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The nature of emission centers in CdS nanocrystals

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Abstract

Photoluminescence (PL) of CdS nanocrystals (NCs) grown in different polymeric matrices is investigated. It is shown that chemical nature of the matrix does not affect the nature of PL centers in NCs. PL centers of NCs are identical to the emission centers in CdS single crystals and are related to their intrinsic defects.
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1. Introduction

Semiconductor nanocrystals (NCs) were extensively studied in the recent years, they are considered as active media for opto-electronic devices (Lakowicz et al., 1999, 2002; Akimov et al., 1992). Their major drawback is a relatively weak emission, which results in inefficiency of the emitter. This inefficiency is mainly due to the interaction of NCs with matrix, interaction of neighboring NCs and surface properties of NCs. The main defects in NCs are vacancies, substitutional impurities, dangling bonds of NC surrounding medium that act as trap states and effect the effectiveness of excitation (Jang et al., 2004; Volkov et al., 2003). At present the problem of the influence of chemical nature of the matrix surrounding NC on generation and recombination processes is not sufficiently investigated. Furthermore, currently there is insufficient information on the physical–chemical nature of defects that play the role of emission centers in NC. A detailed investigation of these issues will make it possible to develop the methods to control the colour of luminescence and its intensity in specified regions of the spectra.

This paper presents the results of investigation of photoluminescence (PL) spectra of CdS NCs obtained by chemical methods in different matrices, which stabilize the size of nanoparticles. The spectra of CdS single crystals were measured for comparison.

2. Experimental procedure

Two kinds of NCs were investigated, which were obtained by chemical methods in stabilizing matrices of differentnature:

1. CdS NCs grown by sol–gel technique in gelatin polymer matrix. NCs, which we obtained in this way, contained an excess of sulfur atoms.
2. CdS NCs obtained by the method of frontal polymerization of metal-containing monomers. For the latter cadmium polyacrylate was used. In this case NCs are contained in the matrix of polyacrylic acid. CdS single crystals were grown by re-crystallization from gas phase. In this case two types of samples were obtained too: samples containing the excess of sulfur (first type) and excess of cadmium (second type).

PL of CdS single crystals and NCs was excited by a laser source with a wavelength of 337 and 441.6 nm. Spectral characteristics of PL were measured at different temperatures and intensities of excitation.

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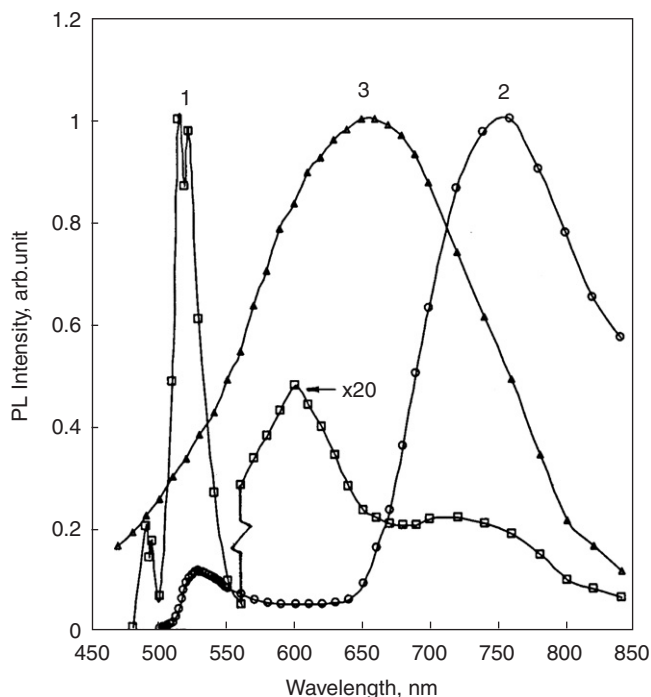*E-mail address:* v_skobeeva@ukr.net (V. Skobeeva).

Fig. 1. Photoluminescence spectra of CdS single crystals (1, 2) and nanocrystals (3) measured at 100 K.

3. Results and discussion

Since the nanoparticles investigated in both cases were contained in polymeric matrices of different chemical nature, the latter could affect both the formation of specific PL centers and the intensity of luminescence. Besides, one should not exclude the possibility that polymeric matrices themselves could show PL and in this way affect spectral characteristics of nanostructure as a whole. In connection to this, to determine individual emission characteristics of CdS NCs we have performed the comparison of spectral characteristics for single crystals and NCs under identical experimental conditions.

Luminescence properties of CdS are quite well investigated and described in books and numerous papers (Georgobiany and Shaikman, 1986; Ermolovich et al., 1985; Shaikman et al., 1988; Lisovoy et al., 1988). It is known that single crystals of CdS have luminescence in blue, green, red and infrared regions of spectra. In Fig. 1 normalized spectra for CdS single crystals of two types (curves 1 and 2) and CdS NCs in gelatin matrix (curve 3) are presented. Spectra were measured at 100 K in a wavelength region of 450–850 nm. For CdS single crystal of the first type (curve 1) the prevalence of short-wavelength bands (blue and green) in comparison with long-wavelength red luminescence was observed. Blue luminescence was represented by discrete narrow lines with $\lambda_{max} = 490$ and 495 nm, which is due to the radiative annihilation of bound excitons (Georgobiany and Shaikman, 1986).

In the green spectra region a structured band in the form of a zero-phonon line and its several phonon repetitions was present too. The maximum of the zero-phonon line was at

$\lambda_{max} = 515$ nm. Energy distance between the peaks of green luminescence was equal to 0.038 eV that corresponds to the energy of longitudinal optical (LO)-phonon. We think that emission in this region of spectrum is due to recombination of donor–acceptor pairs. From the literature it is known that emission in the green region of spectrum is favoured by the following factors: synthesis of crystals (Georgobiany and Shaikman, 1986) and NCs (Lakowicz et al., 2002) under the conditions of excess of atoms of the metal (Cd); doping of semiconductor by atoms of the elements from the first group of Mendeleev periodic table (Lisovoy et al., 1988). Due to high dopant density (10^{17}–10^{18} cm^{-3}) it is possible to observe green luminescence within a wide temperature range (up to 400 K). This fact corresponds very well to our experimental results. In CdS crystals of the second type, which were synthesized under shortage of Cd atoms (and excess of S atoms), green edge luminescence was very weak and blue luminescence was not observed at all (curve 2).

In longer-wavelength region of the spectrum one can observe two structureless PL bands in single crystals: a orange band ($\lambda_{max} = 580$–600 nm) and a wide red band with $\lambda_{max} = 760$–800 nm. Orange luminescence band in single crystals is observed in case of doping with oxygen atoms or in case when interstitial atoms of metal are present in the lattice of the semiconductor. We detected this band in the crystals of the first type (curve 1).

Red band of PL is typically detected in the crystals, which contain a certain concentration of intrinsic defects and it is called self-activated (SA) luminescence. The majority of authors relate luminescence centers responsible for this band to complicated associative centers of the type (V_{Cd}–V_S) or (V_{Cd}–$D_{III,Y}$) (Georgobiany and Shaikman, 1986).

Normally the conditions under which edge luminescence and long-wave luminescence are observed are interrelated. As a rule, if intensity of edge luminescence is high, then the intensity of red luminescence is low. In case when the formation of luminescence centers responsible for edge band is thermodynamically advantageous, SA luminescence has a negligible intensity. This is observed when the concentration of defects in these crystals is low. In the case when the concentration of complicated associative defects is higher, SA band dominates in the luminescence spectra. Recombination parameters of SA luminescence centers also contribute to the increase of the intensity of this luminescence. The centers of red luminescence are slow centers of radiative recombination in CdS crystals (Ermolovich et al., 1985). All the facts mentioned above are visually confirmed by curves 1 and 2 in Fig. 1.

This figure depicts luminescence spectra of CdS NCs in gelatin matrix excited by light with $\lambda_{exc} = 441.6$ nm. One can see that luminescence band of CdS NCs is significantly wider than that of bulk semiconductor. The maximum of luminescence is localized in the red region of spectrum ($\lambda_{max} = 650$–690 nm for different samples) and is always shifted to shorter-wavelength regions of spectra relative to the position of the red PL band of single crystal ($\lambda_{max} = 760$–800 nm). Besides, the profile of the band is not described by Gaussian or Lorenz distributions. All these indicate a non-elementary nature of the band. Inhomoge-
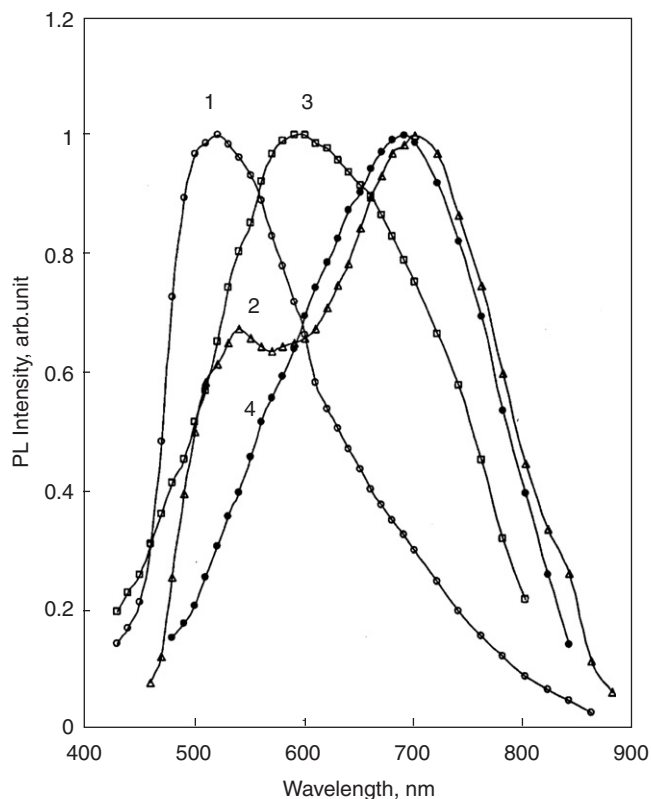
Fig. 2. Photoluminescence spectra of CdS nanocrystals, grown in polyacryl acid (1, 2) and gelatin (3, 4), measured at λ_{exc}: 337 nm (1, 3); 441.6 nm (2, 4).
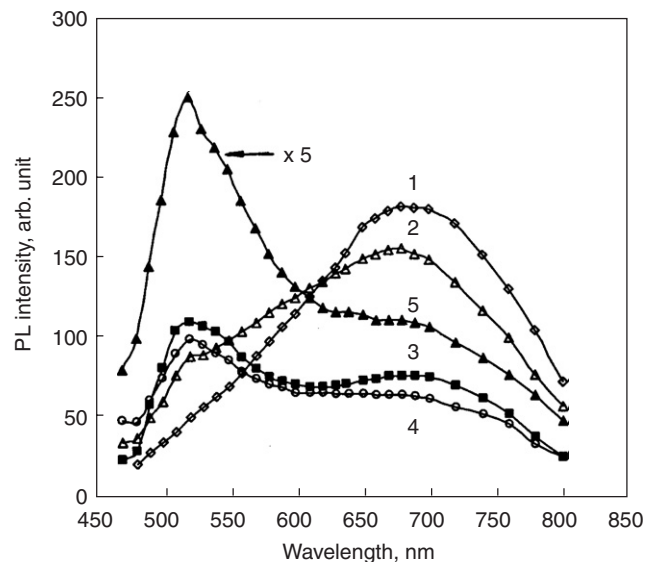

Fig. 3. Photoluminescence spectra of colloid solutions of CdS nanocrystals at dissolution of colloid by distilled water in the ratio: (1) 1:1; (2) 1:3; (3) 1:6; (4) 1:10; and (5) 1:12.

neous broadening of the emission spectrum in the wavelengths range 450–600 nm indicates the presence of a short-wavelength band of luminescence in this spectrum. The total luminescence was detected, i.e. luminescence of NCs together with matrix.

To get more confident extraction of luminescence originating from CdS NCs we measured similar characteristics of CdS NCs in another polymer, namely polyacrylic acid. The results of these measurements are depicted in Fig. 2. The spectra were measured at different wavelengths of exciting light: $\lambda_{exc} = 337$ nm (curves 1 and 3) and $\lambda_{exc} = 441.6$ nm (curves 2 and 4). Two PL bands could be observed in CdS NC luminescence spectra in polyacrylic acid (curves 1 and 2). The maximum of the short-wavelength band was at $\lambda_{max} = 520$ nm and its intensity, at $\lambda_{exc} = 337$ nm (curve 1) is considerably higher than red luminescence. The inverse situation is observed under excitation of the samples by the light with wavelength 441.6 nm and in this case intensity of red luminescence prevails over green. It is important that red luminescence band is localized in the same spectral region as for NCs, contained in gelatin ($\lambda_{max} = 690$HM). This experiment shows that chemical nature of the matrix did not effect the nature of PL centers in NCs, which was connected with their intrinsic defects. At the same time it was found that matrix can play an active role in the processes of luminescence excitation. The presence of gelatin significantly increases the intensity of red luminescence. We have shown experimentally that by the decrease of gelatin concentration in the colloidal solution, in which CdS

NCs are contained, the red luminescence could be completely suppressed. The results of this experiment are shown in Fig. 3.

The weakening in the influence of gelatin matrix was reached by dissolving the colloid by distilled water in the ratio from 1:1 up to 1:12. From comparison of curves 1–5 (Fig. 3) one can clearly see, that the profile of the band changes significantly. The decrease of gelatin concentration results in the decrease of intensity of the red band and the increase of green band intensity. We should note that green band with $\lambda_{max} = 520$ nm was observed also in CdS NCs contained in another matrix (curves 1 and 2, Fig. 2). Thus, the chemical nature of matrix did not affect the emission centers of NC, which are related to the intrinsic defects: (Cd_i) and $(V_{Cd}-V_S)$.

4. Conclusion

The results of the investigations show that CdS NCs grown in polymeric matrices have intrinsic defects of two types, which cause their luminescence in green and red regions of the spectrum. Chemical nature of defects responsible for these bands is identical to analogous luminescence centers in single crystals.

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