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Investigation on photoluminescence quenching of CdSe/ZnS quantum dots by organic charge transporting materials

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The effect of different organic charge transporting materials on the photoluminescence of CdSe/ZnS core/shell quantum dots has been studied by means of steady-state and time-resolved photoluminescence spectroscopy. With an increase in concentration of the organic charge transporting material in the quantum dots solutions, the photoluminescence intensity of CdSe/ZnS quantum dots was quenched greatly and the fluorescence lifetime was shortened gradually. The quenching efficiency of CdSe/ZnS core/shell quantum dots decreased with increasing the oxidation potential of organic charge transporting materials. Based on the analysis, two pathways in the photoluminescence quenching process have been defined: static quenching and dynamic quenching. The dynamic quenching is correlated with hole transporting from quantum dots to the charge transporting materials.

Keywords: *quantum dots; charge transporting; photoluminescence quenching*

1. Introduction

Colloidal fluorescent semiconductor nanocrystals, also known as quantum dots (QDs), have been intensively investigated in the past decades as a luminescent material because of their unique physical and chemical properties [1, 2]. Due to quantum confiement effects, QDs, such as CdSe, CdS, ZnS and ZnSe, possess unique optical properties, including size-tunable photoluminescence (PL), narrow emission bandwidth, high PL quantum yield, broad excitation spectra and superior photostability. So, the QDs have great potential applications in thin-film light-emitting diodes (LEDs), solar cells, lasers, optical amplifier media, biology labels, immunoassay etc. [3–6]. The high surface to volume ratio of QDs means that the surface properties significantly influence their structural and optical properties, because of the large surface area and possible presence of surface states caused by uncoordinated atoms that act as quencher of the

luminescence. It has been proven that overcoating QDs with a shell of a wider band gap semiconductor material can improve the PL quantum yield and photostability by passivating surface nonradiative recombination sites [7]. For example, CdSe/ZnS and CdSe/CdS have been intensively studied over the past decades [8]. However, QDs LEDs are fabricated by sandwiching QDs layer between organic charge transporting material (OCTM) layers [6, 9].

Since the performance of QDs is strongly dependent on their surface properties and structure, the interaction and the dynamic processes between organic molecules and QDs must be deeply investigated for improving the performance of organic and inorganic composite quantum-dots-based optoelectronic devices [10].

In this work, CdSe QDs were synthesised by a successive ion layer adsorption reaction (SILAR) method and were covered by inorganic shell ZnS. With absorption spectroscopy, emission spectrsocopy and time-resolved spectroscopy, the PL quenching of three different organic charge transporting materials,

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NPD (N,N′-di- (1-naphthaleyl)-N,N′-diphenyl-1,1′-biphenyl-4,4′-diamine), TPD (N,N′-diphenyl-N,N′-bis(3-methylphenyl)-1,1′-biphenyl-4,4′-diamine) and TCTA (4,4′,4″-tri(N-carbazolyl)triphenyl-amine) to CdSe/ZnS QDs was studied. The mechanism of the PL quenching with the OCTM was also analyzed in detail.

2. Experimental

2.1. Synthesis of material and characterization

All reagents used here were analytically pure and bought from Sigma Corporation. CdSe/ZnS core/shell QDs were synthesized by typical SILAR method. The detailed procedure can be referred to the litterature [11]. The final products were dispersed in chloroform after removing excess ligands and synthetic byproduct.

Required amounts of organic charge transporting materials NPD, TPD and TCTA were dissolved in 1 mL chloroform to prepare the solutions. Different volumes of OCTM solutions were injected into the sol of CdSe/ZnS QDs to change the concentration of OCTM in the sol.

Steady-state absorption spectra were obtained with a UV-3101PC UV-Vis-NIR spectrometer produced by Shimadzu Corporation. PL spectra were measured with F-4500 fluorescence spectrometer under the excitation of 480 nm. The time-resolved measurements were carried out by a time-correlated single-photo-counting detection system excited at 450 nm with the instrumental response of about 17 ps. The details of the experimental instruments can be referred to the literature [12].

2.2. Results and discussion

The absorption spectra and PL spectra of CdSe/ZnS core/shell QDs are shown in Fig. 1. The emission peak is at about 604 nm. The average particle diameter has been estimated from the wavelength location. The average size of CdSe/ZnS QDs is about 4.2 nm. The calculation shows that the surface of CdSe is covered by two monolayers of ZnS. The CdSe QDs overcoated with the ZnS shell still have strong PL intensity. This is due to the
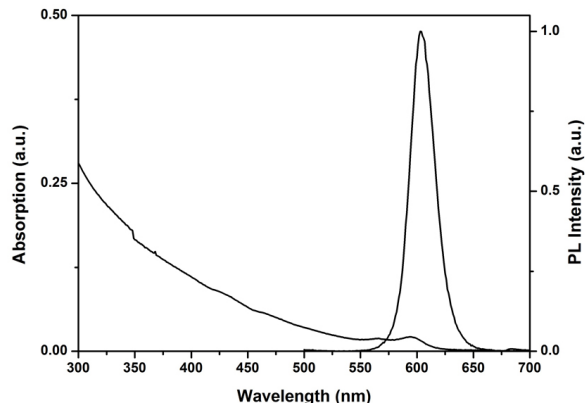

Fig. 1. Absorption and PL spectra of CdSe/ZnS QDs.

passivating effect of the ZnS shell which can modify the surface nonradiative recombination sites of CdSe. The surface-to-volume ratio of CdSe dots is very high, PL of the naked dots is dominated by the broad deep trap emission due to incomplete surface passivation. The growth of ZnS shell on CdSe core should decrease this process by passivating the surface of the core and confine most of the holes and electrons in the core [13].
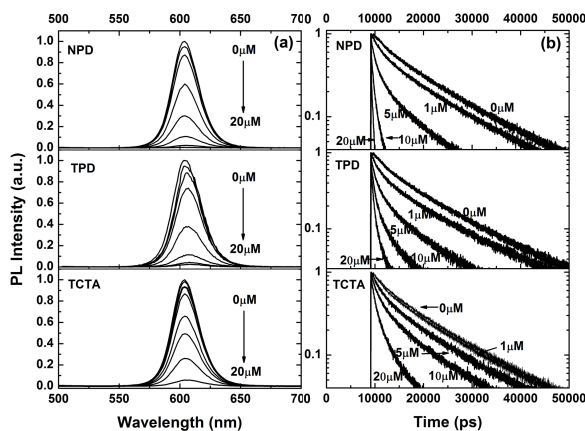

Fig. 2. (a) PL spectra and (b) fluorescence decay curves of CdSe/ZnS QDs with different concentrations of NPD, TPD and TCTA.

In order to investigate the PL quenching of organic molecules in CdSe/ZnS QDs, three different organic charge transporting materials have been chosen: NPD, TPD and TCTA. They are aromatic amine polymers in which N atoms have a strong electron-donating ability. In the process of

continuous electrons transporting, they show hole transporting ability.

Fig. 2a shows the PL spectra of CdSe/ZnS QDs in chloroform with different concentrations of NPD, TPD and TCTA, respectively. With the increase of OCTMs, all the intensities of PL spectra decrease. It can be found that the PL quenching effect of CdSe/ZnS QDs with NPD is the strongest, and that with TCTA is the weakest. This indicates that the PL quenching of CdSe/ZnS QDs is related to the interaction between the organic molecule and the surface of CdSe/ZnS QDs. The potential of oxidation for NPD, TPD and TCTA is 0.27 V, 0.48 V and 0.69 V, respectively. Obviously, the PL quenching effect decreases with the increasing of the oxidation potential of OTCM.

To further clarify the mechanism of PL quenching, the fluorescence decay curves of the mixed solution of CdSe/ZnS QDs and OCTMs were measured. Fig. 2b shows the fluorescence decay curves of the CdSe/ZnS QDs after adding different concentrations of NPD, TPD and TCTA solutions. In general, the fluorescence lifetimes of QDs have been shortened in some degree. For CdSe/ZnS QDs, the shortening of fluorescence lifetime is different for different OCTMs. The reduction of fluorescence lifetime resulting from NPD is greater than that from TPD and TCTA. Considering the value of the oxidation potential, we can conclude that the efficiency of PL quenching increases with the decrease in oxidation potential of OCTMs.

Based on above experimental data, we find that the decay curves are fitted with the kinetic model of a tri-exponential function:

$$I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + A_3 \exp(-t/\tau_3) \tag{1}$$

where τ_j, $j = 1,2,3$ are the lifetimes of the three emission components, respectively, A_j, $j = 1,2,3$ are normalized amplitudes of each component.

In addition, the average lifetimes of QDs are calculated by:

$$\tau_{AV} = (A_1\tau_1^2 + A_2\tau_2^2 + A_3\tau_3^2)/(A_1\tau_1 + A_2\tau_2 + A_3\tau_3) \tag{2}$$

The average lifetimes are listed in Table 1.

In order to intuitively illustrate the effects of OCTMs on PL quenching, the variation of fluorescence intensities and average lifetimes of CdSe/ZnS QDs for different concentrations of OCTMs are shown in Fig. 3. It shows the relation between the PL intensity ratio (I_0/I) and average lifetime (τ_{AV0}/τ_{AV}) of CdSe/ZnS QDs with different OCTMs. Here, I_0 and τ_{AV0} are PL intensity and average lifetime of QDs without OCTMs. It is well known that most PL quenching can be explained by Stern-Volmer equation:

$$I_0/I = 1 + K_{sv}Q \tag{3}$$

where K_{sv} is Stern-Volmer quenching constant, Q is the concentration of quenched material. The results of Fig. 3 are not accord with the Stern-Volmer equation. This implies that there may be static quenching, dynamic quenching or even multiple quenching pathways [14].
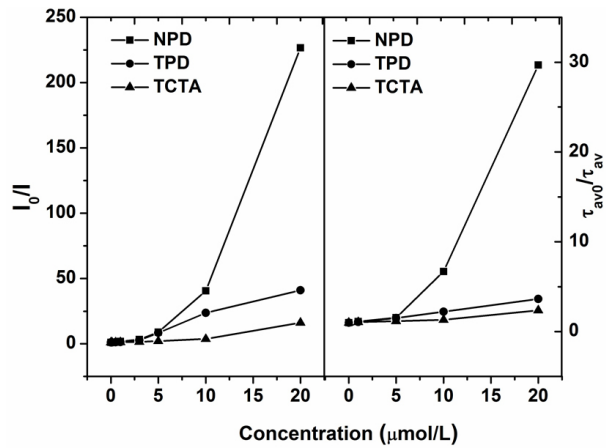

Fig. 3. I_0/I and τ_{av0}/τ_{av} of CdSe/ZnS QDs as a function of OCTMs concentration.

The PL quenching of QDs comes from two possible processes: static quenching and dynamic quenching [15]. There are many hole sites of Zn^{2+} in the ZnS shell, so OCTM molecules occupy these hole sites and then block the combination of electrons and holes. The luminous central ions are easy to be substituted by the charge-transporting molecules adhered to their surface, which may also lead to the static quenching of fluorescence. However, the fluorescence lifetime of QDs cannot be changed by static quenching [16]. On the other

Table 1. Average lifetime of CdSe/ZnS QDs with different concentrations of OCTMs.

Concentration of OCTMs [μmol/L]	Average lifetime of QDs + NPD [ns]	Average lifetime of QDs + TPD [ns]	Average lifetime of QDs + TCTA [ns]
0	12.852	12.852	12.852
1	11.489	11.874	12.151
5	8.236	8.444	11.067
10	1.921	r 5.773	9.689
20	0.433	3.539	5.402

hand, the energy difference between the highest occupied molecular orbital (HOMO) energy level of the OCTMs and the valence band of CdSe/ZnS QDs may lead to dynamic quenching [17]. When the QDs are excited, the holes in their top valence band can be transported to the HOMO energy levels of OCTMs, and then the separation of charge will happen in the interface of QDs and OCTMs. In this work, we selected 480 nm as the excitation wavelength at which only QDs but not OCTMs can be excited. So the holes transporting only happens from QDs to OCTMs. Meanwhile, the oxidation potential of OCTMs indicates that the discrepancy between the holes energy level of QDs and the HOMO energy level of OCTMs is different. According to the theory of hole transporting, the holes transporting probability is inversely proportional to the discrepancy between the hole energy level of QDs and the HOMO energy level of OCTMs. The results of the experiment show that this is the main reason for the decay of PL intensity and the reduction of lifetime of QDs with an increase in the concentration of OCTMs.

3. Conclusions

CdSe/ZnS core/shell QDs have been synthesized by typical SILAR method. The effects of PL quenching of OCTMs on CdSe/ZnS core/shell QDs have been investigated by steady state and time-resolved spectroscopy. With the increase of concentration of OCTMs, the fluorescence of CdSe/ZnS QDs has been effectively quenched. The mechanism of PL quenching consists in transporting of holes originating from QDs to OCTMs. This PL quenching is related to oxidation potential of charge transporting materials. The PL quenching of QDs is due to the static quenching and dynamic quenching.

Acknowledgements

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