

## ELECTRONIC SUPPLEMENTARY INFORMATION

### Corrosion of Self-Propelled Catalytic Microengines

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#### Experimental Section

##### Materials

The cyclopore polycarbonate membranes with pores of 2  $\mu\text{m}$  in diameter and the anodic aluminum oxide membrane with pores of 100 nm 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. (Lot. No.: 12009-2, USA). Hydrogen peroxide (27 %, Lot. No.: 10151507) was purchased from Alfa Aesar, Singapore. 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. The platinum plating solution (Lot No. 20251001) was obtained from Technic Inc., USA. The chemicals were used as received and ultrapure water (18.2 M $\Omega$  cm) from a Millipore Milli-Q purification system was used throughout the experiments.

##### Apparatus

Electrochemical deposition was carried out with a  $\mu$ 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  $^{\circ}\text{C}$ ) using a three-electrode arrangement. 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 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 videos and images were obtained with Nikon Eclipse 50i microscope. Video sequences were processed with Nikon NIS-Elements<sup>TM</sup> software. Concentration of the elements was obtained using an Agilent Inductively Coupled Plasma-Mass Spectrometer (7700 series, Japan) equipped with a 3rd generation He reaction/collision cell (ORS3) to minimize interferences.

##### Methods

**Preparation of Rolled-up Microtubes:** Fabrication of Ti/Fe/Cr/Pt microtubes was carried out with the previously reported protocol.<sup>1</sup> Briefly, a layer of AR-P 3510 photoresist was spin-coated on silicon wafers (1.5 inch) at 3500 rpm for 35 s. After that, a soft bake using a hotplate was carried out at 90 $^{\circ}\text{C}$  for 1 min. The wafer was then exposed to UV light with a Karl Suss MA-56 mask aligner (410–605 nm). The exposed patterns of the photoresist were developed in an AR300-35/ $\text{H}_2\text{O}$  solution (1:1). Microtubes were obtained by a tilted deposition at an angle of about 60 $^{\circ}$  (measured from the horizontal axis) on the photoresist. Metal films with thicknesses of 3 nm (Ti), 5 nm (Fe) and 5 nm (Cr) were deposited layer by layer on the tilted samples. Using magnetron sputtering, a layer of Pt with 1 nm thickness was deposited onto the Ti/Fe/Cr samples. Rolling-up of films into tubular structure was done by immersing the sample into acetone, as it could selectively etch the photoresist layer. Finally,

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supercritical point drying was used to keep the tubes from collapsing due to high fluid surface tension.

**Synthesis and characterizations of Cu/Pt concentric bimetallic microtubes:** The Cu/Pt concentric bimetallic microtubes were synthesized with a modified electrochemical deposition procedure on a cyclopore polycarbonate template.<sup>2</sup> Colloidal graphite ink was applied on the one side of the polycarbonate template with commercial cotton swabs. A piece of flattened aluminum foil was attached to the ink immediately, which serves 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 MΩ cm) for 4 times, and the Cu outer layer was deposited galvanostatically at -4 mA for 450 s in a deposition solution which contained 1 M CuSO<sub>4</sub>. Consequently, after removing the deposition solution, the template was rinsed 5 times with 8 mL of water. The platinum segment was electrodeposited subsequently at -4 mA for 450 s each, 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 for 5 times with 8 mL of water each. After that, the template was ultrasonicated for 3 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 from a centrifugation step at 6000 rpm for 3 min and subsequently washed repeatedly for 3 times with methylene chloride. The solution was then washed with ethanol and water for 2 times each and centrifuged for 3 min after each washing step. The microtubes were stored in water at room temperature.

**Characterization of the blank, control and corrosion solutions:** A number of three different blank solutions were prepared for ICP-MS measurement to determine the amount of relevant elements in the samples. The blank solution (i) contains only 1.74 mL of distilled water, blank solution (ii) contains 1.54 mL of water and 0.2 mL of SDS solution (10 wt %), and blank solution (iii) contains 0.5 mL hydrogen peroxide (27 wt %), 0.2 mL SDS solution (10 wt %) and 1.04 mL of ultrapure water. The solutions were kept in room temperature for one week and an amount of 0.5 mL of the solution was then retrieved and topped up to 3 mL with ultrapure water for ICP-MS measurements.

For the running sample (corrosion) solutions of both rolled-up microtubes and concentric bimetallic microtubes, 0.5 mL hydrogen peroxide (27 wt %) and 0.2 mL SDS solution (10 wt %) was mixed with 1 mL deionized water, and 40 μL of microtube dispersion was then added into the mixture. After that, the solutions were kept in room temperature for one week and filtered through a filter membrane of 100 nm pore size. An amount of 0.5 mL of the solution was then retrieved and topped up to 3 mL with ultrapure water for ICP-MS measurements.

For the control experiment (i), 40 μL of microtube solution was placed into 1.7 mL ultrapure water and the solution was kept in room temperature for one week and filtered through a filter membrane of 100 nm pore size. An amount of 0.5 mL of the solution was then retrieved and topped up to 3 mL ultrapure water for ICP-MS measurement. For the control experiment (ii), 0.2 mL SDS solution (10 wt%) was mixed with 1.5 mL deionized water, and 40 μL of microtube solution was added into the mixture. After that, the solution was kept in room temperature for one week and filtered through a

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filter membrane of 100 nm pore size. An amount of 0.5 mL of the solution was then retrieved and topped up to 3 mL with ultrapure water for ICP-MS measurement.

To determine the total mass of micromotors, the micromotors were digested using microwave digestion and ICP-MS was subsequently carried out. An Anton Paar Multiwave PRO microwave sample preparation system with Rotor 8NXF100 was used to digest the samples. The maximum microwave power was 1200 W. Samples were placed directly in the inner vessel and 3 mL conc. nitric acid and 0.5ml HCl (ULTREX II Ultrapure Reagent, J.T.Baker, Canada) were added to the vessels. Temperature was ramped to 180°C in 20 minutes and then held at this degree for 215 minutes. The reaction vessels were cleaned before each digestion using 5 ml HNO<sub>3</sub> heated for 15 min at 1000 W.

We have also considered 3% whether H<sub>2</sub>O<sub>2</sub> is stable over period of 7 days at room temperature. The commercial solution of H<sub>2</sub>O<sub>2</sub> is always distributed with stabilizer, urea. As such, H<sub>2</sub>O<sub>2</sub> can be shelved for months at room temperature. We show that there is no decrease of mobility of microjets in fresh or 7 days “old” (exposed to room temperature) H<sub>2</sub>O<sub>2</sub>, as shown in Figure S4.

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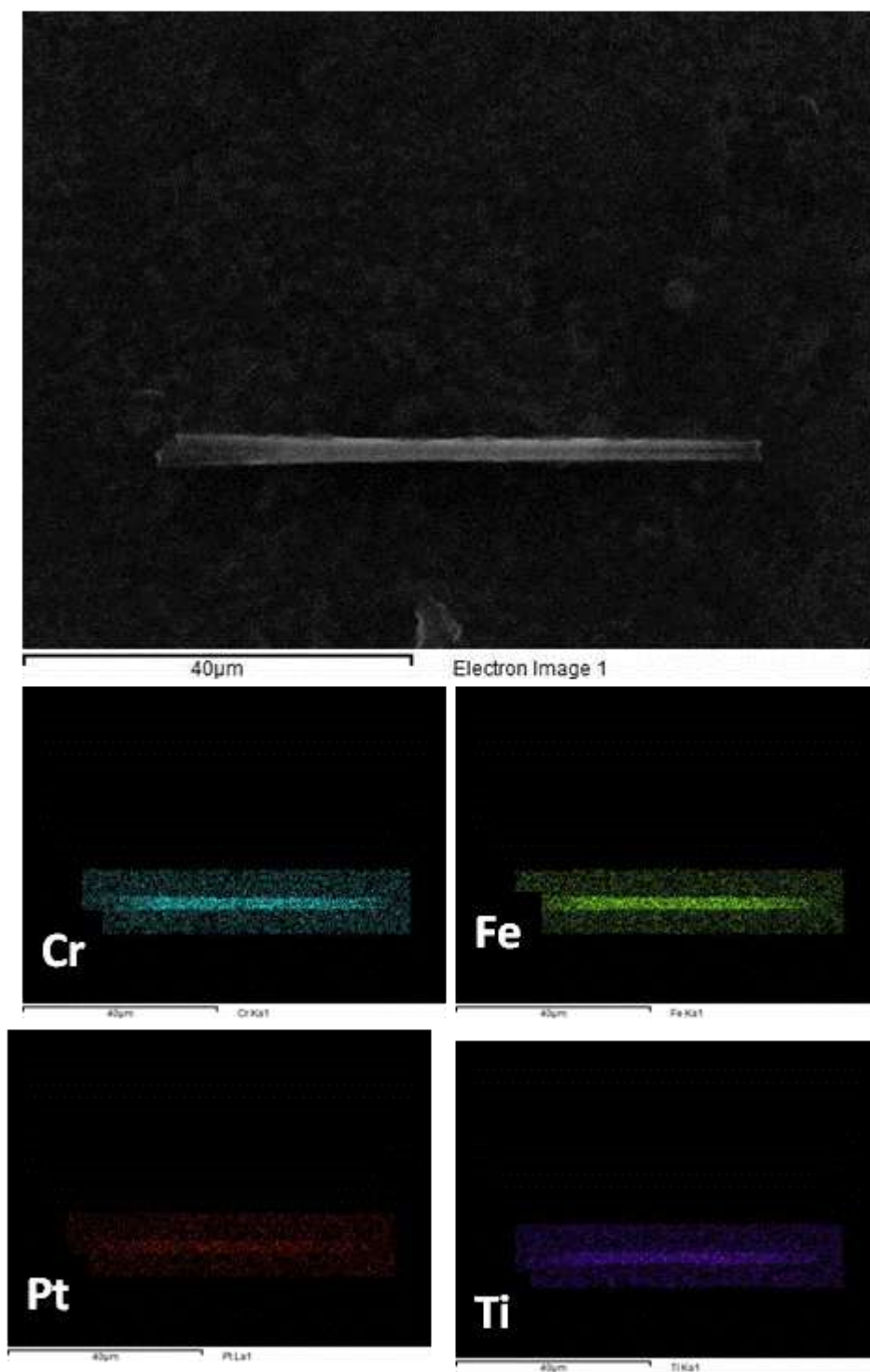


Figure S1. SEM/EDX analysis of roll-up technology fabricated microjet engine.

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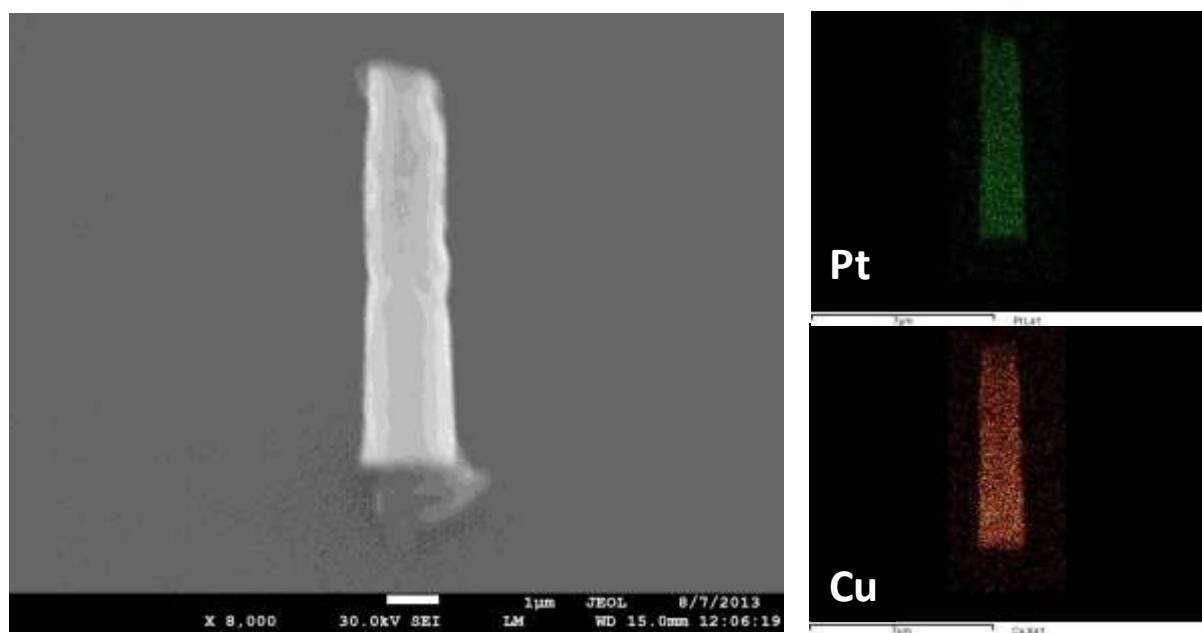


Figure S2. SEM/EDX analysis of Cu/Pt electrodeposited microjet engine.

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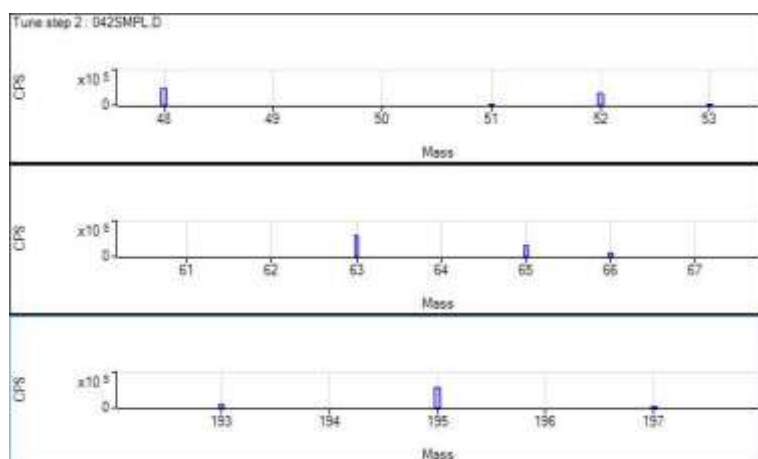
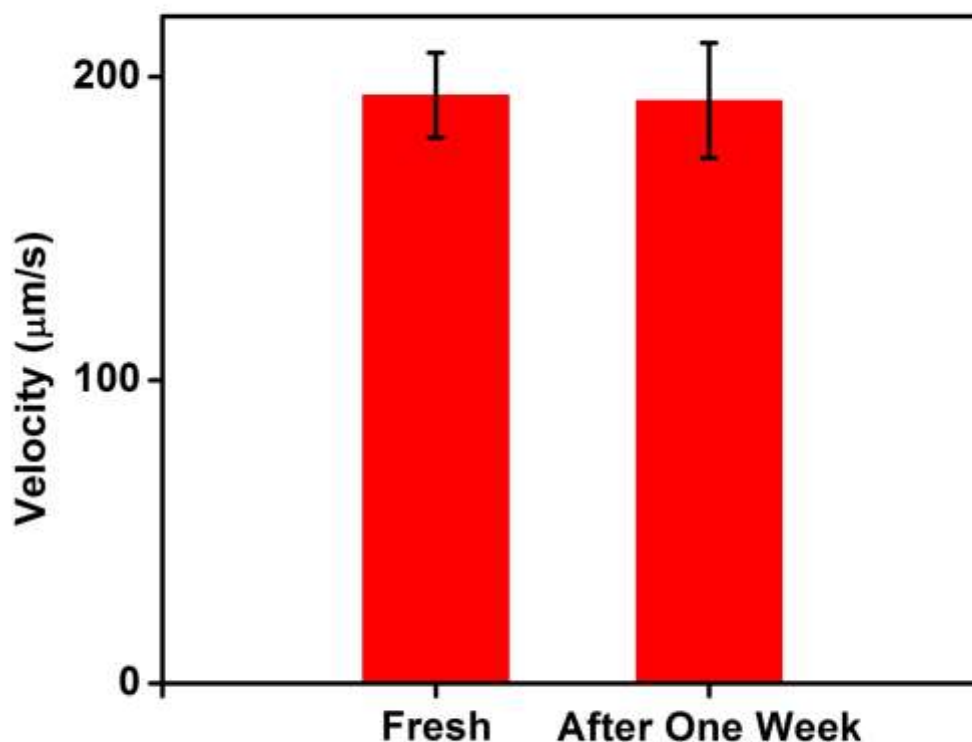


Figure S3. ICP-MS spectra of filtered solution of roll-up microjet engines after exposed to 1.15% SDS solution for one week.

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**Figure S4.** Velocity of microjets in fresh and one week “old” (exposed to room temperature) 7.76% H<sub>2</sub>O<sub>2</sub> and 1.15% SDS solution.

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- 1 Solovev, A. A.; Sanchez, S.; Pumera, M.; Mei, Y. F.; Schmidt, O. G.: Magnetic Control of Tubular Catalytic Microbots for the Transport, Assembly, and Delivery of Micro-objects. *Adv. Funct. Mater.* **2010**, *20*, 2430-2435.  
2 Gao, W.; Sattayasamitsathit, S.; Uygun, A.; Pei, A.; Ponedal, A.; Wang, J. Polymer-Based Tubular Microbots: Role of Composition and Preparation. *Nanoscale* **2012**, *4*, 2447–2453.