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INFLUENCE OF THE SURFACE ON THE SPECTRUM OF LUMINESCENCE OF CdS NANOCRYSTALS IN GELATINE MATRIXS

This paper investigates the optical absorption and luminescence of CdS nanocrystals (NCs) of varying size obtained by colloidal chemistry in an aqueous solution of gelatin. In NCs with a radius of 1.8 nm only long-wavelength luminescence with λ_{max} = 580 nm was observed, which is explained by the surface defects. In NCs of larger size (3.5 nm), the contribution of the recombination with the participation of the surface defects decreases. There is a redistribution of recombination channels to the advantage of recombination of nonequilibrium carriers in the volume of cadmium sulfide nanocrystals, which in that case exhibit intensive exciton band in their luminescence spectra.

1. INTRODUCTION

Phosphors based on semiconductor nanocrystals are promising functional materials for use as fluorescent markers for biochemical and biomedical applications. Compared to traditional organic phosphors nanocrystals have a high absorption coefficient, high brightness and high photostability of radiation [1-7].

Practical application of nanocrystalline semiconductor compounds is made possible by the development of new technologies that will produce nanosystems in a “wet” chemistry - for example, by colloidal chemistry (by sol-gel technology) through a series of simple chemical reactions in solution of the reagents in the presence of stabilizers. The stabilizer prevents the coagulation of particles and their further growth. Colloid-chemical synthesis of nanoparticles is affected by a large number of factors, including the concentration of the starting materials, the type and concentration of the stabilizer, temperature, pH of the solution, kinetics of the chemical reactions.

The most commonly used stabilizers include organic compounds such as polyphosphates [8-11], trioctylphosphine oxide [12] and thiols [13]. Characteristics of semiconductor materials obtained in the above stabilizers are given in [14]. The choice of the stabilizer is determined by many factors. The main factor is its ability to prevent the coagulation of the particles, preventing their further growth. This property is determined by the mechanism of interaction of the stabilizer with the surface of the particles. Adsorption of the molecular groups of the stabilizer on the surface of the nanocrystal leads to the passivation of the surface states that changes the surface potential and decreases the concentration of non-radiative recombination centers. It should be noted that organic compounds are often toxic substances, and the synthesis requires a high temperature and special safety precautions.

In this regard, a topical and emerging technologies nanoparticles are those that use eco-friendly and non-toxic materials.

From this point of view, a suitable stabilizer may be, well-established in the production of photographic materials, natural polymer — gelatin [15]. Gelatin is a high-molecular compound, elementary unit of which is presented in the isoelectronic state as H_2N-R_1-COOH, consisting of amino (H_2N), carboxyl (COOH), polar and non-polar basic and acidic groups (R_1). Gelatin is a good medium for the dispersion of nano - and microparticles. Solution containing ions of the metal and chalcogen quickly penetrate into gelatin. Gelatin solutions can form gels, which after polymerization result in films that are sufficiently transparent and durable. However, the distinctive features of gelatin are not limited to colloid protective functions. Thanks to their acid-base properties of gelatin can take a positive or negative charge. For example, with increasing of pH solution COOH groups dissociate into H^+ and COO^- gelatin molecule acquires a negative charge, which can significantly affect the adsorption interaction with the surface of particles dispersed in it.

From the foregoing, it is of interest to obtain and study the cadmium sulfide nanocrystals obtained by sol-gel technology using gelatin solution as a stabilizing agent, and to explore the effect of size on the NC luminescence spectra.

2. MATERIALS AND FLUORESCENCE MEASUREMENTS

Investigated NC CdS were synthesized by colloidal chemistry. In aqueous solution of gelatin (5%) containing a solution of cadmium salt - Cd $(NO_3)_2$ the salt sulfur — Na_2S solution was injected under continuous stiring. Molar concentration of cadmium salt was 0.025 M and the concentration of sodium sulfide — 0.05 M and 0.5 M. The synthesis of cadmium sulfide happened as a result of exchange chemical reaction between these compounds. The process was carried out at 40 ± 1°C. Colloidal solution of the product was applied to a glass substrate and polymerized by the drying air temperature of 35 ± 2°C. Produced samples correspond to the film with thickness 5-10 microns with nanocrystals of cadmium sulfide dispersed in a gelatin matrix. The thickness of the film depended on the amount of deposited material and the surface tension of the solution.

For spectroscopic studies of quantum dots of cadmium sulfide (light transmission, luminescence) used a spectrometer facility KSVU — 12, based on an MDR — 12 with a resolution at a wavelength of 600 nm 0.1nm.

Luminescence was excited by the solid-state samples pulsed laser with the following specifications: maximum average power of 5 mW, pulse duration at 1 kHz ~ 1 ns, pulse energy at 1 kHz ~ 20 μJ, the emission wavelength of 355 nm. The luminescence was registered with the detector PMT-106, which has a maximum spectral sensitivity in the range of 400-440 nm.

3. DETERMINATION OF THE SIZE OF CdS NC

The average radii of cadmium sulfide nanoparticles were estimated using optical absorption spectra of colloidal solutions of these nanoparticles.
Interband absorption of nanoparticles has a spherical shape and the absorption spectrum is given by a series of discrete lines [15,17]. The threshold value is given by

$$\hbar\omega_{01} = E_g + \frac{\hbar^2\pi^2}{2\mu a^2}, \qquad (1)$$

where E_g — band gap of the bulk crystal;
a — the average radius of the nanocrystal;
$\hbar$ — Planck's constant;

$\mu = \dfrac{m_e m_h}{m_e + m_h}$ — is the reduced mass of the electron and hole.

This implies the law by which the energy of the first optical transition (effective band gap) increases with the decreasing radius of the nanopaticles.

The values of the constants used in the calculations are given by E_g = 2,5 эВ [18], $m_e = 0{,}205\, m_o$ и $m_h = 0{,}7\, m_o$ [19].

4. RESULTS AND DISCUSSION

Fig. 1. shows the spectral dependence of the optical density of the quantum dots for the two samples grown under the same conditions, at different ratio of cadmium salts and sulfur. Sample number 1 corresponded to a lower concentration Na_2S (0,05M) and number 2 to the larger (0.5 M). Curve 1 in this figure corresponds to the absorption of an aqueous solution of gelatin. It can be seen that the spectrum of the gelatin is almost transparent and its absorption spectrum does not

affect the absorption of NC. It is noticeable that the transparency of the two samples are significantly different, and the beginnign of the absorption is shifted to short-wavelength region compared with the absorption spectrum of a cadmium sulfide bulk crystal. According to equation (1), such behavior is characteristic for nanoscale objects and corresponds to the presence of quantum - size effect. Magnitude of the shift of the spectrum with respect to the bulk crystal of nanocrystals depends on the size of the nanocrystals. We estimate that the sample number 1 has an average radius NC 1,8 ±0.1 nm, and the sample number 2 - 3,5 ± 0,1 nm. This clearly shows the dependence of the QD size on the reagent concentrations.

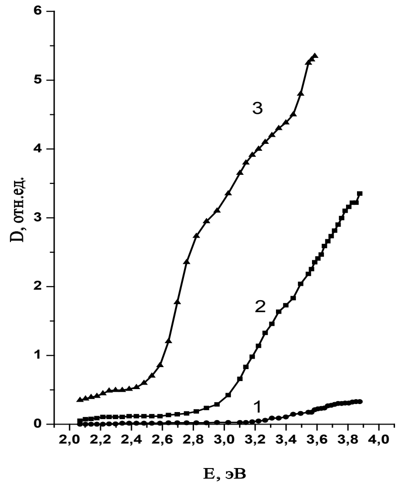

Fig. 1. Absorption spectrums of gelatinous solution (1) and NC of sulfide of cadmium samples: N 1 (2); N 2 (3).

Note that in nanocrystals ratio of surface area to volume of the nanocrystal varies considerably depending on their radius, therefore, changes and number of non-compensated valence atoms leaving the surface. Moreover, the interaction of the gelatin molecules with the surface of the nanocrystals can depend on their size due to the influence of steric factors. Thus, there is every reason to expect the effect of surface defects on the properties that are sensitive to surface recombination of charge carriers, for example, the fluorescent characteristics of NC.

Let us discuss the influence of the surface defects on the photoluminescence characteristics of NC various sizes. Fig. 2. shows the luminescence spectra of CdS QDs (sample number 1) for different powers of the exciting light P, MW: 26.6 (1) 19.5 (2) 45.0 (3). It can be seen that the emission intensity increases with increasing power, but regardless of its size nanocrystals have one broad band with a maximum λ_{max} = 580 nm. The nature of this band is associated with deep centers and radiation appears in the nanocrystals with a high density of defects, including surface [20-22] and this luminescence is called “defective.” It should be noted that the localization of the maxima of the luminescence bands on deep centers depends on the nature of the defects, that is to the energy of ionization. According to our observations [20,21] and the analysis of references [23,24], the long-wavelength region of the spectrum has three luminescence bands that are located at λ_{max} = 580, 670 and 750 nm. The contour of the luminescence bands observed by different authors depends on the technology of the nanocrystals and consists of either one elementary band or emission band formed from the total contribution of the few bands.

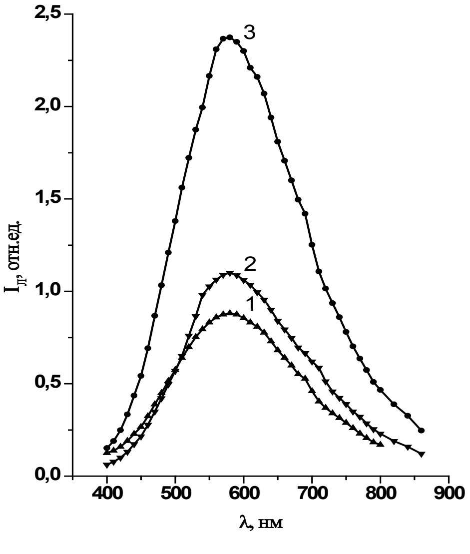

Fig. 2. Luminescence spectrums of NC CdS (sample № 1) at various excitation power, mWt: 26,6 (1) 19,5 (2); 45,0 (3).

Thus, in our case in the sample N 1 we register «defective» emission band and do not observed radiation with energies close to the forbidden band, which is a sign of the dominant role of the luminescence associated with surface defects. The fact that the position of the maximum emission of these samples is independent of the excitation power is indirect evidence of the radiative recombination that is caused by one type of defect.

In contrast, in the spectra of the sample number 2, along with the long-wave radiation, there is a narrow and short-wavelength luminescence band with λ_{max} = 480 nm (Fig. 3), the nature of which is due to the exciton luminescence [25].

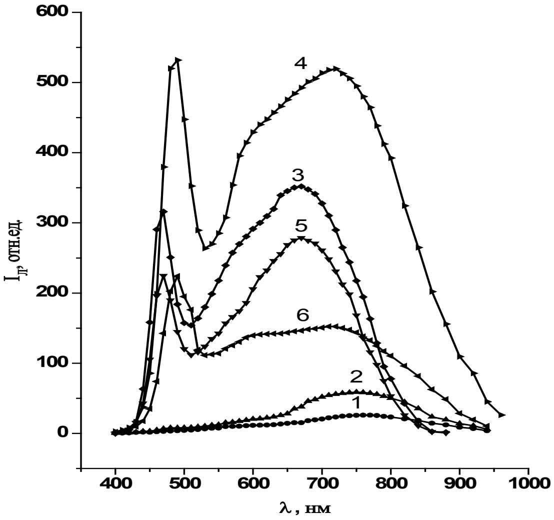

Fig. 3. Luminescence spectrums of NC CdS (sample № 2) at various excitation power, mWt: 19,5 (1); 26,0 (2); 32,0 (3); 42,0 (4); 45,0 (5); 26,6 (6).

The presence of such a band indicates the competitive advantage of the recombination channel, which is associated with the recombination in the cadmium sulfide nanocrystals volume.

It was found that intensity and contour defect luminescence emission of the sample N 2 depend on the power. Thus, the intensity of the bands increases with increasing excitation power luminescence from 19.5 mW to 42 mW, and the ratio of the intensities of the bands that form the total loop «defect» luminescence changes with power. Due to the latter fact there is a possibility of observing the longer wavelengths of several luminescence bands with peaks localized in the wavelength: λ_{max} = 580, 670 and 750 nm. The dependence of the contour on the power of the excitation luminescence is likely to be due to the different parameters of emission centers, and may be the subject of further research.

Conclusion

In this paper we have established a novel dependency of the luminescence spectrum of CdS NC on their size that is associated with different contribution of surface defects in NC of different sizes. In particular the luminescence of NC with an average radius of 1.8 nm is dominated by long-wavelength light with λ_{max}= 580 nm, caused by one type of surface defects. Such NC do not exhibit band-band or exciton luminescence. In NC of larger size (3.5 nm), the contribution of surface recombination is reduced, and the presence of short-wavelength band λ_{max} = 480 nm demonstrates that the dominating recombination channel is due to nonequilibrium carriers in the volume of nanocrystals of cadmium sulfide.

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INFLUENCE OF THE SURFACE ON THE SPECTRUM OF LUMINESCENCE NC CdS IN GELATINE MATRIX

Abstract

The optical absorption and luminescence of nanocrystals (NCs) CdS different sizes obtained by colloidal chemistry in an aqueous solution of gelatin investigated. In NCs with a radius of 1.8 nm was observed only with long-wavelength luminescence λ_{max} = 580 nm due to surface defects. In NCs larger (3.5 nm), the contribution of surface recombination decreases, there is a redistribution of recombination channels. Recombination of nonequilibrium carriers in the volume of cadmium sulfide nanocrystals is primary and their luminescence spectra contains intensive exciton band.

Keywords: nanocrystals CdS, absorption, luminescence

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ВПЛИВ ПОВЕРХНІ НА СПЕКТР ЛЮМІНЕСЦЕНЦІЇ НК CDS В ЖЕЛАТИНОВІЙ МАТРИЦІ

Анотація

Досліджувалося оптичне поглинання і люмінесценція нанокристалів (НК) CdS різного розміру, отриманих методом колоїдної хімії у водному розчині желатини. У НК, що мали розмір з радіусом 1,8 нм спостерігається лише довгохвильове світіння з $\lambda_{макс}$ = 580 нм, яке обумовлене поверхневими дефектами. У НК більшого розміру (3,5 нм) вклад рекомбінації за участю поверхневих дефектів зменшується, відбувається перерозподіл каналів рекомбінації на користь рекомбінації нерівноважних носіїв в об’ємі нанокристалів і спектрі їх люмінесценції реєструється інтенсивна смуга випромінювання екситона.

Ключові слова: нанокристали CdS, поглинання, люмінесценція

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ВЛИЯНИЕ ПОВЕРХНОСТИ НА СПЕКТР ЛЮМИНЕСЦЕНЦИИ НК CDS, В ЖЕЛАТИНОВОЙ МАТРИЦЕ

Аннотация

Исследовалось оптическое поглощение и люминесценция нанокристаллов (НК) CdS разного размера, полученных методом коллоидной химии в водном растворе желатины. В НК с радиусом 1,8 нм наблюдается только длинноволновое свечение с $\lambda_{\text{макс}} = 580$ нм, обусловленное поверхностными дефектами. В НК большего размера (3,5 нм) вклад рекомбинации с участием поверхностных дефектов уменьшается, происходит перераспределение каналов рекомбинации в пользу рекомбинации неравновесных носителей в объеме нанокристаллов сульфида кадмия и спектре их люминесценции регистрируется интенсивная экситонная полоса свечения.

Ключевые слова: нанокристали CdS, поглощение, люминесценция