

# Electronic Supporting Information

## “Electrochemically-Triggered Motion of Catalytic Nanomotors”

Percy Calvo-Marzal, Kalayil Manian Manesh, Daniel Kagan, Shankar Balasubramanian,  
Maria Cardona, Gerd-Uwe Flechsig, Jonathan Posner, Joseph Wang\*

\*E-mail: josephwang@ucsd.edu

**SI Video 1.** Modulated motion of Au-Pt nanomotors by switching the applied potential between +1.0 and -0.4 V at 10 s intervals in a 5 wt% H<sub>2</sub>O<sub>2</sub> solution.

**SI Video 2.** Movement of Au-Pt nanomotors at +1.0 V and -0.4 V in 5 wt % H<sub>2</sub>O<sub>2</sub> solutions.)

### Experimental Section

The gold/platinum (Au/Pt) nanomotors ( $\sim 2 \mu\text{m}$ ) were prepared by sequential electrodeposition of gold and platinum into a porous alumina membrane template (Catalog No. 6809-6022; Whatman, Maidstone, U.K.). The length ( $\sim 1 \mu\text{m}$ ) of each nanomotor segment was obtained by controlling the electrodeposition charge, while its diameter ( $\sim 220 \text{ nm}$ ) was predetermined by the pore size of the membrane. The branched side of the membrane was initially sputtered with silver. A sacrificial silver layer of total charge of 3 C was electrodeposited using a commercial silver plating solution (1025 RTU@4.5 Troy/Gallon; Technic Inc., Anaheim, CA) at a potential of -0.9 V (vs. Ag/AgCl (3 M NaCl), in connection to a Pt wire counter electrode. Subsequently, gold was electrodeposited (1.5 C) at -0.9 V from a gold plating solution (Orotemp 24 RTU RACK; Technic Inc., Anaheim, CA). Platinum was then deposited galvanostatically at -2 mA for 50 min from a platinum plating solution (Platinum RTP; Technic Inc.). In order to obtain free standing nanowires, the sputtered silver layer and the sacrificial silver layer were simultaneously removed by mechanical polishing using cotton-tipped applicators soaked with 35% HNO<sub>3</sub> for ca. 5 min to ensure complete silver dissolution. The membrane template was then dissolved in a 3 M NaOH solution for 30 min to ensure release of the nanowires. These nanowires were collected by centrifugation at 10,000 rpm for 5 min and washed repeatedly with nanopure water (18.2 MΩ·cm) until a neutral pH

was achieved. All nanowire solutions were stored in nanopure water at room temperature and their speed was tested on the same day of preparation.

To study the effect of the applied potential on the nanomotors speed, an electrochemical cell consisting of a 25  $\mu\text{m}$ -diameter gold fiber working and counter electrodes and a Ag|AgCl|100 mM KCl reference electrode in a Viton<sup>®</sup> O-ring embedded in an epoxy-well, was prepared on a microscope glass slide (SI-Scheme 1). Electrochemical measurements were performed using the  $\mu$ Autolab Type II analyzer (Eco Chemie). The distance between the working electrode and the plane of nanomotor were controlled using micrometer screw on the microscope's x-y-z stage, which was previously calibrated using a short (200  $\mu\text{m}$  diameter) gold wire. For our experiments the distance between the working electrode and the plane of nanomotors was maintained in the range of 120 to 200  $\mu\text{m}$ . This is achieved by placing a glass spacer inside the electrochemical cell, as shown in Scheme SI 1. The counter and reference electrode were placed ( $\sim 4$  mm) away from the working electrode to minimize the effect of KCl or silver ions (that may leak from the reference electrode) upon the nanomotor speed. A diluted nanomotor suspension mixed with a freshly prepared 10 % H<sub>2</sub>O<sub>2</sub> solution in ratio of 1:1 was added to the electrochemical cell (defined by a Viton<sup>®</sup> O-ring surrounded by an epoxy well). Speed-potential profiles of Au-Pt nanomotors in a 5% H<sub>2</sub>O<sub>2</sub> solution were studied by stepping the potential from -0.4 V to different positive potentials (0.1, 0.2, 0.4, 0.6, 0.8 and 1.0 V) and from +1.0 V to different negative potentials (-0.1, -0.2, -0.3, -0.4, -0.5 and -0.6 V). The average speed of the nanomotors was tracked from 50 frames taken at 20 s after applying a positive or negative potential. Data shown represent the average speed of 20 nanomotors tracked for each applied potential.

The real time movement of nanomotors was recorded at different potentials. The effect of dissolved oxygen on the nanomotor speed was studied by purging both diluted nanomotor and H<sub>2</sub>O<sub>2</sub> solutions independently with ultra-high purity argon (99.99 %) and oxygen. The speed of the nanomotors under different gaseous atmospheres (each 1 bar) was then recorded by adding a fresh 1:1 mixture of nanomotors and hydrogen peroxide to a closed Petri-dish chamber saturated with respective atmosphere.

Tracking of nanomotors was performed following the protocol reported earlier.<sup>6</sup> Briefly, an inverted optical microscope (Nikon Instrument Inc., Eclipse TE2000-S)

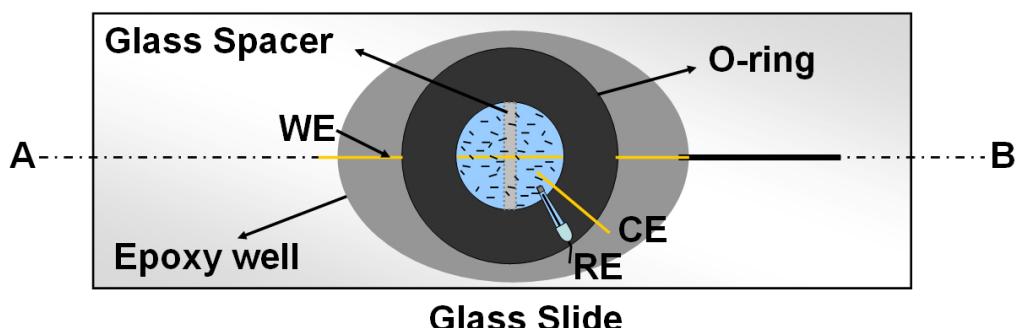
equipped with a 20x objective, a Photometrics CoolSnap CF camera (Roper Scientific, Duluth, GA) and a MetaMorph 7.1 software (Molecular Devices, Sunnyvale, CA) were used for capturing movies at a frame rate of 10 frames per second. The depth of the field was very small (ca. 2  $\mu\text{m}$ ), and only the nanomotors on the glass surface were brought into the focal plane. The nanomotor movement was tracked using Metamorph tracking module and the results were analyzed using OriginPro software. The data were smoothed using in-built smoothing functions in OriginPro.

Tafel plot measurements were used to calculate the mixed potential established at the gold and platinum electrode materials in 5 wt% hydrogen peroxide solution at different atmosphere (argon, air and oxygen). Gold and platinum disk electrodes (CH Instruments, Austin, TX) were used as the working electrode in these electrochemical measurements. Cyclic voltammetry of 5 wt% aqueous hydrogen peroxide (without any electrolyte) was performed using the CH Instrument Model CHI630C at a scan rate of 50  $\text{mV s}^{-1}$  and over a potential range of 0.1 to 0.4 V (vs. Ag/AgCl), along with glassy carbon as a counter electrode. A summation of the anodic ( $i_a$ ) and cathodic ( $i_c$ ) currents at each applied potential was calculated, resulting in the net current ( $i_{\text{net}}$ ). The mixed potential, at which the anodic and cathodic currents are equal (*i.e.*, zero net current), was obtained by extrapolating the linear Tafel regime of the plot of  $\log|i_{\text{net}}|$  *versus* potential<sup>1</sup>. Before each experiment the electrode was successively polished with 0.05  $\mu\text{m}$  alumina powder, subsequently sonicated for 5 min, then washed with running doubly distilled water. The different atmosphere were obtained by bubbling argon or oxygen for 5 min before the experiments and kept the gas flow on the top of the solution (no bubbling) during the experiments. Further details are given in the earlier reports.<sup>2</sup>

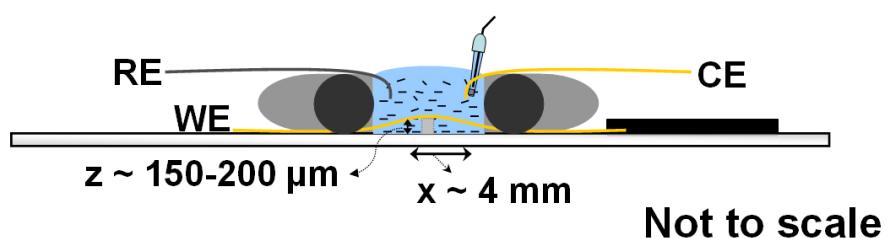
### SI References:

1. Bard, A. J.; Faulkner, L. R. *Electrochemical Method: Fundamentals and Applications*; John Wiley & Sons, Inc.: New York, 2000.
2. R. Laocharoensuk, J. Burdick, J. Wang, *ACS Nano* 2008, **2**, 1069.

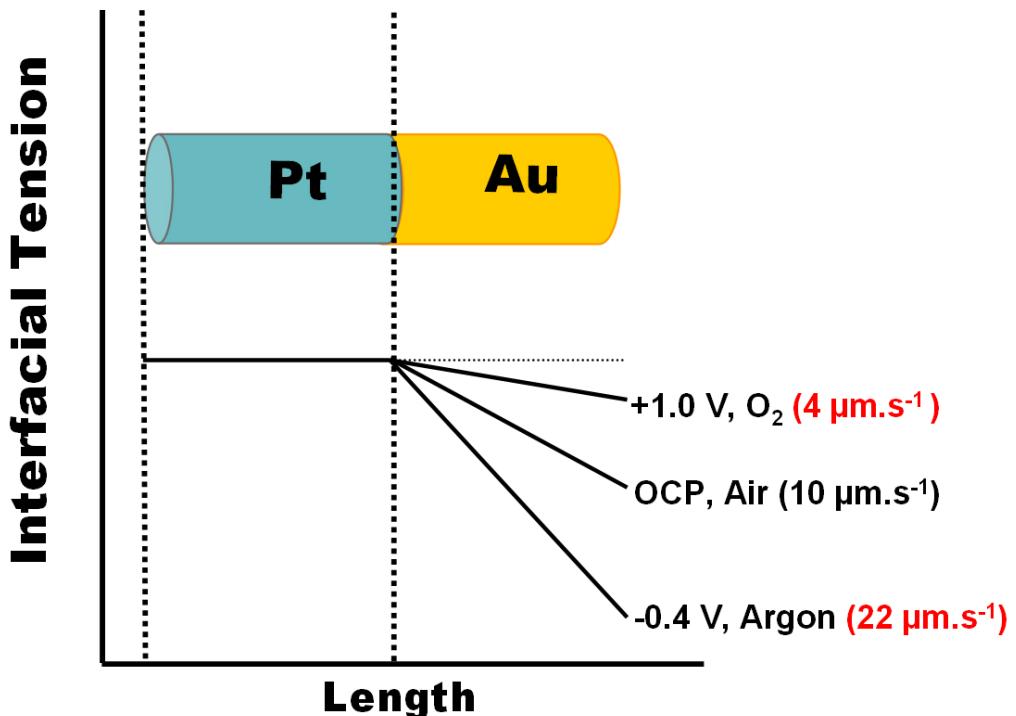
**a) Top View**



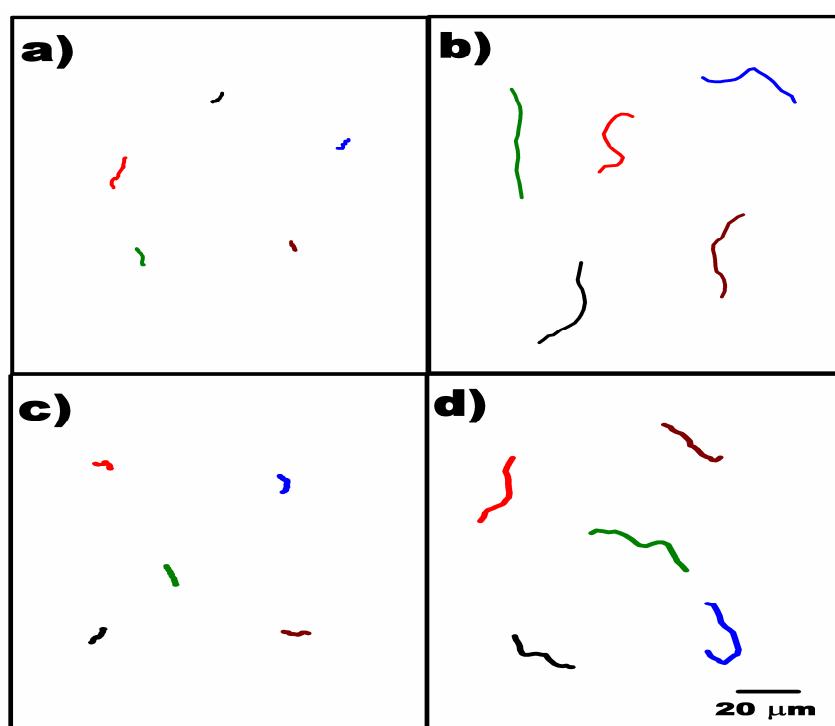
**b) Cross section A – B**



**SI Scheme 1.** Experimental set-up for the potential modulated electrochemical propulsion of catalytic nanowire motors. a) Top view of the experimental setup containing the epoxy well embedded with Viton® O-ring on a microscope glass slide b) Cross-sectional side view of the setup showing the relative positions of nanomotors and the working, reference and counter electrodes (25- $\mu\text{m}$  diameter gold wire, Ag/AgCl(100 mM KCl), and 25- $\mu\text{m}$  diameter gold wire, respectively). The reference and counter electrodes were placed  $\sim 4$  mm away from the working electrode to minimize the interference from leaking ions. The Z-distance indicates the vertical separation between planes of the nanomotor and the working electrode, as was observed through optical microscope at 20 x.



**SI Scheme 2.** Influence of the applied potential and oxygen level upon the interfacial tension gradient along Au-Pt nanowire motors.



**SI Fig. 1.** Tracking lines of Au-Pt nanomotors illustrating the distances traveled in (a) +1.0 V, (b) -0.4 V, (c) oxygen atmosphere and (d) argon atmosphere during a 2 sec period in 5 wt % H<sub>2</sub>O<sub>2</sub> solutions.