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Near-infrared absorption–emission cross-sections of PbSe quantum dots doped in UV gel[☆]

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ABSTRACT

We measure near-infrared absorption spectra of PbSe quantum dots (QDs) with three sizes (4.5, 5.0, and 5.6 nm) doped in UV gel with the concentration of 0.25–1.50 mg mL^{-1} by using an absorption-spectrum method. An empirical formula is proposed to describe the correlation of the first–second absorption-peak wavelengths and QD size. The peak-absorption cross-section is measured as 2.76–3.69 × 10^{-16} cm^2 for 5.6-nm QD, and the absorption coefficient ranges in 0.19–0.59 cm^{-1}, both associated with the doping concentration and the QD size. Furthermore, the emission cross-sections are determined by measuring the photoluminescence spectra of QDs and using the McCumber relationship, which depend weakly on both the doping concentration and the QD size. For 5.6-nm QD, the measured peak-emission cross-section is 3.36–4.48 × 10^{-16} cm^2 within the range of experimental doping concentration.

1. Introduction

Nanocrystal quantum dots (QDs) have drawn considerable research interests in recent years [1]. A series of special optical features are observed in QDs due to the confinement of charge carriers within the physical dimension defined by particle size. IV–VI QDs, such as PbSe, PbS, PbTe etc. emit in the near infrared region as favored in a number of applications. Among them, PbSe QDs with relatively simple electronic structural and high quantum yield have attracted much attention in recent years [2].

Absorption–emission cross-sections are important photo-physical parameters of QDs. For CdSe QDs, the cross sections were measured by the absorption-spectrum method (e.g., [3]). For PbSe QDs, Du et al. [4] measured the absorption and emission spectra of PbSe QD within the range of 1000–1850 nm, and determined the absorption-peak wavelength in 1120–1880 nm for PbSe QD with 3–8 nm diameter. The emission-peak wavelength was in 1210–1450 nm for PbSe QD of 3–4.5 nm, and the photoluminescence (PL) lifetime was 300 ns. Using the absorption-spectrum method, Brumer et al. [5] measured the cross-sections of PbSe (core), PbSe/PbS (core/shell), PbSe/PbSe$_x$S$_{1-x}$ (core/shell), which were prepared by organic thermal synthesis. The absorption–emission-peak cross-sections of PbSe QD with 5.4-nm diameter were determined as 1.25 × 10^{-16} cm^2 and 0.55 × 10^{-16} cm^2, respectively. Cheng et al. [6] measured the absorption and emission spectra of PbSe QD dispersed in *n*-hexane, and obtained absorption-peak cross-section of 3.54 × 10^{-16} cm^2.

In the above work, the reported cross-sections were either only for single size of QD, or only for monodisperse QD, where the doping concentrations were not given, i.e., effect of doping concentration was not considered. This gave an incomplete model as doping concentration inevitably affects the cross sections due to surface effect and fluorescence quenching. In particular, the surface effect arises from difference in dielectric-constant between QD and the media, enhancing the resonance capturing and reducing defect states, which in turnleads to varied cross-sections throughout the media. Therefore, it is considerable to study the cross-sections of QDs with different diameters and doping concentrations in the given media, which has been seldom reported.

Recent studies showed that ultraviolet (UV) gel was an ideal background material for QDs doped fiber laser due to its good transparency in the near infrared region, low reduction of volume during drying and desirable refraction index (n=1.464) that is slightly higher than the SiO$_2$ fiber claddings [7]. QD doped fibers with designed concentration can be obtained if colloidal PbSe QDs are mixed into UV gel and injected into hollow optical fibers to configure the gain fiber, even to constitute QD doped fiber amplifiers and lasers [6,7]. Therefore, we focus on the UV–gel matrix in this paper.

We measured the absorption spectra of PbSe QDs with three sizes which were doped in UV gel, proposing an empirical formula

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describing the first-second absorption-peak wavelengths depending on particle size. By applying the absorption-spectrum method and the Lambert–Beer law, the variance of absorption cross-section and absorption coefficient of QD in respect to the wavelength and doping concentration were determined in the range of 800–2000 nm. Another empirical formula is presented as the dependency of the absorption cross-section on the doping concentration. Furthermore, the emission cross-section of PbSe QDs with different sizes was determined as a function of doping concentration, according to McCumber's relationship between the emission and absorption, and compared with the experimental results reported in literatures. Finally, we present an approximated expression of the dependence of the emission cross section with the wavelength by using Gaussian fitting. We envision the work in this paper to help understand the spectral characteristics of PbSe QD, providing a foundation to constitute next-generation QD doped photo-electronic devices in the future.

2. Experiment

PbSe QDs with the diameter of $d=4.5$, 5.0, and 5.6 nm used in the experiment were prepared by adopting an aqueous route of synthesis, e.g., [8]. Fig. 1 shows the TEM image of PbSe QDs ($d=5.6$ nm) dispersed in *n*-hexane, where the size error is about 5%.

In the experiment, firstly the PbSe QD solution was mixed into UV gel in different concentrations at room temperature. Then the mixture was placed in a three neck flask and heated with magnetic stirring until the *n*-hexane was evaporated completely (heated for 5 min). This was followed by an ultrasonic oscillator to distribute the QDs evenly in UV gel. The chosen concentrations of QD were $c_{1,2,3,4,5,6}=0.25$, 0.50, 0.75, 1.00, 1.25, and 1.50 mg mL^{-1}, in such a doping region, the PL gain and stimulated emission can be generated to benefit experimental observation.

The spectrum measurement was implemented at room temperature. The absorption spectrum was measured by Lambda-750 ultraviolet–visible-near infrared spectrophotometer (PE Corporation, USA), and the emission spectrum was measured by FLS920 steady-transient fluorescence spectrometer (Edinburgh Ltd., England). The used UV gel (UV-6182) was provided by Xinlida Ltd., China.

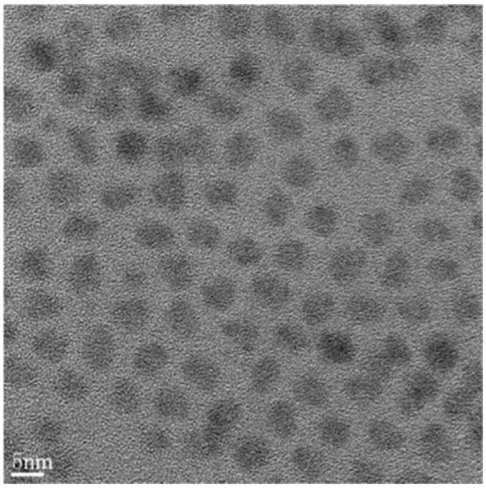

Fig. 1. TEM image of PbSe QDs ($d=5.6$ nm) observed by Tecnai G2 F30.

3. Results and discussion

3.1. Absorption spectrum and absorption cross-section

Light attenuation propagating through media is mainly caused by absorption and scattering. According to the Mie scattering theory [9], when infrared light in hundreds of nanometer wavelength is projected into QDs with a few nanometers, the generated scattering is the Rayleigh scattering whose effect on the extinction is much smaller than the absorption [10]. Thus, the measured light intensity is predominated by absorption. In addition, the absorption of UV gel can be ignored due to very small absorbance in 800–2500 nm [6,7].

Fig. 2 shows the measured absorption spectrum of PbSe QD ($d=5.6$ nm). There are two absorption peaks located at 1310 nm and 1590 nm, respectively. 1590-nm peak is the first absorption-peak wavelength (λ_{P1}), which is from the level transition of $1S_{h(e)}$–$1S_{e(h)}$, i.e., from the top of valence band (VB) to the bottom of conduction band (CB) of the QD. 1310-nm peak is the second absorption-peak wavelength (λ_{P2}), which is from the level transition of $1S_{h(e)}$–$1P_{e(h)}$, i.e., from the top of VB to the upper CB. Due to double absorption peaks appeared in Fig. 2, PbSe QD can be described by a three-level system, as shown in [6].

The absorption varying with the diameter is given in Fig. 3. Notice that the peak wavelengths are moved to $\lambda_{P1,P2}=1475$, 1195 nm for $d=4.5$ nm; and $\lambda_{P1,P2}=1530$, 1250 nm for $d=5.0$ nm, respectively.

From Fig. 3, the absorption-peak wavelength depending on the QD diameter can be expressed as follows:

$$\{\lambda_{P1} = 1006.2 + 104.4d\lambda_{P2} = 726.2 + 104.4d\ (\mathrm{nm},\ 4.5 < d < 5.6\ \mathrm{nm}) \qquad (1)$$

From Eq. (1), the peak wavelength, either for the first or for the second absorption peak, increases linearly with the QD diameter with the same rate of 104.4. Specifically, following the QD diameter increases 1 nm, the first and/or second peak wavelengths increase 104.4 nm. Although Eq. (1) is deduced from only three diameters and limited in a narrow range of diameter, it is still usable in infrared waveband due to the available size of PbSe QD even distributing in 4–6 nm.

Fig. 4 makes a comparison of experimental data, where the black squares are from this paper (QD in UV gel); the red triangles are for PbSe/PbSe$_x$S$_{1-x}$ QD (nuclear/shell) in organic solvents (oleic acid) [5], which can be fitted linearly by $\lambda_{P1}=939+114d$; and the blue dots are for PbSe QD in phosphate glass [11], which can be fitted by $\lambda_{P1}=900+108d$. Namely, the first absorption-peak wavelength increases even with the diameter of PbSe QD in the rate

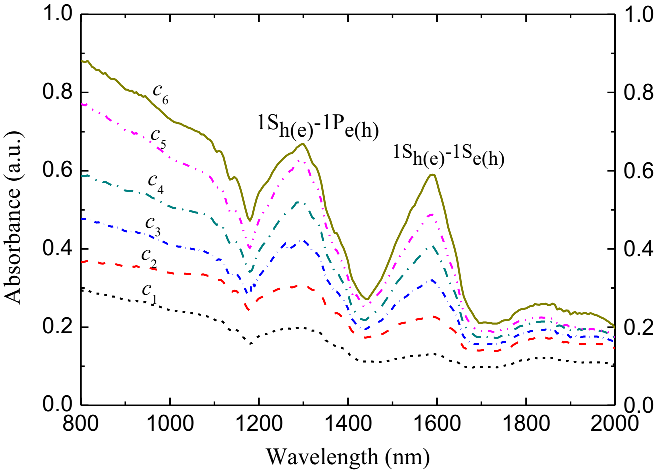

Fig. 2. Absorption spectrum of PbSe QD ($d=5.6$ nm) in UV gel.