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LUMINESCENCE SPECTRA OF QUANTUM-SIZED CdS AND PbI₂ PARTICLES IN STATIC ELECTRIC FIELD

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The influence of external electric field was studied on the luminescence behavior of quantum-sized CdS and PbI₂ nanocrystals, embedded in various polymeric films. The clear increase in the photoluminescence intensity from the quantum-sized particles was observed, as well as the spectral shift of photoluminescence bands. The mechanism proposed is based on the field-induced oxygen desorption from the nanocrystal surface which is the good photoluminescence inhibitor.

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1. Introduction

The nanocrystals of various semiconductors are studied now extensively. When the size of such nanocrystals is below the value of the Bohr radius of exciton in corresponding bulk semiconductors, a number of interesting phenomena appears, related to the effect of the quantum confinement (QC) [1-3]. The spatial confinement of the carriers motion in the semiconductor nanocrystals results in dramatic transformation of their zone structure, as well as the dynamics of excited states. There is a number of papers on the influence of external electric field on the linear and nonlinear absorption spectra of the direct-gap semiconductor nanocrystals in various matrices [4-6]. The development of quantum-confined Stark effect (QCSE) was observed in many experiments [1, 4-6]. The investigation of high electric field influence on the absorption spectra of the quantum-sized (QS) nanocrystals gives the information about the field-induced perturbations in the energetic levels of nanocrystals.

In this paper we present the results of investigation of the external electric field influence on the luminescence spectra of quantum-sized CdS and PbI₂ particles. Such a study can give the information about the relaxation dynamics of excited states in QS-particles. The obtained results can be interpreted in terms of field-induced oxygen desorption from the particles surface, which influences strongly the radiation recombination of excited states in quantum-sized CdS and PbI₂ particles.

2. Experiment

We prepared CdS nanocrystals by the reaction between cadmium acetate, dissolved in methanol, and the gaseous H₂S, bubbled through that solution. The small amount of *ca.* 1% of the polyvinylpyrrolidone PVP was added to the solution to stabilize the colloidal particles. The concentration of Cd²⁺ ions in the initial solution was 10⁻⁴ M. The mean diameter of CdS particles was 3 nm, estimated from the transmitted electron microscopy. The prepared CdS colloidal solution was placed onto the quartz glass with the thin conducting SnO₂ layer as one electrode and dried until the transparent PVP film with CdS particles formed. The thin copper foil serving as a second electrode was placed above the PVP film with the 2 mm teflon spacer.

The PbI₂ nanocrystals were prepared by the fast cooling of a hot saturated PbI₂ solution in water containing 1–2 percents of poly(vinyl alcohol) PVA or gelatin as the polymer-stabilizer. The average size of PbI₂ nanocrystals was determined by X-ray diffraction analysis. We obtained two kinds of PbI₂ nanocrystals depending on that if the PVA or gelatin had been used. The thin hexagonal PbI₂ particles prepared in PVA solution have the thickness of less than 1 nm and the diameter of 3 nm. On the contrary, the thickness of PbI₂/gelatin nanocrystals was about 5 nm and the diameter of more than 10 nm. The samples with PbI₂ particles were prepared in the same way as described above CdS ones.

For the experiment we used the commercial computer-controlled photoluminescence spectrophotometer with the He–Cd cw laser as a pump source, operating at $\lambda = 325$ nm with the 3 mW output. The dc electric field of up to 20 kV was applied from the power block. The polymeric films with CdS or PbI₂ particles were illuminated through the quartz/SnO₂ layer and the luminescence recorded in the backward.

3. Results and discussion

Figure 1 represents the photoluminescence (PL) as well as the relative PL spectra of CdS particles in PVP film before and during the application of electric field. The relative PL spectra were determined as $I(\lambda)/I_0(\lambda)$, where $I_0(\lambda)$ and $I(\lambda)$ are the PL intensity at corresponding wavelength before and during application of high electric field, respectively. Note that pure PVP, as well as PVA and gelatin films have a negligible luminescence at the same conditions. The maximum of PL spectra in Fig. 1 (curve 1) lies around 2.6 eV, therefore the shift on 0.15 eV to the high energy region of the excitonic luminescence band of QS CdS nanocrystals

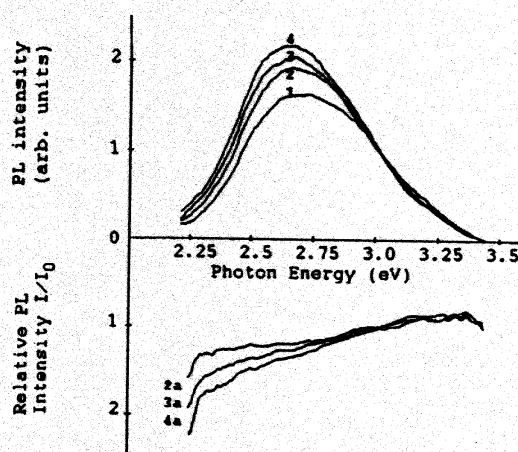


Fig. 1. PL spectra and relative PL spectra of QS CdS nanocrystals in PVP film at the applied dc electric field of different strength, kV/cm: 1 — 0; 2 and 2a — 14; 3 and 3a — 17; 4 and 4a — 20.

takes place comparably with the bulk CdS. We interpreted this shift as the effect of quantum confinement in CdS nanocrystals. The application of the electric field results in clear changes in the low energy side of PL spectra (Fig. 1, curves 2a–4a). The PL intensity grows up with the increase in the electric field strength.

Figure 2 shows the influence of a high electric field on the PL spectra of QS PbI₂ nanocrystals in PVA film. In this case we observed the growth of a high

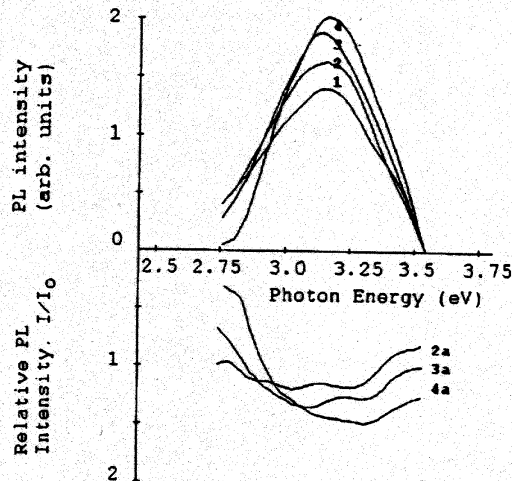


Fig. 2. PL spectra and relative PL spectra of QS PbI₂ particles in PVA film at the applied dc electric field of different strength, kV/cm: 1 — 0; 2 and 2a — 10; 3 and 3a — 14; 4 and 4a — 16.

energy side of PL spectra at the increasing electric field. Simultaneously, the partial decrease in the low energy side of PL spectra develops so that the total narrowing of PL band appears under the electric field action. At least two local maxima can also be seen in the relative PL spectra, which shift to the high energy region with the increase in the field strength.

We interpreted the obtained results on the basis of the three-level model of the excitation and relaxation of excitonic states in QS semiconductor nanocrystals [7]. Since the electron/hole wave functions of excited states in QS particles extend to their surface [1], the electrons or holes can be captured easily at the surface states, caused by the adsorption of the atmospheric oxygen or other impurities. Such excitons bonded with the surface state relax partially through the non-radiative way, decreasing the total PL intensity from QS nanocrystals. Moreover, the mixing of the pure excitonic states with the surface ones causes the substantial inhomogeneous broadening of the PL bands. It is well known that the oxygen molecules or atoms, being good acceptors for photoelectrons, cause the photoluminescence inhibition. Oxygen easily adsorbs both at the covalent and ionic semiconductor surface [8]. Applied electric field results in the field-induced desorption of the oxygen from the surface of QS nanocrystals. Therefore, the narrowing of the QS PbI_2 PL band at the high electric field accompanying the increase in band intensity reflects the "purification" of the excitonic states.

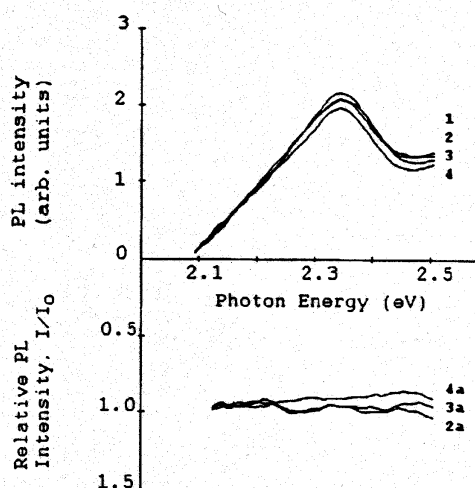


Fig. 3. PL spectra and relative PL spectra of non-QS PbI_2 particles in gelatin at the applied dc electric field of different strength, kV/cm: 1 — 0; 2 and 2a — 10; 3 and 3a — 15.

Figure 3 shows both the PL and relative PL spectra of PbI_2 nanocrystals in gelatin before and during the application of high electric field. These PbI_2 particles have the size slightly larger than the Bohr radius of exciton in bulk PbI_2 . Hence, the probability of electron/hole capturing at the particle surface is smaller, in comparison with QS PbI_2/PVA nanocrystals. Though the external electric field

should cause the similar field-induced desorption of oxygen from the PbI₂/gelatin nanocrystals, as for PbI₂/PVA ones, the increase in PL intensity as well as the shift of PL band are not detected in Fig. 3. Moreover, the clear vanishing of PL intensity occurs when the electric field grows up. We suggest that the field-induced changes in PL spectra of PbI₂/gelatin nanocrystals belong to the pure QCSE, when the exciton dissociation probability increases with the electric field strength. The field-induced changes in the surface states influence less on the PL behavior of such larger particles.

Acknowledgments

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