Supporting information

Nanomotor-based 'Writing' of Surface Microstructures

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Supporting Video Captions

SI-Video 1: Movement of Pt/Ni/Au-Ag catalytic nanomotors in 5% H_2O_2, 5% H_2O_2 with 1 mM $LiClO_4$ and 5% H_2O_2 in the presence of 3 mM aniline (in 1mM $LiClO_4$).

***SI-Video 2*:** Simultaneous magnetically-guided U-Shaped motion of three Pt/Ni/Au-Ag nanomotors in 5% H_2O_2 in the presence of 3 mM aniline (in 1 mM $LiClO_4$).

Experimental Section

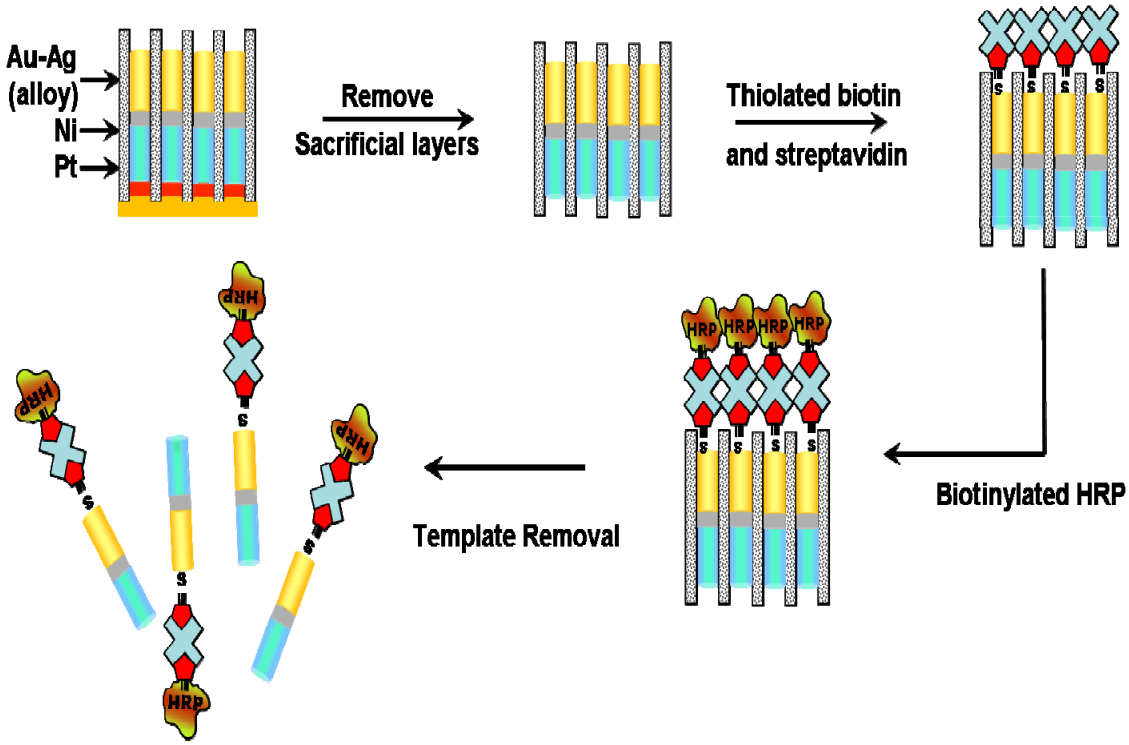
The nanomotors (Pt/Ni/Ag-Au) were prepared by a sequential electrodeposition of the silver-gold (Ag-Au) alloy, Nickel and of the pure platinum segments into a porous alumina membrane template (Catalog no. 6809–6022; Whatman, Maidstone, U.K.). A thin gold film was first sputtered on the branched side 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 electrodeposited into the branched area of the membrane using a 1M cupric sulfate pentahydrate solution ($CuSO_4$ $5H_2O$; Sigma–Aldrich, St. Louis, MO), a total charge of 10 Coulombs (C) and a potential of -1.0 V (vs. Ag/AgCl; along with a platinum wire as a counter electrode). Platinum was then deposited potentiostatically at -0.3 V for 2.8 C from a platinum plating solution (4.6 g L^{-1} hexachloroplatinic acid in 32 g L^{-1} boric acid), followed by electrodeposition of the ferromagnetic Ni segment using a nickel plating solution [20 g L^{-1} $NiCl_2.6H_2O$], 515 g L^{-1} $Ni(H_2NSO_3)_2.4H_2O$, and 20 g L^{-1} H_3BO_3 (buffered to pH 3.4)] at -1.0 V for 2 C. Subsequently, Ag/Au alloys were electrodeposited at -1.1 V from a 1:1 mixture of gold and silver plating solutions (Orotemp 24 RTU RACK and 1025 RTU@4.5 Troy/Gallon, respectively; Technic Inc., Anaheim, CA) until an

alloy-segment length of 1 μm was reached. The sputtered gold layer was removed by mechanical polishing with alumina powder (3-4 μm particle size) and the sacrificial copper layer was removed using a 0.5 M $CuCl_2$- 20% HCl mixture.

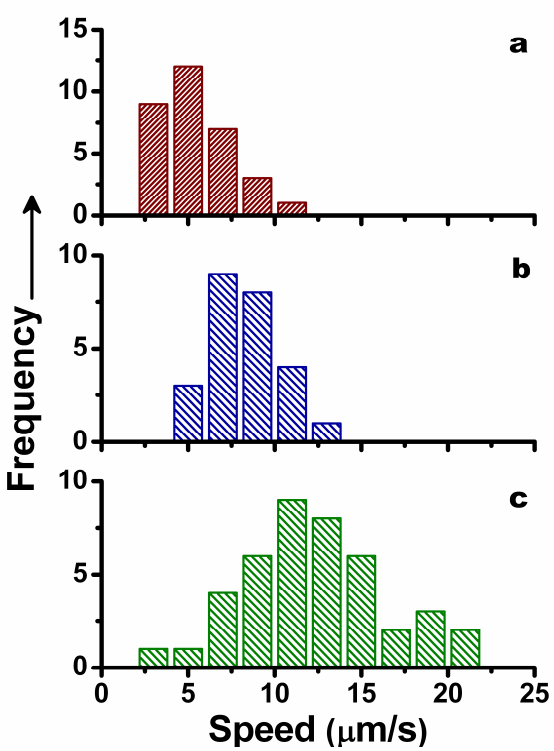
Bio-functionalization of nanowires (SI Fig. 1) was carried out by exposing the alloy ends of the nanowires (while in the membrane) to a 1 mM ethanolic solution biotin-terminated disulfide to form a self-assembled monolayer for overnight at room temperature. The biotin-functionalized nanowires (in membrane) were subsequently functionalized with streptavidin (10 μg/ml in a 0.5 mM phosphate buffer) and biotinylated-HRP (25 μg/ml in 0.5 mM phosphate buffer) by exposing both solutions for 2 h. A diluted NaOH (0.3 M) solution was used to dissolve the membrane and release the enzyme- functionalized nanowires which were washed thoroughly with ultra pure water by repeated centrifugation until a neutral pH was achieved. HRP-functionalized nanowires were stored at 4 °C before testing. The presence of HRP in the nanomotor was confirmed from amperometric (at -0.1 V) and from optical measurements using a solution containing the HRP co-substrate 3,3',5,5'-tetramethylbenzidine (TMB) and H_2O_2 (Enhanced K-Blue TMB substrate, Neogen Co., Lansing, MI).

A 25.4 mm cube-shaped Neodymium (NdFeB) magnet (from K&J Magnetics Inc., Jamison, PA) was used for the magnetic guidance experiments. The magnetic pole (from north to south) of the magnets was perpendicular to the optical axis of the microscope. This position of the magnet allowed for a weak parallel magnetic field to interact with the nanomotors on the gold slide. Freshly prepared HRP-functionalized Pt/Ni/Au-Ag nanowire motors were mixed with a 5 % H_2O_2 and the aniline monomer (0.5 to 3 mM) in 1 mM $LiClO_4$ solution. A 10 μl aliquot of the above mixture was added to a freshly evaporated gold slide for video acquisition and AFM analysis. The precise magnetically-guided motion catalytic Pt/Ni/Au-Ag nanomotors were performed by rotating the magnet at a preselected angle (without changing the position of the magnet). Such guided motion of several functionalized nanomotors has been exploited for direct 'writing' of multiple microstructures.

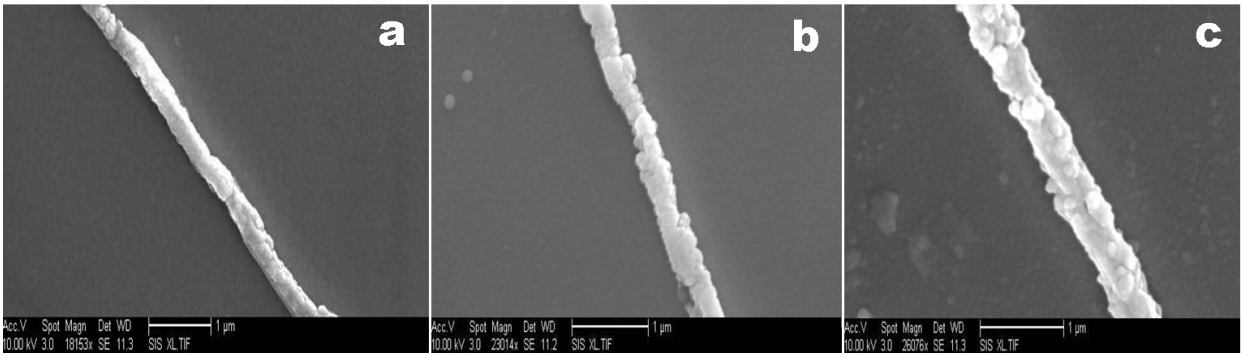
AFM imaging was performed in the tapping mode on a Veeco Scanning Probe Microscope. Imaging was carried out using a scan scale of 5 μm and a scan rate of 1.0 Hz. All writing experiments were conducted under ambient conditions.



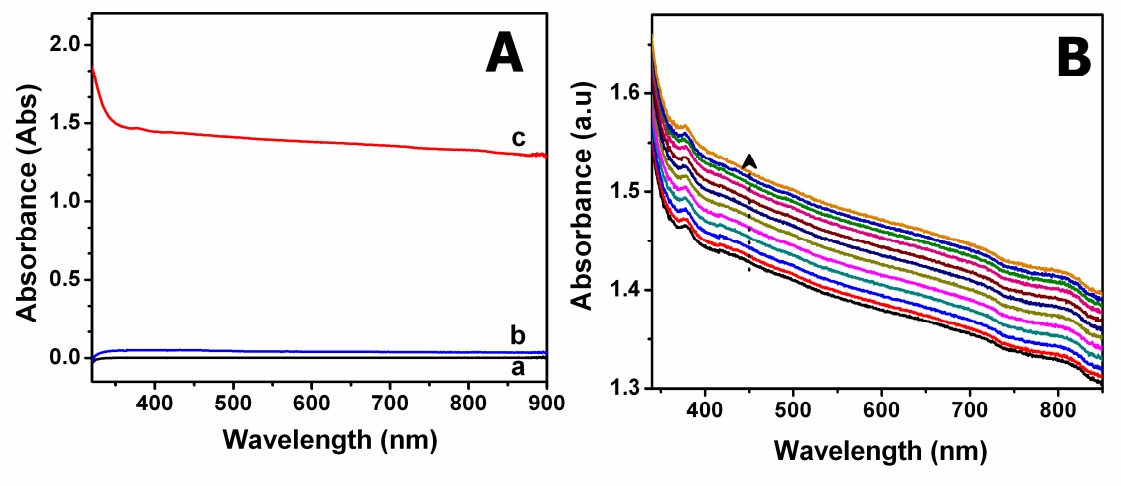
SI-Fig. 1. Schematic representation of the template synthesis of HRP-functionalization of the nanowire motors.



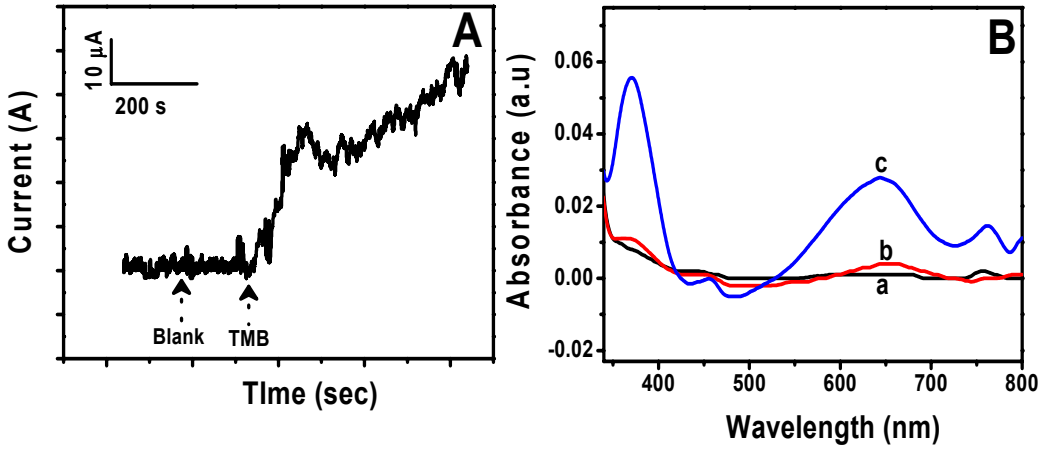
SI Fig. 2: Histograms depicting speed distributions of HRP modified Pt/Ni/Au-Ag nanomotors in (a) 5% H_2O_2 along 3 mM aniline (in 1mM $LiClO_4$), (b) 5% H_2O_2 along with 1 mM $LiClO_4$ and (c) 5% H_2O_2 alone.



SI Fig. 3: SEM image of Nanomotor-based surface 'writing' of catalytic HRP-modified nanomotors in different concentration of aniline (monomer) (a) 0.5 mM, (b) 1 mM, (c) 3 mM in 1 mM $LiClO_4$) in a 5% H_2O_2 solution.



SI Fig. 4: (A) UV-visible Spectra for the for the aniline alone (a), with Au/Ag -Pt (b), with Au/Ag -Pt -HRP (c) and (B) shows course of polymerization of polyaniline with time.



SI- Fig. 5: (A) Amperometric response Au/Ag-Pt-HRP toward the commercial TMB (10 times diluted). (B) UV-visible spectra for the (a) commercial TMB solution (100 times diluted), (b) with Au/Ag –Pt, (c) with Au/Ag -Pt –HRP.