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Nanomotors Responsive to Nerve-Agent Vapor Plumes

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SUPPORTING INFORMATION

1. Supporting Videos description

2. Methods

1. Supporting Videos description

Supporting Video S1. Nerve agent vapor-induced inhibition in the swimming behavior of catalase-modified PEDOT/Au-micromotors: Nerve agent concentration effect (Fixed parameters: 1 min, 0.5 cm).

Supporting Video S2. Nerve agent vapor-induced inhibition in the swimming behavior of catalase-modified PEDOT/Au-micromotors: Distance effect (Fixed parameters: 2 min, 0.1 M).

Supporting Video S3. Nerve agent vapor-induced inhibition in the swimming behavior of catalase-modified PEDOT/Au-micromotors: Time effect (Fixed parameters: 0.01 M, 1 cm).

Supporting Video S4. Nerve agent vapor-induced selective inhibition in the swimming behavior of catalase-modified PEDOT/Au-micromotors. Changes in the swimming behavior of the motors in the presence of: nerve agent (10^{-1} M), methyl paraoxon (1 M), Pb (1 M), phenol (1 M), rhodamine 6G (1 M), and 1,4 phenylenediamine hydrochloride (1 M). (Fixed parameters: 5 min, 1 cm).

2. Methods

Reagents and Apparatus: A Cyclopore polycarbonate membrane, containing 2 µm diameter conical-shaped micropores (Catalog No 7060-2511; Whatman, Maidstone, U.K.), was employed as the template. 3,4-ethylenedioxythiophene (EDOT), sodium dodecyl sulfate (SDS, MW 288.38 g/mol), potassium nitrate, hydrogen peroxide and sodium cholate (NaCh) were purchased from Sigma. Catalase were dissolved in 0.05 M phosphate buffer pH 5.5, prepared from analytical grade KH_2PO_4 and K_2HPO_4. The washing solution (PBST-20X) consisted of 0.05 M phosphate buffer pH 5.5 containing 0.15 M potassium chloride and 0.05% Tween-20. Ultrapure water (18MΩ cm, Millipore Corporation, USA) was used for the preparation of all aqueous solutions

Preparation of the Tubular Micromotors: The microtubular motors 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-thick gold film was first sputtered on one side of the porous membrane to serve as the working electrode using the Denton Discovery 18 sputtering system. The coating was performed at room temperature under base vacuum of 5 × 10^{-6} Torr, DC power 200 W and Ar pressure of 3.1 mT, along with a rotation speed of 65 rpm and sputtering time of 90 s. A Pt wire and Ag/AgCl (3 M KCl) served as counter and reference electrodes, respectively. The membrane was then assembled in the electrochemical plating cell with an aluminum foil serving as a contact.

Poly(3,4-ethylenedioxythiophene) (PEDOT) microtubes were electropolymerized at +0.80 V using a charge of 0.06 C from a plating solution containing 15 mM EDOT, 7.5 mM KNO_3 and 100 mM sodium dodecyl sulfate (SDS); subsequently, gold was plated at −0.9 V for 1 C from a commercial gold plating solution (Orotemp 24 RTU RACK; Technic Inc.). The sputtered gold layer was completely removed by hand polishing with alumina slurry (3–4 μm). Finally, the microtubular engines were collected by centrifugation at 6000 rpm for 3 min and washed repeatedly with methylene chloride, followed by ethanol and ultrapure water (18.2 MΩ cm), three times for each, with a 3 min centrifugation following each wash.

Micromotor functionalization: The inner Au layer of the bilayer microtubes was functionalized first with a mixed MUA/MCH alkanethiol monolayer. A solution mixture of 2.5 mM MUA and 7.5 mM MCH was prepared in ethanol. The microtubes were incubated in the MUA/MCH solution overnight. After rinsing the tubes with water for 5 min, they were transferred to an eppendorf vial containing a 200 μL PBS buffer (pH 5.5) solution with the coupling agents 1-ethyl-3-[3-dimethylaminopropyl] carbodiimide hydrochloride (EDC), N-hydroxylsulfosuccinimide (Sulfo-NHS) at 0.4 and 0.1 M, respectively, and the catalase enzyme (2 mg/mL). This incubation was carried out for 7 h at 37 °C, followed by two 15 min rinsing steps with a PBS solution (pH 5.5) containing 0.05 wt % SDS. Finally, the microengines were washed repeatedly by centrifugation at 6000 rpm for 3 min with water for three times to remove the excess of catalase from the solution, and were suspended in 5.5 pH PBS buffer and stored at 4 °C until use. Such catalase-modified micromotors can be used up to 1 week after their preparation when stored under these conditions.

Equipment: Template electrochemical deposition of microtubes was carried out with a CHI 661D potentiostat (CH Instruments, Austin, TX). An inverted optical microscope (Nikon Instrument Inc. Ti-S/L100), coupled with a 40× objective, a Photometrics QuantEM 512/SC camera (Roper Scientific, Duluth, GA) and MetaMorph 7.6 software (Molecular Devices, Sunnyvale, CA) were used for capturing movies at a frame rate of 30 frames per sec. The speeds of the microengines were tracked using a Metamorph tracking module and the results were statistically analyzed using Origin software.

Vapor experiments: Aqueous diethyl cholorophosphate (DCP) solutions, ranging from (1M to 10^{-4}M), were prepared for the vapor experiments. A 1 µL droplet containing the micromotors (containing 1% of the surfactant and peroxide fuel) was placed first on the glass slide followed by placing a 1 µL droplet of the DCP nerve agent, at distances ranging from 0.5 to 2.0 cm, and allowed to react above a hot plate at 40°C for varied times ranging from 1-5 min. A containment enclosure was placed atop the microscope stage in order to minimize the potential risk of toxic vapor.