

**Geometric Asymmetry Driven Janus Micromotors**

Journal:	<i>Nanoscale</i>
Manuscript ID:	NR-ART-05-2014-002393.R2
Article Type:	Paper
Date Submitted by the Author:	14-Jul-2014
Complete List of Authors:	Zhao, Guanjia; Nanyang Technological University, Division of Chemistry and Biological Chemistry Pumera, Martin; Nanyang Technological University, Chemistry and Biological Chemistry

Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

Geometric Asymmetry Driven Janus Micromotors

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

The production and applications of nano-/micromotors are of high importance. In order for the motors to work, asymmetry in their chemical composition or physical geometry must be present if no external asymmetric field is applied. In this paper, we present a “coconut” micromotor made of platinum through the partial or full etching of the silica templates. It was shown that although both the inner and outer surfaces are made of the same material (Pt), motion of the structure can be observed as the convex surface is capable of the generation of oxygen bubbles. This finding shows that not only chemical asymmetry of the micromotor, but also the geometric asymmetry can lead to fast propulsion of the motor. What’s more, a considerably higher velocity can be seen for the partially etched coconut structures than the velocities of Janus or fully-etched shell-like motors. These findings shall have high importance on the design of the micromotors.

Introduction

Self-propelled autonomous catalytic nano, micro and macromotors are of very high importance and interest as they are the next steps forward for nanotechnology.¹⁻⁷ These tiny devices were suggested to play major roles in future healthcare^{8,9}, environmental remediation^{10,11} and natural resources discovery.¹²

These tiny self-propelled nano/micro-motors and micro robots are typically powered by self-electrophoresis^{13,14}, self-diffusiophoresis^{15,16} or bubble-ejection^{17,18} propulsion. For any propulsion systems with low Reynolds numbers¹⁹, the inertia does not play a role in the propulsion and motion mechanism is based on chemical asymmetry of the surfaces.²⁰ That is, for self-electrophoresis, opposite ends of nano/microrod are made from different metals to create a difference of the electrochemical potential. This leads to asymmetric flow of electrons inside the rod as compared to the hydronium ions on the surface of the rod, propelling it in the opposite direction as to the electron flow.²¹ Self-diffusiophoresis is based on microdevices which have chemically modified surface capable of performing localised chemical reaction while the products are being asymmetrically released, resulting in motion.²² In the case of bubble propulsion-based microtube devices, the interior is made of catalyst (Pt or catalase enzyme),^{23,24} which are capable of decomposing fuel and generating bubbles, while the exterior is made of non-catalytic materials, such as gold. In the case of bubble-propelled Janus particles, as the name suggests, it has two asymmetric sides, where one is catalytic and the other non-catalytic.²⁵ The self-propelled systems are deliberately designed and constructed from a range of materials to ensure asymmetric distribution of the materials resulting in the motion of the device.

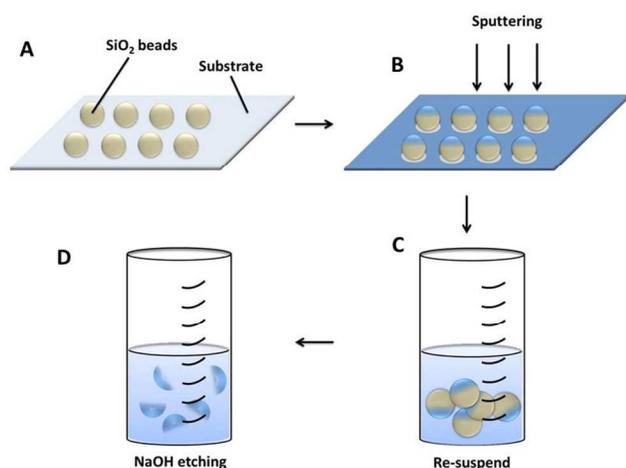
Here we wish to discuss the case where the micromachine is

chemically homogenous, that is it is made from the same material. The propulsion is induced by the geometric difference of the device. Kovtyukhova reported all Pt-based microrods exhibited motion.²⁶ Even though the exact mechanism of the motion was not identified, it is likely that the different active sites on the Pt microrod surface exhibited different catalytic activities and resulted in the different chemical potentials. All Pt microtubes propelled by bubble-ejection were powered from their interior surfaces, as reported recently by our group.²⁷ Here we wish to show that chemically homogeneous Pt hollow semi-spheres made solely of Pt contain geometric asymmetry and can exhibit rapid propulsion.

Results and discussion

Fabrication and characterization of Janus “coconut” motors

We created chemically homogenous micromotor with coconut shell-like hollow structure. Silica beads were used as templates for the fabrication of shelled structure motors. The “coconut” micromotors were made by sputtering a Pt layer on the silica beads and a consequent etching of the silica with 3 M NaOH solution. As shown in **Scheme 1**, the suspension of silica beads in water (20 mg/mL, 100 μ L) was applied on a cover slip, which was pre-treated by washing and O₂ plasma. After drying overnight, a layer of Pt (40 nm) was sputtered on the silica beads. The Pt-capped beads were resuspended in NaOH solution and ultrasonicated. After that, the cover slip was removed and the silica beads were allowed to dissolve under ultrasonication in the NaOH solution. Depending on the reaction time, the Pt-capped silica beads (Janus motors) eventually became half-shelled “coconut” structures or the thoroughly etched shell-like structures. The final products were stored in water suspension at room temperature.



Scheme 1. Fabrication process for the micromotors. (A) The silica beads were suspended in water and applied on the freshly cleaned cover slip. (B) A layer of 40 nm Pt film was sputtered on the beads substrate. (C) The Pt-coated silica beads (Janus motors) were lifted off from the substrate into water by ultrasonication for 3 minutes. (D) The silica was etched in 3 M NaOH for 2 h (for “coconut” motors) or 6 h (for shell-like motors), leaving only the intended structures of the motors.

Figure 1 shows the SEM characterizations of both the Pt-capped silica beads and the coconut structures. There are two SiO₂ beads in Figure 1A, and both are coated with a layer of Pt metal. As the backscattered electron images were taken, difference in brightness indicates the difference in atomic number. The brighter parts of the beads, relative to the background silicon wafer and the darker part of the beads, indicate the presence of elements heavier than silicon, which is platinum in this case. Similarly as shown in Figure 1B, the brighter hollow structure is made of Pt. It should be noted that due to the thin layer of the coconut (40 nm), they collapsed to form flat and folded structures in the vacuum environment. The inset in Figure 1B shows the structure in water suspension, indicating a coconut structure. It can also be seen in the supporting information (Figure SI-1) that the coconuts showed a diameter of 23 μm (with a standard deviation of 4.4 μm), having a similar size to that of the beads.

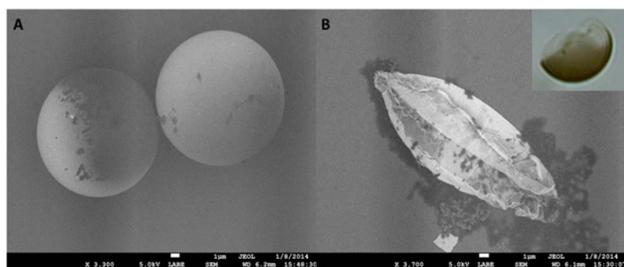


Figure 1. Characterizations of the structures with scanning electron micrographs (SEM). (A) silica beads with a layer of Pt (40 nm) sputtered on surface. (B) After etching with NaOH, the silica was dissolved, leaving only the Pt shell, which appeared to be flattened and folded under SEM. The inset shows one of such shell in water under optical microscope. Scale bars of 1 μm.

Motion of the fully and partially etched “coconut” micromotors

Here we wish to show that chemically homogeneous Pt

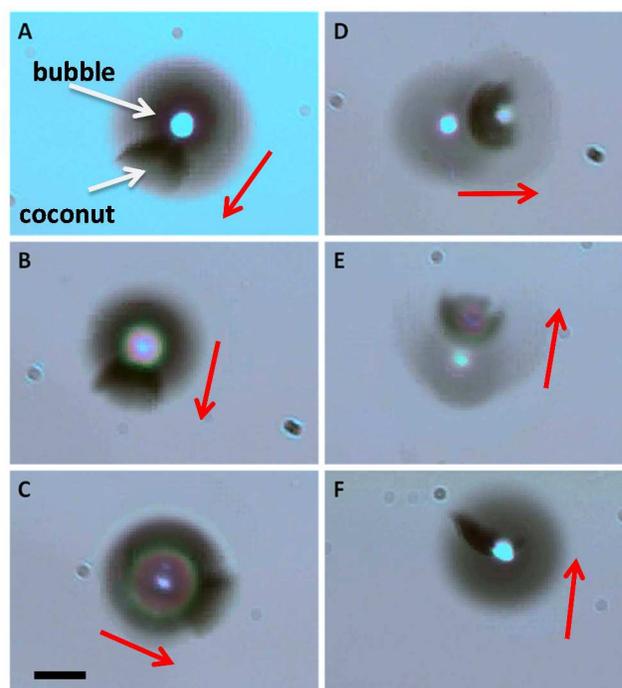


Figure 2. Time lapsed snapshots of fully etched Pt coconut generating bubbles at convex surface of the motor. Time difference ~1 s between the snapshots A-F; see Video S-1 for full motion picture. Diameter of coconut shell 19 μm. Scale bar of 20 μm. Red arrows show direction of the motion of the motor. Conditions, 7% H₂O₂, 1% SDS.

micromotors with geometric asymmetry are capable of motion. Platinum has been reported to be a good catalyst for the decomposition of hydrogen peroxide.²³ In the presence of Pt, disproportionation of hydrogen peroxide occurs vigorously to generate oxygen gas bubbles. When the micromotors were mixed with hydrogen peroxide in the presence of SDS, the detachment of bubbles provides the thrust for the micromotors, in the condition that the fuel concentration is sufficiently high.²⁸

Bubbles are observed as the motors run, and the detachment of bubbles from the convex surface of the coconuts, as shown in Figure 2 (see Video S-1 in Supplementary Information), provides the thrust for the motion. Although both the inner and outer surfaces of the structure are catalytically active as they are made of the same material (Pt), we observe bubble formation at convex surface only.

In the following text we wish to compare motion of chemically homogenous Pt coconut shell structures to chemically heterogeneous microstructures. The fabrication process of the “coconut” micromotors involves the sputtering of a layer of platinum thin film on the silica beads and the subsequent etching of the silica. Thus during this process, a total number of 3 different structures can be generated, namely (i) the Pt-silica Janus structure, (ii) the core-shell structure with Pt encapsulating un-etched silica residues, and (iii) the Pt shelled structures. **Figure 3** shows the characterization of the structures *via* SEM (additional SEM images are shown in Figure SI-2). When the

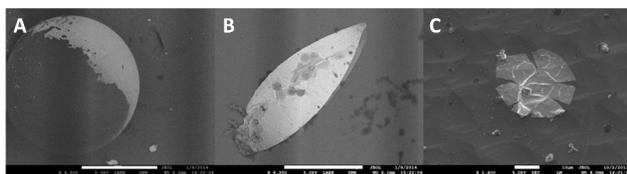


Figure 3. SEM characterizations of three different types of structures through the fabrication process of the “coconut” micromotors. (A) Pt-silica Janus structure, (B) the core-shell structure with Pt encapsulating un-etched silica residues (the coconut structure), and (C) the Pt shelled structure. Scale bars are 10 μm in (C).

backscattered electron image was taken for the Janus structure, the difference in brightness indicates the different elements. It can be seen from Figure 3A that a layer of platinum was coated on the silica bead for the Pt-silica Janus structure. While for the partially etched structure, presence of residual silica gives a darker contrast, as shown in Figure 3B. On the other hand, the fully etched coconut structures will break up under the vacuum conditions for SEM, Figure 3C.

Even though these structures have different extents of asymmetry, they are able to show motion when mixed with sufficient amounts of hydrogen peroxide. Similar velocities were observed for the shell structure and the Janus motors, but the velocities are considerably higher for the partially etched coconut motors, as shown in Figure 4. For the Janus motors (SiO_2 beads with Pt layer on one side), reaction of hydrogen peroxide fuel only occurs on the convex surface of the motor; however, Janus particle motors move slowly due to their large mass due to the bulk of SiO_2 . For the motors of a shell structure, both sides are active and the motion is due to a resultant force from the subtraction of propulsion due to the H_2O_2 decomposition at the convex surface from the one at the concave surface. As the oxygen generation rate is much higher at the convex surface (as inferred from observation of bubbles generated on convex surface) and the coconut shell Pt motors have much lower mass than SiO_2 full Janus motors, a faster speed as compared to that of the Janus motors is observed. It should be mentioned that with decreasing concentration of H_2O_2 the percentage of viable (that is, moving) motors decreases.²⁹ This phenomena was observed previously and it is for this case (in connection with Figure 4) quantified in Figure SI-3.

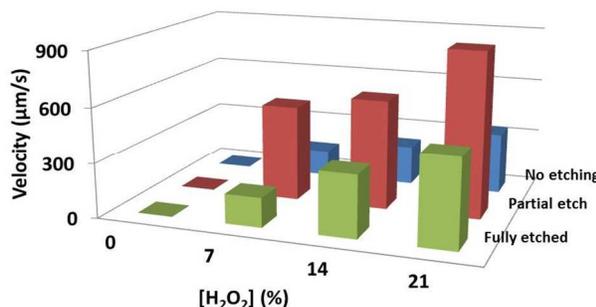


Figure 4. Velocity profiles of the coconut jets with different extents of etching.

All nanoshell motors run based on the bubble propulsion mechanism, and they tend to show a higher capability of motion in comparison to the capability of the Janus motors. When the silica beads were only partially etched, the micromotors possessed a structure similar to the fully-etched shell-structured motors.

Conclusions

In this paper, we introduce the platinum micromotors of shell structures. For the fully-etched shell structures, although there is a lack of asymmetry in chemical composition, the presence of the difference in curvature ensures the generation of asymmetric surface gradients. This is a novel design of asymmetry since both sides of the structure are made of the same material. Additionally, when the silica parts were only partially etched to form the “coconut” motors, a higher ability of motion can be seen as compared to the fully-etched structures. The conclusion that pure geometric asymmetry (without chemical/materials asymmetry) can lead to very efficient motion of motors is of high importance for simplified design of fast-moving motors.

Experimental

Materials The platinum target for sputtering was purchased from Quorum Technologies Ltd, UK. Hydrogen peroxide (27%, Lot. no. 10151507 was purchased from Alfa Aesar, Singapore. Sodium dodecylsulfate (SDS, Lot No. 079K0335) was purchased from Sigma-Aldrich. Silica beads (diameter estimated to be 20 μm) were purchased from Alfa Aesar (Lot # C19W016). All chemicals were used as received and solutions were prepared using ultrapure water (18.2 M Ω cm) from a Millipore Milli-Q purification system.

Apparatus The sputtering of Pt was carried out with JEOL JFC-1600 Auto Fine Coater. The ultrasonication process was carried out with a Fisherbrand FB 11203 ultrasonicator, and centrifugation was carried out with a Beckman Coulter Allegra 64R centrifuge. The O_2 plasma was done with Harrick Plasma Cleaner (PDC-002). Scanning electron microscopy (SEM/EDX) analysis was obtained with a JEOL JSM 7600F instrument. Optical microscope videos and images were obtained with a Nikon Eclipse 50i microscope. Video sequences were processed with Nikon NIS-Elements software.

Methods

Preparation of coconut structures: The cover slips were cleaned with N_2 gas and ultrasonicated subsequently in water, acetone, and isopropanol (IPA) for 3 minutes each. After that, the cover slips were treated in O_2 plasma for 3 minutes. The silica beads were suspended in water at a concentration of 20 mg/mL and a drop of 100 μL was applied on the cover slip to spread over the whole surface. The cover slip was left over night to dry and platinum (40 nm, sputtered at 30 mA for 140 s) was sputtered on the cover slip. The beads were resuspended into NaOH solution (3 M) by ultrasonication. After that, the cover slip was removed and the silica beads were allowed to dissolve under ultrasonication for 2 h. The Pt-coated silica beads became half-shelled “coconut” structures with the partially etched silica residues. The solution was then centrifuged at 10,000 rpm for 10

min. After that, the supernatant was removed and the sample was washed/centrifuged with 2 mL water for 3 times. The structures were stored in water suspension at room temperature. For the preparation of fully-etched shell structures, the silica beads were allowed to dissolve under ultrasonication in NaOH for 6 h and subsequently centrifuged at 10,000 rpm for 40 min. The sample was then cleaned and stored in water suspension at room temperature.

Running of the coconut motors: The experiments for the motion study of the coconut micromotors were carried out in an aqueous solution containing different concentrations of hydrogen peroxide at a constant surfactant concentration (1 wt % of SDS). A mixture of the coconut micromotors, SDS (1 wt %), H₂O₂ and water was applied on a glass slide freshly cleaned with nitrogen gas. Optical microscope videos and images were obtained with Nikon Eclipse 50i microscope. Video sequences were processed with Nikon NIS-Elements™ software. The average velocities were tracked and calculated over 5 s and for each set of data, the standard deviation and average value of recorded velocities ($n=5$) were calculated.

Acknowledgements

M. P. acknowledge Nanyang Technological University and Singapore Ministry of Education Academic Research Fund AcRF Tier 1 (2013-T1-002-064, RG99/13) for the funding support.

Notes and references

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† Electronic Supplementary Information (ESI) available: Additional SEM images, data analysis, Videos S-1 and S-2 See DOI: 10.1039/b000000x/

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