

Supporting Information

Microwave-assisted synthesis of highly luminescent CdSeTe@ZnS-SiO₂ quantum dots and their application in the detection of Cu(II)[†]

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Experimental Section

Materials

Reduced glutathione (GSH, 99%) was purchased from Aladdin Chemistry (China). Tetraethylorthosilicate (TEOS, analytical reagent) was obtained from Sinopharm Chemical Reagent Co. (China). Zinc acetate (Zn(OAc)₂, analytical reagent) was from Shanghai Meixing Chemical Co.(China). All other reagents were of analytical reagent grade and used without further purification.

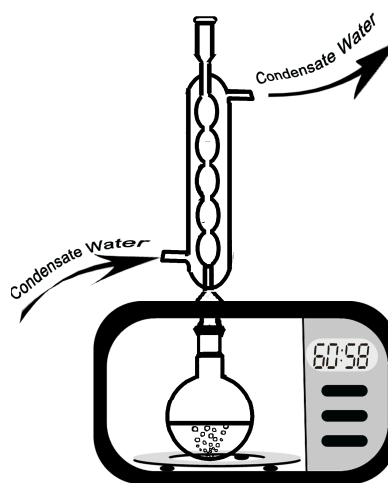
Characterization

The UV-Vis absorption spectra were obtained using a UV-3600 spectrophotometer (Shimadzu, Japan). The fluorescence measurements were carried out using a Bruker RF-5301PC fluorescence spectrometer. High-resolution transmission electron microscopy (HRTEM) images were taken using a JEOL 2010 electron microscope at an accelerating voltage of 200 kV. The elemental analysis of HQdots was carried out on a J-A1100 ICP-AES system. X-ray photoelectron spectroscopy (XPS) was carried out on an ESCALAB MK II X-ray photoelectron spectrometer. All fourier-transform

infrared (FTIR) spectroscopic measurements were performed on a Bruker model VECTOR22 Fourier-transform spectrometer using KBr pressed disks. Microwave reactions were carried out using a WBFY-201 microwave chemical reactor (Nanjing, Keer).

Synthesis of CdSeTe@ZnS-SiO₂ quantum dots (HQdots)

The synthetic pathway for the preparation of CdSeTe@ZnS-SiO₂ quantum dots is shown in Scheme 1. Firstly, 10mL mercaptopropionic acid (MPA) capped green-emitting CdSeTe AQdots were precipitated with ethanol and redispersed in ultrapure water with the concentration unchanged. Secondly, CdSeTe AQdots were coated with silica at room temperature through a Stöber method. Ammonia aqueous solution (70 μL 20%),



microwave chemical reactor

(70 μL 20%), tetraethylorthosilicate (TEOS, 400 μL), Zn²⁺ (0.1 M, 100μL) and GSH (0.1 M, 200 μL) were added into the CdSeTe AQdots solution (pH 10.5). The reaction system was stirred at room temperature for 4 h. Finally, the silica-coated Qdots were refluxed under microwave irradiation (the power was 240W).

Conventional hydrothermal synthesis was similar to that of microwave-assisted synthesis. The only difference was that, at the final step, the silica-coated Qdots were refluxed at 90 °C instead of microwave irradiation.

Fluorescence detection of Cu²⁺

Copper nitrate (Cu(NO₃)₂) aqueous solution was used for the determination of Cu²⁺. The solutions with HQdots and different Cu²⁺ concentrations were mixed in 50mM phosphate buffer solution (PBS 7.4) and equilibrated for 20 min. The fluorescence intensity was measured at 576nm with the excitation wavelength of 450nm.

Selectivity measurements

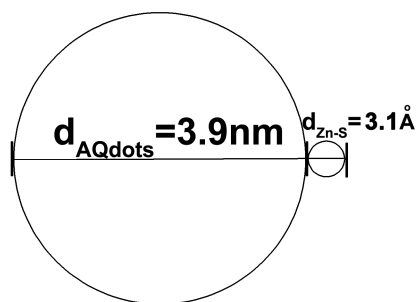
To evaluate the selectivity, the quenching effects of 13 kinds of cations were investigated. The selected inorganic salts is shown in below: potassium chloride, lead

nitrate, aluminum nitrate, barium chloride, calcium chloride, zinc acetate, sodium chloride, magnesium chloride, iron (III) chloride, nickel nitrate, cobalt(II) chloride, cadmium chloride. 1 mM salt solutions were first prepared with ultrapure water, then, diluted with PBS (pH 7.4). Finally, the as-prepared solutions were mixed with HQdots in PBS in the absence of Cu^{2+} .

Sample preparation

The green tea sample was first accurately weighted (about 2.0 g), then ground, digested with 5mL concentrated nitric acid and heated until the solution became clear. The solution was diluted with water and the pH was adjusted to 7.4, before the determination of Cu^{2+} with the HQdots.

Theoretical calculation of ZnS-monolayer capping on the CdSeTe AQdots



The ZnS was assumed to form a monolayer on the CdSeTe AQdots. The $d_{\text{Zn-S}}$ was 3.1 Å,^[S11] while the d_{AQdots} was 3.9 nm. Thus, 72.1 mg zinc would be needed for the ZnS-monolayer in 1 μmol HQdots.

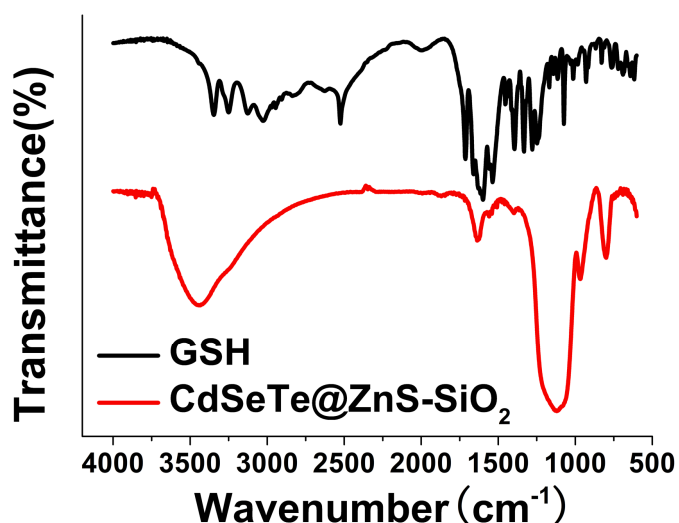


Fig. S1 FTIR spectra of glutathione and CdSeTe@ZnS-SiO₂ Qdots.

The HQdots were characterized by the FTIR spectra. In Fig. S1, the FTIR spectrum of GSH capped HQdots was similar to that of pure GSH. In both samples, the peaks at 1641 cm⁻¹ (C=O) and 3450 cm⁻¹ (COOH) represented the carboxyl group. Furthermore, the peak at 1398 cm⁻¹ was attributed to C-N group, the peak at 968 cm⁻¹ was attributed to the N-H group, and the peak at 1554 cm⁻¹ corresponded to R-CO-NHR. The strong peak at 1117 cm⁻¹ was ascribed to the silica capping on HQdots. The S-H groups could be confirmed by the peaks at 2517 cm⁻¹ (S-H) and 795 cm⁻¹ (C-S). Nevertheless, the peak of S-H group at 2500-2600 cm⁻¹ disappeared for CdSeTe@ZnS-SiO₂ Qdots, which could be ascribed to the covalent bonds between thiols and HQdots. The results indicated that GSH was capped on the surface of HQdots.

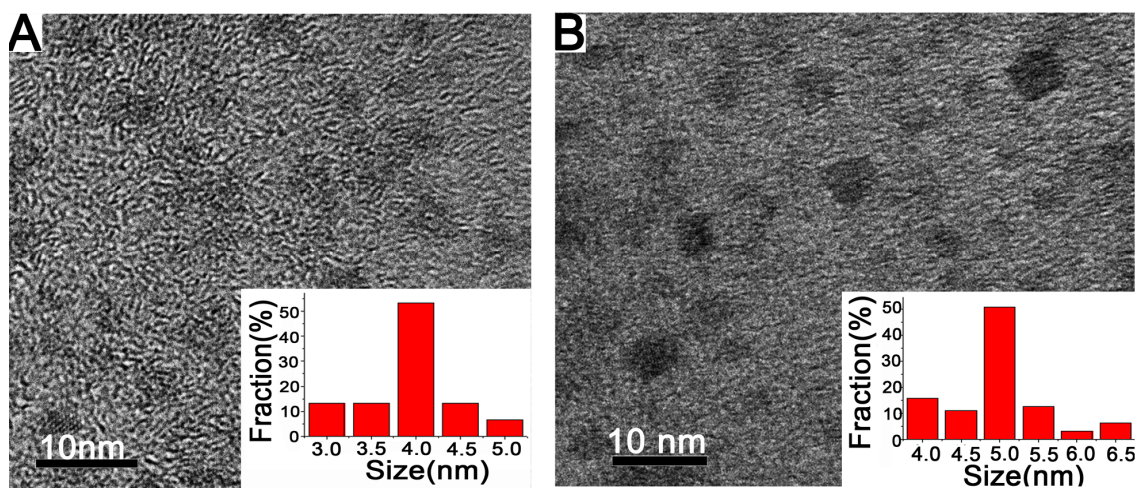


Fig. S2 The size distributions of the CdSeTe AQdots (A) and CdSeTe@ZnS-SiO₂ Qdots (B).

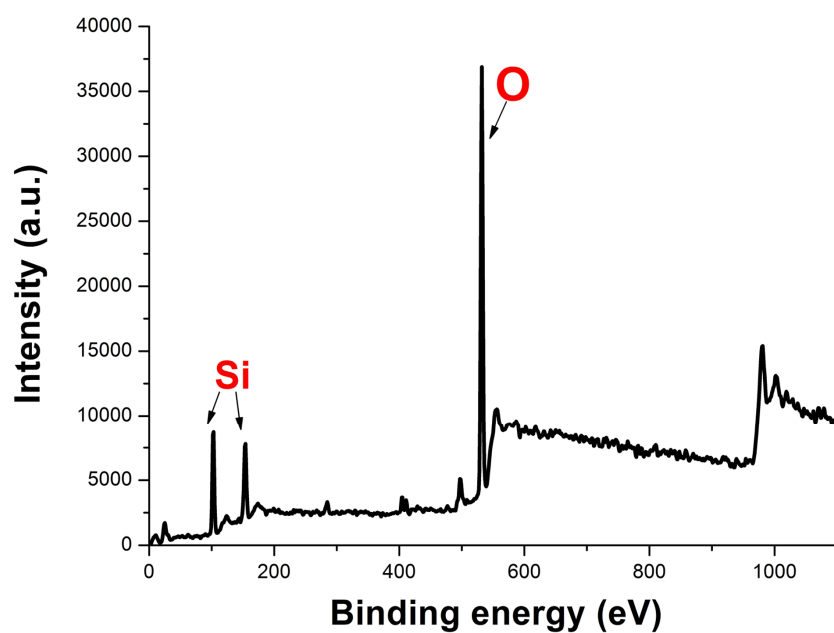


Fig. S3 X-ray photoelectron spectroscopy of the CdSeTe@ZnS-SiO₂ Qdots.

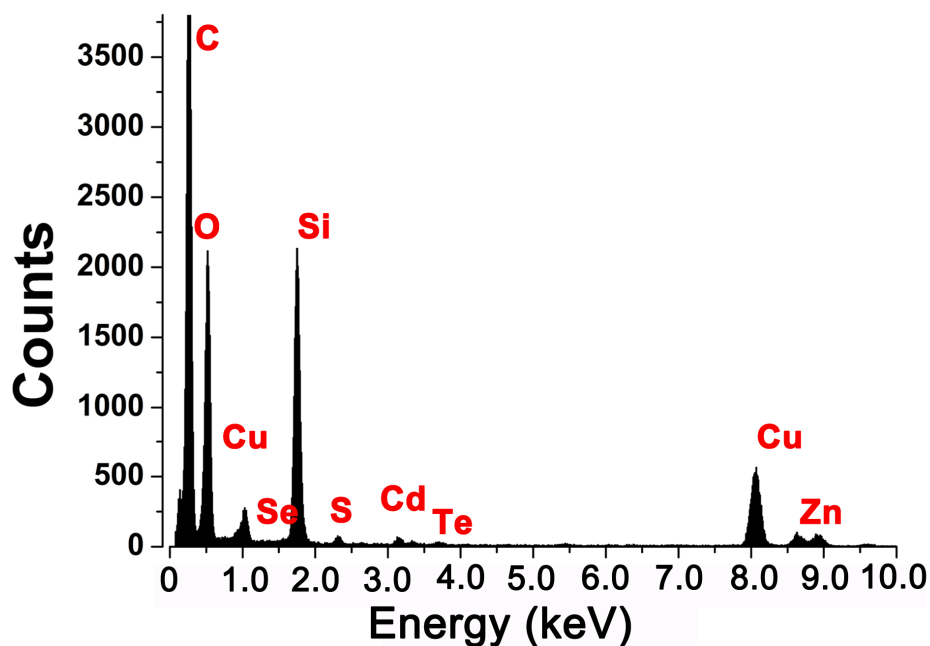


Fig. S4 EDS spectrum of the CdSeTe@ZnS-SiO₂ Qdots.

The result indicated the presence of S (2.3 keV), Zn (8.6 keV), Si (1.7 keV) and O (0.5 keV).

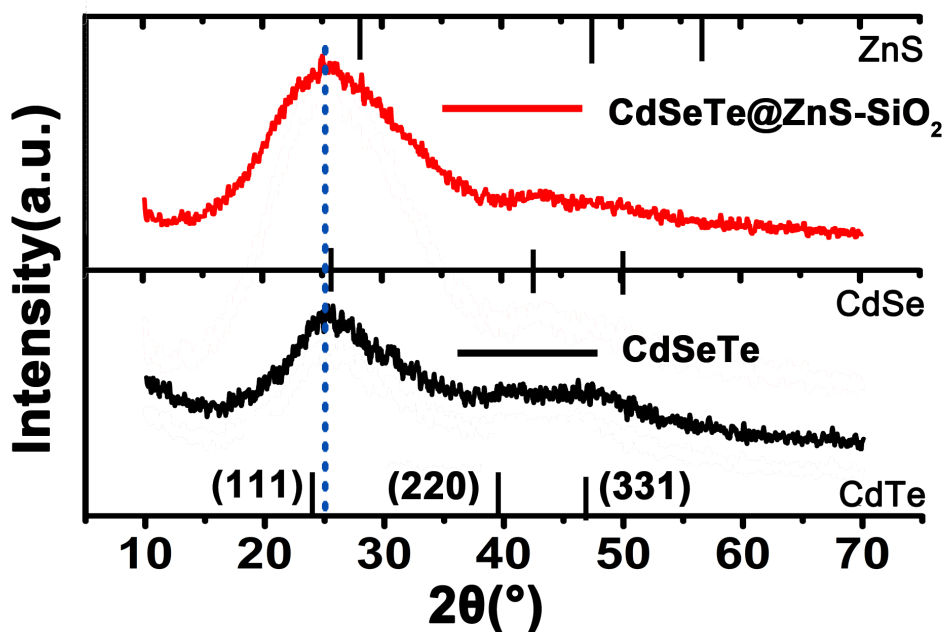


Fig. S5 XRD patterns of CdSeTe AQdots and CdSeTe@ZnS-SiO₂ Qdots.

(CdTe (JCPDS 15-0770), CdSe (JCPDS 19-0191), ZnS (JCPDS NO. 05-0566))

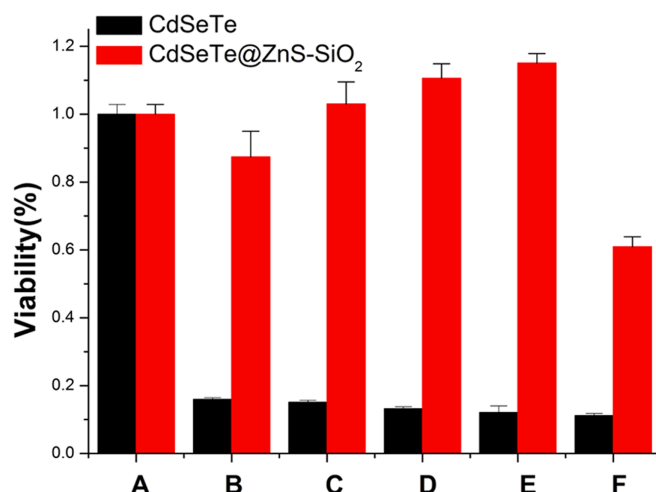


Fig. S6 Cytotoxicity of CdSeTe AQots and CdSeTe@ZnS-SiO₂ Qdots with different concentrations and incubation for 24 h with HeLa cells, blank (A), 5 $\mu\text{g mL}^{-1}$ (B), 10 $\mu\text{g mL}^{-1}$ (C), 50 $\mu\text{g mL}^{-1}$ (D), 100 $\mu\text{g mL}^{-1}$ (E), 500 $\mu\text{g mL}^{-1}$ (F).

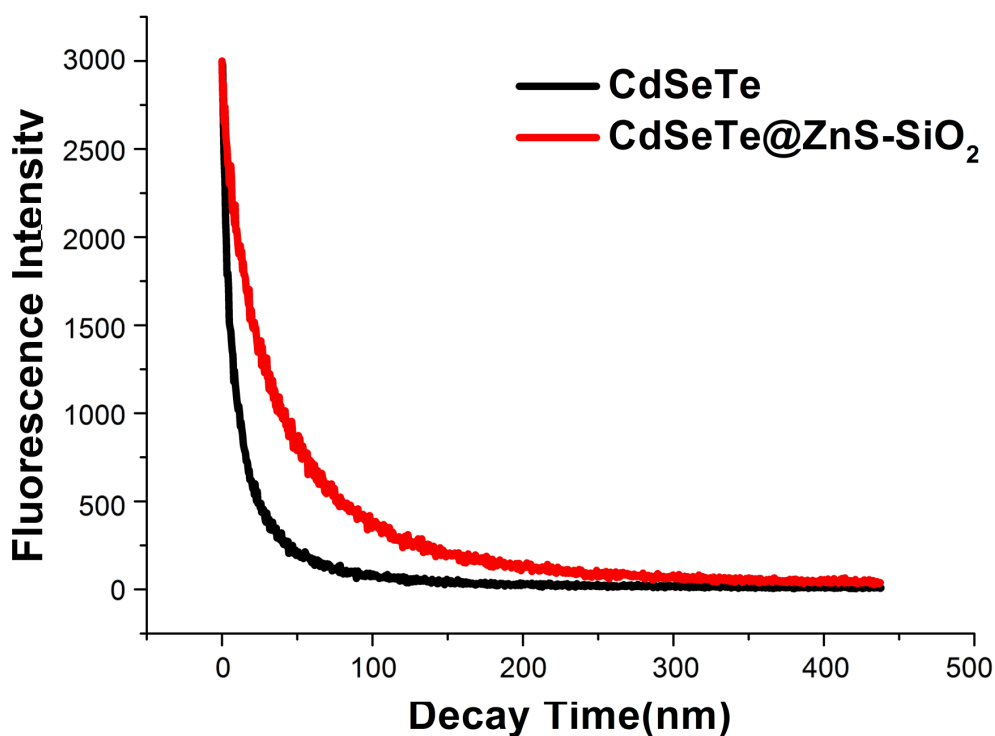


Fig. S7 PL decay curves of CdSeTe AQdots and CdSeTe@ZnS-SiO₂ Qdots.

PL decay lifetime of CdSeTe AQdots is 57.0 ns, and CdSeTe@ZnS-SiO₂ Qdots is 83.8 ns.

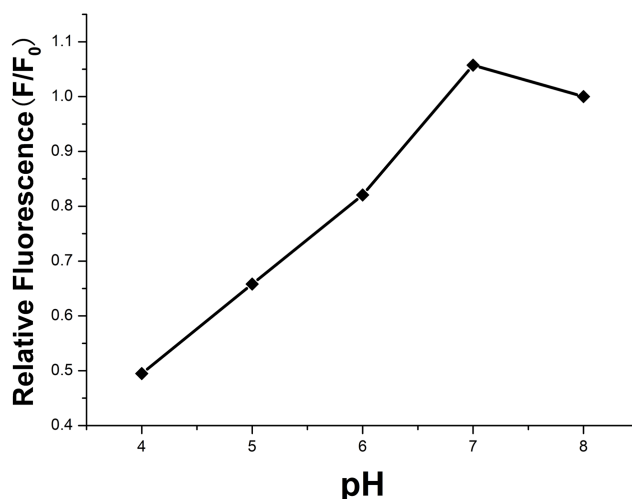


Fig. S8 Fluorescence intensity of the CdSeTe@ZnS-SiO₂ Qdots ($\lambda_{\text{max}} = 576$ nm) in PBS (50 mM) at different pH values.

The effect of pH on the HQdots (Fig. S8) suggested that the HQdots were pH-dependent, due to the protonation and deprotonation of the surface binding thiolates.[SI2]The optimum fluorescence intensity was obtained at the pH ranging from 7 to 8.

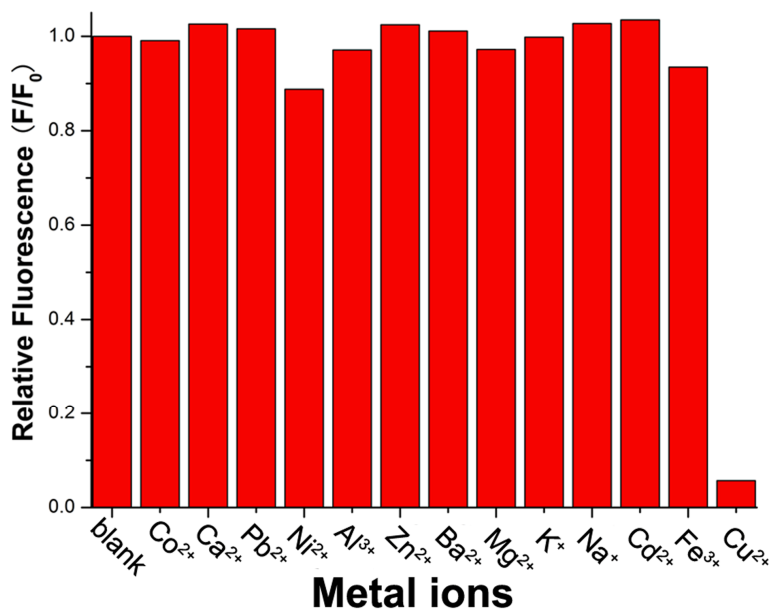


Fig. S9 Relative fluorescence (F/F₀) of CdSeTe@ZnS-SiO₂ Qdots solution in the presence of 5 μ M various metal ions. F₀ and F correspond to the fluorescence intensity of CdSeTe@ZnS-SiO₂ Qdots in the absence and presence of 5 μ M of various metal ions.

To evaluate the selectivity, the quenching effect of 13 kinds of cations was investigated (Fig. S9). After $5\ \mu\text{M}\ \text{Cu}^{2+}$ was added into the HQdots solution ($600\ \text{nM}$) (Fig. S9), the fluorescence quenching of the HQdots was observed. This phenomenon shows that the HQdots can be used for the detection of Cu^{2+} ions. Obviously, the fluorescence of HQdots had little response to $5\ \mu\text{M}\ \text{Co}^{2+}$, Ca^{2+} , Pb^{2+} , Ni^{2+} , Al^{3+} , Zn^{2+} , Ba^{2+} , Mg^{2+} , K^+ , Na^+ , Cd^{2+} , Fe^{3+} , while the same concentration of Cu^{2+} caused almost 92% quenching. This result demonstrated the high selectivity towards Cu^{2+} .

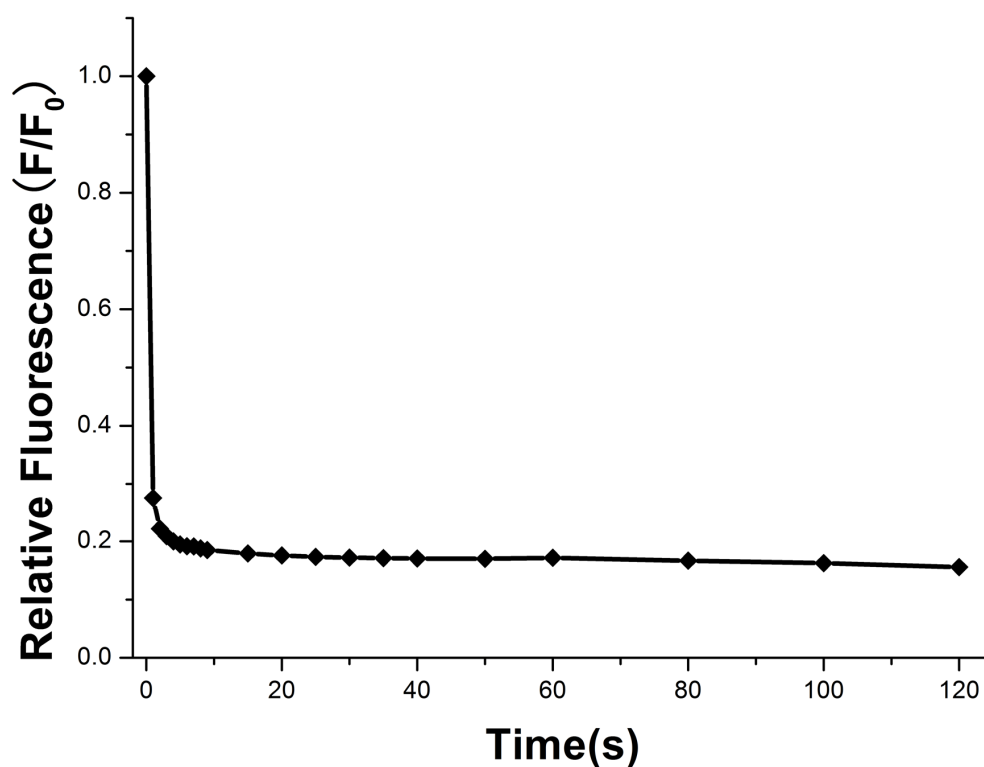


Fig. S10 Time-dependent fluorescence response of the CdSeTe@ZnS-SiO₂ Qdots to Cu^{2+} .

In the case of Fig. S10, fluorescence response was time-dependent. Thus, the fluorescence change was observed after a fixed time of 20 min.

Tab. S1 PL properties and ICP-MS elemental analysis of the CdSeTe@ZnS-SiO₂ Qdots

sample	PL peak (nm)	FWHM (nm)	PL QYs (%)	ICP-AES elemental analysis of Zn (mg/1 μmol HQdots)
a	531	51	11.9	-
b	524	55	11.9	10.8
f	576	52	56.9	10.3

Tab. S2 *K_{sp}* of several compounds mentioned in the detection of Cu²⁺ [SI3]

Compounds	<i>K_{sp}</i>
CuS	6.3×10^{-36}
α-NiS	3.2×10^{-19}
β-NiS	1.0×10^{-24}
γ-NiS	2.0×10^{-26}
CdS	8.0×10^{-27}
α-ZnS	1.6×10^{-24}
β- ZnS	2.5×10^{-22}
PbS	8.0×10^{-24}
α- CoS	4.0×10^{-21}
β- CoS	2.0×10^{-25}

(CaS, BaS, MgS and Fe₂S₃ are easily hydrolyzed, unstable in water system.)

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