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-fluorescense control PEDOT/PSS microrockets in a PBS solution containing 5 % H_2O_2 and 1 % (w/v) sodium cholate

SI video 2. Selectivity of the *'on-the-fly'* mercury detection of Hg^{2+} by CdTe/PEDOT microsensor upon the presence of a high excess of different cations. Medium: PBS buffer, 5 % H_2O_2 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 % H_2O_2 and 1 % (w/v) sodium cholate

SI video 4. Dependence of the fluorescense quenching of CdTe/PEDOT micromotors upon different Hg^{2+} concentrations. Medium: PBS buffer, 5 % H_2O_2 and 1 % (w/v) sodium cholate

SI video 5. Effect of different cations on the fluorescense of CdTe/PEDOT microsensors. Medium: PBS buffer, 2 % H_2O_2 and 1 % (w/v) sodium cholate

SI video 6. Mercury detection and speciation in saliva samples. 2 % H_2O_2 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 H_2O_2 (8-20 %, Sigma-Aldrich, cat. 95313) were dropped in the glass slide, followed by addition of 1 µL of the Hg^{2+} 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 Pb^{2+}, Cu^{2+} and CH_3Hg^+ ions were

performed in a similar fashion. The effect of pH and ionic strength on the fluorescense 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 fluorescense (CCRF). This calculation was performed according to the following equation:

CCRF=Integrated density of the microsensor - (Area of the selected microsensor x mean fluorescense of the background readings)

Integrated density, area and fluorescense 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 fluorescense 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:

$$\alpha h\nu = B\,(h\nu - Eg)^{1/2}$$

where α is the absorption coefficient, hν is the photon energy (calculated as hν = 1240/wavelengt), Eg is the direct band gap energy, and B is a constant. The absorption coefficient (α) was determined by using a relation deduced from Beer–Lambert's relation, α = 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. hν plots on hν 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

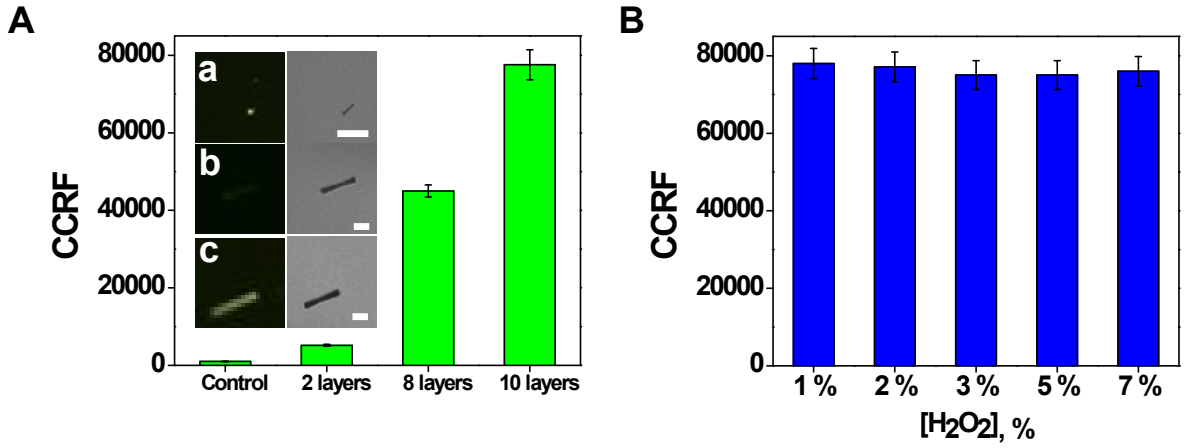

Fig. S1. Effect of the number of polyelectrolite layers (A) and of the hydrogen peroxide concentration (B) on the fluorescense intensity of CdTe/PEDOT microrockets. The inset in Fig S1, A corresponds to fluorescense (left) and bright field (right) microscopy images of microrockets modified with 2 (a),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

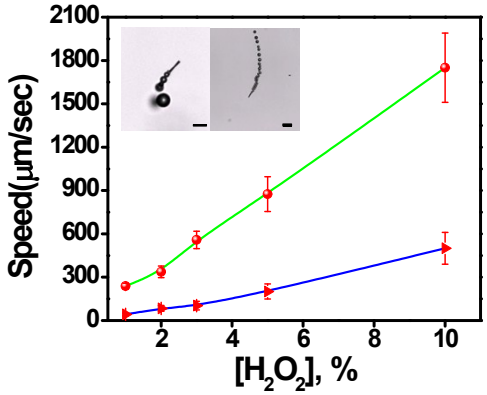

Fig. S2. Dependence of the speed of CdTe/PEDOT (blue line) and control PEDOT/PSS (green line) micromotors upon the hydrogen peroxide concentration over the 1-10 % range, in the presence of 1 % sodium cholate (n=10). Inset: time-lapse images, taken from SI video 3, illustrating the motors propulsion in 1 % H_2O_2 (left) as compared with control PEDOT/PSS micromotors (right). Scale bars, 10 µm.

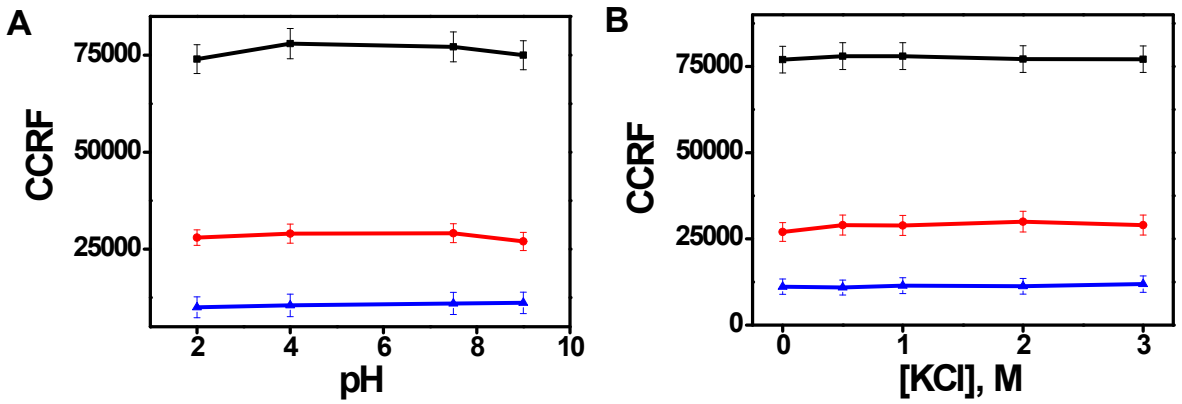

Fig. S3. Effect of pH (A) and ionic strength (B) on the fluorescense intensity of CdTe/PEDOT microrockets under the presence of 0 (black line), 0.5 (red line) and 1 mg/L (blue line) of Hg (II). CCRF, calculated corrected total microsensor fluorescense. Error bar represent the standard deviation resulting from the estimation of the fluorescense of 10 motors (n=10).

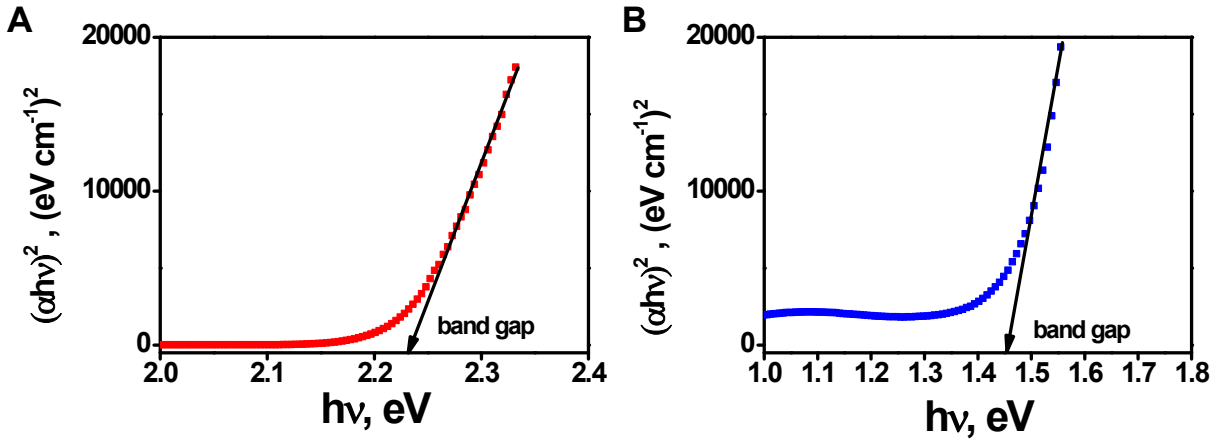

Figure S4. Tauc plots curves for CdTe/PEDOT (A) and $Cd_xHg_{1-x}Te$/PEDOT (B) microsensors. Conditions: 7.5 x 10^5 micromotors/mL, 500 µL solutions .

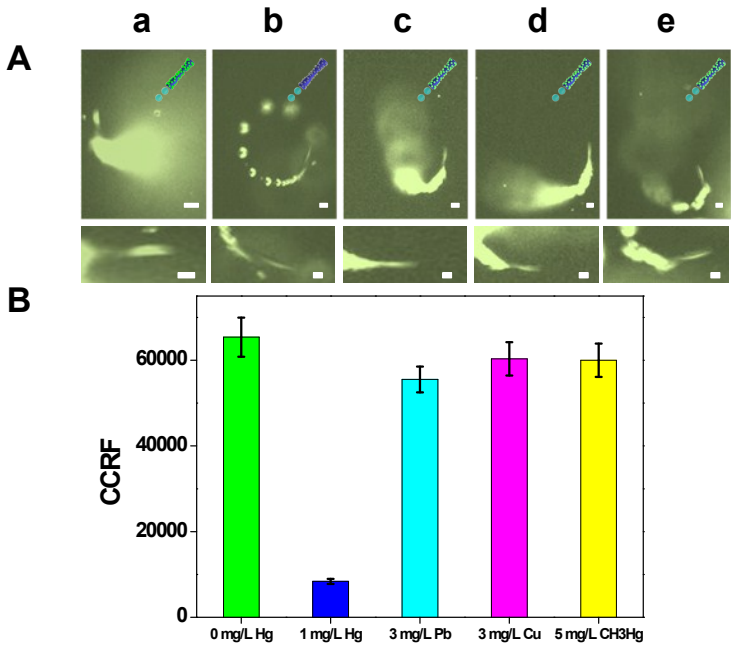

Fig. S5. Selectivity of PEDOT/CdTe micromotors. (A) Time-lapse images, taken from SI videos 2 and 5, showing the effect of different cations on the fluorescense of PEDOT/CdTe micromotors: 0 mg/L Hg^{2+} (a), 1 mg/L Hg^{2+} (b), 3 mg/L Pb^{2+} (c) 3 mg/L Cu^{2+} (d) and 5 mg/L CH_3Hg^{+} (e). Lower part 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 fluorescense intensity (as CCRF) of CdTe/PEDOT microrockets under the absence and presence of Hg^{2+}, Pb^{2+}, Cu^{2+} and CH_3Hg^{+}. Conditions: 2 % peroxide, 1 % sodium cholate, medium, PBS buffer. CCRF (calculated corrected total microsensor fluorescense) was estimated using ImageJ program. Scale bars, 5 µm. Error bar represent the standard deviation of 5 measurements (n=5).