

## 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  $E = 1.6\text{--}2.3$  eV and exciton at  $E = 2.3\text{--}3.0$  eV. An increase of the precursor  $\text{Cd}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$  concentration in polymer matrix does not bring about automatic increase in the light absorption at  $\lambda_{\text{max}}$  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  $\text{A}_2\text{B}_6$  type in nanocrystalline form are of special interest due to their non-linear 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, thin-film 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 nano-dimensional 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 ( $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ) of the “ChDA” qualification (GOST 5824-79).

Sodium sulfide ( $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ ) 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 drying 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-1-hexene-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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[Cd(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O] : [PFPC]. The obtained solution was deposited on the quartz substrate by spin-coating method at 2000 rev/min.

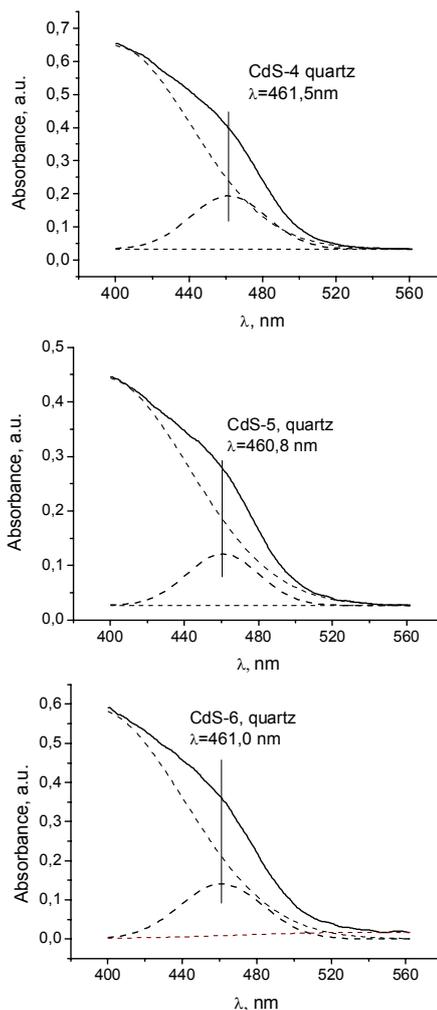
Substrate with obtained polymer film was heated in the oven at 393 K during 2 hours in order to obtain the cross-linked structure, and then it was placed into exsiccator over 10% aqueous solution of Na<sub>2</sub>S for 4 hours at 333 K. As a result of the interaction of Cd<sup>2+</sup> ions embedded in a polymer film with absorbed from gaseous phase H<sub>2</sub>S, which is formed as a result of hydrolysis of Na<sub>2</sub>S, 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 film 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. Cd<sup>2+</sup> and S<sup>2-</sup> 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].

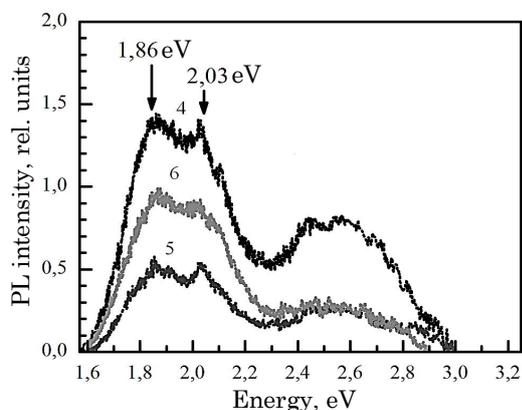
Now we consider the PL spectrum of the sample No5 with the smallest film thickness (90 nm) and content of Cd<sup>2+</sup> salt relative to the PFPC mass  $N_{Cd} = 48\%$ . For this sample PL intensity is minimal in both the doped and exciton spectral regions. Increase in the nanocomposite film thickness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

**Table 1** – Characteristics of nanocomposite films with CdS NC

Sample No	Content of Cd <sup>2+</sup> salt from PFPC mass	Number of layers	Film thickness, nm	Film $\lambda_{\max}$ , nm	Absorption at $\lambda_{\max}$	Size of CdS 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

content of Cd<sup>2+</sup> salt ( $N_{\text{Cd}} = 48\%$ ) 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<sup>2+</sup> salt to  $N_{\text{Cd}} = 36\%$  (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  $N_{\text{Cd}} = 36\%$  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  $N_{\text{Cd}} = 48\%$ . 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<sub>2</sub>S.

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  $N_{\text{Cd}} = 36\%$ .