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Clean room-free rapid fabrication of roll-up self-powered catalytic microengines†

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The fabrication of metallic microtubes which work as self-running micromotors has been a challenging and costly task. In this paper, a newly developed fast and scalable method was introduced, which would help realize the possibility for common laboratories in the world to easily fabricate the high-tech rolled-up micromotors, as long as the magnetron sputtering machines are available.

Introduction

The autonomous self-powered and self-propelled micro- and nanosystems are in the forefront of nanotechnology research. These tiny devices, also dubbed as "microrobots", "microengines" or "smart dust", can navigate in complex environments, follow the source of chemicals or electromagnetic field and deliver tiny cargos; all these are powered by taking chemical energy from the environment and turning it into mechanical energy.[1–5] They are expected to revolutionize the research and development in medicine,[6–12] natural resources discovery[13] or environmental remediation.[14]

Amongst many types of propulsion, such as self-electrophoresis,[15] self-diffusiophoresis[16] and bubble propulsion,[17] the latest one emerged as the preferred mode of powering the microengines (or microrobots as they are called) due to the higher power output. The first and most successful method of fabrication of these bubble-propelled microengines consists of the precise deposition of well-defined thin metal membranes onto silicon wafers, followed by a controlled roll-up step which generates tubular microstructures.[17] This method has been optimized and typically requires clean room conditions for the controlled evaporation and multilayer deposition of various metals to form nanometer thick membranes which roll-up upon lift off procedures.[17] The advantage of this technology is that the microtubes have very thin walls and very high surface-to-mass ratio. However, this method is confined only to a few high-tech laboratories in the world as it requires clean room facilities, such as a mask aligner, photoresist processing and an e-beam evaporator capable of tilting the sample; implementation of these facilities may require investments in the order of several hundreds of thousands of euros/dollars. In addition, the fabrication of microengines by this high-tech methodology takes several days and requires highly specialized operators. A simplified high-tech method for the fabrication of roll-up tubes was recently reported to utilize the dry-releasing approach by burning the sacrificial layers with the assistance of dewetted nanoparticles.[18] An alternative technology, namely the template directed electrodeposition of micro- or nanoengines, has also been proposed but has the drawback of being able to deposit only with the template to form the tubes, and thus the dimensions of the microengines fabricated are limited to commercially available templates and in general generates micro/nanoengines with a larger mass-to-surface ratio.[19] Here we wish to propose a fast and scalable method which could open the door to the fabrication of roll-up catalytic microengines to any laboratory in the world capable of providing only a magnetron sputtering machine and at an extremely low cost.

Results and discussion

In this novel method in order to obtain well-defined metal deposition the mask aligner, normally used in clean-room based methodologies, is replaced with commercially available TEM grids of desired openings which are adopted as masks. The silicon wafer substrate is replaced by a microscope glass slip and the metal deposition is performed using commonly available sputtering equipment. Two simple procedures are proposed and evaluated in this work: (i) a sacrificial layer of poly(methylmethacrylate) (PMMA) is deposited on the glass slip prior to the placement of the TEM grid. The desired metal, Pt in this work, is then sputtered. The final dissolution of the PMMA layer facilitates the roll up of the Pt film due to the internal strain. (ii) A TEM grid is placed directly on the glass slip (no PMMA layer involved), Pt is deposited by sputtering and the microengines are

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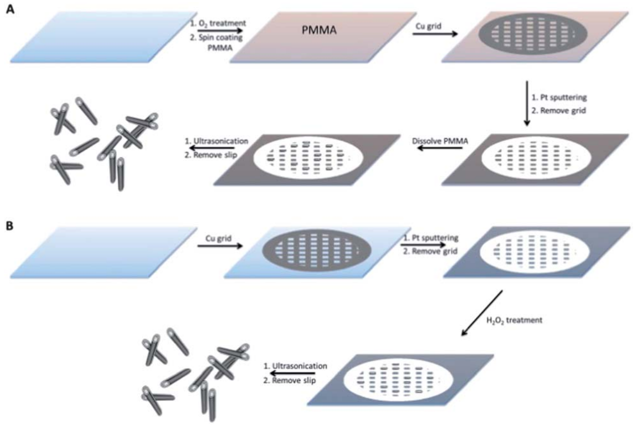


Scheme 1 Depiction of steps used during fabrication of Pt roll-up microengines *via* (A) TEM grid template/PMMA sacrificial layer route or (B) TEM grid template/H_2O_2 assisted lift-off route.

formed by adding hydrogen peroxide which leads to fracture driven lift off of the Pt film and consequent strain induced roll-up of microtubes. See Scheme 1 for an overview of the process. We will address the detailed fabrication procedure and performance of the engines in the following sections.

TEM grid template/PMMA sacrificial layer fabrication of platinum microengines

The process (i) using the PMMA sacrificial layer is illustrated in Scheme 1A. A microscope glass slip was treated in oxygen plasma to remove impurities and created a hydrophilic surface at the same time. The cover slip was consequently spin coated with a layer of PMMA. The PMMA layer serves here for the easy lift-off of the microengines at the end of the process. After drying the PMMA layer, a TEM copper grid of desired openings, in our case of 60 × 60 μm with 23 μm spacing (Fig. 1A), is placed on the PMMA covered glass slip. A thin platinum film is consequently deposited by sputtering. The removal of the TEM grid leaves a well-defined pattern of Pt films. The final dissolution of the PMMA layer in dichloromethane (DCM) solvent favors the formation of microtubes due to the strain induced rolling process (Fig. 1B). The whole fabrication process takes about 2 h. It is important to notice that the direction of the rolling-up can hardly be controlled and thus the resulting microengines exhibit different lengths, as it is evident from the histogram in Fig. 1C. The majority of the microtubes have sizes between 30 and 60 μm with RSD of about 37.2%. It should be mentioned, however, that both the template directed elecrodeposition of microengines as well as the clean room fabrication of microengines showed similarly wide distribution of length, with RSD of 21–28.5% (depending on template used) and 13.2%, respectively (see Fig. S1, ESI†). Therefore the size distribution of microengines fabricated by this simple method is comparable to the size distribution of other alternative methods. In addition, as it is difficult to control the direction of the rolling, the shapes of the tube ends are also different. A layered cylindrical tube with a flat end was formed when the Pt membrane rolled along the axis of the membrane, while a layered cylindrical tube with a sharp end was formed when the Pt membrane was rolled from the membrane with an angle off the axis. The diameter of the microtubes formed using this approach was 4.6 μm (17% RSD, $n = 20$). The rolled-up microengines were then tested for motion in the presence of hydrogen peroxide fuel and exhibited an agile bubble-propelled motion with velocities close to 100 μm s^{-1}, depending on the concentration of fuel, as shown in Fig. 2. Example of motion of the microjet fabricated by this method can be found in Video S-1 (ESI†). The motion is recorded in solution containing 12% H_2O_2 and 1% SDS.

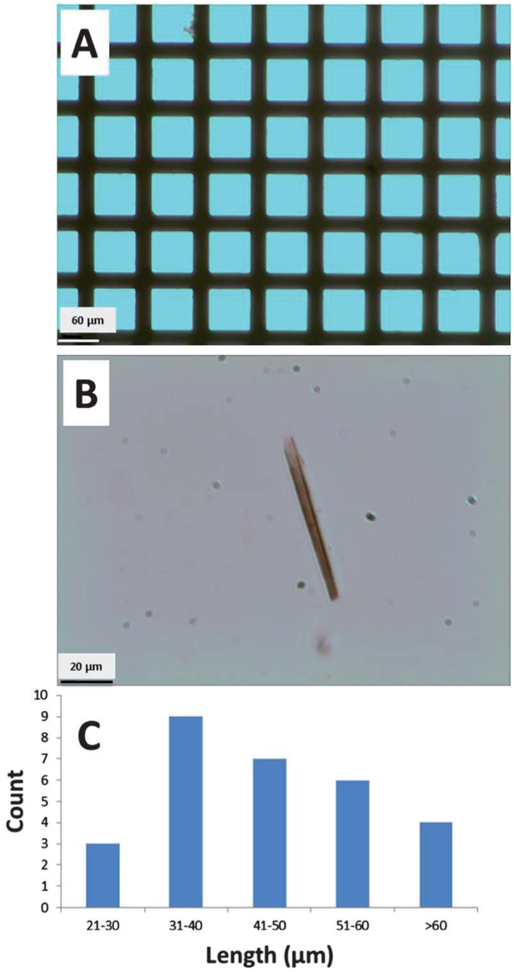


Fig. 1 (A) Optical micrograph TEM grids (300 mesh) used for the production of rolled-up tubes. The openings have sides of ~60 μm; the spacers are ~23 μm wide. Scale bar indicates 60 μm. (B) A typical microscope image of the rolled up tubes, scale bar indicates 20 μm. (C) Length distribution of the tubes, $n = 30$.

TEM grid template/H_2O_2 assisted lift-off fabrication of platinum catalytic microengines

Using procedure (ii) (see Scheme 1B), the TEM grid was directly placed on the glass slip without the preliminary deposition of the PMMA layer followed by the Pt deposition as in method (i). After the removal of the TEM grid, the remaining sputtered area was exposed to H_2O_2 solution. The bubble evolution generated at the edges of the Pt film and in correspondence of the film fractures

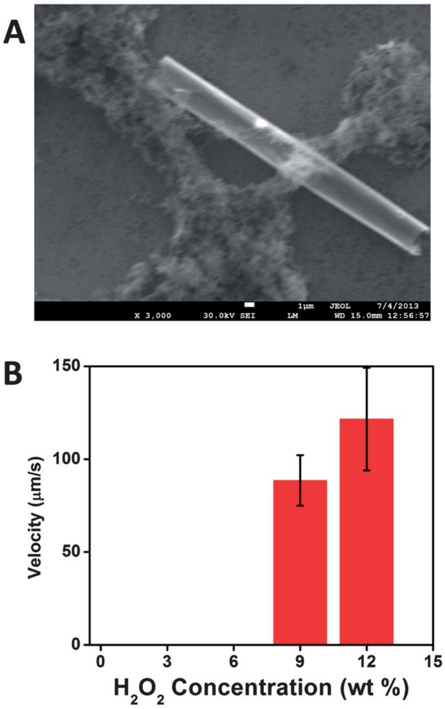
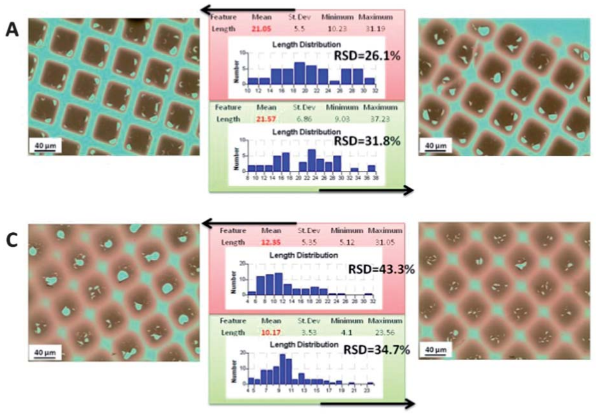


Fig. 2 (A) SEM of platinum microengines fabricated *via* a PMMA sacrificial layer method. (B) Velocity of microengines with different concentrations of hydrogen peroxide containing a constant amount of surfactant (1% SDS).

causes the lifting of the Pt film sections which then rolled up into microtubes. The whole process takes about 2 h. It must be mentioned that unlike the above-mentioned PMMA-based methodology, the size of the microengines generated with this method is not defined by the TEM grid openings, but can be controlled to a certain extent by the concentration of hydrogen peroxide which creates different fracture densities within the 60 × 60 μm Pt squares. The length of microengines decreases, in fact, from ~20 μm for concentrations of 7 and 14 wt% of H_2O_2 to the length of ~10 μm for concentrations of 21 and 28 wt% of H_2O_2 (Fig. 3). Microtubes formed in different concentrations of hydrogen peroxide showed a similar diameter of 2.8 μm (14% RSD, n = 20). The resulting rolled-up microengines showed typically sharp ends (Fig. 4) which were shown to be beneficial for



Feature	Mean	St.Dev	Minimum	Maximum
Length	21.05	5.5	10.23	31.19

Feature	Mean	St.Dev	Minimum	Maximum
Length	21.57	6.86	9.03	37.23

Feature	Mean	St.Dev	Minimum	Maximum
Length	12.35	5.35	5.12	31.05

Feature	Mean	St.Dev	Minimum	Maximum
Length	10.17	3.53	4.1	23.56

Fig. 3 Optical micrographs of H_2O_2 facilitated lift-off of Pt nanomembranes on glass cover slips using (A) 7%, (B) 14%, (C) 21% and (D) 28% of hydrogen peroxide. After sputtering of Pt with a 60° tilt of the slip on the Cu grid-covered glass slips, the hydrogen peroxide solutions were dropped on the Pt part, triggering the rolling up of Pt nanomembranes as the O_2 gas was generated. The length distribution reveals that there are more uniform tubes when 7% H_2O_2 was used.

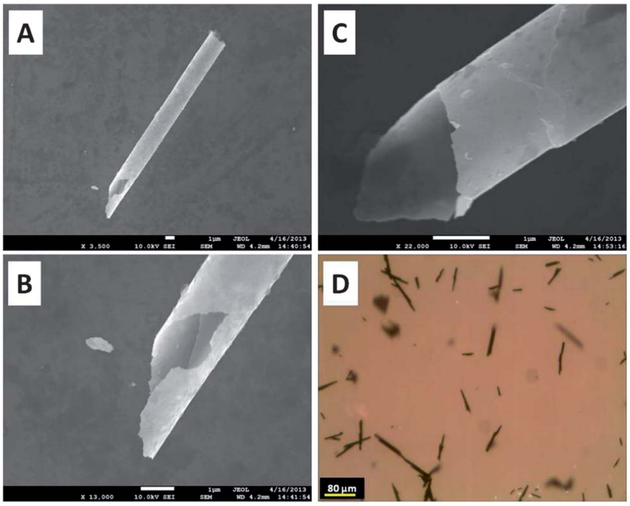


Fig. 4 (A–C) SEM characterization of Pt microengines fabricated through the H_2O_2 (7 wt%) assisted lift-off process. (D) Optical micrograph of the as formed microengines in suspension. Scale bars are 1 μm (A–C) and 80 μm (D).

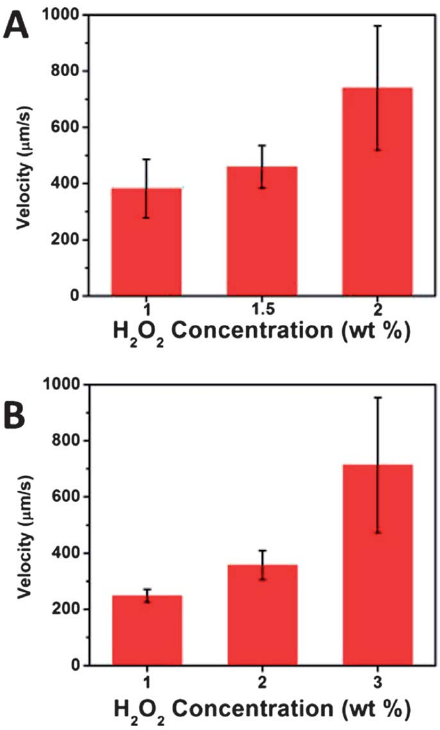


Fig. 5 Comparison of velocities of microengines made *via* (A) a roll-up process with 7% H_2O_2 and (B) galvanostatic deposition using a polycarbonate membrane as the template. A higher velocity of these rolled-up microengines was observed compared to the deposited microengines.

microsurgeries in previous studies.[8] Such sharp ends were formed because when the Pt membrane was torn off by the O_2 bubbles, the as formed Pt membrane was not regular in shape. H_2O_2 assisted lift-off microengines exhibited a very high mobility of 382 μm s^{-1} in 1% H_2O_2 and 740 in 3% of H_2O_2, which corresponds to ~20 to ~40 body length per second, respectively (Fig. 4A). This compares well with the speed of microengines fabricated by the template-based electrodeposition method (Fig. 5B)[20] or the microengines fabricated *via* the rolled-up process under clean room conditions.[21]

In conclusion, we have demonstrated a very simple and rapid method for the fabrication of self-propelled microjet engines. Such a method obviates the needs for clean room and expensive facilities; it uses microscope glass slips instead of silicon wafers, a TEM grid as a template mask instead of the mask aligner and magnetron metal sputter instead of the e-beam evaporator. This is quite a simple technique and can be easily reproduced practically in any materials laboratory around the world, and it has the potential of leading to a dramatic increase in research in this area.

Experimental section

Materials

Hydrogen peroxide (27%, Lot. no. 10151507) and poly(methyl methacrylate) power (PMMA, Lot. no. F02W006) were purchased from Alfa Aesar, Singapore. Dichloromethane (DCM, AR grade) was from RCI Labscan Limited, Thailand. Copper specimen grids (300 mesh) with a formvar/carbon support film (referred to as TEM grids in the text) were purchased from Beijing XXBR Technology Co. The platinum target for sputtering was purchased from Quorum Technologies Ltd, UK. The chemicals were used as received and ultrapure water (18.2 MΩ cm) from a Millipore Milli-Q purification system was used throughout the experiments.

Apparatus

The ultrasonication process was carried out with a Fisherbrand FB 11203 ultrasonicator, and centrifugation was carried out with a Beckman Coulter Allegra 64R centrifuge. Scanning electron microscopy (SEM/EDX) analysis was obtained with a JEOL JSM 7600F instrument. Optical microscope images were obtained with a Nikon Eclipse 50i microscope.

Methods

Pre-treatment of TEM grids and cover slips. The TEM grids were immersed in chloroform for 10 minutes to dissolve the formvar polymer layer. The glass cover slips were cleaned with nitrogen gas and ultrasonicated in water, acetone and isopropanol (IPA) for 3 minutes each. After that, the cover slips were treated in O_2 plasma for 3 min.

Preparation of rolled-up microtubes with hydrogen peroxide treatment. The treated TEM grids were placed on top of the freshly cleaned surface of the cover slip and platinum (3 nm) was sputtered on the cover slip with a current of 20 mA for 30 s. The TEM grids were removed from the cover slip surface simply by shaking the slip, and a drop of 10 μL H_2O_2 (7 wt%) was placed on top of the sputtered area where the TEM grids were placed. The cover slip was placed in water when the bubbling was finished, and it was ultrasonicated for 5 minutes to free the tubes into the suspension. The tubes were stored in water suspension at room temperature.

Preparation of rolled-up microtubes by dissolving the sacrificial polymer layer. PMMA was dissolved in DCM to form a clear solution (5.34 wt%) and a thin layer of the PMMA film was formed by dropping 950 μL of the solution on the surface of the cover slip for the spin coating. The spin coating was carried out with a speed of 5000 rpm for 40 s, with an acceleration time of 15 s and a deceleration time of 0 s. The spin-coated slips work best within two days after the coating. The treated TEM grids were placed on top of the polymer film and the cover slips were placed on the hot plate for 1 min while gently pressing the grids to ensure good contact with the polymer film. After that, platinum (5 nm) was sputtered on the cover slip with a current of 10 mA for 45 s. The TEM grids were removed from the cover slip surface simply by shaking the slip, and a drop of 10 μL acetone was placed on top of the sputtered area where the TEM grids were placed. Rolling-up of films into a tubular structure was accomplished as acetone would selectively etch the polymer layer. The cover slip was placed in ethanol, and it was ultrasonicated for 5 minutes to free the tubes into the suspension. The tubes were stored in ethanol suspension at room temperature.

Conclusion

A fast and scalable method was demonstrated for the simple fabrication of roll-up catalytic microengines. The utilization of hydrogen peroxide or the dissolution of the TEM grids patterned the PMMA layer successfully and generated microtubes of different lengths. These microtubes were able to run in the fuel solution by bubble-propulsion. Although the fabrication of such metallic microtubes was made more feasible and the cost was significantly reduced, the reproducibility of the fabrication needs to be improved. What is more, the experimental parameters are expected to be optimized to fabricate more uniform tubes.

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