PREPARATION OF NANOCOMPOSITE CADMIUM SULFIDE IN A POLYMER MATRIX

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Abstract

A technique for formation of CdS nanocrystals in a Sevilen polymeric matrix by the cluspol method is proposed. The optimum conditions of synthesis of CdS nanocrystals are found. The crystallite sizes are estimated using the X-ray diffraction analysis. The results of studying the luminescent properties of the resultant polymer + nanodimensional CdS structures are described.

1. Introduction

At the present day, much attention is given to obtaining and studying the properties of nanodimensional objects with a view to preparing new materials on their basis whose unique properties are determined by nanoparticles available in their composition, which exhibit developed phase boundaries and excess surface energy as compared to bulk materials.

Literature data analysis shows that the main subject of research is solution-stabilized nanoparticles. These materials are easy to study; however, liquid medium restricts their practical application. Introduction of nanocrystals into an optically transparent polymeric matrix solves this problem and allows obtaining a new process material that can be used in optoelectronics.

Cadmium sulfide as a semiconductor material enjoys wide application in electronics. In particular, it is an active medium in semiconductor lasers and a material for preparation of photoelectric cells, solar cells, and photo- and light-emitting diodes. In this context, we should expect that preparation of composite materials in the form of a polymer matrix containing cadmium sulfide nanoparticles will allow obtaining process materials that will find wide application in the design of optical devices of new generation. These materials must exhibit new properties; one of them is the size effect manifestation in the optical band.

There are methods for obtaining of polymer composites containing cadmium sulfide in such polymer matrices as polystyrol, polymethyl methacrylate, polyvinyl pyrrolidone, and polyvinyl alcohol [1]. For synthesis of CdS in a polystyrol matrix, we used the $Cd(NO_3)_2 \cdot 4H_2O$ salt and preformed cadmium thiolate $Cd(SR)_2$ R = (CH_2) CH_3 as a sulfur precursor. The subsequent thermal annealing in atmosphere of nitrogen or argon led to cadmium thiolate decomposition with precipitation of cadmium sulfide. However, this synthesis of CdS is rather a complex process.

The two-stage process of obtaining of nanocomposite CdS films based on high-pressure polyethylene is described in [2]. At the first stage, the cluspol chemical synthesis method, which is based on thermal decomposition of metalorganic compounds in a polymer solution-melt [3, 4], was used to obtain a nanocomposite powdered material with predetermined ratio of nanoparticles and polymer, a modified high-pressure polyethylene of the PEVD-10803-020 grade was used in the capacity of the latter. The fairly sophisticated technology of polyethylene modification allowed obtaining powder with a highly refined structure (the density was 960 kg/m^3), which is capable of forming under a mechanical attack. The cadmium sulfide particle size ranged within 1 to 70 μm. At the second stage, the resultant powdered material was charged into a press consisting of a fluoroplastic cylinder and a plunger; then it was placed into a muffle furnace and held at a set temperature for 1 h. Despite the considerably high dispersion ability of cadmium sulfide particles, this method appears to be extremely labor-intensive due to the necessity for the process of polyethylene modification.

2. Results and discussion

In this work, we describe the attempt to simplify the method of obtaining of nanocomposite materials without decreasing the degree of dispersion of CdS particles.

The composite material was prepared using the solution-melt technique in a pressure gun equipped with a furnace allowing heating a reaction mixture in the pressure gun body in the temperature range from 20 to 300°C. The maximum pressure of the press plunger is 100 atm. Precursor components for the synthesis were Sevilen (ethylene vinyl acetate copolymer), cadmium acetate, and thiourea pre-dried at a temperature of 80°C. The polymer content in the mixture was 82%. The ratio of cadmium acetate and thiourea was 2:1. The actual composition of the parent mixture is shown in the table 1.

Table 1. Composition and quantitative relationship of the parent mixture.

Reagent name	**Quantity, g**
Ethylene vinyl acetate copolymer	100
Cadmium acetate $Cd(CH_3COO)_2 \cdot 2H_2O$	12
Thiourea SCN_2H_4	6

All the components of the mixture were mixed thoroughly and charged into the pressure gun body; after that, heating was carried out. At a mixture temperature of 100°C, a pressure of 50 atm was set; it remained unchanged until the synthesis was completed. (At temperatures close to 100°C, the polymer and thiourea start melting, and the exchange reaction between cadmium acetate and thiourea takes place). The melt was heated up to the temperature T_{max} = 180°C and held during 10 min, which led to the onset of the formation of cadmium sulfide that embedded into the polymer network. For the CdS formation process to be entirely completed, the melt was held in the same conditions for 20 min more. After that, the resultant solution-melt was charged into press molds and air-cooled to room temperature. The synthesized samples were of a brilliant orange color characteristic of CdS.

This technique allows obtaining composite materials in the form of bulk samples of various shapes (plates, bars, fibers, etc.) and in the form of films.

The resultant material was studied by the X-ray diffraction method using a DRON-3 diffractometer (Fig. 1). The diffraction peaks for 2Θ = 31°, 32.5°, 51°, and 61° were observed, which corresponds to the cubic phase of CdS nanoparticles [3-6]. The size *d* of the CdS particles was determined by the width of the most intense peak by the formula [5]

$$d = k \cdot \lambda / (\beta \cdot \cos\Theta),$$

where k is the constant [5]; λ is the X-ray radiation wavelength equal to 1.7889 Å; β is the full width half maximum (FWHM); and Θ is the diffraction angle.

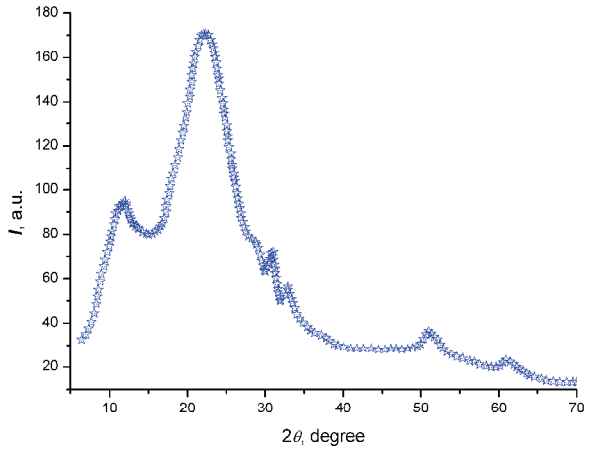


Fig. 1. X-ray diffraction spectrum of CdS nanoparticles in a Sevilen polymer matrix.

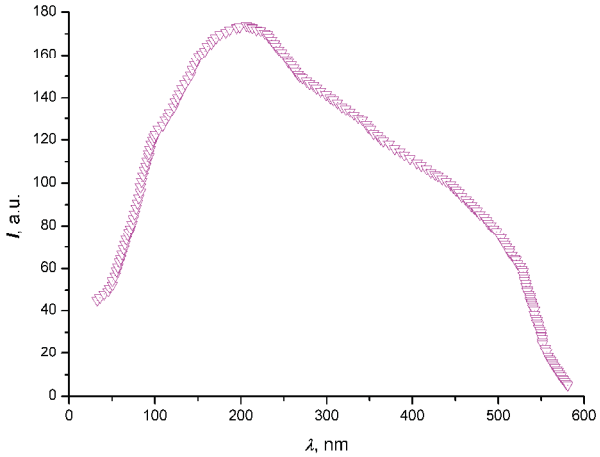


Fig. 2. Photoluminescence spectrum of CdS nanoparticles in a Sevilen polymer matrix measured at a temperature of 300 K.

The particle size calculated by X-ray diffraction line width is 5-10 nm.

The photoluminescence spectrum of the resultant nanocomposite material (Fig. 2) measured at 300 K is a band with a half-width of 90 nm with the peak intensity lying in a range of 520-530 nm. It corresponds to the edge green emission of macroscopic CdS crystals [7].

3. Conclusions

Thus, this technique allows obtaining polymer composites with fillers in the form of ultrafine particles of A_2B_6 semiconductors with sizes on the order of 10 nm, which are promising as photosensitive and electroluminescent materials that exhibit properties of both a polymer and a semiconductor. In particular, this technique will allow solving the problem of obtaining thin-film and monolithic composite materials, using which it will be possible to prepare a number of new devices for recording and processing information in the X-ray and optical bands as well as sensing equipment for environmental monitoring.

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