Bulgarian Chemical Communications, Volume 47, Special Issue B (pp. 168–172) 2015

Low temperature photoluminescence studies of colloidal CdSe nanocrystals

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We present the results from low temperature studies of the PL from colloidal CdSe nanocrystals prepared by the hot injection method in liquid paraffin. The synthesized nanocrystals were all within the quantum confinement range and showed the typical size-dependent UV-vis absorption, PL and Raman spectral characteristics. The photoluminescence spectra and their temperature dependences were measured from room temperature (295 K) down to temperatures as low as 15 K, demonstrating that the exciton PL transitions followed modified Varshni equation accounting for carrier localization. The smallest (2.6 nm in size) CdSe nanocrystals isolated in the beginning of the nanocrystal growth had a relatively symmetric size distribution and showed a single exciton emission band, while the samples isolated at later stages of the growth process showed exciton transitions from subpopulations of nanocrystals.

Key words: CdSe, Nanocrystals, Quantum dots, Photoluminescence, Low temperature

INTRODUCTION

The size-dependent photoluminescence (PL), broad excitation spectra and resistance to photobleaching makes colloidal quantum dots (QDs) quite attractive materials for applications in bioimaging and optoelectronics. For example, differently sized cadmium selenide (CdSe) nanocrystals emitting from blue to red can be used as fluorescent biolabels [1-3], components of light-emitting diodes [4], lasers [5], FRET sensors [6], etc. Therefore, achieving an effective control of the photoluminescence of QDs has been a major goal for scientists in the field of QDs synthesis and there are still unsolved issues of this problem.

The width of the absorption and emission bands in the QDs spectra is a result of homogeneous (thermal) and inhomogeneous broadening. The inhomogeneous broadening comes from the polydispersity of the nanocrystal size [7]. Therefore, the relative changes in the shape and the width of the PL bands during the growth of QDs can be used as an indication for changes in the nanocrystal size distribution [8]. Photoluminescence studies can be more informative when performed at low temperatures, when the thermal broadening of the emission bands is minimized and the effect of quantum confinement is observed in its most clear form. Most of the known low temperature photoluminescence studies of colloidal QDs include investigations of the exciton lifetimes and excitonic radiative decay [9], exciton fine structure [10], single dot spectroscopy [11].

In this work, we report studies on the photoluminescence properties of colloidal CdSe QDs as a function of the temperature, in the range from 15 to 295 K. The nanocrystals were prepared by the hot injection method in liquid paraffin. The synthesized nanocrystals were all within the quantum confinement range. The PL emission bands become narrower at low temperatures due to decrease of the thermal peak broadening, which facilitates the detection of nanocrystal subpopulations of different sizes in a heterogeneous sample.

EXPERIMENTAL SECTION

Nanocrystals of CdSe were synthesized in hot liquid paraffin according to a previously reported method [12]. Briefly, cadmium stearate precursor was prepared in liquid paraffin (15 ml) from cadmium oxide (50 mg; 0.39 mmol) and stearic acid (1.6 g) at 200°C. Tributylphosphine selenide precursor (1.0 ml) was injected to the reaction mixture at 250-260°C and nanocrystals of various sizes and optical properties were prepared by varying the reaction time.

The photoluminescence experiments were performed with a high resolution double monochromator (SPEX Model 1404, f=0.85 m) equipped with Hamamatsu R943 PMTs (GaAs photocathode) with thermoelectric cooler and in photon counting mode. The samples were placed in a closed cycle ARS helium cryostat working in temperature interval from 295 down to 10 K. Argon laser emitting at a wave-

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length of 488 nm (2.54 eV) was used as an excitation source. For the photoluminescence experiments the nanocrystal powders were embedded into potassium bromide (KBr) tablets in order to be placed within the cryostat holder. For that purpose, dried nanocrystal powder (∼20 mg) was homogenized with anhydrous powdered KBr (2 g) and compressed into tablets of suitable sizes (∼2 cm in diameter; 5 mm thickness) by using a tablet press.

RESULTS AND DISCUSSION

Photoluminescence appears as one of the most sensitive methods for analysis of QDs, which allows one to obtain information and to discriminate between different recombination processes, related with various recombination centers in the nanocrystal lattice. In the case of QDs PL measurements could provide information about the energy levels and quantum confinement effects. The correct interpretation of the PL peaks could also provide information about the existence of excitons, the morphology of the heterointerface, the presence of defects and impurities, etc. As mentioned above, the energy of the PL peak, its shape and width could provide information about the average size and size distribution of the nanocrystals. Since the homogeneous (thermal) broadening of the PL bands could be minimized at lower temperatures, we performed PL measurements at low temperatures (down to 15 K) in order to investigate the temperature dependence of the PL peak energy and to evaluate the size homogeneity of the samples.

Fig. 1 represents PL-spectra of three CdSe nanocrystal samples of different size at 15 K. The spectra are normalized to the highest energy peak. The most intensive peak for the three different nanocrystal sizes was shifted toward higher energies than the band gap of the bulk CdSe (1.74 eV). The photoluminescence maximum shifts toward higher energies with decreasing of the nanocrystal size, which is a characteristic observation of quantum-size effects for nanocrystals of sizes that are smaller than the exciton Bohr radius (∼ 5.6 nm for CdSe).

As a result of the quantum confinement effect the energy of the lowest excited state, $E(R)$, according to a simplified version of the effective mass model of Bawendi [13], is given by the following expression (Eq. 1) that is valid for spherical nanocrystals of small radii R.

$$E(R) = E_g + \frac{h^2}{8mR^2} \qquad (1)$$

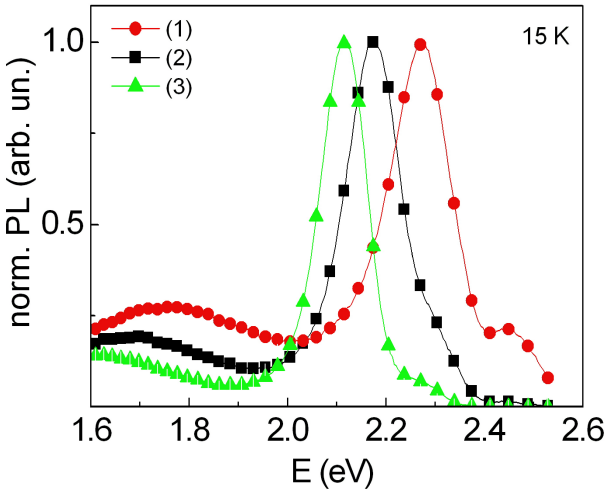

Fig. 1. Normalized PL-spectra of the three samples labeled (1), (2) and (3) at 15 K.

Here, E_g is the energy band gap for the bulk semiconductor, h is the Planck constant, m is the effective mass of the exciton. Accordingly, nanocrystal sizes between 2.6 and 3.6 nm are determined from the PL energy positions.

The temperature dependent PL spectra for two of the samples labeled (1) and (2) measured from 15 K to 295 K are given in Fig. 2 a and b, respectively. Most of the emission spectra show two shoulders at the high-energy side visible also in the room temperature spectra but more pronounced at low temperatures, and a low intensity shoulder at the low energy side. To take into account these features, the PL curves at each temperature were deconvoluted with a sum of Gaussians.

For sample (1) the best fit of the low temperature (15 K) spectrum was done with four Gaussians, while the spectrum of sample (2) was fitted with a combination of five Gaussians. The spectrum of sample (3) is best fitted with five Gaussians similar to (2). The peak at ∼2.5 eV does not depend on the temperature and is situated around the same position for all the three groups of samples. Its nature is currently unclear. The low energy peaks ∼1.8 eV are probably due to surface-state-mediated recombination [14].

The temperature dependences of the main peak and the shoulder (Fig. 2b) correspond to the expected behavior for exciton transitions. The existence of a subpopulation of smaller nanocrystals could be associated with the appearance of a “shoulder” on the shorter wavelength side of the main peak.

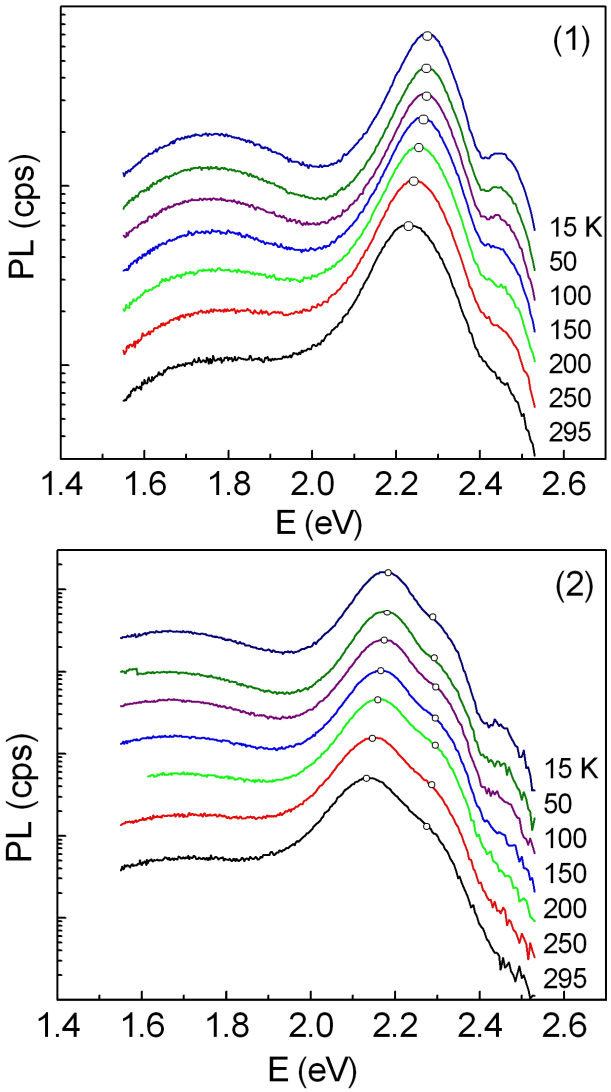

Fig. 2. (a) PL-spectra of sample (1) and (b) of sample (2) at various temperatures (from 15 to 295 K, log scale; offset for clarity).

The temperature dependence of the energy gap of bulk semiconductors is known as the Varshni relation [15] (Eq. 2).

$$E_g(T) = E_g(0) - \alpha \frac{T^2}{T+\beta} \qquad (2)$$

Here, $E_g(0)$ is the energy gap at 0 K, α is the temperature coefficient, and the value of β is close to the Debye temperature of the material. The experimental data for the three QDs were fitted to the Varshni relation. Eq. (2) fits very well the high temperature range 100-295 K (Fig. 3, fits for the three samples) consistent with the known temperature dependence of bulk semiconductor band gap. However, at temperatures lower than 100 K obviously the PL energies deviate from Varshni equation, plateau and even "S-shape" behavior is observed pointing out at involvement of different mechanism connected with relaxation dynamics of localized carriers and confinement. Indeed, better fits in the low temperature range were obtained if a modified equation (Eq. 3) was used:

$$E_g(T) = E_g(0) - \alpha \frac{T^2}{T+\beta} - \frac{\sigma^2}{kT} \qquad (3)$$

where the parameter σ represents a measure of the depth of localization potentials [16] and k is the Boltzmann's constant. Similar behavior is observed in quantum dots and in quantum well structures where it is explained in terms of localized exciton freeze-out at low temperatures, followed by the onset of thermalization of excitons with increasing temperature. The fitted parameters are consistent with the values given in the literature for bulk CdSe: $(2.8\text{-}4.1)\times10^{-4}$ eV/K for α and (181-315) K for β (Ref. [17]). The σ values reveal localization energy $\sim 2 \div 4$ meV from fitting the transition peaks.

Photoluminescence measurements appeared to be a sensitive approach for detection of heterogeneity in the size distribution of nanocrystals. It appears that in the beginning of the nanocrystal growth process there were nanocrystals of uniform size distribution and the size heterogeneity (the observation of a second subpopulation of smaller nanocrystals together with the basic component) appeared in the later stages of the

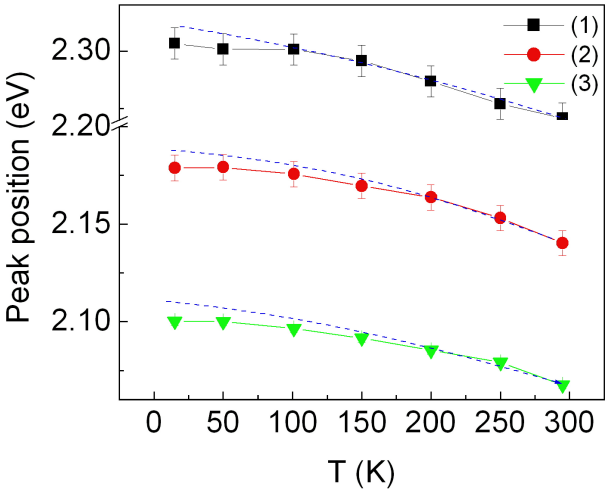

Fig. 3. Temperature dependences of the peak position (energy) of the main peaks of the three samples: sample (1) blacks quare; sample (2) red dot; sample (3) green triangle. Included are Varshni fits (dashed line) and modifiedVarshni fits (solid line).

nanocrystal growth. Our data are likely to be explained by the model of Ostwald ripening. This model of the growth kinetics of QDs in the conditions of the hot-injection synthesis has been described by Talapin et al. [18].

CONCLUSIONS

We reported in this paper results from low temperature photoluminescence studies on colloidal CdSe nanocrystals, prepared by the hot injection method in liquid paraffin. The average nanocrystal size of the nanocrystals was determined to be smaller than the exciton Bohr radius for CdSe. The temperature dependencies of the exciton PL transitions for temperatures higher than 100 K were found to follow the Varshni equation, while from 15 to 100 K the quantum confinement and localization of carriers shows modified Varshni dependance. The CdSe nanocrystals of smallest size (2.6 nm) show uniform size distribution and a single photoluminescence emission band. However, the CdSe samples obtained at later stages of growth, showed an asymmetrical size distribution and photoluminescence from a subpopulation of smaller nanocrystals found together with the larger ones.

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НИСКО-ТЕМПЕРАТУРНИ ФОТОЛУМИНЕСЦЕНТНИ ИЗСЛЕДВАНИЯ НА CdSe НАНОКРИСТАЛИ

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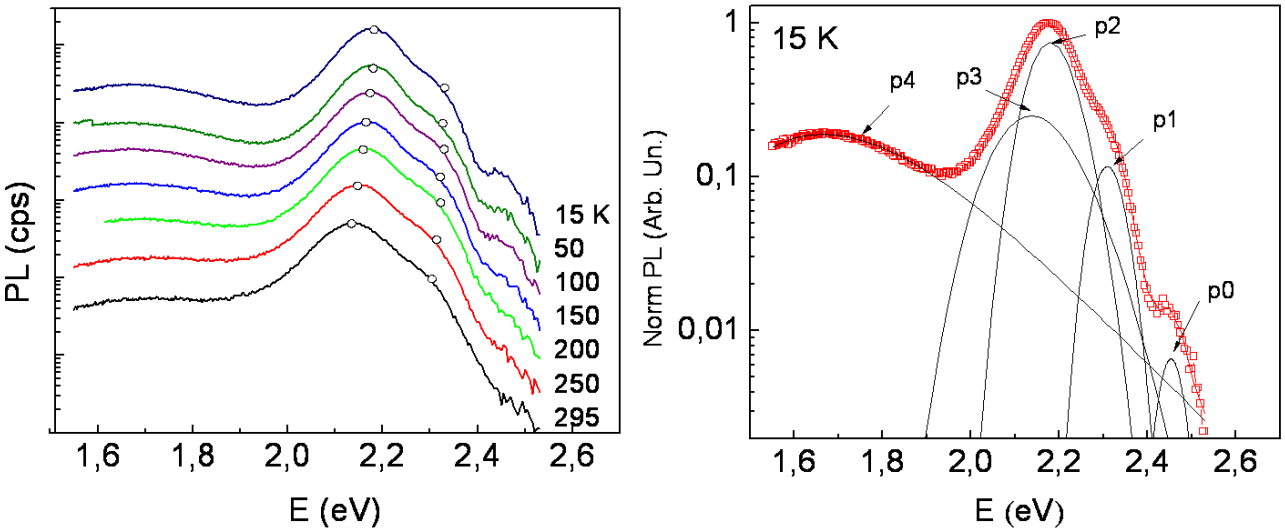
(Резюме)

Полупроводниковите нанокристали (монокристали с размер 2-10 nm в диаметър), известни и като квантови точки (КТ), са перспективни луминесцентни наноматериали, които абсорбират и излъчват видима светлина като резултат от квантовото ограничаване на екситоните [1]. Зависимостта на енергията на фотолуминесценция (ФЛ) от размера на частиците позволява проектиране на приложения в широк енергетичен диапазон. Това прави колоидните КТ атрактивни за използване в оптоелектрониката, медицината и др. Например, наночастици с различен размер от кадмиев селенид (CdSe) излъчват от синьо до червено и могат да се използват като флуоресцентни биомаркери, компоненти в излъчвателни диоди, лазери и др. Затова ефективният контрол на ФЛ от КТ е главна цел за изследователите при синтез на КТ, където има все още нерешени проблеми.

В този доклад представяме резултати от експерименти по ниско-температурна ФЛ на колоидни наночастици CdSe, получени чрез метода на гореща инжекция в течен парафин. Размерите на синтезираните частици са в диапазона на квантово ограничаване и показват типична зависимост от размера на частиците при абсорбция в UV-видимата област, ФЛ и Раманови спектри. ФЛ спектрите и тяхната температурна зависимост бяха измерени от стайна (295 K) до ниска температура от 15 K (Фиг.1), и показаха, че екситонните ФЛ преходи следват модифицирана Varshni-зависимост, показваща ефекта от локализиране на екситоните вследствие квантово-размерен ефект. Най-малките CdSe частици (с диаметър 2.6 nm), изолирани в началото на процеса на израстване, имат относително симетрично разпределение по размер и показват една линия на екситонна емисия, докато частиците, изолирани в по-късни етапи на процеса на израстване показват екситонна емисия от субпопулации от нанокристали.



Фиг. 1. (a) ФЛ-спектри от наночастициCdSe при температури (15 – 295) K; (b) ФЛ спектър (15K), фитиран с пет Гаусиана за определяне на наличието на субпопулации от нанокристали.

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