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Selective recognition of dysprosium(III) ions by enhanced chemiluminescence CdSe quantum dots



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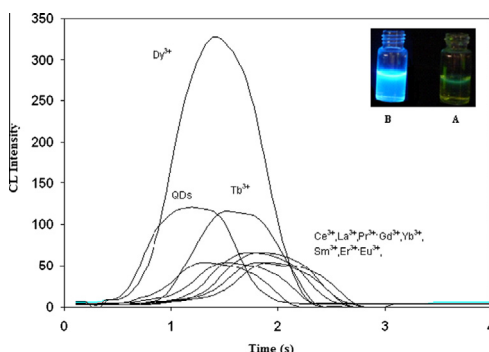
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HIGHLIGHTS

- The intensity of the chemiluminescence reaction of CdSe quantum dots enhances with addition Dy³⁺ ion.
- The chemiluminescence reaction of CdSe quantum dots shows high selectivity and sensitivity to Dy³⁺ ion.
- The sensor has detection limit of 6.0×10^{-8} M for Dy³⁺ ions with linear range 8.3×10^{-7} M– 5.0×10^{-6} M.

GRAPHICAL ABSTRACT

The intensity of emitted light from CdSe quantum dots–H₂O₂ is described as a novel chemiluminescence (CL) reaction for determination of dysprosium. This reaction is based on the catalytic effect of Dy³⁺ ions, causing a significant increase in the light emission, as a result of the reaction of quantum dots (QDs) with hydrogen peroxide.



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ABSTRACT

The intensity of emitted light from CdSe quantum dots (QDs)–H₂O₂ is described as a novel chemiluminescence (CL) reaction for determination of dysprosium. This reaction is based on the catalytic effect of Dy³⁺ ions, causing a significant increase in the light emission, as a result of the reaction of quantum dots (QDs) with hydrogen peroxide. In the optimum conditions, this method was satisfactorily described by linear calibration curve in the range of 8.3×10^{-7} – 5.0×10^{-6} M, the detection limit of 6.0×10^{-8} M, and the relative standard deviation for five determinations of 2.5×10^{-6} M Dy³⁺ 3.2%. The main experimental advantage of the proposed method is its selective to Dy³⁺ ions compared with common coexisting cations, therefore, it was successfully applied for the determination of dysprosium ions in water samples.

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Introduction

Among the miscellaneous functional nanomaterials, quantum dots (QDs) are of considerable interest due to their variety of superior optical and electrical properties. Comparing with conventional organic fluorophores, QDs include significant advantages such as high emission quantum yields, size-tunable emission profiles, and narrow spectral bands [1]. Semiconductor nanoparticles like quantum dots (QDs) have the potential that can overcome to some problems, encountered by organic dye molecules. These QDs are one of the best choices for the detection of heavy metal ions in aqueous media. Unlike organic fluorophores, QDs exhibit high photochemical stability, excellent resistant to chemical degradation and photo-degradation [2–4].

The method of chemiluminescence (CL) has been increasingly used in the studies of kinetics and mechanisms of different reactions as well as qualitative and quantitative analyses of various biological systems. This method just needs a chemical reaction, without any external energy source, that shows more advantage than other luminescence methods. It is characterized by high sensitivity, a large dynamic range of the determined substances concentrations, minimum background, without disturbances and light-scattering, reproducibility, simplicity, and quick analysis [5–10].

Quantum dots (QDs), or colloidal semiconductor nanocrystals (NCs), are extremely interested for their remarkable size-dependent optical and electronic properties in the past two decades [11]. They have been widely used as fluorescence biological probes [12], donors or acceptors in fluorescence resonance energy transfer (FRET) [13], and in bio-imaging [14].

Most CL reactions have weak luminescence, as a result of the low quantum efficiencies; however, this weak emission can be greatly enhanced by sensitizers, usually fluorescent compounds with high quantum efficiency. Thus, it would be more significance to explore the novel CL behavior of semiconductor QDs for developing novel CL sensors. Therefore, the investigation of CL of QDs would be promising for broadening the applications of luminescent nanoparticles [15,16].

The lanthanide ions, which their spectroscopic properties and the ability to react with many biologically active compounds (in which they replace the cations of Ca, Zn, Mg and Fe), were widely applied as structural and analytical luminescent probes, providing information with these materials and the biochemical processes occurring therein [10,17,18].

In recent years, we have studied the chemiluminescence reactions of peroxyoxalate esters, H₂O₂ and the variety of fluorophores in the presence of suitable basic catalysts such as sodium salicylate and imidazole [19–21] and have reported a number of selective optical sensors for lanthanide ions [22–25].

Regarding to our knowledge, there is no previous report pointed out that the enhancing efficiency and selectivity of dysprosium ions on (QDs)–H₂O₂ chemiluminescence reaction in aqueous solutions. In this work, we present a simple CL system imidazol–H₂O₂–CdSe QDs, as dysprosium ions were added to mixed solution, observed a strong CL signal. The emission intensity is dependent on dysprosium ions concentration. Based on this phenomenon, a new, simple, sensitive, and selective method is proposed for the determination of dysprosium ions.

Experimental

Reagents and solutions

All of the reagents and solvents were of analytical grade and used without further purification. Ultrapure water (deionized and

doubly distilled) was used throughout. Cadmium chloride hydrate, selenium powder, sodium hydroxide and hydrogen peroxide (H₂O₂, 30%) were purchased from Merck. Other chemicals were of the reagent grade from Fluka chemical company.

Apparatus

Fluorescence and chemiluminescence spectra were recorded on a Perkin–Elmer LS 50 spectrofluorimeter. The system was equipped with a stirrer that allowed the mixture of reagents to stir at low speeds. The excitation monochromator was set at 375 nm, with a spectral bandwidth (SBW) of 5.0 nm and the emission spectrum was evaluated (SBW 2.5 nm). The experiment was carried out by freshly prepared solutions containing CdSe Quantum dots (5.0 × 10^{−5}–6.0 × 10^{−4} M) in aqueous solution, into a 1-cm quartz fluorimetric cell.

Chemiluminescence detection was performed with Perkin–Elmer LS 50 spectrofluorimeter in lamp-off mode. The voltage applied to the photomultiplier tube was 800 V and the temperature was set at 25.0 °C. The instrument was covered with a black sheet in order to prevent extra lights to the cell, and the apparatus was connected to a personal computer via a suitable interface (Micro-pars, Tehran, Iran).

Procedures

In order to obtain fluorescence spectrum, a fluorimetric cell was filled with 100 μL CdSe QDs and 2 ml double distillation waters, then 40 μL (0.001 M) H₂O₂ in water was added, after vigorous stirring, the chemiluminescence spectrum was recorded.

The CL intensity-time curves were obtained as follows: In a fluorimetric cell containing 100 μL CdSe QDs, 100 μL imidazole (0.01 M in MeOH), 2 ml double distillation water, 50 μL lanthanide ions (1.0 × 10^{−6} M), 40 μL of H₂O₂ (0.001 M) in water was introduced, the CL intensity was recorded with an elapse of time, while the solution was magnetically stirred.

The MPA-Capped CdSe Quantum Dots, 3-mercaptopropionic acid (MPA)-stabilized Cedes QDs were synthesized via arrested precipitation in water as described elsewhere [26]. The preparation of NaHSe included two steps: First, Se powder and NaBH₄ was added into an 100 ml flask with 50 ml redistilled water, protecting N₂ gas and in ambient temperature. Whenever the Se powder in the flask dissolved, the reaction is done successfully. Second, for the preparation of CdSe QDs, 86.6 mg CdCl₂ and 79.22 mg 3-mercaptopropionic acid (MPA) were dissolved in 297 ml redistilled water in a three-necked flask under N₂ gas protection and constant stirring. The pH was adjusted to 9.1 with 1 mol L^{−1} NaOH solution, and then NaHSe solution was dropped to the mixture for about 20 min, heating from room temperature to boiling point (100 °C) with 1 h reflux.

Result and discussion

Characterization of CdSe QDs

The optical properties of MPA capped CdSe QDs were characterized by fluorescence and absorption spectra. Fig. 1(A and B) shows the absorption and fluorescence spectra of different sizes of the MPA capped CdSe QDs respectively.

According to the expression defined in [27], the particle size of the above mentioned CdSe QDs was calculated by following empirical equation.

$$D = (-6.6521 \times 10^{-8})\lambda^3 + (1.9557 \times 10^{-4})\lambda^2 - (9.2352 \times 10^{-2})\lambda + 13.29$$

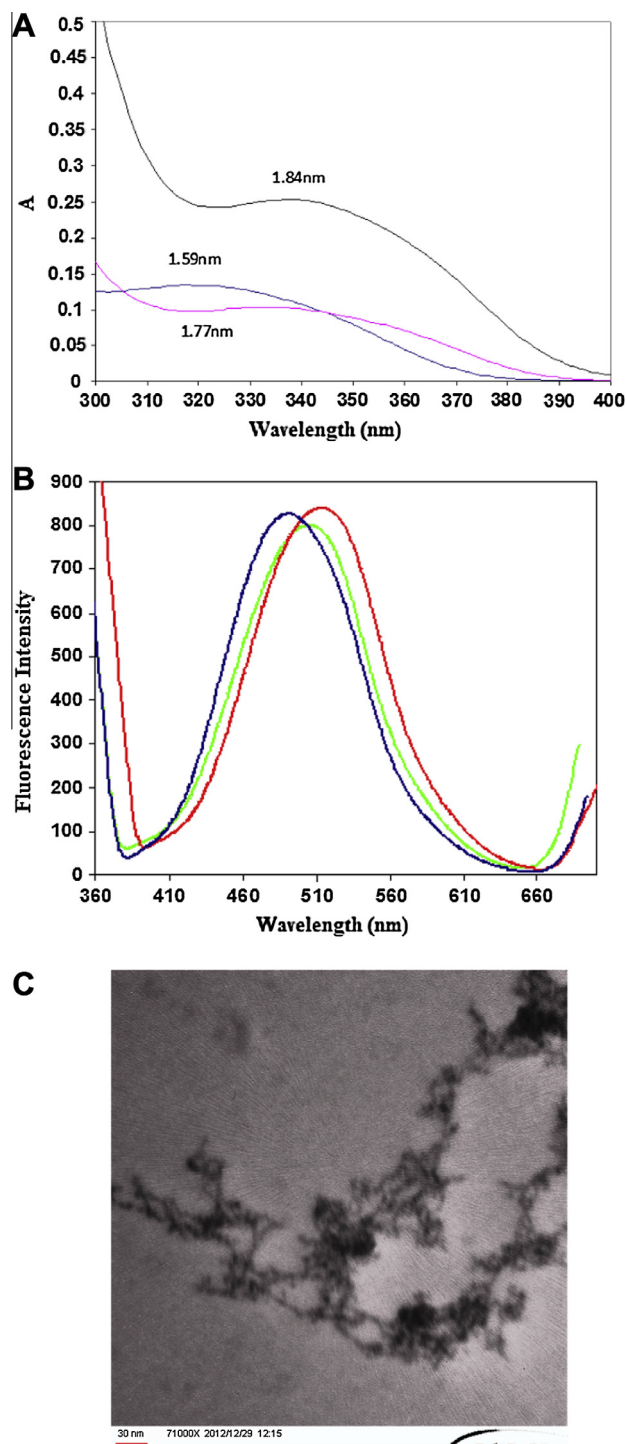


Fig. 1. Characterization of CdSe QDs: (A) UV-Vis absorption spectra; (B) Fluorescence spectra CdSe QDs ($\lambda_{\text{ex}} = 360$ nm); (C) TEM image CdSe QDs.

The results show that the particle diameters of the prepared CdSe QDs are around 1.59, 1.77 and 1.84 nm respectively, corresponding with the fluorescence emission peaks of 482, 498 and 506 nm (Fig. 1B).

The morphology of the functionalized CdSe nanoparticles was studied by TEM. Fig. 1C shows the typical TEM image of CdSe QDs.

Optimization of the CL reaction conditions

Fig. 2 shows the CL system curves (light intensity versus time) obtained at different QDs concentrations, a constant amount of

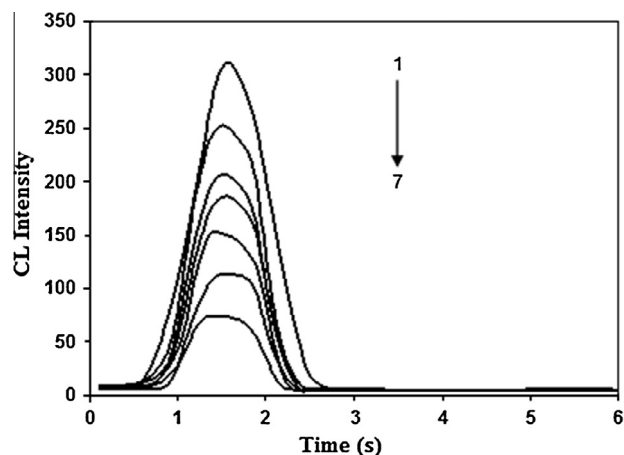


Fig. 2. CL intensity as a function of time for reaction of varying concentrations of QDs (CdSe) with H_2O_2 (4.0×10^{-3} M) in the presence of imidazole (5×10^{-4} M), in aqueous solution: (1) 5.0×10^{-5} , (2) 1.0×10^{-4} , (3) 2.0×10^{-4} , (4) 3.0×10^{-4} , (5) 4.0×10^{-4} , (6) 5.0×10^{-4} and (7) 6.0×10^{-4} .

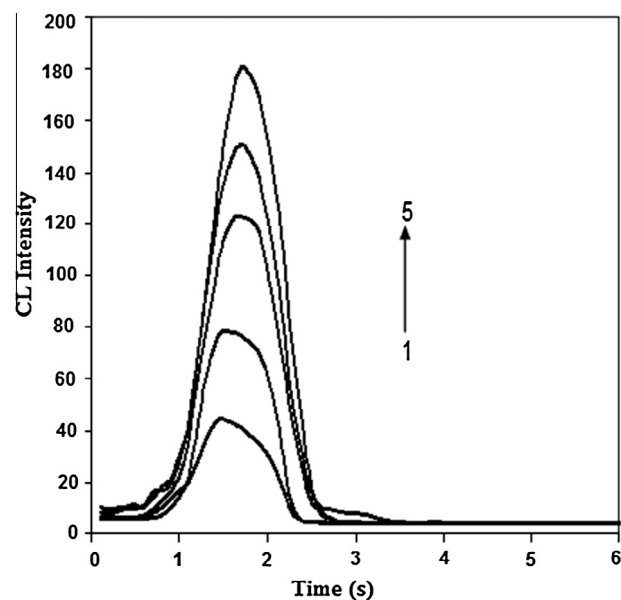


Fig. 3. CL intensity as a function of time for the H_2O_2 -QDs (CdSe) system in the absence and presence of varying concentration of H_2O_2 : (1) 2.0×10^{-3} M, (2) 4.0×10^{-3} M, (3) 6.0×10^{-3} M, (4) 8.0×10^{-3} M and (5) 1.0×10^{-2} M.

imidazole, and a sufficient amount of H_2O_2 . In all cases, as it is seen from Fig. 2 the CL intensity quenches with increasing concentration of QDs. The energy generated during the chemical reaction between H_2O_2 and OH^- was limited and it can excite a certain amount of QDs, so, the CL efficiency was affected. Furthermore, it is observed that an increase in the dense of reactive solution increases collisions and thus the quenching efficiency, therefore, the CL intensity was decreased. Consequently, the QDs concentration was selected 5.0×10^{-5} M as the CL enhancer in this study. This type of behavior has already been reported [28].

The H_2O_2 concentration played an important role in the CL reaction. The influence of the concentration of H_2O_2 on the CL system was studied at a constant QDs concentration (5.0×10^{-3} M) and results are shown in Fig. 3. As it is obvious, the CL intensity strongly increased with increasing hydrogen peroxide concentration in the range of 2.0×10^{-3} – 1.0×10^{-2} M.

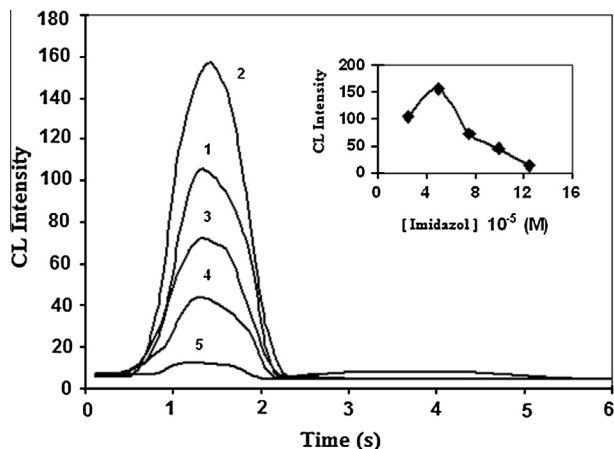


Fig. 4. CL intensity as a function of time for the H_2O_2 -QDs (CdSe) system in the presence of varying concentration of imidazole: (1) 2.5×10^{-5} M, (2) 5.0×10^{-5} M, (3) 7.5×10^{-5} M, (4) 10.0×10^{-5} M and (5) 12.5×10^{-5} M.

In order to investigate the effect of imidazole, the CL intensity of QDs solution (5.0×10^{-5} M), under the constant concentration of H_2O_2 (4.0×10^{-3} M) was measured in the presence of varying concentration of the base, and the resulting CL intensity-time plots are shown in Fig. 4. As it is shown, the CL intensity is strongly dependent on the imidazole concentration. The CL signals exhibited an initial increase due to basic medium with the maximum concentration 2.5×10^{-5} M, followed by a gradual decrease resulting from the negatively charge. The observed enhancement in chemiluminescence intensity caused directly by the catalytic effect of the base [28,29]. Indeed, with increasing pH from 7.0 to 8.9, the more OH^- the CL system contain, the more negatively charge the CdSe QDs surface will feel, and the easier electron transfer from the conduction band of CdSe QDs. Since H_2O_2 reacts with OH^- to generate HO_2^- ions, which leads to the formation of O_2^- radical, and O_2^- species are more stable in basic solution that much more favorably to the CL emission intensity. By contrast, when the concentration of imidazole was higher than 2.5×10^{-5} M, over anions loaded on the surface of CdSe QDs, which would hinder the affinity of negatively charged O_2^- to the CdSe QDs surface, thus causing a decrease in CL intensity. This type of behavior has already been reported [28]. So, further increase in concentration of imidazole revealed a gradual decrease in the CL intensity.

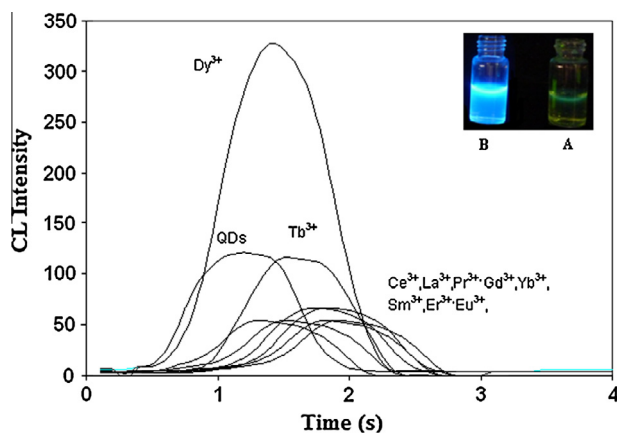


Fig. 5. Effect lanthanide ions $50 \mu\text{L}$ (1.0×10^{-5} M) on CL intensity H_2O_2 -QDs (CdSe) system in optimal conditions. CL intensity H_2O_2 -QDs (CdSe) system in absence (A) and presence of Dy^{3+} ions (B).

The effect of lanthanide ions (1.0×10^{-6} M) on quantum dot chemiluminescence was studied under the optimum experimental conditions were described above, the effect of lanthanide ions on the CL system was investigated in Fig. 5. It was found that some of them have no obvious effect on the CL intensity of QDs- H_2O_2 -imidazole reaction system, except of Tb^{3+} , Eu^{3+} , and Dy^{3+} caused a significant enhance in CL intensity of QDs- H_2O_2 -imidazole reaction system. Other lanthanide ions did not show any noticeable effect on CL system or have quenching effect on CL system.

Typical CL intensity curves in the presence of varying concentration Dy^{3+} ion are shown in Fig. 5. As it is quite obvious, the presence of Dy^{3+} ion in 1.0×10^{-6} M will result in about 3-fold enhanced intensity of the CL of the QD- H_2O_2 -imidazole system.

Analytical parameters

Under the optimum conditions, the calibration curve was obtained for Dy^{3+} ion determination by using a series of five standard solutions (Fig. 6). The calibration curve was found to be linear in the range of 8.3×10^{-7} - 5.0×10^{-6} M, with equation $I = 5.0 \times 10^7 X + 183.8$ ($R = 0.995$), where I is the CL intensity (arbitrary units) and X is the concentration of Dy^{3+} expressed in M. the detection limit as defined by IUPAC, $C_{\text{LOD}} = 3 S_b/m$ (where S_b is the standard deviation of blank and m is the slope of the calibration graph) was found to be 6.0×10^{-8} M. The relative standard deviation (R.S.D) for 2.5×10^{-6} M Dy^{3+} ion was 3.2% based on five replicated measurements.

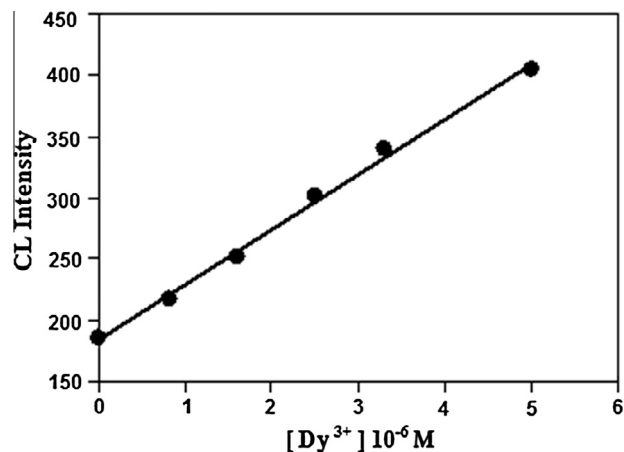


Fig. 6. Calibration curve of CL method of Different concentration of Dy^{3+} .

Table 1

Interference of different metal ions to the CL method for determination Dy^{3+} ion.

M^{n+}	Concentration (μM)	Change of CL intensity (%)
La^{3+}	50	-0.8
Ce^{3+}	50	-0.3
Tb^{3+}	50	+3.4
Sm^{3+}	50	-0.2
Gd^{3+}	50	-0.4
Eu^{3+}	50	+4.1
Lu^{3+}	50	+0.1
Yb^{3+}	50	-0.7
Pr^{3+}	50	-1.2
Nd^{3+}	50	-0.9
Ni^{2+}	100	-3.4
Co^{2+}	100	-2.2
Cd^{2+}	100	-2.9
Pb^{2+}	100	-3.4
Sr^{2+}	100	-3.3
Na^+	100	-0.1

Table 2
Determination of Dy³⁺ ion in water samples and waste water with the proposed method.

Sample	Added (10 ⁻⁶ mol/L)	Found ^a (10 ⁻⁶ mol/L)	Relative error (%)
Tap water	1.6	(1.5 ^a ± 0.2)	6.25
	5.0	(5.3 ± 0.2)	6
River water	1.6	(1.7 ± 0.2)	6.25
	5.0	(5.2 ± 0.2)	4

^a Results are based on three measurements.

Interferences

The selectivity behavior is obviously one of the most important characteristics of a chemosensor, that is, the relative sensor response for the primary ion over other ions present in solution. Physiologically, significant cations have the potential to quench or enhance the chemiluminescence intensity QDs–H₂O₂–imidazole reaction system. The effects of different coexisting ions on the chemiluminescence intensity were studied by mixing a concentration as listed in Table 1. To examine the selectivity of QDs–H₂O₂–imidazole system, we investigated its affinity to the presence of Dy³⁺ ion at 50 μM mixed with different concentration of other cations. A foreign ion was considered to interference seriously when it gave a determining error more than 5%. It was shown from the results that the most important interferences had small or no obvious interference with detection of Dy³⁺ ion.

Analytical application for the proposed method was low level monitoring of the Dy³⁺ ion concentrations in spiked water samples. 10.0 ml of each water sample (tap and river water, Tehran, Iran) was taken and diluted with distilled water in a 25.0 ml volumetric flask. Different amounts of Dy³⁺ ions (5.0 × 10⁻⁶, 1.6 × 10⁻⁶ mol/L) were added to water samples. The proposed sensor was used to determine the Dy³⁺ content and the calibration method was applied. The results obtained with the sensor are summarized in Table 2. It was found that the accuracy of Dy³⁺ detection in different solution samples is almost quantitative.

Conclusion

Water soluble functionalized MPA capped CdSe QDs was synthesized in a one step process to develop a luminescent sensor for Dy³⁺. This sensor is based on the chemiluminescence enhancing of dysprosium ions, which added to QDs solution. Under the optimum conditions, the calibration curve was linear in the range 8.3 × 10⁻⁷ M–5.0 × 10⁻⁶ M and with a correlation coefficient of

0.9950. The detection limit of proposed method is 6.0 × 10⁻⁸ M. There is a little or no interference from various cations ions.

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