Electronic Supplementary Information (ESI) for Chemical Communications

Cathode photoelectrochemical sensing of copper (II) based on analyte-induced formation of exciton trapping

Peng Wang, Xiuyuan Ma, Mengqi Su, Qing Hao, Jianping Lei* and Huangxian Ju*

State Key Laboratory of Analytical Chemistry for Life Science, Department of Chemistry, Nanjing University, Nanjing 210093, P.R. China

Experimental details

Reagents and materials. Cupric nitrate ($Cu(NO_3)_2 \cdot 3H_2O$) was purchased from Shanghai Sinpeuo Fine Chemical Co., Ltd. (China). Meso-2,3-dimercaptosuccinic acid (DMSA) and cadmium chloride ($CdCl_2 \cdot 2.5H_2O$) were purchased from Alfa Aesar China Ltd (China). Tellurium rod (4 mm in diameter) was purchased from Leshan Kayada Photoelectricity Co. (China). All other chemicals were of analytical grade without further purification. H_3BO_3-$Na_2B_4O_7$ (0.1 M, pH 6) buffer was used throughout the photoelectrochemical (PEC) detection. All aqueous solutions were prepared using ultra-pure water obtained from a Millipore system (≥18 MΩ, Milli-Q, Millipore). F-doped tin oxide (FTO) membrane covered glass as the electrode material was purchased from Beijing Midwest Group Technology Co., Ltd (China). The glass was cut into 4.5 cm × 0.8 cm slices and successively bathed in 0.5 M NaOH solution for 10 min, 10% H_2O_2 solution for 10 min, and acetone for 30 min, then

washed with water and dried prior to use. The human hair sample was digested with the mixture of 70% (W/W) nitric acid and 60% (W/W) perchloric acid (3:1 V/V). After digestion, the resulting sample solution was diluted and neutralized to pH 6 with 0.5 M NaOH solution prior to detection.

Apparatus. A CHI 660D electrochemical workstation (CHI, USA) was used to synthesize DMSA capped CdTe QDs. PEC detection was performed on a Zahner intensity modulated photo spectrometer (Zahner, German) with a LW405 LED light as the accessory light source. The inductively coupled plasma (ICP) spectroscopic detection of metal elements in the human hair sample was performed on a J-A1100 inductively coupled plasma spectrometer (Jarrell-Ash Co. USA). The X-ray photoelectron spectra (XPS) data was gained by a PHI5000 VersaProbe X-ray photoelectron spectrometer (ULVAC-PHI Co. Japan). The scanning electron microscopic (SEM) images were obtained by Hitachi S-4800 scanning electron microscope (Japan).

Synthesis of DMSA capped CdTe QDs. The DMSA capped CdTe QDs was synthesized by our reported electrolysis method.[S1] First, 6.5 mg DMSA, 200 μL 1 M NaOH (a.q.), and 120 μL 0.1M $CdCl_2$ (a.q.) were added into 20 mL water in sequence to make a mixture solution. This solution was then electrolyzed under a N_2 atmosphere by the cleaned Te electrode at −1.0 V *vs.* saturated calomel electrode (SCE) until the quantity of electricity was 0.5 coulombs. The resulting solution was refluxed at 50°C for 24 hours to get the product. The final solution of QDs was kept at 4 °C prior to use. After storage for 2 months, the solution remained clear and stable.

PEC performance. PEC detection was performed in a quartz photoelectrochemical cell. The functionalized FTO glass as the working electrode, a platinum wire electrode as the auxiliary electrode and a saturated calomel electrode as the reference electrode were inserted into this cell to form a three-electrode system. 10 mL buffer as the electrolyte was added into the cell. Under illumination, the electrical signal was gained and compared with that gained in dark. The wavelength of the LED light was 405 nm, and the intensity was kept 50 W m^{-2} during illumination.

UV-vis and photoluminescent (PL) spectra of QDs

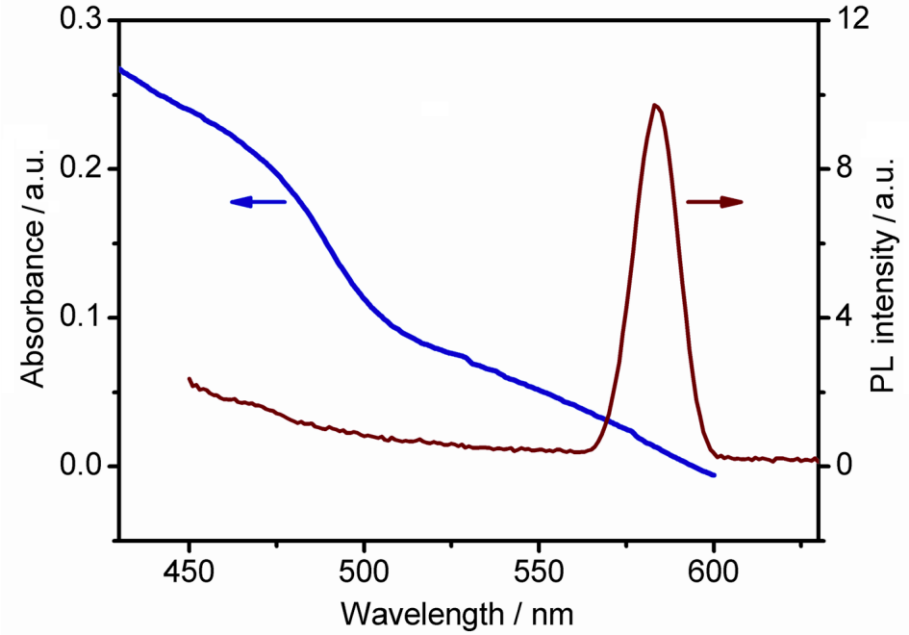

Fig. S1 UV-vis (blue) and PL (red) spectra of the QDs. Excitation wavelength: 380 nm.

Photograph and SEM image of the QDs

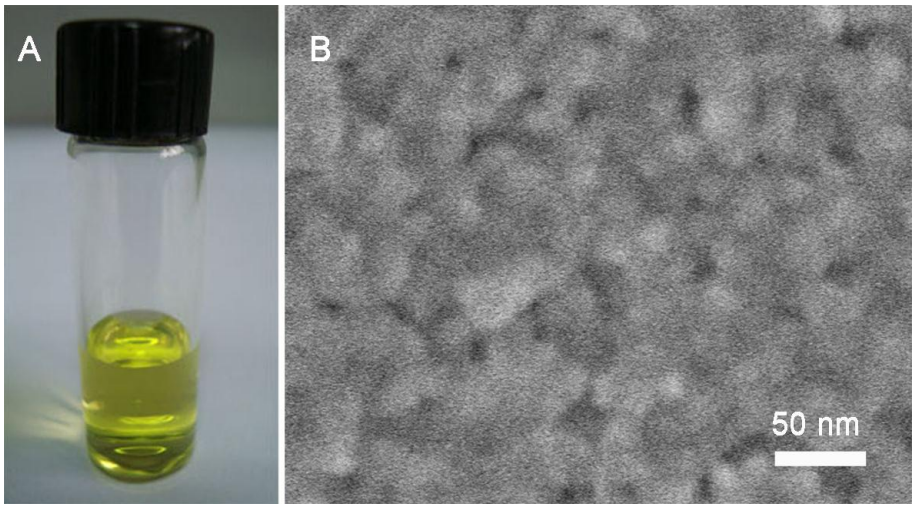

Fig. S2 Photograph (A) and SEM image (B) of the QDs. The average diameter is around 20 nm.

Deoxygenating experiment

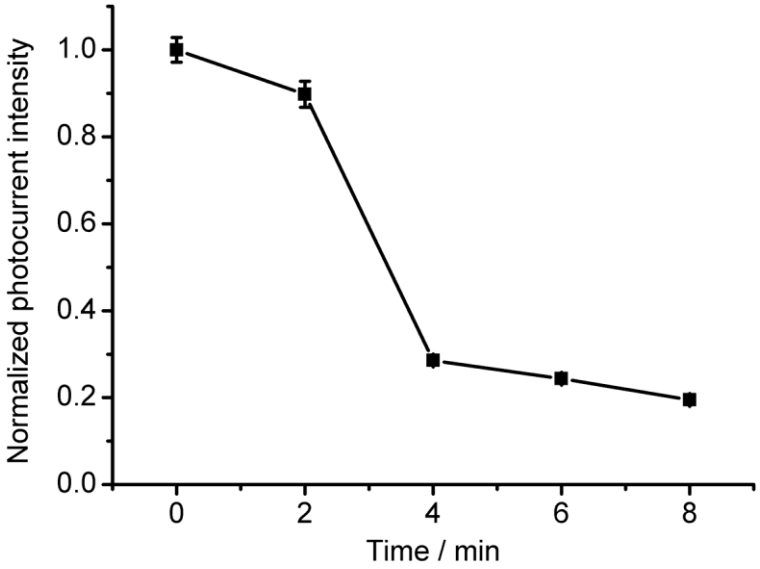

Fig. S3 Normalized increase of photocurrent intensity measured at QDs modified FTO in air-saturated H_3BO_3-$Na_2B_4O_7$ buffer after N_2 bubbling for different times.

pH optimization

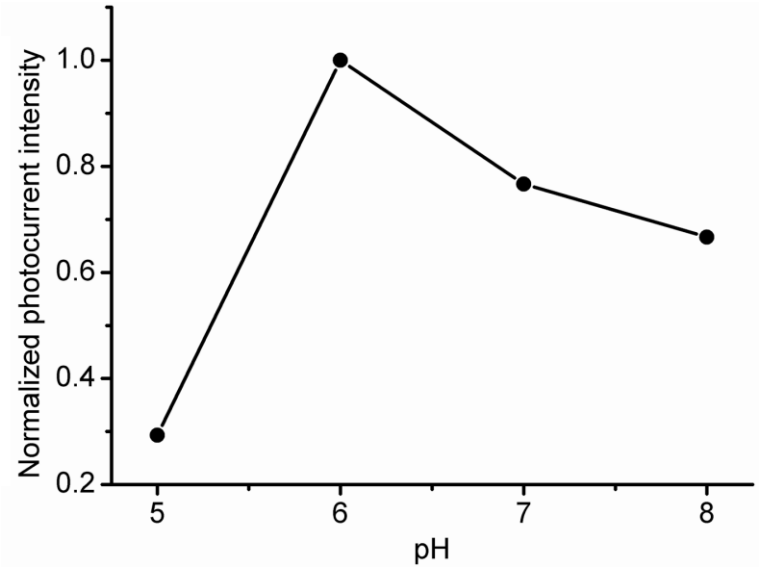

Fig. S4 Normalized photocurrent intensity at different pH values.

XPS spectrum of Cu2p

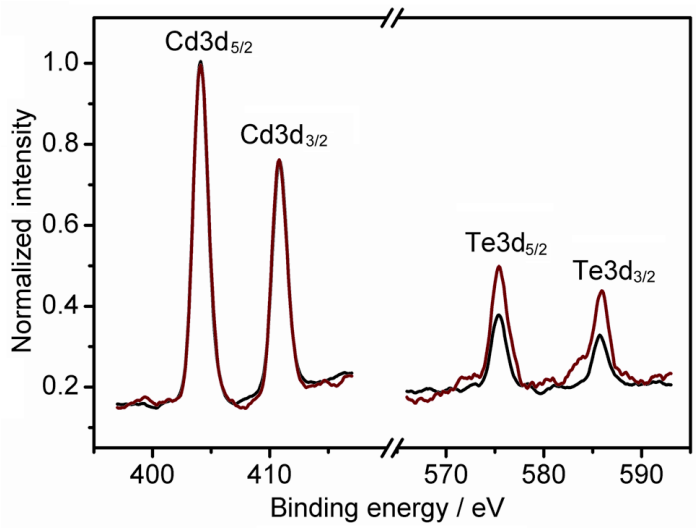

Fig. S5 Normalized XPS intensity of Cd and Te in QDs before (black) and after (red) introducing copper ion into the system.

Table S1 ICP spectroscopic detection results of human hair sample (μg g^{-1}).

Element	Content / ppm	Element	Content / ppm	Element	Content / ppm
Al	5.33	Mg	61.5	Fe	43.4
As	0.33	Mn	0.34	K	2.37
Ba	1.34	Ni	0.36	Sr	2.61
Ca	770	Si	6.34	Zn	264
Cu	10.1				

Reference

S1. X. Liu, L. X. Cheng, J. P. Lei, H. Liu and H. X. Ju, *Chem. Eur. J.*, 2010, **16**, 10764–10770.