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INFLUENCE OF MATRIX ON PHOTOLUMINESCENCE OF CDS NANOCRYSTALS

Photoluminescence (PL) of CdS nanocrystals (NC) grown in different polymeric matrices is investigated. It was shown, that the nature of PL centers of nanocrystals is identical to the nature of emission centers in CdS monocrystals and is connected with their native defects. It was observed, that gelatin matrix could play the active role in processes of luminescence excitation.

INTRODUCTION

Semiconductor nanocrystals (NC) were extensively researched in the recent years and are considered as the active mediums for optoelectronic devices [1–12]. Their major drawback is the relatively weak emission properties, which result in inefficiency of emitter. This inefficiency is mainly due to interaction of nanocrystals with matrix, interaction of neighboring nanocrystals and surface properties of nanocrystals [13]. The main defects in nanocrystals are vacancies, substitutional impurities, dangling bonds of NC surrounding medium that act as trap states and influence on the effectiveness of excitation [8–9]. In the present time the problem for the influence of chemical nature of the matrix surrounded NC on generation and recombination processes is not sufficiently investigated. Furthermore, currently there is not enough information about physical-chemical nature of defects that play the role of emission centers in NC. The detailed investigation of these items will make possible to develop the methods to control the color of luminescence and its intensity in specified regions of the spectra. One must also take into account, that in NC the ratio of the particle surface area to its volume is high. It would be interesting to know which centers are on the surface and which in the volume of semiconductor. These questions were not sufficiently investigated in the past as well.

This paper presents the results for investigation in photoluminescence spectra of CdS nanocrystals obtained by chemical methods in different matrices, which stabilize the size of nanoparticles. The spectra of CdS monocrystals were measured for comparison.

EXPERIMENTAL PROCEDURE

Two kinds of nanocrystals were investigated, which were obtained by chemical methods in stabilizing matrices of different nature.

1. CdS nanocrystals grown by method of sol-gel technology in gelatin polymer matrix. Nanocrystals, which we obtained in this way, contained the excessive atoms of sulphur S [11–15].

2. CdS nanocrystals obtained by method of frontal polymerization of metal-containing monomers. For the latter cadmium polyacrilat was used. In this case nanocrystals are contained in the matrix from polyacrylic acid [9].

We have obtained CdS monocrystals by the method of re-crystallization from gas phase. In this case also two kinds of samples were obtained: samples containing the excesses of sulphur (first kind) and of cadmium (second kind).

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

EXPERIMENTAL RESULTS AND DISCUSSION

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

Luminescence properties of CdS are quite well investigated and described in monographies and numerous papers [16–18]. It is known that monocrystals of CdS have luminescence in blue, green, red and infrared regions of spectra. In Fig. 1. we presented the normalized plots of the

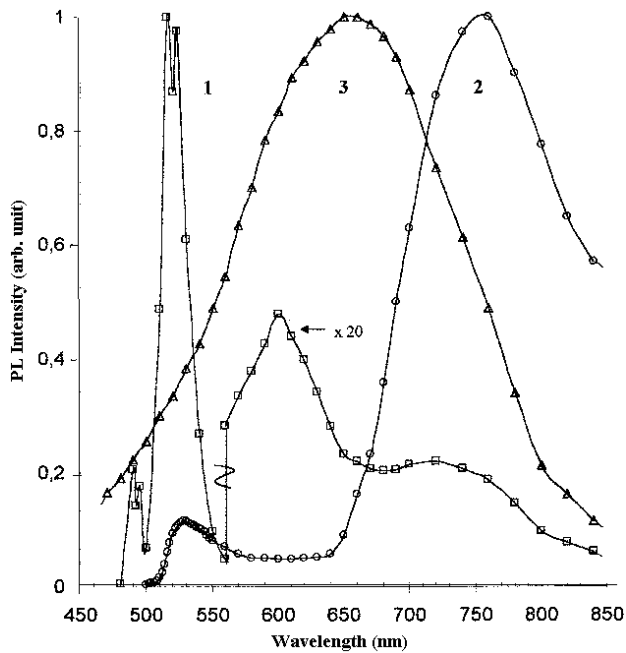


Fig. 1. Photoluminescent spectra of CdS monocrystals (1, 2) and nanocrystals (3), measured at 100K

PL spectra for CdS monocrystals of two types (curves 1, 2) and CdS nanocrystals in gelatin matrix (curve 3). Spectra were measured at temperature of 100 K within the wavelengths 450—850 nm. For CdS monocrystal of the first type the prevalence of short-wave bands (blue and green) in comparison with long-wave red luminescence was characteristic. Blue luminescence was represented as discrete narrow lines with $\lambda_{\text{max}} = 490$ and 495 nm, which is due to annihilation of tie excitons [16]. In the green spectra region the structured band in the form of phononless line and its several phonon repetitions was present too. Phononless maxima was localized at $\lambda_{\text{max}} = 515$ nm. Energy distance between peaks of green luminescence was equal to 0.038 eV that corresponds to the energy of longitudinal optical LO — phonon. We think, that irradiation in this region of spectra is due to recombination of donor-acceptor pairs. From the literature it is known that irradiation in the green region of spectra is favored by the following factors: synthesis of crystals [16] and nanocrystals [4] under the conditions of excess in atoms of a metal (Cd); doping of semiconductor by atoms of the elements from the first group of Mendeleev periodic table [19]. Owing to the high concentration of doped defects (10^{17} — 10^{18} cm^{-3}), which are responsible for edge luminescence, it is possible to observe green luminescence within the wide temperature range (up to 400 K). This fact corresponds very well to our experimental results. In CdS crystals of second type, which were synthesized under shortage of Cd atoms (and excess of S atoms), edge green luminescence was very weak and blue luminescence was not observed at all.

In more long-wave region of spectra one can observe two structureless bands of PL in the

monocrystals: orange ($\lambda_{\text{max}} = 580$ —600 nm) and wide red band with $\lambda_{\text{max}} = 760$ —800 nm. Orange luminescence band in monocrystals is observed in case of doping with oxygen atoms or in case when interstitial atoms of metal are present in the lattice of semiconductor. We have registered this band in the crystals of the first type (curve 1).

Red band of PL is typically registered in the crystals, which contain the considerable concentration of intrinsic defects and is called selfactivated (SA) luminescence. The majority of authors connect the nature of luminescence centers responsible for this band with complicated associative centers of the type ($V_{\text{Cd}} - V_{\text{S}}$) or ($V_{\text{Cd}} - D_{\text{III, V}}$) [16].

It is characteristic that the conditions under which edge luminescence and long-wave luminescence are observed are interconnected. As a rule, if intensity of edge luminescence is high then the intensity of red luminescence is low. This is caused by the fact that the composition of the luminescence centers both of edge luminescence and of SA luminescence includes the same defect (V_{Cd}). In case when the formation of luminescence centers, responsible for edge band is thermodynamically advantageous, SA luminescence will have negligible intensity. This is observed when crystals contain low concentration of defects. In the case when samples have higher concentration of associative defects, SA band prevails in luminescence spectra. Recombinative parameters of SA luminescence centers also contribute to the increase in intensity of this SA luminescence. The centers of red luminescence are slow centers of radiative recombination in CdS crystals [17]. All the facts mentioned above are visually confirmed by curves 1 and 2 in Fig. 1.

This figure depicts luminescence spectra of CdS nanocrystals in gelatin matrix excited by light with $\lambda_{\text{ex}} = 441.6$ nm. One can see, that luminescence band of CdS nanocrystals is significantly wider than the corresponding band of bulk semiconductor. The maximum of luminescence is localized in the red region of spectra ($\lambda_{\text{max}} = 650$ —690 nm for different samples) and is always shifted to the more short-wave regions of spectra comparing to PL red band of monocrystal ($\lambda_{\text{max}} = 760$ —800 nm). Beside that, the shape of the band is not described by Gaussian or Lorenz distributions. All this points to non-elementary nature of the band. The tightened edge of spectral curve within the wavelengths between 450 and 600 nm indicates the presence of shorter-wave band of luminescence in spectra. We should note that the luminescence of the whole structure is registered, i. e. luminescence of nanocrystals together with matrix.

To get more confident extraction of luminescence belonged only to CdS nanocrystals we measured the analogous characteristics of CdS nanocrystals in the other polymer — polyacrylic acid. The results of these measurements are depicted in Fig. 2. The spectra were measured at

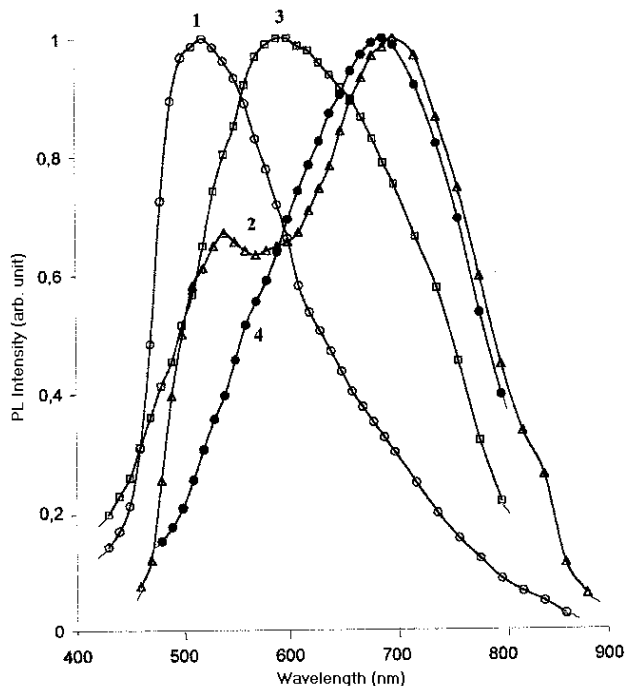


Fig. 2. Photoluminescent spectra of CdS nanocrystals, grown in polyacrilic acid (1, 2) and gelatin (3, 4), measured at λ_{exc} : 337 nm (1, 3) и 441,6 nm (2, 4)

different wavelength of exciting light: $\lambda_{exc} = 337$ nm (curves 1, 3) and $\lambda_{exc} = 440$ nm (curves 2, 4). Two bands of PL could be observed in CdS nanocrystal luminescence spectra in polyacrilic acid. Maximum of short-wave band was localized at $\lambda_{max} = 520$ nm and its intensity, at $\lambda_{ex} = 337$ nm, 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 significant that red luminescence band is localized in the same region of spectra as with nanocrystals, contained in gelatin ($\lambda_{max} = 690$ nm). This experiment shows that chemical nature of the matrix did not influence on the nature of PL centers in nanocrystals, which was connected with their intrinsic defects. At the same time it was found that matrix can play the active role in the processes of luminescence excitation. The presence of gelatin significantly increases the intensity of red luminescence. We showed experimentally, that by decrease of gelatin concentration in the colloidal solution, in which CdS nanocrystals 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 of 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 contour of the band changes significantly. The decrease in gelatin concentration results in 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 nanocrystals contained

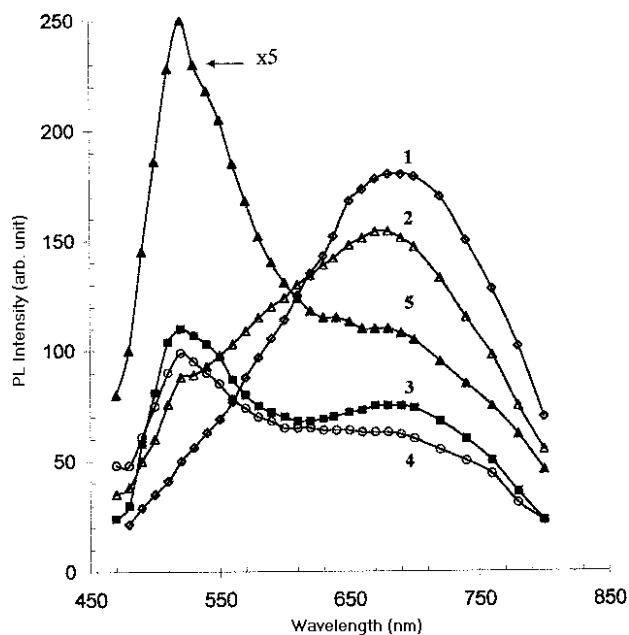


Fig. 3. Photoluminescent spectra for colloid solutions of CdS nanocrystals at dissolution of colloid by distilled water in the ratio 1:1 (1); 1:3 (2); 1:6 (3); 1:10 (4); 1:12 (5)

in the other matrix (curve 1, Fig. 1) (polyacrilic acid).

The fact, that gelatin plays role in increase of red luminescence intensity is also confirmed by the following results. Fig. 4 depicts spectral characteristics of gelatin luminescence (curve 1) and spectra of luminescence for nanoparticle together with gelatin (curve 2). One can see that intensity gelatin luminescence is significantly lower comparing to its luminescence

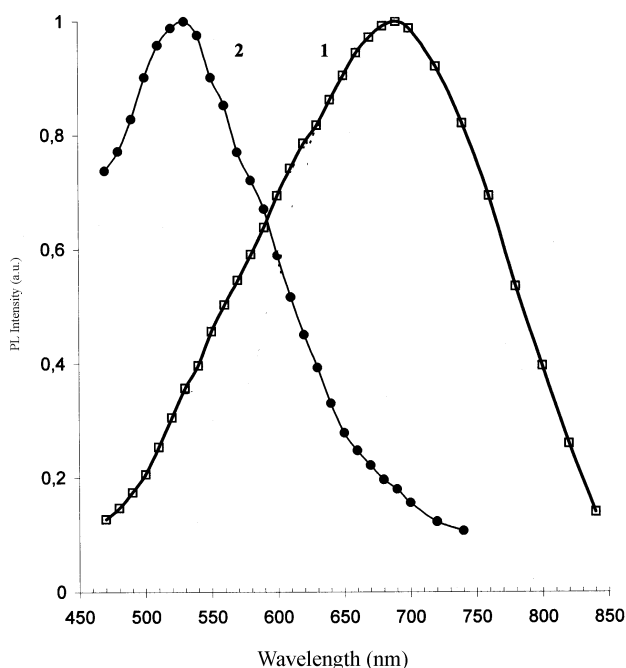


Fig. 4. Photoluminescent spectra of CdS nanocrystals in gelatine (1) and gelatine (2)

without CdS nanoparticles. This can be explained by the fact that energy of gelatin luminescence is absorbed by CdS nanoparticles, since they are closely located geometrically. It is also known [18] that centers of SA red luminescence of CdS are located in the near-surface area of the particle, and that also results in more effective absorption of light quanta by these centers of red illumination [$V_{Cd} - V_s$].

CONCLUSION

In that way, results of the investigations show that CdS nanocrystals, 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 monocrystals. At the same time matrix significantly influences on intensity of luminescence. This influence can have different mechanisms. Probably, the most simple can be the mechanism of reabsorption for light quanta at luminescence of matrix by semiconductor nanocrystals.

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ВЛИЯНИЕ МАТРИЦЫ НА ФОТОЛЮМИНЕСЦЕНЦИЮ НАНОКРИСТАЛЛОВ CdS

Исследованы фотолюминесценция (ФЛ) нанокристаллов CdS, выращенных в различных полимерных матрицах. Показано, что природа центров ФЛ нанокристаллов аналогична центрам свечения в объемных кристаллах CdS и связана с их собственными дефектами. Обнаружено, что желатиновая матрица может выполнять активную роль в процессах возбуждения люминесценции.

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ВПЛИВ МАТРИЦІ НА ФОТОЛЮМІНЕСЦЕНЦІЮ НАНОКРИСТАЛЛОВ CdS

Досліджені фотолюминесценція (ФЛ) нанокристаллов CdS, вирощених у різних полімерних матрицях. Показано, що природа центрів ФЛ нанокристалів аналогічна центрам світіння в об'ємних кристалах CdS і пов'язана з їх

власними дефектами. Виявлено, що желатинова матриця може виконувати активну роль у процесах збудження люмінесценції.

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