

Electronic Supplementary Information

Biocatalytic etching of semiconductor cadmium sulfide nanoparticles as a new platform for optical detection of analytes

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Experimental

Materials: Sodium sulfide (Na_2S) and cadmium sulfate CdSO_4 , cadmium nitrate $\text{Cd}(\text{NO}_3)_2$, horseradish peroxidase type VI and other chemicals were supplied by Sigma-Aldrich. Polyvinyl chloride microspheres with amine functional group (beadBALL-Amine) were purchased from Chemicell (Germany).

Instruments: All assays were performed in black flat-well (330 μL) NUNC 96 wells microtiter plates, and the fluorescence spectra were recorded with a Varioskan Flash fluorimeter (Thermo Scientific). Microscopy studies were done by transmission electron microscopy (TEM) and Axio Observer Microscope (Zeiss). For detection of sulfate ions capillary electrophoresis (CE) with UV/Vis diode-array detector (Agilent CE) and DU[®] 800 Spectrophotometer (Beckman Coulter) were used.

Cadmium sulfide NPs synthesis: To prepare 1000 μL of CdS NPs solution 20 μL of 10 mM Na_2S was mixed with 75 μL of 100 mM Cd^{2+} ions in citrate buffer (3.5 mM, pH 5.0). The mixtures were incubated for 5 min at room temperature and used immediately.

HRP assay: For determination of peroxide, varying concentrations of H_2O_2 were added to a solution containing 100 μL of previously prepared CdS NPs, NaBr 8 mM, HRP 2.5 μM and citrate buffer 3.5 mM pH 5.0, in a final volume of 125 μL . The emission spectra of the resulting mixtures were recorded after 15 min $\lambda_{\text{ex}}=300$. For determination of HRP varying concentrations of HRP were added to a solution containing 100 μL previously prepared CdS NPs, NaBr 8 mM, H_2O_2 0.2 mM and citrate buffer 3.5 mM pH 5.0, in a final volume of 125 μL . The emission spectra of the resulting mixtures were recorded after 15 min at $\lambda_{\text{ex}}=300$.

Sample preparation for sulfate ions detection with CE: Sample 1: To prepare 1000 μL of CdS NPs solution 20 μL of 10 mM Na_2S was mixed with 75 μL of 100 mM $\text{Cd}(\text{NO}_3)_2$ in citrate buffer (3.5 mM, pH 5.0). The mixture was incubated for 5 min at room temperature. Sample 2: NaBr 8 mM, HRP 2.5 μM and H_2O_2 0.2 mM were added to the solution containing 100 μL previously prepared CdS NPs in citrate buffer 3.5 mM pH 5.0. Sample was incubated 15 min. After all samples were centrifuged using an Amicon Ultra filter with a 3000 molecular weight cutoff. 1 mL of filtrate was used.

Sample preparation for sulfate ions detection by a spectrometric method in which sulfate is precipitated as barium sulfate: the samples were prepared like described before. After 1 mL of the sample was mixed with 20 μL of 3.7 % HCl. 47.5 mL of 0.1M BaCl_2 and 2.5 mL of Tween 20 were mixed and 100 μL of this solution were added to the samples. The solutions were agitated for 10 min. The absorbance spectra of the resulting suspensions were recorded after 15 min.

Preparation of polyvinyl chloride microspheres/CdS NPs composites: 40 μL of polyvinyl chloride microsphere-amine (25 mg/mL) were added to 260 μL citrate buffer (3.5 mM, pH 5.0) and centrifuge at 500 x g for 1 min. Supernatant was discarded and 200 μL of previously prepared CdS NPs were added to the beads. After 1 h incubation the beads were washed with 200 μL of citrate buffer 3.5 mM pH 5.0 and resuspended in the same volume of buffer for the further experiments. For monitoring photoluminescence of etching of CdS NPs with Axio Observer Microscope in real time, 400 times diluted solution was used.

HRP assay with polyvinyl chloride microspheres/CdS NPs composites: For determination of etching on polyvinyl chloride microsphere-amine/CdS NPs composites previously mentioned conditions were used. The emission spectra of the resulting mixtures were recorded after 5 min at $\lambda_{\text{ex}}=300$.

Quantification of H_2O_2 in water: Tap water samples (samples were collected in CICbiomagune, San Sebastian, Spain) were spiked with different concentrations of H_2O_2 . Next, prepared polyvinyl chloride microspheres/CdS NPs composites were mixed with water samples and with optimal concentration of HRP and NaBr.

For detection H_2O_2 in rain water collected in San Sebastian, Spain, the sample was diluted by 5 times. For quantification of H_2O_2 in rain water standard addition method was used. According to this method, the same amount of the water sample was split into separate eppendorfs. Varying standard amounts of H_2O_2 were injected into the samples with rain water. The results were plotted with the concentration standard added in the x-axis and the obtained absorbance readings in the y-axis of calibration line. The linear regression was carried out to calculate the position of the recalculated calibration line, which showed the concentration of hydrogen peroxide in samples of rain water.

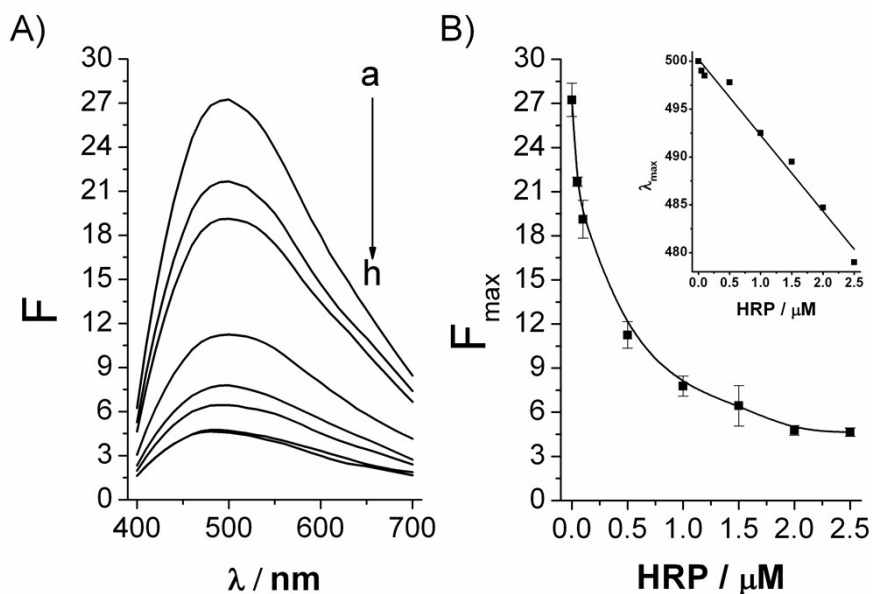


Fig. S1. (A) Fluorescence emission spectra of the system containing CdS NPs, H₂O₂ (0.2 mM), NaBr (8mM) and different concentrations of HRP: a) 0 μM; b) 0.05 μM; c) 0.1 μM; d) 0.5 μM; e) 1 μM; f) 1.5 μM; g) 2 μM; h) 2.5 μM; (B) Calibration curve of HRP obtained using maximum fluorescence intensity of the peak, F_{max}. Inset: the position of emission peaks at different concentrations of HRP.

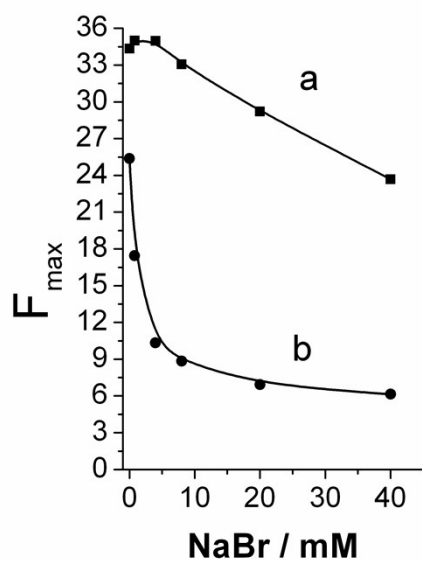


Fig. S2. Effect of different concentrations of NaBr on peak fluorescence intensity, F_{max}, in the system composed of (a) CdS NPs only (b) CdS NPs, H₂O₂ (0.1 mM), HRP (2 μM).

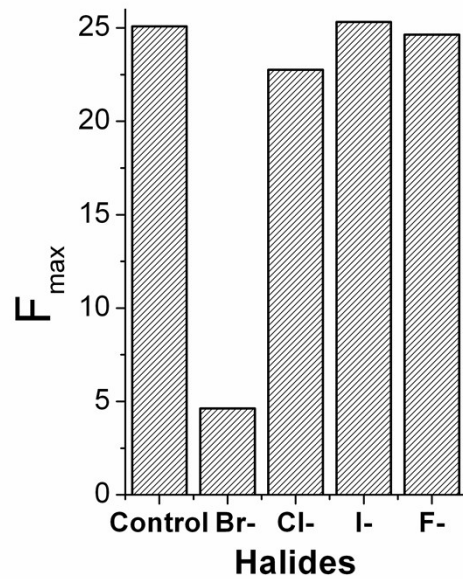


Fig. S3. Effect of different concentrations halides on peak fluorescence intensity, F_{max} in the system composed of CdS NPs, H_2O_2 (0.25 mM), HRP (2.5 μ M) and 8 mM of halides.

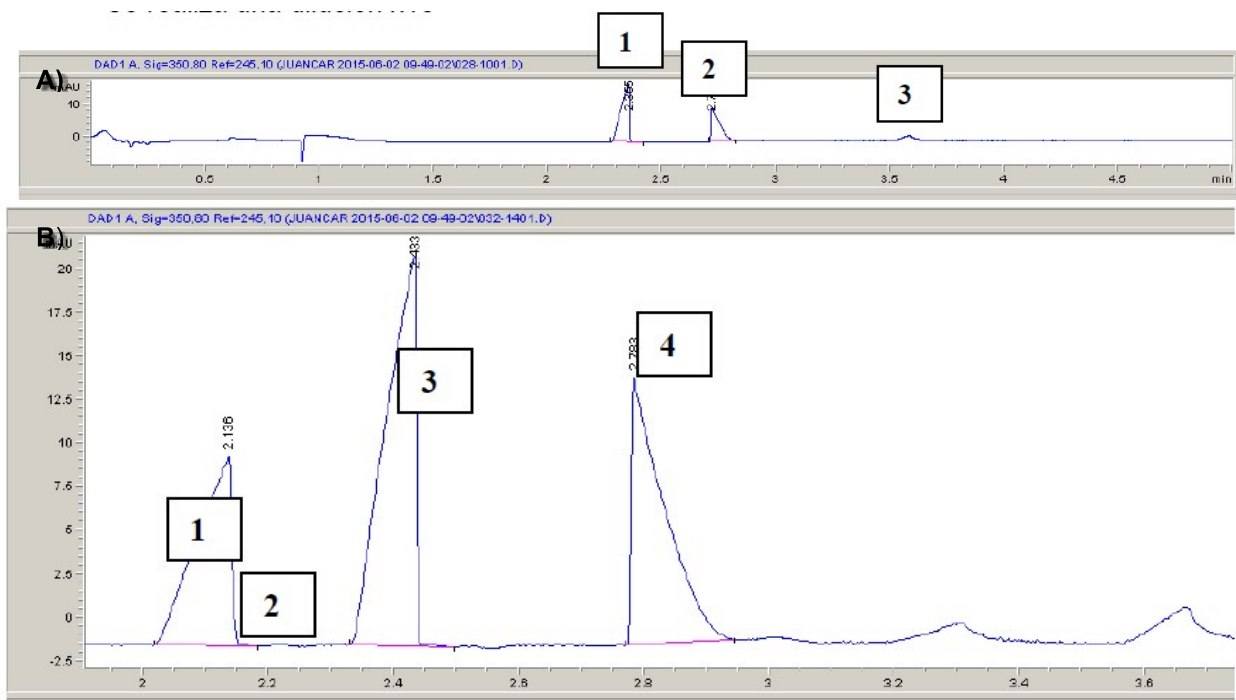


Fig. S4. CE results. (A) Sample 1 (dissolution 10X). peak 1. NO_3^- ; peak 2 citrate ion, peak 3 unknown but not SO_4^{2-} . Conclusion no SO_4^{2-} ions were detected; (B) Sample 2 (dissolution 5X). 1. peak 1 Br^- , peak 2 SO_4^{2-} , peak 3 NO_3^- ; peak 4 citrate ion. Conclusion 2.4 ± 0.3 mg L^{-1} ions were detected.

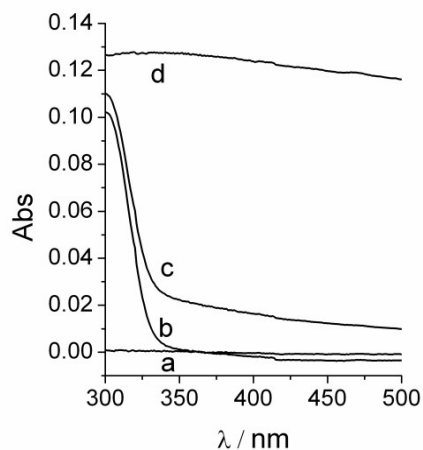


Fig. S5. Absorbance spectra of SO_4^{2-} : a) blank; b) before etching; c) after etching, d) only SO_4^{2-} in citrate buffer.

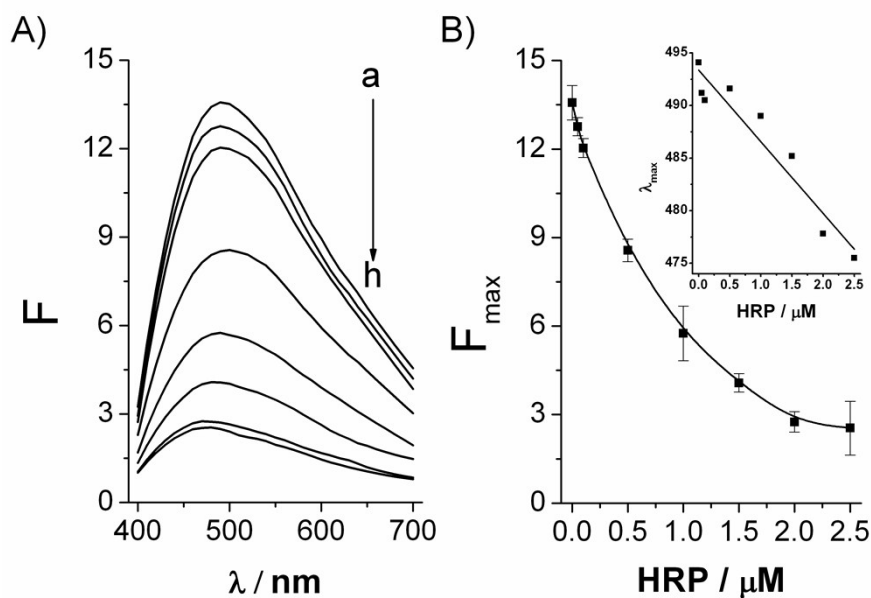
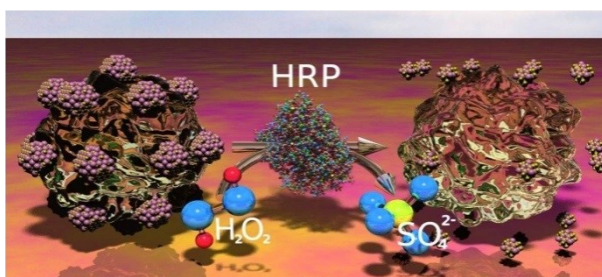


Fig. S6. (A) Fluorescence emission spectra of the system containing polyvinyl chloride microsphere-amine/CdS NPs composites H_2O_2 (0.2 mM), NaBr (8 mM) and different concentrations of HRP: a) 0 μM ; b) 0.05 μM ; c) 0.1 μM ; d) 0.5 μM ; e) 1 μM ; f) 1.5 μM ; g) 2 μM ; h) 2.5 μM ; (B) Calibration curve of HRP obtained using maximum fluorescence intensity of the peak, F_{max} . Inset: the position of emission peaks at different concentrations of HRP.



Scheme S1. Enzymatic etching of CdS NPs immobilized on the surface of polyvinyl chloride microsphere-amine.

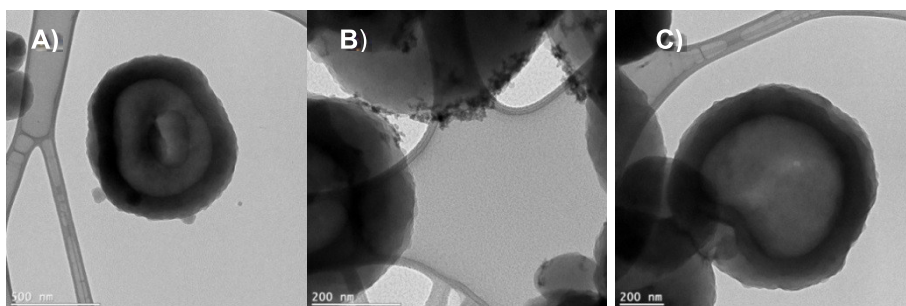


Fig. S7. TEM images of polyvinyl chloride microsphere-amine (A) microspheres only; (B) polyvinyl chloride microsphere-amine/CdS NPs composites before etching; (C) polyvinyl chloride microsphere-amine/CdS NPs composites after etching.

Table S1. Results of the analyses of H₂O₂ in drinking tap water

Water sample	Added, mM	Found, mM	RSD	Recovery
Drinking tap water	0	not found		
	0.0075	0.00743	4.60%	99.0 %
	0.01	0.01082	3.20%	108.2 %
	0.015	0.01447	2.90%	96.5 %

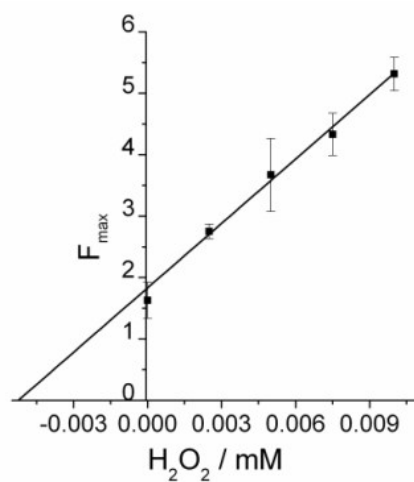


Fig. S8. Quantification of H₂O₂ in rain water with the method of standard addition. The system containing: polyvinyl chloride microsphere-amine/CdS NPs composites, HRP (2.5 μM), NaBr (8 mM).