Electronic Supporting Information (ESI)

Lighting up micromotors with quantum dots for smart chemical sensing

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Supporting videos

SI video 1. Autonomous motion of highly fluorescent CdTe/PEDOT microsensor vs. non-fluorescence control PEDOT/PSS microrockets in a PBS solution containing 5 % H₂O₂ and 1 % (w/v) sodium cholate

SI video 2. Selectivity of the ‘on-the-fly’ mercury detection of Hg²⁺ by CdTe/PEDOT microsensor upon the presence of a high excess of different cations. Medium: PBS buffer, 5 % H₂O₂ and 1 % (w/v) sodium cholate

SI video 3. Effect of the polyelectrolyte layers on the speed of CdTe/PEDOT microsensor (n=10 layers) vs. control PEDOT/PSS microrockets. Medium: PBS buffer, 1 % H₂O₂ and 1 % (w/v) sodium cholate

SI video 4. Dependence of the fluorescence quenching of CdTe/PEDOT micromotors upon different Hg²⁺ concentrations. Medium: PBS buffer, 5 % H₂O₂ and 1 % (w/v) sodium cholate

SI video 5. Effect of different cations on the fluorescence of CdTe/PEDOT microsensors. Medium: PBS buffer, 2 % H₂O₂ and 1 % (w/v) sodium cholate

SI video 6. Mercury detection and speciation in saliva samples. 2 % H₂O₂ and 1 % (w/v) sodium cholate
Experimental Section

Preparation of QDs-based micromotors

For micromotors preparation, a polycarbonate membrane containing 2 µm diameter conical pores (Catalog No. 7060-2511; Whatman, Maidstone, UK) was employed as the template. A thin gold film (75 nm) was first sputtered on the branched side of the membrane to serve as a working electrode. A platinum wire and a Ag/AgCl electrode were used as counter and reference electrode, respectively. The membrane was assembled in a Teflon plating cell with aluminum foil serving as an electrical contact for the subsequent electrodeposition. Poly (3,4-ethylenedioxythiophene) (PEDOT) microtubes, doped with poly(sodium 4-styrene sulphonate) (PSS) were electropolymerized at +0.80 V using a charge of 4 C from a 10 mL plating solution containing 10 mM of 3,4-ethylenedioxythiophene (EDOT) and 125 mM PSS (MW ~70 000). Subsequently, the inner Pt layer was deposited galvanostatically at -2 mA for 3600 s from a commercial platinum plating solution (Platinum RTP; Technic Inc, Anaheim, CA).

For the fabrication of the microsensors, the as obtained PEDOT/PSS micromotors were sequentially incubated with positively charged (poly(diallyldimethylammonium chloride) (PDDA) and negatively charged PSS (1 g/L) for 10 min, respectively. This process was repeated 10 times until ten polyelectrolyte layers were formed, being PDDA the last layer. The resulted microrockets were incubated with a solution containing the negatively-charged COOH-CdTe quantum dots (Sigma Aldrich, cat. 777986, fluorescence λem 510 nm) under vigorous stirring for 1 h at room temperature. The unattached CdTe QDs were isolated by centrifugation (5000 rpm) with ultrapure water, and the resulting micromotors were dispersed in PBS buffer (10 mM, pH 7.5). All microtubes were stored in ultrapure water at room temperature when not in use. These microsensors can be stored for two weeks without any decrease in their fluorescence properties.

Equipment

Template electrochemical deposition of microtubes was carried out using a CHI 661D potentiostat (CH Instruments, Austin, TX). Videos were captured using a C11440 Hamamatsu digital camera, 20X objective and acquired at a frame rate of 5 frames/s using NIS Elements AR 3.2 software. A Nikon optical microscope (Nikon Eclipse Instrument Inc. Ti-S/L100) coupled with a B2-A FITC filter and a 160-W Hg excitation lamp was used to capture fluorescence images and videos. Scanning electron microscopy (SEM) images were obtained with a Phillips XL30 ESEM instrument, using an acceleration voltage of 20 kV. Energy-dispersive X-ray mapping analysis was performed using an Oxford EDX detector attached to SEM instrument and operated by INCA software. An UV-Vis spectrophotometer (UV-2450, SHIMADZU) equipped with a constant temperature circulating bath was used for further characterization of the CdTe/PEDOT microsensors by recording the spectra (350-700 nm) of 500 µL solutions containing 7.5 x 10^5 microsensors/mL before and after addition of 3 mg/L of Hg (II).

‘On-the-fly’ mercury detection experiments

Experiments were performed by placing a total of 4 µL of a solution mixture on a glass slide. First, three different solutions (1µL each), including CdTe/PEDOT micromotors (5 x 10^5 micromotors/ml), sodium cholate (4 %, Sigma-Aldrich, cat. 270911) and H₂O₂ (8-20 %, Sigma-Aldrich, cat. 95313) were dropped in the glass slide, followed by addition of 1 µL of the Hg²⁺ sample solution (in the desired concentration). Hydrogen peroxide acts as a fuel, essential for the microsensor propulsion and its ‘on-the-fly’ mercury detection capacity. Sodium cholate was used as surfactant to reduce the surface tension and stabilize the generated bubbles for the efficient propulsion of the microsensor. Video acquisition started after the micromotors has navigated for 30 s in the above mentioned solutions. Selectivity experiments involving Pb²⁺, Cu²⁺ and CH₃Hg⁺ ions were
performed in a similar fashion. The effect of pH and ionic strength on the fluorescence of the micromotors was evaluated by using several solutions containing the CdTe/PEDOT micromotors (5 x 10^5 micromotors/ml) and the desired pH (2, 4, 7.5 and 9) was adjusted by using diluted HCl or PBS buffer solutions. For the effect of ionic strength, KCl (Fischer Scientific) solutions were used. ImageJ program (developed by National Institute of Health) was used to measure the calculated corrected total microsensor fluorescence (CCRF). This calculation was performed according to the following equation:

\[ \text{CCRF} = \text{Integrated density of the microsensor} - (\text{Area of the selected microsensor} \times \text{mean fluorescence of the background readings}) \]

Integrated density, area and fluorescence of the background readings can be measured directly with ImageJ from the fluorescence microscopy images.

**UV-VIS characterization of CdTe/PEDOT microsensors**

UV-VIS spectroscopy is an important tool for optical characterization of materials, as it provides useful information about the optical band gap of the semiconductors like CdTe QDs. Because of the quantum confinement effect (which is imparted in the developed microsensors by the CdTe QDs) such semiconductor nanoparticles show size-dependant optical properties. In this context, to provide further evidence for the formation of the Cd_xHg_{1-x}Te alloy responsible for the fluorescence quenching behaviour of CdTe/PEDOT microsensors, systematic UV-VIS optical absorption studies were carried out before and after Hg (II) addition. Due to the lower solubility of HgTe than CdTe in water, the Hg^{2+} ions substitute Cd^{2+} ions at the surface of the nanocrystals, forming a Cd_xHg_{1-x}Te and increasing its size, displacing thus the optical band-gap. Using the absorption spectrum, the direct optical band gap energy of the CdTe/PEDOT microsensors before and after Hg (II) addition was calculated by simply plotting \((\alpha h\nu)^2\) versus \(h\nu\), according to the Tauc relation:

\[ \alpha h\nu = B (h\nu - E_g)^{1/2} \]

where \(\alpha\) is the absorption coefficient, \(h\nu\) is the photon energy (calculated as \(h\nu = 1240/\text{wavelength}\)), \(E_g\) is the direct band gap energy, and \(B\) is a constant. The absorption coefficient \((\alpha)\) was determined by using a relation deduced from Beer–Lambert’s relation, \(\alpha = 2.303A/d\), where \(d\) is the path length of the quartz cuvette and \(A\) is the absorbance determined from the UV–VIS spectrum. The average band gap was estimated from the intercept of linear portion of the \((\alpha h\nu)^2\) vs. \(h\nu\) plots on \(h\nu\) axis as shown in Fig. S4. The direct optical band energy gap of the CdTe/PEDOT micromotors before and after addition of 3 mg/L of Hg (II) was calculated to be 2.24 and 1.45, respectively. This shift to a lower bandgap under the presence of Hg (II) is due to the quantum confinement effect as the CdTe QDs grow to larger size due to Hg addition, and this is a good evidence for the formation of Cd_xHg_{1-x}Te alloy on the surface of the microsensor. 23
Figures

**Fig. S1.** Effect of the number of polyelectrolite layers (A) and of the hydrogen peroxide concentration (B) on the fluorescence intensity of CdTe/PEDOT microrockets. The inset in Fig S1, A corresponds to fluorescence (left) and bright field (right) microscopy images of microrockets modified with 2 (a), 4 (b) and 10 (c) polyelectrolite layers. CCRF, calculated corrected total microsensor fluorescence. Image analysis using ImageJ program. Error bar represent the standard deviation resulting from the estimation of the fluorescence of 10 motors (n=10). Scale bars, 9 µm.

**Fig. S2.** Dependence of the speed of CdTe/PEDOT (blue line) and control PEDOT/PSS (green line) micromotors upon the hydrogen peroxide concentration over the 1-10 % range, in the presence of 1 % sodium cholate (n=10). Inset: time-lapse images, taken from SI video 3, illustrating the motors propulsion in 1 % H₂O₂ (left) as compared with control PEDOT/PSS micromotors (right). Scale bars, 10 µm.
Fig. S3. Effect of pH (A) and ionic strength (B) on the fluorescence intensity of CdTe/PEDOT microrockets under the presence of 0 (black line), 0.5 (red line) and 1 mg/L (blue line) of Hg (II). CCRF, calculated corrected total microsensor fluorescence. Error bar represent the standard deviation resulting from the estimation of the fluorescence of 10 motors (n=10).

Figure S4. Tauc plots curves for CdTe/PEDOT (A) and Cd₄HgₓTe/PEDOT (B) microsensors. Conditions: 7.5 x 10⁵ micromotors/mL, 500 µL solutions.
Fig. S5. Selectivity of PEDOT/CdTe micromotors. (A) Time-lapse images, taken from SI videos 2 and 5, showing the effect of different cations on the fluorescence of PEDOT/CdTe micromotors: 0 mg/L Hg$^{2+}$ (a), 1 mg/L Hg$^{2+}$ (b), 3 mg/L Pb$^{2+}$ (c), 3 mg/L Cu$^{2+}$ (d) and 5 mg/L CH$_3$Hg$^+$ (e). Lower part show the magnified images corresponding to each microrocket. Videos were taken after the microrockets had navigated for 30 s in a solution containing the corresponding cation. (B) Plot showing the fluorescence intensity (as CCRF) of CdTe/PEDOT microrockets under the absence and presence of Hg$^{2+}$, Pb$^{2+}$, Cu$^{2+}$ and CH$_3$Hg$^+$. Conditions: 2 % peroxide, 1 % sodium cholate, medium, PBS buffer. CCRF (calculated corrected total microsensor fluorescence) was estimated using ImageJ program. Scale bars, 5 µm. Error bar represent the standard deviation of 5 measurements (n=5).