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The influence of the type of polymer matrix on the photoluminescence from cadmium sulfide nanoparticles

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We report a study of the photoluminescence (PL) from cadmium sulfide nanoparticles formed by successive ion layered adsorption and reaction (SILAR) in samples of different polymeric matrices. The results of our investigation have shown that the character of the PL depends on the type of polymeric matrix. After thermal annealing of samples of CdS:gelatin the intensity of the PL increases. However, in samples of CdS:polybutadien(PB) the intensity after thermal annealing decreases. It is assumed that the character of the PL is mainly determined by interphase interaction between the nanoparticles and the polymeric matrix.

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1. Introduction

One of the perspective directions in the development of materials science is that of nanocomposites formed by semiconductor chalcogenide nanoparticles and a polymer matrix. It is known that the physicochemical properties of the nanoparticles depend on particle size and the shape of the structures formed from them [1-8]. The physical properties of nanostructures often depend on the method of formation and there are many methods of forming nanoparticles of chalcogenide semiconductors. Therefore selective synthetic methods [9-13] have considerable importance for the formation of nanocomposites [14-16]. The growth of thin film thickness in monomolecular layer could be controlled by these methods. The particular property of these methods is that in the growth process full thermodynamic equilibrium is not reached between the growing structure and the crystal environment [17]. This can affect the defect structure of the growing material. The growth of nanoparticles in porous media and polymers by the successive ion-layered adsorption and reaction (SILAR) method is different from the growth conditions of thin films. In the latter case it is the polymer matrix that provides the centers which can adsorb anions or cations of the growing structures. For the formation of nanoparticles in polymers and porous medium by the SILAR method the coalescence processes have particular importance. In the case when a polymer is used as a matrix for the formation of nanocomposites, we must consider the nanoparticle-polymer interaction as well as any change of conformation of polymer molecules. Such interactions can change the energy spectra of nanoparticle-polymer matrix systems and consequently affect the physicochemical properties of the system. Of course such changes must also depend on the type of polymer matrix as well as the interaction that derives from the functional group in polymer matrix. Changing the type of polymeric matrix should lead to a change in the degree of sorbed ion-polymer interaction. It can influence the type of crystal structure, the formation of defects, and also the growth form of the particles. Such changes may be connected with the thermodynamic features of growth [17]. These changes should influence physical properties of nanocomposites.

The purpose of this work is to investigate the influence of the type of polymer matrix on the photoluminescence of cadmium sulfide nanoparticles in the nanocomposite.

2. Experimental techniques

As polymer matrixes we used gelatin and polybutadien (PB). Previously we showed that sorbtion centers are present in the gelatin matrix [14] and this has allowed us to form nanoparticles of cadmium sulfide in the matrix. In contrast, the polybutadien matrix has no sorbtion centers. Therefore, before the synthesis proceeds the polybutadien matrix subject must be subjected to chemical modification [19].

For the formation of cadmium sulfide nanoparticles we used an aqueous solution of cadmium nitrate as a source of cations. As a source of anions we used an aqueous solution of Na_2S*9H_2O. The concentration of both solutions is 0.2 M. The sorption process began with solutions of cadmium nitrate. The method of formation of the nanoparticles, their, growth, optical and structural investigations have been described [14-16]. Nanoparticles of CdS in a polymeric matrix have been prepared using SILAR. After forming polymeric films [14-15] realised sorption of cations and anions in polymeric matrix. Cadmium ions are absorbed from the 0.2 M aqueous solution of $Cd(NO_3)_2$ over 120 minutes. Afterwards any remaining electrolytes are eliminated with the help of double washing in distilled water. Sulphur ions absorbed from the 0.2 M solution of Na_2S*9H_2O also for 120 minutes.

Photoluminescence spectra were measured using laboratory equipment built around an SPM-2 monochromator. As a source of radiation we used a 1 kW

xenon lamp. The emission spectra were measured at the wavelength corresponding to the maximum of excitation spectra of the samples.

3. Results and discussion

PL of CdS:gelatin: The excitation spectra and photoluminescence of cadmium sulfide nanoparticles samples in the gelatin matrix were recorded. These measurements were carried out at the temperature of liquid nitrogen T=90 K. Fig. 1 shows the excitation spectra of CdS:gelatin samples before thermal annealing.

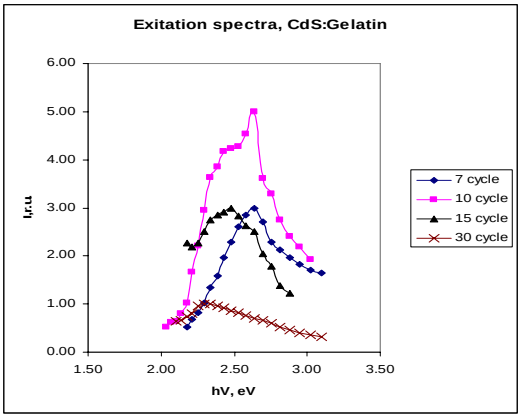

Fig. 1. Excitation spectra of CdS: gelatin before thermal annealing.

This shows that by increasing the number of cycles the maximum of the excitation spectrum shifts towards lower energy in the range (2.64-2.34) eV. In the samples with 10 growth cycles the excitation spectra show 2 maxima: 2.64 eV and 2.43 eV. Emission spectra measurement on CdS:gelatin (Fig. 2) samples do not show the emission for samples with 3 and 5 growth cycles.

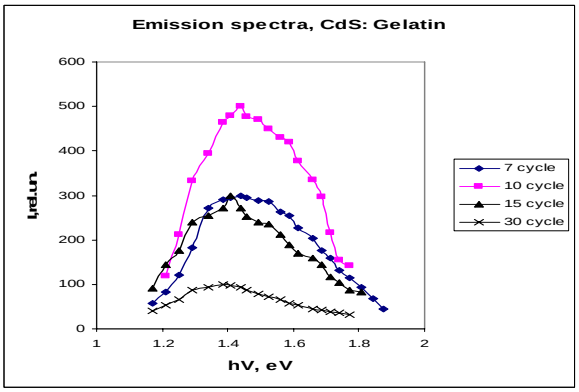

Fig. 2. Emission spectra of the nanocompo-sites CdS:gelatin before thermal annealing.

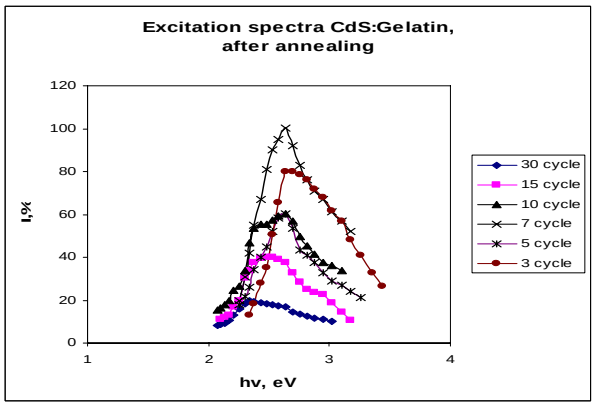

Fig. 3. Excitation spectra of CdS:gelatin after thermal annealing.

In the case of samples with 7-30 growth cycles the maxima of the emission spectra are located in the energy range (1.44-1.38) eV and decrease with increasing numbers of cycles (Fig. 2).

We also measured the excitation spectra of samples after ~12 hours of thermal annealing at 360 K (Fig. 3). The excitation spectra of these samples is shown in Fig. 3. Compared with the un-annealed samples those with 15 growth cycles show additional maxima at 2.8 eV in addition to that at 2.43 eV. In other samples little change is observed. Fig. 4 shows emission spectra of CdS:gelatin samples after thermal annealing. After thermal annealing photoluminescence intensity of samples increased by a factor 2-3. PL is observed from the samples with 3 and 5 growth cycles, from which it was previously absent.

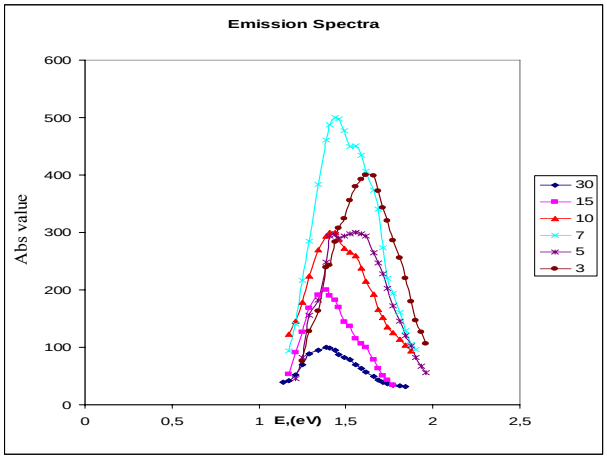

Fig. 4. Emission spectra of the nano-composites CdS:gelatin after thermal annealing.

As shown in Fig. 4 an additional peak appears in the emission spectra by increasing the number of growth cycles to 7 and this component increases with further growth. This is related to the fact that, by increasing the size of the particles the interaction between the particles

and matrix increases. As a result of this increase of interphase interaction this component of the emission will become dominant.

As is shown in Fig. 2, by increasing the number of cycles the intensity of photoluminescence increases at first. After a maximum is reached in 10 cycles (before annealing) and 7 cycles (after annealing – Fig. 4) the photoluminescence intensity decreases. This PL behavior is related to the increasing interaction between the polymer matrix and the nanoparticles by increasing particle size and interphase interaction in the initial stages of growth. This, therefore, increases the number of centres, which are responsible for PL. As a result the PL intensity increases. Further growth of the particle size changes the macromolecular conformation of the polymeric matrix; this decreases the number of centers responsible for PL. Annealing of the structures at T=360 K can change the conformation or arrangement of functional groups. This process must increase the interaction of the nanoparticles with the polymeric matrix; as a result the PL intensity increases. While in the samples with 3 and 5 growth cycles before annealing is not observed PL, then after annealing PL does appear. As shown from Fig. 3 the minimum intensity is observed in the sample with 30 growth cycles. Maximum intensity is observed in the sample with 10 growth cycles. As can be seen from the figures, the photoluminescence spectra are asymmetric. This shows that the nature of the luminescence is related to different centers. In most samples (3,5,7,10) after annealing there are 2 clearly indicated peaks. The peak half-width of all samples was nearly 0.45 eV, essentially the same as the bulk crystals. In most samples (except for the 30 cycle sample) the emission intensity is greater than intensity in bulk crystals.

PL of CdS:PB: We have investigated the photoluminescence of CdS:polybutadiene samples with different degrees of phosphochlorization: high, medium and low. Different degrees of phosphochlorization change the density of absorption centers. This can result in changing the interparticle distance between nanoparticles formed in a polymeric matrix.

We measured the excitation spectra and photoluminescence of the samples. In Fig. 5a are shown the photoluminescence spectra of samples before annealing. It can be seen from Fig. 5a by increasing the concentration of the absorbed centers the intensity of luminescence increases. The maximum of the emission spectra in all samples are situated at hν = 1.69 eV (λ = 735 nm) with half-width of the emission ΔE = 0.5 eV. The emission intensity of samples with a high level of phosphochlorization is nearly 10 times greater than in the samples with a low level of phosphochlorization.

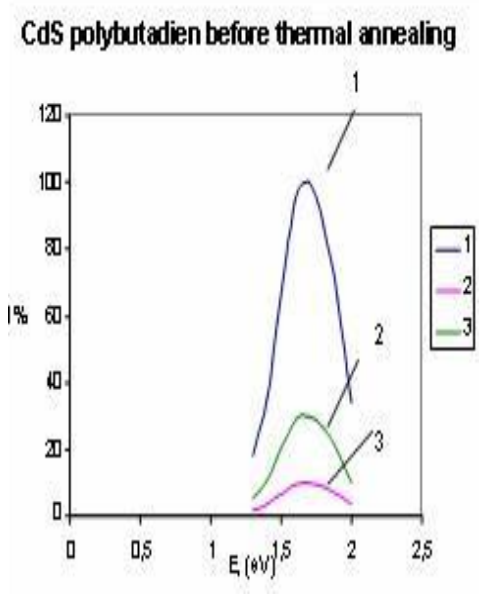

Fig. 5. PL spectra of CdS:polybutadien: a) before thermal annealing, 1- high, 2- medium, 3 – low level of phosphochlorization b) before (1) and after (2) thermal annealing.

The maxima of the excitation spectra are observed in the energy region around hν = 2.82 eV. The half-width of the excitation spectra is ΔE = 0.68 eV. Some CdS:polybutadiene samples were annealed in air at 360 K for 12 hours. The emission spectra measurement showed that, after annealing, the intensity of the photoluminescence decreased by a factor of ~4 (Fig. 5b). The maxima and half-width of the emission did not change. In Fig. 5b are shown the emission spectra of CdS:polybutadiene samples before (curve 1) and after (curve 2) thermal annealing.

As was shown above, the thermal annealing of samples does not result in a change of the maximum of the excitation (E = 2.82 eV) and emission (E = 1.69 eV) spectra. This means that the band gap of nanoparticles does not change after thermal annealing. In previous work [14] it was shown that, after thermal annealing of nanoparticles in a CdS:gelatin matrix the particle size increases as a result of coalescence processes and their band gap decreases. In contrast to the gelatin matrix CdS nanoparticles in the polybutadiene matrix are interacting strongly with the matrix. Annealing of the samples does not result in coalescence between nanoparticles. Nanocomposite samples obtained by different degrees of phosphor-chlorization have the same maximum in the excitation spectra and half-width of the emission spectra. These parameters do not change by annealing the samples. From this it follows that no coalescence process between the nanoparticles occurs.

The size distribution of the nanoparticles does not depend on the level of phosphochlorization and annealing temperature, i.e., the half-widths of the excitation and emission spectra does not change. It is probably affected by conformational changes of the polybutadiene molecules after nanoparticle formation. Conformational changes occur such that nanoparticles cannot move and the coalescence between nanoparticles does not occur. The thermal annealing of samples decreases the intensity of photoluminescence. In previous work [18] it was shown that the PL in CdS nanoclusters formed in Langmuir-Blodgett films is mainly related to the: exciton recombination and recombination via defect levels in matrix. Nevertheless, it is obvious from Figs. 2, 4, 5 that photoluminescence is not related to exciton recombination in CdS nanoparticles, PL maximum energy is well below nanoparticle optical band gap. Hence it could be related to radiative recombination either via interference defects or via defects in the matrix. After thermal annealing the change in the density of states is related to recombination via defect levels in the matrix and interphase interactions. As a result, the intensity of the PL decreases.

4. Conclusion

It was been shown, that the character of PL in nanocomposites CdS:polymer depends on type of a polymeric matrix and temperature of annealing. PL is related to the change of character of interaction nanoparticles-polymer during change of type of the polymeric matrix. Thermal annealing of samples leads to change of conformation of polymeric molecules. It also leads to change of character of interaction polymer-nanoparticles.

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