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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**SYNTHETIC MICRO/NANOMOTORS: FABRICATION,
MOTION STUDIES AND APPLICATIONS**

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SCHOOL OF PHYSICAL & MATHEMATICAL SCIENCES

NANYANG TECHNOLOGICAL UNIVERSITY

2017

SYNTHETIC MICRO/NANOMOTORS: FABRICATION, MOTION STUDIES AND APPLICATIONS

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Epigraph

An experiment is a question which science poses to Nature, and a measurement is the recording of Nature's answer.

Max Planck

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Summary

Micro/nanomachines is an emerging field to design and build miniaturized machines analogous to macroscopic machines in our life to perform various intended tasks at small scales. As mobility is desired in a wide range of applications, micro/nanomotor represents a significant step towards practical tiny machines. Micro/nanomotors, which are micro- or nanoscale devices capable of converting energy into mechanical forces and movement, attract considerable interests as a brand new solution to address problems encountered in many fields, especially in biomedical and environmental area. Aiming at solving the problems that impede the realization of the envisioned applications, this project mainly focuses on fabrication and potential applications of self-propelled micro/nanomotors. In the aspect of fabrication, preparation method of tubular micro/nanomotors was simplified and the influence of geometric parameters was investigated. Furthermore, efforts were made to expand the scope of fabrication materials for the purpose of reducing cost and extending functionality. From the viewpoint of applications, the influence of real-world environment on the mobility of micro/nanomotors was examined and potential functionalization strategies were proposed. These findings would contribute to hastening the application of micro/nanomachines in practice.

List of Publications

1. **Hong Wang**, Bahareh Khezri, Martin Pumera*. Catalytic DNA-Functionalized Self-Propelled Micromachines for Environmental Remediation. *Chem* **2016**, *1*, 473.
2. **Hong Wang**, James Guo Sheng Moo, Martin Pumera*. From Nanomotors to Micromotors: The Influence of the Size of an Autonomous Bubble-Propelled Device upon Its Motion. *ACS Nano* **2016**, *10*, 5041.
3. **Hong Wang**, Martin Pumera*. Fabrication of Micro/Nanoscale Motors. *Chem. Rev.* **2015**, *115*, 8704.
4. **Hong Wang**, Zdenek Sofer, James Guo Sheng Moo, Martin Pumera*. Simultaneous Self-Exfoliation and Autonomous Motion of MoS₂ Particles in Water. *Chem. Commun.* **2015**, *51*, 9899.
5. **Hong Wang**, Guanjia Zhao, Martin Pumera*. Beyond Platinum: Bubble-Propelled Micromotors Based on Ag and MnO₂ Catalysts. *J. Am. Chem. Soc.* **2014**, *136*, 2719.
6. **Hong Wang**, Zdenek Sofer, Alex Yong Sheng Eng, Martin Pumera*. *Iridium-Catalyst-Based Autonomous Bubble-Propelled Graphene* Micromotors with Ultralow Catalyst Loading. *Chem. Eur. J.* **2014**, *20*, 14946.
7. **Hong Wang**, James Guo Sheng Moo and Martin Pumera*. Tissue Cell Assisted Fabrication of Tubular Catalytic Platinum Microengines. *Nanoscale* **2014**, *6*, 11359.
8. **Hong Wang**, Guanjia Zhao, Martin Pumera*. Crucial Role of Surfactants in Bubble-Propelled Microengines. *J. Phys. Chem. C* **2014**, *118*, 5268.
9. **Hong Wang**, Guanjia Zhao, Martin Pumera*. Blood Metabolite Strongly Suppresses Motion of Electrochemically Deposited Catalytic Self-Propelled Microjet Engines. *Electrochem. Commun.* **2014**, *38*, 128.

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11. **Hong Wang**, Guanjia Zhao and Martin Pumera*. Blood Electrolytes Exhibit a Strong Influence on the Mobility of Artificial Catalytic Microengines. *Phys. Chem. Chem. Phys.* **2013**, *15*, 17277.
12. Wei Zhe Teo, **Hong Wang**, Martin Pumera*. Beyond Platinum: Silver-Catalyst Based Bubble-Propelled Tubular Microtors. *Chem. Commun.* **2016**, *52*, 4333.
13. James Guo Sheng Moo, **Hong Wang**, Martin Pumera*. Influence of pH on the Motion of Catalytic Janus Particles and Tubular Bubble-Propelled Micromotors. *Chem. Eur. J.* **2016**, *22*, 355.
14. Wei Zhe Teo, **Hong Wang**, Martin Pumera*. The Gating Effect by Thousands of Bubble-Propelled Micromotors in Macroscale Channels. *Nanoscale* **2015**, *7*, 11575.
15. James Guo Sheng Moo, **Hong Wang**, Guanjia Zhao, Martin Pumera*. Biomimetic Artificial Inorganic Enzyme-Free Self-Propelled Microfish Robot for Selective Detection of Pb^{2+} in Water. *Chem. Eur. J.* **2014**, *20*, 4292.
16. James Guo Sheng Moo, **Hong Wang**, Martin Pumera*. Acetylene Bubble-Powered Autonomous Capsules: Towards in Situ Fuel. *Chem. Commun.* **2014**, *50*, 15849.
17. Guanjia Zhao, **Hong Wang**, Bahareh Khezri, Richard D. Webster, Martin Pumera*. Influence of Real-World Environments on the Motion of Catalytic Bubble-Propelled Micromotors. *Lab Chip* **2013**, *13*, 2937.
18. Guanjia Zhao, **Hong Wang**, Samuel Sanchez, Oliver G. Schmidt and Martin Pumera*. Artificial Micro-Cinderella Based on Self-Propelled Micromagnets for the Active Separation of paramagnetic particles. *Chem. Commun.* **2013**, *49*, 5147.

19. Chee Shan Lim, Zdenek Sofer, Ondrej Jankovsky, **Hong Wang**, Martin Pumera*. Electrochemical Properties of Layered SnO and PbO for Energy Applications. *RSC Adv.* **2015**, 5, 101949.
20. James Guo Sheng Moo, Carmen C. Mayorga-Martinez, **Hong Wang**, Bahareh Khezri, Wei Zhe Teo, Martin Pumera*. Nano/Microrobots Meet Electrochemistry. *Adv. Funct. Mater.* **2017**, DOI: adfm. 201604759.

Thesis Organisation

This thesis is organized into eight Chapters. First of all, the motivations and objectives of this thesis are presented in **Chapter 1**. The following **Chapter 2** will provide a general introduction to the origin and current status of synthetic micro/nanomotors. In-depth discussions on previously reported works with regard to the working principles, fabrication techniques and proof-of-concept applications of existing self-propelled micro/nanomotors are included in independent subchapters of **Chapter 3**. After the scientific background of this thesis outlined in previous chapters, a collection of research towards the objectives established in **Chapter 1** will be provided in **Chapters 4-7**.

In detail, **Chapter 4** will expand on current fabrication methods of micro/nanotubes for better formulation. **Chapter 5** will focus on extending the scope of materials for fabrication of micro/nanomotors. **Chapter 6** will touch on the influence of real-world environment on the mobility of micromotors. **Chapter 7** will highlight the application of micromotors on heavy metal removal and cargo delivery.

Chapter 8 gives a summary and perspective of the work presented in this thesis.

The published version of the results in **Chapters 4-7** are shown in the **Appendices**.

Chapter 1

Objectives of the thesis

The use of tools can be traced back to the beginning of recorded history and represents a significant step in the evolution of mankind. A machine is a tool that can perform intended tasks using energy. Throughout history, humans have developed many machines to help change the world. In fact, machines are not limited to human design. The biomachines created by nature through millions of years of evolution are able to perform complicated tasks precisely, forming the foundations of biological systems. Inspired by the biomachines of nature, humans have devoted considerable effort to the development of artificial micro/nanoscale machines. Micro/nanomotors represent a fundamental step towards the realization of practical nanomachines. A micro/nanomotor is a micro- or nanoscale device that converts energy into movement and force. Micro/nanomotors are expected to bring about revolutionary changes in the ways we address biomedical and environmental issues, owing to the distinct motion element and tiny sizes. All the efforts on the research of micro/nanomotors are to pave way for the ultimate realization of their potential applications. To be employed in a variety of desired tasks, millions of micro/nanomotors need to collaborate with each other in real-world environment. Towards reaching these goals, two overall objectives, as illustrated in Figure 1.1, were established for this thesis. Background knowledge leading to these objectives will be highlighted in **Chapter 3**.

Objective 1: Easy and cost-effective fabrication of micro/nanomotors suitable for applications

The final goal of fabrication is to create micro/nanomotors that are suitable for application in an easy and cost-effective way. The preparation of micro/nanomotors generally requires expensive materials, high-end instruments and complex procedures, thus hindering their widespread applications. To achieve mass production of desired micro/nanomotors at low cost, there are two aspects that we can make efforts on: fabrication methods and materials.

As the representative of self-propelled micro/nanomotors, tubular motors have attracted considerable attention due to their robust performance. The current fabrication of micro/nanotubes mainly depends on two methods: the rolled-up technology and the membrane template-assisted electrodeposition. The conventional rolled-up technology includes top-down photolithography, angled e-beam evaporation as well as stress-assisted rolling of nanomembranes, which demands clean-room conditions and relate high consumption. Simplification of this method is necessary for the consideration of practical applications. In addition, an important factor that needs to be taken into consideration during the fabrication of micro/nanomotors is the dimension of the motor. However, the influence of motor sizes on the mobility of micro/nanomotors has seldom been studied.

The applications of micro/nanomotors mainly rely on integration of functional materials into the propulsion system. Despite the remarkable progress achieved in the field of micro/nanomotors, the limited range of materials currently available is

inadequate for many next generation applications. Considerable challenges remain for translation of proof-of-concept efforts into practical applications. Use of widely accessible materials can reduce the cost of fabrication of micro/nanomotors. Extension of micro/nanomotors into more applications will also require a wider variety of material properties than those currently available. There has been a growing interest in exploring new materials for the functioning of micro/nanomotors. A wide material selection as components of micro/nanomotors would offer a variety of functionality and meet the requirements posed by the ever-increasing assortments of applications.

As such, the simplification of rolled-up technology, influence of motor sizes on mobility and extension of the scope of fabrication materials would be investigated for this objective. The related research direction would be elaborated in **Chapters 4 and 5**.

Objective 2: Investigation on potential applications of micro/nanomotors

The growing sophistication of synthetic micro/nanomotors has provided infinite opportunities in different areas, especially in biomedical and environment field. The envisioned applications of micro/nanomotors require them to carry out various tasks in complex media. Despite the great progress that has been made during the past decade, considerable challenges remain for translation of proof-of-concept efforts into practical applications. Towards reaching this, we need to address two problems: the influence of environment on the mobility of micromotors and the things we can do with micro/nanomotors.

The development in biomedical sciences foresees the inclusion of self-propelled catalytic micromotors for in-vivo therapeutic strategies in the near future. Direct in vivo application of micromotors, however, is impeded by insufficient knowledge on its in vivo mobility. Therefore, it is of great importance to assess the mobility of micromotors in real environments. The potential media for biomedical applications, blood, contains many components that may affect the mobility of micro/nanomotors. Awareness of the impediment to the motion would contribute to overcoming this difficulty. Additionally, the motion of most bubble-propelled micro/nanomotors needs the presence of surfactants, the used amount of which has not been systematically studied.

Functionalization is an indispensable part in the application of micro/nanomotors. Tailored functionalization strategies should be developed according to the characteristics of micro/nanomotors as well as intended applications. Through rational functionalization, micro/nanomotors are able to execute different tasks in a

wide range of areas. The integration of the distinct motion element and exceptional material properties offers a dynamic platform for diverse applications. Enriching the ways to functionalize micro/nanomotors would provide more possibilities for potential applications.

Hence, the influence of blood components and surfactants on the mobility of micromotors as well as demonstrative applications based on new functionalization strategies would be investigated for this objective. The related research direction would be elaborated in **Chapters 6 and 7**.

Figure 1.1 Summary of the challenges and objectives of this project.

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Chapter 2

Introduction

2.1 *Biopropulsion in Nature*

2.2 *Origin of synthetic micro/nanomotors*

2.3 *Challenges of micro/nanomotors*

2.1 Biopropulsion in nature

Through millions of years of evolution, nature has created highly efficient biomotors able to perform specific complicated tasks, which provides the foundation of all the living systems on earth. The biomotors are employed in various cellular activities and functioning processes, ranging from intracellular transport to muscle contractions.

The biomotors are composed of dynamically integrated biochemical components and can harvest energy from biochemical processes. Nature has provided us impressive examples to learn from. Well-studied typical examples include F_0F_1 -ATP synthase, cytoskeletal protein motors, DNA and RNA processing enzymes, and bacteria flagellar motors.¹ F_0F_1 -ATP synthase is a membrane protein complex that can synthesize ATP from ADP and phosphate.² The synthase consists of two rotary motors driven by electro-osmotic energy from proton or sodium ion gradient (Figure 1A). Cytoskeletal protein motors mainly refer to kinesins, myosins, and dyneins.³ These protein motors can transport targets throughout the cell by moving along cytoskeletal filaments in harness with the energy released by hydrolysis of ATP (Figure 1B). DNA and RNA processing enzymes are able to move along DNA or RNA using the chemical energy generated from DNA or RNA polymerization.⁴ Bacteria flagellar motors rotate the flagella to propel the bacteria employing energy from the ion flux.⁵ The extraordinary performance of biomotors in nature provides inspiration for development of synthetic micro/nanomotors that can efficiently convert chemical energy into mechanical work. The replication of biomotors is not able to be achieved with today's technology, but biomimetic systems can be developed with the key concepts and working principles

extracted from nature.

Figure 2.1 Examples of biomotors. A) Schematic illustration of F₀F₁-ATP synthase. B) Schematic illustration Kinesin. Reproduced from Ref. 1.

2.2 Origin of synthetic micro/nanomotors

The prescient speech “There’s Plenty of Room at the Bottom” by Richard Feynman in 1959 laid the conceptual foundation for the nanotechnology toady. The speech described a world full of possibilities if we are able to manipulate and control matter on an atomic scale. He also envisioned tiny machines that “arrange the atoms the way we want”. In 1966, the Hollywood science fiction film *Fantastic Voyage* depicted the navigation of a microscopic submarine in human blood vessels to treat diseases. While this envision has not been realized, researchers have devoted considerable efforts in this field. The pioneering work on self-propelled micro/nanomotors was reported independently by researchers in Penn State University and Toronto University around 10 years ago.^{6, 7} The sophistication of micro/nanomotors has been increasing at a very fast pace in recent years. Inspired from nature, synthetic micro/nanomotors are expected to

perform complicated tasks as biomotors. Nanotechnology provides a way of manipulating individual atoms and molecules. Bottom-up synthesis of complete functional systems is one of the aspiring goals of nanotechnology. Up to now, numerous micro/nanomotors have been developed. The micro/nanomotors can be generally divided into two categories: chemically self-propelled and external stimuli propelled. Self-propelled micro/nanomotors can convert chemical energy into movements and forces, while external power sources include magnetic and electrical fields, light, and ultrasound. Among various micro/nanomotors, chemically powered micromotors have received particular attention as they do not require external energy.^{8, 9} Various approaches for self-propulsion have been proposed based on mechanisms of Marangoni effect,¹⁰ self-electrophoresis,^{11, 12} self-diffusiophoresis,^{13, 14} and bubble propulsion.¹⁵

2.3 Challenges of micro/nanomotors

Design and fabrication of desired structures with featured sizes measured in micro or nanometers is the cornerstone of developing micro/nanomachines.¹⁶ Objects in this dimension cannot be visualized without advanced equipment and cannot be handled by conventional methods used to manufacture macroscopic structures, where arises the first difficulty in the field of micro/nanomotors. Challenges also come from the propulsion of micro/nanoscale objects where Brownian motion and viscosity plays important roles.¹⁷ Common steering strategies in the macroscopic world are not feasible for micro/nanomotors. The difference between motion at nanoscopic scale and macroscopic scale can be seen from Reynolds number, which is the ratio of inertial forces to viscous forces. Reynolds number is defined as $Re = \rho\mu L/\eta$, where μ and L are

the velocity and characteristic dimension of the object, ρ and η are the density and viscosity of the fluid. The motion at small lengths scale is dominated by viscous forces in very low Reynolds regimes ($Re \ll 1$). Purcell's scallop theorem states the difficulty of nanoscale propulsion.¹⁸ The propulsion at low Reynolds number in Newtonian fluids needs non-reciprocal motion of the objects to overcome viscous drag forces. In nature, microorganisms achieve propulsion by displaying screw-like or flexible oar-like movements. Additionally, at the very small scales, the effects of Brownian motion become non-negligible, which will result in speed fluctuation and deviation from intended path.

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Chapter 3

Literature review

3.1 Chemically induced self-propulsion at micro/nanoscale

- 3.1.1 *Self-propulsion induced by surface tension gradients*
- 3.1.2 *Self-propulsion induced by self-diffusiophoresis*
- 3.1.3 *Self-propulsion induced by self-electrophoresis*

3.2 Fabrication of self-propelled micro/nanomotors

- 3.2.1 *Electrochemical/electroless deposition*
- 3.2.2 *Physical vapor deposition*
- 3.2.3 *Strain engineering*
- 3.2.4 *Assembly of materials*
- 3.2.5 *Use of biological materials and original materials*

3.3 Applications of self-propelled micro/nanomotors

- 3.3.1 *Biomedical applications*
 - 3.3.2 *Environmental remediation*
-

The content in this chapter has been published in the following review. All discussions herein are written by the author of the thesis, and reproduced here with permission.

1. **Hong Wang**, Martin Pumera*. Fabrication of Micro/Nanoscale Motors. *Chem. Rev.* **2015**, *115*, 8704.

Article can be retrieved from <http://dx.doi.org/10.1021/acs.chemrev.5b00047>

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3.1 Chemically induced self-propulsion at micro/nanoscale

Self-propelled micro/nanomotors can convert chemical energy to autonomous motion by mechanisms of surface tension gradients, self-electrophoresis, self-diffusiophoresis, and bubble recoil.

3.1.1 Self-propulsion induced by surface tension gradients

Surface tension is the tendency of a fluid surface to have the least surface area. Due to the different attraction between molecules, surface tension gradients at an immiscible interface can lead to an imbalance of forces and hence generate flow, which is known as the Marangoni effect. The velocity and direction of the motion is mainly related to the concentration gradient of the surface active molecular layer. As the attraction force between molecules of liquid with high surface tension gradient is higher than that of liquid with low surface tension gradient, the motion direction is towards area with high surface tension gradient. A typical example of motor relying on surface tension gradient is the camphor boat.¹ The asymmetric dissolution of the camphor grain results in a surface tension gradient around the grain, thus generating motion towards area with lower concentration of camphor. Similarly, our group has reported the motion of hydrazine agglomerate on water surface due to Marangoni effect, demonstrating enhanced diffusion of pollutants induced by self-propulsion.² Additionally, a millimeter-sized polysulfone capsule can exhibit fast motion on the water surface due to surface tension gradient resulted from the asymmetric release of the dimethylformamide inside the capsule.³ Most of the motors based on Marangoni effect stay at macroscale, whereas Zhang *et al.* demonstrated a micrometer-sized motor

propelled by surface tension gradient resulted from the products of a depolymerization reaction (Figure 3.1 A).⁴ Anion-exchange beads that can release OH^- ions were loaded with poly(2-ethyl cyanoacrylate) (PECA) and half-coated with poly(methylmethacrylate) (PMMA). The OH^- ions trigger the depolymerization of PECA, which will release surface active product ethanol in the vicinity and generate surface tension gradients to achieve propulsion.

3.1.2 Self-propulsion induced by self-diffusiophoresis

The motion governed by self-diffusiophoresis relies on the solvent flow induced by the concentration gradients of solute around the particle. The gradients cause the solvent to flow from regions of low solute concentration to high solute concentration area, and the resulting fluid flow will accordingly propel the particle in the opposite direction. Many catalytic Janus micro/nanomotors rely on self-diffusiophoresis to achieve propulsion. A typical example of electrophoretic motor is the Pt-catalyzed Janus particle. The asymmetric decomposition of H_2O_2 catalyzed by half-coated platinum will generate oxygen concentration gradients around the particles, resulting in fluid flow and consequent propulsion of the particles.⁵ Hong *et al.* demonstrated ultraviolet induced motion of silver-coated colloidal spheres in dilute H_2O_2 solution because of the asymmetric release of Ag^+ and OOH^- ions.⁶ In addition to H_2O_2 fuel, diffusiophoretic Janus micromotors utilizing other fuels have been developed. Gao *et al.* developed an iridium-catalyzed Janus micromotor which is a silica particle with one hemisphere coated with iridium using physical vapor deposition.⁷ As shown in Figure 3.2 B, the iridium part catalyzes the decomposition of hydrazine fuel into nitrogen, hydrogen, and

ammonium, thus enabling diffusiophoretic motion of the Janus motor at ultralow levels of hydrazine. Ma *et al.* reported a hybrid capsule micromotor that can exhibit motion at physiological concentration of urea.⁸ The micromotor is a Janus hollow mesoporous silica particle with one side coated with Fe/Au and the other side functionalized with enzyme urease which can catalyze urea into CO₂ and NH₃. The self-generated concentration gradient of these chemical species will lead to propulsion of the particle in the direction of such concentration gradient.

3.1.3 Self-propulsion induced by self-electrophoresis

Typical examples of micro/nanomotors relying on self-electrophoresis are bimetallic catalytic Janus particles and nanowires. Two different electrochemical half reactions occur at two opposite ends of an asymmetric conducting particle, for example, H₂O₂ oxidation and reduction at the two ends of a Pt/Au particle, will cause electron flows inside the particle and accompanied migration of protons outside the particle, which leads to the propulsion of the particle in the opposite direction (Figure 3.1 C).⁹ To increase the mobility of self-electrophoretic motors, materials that can help enhance the redox reactions are employed as a cathode or anode. Replacing the Au segment with Ag/Au alloy as the cathode noticeably accelerates the motion of the nanowires.¹⁰ The incorporation of carbon nanotubes into the anodic Pt can greatly increase the velocity of the nanowire motors.¹¹ On the other hand, increased surface area of the catalytic segment of the nanowires will result in enhanced decomposition of H₂O₂ and thus increase the speed of the nanowires. Ozin and coworkers increased surface roughening of nanowires by mixing silica nanoparticles with plating solution and subsequent etching

away. The introduced porosity increases the catalytic surface area and thus the speed of nanowires.¹² In addition to the commonly used H_2O_2 fuel for the propulsion of electrophoretic nanowires, the motion of Cu-Pt nanowires in dilute aqueous solutions of Br_2 and I_2 has been reported. The Cu end serves as the anode to be oxidized and the Pt end functions as the cathode where reduction of halogen happens.¹³

There are also many catalytic Janus micro/nanomotors relying on self-electrophoretic mechanism to achieve propulsion. Generally, self-electrophoresis needs the particle to consist of two distinct conductive materials, which enables different electrochemical half reactions to occur at opposite ends. Posner and coworkers synthesized bimetallic spherical motors by repeating the process of sputtering and resuspension to coat the entire surface of microspheres with gold, followed by half-coating with Pt.¹⁴ The resulting bimetallic spherical Janus micromotors can swim at velocities comparable to their nanowire counterparts. Zhao and coworkers used glancing angle deposition method to obtain the asymmetric Pt/Au coated catalytic micromotors.¹⁵ After deposition of an adhesive Ti layer and an Au layer, the substrate with microbeads was rotated to a polar angle, and therefore the following Pt deposition left some of the Au layer uncovered. The motion behaviors can be tuned by adjusting the exposed area of the Au layer. Lee *et al.* prepared 30 nm Pt/Au Janus nanomotors by depositing gold onto an array of platinum nanoparticles under fast substrate rotation.¹⁶ All these bimetallic Janus motors depend on the self-electrophoresis mechanism to achieve propulsion. Dong *et al.* demonstrated a light-driven TiO_2 -Au self-electrophoretic micromotor that can exhibit motion in pure water under an extremely low ultraviolet light intensity.¹⁷ Upon exposure to UV light, oxidation of water happens at TiO_2 side and

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the reduction of protons occurs at Au side, which results in self-electrophoretic motion of the particle (Figure 3.1 D).

3.1.4 Self-propulsion induced by bubble recoil

Bubble propulsion depends on the recoil effect of the growth and ejection of bubbles generated through catalytic or non-catalytic reactions of micro/nanomotors. Bubble propulsion has attracted considerable attention due to advantages of high power output, powerful performance and high propulsion speed.¹⁸⁻²⁰ Micro/nanomotors propelled by bubbles are also less susceptible to high ionic environment, compared with self-electrophoretic motors whose mobility decreases with increasing solution conductivity.²¹ A typical example of bubble-propelled micro/nanomotors is the microtube. The oxygen generated by decomposition of H_2O_2 on the inner catalytic surface of the tubes, for example platinum and silver, accumulates in the cavity of the tubes and forms bubbles to be ejected out of the tubes. The hybrid microtubes with catalase enzyme functionalized on the inner Au surface of microtubes, as shown in Figure 3.1 E, have been demonstrated to exhibit motion in H_2O_2 .²² Some catalytic or reactant-based Janus motors can also exhibit bubble-propelled motion. Materials like Al and Mg that can react with the fuel to generate gas have also been developed into micro/nanomotors. Al-Ga alloy microsphere partially coated with Ti can be propelled in water without any additional fuel (Figure 3.1 F).²³ The presence of Ga in the alloy is to remove Al oxide passivation layer that hinders the reaction between Al and water. Attributable to the amphoteric properties of Al, Al microspheres with one hemisphere coated with Pd are able to be propelled in base, acid or H_2O_2 three fuels. Similarly,

hydrogen bubble generation by the reaction of Mg with water is also impeded by the formation of a passivation layer of Mg oxide. The problem can be either solved by addition of NaHCO_3 in the solution or utilization of both macrogalvanic corrosion by an additional gold layer and chloride pitting corrosion.

Figure 3.1 A) Motion of depolymerization-powered motors driven by surface tension gradient. Reproduced from Ref. 4. B) Motion of iridium Janus micromotors driven by self-diffusiophoresis. Reproduced from Ref. 7. C) Motion of bimetallic nanorods driven by self-electrophoresis. Reproduced from Ref. 9. D) Motion of TiO_2 -Au Janus micromotors driven by light-induced self-electrophoresis. Reproduced from Ref. 17. E) Bubble-propelled motion of hybrid microtubes with enzyme catalase immobilized on the inner Au surface. Reproduced from Ref. 22. F) Bubble-propelled motion of Ti/Al-Ga Janus micromotors. Reproduced from Ref. 23.

3.2 Fabrication of self-propelled micro/nanomotors

The rapid development of nanotechnology has resulted in diverse strategies and techniques for the fabrication of self-propelled micro/nanomotors.

3.2.1 Electrochemical/electroless deposition

Electrochemical deposition is a widely-used technique in nanotechnology which allows the synthesis of 3D geometries with different materials such as different metals, graphene and polymers. Electrodeposition uses external electrical current for deposition, while electroless deposition utilizes chemical redox reactions instead of electrical means. With different templates, electrochemical and electroless deposition offer an effective way of preparing desired micro- and nanostructures with various dimensions.

Membrane template-assisted electrodeposition employs the pores in a membrane to synthesize tubes and wires.^{24, 25} Due to the relative monodisperse diameters and large pore densities, similar nanostructures can be prepared in batches. For a certain area of membrane with a fixed pore density, the length of the structure is proportional to the charge and the diameter is the same with the diameter of the pores. The nanostructures can be either hollow or solid relying on the properties of the pore and the deposited material. Nanowire, micro/nanotubes, and helical micromotors have been successfully synthesized by membrane template-assisted electrodeposition.²⁶ In the typical protocol of membrane template assisted electrodeposition shown in Figure 3.2 A,^{19, 27} alumina membranes or track-etched polycarbonate with micro/nanosized pores are utilized and different metals are electrodeposited sequentially into the pores. One side of the membrane is first coated with a layer of silver or gold *via* physical vapor

deposition to serve as the working electrode. The membrane is then assembled in an electrodeposition cell with a piece of flat aluminum foil placed against the deposited metal layer of the membrane to serve as a conductive contact for subsequent electrodeposition. Different kinds of desired materials were electrodeposited sequentially. Removal of the silver or gold backing is achieved by mechanical polishing or chemical etching. The electrodeposited structures can be released by dissolving the membrane and then collected after successive rinsing and centrifugation.

In addition to membrane template, other templates with different shapes can also be used for electro/electroless deposition. For examples, etched silver wires have been reported as templates for deposition of microtubes.²⁸ Besides, asymmetric bipolar electrodeposition is a kind of fabrication method utilizing bipolar electrochemistry. Placed in a strong electric field between two electrodes, a conductive object will have potential differences at the two ends, which can induce the occurrence of asymmetric redox reactions at the opposite poles. Metallic salt can be reduced at the cathode, forming metal deposits on the particles. This method is suitable for large-scale production of Janus micromotors.²⁹

3.2.2 Physical vapor deposition

Physical vapor deposition is a coating technique to deposit thin layers of materials using vaporization from a solid target assisted by high temperature vacuum or gaseous plasma. The vapor is transported to the substrate surface in vacuum or partial vacuum and then condenses to form thin films. Sputtering and electron beam evaporation are the two most common types of physical vapor deposition. Sputtering

generates vapor by bombardment of the target using ionized gas while electron beam evaporation utilizes an electron beam to evaporate the target into vapor. As a direct approach to incorporate target materials into micro/nanostructures to provide desired properties, physical vapor deposition can be used to introduce catalytic or magnetic materials as well as inert materials to block reactions. Without changing the orientation of a substrate, the target materials are only deposited on one face, thus creating asymmetric structures.

Researchers have used physical vapor deposition to break the symmetry of electrodeposited nanowires to exhibit rotational motion instead of linear motion. Qin *et al.* used thermal evaporation to coat one side of electrodeposited Au-Pt-Au nanowires. Breaking the symmetry induces rotation of the nanowires in the presence of H_2O_2 .³⁰ Another asymmetric nanorod reported by Wang *et al.* was fabricated by sequential physical vapor deposition of additional Cr, SiO_2 , Cr, Au, and Pt layers on one side of electrodeposited Au-Ru nanorods (Figure 3.2 B).³¹ The perpendicular force added by the additional Au/Pt catalytic bilayer leads to rotation of the nanorod with a velocity ten times faster than the previous one.

Physical vapor deposition is a widely-used technique in the preparation of Janus micro/nanomotors. The key feature of Janus motors is the asymmetric distribution of materials, which leads to directed force to propel the motion of the object in one direction.³² A common synthetic approach to fabricate Janus motors is to create asymmetry at the interfaces by physical vapor deposition and temporary shielding of one face.³³ Preparation of Janus particles is usually conducted on a self-assembled

monolayer of particles formed by slow evaporation of deposited particle suspension on a substrate. The area of monolayer can be tuned by changing drop size and particle concentration. Catalytic material is then deposited on top of the monolayer to form hemispherical caps on the surface of the particles (Figure 3.2 C). After fabrication, the Janus particles are separated from the substrate via sonication. The diameters of the fabricated catalytic Janus motors usually range from dozens of nanometers to several micrometers. For catalytic Janus micro/nanomotors, catalytic materials are deposited onto one side using physical vapor deposition to catalyze reactions. Some Janus micro/nanomotors are not catalytic as there is consumption of component materials during motion. For non-catalytic Janus micro/nanomotor, physical vapor deposition is used to form an inert coating to generate asymmetric bubble thrust.

For conventional physical vapor deposition, the direction of the vapor flux is almost vertical to the substrate which is parallel with the target. The variation of conventional physical vapor deposition is called glancing angle deposition (GLAD) or dynamic shadowing growth, which utilizes substrates at grazing incidence. The substrate is placed at an oblique angle relating to the vapor flux for geometric shadowing. By controlling the rotation and tilt of the substrate with respect to the vapor flux in the deposition process, a variety of structures of different materials can be obtained.³⁴

GLAD provides an efficient way for preparation of complex 3D structures at large scale. The substrate rotation as well as self-shadowing effect during the deposition of an incident vapor offers a good way for preparation of complex Janus micro/nanomotors. In addition to the most common spherical Janus micromotors, a wide range of Janus micromotors with various shapes have been prepared using GLAD. Interesting structures

like rotary Si/Pt nanorods, L-shaped Si/Pt, and Si/Ag nanorods were prepared by He et al. using GLAD. They first prepared the Si backbone and then utilized geometric shadowing effect to asymmetrically coat the backbone with a Pt or Ag layer on one side (Figure 3.2 D).³⁵ The micromotor reported by Gibbs et al. consists of a silica microbead and a TiO₂ arm deposited at oblique angles.³⁶ Platinum was deposited with no angle and therefore only existed on one side of the arms (Figure 3.2 E). The oblique vapor and rotation of substrate enable deposition on a much larger area of spheres. A Pt-Ag-Au shell micromotor with a small opening was prepared by glancing angle deposition on a spherical template followed by wet chemical etching.³⁷

Figure 3.2 A) Schematic of membrane template-assisted electrodeposition of

microtubes and SEM images of the electrodeposited microtube. Reproduced from Ref. 19. B) SEM image and schematic illustration of a nanorod rotor with asymmetry created by physical vapor deposition. Reproduced from Ref. 31. C) SEM image of monolayer of spherical particles. The inset is the Janus micromotor with one hemisphere coated with metal using physical vapor deposition. Reproduced from Ref. 33. D) Preparation of L-shaped Si/Pt nanorod motors by GLAD. Reproduced from Ref. 35. E) Fabrication of micromotor composed of a silica sphere and a TiO_2 arm coated with Pt on one side. Reproduced from Ref. 36.

3.2.3 Strain engineering

Strain engineering allows rearranging of nanomembranes into 3D structures. Releasing of deposited membranes with an engineered strain gradient enables the formation of desired structures. Strain engineering can be utilized to fabricate microtubes by rolling of deposited nanomembranes.^{38, 39} A photoresist sacrificial layer patterned by photolithography is used as the substrate for deposition of a prestressed nanomembrane. Manipulation of the deposition rate and substrate temperature helps the building of desired strain gradient. When released from the substrate by dissolving the sacrificial layer with acetone, the nanomembrane rolls up into a microtube (Figure 3.3 A). By adjusting the built-in strain and thickness of the nanomembranes, the opening diameters of microtubes range from $1\text{ }\mu\text{m}$ to $30\text{ }\mu\text{m}$.⁴⁰ The sizes of the rolled-up microtubes, with lengths in the range of scores of micrometers, are usually bigger than electrodeposited microtubes. Catalysts like Pt and Ag can be incorporated as the inner wall of microtubes if deposited on the uppermost.⁴¹

The traditional rolled-up technology bears disadvantages such as complex fabrication procedure and relative high costs. Researchers have been working towards simplifying the technique. Deposition of metal layers on graphene oxide nanosheets will lead to the formation of microtubes with GO outer layer upon sonication, due to the weak bonding between GO layers and material strain.⁴² Similarly, fruit cells can be used as the support for deposition of metal layer and subsequent formation of microtubes.⁴³ Zhao *et al.* employed poly(methylmeth -acrylate) (PMMA) as the sacrificial layer, which can be selectively removed after sputtering Pt layer. It is also possible to lift off the Pt layer deposited directly on a glass substrate using H_2O_2 .⁴⁴ To facilitate the formation of relative uniform microtubes, a TEM grid template was used in the fabrication process. Despite the great possibilities of the simplified methods for mass production, future efforts should be devoted to better control of the size and morphology of the prepared microtubes.

A polymeric microtube with Pt inner layer that can respond to temperature changes were developed by Magdanz *et al.*⁴⁵ The polymer can exhibit reversible folding/unfolding with changing the temperature. At reduced temperature, the polymer/Pt layers bend to form microtubes with a catalytic Pt inner layer, while the microtubes unfold at elevated temperature (Figure 3.3 B). The motion can be controlled by tuning the temperature to manipulate the rolling and unrolling of the microtubes. Li *et al.* introduced a new method to reduce the diameters of the rolled-up microtubes by utilizing the surface tension of nanodroplets to facilitate the rolling-up.⁴⁶ Prestressed bilayer of SiO/TiO_2 or Si/Cr was deposited on a sacrificial PMMA layer, followed by the deposition of a platinum layer. Subsequently, the platinum layer was stretched by rapid

thermal annealing (RTA) to separated islands, which brought substantial surface tension for rolling. Simultaneously, the nanomembranes were released as a result of the burning of PMMA. The prepared microtubes have higher mobility than those with a smooth platinum surface.

3.2.4 Assembly of materials

The assembly approach offers a strategy to form desired structures by organizing miniaturized elements. Layer-by-layer (LBL) self-assembly is a method to form multilayers by alternating deposition of oppositely charged materials layers. A wide range of templates can be applied for LBL and it is possible to incorporate various materials, such as inorganic compounds, small organic molecules, colloids and macromolecules. Incorporation of Pt catalyst imparts the ability of propulsion in H_2O_2 to the prepared structures. Membrane template-assisted layer-by-layer (LbL) deposition was used to prepare tubular micromotors.⁴⁷ Pt nanoparticles were assembled on the inner wall of alternatively deposited layers of two oppositely charged biodegradable materials on the membrane template. The multilayer structure formed by LBL is suitable for encapsulation of iron oxide nanoparticles and drugs, which enables control and drug delivery. LbL assembly technique can also be used for preparation of Janus capsule motor using silica particles as templates.⁴⁸ After the deposition of oppositely charged materials shown in Figure 3.3 C, the templates were subjected to microcontact printing with a stamp loaded with Pt NP ink. Removal of the template silica particles resulted in hollow capsules partially coated with Pt NPs, which bears the ability of both propulsion and drug encapsulation.

Asymmetric assembly of nanoparticles is an alternative strategy to fabricate Janus motors. The polymer single crystal (PSC) of α -hydroxyl- ω -thiol-terminated polycaprolactone (HO-PCL-SH) has a large amount of thiol and hydroxyl groups on the surface.⁴⁹ By interacting with these groups, iron oxide, gold and platinum nanoparticles can be incorporated into the PSC template, for the purpose of magnetic control, functionalization and propulsion, respectively (Figure 3.3 D). Wilson *et al.* entrapped Pt NPs in the nanocavities of polymer stomatocytes.⁵⁰ The stomatocyte structures were transformed from spherical polymersomes. Addition of Pt NPs in the solution led to their entrapment by solvent-swollen polymersomes. The entrapped Pt NPs can be accessed by H_2O_2 through the opening of the stomatocytes to generate thrust for motion. The assembly technique also provides possibilities for the construction of micro/nanomotors based on synthetic molecular systems. Feringa *et al.* described the bubble-propelled motion of micro-sized particles covalently tethered manganese catalase mimic.⁵¹

3.2.5 Use of biological materials and original materials

Nature offers a wide range of materials that are readily used for the preparation of micro/nanomotors. Integration of synthetic constituents and biological materials to form biohybrid systems is an alternative strategy for fabrication of micro/nanomotors. Enzyme is an important form of biomaterials that have been widely used in the preparation of micro/nanomotors to catalyze reactions. Mano *et al.* established an enzymatic system that can be bioelectrochemically self-propelled based on the reactions of glucose and oxygen, as shown in Figure 3.3 E.⁵² The two ends of a carbon fiber were

modified with redox polymer wired glucose (GOx) and bilirubin oxidase (BOD), respectively. The internal electron flow within the fiber is accompanied by the external flow of ions, which results in the propulsion of the fiber. The motion of these biocatalytic microtubes will be inhibited with the existence of many aqueous pollutants, which offers a new method of water quality testing. Another spherical hybrid motor was developed by Simmchen *et al.*⁵³ The hybrid motor prepared by immobilizing one side of a mesoporous particle with catalase and single-stranded DNA on the other side. Enzyme immobilization is to achieve propulsion while single-stranded DNA allows capture and transport of the complementary DNA strand. Ma *et al.* described a biocatalytic micromotor which is a Janus mesoporous silica cluster with a Ni layer on one side for magnetic propulsion and catalase enzyme conjugated on the other side for biocatalytic decomposition of the fuel.⁵⁴

Kuhn *et al.* demonstrated the propulsion of metallic microscale objects by a dynamic bipolar self-regeneration mechanism.⁵⁵ In an external electric field, redox reactions occurring at the two ends of the metallic object led to dissolution and deposition of the metal, which will cause directional motion of the object. Another bipolar electrochemical strategy is to produce asymmetric bubble generation at the two ends of a conductive object with the use of an electric field. Water can be used as the media and hydroquinone solution can be used as alternative to increase the propulsion speed due to the lower redox potential of the hydroquinone (HQ) / benzoquinone (BQ) redox couple.⁵⁶⁻⁵⁸ Bubble only forms at one side of the object with hydroquinone solution and therefore results in a higher speed, as illustrated in Figure 3.3 F.

Figure 3.3 A) Schematic of rolling-up of nanomembranes patterned on photoresist and SEM images of the rolled-up microtube. Reproduced from Ref. 41. B) Reversible folding/unfolding of polymeric Pt microtubes with temperature changes. Reproduced from Ref. 45. C) Preparation of (PSS/PAH)₅ hollow capsules using LbL assembly. Reproduced from Ref. 48. D) Preparation of a PSC nanomotor by assembly of nanoparticles. Reproduced from Ref. 49. E) Schematic of bioelectrochemical propulsion of a carbon fiber modified with enzyme. Reproduced from Ref. 52. F) Schematic of the

motion of a conductive particle resulted from bipolar electrochemistry in hydroquinone solution. Reproduced from Ref. 56.

3.3 Applications of self-propelled micro/nanomotors

Potential applications of self-propelled micro/nanomotors mainly focus on biomedical and environmental fields.

3.3.1 Biomedical applications

Micro/nanomotors are envisioned to act as vehicles to transport desired cargoes. Various methods have been developed to transport a wide range of cargoes. The transport of magnetic cargoes can be achieved by magnetic attraction between the cargoes and micromotors. It has been demonstrated that magnetic poly(D,L-lactic-co-glycolic acid) (PLGA) microparticles loaded with drug are able to be transported by nanorods through magnetic attraction.⁵⁹ The transport of charged cargoes can be realized by electrostatic interaction between cargoes and micro/nanomotors. The addition of a polymer segment with negative charge is a widely used strategy to incorporate charged parts into micro/nanomotors. Sen and coworkers introduced a polypyrrole (PPy) segment to the nanorod by electropolymerization, thus allowing the attachment of polystyrene-amidine cargo with opposite charges to the nanorods (Figure 3.4 A).⁶⁰ Unloading of the cargo attached to the nanowires has been demonstrated using photochemically stimulated strategies.⁶¹ Cargo drop-off can be achieved by adding a silver segment to the nanowire, which will dissolve rapidly in the presence of H_2O_2 , Cl^- , and UV light.

Functionalization of micro/nanomotors with materials that are able to interact with corresponding targets is another main method for loading cargo. Self-assembled monolayer (SAM) chemistry is a technique usually used in the functionalization of micro/nanomotors to incorporate materials for desired tasks. Due to the strong thiol-gold interaction, gold is widely employed as the surface for SAM functionalization. Manesh *et al.* modified the Au part of the nanorod with horseradish peroxidase to catalyze the decomposition of H_2O_2 and localized polymerization. Guided motion of the micromotor led to the creation of surface microsurface structures.⁶² Another important interaction commonly used in biotechnology is the interaction between biotin and streptavidin. Through the strong non-covalent interactions, streptavidin-coated cargoes can be attached to the micromotor with a biotin-terminated disulfide self-assembled monolayer at the Au end.⁶⁰ The cargo can be released by photolysis of an additional photocleavable linker (PCL) between the nanorod and the cargo in the presence of UV illumination.⁶¹

Utilizing micro/nanomotors functionalized with bioreceptors to transport biological targets has been demonstrated to be a promising strategy to isolate target materials. The advantages of bubble-propelled microtubes, such as high speed and large towing power, make them an ideal choice for transport vehicles. The transport of various biological targets such as nucleic acids, cancer cells, bacteria, and proteins by microtubes functionalized respectively with single-strand DNA, antibody, lectin, and aptamer receptors has been demonstrated.⁶³ As illustrated in Figure 3.4 B, a mixed alkanethiol monolayer was formed on the sputtered Au layer of the microtube surface, followed by coupling of bioreceptors to obtain functionalized micromotors.⁶⁴ Insertion

of a magnetic part into the functionalized micromotors enables precise manipulation of the transport process.

Cargo binding sites can be embedded in the micromotors during preparation instead of modification after fabrication. The surface of poly (3-aminophenylboronic acid) (PAPBA)/Ni/Pt microtubes has built-in boronic acid which can selectively recognize monosaccharides, enabling transport of yeast cells and glucose-incubated microspheres (Figure 3.4 C).⁶⁵ Ascribed to the higher binding affinity with boronic acid, addition of fructose will trigger the release of captured yeast cells by competitive binding. Molecular imprinting can be employed to introduce specific recognition sites on the outer surface of the microtubes using membrane template containing preadsorbed templates of the target (Figure 3.4 D).⁶⁶ After the electrodeposition process, removal of target templates leaves complementary nanocavities for the targets. In addition, encapsulation or absorption by multilayer or porous structures can be used for nonspecific cargo transport.^{48, 67} It is also possible to incorporate cargoes in the preparation process. A zinc-based micromotor loaded with various cargoes was prepared by membrane template-assisted electrodeposition method.⁶⁸ The loading of different nanoparticles were accomplished by infiltrating them into the pores of the membrane before the electrodeposition of zinc. The zinc-based micromotors can exhibit motion and deliver cargo in mouse stomach.⁶⁹

Tissue penetration is another required ability for micromotors to perform biomedical tasks. Initial microdrillers based on micromotors have been demonstrated. InGaAs/GaAs/Pt microtubes with sharp tips can drill into fixed cells.⁷⁰ Attributed to the

crystal structure of the sacrificial AlAs layer as well as the different etching rates, rolling of the nanomembranes along the InGaAs <100> direction is favored upon etching AlAs with HF. Most of fabricated microtubes have asymmetric structures containing sharp tips and therefore exhibit a screw-like motion suitable for drilling in the presence of H₂O₂. Micro/nanomotors also have the ability to enter cells. Xuan *et al.* prepared nanometer-sized Janus mesoporous silica nanomotors with chromium/platinum caps.⁶⁷ More Janus MSN nanomotors were found to enter the cells in comparison with uncapped MSNs. The MSNs were loaded with doxorubicin drugs and then were covered by an egg phosphatidylcholine (PC) bilayer which will undergo biodegradation in cells to release the drugs.

Biocompatibility is a requirement for practical biomedical applications. It has been demonstrated that Pt/Au nanotubes do not have acute toxicity towards human lung epithelial cells.⁷¹ Hydrogen peroxide is a common fuel to propel micro/nanomotors, but suffers the problem of lacking biocompatibility. Toward eliminating the use of external fuel, simulated body fluids (SBF) and blood plasma have been used to propel the motion of Mg/Pt Janus micromotors, attributable to the chloride pit corrosion and buffering effect.⁷² Thermoresponsive hydrogel layers were coated on the surface of the micromotors to deliver and release the drugs with temperature control.

3.3.2 Environmental remediation

Micro/nanomotors have shown great potential in detection and removal of pollutants. The detection of pollutants is based on either motion behavior of the

micromotors or fluorescence signals. Biocatalytic micromotors using enzyme to catalyze reactions have the ability to sense heavy metals as well as chemical vapor threats and exhibit changes in propulsion behavior accordingly, due to the poisoning of the enzyme catalyst.⁷³ The studies using 2D material-based micromotors for fluorescence detection of pollutants have opened a new door for the application of micromotors. The dye-labeled bioreceptor will lose fluorescence signal upon adsorption onto the graphene or MoS₂ surface through π - π interactions. Due to the higher affinity with the target compounds, the bioreceptor will leave the 2D material surface when combined with the target, which leads to the recovery of the quenched fluorescence signals.^{74, 75}

One of the main applications of micro/nanomotors in environmental field is the adsorption of pollutants. Modification of the surface of micro/nanomotors with a hydrophobic layer allows capturing of oil droplets. As illustrated in Figure 3.4 E, a SAM of alkanethiols was functionalized on the gold outer surface of Au/Ni/PEDOT/Pt microtubes to collect and transport oil droplets.⁷⁶ The surface hydrophobicity can be tuned by changing the lengths of the chain and head functional groups, thus adjusting the extent of interaction. The same strategy worked for magnesium Janus micromotors driven by seawater to collect oil droplets from unmodified seawater.⁷⁷

Using absorbent as starting materials to prepare micro/nanomotors is another method to clean up water bodies.⁷⁸ Janus micromotors based on activated carbon with Pt coating on one side can exhibit efficient bubble propulsion. The adsorption capacity of activated carbon coupling with motion elements allows “on-the-fly” elimination of various pollutants. Microtubes with electrodeposited graphene oxide outer surface have

been used for adsorption of heavy metals.⁷⁹ The zirconia/graphene oxide microtubes prepared by simultaneous electrodeposition of zirconia and reduced graphene oxide are able to remove nerve agents by acid-base Lewis interaction between zirconia and phosphate groups.⁸⁰ Silver-exchanged zeolite micromotors have exhibited excellent adsorption capability towards chemical warfare agents as well as bacterial killing capacity due to the existence of silver ions.⁸¹ Ion-exchange is another common method to remove heavy metals in addition to adsorption. Incorporation of CdS nanocrystals in the polyaniline layer of the microtubes imparts the ability of cation-exchange with mercury to the self-propelled micromachines. The photocatalytic activity of the CdS nanocrystals also enables oxidation of bisphenol A.⁸²

Additionally, remediation agents can be integrated in the structure of micro/nanomotors as the outer surface. The microtubes with Fe outer surfaces have been used for degradation of organic pollutants through the Fenton oxidation process (Figure 3.4 F).⁸³ Corrosion of the Fe surface generates ferrous ions, which acts as reagents for the Fenton reaction together with H₂O₂. A photocatalytic degradation strategy based on TiO₂/Au/Mg spherical micromotors has been employed to decompose biological and chemical warfare agents.⁸⁴ The TiO₂ outer layer will generate highly oxidative species upon UV illumination for decontamination. The movement as well as bubble generation of micromotors will cause convection and mixing, resulting in enhanced efficiency of detoxification.

In comparison with common materials for nanoremediation, micro/nanomachines have the advantage of the unique motion element. The motion

dimension provides innovative solutions of *in situ* and *ex situ* nanoremediation, as well as the potential of accelerating decontamination processes and reducing costs. Catalytic autonomous micro/nanomachines can transport remediation agents to contamination sites and carry out effective mixing at the same time. The miniature sizes of micro/nanomachines enable their navigation in narrow spaces that cannot be reached using conventional methods. Moreover, self-propelled micro/nanomachines are promising to merge sensing and remediation into one platform.

Figure 3.4 A) Attachment of cargo to nanorod by electrostatic interaction. Reproduced from Ref. 60. B) Functionalization of microtubes with DNA probes using SAM. Reproduced from Ref. 64. C) Use of microtubes with built-in boronic acid for transport and triggered release of yeast cells. Reproduced from Ref. 65. D) Schematic of MIP for electrodeposition of micromotor that can selectively capture target protein. Reproduced from Ref. 66. E) Removal of oil droplets by microtubes modified with alkanethiol. Reproduced from Ref. 76. F) Schematic of destruction of organic contaminants by Fe/Pt

microtubes *via* Fenton reaction. Reproduced from Ref. 83.

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Chapter 4

Optimization in the fabrication of micro/nanotubes

4.1 *Introduction*

4.2 *Experimental section*

4.2.1 Materials

4.2.2 Apparatus

4.2.3 Methods

4.3 *Results and Discussion*

4.3.1 Tissue cell assisted fabrication of rolled-up tubular micromotors

4.3.2 The influence of sizes of tubular micromotors upon its motion

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2. **Hong Wang**, James Guo Sheng Moo, Martin Pumera*. From Nanomotors to Micromotors: The Influence of the Size of an Autonomous Bubble-Propelled Device upon Its Motion. *ACS Nano* **2016**, 10, 5041.

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4.1 Introduction

Synthetic micro/nanomotors that can exhibit autonomous motion are in the forefront of nanotechnology. Because of the excellent performance, tubular micro/nanomotors attract the most attention among different kinds of self-propelled micro/nanomotors.^{1, 2} The typical structure of the tubular micromotors is a microtube with platinum catalytic inner surface to generate oxygen bubbles needed for propulsion *via* decomposition of H_2O_2 . The fabrication of micro/nanotubes mainly depends on two methods: the rolled-up technology³ and the membrane template-assisted electrodeposition.⁴ Rolled-up technology is an approach to scroll released membranes on the substrate into tubes utilizing the strain gradient in the deposited multilayers. Membrane template-assisted electrodeposition uses the micro/nanopore in the membrane as template for synthesis of micro/nanotubes. To perform desired biomedical and environmental remediation tasks, millions of autonomous micromotors are required, which makes demand of simple and affordable platform for mass production of the micromotors.

Currently, it is still a highly challenging task to fabricate rolled-up microtubes. The rolled-up technology pioneered by Mei and Schmidt⁵ requires complex procedures. The practical use of this method is largely restricted by the preparation process and high consumption of related experimental conditions. There have been many attempts to develop cheap and simple approaches for fabrication of motors. Biocatalytic motors in millimeter size based on plant tissues⁶ and magnetically powered helical micromotors utilizing spiral water-conducting vessels of plants⁷ have been reported.

We developed a very easy and cost-effective preparation method of tubular micromotors with the use of fruit cells. The replacement of lithographically defined material with cheap and widely accessible fruit cells as the support of metal layers eliminates the etching step and reduces the fabrication costs to a great extent. The prepared microtubes exhibit ultrafast motion in H_2O_2 . The fruit cells assisted method enables rapid and low-cost fabrication of tubular micromotors in large scale.

Owing to the diverse potential applications of micro/nanomotors, the size of micro/nanomotors is an important aspect that requires consideration in order to fit different practical needs. In spite of considerable effort on developing fabrication methods of micro/nanomotors, the studies on their dimensions are limited. Geometric parameters, for instance, diameters of their openings and lengths, have a great influence on the motion of tubular micro/nanoengines. The body-deformation model established by Mei and co-workers studied the dependence of dynamics of tubular micromotors on their geometric parameters, which is verified by experiments using rolled-up microtubes.⁸ Other bubble propulsion models created by Fomin *et al.*⁹ and Manjare *et al.*¹⁰ were tested on rolled-up microtubes as well. Given the need to reduce the size of microtubes in some applications, it is of great interest to understand the motion at an even smaller scale. Membrane template-assisted electrodeposition offers a way to prepare tubes with much smaller dimensions. We prepared different sizes of micro/nanotubes by membrane template-assisted electrodeposition and studied the influence of sizes on the dynamics of micro/nanotubes at a considerably reduced scale down to the nanometer regime.

4.2 Experimental section

4.2.1 Materials

The cyclopore polycarbonate membranes with pore sizes of 5 μm , 2 μm and 200 nm were obtained from Whatman, USA. Pt electrodes with 1 mm diameter and Ag/AgCl/1.0 M KCl were obtained from CH instruments, USA. The platinum plating solution was obtained from Technic Inc., USA. Hydrogen peroxide (35%) was obtained from Alfa Aesar, Singapore. Methylene chloride and ethanol were obtained from Tedia, USA. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (98+%) and sodium dodecyl sulfate (SDS) were obtained from Sigma-Aldrich. The platinum and silver targets for sputtering were obtained from Quorum Technologies Ltd, UK. Cover slips were obtained from CellPath, UK. Bananas and apples were obtained from local markets. Chemicals were used without further purification and the solutions were prepared using ultrapure water (18.2 M Ω cm) generated from a Millipore Milli-Q purification system.

4.2.2 Apparatus

Electrochemical deposition was performed with an Autolab PGSTAT 101 electrochemical analyzer (Eco Chemie, Utrecht, The Netherlands) connected to a computer and controlled by NOVA Version 1.8 software (Eco Chemie). The deposition procedure was carried out at room temperature using a three-electrode setup. A platinum electrode was used as a counter electrode, and Ag/AgCl/1.0 M KCl was employed as the reference electrode. Sputtering was conducted with a JEOL JFC-1600 Auto Fine Coater. Ultrasonication was performed with a Fisherbrand FB 11203 ultrasonicator, and centrifugation was performed with a Beckman Coulter Allegra 64R

centrifuge. Scanning electron microscopy (SEM/EDX) analysis was carried out with a JEOL JSM 7600F instrument. Optical microscope videos and images were acquired via a Nikon Eclipse 50i microscope and a Nikon Eclipse Ti-E microscope fitted with a pco.edge 5.5 scientific CMOS camera, a Photron FASTCAM SA1.1 camera or a DS-Fi1c camera. Nikon NIS-Elements software was used to process video sequences.

4.2.3 Methods

Fruit cells assisted preparation of rolled-up microtubes. The dispersion of fruit cells was prepared by ultrasonication of fruit tissue (500 mg) in 2 mL water. The aqueous suspension (50 μ L) was applied on clean cover slip spreading over the entire surface. After drying overnight, the cover slip coated with fruit tissue cells was sputtered with platinum (15 nm). Subsequently, the cover slip was ultrasonicated in water, resulting in an aqueous suspension of microtubes.

Electrodeposition of Pt micro/nanotubes with different sizes. The Pt micro/nanotubes were prepared with a modified electrodeposition procedure using cyclopore polycarbonate templates. For the microtubes electrodeposited in 5 μ m and 2 μ m pores, silver ($\sim$ 75 nm) was sputtered on one side of the template membrane. The silver-sputtered side of the polycarbonate membrane was attached to copper tape, serving as the working electrode for the plating experiments. For the nanotubes electrodeposited in 200 nm pores, commercial cotton swabs were used to apply colloidal graphite ink on one side of the polycarbonate membrane, immediately after which, a piece of flat aluminium foil was attached to the ink. The aluminium foil together with graphite ink served as the working electrode for electrodeposition. The

membrane template was then assembled into a customized Teflon plating cell. Ag/AgCl reference electrode and platinum counter electrode were used. Electrochemical deposition was performed with an Autolab PGSTAT 101 electrochemical analyzer connected to a computer and controlled by NOVA Version 1.8 software. For the microtubes prepared using templates with 5 μm and 2 μm pores, only platinum was electrodeposited with the use of commercial plating solutions. For Type A and Type B microtubes, platinum was electrodeposited using galvanostatic method at -20 mA for 2000 s. For Type C microtubes, platinum was electrodeposited using galvanostatic method at -20 mA for 600 s. For Type D nanotubes, a copper sacrificial layer was electrodeposited using galvanostatic method at -2 mA for 1000s with a plating solution consisting of 1 M CuSO_4 and 1 M H_2SO_4 . After removal of the deposition solution and rinsing of the template with water, the platinum layer was electrodeposited galvanostatically at -2 mA for 1000 s. The plating cell was disassembled after finishing electrodeposition. For the membranes sputtered with silver, polishing was conducted using 0.06 μm alumina powder to remove the sputtered silver on the membrane. For the membranes applied with graphite ink, the graphite layer was removed by ultrasonication in water. Subsequently, the membranes were placed in Eppendorf tubes with 2 mL of methylene chloride and ultrasonicated until completely dissolved to release all the microtubes. The microtubes were collected by centrifugation at 6000 rpm for 3 min followed by repeatedly washing for 3 times with methylene chloride. The solution was then washed with ethanol and water, twice of each, with a centrifugation for 3 min after each washing step. In the end, concentrated nitric acid was used to treat all the fabricated micro/nanotubes to eliminate the sacrificial copper layer or other

impurities. After washing out nitric acid, the micro/nanotubes were stored in water at room temperature.

Propulsion of micro/nanotubes. The experiments for studying the motion of electrodeposited micro/nanomotors were performed in an aqueous solution consisting of H_2O_2 at different concentrations and SDS at a fixed concentration (0.3 wt%). The experiments for the motion study of the fabricated rolled-up microtubes were performed in an aqueous solution containing H_2O_2 at different concentrations and SDS at a fixed concentration (0.5 wt %). A mixture of micro/nanotubes, SDS, H_2O_2 and water was placed on a freshly cleaned glass slide. Optical microscope videos and images were obtained using a Nikon Eclipse 50i microscope and a Nikon Eclipse Ti-E microscope fitted with a pco.edge 5.5 scientific CMOS camera, a Photron FASTCAM SA1.1 camera or a DS-Fi1c camera. Nikon NIS-Elements software was used to process video sequences.

4.3 Results and discussion

4.3.1 Tissue cell assisted fabrication of rolled-up tubular micromotors

To fabricate microtubes, mashed banana tissue was ultrasonicated in water to prepare an aqueous dispersion of banana fruit cells. After homogenization, the dispersion of banana fruit cells was deposited on glass cover slips. When water is completely evaporated, Pt is deposited on the glass cover slip coated with banana cells *via* sputtering. Upon ultrasonication of cover slip coated with tissue cells and Pt in water, the double-layer film crushed and detached from the cover slip, rolling into scrolls at the same time. Figure 4.1 illustrates the entire fabrication process.

Figure 4.1 Fabrication of rolled-up microtubes with banana fruit cells: (a) coating of the glass cover slip with banana fruit cells, (b) sputtering a Pt layer on top of the dried banana tissue cells, (c) ultrasonication of the cover slip in water.

The optical images of aqueous dispersion of banana fruit cells and the prepared microtubes are shown in Figure 4.2. As can be seen from Figure 4.2 A, the banana fruit cells are flat in shape with a length of several hundred micrometers. After complete evaporation of water, the cells on the cover slip formed a thin layer of membrane that would separate with the glass surface upon exposure to water. No microtubes were observed both before and after sputtering Pt while some cracks of the deposition layers appeared. The formation of microtubes was immediately upon ultrasonication of the cells/Pt-coated glass cover slip in water, as demonstrated in Figure 4.2 B.

Figure 4.2 Optical images of aqueous dispersion of (A) banana tissue cells and (B) microtubes acquired upon ultrasonication. The scale bars are 50 μm .

The SEM images of the prepared microtubes are shown in Figure 4.3 A and B. The rolled-up structure of the microtubes can be clearly seen and they are relative uniform in sizes. As shown in Figure 4.3 C, size distribution analysis was conducted for the obtained microtubes. Most of the fabricated microtubes are 10-15 μm long and the average diameters of the two openings at the opposite ends are around 2.5 μm and 3 μm , respectively. The uniformity of the microtubes prepared *via* this method is comparable with that of microtubes prepared *via* membrane template electrodeposition and rolled-up technology.¹¹

Figure 4.3 (A, B) SEM images of the prepared microtubes. The scale bars are 10 μm and 1 μm, respectively. (C) Length distribution of the tubular microengines. Sixty five samples were taken into account.

As shown in Figure 4.4, EDX mapping elemental analysis of the prepared microtubes clearly demonstrates the presence of platinum, carbon and oxygen, indicating the existence of banana fruit tissue in the microtube structure. In the rolling-up process of nanomembranes, the strain in the film generates the bending moment¹² and strain relaxation drives the rolling process.¹³ The strain in the tissue cells/Pt bilayer structure mainly comes from two sides. The sputtered Pt film has

intrinsic stress resulted from the accumulating effect of crystallographic flaws built during the deposition process.¹⁴ The intrinsic stress depends on the properties of the substrate as well as the deposition conditions.^{14, 15} In addition, the difference between swelling properties of banana tissue cells and metal layer in water leads to uneven changes in volume, which creates swelling-induced strain.^{12, 13} Both the intrinsic stress of platinum film and the swelling-induced strain contribute to the formation of the microtubes.

Figure 4.4 SEM/EDX elemental characterizations of the prepared microtubes. The scale bar is 10 μm .

Control experiment was conducted to prove the role of the banana fruit cells in the preparation of microtubes. Half of the glass cover slip was coated with banana fruit cells whereas the other half of the cover slip was left bare. After subsequent sputtering Pt layer and ultrasonication in water, bare glass surface was still covered with Pt but on the other side of the glass cover slip, the Pt layer and banana fruit cells detached upon

ultrasonication, as shown in Figure 4.5 A. An easily detachable interface between the deposited Pt layer and the glass substrate was provided by the banana fruit cells, enabling the rapid rolling-up of the Pt films upon ultrasonication in water. This method excludes the commonly employed etching approach using other chemical solutions. Additionally, the banana fruit cells serve only as an example and other fruit cells can also be used for fabrication of microtubes. The optical image of a microtube fabricated using apple fruit cells is shown in Figure 4.5 B.

Figure 4.5 (A) Optical image of the cover slip half coated with banana fruit cells (right side) after sputtering Pt and ultrasonication in water. Platinum was still on the bare cover slip after ultrasonication (left side). The scale bar is 50 μm . (B) Optical image of a microtube prepared using apple fruit cells. The scale bar is 20 μm .

The microtubes prepared *via* the fruit cells assisted rolling up display fast propulsion in H_2O_2 fuel. A typical snapshot of the motion of the prepared microtubes in 3% H_2O_2 is shown in Figure 4.6 A. The oxygen bubble released from the microtube formed a tail indicating the motion trajectory. The speed of the microtubes can be tuned by adjusting H_2O_2 concentration. As illustrated in Figure 4.6 B, the average velocity of the fruit cells/Pt microtube had an increase from $\sim 410 \mu\text{m/s}$ to $\sim 680 \mu\text{m/s}$ when increasing H_2O_2 concentration from 2% to 4%. The velocity of some microtubes is up to 1mm/s in 3% H_2O_2 . The mobility of the microtubes prepared with the described method is comparable with that of microtubes prepared by electrodeposition¹⁶ and traditional rolled-up technology.¹⁷ In addition, the cost-effective fabrication process using common fruit like bananas and apples, offers possibilities for production of micromotors at large scale. Thousands of tubular micromotors can be fabricated with only milligrams of fruit tissue.

Figure 4.6 (A) Snapshot of the motion of a microtube in 3% H_2O_2 and 0.5% SDS. The scale bar is 50 μm . (B) Dependence of the average velocity of prepared microtubes on H_2O_2 concentration in 0.5% SDS. To obtain the average velocity, 15 independent running experiments were taken into account. The error bars indicate standard deviation.

4.3.2 The influence of sizes of tubular micromotors upon its motion

The micro/nanotubes used in this study were fabricated by membrane template-assisted electrodeposition. The template is cyclopore polycarbonate membrane containing numerous double-conical pores with a closely controlled pore size distribution, which offers asymmetrical structures required for bubble propulsion. We used three different types of commercially available membranes with pore diameter of 5 μm , 2 μm and 200 nm separately. Despite the widely accepted fact that the motion of Pt microtubes in H_2O_2 is principally governed by bubble propulsion, pure platinum micro/nanotubes were used in the study to rule out the role of electrokinetic mechanisms in the motion. For the microtubes fabricated with 5 μm and 2 μm membrane template, only platinum was electrodeposited, whereas for nanotubes fabricated using 200 nm membrane template, platinum was deposited after the electrodeposition of a layer of copper sacrificial layer. In order to remove the remaining silver backing and the copper sacrificial layer, concentrated nitric acid was used to treat all the fabricated micro/nanotubes in the end. The energy-dispersive X-ray spectroscopy (EDX) analysis showed that the micro/nanotubes only consist of platinum.

Figure 4.7 shows the scanning electron microscopy (SEM) images of the four types of fabricated micro/nanotubes: Type A, microtubes electrodeposited at -20 mA for 2000s in 5 μm pores; Type B, microtubes electrodeposited at -20 mA for 2000s in 2 μm pores; Type C, microtubes electrodeposited at -20 mA for 600s in 2 μm pores and Type D, nanotubes electrodeposited at -2 mA for 1000s in 200 nm pores. The images in column (a) of Figure 4.7 A-D were all obtained at 5000 $\times$ to show the relative size of the four types of micro/nanotubes. Figure A, (a) shows a microtube 15.95 μm long with an aspect ratio of length to average diameter of 3.52. The diameters are 4.67 μm and 4.39 μm at the opposite ends, giving an aspect ratio of 1.06. The microtube shown in Figure B, (a) has a length of 17.27 μm and the diameters are 1.77 μm and 1.88 μm . The aspect ratio of length to average diameter is 9.46 whereas that of opening diameters is also 1.06. The length of microtubes is able to be adjusted by changing the electrodeposition duration. The same kind of membrane was used to prepare the microtubes in Figure C and those in Figure B, and therefore the two types of microtubes share similar opening diameters. Shorter electrodeposition time made the length of microtubes in Figure C smaller. Figure C, (a) shows a microtube with a length of 6.24 μm and opening diameters of 1.87 μm and 1.64 μm . The aspect ratio of length to average diameter is 3.56 and that of large opening to small opening is 1.14. The opening diameters of the nanotubes shown in Figure D, (a) are reduced to hundreds of nanometers. The zoomed-in nanotube shown in Figure D, (c), possesses diameters of 0.21 μm and 0.17 μm , giving an aspect ratio of large opening to small opening of 1.24. The length of the nanotube is 2.32 μm and the aspect ratio of length to average diameter is 12.21. The thickness of the micro/nanotubes can be seen from the images in column (b) of A-D.

The average thicknesses of the four types of micro/nanotubes are 0.53 μm , 0.34 μm , 0.25 μm and 25 nm, respectively from A-D. The images in column (c) of A-C show the unpurified bunches of the three types of microtubes at 800 $\times$. As demonstrated in the images, the sizes and shapes of the fabricated micro/nanotubes are relatively uniform. The observed heterogeneity is largely originated from the difference in the size and alignment of pores in the membrane templates.

Figure 4.7 SEM images of the four types of fabricated micro/nanotubes. A) Microtubes electrodeposited at -20 mA for 2000s in 5 μm pores. B) Microtubes electrodeposited at

-20 mA for 2000s in 2 μm pores. C) Microtubes electrodeposited at -20 mA for 600s in 2 μm pores. Images (a) and (b) in A-C were obtained at the magnification of 5000 $\times$, while images (c) in A-C were obtained at the magnification of 800 $\times$. D) Nanotubes electrodeposited at -2 mA for 1000s in 200 nm pores. Image (a) was obtained at the magnification of 5000 $\times$. Image (b) was obtained at 100000 $\times$. Image (c) was obtained at 30000 $\times$.

The bubble-recoiling propulsion mechanism of the micro/nanotubes decides that the motion is related to the dynamics of bubble growth and detachment.^{9, 10} The oxygen produced on the inner surface of the micro/nanotubes is accumulated and the formed bubbles are expelled to propel the micro/nanotubes gradually. The bubble dynamics is closely related to the H_2O_2 fuel concentration as well as the geometry of the micro/nanotubes. Considering the configuration of the tubes, three main geometric parameters play important roles in their dynamics: the length and diameters of the two openings at the opposite ends. Figure 4.8 shows the motion of the three types of microtubes in 2% H_2O_2 obtained by a high speed camera at 270 frames/s. The microtubes in Figure 4.8 A-C are Type A-C microtubes accordingly. The interval between each frame is 3.7 ms. The first 7 images in A-C are consecutive 7 frames whereas the last ones are 30 frames after the first ones. As shown in the video clips, despite the single platinum composition, the bubbles are only expelled from the cavity of the microtubes, indicating the inner concave surface is more advantageous to the formation and accumulation of oxygen bubbles. The asymmetric bubble formation on the concave and convex surfaces can be ascribed to the heterogeneous nucleation energy as well as asymmetric concentration distribution of oxygen on the concave and convex surfaces.^{18,}

¹⁹ The time of each bubble growth and release cycle is not fixed but for the three types of microtubes in Figure 4.8, the cycles all take a duration of around 7.4 ms to 11.1 ms. Table 4.1 presents the lengths and average diameters of the three microtubes.

Figure 4.8 Motion of the three types of microtubes in 2% H_2O_2 captured by a high speed camera at 270 frames/s. A) A Type A microtube. B) A Type B microtube. C) A Type C microtube. The scale bars are 20 μm . Blue line used for monitoring the motion indicates the position of the motor at $t = 0$.

As bubble ejection provides the thrust for the motion of microtubes, the velocity of the microtubes highly depends on the bubble size and ejection frequency. The

migration of oxygen bubbles in the microtube is driven by difference in Laplace pressure and the direction is along the longitudinal axis of the microtube towards the larger opening.^{9, 20} The pressure difference between the inside and outside of the bubble is called Laplace pressure. Due to the different opening sizes at the opposite ends, the Laplace pressures at the two curved interfaces of the bubble slug in the microtube are different, which drives the motion of the bubble to the larger opening. The Laplace pressure (ΔP) is resulted from the surface tension (γ) of the interface between gas and liquid. Based on the Young-Laplace equation for spheres, $\Delta P = 2\gamma/R$, the radius of the expelled bubbles (R) is mainly related to the Laplace pressure. The bubbles will expand in volume during the expulsion process due to the decrease in the Laplace pressure. Upon the exposure of part of the bubble out of the microtube, the bubble will expand gradually as a result of decrease in Laplace pressure until the bubble is totally expelled out reaching a temporarily stable Laplace pressure. The expelled bubbles with relative uniform sizes formed a clear tail at the end of the microtube. Given the influence of surfactant on the generation and release of bubbles, all of the experiments in the study were conducted at 0.3 wt % of SDS. As illustrated in Table 1, the bubbles generated by the microtube in Figure 4.8 A are larger than those generated by the microtubes in Figure 4.8 B and 4.8 C. Typically, the bubbles ejected by microtubes with larger opening diameters are bigger than those ejected by narrower microtubes, indicating that the bubbles in narrower microtubes experience higher pressure due to the smaller volume inside the microtubes. In addition, it is also meaningful to investigate the effect of length by comparing the two microtubes in Figure 4.8 B and 4.8 C which share similar opening diameters but different lengths. The longer microtube in Figure 4.8 B ejected

larger bubbles than those expelled by the shorter microtube in Figure 4.8 C. Despite the higher oxygen production of the longer microtube due to larger inner surface area, the larger bubbles indicate lower pressure inside the longer microtube, relative to that in the shorter microtube. On the other hand, because the bubbles generated in narrower microtubes experience a more significant change of Laplace pressure in the expulsion process, the volume expansion of bubbles from narrower microtubes is more obvious, which can be observed from the aspect ratio of diameter of the bubble to the microtube. Among the three microtubes in Figure 4.8, the microtube in Figure 4.8 A had the lowest aspect ratio of the diameter of the bubble to the microtube (1.50), which agrees with the previous study that the ratio decreases with increasing the micromotor radius.²¹ The microtube in Figure 4.8 B and Figure 4.8 C had 2.41 and 2.18 as the aspect ratio of the diameter of the bubble to the microtube, respectively. Over time, the bubbles will gradually move towards the surface of the solution and expand at the same time.

The motion of microtubes is driven by bubble recoil and hence it is of great interest to investigate the expulsion process. In this process, both the bubbles and microtubes will experience drag forces opposite to their relative motion in the fluid environment. The average propulsion distance of all the three types of microtubes caused by each bubble growth and release cycle was very close to the radius of the bubbles, which is consistent with previous studies.^{3, 22} As a result, the average velocity of the microtubes is close to the product of the bubble ejection frequency and the bubble radius. The calculated product of the bubble ejection frequency and the bubble radius is the estimated velocity in Table 4.1, whereas the measured velocity in the table

is obtained by tracking using analysis software. The bubble expulsion frequency is the calculated average value from a three-second video and the average bubble diameter is obtained from 20 bubbles ejected in this period. The sizes of bubbles expelled from one microtube are relatively uniform and the standard deviations of bubble diameters are below 0.15 μm . As can be seen from the table, the estimated velocity and the measured velocity are similar for all the three types of microtubes.

As illustrated earlier, the bubble size is related to both the opening size and the length of microtubes, while the bubble ejection frequency is equivalent to the total volume of oxygen generation by the microtube per second divided by the average volume of each bubble. At a fixed concentration of H_2O_2 , the volume of oxygen generation is proportional to the Pt catalytic area.⁸ More oxygen will be generated per unit time by the microtubes with larger inner surface area than by the smaller microtubes. However, due to the unsmooth inner surfaces of the microtubes in the study, the surface area cannot be directly calculated from the geometric parameters. Nevertheless, the general trend still persists. Calculation using the data in Table 4.1 showed that the microtube in Figure 4.8 A has the highest oxygen generation per second, followed by the microtubes in Figure 4.8 B and Figure 4.8 C. The longer moving distance propelled by the large bubbles and the high bubble ejection frequency made the microtube in Figure 4.8 A have the highest absolute value of velocity among the three microtubes. Although the bubble size of the microtube in Figure 4.8 C is smaller than that of the longer microtube in Figure 4.8 B, the higher bubble expulsion frequency leads to a comparable absolute value of velocity with the longer microtube.

The unit of body lengths per second is often used for comparing the velocities of different-sized motors. The velocity by body length offers a way to evaluate the mobility of the microtubes with different sizes. Although the average absolute velocities of the microtubes in Figure 4.8 B and 4.8 C are competitive, the shorter microtube has a much higher velocity by body lengths. Based on the model established by Li *et al.*,⁸ in the small scale studied here, the velocity by body length will decrease with an increase in length, which agrees with our results. The velocity by body length of the microtube in Figure 4.8 A ranked between the microtubes in Figure 4.8 C and 4.8 B. According to the previous reported calculation method of the efficiency of micromotors,²³ we obtained the power conversion efficiency of the microtubes in 2% H₂O₂ using the data presented in Table 4.1. The microtube in Figure 4.8 A processed the highest efficiency of 7.3×10^{-8} while the microtubes in Figure 4.8 B and Figure 2C had 5.9×10^{-8} and 5.4×10^{-8} as the efficiency, respectively.

Table 4.1 Geometric and dynamic parameters of the three microtubes in Figure 4.8.

Microtube	Length (μm)	Average diameter of two openings (μm)	Average bubble diameter (μm)	Bubble frequency (Hz)	Estimated average velocity (μm/s)	Measured average velocity (μm/s)	Average velocity (bodylength/s)
Figure 2A	15.68	4.66	6.99	108.11	377.84	379.77	24.22
Figure 2B	19.58	1.92	4.63	96.49	223.37	215.21	10.99
Figure 2C	6.23	1.82	3.96	117.12	231.90	229.63	36.86

Despite the great interest to minimize the size of micromotors to the nanoscale, there is limited study on the motion of nanoscale tubular motors. We investigated the motion of nanotubes with opening diameter of around 200 nm in H_2O_2 . As can be seen from the motion of nanotubes in 2% and 3% H_2O_2 shown in Figure 4.9, bubbles are expelled from the nanotubes and there is a substantial volume expansion during and after the expelling process due to the very high pressure inside the nanotubes. Given the volume expansion, the diameters of the bubbles were measured once the bubbles detached from the nanotubes. Figure 4.9 A shows the motion of a nanotube (2.65 μm in length) in 2% H_2O_2 captured by a normal camera. The first seven images in Figure 4.9 A are consecutive frames with a time interval of 0.09s, while the last image is 20 frames after the first image. The average diameter of bubbles expelled by nanotube is 2.83 μm and the expulsion frequency is 7.41 Hz, leading to an average velocity of 41.08 $\mu\text{m/s}$. Figure 4.9 B shows the bubble growth and release cycle of a nanotube (2.70 μm in length) in 3% H_2O_2 captured by a high speed camera at 270 frames/s. The time interval between each image in Figure 4.9 B is 7.4 ms. The nanotube displayed an average velocity of 65.05 $\mu\text{m/s}$, with an average bubble diameter of 2.72 μm and a ejection frequency of 30 Hz. For the nanotubes, the average moving distance caused by each bubble cycle is much larger than the bubble radius. External drag forces acted on the microtubes and bubbles are required to be considered into the recoiling propulsion system. Based on the Stokes' law, the drag forces on the bubbles are in proportion to the bubble radius. Compared to the microtubes with micrometer-sized openings, the bubbles expelled by the nanotubes with 200 nm openings have a relatively much larger radius than the tubes themselves. The aspect ratio of the diameter of the bubble to the

nanotube is above 14 in 2% H_2O_2 , which is much higher than that of the microtubes discussed above. As a result, the drag force exerted on the bubbles is significantly larger than that on the microtubes, which causes the average propelled distance by each bubble to be larger than the bubble radius. As to the power conversion efficiency, the efficiency of the nanotube in Figure 4.9 A in 2% H_2O_2 was 1.5×10^{-8} using the same method,²³ which was lower than the three microtubes discussed above.

Figure 4.9 The motion of the Type D nanotubes. A) The motion of a nanotube (2.65 μm in length) in 2% H_2O_2 obtained by a normal camera. B) The motion of a nanotube (2.70 μm in length) in 3% H_2O_2 obtained by a high speed camera at 270 frames/s. The scale bars are 10 μm .

Due to the inhomogeneity of the pores in template and uncontrollable factors in the electrodeposition process, the prepared micro/nanotubes have heterogeneous geometric parameters to some extent. We conducted ensemble analysis to investigate the general effect of chemical environment and geometric parameters on the motion of micro/nanotubes. The diameters of both openings and the lengths of the four types (A-D) of micro/nanotubes are presented in Table 4.2. The data was acquired from 100 samples of each type of micro/nanotubes. The influence of slightly varied geometric parameters within the same type of micro/nanotubes on their dynamics is insignificant relative to that of notably different parameters between different types. To study the effect of chemical environment on the motion of the micro/nanotubes, we investigated the dynamics of the micro/nanotubes in a wide concentration range of H_2O_2 fuel. At lower concentration level of H_2O_2 , the bubble sizes did not have obvious changes. At 1% to 3% concentration of H_2O_2 , the average bubble diameters and standard deviations of Type A-D micro/nanotubes were: A, $7.26 \pm 1.96 \mu\text{m}$; B, $4.96 \pm 1.57 \mu\text{m}$; C, $3.86 \pm 0.96 \mu\text{m}$ and D, $2.51 \pm 0.70 \mu\text{m}$. (60 samples were considered in total for each data; 20 for each concentration, 1%, 2% and 3%.) When the H_2O_2 concentration was increased to relatively higher ranges, the bubbles experienced higher pressure because of the enhanced oxygen production inside the micro/nanotubes, resulting in a tendency to become slightly smaller than the bubbles at lower fuel concentrations.

Table 4.2 Ensemble analysis of the geometric parameters of Type A-D micro/nanomotors.

Type of microtubes	Average length and standard deviation (μm)	Average diameter of larger opening and standard deviation (μm)	Average diameter of smaller opening and standard deviation (μm)
A. Electrodeposited in 5 μm pores	14.12 ± 1.72	4.74 ± 0.18	4.58 ± 0.22
B. Electrodeposited with same current for same duration in 2 μm pores.	17.25 ± 2.19	1.88 ± 0.08	1.76 ± 0.11
C. Electrodeposited with same current for shorter duration in 2 μm pores.	5.82 ± 0.46	1.91 ± 0.09	1.69 ± 0.11
D. Electrodeposited in 200 nm pores	2.25 ± 0.56	0.23 ± 0.02	0.19 ± 0.02

a - Electrodeposition for 2000 s at current of -20 mA.

b - Electrodeposition for 2000 s at current of -20 mA.

c - Electrodeposition for 600 s at current of -20 mA.

d- Electrodeposition for 1000 s at current of -2 mA.

The activity and mobility of Type A-D micro/nanotubes in a wide range of H_2O_2 , from 0.5% to 9%, was investigated. There are differences in the activity of Type A-D micro/nanotubes at very low concentrations of H_2O_2 . Decrease in the numbers of active microtubes is common for all the four types of micro/nanotubes at very low fuel concentrations, but less influence was observed for Type A microtubes with 5 μm

openings. In 0.5% H_2O_2 , there were more moving microtubes for Type A microtubes than the Type B and C microtubes with 2 μm openings. It is of significance to note that the Type D nanotubes did not exhibit any motion below 2% H_2O_2 . The reason may be mainly ascribed to the nanometer-sized openings of the nanotubes. The small opening sizes not only decrease the catalytic area of the tubes, but also increase the difficulty of bubble formation inside the tubes. According to Young-Laplace equation, the formation of smaller bubbles in a narrower microtube needs a higher internal pressure than the bigger bubbles formed in a wider microtube. Only when the dissolved oxygen in the solution exceeds the maximum supersaturation concentration, bubble nucleation begins. However, since the pressure in the restricted cavity of tubes is very high, the maximum attainable oxygen concentration will increase accordingly.²⁴ In order to generate bubbles for propulsion, smaller micro/nanotubes need to generate more oxygen with less catalytic area. As a result, limited fuel is more influential on the activity of smaller microtubes than larger microtubes. For Type D nanotubes with an average inner opening diameter of around 150 nm, the influence was more obvious. The formation of nanometer-sized bubbles inside the nanotube requires a much higher internal pressure. To reach the supersaturation limit and generate bubbles under such high pressure, higher concentrations of H_2O_2 are needed to produce more oxygen from the extremely limited catalytic area. Additionally, for the microtubes with 2 μm openings, the shorter Type C microtubes were more sensitive to low fuel concentrations relative to longer Type B microtubes. The reasons can be similarly ascribed to two aspects. The catalytic area of longer microtubes is larger than that of the shorter ones. For another, based on Young-Laplace equation, the smaller bubbles indicated higher

pressure experienced by the bubbles in the shorter microtubes than those in the longer microtubes.

Similar to previous studies, straight, circular and spiral motion were observed for the micro/nanotubes. The circular and spiral motion reflects the resultant force of bubble propulsion and fluid resistance deviates from the motion direction of micro/nanotubes.^{1, 25} The direction deviation of bubble release and drag forces can be attributed to the asymmetry in the structure of micro/nanotubes, which will lead to asymmetric ejection of bubbles and inhomogeneous fluid flow in the surrounding. To gain a further understanding of the propulsion of microtubes, a high speed camera was used to capture the bubble growth and detachment cycle at 30000 fps. The bubble growth and release process is repeated in a cyclic manner. Figure 4.10 demonstrates the propulsion of microtubes by one bubble growth and release cycle in 2% H₂O₂. Figure 4.10 A and B correspond to Type A and Type B microtubes, respectively. From Figure 4.10, we can see that both bubble growth and release propel the micro/nanotubes forward. The different stages in one bubble propulsion cycle are illustrated in the images on the left side. (a) The motion induced by the release of last bubble was just stopped. (a-b) During a short time after the release of last bubble, there was not obvious displacement for the microtube. (b-c) Before the detachment of the bubble, continuous bubble growth powered the microtube forward. (c-d) The bubble was released providing the tube a thrust. Assuming both bubble growth and bubble release processes propelled the microtube at respective constant speed, the graphs on the right side demonstrate the propelled distance of microtube over time. Bubble growth occupied most of the time in the bubble cycle but the propulsion due to bubble growth

is relatively low. The recoil of bubble release generated a powerful thrust that gave the microtube a very high instantaneous velocity during a time scale of microseconds. To evaluate the contribution of Brownian motion in the motion of micro/nanotubes, we calculated Peclet number ($Pe = VL/D$, V is the mean velocity of the tubes, L is the characteristic linear dimension of the tubes and D is the diffusion coefficient of tubes) of the Type A-D tubes in 2% H_2O_2 . The calculation of diffusion coefficients of the tubes was based on the method set up by Tirado *et al.*²⁶ The Peclet numbers of Type A-D tubes are 3.0×10^4 , 6.3×10^3 , 3.6×10^3 and 16.7, respectively, demonstrating the insignificant effect of Brownian motion. The smaller Peclet number of Type D tubes illustrates stronger effect of diffusion on the nanotubes than on bigger microtubes.

Figure 4.10 The propulsion of microtubes by one bubble growth and release cycle in 2% H_2O_2 . A) Different stages in one bubble propulsion cycle for a Type A microtube. B) Different stages in one bubble propulsion cycle for a Type B microtube. Images on the left side are acquired by a high speed camera at 30000 fps. Blue line indicates the position of the motor at $t = 0$. Graphs on the right side demonstrate the propelled distance of microtube by the bubble over time.

From the perspective of application, we still use average velocity to evaluate the mobility of micro/nanotubes. To obtain more accurate velocities, we only track the micro/nanotubes moving in one focal plane of the microscope. Figure 4.11 A shows the dependence of the absolute average velocity of Type A-D micro/nanotubes on H_2O_2 concentration. At relative low ranges of H_2O_2 concentration, the velocities of Type A-D micro/nanotubes all increased with the H_2O_2 concentration because of the increased decomposition rate. With increasing H_2O_2 concentration, the rise of micro/nanotubes velocity slowed down due to the gradually saturated coverage of the inner Pt surface, which displays a typical trend of Langmuir adsorption model. For the shorter Type C microtubes and Type D nanotubes, the limitations emerged at lower concentrations of H_2O_2 because of relative smaller catalytic area.

To study the general effect of geometric parameters on the motion of micro/nanotubes, Figure 4.11 B was plotted combining the geometric parameters shown in Table 4.2 and the average velocity from 2% to 9% H_2O_2 presented in Figure 4.11 A. The points indicating the four types of tubes at same concentration of H_2O_2 were linked to form a surface. The average opening diameter is the average value of the two

openings at opposite ends. As can be seen from the trend of these surfaces, for the small scale micro/nanotubes we investigated, the absolute average velocity, to a great extent, increases with the tube sizes. The advantage of larger microtubes in mobility becomes more apparent at higher concentrations of H_2O_2 , as limited catalytic area hinders the velocity increase of small tubes. The opening diameter and length influence both the driving force and the drag force of the microtubes. Although drag force resisting the motion of tubes will also increase with sizes, larger length or diameter provides larger catalytic area for the oxygen production to power the micro/nanotubes at a higher velocity. The large moving distance propelled by large bubbles as well as the high bubble ejection frequency offered Type A microtubes the highest average velocity among the four types of micro/nanotubes. It is evident that in the range we investigated, the effect of opening diameters on the mobility of tubes is more significant than that of length. The average velocity of Type B microtubes with larger lengths but smaller openings is lower than Type A microtubes. The influence of length can be observed through the comparison between Type B and Type C microtubes sharing similar opening sizes. As geometric parameters will also affect the bubble sizes, high oxygen production doesn't necessarily mean high bubble ejection frequency. As illustrated above, the bubbles ejected by Type B microtubes were larger than those ejected by Type C. Despite the larger catalytic area and higher oxygen production of the longer Type B microtubes, their bubble expulsion frequency is lower than the shorter Type C microtubes. The two types of microtubes sharing 2 μm openings displayed similar velocities below 7% H_2O_2 , but the limited catalytic area retarded further increase of the velocity of the shorter Type C microtubes at higher H_2O_2 concentrations.

Figure 4.11 C shows the dependence of average velocity by body length against the concentration of H_2O_2 . The average absolute velocity of the Type A microtubes was the highest, but as to body lengths per second, Type C microtubes with smaller opening and length displayed the highest velocity by body length. Type B microtubes with the largest average length were at a disadvantage in terms of velocity by body lengths. Consistent with the previously reported model, at such small scale micro/nanotubes studied here, the velocity by body lengths will decrease as the length of the motor increases.⁸ The tiny Type D nanotubes showed a very high average velocity by body lengths, but it was much lower than the prediction of the model. Possible reasons for the deviation are the trapping by the generated bubbles²⁷ and more significant effect of thermal noise on the nanotubes.^{28, 29}

Figure 4.11 A) The dependence of the average absolute average velocity of Type A-D micro/nanotubes on H₂O₂ concentration. B) Variation of average absolute velocity with average opening diameter of the two ends and length at different concentrations of H₂O₂. C) The dependence of the average velocity by body lengths of the Type A-D micro/nanotubes on H₂O₂ concentration. At least 30 measurements were taken into consideration for each velocity shown in figures. The error bars indicate standard deviation.

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Chapter 5

Development of new materials for fabrication of micro/nanomotors

5.1 *Introduction*

5.2 *Experimental section*

5.2.1 *Materials*

5.2.2 *Apparatus*

5.2.3 *Methods*

5.3 *Results and Discussion*

5.3.1 *Micromotors based on silver and manganese dioxide*

5.3.2 *Micromotors based on graphene*

5.3.3 *Micromotor based on MoS₂*

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1. **Hong Wang**, Guanjia Zhao, Martin Pumera*. Beyond Platinum: Bubble-Propelled Micromotors Based on Ag and MnO₂ Catalyst. *J. Am. Chem. Soc.* **2014**, *136*, 2719.

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2. **Hong Wang**, Zdenek Sofer, Alex Yong Sheng Eng, Martin Pumera*. Iridium-Catalyst-Based Autonomous Bubble-Propelled Graphene Micromotors with Ultralow Catalyst Loading. *Chem. Eur. J.* **2014**, *20*, 14946.

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3. **Hong Wang**, Zdenek Sofer, James Guo Sheng Moo, Martin Pumera*. Simultaneous Self-exfoliation and Autonomous Motion of MoS₂ Particles in Water. *Chem. Commun.* **2015**, *51*, 9899.

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The thesis author was the primary investigator and author of these papers.

5.1 Introduction

Despite the rapid development of micro/nanomotors, the current fabrication still mainly depends on platinum.¹ However, as a kind of noble metal, platinum possesses disadvantages of scarcity and high price. There are only few examples of using materials other than platinum. Sanchez *et al.* developed microtubes with immobilized enzyme on the inner surface to decompose H_2O_2 .² In spite of the innovative use of enzyme, drawbacks such as instability and limited lifetime exist. Complex Ti/Fe/Au/Ag tubular micromotors fabricated by rolling-up of nanomembranes were also reported previously.³ In principle, the development of self-propelled micro/nanomotors can be based on any reaction with gas production. The efforts to develop new materials and fuel have never been stopped. Reported examples include the motion of zinc micromotors in acid fuel,⁴ as well as the motion of aluminium and magnesium micromotors in water.^{5 - 7} The main disadvantage of non-catalyst micro/nanomotors is limited lifespan, as the building substrate will be consumed during motion.

From this viewpoint, materials as catalyst in the reaction are more favoured for the fabrication of micromotors. Considering the high cost of platinum material and related nanofabrication, we want to demonstrate that widely used inorganic materials can be used to prepare bubble-propelled motors. We showed that silver and manganese oxide can be used as catalyst to decompose H_2O_2 fuel efficiently. The generated bubbles lead to fast propulsion of the particles. Silver and manganese dioxide are very promising potential candidate materials for the fabrication of micromotors due to their low costs, excellent catalytic properties, high efficiency and long lifespan. Such

silver and manganese oxide based bubble-propelled micromotors exhibit fast movement even at 0.1% of H_2O_2 . These affordable catalysts offer the possibility of large scale preparation at low costs, which will facilitate widespread use of these motors in practical applications.

The emerging nanomaterials have brought up new opportunities for the development of micro/nanomotors. Graphene is one of the most promising nanomaterials which have been studied extensively. The combination of brand new materials with micromotor offers a platform with a new dimension of motion. In previously reported cases, the catalyst constitutes most of the mass of micromotor (from around 20% to 100%)⁸⁻¹⁰ and therefore the surfaces for functionalization are very limited. We developed a bubble-propelled graphene micromotor with very high surface area. The graphene was loaded with very low content of iridium, a new kind of catalyst, to decompose H_2O_2 . Despite the very low loading of Ir catalyst (0.54 at%), it enables fast movement of graphene microparticles with high surface area up to $316.2 \text{ m}^2/\text{g}$. The preparation of the micromotor is simple and accessible. The iridium catalytic sites catalyze the decomposition of hydrogen peroxide to generate oxygen bubbles, which provides propulsion thrust for the graphene microparticle. The low iridium catalyst loading as well as considerable surface area of the graphene micromotors provides new solutions for enhanced cargo delivery.

Two-dimensional (2D) transitional metal dichalcogenides (TMDCs) are another kind of attractive material which has been receiving growing interest because of their unique properties and exciting prospects. TMDCs have layered structures with strong

intralayer binding and weak interlayer bonding, which allows exfoliation into 2D nanosheets. Each monolayer consists of a transition metal atomic layer sandwiched by two atomic layers of chalcogens.¹¹ Because of the unique properties in a wide range of aspects,^{12, 13} TMDCs have attracted a great deal of effort to develop novel devices for desired applications.¹⁴ In the structure of molybdenum disulfide (MoS_2), a kind of TMDCs, each Mo atom is held by covalent bonds with six S-atoms in either a trigonal prismatic or octahedral system within the layers, whereas adjacent layers are connected by van der Waals interaction.¹⁵ There are great changes in properties from bulk MoS_2 to single layer MoS_2 .¹⁶ As the thickness of the material decreases, the band gap of MoS_2 will increase from an indirect band gap in the bulk form to a direct band gap in the monolayer.¹⁷ The direct band gap, large in-plane carrier mobility, high current on/off ratios, as well as robust mechanical properties of single layer MoS_2 ¹⁸⁻²¹ make it potentially interesting for practical applications ranging from field effect transistors^{22, 23} to optoelectronic devices.²⁴⁻²⁶

The great potential of MoS_2 in biomedical applications has been demonstrated recently. The loss of sulphur atoms lead to defect sites available for surface modification by thiolated compounds.²⁷ The high stability and non-cytotoxicity of MoS_2 nanosheets functionalized with lipoic acid-terminated polyethylene glycol (LA-PEG) makes in vivo applications possible.²⁸ Attributable to the strong near-infrared (NIR) absorbance and high surface area for loading of drugs, 2D MoS_2 exhibit great potential for combined photothermal and chemotherapy of cancer.²⁹ In clinic diagnosis and bioanalysis field, MoS_2 based biosensors have been involved in detection of DNA and other biomolecules.^{30, 31} Additionally, MoS_2 has also demonstrated the potential for

environmental remediation. The use of intercalated MoS_2 as redox-recyclable ion-exchange materials for extraction of heavy metal ions in solution has been reported.³² We reported a MoS_2 based motor able to exhibit simultaneous self-exfoliation and autonomous motion at the surface of water. Exfoliation of bulk MoS_2 into solution-phase 2D MoS_2 can be achieved by sodium intercalation. The self-propulsion of the MoS_2 particle in water is attributed to the surface tension gradients resulted from the naphthalene distributed in the particle. Integration of the self-exfoliation and propulsion in water without additional fuel thus results in a new platform which is promising for new applications of tiny motors and TMDC materials.

5.2 Experimental section

5.2.1 Materials

Silver powder, molybdenum (IV) oxide, molybdenum (VI) oxide, sodium dodecyl sulfate (SDS), sodium, *tert*-butyllithium (1.7M in pentane) and molybdenum disulfide were purchased from Sigma-Aldrich. Manganese dioxide, hydrogen peroxide (35%) and ammonium hexachloroiridate(IV) in spectroscopic purity grade were purchased from Alfa Aesar. Silver microparticles (average size of $\sim 35\ \mu\text{m}$) and MnO_2 microparticles (average size $\sim 5\ \mu\text{m}$) were used as received. Graphite oxide (GO) was from high purity microcrystalline graphite (2-15 μm , 99.9995%), Alfa Aesar, Germany. Sulfuric acid (98 %), potassium permanganate (> 99.5 %), sodium nitrate (>99.5%), naphthalene, THF and hydrochloric acid (37%) were obtained from Penta, Czech Republic. THF was dried by distillation from sodium-benzophenone mixture under argon atmosphere. Nitrogen (99.9999% purity) and hydrogen (99.9999% purity) were obtained from SIAD, Czech

Republic. Hexane was obtained from Lach-ner, Czech Republic. Naphthalene and THF were obtained from Penta, Czech Republic. THF was dried by distillation from sodium-benzophenone mixture under argon atmosphere. Chemicals were used as used without further purification and the solutions were prepared using ultrapure water (18.2 MΩ cm) generated from a Millipore Milli-Q purification system.

5.2.2 Apparatus

A JEOL JSM 7600F instrument was used to obtain scanning electron microscopy (SEM/EDX) analysis. A Phoibos 100 spectrometer with a magnesium X-ray radiation source (SPECS, Germany) was used to perform X-ray photoelectron spectroscopy (XPS). A Nikon Eclipse 50i microscope was used to obtain optical microscope images and videos. Nikon NIS-Elements software was used for processing video sequences. A sorption analyzer Coulter SA 3100 (Backman Coulter) was used for measuring surface area. Before the sorption experiments, outgassing of the samples were performed for 4 hours at 150 °C under high vacuum (VALUE). The temperature is set very low because degradation and decomposition of oxygen functionalities may happen on graphene. BET analysis was conducted with a TCD nitrogen cooled (77 K) detector. XRF analysis was performed using Axios sequential WD-XRF spectrometer equipped with an Rh anode end-window X-ray tube fitted with 50 μm Be window. SuperQ software was used to collect all 11 scans covering 79 measured elements in vacuum. Evaluation of the obtained data was processed with standardless software Omnian. Multimode 8 (Brukers, USA) was used to perform atomic force microscopy analysis with ScanAsyst mode.

5.2.3 Procedures

Synthesis of Graphite Oxide. Five grams of graphite and 2.5g of NaNO_3 were mixed together with 115 ml of concentrated sulfuric acid under stirring. After cooling down to 0 °C, 15g of KMnO_4 was added with vigorous stirring and kept for 2 h. Subsequently, the resulting mixture was cooled down to reach room temperature before heating to 35 °C for 30 min. After that, the mixture was poured into a flask containing 250 mL of deionized water and heated to 70 °C for 15 min, followed by the addition of 1L of deionized water. Removal of the remaining KMnO_4 and MnO_2 was accomplished by the addition of 3 % H_2O_2 . After precipitation, the supernatant was discarded. The resulting graphite oxide was then collected by repeatedly washing with deionized water and centrifugation. The graphite oxide was then dried in a vacuum oven at 50 °C for 2 days.

Synthesis of iridium-doped graphene. Two hundred milligrams of graphite oxide was ultrasonicated in 50 ml water for 30 minutes at 400 W. To the graphite oxide suspension was added Ir precursor $(\text{NH}_4)_2[\text{IrCl}_6]$. The reaction mixture was ultrasonicated for 10 minutes at 400 W followed by evaporation of water in vacuum oven at 50°C for 72 hours. In a vacuum-tight quartz glass reactor, thermal exfoliation of the dried precursor was conducted under controlled atmosphere. Equipped with a porous quartz glass capsule, the reactor is connected to a magnetic manipulator. The setup is able to produce a temperature gradient over 1000 °C/min. The thermal exfoliation was carried out at 1000 °C for 12 minutes under a pressure of 100 kPa. One hundred milligram of HU GO/Ir precursor composite was put into porous quartz glass capsule, followed by flushing the capsule with high purity N_2 for several times and finally filling with H_2 . The sample was

then placed into the preheated furnace with H_2 atmosphere. To remove reaction byproduct, a hydrogen flow 1000 mL/min was used.

Synthesis of MoS_2 motors. Eight grams of naphthalene was dissolved in 100 ml of dry tetrahydrofuran, followed by addition of 1.4 g of sodium. After stirring for 1 hour, to the resulting mixture was added 2.0 g of MoS_2 , after which the solution was further stirred for 12 hours. Suction filtration was used to get the obtained sodium intercalated MoS_2 and it was dried at room temperature. The lithium intercalated MoS_2 in control experiment was prepared by stirring 3 g bulk powder in 20 mL of 1.7 M t-buthyllithium in pentane at 25°C for 3 days. The obtained compound was subsequently separated by suction filtration, followed by repeatedly washing with dried hexane. Glovebox with argon atmosphere was used for all operation.

Motion study. For the motion study of Ag and MnO_2 micromotors, on a clean glass slide freshly was applied a mixture of Ag, MnO_2 and particles for control experiment (1mg/mL), SDS (0.5 wt%) and various concentrations of H_2O_2 . For the graphene micromotors, the motion study was conducted in an aqueous solution of 3% H_2O_2 and 1% SDS. Iridium graphenes (5.6×10^{-5} mg/ μ L), H_2O_2 , SDS, and water were mixed together and applied on a clean glass slide for observation. A Nikon Eclipse 50i microscope was used to obtain optical microscope videos and images. For each of the data points in figures, 6 measurements were taken into account. The motion study of MoS_2 motor was carried out in contained filled with deionized water and a Cannon Ixus 110 camera was used to capture videos and images. Nikon NIS-ElementsTM software was used to process all the video sequences. The velocity data presented was obtained from

at least 6 independent experiments. The error bars indicate standard deviation.

5.3 Results and Discussion

5.3.1 Micromotors based on silver and manganese dioxide

We first described a silver based bubble propelled micromotors. Time-lapse images of the motion of a silver motor in 9% H_2O_2 are shown in Figure 5.1 A. The size of the micromotor in Figure 5.1 A is 20 μm . The silver surface catalyzes the decomposition of H_2O_2 to generate O_2 bubbles, enabling the release of bubbles from one side of the particle. Asymmetry is a key feature of the structure of micro/nanomotors. The asymmetry of spherical Janus motors is usually achieved by a partial coating of inert material, which will lead to asymmetric bubble generation. The absence of the inert coating results in lack of asymmetric bubble thrust, thus causing no directional movement. Although the silver micromotors described here do not have inert coating, they also process the feature of inhomogeneity and asymmetry. The geometry of the motors has a strong influence on bubble generation. Reaching heterogeneous nucleation energy of gases is the prerequisite of bubble nucleation on solid surface. Heterogeneous nucleation energy is related to both the curvature of the surface and the gas saturation concentration. Bubble formation on flat surface requires less energy than on convex surface while bubble formation on concave surface needs even less energy.^{33, 34} We tried coating one side of the Ag micromotors with Au via sputtering, nevertheless, no improvement in mobility was observed relative to the unsputtered ones, which reflects the instinctive morphology of the particles is more important for bubble generation. As reported earlier in the case of microtubes, the silver catalytic

micromotors can exhibit three typical kinds of motion including curved, circular, and self-rotating motions. The different kinds of motion are resulted from the differences in shape, size, and geometry of the micromotor.

Figure 5.1 Motion of silver micromotors. (A) Optical images of the motion of a silver micromotor in 9% H_2O_2 and 0.5 % SDS solution for 3s. Scale bar is 50 μm . (B) Influence of H_2O_2 concentration on the average velocity of silver catalytic micromotors. All experiments were conducted at 23 $^\circ\text{C}$

The H_2O_2 fuel concentration has a great influence on the velocity of silver micromotors. Figure 5.1 B shows the dependence of the average speed of moving silver micromotors on H_2O_2 fuel concentration. As expected, the average velocity of silver micromotors exhibited an increasing trend with an increase of H_2O_2 concentration. The mobility of micromotors and the proportion of moving particles among all the particles depend on both the instinctive morphology of the particles and H_2O_2 fuel concentration. The silver micromotors can exhibit motion at a very low concentration of H_2O_2 down to 0.5%. Figure 5.2 A illustrates the tracking image of the trajectory of a silver catalytic micromotor in 0.5% H_2O_2 for 2s. The velocity by body lengths/s provides a way to evaluate the velocity of motors in spite of different sizes. The trend of velocity expressed in body lengths/s upon H_2O_2 concentration is shown in Figure 5.2 B.

Figure 5.2 A) Tracking image of a silver catalytic micromotor in 0.5% H_2O_2 and 0.5% SDS solution over a 2 s. Scale bar is 50 μm . B) Dependence of the average velocity (body lengths/s) of silver micromotors on H_2O_2 concentration. C) Dependence of the viability of silver micromotors on H_2O_2 concentration. All experiments were conducted at 23 $^{\circ}C$. D) SEM images of the Ag micromotors. Scale bar is 100 μm .

Increasing the concentration of H_2O_2 will cause an obvious increase in the mobility of silver micromotors. The powerful bubble propulsion mechanism provides the silver micromotors very high mobility in comparison with the previously reported Pt catalytic Janus motors powered by diffusiophoresis mechanism.³⁵⁻³⁷ Silver micromotors can exhibit motion at an average velocity of $\sim 25 \mu m/s$ even at 0.1% H_2O_2 and the average velocity of moving silver micromotors can reach over 100 $\mu m/s$ in 12% H_2O_2 . The high bubble frequency shows the high efficiency of silver to catalyze the decomposition of H_2O_2 . Taken the good performance and low costs into consideration, silver has great potential to become an alternative catalyst for fabrication of

micro/nanomotors. However, it should be noted that decreasing the concentration of fuel will decrease the percentage of the particles exhibiting motion, as shown in Figure 5.2 C. SEM images of the silver micromotors are shown in Figure 5.2 D.

Figure 5.3 Motion of manganese dioxide catalytic micromotor. (A) Frames from video of motion of manganese dioxide catalytic motor in 15% H_2O_2 and 0.5% SDS solution at 23 °C. Scale bar: 20 μm . (B) Dependence of the average speed of manganese dioxide catalytic micromotors on H_2O_2 concentration at 23 °C.

Another well-known catalyst for decomposition of H_2O_2 is manganese dioxide, which is more cost-effective and accessible compared to noble metals usually used in the fabrication of micro/nanomotors. MnO_2 is widely used for preparation of cheap carbon/ MnO_2 batteries in industry.³⁸ The mobility of micromotors based on MnO_2 microparticles in H_2O_2 was investigated. MnO_2 micromotors display oxygen bubble propelled motion similar to silver particles. However, the percentage of MnO_2 micromotors exhibiting motion is much less than that for Ag particles and efficient propulsion of MnO_2 micromotors requires higher concentration of H_2O_2 . Figure 5.3 A shows time-lapse images of the motion of a MnO_2 micromotor in 15% H_2O_2 . The size of the micromotor in Figure 5.3 A is 5 μm . As shown in Figure 5.3 B, the average velocity of MnO_2 micromotors exhibiting motion increased from $\sim 50 \mu\text{m/s}$ in 12% H_2O_2 to $\sim 120 \mu\text{m/s}$ in 21% H_2O_2 . Figure 5.4 A illustrates the tracking of a MnO_2 micromotor in 21% H_2O_2 for 2s time interval and Figure 5.4 B shows dependence of the velocity in body lengths/s on fuel concentration. SEM images of the MnO_2 micromotors are shown in Figure 5.4 C and D. The percentage of moving MnO_2 micromotors also increased with increasing H_2O_2 concentration. Nonetheless, the good mobility of MnO_2 micromotors shows that MnO_2 is a promising material for the preparation of micro/nanomotors if appropriate modification in morphology is made.

Figure 5.4 A) Tracking image of a MnO₂ catalytic micromotor in 21% H₂O₂ and 0.5% SDS solution over a 2 s. Scale bar is 50 μm. B) Dependence of the average velocity in body lengths/s of MnO₂ micromotors on H₂O₂ concentration. All experiments were conducted at 23 °C. C) and D) are SEM images of the MnO₂ micromotors. Scale bar is 10 μm in C and 1 μm in D.

As shown in Figure 5.5, to verify that the movement is due to the propulsion by oxygen bubbles generated *via* catalytic decomposition of H₂O₂, various control experiments were conducted. No bubble generation and movement were observed for MoO₂ and MoO₃ in 21% H₂O₂ and 0.5% SDS, because molybdenum oxides lack catalytic properties. Likewise, in the absence of H₂O₂, MnO₂ and Ag particles did not exhibit bubble propulsion. In comparison, the behaviour of MnO₂ and Ag particles in the presence of H₂O₂ reveals efficient bubble propulsion associated with their excellent catalytic properties.

Figure 5.5 Control experiments : (A) Ag and (B) MnO_2 particles in 0.5% SDS solution without H_2O_2 ; (C) MoO_3 and (D) MoO_2 particles in 21% H_2O_2 and 0.5% SDS solution. Scale bars are 50 μm . All experiments were conducted at a temperature of 23 $^\circ\text{C}$ and particle concentrations are 1mg/mL.

The parabolic dependence of the mean square displacement (MSD) of both Ag and MnO_2 motors on time interval proves that the movement is due to bubble propulsion instead of Brownian motion.³⁹ According to the previously reported method, the efficiency of the Ag motor in 9% of H_2O_2 was calculated to be 5.81×10^{-8} while efficiency of MnO_2 motor in 12% H_2O_2 was 1.16×10^{-8} .⁴⁰ Compared to previously reported efficiency of bubble propelled tubular micromotors (2.4×10^{-10}) and Janus particles moving by diffusiophoresis (5×10^{-10}), the Ag and MnO_2 micromotors are in the position of advantage. Less prone to poisoning is another advantage of Ag and MnO_2 materials over Pt. It has been previously reported that Pt based tubular micromotors are vulnerable to thiol poisoning even at micromolar concentration of thiols.⁴¹ We compared the motion of Ag motors in 3% H_2O_2 before and after adding 10 mM of cysteine. The velocity of Ag motors did not have significant difference. Likewise, MnO_2 is not prone to thiol poisoning. It should be noted that Ag and MnO_2 only act as catalyst

and the micromotors stop their motion only when the fuel is exhausted. If the fuel is replenished, the bubble-propelled motion is resumed and micromotors can exhibit motion with the same agility over the span of whole experiment.

5.3.2 Micromotors based on graphene

In order to fabricate iridium-based graphene micromotors, graphite was first oxidized to graphite oxide *via* Hummers method using KMnO_4 in concentrated H_2SO_4 and NaNO_3 . Subsequently, in $(\text{NH}_4)_2[\text{IrCl}_6]$ solutions was added the graphite oxide to form iridium-doped graphite oxide precursors. Thermal exfoliation of the precursors was conducted under a flow of hydrogen gas at 1000°C to produce iridium-doped graphenes. Due to the catalytic property of iridium in the graphenes, the graphene microparticles can display bubble-propelled motion in H_2O_2 .

SEM was conducted to study the morphology of the graphene micromotors. As illustrated in Figure 5.6 A-D, images were taken at different magnifications of $3000\times$, $10000\times$, $30000\times$ and $1500\times$. From the SEM images, it can be seen that the graphene micromotors have typical exfoliated structures with high surface area and the sizes are relatively uniform. Through BET measurements, the surface area of iridium-doped graphene was determined to be $316.2\text{ m}^2/\text{g}$. The H_2O_2 fuel is able to reach the iridium catalytic sites through the gaps between the sheets. The irregular shapes of the particles allow asymmetric distribution iridium catalyst, which is essential for directional motion. EDX elemental mapping analysis of carbon, oxygen and iridium are shown in Figure 5.6 E-G, respectively. The presence of iridium in the graphenes was confirmed by the EDX data. The composition of exfoliated Ir-doped graphene was 90.37 at% C, 0.35 at% N,

7.34 at% H, 1.40 at% O and 0.54 at% Ir. The exfoliated structure of graphene particles enables the decomposition of H_2O_2 at iridium catalytic sites and thus generation of oxygen bubbles to provide continuous thrust.

Figure 5.6 A-D) SEM images and E-G) EDX analysis of prepared graphene micromotors. SEM images were acquired at A) 3000 $\times$, B) 10000 $\times$, C) 30000 $\times$ and D) 1500 $\times$ and scale bars are 1 μm , 1 μm , 100 nm and 10 μm , respectively.

It should be noted that IUPAC defined graphene as semi-infinite sheet of sp^2 hybridized carbon which should be planar theoretically.⁴² However, actually in the preparation process of graphene, there are defective pentagon/heptagon rings resulting in curvature and crumpled structure of graphene.⁴³ Most of studies in related publications have been conducted on graphene in this morphology. In many cases, the crumpled structure is favorable due to the prevention of re-stacking of graphene layers.^{44, 45} Under the synthetic conditions in our study, vast majority of the prepared motors show the form of particles with size of $\sim 20 \mu\text{m}$. The fabricated Ir catalyst based graphene micromotors are essentially different from the previously reported rolled-up micromotor with a graphite oxide layer and a Pt layer,⁴⁶ because the one we studied here works on the principle of Janus particles while the previous one on the principle of

microjets.

X-ray photoelectron spectroscopy was carried out for further investigation on the elemental composition of the graphene micromotors. In order to detect the elements present on the surface, a wide-range XPS scan was first conducted. As shown in Figure 5.7 A, the major peaks that can be observed are a C 1s peak at 284.5 eV, an O 1s peak at 532.5 eV and an Ir 4f peak. High-resolution XPS measurements were also conducted to study the valence state of the doped iridium (Figure 5.7 B). The Ir 4f peak is actually composed of two peaks, which can be clearly seen from the high-resolution XPS spectra. The values for 4f $7/2$ and 4f $5/2$ of metallic Ir (61.35 and 64.35 eV) are very close to the two peaks located at 61.5 and 64.5 eV, respectively.⁴⁷ For IrOx, because of the binding of Ir to the electron-withdrawing O atom, the Ir peaks will be shifted to 62.35 and 65.35 eV.⁴⁷ Consequently, a conclusion can be drawn that most of the iridium in the prepared graphene micromotors is in metallic form instead of the metal oxide.

Figure 5.7 A) Wide-scan XPS and B) Ir 4f high-resolution XPS of prepared graphene micromotors.

Study of the self-propulsion of the iridium-based graphene micromotors was performed under microscope. As can be seen from Figure 5.8, the prepared graphene

micromotors are particles with size of $\sim 20\ \mu\text{m}$ under 10X magnification. The function of Ir dopant is to serve as a catalyst for decomposition of H_2O_2 to generate O_2 . The graphene micromotors demonstrated here work on the bases of bubble-propelled Janus particles. Figure 5.8 A shows the tracking image of the motion of the graphene micromotor in 3% H_2O_2 and 1% SDS over 10 s. It can be seen from the image that the motion of the graphene micromotor is propelled by continuous bubble thrust, unlike the motion of iridium Janus particle in hydrazine powered by diffusiophoresis.⁴⁸ The different tails of bubbles with different sizes illustrates that the graphene micromotor has multiple channels for H_2O_2 to reach various catalytic sites to be decomposed. The asymmetric placement of iridium in the graphene enables bubble generation from one side of the micromotor, thus creating the asymmetric bubble thrust required for directional motion. The iridium-based graphene micromotor exhibited autonomous motion with an average speed of $\sim 40\ \mu\text{m/s}$, corresponding to about 2 body lengths per second. In comparison, no obvious movement was observed for the graphene particles without iridium under microscope. Although Brownian motion is remarkable for objects at nanoscale, it is insignificant for the $20\ \mu\text{m}$ sized graphene particles studied here.

Figure 5.8 Tracking of A) an iridium-doped graphene micromotor and B) a plain

graphene particle in 3% H_2O_2 and 1% SDS for a 10 s interval. Scale bars are 50 μm .

To have a deeper understanding of the motion of graphene micromotors, we plotted the mean square displacement (MSD) of the iridium-doped graphene micromotor and the plain graphene particle against time interval in Figure 5.9. The motion was recorded by a camera connected to the microscope and then tracked using a software. Based on the Einstein's equation for Brownian motion in 2-dimensions, $\Delta L^2 = 4D\Delta t$, the MSD resulting from Brownian motion has a linear relationship with time.^{49, 50} The MSD plot vs. Δt for the graphene particle without iridium shows a straight line, illustrating that the insignificant motion of the particle was only due to Brownian motion. The displacement of a particle exhibiting directional motion is $d = vt$, and hence the MSD is proportional to the square-root of time. The MSD plot for the iridium-doped graphene micromotor under the same conditions shows an upward curvature, indicating the effective bubble propulsion.^{49, 50} The percentage of active graphene micromotors has a dependence on the concentration of H_2O_2 . With increasing the concentration of H_2O_2 , more graphene particles will display bubble-propelled motion. Figure 4B shows the dependence of the percentage of graphene micromotors against H_2O_2 concentration. The percentage of moving micromotors in 9% H_2O_2 is defined to 100%.

Figure 5.9 A) Plots of MSD against time interval for (a) iridium-doped graphene micromotor and (b) the plain graphene in 3% H₂O₂ and 1% SDS. B) The dependence of the percentage of active graphene motors on H₂O₂ concentration.

5.3.3 Micromotor based on MoS₂

Exfoliation into 2D MoS₂ is an important step towards realizing applications. Mechanical exfoliation is a way of obtaining high purity MoS₂ monolayers by peeling from bulk crystals using adhesive tapes, but it has the disadvantage of lack of control and scalability.⁵¹⁻⁵³ An alternative way to prepare 2D nanosheets in large scale is solution-phase exfoliation.⁵⁴⁻⁵⁶ On the other hand, in the field of micro/nanomotors, the widely used toxic H₂O₂ fuel retards their use in practical applications. Alternative fuels, such as hydrazine, I₂, Br₂, as well as acidic and alkaline solutions,⁵⁷⁻⁵⁹ have been brought up to replace H₂O₂.

The intercalation of alkali metal into MoS₂ enables exfoliation in liquid. The intercalation can be accomplished by either use of hot alkali metal vapor⁶⁰ or through soaking in a solution of the corresponding alkali metal-containing compound, usually in solvated metal ammonia solution or a hexane solution of butyl lithium.^{61, 62} An electrochemical intercalation approach capable of monitoring and controlling the intercalation process has also been reported.⁵⁶ The intercalation of alkali metal into MoS₂ makes the material ready for exfoliation. Once exposed to water, the intercalated material will be separated into layers by H₂ gas evolution, leading to a dispersed suspension of 2D sheets of MoS₂.

In our study, sodium intercalation was achieved with the use of sodium

naphthalenide. The intercalation process can be considered as an ion/electron transfer topotactic reaction. The driving force for the intercalation is thought to be the trend of charge transfer from sodium to the MoS₂ lattice.^{15, 60} The electrons are transferred from sodium to the lowest lying unoccupied energy levels, mainly transition metal d bands, of the host MoS₂. For sodium naphthalenide, an electron transfer agent, one electron is transferred from sodium to the aromatic system and results in a radical anion which is an electron donor with strong reducing properties. The electron from sodium is expected to transfer to MoS₂ through the radical anion, followed by the intercalation of sodium ion to balance the charge.⁶³ In addition to the electron transfer, intercalation also leads to the expansion of the interlayer spacing and weakening of van der Waals interactions between the layers.⁶⁰ In order to fabricate the MoS₂ motor, MoS₂ bulk material was submerged in tetrahydrofuran solutions of sodium naphthalenide to intercalate sodium into the laminar structure. Scanning electron microscopy (SEM) was performed to study the morphology of the prepared sodium intercalated MoS₂. The surface characteristics of the intercalated MoS₂ before exfoliation were shown in Figure 5.10 A, B and C at different magnifications. The bulk MoS₂ are stacks of numerous micro-sized plates and each plate actually consists of many monosheets of MoS₂. It is reported that the typical thickness of a single layer MoS₂ is less than 1 nm.⁶⁴

The sodium intercalated MoS₂ shows an excellent exfoliation ability in water. The exfoliation is not only a mechanical process, but also a chemical process based on redox reactions. The separation of MoS₂ layers is forced by hydrogen gas generated by the reaction of water with the intercalated sodium between the layers.⁶⁵ At the same time, the MoS₂ layers experience oxidation as well as hydration.^{15, 60} With the proceeding of

the reaction further into interlayer spaces, spatial separation of the layers increases and finally forms individual single layer or few layers of MoS_2 , leading to a colloiddally dispersed suspension. The MoS_2 particles used in our study have an average diameter of around 2.5 μm . Upon immersing in water, the particles will start self-exfoliation process. The optical image of the formed aqueous MoS_2 dispersion is shown in Figure 5.10 D. It contains MoS_2 flakes with varied exfoliation degrees and the difference in their thickness resulted from the number of layers can be seen from the optical contrast of the flakes. The existence of exfoliated flakes with smaller size, as shown in Figure 5.10 E and F, was proved by scanning transmission electron microscopy (STEM). Figure 5.10 E shows some partially exfoliated MoS_2 flakes while Figure 5.10 F displays more transparent flakes with higher degrees of exfoliation.

Figure 5.10 A-C) SEM images of the MoS_2 microparticles before exfoliation. Scale bars are 10 μm , 1 μm and 1 μm , respectively. D) Optical image of aqueous dispersion of exfoliated MoS_2 . Scale bar is 10 μm . E, F) STEM images of exfoliated MoS_2 . Scale bars are 1 μm and 100 nm, respectively.

Once exposed to water, the MoS_2 particles will display fast movement and simultaneous exfoliation. The motion of the MoS_2 particles in deionized water can be either translational or rotational, as the trajectories shown in Figure 5.11. Due to the exfoliation of sodium intercalated MoS_2 in water, the size of the particle keeps decreasing during motion until the particle totally disappears. Consequently, the lifespan of the MoS_2 particle is affected by the particle size. Generally, it needs more time for the exfoliation of larger MoS_2 particles and therefore larger particles have longer lifetimes. In our study, the MoS_2 particles have an average diameter of 2.5 μm and the motion can last for 20-30 seconds. Although molecular hydrogen and sodium hydroxide are generated by the reaction of intercalated sodium with water, bubbles were not observed during the motion even under microscope, which proves that bubble propulsion is not the main driving force for the motion.

Figure 5.11 Trajectories of the motion of MoS_2 particles in water. A) Translational motion of a MoS_2 particle for 10s. B) Rotational motion of a MoS_2 particle for 2 s. Scale bars are 1 cm.

The asymmetric distribution of sodium intercalated in the MoS_2 particle will result in a concentration gradient of reaction products around the particle during

exfoliation in water. Nonetheless, the effect of diffusiophoresis at such large length scale is not as significant as that in low Reynolds number environment.⁶⁶ Lithium intercalated MoS₂ particle prepared using t-butyl lithium as lithiation agent was employed to conduct control experiment. No motion was observed for the control particle in water, which further excludes the contribution of concentration gradient. Because the MoS₂ particles only exhibit motion at the water surface, Marangoni effect is proposed to be the main driving force for the motion. Naphthalene, an organic compound, was involved in the preparation process. It exists as white crystalline solid at room temperature and has a solubility of 31.6 mg/L in water at 25°C. The motion of a droplet or particle at an interface induced by Marangoni effect has been widely studied.⁶⁷⁻⁷¹ The asymmetric distribution of the surface tension altering material will generate surface tension gradients around the droplet or particle, providing the driving force for the motion. Solid grains of acetylnaphthalene and dihydroxynaphthalene were used to perform control experiment. Their self-propulsion on the surface of water demonstrates the feasibility of Marangoni effect to propel naphthalene derivatives grains. The motion is attributed to the anisotropic distribution of the organic molecules developing asymmetrically from the solid. The generated surface tension heterogeneity will result in motion along the chemical gradient. Likewise, for the MoS₂ motor, the naphthalene molecules developing from the asymmetric distributed naphthalene in the particle generates a surface tension gradient in the surrounding, leading to propulsion of the particle. Greater intermolecular forces exist in a region of higher surface tension. The pulling force from the liquid with a higher surface tension is stronger on the surrounding than that of the liquid with lower surface tension. Consequently, the object will be propelled along the surface tension

gradient towards regions of higher surface tension, where there is lower density of naphthalene.

The simultaneous motion and exfoliation of the MoS_2 particle is illustrated in Figure 5. 12. The motion and exfoliation are actually two distinct processes resulted from two different constituents in the MoS_2 particle. Exfoliation is due to the reaction between intercalated sodium and water while motion is attributed to the concentration gradient of naphthalene developing from the particle. Once immersed in water, the two processes occurred concomitantly, leading to simultaneous exfoliation and motion of the MoS_2 particles. The MoS_2 motor demonstrated here opens a door for fabrication of TMDC based motors through encapsulation of surface tension altering reagents. The motion induced by Marangoni effect can be carried out in non-modified aqueous environment without adding external fuel and surfactants. The exfoliation during motion offers considerable 2D MoS_2 nanolayers for subsequent processing steps. Coupling of the self-propulsion of the MoS_2 motors and their autonomous exfoliation into 2D sheets provides a new platform for potential applications.

Figure 5.12 Schematic illustration of the autonomous motion and simultaneous self-exfoliation of the MoS₂ motor at water surface.

The different motion behaviors of the MoS₂ particles are attributed to the differences in the particle shape and naphthalene distribution inside. The low solubility of naphthalene is very low and only a small amount of naphthalene is able to induce the surface tension gradient needed for the motion of the particle. On the other hand, it takes a very short time for the exfoliation of MoS₂. As a result, different from agglomerates only consisting of diphenylhydrazine,⁶⁸ the lifetime of the MoS₂ motor is not decided by the amount of surface altering material naphthalene. The lifetime is directly determined by the time required for exfoliation of the entire particle, while the mobility of the motor mainly depends on the distribution of naphthalene. The velocity of the particle is related to the concentration gradient of naphthalene that develops from the MoS₂ particle. The distribution of instantaneous speeds of the particle in Figure 5.11 A over time is shown in Figure 5.13. The speed is calculated by dividing the moving distance by the interval between sequential video frames (30 frames/s). In spite of fluctuation, most of the instantaneous speeds of the tracked MoS₂ motor are in the region of around 3 cm/s due to the gradual release of naphthalene. Nevertheless, with the increasing of the naphthalene concentration on the surface of water during motion, the velocity exhibits a slightly decreasing trend because of the reduction of surface tension gradient in the surrounding. The particle can stall for a while once reaching a temporal equilibrium state. When changes in the distribution of naphthalene layer break the balanced state, the particle will resume motion. The average speed acquired from 20 MoS₂ motors over the first 10s is about 2.3 cm/s. In addition, as shown in Figure

5.13 B, atomic force microscopy (AFM) was used to characterize the exfoliated flakes and their average thickness is around 1.4 nm.

Figure 5.13 A) Distribution of instantaneous speed of the MoS₂ motor in Figure 2A over 10s. Time interval is 0.1s. B) AFM image of Na-exfoliated MoS₂ flakes. Height profile along the yellow line is overlaid on the image.

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Chapter 6

Influence of environment on the mobility of tubular micromotors

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6.3.4 *Influence of surfactants on the mobility of microtubes*

The results in this chapter were published in the following manuscripts:

1. **Hong Wang**, Guanjia Zhao, Martin Pumera*. Blood Proteins Strongly Reduce the Mobility of Artificial Self-Propelled Micromotors. *Chem. Eur. J.* **2013**, *19*, 16756.

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2. **Hong Wang**, Guanjia Zhao and Martin Pumera*. Blood electrolytes exhibit a strong influence on the mobility of artificial catalytic microengines. *Phys. Chem. Chem. Phys.* **2013**, *15*, 17277.

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3. **Hong Wang**, Guanjia Zhao, Martin Pumera*. Blood metabolite strongly suppresses motion of electrochemically deposited catalytic self-propelled microjet engines. *Electrochem. Commun.* **2014**, *38*, 128.

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4. **Hong Wang**, Guanjia Zhao, Martin Pumera*. Crucial Role of Surfactants in Bubble-Propelled Microengines. *J. Phys. Chem. C* **2014**, *118*, 5268.

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The thesis author was the primary investigator and author of these papers.

6.1 Introduction

Investigation on the influence of real environments upon the motion of micro/nanomotors is of great significance as they are expected to perform tasks in complex media. Study on the navigation profiles of these self-propelled microengines in blood samples is important for future practical applications involving *in vivo* biomedical procedures. Although remarkable progress towards this goal has been made during the past decade, there are still a lot of problems to overcome. The question of whether the constituents in blood samples would influence the motion of micromotors is seldom studied. Previous studies in our group have shown that the motion of tubular micromotors in both whole blood and blood serum samples is severely hindered, even at very high dilutions.¹ This led us to investigate the possible source of retarded motion of tubular micromotors in blood serum. Blood proteins are important components of serum. Serum albumin is the most rich blood plasma protein and constitutes a percentage of around 50% of mammalian plasma protein. Serum albumin has important roles in helping sustain normal physiological functions such as the regulation of blood volume through retaining colloid osmotic pressure of the blood compartment.² Additionally, γ -globulins are another major component of blood proteins. Immunoglobulins are the key part in the γ -globulins family. As micromotors are envisioned to be employed *in vivo* for biomedical tasks, careful investigations on the impact of serum albumin and γ -globulin on the viability and mobility of micromotors are essential.³

Blood electrolytes are also crucial constituents of serum. Electrolytes in our body

mainly consist of potassium (K^+), sodium (Na^+), calcium (Ca^{2+}), hydrogen phosphate (HPO_4^{2-}), dihydrogen phosphate ($H_2PO_4^-$), chloride (Cl^-), and sulfate (SO_4^{2-}). These electrolytes are involved in a series of physical processes such as regulation of nerve and muscle function, blood pressure, blood pH, hydration level and rebuilding of damaged tissues. As such, keeping the balance of electrolytes is crucial for maintaining regular cell and organ functions. Furthermore, so as to perform these functions, some ions exist in high concentration levels. For example, the concentration of sodium ion in blood is 135-145 mM.⁴ Actually, various mechanisms in the human body keep the concentrations of these electrolytes under stringent control. We examined the influence of these electrolytes on the mobility of bubble-propelled micromotors when they are present at physiological level. The results provide important implications for the functioning of micromotors in high-ionic environments.⁵

In addition to plasma proteins and blood electrolytes, another important component in blood serum that cannot be overlooked is metabolite. Such small metabolite molecules could also potentially influence the motion of micromotors. One of the blood metabolites is uric acid, which is a significant biomarker in medical examination. It is associated with health conditions including diabetes, gout, and kidney stones. Previous studies showed that uric acid can act as a H_2O_2 stabilizer and radical scavenger. These capabilities may reduce the activity of micromotors relying on H_2O_2 fuel to achieve propulsion.⁶

Surfactant is essential for the motion of bubble-propelled micromotors. In spite of numerous researches on development of new materials to fabricate micromotors,⁷⁻¹¹

surfactants have received little attention. Surfactants can change the interface free energy remarkably by absorbing onto the interfaces of a system. The interface free energy is the minimum amount of work needed to expand or create that interface.¹² The oxygen bubbles generated via catalytic reaction on the inner platinum surface propel the motion of tubular micromotors. Upon the addition of surfactants, surfactant molecules will decrease the interfacial free energy by absorbing onto the inner surface of the microtubes, which can facilitate the formation and detachment of the bubbles. In the absence of surfactants, no obvious bubble propulsion was observed for microtubes, which clearly demonstrates that surfactants are of great significance in the motion of bubble-propelled micromotors. For micromotors depending on electrophoresis and diffusiophoresis, e. g. nanorods and some Janus particles, surfactants are generally not a necessity. The types and amounts of surfactants used in previous studies are random to some degree. As such, we conducted systematic study on the influence of surfactants property and concentration on the motion of bubble-propelled microtubes.¹³

6.2 Experimental section

6.2.1 Materials

Template cyclopore polycarbonate membranes with pore diameter of 2 μm were obtained from Whatman, USA. Colloidal graphite in isopropanol base was obtained from Ted Pella, Inc. USA. Ethanol and methylene chloride were purchased from Tedia, USA. Pt electrodes with a diameter of 1 mm and Ag/AgCl/1M KCl reference electrodes were purchased from CH instruments, USA. Hydrogen peroxide (27 %) was purchased from Alfa Aesar, Singapore. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (98+%), sodium dodecyl sulfate (SDS), bovine serum

albumin, γ -globulins from bovine blood, glucose oxidase from *Aspergillus niger* (type X-S), NaCl, CaCl_2 , KCl, K_2HPO_4 , Na_2HPO_4 , Na_2SO_4 , uric acid, cetyltrimonium bromide (CTAB) and Tween 20 were purchased from Sigma-Aldrich. The platinum plating solution was obtained from Technic Inc., USA. Chemicals were used without further purification and all solutions were prepared using ultrapure deionized water (18.2 M Ω cm) generated from a Millipore Milli-Q purification system.

6.2.2 Apparatus

Electrochemical deposition was performed on a μ Autolab type III electrochemical analyzer (Eco Chemie, The Netherlands) connected to a computer and controlled by General Purpose Electrochemical Systems version 4.9 software (Eco Chemie). All the experiments were conducted at room temperature (23 °C). The electrodeposition set-up is a three-electrode arrangement, where Ag/AgCl was utilized as the reference electrode and a platinum electrode was employed as a counter electrode. A Fisher brand FB 11203 ultrasonicator was used for the ultrasonication and centrifugation was performed on a Beckman Coulter Allegra 64R centrifuge. A JEOL JSM 7600F instrument was used to acquire scanning electron microscopy (SEM/EDX) analysis. A Nikon Eclipse 50i microscope was used to obtain optical microscope videos and images. Resulting video sequences and images were processed with Nikon NIS-Elements software.

6.2.3 Procedures

Preparation of Cu/Pt concentric microtubes. The Cu/Pt concentric microtubes employed in the studies were prepared with a modified membrane template assisted electrochemical deposition method. Commercial cotton swabs were used to apply

colloidal graphite ink onto one side of the polycarbonate template, immediately after which, a piece of flat aluminium foil was attached to the ink. The aluminium foil together with graphite ink served as the working electrode for electrodeposition. The membrane template was then assembled into a Teflon plating cell. Ag/AgCl reference electrode and platinum counter electrode were utilized. Electrochemical deposition was carried out with a μ Autolab type III electrochemical analyzer connected to a computer and controlled by General Purpose Electrochemical Systems version 4.9 software. Cu outer layer was first electrodeposited using galvanostatic method at -4 mA for 450 s with plating solution containing 1 M CuSO_4 . Subsequently, after removing the plating solution and rinsing the cell with ultrapure water, the platinum segment was electrodeposited at -4 mA for 450 s with the commercial plating solution. The electrodeposition cell was disassembled once the sequential electrodeposition process was done. The resulting template was washed with ultrapure water and then was ultrasonicated in ultrapure water to remove the graphite. The template was ultrasonicated in methylene chloride until fully dissolved to release all the microtubes. The microtubes were collected by centrifugation at 6000 rpm for 3 min followed by repeatedly washing for 3 times with methylene chloride. The solution was then washed with ethanol and water, twice of each, with a centrifugation for 3 min after each washing step. The prepared tubes were stored in water at room temperature.

Operation of micromotors. The experiments for studying the influence of blood protein, blood electrolytes and uric acid on the motion of microtubes were carried out in an aqueous solution containing constant final concentrations of hydrogen peroxide (3 wt%) and surfactant (1 wt% of SDS). A mixture of microtubes, SDS, H_2O_2 and various

concentrations of influence factors were placed on a glass slide freshly cleaned with nitrogen gas. The experiments for studying the influence of H_2O_2 on the motion of crippled microtubes were carried out in 10 mM phosphate buffer solution containing 1 wt% of SDS. A mixture of microtubes, SDS, phosphate buffer solution (10 mM) and different concentrations of H_2O_2 were placed on a glass slide freshly cleaned with nitrogen gas. The experiments for studying the influence of surfactants were carried out in an aqueous solution containing a constant final concentration (3 wt%) of H_2O_2 . A mixture of microtubes, H_2O_2 and different concentrations of surfactants solutions were placed on a glass slide freshly cleaned with nitrogen gas. Nikon Eclipse 50i microscope was used to acquire optical videos and images. Video sequences and images were processed with Nikon NIS-ElementsTM software. For each data point in the figures of active microtube propulsion, at least 32 measurements were taken into account. The average velocity was obtained by tracking microtubes for duration of 10 seconds from 6 independent running experiments. The error bars indicate standard deviation.

Cyclic voltammetry for the measurement of hydrogen peroxide consumption. All measurements were performed in 0.1 M phosphate buffer solution (pH = 7.2) at scan rate of 100 mV/s. The platinum electrode was polished with alumina slurry before each experiment, and then was washed thoroughly with DI water. The final concentrations of hydrogen peroxide and surfactants were kept constant at 3 wt% and 1 wt%, respectively. For the stock solutions with micromotors inside, 7 μL microtubes were added into the stock solution 1 h before measurement. For each measurement, a mixture of 18 μL stock solution and 2 mL phosphate buffer solution was used to perform cyclic voltammograms.

6.3 Results and Discussion

6.3.1 Influence of blood proteins on the mobility of microtubes

Cu/Pt concentric microtubes utilized in the study were synthesized using membrane template assisted electrodeposition method. To study the effect of blood plasma proteins on the mobility of microtubes, the microtubes were subjected to serum albumin, γ -globulins respectively at physiologically relevant concentrations. The investigation on the mobility of microtubes mainly involved three parameters, which are (i) fraction of microtubes expelling bubbles (as bubble expulsion is one of the necessities for the motion of microtubes), (ii) fraction of microtubes exhibiting motion and (iii) average velocity of microtubes which were propelled by bubbles. The final concentration of hydrogen peroxide and SDS were kept constant at 3 wt% and 1 wt%, respectively. Control experiments were conducted in deionized water without proteins. The microtubes were propelled at an average velocity of 365 $\mu\text{m/s}$ (~ 52 body lengths/s) in the control experiment.

Investigations were first conducted on the influence of serum albumin, which is the most abundant blood protein, on the motility of bubble-propelled microtubes. Bovine serum albumin (BSA) was used in the study. At a concentration of 3 mg/mL of serum albumin, only around 30% of the microtubes expelled bubbles and 25% of the microtubes displayed non-zero velocity motion (Figure 6.1). All data were normalized to the motion of microtubes in the control experiments (motion in deionized water without proteins). Upon increasing the concentration of BSA to 15mg/mL, around 99% of the microtubes stayed stationary and only about 5% of the microtubes ejected

bubbles slowly. The presence of BSA also led to a dramatic reduction in velocities of the propelled microtubes. The average velocity dropped significantly from 365 $\mu\text{m/s}$ to 91 $\mu\text{m/s}$ even at low concentration as 3 mg/mL of BSA. It should be noted that the physiological relevant concentration of serum albumin in blood is in the range of 35-50 mg/mL.¹⁴ Based on our study, the physiological concentration of serum albumin in blood is consequently able to entirely deactivate all the Cu/Pt microtubes at 3% H_2O_2 fuel.

Figure 6.1 Serum albumin significantly reduces the mobility of bubble-propelled Cu/Pt microtubes. (A) The effect of BSA concentration on the population of the microtubes observed to be expelling bubbles (red bar) and propelled (blue bar). (B) The effect of BSA concentration on the velocities of the microtubes exhibiting motion. All the experiments were conducted at room temperature (23°C).

Afterwards, the microtubes were subjected to gamma globulins at different

concentrations, which is another main protein in blood plasma. This study is important to investigate whether the suppressing of microtubes is typical only for serum albumin or a general effect of blood proteins. The results in our study showed that the presence of γ -globulins also affected the mobility of the microtubes. As shown in Figure 6.2, the presence of γ -globulins at 18 mg/mL resulted in a significant loss in the mobility of the microtubes, with about 30% of the microtubes ejecting bubbles and about 20% of the microtubes being propelled. Comparable effect was observed with the existence of 3 mg/mL of serum albumin. The concentration of γ -globulins required to completely deactivate most of microjets (>95%) was found to be 30 mg/mL, which is in the range of physiological concentration of γ -globulins in blood (23-55 mg/mL).¹⁵ Subsequently, according to the obtained results, the γ -globulins in blood serum could restrain the motion of most of the microtubes at their physiological concentrations. It was noticeable that at 6 mg/mL of γ -globulins, the average velocity of the mobile microtubes was 111 $\mu\text{m/s}$, which was much lower than that in the absence of proteins (365 $\mu\text{m/s}$) but higher than the 73 $\mu\text{m/s}$ in a 6 mg/mL albumin solution.

Figure 6.2 γ -Globulins significantly affect the mobility of the bubble-propelled Cu/Pt microtubes. (A) The effect of γ -globulins concentration on the viability of microjets. (B) Influence of γ -globulins concentration upon velocity of moving microtubes. All the experiments were conducted at room temperature (23°C).

After investigating the influences of major blood proteins on the mobility of microtubes, a non-human protein was examined to extend the scope of the study, which is helpful to confirm whether the deactivation of bubble-propelled Cu/Pt microtubes were isolated cases for major blood proteins. Therefore, glucose oxidase (GOx) was selected as representative of non-human protein. The reason of the selection of glucose oxidase was due to the fact that this enzyme has a great potential to be involved in the development of biocompatible micromotors navigating in the human body. Results showed that the bubble-propelled microjets were even more susceptible to the presence of glucose oxidase than to the previous two blood proteins. As illustrated in

Figure 6.3, even at the concentration as low as 0.6 mg/mL of GOx, over half of the microtubes stopped expelling bubbles and only around 30% of the microtubes displayed a suppressed motion at an average velocity of 131 $\mu\text{m/s}$. Similar with blood proteins, the viability and motion of the microjets decreased gradually with increasing the concentration of the glucose oxidase. At 1.5 mg/mL of glucose oxidase, no bubble ejection and motion of microtubes were observed.

Figure 6.3 Glucose oxidase significantly affects the mobility of bubble-propelled Cu/Pt microtubes. (A) The influence of glucose oxidase concentration on the mobility of microjets. (B) Influence of glucose oxidase concentration on the velocity of moving microjets. All the experiments were conducted at room temperature (23°C).

These results apparently demonstrate that the existence of protein molecules led to a decrease in the viability and mobility of bubble-propelled Cu/Pt microtubes. The

deactivation phenomena are possibly attributable to combined effects from two aspects: (i) adsorption of proteins onto the inner surface of the microtubes and/or (ii) increment in the viscosity of solution. The adsorption of proteins on the inner Pt surfaces could potentially decrease the active surface area to catalyze the decomposition of H_2O_2 to generate O_2 bubbles, thus affecting the propulsion of microtubes. The adsorption could result from different ways: (a) physisorption;¹⁶ (b) chemisorption through sulphur containing moieties (R-SH).¹⁷ Furthermore, the increment in protein concentrations will enhance the overall viscosity of the solution. The presence of 3 wt% serum albumin in solution was proved to result in a growth of around 20% in viscosity in comparison with a blank solution.¹⁸ According to Stokes' law, the reduction of the mobility of the microtubes would originate from increased viscosity of the solution.¹⁹ However, the increment in viscosity is inadequate to elucidate the extent of the decreased mobility of microtubes and adsorption of proteins onto Pt surface is expected to mainly account for the deactivation of microtubes.

6.3.2 Influence of blood electrolytes on mobility of microtubes

Sodium is the most copious cation in extracellular fluid, playing important roles in regulation of water amount in the human body and formation of neuron signals. The normal level of sodium in blood is 135-145 mM, which is much higher than other electrolytes. For another, chloride is the most abundant anions in blood processing a concentration of 96-106 mM.⁴ Consequently, we initially studied the influence of NaCl on the motility of bubble-propelled microtubes. The experiments were performed in an aqueous solution containing constant concentration of hydrogen peroxide (3 wt%) and

SDS (1 wt%). If not mentioned otherwise, the final concentration of H_2O_2 and SDS were kept fixed in the following experiments. As illustrated in Figure 6.4 A, with the existence of 10 mM of NaCl, around 30% of the microtubes failed to eject bubbles and even more microtubes lost mobility. Additionally, the moving microtubes exhibited a crippled motion with a great reduction in average velocity from 365 $\mu\text{m/s}$ to 109 $\mu\text{m/s}$. Following study demonstrated that upon increasing the concentration of NaCl to 70 mM, around half of physiological concentration, almost no bubble ejection and motion of microtubes could be observed. In spite of any other factors, only NaCl at physiological concentration was influential enough to suppress the motion of all the microtubes at 3% H_2O_2 fuel concentration.

Potassium and calcium are also major electrolytes in blood. The physiological concentration of K^+ in blood is 3.5 - 5.2 mM and that of Ca^{2+} is 2.2 - 2.6 mM. In spite of the relatively low concentration of these ions in the human body, they are essential to numerous body functions and cannot be overlooked. Potassium and calcium play important roles in the function of muscles and regulation of heartbeat. Furthermore, calcium is also necessary for aiding blood clotting as well as building bones.²⁰ As such, the microtubes were subjected to KCl and CaCl_2 solutions at different concentrations. The study results demonstrated that both salts could apparently reduce the motility of the microtubes. The existence of 10 mM of KCl led to a significant reduction in the mobility of microtubes, with only 38% of the microtubes expelling bubbles and 32% of the microtubes displaying motion. As shown in Figure 6.4 B, the average velocity of the microtubes exhibiting motion considerably decreased from 365 $\mu\text{m/s}$ to 92 $\mu\text{m/s}$.

Figure 6.4 Influence of electrolytes on the mobility of bubble-propelled Cu/Pt microtubes. (A) NaCl solution, (B) KCl solution, (C) CaCl₂ solution. Left: Graph illustrating the influence of electrolytes concentration on the mobility of microtubes. Right: Graph illustrating the influence of electrolytes concentration on the velocity of moving microtubes. Note that all data were normalized to the motion of microtubes in the control experiment using ultrapure water. All the experiments were conducted at room temperature (23 °C).

The microtubes were more sensitive to the existence of CaCl₂ than NaCl and KCl. As can be seen in Figure 6.4C, in the presence of 10 mM of CaCl₂, all the microtubes stayed stationary and only 9% of the microtubes were observed to be ejecting bubbles.

Additionally, a dramatic reduction in velocity was observed from 365 $\mu\text{m/s}$ to 42 $\mu\text{m/s}$ with the existence of only 6 mM of CaCl_2 .

Afterwards, we continue to study the effect of other blood electrolytes with lower physiological concentrations in sub-millimolar ranges. Phosphate constitutes nucleotides, ATP, phospholipids and most coenzymes. Most of phosphate in blood exists in the form of organic phosphate while only around 0.97-1.29 mM is inorganic phosphate such as HPO_4^{2-} and H_2PO_4^- . Phosphate buffer consisting of the buffer pair, HPO_4^{2-} and H_2PO_4^- , is widely used in biological researches.²¹ We used phosphate buffer of pH 7.4, which falls in the blood pH range of 7.35 to 7.45, to study the effect of phosphorus electrolytes on the mobility of bubble-propelled Cu/Pt microtubes.²² As can be seen in Figure 6.5 A, the mobility of the microtubes suffered great reduction with increasing the concentration of the phosphate buffer solution. It is noticeable that at only 2 mM of phosphate buffer solution, more than half of the microtubes stopped bubble expulsion and around 40% of the microtubes exhibited a crippled motion at a much lower average speed of 149 $\mu\text{m/s}$. These findings provide important implications for researches involving microtubes to perform tasks in phosphate buffer.²³

Subsequently we carried on to examine other anions, specifically sulfates. The concentration level of sulfates in blood is relatively low (0.56-1.25 mM).²⁴ In the present study, Na_2SO_4 was demonstrated to obviously suppress the mobility of the microtubes. The existence of 10 mM of Na_2SO_4 resulted in a strong reduction of the mobility of the microtubes, with around 67% of the microtubes ejecting bubbles and about 54% of the microtubes displaying motion at an average speed of $\sim 88 \mu\text{m/s}$.

Figure 6.5 Influence of electrolytes on the mobility of bubble-propelled Cu/Pt microtubes. (A) phosphate buffer solution, (B) sulfate solution. Left: Graph illustrating the influence of electrolytes concentration on the mobility of microtubes. Right: Graph illustrating the influence of electrolytes concentration on the velocity of moving microtubes. Note that all data were normalized to the motion of microtubes in the control experiment using ultrapure water. All the experiments were conducted at room temperature (23 °C).

According to our results, all the main blood electrolytes suppress the mobility of the bubble-propelled Cu/Pt microtubes to different extent, which led us to the conclusion that blood electrolytes could influence the mobility of the microtubes in spite of the bubble-propulsion mechanism. The deactivation of the microtubes with the existence of electrolytes is evidently indicated by the changes in the bubble ejection frequency. The Pt inner surface catalyzed the decomposition of hydrogen peroxide fuel to generate oxygen bubbles to propel the motion of microtubes. The bubble ejection frequency is related to the rate of catalytic decomposition as well as the amount of

surfactant. The rationale for deactivation of the microtubes may include the following aspects: (i) the Pt catalyst was poisoned by the ions, (ii) the radical reaction of H_2O_2 decomposition was interrupted by the ions, and (iii) the formation of larger micellar aggregates of ionic surfactants induced by additional ions increased surface tension, bringing about difficulty in the formation and detachment of bubbles.²⁵⁻²⁷ Nonetheless, further study is needed towards a better understanding on the influence of electrolytes on the mobility of the bubble-propelled microtubes.

Figure 6.6 Influence of H_2O_2 fuel concentration on the mobility of bubble-propelled Cu/Pt microtubes in 10 mM of phosphate buffer solution. (A) A graph illustrating the influence of H_2O_2 concentration on the mobility of microtubes. (B) A graph illustrating the influence of H_2O_2 concentration on the velocity of moving microtubes. Note that all data were normalized to the motion of microtubes in the control experiment using ultrapure water. All the experiments were conducted at room temperature (23°C).

It is important to take this limitation into account when the microtubes are involved in applications in high ionic strength environment. Blood electrolytes can suppress the mobility of bubble-propelled microtubes. Additionally, higher concentrations of H_2O_2 fuel can make up for the decrement in the mobility of microtubes resulted from the ions. As can be seen from Figure 6.6 A, the mobility of

microtubes was to a large extent crippled in 10 mM of phosphate buffer solution at 3 wt% H_2O_2 . The effect of H_2O_2 concentration on the mobility of microtubes in 10 mM of phosphate buffer solution was investigated (Figure 6.6 B). The average velocity of the suppressed microtubes also rose from 46 $\mu\text{m/s}$ to 219 $\mu\text{m/s}$ with increasing the concentration of H_2O_2 from 3 wt% to 15 wt%. These results suggest that it is a possible way to increase the concentration of H_2O_2 fuel to compensate the negative effects of the ions.

6.3.3 Influence of blood metabolite on the mobility of microtubes

Uric acid can scavenge hydroxyl radicals and singlet oxygen, thus providing an antioxidant defense in the human body. Due to the capability of uric acid to scavenge free hydroxyl radicals generated by the decomposition of H_2O_2 , it is often used as an industrial additive to stabilize H_2O_2 solutions.²⁸ Uric acid exists in human blood with a physiological concentration of 0.035-0.075 mg/mL,²⁹ and the mobility of bubble-propelled Cu/Pt microtubes was examined in uric acid solutions in the concentration range of 0.01-0.04 mg/mL. Control experiments were performed in distilled water in the absence of uric acid. The percentages of microtubes ejecting bubbles and exhibiting motion are all normalized to those in the control experiment. As can be seen from Figure 6.7, the mobility of the microtubes decreased significantly as the concentration of uric acid increase. With the existence of only 0.01 mg/mL of uric acid, around 30% of the microtubes stopped bubble expulsion and more than 40% of the microtubes did not display any motion. The average velocity of the moving microtubes suffered a significant decrease from 365 $\mu\text{m/s}$ to 250 $\mu\text{m/s}$. At 0.04 mg/mL

of uric acid, less than 45% of the microtubes remained ejecting bubbles and around 31% displayed crippled motion at an average velocity of 84 $\mu\text{m/s}$. Hydrogen peroxide decomposition is a radical process and hydroxyl radicals are indispensable for the formation of oxygen. The motion of microtubes relies on the propulsion of oxygen bubbles generated catalytically on the inner surface of the microtubes. The function of uric acid as scavenger of singlet oxygen and hydroxyl radicals restricted the formation of oxygen on the Pt surface and thus led to a significant decrease of the mobility of microtubes. As a result, even the very low concentration of uric acid in the blood is sufficient to suppress the motion of microtubes.

Figure 6.7 Influence of uric acid on the mobility of bubble-propelled Cu/Pt microtubes.

(A) A graph illustrating the influence of uric acid on the mobility of microtubes. (B) A graph illustrating the influence of uric acid on the velocity of moving microtubes. Note that all data were normalized to the motion of microtubes in the control experiment

using ultrapure water. All the experiments were conducted at room temperature (23 °C).

6.3.4 Influence of surfactants on the mobility of microtubes

The influence of anionic, cationic and non-ionic surfactants upon the bubble-propelled motion of microtubes was investigated. The case of anionic surfactant was first studied. Sodium dodecyl sulfate (SDS) is an anionic surfactant which is commonly used in cleaning products as well as in nanotechnology. In spite of the extensive use of SDS in the field of micro/nanomotors, little efforts have been devoted to studying the influence of the SDS concentration on the bubble-propelled motion of the microtubes. As such, we first investigated whether the concentration of SDS will influence the mobility of the microtubes. The final concentration of hydrogen peroxide was kept constant in the experiments at 3%. As shown in Figure 6.8 A, in the beginning, the fraction of both the microtubes ejecting bubbles and exhibiting bubble-propelled motion increase significantly upon increasing the SDS concentration. Above 0.3 wt% concentration of SDS, the mobility of microtubes keeps relatively constant. The variance of the average velocity of microtubes on the concentration of SDS also exhibits similar trend (Figure 6.8 B). This result obtained in the experiment agrees well with the theory of adsorption of surfactant at the interfaces.¹² The effect of the surfactant is related to its concentration at the interface. The critical micelle concentration (CMC) of SDS is about 0.24 wt%.³⁰ As the adsorption of SDS onto the microtubes inner surface increases before reaching CMC, the interfacial tension will decrease. Low interfacial tension will then assist the generation and detachment of the bubbles. Consequently, the mobility of microtubes increases with the concentration of SDS below CMC. Usually, the

adsorption is finished around CMC and the interfacial tension will stay relatively constant. As a result, the concentration of SDS will not have significant implications on the mobility of microtubes above CMC in terms of interfacial tension. However, enhanced surfactants concentration will unavoidably increase the viscosity of the solution. Based on the Stoke's equation, the velocity of microtubes will decrease with the increase in viscosity. Until 10 wt%, the negative effect of increasing surfactants concentration is not apparent and the average velocity of microtubes was kept stable at $\sim 365 \mu\text{m/s}$. Further enhancement of surfactant concentration may lead to increased viscous resistance, which will decrease the speed of the microjets.^{10, 31}

Figure 6.8 Influence of the concentration of SDS on the mobility of microtubes. A) Dependence of the percentage of microtubes ejecting bubbles (red bar) and moving (blue bar) on SDS concentration. Note that both the running and bubbling percentages were normalized to those in 3 wt% SDS solution. B) Dependence of the average velocity

of microtubes on SDS concentration. The average speed was obtained by tracking a timescale of 10 seconds from 6 independent running experiments. All the experiments were conducted at a temperature of 23 °C and 3 wt% H₂O₂.

Afterward, we move on to investigate whether the types of surfactants will influence the mobility of microtubes. Tween 20 is a type of nonionic surfactant with good stability and relative non-toxicity, which allows its broad use in various biological applications. Tween 20 possesses a relative low CMC of 0.01 wt%.³² With the use of Tween 20, the mobility of microtubes had a dramatic decrease, with ~ 20% of the microtubes expelling bubbles and ~ 15% of the microtubes displaying bubble-propelled motion above CMC (Figure 6.9 A). Due to the low bubble expulsion frequency, there is also a marked reduction in the velocity of moving microtubes to ~ 65µm/s (Figure 6.9 B). These findings again proved that the mobility of microtubes will stay relative stable while changing the concentration of surfactants above CMC. Another implication obtained from the result is that the properties of surfactants will affect the motion of microtubes.

Figure 6.9 Influence of the concentration of Tween 20 on the mobility of microtubes. A) Dependence of the percentage of microtubes ejecting bubbles (red bar) and moving (blue bar) on Tween 20 concentration. Note that both the running and bubbling percentages were normalized to those in 3 wt% Tween 20 solution. B) Dependence of the average velocity of microtubes on Tween 20 concentration. The average speed was obtained by tracking a timescale of 10 seconds from 6 independent running experiments. All the experiments were conducted at a temperature of 23 °C and 3 wt% H_2O_2 .

Since the performance of microtubes in Tween 20 is very different from that in SDS, we proceed to study the motion of microtubes in the presence of a cationic surfactant, CTAB. As shown in Figure 6.10, bubble-propelled motion was not observed over a wide range of concentrations both below and above CMC of CTAB (0.04 wt%).³³ To confirm that microtubes only exhibit insignificant Brownian motion in the presence of CTAB, we calculate the mean square displacement (MSD) of microtubes in 1 wt% CTAB

solution and that without any surfactants. Both the plots of MSD against time interval for microtubes in the two cases are straight lines, which indicate that the microtubes only exhibit Brownian motion. The diffusion coefficient of microtubes in solution without any surfactants, $\sim 1.29 \mu\text{m}^2 \text{s}^{-1}$, is slightly larger than that of microtubes in CTAB solution, $\sim 0.87 \mu\text{m}^2 \text{s}^{-1}$. The result is consistent with the Stokes-Einstein equation, $D = kT/6\pi\eta r$. When the viscosity of the solution (η) increases, the diffusion coefficient (D) will decrease.^{34, 35}

Figure 6.10 Influence of the concentration of Tween 20 on the mobility of microtubes. Note that both the running and bubbling percentages were normalized to those in 3 wt% Tween 20 solution. B) All the experiments were conducted at a temperature of 23 °C and 3 wt% H_2O_2 .

The mobility of microtubes is related to the bubble frequency. As illustrated in Figure 6.11, microtubes exhibited different bubble frequency in the presence of different surfactants and thus displayed different mobility. The difference between surface tension of SDS, Tween 20 and CTAB solutions above CMC is not significant.³⁶⁻³⁸

The distinct difference between the mobility of microtubes with different surfactants could be related to the adsorption process of surfactant molecules onto the inner surface of the microtubes. According to the radical mechanism of decomposition of hydrogen peroxide on platinum surface, the inner surface of the microtubes has some positively charged sites.³⁹ It is a complicated process for the adsorption of surfactants from aqueous solution to solid surface. The adsorption of ionic surfactants onto substrate with oppositely charged sites initiate with ion exchange, followed by the hydrophobic interaction of the chains of oncoming surfactant ions with those of previously adsorbed surfactant. The adsorption will complete around CMC.¹² Anionic surfactant SDS can be readily adsorbed onto positively charged inner surface of microtubes by electrostatic attraction while cationic surfactant CTAB need to overcome repulsion to be adsorbed onto the inner wall of microtubes. Nonionic surfactant Tween 20 is adsorbed from the solution by moderate hydrophobic interaction with uncharged sites of platinum surface. Consequently, the efficiency as well as effectiveness of the adsorption of CTAB and Tween 20 onto the inner surface of microtubes is lower than that of SDS. Previous studies also showed that the velocity of microtubes in the presence of benzalkonium chloride is much lower than that in other surfactant solutions.⁴⁰ However, there are other reasons that may account for the different behaviors of microtubes in different surfactants solutions except for the adsorption process.

Figure 6.11 Tracking of microtubes in 1 wt% of (A) SDS, (B) Tween 20 and (C) CTAB solutions, as well as (D) solution without any surfactants for 2s. Scale bars are 20 μm . All experiments were conducted at a temperature of 23 $^{\circ}\text{C}$ and 3 wt% H_2O_2 .

Another possibility is that the surfactants will affect the decomposition of hydrogen peroxide to different extents. The influence of salts on the reaction rate of decomposition of H_2O_2 has been studied previously.⁴¹ Here, we investigated the consumption of hydrogen peroxide in the presence of three surfactants using electrochemical method. In Figure 6.12, the cyclic voltammograms show the difference in the consumption of H_2O_2 for SDS, Tween 20 and CTAB. It can be seen that no apparent redox wave was observed for 0.1M phosphate buffer solution at pH 7.2 (blank), but an obvious oxidation wave for H_2O_2 appeared. The difference between the cyclic voltammogram of H_2O_2 solution with surfactant and that of corresponding solution which has been left 1h with micromotors inside reflects the consumption of H_2O_2 . The consumption of H_2O_2 for micromotors in the presence of SDS is the most while the

consumption of H_2O_2 is not obvious in the presence of CTAB. The rate of H_2O_2 decomposition is in agreement with the findings described above. On the other hand, bubble detachment will also influence the decomposition rate since attached bubbles decrease the effective catalytic area of the inner platinum surface of the microtubes. Therefore, the reduced oxygen production may be attributed to the effect of surfactants on the decomposition rate or the difference in effective catalytic area due to bubble detachment. However, we can confirm that different surfactants will affect the bubble expulsion frequency of microtubes. Microtubes generate bubbles with an average radius of $2\ \mu\text{m}$ at a rate of ~ 120 per second in SDS solution and ~ 25 per second in Tween 20 solution. For CTAB, no bubble-propelled motion was observed. According to the method established by Wang *et al.*,⁴² the efficiency calculated for microtubes in the presence of SDS is $\sim 1.40 \times 10^{-7}$ and in the presence of Tween 20 is $\sim 2.14 \times 10^{-8}$.

Figure 6.12 Cyclic voltammograms of H_2O_2 in different surfactants solutions (SDS, Tween 20, CTAB) in the absence and presence of micromotors moving for 1h at 23°C . Scan rate:

100 mV/s.

Other properties of surfactants, such as their effects on foamability wetting ability, and foam stability, may also affect the bubble-propelled of microtubes.⁴³ Surfactants are able to help reduce the hydrophobic nature of the Pt layer, thus improving the Pt wetting with the aqueous H₂O₂ fuel solution.⁴⁰ We tested the wetting ability of running solution with different surfactants (1 wt%) and H₂O₂ (3 wt%) on platinum surface. The trend agreed with the activity of microtubes in the running solution. The contact angles of running solution containing SDS, Tween 20 and CTAB on Pt surface are 36°, 43° and 48°, respectively.

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Chapter 7

Proof-of-concept applications of micro/nanomotors

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7.3.2 *Multifunctional sporopollenin exine capsule micromotors for cargo delivery and heavy metal removal*

The results in this chapter were published in the following manuscript:

1. **Hong Wang**, Bahareh Khezri, Martin Pumera*. Catalytic DNA-Functionalized Self-Propelled Micromachines for Environmental Remediation. *Chem* **2016**, *1*, 473.

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The thesis author was the primary investigator and author of these papers.

7.1 Introduction

Recent developments in nanotechnology have opened up a new way for addressing environmental and biomedical issues. One of the major issues we are facing today is environmental degradation. The shortage of clean water that we lean to survive has attracted world-wide attention. Water scarcity is resulted from diverse causes such as pollution, amplified urbanization, climate changes and overpopulation.¹ Pollution from toxic chemicals threatens life on our planet. As one of the main threatening of people's health, water contamination is putting ever-increasing pressure on human beings.² What is more, water pollution has a widespread impact on the whole ecosystems leading to species mortality and biodiversity reduction.³ Self-propelled micro/nanomachines have brought up new horizons to monitoring and remediation of environment.⁴ Micro/nanomachines functionalized with different materials have been demonstrated effective to remove and destruct a wide range of pollutants. However, the study utilizing micro/nanomotors for clean-up of heavy metal is still very limited.

Able to accumulate in living organism and cause organ damages, mercury is one of the most toxic contaminants.⁵ Industry has dramatically increased mercury content in the environment and it is a worldwide problem as mercury can travel without borders.⁶ Substantial research efforts have been devoted to developing new methods to eliminate mercury from water bodies. As conventional methods such as ion exchange, evaporation and precipitation are ineffective or high-cost to get rid of heavy metal ions, various sorbents for removal mercury including polymers,⁷ hydrogels,⁸ and activated carbon⁹ have been developed by researchers. However, widely used binding sites, such

as thiol and amine groups,^{10, 11} lack selectivity toward mercury. Previous studies have demonstrated that Hg(II) can specifically bind to thymine-thymine (T-T) mismatched DNA base pairs to form T-Hg(II)-T complexes, which are more stable than adenine-thymine (A-T) base pairs.^{12, 13} The binding between T-T mismatched pair and Hg(II) has been shown to be very specific and is not applicable to other ions.^{14, 15} Different Hg(II) sensors with high selectivity and sensitivity towards Hg(II) have been developed based on these findings.¹⁶⁻¹⁸ Here, we demonstrate preliminary efforts to utilize micro/nanomachines to remove Hg(II) from water bodies.

To perform specific tasks in biomedical and environmental fields, such as cargo transport and environmental remediation, additional modification steps are usually required to functionalize the micro/nanomotors accordingly. Looking beyond materials synthesis, nature provides a myriad of unique, widely available biological materials with various microscale and nanoscale architectures that might prove useful for developing autonomous motors. Indeed, the versatile elegant biomaterials structures which have evolved over millions of years are a promising source of templates and materials for the design and fabrication of functional materials. For example, the nanostructures on leaves have inspired the development of superhydrophobic and self-cleaning surface,¹⁹ and the spiral water-conducting vessels of plants have been harnessed to prepare magnetically driven helical micromotors.²⁰ The appropriate modification of plant-derived materials with desirable morphologies offers a cost-effective approach to obtain hybrid structures with high morphological complexity. Additionally, the intrinsic biocompatibility of plant materials makes them promising candidates for biomedical applications.

Here, we demonstrate a bioinspired micromotor based on sporopollenin exine capsules (SECs) which are extracted from sunflower pollen grains, and can encapsulate macromolecular compounds for cargo delivery as well as absorb heavy metals for decontamination of water without further functionalization. The new micromotors are fabricated by partially coating the SEC surface with a layer of platinum catalyst in order to generate oxygen thrust *via* decomposition of H_2O_2 fuel. The direct incorporation of SECs as the main component of micro/nanomotors not only leads to good biocompatibility, but also simplifies the preparation of micro/nanomotors with encapsulation ability. Moreover, sporopollenin is capable of acting as a biopolymeric sorbent to absorb heavy metals from aqueous solution. The raw material, sunflower pollen grains possessing uniform size distribution, can be readily obtained at very low costs, enabling cost-efficient and high-yield preparation of micro/nanomotors.

7.2 Experimental section

7.2.1 Materials

The cyclopore polycarbonate membranes with pore diameters of $3\mu\text{m}$ and 200 nm, as well as anodic aluminum oxide (AAO) membranes with pore size of 200 nm were obtained from Whatman, USA. H_2O_2 (35%) was obtained from Alfa Aesar, Singapore. Ethanol and methylene chloride were obtained from Tedia, USA. Ag/AgCl/1.0 M KCl reference electrode and Pt electrodes with 1 mm diameter were obtained from CH instruments, USA. The Au and Pt electroplating solution were purchased from Technic Inc., USA. Sodium dodecyl sulfate (SDS), oligonucleotides polyT30-SH and DTT were obtained from Sigma-Aldrich. High Purity Nitric Acid and hydrochloric acid were

purchased from J.T Baker, Canada. Defatted sunflower (*Helianthus annuus* L.) pollen grains were procured from Greer labs (NC, USA). Phosphoric acid (85 % w/v), acetone, bovine serum albumin (BSA), and FITC-conjugated BSA were procured from Sigma-Aldrich (Singapore). Vectashield (H-1000) medium was procured from Vector labs (CA, USA) and Sticky-slides, D 263 M Schott glass, No.1.5H (170 μm , 25 mm x 75 mm) unsterile were procured from Ibidi GmbH (Munich, Germany). Stock standard solutions of Pb, Hg (1,000 mg/L) were obtained from inorganic venture (Christiansburg, VA, USA). Ultra-pure 70% HNO_3 was purchased from PlasmaPURE Plus, Canada. Chemicals were used without further purification and the solutions were prepared using ultrapure water (18.2 $\text{M}\Omega\text{ cm}$) generated from a Millipore Milli-Q purification system.

7.2.2 Apparatus

Electrochemical deposition was performed using an Autolab PGSTAT 101 electrochemical analyzer (Eco Chemie, The Netherlands) linked to a computer and controlled by NOVA Version 1.8 software (Eco Chemie). Deposition was carried out at room temperature with a three-electrode arrangement. The counter electrode is a Pt electrode, and the reference electrode is Ag/AgCl/1.0 M KCl. A JEOL JFC-1600 Auto Fine Coater was used to conduct sputtering. A Fisherbrand FB 11203 ultrasonicator was used for ultrasonication process, and a Beckman Coulter Allegra 64R centrifuge was used for centrifugation. A Nikon Eclipse Ti-E microscope with a DS-Fi1c camera was used to obtain optical microscope videos and images. Nikon NIS-Elements software was used to process video sequences. Measurement of mercury was conducted using an Agilent

7700x Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Japan) fitted with a 3rd generation He reaction/collision cell (ORS3) to minimize interference.

7.2.3 Procedures

Preparation of Au/Pt microtubes. The Au/Pt bilayer microtubes were prepared using a modified electrochemical deposition method with cyclopore polycarbonate membranes as templates. On one face of the membrane template was sputtered ~75 nm silver. The sputtered side of the membrane template was attached to copper tape, which together acts as the working electrode for electrodeposition. The membrane template was subsequently assembled into a customized electroplating cell. Using Pt counter electrode and Ag/AgCl/1.0 M KCl reference electrode, an Au layer was deposited galvanostatically at -10 mA for 1000 s, followed by the deposition of Pt at -20 mA for 1000 s. After electrodeposition, the template was polished using 0.06 μm alumina powder to eliminate the remaining silver layer and then was dissolved in methylene chloride. The microtubes were collected by centrifugation at 6000 rpm for 3 min, followed by washing with methylene chloride, ethanol and water. The prepared microtubes were placed in water at room temperature.

Modification of microtubes. The functionalization of micromotubes with DNA was accomplished by an overnight immersion in immobilization buffer solution (1×PBS, pH 7.2) containing 10 μM oligonucleotides. The oligonucleotides with thiol on one end were treated with dithiothreitol (DTT) first to reduce the disulphide bond. The microtubes were washed thoroughly with ultrapure water after immobilization, and

were collected by centrifugation. The functionalized microtubes were stored in immobilization buffer at 4°C.

Propulsion of microtubes. The motion studies of micro/nanomotors were conducted in an aqueous solution containing 3 wt% H₂O₂ and 0.3 wt% of SDS. On a freshly cleaned glass slide was applied a mixture of microtubes, H₂O₂ and SDS. A Nikon Eclipse Ti-E microscope equipped with DS-Fi1c camera was used to acquire optical microscope videos and images. Nikon NIS-Elements software was used to process video sequences.

Removal of Hg(II) from aqueous solution. Mercury removal studies were performed in solutions with a total volume of 2 mL. Bare microtubes or microtubes functionalized with DNA were added into the solution containing Hg(II), yielding a final microtube concentration of 3000 tubes/mL. The final concentration of Hg(II) is fixed as 3ppm. For on-the-fly capture of Hg(II), additional H₂O₂ and SDS were added into the solution, giving final fuel and surfactant concentrations of 3 wt% and 0.3 wt%, respectively. The microtubes were kept in the solution for twenty minutes and then were separated by filtering through a filter membrane with 200 nm pores.

Analysis of Hg(II) concentration using ICP-MS. The processed samples were analyzed using ICP-MS immediately after preparation. The calibration solutions were prepared in nitric acid (3%) and hydrochloric acid (0.5%) with Hg concentrations of 0.1, 0.5, 1, 2.5 and 5.0 µg/L. All solutions were prepared in polyethylene or polypropylene vessels. Using He collision cell allows inclusion of 0.5% HCl in sample preparation which facilitates the formation of a stable complex [HgCl₄]²⁻ to keep the mercury in solution. To maximize ionization of the Hg atoms, the plasma has been operated at the highest

possible temperature.

Isolation of sunflower sporopollenin exine capsules (SECs). The sunflower SECs were extracted by acidolysis using phosphoric acid (85 % v/v): defatted sunflower pollen grains (2 g) were suspended in phosphoric acid (15 ml, H₃PO₄) and mixed gently to form a homogeneous suspension. The pollen grains were heated at 70 °C under gentle stirring for 5 h. The SECs were collected by filtration and washed extensively by using hot water (5 x 50 ml), hot acetone (2 x 50 ml), hot 2M hydrochloric acid (50 ml), hot water (5 x 50 ml), hot acetone (50 ml) and hot ethanol (2 x 50 ml). SECs were dried at 60 °C for 8 h until stable weight and stored in a dry cabinet at 25 °C until further characterization.

Bovine serum albumin (BSA) encapsulation into sunflower SECs. BSA loading into sunflower SECs was performed using a vacuum loading technique.²¹⁻²³ 150 mg of SECs was suspended in 1.2 ml of aqueous BSA solution at a BSA-loading proportion of 54.5 wt% in a polypropylene tube to form a homogeneous suspension and then mixed for 10 min using a vortex mixer (IKA, Staufen, Germany). The tube was transferred to a freeze dryer (Labconco, MO, USA) and a vacuum was applied at 1 mbar for overnight. The tube was collected and the loaded SECs were washed using 2 ml water then centrifuged to remove residual BSA. This washing step was repeated for a total of two times. The BSA-loaded SECs were then placed in a freezer at -70 °C for 30 min before freeze-drying for 24 h. The resultant sunflower SECs were stored at -20 °C until characterization. Placebo SECs were prepared with the same procedure and also stored at -20 °C. In order to determine the localization of BSA within the sunflower SECs, FITC-conjugated

BSA was encapsulated in SECs using the same procedure as the above-mentioned vacuum loading technique.

CLSM imaging of protein-loaded SECs. Fluorescence from sunflower pollen SECs, FITC-BSA loaded SECs, platinum coated SECs, and platinum coated FITC-BSA loaded SECs, were analyzed by CLSM (Carl Zeiss LSM700, Jena, Germany) equipped with three spectral reflected/fluorescence detection channels, six laser lines (405/458/488/514/561/633 nm), and a Z1 inverted microscope (Carl Zeiss, Germany).²⁴ Samples were mounted on sticky slides (Ibidi, Germany) then a drop of mounting medium (Vectashield®) was added before covering with another sticky slide. Images were collected immediately under the following conditions: laser excitation lines 405 nm (5.3 %), 488 nm (11.1 %) and 561 nm (10.0 %) with DIC in an EC Plan-Neofluar 40X 1.3 oil objective M27 lens. Fluorescence was collected in photomultiplier tubes equipped with the following emission filters: 416-477; 572-620. The image size was set at 1024x1024 pixels, with a pixel dwell of 0.79 μ s, and a scan area of 106.17 μ m². The iris was set as optimal for the sample conditions and z-stack images were collected for all samples, with 12 slices at 2 μ m intervals. All settings were fixed for all samples, and per sample, at least three images were captured and processed using ZEISS 2008 software (ZEISS, Germany).

Preparation and motion study of SEC micromotors. The aqueous suspension of empty SECs was applied on a Petri dish. After fully evaporation, platinum was deposited by sputtering using a JEOL JFC-1600 Auto Fine Coater. For SECs loaded with FITC-BSA, they were directly applied on Petri dish by spatula before deposition of platinum. The motion

study of micro/nanomotors was performed in an aqueous solution containing different concentrations of H_2O_2 at constant surfactant concentrations (0.3 wt% of SDS). A mixture of SEC micromotors, SDS, H_2O_2 was applied on a freshly cleaned glass slide. Optical microscope videos and images were obtained using a Nikon Eclipse Ti microscope fitted with a DS-Fi1c camera. Video sequences were processed with Nikon NIS-Elements software.

Removal of lead by SEC micromotors. Lead decontamination studies were carried out in solutions with a final volume of 2 mL. Plain SECs or SEC micromotors ($\sim 1 \times 10^5$ SECs) were added into the lead contaminated solution (1 ppm), yielding a SEC concentration of 5×10^4 SECs/mL. The final concentrations of H_2O_2 and SDS in the solution are 5 wt% and 0.3 wt%, respectively. The SEC micromotors were used to navigate in the lead contaminated solution for different duration (0, 15, 30, 45 min). The plain SECs were allowed in the contaminated solution for 45 min. For each remediation time, three independent experiments were conducted under same conditions. Afterwards, the SECs were separated by filtering through an AAO filter membrane with 200 nm pore size. The filtered solutions were sent for ICP-MS measurement. Prepared samples were acidified and the concentration of the lead was measured using an inductively coupled plasma-mass spectrometer (ICP-MS, Agilent 7700 series, Japan) equipped with a third generation He reaction /collision cell (ORS3) to minimize interferences. Prior analysis of the instrumental parameters such as sample depth, voltages (lenses), torch position, detector (MS, quadrupole) and carrier and dilution gas flow rates were tuned by introducing a $1.0 \mu\text{g L}^{-1}$ solution of Ce, Co, Li, Mg, Tl and Y in 2 wt % HNO_3 (operating

parameters are summarized in Tables 7.1). Then ICP-MS was calibrated using external standard and qualified by known concentration.

Table 7.1 7700x ICP-MS operating parameters for lead measurement.

ICP-MS 7700x settings	
RF power	1550 W
Carrier gas	0.7 L/min
Dilution mode	On
Dilution gas	0.1 L/min
He gas	4.3 mL/min
Data Acquisition	3 readings per replicate

7.3 Results and discussion

7.3.1 DNA-functionalized self-propelled micromachines for mercury removal

The proposed dynamic Hg(II) removal strategy depends on the specific and strong interaction between T-T base pairs and Hg(II). It has been demonstrated by NMR studies that Hg(II) can substitute the imino proton to bind directly to N3 of thymidine, linking two thymidine residues to generate T-Hg(II)-T complexes (Figure 7.1 A).¹³ Hg(II) have been demonstrated highly specific for this binding over other interfering ions.¹⁴⁻¹⁸ Coupling the selective adsorption capability of thymine-rich DNA towards Hg(II) and unique motion dimension of autonomous micromotors leads to a promising platform for various applications. Figure 7.1 B shows “on-the-fly” capture of Hg(II) by micromotors functionalized with DNA in contaminated water. The DNA used in the

study is a polyT30-SH oligonucleotide containing 30 thymine bases as well as a thiolated end. The autonomous micromotor consists of an Au outer surface for functionalization and a Pt inner surface to catalyze H_2O_2 fuel to generate self-propulsion.

Figure 7.1 Working principle of the micromachines. A) Mechanism of the interaction between $\text{Hg}(\text{II})$ and T-T base pairs. B) Schematic illustration of DNA-functionalized self-propelled micromachines for removal of $\text{Hg}(\text{II})$ from aqueous solution.

Given the advantages of tubular micromotors, for instance, high power output and mobility, as well as ease of functionalization, the micromachines were microtubes prepared by membrane template-assisted electrodeposition. Rather than sputtering Au layers on one side of the microtubes,^{25, 26} we electrodeposited an Au layer as the outermost surface of the microtubes, which enables large surface area for following functionalization. A Pt layer is plated afterwards as the inner surface of the microtubes, leading to Au/Pt bilayer microtubes. The scanning electron microscope (SEM) images of the prepared microtubes are shown in Figure 7.2 A-C. The diameters of the openings at

the opposite ends of the microtubes are $2.5\ \mu\text{m} - 3\ \mu\text{m}$ and the microtubes have lengths around $10\ \mu\text{m}$. The top view of a microtube is shown in Figure 7.2 C and bottom is the left-over of sputtered silver layer. The energy-dispersive X-ray (EDX) elemental mapping in Figure 7.2 D shows the distribution of gold and platinum. In general, the fabricated microtubes are concentric Au/Pt structures.

Figure 7.2 Characterization of Prepared Au/Pt Microtubes. A-C) SEM images of fabricated Au/Pt microtubes. D) EDX elemental mapping showing the distribution of Au and Pt in the microtubes. Scale bars in A, B and D are $2\ \mu\text{m}$. Scale bar in C is $1\ \mu\text{m}$.

The polyT30-SH oligonucleotides were attached to the gold outer surface of the microtubes through sulfur-gold covalent bond, which is a robust but modifiable interaction widely used to functionalize surfaces. Sulfhydryl (-SH) functional group is often used to form self-assembled monolayers of thiols on Au surfaces.²⁷ The DNA was

immobilized on the surface of microtubes by immersing overnight in 1×PBS buffer solution containing 10 μM thiolated oligonucleotides. During modification, the microtube concentration in the solution was $\sim 40000 \text{ mL}^{-1}$. The DNA-functionalized microtubes were then washed thoroughly with ultrapure water to eliminate excess DNA. The mobility of microtubes immobilized with DNA was studied with regard to bare microtubes without DNA modification. Ascribed to the heterogeneity of the pores in the template and unmanageable factors in the electroplating process, the fabricated microtubes were inhomogeneous to some degree. As such, the velocities of microtubes vary in a range, but the general trend persists. The immobilization of thiolated oligonucleotides led to a slight decrease in the micromotor velocity. In clean water with 3% H_2O_2 but without Hg(II) , bare microtubes displayed an average velocity of 244 $\mu\text{m/s}$ while the average velocity of DNA-functionalized microtubes was 179 $\mu\text{m/s}$ (Figure 7.3 A). The impact of Hg(II) on the mobility of DNA-functionalized microtubes was also examined. In clean water and Hg(II) polluted water, the functionalized microtubes displayed similar velocity, demonstrating the insignificant influence of Hg(II) . Figure 7.3 B and C are snapshots of the motion of functionalized microtubes in aqueous solution containing Hg(II) . The microbubbles ejected from the microtubes form clear tails indicating the trajectories of microtubes. The Pt inner surface of microtubes catalyzes the decomposition of H_2O_2 to generate oxygen bubbles, which provides continuous thrust for steady propulsion.

Figure 7.3 Motion studies of the micromachines. A) Influence of functionalization with DNA and the presence of Hg(II) on the mobility of microtubes. The average velocity was calculated from 10 independent motion studies. The error bars indicate standard deviation. B, C) Propulsion of DNA-functionalized microtubes in Hg(II) polluted water.

As shown in Figure 7.4 A, we first studied the mercury adsorption capability of stationary DNA-functionalized microtubes. Same amount (~ 6000 microtubes) of functionalized and bare microtubes were added into 2 mL 3 ppm Hg(II) solution respectively in the absence of H_2O_2 and SDS. After twenty minutes, the resulting solution was filtered using a filter membrane with 200 nm pores. Ion conductive plasma-mass spectrometry (ICP-MS) was used to analyze obtained solution. The concentration is the mean value of three measurements with relative standard deviation (RSD) below 2%. Analysis showed that bare microtubes had insignificant effect on the Hg(II) level whereas the solution subjected to microtubes functionalized with DNA had a decrease of 17% in Hg(II) concentration compared to the static control. The difference verifies the existence of DNA on the surface of micromotors. Afterwards, we proceed to study the effect of moving microtubes to remove Hg(II) (Figure 7.4 B). The

decontamination experiment was conducted in solution with 3 % H_2O_2 and 0.3 % SDS. In comparison with moving bare microtubes, the movement of ~ 6000 microtubes functionalized with DNA in 2 mL contaminated solution for twenty minutes eliminated 26% Hg(II) . Under the conditions with 3 % H_2O_2 and 0.3% SDS, the DNA is stable as earlier electrochemical studies have proved that the existence of 5% H_2O_2 and 1% surfactant had a negligible influence on the integrity of self-assembled monolayer of DNA.²⁶ Relative to stationary DNA-functionalized micromachines, moving functionalized micromachines exhibit enhanced adsorption efficiency. Both the motion and bubble generation of the micromachines will result in enhanced mixing of the fluid, thus increasing the remediation efficiency^{28, 29} Previous studies have proved the convection resulted from bubble-propelled microtubes by enhanced transport of passive tracers.³⁰ In addition, compared to the amount of micromotors (10^4 tubes/mL - 10^5 tubes/mL) in other investigations for clean-up of pollutants,^{29, 31} the concentration of micromotors used here, 3000 tubes/mL, is very low. As the adsorption amount is in a positive correlation with the amount of DNA, the removal efficiency will be improved using higher concentration of micromotors functionalized with DNA. Considering the amount of DNA used, the dynamic mercury removal approach based on micromachines shows higher remediation efficiency than earlier studies using DNA condensation.³²

Figure 7.4 Studies on the Hg(II) removal ability of DNA-functionalized microtubes. A) Static bare (control) and functionalized microtubes in Hg(II) polluted water. B) Moving bare (control) and functionalized microtubes in Hg(II) polluted water containing 3 wt% H_2O_2 and 0.3 wt% SDS.

7.3.2 Multifunctional sporopollenin exine capsule micromotors for cargo delivery and heavy metal removal

Pollen grains are considered to be the male partner in the reproductive process of seed plants, and are comprised of microcapsules which protect the genetic material. The microcapsule architecture of each species of pollen grain is highly intricate and unique, yet plants have developed highly efficient processes to renewably produce these microcapsules with high efficiency and reproducibility. The capsules are hollow cavities that are protected by an inner intine layer, which is rich in cellulose, as well as an outer exine layer that is mainly composed of the sporopollenin biopolymer and forms an elaborately sculptured, three-dimensional architecture.³³ As the exine is the

outermost layer to defend against environmental injuries, sporopollenin is highly robust with excellent chemical and structural stability.³⁴ The attractive physicochemical properties as well as biocompatibility of the exine motivate its extraction as a natural 3D biomaterial used for microencapsulation.

The SECs used in the study were obtained from sunflower pollen grains which are abundant in supply and naturally produced by renewable means. In particular, the exines of sunflower possess numerous advantageous features, including highly ordered spikes, a large hollow cavity, and monodisperse size distribution. To obtain empty SECs, the sunflower pollen grains underwent acidolysis using phosphoric acid in order to remove the intine and cytoplasmic materials while retaining the morphology of the exine microstructure. The resulting SECs were then extensively washed with a series of organic solvents and water in order to remove residual constituents and acquire clean SECs. As shown in Figure 7.5 A, the obtained SECs maintain a highly uniform size distribution with an average diameter of $30 \pm 0.4 \mu\text{m}$. The intrinsic morphology of the exine is retained after the extraction processing steps. The zoomed-in images in Figure 7.5 B and C demonstrate that the spikes are intact, surrounded by a number of pores, revealing the porous structure of the SECs. The SEC micromotors were prepared by asymmetrically coating one side of the SECs with a layer of Pt *via* sputtering. The contrast in the optical micrographs shown in Figure 7.5 D and E confirmed that the SECs are partly covered with Pt, which creates the desired asymmetry essential for directional motion. Additionally, the sputtered Pt layer does not damage the natural microstructure of the pollen microcapsules as can be seen from the SEM micrograph in Figure 7.5 F.

Figure 7.5 Structure of SEC and SEC micromotors. A-C) SEM micrographs of plain SECs at different magnifications. D) and E) Optical images of SEC micromotors. F) SEM micrograph of SEC micromotors. Scale bars in A-F are 20 μm , 10 μm , 1 μm , 50 μm , 20 μm and 10 μm , respectively.

It is of great interest to study bubble generation on the unique spiky surface of the SEC micromotors. Figure 7.6A illustrates one bubble generation cycle by a SEC micromotor. Bubble nucleation requires the oxygen concentration to reach a certain level of supersaturation and the accumulated oxygen needs to exceed the critical free energy of heterogeneous nucleation to form bubbles.³⁵ On one hand, the distribution of oxygen is asymmetric around the spiky SEC micromotor. The spikes on the surface of

the SEC micromotors form partially enclosed cavities, which facilitates the accumulation of oxygen. The oxygen molecules generated on the spikes keep diffusing away from the surface and cannot reach the supersaturation level essential for bubble nucleation.³⁶ On the other hand, compared to the convex cone structure of the spikes, the critical free energy for heterogeneous nucleation on the relative smooth planar surface between spikes is lower.³⁷ Taking into account these two factors, heterogeneous nucleation between the spikes is highly favored. The nucleation, growth, and detachment of bubbles are repeated in a cyclical manner: (a) The bubble nucleates between the spikes and grows. (b) At a certain size, the bubble will detach from the nucleation surface but remain stuck between the spikes. (c) The bubble attached to the spikes keeps growing. (d) The bubble eventually detaches from the spikes and a new bubble forms at the nucleation site.

The size of the formed bubbles is related to the space between the spikes where nucleation occurs. Larger gaps between the spikes provide more space for the growth of the bubbles before detachment. The generated defects during preparation, such as tearing of the surface or breaking of the spikes, will result in an enlarged space between the spikes and therefore lead to the formation of larger bubbles. The SEC micromotors exhibit an average velocity of 58.87 $\mu\text{m/s}$ in the presence of 5% H_2O_2 . Figures 7.6 B and C are the tracking trajectories of two SEC micromotors in 5% H_2O_2 for 10 s. The micromotor in Figure 7.6 B only had one nucleation site while the micromotor in Figure 7.6 C possessed multiple nucleation sites. The number of active sites for nucleation is dependent on both the structure of the micromotors and the supersaturation level. At one concentration of H_2O_2 , the number of active sites is mainly related to the surface

area and morphology of the Pt catalyst. At higher concentration of H_2O_2 , increased supersaturation level of oxygen leads to bubble formation at more active sites. High supersaturation of oxygen also promotes higher nucleation rates.^{38, 39} As a result, the SEC micromotors exhibit higher mobility in the presence of higher H_2O_2 concentration due to enhanced bubble propulsion. Figure 7.6 D shows the motion of an SEC micromotor propelled by bubbles generated from multiple nucleation sites on one hemisphere of the micromotor over a time interval of 2.5 s. As shown in Figure 7.6 E, the average velocity of the SEC micromotors increased from 35.48 $\mu\text{m/s}$ in 3% H_2O_2 to 90.83 $\mu\text{m/s}$ in 7% H_2O_2 .

Figure 7.6 Motion studies of SEC micromotors. A) Bubble generation process of a SEC micromotor. B) Trajectory of a SEC micromotor with a single nucleation site in 5% H_2O_2 for 10 s. C) Trajectory of a SEC micromotor with multiple nucleation sites in 5% H_2O_2 for 10 s. D) Trajectory of a SEC micromotor in 7% H_2O_2 for 2.5 s. E) Dependence of the average velocity of SEC micromotors on H_2O_2 concentration. Average velocity at each H_2O_2 concentration was obtained from 10 independent experiments. The error bars indicate standard deviation. Scale bars in A-D are 50 μm .

To demonstrate the encapsulation ability of SECs, we used bovine serum albumin (BSA) as a model biomacromolecule and loaded it within the SECs. The encapsulation was achieved by a vacuum-assisted loading technique.⁴⁰ Suspended in an aqueous solution of BSA, the SECs were able to encapsulate the BSA-containing solution within the internal cavity by suction through the pores due to the change of internal cavity pressure with the application of the vacuum. The BSA-loaded SECs were washed with water to remove residual BSA from the outer surface after loading, followed by freeze-drying. To achieve the goal of cargo delivery within the micromotor design framework, a layer of Pt was deposited on one side of the BSA-loaded SECs, as illustrated in Figure 7.7 A. The BSA-loaded SECs before and after sputtering Pt are shown in Figures 7.7 B and C, respectively. Compared with empty SECs, the loading of BSA does not cause significant changes in the morphology and uniformity of SECs. The partially existed Pt layer on the outer surface imparts catalytic properties towards H_2O_2 decomposition to the BSA-loaded SECs, enabling their motion in the presence of H_2O_2 fuel.

Figure 7.7 Encapsulation and transport of BSA by SEC micromotors. A) Schematic of the cargo transport strategy. B) SEM micrograph of a BSA-loaded SEC. C) SEM micrograph of a BSA-loaded SEC that is partially coated with Pt. Scale bars are 10 μm.

In order to confirm SEC loading and to elucidate the distribution of platinum coating, confocal laser scanning microscopy (CLSM) analysis was performed on all samples (the sunflower pollen-derived SECs, FITC-BSA loaded SECs, platinum coated SECs, and platinum coated FITC-BSA loaded SECs). Z-stack images were collected for each sample and used to construct the 3D cross-sectional images presented in Figure 7.8. All images comprise both blue and green channel fluorescence, with the blue channel depicting SEC autofluorescence, and the green channel depicting FITC fluorescence from the FITC-conjugated BSA. It should be noted that FITC fluoresces in the green light spectrum (excitation: 490 nm, emission: 525 nm)⁴¹ and that pollen is known to exhibit autofluorescence across a broad spectrum of excitation wavelengths.⁴²⁻⁴⁴ However, the green fluorescence intensity from the pollen-derived

SECs is significantly lower than that of FITC, and we ensured that our gain settings were optimal for the detection of FITC, thereby resulting in no visible green fluorescence from the SECs. The unloaded SECs depicted in Figure 7.8 A exhibit a uniform structure with empty internal cavity and micron-sized pollen apertures are clearly present. Loading the SECs with FITC-BSA results in a high proportion of the internal cavity containing FITC-BSA while providing a clean outer SEC surface (Figure 7.8 B). Partial platinum coating of the SECs results in significant fluorescence-quenching over half of the SEC surface, leading to an observable shadowing effect in both the platinum coated SECs (Figure 7.8 C) and the platinum coated FITC-BSA loaded SECs (Figure 7.8 D). These CLSM observations indicate that FITC-BSA loading has been achieved and that the platinum coating is distributed over a single hemisphere of the SECs.

Figure 7.8 CLSM 3D images from Z-Stack data. A) Plain SECs, B) FITC-BSA loaded SECs, C) Plain SECs partly coated with Pt and D) FITC-BSA loaded SECs partly coated with Pt. Images in the first row are with optical background while images in the second row are only with fluorescence. Scale bars in all the images are 10 μm .

The transport of FITC-BSA by SEC micromotors was studied by fluorescence microscopy as well. Figure 7.9 illustrates the movement of a FITC-BSA loaded SEC micromotor in 3% H₂O₂ with an average velocity of 26.40 $\mu\text{m/s}$. Figure 7.9 A displays the time-lapsed images. The results support that encapsulation of FITC-BSA had minimal influence on the mobility of the SEC micromotors. Effective bubble generation was observed on one side of the BSA-loaded SECs, which propels the motion of the transport vehicles. Due to the large number of pores on the SEC surface, the loaded FITC-BSA will be released rapidly upon contact with water. As such, the SEC micromotors will release the encapsulated FITC-BSA during autonomous propulsion. The bubble generation also contributes to the diffusion of released FITC-BSA in the solution. Figure 7.9 B shows the tracking trajectory of the SEC micromotor in Figure 7.9 A. The time interval between adjacent points is 0.78 s. With the cargo loaded inside, the SEC micromotors can still exhibit both linear and circular propulsion behaviors. The circular motion is due to the resultant force of bubble propulsion and drag force deviates from the motion direction of the micromotor.

Figure 7.9 Motion of the FITC-BSA loaded SEC micromotors under fluorescence microscope. A) Time-lapse images of the motion. B) Trajectory of the FITC-BSA loaded SEC micromotor. Scale bars are 50 μm .

In addition to cargo delivery, we also evaluated the potential of the micromotors to address the issue of heavy metal pollution, which is one of the serious threats to public health owing to its detrimental physiological effect even at low concentrations.⁴⁵ Diverse strategies have been developed for elimination of heavy metals in aqueous environments. Among the different methods, adsorption is widely used to remove heavy metals, which is attributable to its easy operation, low cost, and reliable performance. Hence, seeking effective and low-cost adsorbents for heavy metal removal is one of the main directions of research in this field. The use of natural materials derived from renewable resources as adsorbents have recently attracted considerable attention.⁴⁶ The natural abundant biopolymer, sporopollenin, is a

promising bioadsorbent to eliminate heavy metals from aqueous solution. It has been reported that sporopollenin and its derivatives can be used to absorb a wide range of metallic ions.⁴⁷⁻⁴⁹ Sporopollenin has a polymeric porous structure with hydroxyl, carboxyl, and carbonyl groups that can chelate with various metals.⁵⁰ The adsorption is reported to be resulted from both ion-exchange and chelating effects.⁵¹ The self-propulsion and bubble generation of micromotors will result in efficient fluid mixing, which is effective in accelerating the process of sensing and decontamination.^{52, 53} Using self-propelled micromotors to generate effective fluid convection is desirable in circumstances where utilization of mechanical stirring is not suitable.

For proof-of-concept experiments, we used lead as an exemplary metal pollutant in order to compare the decontamination efficiency of static SECs and SEC micromotors. All the decontamination studies were conducted in 1 ppm lead aqueous solution with a fixed concentration of H₂O₂ (5 wt%) and SDS (0.3 wt%). The densities of both static and moving SECs were kept at 5×10^4 SECs/mL in the lead contaminated solution. Figure 7.10 A shows the influence of remediation time using SEC micromotors upon removal of lead over a 0 – 45 min range. The micromotors were allowed to navigate in the contaminated solution for different durations (0, 15, 30 and 45 min). Each point in the figure was obtained from three independent experiments under the same conditions. Inductively coupled plasma mass spectrometry (ICP-MS) was used to measure the concentration of lead. After remediation with SEC micromotors for 15 min, the lead concentration dropped by more than half, from 1 ppm to lower than 500 ppb. If the remediation time is prolonged to 45 minutes, the lead concentration declined to 211 ± 30 ppb, which corresponds to a removal efficiency of $79 \pm 3\%$. In contrast,

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decontamination using static SECs for 45 minutes only led to a mild decrease in concentration to 839 ± 62 ppb, corresponding to a removal efficiency of $16 \pm 6\%$. The greatly enhanced efficiency of SEC micromotors reflects the self-mixing induced by the movement and bubble formation of micromotors. The fluid mixing on one hand enhanced the transport of heavy metals to the micromotor surface, and on the other hand kept the SECs well dispersed in the contaminated solution. The static SECs tended to sink to the bottom, which largely reduced the interaction with heavy metals. Figure 7.10 B shows energy dispersive X-ray spectroscopy (EDX) mapping of the SEC micromotors collected from the filter membrane after the decontamination process described above was completed for 45 minutes. The enhanced signal of lead, compared with that before the decontamination process, further supports its absorption on the SECs.

Figure 7. 10 Decontamination of lead using SEC micromotors. A) Influence of remediation time on lead removal. B) SEM and corresponding EDX mapping of a SEC micromotor after decontamination illustrating the distribution of C, O, Pt and P.

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Chapter 8

Conclusion and Epilogue

8.1 Conclusion

8.1.1 *Material*

8.1.2 *Apparatus*

8.2 Epilogue

8. Conclusion and Epilogue

8.1 Conclusion

As our capabilities to design materials at the microscale and nanoscale levels continue to improve, there is growing interest in developing functional platforms that actively respond to dynamic environmental factors. Such features constitute the basis for micro/nanomachines with autonomous functionalities, as evidenced by the emergence of self-propelled micro/nanoscale motors that can convert chemical energy into motion and forces. Substantial efforts have been made towards addressing practical problems with the use of micro/nanomotors, whereas there are still many difficulties need to overcome to meet the expectation. Among at the shortcomings in effectiveness and practicability, this project has highlighted two aspects in the field of micro/nanomotors, fabrication and application.

8.1.1 Design and fabrication of micro/nanomotors

The first aspect is on the efforts in the direction of large-scale manufacturing of functional micro/nanomotors. The present problems of preparing micro/nanomotors are concentrated in fabrication methods and materials. Conventional preparation methods require complex procedures, high-end instruments and related high cost, which makes it difficult to produce micro/nanomotors in large scale. The current available materials for fabrication largely rely on scarce noble metals, resulting in expensive consumption and limited functionality. **Chapter 4** and **5** present our efforts towards addressing these problems retarding the application of micro/nanomotors.

The simplification of current methods and optimization of geometric parameters of tubular micro/nanomotors were explored in **Chapter 4**. An affordable and simple route for fabrication of rolled-up microtubes, using fruit tissue cells as support of the deposited metal layer, was developed. Given the cheap price of fruits and small amounts needed for the preparation process, the cost of fabrication is only cut down to the consumption of Pt used for sputtering. Microtubes fabricated by this method exhibited good uniformity in the dimensions and excellent mobility. Geometric parameters must be taken into consideration in the design of micro/nanomotors. The influence of dimensions was investigated using micro/nanotubes prepared by membrane template-assisted electrodeposition. Through comparing different sizes of micro/nanotubes, we found that geometric parameters will not only affect the velocity of micro/nanotubes at moderate fuel level. Moreover, it also affects the activity of micro/nanotubes at low fuel concentrations and imposes limitations on the velocity at high fuel concentrations. It needs higher concentration of H_2O_2 for nanotubes with nanometer-sized openings to be activated. High absolute velocity of large tubes does ensure higher velocity by body lengths.

Subsequently, we extended the scope of fabrication materials to widely accessible inorganic materials and emerging nanomaterials in **Chapter 5**. Ag and MnO_2 have been demonstrated to be potential alternative catalyst to Pt. Micromotors based on hot-spot materials, graphene and MoS_2 , were developed using different propulsion mechanisms. Graphene microparticles loaded with a very low amount of iridium catalyst can exhibit fast motion while the high surface area of graphene offers excellent opportunities for various functionalizations desired for practical applications. For the MoS_2 based motor,

naphthalene is to induce surface tension gradient at the water interface for propulsion and intercalated sodium reacts with water to separate the material layers, enabling the simultaneous motion and exfoliation at water surface. The integration of these functional materials would open new horizons for the applications of micro/nanomotors.

8.1.2 Investigation on potential applications of micro/nanomotors

The influences of the main components of blood serum on the motion of Pt catalysed microtubes were investigated in **Chapter 6**. All of blood proteins, electrolytes and metabolite affect the motion of micromotors to some degree. The poisoning effect is not confined to the blood proteins, but is of a general nature, as catalytic microtubes are prone to passivation from other types of proteins such as glucose oxidase. Main blood electrolytes all exhibit passive effect on the motion of the catalytic microtubes. Small metabolite molecule, uric acid, functions as a free radical scavenger which leads to compromised mobility of microtubes. Additionally, the influence of surfactants concentrations and types on the mobility of microtubes was also studied in this chapter. Upon reaching CMC, the concentration of surfactants will not have obvious effects on the motion of microtubes in a moderate range. The mobility of microtubes differ greatly in different surfactants solutions. These findings provide important references for the development of micromotor and its related applications, especially in biomedical field.

The application of micro/nanomotors relies on rational functionalization. Micro/nanomotors intended for different applications demand customized functionalization strategies. Extension of micro/nanomotors to wider applications

requires a wider spectrum of functionalization strategies. Proof-of-concept applications of micro/nanomotors for heavy metal removal and cargo delivery were explored in **Chapter 7**. Towards addressing mercury contamination, we developed DNA-functionalized microtubes that can serve as new generation of self-propelled catalytic micromachines to remove Hg(II) from aqueous solution. The highly specific and strong binding of Hg(II) to T-T mismatched pair in DNA sequences conferred the adsorption capability for Hg(II) on the microtubes and the efficient self-propulsion resulted in enhanced removal of Hg(II). Another multifunctional micromotor based on sporopollenin exine capsules (SECs) was developed for cargo delivery and heavy metal removal applications. The biocompatibility and large internal cavity of SECs make them suitable for encapsulation and delivery of cargo, including macromolecular compounds. The porous polymeric structure and functional groups on the surface offer sporopollenin the ability to absorb heavy metals. The self-propulsion dimension of SEC micromotors enables transport of encapsulated cargo as well as accelerated performance in remediation tasks across large sample volumes in the absence of external mixing.

8.2 Epilogue

We are entering the age of nanotechnology, an era where more expectations have been placed than any previous ages defined by materials such as stone, bronze, iron and silicon. The ability of nanotechnology to control atoms and molecules changes the way we use materials. Researchers are finding diverse approaches to prepare nanomaterials and to build them elaborately into functional systems. While

considerable efforts have led to impressive progress in the great diversity of self-propelled micro/nanomotors, successful realization of their practical applications still requires further improvement.

Focus should be placed on the following several aspects for any future development of micro/nanomotors. First, easy and cost-effective approaches should be developed towards parallel mass production of micro/nanomotors to fulfill the vision that millions of nanomotors are able to cooperate and communicate with each other to accomplish tasks. Quality control is a problem that cannot be overlooked in the process of simplifying preparation procedures. Because the geometry and morphology of micro/nanomotors are critical to their movement, the uniformity of the structures and reproducibility of the methods are of great significance. Second, the discovery of new materials and propulsion methods that are compatible with living systems is a challenge facing the field. The limitations of currently used materials and fuels preclude many potential applications of micro/nanomotors, especially those in the biomedical field. Energy-conversion efficiency can be promoted to increase both the mobility and towing ability of micro/nanomotors for improved transport of heavier and sophisticated cargoes. Third, more functionalization strategies should be developed to expand the scope of potential applications. Current methods relying on magnetic or electrostatic attraction are only suitable for magnetic and charged cargoes, while self-assembled monolayer techniques require specialized interaction between cargoes and receptors on nanomotors. The ability to pick up, transport, and release diverse cargoes is expected to play important roles in numerous practical applications in the environmental and biomedical areas.

Large-scale fabrication of nanomotors with improved efficiency, biocompatibility, and functionality using easy and low-cost approaches can pave the way for the ultimate realization of potential applications. As interest in this cutting-edge field increases and technological breakthroughs emerge, micro/nanomotors are expected to have profound effects on a variety of related fields just like the machines of our macroscopic world.

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Appendices

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Fabrication of Micro/Nanoscale Motors

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1. INTRODUCTION

The use of tools can be traced back to the beginning of recorded history and represents a significant step in the evolution of mankind. A machine is a tool that can perform intended tasks using energy. Throughout history, humans have developed many machines to help change the world. In fact, machines are not limited to human design. The biomachines created by nature through millions of years of evolution are able to perform complicated tasks precisely, forming the foundations of biological systems. Inspired by the biomachines of nature, humans have devoted considerable effort to the development of artificial micro/nanoscale machines analogous to the macroscopic ones in our lives. Micro/nanomotors represent a fundamental step toward the realization of practical nanomachines. A micro/nanomotor is a micro- or nanoscale device that converts energy into movement and force. However, it is not easy to propel microscale objects in liquid because motion at a low Reynolds number is dominated by viscous forces¹ and Brownian motion becomes significant at small length scales. Designing and building new micro/nanomotors and propulsion methods are among the most exciting challenges facing nanotechnology. The same structure/shape of a micromotor can be achieved by different fabrication techniques. Each of these techniques has its own limitations in terms of scalability, precision, cost, or device size. The focus of this review is on the fabrication techniques of the micro/nanomotor itself as they are of key importance in the building of functional devices.

Before discussing details of fabrication techniques, we wish to mention the different approaches used for propulsion as the fabrication techniques serve only one purpose: to create a propelled functional device. Different approaches have been proposed for the propulsion of micro/nanomotors.² The motion of synthetic micro/nanomotors can be either chemically self-propelled or propelled by external energy, including magnetic or electrical fields, light, or ultrasound. In addition to synthetic micro/nanomotors, the propulsion of

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Table 1. General Summary of Propulsion Mechanisms and Fabrication Techniques of Reported Micro/Nanomotors

classes	types	propulsion	fabrication
synthetic chemically self-propelled micro/nanomotors	nanowires	self-electrophoresis	membrane template-assisted electrodeposition ^{49,50}
	micro/nanotubes	bubble propulsion	rolled-up technology ⁵¹
			template-assisted electrodeposition ^{52,53}
	Janus micro/nanomotors	self-diffusiophoresis, self-electrophoresis, bubble propulsion, or surface tension gradients	template-assisted layer-by-layer assembly ⁵⁴ physical vapor deposition ^{16,55–57} asymmetric bipolar electrodeposition ⁵⁸ assembly and trapping of micro/nanoparticles ^{59–61} assembly and incorporation of synthetic molecules ^{5,62}
synthetic magnetically driven micro/nanomotors	helical micro/nanomotors	magnetic forces/torques	self-scrolling technique ⁶³ glancing angle deposition ^{64,65} direct laser writing ^{66,67} deposition on helical templates ^{68,69}
	rigid/flexible nanowires		conventional/modified membrane template-assisted electrodeposition ^{70–72}
	chain of magnetic particles		assembly of magnetic particles ^{73,74}
	Janus micro/nanomotors	magnetically induced thermophoresis	physical vapor deposition ⁷⁵
synthetic ultrasound-driven micro/nanomotors	nanowires	acoustic pressure difference/acoustically driven asymmetric steady fluid streaming	membrane template-assisted electrodeposition ⁷⁶
	perfluorocarbon-loaded microbullets	acoustic droplet vaporization	conjugation of perfluorocarbon in rolled-up or electrodeposited microtubes ³⁹
	magnetic nanoparticle-loaded red blood cells	asymmetric distribution of encapsulated magnetic nanoparticles	loading magnetic particles in red blood cells ⁷⁷
	micro/nanomotors based on photoresponsive surfaces	surface free energy gradient generated by photoisomerization of molecules	modifying substrate surfaces with a photoisomerizable molecule monolayer ^{78,79}
synthetic light-driven micro/nanomotors	doped liquid crystal films/liquid crystal elastomers	photoisomerization of molecular motor induced reorganization/deformation	incorporation of molecular motor into liquid crystal films/liquid crystal elastomers ^{80,81}
	Janus micromotors	diffusiophoresis induced by light	physical vapor deposition ^{82,83} encapsulation ⁸⁴
	micromotors with anisotropic geometry	light torque	direct laser writing ⁸⁵
	particles of photoresponsive inorganic materials	photoinduced self-diffusiophoresis	original particles ^{86,87}
synthetic electrically driven micro/nanomotors	metallic nanowires	electrical driving torque or dielectrophoretic force	membrane template-assisted electrodeposition ^{88,89}
	semiconductor diode nanowires	electroosmotic flow	membrane template-assisted electrodeposition ⁹⁰
	helical micromotors	electroosmotic flow	self-scrolling technique ⁹¹
	metallic microobjects	dynamic bipolar self-regeneration	electrodeposition ⁹²
	conducting microobjects	bipolar chemistry induced asymmetric bubble generation	conducting microobjects of different shapes ⁹³
biohybrid micro/nanomotors	micro/nanomotors based on biomolecular motors	propulsion of biomolecular motors	integration of biomolecular motors with synthetic components ⁹⁴
	micro/nanomotors based on enzymes	propulsion by enzyme-catalyzed reactions	functionalization of synthetic components with enzymes ^{95,96}
	micro/nanomotors based on motile units	propulsion by intact motile cells	integration of motile cells with synthetic components ^{97–100}

various biohybrid micro/nanomotors based on biomaterials existing in nature has been reported. Among a variety of micro/nanomotors, particular attention has been given to chemically powered micromotors.^{3,4} Various self-propelled micro/nanomotors have been developed based on mechanisms of surface tension gradients,⁵ self-electrophoresis,^{6,7} self-diffusiophoresis,^{8,9} and bubble propulsion.¹⁰ Surface tension gradients along an interface can cause an imbalance of forces and thus generate flow, which is known as the Marangoni effect. A number of motors have been reported to exhibit motion on the basis of the Marangoni effect, but most of them are on macroscale.^{11,12} Self-phoresis, which means that an object can generate its own local field or concentration gradient, has been widely employed in the design of self-propelled micro/nanomotors. For micro/nanomotors relying

on self-electrophoresis, typically bimetallic catalytic Janus particles and nanowires, two different electrochemical half reactions happening at the two ends of an asymmetric conducting particle, such as H₂O₂ oxidation and reduction on opposite ends of a Pt/Au particle, will proceed with electron flows inside the particle as well as the migration of protons outside the particle, resulting in the propulsion of the particle in the opposite direction. For self-diffusiophoretic micro/nanomotors, concentration gradients of solute across the particle interfacial region cause water to flow from regions of low to high solute concentrations and the induced fluid flow will propel the particle accordingly. The motion of many catalytic Janus micro/nanomotors is attributed to the self-diffusiophoretic mechanism. Bubble propulsion depends on the recoil mechanism of accumulated gas bubbles generated

through catalytic or noncatalytic reactions. A typical representation of bubble-propelled micro/nanomotors is the microtube design. Some catalytic Janus motors and reactant-based Janus motors can also exhibit bubble-propelled motion. The reported fuels for chemically self-propelled micro/nanomotors include H_2O_2 , Br_2 , or I_2 solutions,¹³ hydrazine,⁹ acidic and alkaline solutions,^{14,15} and so on. Although water has been employed for the propulsion of some micromotors, the limited lifetime of these micromotors restricts their development.^{16,17}

Although autonomous self-propulsion is very attractive, the general requirement for external chemical fuel hinders some biomedical applications of chemically powered micromotors, as most of the fuel used is not compatible with living systems. On the other hand, propulsion by an external energy source provides possibilities for the application of micromotors in vivo, enabling parallel development of self-propelled and external-energy-propelled micro/nanomotors. Propulsion by external energy enables the navigation of micro/nanomotors in various types of fluids with the elimination of chemical fuel requirements. Because low-intensity magnetic fields are considered harmless to living organisms, micro/nanomotors powered by magnetic fields have shown great promise for many biomedical applications. Tiny magnetically driven motors are envisioned to be involved in various biomedical tasks such as kidney stone destruction,¹⁸ cardiovascular intervention,¹⁹ remote sensing,²⁰ treatment of eye diseases,²¹ and so on. Inspired by bacterial flagellum propulsion, researchers have developed a large number of helical motors that can transform rotation around their helical axis into a translational corkscrew motion along the axis.^{22,23} Helical structures are at the heart of magnetically driven micro/nanomotors, because helical motors generally become more desirable than pulling with field gradients as the size of a micromotor decreases or as the distance from the magnetic field source increases.²⁴ Ultrasound is another biocompatible energy that has been widely used in medical applications. A series of nano/microscale motors powered by ultrasound have been developed.²⁵ With the use of ultrasound, propulsion of micromotors inside living cells has also been demonstrated.²⁶ Light and electricity have also been utilized as the source of energy for the propulsion of micro/nanomotors, opening a bright prospect for the development of versatile micro/nanomotors. Additionally, biohybrid techniques offer an alternative strategy for taking advantage of materials existing in nature to achieve micro/nanoscale propulsion.

The ultimate goal of fabrication is to create the micro/nanomotors that are suitable for application in an easy and cost-effective way. Micro/nanomotors are expected to play important roles in various potential applications, ranging from the biomedical area^{27–29} to environmental remediation.^{30,31} Functionalization is a key step toward successful realization of the applications of micro/nanomotors. Tailored functionalization methods should be developed according to characteristics of specific kinds of micro/nanomotors and corresponding intended applications. Through rational functionalization, micro/nanomotors have proved useful for performing diverse biomedical tasks such as directed drug delivery,³² isolation of biological targets,^{33–38} microsurgery,^{39–41} bioassay,^{42,43} and bioimaging.⁴⁴ Recent progress in environmental applications also demonstrated the great potential of micro/nanomotors for use in environmental monitoring and remediation processes.^{45–48}

The rapid development of nanotechnology has resulted in diverse strategies and techniques for the fabrication and functionalization of micro- and nanoscale motors. The objective of this review is to highlight various approaches to the fabrication of micro/nanomotors. The fabrication techniques and the factors that must be considered in the design of micromotors including shape, composition, and distribution of materials as well as functionalization are addressed. By reviewing the progress that has been made in the fabrication of artificial micromotors during the past decade, we intend to illustrate the opportunities and challenges facing fabrication and provide perspectives for the development of new methods. Table 1 provides a general summary of propulsion mechanisms and fabrication techniques of reported micro/nanomotors that will be discussed in the following sections. Please note that only a few representative references are given in the table and all classes are discussed in detail with much more in-depth referencing in the following sections. We have organized the review according to fabrication techniques, as the same techniques can be used for fabrication of different structures propelled by different mechanisms. Because the aim of any fabrication technique is the function of the devices, we closely link fabrication to function and discuss individual examples.

2. FABRICATION TECHNIQUES

2.1. Electrochemical/Electroless Deposition

Electrochemical deposition, or electrodeposition for short, enables the synthesis of arbitrary three-dimensional geometries with different materials ranging from different metals to polymers, thus leading to the widespread application of this technique in nanotechnology. Electrodeposition can easily be performed without the requirements of high-cost instruments and harsh experimental conditions. Additionally, electrodeposition has the ability to be scaled down and scaled up. Therefore, micro- and nanostructures with various dimensions can be fabricated using this technique. While electrodeposition is a process that uses external electrical current to deposit materials, electroless deposition is a technique of deposition by chemical redox reactions rather than electrical means. Utilizing different templates, electrochemical and electroless deposition provide an effective way of making desired structures for micro/nanomotors.

2.1.1. Membrane Template-Assisted Electrodeposition. Membrane template-assisted electrodeposition employs the pores of a membrane to synthesize desired tubes and wires composed of different materials such as polymers, metals, semiconductors, and carbons.^{101,102} Each of the pores is like a reactor where the desired particle is synthesized. Because of the monodisperse diameters and large pore densities in the membrane, similar nanostructures can be mass produced. For membranes of a certain area and pore density, the length of the structure is proportional to the charge while the diameter is equal to the diameter of the pores. Membranes commonly used in the preparation of micro/nanomotors are porous alumina membranes and track-etched polycarbonate membranes. Depending on the chemistry of the pore wall and the properties of the material, the nanostructures can be either solid or hollow. Membrane template-assisted electrodeposition offers a powerful and relatively low-cost method for preparing nanowire, micro/nano tubular motors, and even helical micromotors.¹⁰³ In the

Figure 1. Membrane template-assisted electrodeposition of nanowires: (a) deposition of gold or silver backing on the membrane template, (b) electrodeposition of sacrificial layer, (c) sequential electrodeposition of desired components, and (d) removal of the backing and sacrificial layer; dissolution of the membrane.

following sections, we will discuss membrane template-assisted electrodeposition for the fabrication of nanowires, micro/nanotubes, and helical micromotors.

2.1.1.1. Electrodeposited Nanowires. A synthetic chemically powered microscale motor was reported about 10 years ago. Sen and Mallouk's team described that bisegment Au–Pt nanowires, 370 nm in diameter and 2 μm in length, can exhibit autonomous motion at speeds of ~ 10 body lengths/s in 2–3% hydrogen peroxide.⁴⁹ At that time, Ozin, Manners, and co-workers also reported rotational motion of Au–Ni nanowires.⁵⁰ These original studies have attracted wide attention and have led to considerable subsequent efforts devoted to the field of synthetic micro/nanoscale motors. Other studies found that the motion of the nanowire motors is attributable to self-electrophoresis.⁶ These bimetallic nanowire motors are mainly prepared by membrane template-assisted electrodeposition. In a modified method of preparing nanowire motors,^{50,105} alumina membranes with nanosized pores are used and different metals are deposited sequentially into the pores to form striped rodlike structures (Figure 1). A layer of silver or gold is first deposited on one side of the membrane using physical vapor deposition to serve as the working electrode. The membrane is then assembled in a Teflon plating cell with flat aluminum foil placed against the metal layer to serve as a conductive contact for subsequent electrodeposition. Usually, a sacrificial layer of copper or silver is first deposited, followed by sequential deposition of different desired metals. The silver or gold backing and the sacrificial layer are removed by mechanical polishing or chemical etching. By dissolving the alumina membrane in NaOH solution, the nanowire motors can be released and collected after successive rinsing and centrifugation.

To achieve higher efficiency and speed of bimetallic nanowires, some modifications were made in the fabrication process and resulting nanowire structure. Adopting new materials that can help enhance the redox reactions to serve as a cathode or anode will increase the mobility of self-electrophoretic motors. Employing Ag/Au alloy as the cathode instead of a gold segment dramatically accelerates the movement of the nanowires (Figure 2A).¹⁰⁶ The speed is closely related to the composition of the Ag/Au segment, which can be modulated by varying the proportion of silver

and gold plating solution in the alloy plating solutions. Laocharoensuk et al. showed that the incorporation of carbon nanotubes into the anodic Pt end by adding them to the plating solution can dramatically accelerate the motion of the nanowire motors (Figure 2B).¹⁰⁷ Alternatively, increasing the surface area of the catalytic segment of the nanowires leads to enhancement of the H_2O_2 breakdown rate and therefore the speed of the nanowires. Ozin and co-workers reported a method of increasing surface roughening to increase the speed of nanowires, in which silica nanoparticles were mixed with the metal plating solution for codeposition and then were etched away to introduce porosity.¹⁰⁸ Besides the commonly used H_2O_2 fuel for the propulsion of electrodeposited nanowires, Liu and Sen demonstrated the electrophoretic motion of Cu–Pt nanowires in dilute aqueous solutions of Br_2 and I_2 with the Cu end serving as the anode to be oxidized and the Pt end functioning as the cathode where the halogen is reduced.¹³

In addition to chemically self-propelled motion, nanowires prepared by membrane template-assisted electrodeposition can also exhibit motion powered by ultrasound, electric, or magnetic fields. The behavior of both single material and multisegment metal nanowires prepared by membrane template-assisted electrodeposition in the presence of external electric fields has been widely investigated. Metal nanowires can display controllable rotation due to rotary torque in an electric field provided by applying alternating current voltages to multiple electrodes (Figure 2C).^{88,109} In addition, by using alternating current electric fields applied to strategically designed microelectrodes, the movement of metal nanowires can be controlled by dielectrophoretic force. They can be driven to align, chain, and accelerate in certain directions, as well as to concentrate, disperse, and assemble into complex scaffolds.^{89,110} Chang et al. illustrated that millimeter-sized semiconductor diodes can be powered by an external alternating electric field because of the resulting particle-localized electroosmotic flow.¹¹¹ The miniaturization of diodes was accomplished by using semiconductor diode nanowires. Polypyrrole–cadmium (PPy–Cd) and CdSe–Au–CdSe diode nanowires prepared by membrane template-assisted electrodeposition were demonstrated to be able to exhibit directional motion in the same fashion (Figure 2D).⁹⁰

Figure 2. Propulsion modes of electrodeposited nanowires. (A, B) Schematic representations of the self-electrophoresis mechanism of Ag–Au/Pt and Au/Pt–CNT nanowire motors in H_2O_2 , respectively. Reproduced from refs 106 and 107. Copyright 2008 Wiley-VCH and 2008 American Chemical Society, respectively. (C) Rotation of nanowires by alternating current voltages applied to multiple electrodes: (a) schematic representation of experimental setup of quadruple electrodes and (b) images of free (right) and one end fixed (left) rotating Au nanowires. Reproduced from ref 88. Copyright 2005 American Physical Society. (D) Schematic diagram illustrating the experimental setup for propulsion of PPy/Cd and CdSe–Au–CdSe nanowire diodes in an electric field. The inset shows the corresponding scanning electron microscopy (SEM) images of the nanowire diodes. Reproduced from ref 90. Copyright 2010 Royal Society of Chemistry. (E) Ultrasound-propelled nanowires: (a–c) illustration of the kinds of motion (chain assembly and axial spinning, axial directional motion and in-plane rotation, and pattern formation) of metal nanowires in an acoustic field; (d) and (e) dark field images of typical chain structures and ring patterns formed by Au and AuRu rods. Reproduced from ref 76. Copyright 2012 American Chemical Society. (F) Preparation procedure of flexible metallic nanowires with polyelectrolyte hinges after membrane template electrodeposition. (G) SEM image of a hinged nanowire. (F) and (G) are reproduced from ref 71. Copyright 2007 Nature Publishing Group. (H) SEM image of a Au/Ag_{flex}/Ni nanomotor with flexible central silver segment. Reproduced from ref 72. Copyright 2010 American Chemical Society.

Mallouk and co-workers have demonstrated that metallic nanowires (2 μm long and 330 nm in diameter) can be levitated, propelled, aligned, rotated, and assembled using ultrasound, as illustrated in Figure 2E.⁷⁶ When the acoustic field is turned on, the nanowires levitate to the midpoint plane of a cylindrical cell and exhibit fast axial directional motion or in-plane rotation at a speed of $\sim 200 \mu\text{m/s}$. The nanowires can aggregate into ring or streak patterns without stopping their directional motion or changing direction. The speed of axial propulsion can be tuned by changing the amplitude and frequency of the acoustic wave. The fact that electrodeposited polymer nanorods cannot exhibit directional motion proves that material plays an important role in the axial directional motion. The propulsion mechanism relies on the shape asymmetry of the nanowires, which is derived from their concave and convex ends formed in the electrodeposition process. The ends of the nanowires fabricated by template-assisted electrodeposition are typically concave and convex instead of perfectly flat. They proposed that the scattering of acoustic waves from the concave end concentrates energy while the convex end weakens the energy density, generating acoustic pressure difference between the two asymmetric ends to propel the nanorods directionally. Nadal and Lauga presented another possible mechanism that the asymmetric steady fluid streaming induced by the asymmetry of the nanorod is responsible for the acoustic axial propulsion of the nanowires.¹¹² A sphere lithography technique was introduced for controllable concavity formation at the end of the nanowires.¹¹³ To enhance the concavity, polystyrene (PS) nanospheres were incorporated into the nanopores of silver-sputtered membranes to serve as a second sacrificial template. After sequential deposition of different metals, the nanospheres were dissolved, resulting in the formation of concavity at the bottom of the nanowires.

Magnetic nanowires can act as “surface walkers” in the presence of a rotating magnetic field. Prepared by the membrane template-assisted electrodeposition approach, gold nanowires with subsequent evaporation of nickel on one side¹¹⁴ and pure nickel nanowires⁷⁰ have been demonstrated to be able to move along surfaces and manipulate cargoes with the propulsion of a rotating magnetic field. However, the confinement of the working conditions and the mobility of these magnetically powered rigid nanowire motors are not suitable for some envisioned applications. On the other hand, flexible nanowires can be propelled by external magnetic fields in a variety of fluids. For magnetically driven flexible nanowires, a nickel head and a flexible segment are necessary to achieve magnetic propulsion. The motor is actuated by the alignment of the magnetic nickel segment with the magnetic field, followed by mechanical deformation of the flexible segment essential for propulsion.

Flexible nanowire motors are prepared using a common membrane template-assisted electrodeposition protocol similar to the preparation of rigid nanowire motors, but with some additional steps. Mirkovic et al. described magnetically propelled flexible nanowire motors in which rigid nickel and platinum segments are linked by flexible polyelectrolyte multilayer segments.⁷¹ Fabrication of the flexible polymer hinges was achieved by encapsulation of Ni/Au/Pt nanowires with polyelectrolytes through layer-by-layer electrostatic self-assembly, a technique that will be discussed later, followed by selective etching of the gold part with KI/I_2 solution to expose the soft polymer hinges (Figure 2F). The application

of an external fluctuating magnetic field can induce bending of the nickel segment about the hinge. The flexible nanowires with hinges can also be actuated by a planar oscillating magnetic field to exhibit planar undulation to move forward.¹¹⁵ Wang and co-workers proposed another kind of flexible nanowire motor with a bendable silver part.^{72,116} The flexibility of the silver segment is achieved by partial dissolution of Ag in hydrogen peroxide. The rotation of the nickel head under rotating magnetic field results in the deformation of the Ag part, breaking the symmetry to induce movement. The capability of the Ni/Ag_{flex} motor to deliver drug-loaded magnetic microparticles to *HeLa* cells through a microchannel in biological media has been demonstrated by Gao et al.¹¹⁷ For flexible nanomotors containing an additional gold segment (Figure 2H),⁷² the direction of movement of the Au/Ag_{flex}/Ni nanomotors can be changed from toward the Ni end to away from the Ni end based on the fact that changes in the respective length of the Au and Ni segments can lead to changes in their rotation amplitudes.

2.1.1.2. Electrodeposited Micro/Nanotubes. The electrokinetic self-electrophoresis mechanism of the motion of segmented nanowires in H₂O₂ means that their mobility decreases with increasing solution conductivity, which limits the application of chemically propelled nanowire motors in a high ionic strength environment.¹¹⁸ The emergence of tubular microjet engines blazed a new way for the development of self-propelled micromotors. Such microengines rely on the propulsion of oxygen bubbles generated on the inner surface by catalytic decomposition of H₂O₂. The bubble recoiling mechanism provides microjet engines with higher speed^{119,120} and greater towing ability,²⁸ thus holding great promise for practical applications in biomedical and environmental fields.

Similar to the membrane template-assisted electrodeposition method used in the preparation of nanowires, Gao et al. developed a simplified method for fabricating microtube engines (Figure 3A).⁵² Cyclopore polycarbonate membrane, which has a symmetrical double-cone pore structure, offers a desirable template for the electrodeposition of asymmetric microtubes. The procedure for assembling the electroplating cell is the same as that for preparing nanowires, after which aniline monomers are first electropolymerized for consideration of solvophobic and electrostatic effects. A layer of platinum is subsequently deposited, and bilayer polyaniline (PANI)/Pt microtubes are formed. The resulting microtubes are conical in shape with lengths of several micrometers and diameters depending on the pore size of the membrane template. The microtube engines fabricated by this method exhibit ultrafast speed and require a very low concentration of hydrogen peroxide fuel.

The composition and electropolymerization conditions of polymer-based microtube engines were investigated to realize optimization.¹²¹ A comparison of polypyrrole (PPy)-, poly-(3,4-ethylenedioxythiophene) (PEDOT)-, and PANI-based microtubes illustrated that PEDOT-based bilayer microtubes provide more reproducible yields and consistent morphology. In addition, because of the larger inner opening diameter, the most efficient propulsion is achieved by the PEDOT-based microtubes, which offer a speed of >1400 body lengths/s at physiological temperature. The structure of polymer-based microtubes can be affected by many factors in the electropolymerization process. The most favorable condition is the use of a low monomer concentration together with the proper amount of surfactant and appropriate analyte.

Figure 3. Membrane template-assisted electrodeposition of micro/nanotubes and helical micromotors. (A, B) Polycarbonate membrane-assisted preparation and SEM images of conical PANI/Pt microtubes. Reproduced from ref 52. Copyright 2011 American Chemical Society. (C, D) Anodized aluminum oxide (AAO) membrane-assisted preparation and SEM images of segmented microtubes. Reproduced from ref 53. Copyright 2013 Royal Society of Chemistry. (E) AAO membrane-assisted preparation of helical micromotors. Reproduced from ref 124. Copyright 2014 Royal Society of Chemistry.

Instead of taking advantage of platinum-catalyzed decomposition of hydrogen peroxide as a source of power, Wang's group described tubular PANI/Zn microengines using acid in the environment as fuel.¹⁴ A layer of zinc was electrodeposited to serve as the inner wall of the microtubes after the electropolymerization of PANI. Hydrogen bubble generation and the resulting speed of the zinc microtubes highly depend on acid concentration, thus holding great promise for motion-based pH sensing. Except for polymer-based tubular microengines, complete metallic microtubes can also be prepared via membrane template-assisted electrodeposition. Zhao and Pumera successfully fabricated bimetallic Cu/Pt microtubes and proposed the use of widely available colloidal graphite ink instead of deposited metal backings in the setup of the electroplating cells to simplify the procedure.¹²² A striped metallic nanotube with a diameter of ~300 nm was prepared by electrodeposition employing conductive silver ink on the anodized aluminum oxide (AAO) membrane template together with aluminum foil as the working electrode (Figure 3C).⁵³ Unlike the "Swiss roll"

Figure 4. (A) Silver wire template-assisted layering approach for preparation of microtubes. Reproduced from ref 125. Copyright 2010 American Chemical Society. (B) Preparation of magnetic helical structure using lipids. Reproduced from ref 68. Copyright 2012 Wiley-VCH. (C) Principle of bipolar electrochemistry. (D) SEM image of nickel-modified carbon nanotube prepared by bipolar electrodeposition. Reproduced from ref 129. Copyright 2010 Elsevier Ltd. (E) Schematic illustration of the design of a bipolar electrodeposition cell. (C) and (E) are reproduced from ref 126. Copyright 2013 American Chemical Society.

structure of the rolled-up microtubes and the concentric conical structure of the electrodeposited microtubes, these nanotubes have a unique segmented structure with different metals placed longitudinally. The localized Pt segment can provide efficient propulsion as well.

2.1.1.3. Electrodeposited Helical Micromotors. Park's group reported template-assisted electrosynthesis of palladium nanosprings using nanoporous anodic aluminum oxide membranes.¹²³ Under acid conditions with an appropriate pH, the hydroxyl-terminated surface of the nanopores can selectively adsorb H⁺ ions in the adjacent solution, resulting in a compact layer. An interfacial double layer, localized hydrogen evolution, and screw dislocation were proposed to contribute to the growth of Pd atoms at peripheral positions in the pores to form the desired nanosprings in the electrodeposition process with a plating solution consisting of PdCl₂, CuCl₂, and HCl. The codeposition of palladium and copper in the nanopores of the anodized aluminum oxide membrane using the common membrane template-assisted electrodeposition protocol will result in the formation of homogeneous Pd/Cu nanorods. Upon dissolution of the membrane template and etching of the copper part, the Pd nanosprings can be obtained. Taking advantage of this method, Li et al. deposited a magnetic Ni layer on Pd nanosprings via electron beam evaporation and consequently obtained magnetically driven helical micromotors that display efficient propulsion in a rotating magnetic field (Figure 3E).¹²⁴ Membrane template-assisted electrodeposition also enables convenient tailoring of the geometries and dimensions of helical micromotors. Helical micromotors with different diameters can be fabricated using a membrane template with desired pore size. The length and pitch of the helices can be modulated by tuning the charge density and the Pd²⁺/Cu²⁺ concentration ratio in the plating solution, respectively.

2.1.2. Electrochemical and Electroless Deposition Based on Other Templates. The templates used for electrodeposition are not limited to only porous membranes but can be various shapes according to the desired structures. For the electrodeposition of microtubes, Wang and co-workers reported another approach using etched silver wire as a template (Figure 4A).¹²⁵ After sequential electrodeposition of Pt and Au layers onto the surface, silver wires were diced into microcones of the desired length. With nitric acid treatment, the silver wire template was etched and the Pt/Au bilayer on the wire surface became conical microtubes. The diameter of the larger opening is the same as that of the Ag wire (50 μm). However, this method is not suitable for mass production and the velocity of microtubes fabricated by this method is relatively low. Schuerle et al. employed self-assembled tubes and helical structures of diacetylenic phospholipid 1,2-bis(10,12-tricosadionyl)-sn-glycero-3-phosphocholine (DC_{8,9}PC) as templates for magnetically driven tubular and helical micromotors.⁶⁸ Tubular liposomal microstructures were derived from the dispersion of DC_{8,9}PC in an aqueous ethanol solution by heating and subsequent cooling through the chain-melting temperature, whereas helical liposomal microstructures were formed by adding water to the lipid solution in alcohol. The resulting liposomal microstructures were then activated by electroless deposition of Pd clusters to maintain shape, after which the rigid scaffolds were subjected to an electroless CoNiReP bath to coat them with magnetic multialloy for magnetic manipulation (Figure 4B).

2.1.3. Asymmetric Bipolar Electrodeposition. Bipolar electrochemistry is an important concept, that when a conductive object is placed in a strong electric field between two electrodes, a potential difference will occur between the two ends of the object. The polarization, which is propor-

Figure 5. Micro/nanomotors prepared by conventional physical vapor deposition. (A) Plant-based helical micromotors prepared through physical vapor deposition. Reproduced from ref 69. Copyright 2013 American Chemical Society. (B) SEM image and schematic drawing of a microrotor prepared by sequential deposition of Cr/SiO₂/Cr, Au, and Pt layers on an electrodeposited Au/Ru nanowire. Reproduced from ref 131. Copyright 2009 American Chemical Society. (C) SEM image illustrating an array of self-assembled spherical particles. The inset shows the coating of the Janus particles with metal film providing their catalytic and magnetic properties. Reproduced from ref 55. Copyright 2012 American Chemical Society. (D) Schematic of fabrication of bimetallic Janus micromotors by conventional physical vapor deposition. Reproduced from ref 56. Copyright 2010 American Chemical Society. (E) Formation of sphere dimers via thermal annealing. Reproduced from ref 134. Copyright 2009 Wiley-VCH. (F) Schematic image of a water-driven hydrogen-propelled Al–Ga/Ti micromotor. Reproduced from ref 16. Copyright 2012 American Chemical Society. (G) Schematic diagram of Mg-based seawater-driven Janus micromotor. Reproduced from ref 17. Copyright 2013 Royal Society of Chemistry.

tional to the electric field and the characteristic dimension of the object, generates an asymmetric reactivity on the surface of the object in a wireless manner (Figure 4C).^{58,126} Asymmetric bipolar electrodeposition has shown great promise for the bulk synthesis of Janus particles. Named after the Roman god with two faces, Janus particles refer to nano/microparticles whose surface has distinct chemical or physical properties.¹²⁷ When the polarization is strong enough, electrochemical reactions occur at the opposite poles of the object, which can break the symmetry of the object to generate Janus properties. Bipolar electrodeposition of a wide range of materials including metal, semiconductors, insulators, and molecular layers has been used for the preparation of Janus particles with different sizes and shapes. For bipolar electrodeposition of metal, a perpendicular electric field is applied to induce redox reactions at the opposite poles of the particles. The metallic salt is reduced at the cathodic pole and forms metal deposits on the particles. Janus particles with catalytic or magnetic ends generated by bipolar electrochemistry can be used as self-propelled or magnetically driven micromotors. Carbon microtubes with Pt on one end

synthesized by bipolar electrodeposition were demonstrated to be able to be propelled in H₂O₂ by oxygen bubbles,¹²⁸ whereas carbon microtubes with a Ni particle deposited on one side could be manipulated in the presence of an external magnetic field (Figure 4D).¹²⁹ The developed method of asymmetric bipolar electrodeposition using a cell avoids the immobilization of particles on a surface.^{58,126} Figure 4E shows a typical cell used for bipolar electrodeposition on microparticles. The topology of the deposits can be modulated by varying the orientation and amplitude of the electric field as well as the viscosity of the medium. This technology enables the mass production of Janus motors with different materials, sizes, and shapes.

2.2. Physical Vapor Deposition

Physical vapor deposition is a vaporization coating technique for depositing thin layers of materials. The vaporization of the material from a solid target is assisted by a high-temperature vacuum or gaseous plasma. The vapor is then transported to the surface of the substrate in vacuum or partial vacuum, followed by condensation to generate thin films. The two most common types of physical vapor deposition processes

are sputtering and electron beam evaporation. Sputtering is a technique that creates vapor by bombardment of the target by ionized gas, typically argon, whereas electron beam evaporation relies on an electron beam to evaporate atoms from the target into the gaseous phase. In both techniques, the resulting vapor phase is subsequently deposited onto the surface of the substrate. In the following subsections, we will discuss conventional physical vapor deposition and its variation, glancing angle deposition.

2.2.1. Conventional Physical Vapor Deposition.

Physical vapor deposition provides a direct approach to incorporate target materials into micro/nanostructures to provide desired properties. In the fabrication of micro/nanomotors, it is an important method for introducing materials with catalytic or magnetic properties or inert materials for blocking reactions. Magnetic materials are indispensable components for magnetically driven micro/nanomotors. One strategy for fabricating magnetically driven micro/nanomotors is to prepare templates suitable for magnetic propulsion, followed by physical vapor deposition of magnetic materials. The templates can be prepared through various techniques, such as glancing angle deposition and three-dimensional direct laser writing, or just by the use of structures existing in nature. Gao et al. reported plant-based bioinspired helical micromotors, harnessing intrinsic biological structures.⁶⁹ Spiral water-conducting vessels of different plants were separated, coated with Ti and Ni layers by electron beam evaporation, and then diced (Figure 5A). Helical micromotors with different diameters can be fabricated using spiral vessels from different plants or by controlled mechanical stretching. Instead of relying on magnetic forces and torques, Baraban et al. presented the motion of silica spheres with magnetic caps driven by magnetically induced thermophoresis.⁷⁵ Fe₁₉Ni₈₁ alloy caps were prepared by sputter deposition. By employing an alternating magnetic field to heat the magnetic caps of the particles, a local temperature gradient was generated to induce thermophoretic motion of the particles. To achieve directed motion, the simultaneous application of a homogeneous magnetic field was used to guide the particles.

When the orientation of a substrate is not changed, the materials introduced by physical vapor deposition are only on one side of the structures, thus providing a way of creating asymmetry. To expand the motion styles of nanowires prepared by membrane template-assisted electrodeposition, researchers have developed nanowires that can exhibit rotational motion without tethering instead of linear motion. Qin et al. coated one side of electrodeposited Au–Pt–Au nanowires with a Au/Cr bilayer using a thermal evaporator to break the symmetry, which induced rotation of the nanowires in hydrogen peroxide.¹³⁰ Wang et al. reported a similar asymmetric nanorod fabricated by coating one side of electrodeposited Au–Ru bimetallic rods with additional Cr, SiO₂, Cr, Au, and Pt layers sequentially via physical vapor deposition (Figure 5B).¹³¹ The second Au/Pt catalytic bilayer adds a perpendicular force, which results in rotation of the nanorod about 10 times faster than the one above.

In addition to asymmetric bipolar electrodeposition, physical vapor deposition is another main technique used in the fabrication of Janus micro/nanomotors. The key to the design and fabrication of Janus motors is the asymmetric distribution of catalysts or reactants, which results in directed force exerted on the motor to generate directional motion.¹³²

The preparation of Janus particles should allow selective synthesis of each side of the particle with different properties in high yield. A common synthetic strategy used in the fabrication of Janus motors is to use physical vapor deposition to break the symmetry at the interfaces via temporary shielding of one hemisphere.

For catalytic Janus micro/nanomotors, the preparation process is usually to deposit catalytic materials by physical vapor deposition onto one hemisphere of the particle to introduce asymmetry. As shown in Figure 5C, the typical procedure for preparing Janus particles is to form a self-assembled monolayer of particles by depositing a droplet of particle suspension on a substrate followed by slow evaporation.⁵⁵ Evaporation takes place in a small, tilted box to slow down the process and ensure better quality.¹³³ The desired area of monolayer coverage can be obtained by varying particle concentration and drop size. Catalytic material is then deposited on top of the monolayer to form hemispherical caps on the surface of the particles. After fabrication, the Janus particles are detached from the substrate via sonication. The diameters of the fabricated catalytic Janus motors usually range from dozens of nanometers to several micrometers.

The most common catalytic Janus micromotor is the Pt-catalyzed Janus particle. The motion of the spherical platinum Janus particle relies on a self-diffusiophoretic mechanism. The localized reactions of H₂O₂ catalyzed by asymmetrically distributed platinum will generate concentration gradients around the particles, leading to fluid flow in the vicinity and subsequent propulsion of the particles.^{8,132} Another example of spherical diffusiophoretic Janus micromotors was reported by Gao et al.⁹ They described an iridium-based catalytic Janus micromotor prepared by depositing one hemisphere of silica particles with iridium metal via physical vapor deposition. The iridium cap can catalyze the decomposition of hydrazine fuel into nitrogen, hydrogen, and ammonium. As a result, the Janus micromotor is able to exhibit diffusiophoretic movement in the presence of ultralow levels of hydrazine. Hong et al. reported the propulsion of silver-coated colloidal spheres in dilute H₂O₂ solution upon ultraviolet radiation due to the asymmetrical release of Ag⁺ and OOH[−] ions.⁸² Posner and co-workers demonstrated the synthesis of a bimetallic spherical motor relying on the electrophoretic mechanism for propulsion (Figure 5D).⁵⁶ First, the microspheres were half-coated with gold using a sputter coater. Subsequently, they were resuspended in water and deposited again with random orientation, which was repeated seven or eight times until the entire surface was coated with gold. The fully Au-coated spheres were then half-coated with Pt, resulting in bimetallic spherical Janus micromotors that can swim at velocities comparable to their nanowire counterparts.

On the basis of sphere templates, physical vapor deposition can be used to fabricate not only spherical Janus motors but many other motors with various structures. Valadares et al. proposed a catalytic dimer composed of a silica sphere and a platinum sphere.¹³⁴ The spheres were first coated with a bilayer of Cr/Pt by sputtering, followed by an annealing process, during which the metallic half-shell formed a platinum particle connected to the silica sphere (Figure 5E). Additionally, platinum shell micromotors were obtained by selectively etching silica sphere templates after physical vapor deposition of platinum onto the surface of the templates. The pure Pt shells can display motion propelled by bubbles, but

Figure 6. Micro/nanomotors prepared by glancing angle deposition. (A) Schematic diagram of GLAD technique and SEM image of the helices prepared by this method. Reproduced from ref 142. Copyright 2013 American Chemical Society. (B) GLAD using gold nanodots prepared by micellar nanolithography as nucleation sites. Reproduced from ref 141. Copyright 2013 Macmillan Publishers Limited. (C) Preparation of asymmetric Pt/Au-coated catalytic micromotors by GLAD. Reproduced from ref 143. Copyright 2010 American Institute of Physics. (D) Preparation of electrophoretic Pt–Au Janus nanoparticles by GLAD. Reproduced from ref 57. Copyright 2014 American Chemical Society. (E) Fabrication procedure of L-shaped Si/Pt nanorod motors by GLAD. Reproduced from ref 144. Copyright 2007 American Chemical Society. (F) Synthesis of catalytic micromotor consisting of a spherical silica colloid with a TiO_2 arm coated asymmetrically with Pt. Reproduced from ref 145. Copyright 2009 Wiley-VCH. (G) SEM image of a Pt–Ag–Au shell micromotor fabricated by GLAD. Reproduced from ref 146. Copyright 2013 American Chemical Society.

they possess lower mobility than do the Pt shells with partially etched silica templates.¹³⁵ Tierno et al. illustrated that ellipsoidal particles obtained by elongation of spherical particles can also exhibit motion in H_2O_2 solution when half coated with Pt through physical vapor deposition.¹³⁶

The propulsion of another type of Janus micro/nanomotor is not catalytic because the materials of the motors are consumed during propulsion. Noncatalytic Janus micromotors

usually have sizes of scores of micrometers. For this kind of Janus micro/nanomotor, an inert coating formed by physical vapor deposition is needed to create the asymmetric bubble thrust desired for directional movement. To develop in situ fuel for propulsion, materials that react with water have been involved in the development of micro/nanomotors. Gao et al. reported an example of an Al-based micromotor using water instead of other added external fuel (Figure 5F).¹⁶ The Al–

Ga/Ti Janus micromotors utilized the reaction between aluminum and water to generate hydrogen bubbles. To facilitate continuous hydrogen bubble generation by the reaction between aluminum and water, Al–Ga alloy was employed in the fabrication of the Janus micromotor. Liquid gallium can penetrate into the grain boundaries of the aluminum microspheres via microcontact mixing and effectively remove the aluminum oxide layer hindering the reaction. Titanium was deposited on one side of the microspheres by electron beam evaporation to block the reaction and generate the asymmetric bubble thrust. Because of its amphoteric properties, aluminum is able to react with both strong acid and alkali to generate hydrogen bubbles. It has been demonstrated that the Al/Pd Janus micromotor prepared by coating one hemisphere of an Al microparticle with catalytic Pd through physical vapor deposition has the ability to be propelled by acid, base, or hydrogen peroxide.¹⁵ In acidic and alkaline environments, Pd is used as an inert partial coating to block the reaction between aluminum and the surroundings; in the presence of hydrogen peroxide, Pd is the catalytic material to generate a tail of oxygen bubbles to propel the micromotor.

As another stable material that can react with water, magnesium is highly biocompatible and environmentally friendly. Gao et al. demonstrated the efficient propulsion of a Mg-based Janus micromotor in chloride-rich seawater, as shown in Figure 5G.¹⁷ An inert gold cap deposited by electron beam evaporation is used to generate asymmetric thrust as well as to facilitate the reaction of magnesium with water utilizing the macrogalvanic corrosion mechanism. Chloride in the environment can penetrate the passivation layer and result in local dissolution of magnesium through a pitting process, thus further promoting the reaction. A similar Mg-based micromotor was described by Guan's group.¹³⁷ They proposed adding sodium bicarbonate to water to dissolve the passivation layer on the exposed Mg surface of Mg/Pt Janus micromotors, thus enabling continuous generation of hydrogen bubbles.

2.2.2. Glancing Angle Deposition. In conventional physical vapor deposition methods, the substrate is placed parallel to the target and the vapor flux is deposited almost vertically onto the substrate. Glancing angle deposition (GLAD) or dynamic shadowing growth is a physical vapor deposition technique where the vapor is deposited onto a substrate at grazing incidence. To achieve geometric shadowing, the substrate is set at an oblique angle with respect to the flux. Various structures of a variety of materials can be obtained by manipulating the tilt and rotation of the substrate relative to the incoming vapor flux during deposition.¹³⁸ GLAD offers a good way for mass-producing complex three-dimensional structures. Here, we will mainly introduce the application of GLAD in the fabrication of helical and Janus micro/nanomotors.

2.2.2.1. Helical Micro/Nanomotors by GLAD. The growth of helices can be achieved by azimuthal rotation of a tilted substrate stage during deposition. Figure 6A illustrates the GLAD technique and the fabricated helical structures. To fabricate helical structures with good homogeneity on a large scale, the substrate must be seeded before the GLAD process, which refers to the preparation of arrays of ordered seeds on the substrate. The size, shape, and uniformity of the seeds are critically important to the resulting structures. Ghosh and Fischer reported a helical motor fabricated by glancing angle

deposition.⁶⁴ The silica helical structure was obtained by deposition of SiO₂ vapor flux at an oblique angle on silica beads packed on a rotating substrate. Cobalt was then deposited on the surface of the helical structure by thermal evaporation, enabling magnetic propulsion in the presence of an external magnetic field. The dimensions of the helices strongly depend on the size of the seeds. To reduce the size of the helical motors, Au nanodots produced by micellar nanolithography can be used as seeds.⁶⁵ Figure 6B illustrates GLAD using Au nanodots as nucleation sites. Self-assembled polystyrene-*b*-poly[2-vinylpyridine (HAuCl₄)] diblock copolymer micelles will form into uniform monomeric films upon spin-coating onto a wafer. Subsequent plasma treatment removes the polymer and reduces the gold salt, leaving a regular array of gold nanodots. The spacing and size of the nanodots can be controlled by changing the molecular weight of the diblock copolymers, Au loading, and spin-coating speed. By employing this technique, the size of the helical motors can be scaled down to about 70 nm in filament diameter and 400 nm in length.

Ghosh's group studied the size limit of magnetically driven helical motors using experimental observations and theoretical models.¹³⁹ Because of the overwhelming effect of orientational thermal noise at a small length scale, it was shown that, for helical propellers with a length smaller than 1 μm, an extremely large operational frequency is required to achieve motion in the desired direction in aqueous media. The frequency of the magnetic field for the propulsion system must increase as the inverse cube of the size of the propeller. These findings were confirmed by the motion behavior of the 400-nm-long helical motors described earlier.⁶⁵ Because of their extremely small size, the actuation of these nanohelices in pure water is suppressed by thermal noise. However, they can be actively propelled in high-viscosity hyaluronan solution with significantly higher velocities than in Newtonian fluids, which is opposite to actuation of the larger helices with diameters of several hundred nanometers. In addition, there exists an optimal length for the magnetically driven helical propellers. Theoretical and experimental studies by Fischer, Leshansky, and co-workers showed that the optimal length is only about one full turn.¹⁴⁰

The GLAD technique allows the growth of complex hybrid three-dimensional structures that contain several different functional materials including metals, insulators, semiconductors, and magnetic materials.¹⁴¹ Even binary alloys can be fabricated by codeposition from two evaporators simultaneously. The alloy composition can be readily adjusted by independently controlling the deposition rate from each evaporator. Instead of coating the helical structures released from the wafer with a thin magnetic layer, a ferromagnetic nickel section can be incorporated into the structure during growth, which leads to reproducible production of magnetically driven helical motors with high yield and good uniformity. By changing the rotation direction and speed of the substrate during evaporation, helical structures with different chirality and pitch can be obtained. Schamel et al. demonstrated the propeller effect using a colloidal model system with defined chirality and inbuilt dipole functionality.¹⁴² A racemic mixture of magnetic dipolar chiral colloids was built from helices prepared via GLAD. The helices were magnetized orthogonally to their long axes through application of a strong electromagnetic field before release from the wafer into solution. The left- and right-handed

Figure 7. Rolled-up technology. (A) Rolling-up of nanomembranes patterned with photoresist: (a, b) schematic diagram of a rolled-up microtube consisting of Pt/Au/Fe/Ti multilayers on a photoresist sacrificial layer and an array of rolled-up microtubes; (c) SEM image of a rolled-up microtube. (a) and (c) are reproduced from ref 51. Copyright 2009 Wiley-VCH. (B) Rolled-up microtubes with graphene oxide as an external layer. Reproduced from ref 151. Copyright 2012 American Chemical Society. (C) Reversible rolling and unrolling of thermoresponsive polymeric Pt microtubes. Reproduced from ref 154. Copyright 2014 Wiley-VCH. (D) Particle-assisted rolling process of nanomembrane upon a thermal dewetting treatment. Reproduced from ref 155. Copyright 2013 Wiley-VCH.

diametrically magnetized helical motors will be propelled in opposite directions by application of a rotating field, thus separating the racemic mixture of chiral structures. Another benefit of the GLAD fabrication process is the convenience of on-wafer chemical functionalization of the structures, which offers possibilities for a great number of applications.

2.2.2.2. Janus Micro/Nanomotors by GLAD. On the basis of the self-shadowing effect and substrate rotation during deposition of an incident vapor, glancing angle deposition provides an easier way for fabricating Janus micro/nanomotors with complex structures. Zhao and co-workers reported the asymmetric Pt/Au-coated catalytic micromotors fabricated by this method.¹⁴³ To obtain an asymmetric bimetallic coating, a substrate with silica microbeads was rotated to a polar angle after deposition of an adhesive Ti layer and a Au layer, and accordingly, the subsequent Pt deposition left some of the Au layer exposed (Figure 6C). The motion behaviors can be adjusted by varying the exposed area of the Au layer. Lee et al. fabricated 30 nm Pt/Au Janus nanomotors by glancing angle deposition of gold under fast substrate rotation onto an array of platinum nanoparticles produced by block copolymer micelle lithography (Figure 6D).⁵⁷ Both of the bimetallic Janus motors rely on the self-electrophoresis mechanism for propulsion.

A collection of Janus micromotors with different shapes prepared by GLAD has introduced new possibilities for the development of this area. He et al. reported the fabrication of rotary Si/Pt nanorods, L-shaped Si/Pt, and Si/Ag nanorods where they first used GLAD to prepare the Si nanorod backbone and then asymmetrically coated one side of the nanorod backbone with a Pt or Ag layer via a geometric

shadowing effect.¹⁴⁴ The L-shaped backbone was obtained by a very fast azimuthal rotation of the substrate in the middle of oblique angle deposition (Figure 6E). By controlling the deposition angle and the substrate rotation, complex rolling Si/Ag springs can be obtained. Gibbs and Zhao described the rotational motion of a micromotor consisting of a silica microbead and a TiO₂ arm with asymmetric Pt coating.¹⁴⁵ The arms of the micromotors were deposited on the closely packed microbeads at oblique angles. As such, the Pt coating subsequently deposited with no angle is only on one side of the arms, which provides the asymmetric placement of the catalyst essential for movement (Figure 6F). With oblique vapor direction and rotating substrate, the deposition layer is able to cover a much larger area of the sphere templates than that with conventional vapor deposition. A bubble-propelled Pt–Ag–Au shell micromotor with a smaller opening was fabricated through glancing angle deposition and subsequent wet chemical etching (Figure 6G).¹⁴⁶

2.3. Strain Engineering

Strain engineering offers a useful tool for rearranging nanomembranes into three-dimensional micro/nanostructures, such as wrinkles, tubes, and helices. By incorporating an engineered strain gradient in the deposited membranes, the membranes can form into desired structures when released from the substrate. A variety of materials can be used for this fabrication method, employing suitable deposition techniques and etchant to selectively remove the underlying sacrificial layer. Strain engineering has been widely used in the fabrication of tubular and helical micro/nanomotors.

2.3.1. Rolled-up Technology for Micro/Nanotubes. The rolled-up nanotechnology pioneered by Schmidt and co-

workers employs strain engineering to prepare microtubes from deposited films.^{51,147,148} A prestressed nanomembrane is deposited on a photoresist sacrificial layer patterned by photolithography, which can be selectively removed by acetone. Tilted deposition is used in the physical vapor deposition process to ensure accurate positioning and tube integration on a single chip. Suitable control of substrate temperature and deposition rate, together with the stress evolution during deposition, creates the strain gradient needed for the rolling process. As shown in Figure 7A, the deposited nanomembrane rolls into a microtube once released from the substrate by removal of the sacrificial layer. To avoid collapse of the rolled-up nanomembranes, the critical point drying is used to dry the fabricated microtubes. Microtubes with different opening diameters ranging from 1 to 30 μm can be obtained by changing the thickness and the built-in strain of the nanomembranes.¹⁴⁹ The lengths of the microtube engines are in the range of scores of micrometers. Catalysts such as Pt form the inner wall of the microtubes by simply being deposited on top of the nanomembrane. The wrinkle orientation of the released membrane is determined by the crystal structure of the sacrificial layer and the different etching rates along the crystal axis.¹⁵⁰

Because of the complex nature of the fabrication procedure and the related high cost of the rolled-up technology, considerable efforts have been devoted to simplifying the rolled-up process and reducing its cost. Microtubes with outer layers of graphene oxide (GO) were prepared by depositing metal layers on graphene oxide nanosheets (Figure 7B).¹⁵¹ Because of material strain and weak bonding between GO layers, microscrolls with GO on the outside and Pt at the inner surface were spontaneously formed upon sonication. The diameter can be modulated by varying the thickness of the deposited metal layers. A similar synthetic route of tubular microengines was reported using inexpensive and accessible fruit cells as support for the metallic layers.¹⁵² The tissue-based microjets can exhibit highly efficient bubble propulsion in the presence of hydrogen peroxide. Zhao et al. described the formation of platinum microtubes by selective removal of the poly(methyl methacrylate) (PMMA) sacrificial layer under the sputtered Pt layer or by hydrogen peroxide-assisted lift-off of the Pt layer deposited directly on a glass substrate.¹⁵³ A transmission electron microscopy (TEM) grid template was used to help prepare microtubes of relatively uniform size. Although the simple and low-cost methods described offer great possibilities for large-scale production of microjets, a major problem of these methods is the lack of precise control of the size and morphology of the fabricated microtube engines. On the premise of simplifying the procedures, future efforts should be taken toward better control of the rolled-up process.

Magdanz et al. developed a flexible thermoresponsive polymeric microjet based on the reversible folding/unfolding of the polymer at reduced and elevated temperatures (Figure 7C).¹⁵⁴ Cooling of the polymer/Pt layers leads to bending of the films and formation of 30 μm diameter microtubes with a Pt inner layer as a catalyst, whereas warming results in the unfolding of the microtubes. Therefore, the rolling and unrolling process of the microtubes can be performed reversibly by applying temperature changes to the solution to start and stop the motion of the microtubes. The diameters of the microtubes prepared by the rolled-up methods are all in the microscale range. Li et al. utilized the surface tension of

nanodroplets together with the intrinsic strain relaxation in the nanomembranes to decrease the diameters of the rolled-up tubes to hundreds of nanometers.¹⁵⁵ As illustrated in Figure 7D, a layer of platinum was deposited above a prestrained bilayer of SiO/TiO_2 or Si/Cr on a sacrificial PMMA layer. In the treatment that followed, rapid thermal annealing (RTA) was used to stretch the platinum layer to the separated islands and the nanodroplets brought considerable surface tension for rolling. At the same time, the burning of PMMA led to the release of the nanomembranes. The produced microtubes exhibit higher velocities compared to those with a smooth platinum surface.

2.3.2. Self-Scrolling Technique for Helical Micromotors. Relying on the strain in thin material layers, a straight ribbon can scroll into a helix, which is the desired structure for magnetic propulsion. A microscale helical micromotor prototype based on the self-scrolling technique was presented by Nelson and co-workers.¹⁵⁶ They described the fabrication of a helical micromotor with the size of dozens of microns using traditional thin-film deposition methods (Figure 8A).⁶³ Two or three layers of material were deposited and patterned into straight ribbons by reactive ion etching (RIE), after which a magnetic head for actuation was prepared by chemical vapor deposition of magnetic layers and a lift-off

Figure 8. (A) Fabrication procedure of helical micromotors using self-scrolling technique. (g) SEM image of a self-scrolled helical structure. Reproduced from ref 63. Copyright 2009 American Institute of Physics. (B) Schematic illustration of the electroosmotic propulsion mechanism and experimental setup of helical micromotors. The propulsion direction of helical micromotors can be controlled by the configuration of the two electrodes between which a direct current bias is applied. Reproduced from ref 91. Copyright 2011 Thomson Reuters.

process. Because of the internal stresses in the structure, the ribbon patterns automatically scrolled into helices upon release from the substrate. The parameters of the helical structures can be modulated by tuning the deposition conditions, such as film thickness, ribbon width, and the orientation of ribbon relative to the crystal structure of the metal. A study of the dynamics of the fabricated helical micromotors illustrated the influence of head size on propulsion velocity.¹⁵⁷ At low frequencies, the helix with a small head moves faster than that with a large head due to less viscous drag. However, because of the larger amount of Ni contained in the large head, a stronger magnetic torque can be generated for a helix with a large head, resulting in an increase in maximum velocity.

Hwang et al. demonstrated that helical structures prepared by thin film deposition can also be actuated by an electric field-generated electroosmotic force instead of a rotating magnetic field.⁹¹ The principle of electroosmotic propulsion through an interface between a helical structure surface and a liquid solution is illustrated in Figure 8B. In the presence of an external field, the Stern layer of the helical structure generates a flow that applies hydrodynamic pressure on the surface of the helix, propelling it in the opposite direction. Electrically driven helical micromotors exhibit higher maximum swimming velocity and manipulation force compared to those propelled by a rotating magnetic field. Dielectric polymer-coated helical micromotors show better swimming performance than do those with metallic and semiconductor surfaces.

2.4. Three-Dimensional Direct Laser Writing

The enormous progress in three-dimensional (3D) direct laser writing (DLW) has made it a versatile and routine tool for precise batch fabrication of complex polymer structures in micro- and nanoscale with high resolution. In this technique, a photoresist is deposited on a substrate that can be moved with a piezoelectric stage in three-dimensions following a preprogrammed path to partially expose the photoresist to the focal point of the laser.¹⁵⁸ Photoresists can be divided into two kinds: positive and negative. For positive resists, exposure to light makes the resist more soluble in the photoresist developer and thus it can be washed away by the developer solution, leaving the less-soluble unexposed portion. Negative resists behave in the opposite manner. The exposed region of negative resists becomes polymerized and more difficult to dissolve. As a result, the negative resist remains where it is exposed and the unexposed areas are removed by the developer solution.

Many fabrication strategies for helical motors have been proposed based on 3D direct laser writing. Tottori et al. demonstrated the fabrication of helical motors using this technique (Figure 9A).⁶⁶ A microscaled helical structure was written with negative photoresist deposited on a substrate by DLW. When the laser beam is focused into the photoresist, two-photo polymerization (TPP) occurs at the focal point of the laser. After removal of the unpolymerized photoresist, helical polymer structures were obtained. Subsequently, Ni and Ti thin layers were deposited on the surface of the structure by electron beam evaporation for the use of magnetic actuation and biocompatibility. DLW offers good flexibility for fabricating micromotors of various designs. In the same paper, they also described a helical structure with a microholder consisting of six protrusions at one end for

Figure 9. Micro/nanomotors fabricated by 3D direct laser writing. (A) Procedure for preparing helical micromotors via DLW using negative photoresist. Reproduced from ref 66. Copyright 2012 Wiley-VCH. (B) SEM image of a helical micromotor composed of magnetic polymer composite with 4 vol % Fe_3O_4 particle concentration. Reproduced from ref 159. Copyright 2013 Springer. (C) Fabrication of hybrid helical micromotors by 3D template-assisted electrodeposition. Reproduced from ref 67. Copyright 2013 Wiley-VCH. (D) SEM image of a cylindrical-shaped porous scaffold micromotor for targeted cell delivery. Reproduced from ref 160. Copyright 2013 Wiley-VCH. (E) Schematic drawing of light-driven micromotors prepared by DLW from different views. Reproduced from ref 85. Copyright 2001 American Institute of Physics.

transporting colloidal microparticles. The loading of the particles was achieved by pushing the micromotor slightly downward with a small angle to grasp a microbead lying on the substrate. Once in the microholder, the microparticles can be stably transported in three dimensions without being dislodged because of the forward motion and the confinement of the microholder. Release of the microparticles from the front opening was performed by backward motion of the helical micromotor resulting from reversed rotation.

As an alternative method to include magnetic materials in the helical structure, magnetic nanoparticles can be incorporated in the polymer before the DLW process, enabling distribution of magnetic nanoparticles along the entire helical structure. Helical micromotors that are composed of a magnetic composite material consisting of magnetite nanoparticles and photocurable photoresist were reported by Suter et al. (Figure 9B).¹⁵⁹ A cytotoxicity analysis showed that the magnetic polymer composite structures with up to 10 vol % nanoparticles did not significantly influence the viability of normal human dermal fibroblasts.

Unlike the strategy for negative photoresists to build helical bodies using photoresist, the DLW technique enables fabricating templates containing 3D cavities to be filled by electrodeposition with the use of positive photoresists. The combination of electrodeposition and photolithography facilitates fabrication of complex 3D structures with a wide variety of materials. Adopting the template-assisted, two-step electrodeposition method, Zeeshan et al. synthesized hybrid

Figure 10. Fabrication of micro/nanomotors by assembly of materials. (A) Fabrication of (PSS/PAH)₅ hollow capsules through LbL assembly. Reproduced from ref 59. Copyright 2012 American Chemical Society. (B) Synthetic procedure of a nanoparticle-based PSC nanomotor. Reproduced from ref 60. Copyright 2013 American Chemical Society. (C) Selective and controlled entrapment of Pt NPs inside artificial stomatocytes during shape transformation. Reproduced from ref 61. Copyright 2012 Macmillan Publishers Limited. (D) Schematic of magnetically guided, ultrasound-propelled red blood cell micromotors in whole blood. Reproduced from ref 77. Copyright 2014 American Chemical Society. (E) Schematic illustration of a chain of magnetic particles linked by DNA. Reproduced from ref 73. Copyright 2005 Nature Publishing Group. (F) Schematic illustration of the motion of azobenzene-coated nanoparticles in illumination gradient. Reproduced from ref 78. Copyright 2011 American Chemical Society. (G) Photoresponsive surface based on switchable fluorinated molecular shuttles to expose or conceal fluoroalkane region (orange). Reproduced from ref 173. Copyright 2005 Nature Publishing Group.

helical micromotors with a cobalt–nickel head for magnetic actuation and a biocompatible poly(pyrrole) tail that provides propulsion in liquid (Figure 9C).⁶⁷ The helices were then released from the templates after electrodeposition by dissolving the photoresist with acetone.

In addition to helical structures, the excellent control of direct laser writing over the geometry of the samples enables the fabrication of various micro/nanomotors. Nelson, Choi, and co-workers demonstrated the preparation of a three-

dimensional microscale porous scaffold as a transporter for multiple cells (Figure 9D).¹⁶⁰ When coated with Ni and Ti, the well-defined 3D structure with a customized pore size can be magnetically controlled in body fluids. A light-driven asymmetric L-shaped micromotor fabricated by this technique was reported by Kümmel et al.⁸³ The L-shaped structures were obtained from negative photoresist by photolithography and then coated with a Au layer by thermal evaporation, during which the entire wafer with the attached particles was

tilted to a specific angle with respect to the vapor to deposit at the front side of the short arms. Subsequently, the L-shaped particles were released from the substrate by ultrasonication and suspended in a homogeneous mixture of water and 2,6-lutidine at critical concentration. When the metal layer was heated under illumination by light, a local demixing of the solvent was induced, accordingly resulting in self-phoretic motion of the particles. Subsequent studies of these micromotors showed that shape anisotropy alone is adequate to lead to gravitatic motion with either preferential upward or downward motion.¹⁶¹ Particles with anisotropic geometry can deflect light carrying no angular momentum to generate the torque needed to drive rotation.¹⁶² Micro-fabrication by direct laser writing has been introduced to build complex light-driven rotors that can be manipulated in laser tweezers (Figure 9E).⁸⁵

2.5. Assembly of Materials

The assembly approach occupies an important place in nanofabrication. It is a strategy to combine miniaturized elements to prepare a desired structure. Self-assembly is a spontaneous reorganization process in which a disordered system of components forms an organized structure or pattern. The process is reversible and the formed structures are held together by noncovalent interactions. The building blocks of self-assembly are not limited to atoms and molecules but cover a wide range of nanostructures of different compositions. The unique properties of self-assembled monolayers make them useful for the fabrication of various micro/nanomotors. With a collection of monolayers, three-dimensional structures can be obtained. In addition to employing the self-assembly of materials to build desired structures, desired components can also be included into micro/nanomotors by encapsulating or incorporating them into another material.

2.5.1. Layer-by-Layer Assembly. Layer-by-layer (LbL) self-assembly is a nanofabrication technique for multilayer formation by depositing alternating layers of oppositely charged materials. It is an easy and low-cost process that can incorporate versatile materials, such as small organic molecules, inorganic compounds, macromolecules, and colloids. The LbL technique can be applied to a wide range of solvent-accessible surfaces, allowing the use of different templates. Incorporation of Pt nanoparticles enables the propulsion of the formed multilayer structure to be propelled in H₂O₂ solution.

A method of membrane template-assisted preparation of microtube motors using layer-by-layer (LbL) deposition instead of electrodeposition is illustrated by Wu et al.⁵⁴ Two oppositely charged biodegradable materials, chitosan (CHI) and sodium alginate (ALG), were alternatively deposited on a nanoporous membrane, followed by the assembly of Pt nanoparticles into the template pores. Nanotubes with catalytic Pt nanoparticles on the inner wall can be obtained upon dissolution of the membrane. One advantage of the LbL-assembled nanotube is that the multilayer structure facilitates the encapsulation of drugs and iron oxide nanoparticles, offering possibilities for directed drug delivery. However, low speed and small towing power are problems that must be overcome to achieve this goal.

Wu et al. described the fabrication of a Janus capsule motor partially coated with platinum nanoparticles (NPs) through a template-assisted LbL assembly technique together with a

microcontact printing method.⁵⁹ As shown in Figure 10A, five bilayers of oppositely charged polystyrene sulfonate (PSS)/poly(allylamine hydrochloride) (PAH) were deposited on the surface of template silica particles, followed by the physical contact of a stamp loaded with Pt NP ink on top of the substrate. Upon removal of the template silica particles, hollow capsules partially coated with Pt NPs were obtained. The asymmetric displacement of the Pt NPs enabled the generation of directional forces while the hollow structure enabled drug encapsulation. The loading and release of drugs was achieved by tuning the permeability of the capsules via the use of an organic solvent. The Janus capsule can be magnetically controlled by assembling magnetic particles on the capsule wall.

2.5.2. Assembly and Encapsulation of Micro/Nano-particles.

An alternative strategy for fabricating Janus motors is the asymmetric assembly of nanoparticles that can provide directed propulsion force for the motion. Dong et al. reported the directed self-assembly of nanoparticles on a polymer single crystal (PSC) of α -hydroxyl- ω -thiol-terminated polycaprolactone (HO-PCL-SH) for micromotors (Figure 10B).⁶⁰ Because of the abundant amount of thiol and hydroxyl groups on the surface of the PSC, sufficient gold, iron oxide, and platinum nanoparticles can be introduced into a PSC template through interaction with these groups. Platinum nanoparticles can catalyze the decomposition of H₂O₂, enabling the motion of the PSC in H₂O₂ solution. Gold and iron nanoparticles are used for the consideration of functionalization and remote control. Polymer stomatocytes that can entrap Pt NPs within their nanocavities were described by Wilson et al. (Figure 10C).⁶¹ This method utilized the controlled transformation of spherical polymersomes into stomatocyte structures. Entrapment of the Pt NPs was realized by the addition of nanoparticles to solvent-swollen polymersomes during the transformation process. Hydrogen peroxide can access the catalytic Pt NPs through controlled opening of the stomatocytes to generate thrust and directional motion.

In addition to the micromotors based on the assembly of Pt NPs, Wang et al. showed that the random assembly of Ir particles in graphene can generate oxygen bubbles asymmetrically to propel motion in H₂O₂.¹⁶³ An ultrasound-powered micromotor based on red blood cells was developed by Wu et al.⁷⁷ The loading of iron oxide nanoparticles into red blood cells turns the cells into functional micromotors, because the asymmetric distribution of the nanoparticles within the cells enables magnetic guidance under acoustic propulsion (Figure 10D). Palacci et al. reported the living crystals of synthetic photoactivated colloidal particles, which can form, break, explode, and reform.⁸⁴ Each particle is a polymer sphere encapsulating most of a canted hematite cube with part exposed to the solvent. In the presence of blue-light illumination, hematite can catalyze the decomposition of H₂O₂, generating thermal and chemical gradients. The dynamic assembly of the particles activated by light is due to competition between the self-propulsion of the particles and an attractive interaction induced by osmotic and phoretic effects, respectively.

A common form of magnetically driven micromotor is a chain of magnetic particles. Dreyfus et al. reported a flexible artificial flagellum that is composed of a chain of colloidal magnetic particles (1 μ m in diameter) linked by double-stranded DNA (107 nm long) and an attached red blood cell.⁷³ Preparation of the micromotor is based on

Figure 11. Biohybrid micro/nanomotors. (A) Schematic diagram of F_1 -ATPase biomolecular motor-powered nanodevice. Reproduced from ref 94. Copyright 2000 AAAS. (B) Schematic diagram of a self-propelled carbon fiber powered by bioelectrochemical reaction of glucose and oxygen. I and II are redox polymers. Reproduced from ref 96. Copyright 2005 American Chemical Society. (C) Use of biocatalytic microjets with enzyme immobilized at the inner gold surface as microfish for testing water quality. Reproduced from ref 45. Copyright 2012 American Chemical Society. (D) Phase-contrast optical microscope images showing the path of a PS bead with flagellated bacteria attached to it in 6 s. Reproduced from ref 183. Copyright 2007 American Institute of Physics. (E) Photograph of a MC-1 MTB that can be used as a computer-controllable bioactuator. Reproduced from ref 187. Copyright 2009 The Authors. (F) Microbiorobot consisting of a motile cell trapped inside a rolled-up microtube with a magnetic layer for remote control. Reproduced from ref 99. Copyright 2013 Wiley-VCH. (G) One-dimensional PDMS filament actuated by cardiomyocyte contractions. The image in the red circle shows the contractile cells. Reproduced from ref 192. Copyright 2014 Macmillan Publishers Limited.

streptavidin–biotin interaction between streptavidin grafted on the particle surface and biotinylated DNA and red blood cells. As shown in Figure 10E, the filament can be aligned with an external magnetic field and is able to be propelled by oscillating fields. Tierno et al. demonstrated the propulsion of DNA-linked paramagnetic colloidal particles of different or similar sizes in a magnetic field precessing around an axis parallel to the plane of motion.^{164,165} In addition to the chains of magnetic particles held together by irreversible DNA tethers, self-assembled chains of superparamagnetic beads solely due to magnetic forces have been shown to be able to move along different surfaces when subjected to a rotating magnetic field.^{74,166,167} The assembly and disassembly of the chains are reversible simply by transition between the application and removal of an external magnetic field.

2.5.3. Assembly and Incorporation of Synthetic Molecules.

The development of a wide range of molecular-based systems has paved the way for construction of advanced mechanical machines at the nano- and microscale level based on synthetic molecular systems.^{168–170} Feringa and co-workers reported a molecular-based system in which a covalently tethered synthetic manganese catalase mimic was used to convert chemical energy to mechanical movement of microsized particles.⁶² Zhang et al. developed an autonomous motor powered by depolymerization of poly(2-ethyl cyanoacrylate) (PECA).⁵ Micrometer-sized anion-exchange beads with PECA absorbed on the porous structure were half-coated with PMMA. The OH^- ions generated in the ion-exchange process triggered the depolymerization of PECA on the uncoated side, which generates ethanol to create surface tension gradients to propel the motion of the particle.

Surfaces modified with photoisomerizable molecules have been widely used in the development of light-driven motors. The photoisomerization of azobenzene has been employed in the design of many light-driven motors. The surface tension gradients resulting from the photoisomerization generated by asymmetric illumination can induce a net mass transport of droplets and nanoparticles. Azobenzene-coated polymer nanoparticles of 16 nm in diameter were reported to act as phototriggered nanomotors that can be propelled toward the dark regions of an optical gradient (Figure 10F).⁷⁸ On the basis of the reversible *trans*–*cis* isomerization of azobenzene molecules, the directional motion of a liquid droplet on a substrate surface modified with a monolayer of azobenzene can be reversibly manipulated by light.^{79,171} Rosario et al. demonstrated the same concept using photochromic spiropyran molecules. They found that photoresponsive monolayer coatings on rough, superhydrophobic surfaces exhibit amplification of reversible light-induced contact angle changes.¹⁷² Berna et al. reported the directional transport of a droplet on a photoresponsive surface composed of a monolayer of rotaxane molecular shuttles (Figure 10G).¹⁷³ The millimeter-scale transport of a droplet was accomplished by the changes in surface properties resulting from the collective operation of light-switchable nanoshuttles to expose or conceal fluoroalkane residues.

Another way for collective application of light-driven molecular motors to induce controlled motion of large-scale objects is to embed them in a liquid-crystal film.¹⁷⁴ Feringa and co-workers demonstrated that photoisomerization of a molecular motor dopant can lead to rotational reorganization of liquid crystalline film due to differences in the helical twisting power of the isomers.¹⁷⁵ Employing the collective action of molecular motors, microparticles that exceed the motor in size by 10 000 times can be rotated on the film.⁸⁰ The translational motion of microspheres on the surface of azobenzene-doped liquid crystalline films was accomplished by directional irradiation with an Ar⁺ laser.¹⁷⁶ The intensity of the laser and the concentration of the doped azobenzene compound are two factors that affect the speed of motion. Liquid crystal elastomers (LCEs) are a kind of material obtained by incorporating mesogenic monomers into the backbones or side chains of weakly cross-linked polymers, and therefore they have the properties of both liquid crystals and elastomers. Large reversible deformations of LCEs can be generated with light stimuli through photochemical reactions of incorporated photochromic molecules. Camacho-Lopez et al. illustrated large and rapid shape changes of azobenzene-containing LCEs on illumination as well as their ability to swim away from light.⁸¹ Employing the photoinduced motion of a LCE film, Yamada et al. developed light-driven plastic motors, which can convert light energy directly into rotational motion.¹⁷⁷

2.6. Biohybrid Technique

Nature provides a number of small-scale motors ranging from the molecular to the cellular level. F₁-adenosine triphosphatase (F₁-ATPase), kinesin, myosin, and dynein are well-known motor molecules that can convert chemical energy to mechanical movement. Motile units such as bacteria and muscle sarcomeres are self-powered actuators that can exhibit efficient motion in a low Reynolds environment. In addition to these natural motors, enzymes able to catalyze chemical reactions are forms of biomaterials that have important

implications in the fabrication of micro/nanomotors. The development of biohybrid devices that integrate biological materials and synthetic components offers new possibilities for the micro/nanomotor field. We will discuss the use of single biomolecules as well as whole micro-sized units.

2.6.1. Use of Biological Molecules. Biomolecular motors can be assembled with inorganic components to form hybrid nanomechanical devices. A hybrid system powered by F₁-ATPase was developed by Montemagno and co-workers.⁹⁴ The three elements constituting the device, a Ni post, the F₁-ATPase, and a nanopropeller, were sequentially assembled using different attachment chemistries (Figure 11A). Rotation of the nanopropeller can be initiated with addition of adenosine triphosphate (ATP) and restrained by sodium azide. An alternative for fabrication of hybrid micro/nanomachines could be the incorporation of enzyme molecules into artificial segments. Mano and Heller illustrated a self-propelled bioelectrochemical motor based on the reactions of glucose and oxygen catalyzed by an enzymatic system (Figure 11B).⁹⁶ One end of a carbon fiber was modified with redox polymer wired glucose (GOx), and the other end was coated with redox polymer wired bilirubin oxidase (BOD). Current flow through the fiber is compensated by the flow of ions, which leads to the motion of the fiber. Surface-immobilized enzymes were demonstrated to act as self-powered micropumps in the presence of their respective substrates.¹⁷⁸ The micropumps were easily fabricated by the electrostatic assembly of enzymes on thiol-functionalized Au-patterned surfaces. Fluid flow is a result of a gradient in fluid density generated by exothermic enzymatic reactions.

Catalase has been used to replace inorganic catalysts to achieve the propulsion of micro/nanomotors in H₂O₂. Sanchez et al. reported hybrid biocatalytic tubular micro-engines with enzyme catalase covalently bound to the modified inner surface of Ti/Au microtubes.⁹⁵ Catalase can effectively catalyze the decomposition of H₂O₂ and becomes inhibited in the presence of a wide range of aqueous pollutants, thus providing an alternative to the common method of using live fish for testing water quality (Figure 11C).⁴⁵ Simmchen et al. described a hybrid motor based on a mesoporous particle of 500–700 nm with catalase immobilized on one hemisphere and single-stranded DNA attached to the other side.¹⁷⁹ Enzyme immobilization was performed by amide bond formation between the free amine groups of the catalase and the carboxylic acids of the particles with the assistance of a cross-linker. Single-stranded DNA on the motor enables selective capture and transport of a complementary DNA strand. A biocatalytic micromotor based on Janus mesoporous silica clusters was described by Ma and Sanchez.¹⁸⁰ A layer of Ni was deposited on one side of the aggregated mesoporous silica nanoparticles to provide asymmetry and magnetic properties, followed by the conjugation of catalase enzyme on the uncovered side for the biocatalytic decomposition of H₂O₂.

2.6.2. Use of Motile Units. Given the difficulties of harnessing biological motors outside the cell, intact motile cells have been employed as actuators for engineered systems. Bacteria, in particular, are a suitable choice for controllable microactuators. Efficient conversion of chemical energy from the environment, intelligent sensing ability, taxis behavior, and scalability are all advantages offered by bacteria.¹⁸¹ Bacterial flagellated actuation is one of the most efficient ways to

Figure 12. (A) Optical image of the motion of a Ag particle in H₂O₂. Reproduced from ref 193. Copyright 2014 American Chemical Society. (B) Movement of a TiO₂ particle in a suspension of SiO₂ particles under UV. Reproduced from ref 86. Copyright 2010 Wiley-VCH. (C) AgCl particles in deionized water (a) before UV illumination, (b) after 30 s, and (c) after 90 s of UV exposure. Reproduced from ref 87. Copyright 2009 Wiley-VCH. (D) Scheme illustrating principle of dynamic bipolar self-regeneration. Reproduced from ref 92. Copyright 2010 American Chemical Society. (E) Scheme of proton reduction and HQ oxidation by bipolar electrochemistry. Reproduced from ref 93. Copyright 2011 Macmillan Publishers Limited.

propel motion in a low-Reynolds-number regime. Berg and co-workers found that the motion of a fluid close to a surface that is densely packed with a monolayer of flagellated bacteria was largely enhanced due to the rotation of the bacteria flagella.⁹⁷ They also reported the motion of polystyrene beads and fragments of polydimethylsiloxane (PDMS) attached to the bacteria but without motion control. The motion of a PS bead with flagellated bacteria attached is shown in Figure 11D. The steering of the hybrid motor was demonstrated by Weibel et al. with biflagellated algae using phototaxis to transport polystyrene beads several micrometers in diameter attached to the cell via surface chemistry.¹⁸² Release of the beads can be performed by photocleavage through UV irradiation. Another study by Behkam and Sitti demonstrated that on/off motion control of beads can be achieved by the addition of copper ions to inhibit bacteria flagellar motion and chelating ethylenediaminetetraacetic acid (EDTA) to resume flagellar motion.¹⁸³ Flagellated bacteria have been successfully attached to negative photoresist SU-8 microstructures to act as actuators that can be phototactically controlled.¹⁸⁴ Park et al. demonstrated that selective attachment of flagellated bacteria to SU-8 microstructures by bovine serum albumin (BSA) patterning greatly enhances the mobility of bacteria-actuated microstructures.¹⁸⁵

Substantial work has been done by Martel et al. on integrating magnetotactic bacteria (MTB) with artificial microsystems. They demonstrated controlled manipulation of microbeads with MTB using a directional magnetic field from a small programmed electrical current.⁹⁸ Because MTB can respond to a directional magnetic field as weak as the geomagnetic field, the required electrical energy for steering is extremely low. The combination of flagellated nanomotors with magnetosomes has made MTB the key component of

integrated propulsion and steering of many hybrid microsystems. The structure of MC-1 magnetotactic bacteria is illustrated in Figure 11E. Owing to the small diameter (1–2 μm) of MC-1 MTB, they can pass through tiny capillaries in the human body to reach targets.¹⁸⁶ A platform using magnetic resonance imaging (MRI) has been built to serve as a link between external computerized control and MTB in the human body.¹⁸⁷ MRI provides feedback information, which is essential for real-time control and monitoring of the MTB microsystem.

The flagellar propulsion of sperm cells was introduced for the actuation of rolled-up microtubes (Figure 11F).⁹⁹ A sperm cell can enter the microtube and become trapped in the tube cavity through the interaction of released microtubes with a solution of sperm cells. With incorporation of a magnetic layer into the microtubes, the on-chip separation of a selected microtube by remote magnetic field was accomplished. In addition to flagellated cells, other kinds of bacteria without flagella have been involved in the development of biohybrid microsystems. Hiratsuka et al. described a microrotary motor powered by a species of gliding bacteria.¹⁸⁸ The microrotary motor is formed from three parts, a circular Si track, a SiO₂ rotor with dimensions that just fit into the groove of the track, and gliding bacteria attached to the rotor by biotin–streptavidin interactions. As such, the unidirectional motion of the bacteria results in the rotation of the rotor in one direction. Fernandes et al. developed a two-antibody-based method for selective attachment and triggered release of motile cargo-carrying *E. coli* bacteria from patterned surfaces.¹⁸⁹ Two antibodies were used to sequentially attach the bacteria and cargo to the modified surfaces. On-demand release of motile bacteria–cargo conjugates was realized by the addition of imidazole or EDTA.

Cardiomyocytes are another kind of natural building block, which often serve as the motile unit in hybrid systems. The coupling of muscle and synthetic microstructures enables fabrication of autonomous microdevices powered by glucose present in physiological liquids. Individual cardiomyocytes can grow and self-assemble into muscle bundles. Utilizing the assembly of muscle cells, Xi et al. developed a hybrid microdevice powered by the collective cooperative contraction of muscle bundles.¹⁰⁰ Tanaka et al. reported a cardiomyocyte pump driven by spontaneous contraction of cardiomyocyte sheets.¹⁹⁰ A microspherical heart-like pump was fabricated by wrapping a cultured cardiomyocyte sheet around a hollow elastomer sphere with inlet and outlet. The contractile forces exerted on the sphere by the attached cardiomyocyte sheet reduce the fluid volume in the hollow sphere, generating flow into the fixed capillary. To produce propulsion on a small scale, a series of biohybrid motors mimicking propellers in nature have been developed by integrating cardiomyocyte actuators into substrates of engineered shapes. Nawroth et al. fabricated a millimeter-scale “medusoid” motor by seeding a layer of cardiomyocytes onto an elastic, jellyfish-shaped polydimethylsiloxane (PDMS) thin film.¹⁹¹ Williams et al. prepared a biohybrid flagellum by selectively culturing contractile cardiomyocytes on a PDMS filament with a short, rigid head and a long, slender tail (Figure 11G).¹⁹²

2.7. Use of Original Materials

Besides the fabrication techniques introduced above, some unmodified materials can be used directly as micro/nanomotors. Most of these materials possess unique properties, such as catalytic and photoresponsive properties. Catalytic silver (Figure 12A) and manganese dioxide microparticles were reported to be able to exhibit autonomous motion propelled by bubbles in H_2O_2 .¹⁹³ The asymmetric geometry of the particles facilitates the asymmetric bubble generation needed for directional movement. Uses of photoresponsive inorganic materials that can generate concentration gradients in their surroundings through photoinduced reactions are another common strategy in the development of light-driven micromotors. Researchers have developed micromotor/micropump systems based on the movement of titanium dioxide (TiO_2 , Figure 12B)⁸⁶ and silver chloride (AgCl , Figure 12C)⁸⁷ microparticles in water under UV illumination. The motion of these substances relies on a photoinduced self-diffusiophoretic mechanism. UV-induced reactions generate a concentration gradient around the particles, thus propelling the particles in the direction of the gradient. In addition, Ibele et al. reported that AgCl particles in the presence of UV light and dilute H_2O_2 can exhibit oscillatory movement due to an oscillatory, reversible conversion of AgCl to silver at the particle surface.¹⁹⁴ Duan et al. reported a reaction-induced self-diffusiophoresis system based on Ag_3PO_4 that can exhibit reversible collective behaviors.¹⁹⁵ The transition between two different collective behaviors, exclusion and schooling, can be triggered either by shifts in the equilibrium or in response to light stimuli.

The asymmetric reactivity offered by bipolar electrochemistry provides a way for objects to be propelled in an electric field. Loget and Kuhn introduced a dynamic bipolar self-regeneration mechanism for the propulsion of metallic microscale objects (Figure 12D).⁹² Simultaneous dissolution and deposition of the metal based on redox reactions at the two ends of an object in the presence of an external electric

field will lead to directed motion of the object. Another strategy relies on asymmetric bubble generation due to water splitting at two extremities of a conductive object in the presence of an electric field.⁹³ Propulsion speed can be enhanced by using hydroquinone solution because the hydroquinone (HQ)/benzoquinone (BQ) redox couple has a lower redox potential than does the oxidation potential of water.^{196,197} As a result, bubble formation only occurs at one side of the object, leading to a higher speed (Figure 12E).

3. FUNCTIONALIZATION

Functionalization of micro/nanomotors is a process to make micro/nanomotors suitable for corresponding applications. Functionalized micro/nanomotors are expected to perform diverse and demanding tasks. Because micro/nanomotors are fabricated through different techniques and the requirements for distinct applications vary greatly, a variety of functionalization strategies and methods have been developed. Our discussion here is mainly from the two aims of functionalization: toward control and toward application. Modification in the fabrication procedures and resulting changes in the structures of micro/nanomotors will be illustrated in this section.

3.1. Toward Control

Control of the motion of micro/nanomotors is essential for meeting the demands of various envisioned applications, which require steering toward a destination as well as regulation of speed. The ideal system is to allow precise regulation of micro/nanomotors over both defined times and locations. Due to Brownian motion and low Reynolds numbers, precise control of the motion of micro/nanomotors is not easy. Different approaches have been developed to achieve motion control in micro/nanoscale systems.

3.1.1. Magnetic Control. Directed motion is an indispensable ability needed for micro/nanomotors to navigate in specified trajectories. Among various methods to regulate directionality, remote control by external magnetic fields is the most common method used to steer micro/nanomotors. Magnetically directed movement of micro/nanomotors can be accomplished by incorporating a ferromagnetic part that can be magnetized by an external magnetic field. Depending on different fabrication methods, the magnetic part is usually introduced by electrodeposition or physical vapor deposition. Whether the applied magnetic field will affect the speed of the micro/nanomotors that are not driven by a magnetic field depends on the orientation of the axis of magnetization of ferromagnetic sections with respect to the axis of the axial motion. The ferromagnetic sections will be magnetized along its longest dimensions.¹⁹⁸ As a result, the axis of magnetization is affected by the aspect ratio of the thickness to the diameter of the ferromagnetic sections. For example, magnetic segments shorter than the diameter of the nanowires magnetize perpendicular to the long axis of the nanowires. In this configuration, the applied magnetic field aligns the nanowires perpendicular to the magnetic field and does not exert a net axial force on the motors.¹⁹⁹ However, magnetic segments longer than the diameter of the wires or tubes results in motors magnetized longitudinally. For these micromotors, the velocity is caused by a combination of the driving force and the magnetic field.^{200,201} For the conditions of very weak magnetic field, the

Figure 13. Control of micro/nanomotors. (A) SEM image of Pt/Ni/Au/Ni/Au nanowire. Reproduced from ref 203. Copyright 2005 Wiley-VCH. (B) SEM/energy-dispersive X-ray (EDX) elemental analysis of Au/Ni/Pt nanotube. Reproduced from ref 200. Copyright 2013 American Chemical Society. (C) Scheme illustrating steering of acoustically propelled nanowire toward a HeLa cell. Reproduced from ref 202. Copyright 2013 American Chemical Society. (D) Scheme illustrating magnetic guidance of Janus micromotors. Reproduced from ref 55. Copyright 2012 American Chemical Society. (E) Dynamics study of helical micromotors. Dependence of propulsion speed (red) and angle of precession (blue) on the frequency of the magnetic field. The circles and squares represent experimental data while the solid and dotted lines correspond to data obtained based on the theoretical model. Reproduced from ref 209. Copyright 2012 American Physical Society. (F) Image showing the disintegration of nanowire chain after “sound off” at $t = 0$. Reproduced from ref 216. Copyright 2015 Royal Society of Chemistry. (G) Scheme illustrating ultrasound-modulated bubble propulsion of chemically powered microtubes. Reproduced from ref 217. Copyright 2014 American Chemical Society.

axial magnetic force is much smaller than the propulsion force and their influence on the axial propulsion is negligible.²⁰²

For electrodeposited nanowires and micro/nanotubes, a nickel segment can be introduced into the structure through electrodeposition. A striped, self-propelled Pt/Ni/Au/Ni/Au nanowire was used for one of the earliest demonstrations (Figure 13A).²⁰³ Because the electrodeposited nickel segment was shorter than the diameter of the wire, the nanowire was magnetized transversely rather than longitudinally. Magnetized nanowires can orient their net magnetic moment parallel to an external magnetic field, enabling precise guidance by controlling the orientation of the magnetic field. Experimental studies proved that the magnetic field serves to only align the nanowires without altering their speed. The directed motion of self-propelled Au/Ni/Au/Pt-CNT nanorods as well as their transportation of magnetic microparticle cargoes in micro-channel networks was demonstrated by Burdick et al.²⁰⁴

Magnetic guidance of electrodeposited microtubes can be realized by additional electrodeposition of nickel. For conical microtubes, nickel is electrodeposited to cover the entire inner surface of the microtube before electrodeposition of platinum, and therefore the microtubes are magnetized along the tube axis.⁵² A simplified Pt/Ni alloy inner layer obtained by codeposition of a Pt/Ni layer can provide both catalytic and

magnetic properties.¹²¹ However, the velocity of microtubes with a simplified Pt/Ni alloy inner layer in H_2O_2 is greatly reduced due to decreased catalytic area. For segmented nanotubes with different elements placed longitudinally, because the nickel part has a larger dimension along the axis of the tubes, they also can be magnetized longitudinally, exhibiting behavior similar to that of magnetotactic bacteria (Figure 13B).²⁰⁰

Magnetic guidance can be combined with different propulsion systems. In addition to self-propelled micro/nanomotors, remote control of acoustically powered nanowire can also be realized by steering it with an electrochemically grown ferromagnetic nickel stripe in the presence of a weak magnetic field. In this way, nanowire motors can be steered toward targets of interest. As an example, the magnetic guidance of nanowires toward live HeLa cells in biocompatible buffers was demonstrated (Figure 13C).²⁰² Because of interactions between the nickel parts, nanowires with a thin nickel segment at one end can assemble into geometrically regular dimers, trimers, and higher multimers while being levitated in a fluid acoustic cell.²⁰⁵ The relative number of various assemblies depends on the density of the nanowire suspensions and the speed of their axial motion. N-mer assemblies can exhibit different modes of motion with the

propulsion of ultrasound and can be steered by a weak external magnetic field. They can be isolated from the acoustic cell while remaining intact after drying.

As for rolled-up microtubes, an additional Fe layer can be incorporated into the microtubes during the deposition process to achieve magnetic control. The longitudinally magnetized rolled-up microtubes are able to detect the direction of an external field and orient themselves accordingly.²⁰¹ Magnetized Fe-containing microtubes were demonstrated to be able to selectively capture and transport paramagnetic beads in the absence of an external magnetic field.²⁰⁶ The ability of a platinum Janus particle to transport cargo has been demonstrated by Sanchez and co-workers.⁸ In an attempt to achieve better control of the motion of catalytic Janus motors and the cargo transport process, magnetic caps consisting of [Co/Pt]₅ multilayers were introduced into the structure via physical vapor deposition.⁵⁵ The magnetic caps were designed to align the magnetic moment along the main symmetry axis of the cap, enabling direct manipulation of the Janus motor as well as superparamagnetic cargoes by applying a desired external magnetic field (Figure 13D). Precise control of magnetic Janus particles is further demonstrated by sorting particles between channels in microchip devices.

For magnetically driven micro/nanomotors, variation in the magnetic field will lead to differences in their motion. For example, studies on MTB-based micromotors showed that trapping MTB by a gradient magnetic field in the target site has more advantages than does guidance with uniform magnetic fields.²⁰⁷ Here, we mainly discuss magnetically driven helical micromotors. In most of the reported cases, magnetization of the helical structure was designed to be along its short axis. As such, an external rotating magnetic field will exert a continuous torque on the helical structure and cause it to rotate around the long axis, resulting in a corkscrew motion along the long axis. Ghosh and co-workers studied the motion behavior of ferromagnetic helical structures fabricated using the GLAD technique in the presence of an oscillating magnetic field.²⁰⁸ Helical structures were first prepared by SiO₂ and subsequently coated with a ferromagnetic material. In an oscillating magnetic field, helical structures exhibit reciprocal behavior due to their asymmetric weight distribution brought about by the layer of magnetic coating, whose line of action does not coincide with the direction of the magnetic moment. Using a system of the same helical propellers, the same group investigated the frequency-dependent dynamics of helical micromotors in the presence of a rotating magnetic field.^{209,210} The helices were magnetized along arbitrary directions, thus obtaining a magnetic moment at an arbitrary angle θ_m with the short axis of the propeller under the action of a rotating magnetic field. The dynamics can be described by the precession angle α_p that the long axis of the helix made with the normal axis of the plane defined by the rotating field. As illustrated in Figure 13E, at low frequencies the helix rotates around its short axis in the plane of rotation of the magnetic field, namely, tumbling with $\alpha_p = 90^\circ$, and the velocity of propulsion is negligible. When the frequency was increased beyond a certain frequency Ω_1 , the helix ceased to tumble and started precessional motion at a steady α_p . The precession angle decreased from 90° to 0° with an increase in the frequency of the magnetic field to a step-out frequency Ω_2 , at which point the helical micromotor exhibited a corkscrew motion. In the precession and propulsion configurations, the propulsion

velocity increases with frequency. Beyond the step-out frequency, a helical micromotor slows down because the torque exerted by the magnetic field cannot overcome the viscous drag. In a narrow frequency range around the step-out frequency, the helix shows bistable behavior, switching randomly between tumbling and precessional configurations. Helical structures of the same geometry but with different θ_m under different magnetic fields show the same variation with f/Ω_1 , but the scaled step-out frequency (Ω_2/Ω_1) depends on the direction of magnetization θ_m .

Collective behavior of micro/nanomotors is of great interest as it is the foundation of envisioned collective micro/nanomachines. Assembly of micro/nanomotors is one of the phenomena that have attracted many researchers' attention. Dynamic intermotor interactions between catalytic bimetallic nanowires have been reported. Propelled nanowires can dynamically form staggered doublets and triplets as a result of the catalytically generated electric field.²¹¹ Tadpole-like catalytic nanomotors fabricated by dynamic shadowing growth were reported to be able to self-organize to form two-nanomotor spinning clusters.²¹² Because imparting magnetism to micro/nanomotors is very common, the influence of the introduced magnetic segments on the assembly of micro/nanomotors needs to be considered. Whitesides and co-workers found that nanowires containing nickel sections with length shorter than diameter can form three-dimensional assemblies using magnetic attractions.²¹³ When the length of the nickel section is larger than the diameter, the nanowires align parallel to the magnetic field and the interwire interactions induce the formation of head-to-tail chains.^{213,214}

Because propulsion of micro/nanomotors provides a kind of kinetic energy to induce dissociation of assemblies, assembly of propelled micro/nanomotors due to magnetic attraction is seldom reported. Acoustically propelled nanowires with thin nickel segments at one end instead of in the middle were reported to assemble into multimers.²⁰⁵ Gibbs and Zhao reported a self-assembled multicomponent "helicopter" micromotor consisting of a V-shaped rotor with Ni films on the elbow and a half-coated Ni silica microbead as the body.²¹² The two structures were magnetized in opposite directions and then mix together to assemble into a helicopter structure, where the top V-shaped nanomotor spins slowly on the microbead. The occurrence of the helicopter structure is around 25% in contrast to 0% of the control experiment using nonmagnetized structures. Tottori et al. demonstrated the controlled assembly and disassembly of magnetically propelled helical micromotors in the presence of rotating weak magnetic fields.²¹⁵ The nickel surfaces of the helical micromotors generate attraction forces between the structures, leading to the formation of various assembly configurations. The assembly and disassembly of multiple helical micromotors can be controlled by tuning the direction, speed, and strength of the rotating field. Changes in motion properties can occur depending on the configurations of the assembled structures.

3.1.2. Acoustic Control. Acoustic energy not only provides an alternative power source for the propulsion of micromotors but offers a strategy to control chemically self-propelled micro/nanomotors. The effect of ultrasound on bimetallic nanowires propelled in opposite directions by chemical and acoustic forces was investigated.²¹⁶ The direction of chemically powered movement can be reversed by tuning the power of the ultrasound field. Fast and reversible transition between aggregated and free-moving

states of nanowires in H_2O_2 was observed in response to switching between on and off ultrasound states (Figure 13F). Rapid and reversible stopping and starting of bubble-propelled microtubes is possible with the use of an ultrasound field.²¹⁷ Application of an ultrasound field disrupts normal bubble evolution and ejection by inducing the growth and aggregation of bubbles, thus hindering the movement of the microtubes. Rapid “stop–go” switching of microtube motion can be achieved by “on/off” ultrasound activations (Figure 13G). Furthermore, standing surface acoustic waves (SSAWs) provide a controllable approach for rapid, versatile, and tunable patterning of nanowires through dielectrophoretic forces in an induced piezoelectric field.²¹⁸ Nanowires can be patterned into different geometries by controlling the distribution of the SSAW field while the spacing of the nanowire arrays can be altered by adjusting the frequency of the SSAW.

3.1.3. Chemical/Electrochemical, Electrical, Thermal, And Light Control. The motion of chemically self-propelled micro/nanomotors can be regulated by tuning their fuel level or chemical stimuli. The speed of chemically powered micro/nanomotors was shown to increase with the level of fuel over a certain range.^{10,107} It has been demonstrated that catalytic nanowires, microtubes, and Janus particles all display chemotactic behavior in the presence of a gradient in fuel concentration.^{219,220} They can propel themselves along the gradient toward a region with a higher fuel concentration. As such, controlling the fuel concentration and distribution can be used for guiding and modulating the motion of chemically driven micro/nanomotors. The dynamic swarming of catalytic microtubes was reported to be dependent on the fuel conditions.²²¹ When a droplet of concentrated H_2O_2 is added to the solution of propylene carbonate with low concentrations of H_2O_2 and water, large clusters of microtubes are formed, and subsequently they decay in several minutes. The competition between the attractive capillary force and the repulsion thrust force determines whether the microtubes are in swarming behavior or independent propulsion. Electrochemical control of catalytic nanowires was accomplished by placing a gold wire electrode close to the micro/nanomotor and applying a potential to induce reactions of H_2O_2 or dissolved oxygen.²²² The potential-induced “on/off” switching and speed control are mainly attributed to changes in the local oxygen level. In addition to fuel concentration, the motion of chemically powered micro/nanomotors is affected by the presence of certain other chemicals. The motion of Au/Pt nanowires was shown to be dramatically accelerated upon addition of silver ion due to the underpotential deposition of silver on the nanowires, which leads to differences in surface and catalytic properties.²²³ Hydrazine is another chemical stimulus demonstrated to be useful to speed up the motion of Au/Pt-CNT nanowires.¹⁰⁷ For bubble-propelled micromotors, surfactants are of great significance to the mobility of micromotors because they can facilitate bubble generation and detachment.²²⁴ Thermal control of the motion of catalytic micro/nanomotors was proved to be feasible for both nanowire and microtube motors. The speed of Pt/Au nanowires was substantially increased upon exposure to elevated temperatures.²²⁵ Similar phenomena were found for bubble-propelled microtubes, which have been employed to compensate the effect of reducing the fuel level.¹¹⁹ The motion behavior of electrically driven micro/nanomotors can be modulated by controlling

the applied electric field. Additionally, electrophoretic directional control of two-dimensional movement of hybrid bacterial micromotors can be achieved by direct current electric fields.²²⁶ For most of the light-driven micro/nanomotors and biohybrid micromotors based on bacteria, motion can be guided by light.^{176,182}

3.2. Toward Application

The wide range of potential applications of micro/nanomotors covering different fields requires specific functionalization strategies for each kind of application. Here, we present the functionalization of micro/nanomotors for three main classes of applications: cargo transport, biomedical applications, and environmental remediation.

3.2.1. Cargo Transport. Cargo transport is one of the most important envisioned applications of micro/nanomotors. Depending on the properties of cargoes, tailored methods are needed for their transportation. For the transportation of magnetic cargoes by magnetic micromotors, the cargoes can simply be attached to the micromotors by magnetic attraction.^{55,206} Transportation of drug-loaded, magnetic poly(D,L-lactic-co-glycolic acid) (PLGA) microparticles has been demonstrated with both chemically propelled (Figure 14A) and magnetically driven micromotors through magnetic attraction.^{117,227} For charged cargoes, electrostatic interaction between micro/nanomotors and cargoes can be employed for the loading process. A common strategy to introduce charged parts into micro/nanomotors is to add a negatively charged polymer segment. Sen and co-workers demonstrated that a polypyrrole (PPy) segment introduced to a nanowire via electropolymerization can attach oppositely charged polystyrene amidine cargo through electrostatic interaction (Figure 14B).²²⁸ A photochemically stimulated cargo drop-off strategy was proposed for nanowires loaded with cargoes via electrostatic interaction.²²⁹ An additional silver segment in a nanowire will dissolve rapidly in the presence of hydrogen peroxide, chloride ions, and UV light, resulting in drop-off of the cargo. Garcia-Gradilla et al. described that the addition of a negatively charged polypyrrole polystyrene sulfonate (PPy-PSS) segment to an ultrasound-propelled nanowire can serve as a pH-sensitive carrier for positively charged drugs via electrostatic interaction.¹¹³ Triggered release of the drugs was achieved by a protonated PPy-PSS segment in an acidic environment. The same group prepared drug-loading nanowires based on a nanoporous gold segment with a large surface area.²³⁰ Such a nanoporous structure is obtained by dealloying the Ag component of a Au/Ag alloy prepared by coelectrodeposition of Au and Ag. Loading of the drug doxorubicin in the nanopores via electrostatic interactions with the polymeric coating of the nanowire motors and near-infrared (NIR) light-triggered release are illustrated in Figure 14C.

An alternative way to load cargo is to functionalize micro/nanomotors with materials that can interact with corresponding targets via self-assembled monolayer (SAM) chemistry. SAM chemistry is a common technique employed in the functionalization of micro/nanomotors to introduce desired materials for certain applications. Given the strong interaction of sulfur atoms with gold, gold is often used as a surface for the formation of SAM. For example, the Au head of a flexible nanowire enables the functionalization of a motor with different biomolecules. Manesh et al. demonstrated the creation of a helical gold structure based on a local reaction

Figure 14. Application of micro/nanomotors. (A) Transport and release of magnetic PLGA drug carriers by catalytic nanowire. Reproduced from ref 227. Copyright 2010 Wiley-VCH. (B) Cargo attachment to nanowire motors by electrostatic interaction between negative PPy end of Pt–Au–PPy motor and positively charged polystyrene amidine microsphere. Reproduced from ref 228. Copyright 2008 American Chemical Society. (C) Schematic illustration of drug delivery and triggered release by ultrasound-driven nanoporous Au nanomotors. Reproduced from ref 230. Copyright 2014 Wiley-VCH. (D) Functionalization of outer surface of microtubes using mixed self-assembled monolayer chemistry: (a) selective pick-up of target nucleic acid by capture-probe-modified microjet and (b) surface chemistry involved in functionalization of DNA probe-modified microtubes. Reproduced from ref 37. Copyright 2011 American Chemical Society. (E) Transport and triggered release of yeast cells by microjet with built-in boronic acid recognition. Reproduced from ref 34. Copyright 2012 American Chemical Society. (F) Schematic illustration of preparation of MIP-based micromotor and strategy for capture and transport of target protein. Reproduced from ref 232. Copyright 2013 American Chemical Society. (G) Preparation and propulsion of perfluorocarbon-loaded microbullets. Reproduced from ref 39. Copyright 2012 Wiley-VCH. (H) HeLa cell with internalized gold rods. Reproduced from ref 26. Copyright 2014 Wiley-VCH. (I) Capture of oil droplets by alkanethiol-modified microtubes. Reproduced from ref 46. Copyright 2012 American Chemical Society. (J) Scheme illustration of Fe/Pt microtubes for destroying organic contaminants based on Fenton reaction. Reproduced from ref 48. Copyright 2013 American Chemical Society.

induced by the movement of enzyme-functionalized flexible nanowire motors.²³¹ The interaction of biotin and streptavidin has been widely exploited in biotechnology. On the basis of strong noncovalent interactions, a self-assembled monolayer of biotin-terminated disulfide at the Au end was used to bind streptavidin-coated cargo via the specific biotin–streptavidin interaction.²²⁸ Photoinduced cargo release can be achieved by binding the carboxyl acid groups on the polymer end with the amine terminus of a bifunctional and photocleavable linker, whose biotin end was linked to a streptavidin-coated cargo.²²⁹ Photolysis of the photocleavable linker upon UV illumination will induce release of the cargo.

Active transport of biological targets by micro/nanomotors functionalized with corresponding bioreceptors represents a promising method for the isolation and separation of biomaterials. The high efficiency and large towing power of bubble-propelled microtubes provide considerable possibilities for potential applications. A great deal of progress has been made toward micromotor-based target delivery.³² Various efforts have demonstrated the successful pick-up and transport of different biological targets including bacteria,³³ cancer cells,³⁵ nucleic acids (Figure 14D,a),³⁷ and proteins³⁸ by microtube engines functionalized with lectin, antibody, single-strand DNA, and aptamer receptors, respectively. A layer of gold is sputtered on the microtube surface to facilitate the formation of a mixed alkanethiol monolayer and subsequent coupling of bioreceptors to obtain functionalized micromotors (Figure 14D,b). Magnetic control of the functionalized micromotors enables active pick-up and precise manipulation of the loaded cargoes. The functionalization of ultrasound-propelled nanowires with a self-assembled monolayer of specific bioreceptors on the gold part for selective capture of bacteria was demonstrated by Garcia-Gradilla et al.¹¹³

Other than functionalization after fabrication, binding sites for cargoes can be built into a structure. Kuralay et al. described the pick-up and transport of glucose-incubated microspheres and yeast cells by poly(3-aminophenylboronic acid) (PAPBA)/Ni/Pt microtubes.³⁴ Built-in boronic acid on the polymer surface of microtubes can selectively recognize monosaccharides. On the basis of differences of binding affinity with boronic acid, triggered release of captured yeast cells can be achieved by competitive binding of added fructose (Figure 14E). Molecular imprinting can be introduced in the electropolymerization process to create specific recognition sites on the outer polymer layer for selective capture and transport of targets (Figure 14F).²³² The outer polymer layer of the microtubes is deposited on the inner walls of the pores in the membrane, which contain preadsorbed polymer-based templates of the target. Subsequent dissolution of the membrane simultaneously removes the templates of the target, leaving complementary imprinted nanocavities for desired targets. Nonspecific transport of different cargoes by micro/nanomotors also can be accomplished through encapsulation or absorption by micro/nanomotors with multilayer or porous structures.^{54,59,233}

Cargoes can also be included in the preparation process. Sattayasamitsathit et al. reported a zinc-based micromotor fully loaded with different cargoes.²³⁴ The micromotor was prepared by a modified membrane template-assisted electrodeposition method. Before the electrodeposition of zinc, silica and gold nanoparticles are packed in the micropores of the membrane template via vacuum infiltration. A membrane with pores smaller than the size of the nanoparticles is placed

below to retain the nanoparticles in the upper membrane. After mechanical polishing and membrane dissolution, the nanoparticle-loaded micromotors can be obtained. The fast propulsion of the micromotors in an acidic environment and the autonomous release of the cargoes induced by the dissolution of the zinc body offer different potential applications in the biomedical field. The propulsion of zinc-based micromotors and their cargo delivery in mouse stomach has been demonstrated.²³⁵

3.2.2. Biomedical Applications. Tissue penetration is a desired ability for micromotors to perform in vivo cargo delivery and nanosurgery. Several initial proof-of-concept studies of microdrillers have been reported. Solovev et al. employed InGaAs/GaAs/Pt microtubes with sharp tips as microdrillers to drill into fixed cells.⁴⁰ Due to the crystal structure of the AlAs used as a successive sacrificial layer and the different etching rates of HF, the membranes favor rolling along the InGaAs <100> direction upon etching of the AlAs with HF. Asymmetry in the shape of the microtubes is important in determining their trajectories. The majority of fabricated microtubes containing sharp tips exhibit a screw-like motion in H₂O₂, providing ideal tools for drilling. Xi et al. demonstrated the potential application of magnetically powered rolled-up microtubes with sharp tips in minimally invasive surgery.⁴¹ The microtubes were fabricated by depositing Ti/Cr/Fe layers in a trapezoid pattern to enable the formation of the sharp tips desired for microdrilling. Upon reaching a threshold frequency of the external rotational field, the microtubes changed their rotation from horizontal to vertical, which was applied for mechanical drilling of porcine liver tissue. An ultrasound-triggered tubular microbullet was developed by Kagan et al. for targeted tissue penetration and deformation.³⁹ As shown in Figure 14G, microtubes with a gold inner surface fabricated by rolled-up technology or template electrodeposition were first conjugated with thiolated cysteamine via a thiol-gold bond, followed by electrostatic binding of anionic perfluorocarbon (PFC) emulsion. The microbullets utilize acoustic droplet vaporization (ADV) of the PFCs for propulsion. Rapid expansion during ultrasound-triggered vaporization of the PFCs bound to the inner surface of the microbullets generates an extremely powerful thrust, which can be used to penetrate, deform, and cleave dense materials.

The ability of micro/nanomotors to enter cells has also been studied. Xuan et al. fabricated Janus mesoporous silica nanomotors with sub-100 nm diameters by depositing chromium/platinum caps on mesoporous silica nanoparticles (MSNs).²³⁵ They demonstrated that more Janus MSN nanomotors entered the cells compared to uncapped MSNs. The high surface area of the MSNs enabled the loading of doxorubicin drugs, which was covered by an egg phosphatidylcholine (PC) bilayer, and subsequent release of the drugs by biodegradation of the lipid bilayers in cells. Wang et al. demonstrated the acoustic propulsion of nanorods inside living cells, which opened a new door for intracellular applications (Figure 14H).²⁶ Gold nanorods can strongly attach to the surface of HeLa cells and are readily internalized by the cells when incubated for a prolonged period. The nanorods still exhibit axial propulsion and spinning at different ultrasonic frequencies inside the cells.

Biocompatibility is essential for practical applications in the biomedical field. A toxicity study of Pt/Au nanotubes on the viability of human lung epithelial cells showed that nanotubes

do not exhibit acute toxicity toward the cells, which is of great significance for practical, real-world applications.²³⁶ Coating biocompatible materials on the surface of micro/nanomotors is an easy and direct way of enhancing biocompatibility. Magnetically driven micromotors are usually coated with biocompatible titanium. It has been proved that polymer microdevices coated with Ni/Ti thin bilayers are not cytotoxic to mouse myoblasts.⁶⁶ The cells readily adhered and proliferated over the surface of the devices. By integration of a conformal ferrite coating, Venugopalan et al. reported a cytocompatible magnetically driven helical micromotor that can be propelled in human blood at negligible dilutions.²³⁷ Furthermore, Nelson and co-workers have designed a platform for the biomedical application of magnetically driven motors in the eye.²³⁸ The possibility of targeted retinal drug delivery,²³⁹ retinal vein cannulation, and oxygen sensing²⁴⁰ with the use of magnetic microrobots has been demonstrated. As a common fuel used for chemically propelled micro/nanomotors, H₂O₂ is not biocompatible and should be avoided in biomedical applications. Mou et al. employed the chloride pit corrosion and buffering effect of simulated body fluids (SBFs) or blood plasma to eliminate the need for external fuels and additives, allowing efficient propulsion of micromotors in SBFs and blood plasma.²⁴¹ They also incorporated thermoresponsive hydrogel layers on the surface of the Mg/Pt Janus micromotors as a means of delivery and temperature-controlled release of drugs.

3.2.3. Environmental Remediation. One of the principal environmental applications of micro/nanomotors is the adsorption of contaminants in water. Surface modifications of micro/nanomotors with a hydrophobic layer enable them to capture oil droplets. Guix et al. reported that the functionalization of Au/Ni/PEDOT/Pt microtubes with a SAM of alkanethiols on the gold outer surface enabled the collection and transport of oil droplets due to their strong interactions (Figure 14I).⁴⁶ The extent of interaction can be adjusted by changing surface hydrophobicity by using different chain lengths and head functional groups. Using seawater-driven magnesium Janus micromotors, they were able to collect oil droplets from seawater without additional fuel after modification of the gold surface with SAMs of long-chain alkanethiols.¹⁷ Magnetic steering of these micromotors was accomplished by the addition of a nickel layer. An alternative is to use materials with high adsorption capacity for fabricating the micro/nanomotors. Jurado-Sanchez et al. prepared activated carbon-based Janus micromotors by deposition of a Pt layer on one hemisphere.²⁴² The 60- μ m-diameter carbon Janus micromotors with very rough surfaces can exhibit effective bubble evolution and propulsion. The adsorption properties of activated carbon microparticles enable “on-the-fly” removal of a variety of pollutants. The bubble propulsion of the catalytic Janus micromotors may be attributed to the rough surfaces and large dimensions. Studies by Wang and Wu showed that high catalytic activity and a rough surface can change the propulsion mode from self-diffusiophoresis to bubble propulsion.²⁴³ It was also reported that surfaces with smaller curvature can facilitate the formation of bubbles.²⁴⁴

Remediation agents can also be incorporated in micro/nanomotors as the outer surface to contribute to the decontamination process during motion. Soler et al. reported the use of microtube motors with a Fe outer surface for degrading organic pollutants in water via the Fenton oxidation

process (Figure 13J).⁴⁸ The ferrous ions generated by the corrosion of the Fe surface and the H_2O_2 fuel act together as reagents for the Fenton reaction. On the basis of water-driven Mg Janus micromotors, Li et al. proposed a strategy of using light-activated $\text{TiO}_2/\text{Au}/\text{Mg}$ microspheres for photocatalytic decomposition of biological and chemical warfare agents.²⁴⁵ The coated TiO_2 layer can generate highly reactive oxygen species that are active in the decontamination process under UV illumination. It was also demonstrated that the movement and bubble generation of micromotors provide efficient fluid mixing, leading to acceleration of the detoxification process.⁴⁷

4. CONCLUSIONS

We have reviewed the fabrication methods and techniques of existing micro/nanomotors. Although considerable efforts have led to impressive progress in the great diversity of self-propelled, external-energy-propelled, and biohybrid micro- and nanoscale motors, successful realization of their practical applications still requires further improvement. Several aspects should be taken into consideration for any future development of fabrication methods. First, easy and cost-effective approaches should be developed toward parallel mass production of micro/nanomotors to fulfill the vision that millions of nanomotors are able to cooperate and communicate with each other to accomplish tasks. Quality control is a problem that cannot be overlooked in the process of simplifying preparation procedures. Because the geometry and morphology of micro/nanomotors are critical to their movement, the uniformity of the structures and reproducibility of the methods are of great significance. Second, the discovery of new materials and propulsion methods that are compatible with living systems is a challenge facing the field. The limitations of currently used materials and fuels preclude many potential applications of micro/nanomotors, especially those in the biomedical field. Although diverse micro/nanomotors powered by external energy sources provide alternatives, they are still primitive in the performance of complicated tasks. Energy-conversion efficiency can be promoted to increase both the mobility and towing ability of micro/nanomotors for improved transport of heavier and sophisticated cargoes. Third, more functionalization strategies should be developed to expand the scope of potential applications. Current methods relying on magnetic or electrostatic attraction are only suitable for magnetic and charged cargoes, whereas self-assembled monolayer techniques require specialized interaction between cargoes and receptors on nanomotors. The ability to pick up, transport, and release diverse cargoes is expected to play an important role in numerous practical applications in the environmental and biomedical areas. Large-scale fabrication of nanomotors with improved efficiency, biocompatibility, and functionality using easy and low-cost approaches can pave the way for the ultimate realization of potential applications. As interest in this cutting-edge field increases and technological breakthroughs emerge, micro/nanomotors are expected to have profound effects on a variety of related fields just like the machines of our macroscopic world.

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Notes

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Tissue cell assisted fabrication of tubular catalytic platinum microengines†

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We report a facile platform for mass production of robust self-propelled tubular microengines. Tissue cells extracted from fruits of banana and apple, *Musa acuminata* and *Malus domestica*, are used as the support on which a thin platinum film is deposited by means of physical vapor deposition. Upon sonication of the cells/Pt-coated substrate in water, microscrolls of highly uniform sizes are spontaneously formed. Tubular microengines fabricated with the fruit cell assisted method exhibit a fast motion of ~ 100 bodylengths per s (~ 1 mm s⁻¹). An extremely simple and affordable platform for mass production of the micromotors is crucial for the envisioned swarms of thousands and millions of autonomous micromotors performing biomedical and environmental remediation tasks.

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Introduction

As a leading-edge nanotechnology, self-propelled micro-/nano-scale motors represent a fundamental step towards practical tiny machines.^{1–5} These autonomous nano- and micro-sized devices are expected to perform a wide variety of tasks in the biomedical field,^{6,7} environmental remediation^{8–10} and natural resource discovery.¹¹ Self-propulsion at the nanoscale is achieved mainly by the mechanisms of self-electrophoresis,^{12,13} self-diffusiophoresis^{14,15} or bubble ejection.^{16–18} The last mode of propulsion is of the greatest interest as it exhibits the strongest propulsion power and unprecedented velocity.^{19,20} Bubble-propelled micromotors are typical of microtubes with a catalyst^{17,21} on the inner surface. Hydrogen peroxide fuel is decomposed into oxygen and the resulting bubbles are expelled from one end of the microtube, thus propelling it in the opposite direction.

The fabrication of tubular micro/nanomotors is still a highly challenging task. The rolled-up nanotechnology²² includes top-down photolithography, angled e-beam evaporation and stress-assisted rolling of nanomembranes upon etching away of the photoresist. The practical utility of this method is greatly hindered by the complicated fabrication process and high costs of related clean-room conditions. An alternative method of fabricating tubular micro/nanomotors is anodic aluminum oxide or polymer membrane-templated electrodeposition,^{19,23} but this technique requires highly trained personnel and the cost of templates is not negligible. In addition, toxic

electroplating solutions containing cyanide are usually needed in the electrodeposition process.

Recently, there has been intense interest in developing cheap and easy plant-derived approaches for fabrication of motors. Millimeter sized biocatalytic motors based on plant tissues²⁴ and magnetically driven helical micromotors harnessing spiral water-conducting vessels of different plants²⁵ have been reported. Here, we demonstrate an extremely simple and low-cost fabrication method of tubular microengines with the assistance of fruit cells. The use of cheap and widely accessible fruit cells instead of a lithographically defined material as the support of metal layers omits the etching step and significantly reduces the fabrication costs. The resulting microtubes display ultrafast motion in the presence of hydrogen peroxide. The new fruit cell assisted method allows for rapid and cost-effective fabrication of thousands of copies of tubular microengines using banana and apple fruit tissue cells.

Results and discussion

To prepare the tubular microengines, the aqueous dispersion of banana fruit cells was first prepared by homogenization of mashed banana tissue in water *via* ultrasonication. The homogenized dispersion of banana fruit cells was subsequently deposited on the glass cover slip. After complete evaporation of water, Pt was deposited on the glass cover slip coated with banana cells by sputtering. Upon ultrasonication of the modified cover slip in water, the multilayer film shattered and detached from the glass cover slip, rolling into scrolls. The whole fabrication process is illustrated in Scheme 1.

Fig. 1 shows optical images of aqueous dispersion of banana fruit cells and the fabricated tubular microengines. As can be seen from Fig. 1A, the banana fruit cells are several hundred micrometers in length and are flat in shape. After the

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Scheme 1 Preparation of rolled-up tubular microengines using banana fruit cells: (a) deposition of banana fruit cells on the glass cover slip, (b) deposition of a Pt layer by sputtering, and (c) ultrasonication of the cells/Pt-coated cover slip.

analysis of the obtained microtubes was carried out, as shown in Fig. 2C. The majority of the fabricated tubular microengines are 10–15 μm long and the average opening diameters at opposite ends are around 2.5 μm and 3 μm , respectively. The uniformity of the tubular microengines fabricated by the new method is competitive with that of microtubes prepared by membrane-templated electrodeposition and rolled-up technology.²⁶

The EDX mapping analysis of the fabricated tubular microengines (Fig. 3) clearly shows the presence of platinum, carbon and oxygen, demonstrating the existence of banana fruit tissue in the microtube structure. For the fabrication of rolled-up microstructures, the strain in the film creates the bending moment²⁷ and strain relaxation is the driving force of the rolling

Fig. 1 Optical images of aqueous dispersion of (A) banana fruit cells and (B) tubular microengines obtained upon ultrasonication. Scale bar: 50 μm .

evaporation of water, the cells deposited on the cover slip became a layer of membrane that would detach from the surface upon coming into contact with water. There are no microtubes observed before and after deposition of the Pt layer, where only some cracks of the deposition layers emerged. However, microtubes were immediately obtained upon ultrasonication of the cells/Pt-coated glass cover slip in water, as shown in Fig. 1B.

The SEM images of the resulting microtubes are presented in Fig. 2A and B. The microtubes exhibit excellent size uniformity and the rolled-up structure is clearly visible. A size distribution

Fig. 2 (A and B) SEM images of the fabricated tubular microengines. Scale bars are 10 μm and 1 μm , respectively. (C) Length distribution of the tubular microengines, $n = 65$.

Fig. 3 SEM/EDX elemental characterization of the tubular micro-engine composition. Scale bar: 10 μm .

Fig. 4 (A) Optical image of the cover slip half coated with banana fruit cells (right side) after deposition of Pt and ultrasonication in water. Platinum is still on the uncoated cover slip after ultrasonication (left side). Scale bar: 50 μm . (B) Optical image of tubular micro-engines fabricated using apple fruit cells. Scale bar: 20 μm .

process.²⁸ The strain in the fruit cells/Pt bilayer mainly comes from two aspects. The Pt film deposited by sputtering is in a state of intrinsic stress, because of the accumulating effect of

the crystallographic flaws that are built up during the deposition process.²⁹ The intrinsic stress is related to the deposition conditions and properties of the substrate surface.^{29,30} In addition, the different swelling properties of banana fruit cells and a metal layer in water result in unequal changes in volume, thus generating swelling-induced strain.^{27,28} The intrinsic stress of a platinum film and the swelling-induced strain together lead to the formation of the fruit tissue cells/Pt microscrolls.

Control experiment to prove the necessity of the banana fruit cells for successful formation of the microtubes was carried out. One half of the glass cover slip was covered with banana fruit cells while the other half of the glass was left bare. After deposition of the Pt layer and ultrasonication in water, the Pt layer still covered the bare glass surface while the Pt layer and banana tissue cells on the other side detached from the glass cover slip upon ultrasonication (Fig. 4A, the left and right side, respectively). The banana fruit cells provide an easily detachable interface between the metal layer and the glass substrate, which allows the instantaneous formation of microscrolls upon ultrasonication in water and eliminates the etching step using other chemical solutions. Additionally, we wish to show that banana fruit cells serve only as an example – other fruit cells can be employed to assist the preparation of tubular microengines as well. Fig. 4B shows the optical image of the microtube fabricated using apple fruit cells.

The tubular microengines fabricated with the fruit cell assisted method exhibit high propulsion power in the presence of hydrogen peroxide fuel. Fig. 5A shows a typical snapshot of the motion of the prepared microengines in 3% H_2O_2 . The trajectory can be easily visualized from the oxygen bubble tail released from one end of the microtube. The speed of the tubular microengines can be modulated by varying the concentration of hydrogen peroxide. As shown in Fig. 5B, the average velocity of the fruit cells/Pt microtube engines increases from $\sim 410 \mu\text{m s}^{-1}$ in 2% H_2O_2 to $\sim 680 \mu\text{m s}^{-1}$ in 4% H_2O_2 . Some microengines show ultrafast motion, up to 1 mm s^{-1} in 3% H_2O_2 (Video S1; ESI†). The mobility of the tubular microengines prepared with the introduced method is highly competitive with that of microengines fabricated by electrodeposition¹⁹ and rolled-up technology.²⁰ In addition, the very low cost of the fabrication process using common fruits, such as bananas and apples, offers possibilities for mass production of micromotors. Thousands of microtube engines can be prepared with only milligrams of fruit tissue.

Conclusions

In summary, we demonstrated a very affordable and simple route for the fabrication of rolled-up tubular microengines, using fruit tissue cells as the support of the deposited metal layer. Given the cheap price of fruits and small amounts needed for the preparation process, the cost of fabrication is only cut down to the consumption of Pt used for sputtering. One can envision the use of the other soft tissues for assisted fabrication of microjets. Microtube engines fabricated by this method exhibited good uniformity in the dimensions and excellent mobility, up to ~ 100 bodylengths per s. The fruit tissue cell assisted fabrication process opens doors for mass fabrication of microscale devices at extremely low cost.

Fig. 5 (A) Snapshot of the motion of a microtube engine in 3% H₂O₂ and 0.5% SDS. Scale bar: 50 μm. (B) Dependence of the microjet speed on the H₂O₂ concentration in the presence of 0.5% SDS. Tracking data were obtained from 15 independent running experiments in order to obtain the average speed.

Experimental section

Materials

Hydrogen peroxide (35%, lot no. 10172592) was purchased from Alfa Aesar. Sodium dodecyl sulfate (SDS, lot no. 079K0335) was purchased from Sigma-Aldrich. VFM cover slips (22 × 22 mm, lot no. GP110220001) were purchased from Cellpath, UK. The platinum targets for sputtering were purchased from Quorum Technologies Ltd, UK. Bananas and apples were purchased from local markets. The chemicals were used as received and ultrapure water (18.2 MΩ cm) from a Millipore Milli-Q purification system was used throughout the experiments.

Apparatus

The ultrasonication process was carried out with a Fisherbrand FB 11203 ultrasonicator. Sputtering was carried out with a JEOL JFC-1600 Auto Fine Coater. Scanning electron microscopy (SEM/EDX) analysis was obtained with a JEOL JSM 7600F instrument. Optical microscope images and videos were obtained with a Nikon Eclipse 50i microscope. Video sequences were processed with Nikon NIS-Elements software.

Methods

Preparation of microjets. The cover slips were cleaned with water and dried with nitrogen gas. Fruit tissue (banana or apple,

500 mg) was dispersed in water (2 mL) by ultrasonication and 50 μL of the aqueous suspension was applied on the cover slip to spread over the whole surface. The cover slip was left overnight to dry and platinum (15 nm) was sputtered on the cover slip. The cover slip was ultrasonicated subsequently in water and the aqueous suspension of tubular microengines can be obtained.

Propulsion of microjets. The experiments for the motion study of the fabricated tubular microengines were carried out in an aqueous solution containing different concentrations of hydrogen peroxide at a constant surfactant concentration (0.5 wt% of SDS). A mixture of microjets, SDS, H₂O₂ and water was applied on a glass slide freshly cleaned with a nitrogen gas. Optical microscope videos and images were obtained with a Nikon Eclipse 50i microscope. Video sequences were processed with Nikon NIS-Elements™ software.

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From Nanomotors to Micromotors: The Influence of the Size of an Autonomous Bubble-Propelled Device upon Its Motion

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S Supporting Information

ABSTRACT: Synthetic autonomously moving nano and micromotors are in the forefront of nanotechnology. Different sizes of nano and micromotors have been prepared, but the systematic study of the influence of their sizes on motion is lacking. We synthesized different sizes of tubular micro/nanomotors by membrane template-assisted electrodeposition. The influence of dimensions on the dynamics of micro/nanotubes was studied at a significantly reduced scale than rolled-up microtubes, down to the nanometer regime. Both the geometric parameters and the chemical environment can affect the dynamics of micro/nanotubes. The bubble size and ejection frequency were investigated in correlation with the velocity of micro/nanotubes. The comparison between different sizes of micro/nanotubes showed that geometric parameters of micro/nanotubes will influence the velocity of micro/nanotubes at moderate fuel concentrations. Furthermore, it also affects the activity of micro/nanotubes at low fuel concentrations and imposes limitations on the velocity at very high fuel concentrations. Nanotubes with nanometer-sized openings need a higher concentration of H_2O_2 to be activated. Larger tubes can possess a higher absolute value of velocity than smaller tubes, but do not necessarily have a higher velocity by body lengths per unit time. Insight into bubble ejection/propulsion cycle is also provided. The results presented here provide important implications for the consideration of dimensions in the fabrication of tubular micro/nanomotors.

KEYWORDS: micro/nanomotors, micro/nanojets, size, geometric parameters, dynamics

Nanotechnology provides a way to manipulate matter at the atomic and molecular scale. One of the aspiring goals of nanotechnology is to build complete functional systems from the bottom up. Micro/nanomachines is an emerging field to design and build miniaturized machines analogous to macroscopic machines in our life to perform various intended tasks at small scales.¹ As mobility is desired in a wide range of applications, the use of self-propelled micro/nanomachines represents a significant step toward the realization of practical micro/nanodevices. Up to now, a number of self-powered micro/nanomotors that can convert chemical energy into movements and forces have been developed. The motion of diverse self-propelled micro/nanomotors is mainly attributable to three propulsion mechanisms: self-diffusiophoresis, self-electrophoresis, and bubble propulsion.^{2–4} The motion governed by self-diffusiophoresis relies on the solvent flow induced by the concentration gradient of solute around the micro/nanomotors. Self-electrophoresis generally needs the micro/nanomotors to be composed of two distinct conductive materials, allowing

different electrochemical half reactions to occur at opposite ends. The resulting internal electron flow is accompanied by the migration of protons in the double layer surrounding the micro/nanomotor, which propels the micro/nanomotor in the opposite direction. Bubble propulsion refers to the recoil effect of the growth and ejection of bubbles generated by the micro/nanomotors.

Among different kinds of self-propelled micro/nanomotors, tubular micro/nanomotors attract the most attention due to the robust performance as well as ease of functionalization and control.^{5,6} Recent efforts have demonstrated the great potential of these tubular micro/nanomotors to address problems in biomedical and environmental fields.^{7–11} The most common tubular micromotors are microtubes with platinum inner surface to catalyze the decomposition of hydrogen peroxide

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Figure 1. SEM images of the four types of prepared micro/nanotubes. A) Microtubes electrodeposited at -20 mA for 2000s in $5\ \mu\text{m}$ pores. B) Microtubes electrodeposited at -20 mA for 2000s in $2\ \mu\text{m}$ pores. C) Microtubes electrodeposited at -20 mA for 600s in $2\ \mu\text{m}$ pores. Images (a) and (b) in A–C were taken at the same magnification of $5000\times$. Images (c) in A–C were taken at the same magnification of $800\times$. D) Nanotubes electrodeposited at -2 mA for 1000s in $200\ \text{nm}$ pores. Image (a) was taken at the magnification of $5000\times$. Image (b) was taken at the magnification of $100000\times$. Image (c) was taken at the magnification of $30000\times$.

to achieve propulsion by oxygen bubbles. There are mainly two methods for the fabrication of micro/nanotubes: the rolled-up technology¹² and the membrane template-assisted electrodeposition.¹³ Rolled-up technology relies on the strain gradient in the deposited multilayers for the membranes to scroll into tubes when released from the substrate. Membrane template-assisted electrodeposition utilizes the micro/nanopores in the template for mass electrosynthesis of micro/nanotubes. Compared to rolled-up technology, membrane template-assisted electrodeposition provides an easier way to fabricate tubes with significantly smaller dimensions. Using membranes with different pore sizes, micro/nanotubes of varied dimensions can be prepared.

As the applications of micro/nanomotors cover a wide range of areas, their sizes should be customized to fit the needs. Despite the intensive study of functionalization strategies for micro/nanomotors,^{14–18} the investigations regarding their dimensions are limited. The geometric parameters, such as diameters of their openings and lengths, have a significant influence on the dynamics of tubular micro/nanoengines. Mei and co-workers established a body-deformation model to study the dependence of dynamics of tubular micromotors on their geometric parameters and used rolled-up microtubes to verify the validity of the model.¹⁹ Other bubble propulsion models proposed by Fomin *et al.*²⁰ and Manjare *et al.*²¹ were also tested on rolled-up microtubes. For some of the applications, there is a need to scale down the size of microtubes, so it is of great

significance to understand the motion at an even smaller scale. Here, we use electrodeposited micro/nanotubes with much smaller sizes to investigate the influence of dimensions on their dynamics.

RESULTS AND DISCUSSION

The tubular motors used in the study were prepared by membrane template-assisted electrodeposition using cyclopore polycarbonate membranes. The membranes contain a high density of double-conical pores with a closely controlled pore size distribution, which provide asymmetrical structures desired for bubble propulsion. We employed three different kinds of commercial membranes with double-cone pore structures of $5\ \mu\text{m}$, $2\ \mu\text{m}$, and $200\ \text{nm}$ in diameters separately. Although it is now widely accepted that the motion of platinum based microtubes in H_2O_2 is primarily governed by bubble propulsion, we used pure platinum micro/nanotubes here to rule out the contribution of electrokinetic mechanisms to the motion. For the microtubes prepared using membrane template with pore diameter of 5 and $2\ \mu\text{m}$, only platinum is electrodeposited, while for nanotubes prepared using membrane template with pore diameter of $200\ \text{nm}$, a layer of copper sacrificial layer is first electrodeposited before platinum. Finally, all the prepared micro/nanotubes were treated with concentrated nitric acid to remove the remaining silver backing or the copper sacrificial layer. The energy-dispersive X-ray spectro-

Figure 2. Video frames of the motion of the three types of microtubes in 2% H_2O_2 captured by a high speed camera at 270 frames/s. (A) A microtube electrodeposited at -20 mA for 2000 s in $5\ \mu\text{m}$ pores. (B) A microtube electrodeposited at -20 mA for 2000 s in $2\ \mu\text{m}$ pores. (C) A microtube electrodeposited at -20 mA for 600 s in $2\ \mu\text{m}$ pores. The scale bars are $20\ \mu\text{m}$. Blue line indicates the position of the motor at $t = 0$. It is used for monitoring the motion of the motor.

copy (EDX) images of the micro/nanotubes are shown in [Supporting Information](#).

Figure 1 shows the scanning electron microscopy (SEM) images of the four types of prepared micro/nanotubes: Type A, microtubes electrodeposited at -20 mA for 2000 s in $5\ \mu\text{m}$ pores; Type B, microtubes electrodeposited at -20 mA for 2000 s in $2\ \mu\text{m}$ pores; Type C, microtubes electrodeposited at -20 mA for 600 s in $2\ \mu\text{m}$ pores; and Type D, nanotubes electrodeposited at -2 mA for 1000 s in $200\ \text{nm}$ pores. The images in column (a) of Figure 1A–D were taken at the same magnification of $5000\times$ to illustrate the relative size of the four types of micro/nanotubes. The microtube in Figure 1A,(a) is $15.95\ \mu\text{m}$ long with an aspect ratio of length to average diameter of 3.52. The diameters at the opposite ends are 4.67 and $4.39\ \mu\text{m}$, giving an aspect ratio of 1.06. The length of the microtube shown in Figure 1B,(a) is $17.27\ \mu\text{m}$ and the diameters are 1.77 and $1.88\ \mu\text{m}$. The aspect ratio of length to average diameter is 9.46 while that of large opening to small opening is also 1.06. The length of microtubes can be tuned by varying the electrodeposition duration. The microtubes shown in Figure 1C are prepared using the same kind of membrane as that in Figure 1B, but for a shorter electrodeposition time, thus having similar opening diameters and shorter length. The microtube in Figure 1C,(a) possesses a length of $6.24\ \mu\text{m}$ and opening diameters of 1.87 and $1.64\ \mu\text{m}$, giving 3.56 as the aspect ratio of length to average diameter and 1.14 as that of large opening to small opening. Figure 1D,(a) presents a bunch of unpurified nanotubes, of which the opening diameters are scaled down to hundreds of nanometers. The nanotube in the zoomed-in image, Figure 1D,(c), has an aspect ratio of large opening to small opening of 1.24, with the diameters being 0.21 and $0.17\ \mu\text{m}$. The length of the nanotube is $2.32\ \mu\text{m}$ and the

aspect ratio of length to average diameter is 12.21. The images in column (b) of Figure 1A–D illustrate the thickness of the micro/nanotubes. The average thickness of the four types of micro/nanotubes are $0.53\ \mu\text{m}$, $0.34\ \mu\text{m}$, $0.25\ \mu\text{m}$ and $25\ \text{nm}$, respectively from A–D. The images in column (c) of Figure 1A–C demonstrate the unpurified bunches of micromotors at the same magnification of $800\times$. As can be seen from the images, the prepared micro/nanotubes are relatively uniform in sizes and shapes. The observed heterogeneity is largely due to the inhomogeneity of the size and alignment of pores in the membrane templates.

The bubble-recoiling mechanism of the microtubes means that the motion of microtubes is based on the dynamics of bubble growth and detachment processes.^{20,21} The oxygen generated on the inner wall of the microtubes is accumulated and the formed bubbles are ejected out to propel the microtubes gradually. The bubble dynamics is related to both the H_2O_2 fuel concentration and the geometry of the microtubes. Given the configuration of the microtube, there are three main geometric parameters that influence their dynamics: the length, diameter of large opening, and diameter of opposite smaller opening of the microtube. Figure 2 demonstrates the typical video frames of the motion of the three types of microtubes in 2% H_2O_2 captured by a high speed camera at 270 frames/s. The microtubes in Figure 2A–C correspond to Type A–C microtubes, respectively. The interval between each frame is 3.7 ms. The first 7 images in Figure 2A–C are consecutive 7 frames, while the last ones in A–C are 30 frames after the first ones. As can be seen from the video clips, in spite of the single platinum composition, the bubbles only come out from the cavity of the microtubes, suggesting the inner concave surface is more favorable for the formation and

Table 1. Geometric and Dynamic Parameters of the Three Microtubes in Figure 2

microtube	length (μm)	average diameter of two openings (μm)	average bubble diameter (μm)	bubble frequency (Hz)	estimated average velocity ($\mu\text{m/s}$)	measured average velocity ($\mu\text{m/s}$)	average velocity (body lengths/s)
Figure 2A	15.68	4.66	6.99	108.11	377.84	379.77	24.22
Figure 2B	19.58	1.92	4.63	96.49	223.37	215.21	10.99
Figure 2C	6.23	1.82	3.96	117.12	231.90	229.63	36.86

accumulation of oxygen bubbles. The asymmetric bubble formation on the concave and convex surfaces may be attributed to the heterogeneous nucleation energy and asymmetric concentration distribution of oxygen on the concave and convex surfaces.^{22,23} The time of every cycle of bubble growth and release is not fixed, but for the three types of microtubes presented in Figure 2, the cycles all take an approximate duration of 7.4–11.1 ms intervals. The lengths and average diameters of the three microtubes in Figure 2 are presented in Table 1.

As bubble ejection gives the thrust needed to propel the motion of microtubes, the velocity of the microtubes is closely related to the bubble size and expulsion frequency. The generated oxygen bubbles inside the microtube are driven by difference in Laplace pressure to migrate along the longitudinal axis of the microtube to the larger opening.^{20,24} Laplace pressure is the pressure difference between the inside and outside of the bubbles. Due to the asymmetric shape of the microtubes (along the two differing diameter openings), there exists a difference in Laplace pressure between the two curved interfaces of the bubble slug in the microtube, driving the bubble to move to the larger opening. The Laplace pressure (ΔP) is induced by the surface tension (γ) of the interface between liquid and gas. According to the Young–Laplace equation for spherical shapes, $\Delta P = 2\gamma/R$, the radius of the expelled bubbles (R) mainly depends on the Laplace pressure. The bubbles will experience a volume expansion in the expulsion process because of the decrease in the Laplace pressure. Typically, once a part of the bubble is exposed out of the microtubes, the Laplace pressure will decrease and the bubble will expand accordingly until the bubble is fully ejected out and reaches a temporarily stable Laplace pressure. A clear tail of bubbles with relatively uniform sizes can be observed at one end of the microtube. As the concentration of surfactant can affect the generation and release of bubbles, all of the motion studies were conducted at a fixed concentration of SDS (0.3 wt %). As shown in Table 1, the bubbles generated by the microtube in Figure 2A had larger sizes than those generated by the microtubes in Figure 2B,C. It is typical that the bubbles ejected by microtubes with a larger diameter, to be bigger than those ejected by smaller microtubes, which demonstrates that the bubbles from smaller microtubes experience higher pressure due to the smaller volume inside the microtubes. Additionally, it is also of interest to compare the two microtubes in Figure 2, panels B and C, which are similar in opening diameters but vary in lengths. The bubbles ejected by the longer microtube in Figure 2B were bigger than those ejected by the shorter microtube in Figure 2C. Although the longer microtube has a higher oxygen production due to the larger inner surface area, the bigger bubbles suggest lower pressure inside the longer microtube, compared to that in the shorter microtube. On the other hand, as the change of Laplace pressure in the expulsion process is more significant for bubbles generated in narrower microtubes, the expansion of bubbles from narrower microtubes is more obvious, which can be seen from the aspect ratio

of diameter of the bubble to microtube. The microtube in Figure 2A had the lowest aspect ratio of the diameter of the bubble to the microtube (1.50) among the three microtubes in Figure 2, which is consistent with the previously reported findings that the ratio decreases with an increase in the micromotor radius.²⁵ The aspect ratio of the diameter of the bubble to the microtube in Figure 2B,C was 2.41 and 2.18, respectively. With increasing time, the bubbles will gradually move to the surface of the solution and expand simultaneously.

The driving force for the motion of microtubes is the bubble recoil, and therefore, it is of great significance to study the expulsion process. In this process, both the bubbles and microtubes experience drag forces acting opposite to their relative motion in the fluid environment. Consistent with previous studies,^{12,26} the average moving distance of the three types of microtubes propelled by each cycle of bubble growth and release was very close to the radius of the bubbles. Consequently, the average velocity of the microtubes is approximate to the product of the bubble radius and the bubble ejection frequency. The estimated velocity in Table 1 is the calculated product of the bubble radius and the bubble ejection frequency, while the measured velocity is obtained by tracking using analysis software. The bubble expulsion frequency was the average value calculated from a 3 s video sequence and the average bubble diameter was obtained from 20 bubbles expelled within this period. The bubbles ejected from one microtube are relatively uniform in sizes, and the standard deviations of bubble diameters are below 0.15 μm . For all the three types of microtubes, the estimated velocity and the measured velocity are comparable.

As described earlier, the bubble size is relevant to both the opening size and the length of microtubes, whereas the bubble ejection frequency equals to the total volume of oxygen generated by the microtube inner surface per second divided by the average volume of each bubble. At the same concentration of H_2O_2 , the volume of generated oxygen is proportional to the area of the Pt catalyst surface.¹⁹ The microtubes with larger inner surface area will generate more oxygen per unit time than the smaller microtubes. As the inner surfaces of the microtubes studied here were not smooth, the surface area cannot be directly obtained by calculation from the geometric parameters. However, the general trend still persists. Through calculation using the data in Table 1, we find that the microtube in Figure 2A produces the most oxygen per second, followed by the microtube in Figure 2B and Figure 2C. The longer moving distance propelled by the large bubbles, as well as the high bubble ejection frequency, provided the microtube in Figure 2A the highest absolute value of velocity among the three microtubes. For the microtube in Figure 2C, although the bubble size is smaller than that of the longer microtube in Figure 2B, it has a higher bubble expulsion frequency, which results in a competitive absolute value of velocity with the longer microtube.

When comparing the velocities of different-sized motors, the unit of body lengths per second is often used. The velocity by

body length provides a way to evaluate the mobility of the microtubes regardless of dimensions. The average absolute values of velocities of the microtubes in Figure 2B,C are very similar, but in terms of body lengths per second, the shorter microtube possesses a much higher velocity. According to the model setup by Li *et al.*,¹⁹ for the very small scale microtubes studied here, the velocity in terms of body lengths per unit time will decrease with increasing length, which is consistent with our results. The microtube in Figure 2A has a moderate velocity by body length, ranking between the microtubes in Figure 2C and 2B. According to the method established by Wang *et al.*²⁷ to obtain the efficiency of micromotors, we calculated the power conversion efficiency of the microtubes in 2% H₂O₂ using the data provided in Table 1. For the three microtubes studied here, the microtube in Figure 2A had the highest efficiency of 7.3×10^{-8} , followed by the microtube in Figure 2B with an efficiency of 5.9×10^{-8} and that in Figure 2C with an efficiency of 5.4×10^{-8} .

While it is of great interest to scale down the size of micromotors to the nanoscale, the study on the motion of nanoscale tubular motors is still very limited. Here, we studied the motion of nanotubes with opening diameter of around 200 nm in H₂O₂. Figure 3 illustrates the motion of nanotubes in 2% and 3% H₂O₂. It can be clearly seen that the bubbles are ejected from the nanotubes and the bubbles experience a substantial volume expansion during and after the expelling process owing to the very high pressure inside the nanotubes. Due to the volume expansion, we measured the bubbles only when they are just detached from the nanotubes. Figure 3A are the video frames taken by a normal camera, which shows the motion of a nanotube (2.65 μm in length) in 2% H₂O₂. The first seven images in Figure 3A are consecutive frames with a time interval of 0.09 s. The last image is 20 frames after the first image. The nanotube expelled bubbles of 2.83 μm in average diameter at a frequency of 7.41 Hz, which resulted in an average velocity of 41.08 $\mu\text{m/s}$. Figure 3B clearly demonstrates the cycle of bubble growth and release of a nanotube (2.70 μm in length) in 3% H₂O₂ captured by a high speed camera at 270 frames/s. The time interval between each image in Figure 3B is 7.4 ms. Bubbles with an average diameter of 2.72 μm were ejected out at a frequency of 30 Hz and the nanotube exhibited an average velocity of 65.05 $\mu\text{m/s}$. For these small nanotubes, the average moving steps are much larger than the bubble radius. Given the recoiling mechanism of motion, external drag forces exerted on the microtubes and bubbles are required to be factored into the system. According to the Stokes' law, the drag forces on the bubbles are proportional to the bubble radius. Compared to the cases for microtubes with micrometer-sized openings, the bubbles generated by the nanotubes electrodeposited in 200 nm pores have a relatively much larger radius than the tubes themselves. The ratio of the diameter of the bubble to the nanotube is above 14 in 2% H₂O₂, which is very high compared to that of the microtubes discussed above. The bubbles experience a significantly larger drag force relative to the microtubes. Consequently, the average moving step of the nanotubes is larger than the bubble radius. In terms of power conversion efficiency, similarly, we calculated the efficiency of the nanotube presented in Figure 3A in the presence of 2% H₂O₂ according to the method established by Wang *et al.*²⁷ The efficiency of the nanotube was 1.5×10^{-8} , which was lower than the three microtubes discussed above.

Because of the inhomogeneity of the pores in the membrane template as well as the uncontrollable factors in the

Figure 3. Video frames of the motion of the nanomotors electrodeposited at -2 mA for 1000 s in 200 nm pores. (A) The motion of a nanotube (2.65 μm in length) in 2% H₂O₂ captured by a normal camera at 11 frames/s. (B) The motion of a nanotube (2.70 μm in length) in 3% H₂O₂ captured by a high speed camera at 270 frames/s. The scale bars are 10 μm .

electrodeposition process, heterogeneities of geometric parameters exist in the prepared micro/nanotubes. Ensemble analysis was conducted to study the general effect of geometric parameters and chemical environment on the motion of micro/nanotubes. Table 2 illustrates the distribution of the diameters of the large and small openings, as well as the lengths of the four types (A–D) of micro/nanotubes. The data was obtained by analyzing the three parameters of 100 samples for each type of micro/nanotubes. The effect of the slight variations in geometric parameters within the same type of micro/nanotubes on their motion is insignificant compared to that of the notable differences between different types. To study the influence of chemical environment on the dynamics of different types of micro/nanotubes, we subjected the micro/nanotubes to various concentrations of H₂O₂ fuel. In lower concentration ranges of H₂O₂, the changes of bubble sizes were not obvious. At 1–3% concentration of H₂O₂, the average bubble diameters and standard deviations for the four kinds of micro/nanotubes were as follows: A, 7.26 ± 1.96 μm ; B, 4.96 ± 1.57 μm ; C, 3.86 ± 0.96 μm ; and D, 2.51 ± 0.70 μm (60 separate micro/nanotubes were analyzed in total for each of the

Table 2. Statistical Analysis of the Geometric Parameters of the Four Types of Micro/Nanomotors

type of micro/nanomotors	average length and standard deviation (μm)	average diameter of large opening and standard deviation (μm)	average diameter of small opening and standard deviation (μm)
(A) Electrodeposited in 5 μm pores. ^a	14.12 $\pm$ 1.72	4.74 $\pm$ 0.18	4.58 $\pm$ 0.22
(B) Electrodeposited in 2 μm pores. ^b	17.25 $\pm$ 2.19	1.88 $\pm$ 0.08	1.76 $\pm$ 0.11
(C) Electrodeposited in 2 μm pores (shorter deposition times). ^c	5.82 $\pm$ 0.46	1.91 $\pm$ 0.09	1.69 $\pm$ 0.11
(D) Electrodeposited in 200 nm pores. ^d	2.25 $\pm$ 0.56	0.23 $\pm$ 0.02	0.19 $\pm$ 0.02

^aElectrodeposition for 2000 s at current of -20 mA. ^bElectrodeposition for 2000 s at current of -20 mA. ^cElectrodeposition for 600 s at current of -20 mA. ^dElectrodeposition for 1000 s at current of -2 mA.

presented data; 20 for each concentration, 1%, 2%, and 3%.) As the H_2O_2 concentration was increased to relatively higher levels, the bubbles experienced higher pressure due to the enhanced oxygen production in the micro/nanotubes, and therefore had a tendency to become slightly smaller than those at lower fuel concentrations.

We examined the activity and mobility of the four types of micro/nanotubes in a wide range of H_2O_2 , from 0.5% to 9%. At very low concentrations of H_2O_2 , differences in the activity of the four types of micro/nanotubes exist. Although all the four types of micro/nanotubes will suffer a decrease in the numbers of active microtubes at very low fuel concentrations, it had less influence on the microtubes electrodeposited in 5 μm pores (Type A). In 0.5% H_2O_2 , there were more microtubes exhibiting motion for Type A microtubes than the microtubes electrodeposited in 2 μm pores (Types B and C). It is worthwhile to note that the nanotubes (Type D) did not display any motion below 2% H_2O_2 . The reason may be largely due to the extremely small opening sizes of the nanotubes. The small opening sizes on the one hand decrease the catalytic area of the tubes, and on the other hand increase the difficulty of bubble formation inside the tubes. On the basis of Young–Laplace equation, the formation of smaller sized bubbles inside a narrower microtube needs a higher internal pressure compared to the bigger bubbles formed in a wider microtube. Bubble nucleation starts when the dissolved oxygen in the solution exceeds the maximum supersaturation concentration, whereas the maximum attainable oxygen concentration will increase as the pressure in the confined cavity of tubes is very high.²⁸ To form bubbles for propulsion, micro/nanotubes with smaller opening sizes need to generate more oxygen in the presence of less catalytic area. As a result, low fuel concentration had a bigger influence on the activity of microtubes with smaller opening sizes than the ones with larger opening sizes. For the Type D nanotubes, with a wall thickness of ~ 25 nm and an average inner opening diameter of around 150 nm, the influence was more significant. A much higher internal pressure is needed to form such small-sized bubbles inside the nanotube. To overcome the supersaturation limit and form bubbles under such high pressure, more concentrated H_2O_2 is needed to generate more oxygen on the very limited catalytic area. In addition, for the microtubes electrodeposited in 2 μm pores, the shorter microtubes (Type C) were also more affected by low fuel concentrations, compared to the microtubes (Type B). The reasons can be likewise attributed to two aspects. The longer microtubes have a higher surface area than the shorter ones. For another, according to Young–Laplace equation, the smaller sizes of the ejected bubbles reflected the higher pressure that the bubbles experienced in the shorter microtubes than in the longer microtubes.

Similar to previous reports, the micro/nanotubes can exhibit straight, circular and spiral motion. The circular and spiral motion suggests the resultant force of bubble propulsion and fluid resistance deviates from the motion direction of micro/nanotubes.^{5,29} Such deviation of the direction of bubble release and drag forces can be ascribed to the asymmetry in the structure of micro/nanotubes, which will result in asymmetric expulsion of bubbles and inhomogeneous fluid flow around the tubes. To take a further look at the propulsion of microtubes, we used high speed camera to capture the cycle of bubble growth and detachment at 30 000 frames/s. The process of bubble growth and release is repeated in a cyclic manner. Figure 4 illustrates the propulsion of microtubes by a cycle of bubble growth and release in 2% H_2O_2 . (Figure 4A and 4B are Type A and Type B microtubes, respectively.) As can be seen from Figure 4, both bubble growth and release contribute to the propulsion of the micro/nanotubes. The images on the left side show the different stages in one bubble propulsion cycle.

Figure 4. Propulsion of microtubes by a cycle of bubble growth and release in 2% H_2O_2 . (A) Different stages in one bubble propulsion cycle for a Type A microtube. (B) Different stages in one bubble propulsion cycle for a Type B microtube. Images on the left side are captured by a high speed camera at 30 000 frames/s. Blue line indicates the position of the motor at $t = 0$. Graphs on the right side illustrate the propelled distance of microtube by the bubble against time.

Figure 5. (A) The dependence of the average absolute value of velocity of the four types of micro/nanotubes on the concentration of H_2O_2 . (B) Variation of average absolute value of velocity with average opening diameter of the opposite ends and length at different concentrations of H_2O_2 . (C) The dependence of the average velocity by body length of the four types of micro/nanotubes on the concentration of H_2O_2 . For each velocity shown in figures, at least 30 measurements were taken into account. The error bars indicate standard deviations.

(a) The propulsion caused by the detachment of last bubble was just stopped. (a to b) Within a short period after the detachment of last bubble, the microtube did not have obvious displacement. (b to c) Continuous bubble growth propelled the microtube forward before the release the bubble. (c to d) The bubble was released, giving thrust to the microtube as it departs. Assuming the process of bubble growth as well as bubble release propelled the microtube at respective constant speed, the graphs on the right side show the propelled distance of microtube against time. Bubble growth consumed most of the time in the bubble cycle and propelled the microtube at a relatively low velocity. The recoil of bubble detachment created a powerful thrust that provided the microtube a very high instantaneous velocity over a time scale of microseconds. To assess the role of Brownian motion in the motion of micro/nanotubes, we calculated Peclet number ($Pe = VL/D$, where V is the mean velocity of the tubes, L is the characteristic linear dimension of the tubes, and D is the diffusion coefficient of tubes) of the four types of tubes in 2% H_2O_2 . The diffusion coefficients of the tubes were calculated according to the method established by Tirado *et al.*³⁰ The Peclet numbers of Type A–D tubes are 3.0×10^4 , 6.3×10^3 , 3.6×10^3 , and 16.7, respectively, indicating the insignificant effect of Brownian motion. The smaller Peclet number of Type D tubes demonstrates stronger influence of diffusion on the nanosized tubes compared to other types of microtubes with bigger sizes.

From the viewpoint of application, we still use average velocity to assess the mobility of micro/nanotubes. To obtain the velocities of micro/nanotubes, we only track the micro/nanotubes exhibiting motion in one focal plane of the microscope. Figure 5A shows the dependence of the absolute values of average velocity of the four types of micro/nanotubes upon H_2O_2 concentration. At relative low concentrations of H_2O_2 , the velocities of all four types of micro/nanotubes increased with the H_2O_2 concentration due to the increased decomposition rate. As H_2O_2 concentration increases, the rise

of micro/nanotubes velocity slowed down because of the progressively saturated coverage of the inner Pt surface, which shows a typical trend of Langmuir adsorption model. For the shorter microtubes electrodeposited in 2 μm pores (Type C) and the nanotubes (Type D), the limitations appeared at lower concentration of H_2O_2 due to the effects of relative smaller catalytic area.

To study the general influence of geometric parameters on the mobility of micro/nanotubes, we plot Figure 5B as a combination of the geometric parameters of the four types of tubes presented in Table 2 and the average velocity from 2% to 9% H_2O_2 shown in Figure 5A. The points representing the four types of tubes at same concentration of H_2O_2 were connected to form a surface. The average opening diameter is the average value of the openings at opposite ends. From the trend of these surfaces, we can see that for such small scale micro/nanotubes we studied, the absolute values of average velocity, by and large, increase with the dimensions of the tubes. The advantage of microtubes with large dimensions in mobility becomes more obvious at higher concentrations of H_2O_2 , since limited catalytic area retards the increase of velocity of small tubes. Both the driving force and the drag force of the microtubes are closely related to their opening diameter and length. Despite the fact that drag force resisting the motion of tubes will also increase with dimensions, larger catalytic area provided by larger length or diameter allows the formation of more oxygen gas to propel the micro/nanotubes at a higher velocity. The large average moving step propelled by large bubbles and the high bubble expulsion frequency provided the microtubes electrodeposited in 5 μm pores (Type A) the highest average velocity among the four types of micro/nanotubes. It is apparent that in the range we studied, the influence of opening diameters on the mobility is more significant than that of length. The average velocity of Type B microtubes which possess larger lengths but smaller opening diameters is lower than that of Type A microtubes. The impact of length is more

observable by comparing Type B and Type C microtubes which share similar opening sizes. Since geometric parameters will also influence the bubble sizes, a high volume of oxygen produced does not necessarily mean high bubble expulsion frequency. As described above, the bubbles generated by Type B microtubes were larger than those generated by Type C. As a result, although the longer Type B microtubes possessed larger inner surface area and generated more oxygen, they had a lower bubble expulsion frequency than the shorter Type C microtubes. The two types of microtubes electrodeposited in 2 μm pores exhibited similar velocities below 7% H_2O_2 , while the limitation of catalytic area restricted further increase of the velocity of the shorter Type C microtubes at higher H_2O_2 concentrations.

Figure 5C illustrates the dependence of average velocity by body length on the concentration of H_2O_2 . Although the average absolute value of velocity of the Type A microtubes was the highest, in terms of body lengths per second, Type C microtubes with smaller opening sizes and length exhibited the highest velocity by body length. Type B microtubes, which possess the largest average length, were at a disadvantage from the perspective of velocity by body length. Similar trends were predicted by the reported model that for such small scale micro/nanotubes studied here, the velocity by body lengths per unit time will decrease with increasing length of the self-propelled entity.¹⁹ The tiny Type D nanotubes exhibited a very high average velocity by body length, but it was not as high as the prediction model utilized. The trapping by the generated bubbles³¹ and more significant effect of thermal noise on the nanotubes^{32,33} are possible reasons that cause the deviation.

CONCLUSIONS

In conclusion, we prepared micro/nanotubes of different dimensions by membrane template-assisted electrodeposition. This method allows easy fabrication of microtubes with very small dimensions. With the use of membrane templates with desired pores sizes, micro/nanotubes with diameters ranging from hundreds of nanometers to several micrometers can be prepared. The dynamics of the electrodeposited micro/nanotubes with much smaller dimensions than the rolled-up microtubes was examined. As expected, the dynamics of micro/nanotubes depends on both the geometric parameters and the chemical environment. The mobility of micro/nanotubes with different dimensions at altered fuel concentration was investigated in correlation with the bubble size and bubble expulsion frequency. The geometric parameters of micro/nanotubes will influence the dynamics of micro/nanotubes from several aspects: the activity of micro/nanotubes at low fuel concentrations, the velocity of micro/nanotubes at moderate fuel concentrations, and the limitation of velocity at very high fuel concentrations. The tubes with smaller dimensions tend to be less active at low fuel concentration due to the small catalytic area and high pressure inside. Compared to the microtubes with micrometer sized openings, the nanotubes with opening diameters in nanometer scale need a higher H_2O_2 concentration to be propelled. Geometric parameters will affect the bubble size and expulsion frequency, leading to differences in velocity. In the dimension scales we studied, the bubble size will increase with an increase in the micromotor opening sizes, but the aspect ratio of diameter of the bubble to the tube will decrease accordingly. The influence of length in certain range is not very significant at moderate fuel concentrations. Shorter microtubes which expel smaller bubbles at a higher frequency

can have competitive velocity with longer microtubes. Tubes with large dimensions have an advantage over small tubes at high fuel concentration, as more available catalytic area imposes less limitation on the increase of velocity. Larger tubes also tend to have higher power conversion efficiency than smaller tubes. While micro/nanotubes with high absolute velocity may be desired, in the standpoint of velocity by body lengths per unit time, it may not be as mobile. When employing micro/nanomotors in different applications, it is necessary to consider the influence of geometric parameters in addition to the chemical environment. Although limitations exist for micro/nanomotors that rely on H_2O_2 fuel during employment in practical applications, especially so in biomedical field, we believe the present work will provide some insights into the potential biocompatible tubular bubble-propelled micro/nanomotors that may be developed in the future.

EXPERIMENTAL SECTION

Materials. The cyclopore polycarbonate membranes with pores of 5 μm , 2 μm , and 200 nm in diameter were purchased from Whatman, USA. Hydrogen peroxide (35%) was purchased from Alfa Aesar, Singapore. Methylene chloride and ethanol were purchased from Tedia, USA. Pt electrodes with 1 mm diameter and Ag/AgCl/1.0 M KCl were purchased from CH Instruments, USA. The platinum plating solution was obtained from Technic, Inc., USA. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (98+%) and sodium dodecyl sulfate (SDS) were purchased from Sigma-Aldrich. Chemicals were used as received and the solutions were prepared using ultrapure water (18.2 $\text{M}\Omega \text{ cm}$) from a Millipore Milli-Q purification system.

Apparatus. Electrochemical deposition was carried out with an Autolab PGSTAT 101 electrochemical analyzer (Eco Chemie, Utrecht, The Netherlands) connected to a computer and controlled by NOVA Version 1.8 software (Eco Chemie). The deposition procedure was conducted at room temperature using a three-electrode arrangement. A platinum electrode was utilized as a counter electrode, and Ag/AgCl/1.0 M KCl was used as the reference electrode. Sputtering was carried out with a JEOL JFC-1600 Auto Fine Coater. The ultrasonication process was carried out with a Fisherbrand FB 11203 ultrasonicator, and centrifugation was carried out with a Beckman Coulter Allegra 64R centrifuge. Optical microscope videos and images were obtained using a Nikon Eclipse Ti-E microscope fitted with a pco.edge 5.5 scientific CMOS camera, a Photron FASTCAM SA1.1 camera or a DS-Fi1c camera. Video sequences were processed with Nikon NIS-Elements software.

Preparation of Different Sizes of Pt Micro/Nanotubes. The Pt micro/nanotubes were synthesized with a modified electrochemical deposition procedure on cyclopore polycarbonate templates. For the microtubes prepared using membranes with 5 and 2 μm pores, silver (~75 nm) was sputtered on the one side of the polycarbonate template. Copper tape was attached to the silver-sputtered polycarbonate template, which serves as the working electrode for the plating experiments. For the microtubes prepared using membranes with 200 nm pores, colloidal graphite ink was applied on the one side of the polycarbonate template with commercial cotton swabs. A piece of flattened aluminum foil was attached to the ink immediately, which serves as the working electrode for the plating experiments. The template was then assembled into a customized electrochemical deposition cell. Platinum counter electrode and Ag/AgCl/1.0 M KCl reference electrode were utilized. Electrochemical deposition was carried out with an Autolab PGSTAT 101 electrochemical analyzer connected to a computer and controlled by NOVA Version 1.8 software. For the microtubes electrodeposited in 5 and 2 μm pores, only platinum was deposited with the commercial plating solutions. For Type A and Type B microtubes, platinum was electrodeposited galvanostatically at -20 mA for 2000 s. For Type C microtubes, platinum was electrodeposited galvanostatically at -20 mA for 600 s. For Type D nanotubes, a sacrificial layer of copper was electrodeposited galvanostatically at -2 mA for 1000 s with the

deposition solution containing 1 M CuSO₄ and 1 M H₂SO₄. After the deposition solution was removed, the template was rinsed 5 times with 8 mL of water. The platinum layer was electrodeposited subsequently at −2 mA for 1000 s. When the deposition of microtubes was finished, the electrochemical cell was disassembled. For the membranes with sputtered silver layer, the template was polished with 0.06 μm alumina powder to remove the sputtered silver and was washed 5 times with 8 mL of water by ultrasonication each time. For the membranes applied with graphite ink, the graphite layer can be removed during the ultrasonication in water. It was then placed in an Eppendorf tube with 2 mL of methylene chloride and ultrasonicated until the whole template was dissolved. The electrochemically deposited microtubes were collected by centrifugation at 6000 rpm for 3 min and washed repeatedly 3 times with methylene chloride. The solution was then washed with ethanol and water 2 times each and centrifuged for 3 min after each washing step. Finally, all the prepared micro/nanotubes were treated with concentrated nitric acid to remove the sacrificial copper layer or other impurities. After washing out nitric acid, the resulting tubes were stored in water at room temperature.

Operation of Micromotors. The experiments for studying the dynamics of the motion of micro/nanomotors were carried out in an aqueous solution containing different concentrations of H₂O₂ at constant surfactant concentrations (0.3 wt % of SDS). A mixture of micro/nanotubes, SDS, H₂O₂ was applied on a glass slide freshly cleaned with nitrogen gas. Optical microscope videos and images were obtained using a Nikon Eclipse Ti-E microscope fitted with a pco.edge S.S scientific CMOS camera, a Photron FASTCAM SA1.1 camera or a DS-Fi1c camera. Video sequences were processed with Nikon NIS-Elements software.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.5b07771.

EDX images of micro/nanotubes (PDF)

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Notes

The authors declare no competing financial interest.

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Beyond Platinum: Bubble-Propelled Micromotors Based on Ag and MnO₂ Catalysts

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ABSTRACT: Autonomous bubble-propelled catalytic micro- and nanomachines show great promise in the fields of biomedicine, environmental science, and natural resources. It is envisioned that thousands and millions of such micromachines will swarm and communicate with each other, performing desired actions. To date, mainly platinum catalyst surfaces have been used for the decomposition of a fuel, hydrogen peroxide, to oxygen bubbles. Here we propose Pt-free, low-cost inorganic catalysts for powering micromotors based on silver and manganese dioxide surfaces. Such Ag- and MnO₂-based bubble-powered micromotors show fast motion even at very low concentrations of fuel, down to 0.1% of H₂O₂. These catalysts should enable unparalleled widespread use of such motors in real applications, as it will be possible to make them in large quantities at low cost.

Self-propelled autonomous micromotors and micromachines are at the forefront of research in micro- and nanotechnology.^{1–6} These autonomous devices have the potential to play vital roles in drug delivery,^{7–9} microsurgery,^{10,11} environmental remediation,^{12–14} and natural resources discovery.^{15,16}

There are three types of mechanisms describing the motion of catalytic micro-/nanomotors: (i) self-diffusiophoresis,¹⁷ (ii) self-electrophoresis,¹⁸ and (iii) bubble ejection.¹⁹ Devices relying on (i) self-diffusiophoresis propulsion decompose asymmetrically the fuel presented in their environment.^{20,21} They move in the direction of the self-generated concentration gradient in their vicinity. The motion of micromotors propelled by self-diffusiophoresis does not involve bubble generation, and the micromotors generally exhibit slow motion.²² (ii) Self-electrophoretic micromotors rely on the simultaneous oxidation and reduction of fuel at the opposite ends of the device. Such redox reactions lead to the flow of the electrons across the device, which is accompanied by a flow of hydronium ions at the surface of the microdevice and consequent propulsion.²³ (iii) A bubble-propulsion mechanism for powering micromotors has become highly popular in recent years.^{24–26} Decomposition of hydrogen peroxide over a catalytic surface, such as platinum, creates bubbles and propels the micromotor forward.¹⁹ The advantages of this mechanism are its high power output, its robust performance, and the very high speed the devices can achieve, dramatically overcoming the velocity of the devices powered by mechanisms (i) and (ii).

To date, despite tens of articles published in the field of bubble-propelled micro-/nanomotors, the vast majority of bubble-powered micromotors have used Pt as catalyst,^{25,27,28} with only a few exceptions. A Communication by Sanchez et al. showed the utility of an enzyme to decompose H₂O₂.²⁹ While the use of enzymes shows ingenuity, the disadvantage is their limited lifetime. Complex Ti/Fe/Au/Ag nanomembrane micro-jet motors were also produced previously.³⁰ Given the significant cost of Pt as catalyst and/or nanomachining as fabrication method, we wish to demonstrate that simple and widely available inorganic materials can be used for bubble-propelled motors. We will demonstrate that simple silver and manganese dioxide particles are highly efficient to decompose H₂O₂ fuel, leading to fast bubble-propelled motion of micromotors. The use of Ag and MnO₂ as potential candidate materials for micromotor fabrication is very attractive because of the excellent catalytic properties, low costs, low concentration of fuel needed, high efficiency, and long lifetime.

First we discuss the silver-surface-catalyzed bubble-propelled micromotors. Figure 1A shows time-lapse images of the movement of a Ag micromotor in 9% H₂O₂ (see also Video 1). Figure S-1 (Supporting Information) shows a tracking image for the path of a Ag catalytic micromotor in 0.5% H₂O₂ over a 2 s time interval. Oxygen bubbles are generated by the catalytic decomposition of H₂O₂ by Ag, and they are released from one side of the motor. Asymmetry is the key to the design of micro-/nanomotors. For spherical Janus motors, the motion is usually attributed to asymmetric generation of bubbles achieved by a partial inert coating, without which no directional movement is achieved due to expected lack of asymmetric bubble thrust.^{1,20} However, the Ag micromotors used here feature inhomogeneity and asymmetry. Bubble generation is closely related to the geometry of the motors, and bubble nucleation on solid surface needs gases to reach heterogeneous nucleation energy, which depends on the gas saturation concentration and the curvature of the surface. Less energy is required for bubble formation on a flat surface than on a convex surface, and even less energy is required on a concave surface.^{31,32} We have conducted experiments in which Ag micromotors were half-covered with Au using sputtering, but little difference in mobility was observed compared to the unspattered ones, showing that the bubble generation is more related to the instinctive morphology of the particles. Three typical kinds of trajectories were found for the motion of the Ag

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Figure 1. Motion of silver catalytic micromotors. (A) Time-lapse images of a Ag micromotor in 9% H₂O₂ and 0.5% SDS solution (scale bar = 50 μm). (B) Dependence of the average velocity of Ag catalytic micromotors on H₂O₂ concentration at 23 °C. Video 1 shows the moving Ag micromotor motor in 9% H₂O₂.

catalytic micromotors: circular, curved, and self-rotating motions. The different trajectories derive from the differences in size, shape, and geometry of the catalytic micromotor, similar to the case of tubular micromotors.²⁴

The velocity of the Ag catalytic motor is dependent on the H₂O₂ fuel concentration. Figure 1B illustrates the influence of

H₂O₂ concentration on the average speed of the moving Ag micromotors (see also Figure S-2 for velocity expressed in body lengths per second; the size of the particular micromotor shown in Figure 1A is 20 μm). As expected, Ag micromotors show clearly increased velocities with increasing fuel concentration. The percentage of Ag motors exhibiting motion among all the Ag particles and the mobility of the motors depend on the fuel concentration and instinctive morphology of the Ag particles.

There is an obvious increase in the mobility of Ag micromotors with increasing concentration of H₂O₂. Due to the propulsion by vigorous bubbling, the mobility of the Ag catalytic motor is quite high compared to that of the Pt catalytic Janus motors that move by diffusiophoresis, reported previously.^{33–35} Silver micromotors can move at an average speed of ~25 μm/s, even in 0.1% H₂O₂, and the average speed of Ag catalytic motors exhibiting motion can reach over 100 μm/s in the presence of 12% H₂O₂. The high bubble frequency reflects the high catalytic efficiency of Ag for the decomposition of H₂O₂. Given the low costs and good performance, Ag is a promising candidate catalyst for preparation of micro-/nanomotors. However, it should be noted that, with decreasing amount of fuel, the percentage of motors exhibiting motion decreases, as shown in Figure S-3.

Manganese dioxide is another well-known catalyst that can accelerate the decomposition of H₂O₂, and it is much cheaper and more accessible than the noble metal often used in the preparation of micro-/nanomotors. MnO₂ is widely used in industry for cheap carbon/MnO₂ batteries.³⁶ Next we investigate the motion of micromotors based on MnO₂ microparticles in H₂O₂ solution. Similar to Ag particles, MnO₂ micromotors exhibit motion propelled by oxygen bubbles. However, the proportion of moving MnO₂ micromotors is much less than that for Ag particles, and higher concentrations of H₂O₂ are needed for efficient propulsion. Figure 2A shows time-lapse frames from a video of MnO₂ micromotors in 15% H₂O₂. The size of the particular micromotor in Figure 2A is 5 μm. Figure S-4 tracks a MnO₂ motor in the presence of 21% H₂O₂ for 2 s (see also Videos 2 and 3). As illustrated in Figure 2B, the average speed of moving MnO₂ micromotors increases from ~50 μm/s at 12% H₂O₂ to ~120 μm/s at 21% H₂O₂ (see Figure S-5 for velocity expressed in body lengths/s). The proportion of MnO₂ micromotors exhibiting motion also decreases with decreasing H₂O₂ concentration. Nevertheless, the excellent mobility of MnO₂ micromotors demonstrates the potential of MnO₂ to be involved in the preparation of micro-/nanomotors if modified to proper morphology.

Various control experiments, illustrated in Figure 3, were used to confirm the propulsion by oxygen bubbles generated by catalytic decomposition of H₂O₂. No bubble generation was observed for MoO₂ and MoO₃ in the presence of 21% H₂O₂ and 0.5% sodium dodecyl sulfate (SDS) due to the absence of catalytic property of molybdenum oxides. Similarly, no bubble propulsion was observed for MnO₂ and Ag particles in the absence of H₂O₂. In contrast, the mobility of MnO₂ and Ag particles in H₂O₂ reflects the efficient bubble propulsion associated with their good catalytic properties. The mean square displacement (MSD) of Ag and MnO₂ motors showed a parabolic dependence on time (Figures S-6 and S-7, respectively), which indicates that the motion is driven by bubble ejection instead of Brownian motion.^{33,37} The efficiency of the Ag motor in 9% H₂O₂ was found to be 5.81×10^{-8} , while the efficiency of the MnO₂ motor in 12% H₂O₂ was 1.16

Figure 2. Motion of manganese dioxide catalytic micromotors. (A) Time-lapse images of a MnO₂ catalytic micromotor in 15% H₂O₂ and 0.5% SDS solution (scale bar = 20 μm). (B) Dependence of the average velocity of MnO₂ catalytic micromotors on H₂O₂ concentration at 23 °C. Video 2 shows the moving 5 μm MnO₂ micromotor in 15% H₂O₂. Similarly, Video 3 tracks a MnO₂ micromotor in the presence of 21% H₂O₂ (see Figure S-4).

$\times 10^{-8}$, following the calculation approach previously reported (see Supporting Information for details).³⁸ This compares favorably with previously established efficiencies of other Janus particles that move by diffusiophoresis (efficiency = 5×10^{-10})

Figure 3. Control experiments: (A) Ag and (B) MnO₂ particles in 0.5% SDS solution and (C) MoO₃ and (D) MoO₂ particles in 21% H₂O₂ and 0.5% SDS solution (scale bars = 50 μm). Conditions: temperature, 23 °C; particle concentration, 1 mg/mL.

and bubble-propelled tubular microjets (efficiency = 2.4×10^{-10}).³⁸

An advantage of Ag and MnO₂ materials over Pt is that they are much less prone to poisoning. It has been previously demonstrated that Pt catalytic bubble-propelled microjet engines are susceptible to thiol poisoning, even at micromolar concentration of thiols.³⁹ We compared the motion of Ag motors in 3% H₂O₂ without and with addition of 10 mM cysteine. No observable difference in the velocity of the Ag motors was found. Similarly, MnO₂ is not prone to thiol poisoning. It should be mentioned that the micromotors reported here are truly catalytic, and their motion stops only when the fuel is exhausted. When fuel is replenished, the bubble-propelled motion of the micromotors resumes, and the micromotors move over the span of the whole experiment with the same agility.

In summary, we have presented new materials for catalytic propulsion of bubble-powered micromotors, silver and manganese dioxide. These Pt-free, Ag- and MnO₂-based micromotors, driven by the bubbles from catalytic decomposition of hydrogen peroxide, exhibited fast motion. The speed of the micromotors can be modulated by changing the concentration of H₂O₂, and efficient propulsion can be achieved even at very low concentration (0.1%) of H₂O₂ fuel. The low costs, high efficiency, and good stability of Ag and MnO₂ (compared to Mg- and Al-based micromotors^{12,40,41}) make them attractive alternatives to the currently popular platinum for prolonged propulsion of micro-/nanomotors in diverse ranges of practical applications. Additional efforts should be devoted to further functionalization and modification of Ag and MnO₂ micromotors for applications in biomedical and environmental fields. It is envisioned that such accessible and affordable inorganic materials will replace the need for Pt in these artificial organisms and contribute to their fabrication in millions and millions of copies.

■ ASSOCIATED CONTENT

📄 Supporting Information

Experimental details, tracking of Ag and MnO₂ micromotors, plots of velocities of Ag and MnO₂ micromotors in body lengths/s, MSD analysis, and SEM images. This material is available free of charge via the Internet at <http://pubs.acs.org>.

W Web-Enhanced Feature

Videos 1–3 in .avi format are available in the online versions of the paper.

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Notes

The authors declare no competing financial interest.

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■ Self-Propelled Motors

Iridium-Catalyst-Based Autonomous Bubble-Propelled Graphene Micromotors with Ultralow Catalyst LoadingHong Wang,^[a] Zdeněk Sofer,^[b] Alex Yong Sheng Eng,^[a] and Martin Pumera^{*[a]}

Abstract: A novel concept of an iridium-based bubble-propelled Janus-particle-type graphene micromotor with very high surface area and with very low catalyst loading is described. The low loading of Ir catalyst (0.54 at%) allows for fast motion of graphene microparticles with high surface area of $316.2 \text{ m}^2 \text{ g}^{-1}$. The micromotor was prepared with a simple and scalable method by thermal exfoliation of iridium-doped graphite oxide precursor composite in hydrogen atmosphere. Oxygen bubbles generated from the decomposition of hydrogen peroxide at the iridium catalytic sites provide robust propulsion thrust for the graphene micromotor. The high surface area and low iridium catalyst loading of the bubble-propelled graphene motors offer great possibilities for dramatically enhanced cargo delivery.

Research on micro-/nanoscale motors not only brings deeper insights into locomotion in the low Reynolds number regime,^[1–5] but provides various potential applications ranging from the biomedical field^[6,7] to addressing environmental issues.^[8,9] Considerable efforts have been devoted to the development of chemically powered micro-/nanomotors.^[10,11] Various self-propelled micro-/nanomotors of different structures, such as bimetallic nanowires,^[12] Janus microparticles^[13,14] and tubular microengines,^[15] have been developed with propulsion systems based on self-diffusiophoresis, self-electrophoresis and bubble propulsion. Particular attention has been given to bubble-propelled micro-/nanomotors due to their robust performance and high efficiency. Among these bubble-propelled micro-/nanomotors, platinum tubular microengines that exhibit autonomous self-propulsion in the presence of hydrogen peroxide fuel have traditionally attracted the most attention.^[16,17] There is an intense interest in identifying new compositions for catalytic micromotors, and micromotors based on other materials such as catalase enzyme,^[18] silver and manganese oxide^[19] have been proposed. In the cases mentioned above, the catalyst makes up most of the micromotor mass (from around 20 to 100%)^[16,17,19,20] and there is thus limited surfaces for functionalization needed to perform desired delivery or remediation tasks.

Here, we introduce a new concept of micromotor with high surface area and very low loading of catalyst (0.54 at%). In this case, we go beyond classical Pt as well as Ag and MnO_2 -based catalysts, and introduce a new catalyst for bubble-propelled motors: iridium. The iridium-based graphene micromotor can

display autonomous bubble propulsion in the presence of hydrogen peroxide even at very low concentration of catalyst (0.54 at%). The rest of the micromotor (99.46 at%) consists of graphene which exhibits a large surface area.

To prepare iridium-based graphene micromotors, graphite was first oxidized to graphite oxide with KMnO_4 in concentrated H_2SO_4 and NaNO_3 (Hummers method). The graphite oxide was then dispersed in $(\text{NH}_4)_2[\text{IrCl}_6]$ solutions to generate iridium-doped graphite oxide precursors, which subsequently underwent thermal exfoliation under a flow of hydrogen gas at 1000°C and resulted in iridium-doped graphene. Because of the catalytic property of iridium contained in the graphene, they can exhibit autonomous bubble-propelled motion in the presence of hydrogen peroxide fuel.

The morphology of the graphene micromotor was studied by SEM. Imaging was carried out at various magnifications of $3000\times$, $10000\times$, $30000\times$ and $1500\times$, as shown in Figure 1 A–D. It can be observed from the scanning electron microscope images that the graphene micromotors showed a typical exfoliated structure and have relatively uniform particle sizes with high surface area. The surface area of the graphene/iridium hybrid structure was determined by BET measurements to be $316.2 \text{ m}^2 \text{ g}^{-1}$. The gaps between the sheets provide channels for fuel (hydrogen peroxide) to reach the iridium catalytic sites while the irregular shapes enable the asymmetric placement of the catalyst, which is crucial for the directed motion of micro-/nanomotors.^[3] Figure 1 E–G shows the energy-dispersive X-ray spectroscopy (EDX) elemental mapping analysis of C, O, and Ir, respectively. The EDX data confirm the existence of iridium in the graphene. The composition of graphene after exfoliation with Ir doping was 90.37 at% C, 0.35 at% N, 7.34 at% H, 1.40 at% O and 0.54 at% Ir. The exfoliated structure of graphene particles allows hydrogen peroxide to arrive at the iridium catalytic sites and generate continuous thrust of oxygen bubbles.

One should bear in mind that graphene is, according to the IUPAC definition, a semi-infinite sheet of sp^2 -hybridized carbon which is supposed to be planar.^[21] However, in practice, when graphene is produced, there are defects, pentagon/heptagon rings which lead to curvature and “crump”-like structured graphene.^[22] Such graphene is discussed in the vast majority of related publications. In many cases, this crumpled structure is

Figure 1. SEM images (A–D) and EDX elemental characterization (E–G) of graphene micromotors. SEM images were obtained at: A) $3000\times$, B) $10000\times$, C) $30000\times$, and D) $1500\times$; scale bars are $1 \mu\text{m}$, $1 \mu\text{m}$, 100 nm and $10 \mu\text{m}$, respectively.

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preferable as it prevents restacking of the graphene layers.^[23,24] Under the conditions used in our synthesis, the great majority of the fabricated motors appear to be particles with size of approximately 20 μm . Such Ir-catalyst based Janus-particle-like graphene motors are fundamentally different from the rolled-up motors containing both graphite oxide and Pt layers^[25] reported earlier, as the former work on the basis of Janus particles while the latter operate on the basis of microjet engines.

Further information on the elemental composition of the graphene micromotors can be obtained with X-ray photoelectron spectroscopy. A wide-range XPS scan was first performed to detect the elements that are present on the surface. As can be seen from Figure 2A, the major peaks observed are a C 1s peak at 284.5 eV, an O 1s peak at 532.5 eV and an Ir 4f peak. High-resolution XPS measurements were also performed for the graphene micromotors (Figure 2B). The Ir 4f peak in fact consists of two peaks, which are clearly visible in the high-resolution XPS spectra. The two peaks located at 61.5 and 64.5 eV are very close to the values for 4f_{7/2} and 4f_{5/2} of metallic Ir (61.35 and 64.35 eV).^[26] In the case of IrOx, the Ir peaks would be shifted to 62.35 and 65.35 eV,^[26] due to the binding of Ir to the electron-withdrawing O atom. Therefore, it can be concluded that iridium contained in the graphene micromotors mainly exists in metallic form instead of the metal oxide.

The autonomous propulsion of the iridium-based graphene micromotor was studied under a microscope. The fabricated graphene appears to be particles with size of approximately 20 μm under 10 $\times$ magnification, as shown in Figure 3. The function of doped Ir is similar to Pt (or Ag or MnO₂)^[19] as it is a very efficient catalyst for decomposition of H₂O₂ into H₂O and O₂. The graphene micromotors presented here work on

the principle of bubble-propelled Janus particles. Figure 3A displays the tracking image of the movement of the graphene micromotor in the presence of 3 % hydrogen peroxide fuel and 1 % SDS over a 10 s period. The image illustrates the motion of the graphene micromotor propelled by continuous oxygen bubbles, which is different from the motion of iridium Janus particle in hydrazine relying on a diffusiophoretic mechanism.^[14] The different tails of bubbles in different sizes indicate that the graphene micromotor has more than one catalytic site to decompose hydrogen peroxide fuel. The asymmetric displacement of iridium in the graphene micromotor allows the bubbles to be released from one side of the micromotor, thus creating the asymmetric bubble thrust needed for directed movement. The iridium-doped graphene micromotor exhibited self-propelled motion at an average speed of approximately 40 $\mu\text{m s}^{-1}$, which corresponds to about two body lengths per second. In contrast, no obvious motion was observed for plain graphene containing no iridium at 10 $\times$ magnification. While Brownian motion is significant for objects at nanoscale, it is negligible for the nearly 20 μm sized graphene particles here.

Figure 3. Tracking images of: A) the iridium-doped graphene micromotor, and B) the plain graphene in 3 % H₂O₂ and 1 % SDS for 10 s. Scale bar: 50 μm .

Figure 2. A) Wide-scan X-ray photoelectron spectra, and B) Ir 4f high-resolution X-ray photoelectron spectra of iridium-doped graphene.

To gain a deeper insight into the motion of the graphene micromotor, we calculated the mean square displacement (MSD) of the iridium-doped graphene micromotor and the plain graphene particle, as shown in Figure 4. The movement was recorded by a digital camera connected with the microscope and then analyzed by particle tracking. According to the Einstein's equation for Brownian motion in 2-dimensions, $\Delta L^2 = 4D\Delta t$, the contribution from Brownian motion to MSD is proportional to time.^[27,28] The MSD plot versus Δt for the plain graphene particle gives a straight line, indicating that the insignificant motion of the particle can be solely attributed to Brownian motion. The displacement of a particle being propelled in one direction is $d = vt$, and therefore the MSD is proportional to the square-root of time. The upward curvature shown in the MSD plot for the iridium-doped graphene micromotor under the same conditions reflects the effective bubble propulsion.^[27,28] Additional analysis of motion is provided in the Supporting Information.

In summary, we have described a new concept for a micromotor where iridium catalyst responsible for its motion is present only in very low amounts. Iridium catalyst loaded on graphene microparticles allows for fast motion while the high surface area of the graphene itself (316.2 m² g⁻¹) offers excellent

Figure 4. Plots of MSD against time interval for the plain graphene (b) and the iridium-doped graphene micromotor (a) in 3% H₂O₂ and 1% SDS.

opportunities for various functionalizations desired for practical applications. Due to high surface area of graphene, we can envision environmental applications of these micromotors such as adsorption/removal of oil spills^[29] and catalytic decomposition of harmful chemicals.^[30]

Experimental Section

Materials

Graphite oxide (GO) was from high purity microcrystalline graphite (2–15 μm, 99.9995%; Alfa Aesar). Sulfuric acid (98%), potassium permanganate (>99.5%), hydrogen peroxide (30%), sodium nitrate (>99.5%) and hydrochloric acid (37%) were obtained from Penta (Czech Republic). Ammonium hexachloroiridate(IV), in spectroscopic purity grade was obtained from Alfa Aesar. Sodium dodecyl sulfate (SDS) was purchased from Sigma–Aldrich. Nitrogen (99.9999% purity) and hydrogen (99.9999% purity) were obtained from SIAD (Czech Republic). The chemicals were used as received and ultrapure water (18.2 MΩ cm) from a Millipore Milli-Q purification system was used throughout the experiments.

Apparatus

Scanning electron microscopy (SEM/EDX) analysis was conducted with a Jeol JSM 7600F instrument. X-ray photoelectron spectroscopy (XPS) was performed with a Phoibos 100 spectrometer using a Magnesium X-ray radiation source (SPECS, Germany). Optical microscope images and videos were obtained with a Nikon Eclipse 50i microscope. Video sequences were processed with Nikon NIS-Elements software. Surface area was measured by a sorption analyzer Coulter SA 3100 (Beckman Coulter). The samples were out-gassed for 4 h at 150 °C under high vacuum (VALUE) prior to the sorption experiments. The reason for such low temperature is to avoid degradation and further decomposition of oxygen functionalities, present mainly in chemically reduced graphene. A TCD nitrogen cooled (77 K) detector was employed for the evaluation of the results using BET and Kelvin equations. Axios sequential WD-XRF spectrometer was used to perform XRF analysis. It was equipped with an Rh anode end-window X-ray tube fitted with 50 μm Be window. All eleven scans covering 79 measured elements were collected by software SuperQ in vacuum. The obtained data were evaluated by standardless software Omnian.

Procedures

Graphite oxide synthesis

Graphite (5 g) and sodium nitrate (2.5 g) were stirred together with concentrated sulfuric acid (115 mL). The mixture was then cooled at 0 °C. Potassium permanganate (15 g) was then added with vigorous stirring for 2 h. During the following four hours, the reaction mixture was allowed to reach room temperature before being heated to 35 °C for 30 min. The reaction mixture was then poured into a flask of deionized water (250 mL) and heated to 70 °C for 15 min. The mixture was then poured into deionized water (1 L). The unreacted potassium permanganate and manganese dioxide were removed by the addition of 3% hydrogen peroxide. The reaction mixture was then allowed to settle before being decanted. The obtained graphite oxide was then purified by repeated centrifugation and redispersion in deionized water until all sulfate ions were removed. The graphite oxide slurry was then dried in a vacuum oven at 50 °C for 48 h before use.

Iridium-doped graphene synthesis

Graphite oxide (200 mg) was ultrasonicated in 50 mL water (30 min, 400 W). Ir precursor (NH₄)₂[IrCl₆] was added to the graphite oxide suspension. The mixture was ultrasonicated for 10 min (400 W) and then the water was evaporated to dryness in a vacuum oven (50 °C, 72 h). The thermal exfoliation of the dry precursor was carried out in vacuum-tight quartz glass reactor with controlled atmosphere. The reactor was equipped with a porous quartz glass capsule connected to a magnetic manipulator. This configuration is capable of producing a temperature gradient over 1000 °C min⁻¹. All syntheses were performed at 1000 °C for 12 min under a pressure of 100 kPa. The HU GO/Ir precursor composite (100 mg) was placed into porous quartz glass capsules and the reactor was flushed several times with high purity nitrogen and finally filled with hydrogen. Subsequently the sample was inserted into the preheated furnace with hydrogen atmosphere. The hydrogen flow (1000 mL min⁻¹) was used to remove reaction byproduct.

Operation of the iridium-doped graphene micromotor

The experiments for the motion study of graphene micromotors were carried out in an aqueous solution containing 3% hydrogen peroxide and 1% SDS. A mixture of iridium graphene (5.6 × 10⁻⁵ mg μL⁻¹), SDS, H₂O₂ and water was applied on a glass slide freshly cleaned with nitrogen gas. Optical microscope videos and images were obtained with Nikon Eclipse 50i microscope. Video sequences were processed with Nikon NIS-Elements™ software.

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Keywords: catalysis · graphene · iridium · molecular devices · self-propelled motors

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Simultaneous self-exfoliation and autonomous motion of MoS₂ particles in water†

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Two-dimensional (2D) transitional metal dichalcogenides (TMDCs) have been receiving significant research interest due to their unique physical and electronic properties. We report the design of a MoS₂ based motor that can display simultaneous self-exfoliation and autonomous motion at the surface of water. Exfoliation of bulk MoS₂ via sodium intercalation offers an attractive way to obtain solution-phase 2D MoS₂ nanosheets on a large scale. The motion of the MoS₂ particles results from the surface tension gradients generated by the naphthalene distributed in the MoS₂ particles. A combination of self-exfoliation and propulsion in an unmodified water environment hence leads to a new platform which holds great promise for new applications of TMDC materials in small scale motors.

Transition metal dichalcogenides are layered materials with strong bonding in each layer and weak interactions between the layers, enabling exfoliation into two-dimensional nanosheets with the chalcogen atoms in two hexagonal planes separated by a plane of metal atoms.¹ Because of the unusual electronic, optical, mechanical, chemical and thermal properties,^{2,3} TMDCs have been an emerging class of materials with a range of potential applications in recent years.⁴ For molybdenum disulfide (MoS₂), a widely known layered transition metal dichalcogenide, each Mo atom is coordinated by six S-atoms in either a trigonal prismatic or octahedral system by covalent bonds within each layer, while van der Waals interaction connects the adjacent layers.⁵ The electronic properties of 2D layered nanomaterials are highly associated with their thickness.⁶ Single layer MoS₂ and bulk MoS₂ are inherently different materials with large changes in properties. The band gap of MoS₂ increases with a decrease in the thickness of the material and there exists a transition from an indirect band gap in the bulk form to a direct band gap in

the monolayer.⁷ The direct band gap, significant electrocatalytic properties,⁵⁰ large in-plane carrier mobility and robust mechanical properties of single layer MoS₂^{8–11} open up new prospects for practical applications in novel field effect transistors^{12,13} and optoelectronic devices.^{14–16}

Exfoliation of bulk MoS₂ into 2D layered nanosheets represents a critical step towards translating their unique properties into applications. Individual MoS₂ monolayers of high purity can be peeled from bulk crystals by micromechanical cleavage using adhesive tapes, but this method suffers the problem of scalability and lack of control.^{17–19} Solution-phase preparations provide a promising alternative to obtain exfoliated nanosheets on a large scale.^{20–22} The intercalation of MoS₂ by alkali metals allows the layers to be exfoliated in liquid.²³ The intercalation of alkali metals into the host laminar structure of MoS₂ can be achieved by either the use of hot alkali metal vapor²⁴ or through soaking the bulk material in a solution of the corresponding alkali metal-containing compound, typically, in solvated metal ammonia solution or a hexane solution of butyl lithium.^{25,26} An electrochemical intercalation approach has also been developed with the advantages of being able to monitor and control the intercalation process.²² Once the alkali metal is intercalated into MoS₂, the material is ready for exfoliation. The H₂ gas evolution upon exposing the intercalated material to water rapidly separates the layers, resulting in a dispersed suspension of 2D layers of MoS₂. As an alternative precursor for liquid phase exfoliation, ammoniated MoS₂ can be exfoliated readily in a variety of polar solvents due to the fact that the intercalated NH₃/NH₄⁺ can invite solvent molecules into the interlayer and the evolution of ammonia gas during sonication would facilitate the exfoliation.²⁷

Recent efforts have demonstrated the great potential of MoS₂ to be involved in biomedical applications. Defect sites arising from the loss of sulphur atoms are available for surface modification by thiolated compounds.²⁸ MoS₂ nanosheets functionalized with lipoic acid-terminated polyethylene glycol (LA-PEG) have shown high stability in physiological solutions without obvious cytotoxicity.²⁹ The high surface area suitable for drug loading and strong near-infrared (NIR) absorbance of two-dimensional

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MoS₂ nanosheets make them promising candidates for combined photothermal therapy and chemotherapy of cancer.³⁰ Functionalized MoS₂ based biosensors have been used for the detection of DNA and other biomolecules, providing new opportunities in bioanalysis and clinical diagnosis.^{31–33} In addition, MoS₂ is also a promising material for environmental remediation. It has been shown that intercalated MoS₂ particles can be used as redox-recyclable ion-exchange materials for the extraction of aqueous heavy metal ions.³⁴

Micro/nanomotors, which are micro- or nanoscale devices capable of converting energy into mechanical forces and movement, attract considerable interest as an emerging solution to address problems encountered in many fields, especially in biomedical and environmental area.³⁵ Designing and fabricating micro/nanomotors represents one of the most significant challenges facing nanotechnology. Among various reported micro/nanoscale motors, particular attention has been given to self-propelled micro/nanomotors relying on chemical reactions to harvest energy. Different types of small-scale self-propelled objects, such as striped nanorods, Janus particles and tubular microjets, have been developed on the basis of self-electrophoresis, self-diffusiophoresis and bubble ejection.³⁶ However, in the vast majority of the existing cases, metals, especially noble metals, are employed as indispensable components in the structure of the micro/nanomotors. In addition, the commonly used hydrogen peroxide fuel is toxic, which hinders the development of practical applications of these promising tiny motors. New alternative fuels, including Br₂, I₂, hydrazine, as well as acidic and alkaline solutions,^{37–39} have been put forward to replace hydrogen peroxide. Here, as an initial proof of concept, we report a millimeter-sized TMDC-based motor that exhibits self-propulsion in water. The intercalated MoS₂ particles exhibit fast autonomous motion during the self-exfoliation process in water. In the following sections, we will characterize the fabrication and movement of the MoS₂ based motors.

Sodium intercalated MoS₂ prepared with the use of sodium naphthalenide was employed in this study. The intercalation of sodium into MoS₂ may be regarded as an ion/electron transfer topotactic reaction. The driving force for the intercalation reaction is suggested to be the tendency for charge transfer from sodium to the host MoS₂ lattice.^{5,24} The electrons from the sodium are transferred to the lowest lying unoccupied energy levels of the MoS₂, which are mainly transition metal d bands. Sodium naphthalenide is a kind of electron transfer agent in which sodium transfers an electron to the aromatic system. The resulting radical anion is an electron donor with strong reducing properties. Through the radical anion, the electron from sodium is expected to transfer to MoS₂, followed by the sodium ion intercalation to balance the charge.⁴⁰ Except for the electron transfer from the intercalant sodium to the host MoS₂, another effect of intercalation is the expansion of the interlayer spacing and weakened van der Waals interactions between the layers.²⁴ To prepare the MoS₂ based motor, MoS₂ was submerged in tetrahydrofuran solutions of sodium naphthalenide to insert sodium into the layered structure. The morphology of the resulting sodium intercalated MoS₂ is examined by scanning electron microscopy (SEM). Fig. 1A–C illustrate the surface characteristics of the

Fig. 1 (A–C) SEM images of the pre-exfoliated MoS₂ microparticles. Scale bars are 10 μ m, 1 μ m and 1 μ m, respectively. (D) Optical image of Na-exfoliated MoS₂ dispersion in water. Scale bar is 10 μ m. (E and F) STEM images of Na-exfoliated MoS₂. Scale bars are 1 μ m and 100 nm, respectively.

intercalated MoS₂ before exfoliation at different magnifications. The bulk materials are stacks of many micro-sized plates and each plate is in fact composed of many monolayers of MoS₂. The typical height of a single layer MoS₂ is reported to be less than 1 nm.⁴¹

The sodium intercalated MoS₂ exhibits remarkable ability to exfoliate in water. The exfoliation process is not a purely mechanical process, but a chemical one relying on redox reactions. The reaction of water with the intercalated sodium between the layers generates hydrogen gas, which will force the separation of MoS₂ layers.⁴² Meanwhile, the MoS₂ layers undergo oxidation along with hydration.^{5,24} As the reaction proceeds further into the interlayer spaces, the layers become increasingly spatially separated and eventually turned into individual single layers or few layers of MoS₂, resulting in a colloiddally dispersed suspension. In our study, we used MoS₂ particles with an average diameter of around 2.5 μ m. Once immersed in water, the particles undergo a self-exfoliation process. Fig. 1D shows the optical image of the resulting aqueous MoS₂ suspension containing MoS₂ flakes exfoliated to varying degrees. The different optical contrast of the flakes is attributed to the difference in their thickness, which is governed by the number of layers. Further investigation by scanning transmission electron microscopy (STEM) demonstrates the existence of exfoliated flakes with smaller size (Fig. 1E and F). Fig. 1E displays some partially exfoliated MoS₂ flakes while Fig. 1F shows more transparent flakes indicating higher degrees of exfoliation. The average thickness of the exfoliated flakes was characterized by atomic force microscopy (AFM) to be around 1.4 nm (see ESI† for details).

Upon exposure to water, the MoS₂ particles exhibit fast motion while simultaneously experiencing exfoliation. Fig. 2 illustrates the trajectories of the movement of the MoS₂ particles in deionized water, which can be either translational (SI video-1, ESI†) or rotational motion (SI video-2, ESI†). As the sodium intercalated MoS₂ will exfoliate in water, the size of the particle decreases during motion and continuous motion is observed until the particle totally disappears. Accordingly, the lifetime of the MoS₂ particle is influenced by the size of the particle. It generally needs more time for larger MoS₂ particles to be exfoliated in water, thus allowing longer lifetimes. For the MoS₂ particles with average diameters of around 2.5 μ m used here, the motion and exfoliation

Fig. 2 Trajectories of MoS₂ based motors in water. (A) Translational motion of a MoS₂ based motor for 10 s. (B) Rotational motion of a MoS₂ based motor for 2 s. Scale bars are 1 cm.

process can last for 20–30 seconds. Although the intercalated sodium reacts with water to generate molecular hydrogen and sodium hydroxide, bubbles were not observed during the motion of the MoS₂ particles. We also examined the motion of smaller particles under a microscope and bubbles were still not seen, which demonstrates that bubble propulsion is not the main driving force for motion.

The anisotropic distribution of sodium intercalated in MoS₂ will lead to a concentration gradient of reaction products around the particle during the exfoliation process in water. However, at such a large length scale, the effect of diffusiophoresis is no longer significant as that in the low Reynolds number regime.⁴³ A control experiment using lithium intercalated MoS₂ prepared with *t*-butyl lithium as the lithiation agent demonstrated that they did not exhibit any movement in water, which further rules out propulsion by the concentration gradient (SI video-3, ESI†). Since the MoS₂ particles only move at the air/water interface, we propose that the motion is mainly due to the Marangoni effect. The naphthalene used in the preparation procedure is an organic compound existing as white crystalline solid, which has a solubility of 31.6 mg L⁻¹ in water at 25 °C. The motion of a droplet or solid grain at an interface driven by the Marangoni effect has been extensively reported.^{44–49} Surface tension gradients brought about by the anisotropic distribution of the surface tension altering material around the droplet or grain exterior provide the driving force for the self-motion. Control experiments using acetylnaphthalene (SI video-4, ESI†) and dihydroxynaphthalene (SI video-5, ESI†) demonstrated the ability of naphthalene derivatives, which are solid grains, to exhibit self-propulsion on the surface of water. The motion is due to the non-uniform distribution of the organic molecules that develop asymmetrically from the solid. The resulting surface tension heterogeneity will induce motion along the chemical gradient. Similarly, for the MoS₂ based motor, the naphthalene molecules that develop from the anisotropically distributed naphthalene in MoS₂ generate a surface tension gradient around the particle and thus result in a propulsive force for the motion. A region of higher surface tension means greater intermolecular forces. The liquid with higher surface tension pulls more strongly on the surrounding liquid than the one with lower surface tension. As a result, the surface tension gradient will cause the object to be propelled towards regions of higher surface tension, where there is a region of lower density distribution of naphthalene. Fig. 3 illustrates the

Fig. 3 Schematic diagram illustrating the simultaneous self-exfoliation and autonomous motion of the MoS₂ based motor in water.

simultaneous motion and exfoliation of the MoS₂ particle. The motion and exfoliation are in fact two separate processes due to two different components contained in the MoS₂ particle. Exfoliation is attributed to the reaction between intercalated sodium and water while motion is due to the asymmetric distribution of naphthalene on the water surface. When immersed in water, the two processes occurred at the same time, resulting in concomitant exfoliation and motion of the MoS₂ particles. The MoS₂ based motor presented here provides a strategy for preparation of TMDC based motors by encapsulating surface tension altering reagents. The Marangoni effect induced motion can be performed in an aqueous environment without adding surfactants and external fuel. The exfoliation during motion provides substantial 2D MoS₂ nanosheets for subsequent processing steps. A combination of the mobility of the MoS₂ based motor and its autonomous exfoliation into 2D layers offers a new platform for possible applications.

The different motion modes of the MoS₂ particles are ascribed to the differences in the shape of the particles and distribution of naphthalene in them. The solubility of naphthalene is very low and only a small amount of naphthalene at the water interface can induce the surface tension gradient required for the motion of the particle. On the other hand, the exfoliation of the particle only takes a very short time. As such, unlike the motion of aggregates only constituted of diphenylhydrazine,⁴⁵ the amount of organic surface altering material naphthalene is not the deciding factor of the lifetime of the MoS₂ based motor. The lifespan is directly determined by the time taken for exfoliation of the whole particle, whereas the mobility of the particle is mainly related to the distribution of naphthalene. The velocity of the particle depends on the concentration gradient of naphthalene developing from that in the MoS₂ particle. Fig. 4 shows the distribution of instantaneous speed of the particle in Fig. 2A against time. The speed is calculated by means of dividing the distance covered by the amount of time taken between sequential video frames (30 frames per s). Although fluctuation occurs, the gradual release of naphthalene led to the instantaneous speeds of the tracked MoS₂ based motor to be predominantly distributed around the region of 3 cm s⁻¹. However, as the concentration of naphthalene increases on the surface of water during the motion, the velocity shows a slightly decreasing trend with time due to a reduction of surface tension gradient around the particle. When reaching a temporal equilibrium state, the particle can stall for a moment. Once the balanced state is broken by the changes in the

Fig. 4 Instantaneous speed of the MoS₂ based motor in Fig. 2A over 10 s. Time interval is 0.1 s.

distribution of the naphthalene layer, the particle will resume motion. The average speed obtained from 20 MoS₂ based motors during the first 10 s is about 2.3 cm s⁻¹.

In conclusion, we describe the simultaneous motion and exfoliation of a MoS₂ based motor, in which naphthalene is used to induce surface tension gradient at the water interface for propulsion and intercalated sodium reacts with water to separate the material layers. The Marangoni effect provides a strategy to prepare TMDC based motors that can move autonomously in an aqueous environment without additional surfactants and fuel. The unique properties of MoS₂ offer a lot of potential biomedical applications after rational functionalization. The MoS₂ motor is envisioned to be involved in performing tasks such as sensing and cargo delivery. The simultaneously exfoliated materials can be used for subsequent downstream analysis and the cargo release process. The MoS₂ motor also has the potential to be used as recyclable on-the-fly extractants for removal of heavy metals in aqueous media.

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Blood Proteins Strongly Reduce the Mobility of Artificial Self-Propelled Micromotors

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Abstract: Autonomous self-propelled catalytic microjets are envisaged as an important technology in biomedical applications, including drug delivery, micro/nanosurgery, and active dynamic bioassays. The direct in vivo application of these microjets, specifically in blood, is however impeded by insufficient knowledge on the in vivo viability of the technique. This study highlights the effect of blood proteins on the via-

bility of the microjets. The presence of blood proteins, including serum albumin and γ -globulins at physiological concentrations, has been found to dramatically reduce the viability of the microjets. The reduction of viability has

Keywords: blood proteins • medicinal chemistry • micromotors • microreactors • viability

been measured in terms of a lower number of active microjets and a decrease in the velocity of propulsion. It is clear from this study that in order for microjets to function in biomedical applications, different modes of propulsion besides platinum-catalyzed oxygen bubble ejection must be employed. These findings have serious implications for the biomedical applications of catalytic microjets.

Introduction

Artificial catalytic self-propelled nano/microscale engines have been the subject of intense interest due to their potential use in biomedical applications, such as drug delivery,^[1] isolation of biologically active molecules,^[2] micro/nanosurgery,^[3–5] bioassays,^[6] and artery clean-up.^[7] Study of the navigation profiles of these self-propelled microengines in blood samples is important for future practical applications involving in vivo biomedical procedures. Although remarkable progress towards this goal has been made during the past few years, there are numerous problems to overcome.

The question of whether the components in blood samples would affect the motion of the microjets has seldom been studied. Our group has recently shown that the motions of microjets in whole blood and blood serum samples are severely impeded, even at very high dilutions.^[8] This led to the focus of the present work, which is to investigate the possible origins of impeded motion for microjets in blood serum. We have focused on the most abundant proteins. Serum albumin is the most abundant blood plasma protein and constitutes about 50 % of mammalian plasma protein. Serum albumin helps to sustain normal physiological functions, for example through the regulation of blood volume by maintaining colloid osmotic pressure of the blood compartment.^[9] In addition, γ -globulins constitute another major

class of blood proteins. The most important γ -globulins are immunoglobulins. Since microengines are envisaged as functioning in vivo for biomedical applications, it is important to carefully examine the influences of serum albumin and γ -globulin on the viability and motion of microengines. This work should provide important references for future functionalization and bioapplications of microengines.

Results and Discussion

Cu/Pt catalytic microtubular engines prepared by the membrane template electrodeposition technique were utilized in this work. The preparation procedures have been described previously.^[10] In order to study the influences of blood plasma proteins on the viability of microjets, the microjets were exposed to physiologically relevant concentrations of serum albumin and γ -globulins. Three main parameters associated with the mobility and viability of microjets were investigated, namely: (i) the fraction of the microjets that ejected bubbles (as bubble ejection is one of the prerequisites for motion of the microjets), (ii) the fraction of microjets that were propelled, and (iii) the average velocity of the microjets exhibiting propulsion. Fixed concentrations of hydrogen peroxide (3 wt %) and surfactant (SDS, 1 wt %) were used in the experiments. Control experiments were carried out in distilled water in the absence of proteins. The microjets exhibited an average speed of $365 \mu\text{m s}^{-1}$ (≈ 52 body lengths s^{-1}) in the control experiments.

Initial investigations were carried out on the influence of serum albumin, the most abundant blood protein, on the motion of the microjets. In the presence of 3 mg mL^{-1} of bovine serum albumin (BSA), only about 30 % of the microjets ejected bubbles and 25 % of the microjets exhibited

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Figure 1. The presence of serum albumin in the running solution significantly reduces the viability of the artificial catalytic microjets. A) The influence of BSA concentration on the population of the microjet engines found to be ejecting bubbles (diagonal striped bar) and exhibiting motion (cross-hatched bar). B) The influence of BSA concentration on the velocities of the microjets exhibiting non-zero velocity motion. Conditions: temperature 23 °C, 3 wt % H_2O_2 , and 1 wt % SDS.

non-zero velocity motion (Figure 1). Note that all data were normalized to the motion of microjets in the control solution (motion in the absence of proteins). When the concentration of BSA was increased to 15 mg mL^{-1} , about 99 % the microjets remained stationary and only 5 % of the microjets were observed to eject bubbles periodically. The presence of BSA also resulted in a significant reduction in the velocities of the moving microjets. The average speed decreased dramatically from $365 \mu\text{m s}^{-1}$ to $91 \mu\text{m s}^{-1}$ even in the presence of only 3 mg mL^{-1} of BSA. It should be emphasized that the physiological concentration range of serum albumin in blood is $35\text{--}50 \text{ mg mL}^{-1}$.^[11] According to our study, the physiological concentration of serum albumin in blood would thus be able to completely deactivate all of the catalytic microjets in the presence of 3 % hydrogen peroxide as fuel. No qualitative difference in the microjet behaviour was observed when the concentration of H_2O_2 was significantly increased to 9 %, as shown in Figure S1 in the Supporting Information.

Subsequently, the microjets were exposed to different concentrations of γ -globulins, another class of proteins that are abundant in blood plasma. A key aspect of this study was to ascertain whether the deactivation of microjets is a characteristic of serum albumin or a general effect originating from blood proteins. It was found that the presence of γ -globulins also curtailed the viability and mobility of the microjets. As shown in Figure 2, the presence of 18 mg mL^{-1}

Figure 2. The presence of γ -globulins in the running solution significantly reduces the viability of the catalytic microjets. A) The influence of γ -globulins concentration on the activity of the microjets (ejection of bubbles and mobility of microjet engines). B) Influence of γ -globulins concentration on the velocity of the mobile microjets. Conditions: temperature 23 °C, 3 wt % H_2O_2 , and 1 wt % SDS.

of γ -globulins led to a marked decrease in the mobility of the microjets, with around 30 % of the microjets producing bubbles and only around 20 % of the microjets exhibiting motion. The effect was thus similar to that previously observed in the presence of 3 mg mL^{-1} of serum albumin. The concentration of γ -globulins needed to completely suppress the mobility of $>95\%$ of the microjets was found to be 30 mg mL^{-1} , which falls within the range of physiologically relevant concentrations of γ -globulins in blood ($23\text{--}55 \text{ mg mL}^{-1}$).^[12] Therefore, based on the obtained results, it could be deduced that at physiological concentrations the γ -globulins in blood serum could suppress the motion of almost all of the microjets. It was also of interest to note that at a γ -globulin concentration of 6 mg mL^{-1} , the average velocity of the mobile microjets was $111 \mu\text{m s}^{-1}$. This was much lower than their mobility in a protein-free control solution ($365 \mu\text{m s}^{-1}$) but higher than the $73 \mu\text{m s}^{-1}$ found in a 6 mg mL^{-1} albumin solution.

After the above assessment of the influences of major blood proteins on the viability of microjets, the study was extended to a non-human protein. This investigation was essential to determine whether the observed phenomena of decreasing velocity and viability of catalytic microjets were isolated cases for major blood proteins. Glucose oxidase (GOx) was selected as the protein for these further studies, based on the fact that this enzyme could potentially be employed in the development of biocompatible and navigable

micromotors for use in the human body.^[13,14] The study showed that the self-propelled microjets were even more adversely affected by the presence of glucose oxidase than by the previous two types of proteins, as shown in Figure 3. Even at a low concentration of 0.6 mg mL^{-1} of GOx, more than half of the microjets stopped ejecting bubbles and only around 30 % of the microjets exhibited a crippled motion

Figure 3. The presence of glucose oxidase in the running solution significantly reduces the mobility of the artificial catalytic microjets. A) The influence of glucose oxidase concentration on the activity of the microjets (ejection of bubbles and mobility of microjet engines). B) Influence of glucose oxidase concentration on the velocity of the mobile microjets. Conditions: temperature 23°C , 3 wt % H_2O_2 , and 1 wt % SDS.

with an average velocity of $131 \mu\text{m s}^{-1}$. As in the case of the blood proteins, the viability and motion of the microjets decreased gradually as the concentration of glucose oxidase was increased. No bubble ejection or microjet motion were observed at 1.5 mg mL^{-1} of glucose oxidase.

It was obvious from these results that the presence of protein molecules resulted in a decreased viability of the microjets. This negative effect is most likely caused by a combination of two phenomena: (i) adsorption of proteins on the inner wall of the microjets and/or (ii) increased viscosity of the solution. The adsorption of proteins on Pt catalytic surfaces could potentially decrease the active surface area that promotes the generation of O_2 bubbles and consequently affect the viability of the microjets. Such adsorption could originate from (a) physisorption of proteins on the Pt surface^[15] or (b) chemisorption of proteins on the Pt surface via sulfur-containing moieties (R-SH).^[16] Pt (together with Ag, Au, V, and Cu) can adsorb large amounts of proteins, which is assumed to be due to their greater readiness to chemically

bind to thiol groups thereon.^[17] Electrostatic interaction between Pt and the protein may also play a role.^[18]

Moreover, a larger amount of protein increases the overall viscosity of the solution. For example, a solution containing 3 wt % serum albumin exhibits an increment of about 20 % in viscosity as compared to a blank solution.^[19] Such an increased viscosity of the protein solution would cause a reduction in the mobility of the microjets according to Stokes' law.^[20] However, an increase in viscosity is insufficient to explain the extent of the decreased viability of the microjets, and the major influence is expected to originate from adsorption of proteins on the Pt surface. We also observed that different proteins influence the mobility of the microjets to different extents. There may be various reasons for this, such as different affinities of the proteins towards Pt surfaces caused by their hydrophobicities and/or pI values. It has been established that molecular weight, size, hydrophobicity, charge, and the positions of disulfide bridges and -SH groups influence the degrees of adsorption of different proteins.^[18,21] Maximum adsorption in the isoelectric region is a general property of proteins.^[22]

Conclusion

We have investigated the influences of the main components of blood serum on the motion of Pt-catalyzed microjets. It was discovered that serum albumin and γ -globulins at their physiological concentrations affect the motion of self-propelled microjets. This effect is not restricted to blood proteins, but is of a general nature, since catalytic microengines are prone to passivation by other types of proteins such as glucose oxidase. The mechanism of passivation of the microjets is mainly due to protein adsorption (physi/chemisorption) on the Pt surface. These findings provide important references for the development of microjet engines and related biomedical applications. Considerable effort should be devoted to overcoming these challenges if full use of microjet engines is to be made in the biomedical sphere in the future.

Experimental Section

Materials: Cyclopore polycarbonate membranes with pores of $2 \mu\text{m}$ in diameter were purchased from Whatman, USA (Cat. no. 7060–2511). The pores are conical in shape. Colloidal graphite (isopropanol base) was purchased from Ted Pella, Inc., USA (Lot no. 12009–2). Hydrogen peroxide (27 %; Lot no. 10151507) was purchased from Alfa Aesar, Singapore. Dichloromethane and ethanol were purchased from Tedia, USA. Pt electrodes of diameter 1 mm and Ag/AgCl/1 M KCl electrodes were purchased from CH Instruments, USA. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (> 98 %) was purchased from Sigma–Aldrich. The platinum plating solution (Lot no. 20251001) was obtained from Technic Inc., USA. Sodium dodecyl sulfate (SDS; Lot no. 079K0335), glucose oxidase from *Aspergillus niger* (type X-S; Lot no. 119K1204), bovine serum albumin (BSA; Lot no. 100M1779V), and γ -globulins from bovine blood (Lot no. SLBB9558V) were purchased from Sigma–Aldrich. Chemicals were used as received and the solutions were

prepared using ultrapure water (18.2 M Ω cm) from a Millipore Milli-Q purification system.

Apparatus: Electrochemical deposition was carried out with a μ Autolab type III electrochemical analyzer (Eco Chemie, The Netherlands) connected to a computer and controlled by General Purpose Electrochemical Systems version 4.9 software (Eco Chemie). The deposition procedure was conducted at room temperature (23°C) using a three-electrode arrangement. A platinum electrode was utilized as a counter electrode, and Ag/AgCl was used as the reference electrode. The ultrasonication process was carried out with a Fisherbrand FB 11203 ultrasonicator, and centrifugation was carried out with a Beckman Coulter Allegra 64 R centrifuge. Scanning electron microscopy (SEM/EDX) analysis was carried out with a JEOL JSM 7600F instrument. Optical microscope videos and images were obtained with a Nikon Eclipse TE 2000-E microscope. Video sequences (100 fps) were processed with Nikon NIS-Elements software.

Preparation of Cu/Pt concentric bimetallic microtubes: The Cu/Pt concentric bimetallic microtubes were synthesized by a modified electrochemical deposition procedure on a cyclopore polycarbonate template.^[13] Colloidal graphite ink was applied on one side of the polycarbonate template with commercial cotton swabs. A piece of flattened aluminium foil was immediately attached to the ink, which served as the working electrode in the plating experiments. The template was assembled into a customized electrochemical deposition cell. A platinum counter electrode and an Ag/AgCl reference electrode were utilized. Electrochemical deposition was carried out with a μ Autolab type III electrochemical analyzer connected to a computer and controlled by General Purpose Electrochemical Systems version 4.9 software. The template was rinsed with ultrapure water (18.2 M Ω cm; 4 $\times$ 5 mL), and then the Cu outer layer was deposited galvanostatically at -4 mA for 450 s. The deposition solution contained 1 M CuSO₄. After removing the deposition solution, the template was rinsed with water (5 $\times$ 8 mL). The platinum segment was subsequently electrodeposited at -4 mA for 450 s using a commercial plating solution. When the deposition of the microtubes was complete, the electrochemical cell was disassembled and the template was washed with water (5 $\times$ 8 mL). Thereafter, the template was ultrasonicated in aliquots of ultra-pure water (3 $\times$ 2 mL, each for 3 min). The graphite layer was removed during the ultrasonication procedure. The template was then placed in an Eppendorf tube with dichloromethane (2 mL) and ultrasonicated until the whole template had dissolved. The electrochemically deposited microtubes were collected by centrifugation at 6000 rpm for 3 min and washed three times with dichloromethane. The solution was then washed twice each with ethanol and water and centrifuged for 3 min after each washing step. The tubes were stored in water at room temperature.

Operation of the microjets: The experiments for studying the motion of the microjets were carried out in aqueous solutions containing 3 wt % hydrogen peroxide at constant surfactant concentration (1 wt % SDS). Optical microscope videos and images were obtained with a Nikon Eclipse TE 2000-E microscope. Video sequences (100 fps) were processed with Nikon NIS-ElementsTM software. For each of the data points in the figures,

at least 32 measurements were taken into account. All measurements were performed on multiple microjet engines and therefore different motions of different microjet engines in the same environment are responsible for the error bars and RSD of the data points.

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Blood electrolytes exhibit a strong influence on the mobility of artificial catalytic microengines†

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The developments in biomedical sciences foresee the inclusion of self-propelled catalytic micromotors for *in vivo* therapeutic strategies in the near future. We show here that blood electrolytes, such as Na⁺, K⁺, Ca²⁺, Cl[−], SO₄^{2−} and phosphates, decrease the mobility of the Pt catalyzed tubular microjets. This effect is significant and in many cases, the microjets are completely disabled at physiologically relevant concentrations of the ions. A strategy to counterbalance this negative influence is suggested. These findings have a strong influence in the field of bubble-propelled artificial micromotors, where applications in blood are often envisioned.

Introduction

Self-propelled nano-/microscale machines are a fast developing and important front-line subject in nanotechnology.^{1–6} These artificial autonomous micromachines hold great promise for performing a variety of independent tasks in the biomedical area.^{7–12} One of the most popular propulsion mechanisms of microjet engines is bubble ejection from a tubular catalytic engine, which decomposes fuel (H₂O₂) at its inner walls.⁶ These microengines are currently targeted for applications in general nanomedicine, in particular, drug delivery and/or nano/microsurgeries.^{7–9,12} However, the suitability of the environment of body fluids for catalytic microjet motion remains a pressing issue. We have recently discovered that the blood environment imposed challenging constraints for the motion of microjets,¹³ however, the mechanism of such an effect in blood was not clearly understood/identified.

Here, we investigated the influence of main electrolytes found in blood on the motion of tubular catalytic microjets. Common electrolytes found in the human body include sodium (Na⁺), potassium (K⁺), calcium (Ca²⁺), chloride (Cl[−]), hydrogen phosphate (HPO₄^{2−}), dihydrogen phosphate (H₂PO₄[−]) and sulfate (SO₄^{2−}). These electrolytes regulate nerve and muscle function, hydration level, blood pH, blood pressure, and are involved in rebuilding of a damaged tissue. As such, maintaining the right balance of electrolytes is essential for normal cell and organ functions. Moreover, in order to perform these functions, the ions are usually present in

high concentrations, *i.e.* sodium ion concentration in blood is 135–145 mM. In fact, various mechanisms exist in the human body to maintain the concentrations of these electrolytes under stringent control.¹⁴ We will show that even though these electrolytes are present in small quantities, they can exhibit obvious influences on the mobility of catalytic bubble ejection microjets. This should be taken into account when employing the microjets for different tasks in high-ionic environments.

Experimental section

Materials

The cyclopore polycarbonate membranes with pores of 2 μm in diameter were purchased from Whatman, USA (Cat no. 7060-2511). The pores are conical in shape. Colloidal graphite (isopropanol base) was purchased from Ted Pella, Inc., USA. Hydrogen peroxide (35%) was purchased from Alfa Aesar, Singapore. Methylene chloride and ethanol were purchased from Tedia, USA. Pt electrodes with 1 mm diameter and Ag/AgCl/1 M KCl were purchased from CH instruments, USA. The platinum plating solution was obtained from Technic Inc., USA. CuSO₄·5H₂O (98+%), sodium dodecyl sulfate (SDS), NaCl, KCl, CaCl₂, Na₂HPO₄, K₂HPO₄ and Na₂SO₄ were purchased from Sigma-Aldrich. Chemicals were used as received and the solutions were prepared using ultrapure water (18.2 MΩ cm) from a Millipore Milli-Q purification system.

Apparatus

Electrochemical deposition was carried out using a μAutolab type III electrochemical analyzer (Eco Chemie, The Netherlands) connected to a computer and controlled by General Purpose Electrochemical Systems version 4.9 software (Eco Chemie). The deposition procedure was conducted at room temperature (23 °C)

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using a three-electrode arrangement. A platinum electrode was utilized as a counter electrode, and Ag/AgCl was used as the reference electrode. The ultrasonication process was carried out using a Fisherbrand FB 11203 ultrasonicator, and centrifugation was carried out using a Beckman Coulter Allegra 64R centrifuge. Scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDX) analysis was carried out using a JEOL JSM 7600F instrument. Optical microscope videos and images were obtained using a Nikon Eclipse TE 2000-E microscope. Video sequences (100 fps) were processed using Nikon NIS-Elements software.

Preparation of Cu/Pt concentric bimetallic microtubes

The Cu/Pt concentric bimetallic microtubes were synthesized using a modified electrochemical deposition procedure on a cyclopore polycarbonate template.¹⁵ Colloidal graphite ink was applied on one side of the polycarbonate template using commercial cotton swabs. A piece of flattened aluminium foil was attached to the ink immediately, which serves as the working electrode for the plating experiments. The template was assembled into a customized electrochemical deposition cell. The platinum counter electrode and the Ag/AgCl reference electrode were utilized. Electrochemical deposition was carried out using a μ Autolab type III electrochemical analyzer connected to a computer and controlled by General Purpose Electrochemical Systems version 4.9 software. The template was rinsed with 5 mL of ultrapure water (18.2 M Ω cm) 4 times, and the Cu outer layer was deposited galvanostatically at -4 mA for 450 s. The deposition solution contained 1 M CuSO₄. Consequently, after removing the deposition solution, the template was rinsed 5 times with 8 mL of water. The platinum segment was electrodeposited subsequently at -4 mA for 450 s each, using the commercial plating solutions. When the deposition of microtubes was finished, the electrochemical cell was disassembled and the template was washed 5 times with 8 mL of water each time. After that, the template was ultrasonicated 3 times in 2 mL of ultra-pure water for 3 min each time. The graphite layer was removed during the ultrasonication procedure. The template was placed in an Eppendorf tube with 2 mL of methylene chloride and ultrasonicated until the whole template was dissolved. The electrochemically deposited microtubes were collected by centrifugation at 6000 rpm for 3 min and washed repeatedly 3 times with methylene chloride. The solution was then washed with ethanol and water 2 times each and centrifuged for 3 min after each washing step. The tubes were stored in water at room temperature.

Operation of microjets

The experiments for studying the influence of electrolytes on the motion of microjets were carried out in an aqueous solution containing 3 wt% of hydrogen peroxide at constant surfactant concentrations (1 wt% of SDS). A mixture of microtubes (7 μ L), SDS (1 wt%), H₂O₂ (3 wt%) and various concentrations of electrolyte solutions were applied on a glass slide freshly cleaned with nitrogen gas. The experiments for studying the influence of hydrogen peroxide on the motion of the crippled microjets were

carried out in 10 mM phosphate buffer solution containing 1 wt% of SDS. A mixture of microtubes (7 μ L), SDS (1 wt%), phosphate buffer solution (10 mM) and various concentrations of hydrogen peroxide were applied on a glass slide freshly cleaned with nitrogen gas. Optical microscope videos and images were obtained using a Nikon Eclipse TE 2000-E microscope. Video sequences (100 fps) were processed using Nikon NIS-ElementsTM software. For each of the data points in figures, at least 32 measurements were taken into account.

Results and discussion

Sodium, which is the most abundant cation in extracellular fluid, regulates the total amount of water in the human body and plays a critical role in the generation of neuron signals. Compared with other electrolytes, the normal blood level of sodium (135–145 mM) is much higher. On the other hand, chloride has the highest concentration in blood at 96–106 mM, among the anions.¹⁶ As such, we first investigated the influence of NaCl on the motion of catalytic microjets. The experiments were carried out in an aqueous solution of 3 wt% hydrogen peroxide and 1 wt% SDS (if not mentioned otherwise, all the experiments in the following text were performed under the same conditions). As shown in Fig. 1A, in the presence of 10 mM NaCl,

Fig. 1 Motion of the Pt-catalyzed microjets in electrolyte solutions. (A) NaCl solution, (B) KCl solution, and (C) CaCl₂ solution. Left: graph showing the influence of electrolyte concentration on the percentage of microjets found to be ejecting bubbles (red bar) and moving (blue bar). Right: graph showing the influence of electrolyte concentration on the velocity of the moving microjets. Note that ultrapure water was used in the control experiment, both the running and bubbling percentages of which were defined as 100%. Conditions in all of the experiments: a temperature of 23 °C, 3 wt% H₂O₂ and 1 wt% SDS.

nearly 30% of the microjets stopped ejecting bubbles and even more microjets stopped exhibiting motion. In addition, the average velocity of the microjets suffered a great reduction from $365 \mu\text{m s}^{-1}$ to $109 \mu\text{m s}^{-1}$. Subsequent study showed that when the concentration of NaCl was increased to 70 mM, which was about half of physiological concentration, almost no bubbling and moving microjets could be observed. Regardless of any other factors, the physiological concentration of NaCl in blood was powerful enough to solely inhibit the movement of all the microjets in the presence of 3% hydrogen peroxide fuel.

Other major electrolytes in blood include potassium and calcium. Despite the relatively small amount of these ions in the human body (physiological concentration in blood is 3.5–5.2 mM for K^+ and 2.2–2.6 mM for Ca^{2+}), they possess important functions that cannot be underestimated. Potassium and calcium are best known for the regulation of heartbeat and function of muscles. Moreover, calcium is also important for building bones and aiding blood clotting.^{16,17} Consequently, the microjets were exposed to different concentrations of KCl and CaCl_2 solutions and the study showed that both salts could obviously affect the mobility of the microjets. The presence of 10 mM KCl resulted in a serious reduction of the mobility of the microjets, with only 38% of the microjets ejecting bubbles and 32% of the microjets exhibiting motion. The average velocity of the remaining moving jets dramatically decreased from $365 \mu\text{m s}^{-1}$ to $92 \mu\text{m s}^{-1}$ (Fig. 1B). The presence of CaCl_2 has a much stronger influence on the mobility of the microjets than NaCl and KCl. As shown in Fig. 1C, at 10 mM CaCl_2 , all the microjets stopped moving and only 9% of the jets were ejecting bubbles. In addition, a significant reduction in speed was observed from $365 \mu\text{m s}^{-1}$ to $42 \mu\text{m s}^{-1}$ in the presence of only 6 mM CaCl_2 .

Subsequently, we proceeded to investigate the influence of other electrolytes that are present in blood at lower concentrations, typically in the sub-millimolar concentrations. Phosphate is a component of nucleotides, phospholipids, ATP and most coenzymes. Most of the phosphate in blood is organic phosphate and only 0.97–1.29 mM exists in the form of inorganic phosphates such as HPO_4^{2-} and H_2PO_4^- , the two of which are an important buffer pair. Phosphate buffer is a buffer solution that is commonly used in biological research.¹⁸ We use phosphate buffer of pH 7.4, which is within the narrow blood pH range of 7.35 to 7.45, to study the influence of phosphorus electrolytes on the locomotion of the microjets.¹⁹ As shown in Fig. 2A, the mobility of the microjets decreased significantly as the concentration of the phosphate buffer solution increased. It was only at a concentration of 2 mM phosphate buffer solution more than half of the microjets stopped ejecting bubbles and about 40% of the microjets were moving at a much lower average speed of $149 \mu\text{m s}^{-1}$. This is a significant finding as many experiments involving microjets are carried out in phosphate buffer as well.^{20,21} We will elaborate on this issue further below.

Next we moved on to investigate other anions, specifically sulfates. Sulfates exist in blood in small amounts (0.56–1.25 mM).²²

Fig. 2 Motion of the Pt-catalyzed microjets in electrolyte solutions. (A) phosphate buffer solution, (B) sulfate solution. Left: graph showing the influence of electrolyte concentration on the percentage of microjets found to be ejecting bubbles (red bar) and moving (blue bar). Right: graph showing the influence of electrolyte concentration on the velocity of the moving microjets. Note that the ultrapure water was used in the control experiment, both the running and bubbling percentages of which were defined as 100%. Conditions in all of the experiments: a temperature of 23 °C, 3 wt% H_2O_2 and 1 wt% SDS.

In this study, Na_2SO_4 was found to exhibit an obvious influence on the mobility of the microjets. The presence of 10 mM Na_2SO_4 led to a strong decrement of the mobility of the microjets, with ~67% of the microjets generating bubbles and ~54% of the microjets exhibiting motion at an average speed of $\sim 88 \mu\text{m s}^{-1}$.

To have deeper insight into the problem we plotted all parameters, such as activity of microjets and velocity of the microjets for all solutions vs. ionic strength (Fig. S1 and S2, respectively, ESI†). The activity of the microjets and their velocity decreases with increased ionic strength, however, the difference is not identical for every ion. This is exemplified in the plot of % of active microjet propelling through the solution vs. ionic strength (Fig. S3, ESI†), where Na_2SO_4 exhibits the lowest influence while phosphate buffer exhibits the strongest influence. All the main electrolytes in the blood exhibit a strong influence on the mobility of the microjets to varying degrees. These results led us to the conclusion that blood electrolytes have an influence on the mobility of the microjets despite the bubble-propulsion mechanism.²³ The decreased mobility of the microjets in the presence of electrolytes is clearly indicated by the changes in the frequency of bubble ejection which is responsible for the efficient propulsion of the microjet engines. The oxygen bubbles are generated at the inner surface of the tubular microjets by the Pt-catalyzed decomposition of hydrogen peroxide. The frequency of bubble ejection is related to both the rate of the catalytic decomposition and the amount of surfactant. The possible reasons for decreased mobility of the microjets in the presence of electrolytes may include several aspects: (i) the ions poison the Pt catalyst, (ii) the ions interrupt the radical reaction of the decomposition of H_2O_2 , and (iii) the additional ions in the solution lead to the formation of larger micellar aggregates of ionic surfactants, which increases surface

Fig. 3 Motion of Pt-catalyzed microjets in 10 mM phosphate buffer solution with different concentrations of hydrogen peroxide fuel. (A) A graph showing influence of hydrogen peroxide concentration on the percentage of microjets found to be ejecting bubbles (red bar) and moving (blue bar). (B) A graph showing the influence of hydrogen peroxide concentration on the velocity of the moving microjets. Note that both the running and bubbling percentages of microjets at 15% hydrogen peroxide fuel concentration were defined as 100%. Conditions in all of the experiments: a temperature of 23 °C, 1 wt% SDS.

tension and leads to the difficulty in the detachment of the ejected bubbles from the microjet (however the detachment of bubbles did not show an observable difference in our experiments).^{24–26} Nevertheless, further work is needed for a better understanding of the effects of blood electrolytes on the mobility of the bubble-propelled microtubular engines.

It is of great significance to consider this limitation when employing the microjets to perform different tasks. Although the ions in solution (*i.e.* blood electrolytes) can obviously affect the efficiency of the microjets, we found that a higher concentration of fuel (H_2O_2) can compensate for the reduction of microjets mobility caused by the ions. As shown in Fig. 3A, the mobility of microjets was seriously suppressed in the presence of 10 mM phosphate buffer solution and 3 wt% H_2O_2 fuel. We studied the influence of H_2O_2 concentration on the mobility of the microjets in 10 mM phosphate buffer solution (Fig. 3B). The average velocity of the crippled microjets also increased greatly from $46 \mu\text{m s}^{-1}$ to $219 \mu\text{m s}^{-1}$ as the concentration of H_2O_2 increased from 3 wt% to 15 wt%. Increasing the concentration of H_2O_2 provided a possible way to counterbalance the negative effects of the ions. However, one should note the toxicity of H_2O_2 and realize that the use of H_2O_2 in living systems is prohibited in general.

Conclusions

In this study, we have investigated the influences of main blood electrolytes on the motion of the Pt-catalyzed microjets. The electrolytes, Na^+ , K^+ , Ca^{2+} , Cl^- , $\text{HPO}_4^{2-}/\text{H}_2\text{PO}_4^-$, and SO_4^{2-} all exhibited a strong influence on the mobility of microjets at physiological concentrations. Since this limitation was not initially expected from the bubble-propelled mechanism, more attention should be paid to this effect. These findings suggested that future research involving bubble-propelled microjets in biomedical applications should take into account the negative effects of ions in the solution on the efficiency of the bubble-ejecting catalytic microjets.

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Short communication

Blood metabolite strongly suppresses motion of electrochemically deposited catalytic self-propelled microjet engines

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ABSTRACT

Potential applications of self-propelled catalytic microjet engines in biomedical fields require the ability of microjets to perform tasks in various media, particularly in blood. Here, we show uric acid, a metabolite which is present in blood at a relatively low concentration, acts as a fuel stabilizer and radical scavenger that dramatically reduces the mobility of electrodeposited microjets. These findings would provide significant reference for the development of biomedical applications of electrodeposited microjets.

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1. Introduction

Self-propelled microengines are an important system towards autonomous artificial organisms or autonomous robots [1–6]. The microrobots consist of an important part, which is the propulsion system, the motor. Such motors intended for autonomous motion are typically based on systems converting fuel found in the environment to the motion. This motion can be self-electrophoretic [7], self-diffusiophoretic [8], or rocket-like via bubble propulsion [6]. The bubble-propelled micromotors have become highly popular in recent years due to their large power output. Microrobots are suggested to perform various tasks in biomedical [9,10], environmental remediation [11–13] and natural resource exploration fields [14]. From the application viewpoint, it is important to assess the ability of micromotors to move in the real environments.

We have recently focused on the motion of the microjet engines in real environments to investigate what influence they may have upon the motion of these tiny devices. We found out that thiol containing amino acids and proteins chemisorb on Pt catalytic surface, completely poisoning the catalyst and immobilizing the microjets, even at low and clinically relevant concentrations of such peptides [15]. In different work, we have demonstrated that ions presented in environmental waters significantly reduce viability of the engines [16]. This has important implication to the application of microjets in environmental remediation field. Recently, it was demonstrated that motion of the microjet engines is significantly suppressed in diluted red blood cell suspension and in diluted plasma [17]. Blood proteins and electrolytes can suppress motion of the microjet engines as well [18,19].

In addition to red blood cells and plasma proteins, blood samples may contain small metabolite molecules that could potentially influence the motion of microengines. One of the blood metabolites is uric acid. Uric acid is an important biomarker in medical examination and is associated with health conditions including gout [20], diabetes [21] and kidney stones [22]. In a similar manner, uric acid acts as a H_2O_2 stabilizer [24] and radical scavenger that may reduce the activity of microjets using hydrogen peroxide as fuel.

Here therefore we focused on the influence of one of the most abundant metabolite molecules found in blood serum, uric acid, on the motion of microjet engines.

2. Experimental

2.1. Materials

The cyclopore polycarbonate membranes with pores of 2 μm in diameter were purchased from Whatman, USA (Cat. no. 7060-2511). The pores are conical in shape. Colloidal graphite (isopropanol base) was purchased from Ted Pella, Inc. (Lot no. 12009-2, USA). Hydrogen peroxide (27%, Lot no. 10151507) was purchased from Alfa Aesar, Singapore. Methylene chloride and ethanol were purchased from Tedia, USA. Pt electrodes with 1 mm diameter and Ag/AgCl/1 M KCl were purchased from CH instruments, USA. $CuSO_4 \cdot 5H_2O$ (98+%) was purchased from Sigma-Aldrich. The platinum plating solution (Lot no. 20251001) was obtained from Technic Inc., USA. Sodium dodecyl sulfate (SDS, Lot no. 079K0335) and uric acid (Lot no. STBB1642A0) were purchased from Sigma-Aldrich. The chemicals were used as received and the solutions were prepared using ultrapure water (18.2 M Ω cm) from a Millipore Milli-Q purification system.

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2.2. Apparatus

Electrochemical deposition was carried out with a μ Autolab type III electrochemical analyzer (Eco Chemie, The Netherlands) connected to a computer and controlled by General Purpose Electrochemical Systems version 4.9 software (Eco Chemie). The deposition procedure was conducted at room temperature (23 °C) using a three-electrode arrangement. A platinum electrode was utilized as a counter electrode, and Ag/AgCl was used as the reference electrode. The ultrasonication process was carried out with a Fisherbrand FB 11203 ultrasonicator, and centrifugation was carried out with a Beckman Coulter Allegra 64R centrifuge. Scanning electron microscopy (SEM/EDX) analysis was obtained with a JEOL JSM 7600F instrument. Optical microscope videos and images were obtained with a Nikon Eclipse 50i microscope. Video sequences were processed with Nikon NIS-Elements software.

2.3. Preparation of Cu/Pt concentric bimetallic microtubes

The Cu/Pt concentric bimetallic microtubes were synthesized with a modified electrochemical deposition procedure on a cyclopore polycarbonate template [23]. Colloidal graphite ink was applied on the one side of the polycarbonate template with commercial cotton swabs. A piece of flattened aluminum foil was attached to the ink immediately, which serves as the working electrode for the plating experiments. The template was assembled into a customized electrochemical deposition cell. Platinum counter electrode and Ag/AgCl reference electrode were utilized. Electrochemical deposition was carried out with a μ Autolab type III electrochemical analyzer connected to a computer and controlled by General Purpose Electrochemical Systems version 4.9 software. The template was rinsed with 5 mL of ultrapure water (18.2 M Ω cm) for 4 times, and the Cu outer layer was deposited galvanostatically at -4 mA for 450 s. The deposition solution contained 1 M CuSO₄. Consequently, after removing the deposition solution, the template was rinsed 5 times with 8 mL of water. The platinum segment was electrodeposited subsequently at -4 mA for 450 s each, using the commercial plating solutions. When the deposition of microtubes was finished, the electrochemical cell was disassembled and the template was washed 5 times with 8 mL of water each. After that, the template was ultrasonicated for 3 times in 2 mL of ultra-pure water for 3 min each time. The graphite layer was removed during the ultrasonication procedure. The template was placed in an Eppendorf tube with 2 mL of methylene chloride and ultrasonicated until the whole template was dissolved. The electrochemically deposited microtubes were collected by centrifugation at 6000 rpm for 3 min and washed repeatedly for 3 times with methylene chloride. The solution was then washed with ethanol and water for 2 times each and centrifuged for 3 min after each washing step. The tubes were stored in water at room temperature. The example of microjet fabricated by this technique is shown in Fig. 1.

2.4. Operation of microjets

The experiments for studying the motion of microjets were carried out in an aqueous solution containing 3 wt.% of hydrogen peroxide at constant surfactant concentrations (1 wt.% of SDS). A mixture of microtubes (7 μ L), SDS (1 wt.%), H₂O₂ (3 wt.%) and various concentrations of uric acid solutions were applied on a glass slide freshly cleaned with nitrogen gas. Optical microscope videos and images were obtained with Nikon Eclipse 50i microscope. Video sequences were processed with Nikon NIS-Elements software. For each of the data points in the figures, at least 32 measurements were taken into account.

3. Results and discussion

Uric acid is primarily an antioxidant as well as a scavenger of singlet oxygen and hydroxyl radicals in the human body. The function of uric

Fig. 1. SEM image of microjet engine fabricated by electrochemical deposition method.

acid as a scavenger of free hydroxyl radicals which are created by the decomposition of H₂O₂ (catalytic or not catalytic) predetermines its usage as an industrial additive to stabilize H₂O₂ solutions [24]. The physiological concentration of uric acid in human blood is 0.035–0.075 mg/mL [25], and the microjets were subjected to uric acid solutions of 0.01–0.04 mg/mL concentrations in this study. The bilayer Cu/Pt microjets employed here were fabricated by the membrane template electrodeposition technique. Such microjets have an average length of ~ 7 μ m and the outer diameters are 2.0 and 1.5 μ m at their opposite ends. To assess the viability and mobility of microjets, three parameters were investigated including the fractions of microjets exhibiting bubble ejection and propulsion as well as the average velocity of propelled microjets. Control experiments were conducted in distilled water without uric acid and both the percentages of microjets ejecting bubbles and exhibiting motion in the control experiments are defined as 100%. As shown in Fig. 2, a significant decrease of the mobility of the microjets was observed. In the presence of only 0.01 mg/mL of uric acid, nearly 30% of the microjets stopped ejecting bubbles and more than 40% of the microjets ceased motion. The average speed of the remaining moving microjets dramatically decreased from 365 μ m/s to 250 μ m/s. When the concentration of uric acid was increased to 0.04 mg/mL, no more than 45% of the microjets ejected bubbles and only 31% moved at an average velocity of 84 μ m/s. In the radical process of hydrogen peroxide decomposition, the presence of hydroxyl radicals are essential for the formation of oxygen gas which consequently provides the driving force for the propulsion of microjets. The ability of uric acid to scavenge the singlet oxygen and hydroxyl radicals generated by the Pt surface led to a dramatic decrease of the viability of microjets. Therefore, even a small amount of uric acid in the blood is enough to exhibit a strong influence on the microjet mobility.

4. Conclusion

We found out that small metabolite molecules, such as uric acid, dramatically decrease the mobility of microjets at its physiological concentration. Uric acid is used as a H₂O₂ stabilizer in industry and it is likely due to its function as a free radical scavenger that the mobility of the microjets is compromised by its presence. These findings provide important references for the development of microjet engines and its related biomedical applications. Even though H₂O₂ is not compatible with living systems, this work presents an important concept to be considered when microengine motion is considered in environments

Fig. 2. The presence of uric acid in the running solution reduces the ability of catalytic microjets to move. (A) The influence of uric acid concentration on the activity of microjets (ejection of bubbles and mobility of microjet engines). (B) Influence of uric acid concentration on the velocity of the mobile microjets. Conditions: temperature of 23 °C, 3% (wt.) H_2O_2 and 1% (wt.) SDS.

containing uric acid. Considerable effort should be devoted to overcome these challenges to make full use of microjet engines in biomedical area in the future.

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Crucial Role of Surfactants in Bubble-Propelled Microengines

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ABSTRACT: Bubble-propelled autonomous microengines are expected to perform various tasks in related biomedical and environmental fields. The presence of surfactant in the environment is necessary for movement of microjets because it lowers interfacial tension required for detachment of the bubble from the microjet engine. We study the dependence of the mobility of microjets on the concentration of surfactants and show the different behaviors of microjets in the presence of anionic, cationic, and neutral surfactants. These findings have important implications on the motion of self-propelled microjet engines.

INTRODUCTION

Considerable efforts have been devoted to the field of artificial nano/microscale machines over the past decade owing to their diverse potential applications in directed drug delivery,¹ isolation of objects,^{2,3} detection of pollutants,⁴ and environmental remediation.⁵ Among diverse synthetic micromotors, chemically powered tubular microengines are particularly attractive for high propulsion efficiency^{6–8} and large towing power.^{9,10} These self-propelled microrockets have demonstrated the ability to perform a variety of tasks in different media.^{11–14} Despite the great efforts made in the search of biocompatible fuels to replace hydrogen peroxide,^{15–19} little attention has been paid to surfactants, which is another prerequisite in the motion of bubble-propelled micromotors.

Surfactants can absorb onto the interfaces of a system and alter to a marked degree the interface free energy, which is the minimum amount of work required to create or expand that interface.²⁰ The motion of microjets relies on the propulsion of the oxygen bubbles generated catalytically on the inner platinum surface. Upon adding surfactants, the surfactant molecules will absorb onto the inner surface of the microjets and decrease the interfacial free energy, thus facilitating the generation and detachment of the bubbles.^{21,22} Without surfactants, there is no obvious bubble propulsion observed for microjets. It is thus clear that surfactants play a crucial role in the motion of bubble-propelled microengines. For the motion of micromotors relying on electrophoresis and diffusiophoresis, for example, nanorods and some Janus particles, surfactants are generally not needed. As can be seen from Table 1, which showcases the types and amounts of surfactants used in the literature, the selection of surfactants types and concentrations is usually random, and the lack of systematic study is noteworthy. Here we investigated the influence of surfactants property and concentration on the motion of catalytic tubular microengines.

EXPERIMENTAL SECTION

Materials. The cyclopore polycarbonate membranes with pores of 2 μm in diameter were purchased from Whatman, USA (cat no. 7060-2511). The pores are conical in shape. Colloidal graphite (isopropanol base) was purchased from Ted Pella. (lot no. 12009-2, USA). Hydrogen peroxide (27%, lot no. 10151507) was purchased from Alfa Aesar, Singapore. Methylene chloride and ethanol were purchased from Tedia, USA. Glassy carbon electrode and Pt and Ag/AgCl/1 M KCl electrodes were purchased from CH instruments, USA. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (98+%) was purchased from Sigma-Aldrich. The platinum plating solution (lot no. 20251001) was obtained from Technic, USA. Sodium dodecyl sulfate (SDS, lot. no. 079K0335), cetyltrimonium bromide (CTAB, lot no. 089K0161), and Tween 20 (lot no. STBB2710A0) were purchased from Sigma-Aldrich. Chemicals were used as received, and the solutions were prepared using ultrapure water (18.2 M Ω cm) from a Millipore Milli-Q purification system.

Apparatus. Electrochemical deposition was carried out with a μ Autolab type III electrochemical analyzer (Eco Chemie, The Netherlands) connected to a computer and controlled by General Purpose Electrochemical Systems version 4.9 software (Eco Chemie). The deposition procedure was conducted at room temperature (23 $^{\circ}\text{C}$) using a three-electrode arrangement. A platinum electrode was utilized as a counter electrode, and Ag/AgCl was used as the reference electrode. The ultrasonication process was carried out with a Fisherbrand FB 11203 ultrasonicator, and centrifugation was carried out with a Beckman Coulter Allegra 64R centrifuge. Scanning electron microscopy (SEM/EDX) analysis was obtained with a JEOL JSM 7600F instrument. Optical microscope videos and images were obtained with a Nikon Eclipse 50i microscope. Video

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Table 1. Types and Concentrations of Surfactants Used in the Literature

authors	type of micromotors	surfactants	velocity
1. Mei et al. ¹⁰	Ti/Fe/Pt microjets	1% isopropanol and 0.005 wt % benzalkoniumchloride	80 $\mu\text{m/s}$ (5% H_2O_2)
2. Sanchez et al. ⁷	Ti/Cr/Pt microjets	0.5% (v/v) of soap (anionic tenside, amphoterie tenside, Bronopol, benzisothiazolinone, and methylisothiazolinone)	500 $\mu\text{m/s}$ (1% H_2O_2)
3. Sanchez et al. ²³	InGaAs/GaAs/Cr/Pt microjets	10% (v/v) soap (ditto)	12 $\mu\text{m/s}$ (6% H_2O_2)
4. Sanchez et al. ²⁴	Ti/Fe/Pt microjets	5% (v/v) soap (ditto)	160 $\mu\text{m/s}$ (8.75% H_2O_2)
5. Sanchez et al. ²⁵	Ti/Fe/Pt microjets	0.005 wt % benzalkonium chloride	130 $\mu\text{m/s}$ (4% H_2O_2 in 2.5% cells medium)
6. Wang et al. ⁹	PANI/Pt microjets	1.6% (w/v) sodium cholate	1410 $\mu\text{m/s}$ (5% H_2O_2)
7. Wang et al. ²⁶	PEDOT/PEDOT-COOH/Ni/Pt microjets	2% (w/v) sodium cholate	88 $\mu\text{m/s}$ (1% H_2O_2 in PBS buffer solution)
8. Wang et al. ¹¹	PAPBA/Pt microjets	1.5% (w/v) sodium cholate	40 $\mu\text{m/s}$ (5% H_2O_2 in human serum)
9. Wang et al. ¹²	Ti/Fe/Au/Pt microjets	1% (w/v) sodium cholate	85 $\mu\text{m/s}$ (7.5% H_2O_2 in 1:4 diluted human serum)
10. Wang et al. ²⁷	PEDOT/Au-catalase microjets	5% (w/v) sodium cholate	120 $\mu\text{m/s}$ (2% H_2O_2)
11. Wang et al. ³	Ti/Ni/Au/Pt microjets	0.3% (w/v) sodium cholate	125 $\mu\text{m/s}$ (3% H_2O_2 in protein solutions)
12. Wang et al. ¹⁶	PANI/Zn microjets	1.67% (w/v) Triton X-100	140 $\mu\text{m/s}$ (0.5 M HCl)
13. Wang et al. ²	Au/Ni/PANI/Pt microjets	1.25% (w/v) Triton X-100	150 $\mu\text{m/s}$ (7.5% H_2O_2 in bacteria suspension)
14. Wang et al. ²⁸	PEDOT/Pt microjets	3% (w/v) sodium dodecyl sulfate	980 $\mu\text{m/s}$ (3% H_2O_2)
15. Wang et al. ¹⁵	Al/Ga Janus motor	0.1% (w/v) Triton X-100	3000 $\mu\text{m/s}$ (water)
16. Wang et al. ¹⁷	Al/Pd Janus motor	acid: 1.25% (w/v) Triton X-100 H_2O_2 : 5% (w/v) Triton X-100 base: 1.25% (w/v) sodium cholate	36 $\mu\text{m/s}$ (100 mM HCl) 25 $\mu\text{m/s}$ (100 mM NaOH) 35 $\mu\text{m/s}$ (10% H_2O_2)
17. Pumeret al. ²⁹	Cu/Pt microjets	1 wt % sodium dodecyl sulfate	365 $\mu\text{m/s}$ (3% H_2O_2)

sequences were processed with Nikon NIS-Elements software. Contact angle was measured with CAM101 drop profile analysis device (KSV Instruments, Finland) on fresh platinum substrate.

Preparation of Cu/Pt Concentric Bimetallic Microtubes. The Cu/Pt concentric bimetallic microtubes were synthesized using electrochemical deposition procedure on a cyclopore polycarbonate template.³⁰ Colloidal graphite ink was applied on the one side of the polycarbonate template with commercial cotton swabs. A piece of flattened aluminum foil was attached to the ink immediately, which serves as the working electrode for the plating experiments. The template was assembled into a customized electrochemical deposition cell. Platinum counter electrode and Ag/AgCl reference electrode were utilized. Electrochemical deposition was carried out with μ Autolab type III electrochemical analyzer. The template was rinsed with 5 mL of ultrapure water (18.2 M Ω cm) four times, and the Cu outer layer was deposited galvanostatically at -4 mA for 450 s. The deposition solution contained 1 M CuSO₄. Consequently, after the deposition solution was removed, the template was rinsed five times with 8 mL of water. The platinum segment was electrodeposited subsequently at -4 mA for 450 s each using the commercial plating solutions. When the deposition of microtubes was finished, the electrochemical cell was disassembled and the template was washed five times with 8 mL of water each. After that, the template was ultrasonicated three times in 2 mL of ultrapure water for 3 min each time. The graphite layer was removed during the ultrasonication procedure. The template was placed in an Eppendorf tube with 2 mL of methylene chloride and ultrasonicated until the whole template was dissolved. The electrochemically deposited microtubes were collected by centrifugation at 6000 rpm for 3 min and washed repeatedly three times with methylene chloride. The solution was then washed with ethanol and water two times each and centrifuged for 3 min after each washing step. The tubes were stored in water at room temperature.

Operation of Microjets. The experiments for studying the motion of microjets were carried out in an aqueous solution containing a constant concentration of hydrogen peroxide (3 wt %). A mixture of microtubes (7 μ L), H₂O₂ (3 wt %), and various concentrations of surfactants solutions was applied on a glass slide freshly cleaned with nitrogen gas. Optical microscope videos and images were obtained with Nikon Eclipse 50i microscope. For each of the data points in figures of active microjets percentages, at least 32 measurements were taken into account. Tracking data were obtained for a time scale of 10 s from six independent running experiments to get the average speed.

Cyclic Voltammetry. All measurements were performed in 0.1 M phosphate buffer solution of pH 7.2 at scan rate of 100 mV/s. The platinum electrode was polished prior to each experiment with alumina powder and then washed thoroughly with DI water and dried with nitrogen gas to ensure the cleanliness of the electrode surface. A constant concentration of hydrogen peroxide (3 wt %) and surfactants (1 wt %) was used for stock solutions if mentioned. For the stock solutions with micromotors inside, 7 μ L of microjets was added to the stock solution and left for 1 h before measurement. For each measurement, 18 μ L of the stock solution was mixed with 2 mL of phosphate buffer solution; then, cyclic voltammograms were recorded.

RESULTS AND DISCUSSION

We have investigated the influence of anionic, cationic, and nonionic surfactants upon the motion of microjets. First, we discuss the case of anionic surfactant. Sodium dodecyl sulfate (SDS) is an anionic surfactant used in many cleaning and hygiene products. It is the most common surfactant used in nanotechnology. Despite the wide utilization in this field, little efforts has been devoted to study the influence of the SDS concentration on the motion of the microjets. As such, we first investigated if the concentration of SDS will affect the mobility of the microjets. The experiments were carried out in an aqueous solution with a fixed concentration of hydrogen peroxide (3%). As shown in Figure 1A, initially, there is a

Figure 1. Dependence of the mobility of microjets upon the concentration of SDS in the solution. (A) Influence of SDS concentration on the percentage of microjets found to be ejecting bubbles (red bar) and moving (blue bar). Note that both the running and bubbling percentages in 3 wt % SDS solution were defined as 100%. (B) Influence of SDS concentration on the average velocity of microjets. Tracking data were obtained for a time scale of 10 s from six independent running experiments to get the average speed. Conditions in all of the experiments: a temperature of 23 $^{\circ}$ C and 3 wt % H₂O₂.

marked increase in the fraction of both the microjets ejecting bubbles and exhibiting bubble-propelled motion upon increasing the SDS concentration. After reaching 0.3 wt % concentration of SDS, the mobility of microjets remains relatively constant. Meanwhile, the dependence of the average velocity of microjets on the concentration of SDS also shows the same trend (Figure 1B). This result is consistent with the theory of adsorption of surfactant at the interfaces.²⁰ The performance of the surfactant in many interfacial processes depends on its concentration at the interface. The critical micelle concentration (CMC) of SDS is $\sim$ 0.24 wt %.³¹ Before CMC, the interfacial tension decreases as the adsorption of SDS onto the microjets inner surface increases, while low interfacial tension will facilitate the generation and detachment of the bubbles. As a result, the mobility of microjets is enhanced with the concentration of SDS below CMC. The adsorption is

usually complete in the neighborhood of the CMC, and the interfacial tension will remain relatively constant. Consequently, the concentration of SDS will not have serious implications above CMC for the mobility of microjets in terms of interfacial tension. However, increasing surfactant concentration will inevitably increase the viscosity of the solution. According to the Stoke's equation, the velocity of microjets decreases with an increase in viscosity. Until 10 wt %, the adverse effect of increasing surfactants concentration is not obvious and the microjets maintain an average velocity of $\sim 365 \mu\text{m/s}$. A further increase in surfactant concentration may enhance the viscous resistance and decrease the speed of the microjets.^{18,32}

Subsequently, we proceed to investigate whether microjets will behave distinctively in the presence of different surfactants. Tween 20 is a nonionic surfactant whose stability and relative nontoxicity allows it to be used in a broad range of applications in biological techniques and sciences. Tween 20 has a relatively low CMC of 0.01 wt %.³³ Upon replacing SDS with Tween 20, the mobility of the microjets dropped dramatically, with only $\sim 20\%$ of the microjets generating bubbles and $\sim 15\%$ of the microjets exhibiting bubble-propelled motion over concentrations above CMC (Figure 2A). The velocity of the moving

Figure 2. Dependence of the mobility of microjets upon the concentration of Tween 20 in the solution. (A) Influence of Tween 20 concentration on the percentage of microjets found to be ejecting bubbles (red bar) and moving (blue bar). Note that both the running and bubbling percentages in 3 wt % SDS solution were defined as 100%. (B) Influence of Tween 20 concentration on the average velocity of microjets. Tracking data were obtained for a time scale of 10 s from six independent running experiments to get the average speed. Conditions in all of the experiments: a temperature of 23 °C and 3 wt % H_2O_2 .

microjets also suffered a great reduction to $\sim 65 \mu\text{m/s}$ due to the low frequency of bubble generation (Figure 2B). This result again proved that the mobility of microjets will not greatly change with the concentration of surfactants above CMC. Meanwhile, it posed another issue that the properties of surfactants will significantly affect the motion of microjets.

Because the behavior of microjets in Tween 20 differs greatly from that in SDS, we continue to study the motion of microjets in the presence of CTAB, a cationic surfactant. Figure 3 shows

Figure 3. Dependence of the mobility of microjets upon the concentration of CTAB in the solution. Note that both the running and bubbling percentages in 3 wt % SDS solution were defined as 100%. Conditions in all of the experiments: a temperature of 23 °C and 3 wt % H_2O_2 .

that the microjets do not exhibit any bubble-propelled motion over a wide range of concentrations below and above CMC of CTAB (0.04 wt %).³⁴ To confirm that microjets in the presence of CTAB only display insignificant Brownian motion, we calculated the mean square displacement (MSD) of microjets in 1 wt % CTAB solution and that without any surfactants. Both of the plots of MSD against time interval for microjets under these two conditions give straight lines, indicating that the insignificant motion is solely due to Brownian motion. The diffusion coefficient calculated for microjets in solution without any surfactants of $\sim 1.29 \mu\text{m}^2 \text{s}^{-1}$ is slightly larger than that calculated for microjets in CTAB solution of $\sim 0.87 \mu\text{m}^2 \text{s}^{-1}$, which is in agreement with the Stokes–Einstein equation, $D = kT/6\pi\eta r$. As the viscosity of the solution (η) increases, the diffusion coefficient (D) decreases.^{35,36}

The mobility of microjets highly depends on the bubble frequency. As shown in Figure 4, microjets display different mobility in the presence of different surfactants associated with their influence on bubble frequency. There is little difference between surface tension of SDS, Tween 20, and CTAB solutions above CMC.^{37–39} The huge difference between the mobility of microjets in the presence of different surfactants may be related to the adsorption process of surfactant molecules onto the inner platinum surface. The radical mechanism of decomposition of hydrogen peroxide on platinum surface governs that the inner walls of the microjets have some positively charged sites.⁴⁰ The adsorption of surfactants from aqueous solution to solid surface is a complicated process. For ionic surfactant adsorption onto substrate with oppositely charged sites, the surfactant adsorbs initially by ion exchange, followed by the interaction of hydrophobic chains of oncoming surfactant ions with those of previously adsorbed surfactant. Finally, adsorption in this fashion is complete in the neighborhood of CMC.²⁰ Anionic surfactant SDS can be easily adsorbed onto the positively charged inner surface of microjets due to attraction, while cationic surfactant CTAB has to overcome repulsion to adsorb onto the inner wall of microjets. As a nonionic surfactant, Tween 20 adsorbs from aqueous solution via moderate hydrophobic interaction with uncharged platinum surface. As a result, both the efficiency and effectiveness of adsorption of

Figure 4. Tracking images of microtubes in 1 wt % of (A) SDS, (B) Tween 20, and (C) CTAB solutions as well as (D) solution without any surfactants for 2 s. Scale bars indicate 20 μm . Conditions in all of the experiments: a temperature of 23 $^{\circ}\text{C}$ and 3 wt % H_2O_2 .

CTAB and Tween 20 onto positively charged inner surface of microjets are lower than that of SDS. A similar effect was observed for rolled-up tubes, where the velocity of microjets in benzalkonium chloride solution is much lower than that in other surfactant solutions.¹⁰ However, this may not be the only reason that accounts for the totally different behavior of microjets in different surfactant solutions.

The effect of salts on the reaction rate of decomposition of hydrogen peroxide has been previously reported.⁴¹ Here we studied the consumption of hydrogen peroxide for the respective cases of three surfactants using electrochemical method. The cyclic voltammograms in Figure 5 show the difference in the consumption of hydrogen peroxide for SDS, Tween 20, and CTAB. It can be seen that whereas no significant redox wave was observed for 0.1 M phosphate buffer

Figure 5. Cyclic voltammograms of H_2O_2 in surfactant solutions (SDS, Tween 20, CTAB) in the absence and presence of micromotors moving for 1 h at 23 $^{\circ}\text{C}$. Scan rate: 100 mV/s.

solution at pH 7.2 (blank), an obvious oxidation wave for H_2O_2 appeared. The consumption of H_2O_2 can be easily observed from the difference between the cyclic voltammogram of H_2O_2 solution with surfactant and that of corresponding solution, which has been left 1 h with micromotors inside. As can be seen from Figure 5, micromotors in the presence of SDS consumed the most H_2O_2 , while for CTAB, the consumption of H_2O_2 is not obvious. The rate of H_2O_2 decomposition is consistent with the phenomena previously described. However, bubble detachment will also affect the reaction rate because attached bubbles decrease the effective catalytic area of the inner platinum wall of the microjets. Therefore, it is still difficult to tell whether the effect of surfactants on the reaction rate or the difference in effective catalytic area resulted from bubble detachment accounts for the different behaviors of microjets in the presence of different surfactants. One thing is certain – different surfactants will affect the bubble frequency of microjets. Microjets generate bubbles of 2 μm radius at a rate of ~ 120 per second in SDS solution and ~ 25 per second in Tween 20 solution. For CTAB, no obvious bubbles were observed. The efficiency calculated for microjets is $\sim 1.40 \times 10^{-7}$ in the presence of SDS and $\sim 2.14 \times 10^{-8}$ in the presence of Tween 20, following the method established by Mallouk et al.⁴²

Other properties of surfactants, such as their effects on wetting ability, foamability, and foam stability, can also influence the propulsion of microjets.²¹ Surfactants can help reduce the hydrophobic nature of the Pt layer and improve the Pt wetting with the aqueous hydrogen peroxide fuel solution.²² The trend of wetting ability of running solution with different surfactants (1 wt %) and hydrogen peroxide (3 wt %) on platinum surface is in agreement with the activity of microjets in the running solution. The contact angles of running solution containing SDS, Tween 20, and CTAB on Pt surface are 36, 43, and 48 $^{\circ}$, respectively.

CONCLUSIONS

We have demonstrated the dependence of the mobility of microjets on the concentration of surfactants and the influence

of different surfactants on the motion of microjets. Upon reaching CMC, the concentration of surfactants does not have obvious effects on the motion of microjets. The mobility of microjets differs greatly in different surfactants solutions. Microjets are much more active in the presence of anionic surfactant SDS than nonionic surfactant Tween 20 and cationic surfactant CTAB. Additional work is needed toward a better understanding of the function of surfactants on the motion of microjets. Future studies on microjets should take into account choice of surfactants to achieve the optimized performance of microjets.

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Notes

The authors declare no competing financial interest.

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Article

Catalytic DNA-Functionalized Self-Propelled Micromachines for Environmental Remediation

Mercury is one of the most harmful pollutants faced by humans and wildlife. Micromachines functionalized with DNA on the surface can selectively absorb Hg(II) from water bodies. The distinctive motion element makes the micromachines a dynamic adsorption platform paving the way for next-generation self-powered nanoremediation of contaminated sites.

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HIGHLIGHTS

Microtubes with DNA
immobilized on the Au outer
surface can selectively bind to
Hg(II)

A dynamic adsorption platform
based on micromotors is
proposed

Au/Pt microtubes were prepared
by an electrodeposition method

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Article

Catalytic DNA-Functionalized Self-Propelled Micromachines for Environmental Remediation

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SUMMARY

Toward addressing mercury contamination, DNA-functionalized microtubes that can serve as the next generation of self-propelled catalytic micromachines to remove Hg(II) from aqueous solution are described. The microtubes, prepared via the electrodeposition method, are composed of an inner platinum catalytic surface for self-propulsion and a gold outer surface for functionalization with DNA. The highly specific and strong binding of Hg(II) to T-T mismatched pairs in DNA sequences confers the adsorption capability for Hg(II) on the microtubes. The efficient self-propulsion of these micromachines results in enhanced removal of Hg(II). The autonomous micromotor-based strategy provides a dynamic adsorption platform for decontamination of mercury-polluted water bodies.

INTRODUCTION

Rapid progress in nanotechnology over the past decades has opened up new horizons for addressing environmental problems. As one of the aspiring goals of nanotechnology, recent developments in catalytic autonomous micro- and nanomachines have brought a fresh approach to environmental monitoring and remediation.¹ The great potential of catalytic micro- and nanomachines to detect and remove various pollutants as well as chemical warfare agents has been demonstrated.^{2–4} Enzyme-based artificial microfish are promising for replacing live fish for monitoring heavy metals in water bodies.⁵ Diverse functionalized catalytic micro- and nanomachines have been shown to be useful for the removal and destruction of a wide range of pollutants, including oil droplets,⁶ organic contaminants,^{7,8} bacteria,^{9,10} spores,¹¹ nerve agents,¹² and so forth. Nevertheless, to date, there are few examples of the use of micro- and nanomachine platforms for the uptake of heavy metals. Self-propelled activated carbon Janus micromotors and graphene-based microtubes have been reported to be effective for the removal of various pollutants, including heavy metals, but the adsorption capacity lacks selectivity.^{13,14}

Environmental degradation is one of the largest threats we face in the world today, and it can happen in a number of ways. One major constituent of environmental degradation is the depletion of clean water that we rely on to survive. Many issues such as pollution, overpopulation, amplified urbanization, and climate changes are putting ever-increasing pressure on scarce water resources.¹⁵ Contamination from toxic chemicals threatens life on our planet. Water pollution is suggested to be one of the leading global causes of human diseases and deaths.¹⁶ Moreover, the consequences of water pollution can spread to the whole ecosystem, causing problems such as species mortality and reduction in biodiversity.¹⁷ Mercury is one of the most toxic pollutants and accumulates in both wildlife species and humans. Exposure to mercury, even at low concentrations, is reported to cause damage to the brain, kidneys, and lungs.¹⁸ As a result of human activities in the epoch of

The Bigger Picture

Self-propelled autonomous micromachines, which take chemical energy from the environment and convert it to kinetic energy, are at the forefront of nanotechnology. Great expectations have been placed on nanotechnology for innovative solutions to address challenging problems such as water pollution, a major issue threatening human health and biodiversity on Earth. There are many water pollutants, but mercury remains one of the most toxic and has received global attention. Here, we propose a micromachine-based dynamic adsorption platform for the removal of Hg(II) in an aqueous environment. The micromachines are self-propelled microtubes with immobilized DNA that can selectively bind to Hg(II). These autonomous micromachines can perform remediation tasks over long distances and operate in small narrow spaces that cannot be reached with traditional methods. Nanoremediation based on self-propelled micromachines brings new perspectives to in situ and ex situ environmental remediation protocols.

industrialization, mercury levels in the environment have notably increased over the past centuries, and alarming mercury levels are being reached worldwide as a result of the ease with which mercury travels without borders.¹⁹ Mercury pollution is a worldwide problem that needs a global solution.

The urgent need for reduction in mercury levels has led to considerable research efforts to develop new technologies and innovative solutions to detect and remove mercury from aqueous solution. Realizing the high cost and ineffectiveness of conventional methods, such as precipitation, evaporation, and ion exchange, to remove heavy-metal ions, researchers have developed different kinds of sorbents for mercury uptake. Functional materials with a large surface area, such as polymers,²⁰ hydrogels,²¹ and activated carbon,²² have been used for the removal of mercury. However, some commonly used binding sites on the absorbents, for example, thiol and amine groups,^{23,24} do not show specific selectivity toward mercury. Recent studies have found that Hg(II) can selectively mediate the generation of thymine-thymine (T-T) mismatched DNA base pairs in the form of T-Hg(II)-T complexes, which have even higher stability than adenine-thymine (A-T) base pairs.^{25,26} The interaction between Hg(II) and T-T mismatched pairs has been proved to be highly specific, and other ions do not have a similar effect.^{27,28} These findings have resulted in various Hg(II) probes and sensors with great sensitivity and selectivity toward Hg(II) over other interfering ions.^{29–31}

Compared with usual nanoremediation materials, micro- and nanomachines have the upper hand because of the distinctive motion element. The motion dimension offers not only prospective implementation methods of *in situ* and *ex situ* nanoremediation of contaminated sites but also the potential advantages of accelerated clean-up processes and reduced costs.³² Catalytic self-propelled micro- and nanomachines can carry remediation agents over long distances and conduct powerful mixing. The tiny sizes of micro- and nanomachines also allow their operation in small narrow spaces. In addition, autonomous micro- and nanomachines demonstrate great potential to combine both sensing of pollutants and environmental remediation in one platform. Here, we describe proof-of-concept efforts to use catalytic micro- and nanomachines for cleaning up Hg(II) from aqueous solution. The coupling of micromotors and DNA sequences that can selectively bind with Hg(II) offers a prospective platform for the application of catalytic micro- and nanomachines in the environmental field.

RESULTS AND DISCUSSION

Micromachine-based removal of Hg(II) from aqueous solution relies on strong and highly specific interactions between Hg(II) and T-T base pairs of single-stranded DNA. Nuclear magnetic resonance studies showed that Hg(II) binds directly to N3 of thymidine in substitution for the imino proton and cross-links two thymidine residues to form the T-Hg(II)-T base pair (Figure 1A).²⁶ Hg(II) specificity has been demonstrated for this binding, and other metal ions do not show any stabilizing effect toward the T-T mismatched pair.^{27–31} Bridging the ability of thymine-rich DNA to selective adsorb Hg(II) and attractive properties of self-propelled micromotors results in a prospective platform for diverse applications. Figure 1B illustrates on-the-move capture of Hg(II) by DNA-functionalized micromotors in polluted water. The DNA we used here is a polyT30-SH oligonucleotide that contains 30 thymine bases and a thiolated end. The self-propelled micromotor is composed of a gold outer surface for the purpose of functionalization and a platinum inner surface as the catalyst for decomposition of H₂O₂ fuel to achieve self-propulsion.

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Figure 1. Working Principle of the Micromachines

(A) Mechanism of the interaction between Hg(II) and T-T base pairs.

(B) Schematic illustration of DNA-functionalized self-propelled micromachines for the removal of Hg(II) from aqueous solution.

The micromachines were fabricated in a typical tubular shape with the use of membrane template-assisted electrodeposition, because tubular micromotors possess a number of advantages, such as high mobility, high power output, and ease of functionalization. Instead of building gold layers onto one side of the microtube surface by using physical vapor deposition methods,^{33,34} we plated a gold layer as the outer surface of the microtubes to ensure a large surface area for subsequent functionalization. A platinum layer was electrodeposited subsequently to form the inner surface of the microtubes, resulting in Au/Pt bilayer microtubes. The scanning electron microscope (SEM) images of the fabricated microtubes are shown in Figures 2A–2C. The two openings at both sides of the microtubes are in the range of 2.5–3 μm , and the length of the microtubes is around 10 μm . Figure 2C shows the top view of a microtube, and the bottom is the unremoved sputtered Ag layer. Energy-dispersive X-ray (EDX) elemental mapping showing the distribution of Au and Pt is presented in Figure 2D. The prepared microtubes are generally concentric Au/Pt microtubes.

We attached polyT30-SH oligonucleotides to the Au outer surface of the microtubes via sulfur-gold bonds. The covalent bond between gold and sulfur provides a robust but modifiable interaction, which is widely used in material science to modify and functionalize surfaces. The interaction, usually mediated through the sulfhydryl (-SH) functional group in thiols (R-SH), enables the formation of self-assembled monolayers of thiols on gold surfaces.³⁵ The microtubes were functionalized with DNA by overnight immersion in 10 μM thiolated oligonucleotides prepared in 1 $\times$ PBS buffer solution. The concentration of microtubes in the solution was $\sim 40,000$ microtubes/mL during modification. The modified microtubes with DNA immobilized on the outer surface were subsequently washed repeatedly with ultra-pure water for the removal of excess DNA. The mobility of DNA-functionalized microtubes was investigated in comparison with bare microtubes (without DNA). Because of the inhomogeneity of the pores in the membrane and uncontrollable factors in the electrodeposition process, the prepared microtubes were heterogeneous to some extent. As a result, the velocity of the microtubes was within a certain range,

Figure 2. Characterization of Prepared Au/Pt Microtubes

(A–C) SEM images of a microtube at 6,000 $\times$ magnification (A), three microtubes in a row at 5,000 $\times$ magnification (B), and the top view of a microtube at 20,000 $\times$ magnification (C).

(D) EDX elemental mapping showing the distribution of Au and Pt in the microtubes.

Scale bars represent 2 μm (A, B, and D) and 1 μm (C).

but the general trend could still be seen. The modification with thiolated oligonucleotides resulted in a slight reduction in the velocity of the microtubes. In clean water without Hg(II), bare microtubes exhibited an average velocity of 244 $\mu\text{m/s}$ at 3% H_2O_2 fuel concentration, whereas DNA-modified microtubes were self-propelled at an average velocity of 179 $\mu\text{m/s}$ (Figure 3A). We also examined the influence of Hg(II) on the propulsion of functionalized microtubes. The DNA-modified microtubes demonstrated similar velocity in clean water and Hg(II) polluted water, indicating the insignificant effect of the presence of Hg(II). Figures 3B and 3C show the propulsion behavior of functionalized microtubes in Hg(II)-polluted water. The tails of microbubbles expelled from the cavity of the microtubes sketch the trajectories of the microtubes. The continuous thrust of oxygen bubbles generated via catalytic decomposition of H_2O_2 provides effective and steady propulsion for the functionalized microtubes.

As illustrated in Figure 4A, we first investigated the ability of static DNA-functionalized microtubes to remove mercury. The same amount of bare microtubes and functionalized microtubes ($\sim 6,000$ microtubes) were placed in 2 mL of 3 ppm aqueous solution of Hg(II) respectively without adding H_2O_2 and SDS. After 20 min, the microtubes were separated by filtering through a filter membrane with 200 nm pore size. The processed solution was analyzed by inductively coupled plasma-mass spectrometry (ICP-MS). The concentration of the sample used was the average value obtained from three measurements with relative SD (RSD) below 2%. The results showed that bare microtubes had minimal influence on the concentration of Hg(II) in the solution, whereas the solution exposed to DNA-functionalized microtubes showed a reduction of 17% in the concentration of Hg(II) in comparison with the static control, which indicates the successful immobilization of DNA on the outer surface of the micromotors. Subsequently, we investigated the possibility of utilizing moving microtubes for the removal of Hg(II) from aqueous solution (Figure 4B). The adsorption of Hg(II) was performed in solution containing 3 wt % H_2O_2 and 0.3 wt % SDS. Compared with moving bare microtubes, the navigation of $\sim 6,000$ DNA-functionalized microtubes in 2 mL of polluted solution for 20 min removed 26% of the Hg(II) present in the solution. The DNA was stable under our experimental conditions at 3% H_2O_2 and 0.3% SDS, because previous electrochemical studies by Kagan et al.³⁴ demonstrated that the presence of 5% H_2O_2 and 1% surfactant had a minimal effect on the integrity of the DNA self-assembled monolayer. As opposed to static DNA-functionalized micromachines, moving functionalized micromachines showed increased removal efficiency. Both the movement of the micromachines and the continuous generation of bubbles lead to enhanced motion and

Figure 3. Motion Studies of the Micromachines

(A) Influence of functionalization with DNA and the presence of Hg(II) on the mobility of microtubes. The average velocity was calculated from ten independent motion studies. The error bars indicate the SD.

(B and C) Propulsion of DNA-functionalized microtubes in Hg(II)-polluted water in a linear way (B) and a circular way (C). Scale bars represent 20 μm.

mixing of the fluid, which results in increased remediation efficiency.^{7,36} The convection induced by bubble-propelled microtubes has been characterized by the enhanced transport of passive tracers.³⁷ In addition, compared with the concentration of micromotors (10^4 – 10^5 micromotors/mL) used in other studies for environmental remediation,^{14,36} the concentration of micromachines used in our study, $3,000\text{ mL}^{-1}$, was quite low. Because the adsorption of mercury has a positive correlation with the concentration of DNA, the remediation efficiency increases with higher concentrations of DNA-functionalized micromachines. Given the very small amount of DNA used in the process, the micromachine-based mercury-removal approach exhibits higher removal efficiency than in previous studies using DNA condensation.³⁸

Conclusion

We have presented a micromotor-based approach capable of absorbing Hg(II) from aqueous solution. This strategy is based on the specific interaction between Hg(II) and T-T base pairs in the oligonucleotides immobilized onto the external surface of the micromotors. The proof-of-concept effort demonstrated the effectiveness of using very small amounts of DNA to remove Hg(II). Compared with the corresponding static counterparts, moving micromachines displayed dynamic adsorption of Hg(II) and thus more efficient removal. These self-propelled micromachines represent an alternative solution that holds great promise for reducing mercury pollution. The platform also provides possibilities for combined sensing and remediation of mercury-polluted sites.

EXPERIMENTAL PROCEDURES

Materials

The cyclopore polycarbonate membranes with pores of 3 μm and 200 nm in diameter were purchased from Whatman. Hydrogen peroxide (35%) was purchased from Alfa Aesar. Methylene chloride and ethanol were purchased from Tedia. Pt electrodes with a diameter of 1 mm and Ag/AgCl/1.0 M KCl were purchased from CH Instruments. The gold and platinum plating solutions were obtained from

Figure 4. Studies on the Hg(II) Removal Ability of DNA-Functionalized Microtubes

(A) Static bare (control) and functionalized microtubes in Hg(II)-polluted water.

(B) Moving bare (control) and functionalized microtubes in Hg(II)-polluted water containing 3 wt % H₂O₂ and 0.3 wt % SDS.

Technic. Oligonucleotides polyT30-SH, DTT, and SDS were purchased from Sigma-Aldrich. Chemicals were used as received, and the solutions were prepared with ultrapure water (18.2 MΩ cm) from a Millipore Milli-Q purification system.

Apparatus

Electrochemical deposition was carried out with an Autolab PGSTAT 101 electrochemical analyzer (Eco Chemie) connected to a computer and controlled by NOVA software (version 1.8, Eco Chemie). The deposition procedure was conducted at room temperature with a three-electrode arrangement. A platinum electrode was utilized as a counter electrode, and Ag/AgCl/1.0 M KCl was used as the reference electrode. Sputtering was carried out with a JEOL JFC-1600 Auto Fine Coater. The ultrasonication process was carried out with a Fisherbrand FB 11203 ultrasonicator, and centrifugation was carried out with a Beckman Coulter Allegra 64R centrifuge. Optical microscope videos and images were obtained with a Nikon Eclipse Ti-E microscope fitted with a DS-Fi1c camera. Video sequences were processed with Nikon NIS-Elements software. Analysis of mercury was performed by an Agilent 7700x ICP-MS equipped with a third-generation He reaction-collision cell (ORS³) to minimize interference.

Preparation of Au/Pt Microtubes

The Au/Pt microtubes were synthesized with a modified electrochemical deposition procedure on cyclopore polycarbonate templates. Silver (~75 nm) was sputtered on one side of the polycarbonate template. Copper tape was attached to the silver-sputtered polycarbonate template, which served as the working electrode for the plating experiments. The template was then assembled into a customized electrochemical deposition cell. A platinum counter electrode and Ag/AgCl/1.0 M KCl reference electrode were utilized. Electrochemical deposition was carried out with an Autolab PGSTAT 101 electrochemical analyzer connected to a computer and controlled by NOVA software (version 1.8). A layer of gold was electrodeposited galvanostatically at −10 mA for 1,000 s. After the deposition solution was removed and

the template was rinsed with water, the platinum layer was electrodeposited subsequently at -20 mA for 1,000 s. When the deposition of microtubes was finished, the electrochemical cell was disassembled. The template was polished with $0.06\text{ }\mu\text{m}$ alumina powder for the removal of the sputtered silver and then dissolved in methylene chloride. The microtubes were collected by centrifugation at 6,000 rpm for 3 min and washed repeatedly three times with methylene chloride. The solution was then washed with ethanol and water twice each and centrifuged for 3 min after each washing step. The resulting tubes were stored in water at room temperature.

Modification of Microtubes

The immobilization of DNA on the outer surface of the microtubes was achieved by overnight immersion in $10\text{ }\mu\text{M}$ oligonucleotides in immobilization buffer solution ($1\times$ PBS [pH 7.2]). The thiol-modified oligonucleotides were treated with DTT to reduce the disulfide linkage protection before use. After immobilization, the microtubes were washed with ultrapure water and collected by centrifugation at 6,000 rpm for 3 min. The modified microtubes can be stored in immobilization buffer at 4°C .

Propulsion of Microtubes

The experiments for studying the motion of micro- and nanomotors were carried out in an aqueous solution containing 3 wt % H_2O_2 and 0.3 wt % SDS. A mixture of microtubes, SDS, and H_2O_2 was applied on a glass slide freshly cleaned with nitrogen gas. Optical microscope videos and images were obtained with a Nikon Eclipse Ti-E microscope fitted with a DS-Fi1c camera. Video sequences were processed with Nikon NIS-Elements software.

Removal of Hg(II) from Aqueous Solution

Experiments on the ability of DNA-functionalized microtubes to remove mercury were carried out in solutions with a fixed volume of 2 mL. Bare or DNA-functionalized microtubes ($\sim 6,000$ microtubes) were added to an aqueous solution of Hg(II), giving a microtube concentration of $3,000\text{ mL}^{-1}$. The final concentration of Hg(II) in all experiments was 3 ppm. For on-the-move capture of Hg(II), additional H_2O_2 and SDS were added into the solution to yield final fuel and surfactant concentrations of 3 and 0.3 wt %, respectively. The microtubes remained in the solution for 20 min, after which they were separated by filtering through a filter membrane with a 200 nm pore size.

ICP-MS Analysis of Hg(II) Concentration

The filtered samples were sent for ICP-MS analysis immediately after preparation. The calibration solutions were prepared in nitric acid and hydrochloric acid (3% and 0.5%, respectively) with Hg concentrations of 0.1, 0.5, 1, 2.5, and $5.0\text{ }\mu\text{g/L}$. High-purity nitric acid and hydrochloric acid (J.T. Baker) were used in the preparation. All solutions were prepared in vessels made of polyethylene or polypropylene and sent for ICP-MS analysis immediately after preparation. The use of He collision cells allowed 0.5% HCl to be included in the sample preparation, which ensured the formation of a stable complex $[\text{HgCl}_4]^{2-}$ to keep the mercury in solution. The plasma was operated at the highest possible temperature to maximize ionization of the Hg atoms.

AUTHOR CONTRIBUTIONS

M.P. conceived the project and supervised the studies. H.W. carried out the synthesis, functionalization, and characterization of micromachines, motion studies, and

remediation studies. B.K. performed ICP-MS analysis. H.W. and B.K. interpreted data and wrote the paper.

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