Autonomous propulsion of platinum-based catalytic micro/nanomotors

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

**AUTONOMOUS PROPULSION OF PLATINUM-BASED CATALYTIC
MICRO/NANOMOTORS**

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Abstract

This work focuses on the investigation of platinum-based catalytic micro/nanomotors, including working mechanism, design, fabrication and related characterization. Three different categorized micro/nanomotors have been investigated, and key observations can be summarized as follows:

i. A novel disk-like gold-nickel-platinum nanomotor is proposed. A bubble propulsion mechanism is employed to characterize the locomotion of the proposed nanomotor. The propulsion activities of the nanomotor are investigated at different hydrogen peroxide concentrations and different temperatures. Moreover, the magnetic effect on the propulsion of the nanomotor is also characterized. In addition, for the first time the three-dimensional propulsion of the nanomotor is characterized by using digital holographic microscope.

ii. Two different types of gold-nickel-platinum nanojets are designed. One is with singular off-center nanoengine, the other one is with dual off-center nanoengines. The self-steerable propulsion activities of these two different nanojets are characterized at different hydrogen peroxide concentrations. The results show that the nanojet with singular off-center nanoengine is able to propel forward circularly; while the nanojet with dual off-center nanoengines can move forward linearly.

iii. Another novel micro/nanomotor (platinum-nickel-SU-8 microrocket) is proposed. The microrocket has an eccentric nanoengine. A circularly self-steerable propulsion

mechanism is proposed for characterizing the autonomous locomotion of the microrocket. The circularly steerable propulsion of the microrocket is characterized at different hydrogen peroxide concentrations. The results reveal that the speed of the microrocket increases with the increment of hydrogen peroxide concentrations.

These observations prove the fabrication feasibility of newly designed micro/nanomotors. The wide applications of these micro/nanomotors can be expected.

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List of Abbreviations

a : effective length of particle
ATP: adenosine tri-phosphate
ADP: adenosine di-phosphate
Au: gold
AC: alternate-current
AAO: alumina
Ag: silver
Al: aluminum
 Al_2O_3 : alumina
Ar: argon
BSA: bovine serum albumin
Cu: copper
CNT: carbon nanotube
ConA: concanavalin A
Cr: chromium
CCD: charge-coupled device
 $\text{C}_3\text{H}_6\text{O}$: acetone
D: diffusivity/diffusion coefficient
DAG: dynamic shadowing growth
DOX: doxorubicin hydrochloride
DI: deionized
DNA: deoxyribonucleic acid
e: electron
E: electric field
EDX: energy-dispersive X-ray
EDS: energy dispersive spectrometry
 f : coefficient of friction
Fe: iron
 F_{drag} : aqueous drag force
 F_{drive} : driving force

GLAD: glancing angle deposition
GO: graphene oxide
 H^+ : proton
 H_2O : water molecule
 H_2O_2 : hydrogen peroxide
Hz: Hertz
 H_2SO_4 : sulfuric acid
HMDS: hexamethyldisilazane
HAMLET: human alpha-lactalbumin made lethal to tumor cells
IMF: ion motive force
 k : catalytic reaction rate constant
 k_b : Boltzmann constant
 K_B : Boltzmann constant
K: Kelvin
KOH: potassium hydroxide
LbL: layer-by-layer
 L : traversed distance
 m : mass of one single micro/nanomotor
mT: millitesla
MEMS: micro-electro-mechanical systems
MIP: molecularly imprinted polymer
MSN: mesoporous silica nanoparticle
MAE: Mechanical and Aerospace Engineering
nm: nanometer
Ni: nickel
NaOH: sodium hydroxide
NP: nanoparticle
NIR: near infrared
 Na^+ : sodium ion
NEMS: nano-electro-mechanical systems
 N : number of oxygen bubbles
NTU: Nanyang Technological University

O₂: oxygen molecule
pN: pico Newton
P_i: phosphate molecule
Pt: platinum
PDMS: polydimethylsiloxane
PC: polycarbonate
PVD: physical vapour deposition
PANI: polyaniline
PPy: polypyrrole
PEDOT: polyethylenedioxythiophene
PMMA: polymethyl methacrylate
PSS: polystyrene sulfonate
PAH: polyallylamine hydrochloride
PLGA: poly-lactic-co-glycolic acid
PPyPSS: polypyrrole polystyrene sulfonate
PAPBA: polyaminophenylboronic acid
PECVD: plasma enhanced chemical vapour deposition
 P_{O_2} : pressure inside O₂ bubbles
 P_{atm} : atmospheric pressure
 Q : torque
 r : radius of particle
rpm: revolution per minute
Re: Reynolds number
 R : radius of micro/nanomotor
RTA: rapid thermal annealing
RIE: reactive ion etching
 R_c : propulsion radius
 S : O₂ evolution rate
SEM: scanning electron microscopy
Si: silicon
SiO₂: silicon dioxide
 t : elapsed time

- t_{diff} : diffusion time
T: absolute temperature
TiO₂: titanium dioxide
Ti: titanium
TEM: transmission electron microscopy
 T : absolute temperature
UV: ultraviolet
 v : velocity of object
 v_1 : joint velocity
 v_2 : velocity of micro/nanomotor at detaching moment
 v_3 : velocity micro/nanomotor after detachment
 v_0 : velocity of detached O₂ bubble
 v_B : Brownian motion speed
 x : diffusion distance
 α : Langmuir adsorption constant
 γ : surface tension of solution
 ρ : density of solution
 μ : viscosity of solution
 ξ : zeta potential
 ϵ : permittivity of medium
 ω : angular velocity
 μm : micrometer
 Δm : mass of each individual detached O₂ bubble
 Δt : average bubble growth time
 ΔP : pressure difference
2-D: two-dimensional
3-D: three-dimensional

1

Introduction

This chapter describes the background of the proposed research and explains the existing limitations in this research field. Motivations and objectives for this research project are listed in detail. The outline of this thesis is also presented in this chapter.

1.1 Background and Motivation

Movement is crucial for all different types of lives living in both macroscopic and micro/nanoscale environments. In nature, living organisms have been decorated with intelligent and efficient biomolecular motor proteins through millions of years of biological evolution and employ them in numerous biological processes and cellular activities [1-20]. For instance, bacteria are able to propel themselves forward with the aid of rotary flagellar nanomotors, as shown in Figure 1-1A [21]. Moreover, linear biomolecular motor proteins such as kinesin, myosin and dynein, are capable of harvesting energy from hydrolysing adenosine triphosphate (ATP) into adenosine diphosphate (ADP) and phosphate molecule (Pi) for lateral motion along corresponding tracks, as shown Figure 1-1B [22]. In addition, biological cells are equipped with intelligent biomolecular engines (ATPase) which are demanded to generate biological fuel ATP, as shown in Figure 1-1C [23].

Micro/nanomotors are micro/nanoscale devices, which have the ability to convert chemical energy into mechanical force or movement [24]. Evolution bestows biomolecular motor proteins with fascinating abilities to harness energy from living environments for autonomous movement *in vivo*, as described above. Inspired by the fantasy of naturally occurring motor proteins, researchers paid great attentions into artificial micro/nanomotors in the past decades. In particular, guided by pioneering contributions of Sen and Mallouk's team and Ozin's group, current work mainly focuses

Meanwhile, micro/nanomotors have a wide variety of applications, including cargo towing, water cleaning, chemical sensors and biomedical applications, *etc* [27-50]. Advanced forms of micro/nanomotors may advance and benefit other research. However, designing and powering micro/nanomotors can be considered a significant challenge in today's nanotechnology research. Hence, it is important to review the state of the art of artificial micro/nanomotors and improve them in this research field.

The research of artificial self-propelled micro/nanomotors has rapidly developed in

last few decades. Several advanced developments and excellent contributions had been done in this field. Although the bright future of this research field can be expected, some major existing challenges still are remained to be solved. The design, fabrication and characterization of functional micro/nanomotors require some innovative approaches and ideas to realize. Fabricating micro/nanomotors with individual parts, smartly and precisely controlling motors are still extremely challenging. Hereby, a complete understanding of the physical and chemical mechanisms is necessary. To achieve better control of micro/nanomotors in the future, an industrial level of functional micro/nanomachinery could be realized. Despite the significant advances in micro/nanomotors, challenges still remain to find specific relevant applications, such as biologically compatible fuels, *etc.*

1.2 Special Aspects in Micro/Nanomotor Regime

Synthetic micro/nanomotors can be considered as attractive micro/nanodevices, due to their fundamental relevance as well as their functionality in versatile applications, e.g. ranging from drug delivery to environmental remediation [51-53].

Micro/nanomotors operate in a regime where the physical laws are significantly different from those in which we live. At the micro/nanomotor scale, the effect of viscous drag and Brownian randomization has a determinant effect on motion [4]. The Reynolds number (Re) is a dimensionless quantity which relates to the ratio of the inertial forces to the viscous forces and is given by the equation

$$Re = \frac{\rho va}{\mu} = \frac{\text{Inertial force}}{\text{Drag force}} \quad (1-1)$$

where, ρ is the density of the fluid, v is the velocity of the particle, a is the characteristic length of the particle, and μ is the dynamic viscosity of the medium. A high Re number corresponds to a system where inertial forces dominate over viscous forces, such as the macroscopic world; while at the smaller length scales of bacteria and micro/nanomotors, where the viscous forces largely dominate, the Re number is low. For instance, a person swimming in water has a Re number of about 10^4 , while a swimming bacterium has a Re number of 10^{-4} [2]. The length scale of objects is shown in Figure 1-2.

Figure 1-2. Length scale map of objects.

At low Re number, inertia can no longer sustain motion, as any motile force applied is immediately counteracted by the viscous drag. The system reaches its terminal velocity quickly and contains no momentum. Hence, micro/nanomotors have to be designed to create instantaneous (constant) force to generate continuous motion. The movement of these motors also has to be nonreciprocal. The conventional back and

forth movement that is used to generate motion with high Re numbers can no longer be applied into micro/nanomotors, as no net directional motion can result from it, as summarized in the ‘scallop theorem’. Therefore, to induce motion, time reversal symmetry has to be broken, which adds significant complication to the design of micro/nanomotors.

On the other hand, Brownian motion is the random motion of the particles caused by the thermally driven collisions of solvent molecules with the colloidal particles. Brownian diffusion is characterized by the diffusion coefficient D , which is defined by the Stoke-Einstein relationship and expressed by the equation

$$D = \frac{K_B T}{6\pi\mu r} \quad (1-2)$$

where, K_B is the Boltzmann constant, T is the absolute temperature, μ is the viscosity of the medium, and r is the radius of the particle [3]. The diffusion coefficient is related to the thermal energy of the system and the size of the particle. As the particle size decreases, Brownian motion significantly interferes with the directionality of the motors, thereby leading to random motion and reorientation. Therefore, remote control over the motion of micro/nanomotors is an important aspect to consider when designing artificial micro/nanomotors.

1.3 Objectives

Developing micro/nanomotors which can realize autonomous propulsion, characterizing their detailed physical and chemical properties, and investigating the

respective propulsion performance compared with others are the key aspects in this thesis.

To achieve the above-mentioned goals, efforts shall be devoted to address two primary challenges: the fabrication strategy and the novel shape of micro/nanomotors. These have necessitated the following several major objectives of micro/nanomotors (nanomotor, nanojet and microrocket) to be explored:

- ❖ Firstly, to characterize the propulsion of nanomotor, a disk-like gold-nickel-platinum (Au-Ni-Pt) nanomotor model is proposed. A bubble propulsion mechanism is employed to characterize the locomotion of the proposed nanomotor. After fabrication, the propulsion of the nanomotor will be investigated at either different hydrogen peroxide (H_2O_2) concentrations or different temperatures. Furthermore, the magnetic effect on the propulsion of the nanomotor needs to be investigated. In addition, for the first time the three-dimensional (3-D) trajectory of the nanomotor also demands to be characterized.
- ❖ Afterwards, to characterize the autonomous propulsion of nanojet, two different types of Au-Ni-Pt nanojets are designed, one has singular off-center nanoengine, the other one has dual off-center nanoengines. The self-steerable propulsions of these two different nanojets are characterized at different H_2O_2 concentrations. The results demonstrate that the nanojet with singular off-center nanoengine is able to propel forward circularly, while the nanojet with dual off-center nanoengines can

move forward linearly.

- ❖ Finally, to characterize the autonomous propulsion of microrocket, a novel type of micro/nanomotor (platinum-nickel-SU-8 microrocket) is proposed. The microrocket is with an eccentric nanoengine. A circularly self-steerable propulsion mechanism is proposed for characterizing the autonomous locomotion of the microrocket. The circularly steerable propulsion of the microrocket can be characterized at different H_2O_2 concentrations. The results will reveal the correlation between the speed of the microrocket and the increment of H_2O_2 concentrations.

1.4 Organisation of Thesis and Research Roadmap

This thesis is organized into six chapters. The layout of this thesis is schematically shown in Figure 1-3. Following Introduction in Chapter 1, Chapter 2 reviews the state-of-the-art micro/nanomotors. Various propulsion mechanisms, fabrication methods, propulsion controlling methods and applications of the reported micro/nanomotors are summarised, critiques are assessed and solutions are proposed to overcome the limitations.

Chapter 3 presents a type of disk-like Au-Ni-Pt nanomotor. A bubble propulsion mechanism is employed to characterize the locomotion of the disk-like Au-Ni-Pt nanomotor. The proposed nanomotor is fabricated by a layer-by-layer (LbL) deposition method based on the micro-electro-mechanical systems (MEMS) technology. Moreover,

the propulsion of the fabricated nanomotor is investigated either at different H_2O_2 concentrations or at different temperatures. In addition, for the first time the 3-D trajectory of and the magnetic effect on the propulsion of the nanomotor are presented.

Chapter 4 focuses on two different shaped Au-Ni-Pt nanojets, one is with singular off-center nanoengine, the other one is with dual off-center nanoengines. The self-steerable propulsion of these two different nanojets is characterized at different H_2O_2 concentrations. In conclusion, the nanojet with singular off-center nanoengine is able to propel forward circularly, while the nanojet with dual off-center nanoengines can move forward linearly.

Figure 1-3. Representation of the layout of this thesis.

Chapter 5 introduces a novel micro/nanomotor: Pt-Ni-SU-8 microrocket. The

proposed microrocket has one eccentric nanoengine. The circularly self-steerable propulsion mechanism is proposed for characterizing the autonomous locomotion of the microrocket. The self-steerable propulsion of the microrocket is characterized at different H_2O_2 concentrations. The results reveal that the speed of the microrocket increases with the increment of H_2O_2 concentrations and the microrocket are capable of propelling forward circularly.

Chapter 6 draws conclusions of the accomplished work in this research project and highlights the major contributions of this research and gives perspectives for future work.

1.5 Conclusion

This chapter describes the background of this research work, and explains the special aspects in micro/nanomotor regime. Motivations and objectives for this research project are listed in detail. The organisation of this thesis is also outlined.

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2

Literature Review

This chapter introduces the state of the art of artificial micro/nanomotors fuelled by hydrogen peroxide. The propulsion mechanisms, fabrication methods, propulsion controlling methods, and applications of these artificial micro/ nanomotors developed in the past years will be extensively reviewed and discussed.

2.1 Introduction

Inspired by naturally occurring motor proteins, researchers paid great efforts onto artificial micro/nanomotors in the past decade [1-3]. There still exist some essential issues for developing micro/nanomotors in micro and nanoscale regime, while micro/nanomotors have applications in many fields such as cargo towing, water cleaning, chemical sensors and biomedical applications, *etc* [4-10]. Hence, it is much beneficial for us to review the state of the art of artificial micro/nanomotors. In this chapter, the published works on the propulsion mechanisms, fabrication methods, propulsion controlling, and applications of artificial self-propelled Pt-based micro/nanomotors fuelled by H_2O_2 will be summarized and discussed.

2.2 Propulsion Mechanisms

Whitesides and colleagues in 2002 reported the motion of a millimetre-scale object, which was composed of a thin polydimethylsiloxane (PDMS) plate mounted with a piece of Pt coated porous glass filter using a stainless steel pin, as shown in Figure 2-1 [11]. The assembled object was immersed into H_2O_2 solution. Pt catalyses H_2O_2 decomposition to create oxygen (O_2) bubbles detaching from the surface, which in turn induced a recoil force to propel the object moving forward. This is the foundation in this research field. In micro/nanoscale regime, only asymmetric particles can realize autonomous propulsion. Based on this, researchers focused on two aspects: shape and material compositions of micro/nanomotors for breaking the symmetry; and various

types of micro/nanomotors were invented. Meanwhile, there were different mechanisms proposed to explain the propulsion phenomena, depending on the shapes (e.g. wires, rods, Janus spheres and tubular jets) and material compositions of micro/nanomotors.

Figure 2-1. A) Schematic of a self-propelling object. A thin plate (circa 1-2 mm thick and 9 mm in diameter) was fabricated from PDMS in a desired shape, and specified faces were rendered hydrophilic by oxidation in a plasma formed in air. A $2 \times 2 \text{ mm}^2$ piece of porous glass filter (covered with Pt by an electron beam evaporation) was mounted on the PDMS piece with a stainless steel pin [11]. B) A diagram illustrating self-assembly by capillary interactions [11].

2.2.1 Dielectrophoresis propulsion

In the past decades, a variety of micro/nanomotors have been designed to exploit the concept of dielectrophoresis propulsion, especially micro/nanowires, rods and Janus spheres. Unlike ordinary electrophoresis, these micro/nanomotors do not respond to an external electric field. They generate a local electric field through chemical gradients and move in response to this self-generated electric field.

Electrophoresis describes the movement of micro/nanoscale particles in a fluid. In dielectrophoresis, if a micro/nanoparticle would realize autonomous self-propulsion, the micro/nanoparticle must contain at least two different metals and acts as self-contained electro-chemical cell. For instance, a micro/nanorod is composed of Pt and Au, Au serves as the cathode and Pt is the anode, as shown in Figure 2-2 [12].

Figure 2-2. Schematic representation of dielectrophoresis (bipolar electrochemical) mechanism for the propulsion of a Au-Pt micro/nanomotor in the presence of H_2O_2 . The mechanism involves an internal electron flow from one end to the other end of the motor, along with the migration of protons in the double layer surrounding the motor [12].

The oxidation of H_2O_2 at the Pt side (anode) of the rod generates positively charged protons (H^+) and negatively charged electrons (e^-). The generated protons migrate along the double layer surrounding the rod and electrons internally migrate along the rod from the Pt side to the Au side (cathode) of the rod, thus H_2O_2 can be converted into water (H_2O). The continuous chemical reactions lead to a net flow of electrons from the anode to the cathode as well as the migration of protons to cathode, producing a proton

gradient along the axis of the rod. The electron flow generates a negatively charged rod that responds to the gradient by moving forward to the proton rich environment previously occupied by Au.

In self-electrophoresis, the charged microparticles migrate in a self-generated electric field resulting from an asymmetric distribution of ions. The velocity v of the particle is related to the electric field (E), zeta potential (ζ) of the particle, viscosity (μ) and permittivity (ϵ) of the medium, as shown following

$$v = \frac{\zeta \epsilon E}{\mu} \quad (2-1)$$

2.2.2 Diffusiophoresis propulsion

Self-diffusiophoresis is a propulsion phenomenon in which the movement of particles is induced by a concentration gradient of the reaction products. This propulsion mechanism is more commonly employed in spherical Janus micro/nanomotors, as shown in Figure 2-3 [13, 14]. In this system, the catalyst (Pt) is located at one side of the micro/nanomotor, the reaction products (H_2O and O_2) preferentially accumulate at the site of the catalyst. Hence, a concentration gradient is generated along the surface of the micro/nanomotor. As the reaction products reach a critical point, the local concentration is high and the products start to diffuse away, this diffusion generates a force leading to the movement of the micro/nanomotor.

2.2.3 Interfacial tension induced propulsion

Surface tension gradients along an interface can cause an imbalance of forces and further generate flow, which is known as the “Marangoni effect”. This propulsion mechanism has been employed to explain the propulsion of the micro/nanomotors, and the model was firstly reported by Crespi, Mallouk and Sen, as shown in Figure 2-4 [15]. As H_2O_2 is decomposed at the Pt side of Au-Pt nanorods to produce H_2O and O_2 , leading to an interfacial tension created near the surface of Pt is low due to a larger quantity of O_2 generated. The surface tension difference between the Pt side and the Au side generates a force to thrust the micro/nanomotor propelling.

Figure 2-3. Schematic representation of a micro/nanomotor moving under the diffusiophoresis propulsion mechanism [13, 14].

This model suggests that the velocity v of micro/nanomotors is linearly proportional to the surface tension of the solution, as shown following

$$v = \frac{SR^2\gamma}{\mu DL} \quad (2-2)$$

where, S , R , γ , μ , D , and L are the O_2 evolution rate, micro/nanomotor radius, surface tension of solution, viscosity of solution, diffusion coefficient and length of micro/nanomotor, respectively.

Figure 2-4. Schematic diagram of a Pt-Au nanorod showing the dimensions used in the calculation of interfacial forces [15]. The parameter f is the length ratio of Pt.

2.2.4 Self-acoustophoresis propulsion

One of the potential applications of micro/nanomotors is their utility in biomedicine and diagnostics, there is a demand to develop propulsion mechanisms that can be biocompatible. Ultrasound operates in a range of frequency above 20 kHz, which is biocompatible [16]. Thus, ultrasound is a promising technique for propelling micro/nanomotors (wires/ rods and tubular jets) in biomedical applications. The first autonomous micro/nanomotor propelled by ultrasound was reported by Sen's group in 2012, as shown in Figure 2-5 [16]. In this system, metallic microrods are suspended in water in an acoustic chamber. A vertical standing wave levitates the particles to a plane at the midpoint of the cell where the pressure is a minimum. In that plane the metal microrods exhibit axial motion at speeds up to 200 m/s in water. The particles also form

patterns in the nodal plane resulting from nodes and anti-nodes within the plane. The composition of the microrods was observed to significantly affect their movement, with only metal microparticles showing fast axial motion.

Figure 2-5. Asymmetrically shaped metallic microrods are activated in an ultrasonic standing wave at MHz frequency through a self-acoustophoresis mechanism [16].

2.2.5 Thermophoresis propulsion

Temperature gradient could introduce the motion of micro/nanoparticles (micro/nanowires, rods and Janus spheres). This phenomenon is called thermophoresis, or the ‘Soret effect’. Recently, micro/nanomotors propelled by self-generated temperature gradient have been investigated, as shown in Figure 2-6.

Jiang *et al.* in 2010 demonstrated self-thermophoresis at the single particle level

Au nanowires subjected to elevated temperatures were found to travel significantly faster than those at room temperature. For example, an average speed of 45 $\mu\text{m/s}$ was observed for nanowires at 65 $^{\circ}\text{C}$ compared to 14 $\mu\text{m/s}$ at 25 $^{\circ}\text{C}$. The speed increasing could be attributed to the temperature dependency of the electrochemical process and the reduction in the solution viscosity. The application of heat pulses is a highly reversible process, after combined with magnetic guidance enables a more advanced temporal and spatial control, with the capacity to manipulate both the speed and direction.

2.2.6 Bubble propulsion

Bubble propulsion is probably the most commonly investigated mechanism in the field of micro/nanomotors, which can be suitable for any shapes of motors as long as the motors are decorated with catalysts. The motion of the motors is created by the detachment of micro-sized bubbles from the decomposition of fuel catalysed by the catalyst. The most extensively reported examples of bubble-propelled micro/nanomotors are those decorated with Pt as a catalyst to decompose H_2O_2 into H_2O and O_2 bubbles, as shown in Figure 2-7[19, 20].

Bubble propulsion arises from the spontaneous decomposition of a fuel catalysed by a catalyst into micron-sized gas bubbles whose releasing from the micro/nanomotor's surface generates a recoil force to drive the motion of the motors in the direction away

from the catalyst. These motors, which range in size from a few micrometres to hundreds of micrometres, can realise powerful movement with considerable speed. In bubble-propelled micro/nanojets, Solovev and colleagues reported that the velocity of the micro/nanojets was linear to the product of the bubble radius and the frequency, with the deviations at large values attributed to the potential collisions between bubbles, which diminished the distance travelled from the bubbles inside the tube and limits the releasing stage. They concluded that the dynamics of micro/nanojets is affected by the geometry, viscosity of the medium, and the fuel composition.

Figure 2-7. Examples of bubble propelled micromotors. A) Schematic representation of a tubular micro/nanomotor moving under the bubble propulsion mechanism [19]. B) Janus Pt-SiO₂ spheres moving in H₂O₂ [20].

2.3 Fabrication Methods

Artificial micro/nanomotors could provide a significant advance in the field of

miniaturized devices. However, a major challenge in artificial micro/nanomotor research is the fabrication of such tiny devices with high quality and reliability. Depending on the intended applications, different fabrication strategies must be taken into account, since each specifically shaped micro/nanomotor demands a specialized fabrication technique as well as determines the possible propulsion mechanism. The rapid development of nanotechnology has resulted in diverse strategies and techniques for the fabrication of micro and nanoscale motors. The objective of this section is to highlight various approaches to the fabrication of micro/nanomotors. The fabrication techniques and the factors that ought to be considered in the design of micro/nanomotors, including shapes, compositions and distributions of materials as well as functionalization. By reviewing the progress that has been made in the fabrication of artificial micro/nanomotors during the past decade, we intend to illustrate the opportunities and challenges facing fabrication and provide perspectives for the development of new methods.

2.3.1 Template-assisted electrochemical deposition

Electrochemical deposition is a process that applies external electric current to deposit materials and enables the synthesis of arbitrary 3-D geometries with different materials ranging from metals to polymers, resulting in the widespread applications of this fabrication technique in nanotechnology. Electrochemical deposition can be

conducted without the requirements of high-cost instruments and harsh working environments. Therefore, micro/nanostructures with various dimensions can be fabricated using this method, especially the micro/nanowire, micro/nanorod and tubular micro/nanoengines.

Template-assisted electrochemical deposition, as shown in Figure 2-8, utilizes the pores of a membrane template to synthesize the desired tubes and wires comprising of different materials [21]. Each pore of the template functions as a reactor in which the desired structure is synthesized. Membrane templates commonly used in the synthesis of micro/nanomotors are porous alumina (AAO) membranes and tracketched polycarbonate (PC) membranes. Depending on the chemistry of the pore wall and the properties of the material, the micro/nanomotors can be either solid or hollow. Membrane template-assisted electrodeposition offers a powerful and relatively low-cost method for preparing micro/nanowires, micro/nanorods and tubular micro/nanoengines.

A layer of silver (Ag) or Au is first deposited on one side of the membrane using physical vapour deposition (PVD) to serve as the working electrode. The membrane is then assembled in a Teflon plating cell with flat aluminum (Al) foil placed against the metal layer to serve as a conductive contact for subsequent electrodeposition. Usually, a sacrificial layer of copper (Cu) or Ag is first deposited, followed by sequential deposition of different desired metals. The Ag or Au backing and the sacrificial layer

are removed by mechanical polishing or chemical etching. By dissolving the alumina (Al_2O_3) membrane in sodium hydroxide (NaOH) solution, the nanowire motors can be released and collected after successive rinsing and centrifugation.

Figure 2-8. Membrane template-assisted electrochemical deposition of micro/nanomotors: (a) deposition of Au or Ag backing on the membrane template, (b) electrochemical deposition of the sacrificial layer, (c) sequential electrochemical deposition of desired components, and (d) removal of the backing and sacrificial layer and dissolution of the membrane [21].

The Wang's and Pumera's research groups combined electroplating methods widely utilized in the fabrication of nanowire-based micro/nanomotors with the bubble-propelled performance of tubular microjets, as shown in Figure 2-9 [22-27]. Two geometries (either cylindrical or conical) can be obtained, entirely depending on the geometry and type of porous template (either PC or AAO). In addition to many metals, the combination of polyaniline (PANI), polypyrrole (PPy), or poly(3,4-ethylenedioxythiophene (PEDOT) polymers with Pt produces catalytic microjets. Moreover, the wall can be tailored with molecularly imprinted polymers (MIPs) so that

selective recognition cavities can be implemented for the selective isolation of biomolecules.

Figure 2-9. Examples of micro/nanomotors fabricated by template-assisted electrochemical deposition. A) Electrodeposited Ag–Au/Pt and B) Au/Pt–CNT nanomotors in H_2O_2 [22, 23]. C, D) Polycarbonate membrane-assisted preparation and SEM images of conical PANI/Pt microtubes [24]. E) Preparation procedure of flexible metallic nanowires with polyelectrolyte hinges after membrane template electrodeposition [25]. F, G) Anodized aluminum oxide (AAO) membrane-assisted preparation and SEM images of segmented microtubes [25]. H) SEM image of a hinged nanowire [26]. I) SEM image of a Au/Agflex/Ni nanomotor with flexible central silver segment [27].

2.3.2 Physical vapour deposition

Physical vapour 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 vapour 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 vapour deposition

processes are sputtering and electron beam evaporation. Sputtering is a technique that creates vapour by bombardment of the target by ionized gas, typically argon (Ar), whereas electron beam evaporation relies on an electron beam to evaporate atoms from the target into the gaseous phase. In both techniques, the resulting vapour phase is subsequently deposited onto the surface of the substrate.

Physical vapour deposition has been shown to be an effective fabrication method in micro/nanomotors. Compared with templated-assisted electrochemical deposition, physical vapour deposition has some advantages, such as the ability to deposit a wide range of materials, less fabrication processes, easier to operate, and more complicated geometries of micro/nanomotors can be fabricated. According to the deposition angles, there are two categories: conventional physical vapour deposition and dynamical shadowing growth. In conventional physical vapour deposition, the substrate is placed parallel to the target and the vapoured metal flux is deposited almost vertically onto the substrate. Dynamic shadowing growth (DAG) or glancing angle deposition (GLAD) is a physical vapour deposition strategy in which the vapour is deposited onto a substrate at an oblique angle.

Posner and co-workers demonstrated the synthesis of a bimetallic spherical motor relying on the electrophoretic mechanism for propulsion (Figure 2-10A) [28]. First, the microspheres were half-coated with Au using sputter coater. Subsequently, they were re-suspended in water and deposited again with random orientation, which was repeated

seven or eight times until the entire surface was coated with Au. 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 vapour deposition can be used to fabricate not only spherical Janus motors but also many other motors with various structures. Valadares and co-workers proposed a catalytic dimer composed of a silica sphere and a Pt sphere. 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 Pt particle connected to the silica sphere, as shown in Figure 2-10B [29].

On the basis of the self-shadowing effect and substrate rotation during deposition of an incident vapour, 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. To obtain an asymmetric bimetallic coating, a substrate with silica microbeads was rotated to a polar angle after deposition of an adhesive titanium (Ti) layer and a Au layer, the subsequent Pt deposition left some of the Au layer exposed, as shown in Figure 2-10C [30]. The motion behaviors can be adjusted by varying the exposed area of the Au layer. Lee and coworkers fabricated 30 nm Pt/Au Janus nanomotors by GLAD of Au under fast substrate rotation onto an array of Pt nanoparticles produced by block copolymer micelle lithography, as shown in Figure 2-10D [31]. Both of the bimetallic Janus motors

rely on the self-electrophoresis mechanism for propulsion.

Figure 2-10. A) Schematic of fabrication of bimetallic Janus micromotors by conventional physical vapour deposition [28]. B) Formation of sphere dimers via thermal annealing [29]. C) Preparation of asymmetric Pt/Au-coated catalytic micromotors by glancing angle deposition [30]. D) Preparation of electrophoretic Pt-Au Janus nanoparticles by glancing angle deposition [31]. E) Fabrication procedure of L-shaped Si/Pt nanorod motors by glancing angle deposition [32]. F) Synthesis of catalytic micromotor consisting of a spherical silica colloid with a TiO₂ arm coated asymmetrically with Pt [33]. G) SEM image of a Pt-Ag-Au shell micromotor fabricated by glancing angle deposition [34].

He and colleagues reported the fabrication of rotary Si/Pt nanorods, L-shaped Si/Pt, and Si/Ag nanorods where they firstly 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. The L-shaped backbone was obtained by a high speed

of azimuthal rotation of the substrate in the middle of oblique angle deposition, as shown in Figure 2-10E [32]. 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 TiO_2 arm with asymmetric Pt coating. 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, as shown in Figure 2-10F [33]. With oblique vapour direction and rotating substrate, the deposition layer is able to cover a much larger area of the sphere templates than that with conventional vapour deposition. A bubble-propelled Pt-Ag-Au shell micromotor with a smaller opening was fabricated through glancing angle deposition and subsequent wet chemical etching, as shown in Figure 2-10G [34].

2.3.3 Rolled-up nanotech

By incorporating an engineered strain gradient in the deposited thin membranes, the membranes are able to form into the desired shapes when released from the substrate. The rolled-up nanotechnology pioneered by Schmidt and co-workers employs strain engineering to prepare micro/nanotubes from deposited films. A pre-stressed 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 vapour deposition process to ensure accurate positioning and tube integration on a single chip. Suitable control of the substrate temperature and deposition rate, together with the stress evolution during deposition, creates the strain gradient needed for the rolling process.

Figure 2-11. 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 [35, 36]. B) Rolled-up microtubes with graphene oxide as an external layer [37]. C) Reversible rolling and unrolling of thermoresponsive polymeric Pt microtubes [38]. D) Particle-assisted rolling process of nanomembrane upon a thermal dewetting treatment [39].

As shown in Figure 2-11A, the deposited nanomembrane rolls into a microtube once released from the substrate by removal of the sacrificial layer [35, 36]. 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. 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 the top layer 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.

Because of the complex fabrication procedures and the 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 GO nanosheets (Figure 2-11B) [37]. 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. The tissue-based microjets can exhibit highly efficient bubble propulsion in the presence of H_2O_2 . Zhao and colleagues described the formation of Pt microtubes by selective removal of the poly(methyl methacrylate) (PMMA) sacrificial layer under the sputtered Pt layer or by H_2O_2 -assisted lift-off of the Pt layer deposited directly on a glass substrate. A transmission electron

microscopy (TEM) grid template was used to 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 and colleagues developed a flexible thermoresponsive polymeric microjet based on the reversible folding/unfolding of the polymer at reduced and elevated temperatures (Figure 2-11C) [38]. 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 and his partners 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. As illustrated in Figure 2-11D, a layer of Pt was deposited above a pre-strained bilayer of $\text{SiO}_2/\text{TiO}_2$ or Si/Cr on a sacrificial PMMA layer [39]. In this treatment, 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.

2.3.4 Advanced assemblages

The aforementioned fabrication methods: template-assisted electrochemical deposition, physical vapour deposition (PVD) and rolled-up nanotech, are effective methods for fabricating micro/nanomotors. However, to achieve more complex geometries, the assembly technique must be developed. The construction of devices with multiple individual tiny elements is an extremely challenging task. The assembly approach plays an essential role in micro/nanofabrication. It is a strategy that combines miniaturized components to form a desired device. The unique properties of the assembled structures make them useful for the fabrication of micro/nanomotors. In addition to employing self-assembling of materials to synthesize the desired devices, desired elements can be embedded into micro/nanomotors by encapsulating them into materials.

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 tiny 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 H_2O_2 solution. Taking advantages of low cost, simplicity, and versatility, the LbL assembly, primarily utilizing the electrostatic interaction between oppositely charged species, has been widely used to prepare various multilayer materials.

He's group firstly developed the combination of colloid template-assisted LbL assembly with a microcontact printing method to prepare platinum nanoparticles (Pt NPs) asymmetrically coated autonomous Janus capsule motors, as shown in Figure 2-12A [40]. The silica particles as templates were alternatively immersed into negatively charged polystyrene sulfonate (PSS) solution and positively charged polyallylamine hydrochloride (PAH) solution to form one polyelectrolyte bilayer. After 5 bilayers were deposited, the as-assembled particles were dispersed onto a glass substrate to form a monolayer that was then printed with a PDMS stamp loaded with a drop of dendritic Pt NPs suspension. The Pt NPs partially coated hollow Janus capsule motors were obtained after etching the templates with hydrofluoric acid. Polymer stomatocytes that can entrap Pt NPs within their nanocavities were described by Wilson and collaborators, as shown in Figure 2-12B [41]. 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. H_2O_2 can access the catalytic Pt NPs through controlled opening of the stomatocytes to generate thrust and directional motion.

Figure 2-12. Schematic illustration of various types of controlled self-assembled micro/nanomotors [40]. A) Preparation process of PtNPs-functionalized Janus capsule motors. B) Selective and controlled entrapment of Pt NPs inside artificial stomatocytes during shape transformation [41].

2.4 Controlling Methods

The control of micro/nanomotors is essential for meeting various requirements in practical applications. The precise propulsion control of micro/nanomotors is leading to advances in practical applications, thus it is quite critical to put forward the controlling strategies for micro/nanomotors. In the past years, scientists have realized the propulsion control of micro/nanomotors by using different methods.

2.4.1 Magnetic control

Applying external magnetic field is the most common method used to direct and steer the micro/nanomotors. The pre-determined movement of micro/nanomotors can be realized by incorporating a ferromagnetic or paramagnetic part that can be magnetized by magnetic field. Depending on the shapes of micro/nanomotors, the magnetic part can be introduced by either electrodeposition or PVD. The suitable used magnetic material candidates in micro/nanomotors are Ni and Fe.

Inspired by the work of Mallouk, Wang *et al.* showed a multifunctional nanomotor with three segments (Au–Ni–Au), which was propelled by ultrasound and steered by the magnetic field. A concavity was also adopted at the end of the Au segment by the sphere lithography technique to achieve shape asymmetry. The interaction between the medial magnetic Ni segment and the magnetic field resulted in a predetermined and controlled motion of the nan-motors. The Ni segment was also able to pick up and transport magnetic beads along a preset trajectory, as shown in Figure 2-13A [42].

Magnetic orientation has been proved to be significantly useful to achieve desirable directionality of controlled assembled motors. Sputtering a magnetic layer on one side of the motors is widely used for Janus capsule motors. The catalase-functionalized Janus capsule motor was sputtered with a Ni layer with a thickness of 5 nm before the deposition of Au. Such biocatalytic Janus capsule motors were able to swim in cell media in the presence of H₂O₂ fuel, and were steered by an external magnetic field

toward the targeted HeLa cells, as shown in Figure 2-13B [43]. It should be noted that the applied external magnetic field is exclusively utilized to guide the movement directionality of motors, and is insufficient to trigger the movement of motors by magnetic attraction.

For electrodeposited nanowires and micro/nanotubes, a Ni 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, as shown in Figure 2-13C [44]. Because the scale of the electrodeposited Ni segment was smaller 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 microchannel networks was demonstrated by Burdick et al [23].

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

properties. 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, as shown in Figure 2-13D [45].

Regarding 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. Magnetized Fe-containing microtubes were demonstrated to be able to selectively capture and transport paramagnetic beads in the absence of an external magnetic field. The ability of a Pt Janus particle to transport cargo has been demonstrated by Sanchez and fellows. To achieve better control of the motion of catalytic Janus motors and the cargo transport process, magnetic caps consisting of $[\text{Co/Pt}]_5$ multilayers were introduced into the structure via PVD. 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, as shown in Figure 2-13E [46]. Precise control of magnetic Janus particles is further demonstrated by sorting particles between channels in microchip devices.

Figure 2-13. Micro/nanomotors controlled by magnetic field. A) Schematic illustration of an Au–Ni–Au metal alloy propelled by ultrasound and steered by the magnetic field [42]. B) Magnetically steered movement of Janus capsule motors toward targeted HeLa cell sheets [43]. C) SEM image of Pt/Ni/Au/Ni/Au nanowire [44]. D) SEM/energy-dispersive X-ray (EDX) elemental analysis of Au/Ni/Pt nanotube [45]. E) Scheme illustrating magnetic steering of Janus micromotors [46]. F) Remote control of micro/nanojets by magnetic field [47].

The individual control of microjets in a closed-loop manner and 3-D motion control were the next steps to be taken. Recently, Sanchez’s and Misra’s research groups led to publications on the accurate closed-loop control of microjets [47]. The authors demonstrated precise point-to-point closed-loop control by using weak magnetic fields

(2 mT). Another study demonstrated precise control when a flow was applied against and along the direction of the microjets. An electromagnetic system consisting of two sets of orthogonal arrays of electromagnetic coils with an iron core in conjunction with two microscopic systems was used to control the motion of microjets in 3-D space, as shown in Figure 2-13F [47]. Microjets overcome vertical forces, such as buoyancy forces, interaction forces with O₂ bubbles, and vertical flow, thus they are capable of diving downwards and swimming upwards relative to reference positions.

2.4.2 Acoustic control

Ultrasound not only provides energy for the propulsion of micro/nanomotors but also offers an alternative strategy for controlling self-propelled motors. Using ultrasound to guide micro/nanomotors and rapid “stop/go” switching of micro/nanomotors in response to “on/off” of ultrasound are investigated.

Figure 2-14. A) Scheme illustrating steering of acoustically propelled nanowire toward a HeLa cell [48]. B) Scheme illustrating ultrasound-modulated bubble propulsion of chemically powered microtubes [49].

The movement direction of nanomotors can be reversed by tuning the power of the ultrasound field. Fast and reversible transition between aggregated and free-moving

states of nanomotors in H_2O_2 was observed in response to switching between on and off ultrasound states, as shown in Figure 2-14A [48]. The generation of bubbles can be disrupted by the ultrasound field. Wang *et al.* reported reversible control of the movement of PEDOT/Ni/Pt microengines by tuning the applied voltage of the external transducer which generates the ultrasound field. The authors reported extremely fast changes in the motor speed (< 0.1 s) and reproducible on/off activations that were faster than other reported methods for stopping the motion of microjets, as shown in Figure 2-14B [49].

2.4.3 Electric control

Metal micro/nanomotors can display controllable rotation due to rotary torque in an electric field provided by applying alternating current voltages to multiple electrodes, as shown in Figure 2-15A [50]. In addition, by using alternating current electric fields applied to strategically designed microelectrodes, the movement of metal micro/nanomotors 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, as shown in Figure 2-15B.

2.4.4 Light control

Using the light to control the motion of micro/nanomotors was also studied. For example, Solovev and collaborators demonstrated the control of microjets by using a

white light source as shown in Figure 2-16A [51]. This process was mediated through illumination of the fuel solution above Pt-patterned Si surfaces, which induces a local decrease in the H_2O_2 and surfactant concentration. Although white light could be used to switch off the propulsion of the microjets, shorter wavelengths were observed to suppress the generation of microbubbles faster than longer wavelengths. The phenomenon can be reversible, thus a non-active microjet is activated by dimming the light source. The on/off process is, however, not immediate as it requires a few seconds to completely stop or to acquire a constantly maximum speed.

Figure 2-15. Rotation of micro/nanomotors by alternating current voltages applied to multiple electrodes: A) schematic representation of experimental setup of quadrupole electrodes and B) images of free (right) and one end fixed (left) rotating Au nanowires [50].

Figure 2-16. A) Microengine's propulsion controlled by light [51]. B) NIR light-switchable movement of NIR propelled polymer multilayer rockets [52].

He and colleagues recently reported NIR light-switchable “on/off” motion of gold nanoshell functionalized polymer multilayer rockets, as shown in Figure 2-16B [52]. Application of NIR light irradiation rapidly provides a thermal gradient that enables reversible propulsion of the Au nanoshell-functionalized polymer multilayer rockets. The rockets display on/off/on cycles in connection to a modulated NIR irradiation, along with go/stop/go movements. The directional movement of the rockets were stopped as the NIR irradiation is ‘off’, and resumed upon switching on the NIR light. Accounting for the straight movement behavior of NIR-propelled polymer multilayer rockets, the on/off NIR switching achieves the precisely predefine trajectory of the polymer multilayer rockets. Additionally, the rockets were highly durable and were sustained with negligible damage under 30 times of NIR irradiation.

2.4.5 Thermal control

Thermal control of the propulsion of artificial micro/nanomotors was proved to be feasible for both micro/nanorods and microtube motors. The speed of Pt-Au nanorods was substantially increased upon exposure to elevated temperatures. Similar phenomena were found for bubble-propelled microtubes, which have been employed to compensate the effect of reducing the fuel level.

The temperature of the solution can be controlled by two Peltier elements in connection with a DC power supply placed underneath the sample containing microjets.

By heating the system to a physiological temperature, microjets increase their efficiency and are propelled at extremely low concentrations of H_2O_2 , as shown in Figure 2-17 [53, 54]. In addition, soft micromotors composed of flexible thermo-responsive polymeric microjets can reversibly fold and unfold in an accurate manner in response to changes in the temperature of the solution in which they are immersed, thereby allowing them to rapidly start and stop multiple times in response to the radius of curvature accordingly. The use of stimuli-responsive materials would be ideal for future designs of smart micro/nanomotors.

Figure 2-17. Micro/nanojet's propulsion controlled by temperature [53, 54].

2.4.6 Chemical control

The motion of self-propelled micro/nanomotors can be regulated by tuning the fuel

level or chemical stimuli. In the presence of fuel concentration gradient, micro/nanomotors 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 micro/nanomotors. In addition to fuel concentration, the motion of micro/nanomotors is influenced by the presence of certain other chemicals. For example, the motion of Au/Pt nanomotors was shown to be dramatically accelerated upon addition of silver ion due to the under-potential deposition of silver on the nanomotors, which leads to differences in surface and catalytic properties. Hydrazine is another chemical stimulus demonstrated to be effective to speed up the motion of Au/Pt-CNT nanomotors. For bubble-propelled micro/nanomotors, surfactants are of great significance to the mobility of motors, because they can facilitate bubble generation and detachment.

Solovev *et al.* showed that the generation of large microbubbles from small ensembles of microjets produced a capillary force and a chemophoretic attraction force that pulled other microjets into the swarm. A more sophisticated experiment was reported by Baraban *et al.*, who presented a controllable way of studying the chemotactic behavior of two types of micro/nanomotors-Janus motors and tubular microjets-in microfluidic channels. Both types of motors move towards the gradient of the fuel without the influence of capillary forces, as shown in Figure 2-18 [55].

Figure 2-18. Micro/nanomotor's motion controlled by chemical gradient in microfluidic channel [55].

2.5 Applications

There are many current and potential applications, due to the great advances in motion control, cargo-towing force and lifetime of artificial micro/nanomotors. The wide range of potential applications of micro/nanomotors covering different fields requires specific functionalization strategies in each kind of application. Herein, the functionalization of micro/nanomotors for four main classes of applications is presented as follows: cargo transport, environmental remediation, chemical sensors and biomedical applications.

2.5.1 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 corresponding transportation. An overall process of how to fabricate

micro/nanomotors and use them to transport cargo molecules has been shown in Figure 2-19 [56].

Figure 2-19. Aptamer-functionalized micro/nanomotors for selective binding, transport, and release of a protein cargo [56].

For the transportation of magnetic cargoes by magnetic micro/nanomotors, the cargoes can simply be attached to the motors by magnetic attraction. Transportation of drug-loaded, magnetic poly(D,L-lactic-co-glycolic acid) (PLGA) microparticles has been demonstrated with both chemically propelled, as shown in Figure 2-20A [57-59], and magnetically driven micromotors through magnetic attraction. 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 *et al.* demonstrated that a polypyrrole (PPy) segment introduced to a nanowire via

electropolymerization, which could attach to oppositely charged polystyrene amidine cargo through electrostatic interaction, as shown in Figure 2-20A. A photo-chemically stimulated cargo drop-off strategy was proposed for nanowires loaded with cargoes via electrostatic interaction. An additional silver segment in a nanowire will dissolve rapidly in the presence of H_2O_2 , chloride ions, and ultraviolet (UV) light, resulting in drop-off of the cargo.

Garcia-Gradilla and colleagues described that the addition of a negatively charged polypyrrole polystyrene sulfonate (PPyPSS) segment to an ultrasound-propelled nanowire can serve as a pH-sensitive carrier for positively charged drugs via electrostatic interaction. 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 Au segment with a large surface area. 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 reported.

Xuan *et al.* led to the synthesis of self-propelled Janus nanomotors with a diameter of 75 nm. The method of preparation is illustrated in Figure 2-20B [60]. Spherical mesoporous silica nanoparticles (MSNs) were synthesized by using a base-catalysed sol-gel method. Then, MSNs were spread on a Si wafer to form a monolayer and

subsequently coated with evaporated Cr and Pt. A brief sonication led to the Janus MSNs becoming dispersed in a solution of the anticancer drug doxorubicin hydrochloride to load the cargo, and subsequent mixing with 1 mgmL⁻¹ egg phosphatidylcholine containing 1% folic acid led to encapsulation.

Figure 2-20. A) Examples of the transport of cargo using solid micro/nanorods [57-59]. B) Fabrication procedure for Janus spherical micro/nanomotors, drug loading, lipid bilayer functionalization, and drug release (DOX = doxorubicin hydrochloride) [60]. C) Selective binding and transport of biological analytes and cells by functionalized microjets [61]. D) Direct optical visualization of pick-up, transport, and delivery of *E. coli* bacteria and polymeric drug-carrier spheres [62]. E) In-chip immunoassays for in situ capture and transport of target proteins [53]. F) Selective recognition of monosaccharides for capture and release of yeast cells [64].

The Wang's research group demonstrated a great capability of microtubular motors

for the selective capture, transport and isolation of different target analytes of biological relevance. They bio-functionalized the outer walls of microtubes with ss-DNA, aptamers, antibodies and lectin receptors, thus the isolation modes of nucleic acids, cancer cells, proteins and bacteria could be demonstrated in Figure 2-20C [61]. The authors made use of roll-up microtubes with Au layers for thiolmodification and template-assisted microjets with polymer walls.

Campuzano and colleagues functionalized Au/Ni/PANI/Pt micromotors with Concanavalin A (ConA) to enable selective capture of pathogenic bacteria from fuel-enhanced real samples, as shown in Figure 2-20D [62]. The pick-up, transport, and delivery events were observed by optical microscopy. The transport of pathogenic bacteria by magnetic polymeric drug carriers might represent the basis of an attractive motion-based theranostics strategy. In related work, the same group later functionalized synthetic catalytic micromotors with antibodies to enable in-chip immunoassays, as shown in Figure 2-20E [63]. Kuralay *et al.* created poly(3-aminophenylboronic acid) (PAPBA)/Ni/Pt tubular micromotors that selectively recognize monosaccharides, which were able to capture and release of yeast cells, as shown in Figure 2-20F [64].

2.5.2 Environmental remediation

One of the principal environmental applications of micro/nanomotors is the adsorption of contaminants in water. Remediation agents can 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, as shown in Figure 2-21A [65]. Wang *et al.* illustrated the employment of PEDOT/Pt microtubular motors to boost the degradation of chemical threats, as shown in Figure 2-21B [66]. In brief, the oxidation of an organophosphate nerve agent by H_2O_2 was accelerated by the presence of the self-propelled micromotors, which contributed to an efficient mixing of the treated aqueous solution without the need for external mechanical stirrers.

Figure 2-21. A) Degradation of organic pollutants by employing multifunctional Fe/Pt micromotors in H_2O_2 solutions [65]. B) Accelerated oxidation of organophosphate nerve agents by H_2O_2 by using micromotors as active mixers [66]. C) Capture of oil droplets by alkanethiol-modified microtubes [67]. D) absorption and capture of oil, enabled by a superhydrophobic-modified outer layer [67].

Surface modifications of micro/nanomotors with a hydrophobic layer could also 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, as shown in Figure 2-21C [67]. The same group also functionalized the rough external gold layer of microengines with long chains of self-assembled monolayers to generate a superhydrophobic absorbent layer for oil capture, as shown in Figure 2-21D [67].

2.5.3 Chemical sensors

The use of micro/nanomotors as chemical sensors is based on the fact that the swimming speed of micro/nanomotors can be transformed into an analytically useful signal. The interaction of certain compounds in the sample with the catalytic sites of micro/nanomotors is evaluated from the alteration of their swimming speed and is related to the concentration of an analyte in solution as shown in Figure 2-22. Although the field is still in its infancy, the use of micro/nanomotors for chemical sensing may have a number of advantages over conventional either electrochemical or optical sensors, such as selectivity, sensitivity, immunity to electrical interferences, operation in a wireless manner, and only requiring a minute amount of sample. In the past few years, several research groups reported the capability of micro/nanomotors to detect heavy metals, inorganic electrolytes present in blood, organic compounds such as

dimethyl sulfoxide (Figure 2-22A) [68], uric acid, blood proteins such as bovine serum albumin (BSA), γ -globulin, and glucose oxidase enzymes, amino acids containing thiol groups, for example, cysteine, serine, and methionine (Figure 2-22D) [71], peptides such as glutathione, and DNA (Figure 2-22A).

García and colleagues reported the first antibody-decorated tubular microengines, which were designed to capture and transport target proteins between different microfluidic chambers. Catalytic polymer/Ni/Pt microengines were bio-functionalized with antibodies targeting IgG protein, as a model protein, in order to achieve a micromotor-based immunoassay offering “on-the-fly” capture and isolation/sorting capabilities, as shown in Figure 2-22B [69]. The immunocomplex can be easily visualized through optical microscopy by using an antigen/antibody labelled with a polymeric sphere tracer. This novel work is highly selective and eliminates time-consuming washing steps, simplifying and accelerating the overall immunoassay procedure. Taking advantage of these features, Yu *et al.* exploited antibody-functionalized AuNP/PANI/Pt micromotors to perform rapid “on-the-fly” sandwich immunocomplexes targeting carcinoembryonic antigen. The operation takes 5 minutes with measuring threshold of $1\text{--}1000\text{ ng mL}^{-1}$. In addition, labelling the captured proteins with microscopic particles showing different sizes and shapes facilitates multiplexed analysis of proteins, as proved by Vilela and colleagues (Figure 2-22C) [70]. On the other hand, the aforementioned vortex effect triggered by the micromotors

motion not only promotes the mass transfer of the target toward the functionalized microjet surface (i.e. “on-the-fly”), but also assists the mass transfer of the target molecule within the matrix of a sample solution toward a sensing surface, where the bio-receptor is located and the target is expected to be selectively attached, as shown in Figure 2-22E [72].

Figure 2-22. A) Detection of Ag-tagged nucleic acid, which alters the motion of the micro/nanomotors [68]. B) Antibody-decorated micromotor for protein detection [69]. C) Micromotor-based multiplexed immunoassay via different microscopic tracers [70]. D) Effect of the concentration of DMSO, cysteine, and serine on the swimming speeds of the microtubular motors [71]. E) Microarray immunoassay assisted by microengines [72].

2.5.4 Biomedical applications

The pioneering micro/nanomotors provide considerable promise for biomedical applications, as shown in Figure 2-23 [73]. Here we outline some important advances of micro/nanomotors in the biomedical field.

Micro/nanojets have proven to be capable of drilling into soft tissues and biomaterials. Rolling-up thin nanomembranes asymmetrically can lead to sharp edges being engineered. Nanojets were self-propelled and externally guided towards fixed cancer cells and embedded in their interior, as shown in Figure 2-24A [74]. However, the toxicity of the H_2O_2 fuel used for the propulsion results in the cells undergoing apoptosis after short periods. Therefore, other environmentally friendly sources of motion are urgently needed to replace H_2O_2 . Magnetic actuation can be used as an alternative to the propulsion. Conical microtubes powered by an external rotating magnetic field were placed onto liver tissue and drilled into it for long periods, as shown in Figure 2-24B [75]. After releasing the microtube from the biomaterial, a micrometer-sized hole was observed by SEM, as shown in Figure 2-24C [75]. Ultrasonic waves can also induce the motion of micro/nanomotors, as shown in Figure 2-24D) [76] and E) [77]. Bio-functionalized nanowires moved by ultrasound have been used for bio-sensing and the first results of magnetic guidance towards cells have been reported. Mallouk *et al.* reported the internalization of a nanowire-based motor inside living cells, as shown in Figure 2-24D. Developing biocompatible fuels and materials for artificial

micro/nanomotors or the use of non-invasive external actuated motors may pave the way for biomedical applications of micro/nanomotors in the near future.

Figure 2-23. Categories of biomedical applications of micro/nanomotors, including sensing and isolation, drug delivery, nanosurgery, biomedical imaging [73].

Figure 2-24. A) Catalytic nanojet drilling of a fixed cancer cell [74]. B) SEM image of a magnetic microtube drilling into pig liver tissue, and C) hole after removing the microtube [75]. D) Nanorods inside living HeLa cells. a) A HeLa cell with multiple nanorods inside. b) Subcellular structures (a few are indicated by arrows) can be seen

interacting with active accoustic motors inside a HeLa cell. c) Two vesicular structures in a HeLa cell containing many active but crowded accoustic motors [76]. E) Preparation and propulsion of perfluorocarbon-loaded microbullets (left), computer-generated representation (middle) and images of a microbullet penetrating a tissue after an ultrasound pulse (right) [77].

2.6 Summary

In this chapter, the previously reported artificial micro/nanomotors fuelled by H_2O_2 are summarized. In detail, the propulsion mechanisms, fabrication methods, propulsion controlling methods, and applications of these artificial micro/nanomotors developed in the past years are reviewed. Despite the significant and fast advances in micro/nanomotors, challenges such as specific applications and smart controlling still remain to be solved. In addition, advanced structure design and fabrication methods are needed. In the following three chapters, newly designed micro/nanomotors will be presented in detail.

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3

Gold-Nickel-Platinum Nanomotor

This chapter mainly introduces a disk-like gold-nickel-platinum nanomotor. A bubble propulsion mechanism is employed to characterize the locomotion of the proposed nanomotor. Moreover, experiments are conducted to investigate the correlation between propulsion performance and concentrations of hydrogen peroxide and working temperatures. In addition, the three-dimensional trajectory of and the magnetic effect on the propulsion of the nanomotor are also investigated.

3.1 Introduction

Evolution bestows biomolecular motor proteins with the fascinating capability to harvest energy from surrounding environments for autonomous functions *in vivo* [1-8]. Inspired by naturally occurring molecular nanomotors, researchers paid extensively great attentions to artificial nanomotors in the past decade [9-12]. They designed and fabricated nanostructures, which had the ability to mimic the biomolecular nanomotors existing in living bodies.

The aforementioned artificial nanostructures coated with Pt in H_2O_2 solution are capable of propelling forward. To date, there are several mechanisms such as self-electrophoresis [13], interfacial tension [10] and self-diffusiophoresis [14], to elaborate the aforementioned propulsion phenomena. These mechanisms mainly focused on the chemical reaction process of the decomposition of H_2O_2 to explain the locomotion of the nanostructures, less attention has been paid to momentum change. In this chapter, a disk-like nanomotor consisting of tri-metallic segments: non-catalytic Au, magnetic Ni, and catalytic Pt is designed. A bubble propulsion mechanism originated from momentum change, generated by the detachment of the O_2 bubbles from the Pt-surface, is proposed to elaborate the propulsion of the disk-like Au-Ni-Pt nanomotor. On the other hand, the electrochemical deposition and rolled-up technique have been exploited to fabricate the hollow cylindrical and conical nanomotors with high complexity, but both methods need much higher skills for operation [15, 16]. Meanwhile, the design

and fabrication of the engineered micro and nanomotors is still considered an extraordinary challenge in nanotechnology nowadays. Thus, long-term aims are to develop and fabricate catalytic nanomotors in a low-cost and mass-production manner, as well as suitable of applying in bio-sensing [17], environmental remediation [18] and drug delivery [19]. Herein, the disk-like Au-Ni-Pt nanomotor is fabricated using a high-efficiency layer-by-layer (LbL) deposition method based on the nano-electro-mechanical systems (NEMS) technology. The propulsion of the nanomotor dispersed into H_2O_2 solution either with different concentrations or at different temperatures is experimentally characterized, revealing that the speed of the nanomotor increases with the increment of H_2O_2 concentration and the temperature of the solution. The nanomotor can autonomously propel forward either in a linear or in a circular way. Furthermore, the propulsion direction of the nanomotor is steered by external magnetic field. In addition, the 3-D propulsion of the nanomotor is characterized using holographic technique.

3.2 Bubble Propulsion of Gold-Nickel-Platinum Nanomotor

The newly designed nanomotor, including the structure, size and material composition, is shown in Figure 3-1. The nanomotor is composed of three different metals: Au, Ni, and Pt. These metals are shaped as a concentric disk with 8 μm in diameter. The thicknesses of Au-, Ni- and Pt-disks are 200, 100 and 300 nm, respectively. In this design, Pt is used as a catalyst for the decomposition of H_2O_2 into

both H₂O and O₂ molecules [20]; Au is used as the non-catalyst and purposely to build asymmetric structure for ensuring autonomous propulsion in the micro and nanoscale regime; Ni is magnetic material for steering the propulsion using external magnetic field. As reported in reference 21 and 22, the propulsion direction of a Ni-contained nanomotor can be controlled by external magnetic field.

Figure 3-1. Schematic diagram demonstrating the structure, size and material composition of the disk-like Au-Ni-Pt nanomotor. The proposed nanomotor is composed of three layers: 200 nm thick Au (yellow color), 100 nm thick Ni (black color) and 300 nm thick Pt (white-gray color).

The autonomous propulsion of the disk-like Au-Ni-Pt nanomotor in diluted H₂O₂ solution is induced through the detachment of O₂ bubbles from the Pt-surface, as illustrated in Figure 3-2. In general, the H₂O₂ decomposition can be described as

where, Pt represents the platinum [9-12]. Herein, H₂O₂ is firstly adsorbed onto the

surface of Pt, then is decomposed into H_2O and O_2 bubbles [20].

Before adding H_2O_2 into DI water, the nanomotor is stationary. After adding H_2O_2 , O_2 bubbles are generated and detached from the surface of Pt. According to the Momentum Conservation Law and the Momentum Theorem, a recoil force F'_{drive} is produced to initiate and accelerate the propulsion of the nanomotor, as shown in Figure 3-2. At steady state, the total recoil force F_{drive} is equal to the viscous drag force F_{drag} undergoing the nanomotors in aqueous solution, thus the Au-Ni-Pt nanomotor reaches a constant velocity of v .

Figure 3-2. Schematic diagram of the disk-like Au-Ni-Pt nanomotor's propulsion mechanism. Momentum change induces a recoil force F_{drive} for the propulsion of the Au-Ni-Pt nanomotor due to the detachment of one single O_2 bubble. v_1 , v_2 and v_3 denote the joint velocity of the Au-Ni-Pt nanomotor- O_2 bubble system before the detachment of the O_2 bubble, velocity of the nanomotor at the detaching moment and after the detachment of the O_2 bubble, respectively. v_0 represents the original velocity of the detached O_2 bubble. At steady state, $F_{drive} = F_{drag}$, the nanomotor reaches a constant velocity of v .

In general, H_2O_2 catalysed by Pt can decompose into H_2O and O_2 bubbles. During the H_2O_2 decomposition, O_2 bubbles are firstly generated at the surface of the Pt and subsequently detached from the Au-Ni-Pt nanomotor. Figure 3-2 demonstrates two states of an integrated Au-Ni-Pt nanomotor- O_2 bubble system. At the beginning, O_2

bubbles are attached to the surface of the Au-Ni-Pt nanomotor, called as ‘growing state’, in which the nanomotor and O₂ bubbles have a joint velocity of v_1 . After a short period of time of Δt , O₂ bubbles are detached from the Pt-surface, called as ‘detaching state’. At this state, the nanomotor and O₂ bubbles have a same velocity of v_2 . After the detachment of O₂ bubbles, the nanomotor has a velocity of v_3 , while the O₂ bubbles have a distinct velocity, named v_0 . According to the Momentum Conservation Law, one can obtain the following equations

$$(m+\Delta m)v_2 = mv_3 - \Delta m v_0 \quad (3-2)$$

$$m(v_3 - v_2) = \Delta m(v_2 + v_0) \quad (3-3)$$

where, m is the mass of one single Au-Ni-Pt nanomotor, Δm represents the mass of each individual detached O₂ bubble. According to the Momentum Theorem, the driving force F'_{drive} induced by single detached O₂ bubble can be expressed as

$$F'_{drive} = m \frac{v_3 - v_2}{\Delta t} = \Delta m \frac{v_2 + v_0}{\Delta t} \quad (3-4)$$

After a short period of time of Δt , if N O₂ bubbles are detached from the Pt-surface of the Au-Ni-Pt nanomotor, thus the total driving force F_{drive} can be described as

$$F_{drive} = N F'_{drive} = N \frac{\Delta m}{\Delta t} (v_2 + v_0) \quad (3-5)$$

At steady state, the Au-Ni-Pt nanomotor reaches a constant velocity of v , namely $v_1 = v_2 = v_3 = v$. Hence, one can obtain

$$F_{drive} = N \frac{\Delta m}{\Delta t} (v + v_0) \quad (3-6)$$

3.3 Fabrication of Gold-Nickel-Platinum Nanomotor

The fabrication of the nanomotor has been carried out using the NEMS technology developed in the Micromachines Lab, School of Mechanical and Aerospace Engineering (MAE) at Nanyang Technological University (NTU), Singapore.

To fabricate the structure, a 4-inch silicon (Si) wafer was firstly immersed into sulfuric acid (H_2SO_4) at 120°C to clean the surface for 30 minutes. The Si wafer surface was then deposited with a layer of 1 μm thick silicon dioxide (SiO_2) by plasma enhanced chemical vapor deposition (PECVD) at 300°C for 40 minutes. To improve photoresist adhesion on oxides, SiO_2 -coated Si wafer was transferred into a prime oven for hexamethyldisilazane (HMDS) coating to form a strong chemical bond onto the surface for 2 minutes. Furthermore, a layer of 1.5 μm thick photoresist AZ 7220 was subsequently spin-coated on the SiO_2 surface at 5000 revolutions per minute (rpm) for 30 seconds. Afterwards, the pattern on the glass photomask was exposed onto the photoresist 7220-coated Si wafer using 365 nm wavelength UV light for 4 seconds. The pattern was developed in an AZ 300MIF developer solution for 1 minute (step 1 in Figure 3-3). Thereafter, the patterned Si wafer was coated with a layer of 200 nm thick Au by magnetron sputter for 9 minutes (step 2 in Figure 3-3), following coated with a layer of 100 nm thick Ni via e-beam evaporation for 15 minutes (step 3 in Figure 3-3). Finally, the wafer was coated with a layer of 300 nm thick Pt by magnetron sputter for 9 minutes (step 4 in Figure 3-3). The Au-Ni-Pt nanomotors were formed on the SiO_2

surface by lift-off using acetone to etch off photoresist (step 5 in Figure 3-3). The nanomotors were released from the wafer by reactive ion etching (RIE) and potassium hydroxide (KOH) etchant etching off 1 μm thick SiO_2 (step 6 in Figure 3-3). The fabricated Au-Ni-Pt nanomotors were stored in a glass bottle for experiments.

Figure 3-3. Schematic diagram depicting the disk-like Au-Ni-Pt nanomotor's fabrication steps. The nanomotor was fabricated using an efficient layer-by-layer deposition method based on the NEMS technology, including PECVD, photolithography, sputtering, e-beam evaporation, lift-off, RIE and KOH etching.

3.4 Characterization of Gold-Nickel-Platinum Nanomotor

3.4.1 Energy dispersive spectrometry analysis of gold-nickel- platinum nanomotor

The representative scanning electron microscopy (SEM) image of the fabricated disk-like Au-Ni-Pt nanomotor on Si wafer surface is shown in Figure 3-4(a). To validate the material composition of the nanomotor, the energy dispersive spectrometry (EDS) analysis was conducted, and the corresponding results are shown in Figure 3-4(b). From the EDS analysis results, it has been found that the nanomotor contains three different metals Au, Ni, and Pt, the corresponding weight percentages of these three metals are 94.23%, 0.39% and 5.38%.

Figure 3-4. (a) SEM image of single Au-Ni-Pt nanomotor on Si wafer substrate. (b) EDS analysis results of Au-Ni-Pt nanomotors, the EDS results shows the fabricated nanomotors are made of three different metals: Au, Ni, and Pt.

3.4.2 Observation of oxygen bubble generation

The experimental set-up, as shown in Figure 3-5, was established for investigating the propulsion of the nanomotor. The fabricated Au-Ni-Pt nanomotors dispersed into

aqueous H_2O_2 solution were dropped on the surface of a glass slide using a pipette. The prepared sample was transferred onto a microscope stage. Afterwards, the propulsion of the nanomotors was captured by a microscope equipped with a camera. Finally, the propulsion process was recorded by a computer installed with a video recording software.

Figure 3-5. Microscopy set-up for characterizing and recording the autonomous propulsion of the disk-like Au-Ni-Pt nanomotor in aqueous H_2O_2 solution. The set-up was mainly composed of a microscope, sample stage, sample, camera and computer.

The Au-Ni-Pt nanomotors were suspended in DI (deionized) water without the presence of H_2O_2 , no O_2 bubbles were generated. Once H_2O_2 was added into DI water, O_2 bubbles were initially generated at the surface of Pt, and were detached from the

nanomotor after a short period of time. The diameters of the detaching O₂ bubbles were approximated to be 23 μm (Figure 3-6(a)). The results are consistent with those described by Wang and Wu [23].

3.4.3 Gold-nickel-platinum nanomotor's propulsion at different hydrogen peroxide concentrations

The Au-Ni-Pt nanomotor was immersed into H₂O₂ solution with four different concentrations to characterize the propulsion. A recoil force induced by the detachment of O₂ bubbles thrust the nanomotor propelling forward either in a linear or in a circular way. The time lapses for the linear and circular propulsion of the nanomotor in 12% H₂O₂ solution are shown in Figure 3-6(a) and (b), respectively.

3.4.3.1 Gold-nickel-platinum nanomotor's Brownian motion speed

In micro and nano regime, the linear diffused distance x of an object can be described as in one dimensional (1-D) space

$$\langle x^2 \rangle = 2Dt_{diff} \quad (3-7)$$

where, x , D and t_{diff} are the diffusion distance, diffusivity and diffusion time of the object, respectively. By differentiating equation (3-7), one can obtain that the Brownian motion speed v_B is described as

$$v_B = \frac{D}{\sqrt{2Dt_{diff}}} \quad (3-8)$$

Figure 3-6. Time lapses of the linear (a) and circular (b) propulsion of Au-Ni-Pt nanomotor in 12% H_2O_2 solution, respectively.

Moreover, Einstein and Smoluchowski showed that the diffusivity D of the object moving in a specific fluid is related to the coefficient of the friction f , and the diffusivity can be expressed as

$$D = \frac{k_b T}{f} \quad (3-9)$$

where, $k_b = 1.3806488 \times 10^{-23} \text{ m}^2 \text{ kg}/(\text{s K})$ is the Boltzmann constant and T is the absolute temperature, respectively. The coefficient of the friction can be expressed as

$$f = 6\pi\mu a \quad (3-10)$$

where, $\mu = 0.001 \text{ kg}/(\text{m}\cdot\text{s})$ is the dynamic viscosity of the media (DI water) and a is the effective length of the object, respectively. If $t_{diff} = 1 \text{ s}$ and $T = 300 \text{ K}$, the Brownian motion speed of the fabricated Au-Ni-Pt nanomotor is calculated as follows

$$v_B \approx 0.165 \text{ }\mu\text{m/s} \quad (3-11)$$

3.4.3.2 Gold-nickel-platinum nanomotor's propulsion speed at different hydrogen peroxide concentrations

In the experiments presented above, the elapsed time t and traversed distance L were obtained from the recorded videos. Hence, the propulsion speed v of the Au-Ni-Pt segmented catalytic nanomotors can be calculated as

$$v = \frac{L}{t} \quad (3-12)$$

$$\vec{L} = \vec{X} + \vec{Y} \quad (3-13)$$

where, X and Y are the displacement of the nanomotor at X and Y directions, respectively.

The Au-Ni-Pt nanomotor's propulsion was studied in H_2O_2 solution of four distinct concentrations, namely 3%, 6%, 9% and 12%. Using equation (3-12), the speed of the nanomotor at different H_2O_2 concentrations is calculated, as shown in Figure 3-7. From

the results, the speed of the nanomotor increases with the increment of H_2O_2 concentrations, which was consistent with the theoretical formula [11]. It was obtained that the propulsion speed of the Au-Ni-Pt nanomotor was much larger than Brownian motion speed [24].

Figure 3-7. The propulsion speed of the Au-Ni-Pt nanomotor at different H_2O_2 concentrations.

The instantaneous diameter values of one single O_2 bubble from generation to detachment at 12% H_2O_2 concentration were obtained, as shown in Figure 3-8. The recorded data were analyzed to obtain the size of the detaching O_2 bubbles and the detachment frequency of O_2 bubbles at different concentrations, as shown in Figures 3-9 and -10, respectively. As seen, the radiuses of the detaching O_2 bubbles at higher concentrations were larger than those at lower ones. The generation and detachment rate of O_2 bubbles at higher concentrations were also higher.

Figure 3-8. The instantaneous diameter of O_2 bubbles from generation to detachment at 12% H_2O_2 concentration.

Figure 3-9. The diameter of the detaching O_2 bubbles at different H_2O_2 concentrations.

Figure 3-10. The detachment frequency of O_2 bubbles at different H_2O_2 concentrations.

3.4.3.3 Chemical reaction dependency on gold-nickel-platinum nanomotor's propulsion

It was observed that the fabricated disk-like Au-Ni-Pt nanomotors propelled forward either linearly or circularly. Herein, the mechanism of the nanomotor's propulsion direction was proposed and studied. At steady state, if O_2 bubbles are generated and detached from the center of the nanomotor, in which F_{drive} and F_{drag} are in a line, no torque is generated, resulting in the nanomotor undergoes the linear propulsion, as shown in Figure 3-11(a). On the other hand, since the generated O_2 bubbles are only detached from the off center of the nanomotor, even though the values of F_{drive} and F_{drag} are equal, they are not aligned, a torque Q is reversely generated, which would further lead to the nanomotor propelling forward circularly with a propulsion radius R_c , as shown in Figure 3-11(b).

Figure 3-11. Schematic diagrams for explaining the chemical reaction-dependent propulsion of the disk-like Au-Ni-Pt nanomotor. (a) Au-Ni-Pt nanomotor can move forward towards Au-segment linearly, because the O_2 bubbles generated at the Pt-surface are located along the horizontal axis of the nanomotor, thus the forces F_{drive} and F_{drag} are in a line. (b) Demonstration of the circular propulsion of the Au-Ni-Pt nanomotor with a radius of R_c , resulting from the O_2 bubbles are only generated and detached from one side of the nanomotor, a torque Q is generated.

Stage 1 in Figure 3-11(a) and (b) represents that O_2 bubbles are growing at the Pt-surface, the nanomotor and O_2 bubbles have a joint velocity of v_1 ; after a short period of time, O_2 bubbles are detaching from the Pt-surface (stage 2 in Figure 3-11(a) and (b)), which in turn generates F_{drive} to thrust the nanomotor propelling forward, the motor and O_2 bubbles have a same velocity of v_2 ; after the detachment of the bubbles, the nanomotor continues moving forward with a velocity of v_3 , while the detached bubbles have a different velocity of v_0 (stage 3 in Figure 3-11(a) and (b)). In summary, if F_{drive} and F_{drag} are in a line, no torque is generated and the nanomotor moves forward linearly.

Otherwise, the motor would propel forward in a circular way. The experimental results demonstrated that the propulsion of the nanomotor is chemical reaction-dependent.

3.4.3.4 Discussion on gold-nickel-platinum nanomotor's propulsion

The pressure difference Δp at the interface between two fluids can be described by the Young-Laplace equation [23], thus the pressure inside the O₂ bubbles P_{O_2} can be calculated as follows

$$P_{O_2} = P_{atm} + \Delta P \quad (3-14)$$

where, $P_{atm} = 1.015 \times 10^5$ Pa is the atmospheric pressure.

In our experiments, it was obtained that on average 3.3 O₂ bubbles were generated and detached from the surface of the nanomotor in 12% H₂O₂ solution over 1 second [23]. The speed of the detached O₂ bubbles from the nanomotor was about 80 $\mu\text{m/s}$. Based on the values given above, the pressure inside the O₂ bubbles can be calculated using equation (3-14). Employing the equation derived by Gibbs and Zhao [11], one can obtain that the catalytic reaction rate constant k is 120.6 mol/(m²·s) and the adsorption constant α is 0.053 m³/mol. The results were in good agreement with those shown in reference 11.

Due to the differences from the nanomotor's shape and material composition, the aforementioned propulsion speeds of the nanomotor in our results were higher than those reported in reference 11, while they were much lower than those studied by other

researchers [21, 22]. One can learn the reasons in reference 11 and 25. In fact, there are several parameters determining the speed of the nanomotor, such as the temperature of the media, the size and geometry of the nanomotor, H_2O_2 concentration and the materials.

3.4.4 Magnetic field effect on gold-nickel-platinum nanomotor's propulsion

Figure 3-12. Microscopy set-up for characterizing the propulsion of the disk-like Au-Ni-Pt nanomotor in the presence of magnet. The set-up was mainly composed of a microscope, sample stage, sample, camera, magnet and computer.

Using the set-up shown in Figure 3-12, magnetic field effect on the propulsion of the Au-Ni-Pt nanomotor was investigated. Au-Ni-Pt nanomotor initially moved forward circularly without the presence of external magnetic field, as shown in Figure 3-13(a). The nanomotor changed its propulsion state from circular to linear in the

presence of the magnetic field because of the balance between the magnetic torque Q_M and the driving torque Q_F , as shown in Figure 3-13(b). Due to the location change of the magnet from left-side to right-side, the motor changed its propulsion direction, as shown Figure 3-13(c). After the removal of the magnet, the nanomotor recovered to its initial propulsion state, as shown in Figure 3-13(d). The Au-Ni-Pt nanomotor's propulsion state changed from circular to linear, resulting from the orientation of the nanomotor aligned well with the applied magnetic field, as shown in Figure 3-13(e).

Figure 3-13. Magnetic field effect on the propulsion of the Au-Ni-Pt nanomotor. (a) Au-Ni-Pt nanomotor initially moved forward circularly without the presence of external magnetic field; (b) the nanomotor changed its propulsion state from circular to linear with the presence of the magnetic field; (c) the nanomotor changed its propulsion direction due to the location change of the magnet from left-side to right-side; (d) after the removal of the magnet, the nanomotor recovered to its initial propulsion state. (e) Schematic of the explanation of the nanomotor's propulsion state from circular to linear with magnetic field effect.

From the aforementioned results, one can conclude that the propulsion state and

direction of the Au-Ni-Pt nanomotor can be switched by the magnet, as shown from Figure 3-13(a) to Figure 3-13(b); and the propulsion direction of the nanomotor can be steered by external magnetic field, as shown Figure 3-13b) to Figure 3-13(c). In general, the propulsion controlling of the nanomotor can be magnetic field-dependent.

3.4.5 Gold-nickel-platinum nanomotor's propulsion in hydrogen peroxide solution at different temperatures

Using the set-up shown in Figure 3-14, the fabricated disk-like Au-Ni-Pt nanomotors with two different sizes (4 and 8 μm) were immersed into H_2O_2 solution of 10 mol/m³ (1% weight has a molarity of about 9.79 M, that is 0.37 mol/m³) to observe the autonomous propulsion by changing the temperature of the solution from 7 to 57°C with 10°C interval. The temperature of the solution was firstly cooled down to 7°C by using ice, and the motion of nanomotors was characterized. As can be seen from experiments, H_2O_2 decomposition was very slow, and few O_2 bubbles were generated. Hence, the motion of nanomotors was very slow. Subsequently, the temperature of the H_2O_2 solution was increased to 17°C via reducing the amount of ice to investigate the motion of nanomotors. It was observed that H_2O_2 decomposition was faster, and more O_2 bubbles were generated, nanomotors moved forward faster as well. Thereafter, the temperature of the solution was sequentially heated up to reach 27, 37, 47, and 57°C using a hot plate. As the temperature increased, the H_2O_2 decomposition rate was higher,

more and more O_2 bubbles were generated. Thus, nanomotors propelled forward faster. The motion processes of two different sized nanomotors were recorded at different temperatures. The corresponding time lapses are characterized, as shown in Figures 3-15 and -16. The software “ImageJ” was utilized to process the recorded data to obtain the trajectories of the big and small n nanomotors at different temperatures, as shown in Figures 3-17 and -18, respectively.

Figure 3-14. Microscopy set-up for characterizing the propulsion of the disk-like Au-Ni-Pt nanomotor at different temperatures. The set-up was mainly composed of a microscope, sample stage, sample, camera, thermometer, hot-plate, ice and computer.

3.4.5.1 Gold-nickel-platinum nanomotor's speed in hydrogen peroxide solution at different temperatures

In the aforementioned results, the moving time t (unit in s), as presented in Figures 3-15 and -16, and the traversed distance L (unit in μm), as depicted in Figures 3-17 and -18, are obtained from the recorded data. Thus, the motion speed v (unit in $\mu\text{m/s}$) of Au-Ni-Pt nanomotors can be calculated using equations (3-12) and (3-13).

The Au-Ni-Pt nanomotors' propulsion was studied in H_2O_2 solution of 10 mol/m^3 at 6 different temperatures. The lowest temperature was 7°C (Figures 3-15(a) and -16(a)), the second one was 17°C (Figures 3-15(b) and -16(b)), the following one was 27°C (Figures 3-15(c) and -16(c)), the next one was 37°C (Figures 3-15(d) and -16(d)), the fifth one was 47°C (Figures 3-15(e) and -16(e)), and the last one was 57°C (Figures 3-15(f) and -16(f)). The calculated speeds of the big nanomotor at different temperatures were about 16.2 (Figures 3-15(a) and -17(a)), 19.1 (Figures 3-15(b) and -17(b)), 23.3 (Figures 3-15(c) and -17(c)), 33.4 (Figures 3-15(d) and -17(d)), 42.6 (Figures 3-15(e) and -17(e)), and $57.8 \mu\text{m/s}$ (Figures 3-15(f) and -17(f)), respectively. The determined speeds for the small nanomotor at different temperatures were around 14.5 (Figures 3-16(a) and -18(a)), 18 (Figures 3-16(b) and -18(b)), 24.5 (Figures 3-16(c) and -18(c)), 36.6 (Figures 3-16(d) and -18(d)), 51.7 (Figures 3-16(e) and -18(e)), and $69.5 \mu\text{m/s}$ (Figures 3-16(f) and -18(f)), respectively. The experimental results of the Au-Ni-Pt nanomotors' propulsion speeds at different temperatures are summarized in Figure 3-

19. In addition, the nanomotors can move forward either linearly or circularly, as shown in Figures 3-15 to -18.

As seen from the experimental results, the speed of the small nanomotor was only about 1.05 times larger than that of the big nanomotor at 27 °C in H₂O₂ solution, even though the size of the small nanomotor was about 2 times smaller than that of the big nanomotor. On the other hand, the motion speeds in this research were much lower than those reported by other researchers [21, 22], resulting from the differences of the material compositions and shapes of particles. In such a case, one can learn that there are several factors, such as the size of the particles, the concentration of the solution, and the temperature of the solution, *etc.* [11] which influence the speeds of nanomotors, giving us the guidance how to design and characterize nanomotors in future.

In micro and nano realm, nanomotors in DI water without the presence of the fuel H₂O₂ would undergo thermal fluctuation motion, called as Brownian motion. In this case, no O₂ bubbles were generated, and the nanomotors moved forward very slowly and randomly. As it can be seen, the self-propelled motion speeds of Au-Ni-Pt nanomotors were much larger than Brownian motion speeds [24].

Figure 3-15. Time lapses of the big Au-Ni-Pt nanomotor's motion at different temperatures. (a), (b), (c), (d), (e) and (f) show the time lapses of the big Au-Ni-Pt nanomotor's motion at 7, 17, 27, 37°C, 47 and 57°C in H_2O_2 solution of 10 mol/m^3 , respectively.

Figure 3-16. Time lapses of the small Au-Ni-Pt nanomotor's propulsion at different temperatures. (a), (b), (c), (d), (e) and (f) demonstrated the time lapses of the small Au-Ni-Pt nanomotor's motion at 7, 17, 27, 37, 47 and 57°C in H_2O_2 solution of 10 mol/m^3 , respectively.

Figure 3-17. Trajectories of the big Au-Ni-Pt nanomotor at different temperatures. (a), (b), (c), (d), (e) and (f) illustrate the trajectories of the big Au-Ni-Pt nanomotor at 7, 17, 27, 37, 47 and 57 °C in H_2O_2 solution of 10 mol/m^3 , respectively.

Figure 3-18. Trajectories of the small Au-Ni-Pt nanomotor at different temperatures. (a), (b), (c), (d), (e) and (f) present the trajectories of the small Au-Ni-Pt nanomotor at 7, 17, 27, 37, 47 and 57 °C in H_2O_2 solution of 10 mol/m^3 , respectively.

Figure 3-19. Summary of the disk-like Au-Ni-Pt nanomotor's propulsion speeds in H_2O_2 solution of 10 mol/m^3 at different temperatures.

3.4.5.2 Discussion on disk-like Au-Ni-Pt nanomotor's propulsion at different temperatures

In the aforementioned experiments, it is observed that the radiuses of the detached O_2 bubbles generated from the big nanomotor (Figure 3-15) are always larger than those from the small one (Figure 3-16) at the same temperature. Meanwhile, the generation and detachment rates of O_2 bubbles from the same sized nanomotor at higher temperatures are larger than those at lower temperatures. As it can be seen from the results presented in Figure 3-19, the big nanomotor propels forward faster than the

small one at temperatures below 27 °C, resulting from that the big nanomotor has a larger surface area interacting with more H₂O₂ molecules in a certain time, thus more O₂ bubbles with larger detaching radiuses are generated. In comparison, the small nanomotor moves forward faster at temperatures above 27 °C, because of its smaller diameter with less weight and the higher detachment rate of O₂ bubbles. Hence, the surface area and the size of the nanomotors are the main contributors to the increment of the motion speeds at temperature below and above 27 °C, respectively. In this study, the motion speed of nanomotors is increased with the increment of the temperature of the solution, which is consistent with the theoretical formula [11]. Hence, the propulsion of nanomotors is temperature-dependent.

On the other hand, it was observed that the fabricated Au-Ni-Pt nanomotors moved forward either in a linear (Figures 3-15(a), (b), (d), and Figures 3-16(a), (b), (d)) or in a circular (Figures 3-15(c), (e), (f), and Figures 3-16(c), (e), (f)) way. Herein, the mechanism of the nanomotor's motion direction is proposed and studied. At steady state, if the detached O₂ bubbles are distributed along the centers of nanomotors, *i.e.* the values of F_{drive} and F_{drag} are equal, F_{drive} and F_{drag} are in a line, no torque is generated, thus nanomotors would undergo linear motion. On the contrary, if the generated O₂ bubbles are only located at the off centers of nanomotors, even though the values of F_{drive} and F_{drag} are equal, F_{drive} is not aligned with F_{drag} , then a torque Q is generated, which would further lead to n nanomotors propelling forward circularly with a motion

radius R_c . In general, if F_{drive} and F_{drag} are in a line, no torque is generated, thus Au-Ni-Pt nanomotors move forward linearly. Otherwise, the torque Q is generated, nanomotors would propel forward in a circular way.

3.4.6 Three-dimensional characterization of gold-nickel-platinum nanomotor using digital holographic imaging microscopy

In the aforementioned results, the propulsion of Au-Ni-Pt nanomotor was only studied and characterized in planar system (e.g. oxy). In fact, the nanomotor can move forward in 3-D space (e.g. oxyz), as represented in Figure 3-20.

Figure 3-20. 3-D velocity representation of nanomotor in 3-D corordinate system.

Herein, the total speed v_t of the nanomotor can be expressed as

$$v_t = \sqrt{v_x^2 + v_y^2 + v_z^2} \quad (3-15)$$

where, v_x , v_y and v_z are the speed of the nanomotor along x, y and z directions, respectively.

3.4.6.1 Working principle of digital holographic image microscopy

A digital holographic microscopy is a powerful imaging tool, which is extremely beneficial for studying the 3-D information of an object. From the recorded hologram by the holographic microscopy, one can obtain the size, location and distribution of the object [27]. To create the necessary hologram, the illumination needs to be a coherent (monochromatic) light source, such as a laser. As it can be seen from Figure 3-21, the laser light is split into an object beam and a reference beam. The expanded object beam illuminates a sample to create the object wave front. After the object wave front is collected by a microscope objective, the object and reference wave fronts are joined by a beam splitter to interfere and create the hologram acquired by an image sensor. Using the digitally recorded hologram, a computer acts as a digital lens and calculates a viewable image of the object wave front by using a numerical reconstruction algorithm to demonstrate the 3-D location of the object.

3.4.6.2 Three-dimensional propulsion of gold-nickel-platinum nanomotor

The fabricated Au-Ni-Pt nanomotors were immersed in the diluted H_2O_2 solution to investigate the autonomous propulsion using the digital holographic microscopy, as shown in Figure 3-22. The time lapses for the propulsion of the nanomotors are

characterized, as shown in Figure 3-23. The recorded hologram data is used to reconstruct the two-dimensional (2-D) and 3-D trajectories of nanomotors using “ImageJ” and “Matlab”, as shown in Figures 3-24 and -25, respectively.

Figure 3-21. Schematic diagram of the working principle of the digital holographic microscopy. A beam of the coherent laser light is split into an object beam and a reference beam. The expanded object beam illuminates a sample to create the object wave front. After the object wave front is collected by a microscope objective, the object and reference wave fronts are joined by a beam splitter to interfere and create the hologram acquired by an image sensor.

The 3-D velocity of the nanomotor can be expressed as follows:

$$\vec{v}_{x_i} = \frac{\vec{X}_{i+1} - \vec{X}_i}{\Delta t_i} \quad (3-16)$$

$$\vec{v}_{y_i} = \frac{\vec{Y}_{i+1} - \vec{Y}_i}{\Delta t_i} \quad (3-17)$$

$$\vec{v}_{z_i} = \frac{\vec{Z}_{i+1} - \vec{Z}_i}{\Delta t_i} \quad (3-18)$$

$$v_{t_i} = \sqrt{\vec{v}_{x_i}^2 + \vec{v}_{y_i}^2 + \vec{v}_{z_i}^2} \quad (3-19)$$

where, $\vec{X}_i$, $\vec{Y}_i$, and $\vec{Z}_i$ are the displacement of the nanomotor along x, y and z directions at the i^{th} moment, respectively. $\vec{X}_{i+1}$, $\vec{Y}_{i+1}$ and $\vec{Z}_{i+1}$ are the displacement of the nanomotor along x, y and z directions at the $i+1^{\text{th}}$ moment, respectively. $\vec{v}_{x_i}$, $\vec{v}_{y_i}$

and $\vec{v}_{z_i}$ are the velocity of the nanomotor along x, y and z directions at the i^{th} moment, respectively. Δt_i and v_{t_i} are the total time period and the total speed of the nanomotor at the i^{th} moment, respectively. Using equations (3-16) to (3-19), the 3-D velocity of the nanomotor is calculated at different H_2O_2 concentrations, as shown in Figure 3-26.

Figure 3-22. Microscopy set-up for characterizing the 3-D propulsion of the disk-like Au-Ni-Pt nanomotor in aqueous H_2O_2 solution using digital holographic microscope. The set-up was mainly composed of a microscope, sample stage, sample, camera and computer.

Figure 3-23. Time lapses of the Au-Ni-Pt nanomotor's propulsion recorded by the holographic imaging microscope.

Figure 3-24. Time lapses of the reconstructed 2-D trajectory of the Au-Ni-Pt nanomotor.

Figure 3-25. Time lapses of the reconstructed 3-D trajectory of the Au-Ni-Pt nanomotor.

3.4.6.3 Discussion on three-dimensional propulsion of disk-like gold-nickel-platinum nanomotor

In our experiments, it was observed that about 3~5 O₂ bubbles were generated and detached from the surface of the nanomotors at different H₂O₂ concentrations in 1 second, as shown in Figure 3-27. The speed of the detached O₂ bubbles from the Au-Ni-Pt nanomotors was about 80 μm/s, as shown in Figure 3-28. Based on the values given above, the pressure inside O₂ bubbles can be calculated using equation (3-14). Employing the equation derived by Gibbs and his colleague [11], one can obtain that the catalytic reaction rate constant k is about 128.1 mol/(m²·s) and the adsorption

constant α is approximately $0.067 \text{ m}^3/\text{mol}$. The results were in good agreement with those reported in reference 11. On the other hand, the speed of the nanomotors in our results was higher than those presented in reference 11, while it was lower than those studied by other researchers [21, 22], due to the differences from the nanomotor's shape and material compositions [11]. In fact, there are several parameters which influence the speed of nanomotors, giving us the guidance how to design and characterize nanomotors in future work. In addition, the radius variation of the bubble can be well fitted with γt^n , as shown in Figure 3-28.

3.5 Conclusion

A bubble propulsion mechanism stemming from momentum change induced by the detachment of O_2 bubbles from the surface of Pt was applied to study the linear and circular movement of a disk-like Au-Ni-Pt nanomotor in H_2O_2 solution. A high-efficiency LbL deposition method was employed to fabricate the Au-Ni-Pt nanomotor based on the NEMS technology. The propulsion of the Au-Ni-Pt nanomotor was experimentally investigated in H_2O_2 solution either with different concentrations or at different temperatures, revealing that the propulsion speed of the nanomotor increased with the increment of H_2O_2 concentration and the temperature of the solution. Moreover, the nanomotor could autonomously propel forward linearly due to O_2 bubbles were generated from the center of the nanomotor, while the nanomotor moved forward

circularly resulting from that O_2 bubbles were only generated from the off center of the nanomotor.

Figure 3-26. The 3-D velocity of the Au-Ni-Pt nanomotor at different H_2O_2 concentrations.

Figure 3-27. Bubble radius variation with time at different H_2O_2 concentrations.

Figure 3-28. Bubble radius variation fitting with γt^n , where n is the growth exponent and γ is the proportionality constant.

Furthermore, the propulsion controlling of the nanomotor was characterized using a magnet, revealing that the nanomotor could be steered by external magnetic field. It was concluded that the propulsion of the nanomotor was chemical reaction- and magnetic field-dependent. In addition, the 3-D trajectory of the nanomotor was also reconstructed based on the recorded hologram data using digital holographic imaging microscope. The results of this research will encourage further studies, such as the propulsion characterization of the nanomotor placed in micro-channels. Such nanomotors could be used for environmental sensing [17, 18] and other applications [19, 27].

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4

Gold-Nickel-Platinum Nanojet

This chapter presents two different shaped gold-nickel-platinum nanojets, one is with singular off-center nanoengine, the other one is with dual off-center nanoengines. The self-steerable propulsion of these two different nanojets is characterized at different hydrogen peroxide concentrations. In conclusion, the nanojet with singular off-center nanoengine is able to propel forward circularly, while the nanojet with dual off-center nanoengines can move forward linearly.

4.1 Introduction

Evolutions bestow biomolecular motor proteins to be evolved with fascinating functions in cells, as described in Chapter 2. Inspired by naturally occurring biomolecular nanomotors, researchers have devoted extensively great efforts on the development of artificial nanojets in the last few years [1]. For instance, Sanchez *et al.* developed the smallest man-made jet engine using rolled-up nanotech [2]. Meanwhile, Zhao *et al.* reported the bimetallic nanojets fabricated by template-assisted electrochemical deposition [3]. These nanojets have a wide range of applications such as isolation of cells, drug delivery, and nanosurgery [4]. In recent years, nanojets have been used for motion-based (bio)sensing [5]. The propulsion of nanojets can improve the mixing of the fluids and increase the possibility of a target binding to the receptor-immobilized nanojets, which in turn enhances the sensitivity [6]. In particular, the circular propulsion of nanojets plays a great role in enhancing motion-based (bio)sensing.

In other researchers' works, nanojets were shaped as horizontally symmetrical either cones or cylinders, which cannot realize the circularly self-steering propulsion without the guidance of an external control source [7]. Meanwhile, the aforementioned methods used for the fabrication of nanojets are very complicated techniques, which require sophisticated skills to operate and also need enormous of time and money to finalise [2, 3]. In this chapter, a novel self-steering propulsion mechanism is proposed to

investigate the propulsion of a nanojet with off-center nanoengines. The nanojet has a form of disk, consisting of three different metals: Au, Ni and Pt. The disk-like Au-Ni-Pt nanojet is fabricated by a highly efficient LbL deposition method based on the NEMS technology. The propulsion of the nanojet is characterized in H_2O_2 solution of different concentrations. Experimental observations show the nanojet with singular off-center nanoengine can move forward circularly without any external control, while the nanojet with dual off-center nanoengines is able to propel forward linearly.

4.2 Gold-Nickel-Platinum Nanojet with Singular Off-Center Nanoengine

A novel nanojet with singular off-center nozzle nanoengine is designed. The schematic and the material composition of the nanojet are shown in Figure 4-1. In detail, the nanojet is composed of three different metals: non-catalytic Au, magnetic Ni, and catalytic Pt. Au and Ni are shaped as a concentric disk with 12 μm in diameter. The thicknesses of Au- and Ni-disks are 200 and 100 nm, respectively. The off-center nozzle nanoengine Pt has a tubular shape with a solid base, which is located at one side of the plate of the Au-Ni disk. The diameter, base-thickness, wall-thickness and wall-height of the nanoengine are 3 μm , 300 nm, 300 nm and 1.5 μm , respectively. Au is employed as a non-catalyst for building asymmetric structure to ensure autonomous propulsion in micro and nanoscale regime [8]. Ni is a paramagnetic material which can be used for controlling the propulsion of the nanojet in future work. For instance, the movement of

a Ni-contained nanodevice can be directed by external magnetic field [9, 10]. Pt is served as a chemical catalyst which prompts H_2O_2 to decompose into H_2O and O_2 bubbles [11].

Figure 4-1. Schematic diagram of Au-Ni-Pt nanojet with singular off-center nanoengine. The nanojet has a form of disk comprising of three different metals: Au, Ni, and Pt. Au- and Ni-disks are concentric. Pt forms a tubular cylinder, which is the nanoengine of the nanojet and is only located at one side of the plate of the Au-Ni disk.

4.2.1 Circularly self-steering propulsion mechanism for gold-nickel-platinum nanojet with singular off-center nanoengine

At initial state, the nanojet is sunk in the DI water with a relatively static situation. Once H_2O_2 is added into the DI water, O_2 bubbles are generated and grow gradually bigger and bigger (growing state). The generated O_2 bubbles could detach from the surface of the off-center nozzle nanoengine Pt after a short period of time (detaching state), as shown in Figure 4-2(a). The self-steering propulsion of the disk-like Au-Ni-Pt nanojet with singular off-center nozzle nanoengine is triggered by the detachment of O_2 bubbles from the off-center nanoengine Pt, as illustrated in Figure 4-2. The

decomposition of H_2O_2 in general can be described as

where, Pt denotes the catalyst platinum [2, 3]. Herein, H_2O_2 is firstly adsorbed onto the surface of Pt, then is decomposed into H_2O and O_2 bubbles [11]. According to the Momentum Conservation Law and the Momentum Theorem, a recoil force F_{drive} , as shown in Figures 4-2(b) and (c), will be generated to initiate and accelerate the propulsion of the nanojet, resulting from the detachment of O_2 bubbles.

In Space, a rocket can orbit around Earth and realize the self-steering movement using self-equipped jet engine. Similarly, the Au-Ni-Pt nanojet with singular off-center nozzle nanoengine will propel forward circularly, because the recoil force F_{drive} and the viscous drag force F_{drag} are not aligned in a same line, as O_2 bubbles can only be generated and detached from one side of the nanojet. In particular, if the Pt nozzle nanoengine is located at the left-hand side of the nanojet, the generated O_2 bubbles will only be detached from the left-hand side of the nanojet, thus forcing the nanojet to move forward circularly in a clockwise direction, as shown in Figure 4-2(b). On the contrary, if the Pt nozzle nanoengine is located at the right-hand side of the nanojet, the generated O_2 bubbles will detach from the right-hand side of the nanojet. Hence, the nanojet will propel forward circularly in a counter-clockwise direction, as shown in Figure 4-2(c). Stage 1 in Figures 4-2(b) and (c) represents O_2 bubbles are g-

Figure 4-2. Schematic diagram of the circularly self-steering propulsion mechanism for the disk-like Au-Ni-Pt nanojet with singular off-center nozzle nanoengine in H_2O_2 solution. (a) Illustration of the Au-Ni-Pt nanojet's propulsion originating from momentum change, a driving force F'_{drive} induced by the detachment of one single O_2 bubble from the Pt-surface catalysing H_2O_2 decomposition thrusts the nanojet to move forward. (b) Schematic representation of the circular propulsion of the Au-Ni-Pt nanojet in a clockwise direction, as the off-center nozzle nanoengine is located at the left-hand side of the nanojet. (c) Demonstration of the circular propulsion of the Au-Ni-Pt nanojet in a counter-clockwise direction, since the off-center nozzle nanoengine is located at the right-hand side of the nanojet.

enerated at the surface of the off-center nanoengine Pt. The nanojet and O_2 bubbles have a joint velocity of v_1 . Afterwards, the generated O_2 bubbles grow bigger, and detach from the surface of the nanoengine Pt after a short period of time, which in turn generates F_{drive} to thrust the nanojet to move forward, as shown in stage 2 of Figures 4-

2(b) and (c). At this stage, the nanojet and O₂ bubbles have a same velocity of v_2 . After the detachment of O₂ bubbles, the nanojet continues to move forward with a velocity of v_3 , while the detached O₂ bubbles have a different velocity of v_0 , as shown in stage 3 of Figures 4-2(b) and (c). At steady state, the values of F_{drive} and F_{drag} are equal, thus the Au-Ni-Pt nanojet reaches a constant velocity of v .

Figure 4-3. Diagram of the fabrication steps of the nanojet with singular off-center nozzle nanoengine. The Au-Ni-Pt nanojets were fabricated using a high-efficiency LbL deposition method based on the NEMS technology. The fabrication processes include PECVD, photolithography, sputtering, e-beam evaporation, lift-off and KOH etching.

4.2.2 Fabrication of gold-nickel-platinum nanojet with singular off-center nanoengine

The fabrication of the proposed nanojet was carried out using an advanced NEMS technology developed in Micromachines Lab, School of Mechanical and Aerospace Engineering (MAE) at Nanyang Technological University (NTU), Singapore [12, 13]. The detailed fabrication steps are illustrated in Figure 4-3.

To fabricate the structures, a 4-inch Si wafer was firstly immersed into H_2SO_4 at 120 °C for 30 minutes to clean its surface. The Si wafer surface was then deposited with a layer of 1 μm thick SiO_2 by PECVD at 300 °C in 40 minutes. In order to improve photoresist adhesion on oxides, SiO_2 -coated Si wafer was transferred into a prime oven for hexame-thyldisilazane HMDS coating for 2 minutes to form a strong chemical bond onto the surface of SiO_2 . Subsequently, a layer of 1.5 μm thick photoresist AZ7220 was spin-coated on the SiO_2 surface at 5000 rpm for 30 seconds. Afterwards, the features on the glass photomask were exposed onto the photoresist 7220 using UV light beam of 365 nm wavelength for 4 seconds. The pattern was developed in AZ 300MIF developer solution over 1 minute (step 1 in Figure 4-3). The patterned Si wafer was firstly coated with a layer of 200 nm thick Au by magnetron sputter for 9 minutes (step 2 in Figure 4-3), which was subsequently coated with a layer of 100 nm thick Ni via e-beam evaporation for 15 minutes (step 3 in Figure 4-3). Thereafter, the wafer was immersed into acetone etching off the photoresist, a process called lift-off (step 4 in

Figure 4-3). The photolithography process was performed one more time, followed by coating a 300 nm thick Pt-layer onto the surface by magnetron sputter for 9 minutes (step 5 in Figure 4-3). Finally, the Au-Ni-Pt nanojets were formed on the SiO₂ surface by lift-off (step 6 in Figure 4-3). The nanojets were released from the Si substrate using KOH etchant to etch off the SiO₂ layer (step 7 in Figure 4-3).

4.2.3 Energy dispersive spectrometry analysis of gold-nickel- platinum nanojet with singular off-center nanoengine

The Au-Ni-Pt nanojet was fabricated by a LbL deposition method based on the NEMS technology. The SEM images of one fabricated Au-Ni-Pt nanojet with singular off-center nozzle nanoengine on Si wafer, obtained from the top and side views, are shown in Figures 4-4(a) and (b), respectively.

In order to identify the material composition of the fabricated Au-Ni-Pt nanojet with singular off-center nozzle nanoengine, EDS analysis was performed, and the corresponding results are shown in Figure 4-5. It can be seen that the disk plate of the nanojet contains two different metals: Au and Ni, as shown in Figure 4-5(a). On the other hand, Pt is detected in the region of the singular off-center nanoengine, as shown in Figure 4-5(b). Hence, the fabricated nanojet is consistent with the proposed one.

Figure 4-4. SEM images of the fabricated Au-Ni-Pt nanojet with singular off-center nozzle nanoengine. Top view (a) and side view (b) of single Au-Ni-Pt nanojet with singular off-center nozzle nanoengine, respectively.

4.2.4 Oxygen bubble generation

To characterize the self-steering propulsion of the fabricated Au-Ni-Pt nanojets, the experimental set-up was established, as shown in Figure 4-6. The fabricated Au-Ni-Pt nanojet was dispersed into H_2O_2 solution to study the generation of O_2 bubbles. The

generation and detachment of O_2 bubbles associated with the propulsion of the nanojet were characterized and captured by a camera installed onto an optical microscope. The results were recorded by a computer installed with a video recording software. It could be observed that the nanojet was stationary in DI water without the presence of H_2O_2 , and no O_2 bubbles were generated. After the addition of H_2O_2 into DI water, O_2 bubbles were initially generated at the Pt-surface. Thereafter, the generated O_2 bubbles grew bigger and bigger. Finally, O_2 bubbles were detached from the nanojet and next O_2 bubbles were generated and grew, as shown in Figure 4-7. The diameters of the detaching O_2 bubbles from the nanojet immersed in 5% H_2O_2 solution were approximately of 20 μm (Figure 4-7(a)).

4.2.5 Self-steering propulsion of gold-nickel-platinum nanojet with singular off-center nanoengine

The fabricated Au-Ni-Pt nanojets were separately immersed into H_2O_2 solution with three different concentrations to investigate the self-steering propulsion. The corresponding data of the propulsion of the disk-like nanojet were recorded. The circularly self-steering propulsion of the nanojet in a clockwise direction is shown in Figure 4-7(a), while Figures 4-7(b) and (c) depict the time lapses of the circular propulsion of the nanojets in a counter-clockwise direction.

Figure 4-5. EDS analysis results of the fabricated Au-Ni-Pt nanojet with singular off-center nozzle nanoengine. (a) EDS spectrum of the plate of Au-Ni disk, which shows the disk plate of the nanojet contains two different metals: Au and Ni. (b) EDS spectrum of the nozzle nanoengine of the nanojet, which reveals the nozzle nanoengine is made of another distinct metal: Pt.

Figure 4-6. Microscopy set-up for characterizing and recording the disk-like Au-Ni-Pt nanojet's self-steering propulsion in aqueous H_2O_2 solution. The set-up was mainly composed of a microscope, sample stage, sample, camera and computer.

Figure 4-7. Time lapses of the circularly self-steering propulsion of the disk-like Au-Ni-Pt nanojet with singular off-center nozzle nanoengine in H_2O_2 solution with three different concentrations. (a) Time lapses of the circular propulsion of the Au-Ni-Pt nanojet in a clockwise direction in 5% H_2O_2 solution. Time lapses of the circular propulsion of the Au-Ni-Pt nanojets in a counter-clockwise direction in 10% (b) and 20% (c) H_2O_2 solutions, respectively.

4.2.5.1 Propulsion speed and angular velocity of gold-nickel-platinum nanojet with singular off-center nanoengine in hydrogen peroxide solution

Figure 4-8. Trajectory analyses of the Au-Ni-Pt nanojet in H_2O_2 solution with three different concentrations. (a) Trajectory of the Au-Ni-Pt nanojet in a clockwise direction in 5% H_2O_2 solution. Trajectories of the Au-Ni-Pt nanojet in a counter-clockwise direction in 10% (b) and 20% (c) H_2O_2 solutions, respectively.

The recorded data were processed by “ImageJ” software to obtain the corresponding

trajectories of the Au-Ni-Pt nanojet in H₂O₂ solution with three different concentrations, as shown in Figure 4-8. In the experiments described above, the elapsed time t (unit in s) and the period time T (unit in s), as shown in Figure 4-7, and the traversed distance L (unit in μm), as shown in Figure 4-8, can be obtained. Hence, the speed v (unit in $\mu\text{m/s}$) and the angular velocity ω (unit in rad/s) of the Au-Ni-Pt nanojet can be calculated as [14]

$$v = \frac{L}{t} \quad (4-2)$$

$$\omega = \frac{2\pi}{T} \quad (4-3)$$

The self-steering propulsion of the Au-Ni-Pt nanojet was studied in H₂O₂ solution with three different concentrations (5%, 10% and 20%), whereby H₂O₂ concentration was the ratio of the pure H₂O₂ volume to the DI water volume. Based on equations (4-2) and (4-3), the propulsion speeds and angular velocities of the nanojet at these three different concentrations are about 80 $\mu\text{m/s}$ and 2.62 rad/s, 120 $\mu\text{m/s}$ and 15.70 rad/s, 150 $\mu\text{m/s}$ and 20.93 rad/s, respectively. The experimental results reveal that the speed and angular velocity of the nanojet increases with the increment of H₂O₂ concentration, as shown in Figure 4-9. In this work, the concentrations of H₂O₂ are lower than that reported in the previously published paper [12], thus the speeds of the nanojet are lower.

Figure 4-9. Summary of the propulsion speed and angular velocity of Au-Ni-Pt nanojet with singular off-center nanoengine in H_2O_2 solution.

4.2.5.2 Discussion on gold-nickel-platinum nanojet's self-steering propulsion in hydrogen peroxide solution

In this experiment, it was observed that the nanojets moved forward in a circular way. Herein, the circularly self-steering propulsion mechanism for the disk-like nanojet with singular off-center nanoengine can be proposed and studied. Since the nozzle nanoengine Pt is located at one side of the nanojet, even though the values (~ 10 pN) of F_{drive} and F_{drag} are equal, F_{drive} is not aligned with respect to F_{drag} . Therefore, a torque Q is generated, which guides the nanojet to propel forward circularly with a radius of

R_c , as shown in Figure 4-10. At steady state, if the Pt nozzle nanoengine is located at the left-hand side of the nanojet, the generated O_2 bubbles are only detached from the left-hand side of the nanojet, the nanojet hence moves forward circularly in a clockwise direction, as shown in Figure 4-10(a). On the other hand, if the Pt nozzle nanoengine is located at the right-hand side of the nanojet, the generated O_2 bubbles are detached from the right-hand side of the nanojet, thus the nanojet moves forward circularly in a counter-clockwise direction, as shown in Figure 4-10(b).

In particular, the experimental results reveal that O_2 bubbles are firstly generated at the surface of the singular off-center nanoengine Pt which catalyzes the decomposition of H_2O_2 . The generated O_2 bubbles then grow bigger. When O_2 bubbles reach a certain diameter, they are detached from the nanojet. After the detachment of O_2 bubbles, an off-center recoil force is in turn generated to thrust the circularly self-steering propulsion of the nanojet. Hence, the experimental results are in good agreement with the aforementioned modeling analysis.

Figure 4-10. Schematic illustrations of the circularly self-steering propulsion of the Au-Ni-Pt nanojet with singular off-center nozzle nanoengine. (a) Au-Ni-Pt nanojet can move forward towards the Au-segment circularly in a clockwise direction, as O_2 bubbles generated at the surface of the off-center nozzle nanoengine Pt are only detached from the left-hand side of the nanojet. (b) Explanation of the circular propulsion of the Au-Ni-Pt nanojet in a counter-clockwise direction, since the nozzle nanoengine Pt is located at the right-hand side of the nanojet.

4.3 Gold-Nickel-Platinum Nanojet with Dual Off-Center Nanoengines

4.3.1 Linearly self-steerable propulsion mechanism

It is well known that a launch vehicle can orbit around Earth and steer its motion using self-equipped jet engines in Space. Inspired by the launch vehicle, a novel disk-like nanojet with dual off-center nozzle nanoengines is proposed, as shown in Figure 4-11. The nanojet has a form of disk, consisting of three different metals: non-catalytic Au, magnetic Ni, and catalytic Pt.

Figure 4-11. Schematic diagram of the structure, material compositions and size of the disk-like nanojet with dual off-center nanoengines. The nanojet is composed of three different metals: Au, Ni, and Pt. Au and Ni are concentric disks, two identical off-center nozzle nanoengines Pt are shaped as hollow cylinders and symmetrically located on the plate of the Au-Ni disk.

The Au-Ni-Pt nanojet suspended in DI water without the presence of H_2O_2 is stationary. Once H_2O_2 is added into DI water, O_2 bubbles are firstly generated at the surface of the off-center nanoengines of the nanojet, in which the nanojet and O_2 bubbles have a joint velocity of v_1 . Afterwards, the generated O_2 bubbles grow bigger and bigger (growing state in Figure 4-12(a)). When O_2 bubbles reach a certain diameter, they detach from the nanojet (detaching state in Figure 4-12(a)). The nanojet and O_2 bubbles have a same velocity of v_2 at the detaching moment. After the detachment of O_2 bubbles, rockets continue to propel forward with a velocity of v_3 , while the detached bubbles have a different velocity of v_0 . The H_2O_2 decomposition in general can be described as

where, Pt denotes the catalyst platinum [2, 3, 11].

Figure 4-12. Schematic diagram of the self-steerable propulsion of the proposed nanojet with dual off-center nozzle nanoengines. (a) Illustration of the propulsion of the nanojet originated from the detachment of O_2 bubbles from the dual off-center nanoengines Pt catalyzing the decomposition of H_2O_2 . During the growth of O_2 bubbles, the nanojet and growing O_2 bubbles have a joint velocity of v_1 ; at the detaching moment, the nanojet and detaching bubbles have a same velocity of v_2 ; after the detachment of O_2 bubbles, the nanojet moves forward with a velocity of v_3 , while the detached O_2 bubbles have a different velocity of v_0 . (b) Demonstration of the linearly self-steerable propulsion of the nanojet in H_2O_2 solution. The recoil force F_{drive} is well aligned with the drag force F_{drag} , thus the nanojet moves forward linearly. At steady state, the nanojet move forward linearly with a speed of v .

The self-steerable propulsion of the nanojet is produced by the detachment of O_2 bubbles from the surface of Pt, as shown in Figure 4-12(a). According to the

Momentum Conservation Law and the Momentum Theorem, a recoil force F_{drive} will be generated to thrust the nanocket's propulsion. In principle, the dual off-center nanoengines are symmetrically located on the disk-plate of the nanojet, thus O_2 bubbles are identically generated and detached from the nanojet. In turn, the total recoil force F_{drive} is aligned with the drag force F_{drag} , as shown in Figure 4-12(b). Hence, the microrocket is capable of propelling forward linearly. At steady state, the values of F_{drive} and F_{drag} are equal, thus the nanojet reaches a constant velocity of v .

4.3.2 Fabrication of nanojet with dual off-center nanoengines

The schematic of the structure, material compositions, and size of the proposed nanojet with dual off-center nanoengines are shown in Figure 4-11. The nanojet consists of three parts: non-catalytic Au, magnetic Ni, and catalytic Pt. Au and Ni are shaped as a concentric disk with 12 μm in diameter. The thicknesses of Au- and Ni-disks are 0.2 and 0.1 μm , respectively. Two identical off-center Pt nozzle nanoengines form hollow cylinders and are symmetrically located on the plate of the Au-Ni disk. The diameter, bottom-thickness, wall-height and wall-thickness of the Pt nanoengines are about 3, 0.3, 1.5, 0.3 μm , respectively. Au functions as a non-catalyst and is purposely used to build asymmetric structure for ensuring the autonomous propulsion in micro and nanoscale regime [8]. Ni is a paramagnetic material, and the orientation of the magnetic material will be directed by magnetic field [9, 10]. Thus, the propulsion direction of the nanojet

can be steered and controlled by magnetic field in future work. Pt acts as a chemical catalyst to prompt the decomposition of H_2O_2 into H_2O and O_2 bubbles [11]. The nanojets were fabricated using the mature NEMS technology developed in Micromachines Lab, School of Mechanical and Aerospace Engineering (MAE) at Nanyang Technological University (NTU), Singapore [12, 13].

Figure 4-13. Diagram of the fabrication procedures of the nanojet with dual off-center nozzle nanoengines. The nanojet is fabricated by a high-efficiency layer-by-layer deposition method based on the NEMS technology, which includes PECVD, photolithography, sputtering, e-beam evaporation, lift-off and KOH etching.

Firstly, a 4-inch Si wafer was immersed into diluted H_2SO_4 solution at $120\text{ }^\circ\text{C}$ to clean the wafer surface for 30 minutes. The Si wafer was then coated with a layer of $1\text{ }\mu\text{m}$ thick SiO_2 by PECVD at $300\text{ }^\circ\text{C}$ for 40 minutes. In order to improve the adhesion of photoresist onto oxide, SiO_2 -coated wafer was kept inside an oven at $120\text{ }^\circ\text{C}$ for HMDS coating to form a strong chemical bond onto the surface in 4 minutes. Subsequently, a layer of $1.5\text{ }\mu\text{m}$ thick photoresist 7220 was spin-coated onto the surface of SiO_2 at 5000 rpm for 30 seconds. Afterwards, the features of nanojets plotted on the glass photomask were exposed onto the surface of photoresist-coated wafer using a beam of 365 nm wavelength UV light for 5 seconds. The pattern was developed in AZ-300MIF developer for 2 minutes (step 1 in Figure 4-13). The patterned Si wafer was firstly coated with a layer of 200 nm thick Au by magnetron sputter for 9 minutes (step 2 in Figure 4-13), following deposited with a layer of 100 nm thick Ni via e-beam evaporation for 15 minutes (step 3 in Figure 4-13). Thereafter, the wafer was immersed into acetone ($\text{C}_3\text{H}_6\text{O}$) etching off photoresist, a process called “*lift-off*” (step 4 in Figure 4-13). The photolithography process was conducted one more time. A layer of 300 nm thick Pt was coated onto the wafer using magnetron sputter for 9 minutes (step 5 in Figure 4-13). Finally, Au-Ni-Pt nanojets were formed on the surface of SiO_2 via lift-off without using ultrasound (step 6 in Figure 4-13). The fabricated nanojets were released from the surface of Si wafer using KOH to etch off SiO_2 (step 7 in Figure 4-13). The released nanojets were stored in a glass bottle for experiments. The SEM top-down and

side views of the nanojets are shown in Figures 4-14(a) and (b), respectively.

4.3.3 Energy dispersive spectrometry analysis of gold-nickel- platinum nanojet with dual off-center nanoengine

In order to confirm the material compositions of the nanojet, EDS analysis was conducted. The EDS analysis results of the disk plate and the dual nanoengines of the nanojet are shown in Figures 4-15(a) and (b), respectively. As can be seen, the disk plate of the nanojet contains two different metals: Au and Ni, whereas the nozzle nanoengines of the nanojet are made of another distinct metal: Pt. Hence, the fabricated nanojet is consistent with the proposed one.

4.3.4 Oxygen bubble generation

Using the set-up shown in Figure 4-6, the fabricated Au-Ni-Pt nanojet was dispersed into H_2O_2 solution to study the generation of O_2 bubbles. The generation and detachment of O_2 bubbles associated with the propulsion of the nanojet were characterized and captured by a camera installed onto an optical microscope. The results were recorded by a computer installed with a video recording software. It could be observed that the nanojet was stationary in DI water without the presence of H_2O_2 , and no O_2 bubbles were generated. After the addition of H_2O_2 into DI water, O_2 bubbles were initially generated at the Pt-surface. Thereafter, the generated O_2 bubbles grew bigger and bigger. Finally, O_2 bubbles were detached from the nanojet and next O_2

bubbles were generated and grew, as shown in Figure 4-16. The diameters of the detaching O_2 bubbles from the nanojet immersed in 5% H_2O_2 solution were approximately of 20 μm (Figure 4-16(a)). The results were consistent with those reported by Wang and Wu [15].

Figure 4-14. SEM images of the fabricated Au-Ni-Pt nanojet with dual off-center nozzle nanoengines. SEM top-down (a) and side (b) views of the nanojets on the surface of silicon (Si) wafer, respectively.

4.3.5 Self-steerable propulsion of nanojet with dual off-center nanoengines in hydrogen peroxide solution

The fabricated nanojet with dual off-center nanoengines was immersed into three different concentrated H_2O_2 solutions to investigate the self-steerable propulsion. The nanojet propelled forward linearly, as shown in Figure 4-16. The corresponding trajectories of the nanojet are shown in Figure 4-17.

4.3.5.1 Self-steerable propulsion speeds of nanojet in hydrogen peroxide solution

The “ImageJ” software was employed to process the recorded data, and the corresponding trajectories of the nanojet in three different concentrated H_2O_2 solutions are shown in Figure 4-17. From the aforementioned experimental results, the elapsed time t (unit in s), as shown in Figure 4-16, and the corresponding traversed distance L (unit in μm) of the nanojet, as shown in Figure 4-17, can be obtained. Hence, the speed v (unit in $\mu\text{m/s}$) of the nanojet can be expressed as [14]

$$v = \frac{L}{t} \quad (4-5)$$

The self-steerable propulsion of the nanojet was investigated in H_2O_2 solution with three different concentrations. The lowest concentration was 5%, the medium one was 10%, and the highest one was 20%, respectively. Using equation (4-5), the corresponding propulsion speeds of the nanojet at these three different concentrations were about 30, 75, and 135 $\mu\text{m/s}$, as shown in Figure 4-18. In general, the speeds of the nanojet are increased with the increment of H_2O_2 concentration, in consistency with the

theoretical derivation [16].

Figure 4-15. EDS analysis results of the nanojet with dual off-center nozzle nanoengines. (a) EDS analysis results of the disk plate of the nanojet, which confirm

that the disk plate of the nanojet contains two different metals: Au and Ni. (b) EDS analysis results of the nozzle nanoengines of the nanojet, which reveal that the nozzle nanoengines of the nanojet are composed of another different metal: Pt.

Figure 4-16. Time lapses of the self-steerable propulsion of the nanojet in different concentrated H_2O_2 solutions. The instantaneous locations of the nanojet are shown in 5% (a), 10% (b), and 20% (c) H_2O_2 solutions, respectively.

Figure 4-17. Trajectories of the nanojet with dual off-center nozzle nanoengines in different concentrated H_2O_2 solutions. The corresponding trajectories of the nanojet in 5% (a), 10% (b), and 20% (c) H_2O_2 solutions.

In micro and nano realm, the nanojet in DI water without the presence of the fuel H_2O_2 can undergo thermal fluctuation motion, called Brownian motion. In such a case, no O_2 bubbles are generated, and the nanojet moves forward very slowly and randomly. As seen, the steerable propulsion speeds of Au-Ni-Pt nanojet are much larger than Brownian motion speed [17]. Hence, the Brownian motion speed is smaller and can be negligible.

Figure 4-18. Summary of the propulsion speed of Au-Ni-Pt nanojet with dual off-center nanoengine in H_2O_2 solution.

As it can be seen, the nanojet generated multiple beams of O_2 bubbles detaching

from the surface of the dual off-center nanoengines. After the detachment of O₂ bubbles, a total recoil force was generated to thrust the nanojet propelling forward linearly, resulting from the generated O₂ bubbles which were identically and symmetrically distributed on both sides of the nanojet and the total recoil force was well aligned with the drag force.

4.3.5.2 Discussion on the self-steerable propulsion of nanojet with dual off-center nanoengines

The material composition and the shapes of the fabricated nanojet are significantly different from those studied by other researchers [2, 3, 17, 18, 16, 19]. The propulsion speeds in this work are smaller than those published in reference 2, 3, 17 and 18, while they are much larger than those reported in 16 and 19. The differences between them are coming from the different structures and material compositions of the particles. One can learn the reasons from the reference 16. In fact, the propulsion speed of the nanojet is affected by some factors, such as the size of the nanojet, the temperature of solution, *etc.* giving us the guidance how to design and characterize the nanojet in future.

As observed in this study (Figure 4-16), the values of the generation rate and the detachment rate of O₂ bubbles from the nozzle nanoengines at higher concentrations are larger than those at lower ones, resulting from the fact that more H₂O₂ molecules at higher concentrations are decomposed to generate more O₂ bubbles at a certain period of time. Hence, a larger recoil force is generated, which propels the nanojet forward

faster. In the experimental results, the propulsion speeds of the nanojet at higher concentrations are larger, which are consistent with the physical phenomenon. The experimental results are in good agreement with our theoretical analysis, thus our model and theory are verified.

4.4 Conclusion

The self-steering propulsion mechanism stemmed from momentum change induced by the detachment of O_2 bubbles from the surface of the catalyst Pt was proposed to investigate the propulsion of Au-Ni-Pt nanojets with off-center nanoengines in H_2O_2 solution. A high-efficiency and mass-production layer-by-layer deposition method was utilized to fabricate two different shaped Au-Ni-Pt nanojets based on the NEMS technology. The steerable propulsion of the disk-like Au-Ni-Pt nanojets was experimentally investigated in diluted H_2O_2 solution with different concentrations. The results showed that the speed of the nanojets increased with the increment of H_2O_2 concentration. In addition, the nanojets with singular off-center Pt nozzle nanoengine could move forward circularly in H_2O_2 solution due to the presence of a torque, while the nanojets with two identically and symmetrically distributed Pt nozzle nanoengines could propel forward linearly. The results of this research will encourage further studies, such as the exploration of the steerable trajectories of the nanojets via the geometry design of Pt nanoengines [20], the motion observation of the nanojets placed in

micro-channels [21] and the controlling by the external magnetic field [9, 10, 22, 23]. Such nanojets may be a promising for environmental sensing [24, 25] and other applications [26-29].

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5

Platinum-Nickel-SU-8 Microrocket

This chapter introduces an innovative micro/nanomotor: platinum-nickel-SU-8 microrocket with eccentric nanoengine. A circularly self-steerable propulsion mechanism is proposed for characterizing the autonomous locomotion of the microrocket. The circularly steerable propulsion of the microrocket is characterized at different hydrogen peroxide concentrations. The results reveal that the speed of the microrocket increases with the increment of hydrogen peroxide concentrations.

5.1 Introduction

The previously reported artificial structures are designed as horizontally symmetrical either cone or cylinder, in which the self-steering trajectory can only be achieved with external control sources, such as electrical, optical and magnetic, *etc.* However, none of them has realized a truly self-steering in artificial micro and nanodevice. On the other hand, the rolled-up technique and the electrochemical deposition exploited to fabricate the hollow either conical or cylindrical structures are very complex techniques, both methods need much higher skills to operate [1-4]. Therefore, the design and fabrication of the engineered micro and nanodevices is still considered an extraordinary challenge in nanotechnology nowadays. Therefore, it is highly demanded to develop and fabricate micro and nanodevices in a high-efficiency manner.

In this chapter, a novel microrocket with an eccentric nanoengine is designed, composing of three parts: polymer SU-8, magnetic Ni, and catalytic Pt. A circularly steerable propulsion mechanism originated from a microrocket-oxygen bubble integral system is proposed to investigate the steerable propulsion of the microrocket with the eccentric nanoengine. Herein, the proposed Pt-Ni-SU-8 microrockets are fabricated using a high-efficiency LbL deposition method based on the NEMS technology. The steerable propulsion of the fabricated microrockets is characterized in H_2O_2 solution with different concentrations. The results reveal that the speed of the rockets increases

with the increment of H₂O₂ concentration. In addition, the Pt-Ni-SU-8 microrockets can propel forward circularly either in a clockwise or in a counter-clockwise direction.

5.2 Platinum-Nickel-SU-8 Microrocket with Eccentric Nanoengine

5.2.1 Circularly steerable propulsion mechanism for platinum-nickel-SU-8 microrocket with eccentric nanoengine

It is well known that a launch vehicle can soar around Earth and control its motion direction using self-equipped jet engine in the space. Inspired by the launch vehicle's configuration, an innovative microrocket with an eccentric nanoengine is proposed. The circularly self-steering propulsion mechanism for the proposed microrocket in H₂O₂ solution is schematically drawn, as demonstrated in Figure 5-1.

The microrocket is stationary in DI water without the presence of H₂O₂. Once H₂O₂ is added into DI water, O₂ bubbles are generated at the surface of the eccentric nanoengine of the microrocket (attached state), then are detached from the microrocket (detached state) after a while, as shown in Figure 5-1(a). The H₂O₂ decomposition in general can be described as

where, Pt denotes the catalyst platinum [2, 3, 5].

According to the Momentum Conservation Law and the Momentum Theorem, a recoil force F_{drive} will be generated to initiate and accelerate the microrocket's

propulsion, resulting from the detachment of O₂ bubbles. Theoretically, the nanoengine is eccentrically located on one side of the microrocket. Hence, O₂ bubbles are only generated and detached from one side of the microrocket. In turn, the generated recoil force F_{drive} is off-center and not aligned with the drag force F_{drag} , as shown in Figures 5-1(b) and (c). Hence, the microrocket is capable of propelling forward circularly. In specific, if the nanoengine is located on the left-hand side of the rocket, the rocket will move forward circularly in a clockwise direction, as shown in Figure 5-1(b). Whereas, the rocket propels forward circularly in a counter-clockwise direction, if the nanoengine is located on the right-hand side of the rocket, as shown in Figure 5-1(c). Stage 1 in Figures 5-1(b) and (c) demonstrates the generation of O₂ bubbles at the Pt-surface, in which microrockets and O₂ bubbles have a joint velocity of v_1 . Thereafter, O₂ bubbles are growing bigger, and detach from the Pt-surface after a period of time, as shown in Stage 2 of Figures 5-1(b) and (c). In turn, F_{drive} is generated to thrust microrockets moving forward, rockets and O₂ bubbles have a same velocity of v_2 at the point of detaching. After the detachment of O₂ bubbles, rockets continue to propel forward with a velocity of v_3 , while the detached bubbles have a different velocity of v_0 , as shown in Stage 3 of Figures 5-1(b) and (c). At steady state, the values of F_{drive} and F_{drag} are equal, thus Pt-Ni-SU-8 microrockets reach a constant velocity of v .

Figure 5-1. Schematic diagram of the steerable propulsion of a Pt-Ni-SU-8 microrocket with an eccentric nanoengine in H_2O_2 solution. (a) Demonstration of a recoil force F'_{drive} induced by the detachment of one single O_2 bubble from the Pt-surface for the propulsion of Pt-Ni-SU-8 microrocket; v , v' and v_0 denote the joint velocity of microrocket and O_2 bubble before the detachment of O_2 bubble, the velocity of the rocket after the detachment of O_2 bubble and the original velocity of the detached O_2 bubble, respectively. (b) Representation of the circular motion of Pt-Ni-SU-8 microrocket in a clockwise direction, due to the eccentric nanoengine is located on the left-hand side of the rocket. (c) Illustration of the circular motion of Pt-Ni-SU-8 microrocket in a counter-clockwise direction, resulting from the eccentric nanoengine is located on the right-hand side of the rocket.

5.2.2 Fabrication of platinum-nickel-SU-8 microrocket with eccentric nanoengine

The schematic of the structures, material compositions, and sizes of the proposed microrocket are shown in Figure 5-2. The microrocket consists of three parts: polymer SU-8, magnetic Ni and catalytic Pt. SU-8 forms the body of the microrocket, which is shaped as a solid cylinder with 4.5 μm in diameter and 15 μm in length. Ni and Pt are concentric and have a form of disk with 4 μm in diameter. The thicknesses of Ni- and Pt-disks are 100 and 50 nm, respectively. Pt-Ni disk serves as the nanoengine of the rocket, which is eccentrically located on one side of the SU-8 cylinder. Pt is used as a catalyst to chemically catalyse the decomposition of H_2O_2 into both H_2O and O_2 bubbles [5, 6]. Ni is a paramagnetic material for controlling the propulsion in future work [7, 8]. SU-8 is employed as a non-catalyst and purposely used to build asymmetrical structure for ensuring autonomous propulsion in micro and nanoscale regime.

A 4-inch Si wafer was firstly immersed into H_2SO_4 to clean the surface at 120 $^\circ\text{C}$ in 30 minutes. The Si-wafer surface was then deposited with a layer of 500 nm thick SiO_2 by PECVD at 300 $^\circ\text{C}$ for 20 minutes. In order to improve photoresist adhesion onto oxides, SiO_2 coated Si-wafer was transferred into a prime oven for HMDS coating to form a strong chemical bond onto the oxide surface in 120 seconds. Afterwards, a layer of 1.5 μm thick photoresist was spin-coated on the SiO_2 surface

Figure 5-2. Schematic of the structures, material compositions, and sizes of the proposed Pt-Ni-SU-8 microrocket with the eccentric nanoengine. SU-8 (brown) is the body of the rocket and is shaped as a solid cylinder with $4.5\ \mu\text{m}$ in diameter and $15\ \mu\text{m}$ in length. Ni (golden yellow) and Pt (blue) are the nanoengine of the microrocket which has a form of disk with $4\ \mu\text{m}$ in diameter. The Pt- and Ni-disks are concentric, and the corresponding thicknesses are 100 and 50 nm.

at 5000 rpm for 30 seconds. The pattern on the glass photomask was exposed onto the photoresist coated Si-wafer using 365 nm UV light over 4 seconds. The pattern was subsequently developed in an AZ 300MIF developer solution for 1 minute (step 1 in Figure 5-3). The patterned Si-wafer was coated with a layer of 50 nm thick Pt by magnetron sputter in 4 minutes and following deposited with a layer of 100 nm thick Ni using e-beam evaporator for 15 minutes (step 2 in Figure 5-3). The wafer was immersed in acetone etching off photoresist, called *lift-off* (step 3 in Figure 5-3). Thereafter, the Pt-Ni-nanoengine patterned wafer was spin-coated with a layer of $15\ \mu\text{m}$ thick SU-8 at 5000 rpm in 30 seconds, and the photolithography was performed

once again. Pt-Ni-SU-8 microrockets with eccentric nanoengines were formed on the SiO₂-surface using the SU-8 developer to release the unexposed SU-8 over 3 minutes (step 4 in Figure 5-3). Finally, the microrockets were released from the Si-wafer using KOH etching off 1 μ m thick SiO₂ (step 5 in Figure 5-3). The fabricated Pt-Ni-SU-8 microrockets were stored in a glass bottle for the following experiments.

Figure 5-3. Schematic diagram of the fabrication procedures of Pt-Ni-SU-8 microrockets with eccentric nanoengines. The microrockets are fabricated using a high-efficiency layer-by-layer method based on NEMS technology, including PECVD, photolithography, sputtering, e-beam evaporation, lift-off and KOH etching.

5.2.3 Energy dispersive spectrometry analysis of platinum-nickel- SU-8 microrocket with eccentric nanoengine

The microrockets are fabricated using a layer-by-layer deposition method based on

the developed NEMS technology [9, 10]. The SEM images of the fabricated microrockets are captured, as shown in Figure 5-4. The inset shows the side view of one single enlarged microrocket. The material compositions of the eccentric nanoengine of the fabricated microrocket are confirmed via EDS analysis, as shown in Figure 5-5.

Figure 5-4. SEM images of the Pt-Ni-SU-8 microrocket with the eccentric nanoengine. The nanoengine of the microrocket is eccentrically located on one side of the rocket. The inset shows the side view of one single enlarged microrocket.

Figure 5-5. EDS analysis results of the eccentric nanoengine of the fabricated Pt-Ni-SU-8 microrocket. The results show that the eccentric nanoengine contains two different metals: Ni and Pt, and the corresponding weight percentages are 30.84% and 69.16%.

5.2.4 Oxygen bubble generation

The experimental set-up was established, as shown in Figure 5-6. The generation and detachment of O_2 bubbles associated with the motion of microrockets were characterized and captured by a camera installed onto an optical microscope. The results were recorded by a computer installed with a video recording software. The fabricated Pt-Ni-SU-8 microrockets were immersed into diluted H_2O_2 solution to study the steerable motion. It could be observed that the microrocket was stationary in DI water without the presence of H_2O_2 , as shown in Figure 5-7(a), and no O_2 bubbles were

generated. After the addition of H_2O_2 into DI water, the first O_2 bubble was initially generated at the Pt-surface, as shown in Figure 5-7(b). Thereafter, the generated O_2 bubble grew bigger and bigger, as shown in Figure 5-7(c). Finally, the first generated O_2 bubble was detached from the microrocket and the next O_2 bubble was growing, as shown in Figure 5-7(d). The diameters of the detaching O_2 bubbles from the microrocket immersed in $2 \text{ mol/m}^3 \text{ H}_2\text{O}_2$ solution were approximately of $20 \text{ }\mu\text{m}$ (Figure 5-7(c)). The results were consistent with those reported by Wang and Wu [11].

Figure 5-6. Experimental set-up for characterizing the Pt-Ni-SU-8 microrocket's self-steering propulsion in diluted H_2O_2 solution. The set-up mainly includes a microscope, sample stage, camera and computer.

Figure 5-7. The generation and detachment of O_2 bubbles from the microrocket. (a) Pt-Ni-SU-8 microrocket was suspended in DI water without the presence of H_2O_2 , no O_2 bubbles were generated. (b) Pt-Ni-SU-8 microrocket was immersed in diluted H_2O_2 solution, the first O_2 bubble was generated at the surface of the nanoengine; (c) The generated O_2 bubble grew bigger and bigger; (d) The first generated O_2 bubble with about $20\ \mu m$ in diameter was detached from the microrocket and the next O_2 bubble was generated and growing.

5.2.5 Steerable propulsion of microrocket in hydrogen peroxide solution

The fabricated microrockets with eccentric nanoengines were immersed into H_2O_2 solution with different concentrations to investigate the steerable propulsion. The microrockets propelled forward circularly either in a clockwise or in a counter-

clockwise direction, as shown in Figure 5-8. The time lapses of the steerable propulsion of the microrockets in $10 \text{ mol/m}^3 \text{ H}_2\text{O}_2$ solution are characterized, as depicted in Figure 5-9. The corresponding circular trajectories of the microrockets are shown in Figure 5-10.

Figure 5-8. Circular propulsion of Pt-Ni-SU-8 microrockets in H_2O_2 solution with three different concentrations. (a) and (b) Microrockets immersed in $10 \text{ mol/m}^3 \text{ H}_2\text{O}_2$ solution moved forward circularly in a clockwise and a counter-clockwise direction with a speed of $80 \mu\text{m/s}$, respectively. (c) The rocket suspended in $20 \text{ mol/m}^3 \text{ H}_2\text{O}_2$ solution propelled forward circularly in a counter-clockwise direction at a speed of $150 \mu\text{m/s}$. (d) The rocket immersed into $30 \text{ mol/m}^3 \text{ H}_2\text{O}_2$ solution moved forward circularly in a clockwise direction, the motion speed of the rocket was $200 \mu\text{m/s}$.

Figure 5-9. Time lapses of the circular propulsion of Pt-Ni-SU-8 microrockets in 10 mol/m³ H₂O₂ solution. (a) Time lapses of the motion of the rocket in a clockwise direction and (b) time lapses of the movement of the rocket in a counter-clockwise direction, respectively.

5.2.5.1 Steerable propulsion speed and angular velocity of microrocket in hydrogen peroxide solution

In the experiments, the Pt-Ni-SU-8 microrocket's steerable motion was investigated

in H_2O_2 solution with three different concentrations. The lowest H_2O_2 concentration was 10 mol/m^3 (Figures 5-8(a) and (b)), the medium one was 20 mol/m^3 (Figure 5-8(c)) and the highest one was 30 mol/m^3 (Figure 5-8(d)). The elapsed time t (unit in s) and the period time T (unit in s), as shown in Figure 5-9, and the traversed distance L (unit in μm) and the angular velocity ω (unit in rad/s), as shown in Figure 5-10, are obtained from the recorded videos. Thus, the speed v of microrockets can be calculated as

$$v = \frac{L}{t} \quad (5-2)$$

$$\omega = \frac{2\pi}{T} \quad (5-3)$$

Figure 5-10. Trajectories of Pt-Ni-SU-8 microrockets in 10 mol/m^3 H_2O_2 solution. (a) Trajectories (red dashed line) of the rocket propelling forward in a clockwise direction and (b) trajectories (green dashed line) of the microrocket moving forward in a counter-clockwise direction, respectively.

The corresponding speeds and angular velocities of the microrockets are calculated using equations (5-2) and (5-3), which are about $80 \mu\text{m/s}$ and 1.57 rad/s (Figure 5-8(a) and (b)), $150 \mu\text{m/s}$ and 6.28 rad/s (Figure 5-8(c)) and $200 \mu\text{m/s}$ and 7.85 rad/s (Figure

5-8(d)), respectively. The results are shown in Figure 5-11. In micro and nano realm, catalytic microrockets in DI water without the presence of the fuel H_2O_2 can undergo thermal fluctuation motion, called Brownian motion. In such a case, no O_2 bubbles are generated (Figure 5-7(a)), and microrockets move forward very slowly and randomly. As seen, the steerable propulsion speeds of Pt-Ni-SU-8 microrockets are much larger than Brownian motion speed [12]. In general, the speeds and angular velocities of microrockets are increased with the increment of H_2O_2 concentration, in consistency with the theoretical derivation [13].

Figure 5-11. Summary of the propulsion speed and angular velocity of Pt-Ni-SU-8 microrocket with an eccentric nanoengine in H_2O_2 solution.

The time lapses of the steerable motion of the microrockets in 10 mol/m³ H₂O₂ solution are further characterized, as depicted in Figure 5-9. As it can be seen, the microrockets are suspended in H₂O₂ solution, O₂ bubbles are continuously generated from the eccentric Pt nanoengines, then detached from the micro-rockets after a period of time. The off-center recoil force F_{drive} , induced by the detachment of O₂ bubbles, thrusts the microrockets to propel forward towards the SU-8 cylinders circularly either in a clockwise (Figure 5-9(a)) or in a counter-clockwise direction (Figure 5-9(b)). The corresponding steerable trajectories of microrockets in 10 mol/m³ H₂O₂ solution, as shown in Figures 5-10(a) and (b), are processed using “ImageJ” software.

5.2.5.2 Discussion on the steerable propulsion of microrocket

The material composition and the shapes of the fabricated microrockets are significantly different from those studied by other researchers [7, 8, 13], like the speeds of microrockets, which in our experiments are much lower than those (above 500 μm/s) studied in reference 7, 8 or larger than those (below 10 μm/s) reported by Gibbs *et al.* [13]. The differences observed may be caused by the size and shape of the particles, and the surface tension of the solution as proposed by Gibbs *et al.* [13], giving us the guidance how to design and investigate the microrockets in future.

In addition, microrockets with eccentric nanoengines can move forward circularly either in a clockwise direction or in a counter-clockwise direction, as shown in Figure

5-8. The nanoengines are located on one side of the microrockets, thus O_2 bubbles are only generated at the surface of the eccentric nanoengines and detached from the rockets, resulting in the generated recoil force F_{drive} is off-center and not aligned with the drag force F_{drag} , which in turn introduces a torque of Q , as shown in Figure 5-12, which further leads to microrockets propelling forward circularly with a radius of R_c . At steady state, if the eccentric nanoengines are located on the left-hand side of the rockets, the rockets will move forward circularly in a clockwise direction, as shown in Figure 5-12(a). On the other hand, the rockets propel forward circularly in a counter-clockwise direction, due to the nanoengines are located on the right-hand side of the rockets, as shown in Figure 5-12(b). The experimental results are in good agreement with our theoretical analysis, thus our model and theory are verified.

Further investigations can be conducted, including the propulsion characterization of the microrocket placed in micro-channels [15] and the motion controlling using external magnetic field [16, 17]. Such microrocket may be useful for environmental remediation [18] and other applications [19, 20]. In special, H_2O_2 , belongs to the class of reactive oxygen species (ROS) like O_2^- , $HO^\bullet$, H_2O_2 , $RSSR^\bullet$ -, $RS^\bullet$ or $RSOO^\bullet$, and is well recognized for playing a dual role as both deleterious and beneficial species in biological cells. Sustaining the balance of ROS, called, redox homeostasis (RH) is crucial for every organism in order to effectively harness the reducing power through catabolism of various substrates and to utilize this power in the anabolism of cellular

components such as DNA, lipids, and proteins. Imbalance of ROS is implicated in aging, cancer, cardiovascular diseases, diabetes and neurodegeneration [21]. Among biologically relevant ROS, H_2O_2 has the highest intracellular concentration (mol). Therefore, the high efficiency of SU-8 microrockets forms a novel platform to sense excess of intracellular concentrations of H_2O_2 in living cells.

Figure 5-12. Schematic diagrams for explaining the circularly steerable propulsion of Pt-Ni-SU-8 microrockets with eccentric nanoengines. (a) Pt-Ni-SU-8 microrocket can move forward towards the SU-8 cylinder circularly in a clockwise direction. O_2 bubbles generated at the Pt nanoengine are detached from the left-hand side of the rocket. (b) Diagram of the explanation of the circular motion of the Pt-Ni-SU-8 microrocket in a counter-clockwise direction, O_2 bubbles generated at the Pt nanoengine are located at the right-hand side of the rocket.

5.3 Conclusion

A circularly steerable propulsion mechanism was proposed for the first time to investigate the steerable movement of Pt-Ni-SU-8 microrocket with an eccentric nanoengine in H_2O_2 solution. The microrocket was fabricated by a high-efficiency LbL deposition method based on the NEMS technology. The steerable movement of the microrocket was experimentally characterized in H_2O_2 solution with different concentrations. The steerable propulsion was proved to be induced by the detachment

of the off-center O₂ bubbles from the surface of the eccentric Pt nanoengine. The speeds and angular velocities of the microrocket were increased with the increment of the concentration of the fuel H₂O₂. Microrockets were able to self-steer and propel forward circularly either in a clockwise or in a counter-clockwise direction. The results of this research will enhance the exploration on the steerable propulsion of the microrocket via the design of the Pt-nanoengine [10, 14].

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6

Conclusion and Future Work

This chapter draws conclusions for the work presented in this research project. An insight into versatile future projects that could be of significance as a continuation to this research is also presented.

6.1 Conclusions

This research work focuses on Pt-based catalytic micro/nanomotors. Three different categorized micro/nanomotors have been investigated. The main conclusions can be summarized as follows:

(i) A disk-like Au-Ni-Pt nanomotor is proposed. A bubble propulsion mechanism is employed to characterize the locomotion of the proposed nanomotor. The propulsion of the nanomotor is investigated at different H_2O_2 concentrations and different temperatures. Furthermore, the magnetic effect on the propulsion of the nanomotor is characterized. In addition, for the first time the 3-D propulsion of the nanomotor is investigated by using digital holographic microscope.

(ii) Two novel shapes of Au-Ni-Pt nanojets are designed, one is with singular off-center nanoengine, the other one is with dual off-center nanoengines. The self-steerable propulsions of these two different nanojets are characterized at different H_2O_2 concentrations. The results reveal that the nanojet with singular off-center nanoengine is able to propel forward circularly, while the nanojet with dual off-center nanoengines can move forward linearly.

(iii) Another novel micro/nanomotor (Pt-Ni-SU-8 microrocket) is proposed. The microrocket is with an eccentric nanoengine. A circularly self-steerable propulsion mechanism is proposed for characterizing the autonomous locomotion of the microrocket. The circularly steerable propulsion of the microrocket is characterized at

different H_2O_2 concentrations. The results reveal that the speed of the microrocket increases with the increment of H_2O_2 concentrations.

6.2 Major Contributions

In this study, some major works have been done to better understand the physical and chemical performance of micro/nanomotors. The major contributions are listed as follows:

(i) Three newly designed micro/nanomotors (Pt-Ni-Au nanomotor, Pt-Ni-Au nanojet and Pt-Ni-SU-8 microrocket) have been proposed and fabricated. The autonomous propulsion of these micro/nanomotors have been investigated in H_2O_2 solution of different concentrations, which revealed that the speed of micro/nanomotors increases with the increment of H_2O_2 concentrations.

(ii) The propulsion of Pt-Ni-Au nanomotor at temperatures ranging from $7\text{ }^\circ\text{C} \sim 57\text{ }^\circ\text{C}$ was investigated. The propulsion controlling of Pt-Ni-Au nanomotor by external magnetic field was also studied.

(iii) For the first time, the 3-D propulsion of Pt-Ni-Au nanomotor was investigated by using digital holographic microscope.

(iv) The linearly self-steerable propulsion of Pt-Ni-Au nanojet with singular off-center nanoengine at different H_2O_2 concentrations was conducted.

(v) The circularly self-steerable propulsion of Pt-Ni-Au nanojet with dual off-center nanoengines at different H_2O_2 concentrations was studied.

(vi) The circularly self-steerable propulsion of Pt-Ni-SU-8 microrocket with an eccentric nanoengine at different H_2O_2 concentrations was investigated.

The aforementioned work conducted in this thesis can be a great part of research on micro/nanomotors.

6.3 Future Work

As stated in conclusions, the autonomous propulsion of three different categories of micro/nanomotors are characterized. In future work, purifying and extracting HAMLET (Human Alpha-lactalbumin Made Lethal to Tumor cells) antitumor protein from human milk by using biochemical approach will be the feasible research direction. Also, assembly of separated samples into a hybrid nanodevice for drug delivery is another interesting issue to be addressed. Besides of them, the research of hybrid nanodevice to be characterized in a microchannel integrated microheater device is also very promising. The main outlines and composition of the future work about this research project are as follows.

6.3.1 Propulsion controlling of micro/nanomotors by magnetic field

The fabricated micro/nanomotors contain Ni. Since the magnetic material can exhibit the magnetic performance under magnetic field [1, 2]. In the future work, the realization of the controlled propulsion of the micro/nanomotors needs to be addressed. A reasonable approach is to apply an external magnetic field to control the device.

However, both simulation and practical experiments need to be done with sufficient theoretical research background support.

6.3.2 Propulsion investigation using microchannel integrated with microheater

6.3.2.1 Fabrication of microchannel integrated with microheater device

Microchannel is a microfluidic chip for characterizing objects or assembled systems in liquid environment. To observe the locomotion of micro/nanomotors, a microchannel device with high sensitivity and accuracy is needed to be designed and fabricated [3, 4]. On the other hand, temperature has a great effect on the propulsion of micro/nanomotors as suggested in this research and other published work, thus a microheater is demanded [5]. Combined these two demands, a microchannel integrated microheater device is proposed, as shown in Figure 6-1 and 6-2. The proposed device will be fabricated by using the MEMS technology.

Figure 6-1. The schematic diagram of microchannel integrated with microheater

6.3.2.2 Propulsion characterization of micro/nanomotors using microchannel integrated with microheater device

As reported in Chapter 3, the speed of the nanomotor is related to the temperature. In order to investigate the effect of the temperature on the propulsion of catalytic micro/nanomotors, the microchannel integrated with microheater device is proposed, as described above. Microchannel is used as the tract for guiding the catalytic micro/nanomotors. Microheater is used as the heating device to increase the temperature. The integrated device is shown in Figure 6-1. The 3-D structure is shown in Figure 6-2.

Figure 6-2. The 3-D diagram of microchannel integrated with microheater

6.3.3 Hybrid nanodevice for drug delivery

6.3.3.1 The purification of HAMLET protein

Since it is reported that HAMLET protein can be purified from human milk, the reported method will be employed to extract the HAMLET protein in future study [6-9].

6.3.3.2 Assembling of hybrid nanodevice for drug delivery

To realize the drug delivery, a hybrid nanodevice is proposed, as shown in Figure 6-3. The device is composed of the artificial micro/nanomotor and the biological HAMLET protein. The HAMLET protein can be engineered with his-tag, and his-tag can react with Ni to form a strong chemical bond. Hence, the his-tagged HAMLET protein can be linked to the micro/nanomotor. In this way, the assembled hybrid device can deliver the drug molecule HAMLET to the target.

Figure 6-3. The hybrid nanodevice model.

6.3.3.3 Delivery characterization of hybrid nanodevice in microchannel

The hybrid nanodevice is composed of two major components, which are catalytic micro/nanomotor and antitumor HAMLET protein. To observe the property and

performance of the hybrid nanodevice, the device can be characterized in the microchannel integrated with microheater device.

6.4 Summary

This chapter mainly concluded the accomplished work of this research project. The future work about this research project and some perspectives on research directions are also presented.

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List of Publications

A. Journal Publications

1. **Liangxing Hu**, Jianmin Miao and Gerhard Grüber, “Disk-like nanojets with steerable trajectory using platinum nozzle nanoengines”, *RSC Advances*, 6(5): 3399-3405, January 2016.
2. **Liangxing Hu**, Kai Tao, Jianmin Miao and Gerhard Grüber, “Hydrogen-peroxide-fulled platinum-nickel-SU-8 microrocket with steerable propulsion using eccentric nanoengine”, *RSC Advances*, 6(104): 102513-102518, October 2016.
3. **Liangxing Hu**, Jianmin Miao and Gerhard Grüber, “Temperature effects on disk-like gold-nickel-platinum nanoswimmer’s propulsion fuelled by hydrogen peroxide”, *Sensors and Actuators B: Chemical*, 239: 586-596, February 2017.
4. Kai Tao, Jin Wu, Lihua Tang, **Liangxing Hu**, Sun Woh Lye and Jianmin Miao, “Enhanced electrostatic vibrational energy harvesting using integrated opposite-charged electrets”, *Journal of Micromechanics and Microengineering*, 27: 044002, April 2017.
5. Yu Dian Lim, **Liangxing Hu**, Alexander Avramchuck, Dmitry Grapov, Beng Kang Tay, Sheel Aditya, Jianmin Miao and Vladimir Labunov, “Temperature-dependent selective growth of carbon nanotubes in Si/SiO₂ structures for field emitter array applications”, *Materials Research Bulletin*, July 2017, DOI: 10.1016/j.materresbull.2017.07.022.
6. Sanathanan Muttikulangara, Maciej Baranski, Shakil Rehman, **Liangxing Hu** and Jianmin Miao, “MEMS tunable diffraction grating for spaceborne imaging spectroscopic applications”, *IEEE Sensors*, 17(10): 2372, October 2017.
7. Yu Dian Lim, **Liangxing Hu**, Xin Xia, Zishan Ali Syed Mohammed, Shaomeng Wang, Beng Kang Tay, Sheel Aditya and Jianmin Miao, “Field emission properties of SiO₂-wrapped CNT field emitter”, *Nanotechnology*, October 2017, DOI: 10.1088/1361-6528/aa96ed.
8. Yu Dian Lim, Dmitry Grapov, **Liangxing Hu**, Qinyu Kong, Vladimir Labunov, Sheel Aditya, Jianmin Miao and Beng Kang Tay, “Enhanced field emission properties of carbon nanotube bundles confined in SiO₂ pits”, *Nanotechnology*, December 2017, DOI: 10.1088/1361-6528/aaa1bb.

9. Dang Minh Nguyen, **Liangxing Hu**, Jianmin Miao and Claus-Dieter Ohl, "Oscillate boiling with electrical microheaters", *Physical Review Applied*, June 2017. (under revision).
10. Yu Dian Lim, Dmitry Grapov, **Liangxing Hu**, Xin Xia, Shaomeng Wang, Beng Kang Tay, Sheel Aditya, Vladimir Labunov and Jianmin Miao, "Design and fabrication of carbon nanotubes field emitter for microfabricated traveling-wave tube", *IEEE Transactions on Nanotechnology*, October 2017. (submitted)

B. Conference Presentations

1. **Liangxing Hu**, Jianmin Miao and Gerhard Grüber, "Au-Ni-Pt striped nano-swimmer motion: theory and experiments", *2nd IBN International Symposium: Nanomedicine and nanoassays*, Institute of Bioengineering and Nanotechnology, A*STAR, Singapore, December 2014.
2. **Liangxing Hu**, Jianmin Miao and Gerhard Grüber, "H₂O₂ fuelled Au-Ni-Pt nano-swimmer's autonomous propulsion thrust by recoil force induced from O₂ bubble detachment", *4th Nano Today Conference*, Dubai, United Arab Emirates, December 2015.
3. **Liangxing Hu**, Zhiyuan Shen, Jianmin Miao and Gerhard Grüber, "Steerable trajectory of gold-nickel-platinum nanojets with nozzle nanoengines", *IEEE NEMS 2016*, Matsushima and Sendai, Japan, April 2016.
4. **Liangxing Hu**, Jianmin Miao and Gerhard Grüber, "Gold-nickel-platinum nanojets with steerable propulsion using nozzle nanoengines", *IEEE INEC 2016*, Chengdu, China, May 2016.
5. **Liangxing Hu**, Nan Wang, Jianmin Miao and Gerhard Grüber, "Investigation of temperature dependency on the propulsion of disk-like nanoswimmers", *Biosensors 2016*, Gothenburg, Sweden, May 2016.
6. **Liangxing Hu**, Jianmin Miao and Gerhard Grüber, "Pt-Ni-SU-8 microrocket with steerable trajectory using eccentric Pt nanoengine", *International Conference on Electrified Interfaces 2016*, Singapore, Singapore, July 2016.
7. Kai Tao, Jin Wu, Ajay Giri Prakash Kottapalli, Lihua Tang, **Liangxing Hu**, Nan Wang, Sun Woh Lye, Michael Triantafyllou and Jianmin Miao, "Electrostatic/triboelectric hybrid power generator using folded electrets", *Conference: Micro Electro Mechanical Systems (MEMS), 2017 IEEE 30th International Conference on*, Las Vegas, United States of America, January 2017.

8. Kai Tao, H. L. Chang, Jin Wu, Lihua Tang, Ajay Giri Prakash Kottapalli, **Liangxing Hu**, Sun Woh Lye and Jianmin Miao, “Enhanced performance of electrostatic energy harvester with integrated opposite-charged electrets”, *Conference: 19th International Conference on Solid-State Sensors, Actuators and Microsystems (TRANSDUCERS)*, Taipei, Taiwan, June 2017.
9. Solange E. Astorga, **Liangxing Hu**, Enrico Marsili and Yizhong Huang, “Ordered structured array electrode for enhancing bioelectrochemical sensors”, *1st Singapore ECS international Symposium on Energy Materials*, Research Techno Plaza, Nanyang Technological University, Singapore, December 2017.
10. Sanathanan Muttikulangara, Maciej Baranski, Shakil Rehman, **Liangxing Hu** and Jianmin Miao, “In-plane rotational tuning of polymer diffraction grating for diverse imaging spectroscopy”, *8th IEEE International NanoElectronics Conference (INEC 2018): Nanoelectronics for IoT*, Kuala Lumpur, Malaysia, January 2018.
11. Sanathanan Muttikulangara, Maciej Baranski, Shakil Rehman, **Liangxing Hu** and Jianmin Miao, “Diffraction grating integrated on micromachined stepper motor for diversity implementation in imaging spectroscopy”, *Conference: Micro Electro Mechanical Systems (MEMS), 2018 IEEE 31th International Conference on*, Paris, France, January 2018.

C. Patents

1. Dang Minh Nguyen, **Liangxing Hu**, Jianmin Miao and Claus-Dieter Ohl, “Electric-powered heat transfer device to enhance heating and cooling of substrates in contact with liquids”. (filed by Nanyang Technological University, Singapore)