Double-Emission Ratiometric Fluorescent Sensors Composed of Rare-Earth-Doped ZnS Quantum Dots for Hg\(^{2+}\) Detection

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**ABSTRACT:** Quantum dots (QDs) are a class of zero-dimensional nanocrystal materials, whose lengths are limited to 2–10 nm. Their unique advantages such as wide excitation spectra, narrow emission spectra, and high quantum yield make their application possible in fluorescence sensing, wherein QDs such as CdSe, CdTe, and CdS are used. Indeed, QDs have a wide range of applications in fluorescence sensing, and there have been many reports of applications based on QDs as ion probes. The emission spectra of QDs can be adjusted by changing the size of the QDs or doping them with other ions/elements. However, the high toxicity of Cd and the poor anti-interference ability of single-emission fluorescent probes greatly limit the applications of QDs in many fields. In this paper, ZnS QDs are doped with the rare-earth element Ce to form a low-toxicity double-emission ratiometric fluorescent sensor, ZnS:Ce, for Hg\(^{2+}\) detection. The results of transmission electron microscopy (TEM), X-ray diffractometry, X-ray photoelectron spectroscopy, and optical spectroscopy show that ZnS:Ce QDs were successfully synthesized. Under the optimal conditions, the concentration of Hg\(^{2+}\) was in the range of 10–100 μM, which had a linear relationship with the fluorescence intensity of the ZnS:Ce QDs: the linear correlation coefficient was 0.998, and the detection limit was 0.82 μM L\(^{-1}\). In addition, the fluorescent sensor had good selectivity for Hg\(^{2+}\), and it was successfully applied to the detection of Hg\(^{2+}\) in laboratory water samples.

1. **INTRODUCTION**

Hg\(^{2+}\) is a strong carcinogen. Long-term exposure to Hg\(^{2+}\) can damage the urinary system, nervous system, reproductive system, and immune system of humans, thus leading to cancer, biological malformation, and gene mutations. At present, there are many methods used to identify Hg\(^{2+}\), such as atomic absorption spectrometry, inductively coupled plasma mass spectrometry, electrochemical methods, and ion chromatography. The above methods have certain advantages in terms of detection sensitivity and selectivity, but they are complicated to conduct, incur high costs, require large-scale instruments, and take a long time to yield detection. Therefore, it is of practical significance to develop a simple and efficient method to determine Hg\(^{2+}\) in water.

Quantum dots (QDs) are zero-dimensional semiconductor nanomaterials, and their particle sizes are smaller than, or close to, the Bohr radius of self-trapped excitons in three spatial dimensions. QDs are ideal fluorescent materials with wide excitation spectra, narrow and symmetrical emission spectra, high quantum yields, and stable optical properties. Based on these unique properties, QDs are widely used as fluorescent probes in the field of fluorescence sensing.

The fluorescence emission spectra of QDs can be adjusted by changing the size of the QDs and by introducing doped ions, which can be used to prepare QDs for detecting specific targets. Up to now, there have been many reports that Cu\(^{2+}\), Pb\(^{2+}\), Hg\(^{2+}\), and other heavy metal ions have been detected using the fluorescence characteristics of Cd QDs. However, the fluorescence spectra of fluorescent probes constructed by a single fluorophore are easily affected by changes and impurities in the environment, which thus generate systematic errors and affect the detection results. Moreover, Cd-based QDs are mostly synthesized in organic phases, and because Cd is a heavy metal, its usage causes pollution. Doped QDs can replace traditional Cd-containing QDs. On the one hand, doped QDs have low toxicity, and on the other hand, doped QDs have double fluorescence emission and can form ratio-type fluorescent probes.

A ratiometric fluorescent probe can obtain two different emission wavelengths under single wavelength excitation, and it can detect an object based on the ratio of the fluorescence intensities of two independent emission peaks. The internal standard emission wavelength of a ratiometric fluorescent sensor endows fluorescent probes with anti-interference capabilities, effectively weakening the influence caused by changes in the excitation light, environment, and probe concentration...

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and improving the accuracy of fluorescence detection.\textsuperscript{37–42}
Therefore, in this work, rare-earth Ce ions are doped on the basis of low-toxicity ZnS QDs to form a double-emission ratiometric fluorescent sensor, ZnS:Ce, which is used as a fluorescent probe to detect Hg\textsuperscript{2+} in a pH = 7 phosphate buffer solution. The interaction mechanism between ZnS:Ce QDs and Hg\textsuperscript{2+} is subsequently discussed. The probe is then successfully applied to the determination of trace Hg\textsuperscript{2+} in laboratory tap water.

2. CHARACTERIZATION OF ZnS:Ce QDs

2.1. Fluorescence Characterization of ZnS:Ce QDs.
First, ZnS:Ce QDs were tested for fluorescence performance. Figure 1 shows the fluorescence spectrum of ZnS:Ce QDs. At an excitation wavelength of 230 nm, it can be seen that the fluorescence spectrum of the ZnS:Ce QDs has two obvious emission peaks located at 459 and 689 nm, wherein the emission peak at 459 nm belongs to Zn\textsuperscript{2+} defect luminescence of deep electron wells and the emission peak at 689 nm belongs to doped Ce\textsuperscript{3+} luminescence.

2.2. X-ray Photoelectron Spectroscopy (XPS) Characterization of ZnS:Ce QDs.
X-ray photoelectron spectroscopy

Figure 1. Fluorescence spectrum of ZnS:Ce QDs.

Figure 2. XPS survey spectra of ZnS:Ce QDs for ZnS:Ce (A), Ce 3d (B), Zn 2p (C), and S 2p (D).
experiments were carried out on ZnS:Ce QDs. As shown in Figure 2, Zn 2p has split into two peaks, Zn 2p3/2 (1021.58 eV) and Zn 2p1/2 (1044.68 eV); Ce 3d has divided into two peaks, Ce 3d3/2 (917.08 eV) and Ce 3d5/2 (882.48 eV); the valence of S is $S^{2-}$ (2p1/2, 161.28 eV). Based on the valence states of Zn, Ce, and S elements, the successful synthesis of ZnS:Ce QDs is proved.

2.3. X-ray Diffraction Characterization of ZnS:Ce QDs. Figure 3 shows the X-ray diffraction pattern of ZnS:Ce QDs.

![X-ray diffraction (XRD) pattern of ZnS:Ce QDs.](image1)

It can be seen from the figure that the diffraction angles of the XRD peaks of the ZnS:Ce QDs prepared in this experiment are 28.68, 47.84, and 56.56°, which are, respectively, consistent with the (111), (220), and (311) crystal planes of ZnS, which has a cubic sphalerite structure. This proved the successful synthesis of ZnS:Ce QDs.

2.4. TEM Characterization of ZnS:Ce QDs. The morphology of the synthesized ZnS:Ce QDs was characterized by transmission electron microscopy. As shown in Figure 4, the particle size of the composite is about 3.5 nm, and some quantum dots are polymerized.

3. RESULTS AND DISCUSSION

3.1. Effect of Hg$^{2+}$ on the Fluorescence Intensity of ZnS:Ce QDs. In this study, it is found that Hg$^{2+}$ can quench the fluorescence peak generated by Zn$^{2+}$ defects in a deep electron trap at 459 nm and the fluorescence peak generated by the doped Ce at 689 nm in ZnS:Ce QDs as illustrated in Scheme 1. Therefore, a ratiometric fluorescent sensor is proposed to detect Hg$^{2+}$ ions according to the change in the intensity ratio of the double-emission fluorescence peaks. The ratiometric fluorescent sensor was constructed based on measuring the ratio of fluorescence intensities of two independent emission peaks, which can effectively reduce the influence caused by changes in the excitation light, environment, and probe concentration and improve the accuracy of Hg$^{2+}$ detection. Other metal ions (Cd$^{2+}$, Pb$^{2+}$, Fe$^{3+}$, Co$^{2+}$, Na$^{+}$, Mn$^{2+}$, Zn$^{2+}$, K$^+$, Al$^{3+}$, Cu$^{2+}$, and Mg$^{2+}$) did not significantly affect the intensity of the double-emission fluorescence peaks of the sensor, indicating that the sensor has excellent selectivity for Hg$^{2+}$.

Therefore, in this experiment, the concentration of Hg$^{2+}$ is detected by a ratiometric fluorescent sensor composed of ZnS:Ce QDs. The sensor is used for the quantitative detection of Hg$^{2+}$, and experimental conditions such as the pH value of the solution and the reaction time with Hg$^{2+}$ were optimized. The method is simple to operate and has a strong anti-interference capability.

3.2. Effect of pH on the Ratiometric Fluorescent Sensor. Different pH solutions will affect the sensitivity and selectivity of detection substances. Figure 5 depicts the effect of a range of pH values, from 5 to 9, on the fluorescence intensity of ZnS:Ce QDs $F_{459}/F_{659}$ in the presence and absence of Hg$^{2+}$. It can be seen from the figure that the fluorescence intensity ratio of the ZnS:Ce QDs with the same concentration is the strongest at pH = 7, indicating that fluorescence quenching is most obvious when Hg$^{2+}$ is added. Therefore, it is suggested that a pH value of 7 should be used for Hg$^{2+}$ detection.

3.3. Determination of Reaction Time between the Ratiometric Fluorescent Sensor and Hg$^{2+}$. The effect of the reaction time on the fluorescence intensity was studied at room temperature, and the results are shown in Figure 6. The experimental results show that the fluorescence intensity of the ZnS:Ce QDs rapidly quenched in the presence of Hg$^{2+}$ and reached equilibrium within 10 min, whereby the fluorescence signal stabilized for at least another 20 min. Therefore, the experiment was carried out after 10 min.

3.4. Anti-Interference Ability of the Ratiometric Fluorescent Sensor. We investigated the effects of other interfering ions on ZnS:Ce QDs. In the presence and absence of Hg$^{2+}$, an interfering substance with a concentration of 100 μM was added to ZnS:Ce QDs. Figure 7 shows that in the presence of Hg$^{2+}$ at a concentration of 100 μM, the fluorescence of ZnS:Ce QDs is significantly broken, while other interfering ions have little effect on the fluorescence of ZnS:Ce QDs in the absence of Hg$^{2+}$. This fully illustrates the selectivity of this method for Hg$^{2+}$.

![Transmission electron microscopy (TEM) (inset shows high-resolution) images of ZnS:Ce QDs.](image2)
3.5. Detection of Hg$^{2+}$ Using the Sensor. As shown in Figure 8, the experimental results demonstrate that the fluorescence intensity of the Zn:Ce QDs at 459 and 689 nm gradually decreased in the presence of Hg$^{2+}$ with different concentrations. The fluorescence quenching efficiency ($F_{459}^0/F_{689}^0 - F_{459}/F_{689}$) had a linear relationship with Hg$^{2+}$ concentration in the range $10^{-10}$ to $10^{0}$ μM. The best-fitting linear equation is $F_{459}^0/F_{689}^0 - F_{459}/F_{689} = 0.0194C - 0.0024$, with a correlation coefficient of $R^2 = 0.998$. $F_{459}^0/F_{689}^0$ represents the fluorescence intensity ratio at 459 nm without Hg$^{2+}$, and $F_{459}/F_{689}$ represents the fluorescence intensity ratio at 689 nm in the presence of Hg$^{2+}$. The detection limit (limit of detection (LOD) = 3σ/K) is 0.82 μM L$^{-1}$.

3.6. Application to Actual Water Samples. To demonstrate the ability of our proposed ratiometric fluorescent probe, it was used to detect Hg$^{2+}$ in laboratory tap water. The results are shown in Table 1. The recovery rate after the standard addition was 96–116%, and the relative standard deviation was less than 10%, which indicates the accuracy and precision of our method for determining Hg$^{2+}$ concentrations in actual samples.

3.7. Mechanism of ZnS:Ce QDs for Selective Detection of Hg$^{2+}$. The interaction mechanism between ZnS:Ce QDs and Hg$^{2+}$ is discussed here. As shown in Figure 9A, Hg$^{2+}$ has almost no ultraviolet absorption, so fluorescence energy resonance transfer is not the cause of fluorescence quenching of the ZnS:Ce QDs. As shown in Figure 9B, by monitoring the changing double-emission fluorescence peak intensity of the ZnS:Ce QDs solution, it is found that the fluorescence peak intensity at 459 nm obviously reduced, and the fluorescence peak intensity at 689 nm slightly reduced, after adding Hg$^{2+}$. According to Fajans’ rule, ions that can form insoluble or insoluble substances with ions that make up a crystal are preferentially adsorbed.43−50 On the other hand, the solubility product of HgS is much smaller than that of ZnS, which indicates that the ZnS:Ce QDs preferentially adsorbed Hg$^{2+}$, and some ZnS was converted into HgS, resulting in the aggregation and precipitation of the ZnS:Ce QDs. Due to the change of surface structure, thus causing fluorescence quenching. The decrease of fluorescence intensity had a quantitative relationship with the concentration of Hg$^{2+}$. Therefore, it can be predicted...
that the ratio change of the double-emission fluorescence peak intensities of the system has a quantitative relationship with the concentration of Hg$^{2+}$.

3.8. Comparison with Other Sensors that Detect Hg$^{2+}$ Ions. Compared with the Hg$^{2+}$ detection methods used in other studies, as shown in Table 2, the prepared ZnS:Ce double-emission ratiometric fluorescent sensor not only has low toxicity but also can reduce the effects of interference caused by excitation light, the environment, and probe concentration changes, and it has improved the detection accuracy relative to other methods.

4. CONCLUSIONS

ZnS:Ce-doped QDs were synthesized using a hydrothermal method, which were then utilized as ratiometric fluorescent probes for the quantitative determination of Hg$^{2+}$. The ZnS:Ce-doped QDs are not only less toxic than other QDs but also have the advantages of being very suitable ratiometric fluorescent probes. The proposed method has good stability and dispersibility in aqueous solutions (Cd$^{2+}$, Pb$^{2+}$, Fe$^{3+}$, Co$^{3+}$, Na$^+$, Mn$^{2+}$, Zn$^{2+}$, K$^+$, Al$^{3+}$, Cu$^{2+}$, and Mg$^{2+}$), and they can realize the selective detection of Hg$^{2+}$. Their detection sensitivity is high in the linear detection range of 10−100 μM, and the LOD was 0.82 μM L$^{-1}$.

The synthesis method of the probe is simple and cheap, and it

...
can realize the detection of trace amounts of Hg\(^{2+}\) in actual water samples.

5. EXPERIMENTAL SECTION

5.1. Materials. (CH\(_3\)COO\)\(_2\)Zn, Na\(_2\)S\(_9\)H\(_2\)O, CeCl\(_3\), NaOH, CH\(_3\)CH\(_2\)OH, Ca(NO\(_3\))\(_2\), Cd(CH\(_3\)COOH)\(_2\), FeCl\(_3\), Pb(NO\(_3\))\(_2\), CoCl\(_2\), NaCl, MnCl\(_2\), ZnCl\(_2\), KCl, A1Cl\(_3\), HgSO\(_4\), and Zn(NO\(_3\))\(_2\)-6H\(_2\)O were used.

5.2. Instruments. A fluorescence spectrometer, a UV spectrophotometer, an X-ray photoelectron spectroscopy analyzer, an X-ray diffractometer, a transmission electron microscope, and a scanning electron microscope were used.

5.3. Preparation of ZnS:Ce QDs. ZnS:Ce QDs were prepared according to the synthetic methods reported in the literature.\(^{21-24}\) First, 2.201 g of zinc acetate was added to 20 mL of ultrapure water, which was stirred until the zinc acetate was completely dissolved. Then, 0.4732 g of cerium trichloride was added and stirred until the solution became clear and transparent. Next, the pH was adjusted to 10 with sodium hydroxide and the process of removing air with nitrogen was repeated three times. Under the protection of nitrogen, 20 mL of a solution containing 2.883 g of sodium sulfide nonahydrate was added dropwise and stirred for 20 min. The mixture was then stirred at 60 °C for 6 h. The obtained ZnS:Ce QDs were purified three times by anhydrous ethanol precipitation to remove impurities and unreacted precursors, and then the pure ZnS:Ce QDs were dried under vacuum at 60 °C for 12 h. After drying, they were ground into powder. Finally, the obtained ZnS:Ce QDs were re-dispersed in ultrapure water for further analysis and testing.

5.4. Hg\(^{2+}\) Detection. ZnS:Ce QDs with a concentration of 10 mg mL\(^{-1}\) were prepared with phosphate-buffered saline at pH = 7, and the same volume of ZnS:Ce QDs solution (0.9 mL) was added to a test tube and then added to additional test tubes containing 100 μL of different concentrations (10–100 μM) of Hg\(^{2+}\) solution. The reaction was mixed at room temperature for 15 min, and the fluorescence emission spectra were recorded at an excitation wavelength of 230 nm. The fluorescence quenching efficiency was calculated using the formula $F_{459} / F_{688} = F_{459} / F_{688}$, where $F_{459} / F_{688}$ represents the ratio of fluorescence intensity at 459 nm without Hg\(^{2+}\), and $F_{459} / F_{688}$ represents the ratio of fluorescence intensity at 688 nm in the presence of Hg\(^{2+}\).

5.5. Detection of Hg\(^{2+}\) in Actual Samples. The actual samples were laboratory tap water and ultrapure water. The specific measurement method is the same as that used in Section 4.4.

![Figure 9. (A) (a) Ultraviolet–visible (UV–vis) absorption spectra of Ce:ZnS and (b) UV–vis absorption spectra of Hg\(^{2+}\). (B) (a) Fluorescence emission spectrum of Ce:ZnS QDs and (b) fluorescence emission spectrum of Ce:ZnS QDs solution after adding 100 μM Hg\(^{2+}\).](https://pubs.acs.org/doi/abs/10.1021/acsomega.0c00861)

Table 2. Comparison of the Reported Methods for Hg Detection Using QDs

| QDs                      | modification method | biological toxicity | whether ratiometric fluorescent probe | references |
|--------------------------|---------------------|---------------------|---------------------------------------|------------|
| ZnS                      | doped Ce            | low toxicity        | dual emission                         | this work  |
| CdTe                     | bovine serum albumin (BSA) | highly toxic       | single emission                       | 51         |
| CdTe                     | N-acetyl-L-cysteine | highly toxic        | single emission                       | 52         |
| CdTe                     | Au nanocluster, bovine serum albumin (BSA) | highly toxic       | single emission                       | 53         |
| CdTe                     | 2-mercaptoethanesulfonate (MES) | highly toxic       | single emission                       | 54         |
| CdTe                     | thioglycolic acid   | highly toxic        | single emission                       | 55         |
| CdTe                     | cysteamine          | highly toxic        | single emission                       | 56         |
| CdTe/CdS                 | unmodified          | highly toxic        | dual emission                         | 57         |
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Notes
The authors declare no competing financial interest.

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REFERENCES
(1) Li, L.; Jia, C.; Wang, F.; Fan, H.; Jiao, W.; Shao, Z. Facile Synthesis of Magnetic Fluorescent Nanoparticles: Adsorption and Selective Detection of Hg(II) in Water. J. Mater. Chem. C 2018, 6, 2360–2369.
(2) Sardans, J.; Montes, F.; Peñuelas, J. Determination of As, Cd, Cu, Hg and Pb in biological samples by modern electrothermal atomic absorption spectrometry. Spectrochim. Acta, Part B 2010, 65, 97–112.
(3) Romanovskiy, K. A.; Bolshov, M. A.; Münz, A. V.; Temerdashev, Z. A.; Burlyn, M. Y.; Sirota, K. A. A novel photochemical vapor generator for ICP-MS determination of As, Bi, Hg, Sb, Se and Te. Talanta 2018, 187, 370–378.
(4) Sacilotto, T. R.; Cervini, P.; Cavalliero, E. T. G. Simultaneous Voltammetric Determination of Zn(II), Pb(II), Cu(II), and Hg(II) in Ethanol Fuel Using an Organofunctionalized Modified Graphite-Polyurethane Composite Disposable Screen-Printed Device. Electroanalysis 2014, 26, 2664–2676.
(5) Dago, A.; González-García, O.; Arino, C.; Díaz-Cruz, J. M.; Esteban, M. Liquid chromatographic analysis of Hg(II) binding by thiol-rich peptides using both UV-vis and electrochemical detection. J. Chromatogr. A 2009, 1216, 6752–6757.
(6) Chan, Y. H.; Ye, F. M.; Gallina, M. G.; Zhang, X. J.; Jin, Y. H.; Wu, I.-C.; Chiu, D. T. Hybrid Semiconducting Polymer Dot–Quantum Dot with Narrow-Band Emission, Near-Infrared Fluorescence, and High Brightness. J. Am. Chem. Soc. 2012, 134, 7309–7312.
(7) Li, Y.; Hou, X. Q.; Dai, X. L.; Yao, Z. L.; Lv, L. L.; Jin, Y. Z.; Peng, X. G. Stoichiometry-Controlled InP-Based Quantum Dots: Synthesis, Photoluminescence, and Electroluminescence. J. Am. Chem. Soc. 2019, 141, 6448–6452.
(8) Albers, A. E.; Chan, E. M.; Mcbride, P. M.; Ajo-Franklin, C. M.; Cohen, B. E.; Helms, B. A. Dual-Emitting Quantum Dot/Quantum Rod-Based Nanothermometers with Enhanced Response and Sensitivity in Live Cells. J. Am. Chem. Soc. 2012, 134, 9565–9568.
(9) Xu, Y. L.; Niu, X. Y.; Zhang, H. J.; Xu, L. F.; Zhao, S. G.; Chen, H. L.; Chen, X. G. Switch-on Fluorescence Sensing of Glutathione in Food Samples Based on a Graphitic Carbon Nitride Quantum Dot (g-C3N4QDs)-Hg2+ Chemosensor. J. Agric. Food Chem. 2015, 63, 1747–1755.
(10) Bagalkot, V.; Zhang, L. F.; Levy-Nissenbaum, E.; Jon, S.; Kantoff, P. W.; Langer, R.; Farokhzad, O. C. Quantum Dot-Aptamer Conjugates for Synchronous Cancer Imaging, Therapy, and Sensing of Drug Delivery Based on Bi-Fluorescence Resonance Energy Transfer. Nano Lett. 2007, 7, 3065–3070.
(11) Weaver, A. L.; Gamelin, D. R. Photoluminescence Brightening via Electrochemical Trap Passivation in ZnSe and Mn2+-Doped ZnSe Quantum Dots. J. Am. Chem. Soc. 2012, 134, 6819–6825.
(12) Wang, C.; Gao, X.; Ma, Q.; Su, X. G. Aqueous synthesis of mercaptopropionic acid capped Mn2+-doped ZnSe quantum dots. J. Mater. Chem. 2009, 19, 7016–7022.
(13) Dong, B. H.; Cao, L. X.; Su, G.; Liu, W.; Qu, H.; Jiang, D. X. Synthesis and characterization of the water-soluble silica-coated ZnS:Mn nanoparticles as fluorescent sensor for Hg2+ ions. J. Colloid Interface Sci. 2009, 339, 78–82.
(14) Ma, Y. J.; Xu, G. H.; Wei, F. D.; Cen, Y.; Ma, Y. S.; Song, Y. Y.; Xu, X. M.; Shi, M. L.; Muhammad, S.; Hu, Q. A Dual-emissive fluorescent sensor fabricated by encapsulating quantum dots and carbon dots into metal–organic frameworks for ratiometric detection of Cu2+ in tap water. J. Mater. Chem. C 2017, 5, 8566–8571.
(15) Xu, H.; Wang, Z. P.; Li, Y.; Ma, S. J.; Hu, P. Y.; Zhong, X. H. A quantum dot-based “off–on” fluorescent probe for biological detection of zinc ions. Analyst 2013, 138, 2181–2191.
(16) Li, W. W.; Liu, J.; Sun, K.; Dou, H. J.; Tao, K. Highly fluorescent water soluble CdZnS:Te alloyed quantum dots prepared in aqueous solution: one-step synthesis and the alloy effect of Zn. J. Mater. Chem. B 2010, 2, 2133–2138.
(17) Sun, X.; Liu, B.; Xu, Y. B. Dual-emission quantum dots nanocomposites bearing an internal standard and visual detection for Hg2+. Analyst 2012, 137, 1125–1129.
(18) Huang, K.; Dai, R.; Deng, W. Q.; Lin, L.; Zhang, A.; Yuan, X. Aqueous Synthesis of CdTe Quantum Dots by Hydride Generation for Visual Detection of Silver on Quantum Dots Immobilized Paper. Anal. Methods 2017, 9, 5339–5347.
(19) Geszke-Moritz, M.; Piotrowska, H.; Murias, M.; Balan, L.; Moritz, M.; Lulek, J.; Schneider, R. Thioglycerol-capped Mn-doped ZnS quantum dot bioconjugates as efficient two-photon fluorescent nano-probes for bioimaging. J. Mater. Chem. B 2013, 1, 698–706.
(20) Ban, R.; Li, J. J.; Cao, J. T.; Zhang, P. H.; Zhang, J. R.; Zhu, J. J. Highly luminescent glutathione-capped ZnS:Mn/ZnS core/shell doped quantum dots for targeted mannosyl groups expression on the cell surface. Anal. Methods 2013, 5, 5929–5937.
(21) Tu, R. Y.; Liu, B. H.; Wang, Z. Y.; Gao, D. M.; Wang, F.; Fang, Q. L.; Zhang, Z. P. Amine-capped ZnS-Mn2+ nanocrystals for fluorescence detection of trace TNT explosive. Anal. Chem. 2008, 80, 3458–65.
(22) Ren, H.-B.; Wu, B.-Y.; Chen, J.-T.; Yan, X.-P. Silica-Coated S2−-Enriched Manganese-Doped ZnS Quantum Dots as a Photoluminescence Probe for Imaging Intracellular Zn2+ Ions. Anal. Chem. 2011, 83, 8239–8244.
(23) Wu, P.; He, Y.; Wang, H.-F.; Yan, X.-P. Conjugation of Glucose Oxidase onto Mn-Doped ZnS Quantum Dots for Phosphorescent Sensing of Glucose in Biological Fluids. Anal. Chem. 2010, 82, 1427–1433.
(24) Sotelo-Gonzalez, E.; Fernandez-Arguelles, M. T.; Costa-Fernandes, J. M.; Sanz-Medel, A. Mn-doped ZnS quantum dots for the determination of acetone by phosphorescence attenuation. Anal. Chim. Acta 2012, 712, 120–126.
(25) Liu, J.; Chen, H.; Lin, Z.; Lin, J.-M. Preparation of Surface Imprinting Polymer Capped Mn-Doped ZnS Quantum Dots and Their Application for Chemiluminescence Detection of 4-Nitrophenol in Tap Water. Anal. Chem. 2010, 82, 7380–7386.
(26) Geszke, M.; Murias, M.; Balan, L.; Medjahd, G.; Korczynski, J.; Moritz, M.; Lulek, J.; Schneider, R. Folic acid-conjugated core/shell ZnS:Mn nanoparticles as fluorescent sensor for Hg2+ ions. Microchim. Acta 2010, 170, 147–153.
(27) Chang, S.-Q.; Kang, B.; Dai, Y.-D.; Zhang, H.-x.; Chen, D. One-step fabrication of biocompatible chitosan-coated ZnS and ZnS:Mn2+ quantum dots via a γ-radiation route. Nanoscale Res. Lett. 2011, 6, No. 591.
(28) Wu, P.; Zhao, T.; Tian, Y. F.; Wu, L.; Hou, X. D. Protein-Directed Synthesis of Mn-Doped ZnS Quantum Dots: A Dual-Channel Biosensor for Two Proteins. Chem. - Eur. J. 2013, 19, 7473–7479.
(29) Zhang, B.-H.; Qi, L.; Wu, F.-Y. Functionalized manganese-doped zinc sulphide core/shell quantum dots as selective fluorescent chemodosimeters for silver ion. Microchim. Acta 2010, 170, 147–153.
(30) Shang, Y.; Qi, L.; Wu, F.-Y. Functionalized manganese-doped zinc sulfide quantum dot-based fluorescent probe for zinc ion. *Microchim. Acta* 2017, 184, 1199–1206.

(31) Xu, X.-Y.; Yan, B. Fabrication and application of ratiometric and colorimetric fluorescent probe for Hg²⁺ based on dual-emissive metal-organic framework hybrids with carbon dots and Eu³⁺. *J. Mater. Chem. C* 2016, 4, 1543–1549.

(32) Ma, Y. J.; Xu, G. H.; Wei, F. D.; Cen, Y.; Xu, X. M.; Shi, M. L.; Cheng, X.; Chai, Y. Y.; Sohail, M.; Hu, Q. One-pot synthesis of a magnetic, ratiometric fluorescent nanoprobe by encapsulating Fe₃O₄ magnetic nanoparticles and dual-emissive rhodamine B modified carbon dots in metal–organic framework for enhanced HClO sensing. *ACS Appl. Mater. Interfaces* 2018, 10, 20801–20805.

(33) Algar, W. R.; Susumu, K.; Delehanty, J. B.; Medintz, I. L. Semiconductor Quantum Dots in Bioanalysis: Crossing the Valley of Death. *Anal. Chem.* 2011, 83, 8826–8837.

(34) Yu, J. L.; Su, J.; Zhang, J.; Wei, X. T.; Guo, A. L. CdTe/CdS quantum dot-labeled fluorescent immunochromatography test strips for rapid detection of Escherichia coli O157:H7. *RSC Adv.* 2017, 7, 17819–17823.

(35) Mu, Q.; Li, Y.; Xu, H.; Ma, Y. F.; Zhu, W. H.; Zhong, X. H. Quantum dots-based ratiometric fluorescent probe for merHg in biological fluids. *Talanta* 2014, 119, 564–571.

(36) Wang, K.; Qian, J.; Jiang, D.; Yang, Z. T.; Du, X. J.; Wang, K. Onsite naked eye determination of cysteine and homocysteine using quencher displacement-induced fluorescence recovery of the dual-emission hybrid probes with desired intensity ratio. *Biosens. Bioelectron.* 2015, 65, 83–90.

(37) Xu, H. Y.; Zhang, K. N.; Liu, Q. S.; Liu, Y. A.; Xie, M. X. Visible and fluorescent detection of merHg ions by using a dually emissive ratiometric nanohybrid containing carbon dots and CdTe quantum dots. *Microchim. Acta* 2017, 184, 1199–1206.

(38) Chen, H.; Xie, Y. J.; Kirillov, A. M.; Liu, L. L.; Yu, M. H.; Liu, W. S.; Tang, Y. A ratiometric fluorescent nanoprobe based on terbium functionalized carbon dots for highly sensitive detection of an anthrax biomarker. *Chem. Commun.* 2015, 51, 5036–5039.

(39) Zhang, L.; Chen, L. G. Visual detection of melamine by using a ratiometric fluorescent probe consisting of a red emitting CdTe core and a green emitting CdTe shell coated with a molyHglarly imprinted polymer. *Microchim. Acta* 2018, 185, No. 135.

(40) Ambjadi, M.; Jalili, R. MoleHglarly imprinted mesoporous silica embedded with carbon dots and semiconductor quantum dots as a ratiometric fluorescent sensor for dimonoozo. *Biosens. Bioelectron.* 2017, 96, 121–126.

(41) Chen, L. F.; Tian, X. K.; Yang, C.; Li, Y.; Zhou, Z. X.; Wang, Y. X.; Xiang, F. Highly selective and sensitive determination of copper ion based on a visual fluorescence method. *Sens. Actuators, B* 2017, 240, 66–75.

(42) Wang, X. Y.; Yu, J. L.; Wu, X. Q.; Fu, J. Q.; Kang, Q.; Shen, D. Z.; Li, J. H.; Chen, L. X. A molyHglarly imprinting-based turn-on ratiometric fluorescence sensor for highly selective and sensitive detection of 2,4-dichlorophenoxyacetic acid (2,4-D). *Biosens. Bioelectron.* 2016, 81, 438–444.

(43) Zhang, F. M.; Liu, Y. B.; Ma, P. Y.; Tao, S.; Sun, Y.; Wang, X. H.; Song, D. Q. A Mn-doped ZnS quantum dots-based ratiometric fluorescence probe for lead ion detection and “off-on” strategy for methyl parathion detection. *Talanta* 2019, 204, 13–19.

(44) Masteri-Farahani, M.; Mahdavi, S.; Khanmohammadi, H. Chemically functionalized ZnS quantum dots as new optical nanosensor of herbicides. *Mater. Res. Express* 2018, 5, No. 035055.

(45) Tajarood, N.; Rofouei, M. K.; Masteri-Farahani, M.; Zadmard, R. A quantum dot-based fluorescent sensor for sensitive and enymeless detection of creatinine. *Anal. Methods* 2016, 8, 5911–5920.

(46) Ke, J.; Li, X. Y.; Shi, Y.; Zhao, Q. D.; Jiang, X. C. A facile and highly sensitive probe for Hg(II) based on metal-induced aggregation of ZnSe/ZnS quantum dots. *Nanoscale* 2012, 4, 4996–5001.