

THE EFFECT OF ELECTRIC DISCHARGE TREATMENT ON THE OPTICAL PROPERTIES OF HYBRID PP/PbS/CdS NANOCOMPOSITES

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In given paper, were studied UV spectra of nanocomposites obtained on base of PP+PbS, PP+CdS, PP+PbS/CdS and showed that UV absorption spectra blue shifted when the dimensions of semiconductor nanoparticles decrease. In this work measured optical band gap for PP/PbS, PP/CdS, PP/PbS/CdS nanocomposites based on PP powder which was treated by electrical discharge during 0.5 hour. SEM analysis of PP + PbS, PP + CdS, PP + PbS /CdS nanocomposites was carried out and it was shown that particle size in nanocomposites was the range of 13-18nm, 16-26nm and 9-12 nm in respectively. It has been established that the luminescence of PP + PbS / CdS hybrid nanocomposite has a spectrum of superposition of PbS and CdS spectra, and also has different maximum than the luminescence spectrum of individual nanoparticles. This type of spectrum in mixed systems is associated with the activation of luminescent centers of individual nanoparticles, and also leads to the absorption of luminescence at other wavelengths. Simultaneous decreasing of the particle size also leads to an increase in the band gap, which ultimately results in the slope of the wavelength of the maximum of the luminescence spectrum.

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1. Introduction

In recent years, the study of the optical properties of nanomaterials have been drawing special attention. Due to the quantum-confinement effects, the use of nanomaterials based on the unique optical properties of nanoparticles is enormous. Among such materials, a special place is occupied by hybrid semiconductor nanocomposites based on polymers. Recent research has shown that polymeric nanocomposite materials based on metal chalcogenides have wide application possibilities in terms of electrical and optical properties of electronics, solar cells, converters, etc. It is known that bulk crystalline PbS is a narrow-gap (0,44 eV, 300 K) semiconductor, especially have applications in the IR region. CdS is broad band (2,42eV, 300K) semiconductor, with a wide range of applications in solar cells. Because the properties of semiconductor nanoparticles can be varied by the influence of many factors, nanomaterials obtained based of them can be used in devices (sensors, solar cells, detectors, etc.) with a wide range of applications. In the presented article, have been investigated the optical properties of PP / PbS / CdS hybrid nanocomposites obtained on a based polypropylene powder (PP). It was found that the PP / PbS / CdS hybrid nanocomposites have luminescence in a wide spectral range. At the same time, it is known that the formation of nanoparticles in a polymer can be controlled by exposing the polymer matrix to various effects (electrical discharge treatment, gamma radiation, etc.). In this paper, the optical properties of PP / PbS / CdS nanocomposites prepared on a polypropylene powder subjected to an electric discharge treatment for 0.5 hours are considered.

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2. Experimental part

2.1 Materials

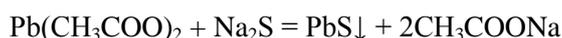
The isotactic polypropylene (PP brand Sigma Aldrich P code 1001326963) has a density of 0,9 g/ml at 25°C, refractive index- n_{20/D} 1.49, transition temp - T_g -26 ° C, mol.wt-average Mw ~ 250000 by GPC, autoignition temp -> 674 ° F, mp - 189°C, toluene, lead acetate Pb(CH₃COO)₂, cadmium chloride (CdCl₂·x2,5H₂O), Na₂S·x9H₂O, (1-hexadecyl)trimethylammonium bromide (C₁₉H₄₂BrN ,98%) have been purchased from Sigma Aldrich.

2.2 Characterization

The images of the samples have been obtained by a scanning electron microscopy (SEM, Jeol JSM-7600 F). Scanning was performed in SEI mode at an accelerating voltage of 15 kV and a working distance of 4.5 mm, 14.7mm and 15.1 mm. Energy dispersive micro-X-ray analysis was performed using the device X-Max 50 (Oxford Instruments), fitted in the used SEM. The UV spectra have been recorded on Spectrophotometer Specord 250 Plus. UV spectra were recorded at 200-1000 nm and ambient temperature. Photoluminescent properties of nanocomposite films were examined using a spectrofluorometer Varian Cary Eclipse at wavelength range 200-900 nm.

2.3 Synthesis of nanocomposites

Synthesis of nanocomposite materials was carried out as follows: Initially, the polypropylene powder was treated by electric discharge during 0.5 hour. The synthesis of PbS and CdS nanoparticles was carried out as follows: 20 ml, 0.01 M solution of lead acetate mixed with a 0.5% solution of CTAB was stirred for 30 minutes in a magnetic mixer and 20 ml, 0.01 M of sodium sulfide solution is added and stirred vigorously in a magnetic stirrer for 2 hours. Therefore, synthesized PbS nanoparticles are washed in a centrifuge several times with distilled water and dried. By the same procedure, for the synthesis of CdS nanoparticles 20 ml, 0.01 M cadmium chloride solution mixed with 0.5% CTAB solution for 30 min and then mixed with 20 ml, 0.01 M sodium sulfide solution for 2 hours intensively in a magnetic mixer. The resulting CdS nanoparticles are centrifuges in several times with distilled water and dried. The synthesis was carried out in accordance with the following reactions:



0.1g of polypropylene powder (PP) which was treated by electric discharge during 0.5 hours was solved in toluene solution for in to synthesize nanocomposites. For the synthesis of PP / PbS and PP / CdS nanocomposites polypropylene solved in a toluene solution and was added of 3% PbS and 3% CdS nanoparticles in to magnetic stirrer and mixed during for 2 hours. After obtain homogeneous system mixture transferred to petri dish and dried during the day. The hybrid nanocomposite PP / PbS / CdS is synthesized as follows: 0,1g polipropilen powder (PP) treated by an electrical discharge during 0,5 hours was solved in toluene and added 3% PbS nanoparticles and stirred in a magnetic stirrer for an hour. In the next step, 3% CdS nanoparticles are added to the mixture and mixed in a magnetic mixer for 2 hours After obtain homogeneous system mixture transferred to petri dish and dried during the day.

3. Results and discussion

Fig. 1 shows the UV spectra of polymer nanocomposites PP/PbS, PP/CdS and PP + PbS/CdS. It is known that a decrease of the semiconductor nanoparticles size leads to a shift in the edge of the UV spectrum to the blue part of the spectrum. It is seen from Figure 1 (a) that for the nanocomposite PP/PbS, the absorption edge shifts to the blue part of the spectrum. From the UV

spectra by extrapolation, the optical band gap was calculated for polymer nanocomposites. Optical band gap of nanocomposites was determined by using following equation

$$\alpha = A(h\nu - E_g)^n / h\nu$$

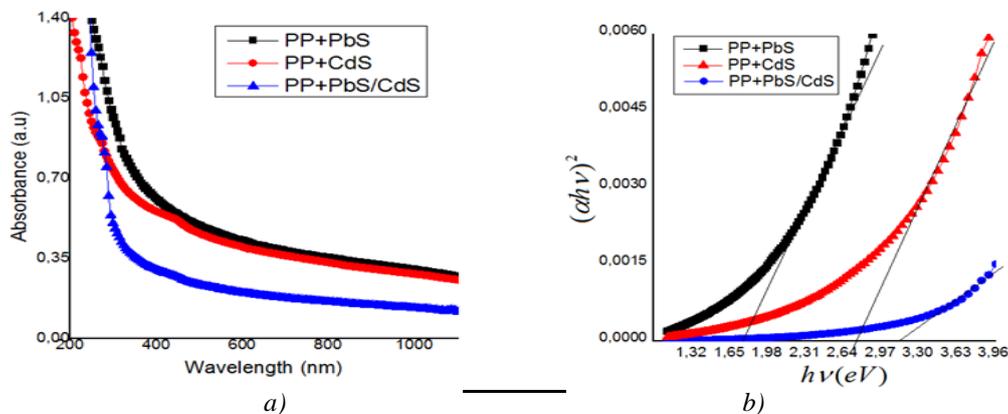


Fig. 1. UV absorptions spectra (a) and band gap calculation (b) for PP/PbS ,PP/CdS and PP+PbS/CdS nanocomposites

As can be seen from the graphs, the optical band gap for PP + PbS, PP + CdS, PP + PbS / CdS nanocomposites based on PP powder was treated by electrical discharge 0.5 hours is changed as follows:

Table 1. Optical band gap for PP + PbS, PP + CdS, PP + PbS / CdS nanocomposites

Sample	Optical band gap (eV)
PP+PbS	1,65
PP+CdS	2,6
PP+PbS/CdS	3,0

The morphology of nanocomposites and the distribution of nanoparticles in a polymer matrix were also studied by means of scanning electron microscopy. Figure 2 shows SEM images of nanocomposites PP + PbS (a), PP + CdS (b), PP + PbS / CdS (c) obtained on PP powder subjected to electric discharge treatment during 0.5 hours. SEM images of nanocomposites PP+PbS,PP+CdS,PP+PbS/CdS in the figure 2 show average sizes of nanoparticles in the polypropylene matrix in the range of 13-18nm,16-26nm and 9-12 nm in respectively.

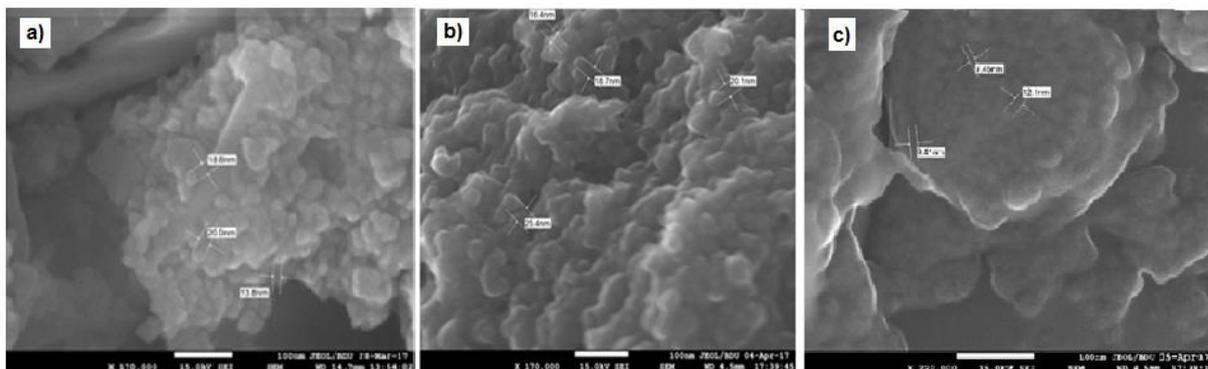


Fig. 2. SEM images of PP/PbS(a) ,PP/CdS (b) and PP+PbS/CdS (c) nanocomposites.

Fig. 3 reports the EDS spectrum of nanocomposites PP+PbS(a), PP+CdS(b), PP+PbS/CdS(c) based on PP powder which was treated by electric discharge during 0.5 hours. Fig. 3 shows that nanoparticles PbS, CdS and PbS / CdS in nanocomposites PP + PbS, PP + CdS and PP + PbS / CdS have been obtained cleanly.

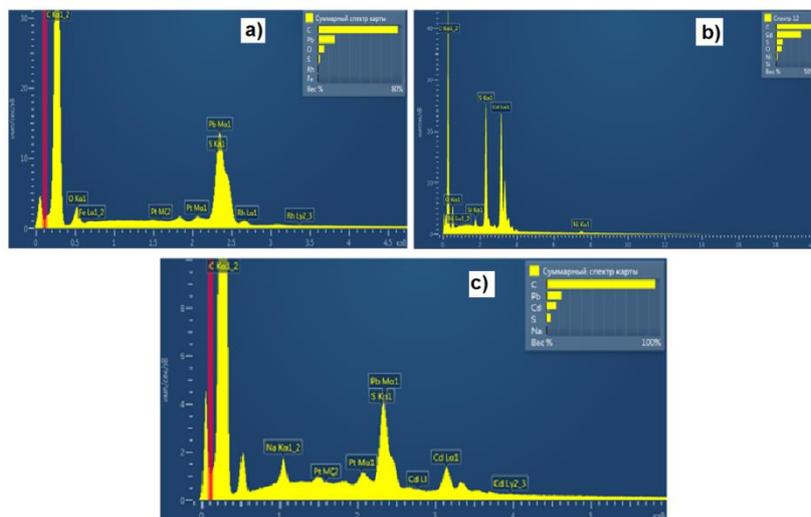


Fig. 3. EDS spectra of PP/PbS(a), PP/CdS (b) and PP+PbS/CdS (c) nanocomposite

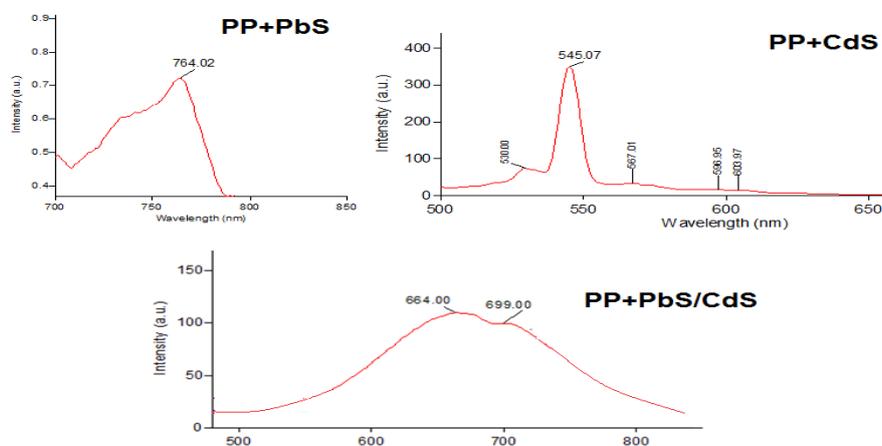


Fig. 4. Photoluminescence spectrum of PP/PbS, PP/CdS and PP+PbS/CdS Nanocomposites

Fig. 4 shows the luminescent spectra of the nanocomposites PP/PbS, PP/CdS and PP+PbS/CdS. As can be seen from the figure, for PP/PbS nanocomposite peaks are observed at wavelengths of 745 nm and 764 nm. It is known that bulk crystalline PbS is a narrow-gap semiconductor. The luminescence region for PP/PbS nanocomposite falls into the infrared region of the spectrum. The PP + CdS nanocomposites, as seen from the graph, give the luminescence of wavelengths 530 nm, 545 nm and 567 nm. The energy of the photon at the $\lambda = 534$ nm for PP + CdS nanocomposites is 2.4 eV, and $\lambda = 545$ nm wavelength is 2.2 eV. Figure 4 shows that the maximum intensity at $\lambda = 545$ nm wavelength is greater than the 534 nm and 567 nm wavelength. At the same time Fig. 4 shows that the luminescence spectrum of hybrid nanocomposites based on PP + PbS / CdS is in the wide wavelength range. Figure shows that luminescence of PP + PbS / CdS hybrid nanocomposites have a spectrum of superposition of PbS and CdS nanoparticles and at the

same time have different maxima than the luminescence spectrum of individual nanoparticles. This kind of spectrum is associated with the activation of separate nanoparticles luminescence centers in mixed systems, causing of absorption luminescence in other wavelengths. Simultaneous decreasing of the particles size also leads to the increase of the band gap, which ultimately leads to the sliding of the wavelength of the maximum of the luminescence spectrum.

4. Conclusions

In the given article, UV spectra of nanocomposites obtained on PP + PbS, PP + CdS, and PP + PbS / CdS have been studied and it has been shown that the blue shifted occurs in UV absorbance spectra when the dimensions of semiconductor nanoparticles are decreased. In this work the optical band gap calculated for PP + PbS, PP + CdS, PP + PbS / CdS nanocomposites which obtained based on PP powder which was treated by electrical discharge during 0.5 hours. SEM images of nanocomposites PP+PbS,PP+CdS,PP+PbS/CdS show average sizes of nanoparticles in the polypropylene matrix is in the range of 13-18nm,16-26nm and 9-12 nm in respectively. It is found that luminescence of PP + PbS / CdS hybrid nanocomposites have a spectrum of superposition of PbS and CdS nanoparticles and at the same time have different maximum than the luminescence spectrum of individual nanoparticles. This kind of spectrum is associated with the activation of separate nanoparticles luminescence centers in mixed systems, causing of absorption luminescence in other wavelengths. The decreasing of the particles size also leads to the increase of the band gap, which ultimately leads to the sliding of the wavelength of the maximum of the luminescence spectrum.

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