

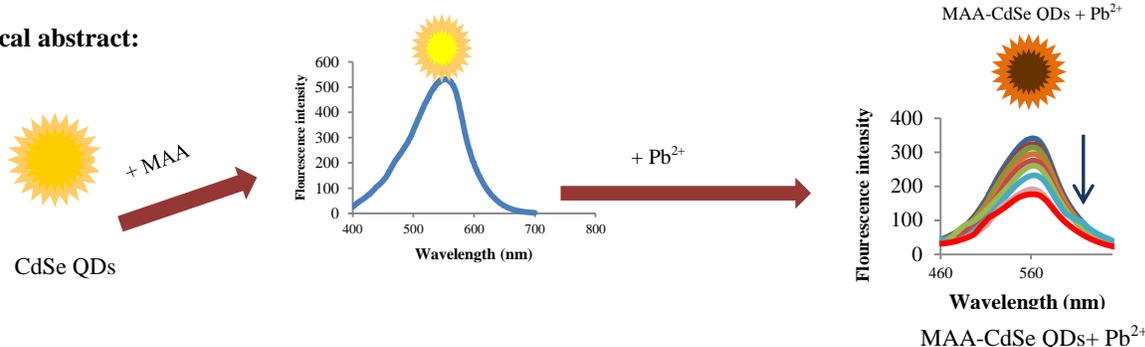


MERCAPTOACETIC ACID CAPPED CDSE QUANTUM DOTS AS FLUORESCENCE PROBE FOR SIMPLE DETERMINATION OF Pb^{2+} IN AQUEOUS SOLUTIONS BY LUMINESCENT MEASUREMENTS

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Graphical abstract:



ABSTRACT

A new chemiluminescence (CL) method using water-soluble mercaptoacetic acid (MAA) capped CdSe quantum dots (QDs) as sensitizers is proposed for the determination of Pb^{2+} . MAA-CdSe QDs were synthesized by using MAA as stabilizer in aqueous solutions. The stability of QDs was studied. The shape, size and spectral properties of MAA-capped-CdSe QDs were characterized by Ultra Violet-Visible absorption Spectroscopy, transmission electron microscopy (TEM) and spectrofluorometry. A pH 6 was selected for measurement. Also the influence of the foreign cations, drugs and amino acids on the fluorescence intensity of MAA-CdSe QDs was studied and Results showed a high selectivity of the MAA-CdSe QDs towards Pb^{2+} ions. There is a good linear relationship between the relative chemiluminescence intensity and the concentration of Pb^{2+} in the range of 1.6×10^{-9} – 1.3×10^{-8} M of Pb^{2+} ions with a correlation coefficient (R_2) of 0.9967. The limit of detection of this system was found to be 1.1×10^{-9} M. This method is simple, sensitive and lowcost.

Keywords: Mercaptoacetic acid; CdSe quantum dots; Pb^{2+} ions; Chemiluminescence.

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INTRODUCTION

Quantum dots is semiconductor nanoparticles which are recognized to be novel, high performance probes

that are at the forefront of nano-biotechnology research because they possess many attractive optical properties, including strong photostability, a broad absorption spectrum coupled with narrow emission, and a high photoluminescent quantum yield (PLQY) [1–8]. The

surface modification of QDs may change their chemical, optical and photophysical properties such as enhancement of their emission intensities and improvement in the photostability of semiconductor nanoparticles. Modification of QDs lead to the appearance of new emission bands, enhancement of selectivity and stability of the QDs, etc [9]. Highly luminescent QDs have been thoroughly developed and used in various bioapplications, including bioimaging [10-12], cell label, DNA probe [13-15], drug determination [16] and etc.

Lead is most toxic heavy metal element that in drinking water is pollutant and it has been extensively studied due to its properties as a highly toxic cumulative poison in humans and animals. Therefore, accurate, simple and reliable determination of rare Pb^{2+} is of great importance. A variety of quantitative analytical methods have been reported to determination of Pb^{2+} , including spectrophotometry [17], gas chromatography mass spectrometry [18], and atomic absorption spectrometry [19, 20]. But spectrofluorimetric method has attracted increasing attention because of its good selectivity, high sensitivity, rapid response, extreme simplicity and low cost.

EXPERIMENTAL

Reagents

All chemical reagents were of analytical grade and used as received without further purification. Ultrapure water (deionized and doubly distilled) was used throughout. All The metal salts such as $CdCl_2 \cdot 2H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$, $Ca(NO_3)_2 \cdot 4H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$ and etc were purchased from Merck (Germany). Mercaptoacetic acid and ascorbic acid and all amino acids was purchased from Merck (Germany). KH_2PO_4 and K_2HPO_4 were used preparing buffer solutions.

Apparatus

UV-vis absorption spectra were recorded by a WPA- Biowave II instrument. Fluorescence spectra were measured with a JASCO- FP-6500PC spectrofluorimeter. Metrohm 827 PH-Lab pH-meter was used for determination of pH . The structure and morphology of QDs were investigated by high resolution transmission electron microscopy (HRTEM) using a Philips-CM 30 model under the accelerating voltage of 200 kv.

Synthesis of MAA-capped CdSe QDs

In order to simple determination of mercaptoacetic acid capped CdSe QDs, 0.4026 g of $CdCl_2 \cdot 2H_2O$ and 3.2 mM of mercaptoacetic acid and 100 ml of deionized water were added to a three necked flask and the pH of the solution was adjusted to 11.8 By adding 1 $molL^{-1}$ NaOH. Then 0.3522g of ascorbic acid and 0.222g of selenium dioxide were added to the solution under vigorous stirring and the pH of the solution was adjusted to

11.8 The solution, The solution, was then purged with pure nitrogen for 9 hours at $100^{\circ}C$ under vigorous stirring.

Fluorescence measurement of Pb^{2+} ions

The concentration of Pb^{2+} ions was estimated by adding 9 μl of MAA-CdSe QDs to 2.5 ml of deionized water and 0.5 ml buffer. The fluorescence intensity of the quantum dot solution after adding Pb^{2+} ions was measured at 385/550 nm.

RESULTS AND DISCUSSION

Characterization of MAA-capped CdSe QDs

The optical characteristics of the synthesized MAA-CdSe quantum dots were optically characterized by UV-Vis absorption spectroscopy and fluorometry. The characteristic absorption spectrum of MAA-capped CdSe QDs occurs in 385 nm as shown in (Fig.1). The absorption spectra of MAA-capped CdSe QDs exhibited a broad excitation peak at 385 nm. When QDs were excited with 385 nm the symmetric and narrow emission spectrum of MAA-CdSe displayed an emission maximum around 550 nm. MAA-CdSe QDs was studied by high resolution transmission electron microscopy (HRTEM) as shown in (Fig.3). TEM results showed that the CdSe QDs were spherical particles with diameters of about 8-10 nm.

Stability of MAA-Capped CdSe QDs

In order to study the fluorescence stability of MAA-capped CdSe QDs the fluorescence intensity of QDs was recorded every 2 minutes (Fig.4). The result showed that up to 20 minutes the fluorescence intensity of MAA-CdSe QDs didn't changed significantly that shows the stability of QDs.

Effect of the pH on the determination of Pb^{2+} ions

The fluorescence intensity of QDs is influenced by pH. In order to select the optimum conditions for the determination of Pb^{2+} with the MAA capped CdSe QDs The effect of pH in a range between 5 and 10 was studied and because of that the fluorescence intensity of QDs before and after the addition of Pb^{2+} ions was recorded and result showed that in pH =6 maximum quenching occurs (Fig.5).

Selectivity of the MAA-CdSe QDs

The effects of different metal ions (Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Sn^{2+} , Cu^{2+} , Ni^{2+} , Ba^{2+} , Zn^{2+} , Pb^{2+}), drugs and amino acids on the fluorescence properties of MAA-CdSe QDs were further investigated. As can be seen from Fig. 6, the competitive metal ions and other drugs and amino acids studied here did not cause any significant change in the fluorescence intensity of MAA-CdSe QDs. Only Pb^{2+} led to strong fluorescence quenching of MAA-CdSe QDs, which indicated that MAA-CdSe QDs exhibited excellent selectivity over Pb^{2+} ions.

Fluorescence detection of Pb²⁺ by the quenching emission of MAA-Capped CdSe QDs

It was found that the fluorescence intensity of MAA-capped CdSe QDs was greatly quenched with the addition of Pb²⁺ that is shown in (Fig.7A). At the optimized condition, Pb²⁺ concentrations ranging from 1.6×10⁻⁹-1.3×10⁻⁸M were added to the MAA-CdSe QDs. It was found that PL intensities of MAA-CdSe QDs decreased as the concentration of Pb²⁺ was increased. (Fig.7B) showed the corresponding Stern–Volmer plot that illustrates the relationship between fluorescence intensity of MAA-CdSe QDs and concentration of the Pb²⁺. the calibration equation is (1):

$$I_0/I = K_{SV}C + 1 \quad (1)$$

That I₀ is the fluorescence intensity in the absence of Pb²⁺ and I is the fluorescence intensity in the presence of Pb²⁺. C is the Pb²⁺ concentration and K_{SV} is quenching constant of the Stern–Volmer equation.

Measuring Pb²⁺ in real samples:

The proposed method was applied to determine Pb²⁺ in 2 samples. The results obtained by the proposed sensor were showed in **Table 1**. Good recoveries for the determination of Pb²⁺ were obtained in all cases, thus indicating the validity of the proposed method for direct analysis of Pb²⁺ in all samples.

Table 1. Determination of Pb²⁺ in real samples.

Real samples	Recovery (%)	RSD(%)
Sample1	101	1.2
Sample2	102.3	2.2

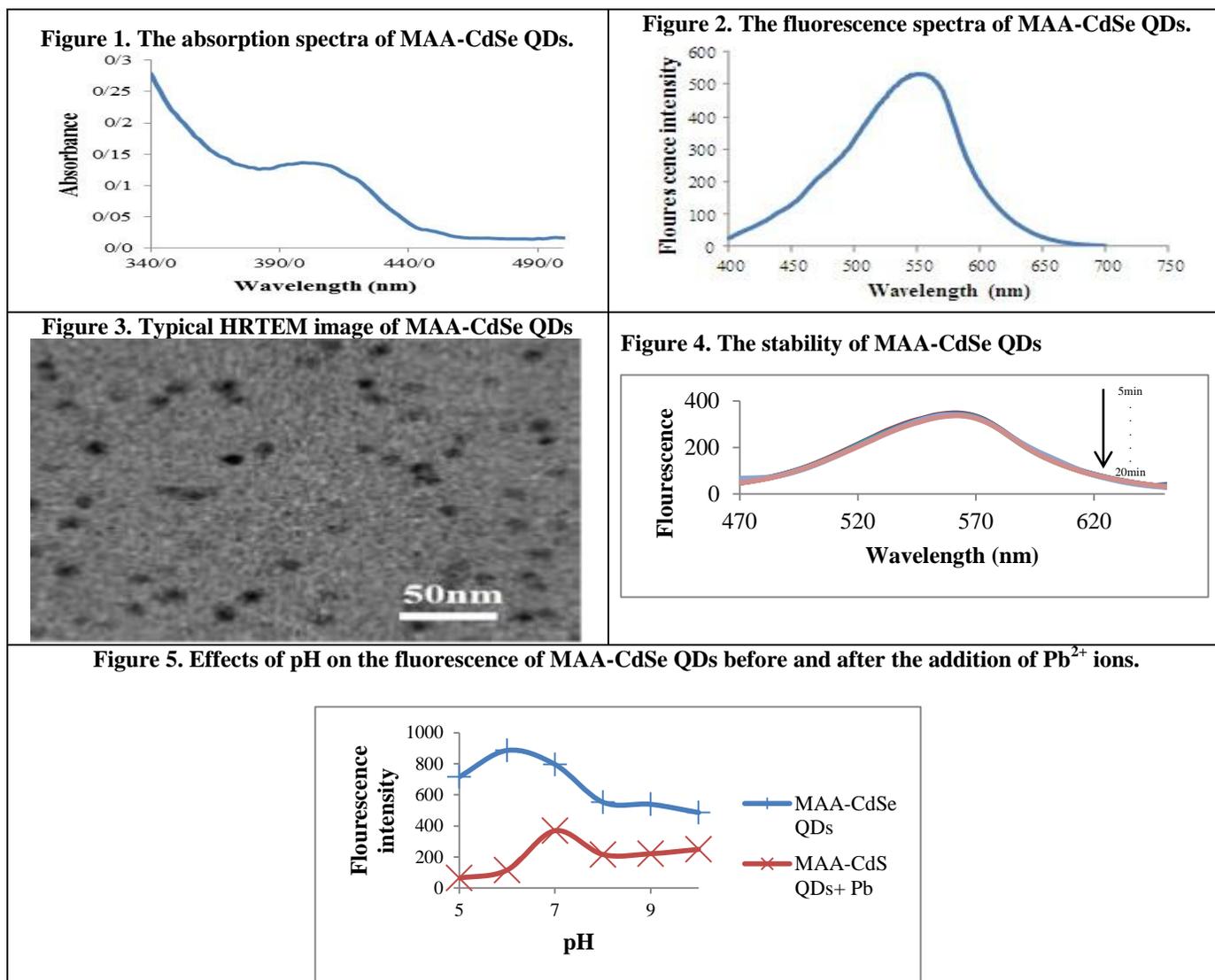


Figure 6. Effect of A) ions, B) drugs and c) amino acids on the luminescence of MAA-Capped CdSe QDs.
 Concentrations of ions and drugs and amino acids are all $1.66 \times 10^{-4} \text{ mol L}^{-1}$.

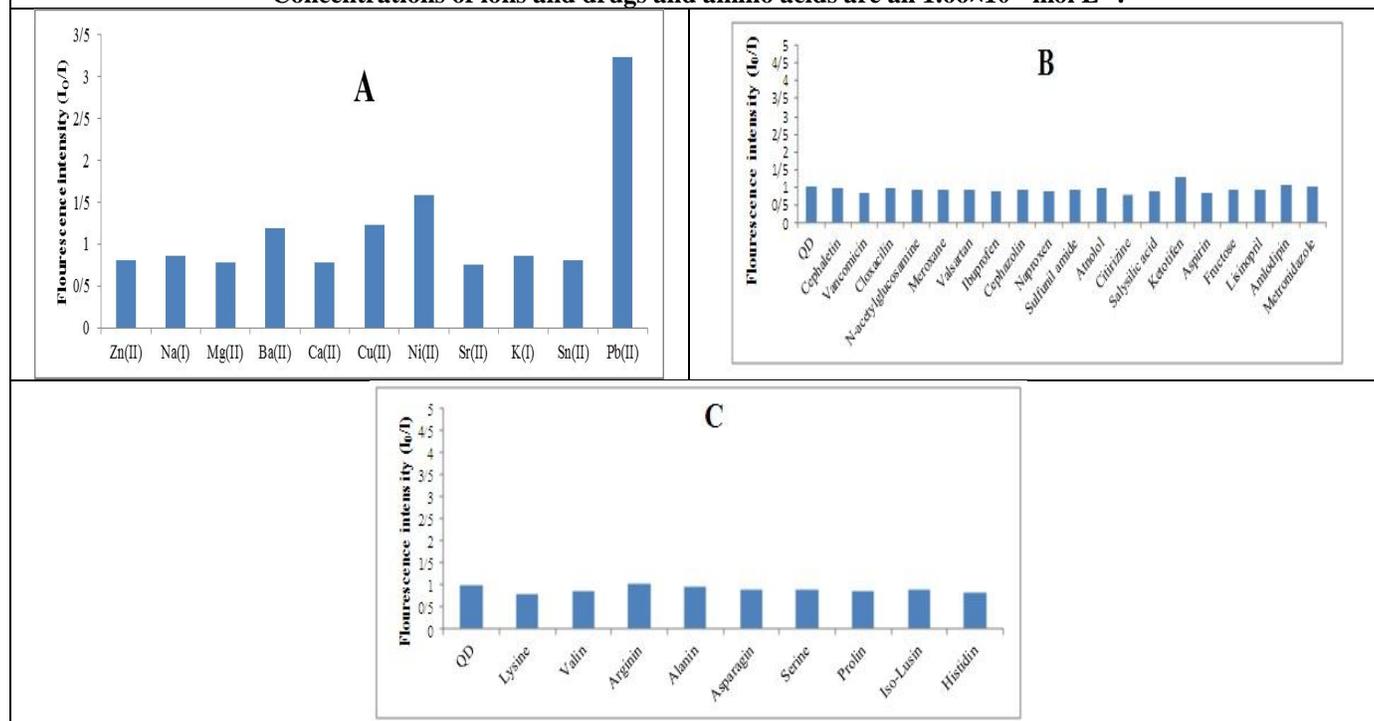
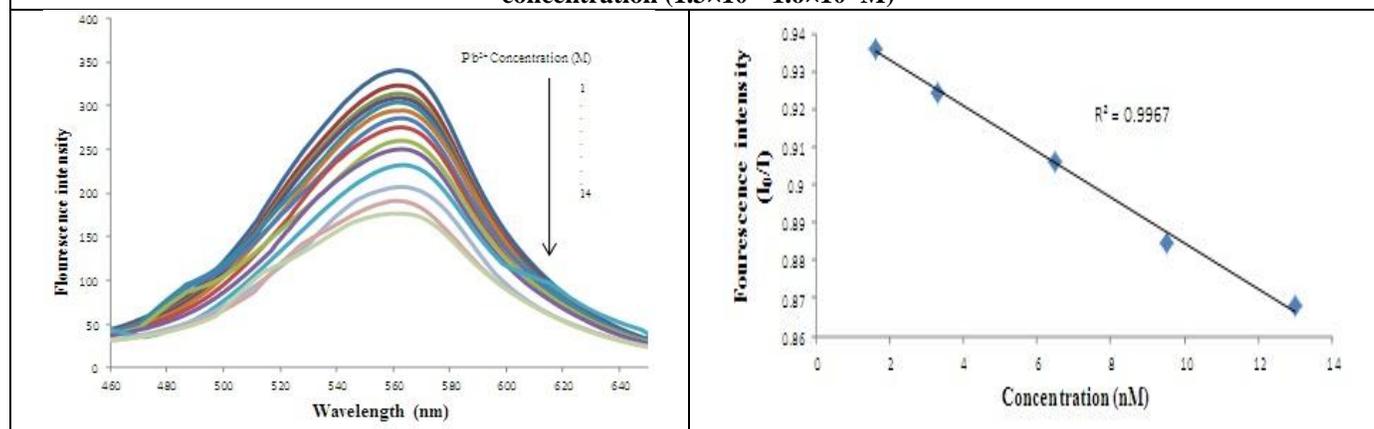


Figure 7. (A) Fluorescence spectra of MAA-CdSe QDs in the presence of Pb^{2+} , from top to bottom, the concentrations of Pb^{2+} 1) 0 2) 1.6×10^{-9} 3) 3.3×10^{-9} 4) 5.6×10^{-9} 5) 1.3×10^{-8} 6) 3.2×10^{-8} 7) 1.1×10^{-7} 8) 1.7×10^{-7} 9) 3.3×10^{-7} 10) 8.3×10^{-7} 11) 1.8×10^{-6} 12) 1.9×10^{-6} 13) 2.1×10^{-6} . (B Stern-Volmer plot the fluorescence intensity of MAA-Capped CdSe QDs vs Pb^{2+} concentration (1.3×10^{-8} - $1.6 \times 10^{-9} \text{ M}$)



CONCLUSION

In this paper, CdSe capped with mercaptoacetic acid QDs were synthesized for selective determination of Pb^{2+} based on fluorescence quenching of QDs. MAA-CdSe QDs sensor showed good selectivity and sensitivity toward the detection of Pb^{2+} compared to other tested drugs,

Amino acids and metal ions. the calibration plot was linear in the range between $1.6 \times 10^{-9} \text{ molL}^{-1}$ to $1.3 \times 10^{-8} \text{ molL}^{-1}$ and a correlation coefficient of 0.9967. The detection limit of this sensor is 1.1 nM. this method is sensitive, selective and simple for determination of Pb^{2+} .

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