Detection of Hg\(^{2+}\) by a Dual-Fluorescence Ratio Probe Constructed with Rare-Earth-Element-Doped Cadmium Telluride Quantum Dots and Fluorescent Carbon Dots

Hongtao Chu, Dong Yao, Jiaqi Chen, Miao Yu, and Liqiang Su

ABSTRACT: Quantum dots (QDs) and carbon quantum dots (CDs) are classes of zero-dimensional materials whose sizes can be ≤10 nm. They exhibit excellent optical properties and are widely used to prepare fluorescent probes for qualitative and quantitative detection of test objects. In this article, we used cerium chloride as the cerium source and used the in situ doped cerium (rare-earth element) to develop cadmium telluride (CdTe) quantum dots following the aqueous phase method. CdTe: Ce quantum dots were successfully synthesized. The solution of CdTe:Ce QDs was mixed with the CD solution prepared following the green microwave method to form a ratio fluorescence sensor that can be potentially used for the selective detection of mercury ions (Hg\(^{2+}\)). We used transmission electron microscopy, X-ray photoelectron spectroscopy, X-ray diffraction, and other microscopy and spectral characterization techniques to validate that Ce had been successfully doped. The test results on the fluorescence performance revealed that Ce doping enhances the predoped fluorescence performance of the CdTe QDs. We have quantitatively detected Hg\(^{2+}\) using a ratiometric fluorescence sensor to show that in the range of 10−60 nM, the fluorescence quenching efficiency increases linearly with the increase in Hg\(^{2+}\) concentration. The linear correlation coefficient \(R^2 = 0.9978\), and its detection limit was found to be 2.63 nM L\(^{-1}\). It was observed that other interfering ions do not significantly affect the fluorescence intensity of the probe. According to the results of the blank addition experiment, the developed proportional fluorescence probe can be used for the detection of Hg\(^{2+}\) in actual samples.

1. INTRODUCTION

Hg\(^{2+}\) is a strong carcinogen. Excessive exposure to this ion can cause adverse physiological reactions (such as vomiting, diarrhea, headache, and nausea). Prolonged exposure can lead to kidney failure, liver poisoning, and damage to the human central nervous system.\(^{1−5}\) With the advancement of industrial technology, increasing amounts of Hg\(^{2+}\) are being used, which inevitably pollute water sources and soil.\(^{6−9}\) Therefore, it is important to detect Hg\(^{2+}\) present in the environment.\(^{10−14}\) At present, atomic absorption spectroscopy, atomic fluorescence spectrometry, and inductively coupled plasma mass spectrometry (ICP-MS) techniques are used to detect Hg\(^{2+}\).\(^{15−20}\) Although these instruments are very accurate and sensitive, they are expensive and complex.\(^{21}\) These factors limit their widespread use. Developing a detection method for Hg\(^{2+}\), which involves relatively low-cost and simple instruments, is a major research focus.\(^{22−26}\)

Fluorescent probes are widely used for detection and analysis as they are simple, highly sensitive, and precise.\(^{27−30}\) Quantum dots (QDs) are tiny semiconductor materials that are widely used as fluorescent probes as they exhibit excellent optical properties. However, the toxicity of the Cd element limits the application of Cd QDs as fluorescent probes. The emergence of doped QDs has provided a barrier around this issue.\(^{31−35}\) Doped QDs have several advantages, such as high stability and the generation of the tunable emission spectrum.\(^{36−40}\) Doping transition elements to CdTe QDs or rare-earth metal ions does not only reduce the Cd content but also effectively modifies the surface defects and enhances the fluorescent properties of QDs.\(^{41−43}\) Doped QDs have a longer emission lifetime than undoped QDs.\(^{44}\) Due to their high fluorescence stability and low toxicity, carbon quantum dots (CDs) have received extensive attention in the field of fluorescent probes.\(^{45}\) CDs can be directly used as probes to interact with the target analyte or can be combined with other fluorescent probes to form a ratio fluorescent probe that can be used to detect the target analyte. The ratio fluorescent probe combines two fluorescent materials
with different emission wavelengths. The ratio of the intensity of the two fluorescent materials is linearly related to the concentration of the target analyte. It is a detection method with strong anti-interference ability. An internal standard is established, and the ratio fluorescent probe exhibits a self-regulating function that reduces the interference from other factors to obtain more accurate data.

In this paper, CdTe QDs are doped with rare-earth Ce ions to form CdTe:Ce QDs, which reduce the content of Cd on the one hand and enhance the emission peak intensity of CdTe QDs on the other. The solution of CdTe:Ce QD and the solution of CD are mixed to produce the dual-emission ratio fluorescence sensor that can be used for the selective detection of Hg²⁺ in the solution. Dual-emission ratio fluorescent probes can effectively reduce the influence of excitation light and concentration changes and improve the ability of the probe to resist interference. We have thoroughly studied the interaction mechanism of CdTe:Ce QDs with Hg²⁺ and applied the probe to determine the amount of Hg²⁺ present in tap water. QDs are widely used for heavy metal ion detection. However, the traditional Cd-based QDs exhibit a high Cd content, which reduce the in...

2. CDTE: CHARACTERIZATION OF CE QDS

2.1. CdTe: Fluorescence Characterization of Ce QDs. Figure 1 shows the fluorescence spectra recorded with CdTe QDs and CdTe:Ce QDs. At an excitation wavelength of 300 nm, the concentrations of CdTe QD and CdTe:Ce QD solutions are similar. The fluorescence emission peak intensity of CdTe:Ce QDs is significantly higher than that of the undoped compound. Ce doping minimizes the surface defects of CdTe QDs, fills the trap state, and enhances the radiation rate. The fluorescence intensity of CdTe:Ce QDs is observed to be higher than that of CdTe QDs. It also helps reduce the Cd content in the QDs, thereby reducing the quantum dot toxicity.

2.2. Characterization of CdTe:Ce QDs Using X-ray Photoelectron Spectroscopy (XPS) Technique. We used the X-ray photoelectron spectroscopy technique to determine the elemental composition of CdTe:Ce QDs. Characteristic peaks corresponding to the rare-earth Ce were observed (Figure 2A). This proved the successful doping of Ce. Ce 3d was split into two peaks: Ce 3d₃/₂ (904.08 eV) and Ce 3d₅/₂ (886.08 eV). Te 3d was split into four peaks: Te 3d₃/₂ (582.68 eV), Te 3d₅/₂ (576.08 eV), and Te 3d₃/₂ (572.28 eV). Cd 3d was split into two peaks: Cd 3d₅/₂ (411.78 eV) and Cd 3d₃/₂ (404.98 eV). Cd doping was proved when the combined Te and Ce energy was analyzed. The results indicate that simple mixing or coating does not occur.

2.3. X-ray Diffraction (XRD) Patterns Recorded for CdTe:Ce QDs. Figure 3 shows that the CdTe:Ce QDs exhibit three major diffraction peaks. The diffraction angles were recorded to be 24.56, 40.04, and 47.46⁰, which corresponded to the (111), (220), and (311) crystal planes, respectively. Thus, the successful synthesis of CdTe:Ce QDs was proved. The XRD patterns of CdTe:Ce QDs and CdTe QDs were compared, and it was observed that the doping of Ce elements did not hamper the structure of the CdTe QDs.

2.4. Characterization of the Samples Using Transmission Electron Microscopy (TEM) Technique. Figure 4 shows the TEM images of CdTe:Ce QDs. The images revealed that the particle sizes of the CdTe:Ce QDs were approximately 4 nm. It can be seen from the figure that the samples exhibited good dispersibility properties and were uniform in size.

3. CHARACTERIZATION OF CDS

3.1. Fluorescence Characterization of CDS. Figure 5 shows the fluorescence spectrum of CDS. Under the excitation wavelength of 300 nm, the emission peak of the fluorescent probe exhibits a self-regulating ability. Ions that make up the crystal are preferentially adsorbed. The fluorescence intensity of CDS is linearly related to the concentration of target analyte. It is a detection method with strong anti-interference ability. An internal standard is established, and the ratio fluorescent probe exhibits a self-regulating function that reduces the interference from other factors to obtain more accurate data.

3.2. X-ray Photoelectron Spectroscopy (XPS) Technique for the Characterization of CDS. We used the XPS technique to analyze the elemental composition of the CDs. Figure 6 reveals that the CDs are composed of three elements: C, N, and O. Figure 6B reveals that the high-resolution XPS spectrum of C 1s consists of three peaks, namely, C-≡C (284.6 eV), C≡N (285.4 eV), and C≡O (289.0 eV). Figure 6C reveals three fitting peaks in the N 1s high-resolution XPS spectrum. This indicates that they are primarily present in the form of CNC (398.3 eV), CN (399.7 eV), and NH (400.1 eV). The high-resolution energy spectrum of O 1s reveals that there are C-OH (531.2 eV) and C-O (533.2 eV) bonds in the CDs (Figure 6D).

3.3. Characterization of C QDs and CdTe/C QDs Using the Hybrid Transmission Electron Microscopy Technique. Figure 7 shows the TEM images of the CDs and CdTe/C QDs. It could be seen from the figure that the particle size of CDs was approximately 5 nm. When CdTe/C QDs and CDs were mixed, the morphology was not hampered and uniform dispersion was achieved.

4. RESULTS AND DISCUSSION

4.1. Effect of Hg²⁺ on the Ratio Fluorescent Probe Composed of CdTe:Ce QDs and CDS. We found that Hg²⁺ could significantly quench the fluorescence intensity of the CdTe:Ce QDs (quenching of the peak intensity at 599 nm; Scheme 1). This ion exerted little effect on the fluorescence peak at 445 nm corresponding to the CDs. According to the Fajans rule, ions that can form insoluble or insoluble substances with the ions that make up the crystal are preferentially adsorbed. The solubility product of HgS was significantly smaller than that of

Figure 1. CdTe:Ce QD fluorescence spectrum and CdTe QD fluorescence spectra.
CdS, indicating that CdTe:Ce preferentially adsorbs Hg$^{2+}$. A part of CdS was converted to HgS, which caused MPA to change from CdTe:Ce quantum. The dot surface falls off under these conditions, resulting in a decrease in the fluorescence intensity. Thus, fluorescence quenching was observed. The ion did not exert a significant effect on the fluorescence intensity of the carbon dots. The relationship between the fluorescence quenching efficiency of the ratio fluorescent probe composed of the CdTe:Ce QDs and CDs and the concentration of Hg$^{2+}$ was studied. A ratio fluorescence sensor was proposed for the detection of Hg$^{2+}$. Other interfering ions did not significantly impact the fluorescence intensity of the fluorescent probe sensor composed of CdTe:Ce QDs and CDs. This indicated that the sensor was selective toward Hg$^{2+}$.

A ratio fluorescence probe sensor composed of CdTe:Ce QDs and CDs was used to quantitatively detect Hg$^{2+}$. The experimental conditions were optimized (including the pH value of the ratio fluorescence probe sensor solution and the ratio fluorescence probe). Conditions such as the reaction time of the needle sensor and Hg$^{2+}$ were also optimized. The method is simple and has a strong anti-interference ability. This method can be popularized.

4.2. Effect of Ce Doping on the Synthesis of CdTe:Ce QDs. The introduction of the doped rare-earth element Ce usually does not change the specific lattice structure of the bulk quantum dots. However, interference effect on the electronic energy level of the bulk was observed, and new electronic energy levels were generated. The characteristics of the quantum dots were improved. It was observed that the maximum fluorescence intensity of the quantum dots was achieved under conditions of $n$(Cd):$n$(Ce) = 1:0.2 (Figure 8). The ratio of Cd to Ce was selected to be 1:0.2 for the synthesis of CdTe:Ce.

4.3. Effect of pH on the Ratio of CdTe:Ce QDs and CDs to Fluorescent Probes. Different pH buffer solutions exerted different effects on the fluorescence intensity of the ratio fluorescent probe sensor. Figure 9 depicts the effect of pH (pH = 5–9) on the CdTe:Ce QDs and CDs in the presence and absence of Hg$^{2+}$. The effect of ratio fluorescence probe fluorescence. It can be seen from the figure that the ratio fluorescent probe composed of the same concentration of CdTe:Ce QDs and CDs exhibit the maximum fluorescence intensity.
intensity when the pH is 7. Significant fluorescence quenching was observed when Hg\(^{2+}\) was added. Therefore, Hg\(^{2+}\) was added at pH 7 for conducting the tests.

4.4. Determination of the Reaction Time for the Reaction between Hg\(^{2+}\) and the Ratio Fluorescent Probe System. The effect of reaction time on the ratio of fluorescence intensity of fluorescent probes was studied at room temperature, and the results are shown in Figure 10. Experimental results show that the ratio of fluorescence intensity to the fluorescent probe decreases rapidly in the presence of Hg\(^{2+}\) and reached equilibrium after 5 min. The ratio of fluorescence intensity can be stable for 30 min. Therefore, the reaction time of this experiment was selected as 5 min.

4.5. CdTe: The Ratio of Ce QDs to CDs Constitutes the Anti-interference Ability of the Fluorescent Probe Sensors. The fluorescence intensity of the probe was significantly reduced in the presence of 60 nM of Hg\(^{2+}\). The concentrations of the other interfering ions at 60 nM caused a very slight change in the fluorescence intensity ratio (Figure 11). This result indicated that the fluorescent probe (ratio) was selective toward Hg\(^{2+}\). The effect of fluorescence quenching of the ratio fluorescent probe under the coexistence of some interfering ions and Hg\(^{2+}\) was further studied. As shown in the figure, even if Hg\(^{2+}\) coexisted with interfering ions, the ratio fluorescent probe could still selectively detect Hg\(^{2+}\).

4.6. CdTe:Ce QDs and CDs to Detect Hg\(^{2+}\) by Ratio Fluorescent Probe. We observed that the fluorescence intensity of the CdTe:Ce QDs gradually decreased under conditions of varying Hg\(^{2+}\) concentrations. As shown in Figure 12, the fluorescence quenching efficiency \(\left(\frac{F_{445}}{F_{599}}\right) - \frac{F_{445}}{F_{599}}\) linearly increased with the Hg\(^{2+}\) concentration in the range of 10\(^{-6}\)–60 nM. The linear equation used was \(\frac{F_{445}}{F_{599}} = 0.0292C - 0.0515\), and the correlation coefficient \(R^2\) was 0.9978. \(\frac{F_{445}}{F_{599}}\) represents the ratio of the fluorescence intensity in the absence of Hg\(^{2+}\). \(\frac{F_{445}}{F_{599}}\) represents the ratio of fluorescence intensity in the presence of Hg\(^{2+}\). The detection limit (LOD = 3\(\sigma\) \(K^{-1}\)) was 2.63 nM L\(^{-1}\). The present detection method was compared with the Hg\(^{2+}\) detection methods developed using the state-of-the-art research technique. Our dual-emission ratio fluorescence sensor composed of CdTe:Ce QDs, CDs can detect low levels of Hg\(^{2+}\) and can reduce the toxicity of CdTe QDs to a certain extent. The sensor can reduce the influence of other interference factors, thereby improving the accuracy of the probe.

4.7. Blank Spike Recovery Experiment. A ratio fluorescent probe composed of CdTe:Ce QDs and CDs was used to detect the Hg\(^{2+}\) levels in water (Table 1). The results are shown in the table. The sample recovery rate was 91–114%, and the relative standard deviation (RSD) was less than 10%. This indicates that the accuracy and precision of the established method for the detection of Hg\(^{2+}\) in an actual sample.

4.8. Selective Detection of Hg\(^{2+}\) Using Fluorescent Probe Sensors: Use of CdTe:Ce QDs and CDs. It can be hypothesized that Hg\(^{2+}\) destroys the Cd–S bond formed by Cd and 3-MPA and quenches the fluorescence of CdTe:Ce QDs.\(^{51-54}\) As the formation of metal sulfides is determined by their \(K_{sp}\) value, the \(K_{sp}\) value can potentially be a key factor to determine the extent of fluorescence quenching (of quantum dots) in the presence of metal ions.\(^{65-69}\) The \(K_{sp}\) value of the Hg–S bond (6.3 \(\times\) \(10^{-36}\)) was much smaller than the \(K_{sp}\) value of Cd–S (8.0 \(\times\) \(10^{-27}\)).\(^{66}\) When Hg\(^{2+}\) was added to the vector dot solution, Hg\(^{2+}\) combined with S in MPA and replaced Cd. Thus, fluorescence fragmentation could be achieved.
5. CONCLUSIONS

In short, quantum dots doped with CdTe:Ce quantum dots were synthesized following the hydrothermal method. They were mixed with carbon dots synthesized following the microwave method to form a ratio fluorescent probe for the quantitative determination of Hg$^{2+}$. The Hg$^{2+}$ can effectively quench the fluorescence of CdTe:Ce quantum dots without significantly affecting the fluorescence intensity of the carbon dots. A dual-emission ratio fluorescence sensor with CdTe:Ce quantum dots and carbon dots was developed to quantitatively
detect Hg$^{2+}$. When Ce quantum dots were mixed with CDs, fluorescent probes exhibiting strong anti-interference properties were produced. This ratio fluorescent probe exhibited a good fluorescence response to low concentrations of Hg$^{2+}$ and can be used for sensitive and selective detection of low concentrations of Hg$^{2+}$. Several detection conditions have been optimized. Selectivity and interference experiments were carried out to explore the selectivity of the fluorescent probes. The results showed that the selectivity of the probe was very good. The linear range of detection was 10$^{-6}$ - 60 nM, and the LOD was 2.63 nM L$^{-1}$. The mixed ratio fluorescent probe can be synthesized following a simple method that is convenient to operate. The probe can be used for the detection of Hg$^{2+}$ in actual water samples. Finally, the mechanism of fluorescence fracture has been discussed.

6. EXPERIMENTAL SECTION

6.1. Experimental Materials. The chemicals used were Te (analytically pure), NaBH$_4$ (analytically pure), CdCl$_2$ (analytically pure), C$_3$H$_6$O$_2$S (analytically pure), CeCl$_3$ (analytically pure), and H$_2$O.

Figure 8. Selection of rare-earth element Ce doping content.

Figure 9. Fluorescence responses of the ratio fluorescence sensor in the absence and presence of Hg$^{2+}$ at different pH values.

Figure 10. Determination of the reaction time of Hg$^{2+}$ and ratio fluorescent probe system.
pure), NaOH (analytically pure), C₃H₆O₂ (analytically pure), CH₄N₂O (analytically pure), CH₃CH₂OH, HgSO₄, Cd(CH₃COOH)₂ (analytically pure), FeCl₃ (analytically pure), Ca(NO₃)₂ (analytically pure), Pb(NO₃)₂ (analytically pure), CoCl₂ (analytically pure), AlCl₃, Zn(NO₃)₂·6H₂O, CuSO₄·SH₂O (analytically pure), MnCl₂ (analytically pure), Na₂HPO₄ (analytically pure), NaSO₄ (analytically pure), NaNO₃ (analytically pure), KCl (analytically pure), Na₂CO₃ (analytically pure), and CH₃COONa (analytically pure).

6.2. Experimental Instrument. The instruments used were fluorescence spectrometer (Shimadzu), X-ray photoelectron spectrum analyzer (Shimadzu), X-ray diffractometer (malvern-panalytical), and transmission electron microscope (FEI).

6.3. Preparation of NaHTe Precursor. Tellurium powder (0.06 g) and 10 mL of ultrapure water were added to a three-necked flask. After deoxygenating with nitrogen, 0.04 g of NaBH₄ was added and the mixture stirred and heated at 80 °C for 30 min to obtain the NaHTe precursor.

6.4. Preparation of CdTe:Ce QDs. In a 250 mL three-necked flask, 0.55 g of CdCl₂ was dissolved in 100 mL of deionized water, N₂ was passed to remove oxygen, 0.08 g of mercaptopropionic acid was added, and 1.0 mol L⁻¹ NaOH solution was used to adjust the pH to 11.8 to obtain the Cd precursor. The newly prepared NaHTe aqueous solution was added to the CdCl₂ solution under the protection of N₂, and the color of the solution became orange and then transparent. The prepared mixture was heated under the reflux, and 10 mL of CeCl₃ solution of different concentrations was added to synthesize CdTe:Ce QDs doped with different concentrations of the rare-earth element Ce.

Table 1. Determination of Hg²⁺ in Real Samples (n = 3)

| sample          | spiked (nM) | found (nM) | recovery (%) | RSD (%) |
|-----------------|-------------|------------|--------------|---------|
| purified water  | 10.0        | 11.4       | 114          | 5.2     |
|                 | 20.0        | 18.2       | 91           | 6.4     |
|                 | 30.0        | 32.4       | 108          | 3.5     |
|                 | 40.0        | 42.6       | 106          | 7.1     |
|                 | 50.0        | 47.7       | 95           | 8.3     |
|                 | 60.0        | 57.9       | 97           | 4.6     |
6.5. Preparation of Carbon Dots. The citric acid (1.5 g) and 1.5 g of urea were weighed and 5 mL of ultrapure water was added for ultrasonic dissolution; the mixture was heated by microwave heating for 10 min at a power of 1 kW and then for 10 min; 50 mL of ultrapure water was added, dissolved again by ultrasonication, centrifuged at high speed, and the supernatant taken. The solution was diluted to obtain the required cyan carbon dot solutions (CDs).

6.6. Preparation of Mixed CdTe QDs and CDs. CdTe QDs solution (9.7 mL) was mixed with 0.3 mL of carbon dot solution to obtain mixed QD-CdTs and CDs.

6.7. Detection of Hg²⁺. We prepared a CdTe:Ce QD suspension with a concentration of 0.8 g L⁻¹ in the PBS buffer with pH 7, added the same volume of CdTe:Ce QDs solution (9.8 mL) to the test tube, and then added it to each test tube. We added 100 µL of Hg²⁺ solution of different concentrations to each test tube. The reaction was mixed at room temperature for 5 min, and the fluorescence emission spectrum was recorded at an excitation wavelength of 300 nm.

6.8. Interference Experiment. In the water phase, we added interfering ions with a concentration of Hg²⁺ 10 times to the ratio fluorescent probe system and measured the fluorescence.

6.9. Detection of Hg²⁺ in Actual Samples. The actual sample comes from tap water in the laboratory, and the specific determination method is the same as the operation step 1 in Section 6.5.

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Notes
The authors declare no competing financial interest.

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