

Luminescence and resonant energy transfer of two sizes of CdTe quantum dots embedded in gelatin films

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Received: 5 December 2006 / Accepted: 13 June 2007 / Published online: 31 July 2007
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Abstract We have used two sizes of highly monodisperse colloidal CdTe nanocrystals (or quantum dots) and gelatin to form quantum dots (QDs)-gelatin films. Photoluminescence (PL) results for the mixed systems show that the quenching of the emission of the small dots was accompanied by the enhancement of the emission of the large dots as their average separation decrease. The phenomena were attributed to the occurrence of the long-range resonance transfer (LRRT) between two different sizes of QDs when the concentration of the gelatin is low enough to ensure the close proximity of the dots. Determined by the overlap between the emission spectrum of the donor QDs (small dots) and the absorption spectrum of the acceptor QDs (large dots), FRET provides efficient coupling between two different sizes of QDs via long-range dipole-dipole interaction. The PL spectrum changes were also confirmed by true-color images of the mixed QDs system, which show that the colors change gradually from red to green at the gelatin concentrations varying from 0.01% to 0.25 wt% in their initial solution. The experimental results are expected to open new opportunities to modulate the luminescence of semiconductor QDs in a simple way.

Introduction

These years, colloidal semiconductor nanocrystals or quantum dots (QDs) with narrow size distribution and high

luminescence quantum yields have found a variety of uses in the field of electronic, optoelectronic devices and biological labeling. For the application of QDs to biological labeling, the easy tuning of the absorption and emission bands through size variation together with high photo-stability gives the QDs advantages over classical fluorescence dye markers. The conjugation of QDs to biomolecules may make these NCs and biomolecules close enough in QDs-labeled samples and may results in the changes of their luminescence due to the fluorescence resonance energy transfer (FRET) between them. FRET process takes place not only between a molecule-pair, organic dyes [1, 2], but also between a molecule or an ion and a solid [3] and even happens between mixed-size of CdSe QDs [4]. The FRET-based luminescence studies for the mixed system can not only provide information about biomolecular structure and ligand-receptor binding [5, 6] but also provide a simple and convenient mechanism for tuning the emission wavelength of quantum dot.

In this paper, luminescence and energy transfer process of two sizes of CdTe nanocrystals embedded in gelatin films are investigated using PL and PLE spectra. By varying the amount of added gelatin, the separations between dots in thin solid films can be controlled. The true-color images and PL for the QDs-gelatin films were also studied.

Experiments

Material

Colloidal thioglycolic-acid-stabilized CdTe QDs with different diameter sizes were synthesized by the method reported in Ref. [7]. Mainly two types of colloidal

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gelatin aqueous solution containing CdTe QDs were utilized here:

- 1) Mixed sample series: about $4 \times 10^{19}/L$ small dots (averaging 2.3 nm in diameter, with standard deviations between 5.0% and 6.5%) and $3 \times 10^{19}/L$ large dots (averaging 4.0 nm in diameter, with standard deviations between 9% and 10%) were dispersed in gelatin aqueous solution.
- 2) Pure small dots sample series: pure above small dots ($4 \times 10^{19}/L$) dispersed in gelatin aqueous solution.
- 3) Pure larger dot sample series: pure above large dots ($3 \times 10^{19}/L$) dispersed in gelatin aqueous solution.

Composite thin films of QDs-gelatin were produced by putting 5 μ L of above sample colloidal solutions onto a Teflon template (with a hole of 10 mm in diameter) on glass and let it dry at room temperature. The resultant composite thin films was about 5–10 μ m in thickness which was transparent to the light. The gelatin concentrations of above colloidal solutions prior to the dropping can range from 0 to 0.5 wt%. If no gelatin were added onto the colloidal solution prior to the dropping, closely packed QD solid films with inorganic capping group on the top of the nanocrystals can be prepared. When gelatin was added, QDs-gelatin composite films will be formed and the interdot distances varied with the amount of added gelatin.

In order to make stable and optical clear films, gelatin was chosen here. The distances between QDs can be changed by adding a variable amount of gelatin in the initial colloidal CdTe QD solutions. Moreover gelatin doesn't influence the structure and optical properties of QDs ($n = 1.005$) in visible region.

Results and discussion

Figure 1 shows a series of room temperature photoluminescence (PL) spectra for mixed QDs in aqueous solution (curve a), pure small in close-packed film (curve b), pure large QDs in close-packed film (curve c), and mixed QDs in QDs-gelatin composite solid films prepared with different gelatin concentrations (from curves d1 to d5), respectively. Generally speaking, all the PL spectra of mixed QDs (curve a and curves d1 to d5) show two emission bands, blue band of small dot luminescence and red band of large dot luminescence. As the gelatin concentration in the initial colloidal solutions decrease from 0.25% to 0, the ratios of large to small dot luminescence intensities of mixed QDs in solid films (curves d1 to d5) increase, that is the quenching of the emission of the small dots was accompanied by the enhancement of the emission of the large dots.

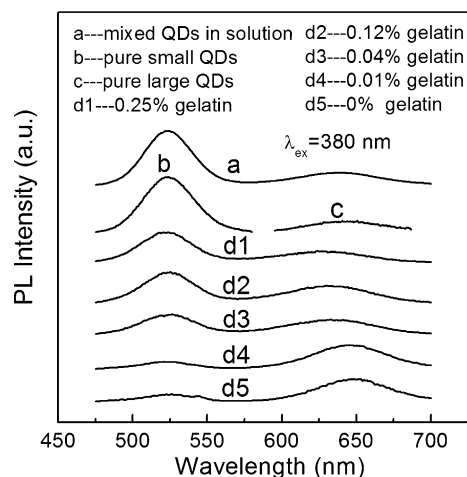


Fig. 1 PL spectra of (a) mixed QDs in solution and, (b) pure small size QD in solid film, (c) pure large size QD in solid film, and (d1) to (d5) gelatin-QDs composite film prepared from gelatin concentration of 0.25%, 0.12%, 0.04%, 0.01% and 0% in initial solution, respectively

True-color images of thin gelatin solid films containing pure large QDs, mixed QDs with various gelatin concentration in initial solution, and pure small QDs were presented in Fig. 2a, b and c respectively. It shows that the colors of the mixed system change gradually from red, orange to green when the concentrations of gelatin in the initial solutions vary from 0.01% to 0.25%.

The above changes in PL spectra and true-color images for the mixed system arise from dipole-dipole interdot interaction between proximal QDs. Due to the energy overlap in the 2.3 nm dots' (serve as donors) PL spectrum with the 4.0 nm dots' (serve as acceptor) absorption spectrum, electronic energy is transferred from the former to the latter dots (shown in the Fig. 3) when they are close enough. The interdot distances in the gelatin films are changed by varying the concentration of gelatin in initial colloidal solution prior to the dropping. A decrease in gelatin concentration leads to a decrease in distances and a close proximity between QDs, which results in the occurrence of FRET between QDs and the changes in the relative luminescence intensities of the two sized QDs.

In Fig. 1, curve d1 to curve d5, it can also be seen clearly that the energy transfer process not only take place between samples of different size dots, but also take place from the smaller to larger dots within the sample in homogenous distribution when the dots get close enough. The electronic energy transfer within "single" size dots account for the red shifts of both small dot emission bands (521–525 nm) and large dot emission bands (from 620 nm to 645 nm) when interdot distances decrease. A broader distribution of 4.0 nm dots (with a FWHM of 65 nm) results in a larger red shift than that of the 2.3 dots (with a

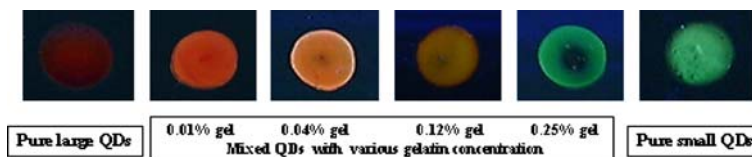


Fig. 2 True-color images of thin solid films containing (a) pure large QDs (averaging 4.0 nm in diameter), (b) mixed QDs with various gelatin concentration in initial solution, (c) pure small QDs (averaging

2.3 nm in diameter). All the samples were illuminated with a UV-lamp

FWHM of 40 nm). The similarity of the PL spectra for mixed QD solid with largest gelatin concentration (curves d1, with a maximal interdot distances) and that of mixed QDs in aqueous solution (curve a) reveal that both QDs possess the optical properties of individual and independent dots.

The average distances, *d* between dots can be estimated approximately from the volumes of gelatin and that of the QDs in the composite films using the following equation:

$$(V_{\text{gelatin}} + V_{\text{QDS}}) / N_{\text{QDS}} = 1/6 \Pi d^3$$

where V_{gelatin} , V_{QDS} , and N_{QDS} are the volume of gelatin, the volume of QDs, and the number of QDs, respectively.

For simplicity we assume that the donor fluorescence is solely quenched by the energy transfer that is the quenching efficiencies χ would be equal to the energy-transfer efficiency. Quenching efficiencies for the mixed QD system could be estimated using the following equation,

$$\chi = 1 - (I_{\text{donor}}^{\text{film}} / I_{\text{donor}}^{\text{solu}})$$

where $I_{\text{donor}}^{\text{film}}$ and $I_{\text{donor}}^{\text{solu}}$ are donor’s emission intensities for the gelatin films and that of the initial colloidal solution

respectively. These intensities are obtained by the integration of the blue emission band (donor’s) from 470 nm to 575 nm and are normalized with their absorption.

The obtained curve of quenching efficiencies χ versus average distance *d* was plotted in Fig. 4. At smaller distance (6–11 nm), a relatively sharp decrease of χ is observed when *d* increase. As larger distance *d* beyond 11–12 nm, the χ tends gradually settle to a saturation minimum value about 0.33–0.38. These remaining quenching efficiencies at larger distances may come from the conglomeration of the dots.

Follow Olga I. Micic etc. [8], we could estimate the critical distance from $\chi(t)$ - *d*(*t*) curves. Taking 50% of χ to be critical distance we obtained $R_0 = 9.3$ nm. This critical distance from our mixed system agrees well with other’s results obtained in solid films.

In order to confirm that the changes of the luminescence for the mixed QD system originate from the energy transfer between the QDs, PLE spectra for the composite films (monitoring at the emission peak of the 4.0 nm dots) were also measured. As shown in Fig. 5, at lower gelatin concentration (lower than 0.04%) two peaks are observed (480 and 620 nm respectively) which reveal that the fluorescence peak of the red dots arises not only from red dot absorption but also that of green dots absorption. These

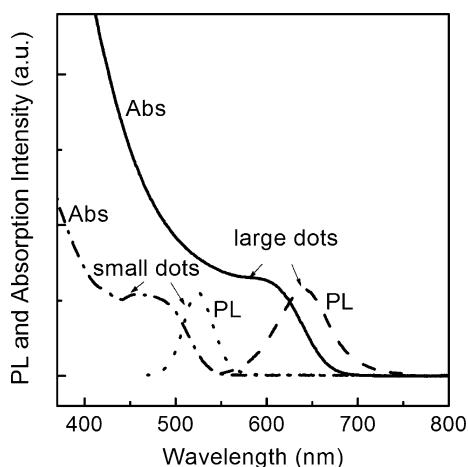


Fig. 3 Energy overlap in the 2.3 nm dots’ PL spectrum with the 4.0 nm dots’ absorption spectrum

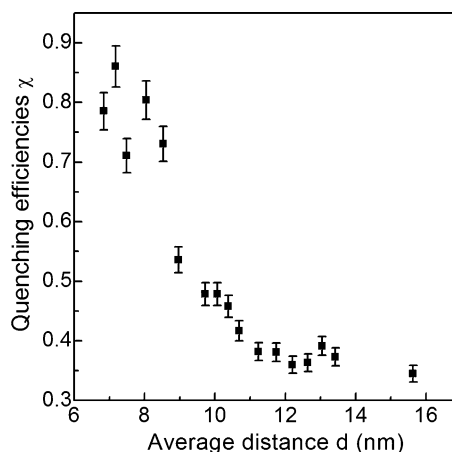


Fig. 4 Plot of luminescence quenching efficiencies χ versus average distances between QDs for the mixed solid films

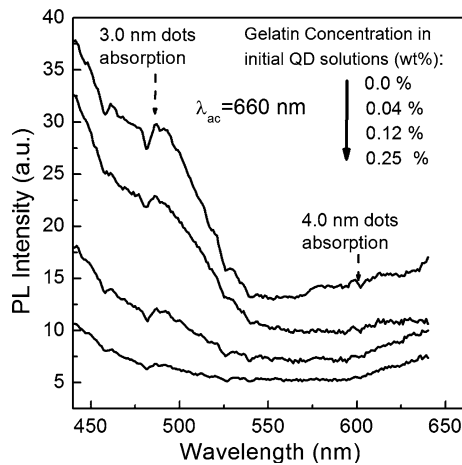


Fig. 5 PLE spectra for gelatin-QDs composite films prepared from gelatin concentration of 0.25%, 0.12%, 0.04% and 0% respectively, in initial solution (monitoring at the emission peak of the 4.0 nm dots)

results strongly indicate that energy transfer, which is LRRT occurs from the small to the large dots when the concentration of the gelatin is low enough to ensure the close proximity of the dots [9, 10].

Conclusion

Thin QDs-gelatin films were produced by two size of highly monodisperse colloidal CdTe QDs. PL results exhibit that luminescence for the mixed QDs system can be tuned when the interdot distances in the thin solid films are changed by adding a variable amount of gelatin. The

results of PLE and true-color images confirm that the changes of the luminescence were attributed to the energy transfer between the QDs in the mixed system. These experimental results are expected to open new opportunities to modulate the luminescence of semiconductor QDs in a simple way.

Acknowledgements The supports of this work by National Natural Science Foundation of China under Grant No. 10574069, No. 60508009 and National Basic Research Program of China (No. 2007CB613401 and No. 2006CB932202) are gratefully acknowledged.

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