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Quantitative Model for the Surface-related Electron Transfer in CdS Quantum Dots

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Abstract The influence of surface S^{2-} dangling bonds and surface doped ions(Se^{2-}, Cu^{2+}, and Hg^{2+}) on the photoluminescence of Cd^{2+}-rich CdS QDs was investigated. A quantitative model was proposed to understand the complex transfer processes of excited electrons in CdS QDs. The transfer of excited electrons from either the conduction band or the Cd^{2+}-related trap-state to the surface S^{2-}-related shallow hole trap-state is effective. However, the trap of excited electrons by surface doped ion trap-states from the Cd^{2+}-related trap-state is more effective than that from the conduction band. The efficiency of trapping electrons from both the conduction band and the Cd^{2+}-related trap-state can be quantitatively understood with the help of the proposed model. The results show that the transfer efficiency of excited electrons is dependent on the location of the energy-level of the relevant surface-related trap-state. The trap of excited electrons by the surface trap-state with energy-level closer to that of the conduction band is more effective, especially for the trap of excited electrons from Cd^{2+}-related trap-state.

Keywords Photoluminescence; Quantitative model; CdS quantum dots; Surface

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1 Introduction

The photoluminescence of semiconductor QDs, especially II-VI semiconductor QDs such as CdS and CdSe nanocrystals, has been investigated intensively by means of various techniques[1—3]. Several groups have studied these QDs in order to characterize the relationship between nanocrystal size, shape, surface structure, and photoluminescent property[2—6]. The photoluminescence technique is one of the most useful tools for investigating the electronic structure, energy state, and property of trap-state on the surface of semiconductor QDs.

Since semiconductor QDs possess a high ratio of surface area to volume, many of their photoluminescent properties are related to the nature of the surface. The surface properties of QDs such as surface vacancies, defects, dangling bonds, local lattice mismatches, and organic ligands, which can result in trap-states on the surface of QDs, are critical for photoluminescent properties[6—12]. The excited electrons or holes can be rapidly trapped by these local trap-states, leading to less effective direct radiative recombination. The emission from the radiative relaxation of the trapped electrons and holes is characterized by broad, highly red-shifted photoluminescence, and sometimes exhibits multiple bands[13]. More recently, the investigation on the influence of the surface structure on the photoluminescent properties of QDs has been a topic of interest[6—12].

CdS QDs are important direct band gap materials with a broad range of potential applications[14,15]. Of many semiconductor QDs investigated, CdS QDs can be considered as a model system for understanding direct band gap QDs[13]. The influence of various parameters on the photoluminescent properties of CdS QDs has been investigated in detail, such as light illumination, size, surface termination(S^{2-} and Cd^{2+} dangling bonds), and surface adsorbates[4,6,13,14]. Either excitonic or trap-state photoluminescence is related to the surface properties of CdS QDs. Surface states of CdS QDs act as temporary traps for excited electrons or holes, preventing them from direct radiative recombination and thus reducing the overall quantum yield of excitonic photoluminescence. The trap-state photoluminescent efficiency is determined by both radiative and nonradiative relaxations of trapped electrons and holes. However, the quantitative relationship

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between radiative, nonradiative processes of excited electrons and holes and various surface-related trap-states has not been well understood. A quantitative model for describing the relation will be readily invited.

Besides the well developed studies of the optical properties and applications of semiconductor QDs, considerable interest has also been focused on the photoluminescent properties of the semiconductor QDs doped with optically active impurities such as transition metal ions, rare earth ions, and other donor or acceptor impurities[16—21]. The interest in the doped semiconductor QDs is owing to their tunable impurity emission properties and application in the area of magnetism[15,17]. Successful doping of semiconductor QDs results in the increase of photoluminescence intensity from the doping centers and the decrease of the photoluminescence intensity of the host QDs. The mechanism of excited electron transfer in such doped semiconductor QDs systems is the subject of numerous studies, especially those for doped ZnS, CdS, and ZnSe QDs systems[16—19,22—24]. The presence of doped impurities within a nanocrystal leads to the faster trap of excited electrons and holes by impurities, corresponding to direct recombination or surface-related recombination. Taking impurity doped CdS QDs as an example, their photoluminescent properties strongly depend on their core/surface structure and surrounding chemical environment such as size, surface defect, impurity content, impurity location, and temperature[18,25,26].

Although the photoluminescence spectra and dynamics of doped semiconductor QDs have been widely investigated, owing to the intricate and surface-related photolumeniscent properties of pure semiconductor QDs, the transfer processes of excited electrons and holes from host QDs to impurities have not been well understood yet. The quantitative understanding of various processes is, however, of utmost importance for both fundamental research and application of doped semiconductor QDs.

In the present article, in order to quantitatively understand the surface-related radiative and nonradiative processes of excited electrons and holes, the influence of surface S^{2-} dangling bonds on the photoluminescence intensity of CdS QDs is examined. An increase in the content of surface S^{2-} dangling bonds can create more nonradiative centers, resulting in the decrease of the photoluminescence intensity. With an analysis of the radiative and nonradiative processes of excited electrons, holes, and surface-related trap states in CdS QDs, a quantitative model is proposed and discussed, which offers an insight into the complex relaxation processes of excited electrons and holes. Additionally, to quantitatively understand the transfer or trap processes of excited electrons and holes from host QDs to impurities in doped QDs, the effects of adsorbed Se^{2-} and transition metal ions(Cu^{2+} and Hg^{2+}) on the photoluminescence intensity of CdS QDs are investigated, wherein the proposed quantitative model is applied to the analysis of the transfer processes of excited electrons from host CdS QDs to impurities(Se^{2-}, Cu^{2+} and Hg^{2+}) in doped CdS QDs.

2 Experimental

2.1 Chemicals

Mercaptoacetic acid($HSCH_2COOH$), cadmium chloride($CdCl_2\cdot10H_2O$), sodium sulfide($Na_2S\cdot9H_2O$), selenium powder(Se), sodium borohydride($NaBH_4$), copper sulfate($CuSO_4$), mercury chloride($HgCl_2$), and other routine chemicals were purchased from Shanghai Reagents Factory, China, and used as received without further purification. NaHSe solution was prepared from the reaction between selenium powder and $NaBH_4$. All chemicals used were of analytical-reagent grade. Doubly deionized water was used throughout the experiment.

2.2 Preparation of Water-soluble Cd^{2+}-rich CdS QDs

Water-soluble Cd^{2+}-rich CdS QDs capped by mercaptoacetic acid were synthesized by means of the method reported by Winter *et al.*[27] with modifications. Firstly, 10 mmol of $CdCl_2\cdot10H_2O$ and 110 mmol of mercaptoacetic acid were dissolved in 100 mL of deionized water in a 250 mL rockered flask, and then the pH value was adjusted to 6.5 with NaOH solution. Then, 7.5 mmol of $Na_2S\cdot9H_2O$ dissolved in 40 mL of deionized water was added dropwise to the Cd^{2+} solution with vigorous stirring, and the solution gradually turned into yellow. After stirring overnight(~12 h), 100 mL of acetone was added to the yellow solution for precipitating the CdS QDs. The resultant precipitation was filtrated, washed with a copious amount of acetone, and dried. The prepared Cd^{2+}-rich CdS QDs powder was finally resuspended in doubly deionized water for further investigation.

2.3 Procedures

Stock solutions were prepared by dissolving the pure solid into doubly distilled water. Diluted solutions were prepared from the stock ones. Stock solutions of Cd^{2+}-rich CdS QDs were kept in the darkness.

CdS QDs with different contents of surface S^{2-} dangling bonds were obtained by adding various amounts of S^{2-} ions to the initial solutions of Cd^{2+}-rich CdS QDs. First, 7.5 mg of Cd^{2+}-rich CdS QDs was added to 150 mL of rockered flasks and dissolved with 100 mL of deionized water. Then, different amounts of S^{2-} ions(1×10^{-3} mol/L, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35, 0.40, 0.50, 0.60, 0.70, 0.80, 0.90, 1.00, 2.00 and 3.00 mL) were added to the solutions of Cd^{2+}-rich CdS QDs, respectively. The prepared CdS QDs with different contents of surface S^{2-} dangling bonds were used for fluorescence measurements.

Different ions(Cu^{2+}, Hg^{2+} and Se^{2-}) doped CdS QDs(surface doped) were obtained by adding relevant ions to the initial solutions of Cd^{2+}-rich CdS QDs (same as the procedure described above), and the doped content was determined by the amount of relevant ions added. Experiments involving Se^{2-} ions were performed in N$_2$ atmosphere.

A Tris-HCl buffer solution with a pH value of 7.4 was chosen to run the spectroscopy measurements. A Varian Cary 300 UV-Vis spectrophotometer was used for recording the absorption spectra. A Shimadzu RF-5301pc spectrofluorometer was used for recording the photoluminescence spectra. All photoluminescence spectra were recorded at room temperature using a Xenon lamp as the source of excitation and a 3-mL standard quartz cuvette(10 mm×10 mm). The optical density(absorbance) of the sample was kept below 0.05 to avoid inner filter effects. The emission intensity integrated from 410 to 690 nm($\lambda_{\rm ex}$=350 nm) was used for quantitative analyses. The relative photoluminescence quantum yield was determined by the comparison of the wavelength-integrated photoluminescence intensity of the sample with that of a standard one[28]. The initial Cd^{2+}-rich CdS QDs were chosen as the standard and their quantum yields were all regarded as 1.0 in order to conveniently and quantitatively analyze the influence of the surface states of CdS QDs on the photoluminescence intensity.

High-resolution transmission electron microscopy(HRTEM) was performed on a Tecnai F30 electron microscope. The sample preparation was done by placing a drop of the freshly prepared colloidal solution on a carbon coated copper grid, and the excess solution was then removed.

3 Results and Discussion

3.1 Spectroscopic Properties of Cd^{2+}-rich CdS QDs

Fig.1 curve *a* depicts the absorption spectrum of the initial Cd^{2+}-rich CdS QDs. The value of $E_{\rm g}$ obtained at the absorption onset was calculated to be 2.83 eV. Using the three-dimensional confinement model[29,30], the average particle diameter was estimated to be 3.5 nm. The morphology of the prepared Cd^{2+}-rich CdS QDs was also studied by the HRTEM. Based on the TEM image shown in Fig.2, it is found that the shape of these nanoparticles is closely spherical, though the average diameter of the particles(~5 nm) is larger than that estimated from the three-dimensional confinement model.

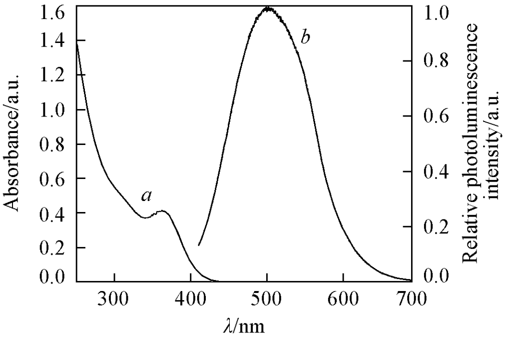

Fig.1 Absorption(*a*) and photoluminescence(*b*) spectra of initial Cd^{2+}-rich CdS QDs

[Cd^{2+}-rich CdS QDs]$_a$=10[Cd^{2+}-rich CdS QDs]$_b$.

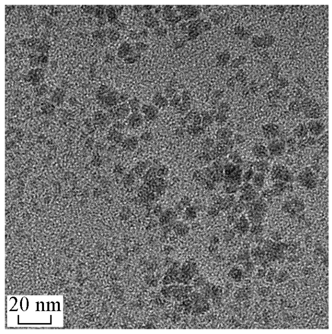

Fig.2 TEM image of CdS QDs

The photoluminescence spectrum($\lambda_{\rm ex}$=350 nm) given in Fig.1 curve *b* shows that the emission peak at 510 nm is red shifted by *ca.* 60 nm from the absorption onset. The photoluminescence of Cd^{2+}-rich CdS QDs with a large Stokes' Shift is usually considered to originate from Cd^{2+} dangling bonds on the particle surface[29,31]. Thus, it should be mentioned that CdS QDs synthesized with an excess of Cd^{2+} ions are indispensable for a large number of Cd^{2+} dangling bonds on the CdS QDs surface and a higher quantum yield of trap-state photoluminescence[27]. In addition, the photoluminescence emission of CdS QDs is broadly banded(Fig.1 curve *b*), and the full width at half maximum(FWHM) of the emission is *ca*. 120 nm. Since the photoluminescence emission is usually red shifted with the average size of the particles increase, QDs in aqueous solution with wide size distribution can extend the emission band. However, even when the size distribution of the sample has been eliminated by the fluorescence line narrowing technique where only the largest QDs are excited, the emission band is still broad. The broad band emission of the prepared Cd^{2+}-rich CdS QDs is thus mostly caused by a large number of surface trap-states on the surface of CdS QDs.

3.2 Trap-state Photoluminescence of Cd^{2+}-rich CdS QDs

The band edge excitonic photoluminescence was not observed for the prepared CdS QDs. The broad, large Stocks' Shift emission from Cd^{2+}-rich CdS QDs is defined as the surface trap-state photoluminescence. Numerous researches have been performed to explore the essential mechanism of the photoluminescence process. To the best of our knowledge, the recombination of shallow trapped electrons and deep trapped holes has been considered as a dominant source of the surface trap-state photoluminescence in Cd^{2+}-rich CdS QDs[6,13,29]. The density of such trap-states is positively related to the content of surface Cd^{2+} dangling bonds in CdS QDs. The higher content of surface Cd^{2+} dangling bonds results in more shallow-trapped electrons and deep-trapped holes, and hence the more effective surface trap-state photoluminescence[6,13].

The process of the surface trap-state photoluminescence can be understood in terms of the energy level diagram[32] described in Fig.3. The surface-related shallow and deep trap-states were both defined as Cd^{2+}-related trap-state on the basis of the above discussion. The other nonradiative processes of excited electrons and holes are not shown in the energy-level diagram, because the photoluminescence quantum yield of the initial Cd^{2+}-rich CdS QDs is defined as 1.0. Thus, the other nonradiative processes of excited electrons and holes in initial Cd^{2+}-rich CdS QDs are not considered when the influence of surface S^{2-} dangling bonds, Cu^{2+}, Hg^{2+}, and Se^{2-} ions on the photoluminescence intensity is investigated.

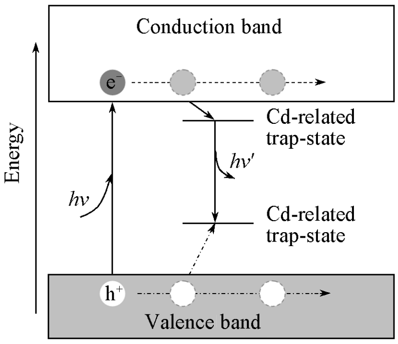

Fig.3 Energy-level diagram describes the process of the surface trap-state photoluminescence

3.3 Influence of Surface S^{2-} Dangling Bonds on the Photoluminescence of Initial Cd^{2+}-rich CdS QDs

After the addition of S^{2-} ions, the absorption spectrum is red shifted[Fig.4(A)], indicating that the introduction of S^{2-} enlarges the CdS QDs. A fresh CdS layer is probably formed outside the CdS QDs where several Cd^{2+} dangling bonds can exist on the surface in the case of Cd^{2+} excess under the current synthesis conditions. The binding of S^{2-} onto the surface of Cd^{2+}-rich CdS QDs is owing to the strong association constant between S^{2-} ions and Cd^{2+} dangling bonds existing at Cd^{2+}-rich CdS QDs surface. In addition, excess S^{2-} ions also compete with —SH groups in mercaptoacetic acid, which bind with surface Cd^{2+} for the stability of the CdS QDs, resulting in particles with less surface protective groups and lower stability. However, such competitive effect is speculated to be

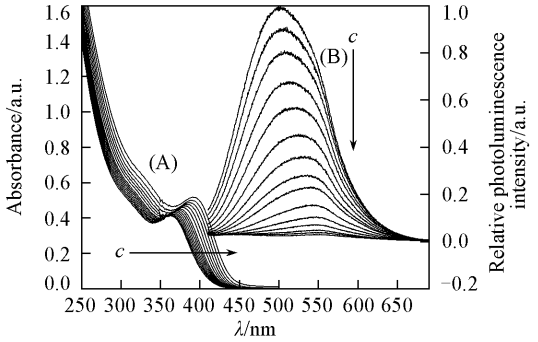

Fig.4 Absorption spectra of CdS QDs(75 mg/L) in the presence of additive S^{2-} ions at various concentrations(A) and the fluorescence emission spectra of CdS QDs(7.5 mg/L) in the presence of additive S^{2-} ions at various concentrations(B)

(A) 10^4 $c/(mol\cdot L^{-1})$: 0, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35, 0.40, 0.50, 0.60, 0.70, 0.80, 0.90, 1.00, respectively, pH=7.4; (B) 10^5 $c/(mol\cdot L^{-1})$: 0, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35, 0.40, 0.50, 0.60, 0.70, 0.80, 0.90, 1.00, respectively, pH=7.4. λ_{ex}=350 nm.

not effective while the amount of the additive sulfide is not excess enough. This speculation is supported by the absence of the scattering background in absorption spectra shown in Fig.4(A) because the dissociation of the surface ligands can cause the precipitation of QDs and thus a significant scattering in the sample[33]. A significant scattering background is just evidenced in the solution of Cd^{2+}-rich CdS QDs with sufficiently excess additive S^{2-} ions.

The quenching together with a red shift of the photoluminescence emission of Cd^{2+}-rich CdS QDs by the addition of S^{2-} ions is shown in Fig.4(B). The photoluminescence quenching is owing to the removal of the Cd^{2+} dangling bonds and the creation of S^{2-} dangling bonds by the binding of S^{2-} ions to Cd^{2+} ions on the surface of Cd^{2+}-rich CdS QDs. The photoluminescence red shift results from the enlargement of CdS nanoparticles.

Based on the above discussion, the influence of additive S^{2-} ions on the photoluminescence of Cd^{2+}-rich CdS QDs is quantitatively related to the influence of the surface S^{2-} dangling bonds. The binding of ions to the surface of nanoparticles can be effectively described by the Langmuir-type binding isotherm[34]. The surface of initial Cd^{2+}-rich CdS QDs consists of a finite number of Cd^{2+} dangling bonds. Each Cd^{2+} dangling bond can adsorb one S^{2-} ion. The fraction of surface Cd^{2+} dangling bond covered by S^{2-} ions is defined as θ. According to the Langmuir-type binding isotherm model, the relation between surface S^{2-} coverage θ and the concentration of S^{2-} ions c in the solution can be expressed as follows:

$$\theta/(1-\theta)=Kc \tag{1}$$

where, $1-\theta$ is the fraction of residual Cd^{2+} dangling bonds, and K is the equilibrium constant for binding.

The energy-level diagram described in Fig.5 shows the influence of surface S^{2-} dangling bonds on the transfer or trap of excited electrons and holes in CdS QDs. The trap-state photoluminescence arises from the Cd^{2+}-related trap-state. Addition of S^{2-} ions covers the surface of CdS QDs with S^{2-} ions and thus creates surface S^{2-} dangling bonds. S^{2-} dangling bonds on the surface of CdS QDs result in the creation of shallow hole trap-states, which trap excited electrons from both the conduction band(process ②) and the Cd^{2+}-related trap-state(process ④). The quantum yield of the Cd^{2+}-related trap-state photoluminescence is determined by two processes. Firstly, the efficiency of trapping excited electrons from the conduction band by Cd^{2+}-related trap-states(process ①), which is determined by both processes ① and ②. Secondly, the efficiency of the recombination of trapped electrons and holes(process ③), which is determined by both processes ③ and ④. Thus, both processes ③ and ④ cause the decrease of the surface trap-state photoluminescence.

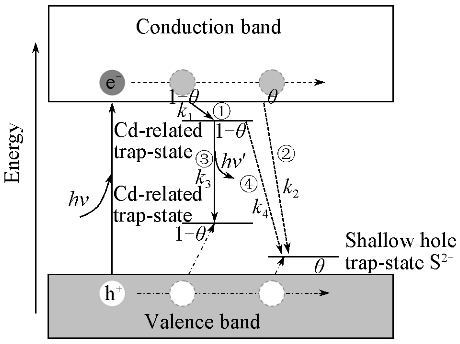

Fig.5 Energy-level diagram describes the influence of surface S^{2-} dangling bonds on the transfer or trap of excited electrons and holes in CdS QDs

Processes ① and ② in CdS QDs can be expressed as follows: $CdS(e_1)+Cd^{2+}\text{-related trap-state} \longrightarrow CdS+Cd^{2+}\text{-related trap-state}(e_1)$, process ①; $CdS(e_2)+\text{shallow hole trap-state(h)} \longrightarrow (he_2)+\text{nonradiation}$, process ②. Where, $CdS(e_1)$ represents the excited electrons located near surface Cd^{2+} dangling bonds(Cd^{2+}-related trap-state) and $CdS(e_2)$ represents those near surface S^{2-} dangling bonds(shallow hole trap-state). It is speculated that the density of the Cd^{2+}-related trap-state and $CdS(e_1)$ is directly proportional to the fraction of the surface Cd^{2+} dangling bonds($1-\theta$), while that of the shallow hole trap-state and $CdS(e_2)$ is directly proportional to the fraction of surface S^{2-} dangling bonds(θ). The reaction rate of process ① is determined by the density of the Cd^{2+}-related trap-state and $CdS(e_1)$. Likewise, the reaction rate of process ② is determined by the density of the shallow hole trap-state and $CdS(e_2)$. The rate of processes ① and ② can be given by the following equations

$$R_1 = k_1(1-\theta)(1-\theta) \tag{2}$$

$$R_2 = k_2\theta\theta \tag{3}$$

where, k_1 and k_2 are the rate constants of processes ① and ②, respectively. The efficiency of trapping excited electrons from the conduction band by Cd^{2+}-related trap-states can be, therefore, described by

$$\varphi_1 = \frac{R_1}{R_1 + R_2} = \frac{k_1(1-\theta)(1-\theta)}{k_1(1-\theta)(1-\theta) + k_2\theta\theta} \qquad (4)$$

By combining Eq.(1) with Eq.(4), it can be written that

$$\varphi_1 = \frac{1}{1+[(k_2/k_1)K^2]c^2} = \frac{1}{1+p_1c^2} \qquad (5)$$

The above equation quantitatively describes the influence of the surface S^{2-} dangling bonds on the efficiency of trapping excited electrons from the conduction band by Cd^{2+}-related trap-states.

Similarly, processes ③ and ④ in CdS QDs can also be described by the following reaction equations: Cd^{2+}-related trap-state(e$_1$)+Cd^{2+}-related trap-state(h) → (he$_1$)+$h\upsilon$ process ③; Cd^{2+}-related trap-state(e$_1$)+shallow hole trap-state(h) → (he$_1$)+non-radiation Process ④.

The rate of processes ③ and ④ can be given by

$$R_3 = k_3(1-\theta)(1-\theta) \qquad (6)$$

$$R_4 = k_4(1-\theta)\theta \qquad (7)$$

where, k_3 and k_4 are the rate constants of processes ③ and ④, respectively. The efficiency of the recombination of trapped electrons and holes can be described by the following equation:

$$\varphi_2 = \frac{1}{1+[(k_4/k_3)K]c} = \frac{1}{1+p_2c} \qquad (8)$$

Eq.(8) quantitatively describes the influence of surface S^{2-} dangling bonds on the efficiency of the recombination of trapped electrons and holes.

Based on the above discussion, the relative quantum yield of the Cd^{2+}-related trap-state photoluminescence can be calculated *via*

$$\varphi = \varphi_1\varphi_2 = \frac{1}{1+p_1c^2}\frac{1}{1+p_2c} \qquad (9)$$

where, p_1 and p_2 quantitatively describe the contributions of the influence of processes ② and ④ on the trap-state photoluminescence of CdS QDs, respectively. Eq.(9) together with the energy-level diagram can be used as a quantitative model for investigating the influence of surface S^{2-} dangling bonds on the photoluminescence of CdS QDs. Additionally, as can be calculated from Eq.(9), the quantum yield of initial Cd^{2+}-rich CdS QDs without the addition of S^{2-} ions is 1.0 because the other nonradiative processes in initial Cd^{2+}-rich CdS QDs are not considered.

Based on the above analysis, it is expected that the relative photoluminescence quantum yield as a function of the content of surface S^{2-} dangling bonds can be well fitted using Eq.(9). As an example, a plot of the relative quantum yield of CdS QDs with different contents of surface S^{2-} dangling bonds is shown in Fig.6(A). The fitted curve closely matches the experimental data, supporting the proposed quantitative model in the current study. The obtained values for p_1 of 1.305×10^5 L/mol and p_2 of 1.051×10^5 L/mol, respectively, are not largely different, indicating that the trap of the excited electrons from the conduction band(process ②) and Cd^{2+}-related trap-state(process ④) by the surface S^{2-} related shallow hole trap-state is effective. Thus, it is suggested that the proposed quantitative model provides a feasible method for an insight into the complex relaxation processes of excited electrons and holes in CdS QDs.

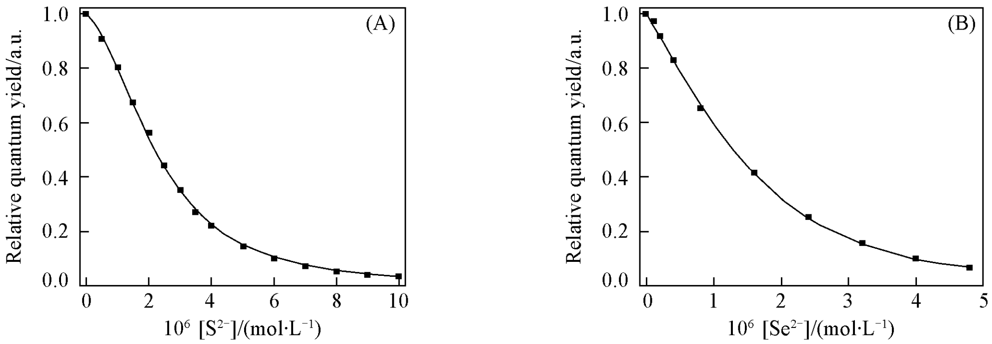

Fig.6 Quantitative model plots for the influence of the additive S^{2-}(A) and Se^{2-}(B) ions on the relative quantum yield of CdS QDs

3.4 Influence of Surface Doped Se^{2-} Ions on the Photoluminescence of Initial Cd^{2+}-rich CdS QDs

Since Se^{2-} ions are analogous to S^{2-} ions in property and structure, and are even more highly reactive toward Cd^{2+} than S^{2-}, they can also effectively bind with Cd^{2+} dangling bonds existing on the surface of initial Cd^{2+}-rich CdS QDs. The introduction of Se^{2-}

ions forms a fresh CdSe layer outside of the CdS QDs, resulting in the enlargement of the particle size(judged by absorption spectra). The quenching and red shift of the photoluminescence emission, which parallels the observation with the addition of S^{2-} ions, are owing to the removal of the Cd^{2+} dangling bonds and the creation of surface doped Se^{2-} ions(Se^{2-} dangling bonds). Se^{2-} dangling bonds on the surface of CdS QDs also result in the creation of shallow hole trap-states, and trap excited electrons from both the conduction band and the Cd^{2+}-related trap-state. However, the quenching efficiency of Se^{2-} ions is higher than that of S^{2-} ions, indicating that the trap of excited electrons by the surface Se^{2-}-related shallow hole trap-state is more effective than that by the surface S^{2-}-related shallow hole trap-state. It is well known that QDs coated with a larger band-gap semiconductor layer result in the enhancement of the photoluminescence partly owing to the localization of electrons and holes in core QDs[14]. Conversely, an outer semiconductor layer with smaller band-gap provides an additional area of delocalization for electrons and holes, resulting in the repression of the photoluminescence[14]. Since the band-gap of CdSe is smaller than that of CdS, the more effective quenching of the photoluminescence of CdS QDs by the surface Se^{2-} ions than that by the surface S^{2-} ions is quite reasonable. In addition, the energy-level of surface Se^{2-}-related shallow hole trap-state in CdS QDs is related to the band-gap of CdSe and is thus deeper than that of surface S^{2-}-related shallow hole trap-state. Therefore, the deeper the hole trap-state, the more effective is the trap of excited electrons.

Based on the above analysis, the quantitative model proposed can also be introduced for investigating the influence of surface doped Se^{2-} ions on the photoluminescence of CdS QDs. With the aid of Eq.(9), a plot of the relative quantum yield of CdS QDs as a function of the different contents of surface doped Se^{2-} ions is shown in Fig.6(B). This yields the values for p_1 of 1.613×10^5 L/mol and p_2 of 4.483×10^5 L/mol, respectively. The fitted curve closely matches the data, further supporting the quantitative model. However, the obtained value of p_2 is larger than that of p_1, indicating that the transfer of the excited electron from the Cd^{2+}-related trap-state to the Se^{2-}-related shallow hole trap-state is more effective than that from the conduction band.

3.5 Influence of Surface Doped Metal Ions(Cu^{2+} and Hg^{2+}) on the Photoluminescence of Initial Cd^{2+}-rich CdS QDs

The association constants between doped metal ions(Cu^{2+} and Hg^{2+}) and S^{2-} ions are considerably larger than that between Cd^{2+} ions and S^{2-} ions. The introduction of Cu^{2+} ions or Hg^{2+} ions into the solution of initial Cd^{2+}-rich CdS QDs causes a rapid substitution of surface Cd^{2+} ions with Cu^{2+} ions or Hg^{2+} ions[29,35,36]. The adsorbed metal ions create a new surface state, which is defined as the deep electron trap-state(a mid-gap energy level located near the middle of the band-gap of CdS QDs)[29]. The deep electron trap-state can trap excited electrons from both the conduction band and the Cd^{2+}-related trap-state, leading to the photoluminescence quenching of Cd^{2+}-rich CdS QDs and the creation of photoluminescence from doping centers. However, the photoluminescence from doping centers was not observed here perhaps owing to the unfavorable impurity location. Moreover, the quenching of the photoluminescence of CdS QDs by the surface doped Cu^{2+} and Hg^{2+} ions is more effective than that by surface S^{2-} and Se^{2-} ions, indicating that the trap of excited electrons by the deep electron trap-state is more effective than that by the shallow hole trap-state. Therefore, it can be concluded that the trap efficiency of the surface-state increases with increasing the energy gap between the conduction band and energy-level of the relevant surface trap-state.

The binding of metal ions(Cu^{2+} and Hg^{2+}) onto the surface of Cd^{2+}-rich CdS QDs results in the formation of new electron trap-states together with a decrease of the surface Cd^{2+}-related trap-states. Thus, the quantitative model proposed is also effective for investigating the influence of surface doped Cu^{2+} and Hg^{2+} ions on the photoluminescence of CdS QDs. Fig.7 depicts the plots of the relative quantum yield changes of CdS QDs with different contents of surface doped Cu^{2+} ions(A) and Hg^{2+} ions(B) fitted by Eq.(9). The values for p_1 of 4.000×10^4 L/mol and p_2 for 3.913×10^6 L/mol obtained from the fitted curve a and the value of 2.150×10^4 L/mol and 2.973×10^6 L/mol, respectively, obtained from the fitted(B) both indicate that the transfer of excited electron from Cd^{2+}-related trap-state is considerably more effective than that from the conduction band. As compared to

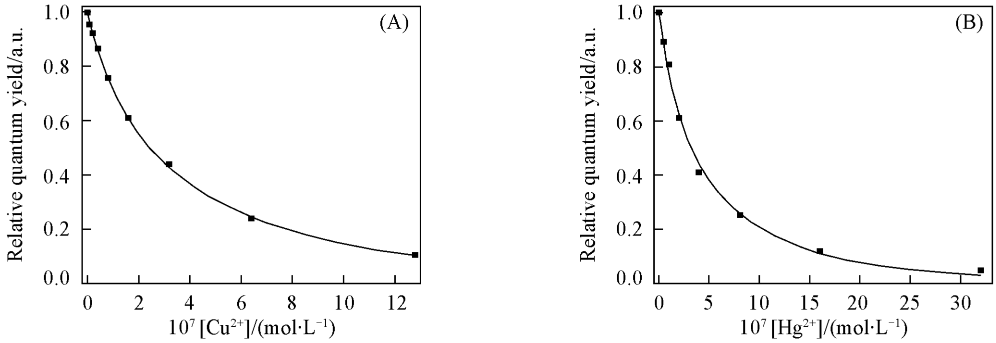

Fig.7 Quantitative model plots for the influence of the additive Cu^{2+}(A) and Hg^{2+}(B) ions on the relative quantum yield of CdS QDs

the results obtained from Fig.6(A) and (B), it is possible to conclude that the smaller energy gap between the conduction band and the surface trap state will be favorable for trapping excited electrons from Cd^{2+}-related trap-state. The energy gap between the conduction band and the energy-level of the surface state follows the order, $S^{2-}>Se^{2-}>Hg^{2+}$, Cu^{2+}(see Fig.8).

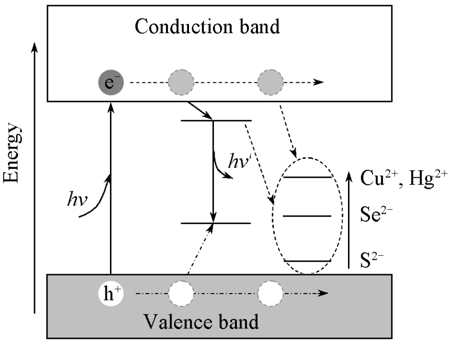

Fig.8 Energy-level diagram describes the influence of surface-related trap-states on the transfer or trap of excited electrons and holes in CdS QDs

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