

Study on the interaction between 2-mercaptoethanol, dimercaprol and CdSe quantum dots

Fei Dong, Heyou Han*, Jiangong Liang and Donglian Lu

ABSTRACT: The interactions between 2-mercaptoethanol, dimercaprol and CdSe quantum dots (QDs) in organic media have been investigated by spectral methods. The results showed that the fluorescence (FL) emission of CdSe QDs gradually decreased, with a slight red-shift, after adding thiols to CdSe QDs solutions. With the increase of the concentrations of thiols, the resonance light scattering (RLS) signal of CdSe QDs had been strongly enhanced in the wavelength range 300–500 nm, which was confirmed by the formation of larger CdSe QDs particles. The effect of thiols on the FL emission of CdSe QDs could be described by a Stern–Volmer-type equation with the concentration ranges 1.0×10^{-6} – 7.5×10^{-4} mol/L for 2-mercaptoethanol and 1.0×10^{-7} – 2.5×10^{-5} mol/L for dimercaprol. The possible mechanism of the interaction was proposed according to the results of UV-vis absorption and micro-Raman spectroscopy. The results indicated that FL quenching was mainly attributable to the exchange of the QDs surface molecules. Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: CdSe QDs; 2-mercaptoethanol; dimercaprol; interaction; fluorescence spectroscopy; Raman spectroscopy

Introduction

Quantum dots (QDs) have attracted great attention due to the enormous advantages over conventional organic fluorophores in recent decades (1–4). Recently, having intrinsic excellent optical properties, QDs have been tested as luminescent probes for biological processes, especially fluorescent biological labels and imaging, which have shown the potential biological applications of QDs (5–8). Nowadays, however, highly efficient QDs are often synthesized in organic media, as such synthesis processes allow for advanced shape and composition control (9). For further applications in biological processes, QDs must be rendered hydrophilic, so that they are soluble in aqueous buffers (10, 11). So far, many methods have been developed for the phase transfer of QDs to aqueous solution, including ligand exchange, surface silanization, embedding in a polymer shell, incorporation in micelles and so forth (6–9). As a result of their simplicity and high efficiency, especially without increasing the overall sizes of QDs, the exchange of ligands with small molecular thiols is probably the most commonly utilized method in making hydrophobic QDs water-soluble for further utilities, but this method suffers from the major drawback that it can reduce the fluorescence (FL) emission from CdSe QDs (12–15). Although the FL emission quenching of thiols to CdSe QDs has been reported, further research for probing the mechanism of the interaction is very necessary. This motivated us to investigate the interaction of CdSe QDs with thiols. This could not only provide useful information to understand FL quenching of the emissions from CdSe QDs when transferred into aqueous solution, but also be used as a reference for the surface functionalization of QDs.

In this study, the interactions between 2-mercaptoethanol, dimercaprol and CdSe QDs in organic media were investigated using various spectral methods, including ultraviolet and visible

(UV-vis) absorption spectroscopy, FL spectroscopy, resonance light scattering (RLS) spectroscopy and micro-Raman spectroscopy. It was found that the FL emission of CdSe QDs gradually decreased with a slight red-shift after adding 2-mercaptoethanol or dimercaprol to the solutions of QDs. For quenching of the emission from CdSe QDs, dimercaprol was more effective than 2-mercaptoethanol. The effect of thiols on the FL emission of CdSe QDs was linearly proportioned in fixed concentration ranges, which could be described by the Stern–Volmer-type equation. UV-vis and micro-Raman spectroscopy were used to probe the mechanism of the FL quenching. The results showed that the quenching phenomenon would be mainly due to the exchange of the capping molecules.

Experimental

Reagents and chemicals

Selenium powder (200 mesh), CdO, hexane, methanol, chloroform, stearic acid, 2-mercaptoethanol were purchased from Shanghai Reagent Factory and used as received without any further purification. Dioctylamine (DOA), dimercaprol, tri-*n*-octylphosphine (TOP), tri-*n*-octylphosphine oxide (TOPO) and hexadecylamine (HDA) were purchased from Aldrich (Milwaukee, WI, USA). All other chemicals used were of analytical reagent grade.

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Apparatus

The UV-vis absorption spectra were acquired on a Thermo Nicolet Corporation Model Evolution 300 UV-visible spectrometer. The FL and the RLS spectra were performed on a Perkin-Elmer Model LS-55 luminescence spectrometer equipped with a 20 kW xenon discharge lamp as a light source. The excitation wavelength was 380 nm. The Raman spectra were acquired with an inVia micro-Raman spectroscopy system (Renishaw, UK), equipped with a He-Ne laser excitation source emitting wavelength at 633 nm.

Procedure

CdSe QDs were prepared according to the method reported previously, with minor modifications (16). Briefly, in a three-necked flask, 0.033 g CdO and 0.58 g stearic acid were heated to 150°C under a nitrogen atmosphere. When CdO was completely dissolved, the mixture was kept in air to cool to room temperature; meanwhile, 4.87 g TOPO and 4.87 g HDA were added to the flask, then the mixture was heated to 320°C under a nitrogen atmosphere. At this temperature, the selenium solution, prepared previously by dissolving 0.20 g selenium powder in 1.62 g TOP and 3.20 g DOA in a nitrogen-filled dry-box, was quickly injected into the reaction flask. After the injection of the stock solution, the reaction temperature was maintained at 280°C for 5 min. Monodisperse CdSe QDs were purified by precipitation, centrifugation and decantation and redispersed in hexane, then kept in the dark until further use.

2-Mercaptoethanol and dimercaprol were dissolved in chloroform and diluted to appropriate concentrations with hexane. The UV-vis absorption, FL and RLS spectra were obtained by adding different concentrations of 2-mercaptoethanol and dimercaprol into CdSe QDs solution, and then diluting with hexane to the mark. The Raman spectra were performed at a spectral range of 300–2000/cm. The samples were measured on quartz slides and each spectrum was obtained in 10 s × 6 collection times.

Results and discussion

Characterization of CdSe QDs

The UV-vis absorption (a) and room temperature FL (b) spectra of CdSe QDs are presented in Fig. 1. The curve (a) shows that the absorbance maximum of CdSe QDs was centred at 543 nm. From curve (b) it can be seen that the line width of the FL spectrum was narrow (with the full width at half-maximum about 30 nm), which shows that as-prepared CdSe QDs were nearly monodis-

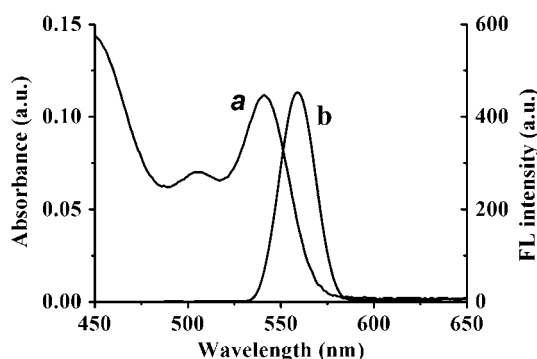


Figure 1. UV-vis absorption and FL spectra of CdSe QDs: (a) UV-vis absorption spectrum; (b) FL spectrum.

perse and homogeneous (17). The maximum of the emission was observed at 553 nm. A quantum yield (QY) in emission of ~18% was obtained in comparison to the FL emission of rhodamine 6G (QY 95%) (18). The average size ($\sim 3.2 \pm 0.2$ nm) and concentrations ($\sim 4.2 \times 10^{-5}$ mol/L) of the CdSe QDs were estimated according to the method reported by Schmelz *et al.* (19).

Effect of reaction time on the interactions between thiols and CdSe QDs

The effect of reaction time on the interactions between thiols and CdSe QDs was investigated. The results showed that the quenching of 2-mercaptoethanol and dimercaprol toward CdSe QDs was finished within 5 min and then the FL signals were stable for more than 60 min. In order to make CdSe QDs and thiols react completely, the FL intensity was collected after 10 min.

Effect of thiols on the FL spectra of CdSe QDs

Figure 2 shows the effect of 2-mercaptoethanol on the FL spectra of CdSe QDs. It was found that the FL emission of CdSe QDs gradually decreased with increasing amounts of 2-mercaptoethanol. At the concentration of 7.5×10^{-4} mol/L, almost all the emission was quenched. After the addition of 2-mercaptoethanol, a slight red shift (0–4 nm) was observed. The interaction between dimercaprol and QDs was similar to that of 2-mercaptoethanol. As shown in Fig. 3, with the increase of the concentration of dimercaprol, the FL emission of CdSe QDs was progressively quenched. When the concentration of dimercaprol was $2.5 \times$

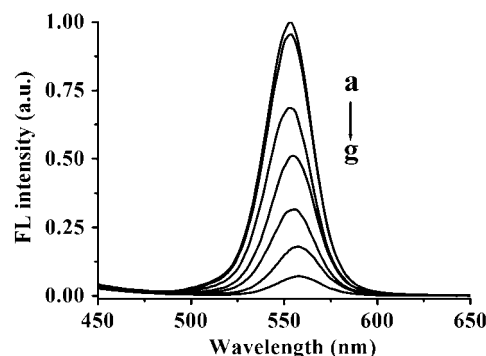


Figure 2. FL response of CdSe QDs to addition of 2-mercaptoethanol. Aliquots of 5.0×10^{-3} , 5.0×10^{-4} , 5.0×10^{-5} mol/L 2-mercaptoethanol were added to yield final 2-mercaptoethanol concentrations of: (a) 0; (b) 1.0×10^{-6} ; (c) 1.5×10^{-6} ; (d) 5.0×10^{-6} ; (e) 7.5×10^{-6} ; (f) 2.5×10^{-5} ; (g) 1.0×10^{-4} mol/L, $\lambda_{\text{ex}} = 380$ nm.

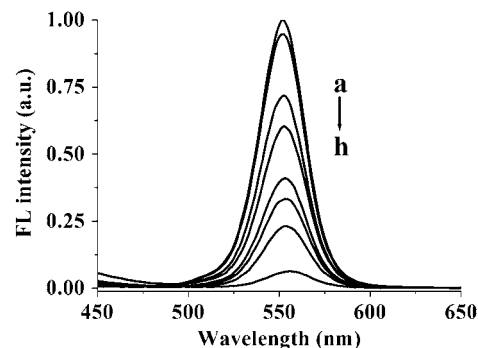


Figure 3. FL response of CdSe QDs to addition of dimercaprol. Aliquots of 5.0×10^{-5} , 5.0×10^{-6} and 5.0×10^{-7} mol/L dimercaprol were added to yield final dimercaprol concentrations of: (a) 0; (b) 1.0×10^{-7} ; (c) 2.5×10^{-7} ; (d) 7.5×10^{-7} ; (e) 1.5×10^{-6} ; (f) 2.0×10^{-6} ; (g) 2.5×10^{-6} ; and (h) 5.0×10^{-6} mol/L, $\lambda_{\text{ex}} = 380$ nm.

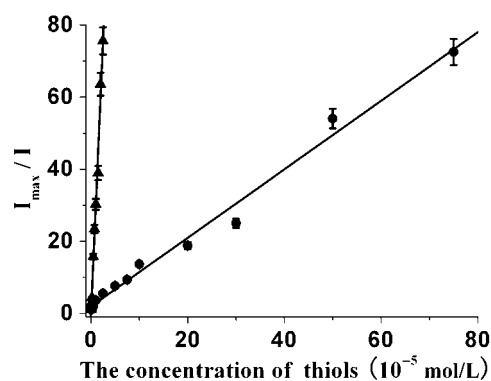


Figure 4. Stern–Volmer plot of thiols concentration dependence on the FL intensity of QDs. (▲), Dimercaprol; (●), 2-mercaptoethanol.

10^{-5} mol/L, the emission from CdSe QDs was nearly completely quenched, which indicated that dimercaprol was a more effective quencher than 2-mercaptoethanol for CdSe QDs emission. The FL emission of QDs was also observed to have a slight red-shift of about 0–4 nm in the presence of dimercaprol.

It was found that thiols quenched the FL intensity of CdSe QDs in a concentration dependence that was best described by a Stern–Volmer-type equation:

$$\frac{I_{\max}}{I} = 1 + K[Q]$$

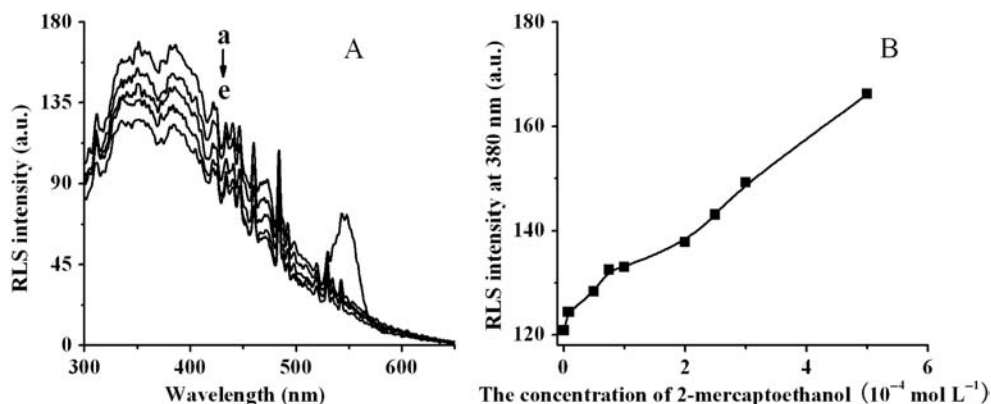


Figure 5. (A) RLS intensity changes of CdSe QDs upon the addition of: (a) 5.0×10^{-4} ; (b) 3.0×10^{-4} ; (c) 2.5×10^{-4} ; (d) 7.5×10^{-5} ; and (e) 0 mol/L 2-mercaptoethanol. (B) RLS intensity of CdSe QDs in 380 nm vs. 2-mercaptoethanol concentration.

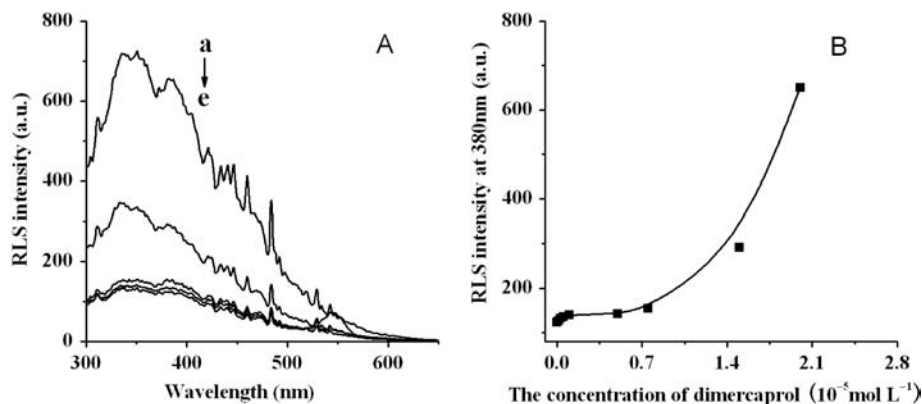


Figure 6. (A) RLS intensity changes of CdSe QDs upon the addition of: (a) 2.0×10^{-5} ; (b) 1.5×10^{-5} ; (c) 7.5×10^{-6} ; (d) 5.0×10^{-7} ; and (e) 0 mol/L dimercaprol. (B) RLS intensity of CdSe QDs in 380 nm vs. dimercaprol concentration.

where I_{\max} is the FL intensity of the fluorophore in the absence of the quencher; I is the FL intensity of the fluorophore when the quencher is present at concentration $[Q]$ and K is the Stern–Volmer constant. As shown in the Fig. 4, in the range 1.0×10^{-6} – 7.5×10^{-4} mol/L for 2-mercaptoethanol and 1.0×10^{-7} – 2.5×10^{-5} mol/L for dimercaprol, the linear relationship between I_{\max}/I and $[Q]$ had been obtained. The values of K for 2-mercaptoethanol (K_1) and dimercaprol (K_2) were found to be 9.5×10^4 L/mol and 3.0×10^6 L/mol, respectively. The value of K_2 was larger than K_1 , which revealed that the interaction between dimercaprol and CdSe QDs was stronger than that of 2-mercaptoethanol. This showed that dimercaprol was more effective than 2-mercaptoethanol for the quenching of FL emission from CdSe QDs, which may be attributed to the increasing of the amounts of sulphhydryl.

Effect of thiols on the RLS spectra of CdSe QDs

Figure 5A shows the RLS spectra of CdSe QDs in the presence of 2-mercaptoethanol of different concentrations and Fig. 5B indicates the RLS intensity of CdSe QDs at 380 nm vs. the concentration of 2-mercaptoethanol. As shown in Fig. 5, with increasing concentrations of 2-mercaptoethanol the scattering signal of CdSe QDs was strongly enhanced in the 300–500 nm wavelength range. The effect of dimercaprol on the RLS spectra of CdSe QDs is presented in Fig. 6. With increasing concentrations of dimercaprol, the RLS intensity of CdSe QDs was enhanced in the same wavelength range as for 2-mercaptoethanol and the signal were stronger. When the concentration of dimercaprol

was $>7.5 \times 10^{-6}$ mol/L, the enhancement of RLS intensity was significant. The result showed that the enhancement became stronger with increasing amounts of sulphhydryl, which was in accordance with the effect of thiols on the FL emission of CdSe QDs.

The RLS theory elucidates that the increase of the extent of particle aggregation was a main reason for the RLS enhancement (20). Many previously reported studies have shown that the aggregation of nanoparticles would induce the enhancement of the RLS intensity (21). In organic media, Liang *et al.* have demonstrated that CdSe QDs become larger in the presence of ethylenediamine and 1,6-hexanediamine, in which a significant increase of the RLS intensity was also observed (22). A similar mechanism, that the larger particles of CdSe QDs were formed in the presence of thiols, could be used to explain the phenomena in this study. The results showed that the sulphhydryl played a vital role in making the CdSe QDs aggregate. Dimercaprol, with more sulphhydryl, was therefore more efficient than 2-mercaptoethanol.

The mechanism of reaction between thiols and CdSe QDs

Previously reported studies have shown that the surface capping molecules have a deep influence on the FL properties of QDs (15). The exchange of the capping molecules may play a vital role in the quenching of the emission from CdSe QDs after the hydrophobic QDs become water-soluble (23). In organic media, strong binding of thiols onto the surface of CdSe QDs may also result in changes in the surface-bound organic molecules (24), which may be the reason of the quenching of the FL emission from CdSe QDs.

To probe the interaction mechanism, the UV-vis absorption spectra were investigated in the absence and presence of the thiols (not shown). The results indicated that neither 2-mercaptoethanol nor dimercaprol have absorption in the 300–700 nm wavelength range. The quenching of FL emission of CdSe QDs is therefore not attributable to the absorption of the emission wavelength by thiols. With adding each of thiols to CdSe QDs solutions, a slight red-shift can be observed for the absorption spectra of CdSe QDs. The fact that the larger particles of CdSe QDs are formed in the presence of the thiols could explain this phenomenon. The result is in agreement with the study of the effect of thiol concentration on the RLS spectra of CdSe QDs. With increasing thiols in CdSe QDs solutions, the intensity of RLS was greatly enhanced (Figs 5, 6), which meant that the size of CdSe QDs became larger. Many studies have shown that CdSe QDs synthesized in organic media could only be dispersed in non-polar organic solvents, such as chloroform and hexane (3). Due to the strong binding of thiols onto the surface of the CdSe QDs, previous ligands on the QDs surface may be replaced after adding thiols into the non-polar QDs solution (24). However, with increasing the amounts of the thiols into the CdSe QDs solutions, the polarity of the solution was changed significantly, which resulted in the aggregation of the monodisperse CdSe QDs. The aggregation of QDs in the presence of thiols had been confirmed by changes in the UV-vis and RLS spectra.

To prove the exchange of the surface capping ligands, the micro-Raman spectra of CdSe QDs were measured in the absence and presence of thiols for further investigation. Figure 7 shows the Raman spectra of normal CdSe QDs (Fig. 7a) and CdSe QDs in the presence of 2-mercaptoethanol (Fig. 7b) or dimercaprol (Fig. 7c). As shown in Fig. 7, the peak at 460 cm^{-1} is the char-

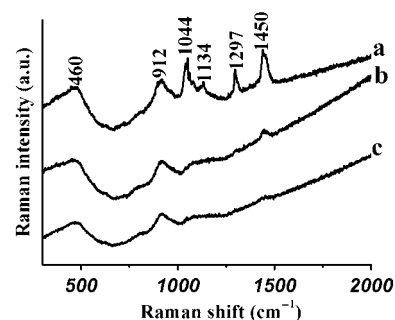
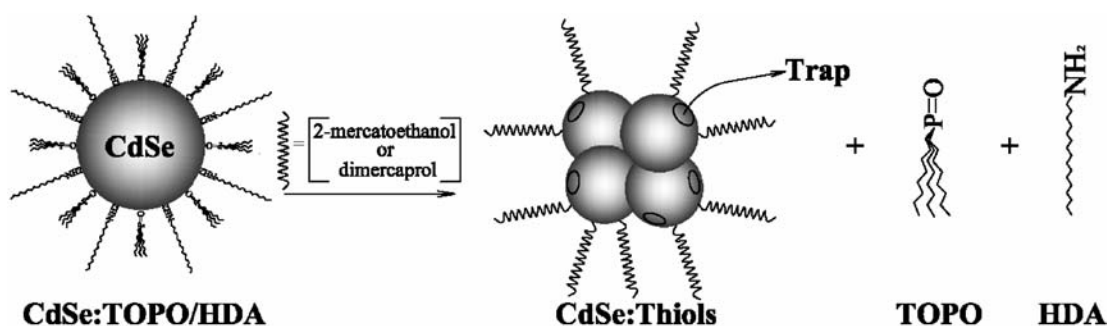


Figure 7. Raman spectra of CdSe QDs in the absence (a) and presence of 2-mercaptoethanol (b) and dimercaprol (c); the concentration of CdSe QDs was 4.2×10^{-5} mol/L; the concentrations of 2-mercaptoethanol and dimercaprol were 5.0×10^{-4} mol/L.

acteristic band for CdSe QDs (25). Comparing with the previous reported results, the shift of the Raman peaks may be due to the changes of the QDs sizes. The peak at 912 cm^{-1} is found to be unchanged in the presence or absence of thiols, which is assigned to C–C stretching vibrations for all of the ligands. A distinct feature of curve a compared to curves b and c is the disappearance of the peak at 1297 cm^{-1} , which is assigned to C–N stretching vibrations (26). Compared to thiols, amine capping molecules are not very strongly bound ligands, which is ascribed to the fact that the Cd–thiol bond is much stronger than the Cd–amine bond (24). So the disappearance of the peak at 1297 cm^{-1} is attributed to the surface capping amine molecules being replaced efficiently by the thiols. The 1134 cm^{-1} band is assigned to $P = 0$ stretch vibrations (27). The peak became weak after adding thiols into the QDs solutions, indicating that TOPO at the surface of QDs were partially replaced. These were in agreement with previously reported results (28). The peak at 1044 cm^{-1} is CH_3 wagging modes and the peak at 1450 cm^{-1} is H–C–H bend vibrations (27). Both of these peaks became weak in the presence of thiols, which may be attributed to the decrease of the long-chain alkyl compounds. The Raman spectra showed that the surface capping organic molecules of CdSe QDs were exchanged after adding the thiols into the QDs solutions. Moreover, it was found that the changes of Raman peaks were more distinct in the presence of dimercaprol than that of 2-mercaptoethanol, which indicated that dimercaprol was more effective for exchanging of the capping molecules, ascribing to the suggestion that dimercaprol had a more sulphhydryl. The changes of Raman peaks after adding the thiols into the QDs solutions were consistent with those of UV-vis, FL and RLS spectra that we had investigated.

It is known to all that the passivation of surface layer plays a vital role in improving the FL efficiency of QDs (3, 6, 29). Therefore, the changes of the surface situation will greatly affect the FL properties of QDs. This is because, after changing the surface layer, previous perfect surface passivation of the QDs would be altered, leading to an increase of surface defects and then a significant FL quenching of QDs (30, 31). As shown in Scheme 1, the CdSe QDs fabricated in this work were capped with a TOPO/HDA layer, which had a very strong passivation effect (15, 16). Thus, the CdSe:TOPO/HDA QDs had a very high FL efficiency. However, after adding thiols into the CdSe QDs solutions, strong binding of thiols onto the surface of CdSe QDs resulted in changes of the surface capping molecules, which had been demonstrated by the Raman spectra results. Furthermore, with increasing amounts of thiols, the polarity of the solution was changed significantly,



Scheme 1. A model of CdSe QDs before and after the ligand exchange.

which resulted in the aggregation of the monodisperse CdSe QDs. These results indicated that the surface situation of the as-prepared CdSe QDs had been changed in the presence of thiols. Therefore, the previously perfect surface passivation attained by capping a TOPO/HDA layer would no longer be perfect, resulting in an increase of surface defects and then the quenching of the FL emission from CdSe QDs.

Conclusions

In this study we have explored the interaction between two kinds of thiols and CdSe QDs in organic media by spectral methods. The results showed that thiols were effective quenchers for the emission of CdSe QDs and that the nearly monodisperse CdSe QDs had slight aggregation in the presence of thiols. The FL quenching would be mainly due to the exchange of the capping molecules. Quenching of the FL emitted by CdSe QDs may also develop to be a potential sensor for the detection of thiols.

Acknowledgements

The authors gratefully acknowledge the support for this research by the National Natural Science Foundation of China (Grant No. 20675034), the Key Programme of the Chinese Ministry of Education (Grant No. 106120), New Century Excellent Talents in Chinese Ministry of Education (Grant No. NCET-05-0668) and the Nature Science Foundation from Hubei Province of China (Grant No. 2006ABA160).

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