Supporting Information

CHEMICAL SENSING BASED ON CATALYTIC NANOMOTORS:

MOTION-BASED DETECTION OF TRACE SILVER

Daniel Kagan[1], Percy Calvo-Marzal[1], Shankar Balasubramanian[1], Sirilak Sattayasamitsathit[1], Kalayil Manian Manesh[1], Gerd-Uwe Flechsig[2] and Joseph Wang[1]*

[1]University of California San Diego, Department of Nanoengineering, La Jolla, CA 92093, USA
[2]Department of Chemistry, University of Rostock, Dr.-Lorenz-Weg 1, D-18051 Rostock, Germany

SI Video 1. Depicts the disparity in speed between nanomotors in 100 µM Ag^+ solution (center video) and nanomotors placed in other metal ion 100 µM solutions i.e (K^+, Pd^{2+}, Ni^{2+}, Mn^{2+}, Cd^{2+}, Ca^{2+}, Cu^{2+}, Pb^{2+} and Bi^{3+}).

SI Video 2. Movement of Au-Pt nanomotors in the presence of different Ag(I) concentrations: 0 (A), 1.0 (B), 10 (C) and 100 (D) µM, along with 5 wt% H_2O_2 fuel solution.

SI Video 3. Influence of Ag(I) on the motion of mono-component platinum nanowires in 5% H_2O_2 fuel source. Motion observed in the absence (left) and presence (right) of 10µM $AgNO_3$.

SI Figure 1. Atomic % of Ag on monocomponent Pt and Au nanowires obtained from EDX measurements. In all experiments, monocomponent Pt and Au nanowires were individually mixed with 5% H_2O_2 and 50 µM $AgNO_3$ and analyzed at different times.

Experimental Section

The gold/platinum nanomotors were prepared by sequential electrodeposition of gold and platinum into 200-nm-diameter nanopores of a 60 µm-thick alumina membrane template (Catalog No. 6809-6022; Whatman, Maidstone, U.K.). A thin gold film was first sputtered on the branched side of the membrane to serve as a working electrode. The membrane was assembled in a Teflon plating cell with aluminum foil serving as an electrical contact for the subsequent electrodeposition. A sacrificial copper layer was first electrodeposited into the branched area of the membrane using a 1 M cupric sulfate pentahydrate solution ($CuSO_4.5H_2O$; Sigma-Aldrich, St. Louis, MO), using a charge of 10 Coulombs and a potential of -1.0 V (*vs*. Ag/AgCl reference electrode) along with platinum wire as a counter electrode. Subsequently, Au segment was plated from a gold

plating solution (Orotemp 24 RTU RACK; Technic Inc., Anaheim, CA) and electrodeposited at a total charge of 1.5 Coulombs and a potential of -0.9 V. Platinum was then deposited galvanostatically using a current of -2 mA for 50 min from a platinum plating solution (Platinum RTP; Technic Inc). The resulting Au-Pt nanowires had a length of around 2 µm. The sputtered gold layer and the copper sacrificial layer were simultaneously removed by mechanical polishing using cotton tip applicators soaked with 0.5 M $CuCl_2$ solution in 20% HCl. The nanomotors were then released by immersing the membrane in 3 M NaOH for 30 minutes. The synthesized nanomotors were separated from solution using by centrifugation at 10,000 rpm for 5 min and washed repeatedly with ultrapure water (18.2 MΩ cm) until a neutral pH was achieved. Between the washing steps the nanomotors solution was mixed with ultrapure water and briefly sonicated (2-5 seconds) to ensure the complete dispersion of nanomotors in the washing water. All nanomotors were stored in ultrapure water at room temperature and their speed was tested before each experiment.

To prepare, 2 µm monocomponent nanowires, Pt was deposited for 70 min and Au was deposited for 2.5 C using the method described above. To study the deposition of Ag, bimetallic and monocomponent nanowires were individually mixed with 5% H_2O_2 and 50 µM $AgNO_3$ for different times. The residual silver ions and peroxide were removed by repeated washing with ultrapure water. Energy dispersive X-ray analyses (EDX) of the nanowires were performed using Phillips XL30 ESEM instrument to confirm the metal composition of nanowires.
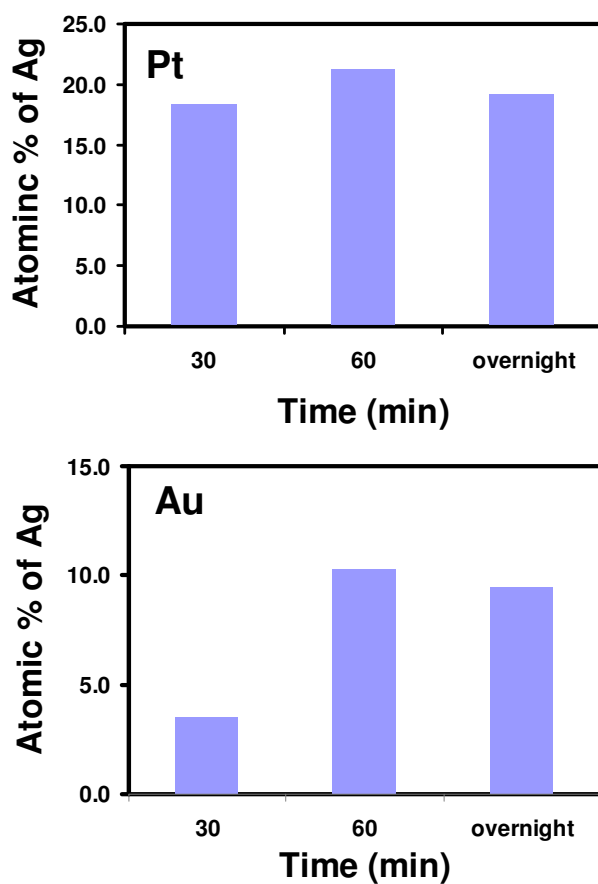
To study the effect of silver ion (and of other cations) upon the motion of Au-Pt nanowire motors, the nitrate salts of the various metals were mixed with the nanomotor/fuel solution. Metal nitrate salts were purchased from Sigma or Fisher with a purity of 99.99% (or higher) to minimize potential impurity effects. The speed of the nanowire motors was examined in a solution prepared by mixing 50µl of equal parts (1:1:1) of the diluted nanomotors suspension, the metal nitrate solution, and a freshly prepared 15 wt% H_2O_2 solution. A 10µl aliquot of this solution was then added to the glass slide for immediate video acquisition.

The tracking of nanomotors was performed following the protocol reported earlier.[1] 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 MetaMorph 7.1 software (Molecular Devices, Sunnyvale, CA, USA) was used for capturing movies at a frame rate of 10 fps. This software calculates the instantaneous velocity by tracking the object's center-to-center displacement from frame to frame. The program averages the instantaneous velocities over the 50 frames tracked to yield an overall average speed. Usually 5 videos from randomly selected glass slide areas (200 µm X 200 µm) were recorded to ensure accurate population sampling. Approximately, 20 random nanomotors were tracked for 50 frames to obtain a representative nanomotor speed. To distinguish between Brownian and non-Brownian motions, the motion of the nanomotors was compared to that observed without fuel. Typically, nanomotors in water display a Brownian motion, i.e. tumbling and/or sideways motion, with speeds of ~3 μm s^{-1}.

References

1. Laocharoensuk, R., Burdick, J., Wang, J., *ACS Nano* **2008,** *2*, 1069.

SI Figure 1

SI Figure 1: Atomic % of Ag on monocomponent Pt and Au nanowires obtained from EDX measurements. In all experiments, monocomponent Pt and Au nanowires were individually mixed with 5% H_2O_2 and 50 µM $AgNO_3$ and analyzed at different times.