Supporting Information

Highly Selective Detection of Glutathione Using Quantum-Dots-Based OFF-ON Fluorescent Probe

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1. Experimental section:

Materials: Deionized water was used in all the experiments. Orange-fluorescence core/shell CdSe/ZnS quantum dots in chloroform were prepared by Prof. Xinhua Zhong's group, and NaOH solution was used to adjust the pH value of the QDs' solutions and the pH value of system in Figure S1 and S2. All reagents were of commercial quality and used without further purification.

Characterization: Absorption spectra were recorded on a Shimadzu UV-2550 UV-vis spectrometer. The steady-state fluorescence experiments were performed on a Varian Cary Eclipses fluorescence spectrometer. ^{1}H NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer. Chemical shifts were collected in D_2O.

Preparation of water-soluble TGA capped QDs: QDs was precipitated twice from the chloroform solution (4mL) by addition of acetone (10 mL) and subsequent centrifugation for 10 min at 3000 rpm. The resulting precipitate was dissolved in 2 mL chloroform again, and a 200 μL TGA solution (containing 100 mg TGA and 100 mg NaOH in 5 mL methanol) was added, the mixture was then shaken for 3 min. After addition of 2 mL of 1 mM NaOH solution in water, all the particles were transferred to the water phase and the chloroform became clear. The water phase with QDs solution was separated from the chloroform, and two successive precipitation steps of QDs with acetone followed by centrifugation were used to remove excess ligand. The obtained QDs were dissolved in 2 mL water, and kept in the dark. The final concentration was estimated to be 0.1 μM using

methods reported by Yu. [W. W. Yu，L. H. Qu, W. Z. Guo, X. G. Peng, *Chem. Mater.*, 2003, **15**, 2854-2860.]

General procedure for the detection experiments: To the above 0.2 mL QDs solution, water (2 mL) or water solution with different pH value was added, and then MV^{2+} solution was added to quench the fluorescence of the QDs. Because of ET, the fluorescence of QDs was quenched, and it was ready for analytes such as thiols or amino acids in both qualitative and quantitative detection.

2. PL quenching efficiency and restoration spectra at different pH values.

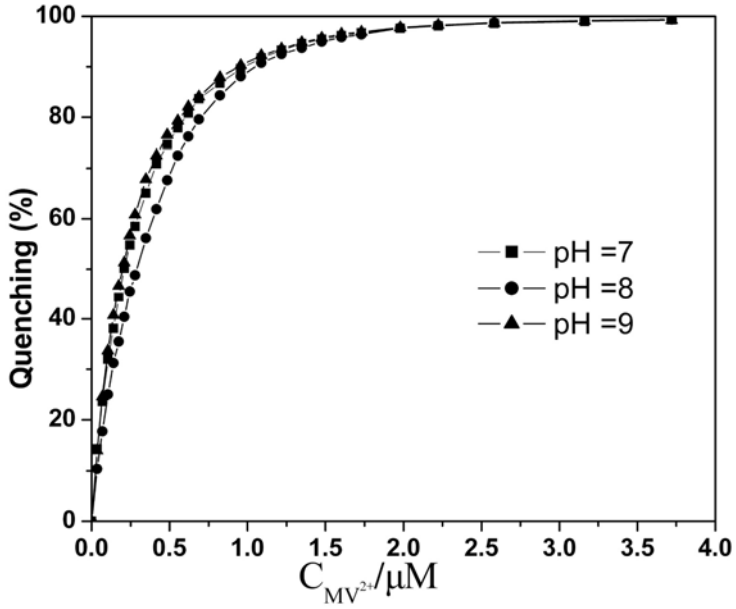


Figure S1. PL quenching efficiency of QDs vs the increment of the MV^{2+} (0-3.8 μM) concentration at different pH values.

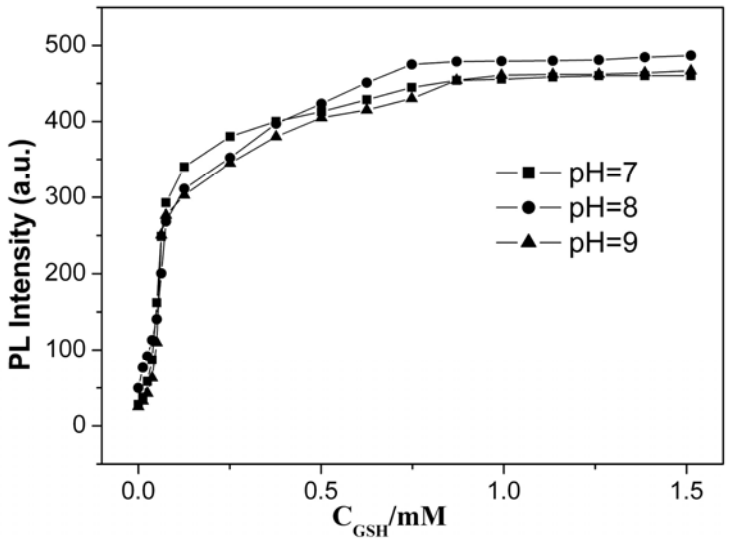


Figure S2. PL restoration of QDs/MV^{2+} system (Mv^{2+} =2.1 μM) vs the increment of the concentration of GSH at different pH values.

3. Effect of MV^{2+} concentration on the detection of GSH

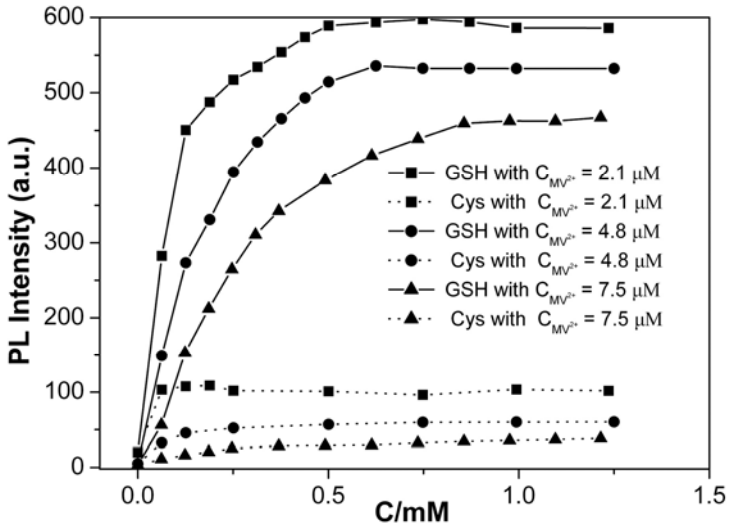


Figure S3. Effect of MV^{2+} concentration (at 2.1, 4.8, 7.5 μM) on the probe's selectivity, which suggested that the selectivity resolution between the GSH and Cys detection was optimum when the concentration of the MV^{2+} was 4.8 μM (since the response for Cys

was too high when C_{MV}^{2+} was 2.1μM and the response for GSH is too low when C_{MV}^{2+} was 7.5μM.)

Figure S1 showed that the quenching efficiency increased depending on the amount of the MV^{2+}. When the concentration of MV^{2+} was 2.1 μM, the percentage of quenching, Q%, was almost highest, 98%. To optimize the detection condition for our probe system, we initially selected three concentrations for MV^{2+}, 2.1 μM (appropriate), 4.8 μM (excessive), and 7.5 μM (large excessive), respectively. From figure S3, it was confirmed that the resolution for the detection between GSH and Cys was optimum when C_{MV}^{2+} was 4.8 μM.

4. The selectivity of QDs-based probe for GSH.

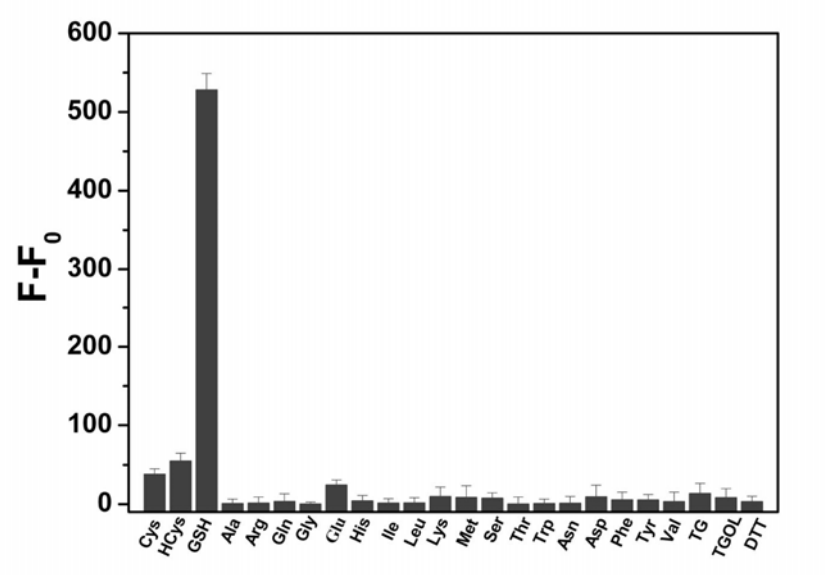
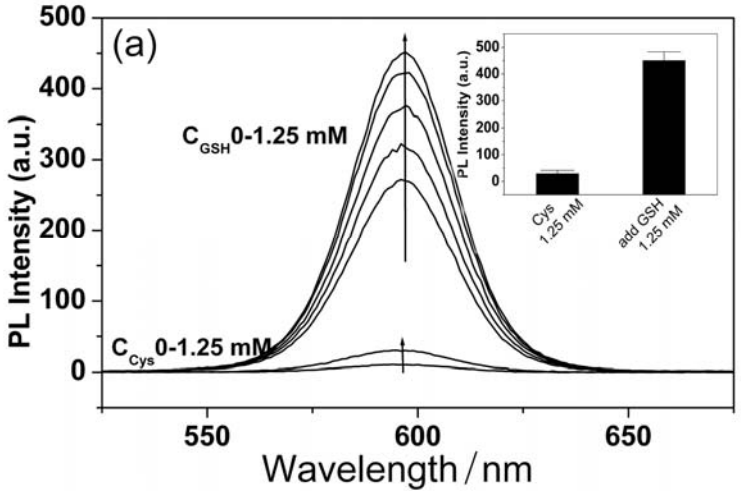


Figure S4. Enhanced fluorescence ($F-F_0$) response at 591 nm of QDs-based probe to diverse thiols and amino acids (1.25 mM) in DI water. (C_{Mv}^{2+} = 4.8 μM, λ_{ex} = 400 nm, $C_{analytes}$ = 1.25 mM)

5. Fluorescence photograph

Figure S5 Fluorescence photograph of QDs systems in the absence and presence of MV^{2+} (4.8 μM), GSH, Glu and Cys (1.5 mM) under irradiation of 365 nm Uv light.

6. Competition experiments between GSH and Cys, and the effect of the addition of heavy metal ions Hg^{2+} and Pb^{2+} on the detection of GSH



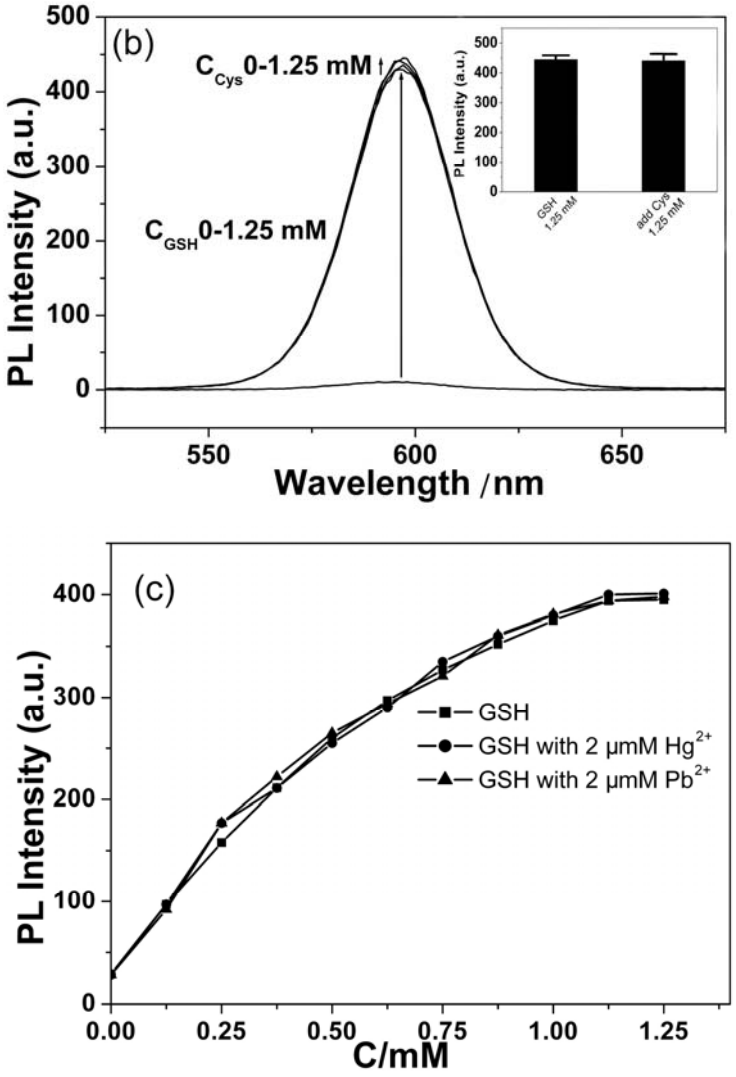


Figure S6 Competition experiments between GSH and Cys: (a) Fluorescence QDs probe (C_{Mv}^{2+} = 4.8 μM) was exposed to Cys (1.25 mM) first and then GSH (1.25 mM). The presence of Cys just produced a small fraction of the response generated by the GSH; (b) Fluorescence response of QDs probe (C_{Mv}^{2+} = 4.8 μM) to GSH (1.25 mM) in the absence and presence of Cys (1.25 mM). The presence of Cys did not alter the GSH detection; (c) The fluorescence response at 586 nm vs the increment of the concentration of GSH in the presence of Hg^{2+} and Pb^{2+}, respectively: C_{Mv}^{2+} = 4.8 μM, C_{GSH} = 0-1.25 mM, C_{Hg}^{2+}= C

$_{Pb}{}^{2+}$= 2 μM, the QDs used in Figure S6c was not from the same batch as previous, the maximum emission wavelength locates at 586 nm.