Supporting Information:

Fabrication of "Ion-Imprinted" Dual-Emission Quantum Dots Nanohybrid for Selective Fluorescence Turn-On and Ratiometric Detection of Cadmium Ions

Jing Wang[a*], Chenxing Jiang[a], Xiaoqi Wang[a], Ligeng Wang[a], Aimin Chen[a], Jun Hu[a], Zhihui Luo[b*]

[a]*College of Chemical Engineering, Zhejiang University of Technology. Hangzhou310014, PR China.*

[b]*Guangxi Key Laboratory of Agricultural Products Processing (Cultivating Base), Guangxi Colleges and Universities Key Laboratory for Efficient Use of Agricultural Resources in the Southeast of Guangxi, College of Chemistry and Material, Yulin Normal University, Yulin 537000, PR China.*

*E-mail: Jingw1986@zjut.edu.cn;Lzhui_1980@163.com

Experimental detail

Synthesis of red-emitting MPA-stabilizedCdTe QDs

Water-soluble CdTe QDs were synthesized according to the one-pot method with some modification.Typically, $CdCl_2 \cdot 2.5H_2O$ (0.2284 g) was dissolved in 500 mL deionized water in a three-necked flask, MPA (100 μL) was added and the pH of the mixture was adjusted to 11.0 with 1.0 M NaOH under stirring. Then trisodium citrate dihydrate (0.5380 g), Na_2TeO_3 (0.0444 g) and $NaBH_4$ (0.1000 g) were successively added into the mixture. The final molar ratio of Cd^{2+}, TeO_3^{2-} and MPA is 5: 1: 6. When the color of solution changed to pale green, the mixture was refluxed at 100 °C. All reactions were carried out under ambient atmospheric conditions. Red fluorescent CdTe QDs were obtained after refluxing for about 6 h. The preparedCdTe QDs solution was purified by centrifugation after adding the same volume of ethanol. The purified CdTe QDs were finally redispersed in ultrapure water and stocked at 4 °C for further use.

Synthesis of green-emitting dual-stabilizers-capped CdSe QDs

Dual-stabilizers-capped CdSe QDs were prepared according to a reported method. For a typical synthesis, 0.80 mL $CdCl_2$ solution (0.20 M) wasadded to a three-necked flask containing 50 mL H_2O, and then SHMP (72.5 mg) and MPA (34.6 μL) were introduced to the solution under magnetic stirring. After thesolution pH was adjusted to 9.0 with 1.0 M NaOH, 0.80 mLNa_2SeO_3 solution (0.020 M) was added to the above solution. Afterthe resulting mixture was refluxed at 100 °C for 10 min, 3.70 mL $N_2H_4 \cdot H_2O$ was injected into the above solution, and then the finalmixed solution was refluxed under open-air conditions for about 9 h to obtain the greenCdSe QDs. The obtained crude products were purified by centrifugation after adding the same volume of ethanol. The purified CdSe QDs were finally redispersed in ultrapure waterand stocked at 4 °C for further use.

Results

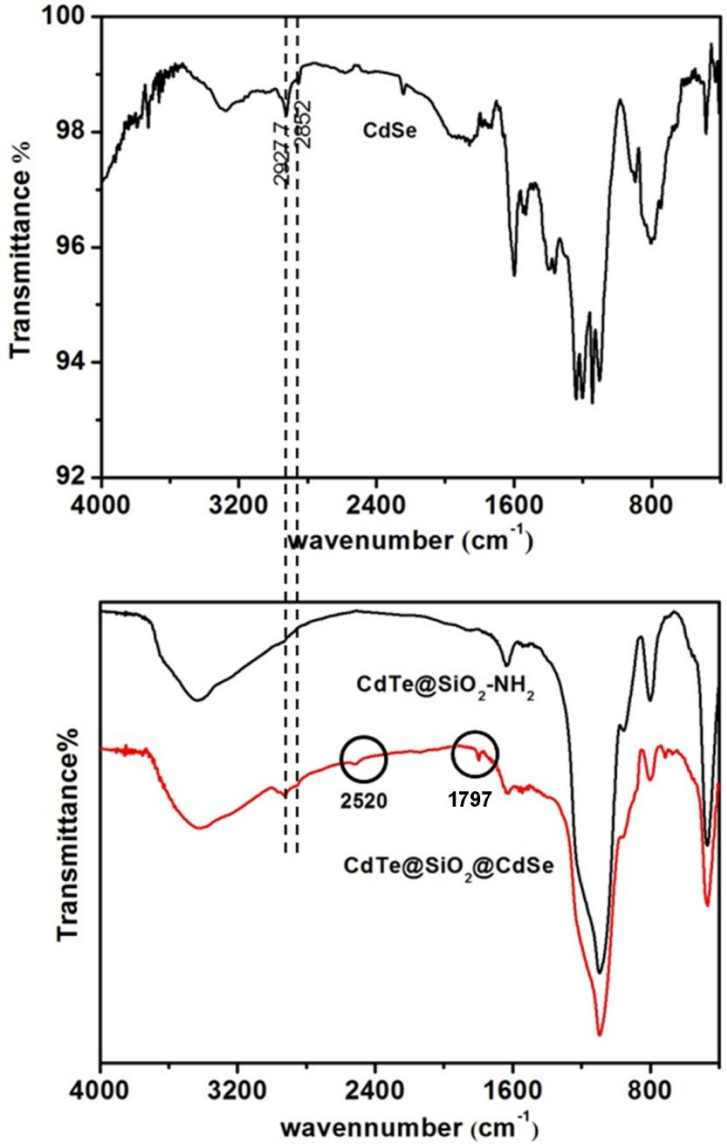

Fig. S1. FTIR spectra of CdSe, CdTe@SiO_2-NH_2 and CdTe@SiO_2@CdSe NPs

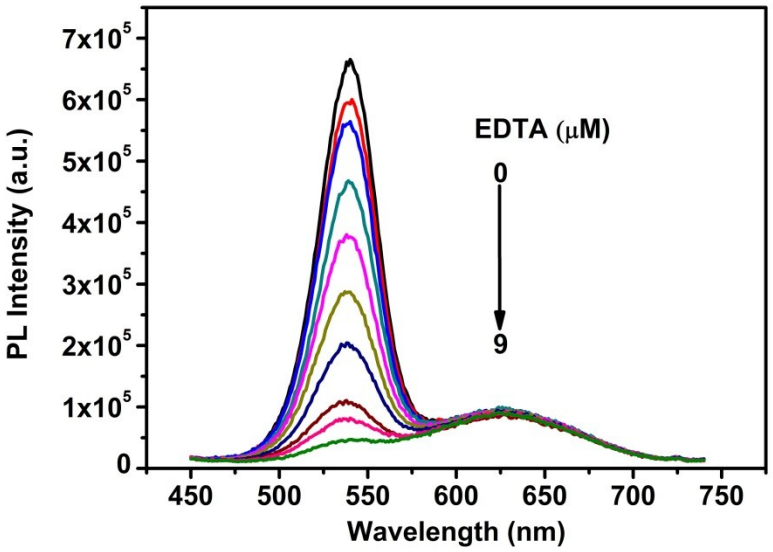

Fig. S2. The PL spectra (λex = 380 nm) of the CdTe@SiO_2@CdSe NPs (50 μg/mL) upon the exposure to different concentrations of EDTA. The concentrations of EDTA from top to bottom are 0, 1, 2, 3, 4, 5, 6, 7, 8, and 9 μM, respectively.

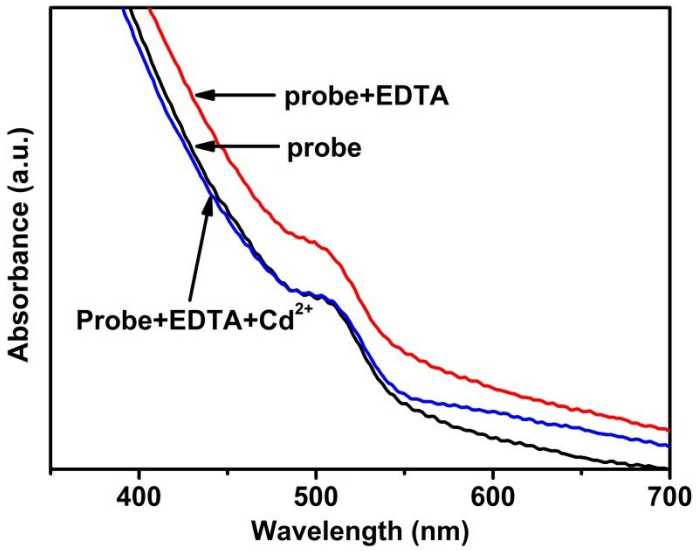

Fig. S3. UV-Vis spectra of the ratiometric probe (1 mg mL^{-1}) in the absence of EDTA, in the presence of EDTA (160 μM), and in the presence of EDTA (160 μM) and Cd^{2+} (160 μM).

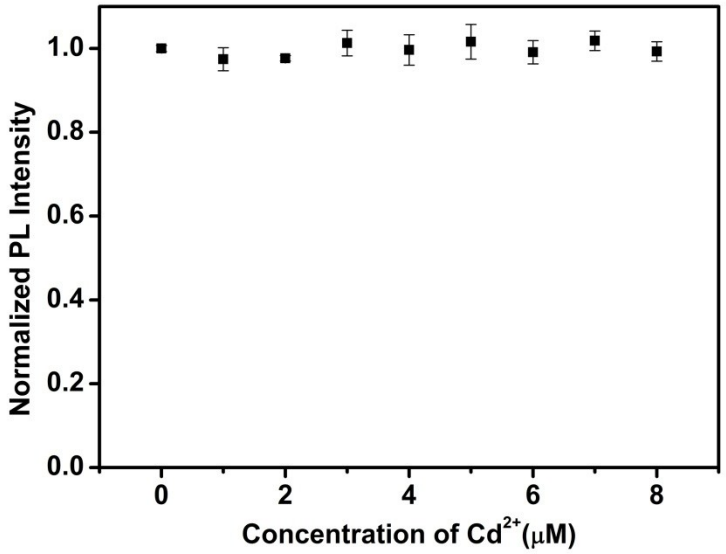

Fig. S4. The influence of Cd^{2+} on the PL of CdTe@SiO_2@CdSe NPs (50 μg/mL).

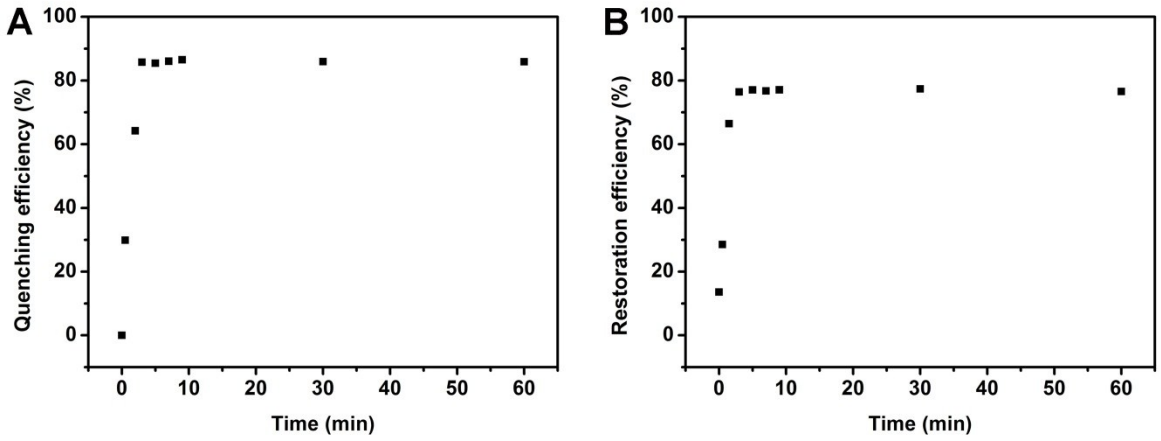

Fig. S5. Time-dependent PL quenching efficiency (A) of the outer CdSe QDs in ratiometric probe (CdTe@SiO_2@CdSe,50 μg/mL)to EDTA (8 μM) and subsequent PL restoration efficiency (B) by Cd^{2+} (8 μM).

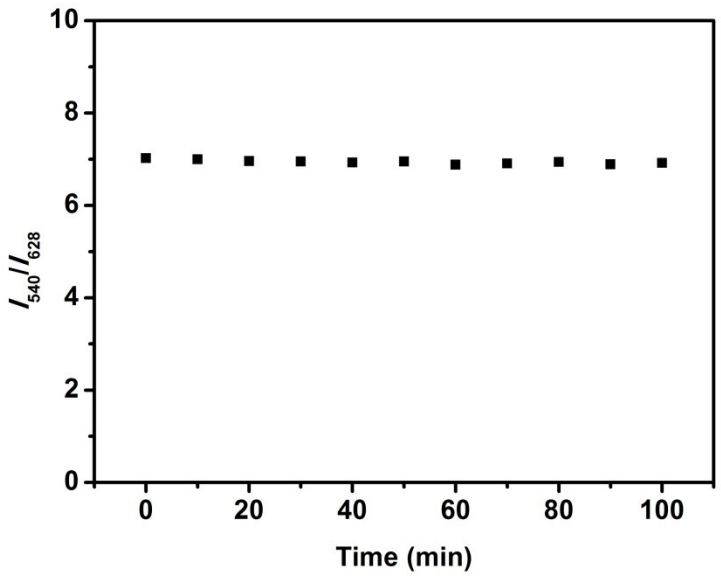

Fig. S6. Stability of the PL intensity ratios of the ratiometric probe (CdTe@SiO_2@CdSe) at 540 nmversus that at 628 nm.

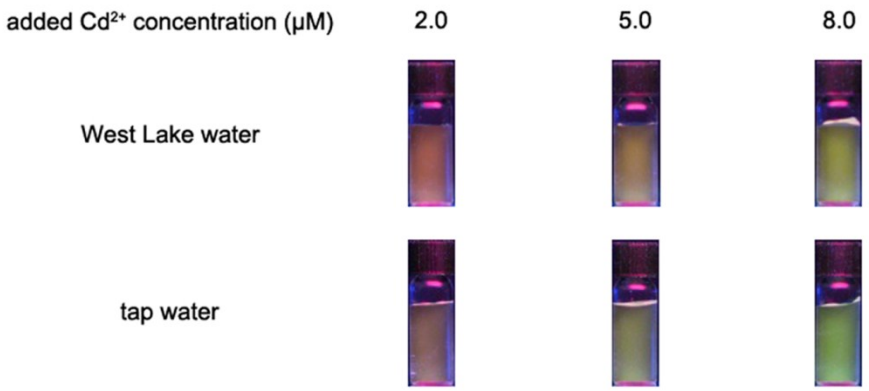

Fig. S7. Digital photos of detection of Cd^{2+} in spiked tap water and West Lake water by the ratiometric sensor

Table S1. Comparison of this work with some QDs-based fluorescence sensors for Cd^{2+} detection.

References	Probes	Methods	modes	Linear range (μM)	Detection limit (nM)
This study	CdTe@SiO_2@CdSe	ratiometric	turn-on	0.1-9	25
Ref. 1	FITC–CdTe	ratiometric	turn-on	0.1-15	12
Ref. 2	CQDs/AuNCs	ratiometric	turn-off	0.15-15	32.5
Ref. 3	InP	single	turn-on	0.2-10	100
Ref. 4	CdSe/ZnS	single	turn-on	0-50	150
Ref. 5	CdTe	single	turn-on	1.3-25	500

Reference

1. Gui, R.; An, X.; Huang, W. An improved method for ratiometric fluorescence detection of pH and Cd^{2+} using fluorescein isothiocyanate-quantum dots conjugates. *Anal. Chim. Acta* **2013,***767*, 134-140.
2. Niu, W.-J.; Shan, D.; Zhu, R.-H.; Deng, S.-Y.; Cosnier, S.; Zhang, X.-J. Dumbbell-shaped carbon quantum dots/AuNCs nanohybrid as an efficient ratiometric fluorescent probe for sensing cadmium (II) ions and l-ascorbic acid. *Carbon* **2016,***96*, 1034-1042.
3. Zhang, Y.; Zhang, Z.; Yin, D.; Li, J.; Xie, R.; Yang, W. Turn-on fluorescent InP nanoprobe for detection of cadmium ions with high selectivity and sensitivity. *ACS Appl. Mater. Interfaces* **2013,***5*, 9709-9713.
4. Li, H.; Zhang, Y.; Wang, X. l-Carnitine capped quantum dots as luminescent probes for cadmium ions. *Sens. Actuators, B***2007,***127*, 593-597.
5. Xu, H.; Miao, R.; Fang, Z.; Zhong, X. Quantum dot-based "turn-on" fluorescent probe for detection of zinc and cadmium ions in aqueous media. *Anal. Chim. Acta* **2011,***687*, 82-88.