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碲化镉纳米晶中温度相关的能量转移

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摘要:为了获得纳米晶之间以及单个纳米晶内部本体态至缺陷态两种能量转移在不同温度下对发光强度的影响,测量了碲化镉纳米晶层发光光谱随温度(78~300 K)的变化情况.碲化镉纳米晶层发光光谱显示:碲化镉纳米晶层在低温下有明显的本体(约 520 nm)和缺陷(约 605 nm)发光,且发光强度随温度的改变呈现出不同的变化规律.在温度变化的第一阶段(78~140 K),大尺寸碲化镉纳米晶发光效率高、表面缺陷少,小尺寸纳米晶至大尺寸纳米晶间的能量转移使得纳米晶本体发光强度逐渐升高、缺陷发光强度迅速降低.在温度变化的第二阶段(140~300 K),随着温度的升高,无辐射跃迁几率的增大使得碲化镉纳米晶缺陷态和本体态发光强度均逐渐降低.因此,能量转移仅在温度变化的第一阶段对发光强度的影响起主要作用,在第二阶段起次要作用.为了进一步验证能量转移对发光强度的影响,将碲化镉纳米晶用聚乙二醇包裹以减少纳米晶间的能量转移;将纳米晶层的干燥过程放在近真空环境下进行以减少单个纳米晶内部本体至缺陷态的能量转移.光谱结果显示在温度变化的第一阶段,这两种方式下得到的纳米晶层发光强度均逐渐降低,能量转移对发光强度的影响不再起主要作用.证实了能量转移对发光强度的影响规律的合理性.

关键词:发光学;能量转移;温度;缺陷;碲化镉纳米晶

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Two Temperature-dependent Energy Transfers in CdTe Nanocrystal Films

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Abstract: In order to obtain the influence of two temperature-dependent energy transfers (the one Energy Transfers (ET) from band edge to defect states in one nanocrystal and the other energy transfers from different size nanocrystals) on fluorescence emission intensity of CdTe nanocrystals, the fluorescence emission spectra of CdTe nanocrystals films at temperature from 78 to 300 K were investigated. The results of the experiment show that the fluorescence emission spectra of CdTe nanocrystals films exhibit band edge emission centered at about 520 nm and defect fluorescence emission centered at about 605 nm, and the fluorescence intensity presents different change regularity with temperature increasing. At the first stage of temperature(78~140 K), for the green-emitted CdTe NCs, large size ones have fewer defect sites and the fluorescence emission efficiency is higher than the small size ones. The energy transfers from small size ones to large, resulting in increasing of the band edge fluorescence emission intensity. At the second temperature stage(140~300 K), the defect and band edge fluorescence emission intensity gradually decreases. Therefore, the ET rates with temperature are prominent at the first stage of temperature and subordinate at the second temperature stage, compared to the nonradiative recombination rates. To further prove the influence of ET on the fluorescence emission intensity, the CdTe NC films were dried under vacuum conditions, which could avoided the atmospheric oxidation and therefore had fewer defects on the NCs surface. CdTe NCs were put in PEG matrix film in order to

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reduce the ET rates from different size nanocrystals. Fluorescence emission intensities of as-prepared CdTe NC films were decreased with temperature at the first stage and coincided with the variations of ET rates with temperature.

Key words: Fluorescence emission; Energy transfer; Temperature; Defect; CdTe nanocrystals

OCIS Codes: 160.4670; 160.6000; 260.2160; 300.6280; 310.6860

0 Introduction

Nanocrystals (NCs) are nanometer sized semiconductor crystallites, which exhibit unique properties compared to the respective bulk semiconductor material. As a typical semiconductor NC material, CdTe NCs are currently receiving widespread attention due to their size dependent electronic and optical properties, and have been used in, light-emitting diodes, solar cells, fluorescent probe, etc^[1]. However, despite significant progress in CdTe NCs device development, a detailed understanding of the effect of NCs size and morphology on their optical properties remains limited. Fluorescence emission from the CdTe NCs depends largely on defect content, stoichiometry, dopant type and concentration, grain size and morphology, and sample temperature. Thus, the study of the optical properties of CdTe NCs is important to both the fundamental and applied points of view.

Additionally, NCs can be chemically manipulated like large molecules. They can be incorporated into polymer and glass matrices and into different photonic structures, including microcavities and photonic crystals. NCs can also be assembled into close packed ordered and disordered arrays. The combination of tunable electronic energies and chemical flexibility makes NCs ideal building blocks for the bottom-up assembly of optical device structures, including optical amplifiers and lasers^[2]. In the limit of large numbers of coupled dots, colloidal semiconductor NCs provide a promising route towards large-scale nanoassemblies that can be treated as "artificial solids". In addition, communication, coupling, and coherence between NCs are central themes in numerous scientific effort of present physical and technological interest^[3]. In strongly coupled NC assemblies, electronic excitations can delocalize across multiple NCs leading to new states described by coherent superpositions of individual NC wave functions in principle.

An alternative approach exploits the readily achievable coupling via incoherent long-range dipolar interactions, which allow interdot communication via Förster Energy Transfer (ET)^[4], an effect well known in organic dyes, polymers, and biomolecules, and recently observed in NC quantum dots/dye systems^[5]. Recently, a close-packed layered NC film has been demonstrated not only to efficiently transfer excitation energy to desired fluorescence emission energy, but

also to increase the fluorescence emission intensity by recycling of otherwise trapped excitons^[6]. However, in close-packed films of CdTe NCs, besides ET between different size NCs, the ET from band edge to defect in one NC is also closely related to the electronic and optical properties.

In this paper, we investigated these two temperature-dependent ET through the fluorescence emission spectra of CdTe NC films in the temperature range of 78-300 K. Both band edge and defect fluorescence emission characteristics of CdTe NC films show different temperature dependence. A model for the transition states and processes was established and the thermally related ETs were used to explain these emission characteristic variations at different temperatures.

1 Experiment

1.1 Materials

All materials used in this work were analytical reagents. Cadmium chloride (CdCl_2) (99 + %), sodium borohydride (NaBH_4) (99%), and Poly Ethylene Glycol (PEG) were purchased from the Beijing Chemical Factory, China. 3-Mercaptopropionic Acid (MPA) (99 + %) and Tellurium (Te) powder (99.8%) were purchased from Alfa Aesar. Sodium hydrogen telluride (NaHTe) solution was prepared by using Te powder and NaBH_4 in accordance with reference methods^[7]. By a molar ratio of 2:1, NaBH_4 was used to react with Te powder in water to produce NaHTe . Briefly, 0.337 g of NaBH_4 was transferred to a small flask; then 6 mL of deionized water was added. After 0.51 g of Te powder was added in the flask, the reacting system was cooled by ice water. During the reaction, a small outlet connected to the flask was kept open to discharge the pressure from the resulting hydrogen. After approximately 8 h, the black Te powder disappeared and sodium tetraborate white precipitation appeared on the bottom of the flask instead. The resulting NaHTe in clear supernatant was separated and used in the preparation of CdTe NCs.

1.2 Synthesis of CdTe NCs

CdTe NCs were synthesized according to a previous synthesis method^[7]. Typically, the pH of CdCl_2 and MPA mixed solution was adjusted to 9.1, then freshly prepared NaHTe solution was injected into the solution after being degassed with nitrogen gas for 30 min. To obtain CdTe NCs, the crude solution was refluxed at 100°C for 2.5 h and then cooled to room

temperature in the open air. The feed molar ratio of Cd²⁺/MPA/NaH₂Te was 1:2.4:0.2. The as-prepared CdTe NCs exhibit PL at wavelengths of about 540 nm in solution at room temperature.

1.3 The preparation of CdTe NC films

The close-packed CdTe NC films were prepared by the CdTe NCs which were directly dispersed in aqueous solution. Typically, CdTe NCs solution were deposited on quartz substrate and then dried in the air, resulting in close-packed CdTe NC films. The Poly Ethylene Glycol (PEG) matrix films of CdTe NCs were prepared in a similar way. Briefly, the PEG aqueous solution at pH 9.0 was added into CdTe NCs solution, stirring for 15 h. Then the solution were deposited on quartz substrate and dried in the air.

1.4 Characterization

Fluorescence spectrum measurements were performed with a FLS920 combined fluorescence steady state and lifetime spectrometer. In the fluorescence spectra experiments, the source of exciting light was a 450 W xenon lamp. For temperature-dependent measurements, the samples were loaded into an Oxford closed cycle liquid nitrogen cryostat, and the temperature of CdTe NCs films was regulated from 78 K to room temperature. Transmission Electron Microscopy (TEM) was recorded by Tecnai F20 electron microscope with an acceleration voltage of 200 kV. The as-prepared CdTe NCs directly used for TEM measurement without further post-synthesis treatment.

2 Results and Discussion

In order to investigate the ET of NCs, green-emitted CdTe NCs were used. The TEM image of CdTe NCs is shown in Fig. 1. The TEM images show the formation of CdTe NCs, which are nearly spherical in shape. To estimate the average size, 30 CdTe NCs were measured and the average result was used. TEM image shows as-prepared CdTe NCs with average sizes of 2.4 nm in diameter. Although room temperature PL is essential for determining the optical applications of such fluorescent semiconductor NCs, temperature-dependent PL can especially reveal not only the physical process in band edge fluorescence emission but also

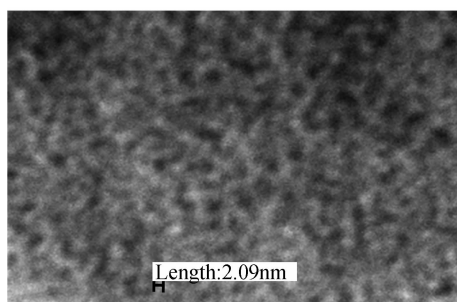


Fig. 1 TEM image of CdTe NCs

the dissociation processes of defects in NCs^[8]. Hence the PL spectra of CdTe NCs in the close-packed film have been measured at temperature range of 78 ~ 300 K, as shown in Fig. 2. The PL spectra of green emitted CdTe NCs in the close-packed film (Fig. 2(a)) exhibit band edge fluorescence emission centered at about 520 nm and defect fluorescence emission centered at about 605 nm at low temperature of 78 K. The fluorescence emission peaks show obviously red shift with the increase of sample temperature because the band gap narrows gradually with rise of temperature^[9].

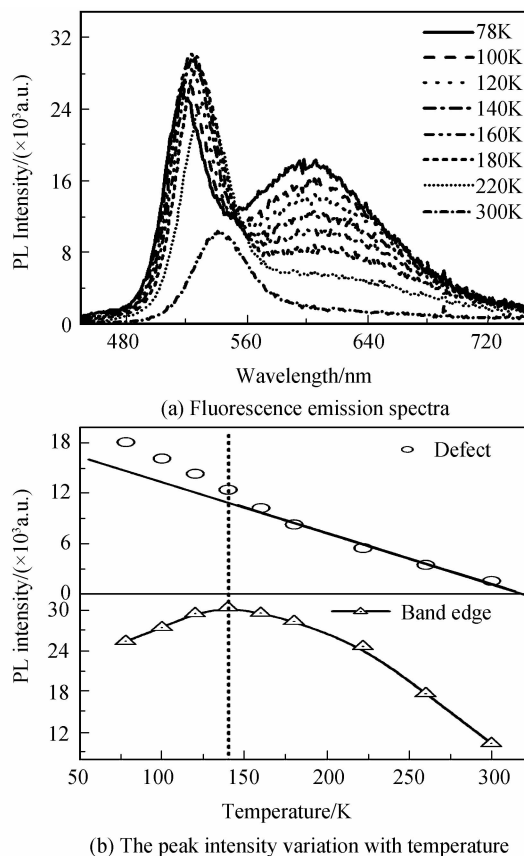


Fig. 2 Temperature-dependent fluorescence emission spectra of CdTe NCs in close-packed films which were dried in the air

The intensities of band edge and defect fluorescence emission show obviously different change regularity with the sample temperature increasing. The intensity of defect fluorescence emission significantly decreased with temperature increment and the defect fluorescence emission nearly disappears at room temperature. Compared to the intensity changes of defect fluorescence emission, the band edge fluorescence emission intensity shows dissimilar variation with sample temperatures, as shown in Fig. 2 (b). Interestingly, the intensity changes of both band edge fluorescence emission and defect fluorescence emission with temperature can be divided into the same two stages: the first stage with the temperature of 78 K to 140 K and the second stage with the

temperature of 160 K to 300 K. The experimental results of PL intensities at different temperatures can be concluded as follows: 1) with the temperature increasing, the intensity of defect fluorescence emission decreases sharply at the first temperature stage and decreased slowly at the second temperature stage. 2) The intensity of band edge fluorescence emission begins to increase at the first temperature stage and then decreases gradually at the second temperature stage, which is obviously different from the intensity changes of defect fluorescence emission.

A defect states in CdTe NCs capable of binding excitons can be in one of three states, which has no carriers bound to it, one bound carrier, or two bound carriers of opposite signs (a bound exciton). These will be referred to as states 0, 1, 2 and the concentrations of defects in states 0, 1, 2 will be referred to as n_1 , n_2 , n_3 , respectively. The defect is capable of transitioning between any pair of these states. The intensity of defect fluorescence emission will be proportional to n_2 .

Table 1 lists all the physical process that can occur in the defect. Several processes may be ignored as follows. 1) The concentration of free excitons is negligible compared to the concentration of free carriers, because the CdTe NCs are optically pumped materials. Accordingly, the rate R_{02} (free exciton capture) could be ignored. 2) A localized state and a delocalized state have a small interaction. The rate of recombination of a bound carrier with a free carrier is small relative to the rates of capture and emission of free carriers. The rate R_{10} (bound h^+ or free e^- recombination) and R_{21} (bound e^- or free h^+ recombination) could be ignored. 3) Pair generation

Table 1 Physical processes contributing to each transition rate

Rate	Process	Δ free e^-	Δ free h^+	Δ Free exciton
R_{01}	h^+ capture	0	-1	0
R_{01}	Bound h^+ or free e^- generation	+1	0	0
R_{12}	e^- capture	-1	0	0
R_{12}	Bound e^- or free h^+ generation	0	+1	0
R_{02}	Free exciton capture	0	0	-1
R_{02}	Bound exciton generation	0	0	0
R_{10}	h^+ emission	0	+1	0
R_{10}	Bound h^+ or free e^- recombination	-1	0	0
R_{21}	e^- emission	+1	0	0
R_{21}	Bound e^- or free h^+ recombination	0	-1	0
R_{20}	Nonradiative bound exciton recombination	0	0	0
R_{20}	Radiative bound exciton recombination	0	0	0
R_{20}	Bound exciton emission	0	0	1

processes localized at a defect can be ignored. This assumption is essentially equivalent to stating that the rate at which pump photons generate carriers at the luminescent defects is small relative to the rate at which the defects capture free carriers. Consequently, the rate R_{01} (bound h^+ or free e^- generation), R_{12} (bound e^- or free h^+ generation), and R_{02} (bound exciton generation) could be ignored. The concentration of defects in CdTe NCs is small relative to the concentrations of free electrons and free holes. Applying charge neutrality allows free carriers to be removed from the bookkeeping according to which is $n_{freee^-} \approx n_{freeh^+} = n_c$ independent of temperature.

Under these assumptions, Table 1 translate into the following equations

$$\begin{cases} R_{01} = n_0 n_c c_{01} \\ R_{12} = n_1 n_c c_{12} \\ R_{10} = n_1 e_{10} \\ R_{21} = n_2 e_{21} \\ R_{20} = n_2 e_{20} \end{cases} \quad (1)$$

where the c_{ij} and e_{ij} are capture and emission coefficients, respectively. The n_2 yields^[10] is

$$n_2 = \frac{\beta n_D n_C^2}{\beta(K_{01}K_{12} + K_{12}n_C + n_C^2) + \alpha(K_{01} + n_C) + \alpha\beta n_C} \quad (2)$$

where $\alpha = e_{20}/c_{01}$ and $\beta = c_{12}/c_{01}$ are fitting parameters with units of concentration and no units, respectively. The $K_{01} = e_{10}/c_{01}$ and $K_{12} = e_{21}/c_{12}$ are in portion to the conduction and valence band effective densities of states ($\propto T^{3/2}$). The n_2 decreases with temperature increasing, result in the reduced intensity of defect fluorescence emission.

The intensity change features of band edge fluorescence emission in close-packed CdTe NC films with temperature are similar to the results have been observed in PbS quantum dot film^[11]. However, the situation changes dramatically in the case of CdTe NC films in our experiments. Unlike the PbS quantum dot film, there are obviously defect fluorescence emission at low temperatures in CdTe NC films. The defect states lead to additional competing relaxation pathways by excited electron in the conduction band into defect sites and accelerate depopulation from the band edge^[12]. Accordingly, in the close-packed CdTe NC film, transfer of excitation energy not only takes place between the NCs of different sizes, but also from band edge to defect states in one NC. To understand the PL intensity change features in CdTe NC films at different temperatures, we take these two ET into account together.

Based on these results and discussions, a model including the two ET was proposed to explain the PL intensity change features in the close-packed film, as shown in Fig. 3. Under the conditions of steady-state excitation, some electrons are excited to the conduction

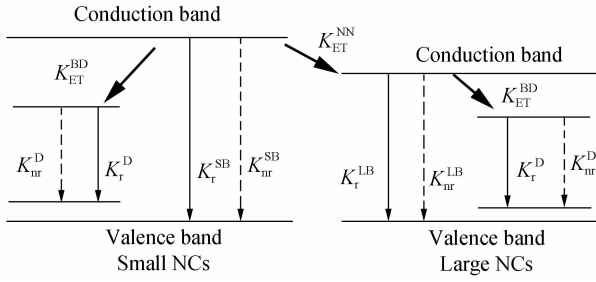


Fig. 3 Schematic model for the relaxation processes of CdTe NCs in close-packed film

band and holes appear in the valence band. The recombination rate consists of a radiative term with rate K_r^B (K_r^{SB} and K_r^{LB} are the radiative rates of small size CdTe NCs and large size CdTe NCs, respectively), namely the band edge fluorescence emission of the close-packed CdTe NC film, a nonradiative term with rate K_{nr}^B , a term corresponding to ET between the NCs of different sizes with rate K_{ET}^{NN} , and a term corresponding to ET from band edge to defect states with rate K_{ET}^{BD} . Similarly, the recombination of the trapped electrons and holes in the defect state consists of a radiative term with rate K_r^D and a nonradiative term with rate K_{nr}^D . The efficiencies of the defect fluorescence emission, the band edge fluorescence emission of small size CdTe NCs and large size CdTe NCs, ϕ^D , ϕ^{SB} and ϕ^{LB} , respectively can be expressed by Eqs. (3) ~ (5); the quantum yield (QY) of defect and band edge fluorescence emission, QY^D and QY^B , respectively can be expressed by Eqs. (6) ~ (7)

$$\phi^D = \frac{K_r^D}{K_r^D + K_{nr}^D} \quad (3)$$

$$\phi^{SB} = \frac{K_r^{SB}}{K_r^{SB} + K_{nr}^{SB} + K_{ET}^{BD}} \quad (4)$$

$$\phi^{LB} = \frac{K_r^{LB}}{K_r^{LB} + K_{nr}^{LB} + K_{ET}^{BD}} \quad (5)$$

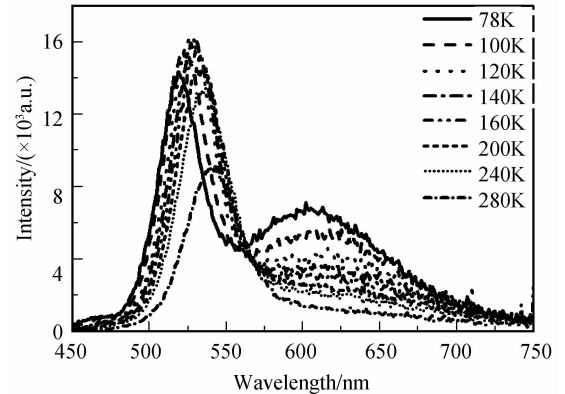
$$QY^D = K_{ET}^{BD} * \phi^D \quad (6)$$

$$QY^B = \phi^{SB} + \phi^{LB} + K_{ET}^{NN} * \phi^{LB} \quad (7)$$

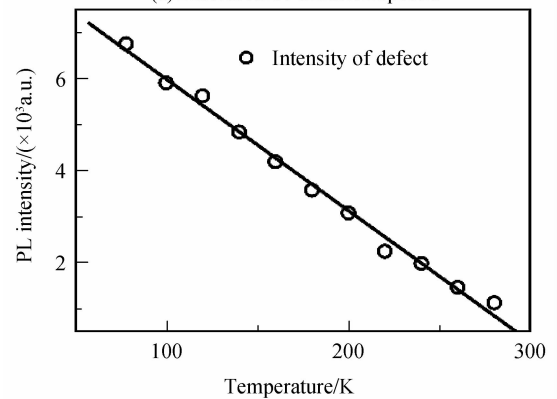
From the Eq. 6, it can be seen that intensities of defect fluorescence emission in close-packed CdTe NC film at different temperatures are related to the rates K_{ET}^{BD} and K_{nr}^D . The ET rate K_{ET}^{BD} decreases and the nonradiative recombination rate K_{nr}^D increases with temperature^[11]. At the first stage of the sample temperature, the decrease of the ET rate K_{ET}^{BD} with temperature and the increase of the rate K_{nr}^D are both very prominent, resulting in the sharply decrease of the defect fluorescence emission intensity at the first temperature stage. At the second temperature stage, the ET rate K_{ET}^{BD} decreases to a relatively small value and the increase of nonradiative recombination rate K_{nr}^D with temperature play a predominant part, resulting in the slowly decrease of the defect fluorescence emission intensity.

To further prove our point, confirmatory

experiments were performed to improve the understanding on the variation of defect fluorescence emission intensity at different temperatures. The aforementioned close-packed CdTe NC films were dried in the air. There are lots of defects on the surface of CdTe NCs because of atmospheric oxidation^[13], resulting in great influence of the rate K_{ET}^{BD} on the defect fluorescence emission intensity at the first temperature stage. To reduce the defects on the CdTe NCs surface, namely, reduce the effect of the rate K_{ET}^{BD} on the defect fluorescence emission intensity at the first temperature stage, we changed the drying process of the CdTe NC films. To avoid the atmospheric oxidation, the CdTe NC films were dried under vacuum conditions at room temperature. The as-prepared CdTe NC film exhibits different defect fluorescence emission intensity variation with temperature, and the results are shown in Fig. 4 (a). The lowering of fluorescence emission intensity had a high correlation with the defect state, nonradiative rates and ET rates. Fig. 4 (b) presents the peak intensities of the defect fluorescence emission at different temperatures. The high ET rate K_{ET}^{BD} from band edge to defect states and low nonradiative rate K_{nr}^D make the defect of CdTe NCs films with bright fluorescence emission at low temperature of 78 K. The ET rate K_{ET}^{BD} decreases and the nonradiative recombination rate K_{nr}^D increases with temperature



(a) Fluorescence emission spectra



(b) The peak intensity variation with temperature

Fig. 4 Fluorescence emission spectra of the close-packed film dried under vacuum conditions

increasing, resulting in gradually decrease of defect fluorescence emission intensity. The intensity variation with temperature is nearly the same at the whole temperature range (from 78 K to 300 K), which is different from the fluorescence emission of CdTe NCs films dried under air conditions. The CdTe NCs films dried under vacuum conditions avoided the atmospheric oxidation and therefore had fewer defects on the NCs surface. The nonradiative recombination rate K_{nr}^D increases and the ET rate K_{ET}^{BD} decreases with temperature play a predominant part at both temperature stages.

By using the aforementioned model, the intensity variation of band edge fluorescence emission with temperature in close-packed CdTe NC film could also be understood. On the one hand, it can be seen that intensities of band edge fluorescence emission with temperature are closely related to the fluorescence emission efficiency ϕ^{SB} , ϕ^{LB} and the ET rate K_{ET}^{NN} between NCs from the Eq. (7). Here, both the ET rate K_{ET}^{NN} between NCs and the nonradiative recombination rate K_{nr}^B increase with temperature^[14]. At the first temperature stage, the increase of the ET rate K_{ET}^{NN} between NCs is more prominent, which induces trapped carriers to replenish to the excited state of large CdTe NCs. For the green-emitted CdTe NCs, the fluorescence emission efficiency of large size ones are higher than the small size ones^[15], which results in increasing of the whole fluorescence emission intensity. The difference in the fluorescence emission efficiency originates from the variation of the surface quality. High surface quality refers to a smooth, defect-free, and thus a charge carrier trap-free surface. The distribution of fluorescence emission efficiencies can be explained in terms of “kinetic roughening”, the phenomenon well known for the growth of crystalline solids. When growth rate of a nanocrystal increases, the critical size of two-dimensional nucleation sites at the surface becomes so small that the nucleation barrier vanishes. As a result, the crystal surface becomes microscopically rough and macroscopically rounded. In an ensemble of nanocrystals in colloidal solution, the particle growth rate is strongly size-dependent. For the green-emitted CdTe NCs, the main concept of the Ostwald ripening implies that larger NCs with lower growth rate, compared to the smaller NCs, and consequently the fluorescence emission efficiency of large size ones are higher. At the second temperature stage, the nonradiative recombination rates K_{nr}^{SB} and K_{nr}^{LB} increase more rapidly with increasing temperature than the ET rate K_{ET}^{NN} between NCs, accordingly, the whole fluorescence emission intensity gradually decreases. On the other hand, the aforementioned ET rate K_{ET}^{BD} from band edge to defect states decrease with

temperature, which also results in the increase of the band edge fluorescence emission intensity at the first temperature stage.

To further testify the influence of the ET rate K_{ET}^{NN} between NCs on the intensity variation of band edge fluorescence emission, correlative confirmatory experiments were performed. The ET rate K_{ET}^{NN} is closely related to the distance between the NCs^[4] and can be expressed by equation^[16]

$$K_{ET}^{NN} = \frac{1}{\tau_D} \left(\frac{R_0}{r} \right)^6 \quad (8)$$

where R_0 is the Förster distance, τ_D is the lifetime of the donor in the absence of acceptor in the ET process, and r is the donor-to-acceptor distance, namely the average distance from small size CdTe NCs to large size ones. From Eq. (8), we can see that if we increase the distance r from small size CdTe NCs to large size ones, the ET rate K_{ET}^{NN} will be decreased drastically and certainly the influence of the ET rate K_{ET}^{NN} on band edge fluorescence emission intensity variation will also be remarkably weakened. We put the CdTe NCs in PEG matrix film in order to increase the distance r . The PL spectra of the CdTe NCs in PEG matrix film are shown in Fig. 5. Fig. 5 (b) presents the peak intensities of the band edge fluorescence emission in PEG matrix film at different temperatures. The band edge fluorescence

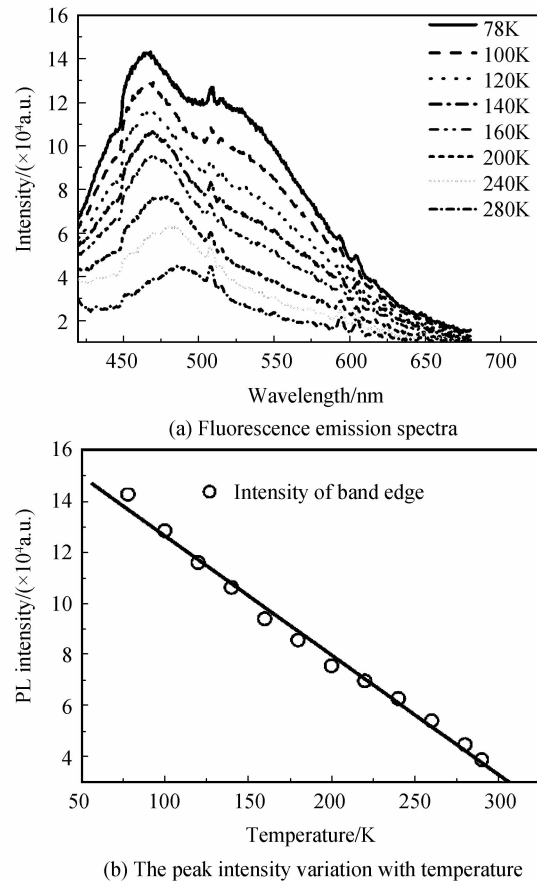


Fig. 5 Fluorescence emission spectra of CdTe NCs in PEG matrix film

emission intensities of PEG matrix films decrease with increasing temperature at the first temperature stage, which are obviously different from the close-packed CdTe NC films. The intensity variation of band edge fluorescence emission with temperature is nearly the same at the range from 78 K to room temperature. That is because the ET rate K_{ET}^{NN} between NCs is relatively low due to the increase of distances r between CdTe NCs in PEG matrix films, resulting in the increase of nonradiative recombination rate of band edge with temperature play a predominant part at both temperature stages.

Semiconductor NCs belong to a state of matter lying in the transition regime between molecules and bulk materials^[17]. NCs possess the photophysical properties necessary to overcome the limitations of conventional bulk materials. Their broad excitation spectra, size-tunable narrow fluorescence emission spectra, high quantum yields, and resistance to photodegradation make them superior to conventional bulk materials in several ways. The unique optical properties of NCs originate from the quantum confinement of the electron-hole pair. Quantum confinement arises when one of the dimensions of the object is of the order of the exciton Bohr radius. This quantum confinement leads to the emergence of discrete electronic states in the nanocrystal and size-dependent electronic and optical properties. Therefore, a smaller nanocrystal leads to a larger difference in energy levels and, consequently, a shorter wavelength emission.

3 Conclusion

In summary, the temperature-dependent band edge and defect fluorescence emission dynamics of CdTe NC films have been investigated. We observed the distinctly dissimilar intensity variation of band edge fluorescence emission with temperature, compared to the defect fluorescence emission. It is suggested that ET processes from band edge to defect states in one NC and ET from a trap state of smaller NCs to excited state of larger NCs in ensemble are thermally activated processes. A model including both ET processes has been proposed for explaining the fluorescence emission intensities variation with temperature, which is supported by relative verifying experiments.

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