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The behaviors of metal ions in the CdTe quantum dots–H_2O_2 chemiluminescence reaction and its sensing application

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ABSTRACT: The behaviors of 15 kinds of metal ions in the thiol-capped CdTe quantum dots (QDs)–H_2O_2 chemiluminescence (CL) reaction were investigated in detail. The results showed that Ag^+, Cu^{2+} and Hg^{2+} could inhibit CdTe QDs and H_2O_2 CL reaction. A novel CL method for the selective determination of Ag^+, Cu^{2+} and Hg^{2+} was developed, based on their inhibition of the reaction of CdTe QDs and H_2O_2. Under the optimal conditions, good linear relationships were realized between the CL intensity and the logarithm of concentrations of Ag^+, Cu^{2+} and Hg^{2+}. The linear ranges were from 2.0×10^{-6} to 5.0×10^{-8} mol L^{-1} for Ag^+, from 5.0×10^{-6} to 7.0×10^{-8} mol L^{-1} for Cu^{2+} and from 2.0×10^{-5} to 1.0×10^{-7} mol L^{-1} for Hg^{2+}, respectively. The limits of detection (S/N = 3) were 3.0×10^{-8}, 4.0×10^{-8} and 6.7×10^{-8} mol L^{-1} for Ag^+, Cu^{2+} and Hg^{2+}, respectively. A possible mechanism for the inhibition of CdTe QDs and H_2O_2 CL reaction was also discussed. Copyright © 2009 John Wiley & Sons, Ltd.

Keywords: quantum dots; chemiluminescence; inhibition effect; metal ions

Introduction

Chemiluminescence (CL) is the generation of electromagnetic radiation as light by the release of energy from a chemical reaction (1, 2). Compared with fluorescence (FL) analysis, CL analysis has some excellent advantages, such as high sensitivity, wide linear range, simple instrumentation and no interference from background scattering light (3, 4). As a kind of novel CL and electrogenerated chemiluminescence (ECL) material, quantum dots (QDs), also known as semiconductor nanocrystals, have attracted considerable attention in recent years (5–8). The CL of QDs displays size-dependent effects and its intensity increases with increasing size of the QDs. The CL emission spectra are directly controlled by the size and composition of the QDs (9, 10). In addition, QDs have a good biocompatibility and can be linked easily to some biomacromolecules such as protein and DNA (10). Therefore, QDs have potential advantages in the CL analysis compared with commercial CL materials such as luminol, lucigenin and tris(2,2-bipyridyl)ruthenium(II). In 2002, Bard's group first reported the ECL of Si QDs in organic media (11). Subsequently, Zou *et al.* developed a H_2O_2 ECL sensor by depositing CdSe QDs on a paraffin-impregnated graphite electrode (12). Recently, our group investigated the direct ECL of water-soluble QDs, which have been applied to detect pyrogallol and hydrogen peroxide in aqueous solution (13, 14).

In comparison with ECL of QDs, there are few reports concerning CL of QDs, especially in analytical applications (15). In addition, previous studies revealed that the use of QDs as a novel luminophor has some potential advantages in CL analysis, such as high sensitivity, simple instrumentation and ease of multicolor labeling. Therefore, the investigation of analytical applications of QD CL is of interest.

In the present work, thiol-capped CdTe QDs as a novel CL emitter were used in metal ion analysis. The behaviors of 15 kinds of metal ions in the CdTe QDs–H_2O_2 CL reaction were studied and a novel inhibition CL method for the selective determination of Ag^+, Cu^{2+} and Hg^{2+} using the reaction of CdTe QDs and H_2O_2 was developed. Under the optimal conditions, relatively wide linear range, low detection limits and rapid response to metal ions were obtained. A possible mechanism for the inhibition of thiol-capped CdTe QDs CL reaction was also proposed.

Experimental

Reagents and chemicals

Tellurium powder (99.9%) and $NaBH_4$ (96%) were obtained from Shanghai Chemical Reagent Co. Ltd. Thioglycolic acid (TGA, 90%), KCl (99.8%), NaCl (99.5%), $AgNO_3$ (99.0%), $CdCl_2{\cdot}2.5H_2O$ (99.0%), $MgCl_2$ (98%), $CuSO_4{\cdot}5H_2O$ (99%), $MnSO_4{\cdot}H_2O$ (99%), $Zn(NO_3)_2{\cdot}6H_2O$ (99%), $CoCl_2{\cdot}6H_2O$ (99%), $CaCl_2{\cdot}2H_2O$ (98%), $BaCl_2{\cdot}2H_2O$ (99.5%), $FeCl_2{\cdot}2H_2O$ (99%), $FeCl_3{\cdot}6H_2O$ (99%), $HgCl_2$ (99%) $CrCl_3{\cdot}6H_2O$ (99%) and Na_2TeO_3 (99%) were obtained from Sinopharm Chemical Reagent Co. Ltd. Milli-Q water was used throughout the experiments. All other chemical reagents were of analytical grade and were used without further purification.

Apparatus

The CL signals were detected and recorded with a BPCL-Ultra-Weak Luminescence Analyzer (Beijing, China). The absorption spectra were acquired on a Thermo Nicolet Corporation Model evolution 300 UV–vis spectrometer. The FL spectra were acquired using a Perkin Elmer Model LS-55 luminescence spectrometer. The transmission electron microscopy (TEM) image of the CdTe QDs was acquired on an H-7650 TEM (Japan). The pH measurements were made using a model pHS-3C meter (Shanghai Leici Equipment Factory, China).

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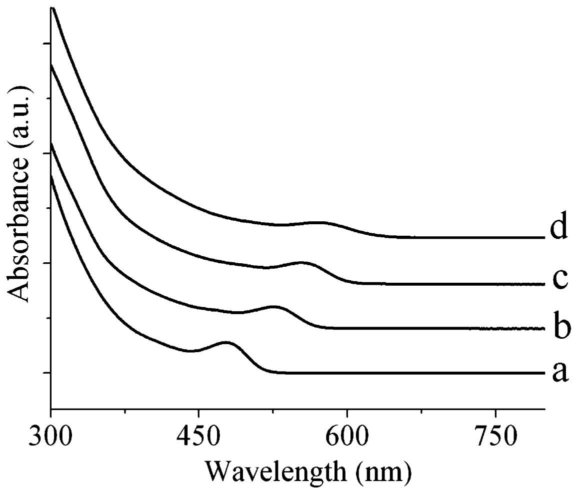

Figure 1. The absorption spectra of thiol-capped CdTe QDs with different sizes: (a) 1.56 nm, (b) 2.88 nm, (c) 3.28 nm, (d) 3.42 nm.

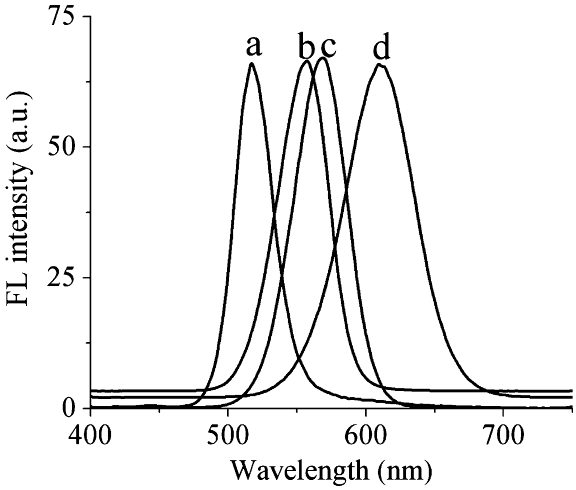

Figure 2. The FL spectra of thiol-capped CdTe QDs with different sizes: (a) 1.56 nm, (b) 2.88 nm, (c) 3.28 nm, (d) 3.42 nm. Excitation wavelength, 380 nm.

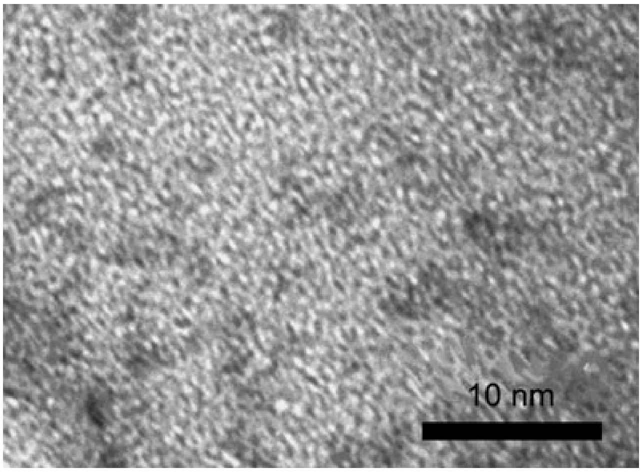

Figure 3. TEM image of thiol-capped CdTe QDs.

Procedure

Thiol-capped CdTe QDs were synthesized via the hydrothermal route with some modifications (16, 17). In a typical synthesis procedure, $CdCl_2$ (10 mL, 0.01 mol L^{-1}) and TGA were dissolved in 35 mL of water followed by adjustment to pH 10 under N_2 atmosphere. Then, trisodium citrate dehydrate (60 mg), Na_2TeO_3 (1.7 mL, 0.01 mol L^{-1}) and $NaBH_4$ (50 mg) were added with stirring. When the color of the solution had changed to yellow, it was put into a Teflon-lined stainless steel autoclave with a volume of 50 mL. The autoclave was maintained at 180°C for different times to control the size of the CdTe QDs and then cooled to room temperature. The resulting products were precipitated with acetone and centrifuged. Finally, the precipitate was dissolved in phosphate-buffered saline (PBS) (0.1 mol L^{-1}, pH = 7.4).

The as-prepared thiol-capped CdTe QDs were charactered by absorption spectra (Fig. 1), FL spectra (Fig. 2) and TEM (Fig. 3). The particle diameters of the CdTe QDs were 1.56, 2.88 and 3.42 nm, respectively, and were calculated as follows (18):

$$D = (9.8127 \times 10^{-7})\lambda^3 - (1.7147 \times 10^{-3})\lambda^2 + (1.0064)\lambda - (194.84)$$

where λ (nm) is the wavelength of the first excitonic absorption peak of the CdTe QDs, which can be obtained using UV–vis absorption spectrum. Owing to the quantum confinement, the absorption and FL spectra of thiol-capped CdTe QDs were shifted to the longer wavelength with increasing size of the QDs (19). As shown in Fig. 3, the size of the prepared CdTe QDs was about 3.5 nm, which is consistent with the calculated result (3.42 nm) according to the UV–vis absorption spectrum.

A 0.04 mL aliquot of thiol-capped CdTe QDs or the mixed solution of thiol-capped CdTe QDs and metal salt solution was injected into the mixture solution of NaOH and H_2O_2, and the average value of CL signals determined from five parallel measurements using a BPCL analyzer.

Results and discussion

Properties of CdTe QDs–H_2O_2 CL reaction

Hydrogen peroxide could directly oxidize thiol-capped CdTe QDs to produce strong CL emission in basic conditions. As shown in Fig. 4, the CL spectra of the QD–H_2O_2 reaction show a size-dependent property. With the increasing size of CdTe QDs, the CL spectrum is red-shifted. In addition, the CL intensity is closely related to the sizes of thiol-capped CdTe QDs. Figure 5 depicts CL kinetic curves of different sizes of CdTe QDs. It was found that CdTe QDs–H_2O_2 CL reaction proceeded very quickly. Moreover, the relative CL intensity was enhanced with the increasing size of CdTe QDs, which can be explained by CL energy match theory. The more energy matched the degree between the chemical energy generated during CL redox reaction and the required excitation energy for the formation of excited state of luminophor, the stronger the CL intensity was (18). Therefore, 3.42 nm CdTe QDs was used in the subsequent experiments.

Optimization of thiol-capped CdTe QDs–H_2O_2 CL system

The reaction conditions were optimized as follows: the concentration of CdTe QDs was linear with the CL intensity ranging from 1.0×10^{-7} to 8.0×10^{-7} mol L^{-1} (linear equation: $y = 101.6 + 88.3x$). Taking account of the consumption of CdTe QDs, 4.0×10^{-7} mol L^{-1} of CdTe QD solution was chosen in the following experiments.

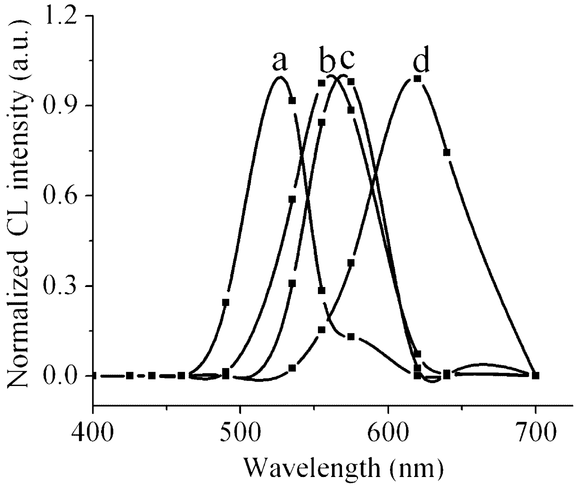

Figure 4. The CL spectra of thiol-capped CdTe QDs with different sizes: (a) 1.56 nm, (b) 2.88 nm, (c) 3.28 nm, (d) 3.42 nm. Conditions: 8.0×10^{-7} mol L^{-1} CdTe QD solution, 0.3 mol L^{-1} NaOH solution, 1.1 mol L^{-1} H_2O_2, high voltage 800 V.

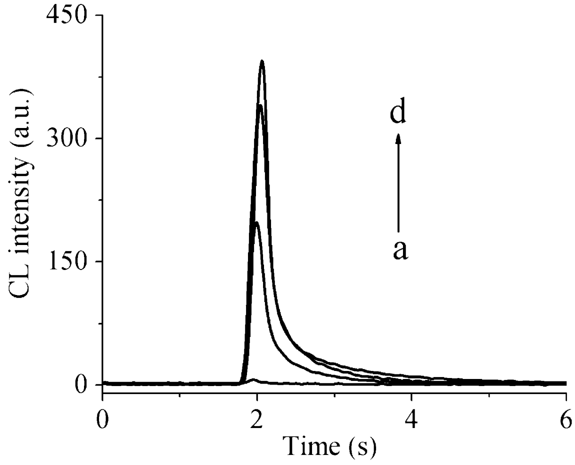

Figure 5. The CL kinetic curves of different sizes of CdTe QDs and H_2O_2 CL reaction. Conditions: 40 μL, 4.0×10^{-7} mol L^{-1} CdTe QDs with a particle size of around 1.56 nm (a), 2.88 nm (b), 3.28 nm (c) and 3.42 nm (d) were injected into a mixture of H_2O_2 (1.1 mol L^{-1}) and NaOH (0.3 mol L^{-1}). High voltage: 600 V.

The effect of NaOH concentration on the relative CL intensity was investigated, ranging from 0.1 to 0.6 mol L^{-1}. The optimized NaOH concentration for CdTe QDs–H_2O_2 CL system was 0.3 mol L^{-1}. The effect of H_2O_2 concentration on the relative CL was studied in the range 0.9–1.3 mol L^{-1}, the relative CL intensity increased with increasing H_2O_2 concentration in the range 0.9–1.1 mol L^{-1} and obvious changes in light intensity were observed when the H_2O_2 concentration was larger than 1.1 mol L^{-1}. The concentration of 1.1 mol L^{-1} H_2O_2 was chosen in the following experiments.

The behaviors of 15 kinds of metal ions in the CdTe QDs–H_2O_2 CL reaction

Under the optimum experimental conditions described above, the behaviors of 15 kinds of metal ions in the CdTe QDs–H_2O_2 CL reaction were investigated in detail (Table 1). It was found that K^+ and Na^+ had no obvious effect on the CL intensity of CdTe QDs–H_2O_2 reaction system. However, Ag^+ had an evident restraining effect on the CL reaction of CdTe QDs and H_2O_2. Among the different divalent metal ions, only Cu^{2+} and Hg^{2+} caused a significant decrease in CL intensity of CdTe QDs–H_2O_2 reaction system, while the other metal ions did not produce any noticeable effect (relative error <±5%). The behaviors of trivalent metal ions (Fe^{3+} and Cr^{3+}) in the CdTe QDs–H_2O_2 reaction system were similar to Mg^{2+} and Ba^{2+}. Hence, the CdTe QDs–H_2O_2 CL reaction could be used to detect Ag^+, Cu^{2+} and Hg^{2+}.

Calibration and sensitivity

Under the optimal conditions, the relative CL intensity ($\Delta I = I_0 - I$) was log–linear with Ag^+, Cu^{2+} and Hg^{2+} concentrations in the ranges 2.0×10^{-6} to 5.0×10^{-8}, 5.0×10^{-6} to 7.0×10^{-8} and 2.0×10^{-5} to 1.0×10^{-7} mol L^{-1}, respectively (Table 2). The experimental detection limits were 3.0×10^{-8} mol L^{-1} for Ag^+, 4.0×10^{-8} mol L^{-1} for Cu^{2+} and 6.7×10^{-8} mol L^{-1} for Hg^{2+}. In comparison with the luminol–H_2O_2 CL system, the thiol-capped CdTe QDs–H_2O_2 CL system had higher selectivity for the determination of metal ions.

Table 1. Effects of 15 kinds of metal ions on the CL intensity of CdTe–H_2O_2 CL reaction[a]

Metal ions	I	I/I_0	Metal ions	I	I/I_0
Blank	473		Ba^{2+}	482	1.02
K^+	465	0.983	Mg^{2+}	466	0.985
Na^+	465	0.983	Mn^{2+}	461	0.975
Ag^+	200	0.423	Co^{2+}	480	1.02
Ca^{2+}	466	0.985	Hg^{2+}	347	0.734
Fe^{2+}	468	0.989	Cu^{2+}	296	0.656
Zn^{2+}	467	0.987	Fe^{3+}	464	0.981
Cd^{2+}	483	1.02	Cr^{3+}	489	1.03

[a] The percentage of restraining CdTe–H_2O_2 CL reaction was calculated as I/I_0. The blank CL signal I_0 obtained by CdTe QDs–H_2O_2 CL reaction without metal ions was 473. The concentration of K^+ and Na^+ was 1.0×10^{-4} mol L^{-1}. The concentration of Ca^{2+}, Mg^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Fe^{2+}, Mn^{2+}, Ba^{2+}, Fe^{3+} and Cr^{3+} was 1.0×10^{-5} mol L^{-1}. The concentration of Ag^+, Cu^{2+} and Hg^{2+} was 1.0×10^{-6} mol L^{-1}.

Detection metal ions in simulated samples

In order to verify the practical application of the proposed method, three simulated samples were prepared with appropriate amounts of some foreign species. Sample 1 contained 1.0×10^{-7} mol L^{-1} Ag^+ and 1.0×10^{-5} mol L^{-1} K^+, Na^+, Zn^{2+}, Mg^{2+}, Ca^{2+} and Ba^{2+}; sample 2 contained 5.0×10^{-7} mol L^{-1} Cu^{2+} and 1.0×10^{-5} mol L^{-1} K^+, Na^+, Zn^{2+}, Mg^{2+}, Ca^{2+} and Ba^{2+}; while sample 3 contained 1.0×10^{-6} mol L^{-1} Hg^{2+} and 1.0×10^{-5} mol L^{-1} K^+, Na^+, Zn^{2+}, Mg^{2+}, Ca^{2+} and Ba^{2+}. The results of the determination are given in Table 3. The relative standard deviations less than 7.4% and the recoveries between 105% and 108% were highly satisfactory and illustrated the good performance of the proposed method.

Table 2. Analytical performance of the proposed CdTe QDs–H_2O_2 CL reaction

	Linear range (mol L^{-1})	Equation of linear regression (C, mol L^{-1})	Related coefficient	Detection limit (S/N = 3 mol L^{-1})
Ag^+	2.0×10^{-6}–5.0×10^{-8}	$\Delta I = 979.8 + 123.3 \lg C$	0.9973	3.0×10^{-8}
Cu^{2+}	5.0×10^{-6}–7.0×10^{-8}	$\Delta I = 693.5 + 86.1 \lg C$	0.9996	4.0×10^{-8}
Hg^{2+}	2.0×10^{-5}–1.0×10^{-7}	$\Delta I = 522.3 + 66.0 \lg C$	0.9907	6.7×10^{-8}

Table 3. Determination results of simulated samples ($n = 11$)

Analyte	Added (mol L^{-1})	Foreign ions (1.0×10^{-5} mol L^{-1})	Found (mol L^{-1})	Recovery (%)	RSD (%)
Sample 1	1.0×10^{-7}	K^+, Na^+, Zn^{2+}, Mg^{2+}, Ca^{2+}, Ba^{2+}	1.07×10^{-7}	107	7.4
Sample 2	5.0×10^{-7}		5.4×10^{-7}	108	5.9
Sample 3	1.0×10^{-6}		1.05×10^{-6}	105	6.2

A possible mechanism for the inhibition of CdTe QDs–H_2O_2 CL reaction

The CL process of CdTe QDs can be mainly divided into three steps in the presence of H_2O_2 (8). To begin with, the superoxide radical (O_2^-) and hydroxyl radical (OH·) were produced under TGA and H_2O_2 existed condition [reactions (1) and (2)]. Then, the superoxide radical injected an electron into the $1S_e$ quantum-confined orbital of CdTe QDs [reaction (3)]. Meanwhile, the hydroxyl radical (OH·) injected a hole into the $1S_h$ quantum-confined orbital of CdTe QDs [reaction (4)]. Finally, the CL emission was produced by the exciton reaction [reaction (5)]:

$$O_2 + 2TGA + 4OH^- \rightarrow 2O_2^- + 2TGA^- + 2H_2O \tag{1}$$

$$O_2^- + H_2O_2 \rightarrow 2OH\cdot + 1O_2 \tag{2}$$

$$O_2^- + CdTe \rightarrow CdTe(e^-_{1se}) \tag{3}$$

$$OH\cdot + CdTe \rightarrow CdTe(h^+_{1sh}) \tag{4}$$

$$CdTe(e^-_{1se}) + CdTe(h^+_{1sh}) \rightarrow (CdTe\ QDs)^* \rightarrow h\nu \tag{5}$$

When the Ag^+, Cu^{2+} and Hg^{2+} were added to the CdTe QD solution, the electron transferred from $1S_e$ quantum-confined orbital of CdTe QDs to metal ions during the CL process. The exciton reaction [reaction (5)] was inhibited, and the CL intensity of CdTe QDs and H_2O_2 reaction was decreased. The FL data favor that transfer process. As shown in Fig. 6, the FL spectrum of CdTe QDs was red-shifted and light intensity was significantly decreased in the presence of Cu^{2+}. The results are similar to previous reports, and the reason may be electron transfer from the $1S_e$ quantum-confined orbital of CdTe QDs to metal ions (20–22). The experimental phenomena of Ag^+ and Hg^{2+} were similar to those of Cu^{2+}. It is well know that the difference between CdTe QDs CL and FL is the way of generating the excited state. However, the CL process of CdTe QDs is the same as the FL process. That is to say, the light emission was produced by the exciton reaction [reaction (5)]. Therefore, electron transfer from $1S_e$ quantum-confined orbital of CdTe QDs to metal ions is possible. Excluding Ag^+, Cu^{2+} and Hg^{2+}, the other 12 kinds of metal ions had little effect on the CL intensity of CdTe QDs and H_2O_2 reaction, which may be ascribed to the variation in ion strength of the solution. Owing to the complexity of the inhibition of the CdTe QDs–H_2O_2 CL reaction, further research is underway in this laboratory.

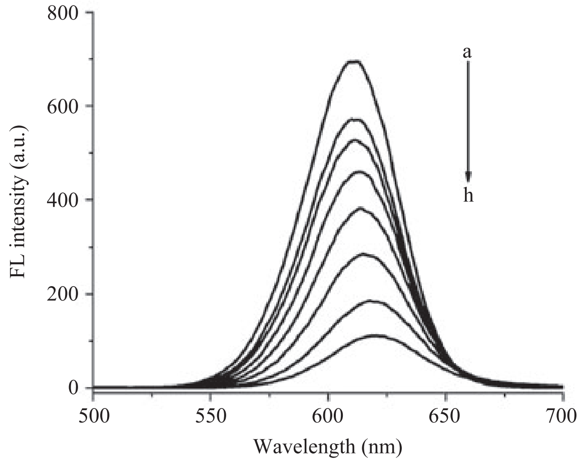

Figure 6 Effect of Cu^{2+} concentrations on FL intensity of CdTe QDs (from a to h: 0, 1.0×10^{-6}, 2.0×10^{-6}, 5.0×10^{-6}, 1.0×10^{-5}, 2.0×10^{-5}, 5.0×10^{-5} and 1.0×10^{-4} mol L^{-1}); the size of CdTe QDs is 3.42 nm.

Conclusions

In summary, the behaviors of 15 kinds of metal ions in CdTe QDs–H_2O_2 CL reaction were investigated in detail. It was found that the Ag^+, Cu^{2+} and Hg^{2+} ions had a restraining effect on the CdTe QDs–H_2O_2 CL reaction. A novel method for the determination of Ag^+, Cu^{2+} and Hg^{2+} was developed based on their inhibition of the CdTe QDs–H_2O_2 CL reaction. This work is important for the development of the CL of QDs in metal ion analysis.

Acknowledgments

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