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Synthesis Structure and Optical Properties of PP+PbS/CdS Hybrid Nanocomposites

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In this paper, we report the synthesis of hybrid polymer nanocomposites PP+PbS/CdS, characterization of their structure and study of their optical properties. The structure and distribution of nanoparticles in the polymer were studied by means ofthe Scanning electron microscopy (SEM). It was found that the average nanoparticle size for a hybrid nanocomposite PP+PbS/CdS is 9-12 nm. Optical and photoluminescent properties of nanocomposites were also studied. From UV spectra of nanocomposites by extrapolation method the width of the forbidden band for polymer nanocompositeswas determined. The band gap was equal to 1.65 eV for PP/PbS nanocomposites, to 2,6 eV for PP/CdS and to 3.0 eV for PP+PbS/CdS nanocomposites. Photoluminescence analysis of nanocomposites PP+PbS/CdS shows two luminescent peaks at the wavelengths of 680 nm and 715 nm of the luminescence spectrum. Therefore, for such systems, it was proved that the spectral region is expanded and it makes possible to apply such nanocomposites in various fields of science and technology.

1. Introduction

The size dependent properties of semiconductor/polymer nanocomposites make these materials very attractive in terms of their possible application in various fields of technic such as optical switching, single electron transistors, solar cells, nonlinear optics, optoelectronic device and heterogeneous photo catalysis. There are a lot of methods that have been developed to produce nanoparticles/polymer composites. Among them we can mention the mechanical blend of separately prepared polymers and inorganic nanoparticles, leading to the desired polymer nanocomposites. Another approach is based on the reduction or coordination of the generating nanoparticles precursors, in the presence of polymer matrix in-situ, and ex-situ, when the nanoparticles are previously synthesized and then are introduced within the polymer matrix (Z.I.Ali et.al, 2015) .The high surface-to-volume ratio of semiconductors nanoparticles in comparison with their bulk analogues differentiates their properties and emphasizes the use of their optical and optoelectronic properties that mainly depend on their size and shape. The CdS is a semiconductor that is able to absorb the light from the visible region of spectra. Due to its wide band gap, the CdS are applicable for hetero-junction solar cells (Singh V et.al, 2010). The energy of forbidden band and high optical absorption makeCdS a very attractive material in terms of its application in different fields of optoelectronic, photovoltaic, catalysis, biological sensing catalysis, and thin film solar cells (Thambidurai M et.al, 2011). Lead sulphide is widely used for infrared technique as well as for micro-and optoelectronics. The electrical properties of the lead sulphide significantly change upon transition from bulk crystalline to nanocrystalline state as well as other semiconductors. This fact promises new opportunities for the use of its optical features in the visible and infrared regions. As a narrow band semiconductor the lead sulphide is widely used to obtain temperature sensitive transducers, detectors operating in the infrared region (850-3100nm) of spectrum, photo-resistors and selective sensors. Properties of lead sulphide significantly change with the decrease of the particles sizes down to the nanometer range (A.M.Maharramov et.al, 2016).Therefore the production process ofpolymer nanocomposite materials including very small nanoparticles of lead sulphide and cadmium sulphide is of great scientific and practical interest.

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This work deals with the stabilization ofPbS and CdS nanoparticles in a thermoplastic polymeric matrix such as isotactic polypropylene. In particular, a new synthesis of hybrid polymer nanocomposites, based onPP+PbS/CdS, was developed, the optimal conditions of formation of PbS and CdS nanoparticles in the polymermatrix were determined and structure and optical properties of the produced hybrid polymer nanocomposites were investigated. The main purpose of the present work was to obtain polymeric luminescent films of the PP+PbS/CdS nanocomposites with wide spectral diapason.

2. Experimental procedure

2.1 Materials

All chemicals were used as received. Isotactic polypropylene (PP grade Moplen HF500N, homopolymer); density 0,92g/cm3 at 25 °C, Mw = 250000, Mn = 67000, Melt Mass-Flow Rate- MFR = 11,5g /10 min (2300 C, 2,16 kg), melting T=162 °C). Lead acetate $Pb(CH_3COO)_2$,cadmium chloride ($CdCl_2x2,5H_2O$), sodium sulfide (Na_2Sx9H_2O) have been purchased from Sigma Aldrich; deionized water.

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 LEI mode at an accelerating voltage of 15 kV and a working distance of 4.5mm,14,7mm and 15.1 mm. Energy dispersive micro-X-ray analysis was performed using the device X-Max 50 (Oxford Instruments). The UV spectra have been recorded on Spectrophotometer Specord 250 Plus. UV spectra were recorded at 200-700 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 hybrid semiconductor nanocomposite materials PP+PbS/CdS was carried out by the sorption method. The synthesis was carried out as follows:
In order to obtain PbS and CdS nanoparticles in a polymeric matrix, sorption of transition metal ions Pb2+ and Cd2+ into isotactic polypropylene powders was firstly carried out. The production of hybrid nanocomposites PP+PbS/CdS occurs in subsequent stages: firstly thesynthesis of the nanocomposites PP/PbSand PP/CdS, respectively, andthen the mixing of the two previously produced nanocomposites.
The preparation of PP/PbS nanocomposites was carried out as follows. 0.1 g of isotactic polypropylene powder was first treated with 20 ml 0.01M $Pb(AsO)_2$ solution and mixed intensively at room temperature for 30 minutes. Then the solution of the polypropylene powder in the lead acetate solution was transferred to a Petri dish and left for a day for deeper sorption of Pb2+ ions. After 24 hours, the powders were filtered and washed with distilled water several times to remove loosely bound Pb^{2+} ions. The powder was then dried in the air for 24 hours. Afterwards, the dried polypropylene powder containing Pb^{2+} ions was treated with 20 ml 0.01M Na_2S solution and vigorously mixed for 30 min. Similarly, the powder was left for 24 hours for complete sorption of S^{2-} ions. The powder was then rinsed with distilled water and dried overnight. As a result, a PbS nanophase was formed in the pores of the isotactic polypropylene powder. By varying the concentration of solutions of $Pb(AsO)_2$ and Na_2S, it was possible to obtain nanoparticles with sufficiently uniform distribution in the polymer matrix (A.M. Maharramov et al, 2014, 2016).
In a similar way, nanocomposites based on PP/CdS were synthesized. 0.1 g of polypropylene was gradually treated with solutions of 20 ml 0.01M $CdCl_2\times 2.5H_2O$ and 20 ml 0.01M Na_2S.
Formation of nanophases PbS andCdS in the pores of isotactic polypropylene occurs according to the following reactions:

$$Pb(CH_3COO)_2 + Na_2S = PbS\downarrow + 2CH_3COONa$$
$$CdCl_2 + Na_2S = CdS\downarrow + 2NaCl$$

To synthesize hybrid nanocomposites based on PP+PbS/CdS, the polymer nanopowders PP/PbS and PP/CdSat a weight ratio equal to 1 were mechanically mixed. Nanocomposite films based on PP+PbS/CdS were obtained by hot pressing at the melting temperature of polypropylene and at a pressure of 15 MPa. The films were cooled in water at a cooling rate of 200 deg/min.

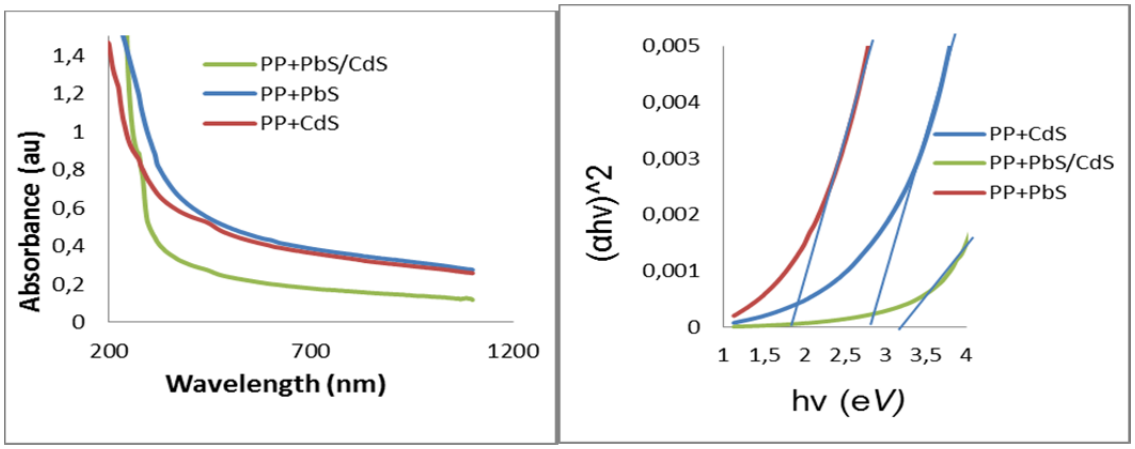
3. Results and discussion

Figure 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 (T.Serrano, et.al, 2014).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 width of the forbidden band was calculated for polymer nanocomposites.Optical band gap of nanocomposites was determined by using following equation Eq(1):

$$\alpha = A(h\nu - E_g)^{1/2}/h\nu (1)$$

where A is a constant and n=1/2 for allowed direct transition.The variation of optical absorption coefficient with wavelength was also analysed in order to find out the nature of the electronic transition across the optical band gap. Figure 1 (b) reports the plot of (αhv)2 versus the energy for the nanocomposite samples. By extrapolating the linear portion near the onset of absorption edge to the energy axis the band gap energy of nanocomposite samples can be optioned (YasharAzizian, et al,2007).It was found that the band gap is 1.65 eV for PP/PbS nanocomposites, 2.6 eV for PP/CdS and 3.0 eV for PP+PbS/CdS nanocomposite.



(a) (b)

Figure1. UV absorbtions spectra (a) and band gap calculation (b) for PP/PbS ,PP/CdS and PP+PbS/CdS nanocomposites.

The morphology of nanocomposites and the distribution of nanoparticles in a polymer matrix were also studied by means of scanning electron microscopy (SEM). SEM images of nanocomposites PP/PbS in Figure 2 show average size of nanoparticlesPbS in the polypropylene matrix in the range 13-18 nm. Figure 3.reports the EDS spectrum of nanocomposite PP/PbS. From the EDS spectrum it can be seen that the composite containsPb and S as the main elements.

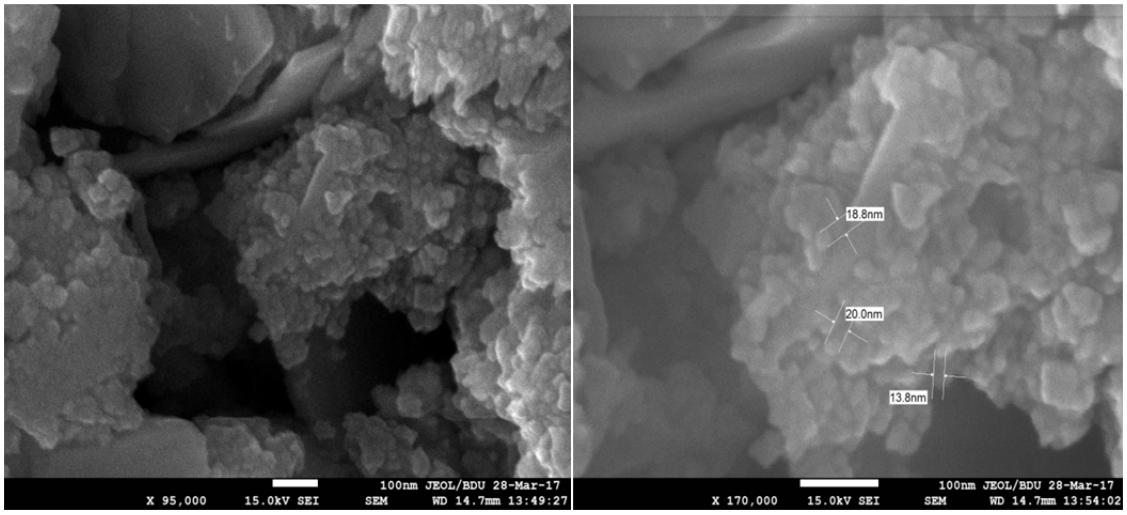


Figure 2.SEM images of PP/PbS nanocomposite

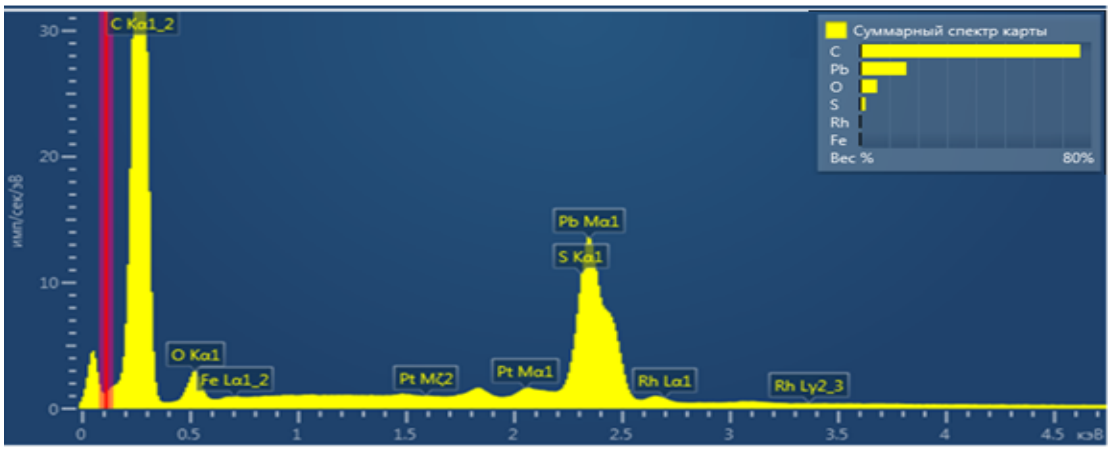


Figure 3. EDS spectra of PP/PbS nanocomposite

Figure 4 shows SEM images of nanocomposites PP/CdS. CdSnanoparticles in the polypropylene matrix in the range size 16-26 nm can be noticed. Figure 5 shows the EDS spectrum of nanocomposite PP/CdS. From the EDS spectrum it can be seen that the composite contain Cd and S as the main inorganic elements, the week signal of Ni is coming from substrate.

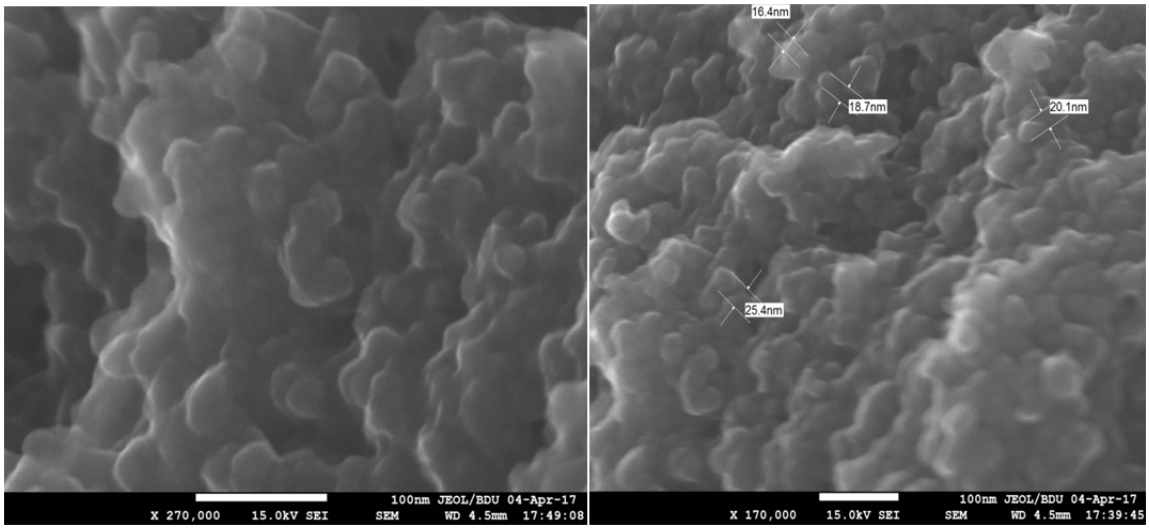


Figure 4. SEM images of PP/CdS nanocomposites

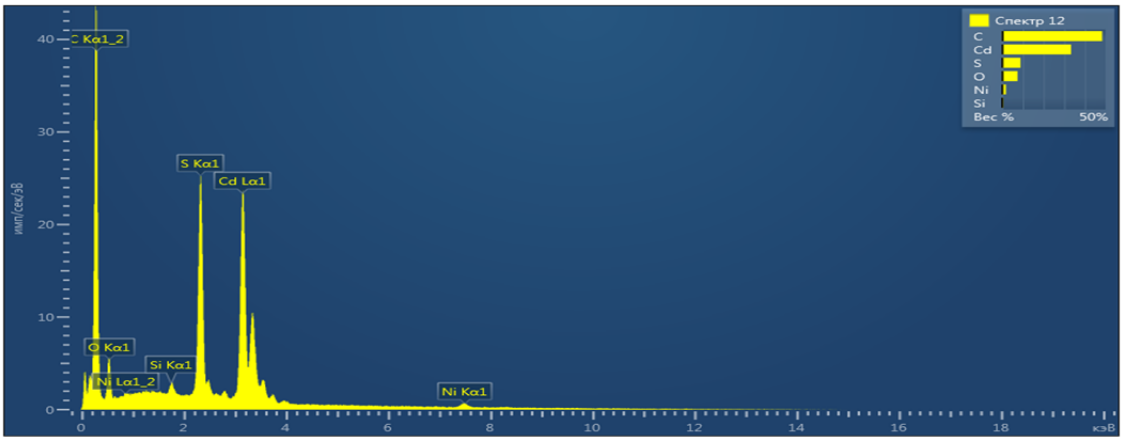


Figure 5. EDS spectra of PP/CdS nanocomposite

The Figures 6 and 7 report the SEM and EDS spectra of hybrid nanocomposite PP+PbS/CdS, respectively. As it can be seen from the figure 6 the average size of nanoparticles is in the raneg 9-12 nm. The EDS spectra shows that the main elements of hybrid nanocomposite, apart carbon, are Pb, Cd and S, thus the nanocomposites consists of CdS and PbS nanophases.

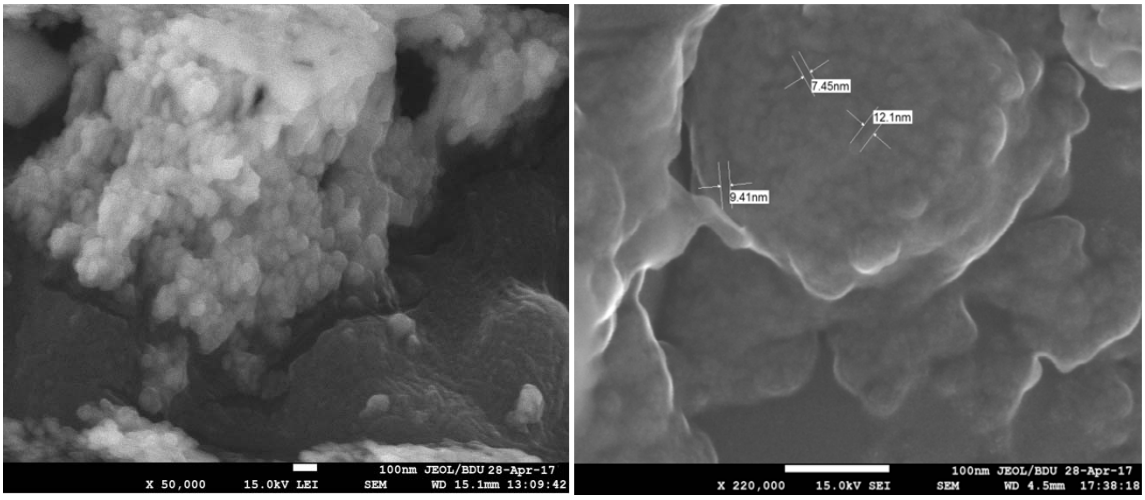


Figure 6. SEM images of PP+PbS/CdS nanocomposites.

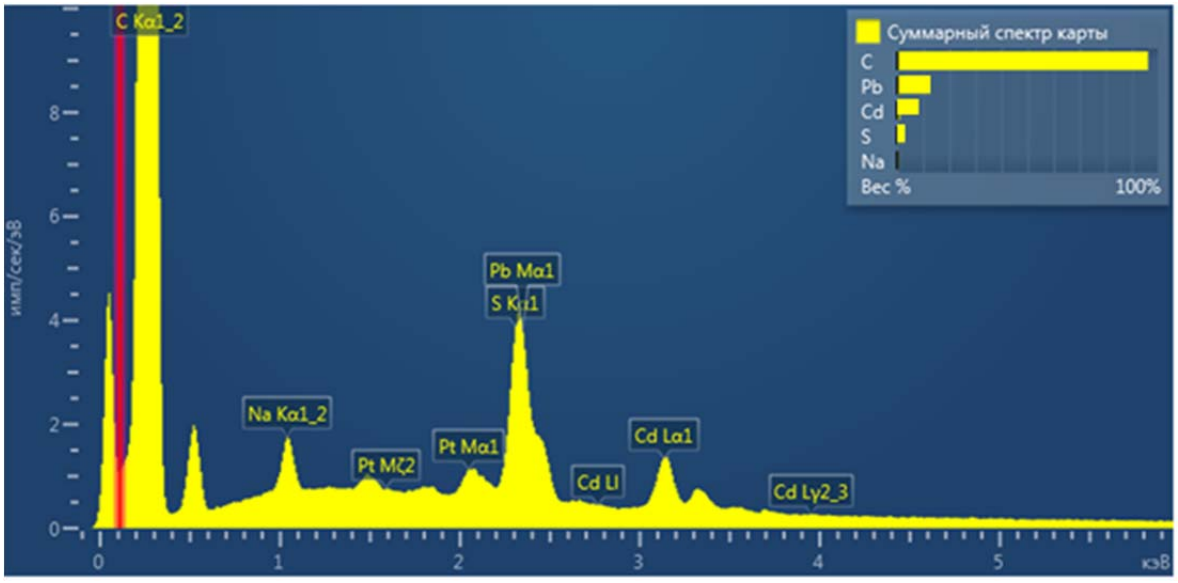


Figure 7. EDS spectra ofPP+PbS/CdS nanocomposite

Finally, the photoluminescence properties of the obtained polymer nanocomposites were studied. Figure 8 shows the luminescent spectra of the nanocomposites PP/CdS and PP+PbS/CdS. The photoluminescence spectrum of PP/CdS nanocomposites was measured in the wavelength range 300-700 nm with excitation at 342 nm wavelength. The photoluminescence spectra of PP+PbS/CdS nanocomposites were studied in the wavelength range 300-900 nm with excitation at 330 nm wavelength. As can be seen from Fig. 8 (a), peaks at 511 nm and 560 nm wavelengths belong to CdS nanoparticles. From the literature data it is known that the luminescence region for PbS nanoparticles falls into the infrared region of the spectrum (LudmilaBakueva, et.al, 2004). Figure 8 (b) shows the luminescence spectrum of a hybrid nanocomposite based on PP+PbS/CdS. As can be seen from the figure, luminescent peaks are observed at wavelengths of 680 nm and 715 nm. From the luminescence spectrum of the hybrid nanocomposite PP+PbS/CdS, it can be seen that the spectral-sensitive region broadens.

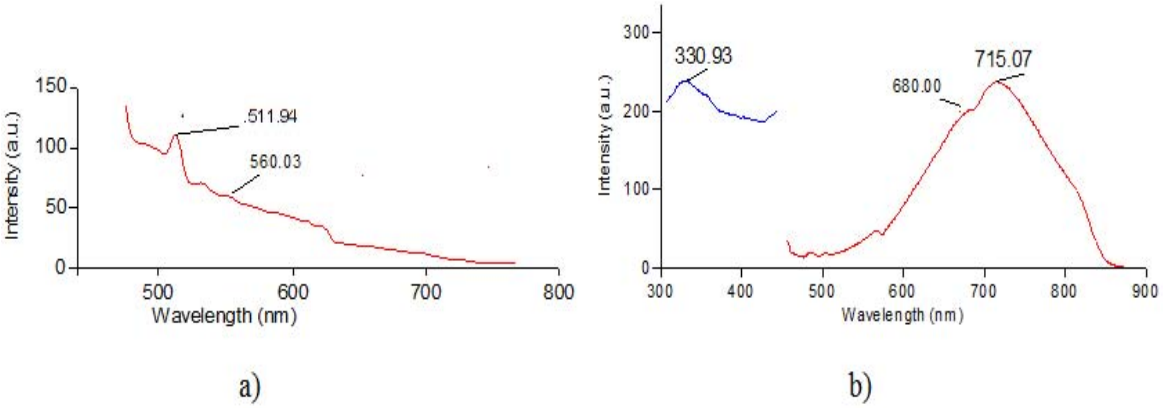


Figure 8. Photoluminescence spectrum of PP/CdS (a) and PP+PbS/CdS (b) nanocomposites

4. Conclusions

In this paper, we have reporteda study on the synthesis of hybrid polymer nanocomposites PP+PbS/CdS, their structure characterization and their optical properties. The structure and the size distribution of nanoparticles in the polymer matrix were studied by using SEM analyses. It was found that the average nanoparticle size of the hybrid nanocomposite PP+PbS/CdS is in the range 9-12 nm. Optical and photoluminescence properties of nanocomposites were also studied. From UV spectra of nanocomposites by extrapolation method was calculated the width of the forbidden band of polymer nanocomposites. It was found that for PP/PbS nanocomposites, the band gap is 1.65 eV, for PP/CdS 2.6 eV, whereas for PP+PbS/CdS nanocomposite is 3.0 eV. Photoluminescence analysis of nanocomposites PP+PbS/CdS shows 2 luminescent peaks at the wavelength of 680 nm and 715 nm, respectively, ofthe luminescence spectra. Therefore, for such systems, the spectral sensitive region is broadenand it allows to use such nanocomposites for creation of luminescent screens.

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