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Self-propelled nanojets *via* template electrodeposition†

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In this paper, we present a rapid, high-yield, low-end and low-cost fabrication of nanojet motors using a template directed electrochemical deposition method. Using an electrochemical deposition method, the bubble-ejecting nanojets were grown within the alumina template, which is commercially available. These fabricated nanosized devices have typical dimensions of 300 nm (diameter) by 4.5 μm (length), and they are able to move in a hydrogen peroxide fuel solution with velocities up to approximately 40 body lengths per second. They are also capable of exhibiting various modes of movement such as straight, screw-like and circular motions, in a similar manner comparable to larger micro-sized jets. In addition, due to their small dimensions, the movements of these nanojets can be strongly influenced by colliding them with microbubbles. This highly parallel method which is of low-cost and requires the usage of low-end equipment that can be easily located in any laboratory opens up the doors for world-wide nanojet fabrication in the near future.

Introduction

It is envisioned that self-propelled nanoscale machines will have a significant effect in biomedical, security and environmental applications.^{1–3} Self-propelled nanomotors consisting of two metallic segments were first introduced less than a decade ago.^{6–8} These nanomotors have been based on template-grown bi- or multi-metallic nanorods (typically Au and Pt), with a diameter of about 300 nm and a typical length of several micrometers.⁹ The propulsion mechanism is based on the oxidation/reduction of the fuel (typically hydrogen peroxide) at individual metallic segments, yielding the flow of the electrons into the rod and the flow of hydronium ions at the surface of the rod, effectively propelling it in the opposite direction to this flow *via* self-electrophoresis.¹⁰ The velocity of these devices ranges from 4–15 body lengths per second (bl s^{-1}) to 30–75 bl s^{-1} , depending on the composition of the segments.^{6,11–13}

A new class of the self-propelling devices of micro-scale sizes was developed recently. These devices have the shape of a microtube with a diameter of several micrometers and the length of approximately 50 μm , and the propulsion mechanism is based on the bubble ejection that is generated by the catalytic reaction of the fuel (H_2O_2).^{14,15} The self-propelled microjet engines are typically prepared using a high-end technology which requires a clean room, metal evaporation and deposition with the consequent roll-up of thin films.^{14–21} The alternative technology of microjet fabrication is by utilizing

electrochemical template deposition.^{13,22–24} It is of high interest to scale down the size of these microjets to nanoscale dimensions which are comparable to biological structures. The first case of bubble propelled nanojets has been reported recently by Sanchez *et al.*²⁵ The devices of about 300 nm $\times$ 10 μm were fabricated by a rolled-up technology. This technology requires the top-down photolithography in a clean room, electron-beam evaporation and the stress-induced rolled up of the nanotubes. Developing a batch of nanojets using these processes would take several days to complete, and necessitates a high-end environment for production. Here we describe a highly parallel, simple, fast and low-cost fabrication of nanojets by the template electrochemical deposition method. These nanojets have the dimensions of 300 nm $\times$ 4.5 μm and are smaller than typical micro/nanojets (dimensions 300–5000 nm $\times$ 10–50 μm) and they represent the smallest bubble jet engines fabricated to date.²⁶ We will proceed to demonstrate that these nanojets can exhibit fast motions up to 40 bl s^{-1} as well as display the same modes of motion as their microjets counterparts. In addition, due to their small size, they are also able to exhibit strong interactions with the microbubbles encountered during their movement.

Experimental part

Synthesis of Au–Pt bimetallic nanotubes

The Au–Pt bimetallic nanotubes were synthesized with an improved electrochemical deposition procedure on an aluminum oxide (AAO) template. The aluminum oxide templates with pore size of 200 nm were purchased from Whatman® (Cat. no. 6809-6022, Germany). Silver conductive ink (Lot # L18U007, Alfa Aesar, Singapore) was applied on one side of the AAO template with commercial cotton swabs. A piece of flattened

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aluminum foil was attached to the ink immediately, which serves as the working electrode. The template was assembled into a customized electrochemical deposition cell. A platinum counter electrode and a Ag/AgCl reference electrode were utilized. Electrochemical deposition was carried out with a μ Autolab type III electrochemical analyser (Eco Chemie, The Netherlands) connected to a computer and controlled by General Purpose Electrochemical Systems Version 4.9 Software (Eco Chemie). The template was rinsed with 5 ml of ultrapure water ($18.2 \text{ M}\Omega \text{ cm}$) for 4 times, and a Cu sacrificial layer was deposited galvanostatically at -10 mA for 900 s. The deposition solution contains 1 M CuSO_4 . Consequently, after removing the solution, the template was rinsed 5 times with 8 ml of water. Pt and Au were then deposited at -5 mA for 2700 s each, using the commercial plating solutions (Technic, Inc). After washing for 5 times with 8 ml of water each, the template was ultrasonicated for 3 times in 2 ml of diethylene glycol monoethyl ether acetate (Alfa Aesar) for 60 s each time. The silver ink layer was removed completely during the sonication procedure. The template was then soaked in 3 ml of 5 M HNO_3 (Alfa Aesar) solution until the Cu layer is no longer visible. After washing with water, the template was placed in an Eppendorf tube with 2 ml of NaOH (Alfa Aesar) and ultrasonicated till no shards remain. The solution was washed and centrifuged at 1500 rpm for 1 min for 10 times with 2 ml of water to completely remove the salt impurities. The final aqueous solutions of nanotubes were stored at room temperature. Scanning electron microscopy (SEM/EDX) analysis was obtained with a JEOL JSM 7600F instrument.

Nanojet motion

Motion of the nanojet engines was investigated in an aqueous solution containing 9 wt% of hydrogen peroxide at constant surfactant concentrations (1 wt% of SDS). Both were obtained from Alfa Aesar. Optical microscope videos and images were obtained with a Nikon Eclipse TE 2000-E microscope, CFI 10 $\times$ optics. Video sequences were processed with Nikon NIS-ElementsTM software.

Results and discussion

The highly parallel fabrication of template-based nanojets by electrodeposition is presented in Scheme 1. We used a commercially available alumina template membrane. Briefly, the fabrication process involves the placement of a conducting silver paste at the alumina membrane, followed by the electrochemical deposition of a copper sacrificial layer, with the Pt and Au components being introduced by means of chronocoulometry.²⁷ Subsequently, the membrane template and sacrificial layers are dissolved, yielding the Au–Pt nanotubes in large arrays, as we have shown with scanning electron microscopy (Fig. 1). These nanotubes consist of two longitudinal segments, gold and platinum, which are confirmed by using SEM/X-ray energy dispersive spectroscopy mapping (SEM/EDX; Fig. 2A). Note that the longitudinal placement of various segments is impossible when using any of the previously described technologies for microjet fabrication.^{14–24,28} It should

Scheme 1 Growth procedure for the bimetallic nanotubes. Silver ink was applied on one side of the AAO template followed by the attachment of flattened aluminium foil. Sequential plating of Cu, Pt and Au was carried out at fixed currents. The Au–Pt nanotubes were freed after removing the silver ink and etching away the template.

Fig. 1 Scanning Electron Microscope (SEM) characterizations of the Au–Pt nanotubes. (A) View of the nanotubes before the removal of the Cu layer; (B) nanotubes on Si wafer after the removal of the Cu layer. Scale bars indicate $1 \mu\text{m}$ (A) and $10 \mu\text{m}$ (B).

be noted that the SEM/EDX is a preferred method for the identification of the segments, as the individual segments show a negligible contrast difference in the SEM imaging mode. The purpose of fabricating the bimetallic Au–Pt tubes is that each individual segment can be specifically functionalized. It should be noted that using a similar method the nanorods can be

Fig. 2 (A) Elemental mapping using SEM/EDX. Red color denotes Pt and green color denotes Au. (B) Secondary Electron Image (SEI) of the same tube showing different brightness of Pt and Au. Scale bars indicate 2 μm (A) and 1 μm (B).

prepared. The driving element which determines whether the nanoobject will be hollow (nanotube) or filled (nanorod) is the fabrication of the first conductive layer (Ag) as described previously. If the first conductive layer is deposited in the way that it enables electrochemical deposition only at the walls of the nanopores, the resulting structures are nanotubes. If the first conductive layer allows electrodeposition across the nanopores, the resulting structures are nanorods.^{29–31}

It is important to discuss the shape and size distribution of the mass-fabricated nanojets. The length is dictated by the duration of the electrolytic process. However, at given conditions, the length can vary across the same batch nanojet fabrication. As depicted in Fig. 3, the typical length is 4.5–5.0 μm with about 65% of the nanotubes having lengths in the range of 4.0–6.0 μm and whole distribution ranging from 2.2 to 7.06 μm ($n = 50$, standard deviation (σ) = 1.16 μm). The presence of very short (2–3 μm) tubes is likely to be due to breakage of the longer nanotubes during the processing. The mean outer diameter is 310 nm with distribution from 200 to 410 nm ($n = 100$; $\sigma = 50$ nm). The mean inner diameter is 230 nm, whole distribution

Fig. 3 The distribution of dimensions of nanojet motors fabricated by electro-deposition. (A) Length of nanotubes ($n = 50$); (B) inner nanotubes diameter ($n = 100$) and (C) outer nanotubes diameter ($n = 100$).

is ranging from 120 to 330 nm ($n = 100$; $\sigma = 40$ nm). The shape of the nanotubes is dictated by the template and its quality. It is possible to observe nanotubes which are not straight or are merged.

We investigated motion of the Au–Pt nanotubes. We also investigated whether these nanobubbles detach from the nanojets to give rise to their motion. In Fig. 4, we show that

Fig. 4 Influence of the hydrogen peroxide concentration on the velocity of the nanojets. As the concentration of fuel increases, the nanojets run with a higher average velocity. The tracking data were obtained for a time scale of 10 seconds from 6 independent experiments. The inset shows the tracking image for typical nanojets running in the fuel solution (H_2O_2 concentration of 9%). Scale bar indicates 20 μm .

Fig. 5 Different modes of motion were observed for the nanojets: (A) jets running in a straight path; (B) circular motion of the nanojet; (C) screw-like motion; (D) snapshots of a nanojet moving in the circular path of small radius. Scale bars indicate 10 μm in (A–C) and 2 μm in (D).

indeed the Au–Pt nanotubes exhibit movement in 3–15% H_2O_2 , with the velocity ranging from 20 to 40 $\mu\text{m s}^{-1}$. The velocity in $\mu\text{m s}^{-1}$ units is highly comparable with that of typical microjet motors, as well as that of the fastest bimetallic nanorods.³² It is

also obvious that the concentration of the fuel, hydrogen peroxide, strongly influences the motion of these nanojets. The average velocity of the motion of nanojets is $71 \mu\text{m s}^{-1}$ ($n = 6$) at a concentration of H_2O_2 of 3%. With the increment of the H_2O_2

Fig. 6 Effect of bubbles on the motion of nanojets. Due to their small size, the motion of the nanojets could be affected by the bubbles generated by themselves. (A) Abrupt change in the direction when the nanojet collides with the bubble; (B) the nanojets can be engulfed when colliding with the bubble it previously generated. Scale bars are of 10 μm.

concentration to 15% (wt), the velocity of the jet engines increases to $111 \mu\text{m s}^{-1}$. See Video S1 (ESI†) for the related motion picture. We know that microjets motors can exhibit a variety of motions such as straight, screw-like or circular, depending on the small variations of their shape. To that, we have also shown in Fig. 5 that the nanojets are capable of exhibiting the same styles of the movement as their microscopic counterparts, and that is (A) straight, (B) circular and (C) screw-like motion. Fig. 5D exhibits the time-lapse images of the circular motion of the nanojet. See Videos S2–S5 (ESI†) for corresponding motion pictures.

It is of interest to investigate whether O_2 bubbles expelled by the nanojet influence its motion. Previously, the interactions of bubbles were studied with microjets.^{14,33,34} Due to the nanometer size of nanojets studied here and their bubble-propulsion mechanism, it is possible to observe interactions of these nanojets with microscopic gas bubbles in the solution in a different manner from that with microjets. Fig. 6A shows time-lapsed microscopic images of the nanojet colliding with the microscopic bubble, and this collision results in a dramatic change in the direction of motion by about 160° (“bouncing back”; see Videos S6 and S8† for related motion pictures). Another interaction of nanojet with gas bubble is demonstrated in Fig. 6B. The nanojet is trapped on the liquid–air interface of the microbubble which was previously ejected from the nanojet and it moves on the air–liquid interface of the bubble in a circular fashion. The ejected O_2 gas yielded an increase in the bubble diameter which will eventually burst when the bubble reaches a certain size, freeing the nanojet to continue its motion in the solution. Note that these data are qualitative as it is not possible at present to navigate the nanojets directly into the bubble surface in a controlled manner. Nevertheless, these interactions can be seen often; see Videos S7 and S9† for related motion pictures.

Conclusions

We have presented in this study a method for an equivalent, rapid and inexpensive fabrication of nanojet engines, *via* the electrodeposition in a commercially available alumina membrane template. These nanojet engines exhibit fast movements in hydrogen peroxide solution with speeds up to 40 body lengths per second. The nanojets can exhibit different movements, such as straight, screw-like and circular motions, which are analogous to their microjet counterparts. In addition, the nanoscale size of the nanojets when compared to sizes of the ejected microbubbles actually allows the nanojet motion to be strongly influenced whilst encountering such bubbles. The nanojets presented in this work represent the smallest nanojet engines (from the viewpoint of length $\times$ diameter) presented to date. In addition, the simplicity of the template assisted electrochemical deposition fabrication method and its low-end requirements open the doors for fabrication of such nanojets in practically any laboratory.

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