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Spectrochimica Acta Part A 70 (2008) 247–252

SPECTROCHIMICA
ACTA
PART A

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Fluorescence quenching of CdSe quantum dots by nitroaromatic explosives and their relative compounds

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Received 29 November 2006; received in revised form 12 July 2007; accepted 24 July 2007

Abstract

CdSe quantum dots (QDs) were synthesized in oleic acid and octadecene medium under high-temperature and dispersed in chloroform. Nitroaromatic explosives and their relative compounds, 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (DNT), nitrobenzene (NB), 2,4-dinitrochlorobenzene (DNBCl) and *p*-nitrotoluene (NT) can obviously cause the fluorescence quenching of the synthesized QDs. Under the optimum conditions, a nonlinear response was observed over the concentration range of 10^{-8} to 10^{-5} M for them all. The modified Stern–Volmer quenching equations of $\ln I_0/I$ versus C show a good linear relation in 10^{-5} M order of magnitude, and the detection limits approach 10^{-6} to 10^{-7} M.

Keywords: Quantum dots; Fluorescence quenching; Explosives; Nitroaromatic compounds

1. Introduction

With the surge of terrorism and the increased use of modern bombs in terrorist attacks, the detection of hidden explosives as well as unrecovered land mines has become an important but difficult international problem. The development of new devices capable of rapidly and cost-efficiently detecting explosives has become an urgent worldwide necessity [1]. Various physical methods such as gas chromatography coupled with a mass spectrometer, nuclear quadrupole resonance, energy-dispersive X-ray diffraction as well as electron capture detection have been used for this purpose [2–5]. These techniques are highly selective, but some of them are expensive and others are difficult to be fielded in a small, low-power package. Over the past several years, chemical sensors based on absorption, fluorescence and conductivity transduction mechanisms have attracted much attention in the rapid detection of explosives because they can be easily incorporated into inexpensive and portable microelectronic devices. In this respect, the fluorescence-based sensor schemes are very promising [6–10].

Quantum dots (QDs), a brand new class of fluorescent nanoprobes, are advantageous over fluorescent dyes because of their tunable emission color, high quantum yield and long-term photostability. Moreover, the emission of QDs is narrow, symmetric, and independent of the excitation wavelength [11,12]. Due to their unique properties, QDs have found increased uses in a variety of practical biological applications [13–16]. As novel luminescent probes, QDs have also attracted considerable attention for the development of sensitive and selective fluorescence sensors in recent years [17,18]. The studies revealed that the interactions between some substances and the surface of QDs would change their physical properties. Thus, expanding applications of QDs to develop sensitive and simple sensors for the detection of different analytes is a topic of current interest [19–24]. Also the potential applications of QDs in the detection of nitroaromatic explosives based on directive fluorescence quenching of QDs [25,26] or fluorescence resonance energy transfer [27] have been paid to attention.

Herein, we report that fluorescence of oleic acid covered CdSe QDs could be efficiently quenched by nitroaromatic analytes, which might provide a new pathway to detection of the nitroaromatic explosives and their relative compounds.

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1386-1425/$ – see front matter © 2007 Published by Elsevier B.V.
doi:10.1016/j.saa.2007.07.054

2. Experimental

2.1. Reagents

Cadmium oxide (CdO, 99.99%), selenium (Se, power, 100 mesh, 99.99%), trioctylphosphine (TOP, 90%), oleic acid (OLE, 90%) and octadecene (ODE, 90%) were all purchased from Aldrich (Milwaukee, WI, USA). Chloroform was purchased from Beijing Reagent Factory. The *p*-nitrotoluene (NT), 2,4-dinitrochloro benzene (DNBCl), nitrobenzene(NB) was purchased from Shanghai Reagent Factory. DNT was purchased from The British Drug Houses Ltd. and used as received. TNT was obtained from the PSB of Shanxi and recrystallized from methanol–water (2:1). Stock solutions of nitroaromatic compounds were prepared in chloroform at 1.00×10^{-2} M. As used they were diluted to the concentration needed.

2.2. Instrumentation

Steady state fluorescence was measured using a Cary Eclipse luminescence spectrometer (Varian, USA). The samples were excited at 260 nm and the fluorescence signal was monitored at 602 nm. The excitation and emission slit widths were set at 5 and 10 nm, respectively. Fluorescence decay studies were carried out on FL920 Fluorescence Lifetime Spectrometer (Edinburgh Instruments Ltd.) with the pulse width of Xe lamp 1 ns.

2.3. Synthesis of QDs

QDs were synthesized according to the previously described procedures referenced in the body of the paper [28–30]. Some modifications were made. In brief, 25.6 mg CdO (0.2 mmol), 1.2 ml oleic acid and 1.6 ml octadecene were loaded in a 150 ml three-neck flask and heated to 150 °C under N_2 flow. After CdO was completely dissolved, the flask was cooled to room temperature, and then 15.8 mg Se (0.2 mmol) and 0.2 ml TOP were added. The mixture was stirred until the Se was completely dissolved. While 5 ml octadecene in another flask was heated to 310 °C, 2 ml of the previously prepared CdO–Se–TOP mixture was quickly injected at 300–310 °C with vigorously stirring for the nucleation and growth of quantum dots. After the injection, the solution was kept at this temperature for 30 s and then the heat source was removed immediately. Afterward, 30 ml chloroform was rapidly injected to stop the reaction. And CdSe QDs were precipitated out from the solution by methanol. After centrifugalated, the solid QDs was dispersed and stored in chloroform. Stock solution of QDs was prepared by transferring 10 μl of the synthesized QDs solution into a comparison tube of 10 ml and diluting to final volume with chloroform.

2.4. Procedures

Fluorescent titration was performed by addition of varying concentrations of nitroaromatic compounds under the constant concentration of CdSe QDs. The working solutions were stirred thoroughly prior to the fluorescence measurements. All measurements were made at room temperature.

3. Results and discussion

3.1. TEM images of CdSe QDs

Fig. 1A and B shows TEM image of the synthesized CdSe QDs with the excitonic absorption peak at 587 nm. As seen in Fig. 1A, the size distribution of QDs was nearly monodisperse with the average size of 4 nm. Absorption and photoluminescence measurements in chloroform solutions of QDs confirmed their quantum-confined nature and considerable quantum yield (Fig. 1B). Taken together, these data confirm the successful preparation of high-quality QDs.

3.2. Selection of the QDs concentration

The fluorescence intensity of CdSe QDs solution, especially at low concentration, decreased slightly with standing time under ambient condition. Removal of oxygen from QDs solution by nitrogen-purging, however, was found to increase its stability. Also, a slight blue-shift of the emission maximum spectra was observed. This indicates that oxygen in the air has some oxidation effect on the surface of QDs. Bawendi and co-workers [31] reported that the molar absorption coefficient of CdSe QD

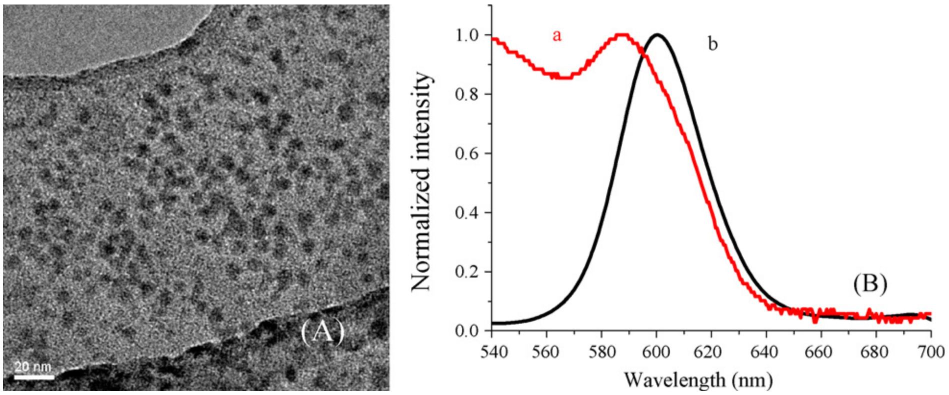

Fig. 1. (A) TEM of CdSe QDs and (B) normalized absorption spectrum (a, band-edge absorption at 587 nm) and fluorescence spectrum (b, emission maximum at 602 nm; fwhm 37 nm) of QDs.

was about 10^5 to $10^6\,\mathrm{mol\,l^{-1}\,cm^{-1}}$ and varies with excitation wavelength and particle size. In this paper we estimate the concentration of CdSe QD through ε $10^6\,\mathrm{mol\,l^{-1}\,cm^{-1}}$ for CdSe QD. According to stability of fluorescence of QDs and amplitude of signal change, 5.0×10^{-8} M QDs was selected in the further experiment, and the effect of the air was negligible at the selected concentration.

3.3. Measurements of fluorescence spectra

The nitroaromatic explosives and their relative compounds inclusive of TNT, DNT, NB, DNBCl and NT were found to quench the QDs fluorescence strongly. As seen in Fig. 2, the fluorescence intensity of QDs decreases progressively with increasing concentration of these analytes from 8.0×10^{-8} to 8.0×10^{-5} M. The data were plotted according to the Stern–Volmer equation and noticeable nonlinearity was observed, as shown as insets in Fig. 2. This may be a typical property of quantum dots as fluorescence sensors in solution [17,32]. If the quenching power of analyte is expressed with k value in exponential term e^{kx}, the following order can be obtained in quenching power, NB (1.85) > DNBCl (1.29) > TNT (1.06) ~ DNT (1.04) > NT (0.91). NB shows the strongest quenching, also I_0/I being over 30. TNT and DNT do not display considerable difference. The experiments show that toluene or benzene did not show any significant quenching up to 10.0×10^{-5} M.

From Fig. 2 it can be seen that the fluorescence of CdSe QDs were quenched by the nitroaromatic compounds investigated here in a very wide range from 10^{-8} to approaching 10^{-4} M. However, in the lower concentration range, we could not achieve a good linear correlation between I_0/I and C or their other forms.

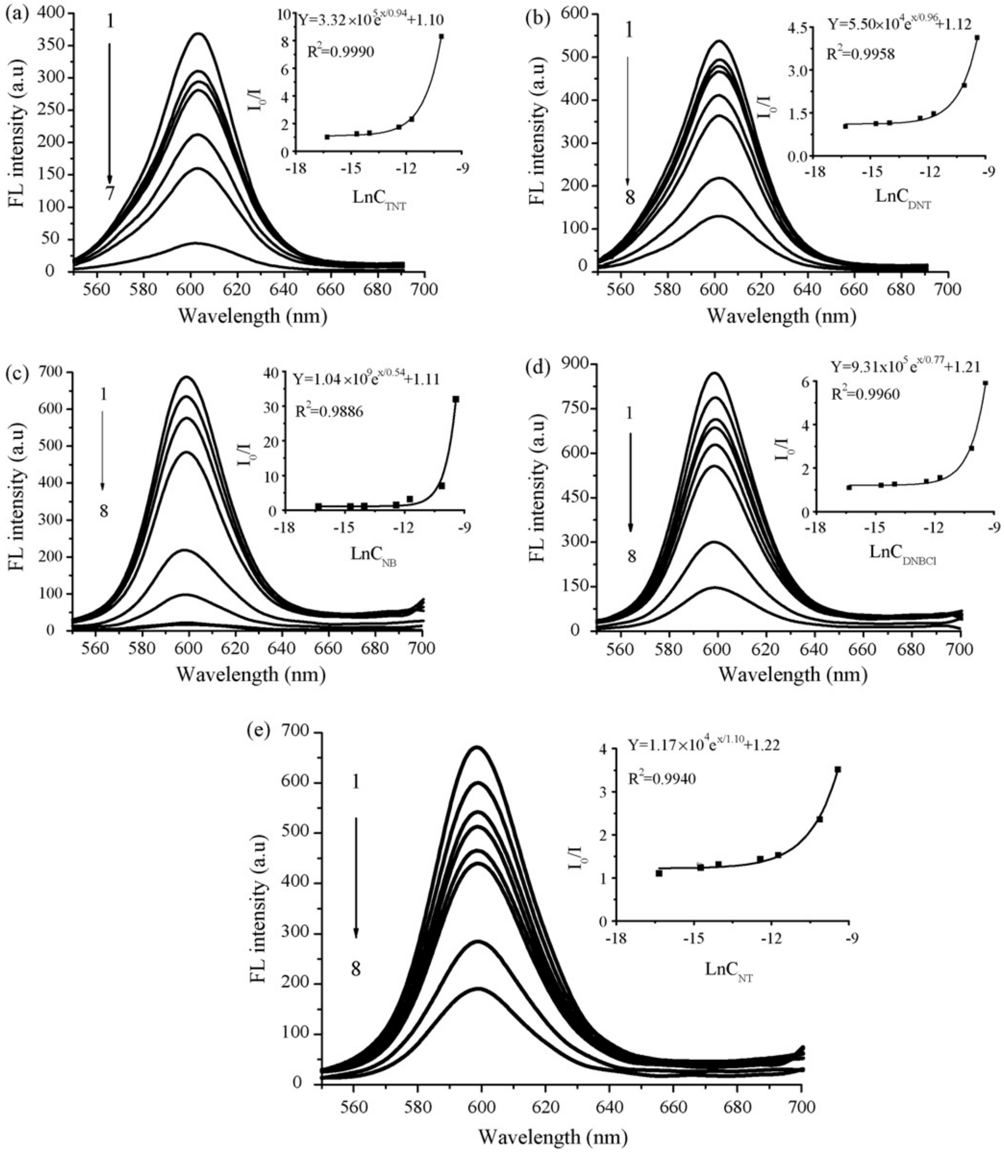

Fig. 2. Fluorescence quenching spectra of CdSe QDs with increasing concentration of TNT (a), DNT (b), NB (c), DNBCl (d) and NT (e). (The concentration, C, of quenchers represents, respectively, from no. 1 to 8: 0.0, 8.0×10^{-8}, 4.0×10^{-7}, 8.0×10^{-7}, 4.0×10^{-6}, 8.0×10^{-6}, 4.0×10^{-5}, 8.0×10^{-5} M; Y and x represent I_0/I and $\ln C$, respectively, in insets and I and I_0 are the fluorescence intensity of QDs in the presence and in the absence of quencher, respectively.)

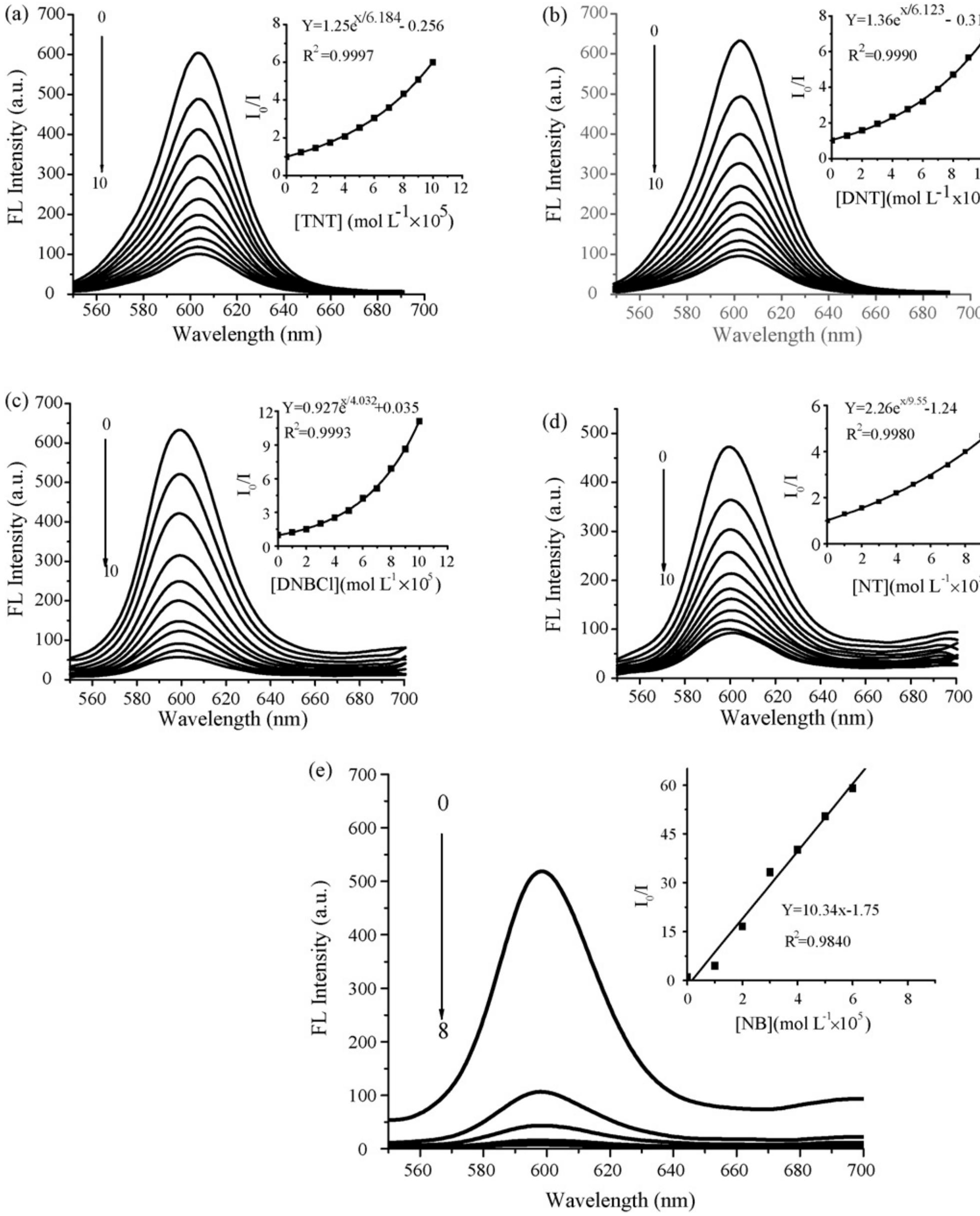

Fig. 3. Fluorescence quenching spectra of CdSe QDs by TNT (a), DNT (b), DNBCl (c), NT (d) and NB (e) in 10^{-5} M scale. (The concentration, *C*, of quenchers represents, respectively, from no. 0 to 10: 0, 1.0×10^{-5}, 2.0×10^{-5}, 3.0×10^{-5}, 4.0×10^{-5}, 5.0×10^{-5}, 6.0×10^{-5}, 7.0×10^{-5}, 8.0×10^{-5}, 9.0×10^{-5}, 10×10^{-5} M; *Y* and *x* represent I_0/I and $\times 10^5$ M, respectively, in insets.)

So we focused the quenching concentration on 10^{-5} M order of magnitude.

Fig. 3 shows the fluorescence quenching spectra of CdSe QDs by nitroaromatic explosives and their relative compounds in 10^{-5} M scale and the plots of I_0/I versus quencher concentration were depicted in insets, I and I_0 being the fluorescence intensity of QDs in the presence and in the absence of analytes. Also the quenching plots showed the nonlinear property in this concentration scale except for NB, as shown as in insets. The modified Stern–Volmer plots, i.e., $\ln I_0/I$ versus C, showed good linear relationship ($r > 0.9971$), as shown as Fig. 4. If we fit the quenching data by the modified Stern–Volmer equation in lower NB concentration, also a more sensitive straight can be obtained. The slope for NB is higher than that for other compounds. The

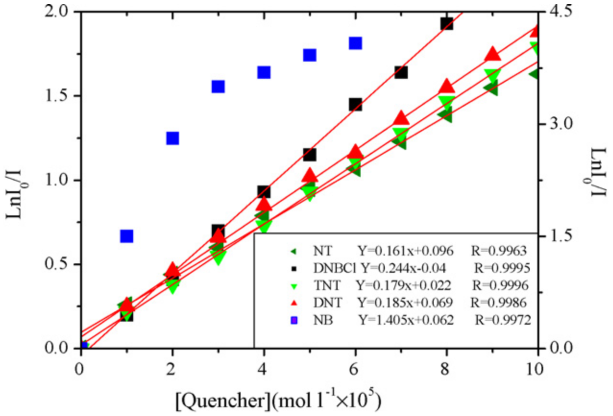

Fig. 4. Modified Stern–Volmer plot of QDs with increasing concentration of analytes (NB in right *y*-axial).

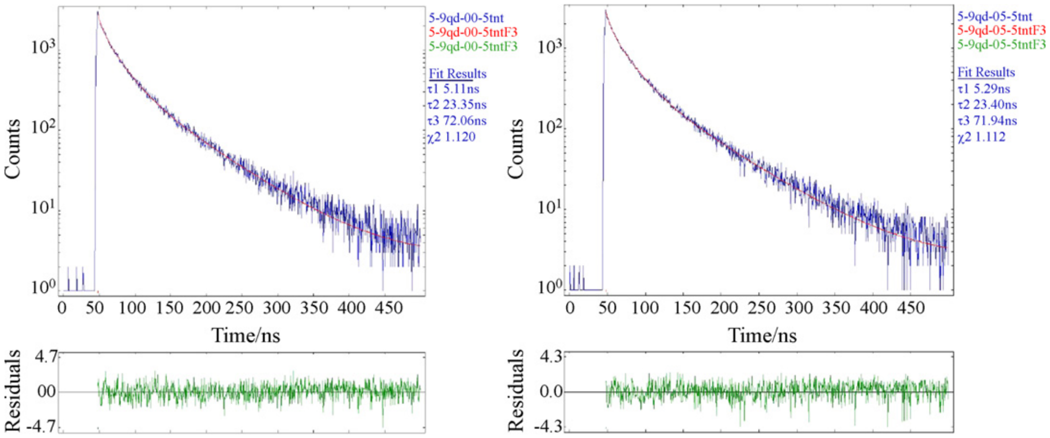

Fig. 5. Fluorescence decay curves of QDs in the absence of quencher (left) and in the presence of quencher (right). [QDs] = 5.0×10^{-8} M; [Q] = 5.0×10^{-5} M.

Table 1
The potential analytical characteristic of nitroaromatic explosives and relative compounds

Condition	LDR (mol l^{-1})	LOD (mol l^{-1})	R.S.D. (%) ($n = 5$)	r
TNT	1.0×10^{-5} to 1.0×10^{-4}	1.5×10^{-6}	2.7 (at 2.0×10^{-5} mol l^{-1})	0.9996
DNT	1.0×10^{-5} to 1.0×10^{-4}	1.2×10^{-7}	3.6 (at 2.0×10^{-5} mol l^{-1})	0.9985
NT	1.0×10^{-5} to 1.0×10^{-4}	1.1×10^{-6}	3.5 (at 2.0×10^{-5} mol l^{-1})	0.9963
NB	8.0×10^{-8} to 2.0×10^{-5}	6.5×10^{-8}	3.1 (at 2.0×10^{-6} mol l^{-1})	0.9996
DNBCl	1.0×10^{-5} to 1.0×10^{-4}	4.5×10^{-6}	2.4 (at 2.0×10^{-5} mol l^{-1})	0.9995

LDR, Linear dynamic range; LOD, limit of detection; *r*, correlation coefficient.

limits of detection calculated from the calibration equation are listed in Table 1.

The LOD values seem poor compared with the fluorescence polymer sensors. But from the results in Fig. 2, they appear to be expandable by improving conditions, for example, types, components, modification of surface, size and shape (quantum dots, quantum wire or quantum ring) of QDs, etc., in further researches. Although the method proposed here is not a specific one, generally, the detection of explosives and their relative compounds can provide very useful information for probing landmines or other exposive devices. Therefore, as a screening method it should be acceptable.

3.4. Measurements of fluorescence lifetime

Deviations from typically linear Stern–Volmer fashion are frequently due to quenching of more than one electronic state, or to a combination of static and dynamic quenching. In the case of dynamic quenching, the fluorescence lifetimes vary proportionally with quencher concentration. In the case of static quenching, however, lifetimes are invariant with quencher concentration [33]. Fluorescence lifetimes of QDs with and without quenchers were measured to further study the quenching mechanism.

Fig. 5 shows the fluorescence decay curves and the residual analysis for CdSe QDs. In our study, the fluorescence decay measured from 5.0×10^{-8} M QDs solutions was best fitted to a triexponential pattern with the lifetimes of 5.13, 23.4 and 72.1 ns. The fluorescence decay curves were unchanged by added analytes, implying the fluorescence quenching occurs by a static mechanism. We speculated the quencher molecules can intercalate between the hydrophobic layer around the CdSe cores and interact with the QDs. Such interactions could affect the efficiency of the core electron–hole recombination, and thus the luminescent emission [34]. But the exact quenching mechanism remains to be discussed in the future study.

4. Conclusions

In conclusion, the nitroaromatic explosives or their relative compounds caused the fluorescence quenching of CdSe QDs. Recently the detect limit reported were general 10^{-6} to 10^{-7} mol l^{-1} [35–38]. The most sensitive method may detect 10^{-12} mol l^{-1} TNT [39,40]. Here we demonstrated the potential application of luminescent QDs to develop new fluorescence sensors for the detection of explosives. The synthesized CdSe QDs show large fluorescence quenching effects with exposives, making this system an interesting candidate for exposives measurement. A good linear relationship ($r > 0.9971$) was observed up to concentrations of at least 1.0×10^{-4} M when using a modified Stern–Volmer plot. The detection limits are from 10^{-6} to 10^{-7} M level in present state. The fact that QDs showed high fluorescence quenching sensitivity towards nitrocompounds investigated indicated that they are potential candidates materials for detection of landmines or other exposive devices.

Acknowledgements

We gratefully acknowledge the financial support from NSFC (Nos. 20475035 and 20239486), The Liuxue Guiguo Foundation of Shanxi Province and the Ministry of Education CFKSTIP (705010).

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