

## Supporting Information

# Selective detection of trace amount of $\text{Cu}^{2+}$ using semiconductor nanoparticles in photoelectrochemical analysis

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### Materials

$\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$  was purchased from Shanghai Jinshan Tingxin Chemical Plant.  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  was purchased from Shanghai Lingfeng Chemical Reagent Co. LTD. Thioglycolic acid (TGA) and triethanolamine (TEA) were obtained from Sinopharm Chemical Reagent Co., LTD. PDDA (20%, w/w in water, Molecular Weight = 200,000–350,000) was obtained from Aldrich. All other chemicals used in this work are of analytical reagent grade. All aqueous solutions were prepared with doubly distilled water ( $18 \text{ M}\Omega \text{ cm}^{-1}$ ), which was obtained from a Milli-Q water purification system. The stock solutions ( $1.0 \times 10^{-3} \text{ M}$ ) of  $\text{Cu}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Al}^{3+}$  and  $\text{Mn}^{2+}$  ions were prepared by dissolving suitable amount of compounds like  $\text{CuSO}_4$ ,  $\text{AgNO}_3$ ,  $\text{Zn}(\text{NO}_3)_2$ ,  $\text{CdCl}_2$ ,  $\text{NiCl}_2$ ,  $\text{Fe}(\text{NO}_3)_3$ ,  $\text{FeSO}_4$ ,  $\text{CoCl}_2$ ,  $\text{Cr}(\text{NO}_3)_3$ ,  $\text{KCl}$ ,  $\text{NaCl}$ ,  $\text{MgSO}_4$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{CaCl}_2$ ,  $\text{BaCl}_2$ ,  $\text{Al}(\text{NO}_3)_3$  and  $\text{MnCl}_2$  in Milli-Q water. The stock solution of  $\text{Hg}^{2+}$  was prepared by dissolving 14.8 mg of  $\text{HgSO}_4$  in 50 mL doubly deionized water containing 0.3 mL concentrated HCl. The stock solutions were further diluted whenever necessary.

## **Apparatus**

Photoelectrochemical measurements were performed with a home-made photoelectrochemical system. A 500 W Xe lamp equipped with monochromator was used as irradiation source. The monochromatic illuminating light intensity was about  $400 \mu\text{W}/\text{cm}^2$  estimated with a radiometer (Photoelectric Instrument Factory of Beijing Normal University). Photocurrent was measured on a CHI 750a electrochemical workstation. CdS QDs modified ITO electrode with the area of  $0.2 \text{ cm}^2$  was employed as working electrode. A Pt wire was used as a counter electrode and a saturated Ag/AgCl as a reference electrode. All the photocurrent measurements were performed at a constant potential of 0 V (vs. saturated Ag/AgCl). 0.1 M phosphate buffer solution (PBS, pH=7.0) containing 0.1 M triethanolamine (TEA) was used as the supporting electrolyte for photocurrent measurements. The solution was deaerated by highly pure nitrogen for 15 min before photoelectrochemical experiments and then keeping  $\text{N}_2$  atmosphere over the solution in all the experimental process. UV-vis absorption spectra were obtained on a Shimadzu UV-3600 UV/vis spectrophotometer (Shimadzu corporation, Japan). All pH measurements were made with a Model PB-10 meter (Sartorius, German).

## **Synthesis of TGA capped CdS QDs**

TGA stabilized CdS QDs were synthesized using a slightly modified procedure reported by Feng et al.<sup>27</sup> 250  $\mu\text{L}$  TGA were added to 50 mL of  $2.0 \times 10^{-2}$  M  $\text{CdCl}_2$  aqueous solution, after that, 1.0 M NaOH was added to adjust the pH of the above solution to 7.0. During the above process,  $\text{N}_2$  was bubbled throughout the solution to remove  $\text{O}_2$  and lasted for 30 min. Then, 5.0 mL of 0.1 M  $\text{Na}_2\text{S}$  aqueous solution was injected into this solution to obtain TGA capped water-soluble CdS QDs and the

reaction mixture was refluxed under N<sub>2</sub> atmosphere for 4 h. The finally obtained TGA capped CdS QDs were stored in a refrigerator at 4 °C for use.

### Modification of electrodes

The ITO slices (type N-STN-S1-10, China Southern Glass Holding Co., LTD, Shenzhen, China, ITO coating 180±20 nm, sheet resistance 8.1±0.6 Ω/square) were boiled in 2 M KOH for about 20 min, then rinsed thoroughly with distilled water, and finally dried at 120 °C for 2 h. The PDDA/CdS film was grown by alternately dipping the cleaned ITO slices into a solution of 2% PDDA containing 0.5 M NaCl and the as obtained QDs solution for 10 min, respectively. The electrode was carefully washed with doubly distilled water after each dipping step.

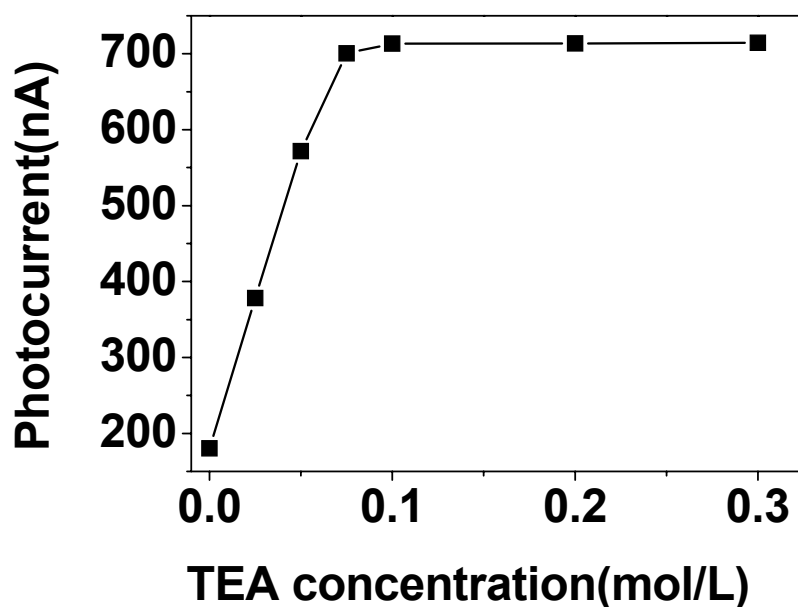
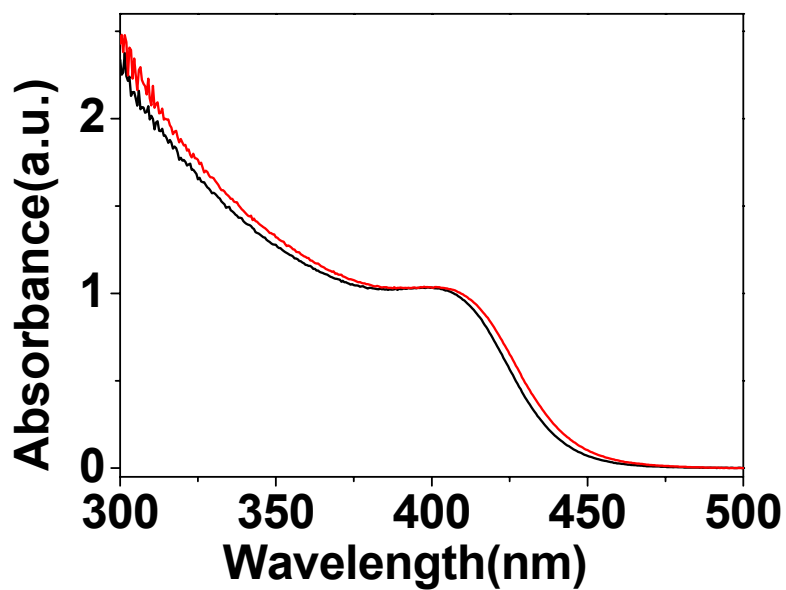
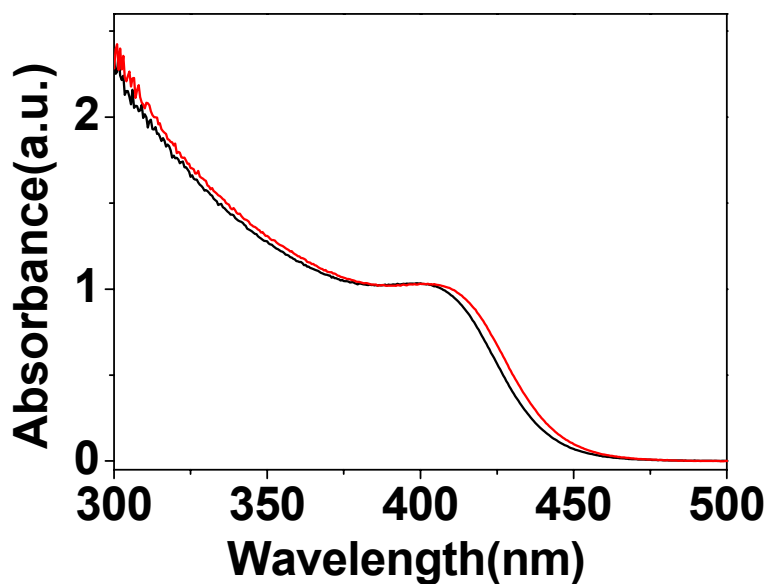


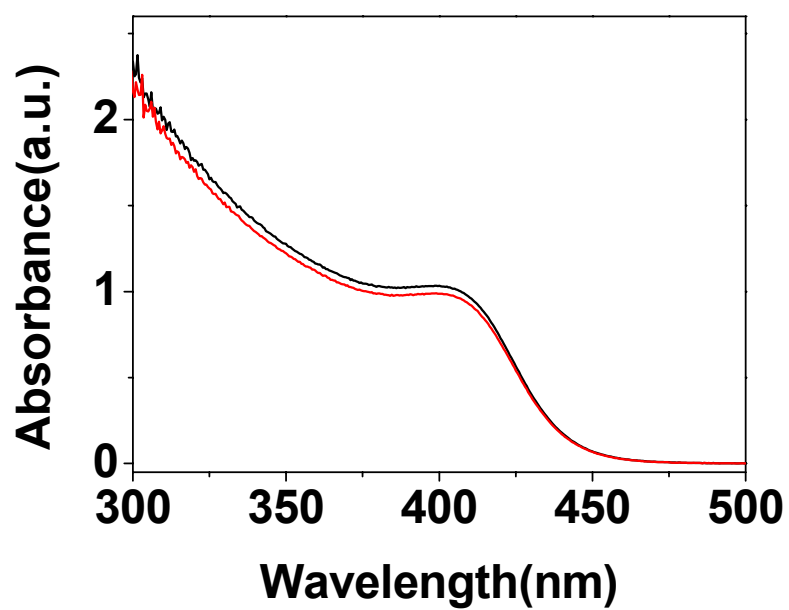
Fig. S1 The dependence of photocurrent of the ITO/(PDDA/CdS) electrode on the concentration of TEA in 0.1 M PBS (pH 7.0).



**Fig. S2** Absorption spectra of TGA-capped CdS QDs in the absence (black line) and presence of  $2.0 \times 10^{-5}$  M  $\text{Cu}^{2+}$  (red line) in 0.1 M TEA - PBS (pH 7.0) solution.



**Fig. S3** Absorption spectra of TGA-capped CdS QDs in the absence (black line) and presence of  $2.0 \times 10^{-5}$  M  $\text{Ag}^{+}$  (red line) in 0.1 M TEA- PBS (pH 7.0) solution.



**Fig. S4** Absorption spectra of TGA-capped CdS QDs in the absence (black line) and presence of  $2.0 \times 10^{-5} \text{ M Hg}^{2+}$  (red line) in 0.1 M TEA-PBS (pH 7.0) solution.