

Supplementary Information

Efficient ratiometric fluorescence probe based on dual-emission fluorescent silica nanoparticle for visual determination of Hg²⁺

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Experimental Details

Reagents

All the starting materials of the FITC-silica and dual-emission silica nanoparticles synthesis were used without further purification. CdCl₂·2.5H₂O (99.0%), NaBH₄ (96.0%), tellurium powder (99.9%) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Tetraethoxysilane (TEOS), fluorescein isothiocyanate isomer I (FITC, ≥90%), N-Acetyl-L-cysteine (NAC), 3-aminopropyltriethoxysilane (APTES, 99%), poly (allylamine) hydrochloride (PAH, molecular weight (MW)≈56000 g mol⁻¹) and poly(sodium 4-styrene-sulfonate) (PSS, MW≈70000 g mol⁻¹) were obtained from Sigma-Aldrich Chemicals Co. Mercury nitrate (Hg(NO₃)₂) and other common solvents and salts were obtained from Aladdin Reagent Co. Ltd. For all aqueous solutions, high-purity ultrapure water from a Millipore (18.2 MΩ·cm) system was used throughout the experiments.

Experimental measurements

The optical absorption spectra were acquired on the Nicolet Evolution 300 UV-Vis spectrometer (Thermo, USA) coupled with a 1.00 cm quartz cell. Fluorescence spectra and fluorescence lifetime study were performed on an Edinburgh FLS920 spectrometer (Edinburgh Instruments Ltd, UK) with an integrating-sphere attachment under excitation of 365 nm. Measurements of Zeta potential in aqueous solution were

acquired on a Zetasizer Nano-ZS90 (Malvern Instruments Ltd, UK). The FL QY of the as-prepared FITC-doped silica nanoparticles (85.6%) and CdTe/CdS QDs (33.4%) were determined through comparison using a Rhodamine G6 standard organic dye. Transmission electron microscopy (TEM) images were acquired using a Tecnai G² F30 S-Twin transmission electron microscope (FEI, Holland) operating at an acceleration voltage of 200 kV. The concentration analysis of Hg²⁺ in real water samples were carried out on an AFS-830 cold-vapour atomic fluorescence spectrophotometer (CV-AFS).

Synthesis of FITC-doped silica nanoparticles

Fluorescein isothiocyanate (39 mg, 0.10 mmol) was mixed with APTES (23 μ L, 0.10 mmol) in 100 mL of absolute ethanol, and was stirred at 42 °C for 24 h to yield the FITC-silane precursor. The FITC-doped silica nanoparticles were prepared following a modified protocol from the classic Stöber method.¹ The FITC-silane precursor solution (5 mL) was mixed with TEOS (2.8 mL), and the mixture was added to absolute ethanol (34 mL) followed by NH₃·H₂O (25%, 2.8 mL). The reaction was allowed to proceed at room temperature for at least 8 h with vigorous stirring to yield a bright yellow colloidal solution. The resultant product were collected by centrifugation and washed three times with ethanol.

Synthesis of dual-emission silica nanoparticles (ratiometric fluorescence probe)

The NAC-capped CdTe/CdS QDs were prepared according to the previous report with a reaction time of 55 min at 200 °C.² The self-assembled, three-layer film was formed by incubating sequentially a FITC-doped silica nanoparticle dispersion (0.5 mL, 5 mg mL⁻¹) with PAH, PSS and PAH solutions (1 mL, 1 mg mL⁻¹ in 0.5 mol L⁻¹ NaCl) for 30 min for each polyelectrolyte layer. Before incubation in the next solution, the resulting particles underwent centrifugation three times with ultrapure water to remove excess polyelectrolyte. The dual-emission silica nanoparticles were prepared by mixing a 500 μ L dispersion of the microspheres and a 1.0 mL dispersion of the CdTe/CdS QDs (5 mg mL⁻¹). After absorption for 2 h, unbound QDs were removed by successive centrifugation and washing with water several times. The obtained dual-emission silica nanoparticles were dispersed in 1 mL of ultrapure water and stored at 4 °C.

Ratiometric fluorescence assay for Hg²⁺

Mercury nitrate (Hg(NO₃)₂) aqueous solution was used for the determination of Hg²⁺. To a 2 mL calibrated test tube 100 μL the ratiometric probe solution (5 mg mL⁻¹) and certain amounts of Hg²⁺ were sequentially added. The mixture was then diluted to volume with 0.01 M phosphate buffer solution (PBS, pH 7.4) and mixed thoroughly. Two minutes later, the mixture was transferred to a 3 mL cuvette and the fluorescence intensity of solution was recorded with the excitation wavelength of 365 nm.

Detection of Hg²⁺ in real water samples

The lake water sample was obtained from West Lake and filtered twice using a 0.02 μm membrane to remove the solid suspensions. The tap water was obtained from the lab. Water samples with various concentrations of Hg²⁺ were added to our sensing system, and then the fluorescence spectra were collected.

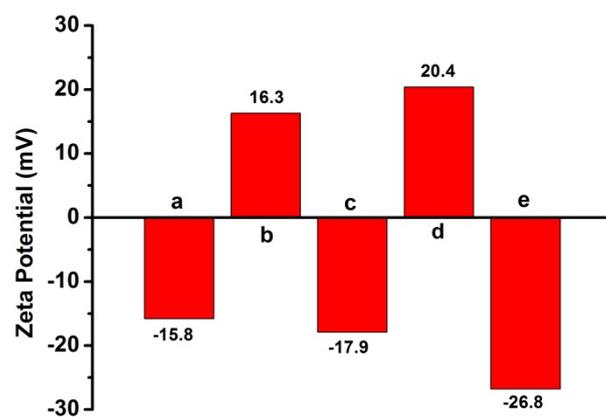


Fig. S1 Zeta potential of FITC-SiO₂ (a), FITC-SiO₂/PAH (b), FITC-SiO₂/PAH/PSS (c), FITC-SiO₂/PAH/PSS/PAH (d), and CdTe/CdS QDs (e).

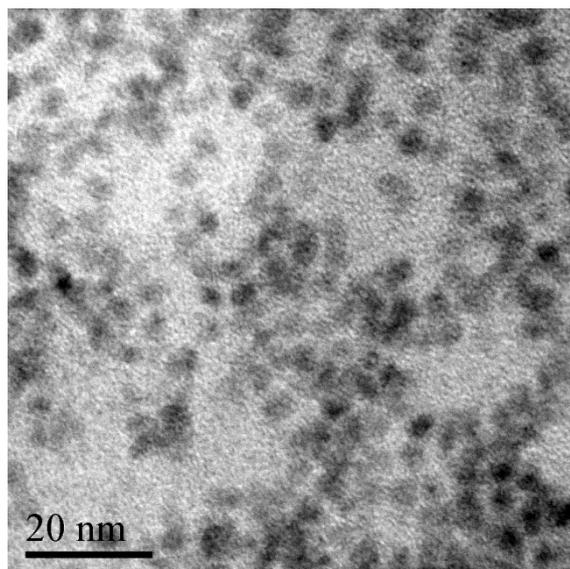


Fig. S2 TEM of NAC-capped CdTe/CdS QDs.

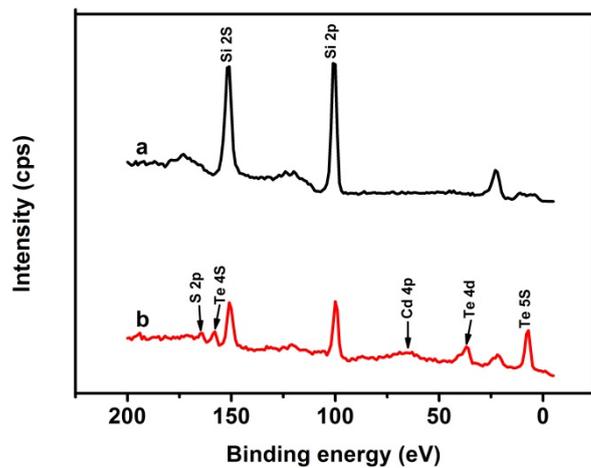


Fig. S3 XPS spectra from 200 to 0 eV of FITC-doped silica nanoparticles (curve a) and dual-emission silica nanoparticles (curve b).

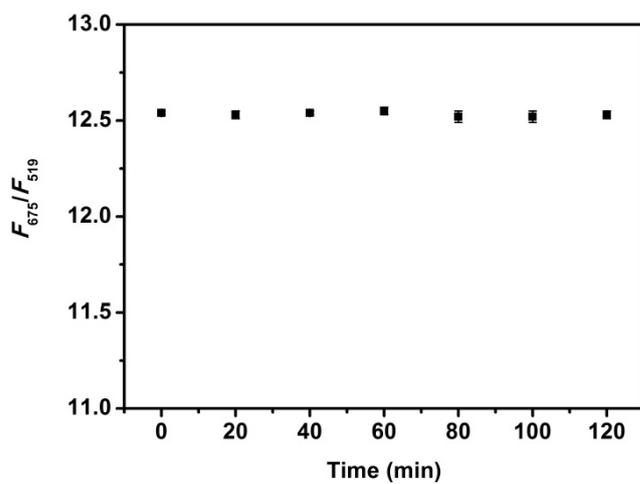


Fig. S4 Photostability of the fluorescence intensity ratio (F_{675}/F_{519}) of the ratiometric fluorescence probe. F_{675} and F_{519} are the fluorescence intensity of the ratiometric probe at the emission wavelength of 675 and 519 nm, respectively.

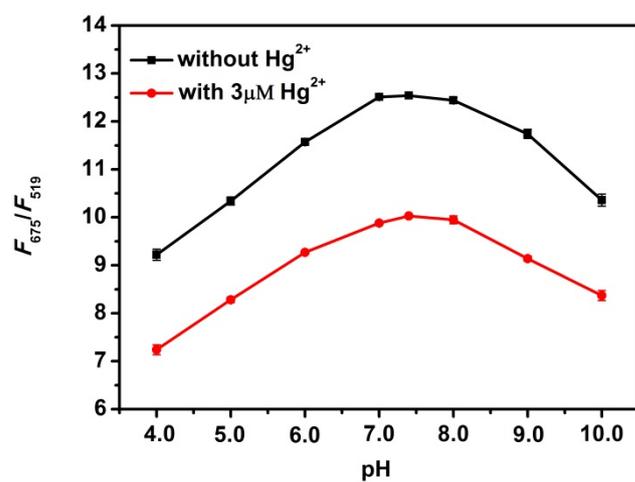


Fig. S5 The pH dependent response of the ratiometric fluorescence probe in the absence and presence of Hg²⁺ (3 μM).

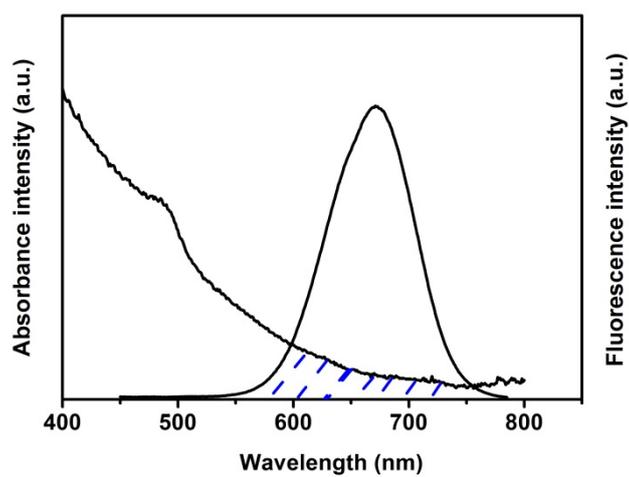


Fig. S6 Absorption spectrum of FITC-doped silica nanoparticle (left) and emission spectrum of QDs (right), excited at 365 nm.

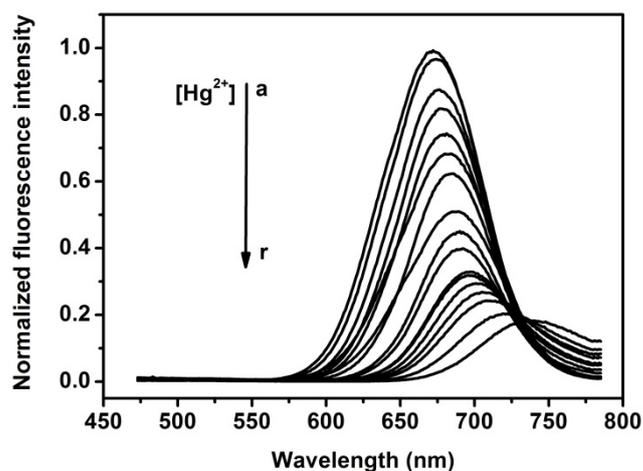


Fig. S7 The corresponding fluorescence spectra ($\lambda_{ex} = 365$ nm) of the pure red NAC-capped CdTe/CdS QDs upon the exposure to different concentrations of Hg^{2+} . The concentration of Hg^{2+} from the top to the bottom (a-r): 0, 0.5, 1, 2, 3, 4, 5, 6, 9, 12, 15, 18, 21, 24, 27, 30, 36, 42 μM , respectively. The final concentration of the CdTe/CdS QDs was 1.0×10^{-7} mol L^{-1} .

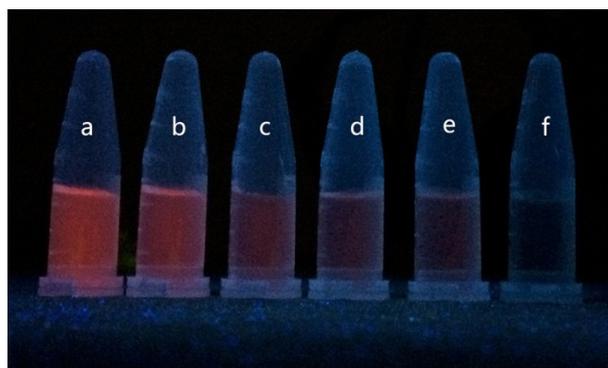


Fig. S8 The fluorescence photos were taken under a UV lamp at excitation wavelength of 365 nm. The concentrations of Hg^{2+} from left to right (a-f) are 0, 2, 4, 9, 15, 21 μM , respectively. The final concentration of the CdTe/CdS QDs was 1.0×10^{-7} mol L^{-1} .

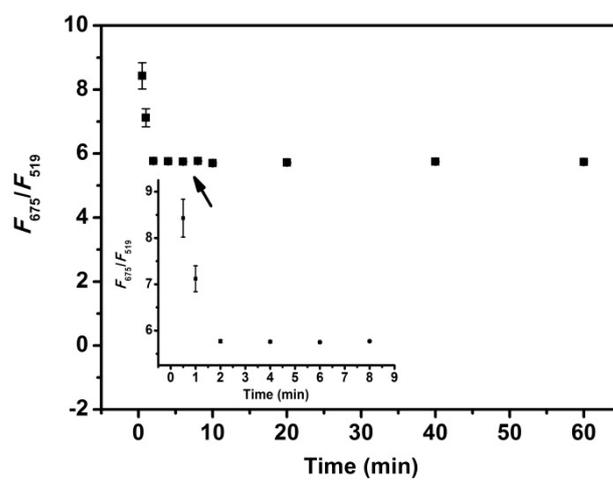


Fig. S9 Time-dependent fluorescence intensity ratio (F_{675}/F_{519}) of the ratiometric fluorescence probe to Hg^{2+} ($9 \mu\text{M}$).

Reference

1. W. Stöber, A. Fink and E. Bohn, *J. Colloid Interf. Sci.*, 1968, **26**, 62-69.
2. D. Zhao, Z. He, W. H. Chan and M. M. F. Choi, *J. Phys. Chem. C*, 2009, **113**, 1293-1300.