

Supplementary data

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Signal Amplification via Cation Exchange Reaction: An Example in the Ratiometric Fluorescence Probe for Ultrasensitive and Selective Sensing of Cu (II)

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Instruments

TEM images were recorded by a transmission electron microscopy (TEM, FEI-Tecna G² 20) equipped with an energy-dispersive X-ray spectrometer (EDX). Samples were prepared by casting one drop of the sample solution onto a standard carbon-coated copper grid.

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The light source for photochemical synthesis was a 500 W Xe lamp (Shanghai Jiguang Lighting Co.). The intensity of the light was measured by a radiometer (Photoelectric Instrument Factory Beijing Normal University) in mW cm⁻².

UV-Vis absorption spectra were recorded with a Hitachi UV-2450 spectrophotometer.

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FL measurements were performed using a Hitachi F-4500 spectrofluorimeter. All measurements were performed at ambient conditions.

The IR measurements on powdered samples were made using a Hitachi IR Prestige-21 spectrometer in transmission mode with a KBr window.

Synthesis

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Preparation of CdTe quantum dots (QDs)

The preparation of CdTe QDs was performed according to the literature with major modifications.¹ Briefly, freshly prepared aqueous NaH₂Te solution was injected into N₂-saturated CdCl₂ solution at pH 11.2 in the presence of stabilizing agent, thioglycolic acid (TGA). The concentration of the precursor was 4.4 mM with respect to Cd²⁺, and the molar ratio of Cd²⁺: NaH₂Te: TGA was fixed at 8:1:1.2. At ambient temperature, 100 mL CdTe precursor solution was directly transferred into a sealed quartz vessel, and then subjected to illumination using a 500 W Xe lamp under vigorous stirring. The intensity of the light was approximately 150 mW cm⁻². It was observed that the quantum yield (QY) of QDs could reach 60% after 6 h illumination (rhodamine B (quantum yield = 89%) as a reference standard). Major reasons for high-quality CdTe QDs formation should be multifold. Above all, relatively low temperature during photoillumination (PI) process would effectively lead to temporal separation of nucleation and crystal growth in the preparation of CdTe QDs², which was similar to monodisperse high QY of QDs formed in organic media. And high molar ratio of Cd: Te (8:1) would be beneficial to perfect the surface of CdTe QDs, considering the surface Te atoms with dangling bonds were responsible for the low QY as reported by Weller and co-workers³. In addition, during the slow growth of QDs, PI could further reduce charge-carrier recombination at the surface of CdTe QDs⁴. It was noted that further increasing irradiation time would result in the precipitation of CdTe QDs. Therefore, the resulting CdTe QDs were obtained by 6 h irradiation and visualized by TEM.

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Preparation of luminescent CdTe nanorods (NRs)

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CdTe NRs were prepared on the basis of CdTe QDs in the presence of excess TGA. As suggested in the literature⁵, due to the secondary coordination of TGA-like structure and low temperature reaction, 1D colloiddally stable CdTe

nanostructures could be prepared by anisotropic growth in solution. Meanwhile, in view of the effect of PI in the preparation of QDs, we presented a facile approach for synthesis of high-quality CdTe NRs. In brief, 30 μ L of TGA was added into the before-mentioned CdTe QDs solution under stirring. After 1 h illumination, another 30 μ L of TGA was added. About 20 min illumination, the color of the solution shifted from green to dark. TEM imaging demonstrated that the presence of excess TGA led to the formation of NRs. It should be noted that the illumination time was rigorous. Otherwise, precipitation would be formed in the solution with increasing irradiation time.

Preparation of dual-fluorophores sensor

2-propanol was added to 20 mL CdTe NRs solution. The precipitate was isolated by centrifugation and washed by ethanol for 3 times, respectively. Then the resulting CdTe NRs were mixed with 0.1 % cationic PEI solutions and sonicated for 10 min. At ambient condition, calcein blue and KOH were mixed with the CdTe NRs solution. The mixture were stirred for 20 min and diluted to 100 mL with Mill-Q water. The final concentrations of CdTe NRs, calcein blue and KOH were 0.88 mM, 0.5 μ M, and 1 μ M, respectively. The stock solution was stored at 4 $^{\circ}$ C and employed in the following detection experiments.

Figures

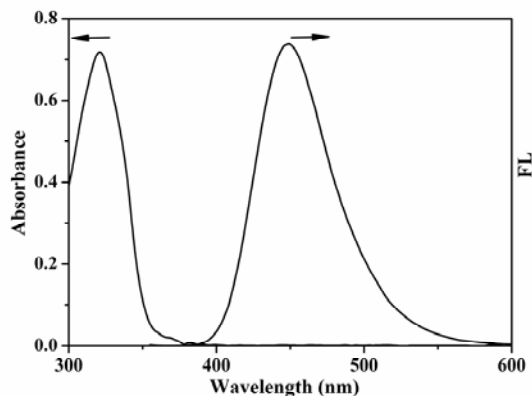


Fig. S1 UV-vis absorbance and FL spectrum of calcein blue recorded in aqueous solution (excitation at 350 nm).

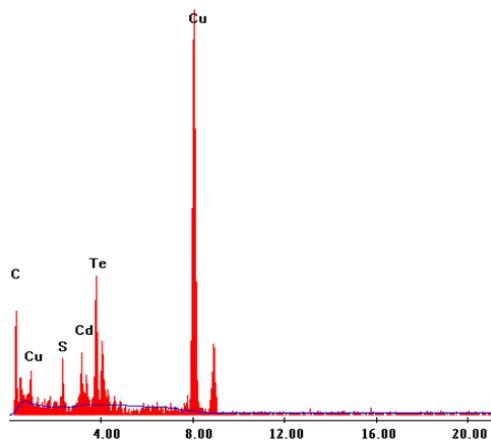


Fig. S2 EDS spectrum of CdTe NRs showing that the major elements are Cd, Te, S.

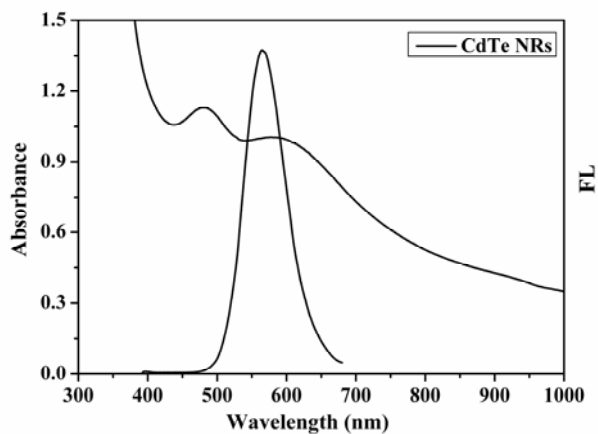


Fig. S3 UV-vis absorbance and corresponding FL spectrum of CdTe NRs prepared by photoillumination approach. (excitation at 350 nm).

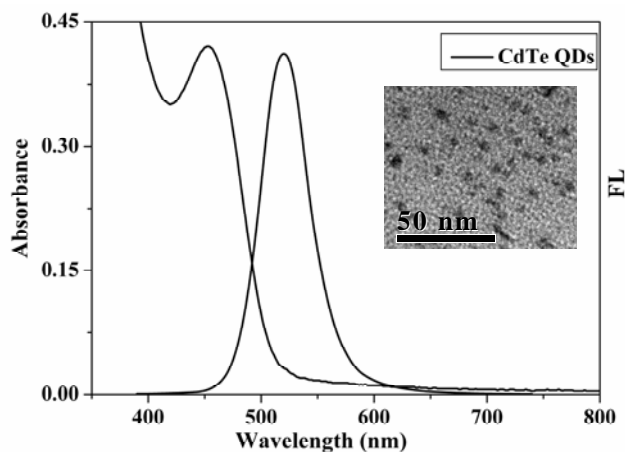


Fig. S4 UV-vis absorbance and corresponding FL spectrum of CdTe QDs obtained by 6 h photoillumination (excitation at 350 nm). The inset is the TEM image of CdTe QDs (scale bar 50 nm).

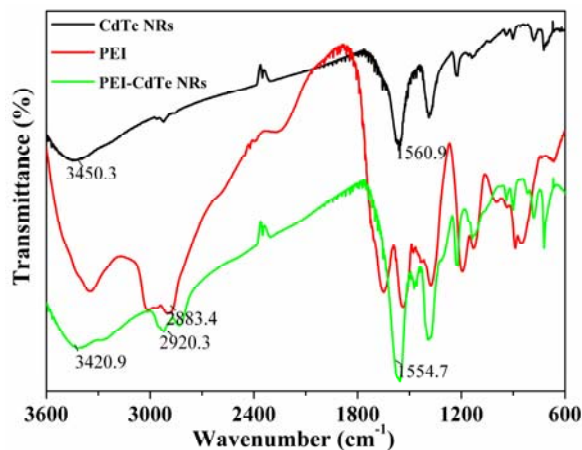


Fig. S5. IR spectra of CdTe NRs (black), PEI (red) and PEI-CdTe NRs (green). Peaks at 3450.3 and 1560.9 cm^{-1} , are ascribed to O-H and COO^- vibration of CdTe NRs, respectively. The absence of the S-H stretching mode around 2550 cm^{-1} indicates that thiol group of TGA are bound to surface of QDs through Cd-S bond. The peak at 2920.3 cm^{-1} is due to the vibrational mode of NH_3^+ , which imparts the positively charged PEI-CdTe NRs backbone.

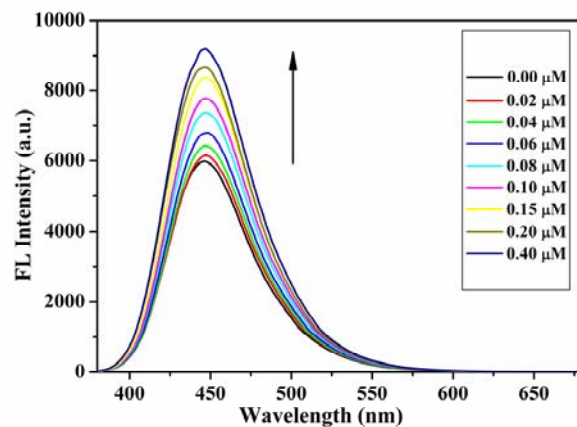
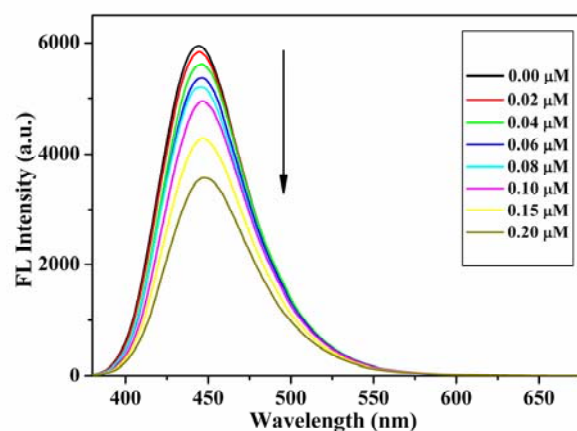
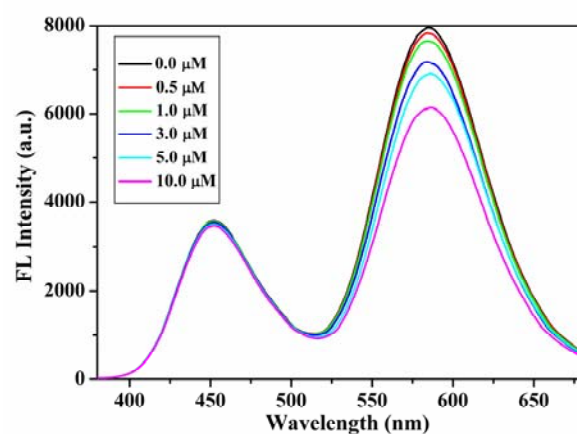


Fig. S6 FL emission spectra of calcein blue with addition of different concentrations of Cd (II) ions in aqueous solution, containing calcein blue (0.5 μM) and KOH (1 μM) (excitation at 350 nm).



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Fig. S7 FL emission spectra of calcein blue with addition of different concentrations of Cu (II) ions in aqueous solution, containing calcein blue (0.5 μM) and KOH (1 μM) (excitation at 350 nm).



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Fig. S8 Changes in FL emission spectra upon additions of different concentrations of Ag (I) ions in our system, containing CdTe NRs (0.88 mM) and calcein blue (0.5 μM) and KOH (1 μM) (excitation at 350 nm).

References:

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