

Beyond Platinum: Silver-catalyst Based Bubble-propelled Tubular Micromotors

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Experimental Section

Chemicals

Cyclopore polycarbonate membranes with conical-shaped pores of 3 μm in diameter were purchased from Whatman, USA (Cat. no. 7060-4712), hydrogen peroxide (H_2O_2 ; 35%) from Alfa Aesar, Singapore, methylene chloride and ethanol from Tedia, USA, platinum electrode (1 mm diameter) and Ag/AgCl/1M KCl electrode from CH instruments, USA, copper (II) sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 98+%), and sodium dodecyl sulfate (SDS, Product No.: L3771) from Sigma–Aldrich, platinum-plating solution from Technic Inc., USA, and silver sputtering target from Electron Microscopy Sciences, USA. 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 throughout the experiments.

Apparatus

Autolab PGSTAT 101 electrochemical analyser (Eco Chemie, Utrecht, The Netherlands) connected to a computer and controlled by NOVA version 1.8 software (Eco Chemie) was used for electrochemical deposition of Cu and Ag on polycarbonate membrane. A three-electrode configuration was adopted for the deposition procedure, in a customised electrochemical deposition cell at room temperature (23 $^\circ\text{C}$). The auxiliary electrode was a platinum electrode while the reference electrode was an Ag/AgCl electrode. A JEOL JFC-1600 Auto Fine Coater was utilized to sputter the polycarbonate membrane. Ultrasonication process was carried out with a Fisherbrand FB 11203 ultrasonicator, and centrifugation was carried out with a Beckman Coulter Allegra 64R centrifuge. Video recordings were obtained using Nikon Eclipse 50i optical microscope, which in turn were analysed with Nikon NIS-Elements software. SEM images were captured using JEOL-7600F semi-in-lens FE-SEM, in SEM mode with an accelerating voltage of 15 kV, at a working distance of 7.2 mm.

SEM/EDX data were measured with JEOL-7600F semi-in-lens FE-SEM, in SEM mode with an accelerating voltage of 30 kV, at a working distance of 15.2 mm.

Preparation of Cu/Ag segmented bimetallic microtubes

Cu/Ag segmented bimetallic microtubes were synthesized through an electrochemical deposition method with a cyclopore polycarbonate template. Prior to the electrochemical deposition experiment, the polycarbonate template was sputtered with silver (15 nm) on one side of the membrane and subsequently attached to a piece of copper tape. The template, which will serve as the working electrode, was then assembled into a customised electrochemical deposition cell. A layer of Cu was first deposited along the pores of the template by adding 1M CuSO₄ electrolyte into the cell after rinsing the template thoroughly with ultrapure water (18.2 MΩ cm). The electrochemical deposition of Cu was carried out galvanostatically at -5 mA for 900 s. Subsequently, the CuSO₄ electrolyte was removed, the cell rinsed thoroughly with ultrapure water and replaced with commercial silver-plating solution. Following that, the silver segment was electrodeposited at -5 mA for 1200s. Upon completion of the deposition of microtubes, the template was removed from the electrochemical cell and washed with ultrapure water. Methylene chloride was then used to dissolve the template and ultrasonication was performed to enhance the dissolution of the template. The Cu/Ag microtubes were then collected by centrifuging the solution at 6000 rpm for 3 min. The process of ultrasonication and centrifugation was repeated 3 times with methylene chloride to ensure complete dissolution of the template. Finally, impurities in the Cu/Ag microtubes solution were removed by washing with ethanol and water for 2 times each, with 3 min of centrifugation at 6000 rpm following each washing step. The Cu/Ag microtubes were stored in water at room temperature.

Micromotors propulsion study

The Cu/Ag micromotors were dispersed in aqueous solutions containing different concentrations of hydrogen peroxide (0.5% – 3%) and 1 % SDS surfactant for the motion study experiments. At the start of each experiment, the micromotor mixture was placed on a freshly cleaned glass slide. Then, the glass slide is mounted on Nikon Eclipse 50i optical microscope where videos and optical images of the bubble propulsion process were taken. Finally, the recordings were processed and analysed with the Nikon NIS-Elements software.

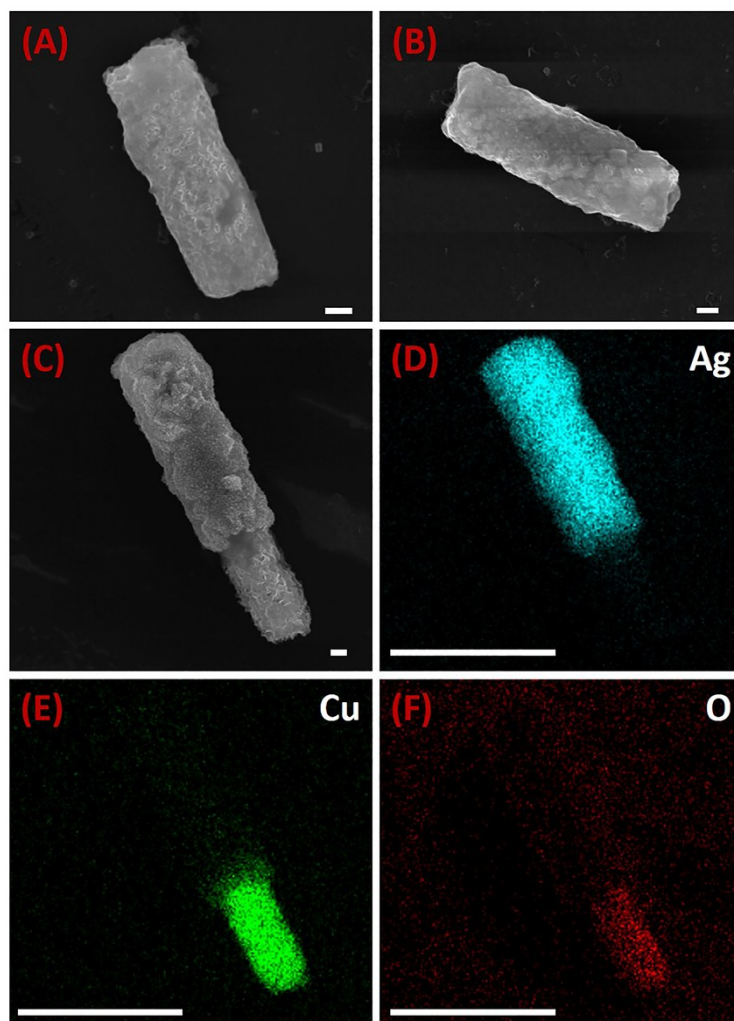


Figure SI-1. SEM images of Cu/Ag micromotors before (A & B) and after (C) propelling in 3 % H_2O_2 running solution. Elemental mapping was carried out on the Cu/Ag micromotor, which was immersed in the H_2O_2 running solution, using SEM/EDX (D – F) to determine if Ag was oxidized while in the H_2O_2 solution. Scale bars in A – C and D – F represent 1 μm and 10 μm respectively.

Video SI-1. Recording of Cu/Ag micromotor propulsion under a microscope. Conditions: 1.5% H_2O_2 and 1% SDS.