

# Hydrogen-Bubble Propelled Zinc-based Microrockets in Strongly Acidic Media

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## SI Video Captions

**SI Video 1.** The propulsion of PANI/Zinc microrocket in hydrochloric acid solution.

**SI Video 2.** The prolonged motion of PANI/Zn microrocket with 5  $\mu\text{m}$  diameter (60 mM HCl, 1.67% Triton X-100).

**SI Video 3.** The propulsion of PANI/Zn microrocket in different acid solutions.

**SI Video 4.** Magnetic Control of PANI/Zn microrocket in an acidic solution (400 mM HCl, 1.67% Triton X-100).

**SI Video 5.** Magnetic guided cargo pick-up and transport in acidic environment.

**SI Video 6.** PANI/Zn microrocket in biological media - human serum (400 mM HCl, 1.25% Triton X-100).

## Experimental Section

### *Synthesis of Zinc based Microrockets*

The PANI/Zn microtubes were prepared using a common template directed electrodeposition protocol. The Cyclopore polycarbonate membranes, containing 2  $\mu\text{m}$  diameter (Catalog No 7060-2511; Whatman, Maidstone, U. K.) and 5  $\mu\text{m}$  diameter

(Catalog No 7060-2513; Whatman, Maidstone, U. K.) conical-shaped micropores, were employed as the templates. A 75 nm gold film was first sputtered on one side of the porous membrane to serve as working electrode using the Denton Discovery 18. 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 a contact. Polyaniline microtubes were prepared by modifying the previously described method.<sup>[1]</sup> Briefly, aniline (Sigma-Aldrich, St Louis, MO) was distilled before use at a vapor temperature of 100 °C and a pressure of 13 mm Hg. Polyaniline (PANI) microtubes were electropolymerized at +0.80 V for 0.02 C (0.1 C for membrane with 5 µm pore size) from a plating solution containing 0.1 M H<sub>2</sub>SO<sub>4</sub>, 0.5 M Na<sub>2</sub>SO<sub>4</sub> and 0.1 M aniline; subsequently, the inner zinc tube was deposited galvanostatically at -6 mA for 1800 sec (2400s for membrane with 5 µm pore size) from a commercial zinc plating solution containing 80 g l<sup>-1</sup> ZnSO<sub>4</sub>, and 20 g l<sup>-1</sup> H<sub>3</sub>BO<sub>3</sub> solutions (buffered to pH = 2.5 with sulfuric acid).<sup>[2]</sup> The sputtered gold layer was completely removed by hand polishing with 3-4 µm alumina slurry. The membrane was then dissolved in methylene chloride for 10 min to completely release the microtubes. The latter were collected by centrifugation at 6000 rpm for 3 min and washed repeatedly with methylene chloride, followed by ethanol, three times of each. All microtubes were stored in ethanol at room temperature since zinc is an active metal and slowly react with water. Before usage, the microtubes were washed twice with ultrapure water (18.2 MΩ cm) at 6000 rpm for 3 min. To achieve the magnetic directional control, the microrocket solution (ethanol) was evaporated onto glass slides before the sequential E-beam deposition of 10 nm Ti (adhesion layer), 20 nm Ni (magnetic layer), over the microtubes. Experiments in human serum samples, from human male AB plasma (Sigma-Aldrich, St. Louis, MO), were carried out by mixing sequentially 5 µL of the microrocket solution with 5 µL 5% Triton X-100, 5 µL biological media and 5 µL 2 M HCl, leading to a final solution corresponding to 25% of the raw samples.

#### *Equipments*

Template electrochemical deposition of microtubes 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. The SEM images were taken shortly after the microtube samples in ethanol suspension freshly dried up. Videos are captured by an inverted optical microscope (Nikon Instrument Inc. Ti-S/L100), coupled with a 10x objective, a Hamamatsu digital camera C11440 using the NIS-Elements AR 3.2 software.

*References:*

- [1] Gao, W.; Sattayasamitsathit, S.; Orozo, J.; Wang, J. *J. Am. Chem. Soc.* **2011**, *133*, 11862.
- [2] Pang, Y. T.; Meng, G. W.; Zhang, L. D.; Shan, W. J.; Zhang, C.; Gao, X. Y.; Zhao, A. W. *Solid State Sci.* **2003**, *5*, 1063-1067.