Supporting Information

Highly Efficient Catalytic Microengines: Membrane Electrodeposition of Bilayer Polyaniline-Platinum Conical Microtubes

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SI FIGURES and VIDEOS CAPTIONS

SI Figure 1. EDX mapping analysis of a bilayer PANI/Pt microtube. a) SEM image of a bilayer microtube; b) EDX Mapping result of the distribution of carbon; c) EDX mapping result of the distribution of platinum.

SI Figure 2. Influence of sodium cholate concentration on the speed of the microengines in the presence of 1% and 2% hydrogen peroxide.

SI Figure 3. Motion of the bilayer microengine in different biological media: A) Cell Culture Media; B) Human Serum, spiked with 1.5% H_2O_2, 2% sodium cholate.

SI Video 1. Spiral motion of a microengine in 1% H_2O_2 with 0.33% sodium cholate.

SI Video 2. Circular motion of a microengine in 1% H_2O_2 with 0.33% sodium cholate.

SI Video 3. Magnetic motion control of a PANI/Ni/Pt trilayer microengine.

SI Video 4. Ultrafast propulsion of the bilayer microengine.

SI Video 5. Fastest bilayer microengine (3 mm s^{-1}).

SI Video 6. Motion of a microengine in low fuel level (0.2% H_2O_2).

SI Video 7. Motion of a microengine in 0.05% H_2O_2 with the presence of 0.05% hydrazine.

SI Video 8. Motion of a bilayer microengine in cell culture media.

SI Video 9. Motion of a bilayer microengine in human serum.

EXPERIMENTAL SECTION

Synthesis of multilayer microtube engines

The multilayer microtubes were prepared using a common template directed electrodeposition protocol. A cyclopore polycarbonate membrane, containing 2 μm diameter conical-shaped micropores (Catalog No 7060-2511; Whatman, Maidstone, U. K.), was employed as the template. A 75 nm gold film was first sputtered on one side of the porous membrane to serve as working electrode. A Pt wire and an Ag/AgCl with 3 M KCl were used as counter and reference electrodes, respectively. The membrane was then assembled in a plating cell with an aluminum foil serving as contact. Polyaniline microtubes were prepared by modifying the previously described method.[1,2] Briefly, polyaniline (Sigma-Aldrich, St Louis, MO) was distilled before used at a vapor temperature of 100 °C and a pressure of 13 mm Hg. It should be pointed out that such freshly distilled aniline solution should be used within 3 days. Polyaniline microtubes were electropolymerized for 5 sec at +0.80 V from a plating solution containing 0.1 M H_2SO_4, 0.5 M Na_2SO_4 and 0.1 M aniline; subsequently, the inner Pt tube was deposited galvanostatically at -2 mA for 3600 sec from a commercial platinum plating solution (Platinum RTP; Technic Inc, Anaheim, CA). For PANI/Ni/Pt trilayer microtube, polyaniline microtubes were deposited from a plating solution containing 0.1 M H_2SO_4, 0.5 M Na_2SO_4 and 0.1 M aniline and electropolymerized at +0.8 V for 5 sec; then a nickel layer was deposited from a nickel plating solution containing 20 g L^{-1} $NiCl_2 \cdot 6H_2O$, 515 g L^{-1} $Ni(H_2NSO_3)_2 \cdot 4H_2O$, and 20 g L^{-1} H_3BO_3 at -1.0 V (vs. Ag/AgCl) for 1 C; finally, the inner Pt tube was deposited galvanostatically at -2 mA for 1800 sec. For the opening size study, the inner Pt layer of the PANI/Pt microengine was deposited galvanostatically at -2 mA for 10000 sec (after 5 s of PANI), which provides a ~150 nm opening diameter, compared to the 500 nm diameter used throughout this study (measured from in smaller side of the tube). The sputtered gold layer was completely removed by hand polishing with 3-4 μm alumina slurry (as indicated by visual inspection of the membrane color). Incomplete removal will result in bubbles emerging from the smaller opening of the microengine (yet without compromising the performance). The membrane was then dissolved in methylene chloride for 10 min to completely release the microtubes. They were collected by centrifugation at 6000 rpm for 3 min and washed repeatedly with methylene chloride (three times), followed by ethanol and ultrapure water (18.2 MΩ cm), twice of each, with a 3 min centrifugation following each wash. All microtubes were stored in nanopure water at room temperature when not in use. The microengine preparation method is characterized with good reproducibility. For example, two batches tested from different membranes yielded average

speeds of 286 and 281 μm s^{-1}, with relative standard deviations of 16.4 and 18.2%, (n=30 for each batch, using 1.0% H_2O_2 and 1.6% sodium cholate). Typically, such microengines can propel continuously for over 20 min in 15 μL mixed solution (until the sample solution dries up).

Equipments

Template electrochemical deposition of microtube was carried out with a CHI 661D potentiostat (CH Instruments, Austin, TX). Scanning electron microscopy (SEM) images were obtained with a Phillips XL30 ESEM instrument, using an acceleration potential of 20 kV. Mapping analysis was investigated by Oxford EDX attached to SEM instrument and operated by Inca software. An inverted optical microscope (Nikon Instrument Inc. Ti-S/L100), coupled with a 40x objective, a Photometrics QuantEM 512/SC camera (Roper Scientific, Duluth, GA) and a MetaMorph 7.6 software (Molecular Devices, Sunnyvale, CA) were used for capturing movies at a frame rate of 30 frames per sec. The speed of the microengines was tracked using a Metamorph tracking module and the results were statistically analyzed using Origin software.

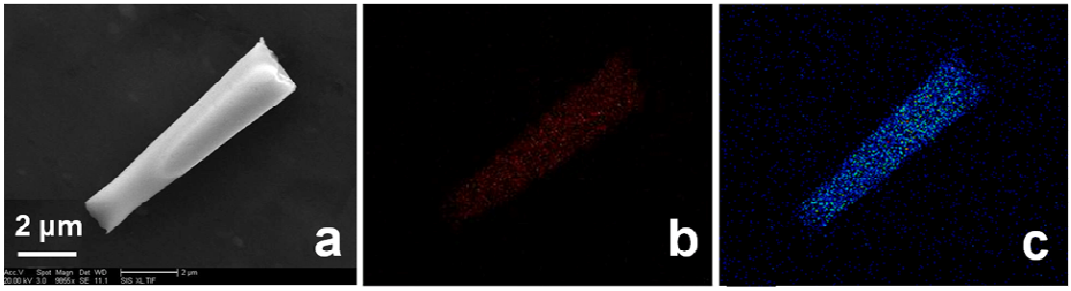
Reagents and Solutions

In order to self-propel catalytic microengines, aqueous hydrogen peroxide solutions with concentrations ranging from 0.2–5.0% were used as chemical fuels, containing 0.33-5.0% (w/v) sodium cholate (Sigma-Aldrich, St Louis, MO) to reduce the surface tension, hence facilitating the engine propulsion. Below 0.5% peroxide, the fraction of moving microengines decreases greatly due to the lower bubble frequency (i.e., weaker bubbling thrust). The hydrazine study was carried out by mixing 5 ml of each of the following solutions: microengine sample, 5% sodium cholate, 0.2% hydrazine and 0.2% H_2O_2. The experiments of the microengines in human serum samples from human male AB plasma (Sigma-Aldrich, St. Louis, MO) and cell culture media (Catalog No. 15-040-CV, Mediatech Inc, Manassas, VA) were carried out by mixing sequentially 5 μL microengine solution, 5 μL 10% sodium cholate, 10 μL biological media and 5 μL 7.5% H_2O_2, i.e., a final solution corresponding to 40% of the raw samples.

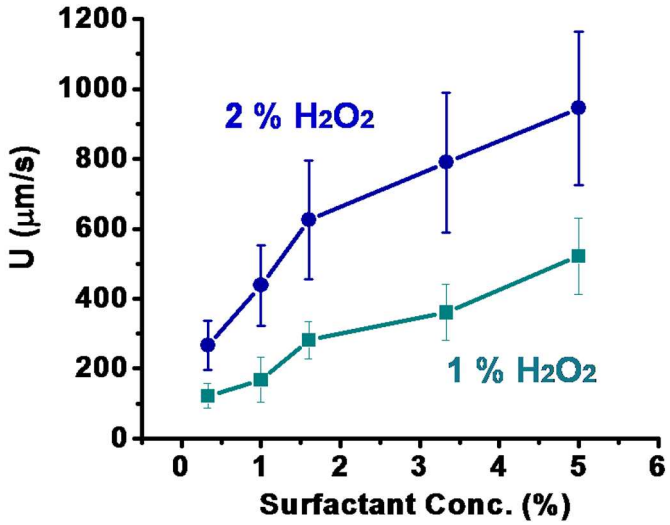
References

1. Lahav, M., Weiss, E., Xu, Q., Whitesides, G. M., *Nano Lett.* **2006**, 6, 2166.
2. Cao, Y., Mallouk, T. E., *Chem. Mater*. **2008**, 20, 5260.

SI Figure 1



SI Figure 2



SI Figure 3