

SPECTRAL LUMINESCENCE PROPERTIES OF CdS NANOCOMPOSITES IN A POLYMER SHELL

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Nanocomposites of different concentrations of cadmium sulfide nanoparticles in a polyacrylamide shell were obtained as a result of the reaction of cadmium nitrate with acrylamide and a tiouresulfiding agent (thiourea) in certain stoichiometric ratios followed by thermal polymerization of the reaction mixture. The samples were studied by the methods of elemental analysis, X-ray diffraction, scanning electron microscopy, and optical and luminescent spectroscopy. The sizes of sulfide nanoparticles as well as their distribution in the polymer were determined. It was shown that the absorption spectra have characteristic features of the spectra of composite systems with nanosized semiconductor crystals that manifested "defective" luminescence with a maximum in the 550–570 nm region.

KEY WORDS: *nanocomposites, cadmium sulfide, polyacrylamide shell, frontal polymerization of metallic monomers*

1. INTRODUCTION

Great interest in semiconductor materials, in both the terms of fundamental science and applied developments, is explained by their application as light-emitting

diodes, photocatalysts, biological marks, and gas sensors (Pomogailo et al., 2000; Magerramov et al., 2008; Gubin et al., 2005; Rogach, 2008; Nikolenko and Razumov, 2013) in aviation and space vehicles and other equipment. The most topical of these materials are polymer nanocomposites with chalcogenides of transition metals that possess a whole range of optical, electrophysical, photochemical, and magnetic properties which allows their use in creation of luminescent screens, converters, sensors, light-emitting diodes, and other devices (Pomogailo et al., 2000, 2014; Magerramov et al., 2008; Gubin et al., 2005; Rogach, 2008; Nikolenko and Razumov, 2013; Biryukov et al., 2013; Bochenkov and Sergeev, 2007; Yuan et al., 2010). Moreover, a specific feature of multifunctional nanostructured coatings of "chameleon" type, designed for spacecrafts, is that during friction the chemical composition of tribological layers on the coating surfaces change depending on the composition and environmental temperature. For instance, chalcogenides in vacuum or dry nitrogen reduce the friction coefficient to values below 0.1, whereas chalcogenides surrounded by a ceramic matrix at a high temperature of about 500°C to 0.2 (Kochanov, 2010).

In this case, the polymer matrix ensures high physicomechanical characteristics of nanocompositions (flexibility and processing properties), while active fillers ensure high sensitivity and effective photoluminescence properties. By varying the synthesis conditions and composition it is possible to control the structure of the material, as well as its chemical, catalytic, and sensory properties (Biryukov et al., 2013; Bochenkov and Sergeev, 2007; Pomogailo et al., 2014). There exist two approaches to the production of nanocomposites. One approach is to introduce presynthesized nanoparticles to the polymer matrix, and the second approach is to produce them *in situ*, i.e., at the time when the composite is produced nanoparticles are generated in the polymerized matrix, which facilitates even distribution of nanoparticles. In the present study, the second approach was used to obtain *in situ* nanocomposites of different compositions based on cadmium sulfide nanoparticles in a polymer matrix, to characterize their structure, to establish the relation between the original concentrations of precursors and the size of the nanoparticles formed, and to investigate their spectral and luminescence properties.

2. EXPERIMENTAL

The work was performed using the following reagents: $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (chemically pure), acrylamide (AAM, Fluka), thiourea (chemically pure), and dimethyl sulfoxide (DMSO, Sigma-Aldrich, 99.9%).

2.1 Obtaining Cadmium Sulfide Nanocomposites in a Polyacrylamide Matrix by Thermal Polymerization

Mixtures of cadmium nitrate, sulfonating agent, and acrylamide in various quantities, indicated in Table 1, were pressed by a hand-operated press in the form of cy-

TABLE 1: Composition of the initial components of charge mixtures

Samples	Weight Ratio, g			Mole Ratio Cd(NO ₃) ₂ ·4H ₂ O:Thiourea:AAM
	Cd(NO ₃) ₂ ·4H ₂ O	AAM	Thiourea	
1CdS-pAAM	0.52	4.75	0.129	1:1:40
2CdS-pAAM	1.04	4.5	0.5	1:1:20
3CdS-pAAM	1.54	4.25	0.38	1:1:11
4CdS-pAAM	2.5	2.55	0.675	1:1:4

lindrical workpieces and placed in test tubes. Then the lower part of the workpiece was heated for several minutes in a Wood alloy bath at 180–190°C. The thermal initiation causes frontal polymerization of acrylamide, accompanied by strong heating of the cadmium nitrate–thiourea mixture. As a result, thiourea is decomposed in the melted cadmium nitrate, whose subsequent dissociation leads to the formation of cadmium ions that react with the sulfur ions (II) in the melt obtained. Thus, cadmium sulfide nanoparticles are formed in a polyacrylamide shell. Table 1 lists the data on the composition of the initial components of charge mixtures.

The structure of the materials obtained was investigated by the X-ray phase analysis at room temperature using a DRON UM-2 diffractometer; the morphology of the surface of nanocomposite samples was studied by an FEI QUANTA 200 FEG scanning electron microscope.

The absorption spectra of samples were measured by a Shimadzu UV-3101PC spectral photometer, and the luminescence spectra were recorded by a Perkin Elmer LS55 spectrofluorimeter.

3. RESULTS AND DISCUSSION

As a result of thermal polymerization of acrylamide in the presence of cadmium nitrate and thiourea (for their concentrations see Table 1) at 180°C we obtained nanocomposites of various compositions (Table 2).

The comparative analysis of the data, listed in Table 2, with the data on the composition of the initial components of the charge mixture (Table 1) indicated to the pos-

TABLE 2: Elemental analysis of the nanocomposites obtained

Samples	Found, %				Content of Metal Sulfide, %
	C	H	S	Dry Residue	
1CdS-pAAM	46.52	6.81	0.69	4.71	3.10
2CdS-pAAM	40.04	6.47	2.23	8.35	9.38
3CdS-pAAM	40.48	5.88	3.5	11.59	13.03
4CdS-PAAM	30.07	6.00	4.5	21.71	24.41

sibility of targeted production of composites with a high content of cadmium sulfide (Table 2).

The electron microscopy images of nanocomposites, containing different concentrations of cadmium sulfide nanocrystals, do not allow identification of the nanoparticles themselves due to insufficient resolution of the microscope. However, a noticeable influence of their concentration on the surface morphology can be seen (Fig. 1),

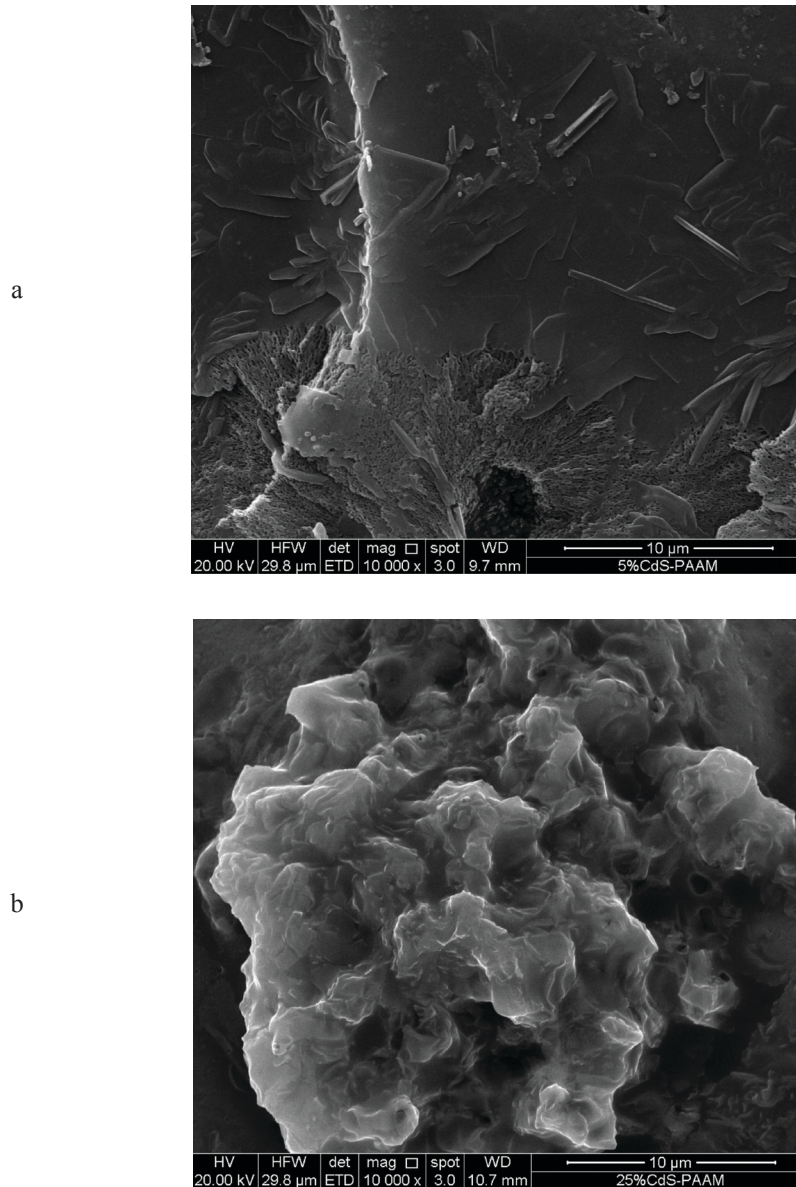


FIG. 1: Electron microscopy images of nanocomposites: a) 1CdS-pAAM; b) 4CdS-pAAM

namely, the increasing concentration of cadmium sulfide enhances the compactness and structuring of the composite (Fig. 1b).

The X-ray phase analysis of the nanocomposites obtained (Fig. 2) revealed the following reflexes at 2Θ : 26.35, 43.85, and 51.85 with $d = 3.357$, 2.085, and 1.756 that are typical of hexagonal cadmium sulfide with a wurtzite structure. An intense broad band in the region of $2\Theta = 21^\circ$ belongs to polyacrylamide. It is characteristic that the intensity of the peaks of the CdS-containing phase decreases with increase in the concentration of cadmium sulfide in the composite and with simultaneous increase in the interplanar spacings, which testifies to binding of nanocrystals to the polymer matrix. The mean sizes of crystallites (nanoparticles) D that correspond to the sizes of the regions of X-rays coherent diffusion were estimated by the width of reflexes on X-ray diagrams using the Debye–Scherrer formula:

$$D = 0.89\lambda / (l \cos \theta), \quad (1)$$

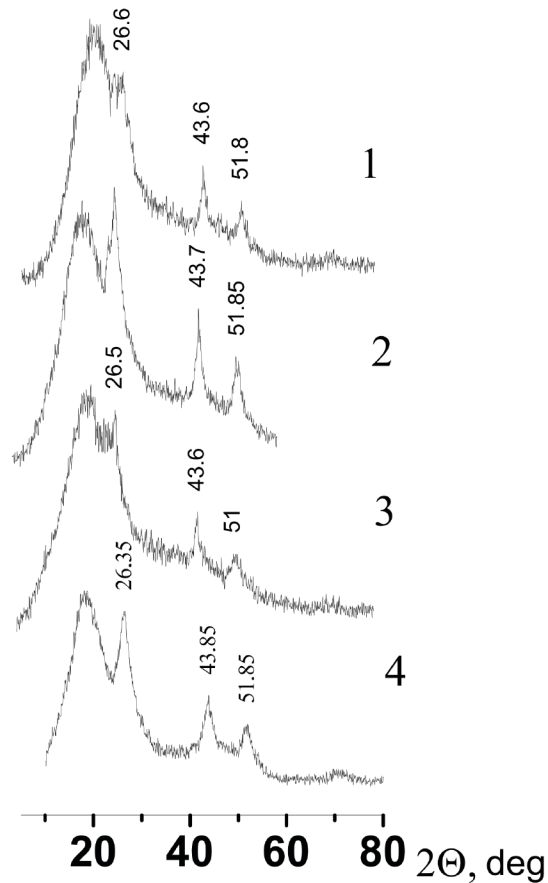


FIG. 2: X-ray diffractograms of nanocomposites: 1) 1CdSpAAM; 2) 2CdSpAAM; 3) 3CdSpAAM; 4) 4CdSpAAM

where λ is the wavelength of X-ray radiation [$\lambda(\text{CuK}\alpha) = 1.54051 \text{ \AA}$], l is the peak width at half-height (rad), and θ is the diffraction angle (rad).

According to data obtained by the Debye–Scherrer equation (Table 3), the size of particles varies in a narrow range of values, changing from 4 to ~15 nm with increasing fraction of CdS in the composite (Table 3). An increase in the CdS concentration decreases the size of CdS crystallite particles.

The investigations conducted with the aid of optical and luminescent methods that are the most informative contactless methods for characterizing the properties of nanosized objects show that in the case of nanocrystals the energy spectrum of charge carriers is discrete. The energy levels of electrons and holes in the conduction band and the valence band are as follows (Ekimov et al., 1985; Kulish et al., 1992, 1997):

$$E_{e,h}^{l,n} = \frac{\hbar^2 \varphi_{l,n}^2}{2m_{e,h} R^2}, \quad (2)$$

where l and n are the orbital and main quantum numbers, $\varphi_{l,n}$ are the roots of the Bessel function, R is the mean radius of the nanocrystal, \hbar is the Planck constant, and m_e is the effective mass of an electron.

The threshold energy of interband absorption, having the meaning of the effective width of the forbidden band in quantum points, is described by the following expressions:

$$h\nu_{01} = E_g + \frac{\hbar^2 \pi^2}{2\mu R^2}, \quad (3)$$

$$\mu = \frac{1}{m_e} + \frac{1}{m_h}, \quad (4)$$

where E_g is the width of the forbidden band of a macrocrystal, μ is the reduced mass, and m_e and m_h are the effective masses of electron and hole, respectively.

When the particles have the same size, the absorption spectrum will contain a set of lines that correspond to transitions between the electron and hole levels with corresponding quantum numbers l and n . The coefficient of absorption in each line is proportional to the product of the reduced density of the state of levels that participate

TABLE 3: Sizes of the CdS crystallites, calculated by the data of X-ray phase analysis and the absorption spectra

Samples	Particle Sizes, nm	
	X-ray Phase Analysis	Absorption Spectra
1CdS-pAAM	11.7	8.4
2CdS-pAAM	7.2	7.0
3CdS-pAAM	15.0	5.4
4CdS-pAAM	4.2	4.6

in transitions in a separate crystal by the total number of nanoparticles. In the real case, the size distribution of particles is always present, and the absorption spectrum represents a curve consisting of overlapping bands.

It can be seen from the presented theoretical ideas that the spectra of optical absorption of the samples under investigation (Fig. 3) have typical features of spectra of the composite systems with nanosized semiconductor crystals.

Curve 1 in Fig. 3, belonging to 1CdS-pAAM with the minimum quantity of cadmium sulfide, has an ill-defined band in the 470-nm region, which corresponds to the first optical transition. With increasing content of CdS, this band shifts towards short waves and is localized in the region of 460-, 435-, and 420-nm wavelengths (curves 2, 3, and 4, respectively). In conformity with these values and based on the calculated mean radius of nanocrystals, the dimensions (diameters) of the obtained samples 1, 2, 3, and 4 are equal to 8.4, 7.0, 5.4, and 4.6, respectively (Table 3). It is seen that the dimensions of nanocrystals decrease monotonously with increase of their concentration in the composite, which is in qualitative agreement with the data of X-ray phase analysis.

Figure 4 presents the luminescence spectra of the studied composites excited by the light with the 460-nm wavelength in DMSO. It should be noted that polyacrylamide *per se*, as well as polyacrylamide cadmium complex did not luminesce in these conditions. All samples are characterized by a broad luminescence band with a maximum in the 550–570-nm region, correspondent to CdS nanoparticles (Pucci et al.,

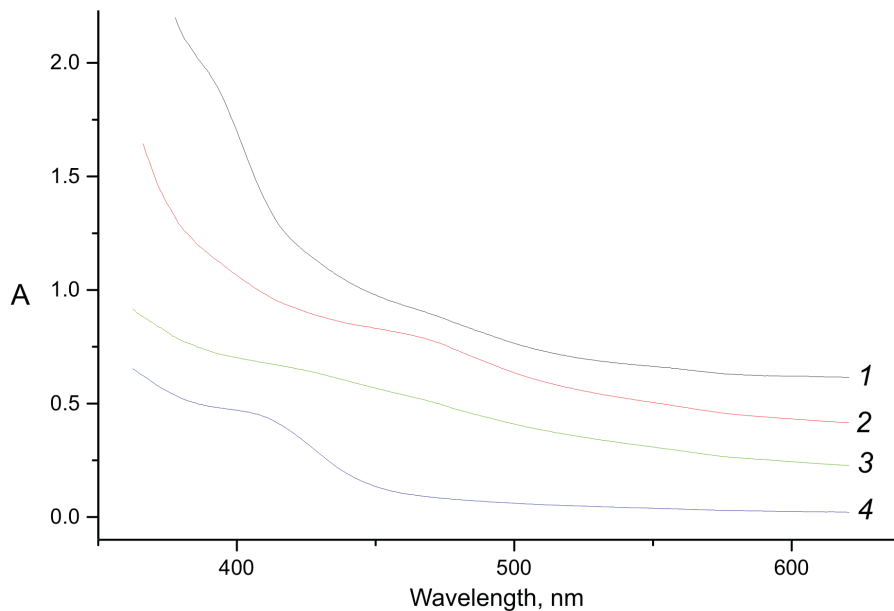


FIG. 3: The absorption spectra of the samples in DMSO: 1) 1CdS-pAAM; 2) 2CdS-pAAM; 3) 3CdS-pAAM; 4) 4CdS-pAAM

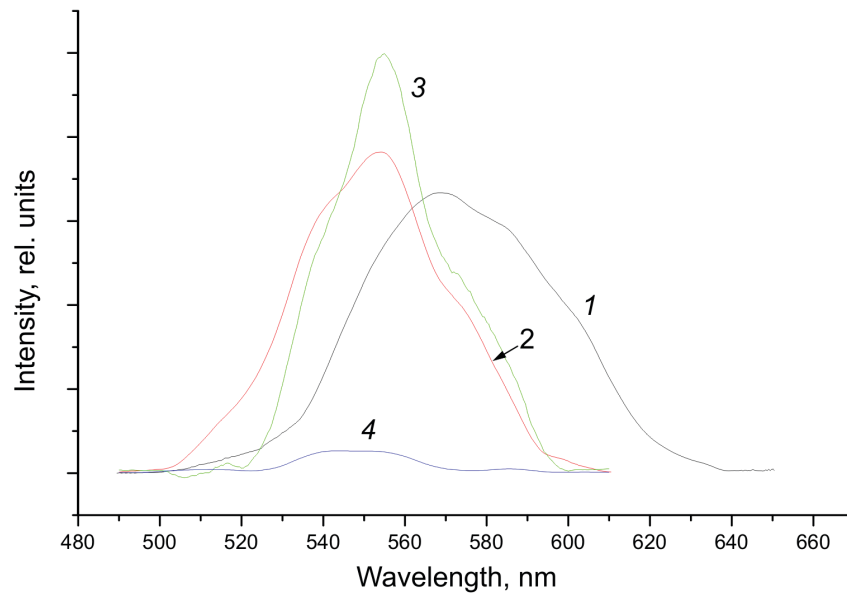


FIG. 4: The luminescence spectra of the samples in DMSO: 1) 1CdS-pAAM; 2) 2CdS-pAAM; 3) 3CdS-pAAM; 4) 4CdS-pAAM. The excitation wavelength is 460 nm

2008). Evidently, this band is complex and represents a superposition of elementary bands, with its intensity for the sample 4CdS-pAAM (curve 4) decreasing compared to luminescence of the samples 1CdS-pAAM, 2CdS-pAAM, and 3CdS-pAAM. It was found that the use of light for excitation of luminescence in the region of 300–460-nm wavelengths did not lead to substantial changes in the position of the maximum or intensity of the band. Therefore, the observed decrease in the peak amplitude with decrease in the particle size is related, most probably, to the fact that the ratio of the surface to the volume of the particle increases, and the number of nonradiative recombination centers decreases as well.

The fact that this luminescence refers namely to the cadmium sulfide is confirmed by the excitation spectra of the samples 2CdS-pAAM (curve 1) and 3CdS-pAAM (curve 2), presented in Fig. 5 and observed at the 550 nm wavelength (in the luminescence band maximum). It is seen that these curves reproduce qualitatively the absorption spectra, correspondent to these samples.

Given the fact that in our case the Stokes shift is about one hundred nanometers and that the luminescence bands are rather broad (>50 nm), it is possible to state that the luminescence mechanism occurs with involvement of defects (Chandrasekharan and Kamat, 2002). Such defects can be, for example, unsaturated atoms of sulfur or interstitial ions of cadmium. In their works, Smyntyna et al. (2006, 2007) discussed the nature of the luminescence centers in cadmium sulfide nanocrystals in different polymer matrices. According to the authors, the nature of luminescence in the green

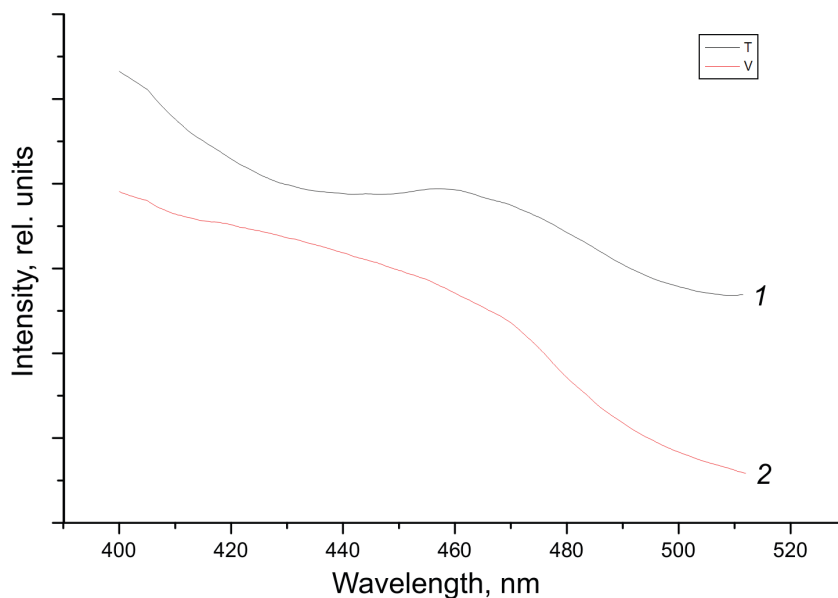


FIG. 5: The excitation spectra of the samples in DMSO at a wavelength of 550 nm: 1) 2CdS-pAAM and 2) 3CdS-pAAM

band of the spectrum is related to the presence of interstitial ions of cadmium and does not depend on the nature of the matrix.

4. CONCLUSIONS

We investigated nanocomposites that contain semiconducting CdS nanocrystals and are obtained by frontal polymerization in a polymer. The conditions that provide the formation of cadmium sulfide nanocrystals in the polymer matrix are defined.

The electron microscopy data demonstrated the structuring of composites with increase in the cadmium sulfide concentration. The average size of nanocrystals varied in the range 4.6–8.4 nm and decreased with increase in their concentration in the composite, which is in qualitative agreement with the data of X-ray phase analysis.

A shortwave shift of the optical absorption band testifies to the influence of dimensional quantization on the energy structure of nanocrystals. Luminescence of the samples represented the radiation transitions involving the defects of nanocrystals. The luminescence intensity is substantially affected by nonradiative processes involving the surface defects at the nanocrystal–matrix boundary.

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