

Photoactivated CdTe/CdSe Quantum Dots as a Near Infrared Fluorescent Probe for Detecting Biothiols in Biological Fluids

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The important roles of biothiols in biological systems have attracted great interest in the determination of biothiols. Although great progress has been made in fluorescent biothiol probes, near-infrared (NIR) fluorescent probes for biothiols are rather few even such NIR probes can avoid interference from biological media such as tissue autofluorescence and scattering light, and thereby facilitate relatively interference-free sensing. Herein, we report photoactivated CdTe/CdSe quantum dots (QDs) as a novel NIR fluorescent probe for biothiols. The photoactivated CdTe/CdSe QDs based NIR fluorescent probe offers good sensitivity and selectivity for detecting cysteine (Cys), homocysteine (Hcy), and glutathione (GSH) in the presence of 20 other amino acids, main relevant metal ions, and some other molecules in biological fluids. The recovery of spiked 5.0 μM thiols in human urine, plasma, and cell extracts ranges from 90% to 109%. The precision for nine replicate measurements of the thiols at 5.0 μM is in the range from 1.6% to 1.8%. The detection limits for Cys, Hcy, and GSH are 131, 26, and 20 nM, respectively. This assay is based on both the superior photoactivity of CdTe/CdSe QDs and the strong affinity of thiols to photoactivated CdTe/CdSe QDs. The addition of thiols into the photoactivated CdTe/CdSe QDs improves the passivation of the illumination-induced traps, meanwhile reduces most of Se(IV) and Te(IV) on the surface of photoactivated CdTe/CdSe QDs so as to improve the fluorescence property.

Biothiols play a crucial role in the physiological matrix for their participation in the process of reversible redox reactions and important cellular functions including detoxification and metabolism.^{1–4} The level of homocysteine (Hcy) in plasma is an indicator for disorders including cardiovascular and Alzheimer's

disease.⁵ Cysteine (Cys) deficiency is involved in slowed growth, hair depigmentation, edema, lethargy, liver damage, muscle and fat loss, skin lesions, and weakness.⁶ The ratio of glutathione (GSH) to glutathione disulfide is a key indicator for monitoring the cellular oxidative stress.^{1–4} The level of thiol-containing amino acids and peptides in plasma is also linked to AIDS.⁷ Because of the important roles of thiols in biological systems, there is a rapidly growing interest in the determination of biothiols.^{8–21} Great attention has been paid to fluorescent probes for biothiol detecting or imaging owing to the apparent advantages of fluorescent probes over other methods in virtue of sensitivity and convenience.^{14–21}

Efficient near-infrared (NIR) lumophores have generated much interest in biosensor applications because biosensors operating in the NIR region (generally wavelengths >650 nm) can avoid interference from biological media such as tissue autofluorescence and scattering light and thereby facilitate relatively interference-free sensing.¹⁸ Although great progress has been made in the field of fluorescent biothiol probes, NIR fluorescent probes for biothiols are rather few.^{15,16}

Colloid semiconductor quantum dots (QDs) are promising lumophores for biosensors since QDs offer many advantages over

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conventional organic fluorophores such as high photoluminescence efficiency, size-dependent emission wavelengths, and sharp emission profile. QDs have been widely explored for detecting either ions or molecules, and for tracing biorecognition events or biocatalytic transformations.^{19–38} However, to our knowledge, QDs based NIR fluorescent probes for biothiols have not been reported before.

Herein, we report a novel NIR fluorescent probe for biothiols based on photoactivated CdTe/CdSe core/shell QDs. Important biothiols of Cys, Hcy, and GSH were employed as targets. The present photoactivated QDs based NIR fluorescent probe offers good sensitivity and selectivity for the studied thiols and effectively eliminates interference from autofluorescence and scattering light from the biological matrix.

EXPERIMENTAL SECTION

Chemicals. All chemicals used were at least analytical grade. Ultrapure water (18.2 MΩ cm) obtained from a WaterPro water purification system (Labconco Corporation, Kansas City, MO) was used throughout. Te and Se powder, CdCl₂, KBH₄, Tris, HCl, NaOH, and NaCl were from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China). Hcy was from Aldrich (Steinheim, Germany), and all the other amino acids and reduced GSH were from Beijing Newprobe Biotechnology Co. Ltd. (Beijing, China). KHTe and KHSe solutions were freshly prepared according to a published procedure.³⁹

Synthesis of CdTe/CdSe QDs. CdTe/CdSe QDs were prepared in aqueous solution with a layer-by-layer epitaxy approach.⁴⁰ Typically, freshly made KHTe solution was injected into a mixture solution (pH 11.0) of CdCl₂ and Cys after 30 min of degassing with argon. The molar ratio of Cd/Te/Cys was set to 1/0.45/2.5 when the concentration of CdCl₂ was 5.0 mM. The crude solution was refluxed at 100 °C for 3 h to promote the growth of CdTe QDs. After that, in order to form a single layer of CdSe shell on the CdTe QDs, a degassed mixture solution (pH 11.0) of CdCl₂ and Cys and a solution of freshly

made KHSe were injected into the reaction system of the CdTe QDs solution sequentially by a syringe and then refluxed for 30 min. Thus, the first layer of CdSe shell came into being. Repeating the above procedure five times resulted in the CdTe/CdSe QDs with a diameter of 5 nm, giving a fluorescence emission maximum at 750 nm.⁴⁰

Photoactivation of the CdTe/CdSe QDs. One portion of freshly made CdTe/CdSe QDs solution in colorless glass tubes was open to air and stored in a simulate climate box (SPX-250IC (Shanghai Boxun Industry & Commerce Co. Ltd., Shanghai, China) equipped with 10 daylight lamps of 30 W and 6500 K (Foshan Electrical and Lighting Co., Ltd., Foshan, China)) with an average illumination intensity of 6 500 lx at 30 °C, then an aliquot of the solution was taken at a certain interval to monitor the fluorescent property of the QDs. However, the CdTe/CdSe QDs solution used for analytical application was activated only for 1 day and then stored in sealed brown bottles in the dark to avoid further illumination. Before use, the solution of photoactivated CdTe/CdSe QDs was precipitated with ethanol, dried by argon, and redissolved in ultrapure water for probing the biothiols. Samples for any parallel experiments were prepared with the same batch of CdTe/CdSe QDs on the same day and worked out as parallel as the conditions allowed. Key experiments were repeated with different batches of QDs.

Characterization. Absorption spectra were recorded on a Shimadzu UV-3600 UV–vis-NIR spectrophotometer. The steady-state fluorescence experiments were performed on a Hitachi FL-4500 fluorescence spectrometer. The fluorescent lifetime of the QDs was measured on an Edinburgh FLS920 spectrometer with an integrating sphere attachment under excitation of 450 nm. The X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Kratos Axis Ultra DLD spectrometer fitted with a monochromated Al Kα X-ray source ($h\nu = 1486.6$ eV), hybrid (magnetic/electrostatic) optics, and a multichannel plate and delay line detector. All XPS spectra were recorded using an aperture slot of 300 × 700 μm. Survey spectra were recorded with a pass energy of 160 eV and high resolution spectra with a pass energy of 40 eV. All the results were corrected with charge shift.

Samples. The urine and plasma samples were collected from two healthy volunteers, centrifuged, and reduced by dilute HCl. An appropriate dilution of urine (66-fold) and plasma (100-fold) were adopted for detection. Aliquots were mixed with photoactivated CdTe/CdSe QDs, and the other aliquots were pretreated with 0.1 mM *N*-ethylmaleimide (NEM) as a thio-blocking compound before reaction with the photoactivated CdTe/CdSe QDs.¹⁷

The human cervical carcinoma (Hela), human hepatoma (HepG2) and human leukemic cell line (HL60) were cultured in Dulbecco's modified Eagle's medium (DMEM) with 10% fetal bovine serum to get a suitable density (70–80% confluence). The complete DMEM was removed, and cells were harvested by centrifugation after treating by 0.25% trypsin. Healthy human leukocyte (HHL) cells were collected from healthy volunteers' blood. The blood was centrifuged in the presence of EDTA as a gelation inhibitor, extracted the white layer in the medium, dissolved in 0.83% NH₄Cl, and then centrifuged once again to get HHL cells to precipitate. All kinds of the cells were then suspended in phosphate buffer solution (PBS, pH 7.4) and counted under the microscope (Nikon, Japan). To detect the

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intracellular nonprotein thiols, cells were washed with cold PBS three times, sonicated to make cells homogeneous, and then centrifuged. The supernatant was collected, reduced by dilute HCl, and diluted with PBS for detection. Aliquots were mixed with photoactivated CdTe/CdSe QDs, and the other aliquots were pretreated with 0.1 mM NEM before reaction with the photoactivated CdTe/CdSe QDs.¹⁷

Measurement Procedures. In a typical test, to a 10-mL calibrated test tube, 0.1 mL of photoactivated CdTe/CdSe QDs (1.6 g L^{-1} , purified), 1.0 mL of Tris-HCl buffer solution (0.1 M, pH 7.0), and certain amounts of analytes were sequentially added. The mixture was diluted to volume with ultrapure water, set for 15 min, and measured with a fluorescence spectrometer at 750 nm under excitation at 600 nm.

RESULTS AND DISCUSSION

Photoactivation of CdTe/CdSe QDs for Probing Biothiols. The photoactivation of QDs is an established phenomenon,^{33,34,41–44} for which different mechanisms have been proposed, including photoinduced surface reconstruction of the surface atoms of the QDs or the optimization of surface-ligand passivation induced by photon–photon coupling.^{33,34,41–44} However, only a few publications concern the use of photoactivated QDs for the generation of sensitive luminescent probes, i.e., photoactivated CdSe QDs as sensitive probes for cyanide^{33,34} and as nanosensors for gases.⁴² In the present work, we report a photoactivated CdTe/CdSe QDs based NIR fluorescent probe for biothiols.

Photoactivation of QDs under sunlight irradiation may be not very robust nor reproducible owing to the uncontrolled variation of the sunlight intensity and temperature resulting from different weather conditions and locations. For this reason, in this work we carried out the photoactivation of CdTe/CdSe QDs under well-controlled conditions, i.e., in a simulate climate box with an average illumination intensity of 6 500 lx at 30 °C for a fixed period.

To obtain better performance of the photoactivated QDs for probing biothiols, the effect of photoactivation time on the enhanced fluorescence intensity of the CdTe/CdSe QDs due to addition of thiols was investigated (Figure 1). Without photoactivation (e.g., freshly made or after 1-day storage in the dark), no significant enhancement effect of the thiols on the fluorescence of the CdTe/CdSe QDs was observed. However, the thiols enhanced the fluorescence intensity of the CdTe/CdSe QDs after photoactivation, and the enhanced fluorescence intensity of the QDs varied with photoactivation time. The best enhancement effect of thiols was observed for the CdTe/CdSe QDs after 1-day photoactivation. As the 1-day photoactivated QDs had good stability in the dark (Figure S1 in the Supporting Information), they were stored in the dark for further experiments.

Factors Affecting the Enhanced Fluorescence of the Photoactivated CdTe/CdSe QDs. Besides photoactivation time, several other factors that may affect the performance of the

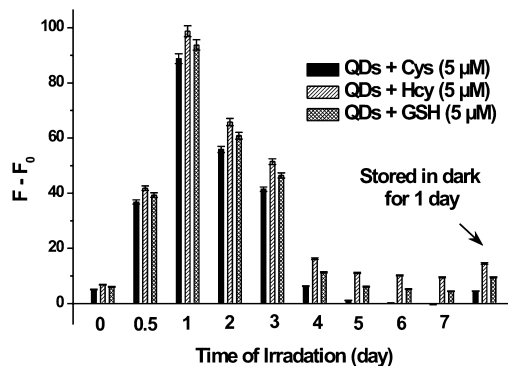


Figure 1. Effect of photoactivation time on the enhanced fluorescence intensity ($F - F_0$) of the CdTe/CdSe QDs by added thiols. F_0 and F are the fluorescence intensity of the CdTe/CdSe QDs at 750 nm ($\lambda_{\text{ex}} = 600 \text{ nm}$) before and after adding thiols, respectively.

photoactivated CdTe/CdSe QDs based NIR fluorescent probe were optimized, such as the concentration of the photoactivated CdTe/CdSe QDs, pH value, and ionic strength.

The concentration of the photoactivated CdTe/CdSe QDs not only affected the fluorescence intensity but also influenced the sensitivity of the photoactivated CdTe/CdSe QDs to thiols (Figure S2 in the Supporting Information). A 16 mg L^{-1} solution of the photoactivated QDs not only gave the strongest enhanced fluorescence intensity but also the best sensitivity to the thiols.

The effect of pH on the enhanced fluorescence intensity of the photoactivated CdTe/CdSe QDs is shown in Figure S3 in the Supporting Information. Maximal enhanced fluorescence intensity of these photoactivated QDs by thiols was obtained at pH 7.0, and thus in further experiments, a pH 7.0 Tris-HCl buffer was chosen.

Temporal change of the enhanced fluorescence intensity of the photoactivated QDs in the presence of Cys, Hcy, or GSH was also monitored for 35 min (Figure S4 in the Supporting Information). Maximal and stable enhanced fluorescence intensity was observed after 15 min of interaction for all three thiols tested. In addition, the enhanced fluorescence was not affected by ionic strength at least up to 600 mM NaCl (Figure S5 in the Supporting Information).

Dependence of the Fluorescence of the Photoactivated CdTe/CdSe QDs on the Concentration of Biothiols. The effect of the concentration of Cys, Hcy, and GSH on the fluorescence of the photoactivated CdTe/CdSe QDs is shown in Figure 2. Addition of these thiols up to $500 \mu\text{M}$ resulted in an increase in the fluorescent intensity along with a red-shift of $\sim 4 \text{ nm}$ in the fluorescence spectra (Figure 2a–c). A linear relationship between the enhanced fluorescence intensity of the photoactivated CdTe/CdSe QDs and the logarithm of the concentration of added thiols was found over the range from 0.2 to $100 \mu\text{M}$ with a correlation coefficient $R > 0.990$ (Figure 2c).

The concentration dependence of the luminescence intensity of the photoactivated CdTe/CdSe QDs follows a Langmuir-type binding isotherm equation ($C/F = 1/(BF_{\text{max}}) + (1/F_{\text{max}})C$, where C is the concentration of the added thiol, F is the fluorescence intensity at the concentration of the added thiol (C), and F_{max} is the maximum fluorescence intensity, B is the binding constant) with a correlation coefficient $R > 0.999$ (Figure 2d). The binding constant B between the thiols and the photoactivated

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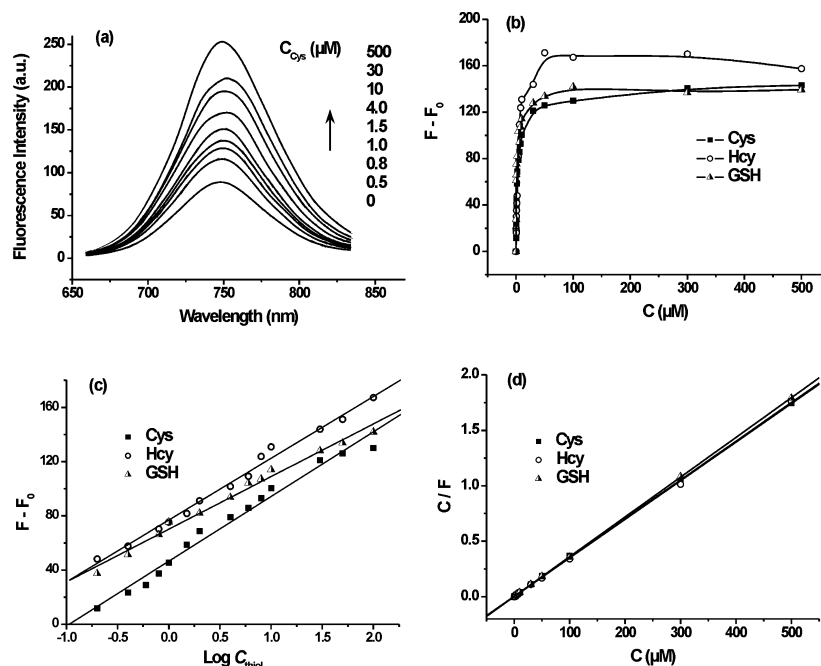


Figure 2. (a) Variation of the fluorescence emission spectra of the 1-day photoactivated CdTe/CdSe QDs with the concentration of added Cys. (b) Enhanced fluorescence intensity of the 1-day photoactivated CdTe/CdSe QDs at 750 nm ($\lambda_{\text{ex}} = 600$ nm) vs the concentration of the added thiol. (c) Enhanced fluorescence intensity of the 1-day photoactivated CdTe/CdSe QDs at 750 nm ($\lambda_{\text{ex}} = 600$ nm) vs the logarithm of the concentration of the added thiol from 0.2 to 100 μM . (d) Langmuir binding isotherm showing a linear fit for the added thiols from 0 to 500 μM with a correlation coefficient $R > 0.999$.

QDs was calculated to be $\sim 2.5 \times 10^3 \text{ M}^{-1}$. The excellent Langmuir fit suggests a possible multisite binding on a single QD for the thiols.

Possible Mechanism. A time-resolved spectroscopic technique was employed to gain insight into the mechanism of fluorescence changes with photoactivation in the absence or presence of thiols (Figure 3) since time-resolved fluorescence is sensitive to both electron and hole dynamics.⁴⁵ A significant decrease in the average fluorescence lifetime from 75.5 to 61.2 ns was observed after 1-day photoactivation (Table S1 in the Supporting Information), indicating that photoactivation resulted in an increased nonradiative decay of QDs.^{46–48} Furthermore, the addition of Cys as an electron donor into the solution of the photoactivated QDs improved the passivation of the electron traps and increased the average lifetime up to 85.6 ns (Table S1 in the Supporting Information), which was consistent with the improvement in the steady-state fluorescence.^{20,46} The results indicate that thiols not only affected the radiation process but also reduced the nonradiation relaxation pathways.

To probe whether the surface of the CdTe/CdSe QDs was photooxidized after 1-day photoactivation, three samples were prepared for the analysis by XPS, i.e., QD-1 for freshly made CdTe/CdSe QDs before photoactivation and QD-2 and QD-3 for 1-day photoactivated CdTe/CdSe QDs in the absence and presence of added Cys (100 μM), respectively. Typical survey spectra

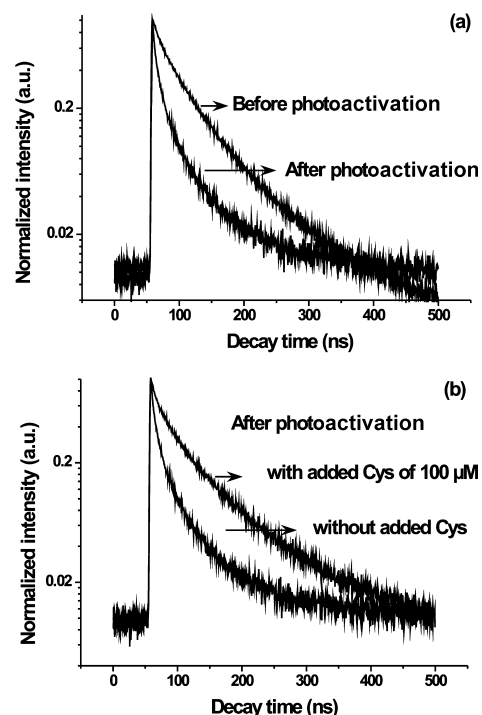


Figure 3. Fluorescence lifetime of (a) CdTe/CdSe QDs before (QD-1) and after (QD-2) 1-day photoactivation; (b) 1-day photoactivated CdTe/CdSe QDs in the absence (QD-2) and presence (QD-3) of Cys (100 μM). Other conditions: Tris-HCl solution (pH 7.0), $\lambda_{\text{ex}} = 450$ nm, $\lambda_{\text{em}} = 750$ nm.

shows the presence of Cd, S, Se, and Te from the QDs and their surface, and C, N, and O from the QDs surface and from absorbed gaseous molecules (Figure S6 in the Supporting Information).

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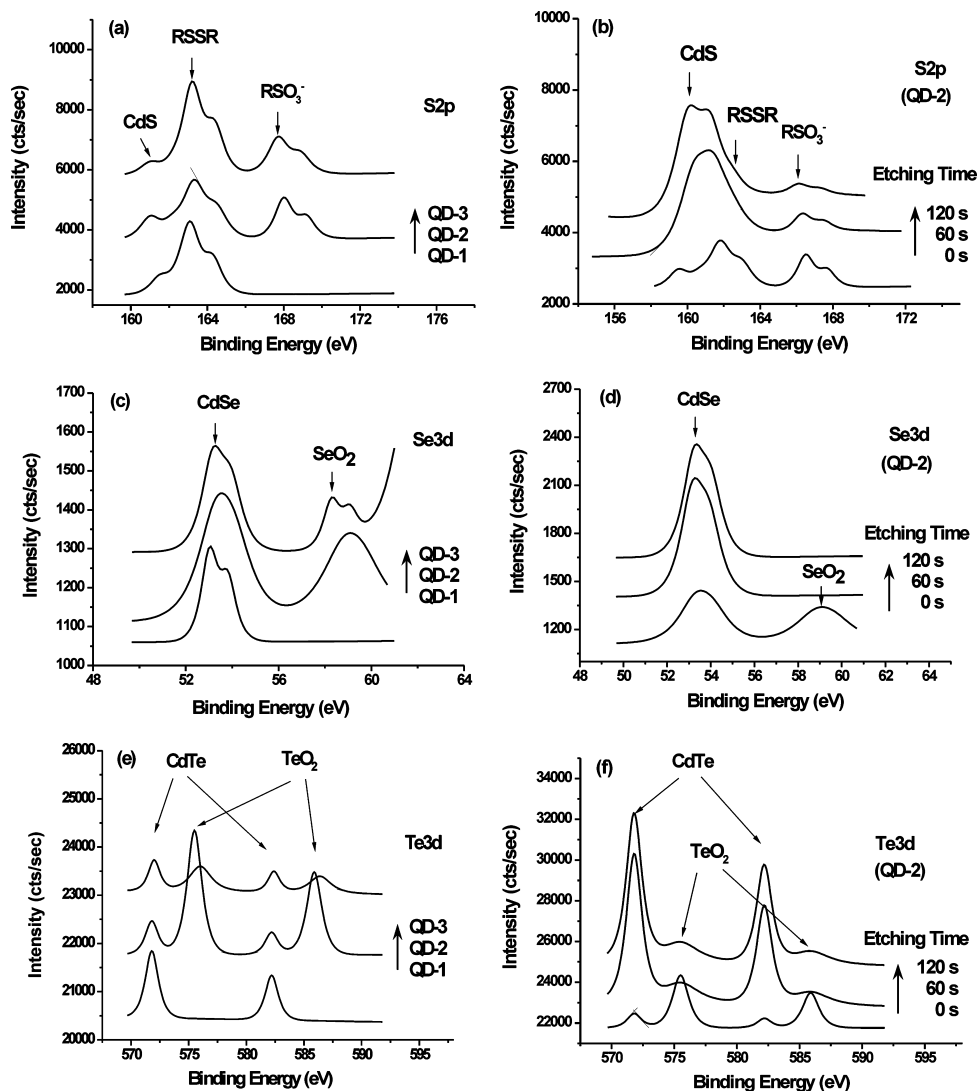


Figure 4. XPS spectra of S 2p, Se 3d, and Te 3d for the freshly prepared CdTe/CdSe QDs (QD-1), 1-day photoactivated CdTe/CdSe QDs in the absence (QD-2) and in the presence (QD-3) of Cys (100 μ M) (a, c, e) without etching and (b, d, f) QD-2 etched for 0, 60, and 120 s.

Higher-resolution XPS spectra were taken in the regions of Cd 3d, S 2p, Se 3d, and Te 3d, and the binding energy and possible states were compared for the three samples of QDs (Figure 4; Figure S6b and Table S2 in the Supporting Information). The Cd 3d_{5/2} peak in all of the three samples, which correspond to that of Cd in cadmium chalcogenide,^{49–51} centered around 404.5 ± 0.1 eV, shows no obvious difference (Figure S6b in the Supporting Information). An inspection of the S 2p spectral region (Figure 4a) indicates that after photoactivation, a new valence state of sulfur appeared on the surface of both QD-2 and QD-3, with S 2p binding energy of about 168 eV. The new peak was attributed to the S(IV) in sulfite. The area of this peak in both QD-2 and QD-3 was quite similar. So, photoactivation turned part of sulfur from the L-cysteine ligand on the surface of the CdTe/CdSe QDs into higher oxidation state, which was not reduced by the addition of thiols.

Photoactivation also produced the peaks of oxidized Se (SeO₂) (Figure 4c) and Te (TeO₂) (Figure 4e) in QD-2. Depth profile experiments show that the photooxidation of the Se and Te occurred on the surface of the QDs as the peak areas of the oxidized Se (SeO₂) and Te (TeO₂) significantly decreased while those of the reduced Se (CdSe) and Te (CdTe) increased with increasing the etching time (Figure 4d,f). Addition of free thiols reduced most of Se(IV) and Te(IV) and resulted in a sharp decrease in the peak area of the SeO₂ and TeO₂ (Figure 4c,e). Therefore, the added thiols not only improved the passivation of the surface of the QDs by decreasing traps but also reduced the opaque SeO₂ and TeO₂ which possibly made contribution to the recovery of the fluorescence property.

Selectivity of the Photoactivated CdTe/CdSe QDs for Detecting Biothiols. One of the significant features of the present photoactivated CdTe/CdSe QDs as the NIR fluorescent probe is the ability to detect Cys, Hcy, and GSH in the presence of various other amino acids. To evaluate the selectivity of the photoactivated CdTe/CdSe QDs for detecting thiols, we studied the fluorescent response of the photoactivated QDs to 22 essential amino acids and GSH (5 μ M for Cys, Hcy and GSH and 5 mM for the other

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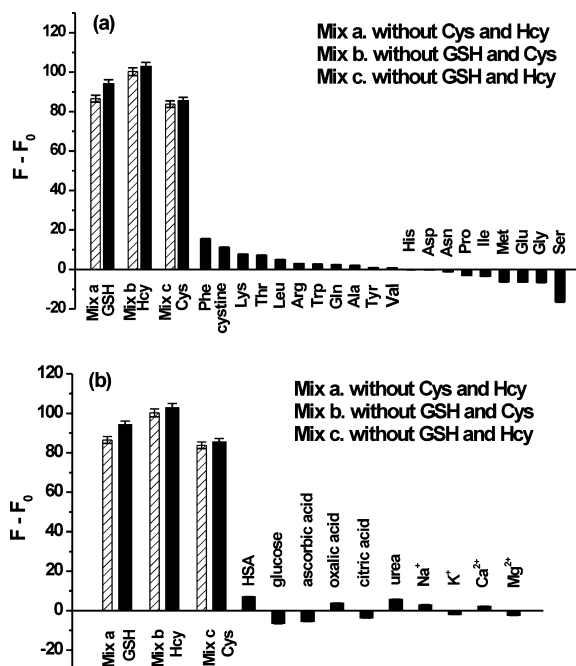


Figure 5. (a) Fluorescence responses of the 1-day photoactivated CdTe/CdSe QDs to 22 essential amino acids and GSH (5 μM for Cys, Hcy, and GSH and 5 mM for the other 20 amino acids) in pH 7.0 Tris-HCl buffer. Mix a, GSH with all the other nonthiol amino acids; Mix b, Hcy with all the other nonthiol amino acids; Mix c, Cys with all the other nonthiol amino acids. (b) Fluorescence responses of the 1-day photoactivated CdTe/CdSe QDs to Cys, Hcy, GSH (5 μM), HSA (25 mg L^{-1}), glucose, ascorbic acid, oxalic acid, citric acid (50 μM), urea (1 mM), Na^+ (0.6 M), K^+ (0.1 M), and Ca^{2+} and Mg^{2+} (5 mM). Mix a, all the above substances except Cys and Hcy; Mix b, all the above substances except GSH and Cys; Mix c, all the above substances except GSH and Hcy. F_0 and F are the fluorescence intensity of the photoactivated CdTe/CdSe QDs at 750 nm ($\lambda_{\text{ex}} = 600$ nm) before and after adding the corresponding substances, respectively.

20 amino acids) (Figure 5a). Cys, Hcy, and GSH exhibited a significant enhancing effect on the fluorescent intensity of the photoactivated QDs, whereas other amino acids even at 1000-fold higher concentration of Cys, Hcy, and GSH did not induce obvious fluorescence changes. In addition, the increased fluorescence of the photoactivated QDs by Cys, Hcy, and GSH was affected by less than 10% with the coexistence of other 20 amino acids. These results show that the proposed method is practical for detecting the thiols in the presence of other 20 amino acids, indicating the diagnostic potential of the photoactivated CdTe/CdSe QDs for probing thiols in biological samples.

To further evaluate the selectivity of the photoactivated CdTe/CdSe QDs for detecting biothiols, we studied the effect of main relevant metal ions and other molecules in biological fluids, such as K^+ , Na^+ , Ca^{2+} , Mg^{2+} , urea, human serum albumin (HSA), glucose, ascorbic acid, oxalic acid, and citric acid on the enhanced fluorescence intensity of the photoactivated CdTe/CdSe QDs for 5 μM Cys, Hcy, or GSH. As shown in Figure 5b, the enhancement of the fluorescence emission due to the addition of thiols at 5 μM was unaffected by 120 000-fold excesses of Na^+ , 20 000-fold excesses of K^+ , and 1 000-fold excesses of Mg^{2+} and Ca^{2+} . Typical coexisting molecule urea was permitted at 200-fold excess. HSA (25 mg L^{-1}) and 10-fold excesses of

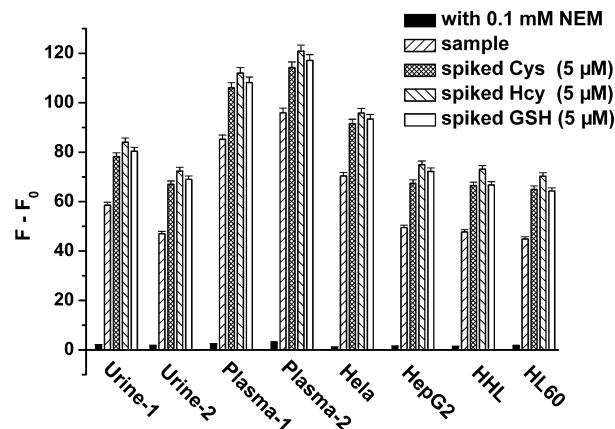


Figure 6. Enhanced fluorescence response of the 1-day photoactivated CdTe/CdSe QDs (16 mg L^{-1}) toward the urine, plasma, and cell extracts of Hela, HepG2, HHL, and HL60.

glucose, ascorbic acid, oxalic acid, and citric acid induced less than 10% interference with the detection of the thiols.

Figures of Merit for the Photoactivated CdTe/CdSe QDs for Detecting Biothiols. The calibration function, linearity, precision, and detection limits (DLs) for the photoactivated CdTe/CdSe QDs based NIR fluorescent probe for detecting Cys, Hcy, and GSH are summarized in Table S3 (Supporting Information). The calibration graphs (ΔF vs $\lg C$) are linear in the concentration range of thiol from 0.2 to 100 μM , corresponding to a linear range of 3 orders of magnitude (Figure 2c). The reproducibility for nine replicate measurements of the thiols at 5 μM ranges from 1.6% to 1.8% (relative standard deviation). The DLs (3σ) for Cys, Hcy, and GSH are 131, 26, and 20 nM, respectively. The DLs are much lower than the concentration of the thiols in healthy human fluids (0.1–10 mM of GSH in cells,⁵² 50–300 μM of Cys in plasma,⁵³ and 5–15 μM of Hcy in plasma⁵⁴). The main advantages of the present NIR fluorescent probe for biothiols include the effective reduction of interferences from biological media such as tissue autofluorescence and scattering light (Figure S7 in Supporting Information) and the avoidance of complex modification/immobilization of the QDs.

Application of the Photoactivated CdTe/CdSe QDs-Based NIR Fluorescent Probe for Detecting Thiols in Biological Fluids. The photoactivated CdTe/CdSe QDs-based NIR fluorescent probe was applied for detecting the thiols in human urine, plasma, and cell extract samples. No fluorescence background from urine and plasma was observed in the NIR region with excitation at 600 nm although there was high fluorescence background in the visible region from urine and plasma under excitation at <550 nm (Figure S7 in the Supporting Information). Thus, fluorescence background interference was avoided successfully when the photoactivated QDs were applied to NIR fluorescence detection with excitation at 600 nm. All of the biological fluid samples gave a clear increase in the fluorescence intensity of the photoactivated QDs (Figure 6). The pretreatment of the samples with the thiol-blocking reagent NEM resulted in a distinct decrease of the fluorescence intensity, confirming that

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the fluorescence changes were caused by the thiols in the samples. Appropriate dilution of urine (66-fold), plasma (100-fold), and cell extracts (final concentration of 2×10^4 cells mL⁻¹) was necessary to ensure the concentration of biothiols in the linear range and to obtain quantitative recovery of the spiked thiols. The recovery of the thiols in the diluted samples of urine, plasma, and cell extracts ranged from 90% to 109% (Table S4 in the Supporting Information), indicating that no significant interference with the determination of the thiols in the samples of urine, plasma, and cell extract was encountered after an appropriate dilution of the samples. The above results demonstrate that the photoactivated QDs-based NIR fluorescent probe possesses great potential for detecting thiols in biological fluids.

CONCLUSIONS

We have developed a novel NIR fluorescent probe based on photoactivated CdTe/CdSe QDs for biothiols. The present NIR fluorescent probe not only effectively eliminates the interference from autofluorescence and scattering light from biological matrix but also allows sensitive and selective detecting Cys, Hcy and GSH in biological fluids.

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SUPPORTING INFORMATION AVAILABLE

Evolution of the fluorescence emission, absorption spectra, and photographs of QDs before and after photoactivation; typical survey spectra and Cd 3d spectra from XPS data of QDs-3 in the absence or presence of Cys (100 μ M); enhanced fluorescence intensity vs thiol concentration, pH, and interaction time at different concentration of the 1-day photoactivated CdTe/CdSe QDs; and fluorescent spectra of urine and plasma excited at 450 and 600 nm. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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