Synthesis and Photoluminescence Spectra of the Composite Films with Cadmium Sulfide Nanocrystals

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The paper describes the features of the optical properties of the composite films with embedded cadmium sulfide nanocrystals (CdS NC) which have been obtained *in situ* via sol-gel method. Photoluminescence spectra comprise two areas: the doped due to surface defects at E = 1.6-2.3 eV and exciton at E = 2.3-3.0 eV. An increase of the precursor Cd(Ac)₂·2H₂O concentration in polymer matrix does not bring about automatic increase in the light absorption at λ_{max} and photoluminescence intensity of the composite film; perhaps this is caused by the formation of less perfect CdS structures in this case.

Keywords: CdS nanocrystals, Composite film, Photoluminescence spectrum.

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1. INTRODUCTION

Quantum effects, caused by the splitting of energy levels on the edges of the valence band and conduction band with the decrease in the size of metal and semiconductor particles less than the Bohr radius, are the objects of intensive theoretical and practical investigations of the last decade. This, in turn, stimulated the development of a new field of science – nanotechnology connected with the elaboration of methods for obtaining, investigation, handling and application of the objects of reduced dimension.

Semiconductor materials of the A₂B₆ type in nanocrystalline form are of special interest due to their nonlinear optical properties [1, 2], luminescent properties [3, 4], appreciable quantum-size effect [5] and other properties that makes them promising materials for the application in photodetectors, light-emitting devices, thinfilm transistors, solar cells, etc. CdS is one of the most promising materials among them, since its fundamental absorption edge is located in the visible spectral region, and band-to-band transition occurs in this region that is important for application in many opto-electrical devices [6]. This has stimulated intense investigations of the development of different methods for obtaining nanodimensional CdS structures: vacuum evaporation and deposition, pyrolysis sputtering, molecular-beam epitaxy, chemical deposition and some others. Chemical deposition which occurs via sol-gel mechanism is a cheap alternative to all the above mentioned methods, although less perfect structures are formed in this case, too.

The so-called organic-inorganic hybrid materials, in particular, nanocrystals (NC) of semiconductors embedded in polymer matrix are of special attention. In such materials, not only the role of the interphase interaction of matrix and inclusions considerable increases, but also the nature of matrix itself can influence the NC properties, and, thus, can be one more reason of their regulation or amplify NC sensitivity to the action of external factors in different sensors. Usually, organic-inorganic composites are produced from inorganic nanoparticles pre-formed in the aqueous environment which are transferred by some means into organic environment which contains matrix polymer. Here, it is almost impossible to avoid agglomeration of nanoparticles and provide their uniform distribution in a polymer matrix. We have developed the *in situ* method of CdS NC synthesis in thin polymer films without these disadvantages [7].

In the present work we discuss the features of the luminescence spectra of CdS NC embedded in polymer matrix obtained via the sol-gel method directly in hydrogel film of cross-linked (structured) polymer deposited on a solid substrate (quartz glass).

2. EXPERIMENTAL PART

2.1 Materials

Cadmium acetate (Cd(CH₃COO)₂ \cdot 2H₂O) of the "ChDA" qualification (GOST 5824-79).

Sodium sulfide ($Na_2S \cdot 9H_2O$) of the "ChDA" qualification (GOST 2053-77).

Solvents, acetone of the "ChDA" qualification (GOST 2603-79); ethyl acetate (EA) of the mark A, superior quality (GOST 8981-78); dimethyl formamide (DMF) of the "KhCh" qualification (GOST 20289-74), were cleaned by drving over calcium chloride with further distillation.

Polyethylene glycol PEG-200 (Merck, Germany) was used without additional cleaning.

For synthesis of polyfunctional peroxide-containing copolymer (PFPC) the following monomers were applied: butyl methacrylate (BMA) (Merck, Germany) was cleaned by vacuum distillation; maleic anhydride (MA) (Merck, Germany) was cleaned by recrystallization from chloroform; peroxide monomer 5-tert-butylperoxy-5-methyl-1hexene-3-yne (VEP) was synthesized at the department of organic chemistry of the Lviv Polytechnic National University by the technique of [8]; dimethylaminoethanol (DMAE) (Merck, Germany) was used without additional cleaning.

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PFPC was synthesized in two stages: terpolymer VEP-BMA-MA was obtained on the first stage by radical copolymerization of the corresponding monomers by the known technique [9]; on the second stage obtained terpolymer VEP-BMA-MA was dissolved in EA at their ratio of 1:7.5 in three-necked reactor with impeller mixer and backflow condenser at the temperature of 333 K. After total dissolution of terpolymer, 10% solution of DMAE in EA was dripped into reactor during 1 hour at constant agitation in order that mole ratio [MA]:[DMAE] was equal to 2:1. After dripping, reaction mixture was agitated during 4 hours more at 333 K, and then the obtained product was doubly re-precipitated in hexane and dried under vacuum at room temperature to constant mass. As a result, we have obtained PFPC of the following structure:



where k = 27 % mol., m = 33 % mol., n = 24 % mol., and p = 16 % mol., and the following characteristics:

- external view yellowish powder;
- characteristic viscosity in acetone, length/g 0.01;
- content of active oxygen, % − 2.8.

Quartz substrates $24 \times 24 \times 0.18$ mm, on which thin polymer films with NC of metal sulfides were formed, were cleaned by washing in "piranha" solution (mixture [NH₄OH 25%] : [H₂O₂ 35%] : [bidistilled water] = 1:1:1) and then washed many times in bidistilled water.

2.2 Analysis techniques

2.2.1. Characteristics of polyfunctional peroxide-containing copolymer. Composition of PFPC was calculated based on the results of the functional analyses for the content of active oxygen, carboxyl groups, and nitrogen.

Content of active oxygen and, correspondingly, VEP links in PFPC was determined by the method of gas chromatography analysis of the thermal decomposition products of PFPC at the isokinetic point T = 483 K in accordance with [10].

Content of MA links in PFPC was defined by the reverse potentiometric titration of carboxyl groups in alkaline aqueous solution of PFPC.

Content of DMAE fragments in PFPC was calculated from the results of determination of nitrogen content by the Dumas method [11].

Characteristic viscosity of PFPC was defined in acetone at 293 K using Bischoff viscometer with line level.

2.2.2. Characteristics of nanocomposite films with CdS NC. Scanning electron microscopy, energydispersion X-ray microanalysis, spectroscopy in the visible region, and photoluminescence spectroscopy were used for the analysis and investigation of the properties of nanocomposite films with CdS NC.

Estimation of the thickness of nanocomposite films and composition of CdS NC was carried out using the scanning electron microscope – X-ray microanalyzer REMMA-106i (public corp. "SELMI", Sumy, Ukraine). Spectra in the visible region of nanocomposite films with CdS NC were recorded on the spectrophotometer Specord-M40.

Size of CdS particles was defined by the formula [5]

$$D = -6,6521 \cdot 10^{-8} \lambda^3 + 1,9557 \cdot 10^{-4} \lambda^2 - -9,2352 \cdot 10^{-2} \lambda + 13,29.$$
 (1)

where λ is the wavelength, at which absorption maximum on the sample spectrum is observed.

Measurements of the photoluminescence spectra were performed on the automated experimental plant for the investigations of the optical and luminescence spectra, which consists of the radiation source (optical quantum generator), optical cryostat, optical monochromator MDR-23 with working spectral range of 200-1000 nm, photoreceiving device, amplifier, and personal computer. Continuously working helium-cadmium laser LG-70 with the wavelength of $\lambda = 325.0$ nm and power of 10 mW (production of "Lviv-Electronics", Lviv, Ukraine) was used for the excitation of photoluminescence (PL).

PL signal with the aid of the system of lenses was focused on the entrance slit of optical monochromator MDR-23. PL spectrum was analyzed by monochromator with the resolution which in all cases was not less than 1 meV. Light filter was located in front of the entrance slit in order to avoid a hit of the reflected laser beam on photodetector. As radiation detector we have used uncooled photo-multiplier FEU-100, for which spectral dependence of the sensitivity was obtained, and PL spectra of the investigated samples were plotted taking into account this dependence. Registration of the PL signal was realized in the mode of constant current by amplifier with high zero stability and low intrinsic noise ($\approx 10^{-15}$ A). Electric signal of photodetector after amplification came to the entrance of the analog-digital converter with further electronic processing.

3. RESULTS AND DISCUSSION

3.1 Production of nanocomposite films with CdS NC

Production of nanocomposite films with CdS NC included three sequential stages, namely, formation on a solid substrate of a polymer film with coordinately and chemically bonded Cd²⁺ ions, its structuring and treatment by hydrogen sulfide from gaseous phase.

Formation of a polymer film was performed from the solution containing PFPC, cadmium salt, and structureforming agent in organic solvent at the content of cadmium salt of 36-48% of PFPC mass. To this end, 10% solution of PFPC in DMF was prepared, and structureforming agent PEG-200 was added to it. Usage of the mixture of PFPC and PEG-200 provides the possibility of obtaining polymer films of the cross-linked structure with the given ratio of polar and nonpolar fragments as well as interstitial distance in whose cells NC of metal sulfides are formed that allows to control the size and distribution density of the synthesized nanocrystals in such nanocomposite film. Saturated solution of cadmium acetate in DMF was prepared separately. Both solutions were admixed with intensive agitation in such proportion in order to provide the specified correlation

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 $[Cd(CH_3COO)_2 H_2O]$: [PFPC]. The obtained solution was deposited on the quartz substrate by spin-coating method at 2000 rev/min.

Substrate with obtained polymer film was heated in the oven at 393 K during 2 hours in order to obtain the cross-linked structure, and then it was placed into exsiccator over 10% aqueous solution of Na₂S for 4 hours at 333 K. As a result of the interaction of Cd^{2+} ions embedded in a polymer film with absorbed from gaseous phase H₂S, which is formed as a result of hydrolysis of Na₂S, CdS NC were formed in a polymer film.

Nanocomposite films with the average thickness of ≈ 50 nm which contain 15-20% of CdS NC are formed by this technique. Some layers of nanocomposite film are additionally formed on the produced nanocomposite films in order to obtain nanocomposite films with larger thickness. This allows to obtain multilayer nanocomposite films of the specified thickness which depends on the amount of layers and, correspondingly, govern their optical and other properties, first of all, absorption and luminescence intensities.

3.2 Investigation results of the absorption spectra

Absorption spectra of nanocomposite films with CdS NC in the visible region are represented in Fig. 1a and their characteristics are given in Table 1.

As seen from the presented data, CdS NC are formed in polymer films as a result of the sol-gel process and their sizes depend weakly on the formation conditions: number of deposited layers (Table 1, samples 5 and 6) and precursor concentration (Table 1, samples 4 and 6) and also sufficiently narrow unimodal size distribution (Fig. 1). This is conditioned by the fact that method we have developed considerably differs from other methods of NC synthesis, since formation and growth of NC occurs in hydrogel matrix - swollen layer of cross-linked polymer. Structure of such matrix can be represented in the form of a net of polymer chains, in whose cells water molecules (solvent) and cadmium ions are placed. If place hydrogel matrix into the atmosphere saturated by gas-like hydrogen sulfide, it is absorbed by aqueous phase of a matrix and partly dissociates in it. Cd²⁺ and S² ions are mobile, can easily diffuse due to small sizes and react in hydrogel matrix with the formation of CdS molecules. The latter are also sufficiently mobile and interact with each other with the formation of clusters, which are extracted into separate phase because of low solubility in water. With the growth of clusters their mobility rapidly decreases and therewith is suppressed by interstitial sizes of hydrogel net. Since the same polymer matrix with the same parameters was used in all cases of the given investigation, nets formed by CdS NC have rather similar sizes. With the increase in the number of layers, as it was expected, the value of the optical density of films with NC increases (Table 1, samples 5 and 6), but increase in the precursor concentration does not lead to mechanical increase in the optical density. Reasons of this phenomenon are not completely clear and require additional investigations.



Fig. 1-UV absorption spectra of the obtained nanocomposite films. Solid lines are the integral absorption spectra; dotted lines are the approximation of the absorption spectra by the normal Gauss distribution

3.3 Investigation results of the PL spectra

In Fig. 2 we present the PL spectra of CdS NC No4, No5, and No6, whose characteristics are given in Table 1. We note that initial PL spectra contained also the contribution of quartz luminescence in the vicinity of 3.1 eV [12]. Therefore, from the initial PL spectra we have excluded the component responsible for quartz glow, and in Fig. 2 we illustrate the PL spectra which correspond to the glow of CdS NC solely. According to the literature data, PL spectrum of CdS NC shown in Fig. 2 consists of two areas: the doped area with E = (1.6-2.3) eV conditioned by surface defects and the exciton one with E = (2.3-3.0) eV [4, 13, 14].

Now we consider the PL spectrum of the sample No5 with the smallest film thickness (90 nm) and content of Cd^{2+} salt relative to the PFPC mass $N_{Cd} = 48\%$. For this sample PL intensity is minimal in both the doped and exciton spectral regions. Increase in the nanocomposite film thickness to 120 nm (sample No6) at the constant

Sam-	Content of Cd ²⁺ salt	Number of	Film	Film λ_{\max} , nm	Absorption	Size of CdS
ple No	from PFPC mass	layers	thickness, nm		at λ_{\max}	NC, nm
4	36	4	120	461.5	0.39	5.78
5	48	3	90	460.8	0.28	5.75
6	48	4	120	461.0	0.36	5.76

Table 1 - Characteristics of nanocomposite films with CdS NC

content of Cd^{2+} salt ($N_{Cd} = 48\%$) did not lead to the increase in the intensity of exciton PL, while intensity of impurity PL increased approximately 1.6 times. That is, concentration of surface defects responsible for the impurity PL considerably increases with the increase in the nanocomposite film thickness from 90 nm to 120 nm. It is interesting that decrease in the content of Cd^{2+} salt to $N_{Cd} = 36\%$ (sample No4) leads to the significant (almost three-fold) increase in the intensity of exciton PL, and this is the indicator of the decrease in the radiationless losses.

Thus, nanocomposite films with $N_{Cd} = 36\%$ contain more structurally perfect CdS NC than the correspond-



Fig. 2 – PL spectra at T = 300 K of CdS NC No4, No5, No6, whose characteristics are given in Table 1

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ing films with $N_{Cd} = 48\%$. Excess concentration of cadmium, probably, leads to the increase in the number of defects, which are the centers of radiationless recombination. As for the increase in the intensity of impurity PL for sample No4, it is induced, to our opinion, not by the increase in the concentration of surface defects in comparison with sample No6 (number of layers in samples No4 and No6 is the same), but by the total increase in the rate of the radiative recombination.

4. CONCLUSIONS

1. Synthesis technique of CdS NC in polymer matrices has been developed *in situ* via sol-gel method which includes deposition of a layer of polymer matrix with precursor – cadmium salt – on a solid substrate, structuring of the matrix and formation of CdS NC in a swollen matrix as a result of the interaction of precursor and H_2S .

2. It is established that sizes of the formed CdS NC insignificantly depend on the preparation conditions and are determined, mainly, by the parameters of matrix net and are in the range of 5.75-5.78 nm.

3. PL spectra of CdS NC synthesized in a polymer matrix consist of two areas, namely, the doped area with E = 1.6-2.3 eV conditioned by surface defects and the exciton one with E = 2.3-3.0 eV.

4. Maximum PL intensity of CdS NC is achieved if use the precursor content – cadmium salt with respect to the PFPC mass $N_{Cd} = 36\%$.

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