

PAPER

Concentric bimetallic microjets by electrodeposition†

Cite this: DOI: 10.1039/x0xx00000x

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Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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Self-propelled micro and nanosystems are at the forefront of nanotechnology research. Here we describe a method for fabrication of concentric bimetallic microjets *via* an electrochemical deposition route. These microjet engines consist of an inner platinum layer which is responsible for the catalytic decomposition of H_2O_2 , which subsequently results in bubble-propelled movement. The outer copper layer allows for further functionalization of the microjet engines. These microjet engines are able to move at speeds of ~ 7 bodylengths s^{-1} at fuel concentrations as low as 0.2% (wt.) of H_2O_2 . The described method obviates the need to use physical vapor deposition (sputtering) and thus is applicable in any low-end equipped laboratory. Such an accessible method is expected to lead to a dramatic increase in the research activity on artificial self-propelled systems.

Introduction

Self-propelled nano and micromotors are at the forefront of nanotechnology research.^{1–6} These artificial machines are expected to be able to engage in various tasks, ranging from drug delivery to environmental remediation and discovery of natural resources.^{7–10} There has been a recent increase of interest in bubble-propelled catalytic microjet and nanojet engines.^{11–15} These micro and nanojets operate based on the same propulsion principle, which is the catalytic decomposition of fuel, typically H_2O_2 , on platinum (Pt) surfaces to create oxygen bubbles that subsequently propel the devices. Microjets were originally rolled-up microtubes prepared using thin-film technology, based on the depositions of nanometer thin layers of various metals which rolled up into tubular shapes.^{12,16–21} This technology is rather demanding since it requires clean room facilities. On the other hand, a more cost-effective method for fabrication of microjets was developed and involves the electrochemical polymerization of conducting polymers and subsequent electroplating of Pt in a membrane template.^{13,14,20,21} Such microjets consist of concentric layers of inner catalytic Pt and outer conducting polymer. The template-based plating method significantly simplified the fabrication of microjets.²² The polymer outer layer can lead to limitations with respect to further functionalizations on the microjets. For example, to utilize a thiolated gold surface, typically, another metallic Au layer must be deposited onto the polymer *via* physical vapor deposition to allow for subsequent functionalizations.^{20–23}

Here we wish to demonstrate an electrochemical deposition method that allows for the fabrication of concentric bimetallic microjets. This method results in the creation of microjets with catalytic Pt inner surfaces and metallic outer surfaces. In addition, this method completely obviates the use of physical vapor deposition (metal sputtering) in its fabrication steps, which makes it extremely simple and accessible for most laboratories.

Experimental section

Materials

Cyclopore polycarbonate membranes with pores of 2 μm in diameter were purchased from Whatman, USA (Cat. No. 7060-2511). The pores are conical in shape. Colloidal graphite (isopropanol base) was purchased from Ted Pella, Inc., USA (Lot. No. 12009-2). Hydrogen peroxide (27%) was purchased from Alfa Aesar, Singapore (Lot. No. 10151507). Dimethyl sulfoxide (DMSO), methylene chloride and ethanol were purchased from Tedia, USA. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (98+%) and sodium dodecylsulfate (SDS, Lot. No. 079K0335) were purchased from Sigma-Aldrich. Platinum plating solution was obtained from Technic Inc., USA (Lot No. 20251001). The chemicals were used as received and ultrapure water (18.2 $\text{M}\Omega \text{ cm}$) from a Millipore Milli-Q purification system was used for all of the experiments.

Apparatus

Electrochemical deposition was carried out using a $\mu\text{Autolab}$ type III electrochemical analyzer (Eco Chemie, The Netherlands) connected to a computer and controlled by General Purpose Electrochemical Systems version 4.9 software (Eco Chemie). The deposition procedure was conducted at room temperature (25 °C) using a three-electrode arrange-

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† Electronic supplementary information: Videos S3A and S3B exhibiting the behaviour of microjets in the absence (S3A) and presence (S3B) of 1% H_2O_2 . Video S1 for their motion in 0.2% H_2O_2 .

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

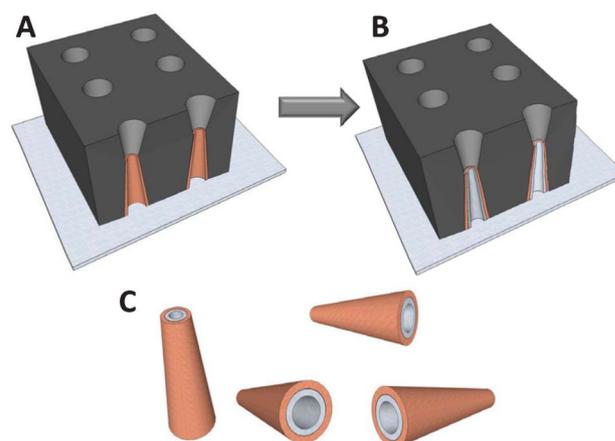
Methods

Synthesis of Cu/Pt concentric bimetallic microtubes

The Cu/Pt concentric bimetallic microtubes were synthesized *via* a modified electrochemical deposition procedure on a cyclopore polycarbonate template.²² Colloidal graphite ink was applied to one side of the polycarbonate template using commercial cotton swabs. A piece of flattened aluminium foil was attached to the ink immediately, to serve as a working electrode for the plating experiments. The template was assembled into a customized electrochemical deposition cell. The template was rinsed with 5 mL of ultrapure water (18.2 M Ω cm) four times, and the Cu outer layer was deposited galvanostatically at -4 mA for 450 s from a deposition solution which contained 1 M CuSO₄. Subsequently, after removing the deposition solution, the template was rinsed five times with 8 mL of water. The platinum segment was then electrodeposited at -4 mA for 450 s, using a commercial plating solution. When the deposition of Pt layer on the microtubes was completed, the electrochemical cell was disassembled and the template was washed five times with 8 mL of water each time. After that, the template was ultrasonicated three times in 2 mL of water for 3 min each time. The graphite layer was removed during the ultrasonication procedure. The template was placed in an Eppendorf tube with 2 mL of methylene chloride and ultrasonicated until the whole template was dissolved. The electrochemically deposited microtubes were collected as a pellet after centrifugation at 6000 rpm for 3 min and subsequently washed three times with methylene chloride. The solution was then washed with ethanol and water two times each and centrifuged for 3 min after each washing step. The microtubes were stored in water at room temperature.

Operation of microjets

The microjets were set into motion for propulsions in aqueous solutions containing various concentrations of hydrogen peroxide with a fixed surfactant concentration. A mixture of microjets (5 μ L), SDS (1 wt%) and H₂O₂ was applied to a glass slide which had been freshly cleaned with nitrogen gas. The behaviour of the microjets was then observed under the microscope. Optical microscope videos and images were obtained using a Nikon Eclipse TE 2000-E microscope. Video sequences (100 fps) were processed with Nikon NIS-ElementsTM software.



Scheme 1 Template-based electrodeposition of concentric bimetallic microjets. (A) The copper layer is grown electrochemically in a template micropore connected to a carbon electrode. (B) The Pt layer is grown. (C) The template membrane is dissolved and the microjets are freed.

Results and discussion

The concentric bimetallic microjets were fabricated in cyclopore polycarbonate membranes *via* an electrodeposition process. The conductive colloidal graphite ink was applied to one side of the polycarbonate membrane to provide a conductive contact for subsequent metal deposition. The copper outer layer was electroplated from a CuSO₄ solution based on a galvanostatic deposition method and the inner Pt layer was electroplated from a commercial plating solution (Scheme 1).

Upon dissolution of the template, the microtubes were examined using scanning electron microscopy (SEM) and found to exist as conical shapes. We noted that in previous work by other authors, the Au outer layer was deposited in DMSO solution. This solution led into dissolution of polymer membrane and poor yields of microtubes.²² However, the Au/Pt microtubes synthesized showed agile motion.²² Fig. 1 shows the membrane (A) before and (B) after plating the microtubes, demonstrating that our method does not lead to damage of the membrane; instead it leads to large parallel fabrication of concentric bimetallic microtubes.

Fig. 2 A, B and C show SEM images of the fabricated Cu/Pt microjet engines at various magnifications. It is observed from the SEM images that the microtubes retain the conical shape of the template membrane pores; the average length of the microtubes was approximately 7 μ m and the diameters of the tubes are ~ 1.5 and ~ 2 μ m at their opposite ends. Fig. 2 D and E show the energy dispersive X-ray spectroscopic (EDX) investigation of the prepared bimetallic microtubes. The SEM/EDX images clearly show the presence of Cu and Pt layers on the microtubes. Statistical analysis of 20 microjets ($n = 20$) showed that the average length is 10.4 μ m ($\sigma = 2.6$), the diameter at the larger opening end is 1.92 μ m ($\sigma = 0.34$), and the diameter at the smaller opening end is 1.43 μ m ($\sigma = 0.31$).

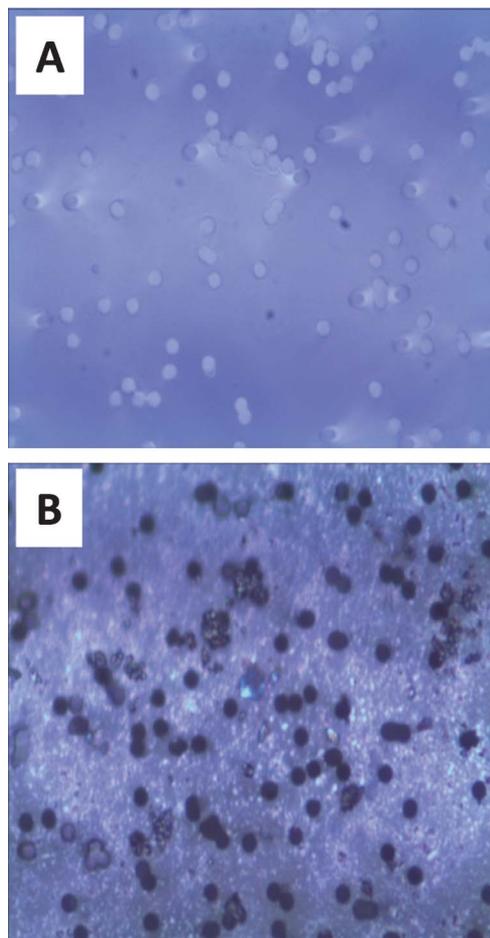


Fig. 1 Optical micrograph of the polycarbonate membrane (A) before and (B) after electrochemical growth of concentric bimetallic Cu/Pt microjets.

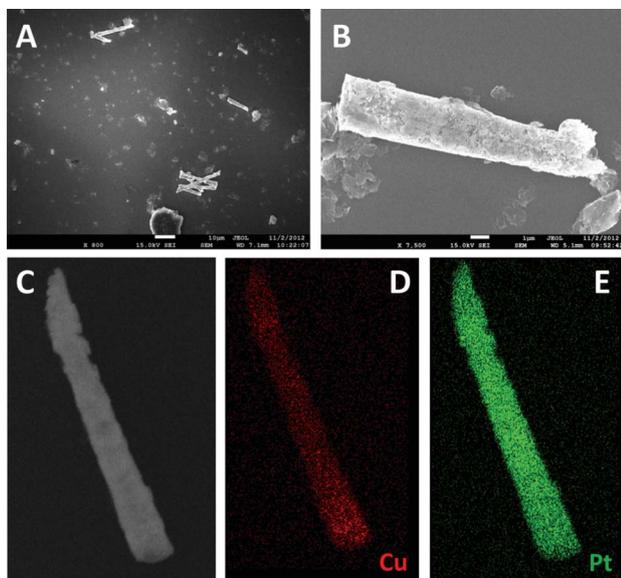


Fig. 2 Scanning electron micrographs of microtubes freed from the membrane (A, B, C). Note that debris around microtubes is graphite from the graphite ink. SEM/EDX elemental characterization of microjet composition (D, E).

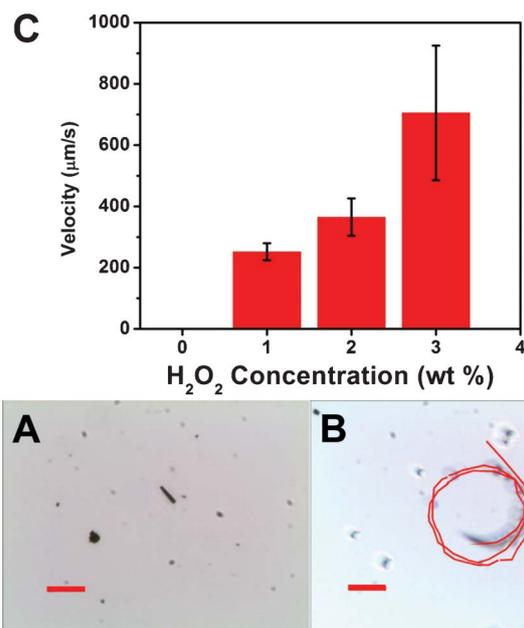


Fig. 3 Optical micrographs of the microjets in (A) the absence and (B) the presence of 1% (wt.) H₂O₂ fuel. Scale bars of 20 μm; tracking line for 5 s. (C) Plot showing dependence of average velocities of microjets on concentration of fuel.

The bimetallic microjets moved in the hydrogen peroxide solutions at high speeds, similar to previously fabricated rolled-up microjets or polymer/Pt microjets. The microjet engines show fast movement speeds of ~ 7 bodylengths s^{-1} ($bl s^{-1}$), even in a very low concentration of 0.2% hydrogen peroxide fuel (Video S1†). Fig. 3 shows the microtubes in the (A) absence of H₂O₂ and (B) in the presence of 1% H₂O₂. See also the corresponding supplementary videos S3A and S3B (ESI†). The dependence of the microjets velocities on the concentration of H₂O₂ is highlighted in the graph shown in Fig. 3C).

Conclusions

In summary, we have demonstrated the possibility of preparing functional concentric bimetallic catalytic microjet engines using an electrochemical deposition method. This method obviates the use of physical vapor deposition during the preparation procedure. This method also obviates the use of an organic solvent for outer metal layer plating, allowing parallel production of microjets. The resulting microjet engines exhibited excellent performances and high velocities of ~ 7 $bl s^{-1}$ even at very low fuel (0.2% (wt.) H₂O₂) concentrations. Such a simple methodology for the preparation of functional²⁴ microjet engines is of high importance as it can be practically employed in most laboratories.

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