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STRUCTURE AND PHOTOLUMINESCENCE PROPERTIES OF HYBRID NANOCOMPOSITES ON THE BASE OF POLYVINYLIDENE FLUORIDE (PVDF) AND PbS/CdS NANOPARTICLES

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Abstract. Hybrid nanocomposites based on polyvinylidene fluoride (PVDF) and PbS/CdS nanoparticles with a wide spectral region of luminosity were synthesized by teams using the co-precipitation method. The optical properties of the obtained nanocomposite films were investigated by absorption and photoluminescence spectroscopies. The optical band gap, which is calculated on the basis of the UV absorption spectra, shows that with increasing concentration, the band gap is decreasing. The structure of PVDF/PbS/CdS nanocomposite films was characterized using X-ray diffractometry. The particle size in PVDF+3%PbS/CdS, PVDF+5%PbS/CdS, and PVDF+10%PbS/CdS nanocomposites was 48-83 nm, 73-88 nm, and 79-90 nm, respectively, according to SEM analysis. It was determined that hybrid nanocomposites on the basis of PVDF+PbS/CdS with an increasing concentration of semiconductor nanoparticles, the optical band gap is starting to decrease. It was found that hybrid nanocomposite films synthesized based on PVDF+PbS/CdS have luminescence in a wide spectral region. This type of nanocomposites can be used in a variety of sensor techniques that operate over a broad spectral range.

Keywords: *polymer, polivinildenfluoride, PbS, CdS, photoluminissence, hybrid nanocomposite, nanoparticle.*

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1. Introduction

This paper discusses semiconductor nanoparticle-polymer composites. Within the last decade, polymer-inorganic nanocomposites became one of the emerging classes of advanced materials. Composites consisting of an insulating polymer matrix filled with nanosized particles are of interest for their stability and also for unique properties due to interactions that will happen between the matrix and nanoparticles. Semiconductor nanomaterials and nanocomposites possess interesting photoluminescence emission and nonlinear optical properties due to the quantum confinement effect. Nanocomposite materials obtained with the addition of nanoparticles can further improve the properties of the polymer by increasing it. Synthesis, characterization and measurement of optical properties of nanocomposites with different fillers have also drawn significant attention. Recently, a lot of research focus has been given on the preparation of polymer-based semiconductor nanocomposite materials that have potential applications in different optoelectronic and photonic devices. The incorporation of nanoparticles in polymer matrices offers the possibility of improvements to the optical, mechanical, and chemical properties of the materials. Since they can influence strongly the physical properties of the host polymeric matrices but also give new characteristics and properties to the material, like light emission. Polymer based nanocomposites presents some advantages

compared to the intrinsically photoluminescent polymer. The potential use of photoluminescent polymers is, in fact, ultimately limited by their low quantum efficiency as well as by their poor stability due to oxygen interaction. The typical representative of polymeric materials is poly (vinylidene fluoride), PVDF, which has interesting scientific and technological properties (Lovinger, 1982).The most recent research presents the major classes of photoluminescent nanofillers dispersed in polymeric matrices, as well as the most important applications of photoluminescent polymer nanocomposites. PVDF has good physical and electrical properties of a kind for many applications (Zhao *et al*., 2013). PVDF has various favorable advantages, including excellent dielectric properties, high mechanical strength, flexibility, and thermal and chemical stability (Chen *et al*., 2007). Generally, some reports demonstrate the crystalline structures of PVDF and show a minimum of five possible kinds of the crystal phase, namely, α, β, γ, ε and δ phases (Liu *et al*., 2013). Other than the most well-known, the -phase is a more attractive crystal type in PVDF, which is described by an all-trans planar zigzag conformation with all the fluorine atoms situated on the same side of the polymer chains (Nalwa, 1991). At the same time, nanocomposite materials obtained with the addition of nanoparticles can further improve the properties of the polymer by increasing its stiffness. Recently, in scientific journals, many publications have been published on the acquisition, research, and application of two-phase and multiphase polymer nanocomposite structures. PbS and CdS were used as nanoparticles in the article. Cadmium sulphide (CdS) is one such semiconductor which absorbs in the visible region of the electromagnetic spectrum. It is known that bulk crystalline PbS is a narrow-gap (0.44 eV, 300 K) semiconductor and has applications in optoelectronic devices (Ramazanov, 2018). The article discusses the photoluminescent properties of hybrid nanocomposites synthesized based on PVDF+PbS/CdS. It was found that hybrid nanocomposite films synthesized based on PVDF+PbS/CdS have luminescence in a wide spectral region. Studying the effect of changes in the composition and concentration of nanoparticles on the luminescence spectrum and properties of nanocomposites is an actual problem.

2. Experimental

All chemicals were used without any additional purification. The polar polymer PVDF has a density of 1.78 g/cm^3 at 250°C and a melting point of 177° C. Sigma Aldrich provided lead acetate $Pb(CH_3COO)_2$, cadmium chloride ($CdCl_2x2,5H_2O$), Na_2Sx9H_2O, (1-hexadecyl) trimethylammonium bromide ($C_{19}H_{42}BrN$,98%) and DMF solvent. Polymer composite materials were prepared as follows: PVDF was solved in a DMF solution at room temperature, then nanoparticles of PbS and CdS were added to the polymer solution at a constant concentration of 1%, 3%, 5%, 10% and 15% and stirred for two hours to obtain a homogeneous mixture. The mixture was transferred to a petri dish and dried for 24 hours. Thin films of nanocomposite were obtained from these samples by hot pressing and applying a pressure of 15 MPa. The films, after hot pressing, were cooled in water at a cooling rate of 200°C per minute. The images of the samples have been obtained by 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 15 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 the Spectrophotometer Specord 250 Plus. At 200-1000

nm, UV spectra were recorded at the ambient temperature. The photoluminescent properties of nanocomposite films were examined using a spectrofluorimeter, Varian Cary Eclipse, at a wavelength range of 200–900 nm.

3. Results and discussions

Fig. 1 shows the X-ray diffraction pattern of neat PVDF and PVDF+PbS/CdS nanocomposites. It is clear that with an increase in the content of CdS and PbS nanoparticles in the polymer matrix, the degree of crystallinity of polymer nanocomposites based on PVDF+PbS/CdS increases. It is known that PVDF exists mainly in two forms: α- and β-forms. α-phase occurs during a helical conformation of the polymer chain and the identity period is 4.64 Å, including two monomeric units. The crystal structure of β-phase of PVDF has planar-zigzag chain conformation with an identical period of 2.56 Å, including one monomeric unit. As seen from Fig. 1, at 18.83°; 20.41° and 26,8° of 2θ angle, three peaks are observed, which belong to the α-phase of PVDF. The peak at 20.60 belongs to β-phase of PVDF. Also, the diffraction pattern shows peaks at 35.43° and 41.19°, which are characteristic peaks of the α-phase of PVDF. It was found that with the introduction of CdS and PbS nanoparticles, the intensity of the peaks belonging to the α- decreases, and for the β-phase, it increases (Bohlen & Bolton, 2014; Rastogi & Desu, 2016; Ren & Dzenis, 2006; Yee *et al*., 2007; Sencadas *et al*., 2006; Ameduri, 2009; Ma *et al*., 2008).

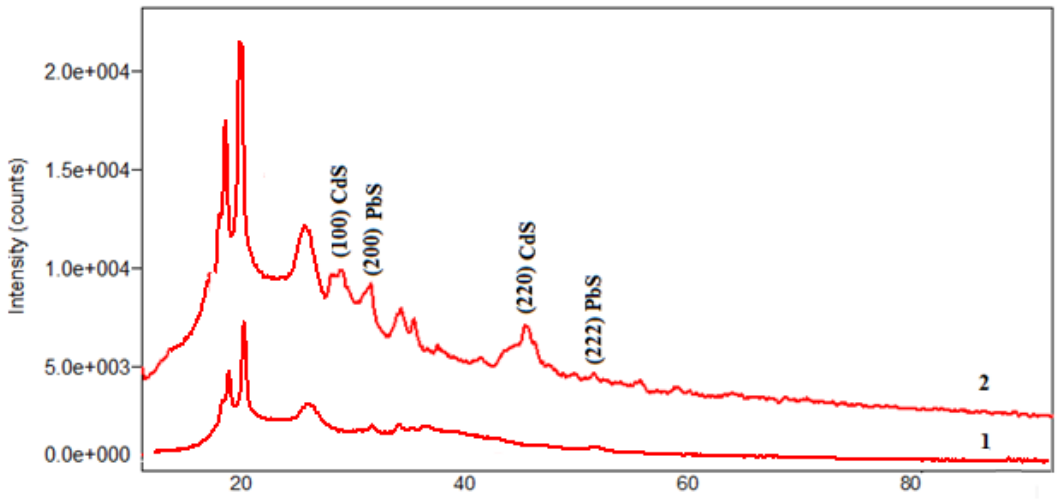

Fig. 1. X-Ray diffraction patterns: 1-neat PVDF, 2- PVDF+PbS/CdS base nanocomposite

It was also found that with an increase in the content of nanoparticles, peaks appeared that were characteristic of both CdS and PbS nanoparticles. As can be seen, the diffractogram of PVDF+PbS/CdS nanocomposite exhibits at 2θ the peaks 25.2° (100), and 43.65° (220) characteristics of CdS and those ones 30.01º (200) and 53.70° (222) characteristics of PbS. Other peaks in the diffractogram belongs to the surfactant CTAB, which coats and stabilizes the surface of nanoparticles.

Fig. 2 shows the UV spectra and optical band gap calculation of PVDF+PbS/CdS nanocomposites with various volume content of PbS/CdS.

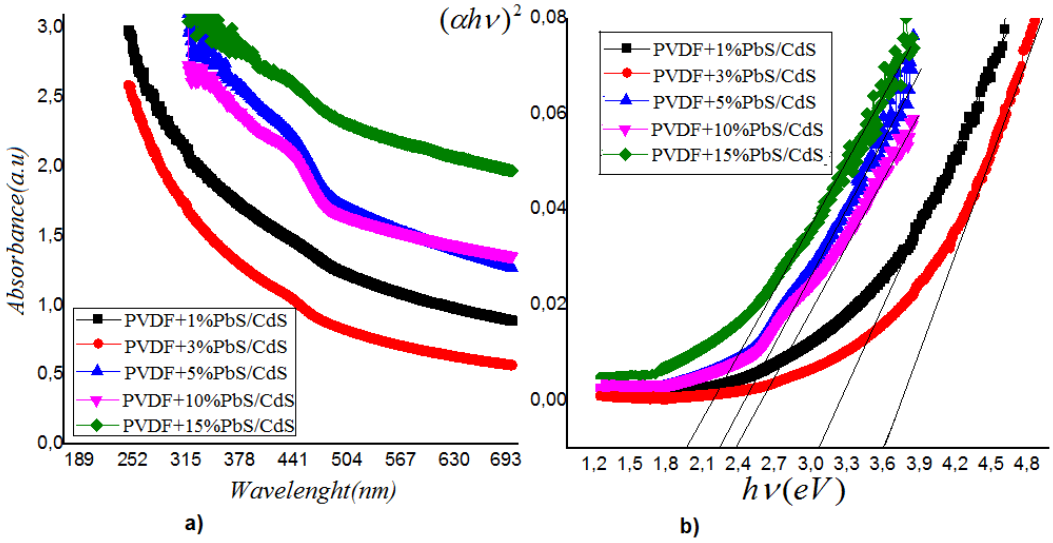

Fig. 2. UV absorbtions spectra (a) and band gap calculation (b) for PVDF+(1%,3%,5%,10%,15%)PbS/CdS nanocomposites

From the UV spectra by extrapolation, the optical band gap was calculated for polymer nanocomposites According to authors (Jia *et al*., 2019; Kang & Haynes, 2019; Jang *et al*., 2019), the energy gap of each nanocomposite film was determined by applying the Urban relationship (1).

$$\alpha = A\left(h\nu - E_g\right)^n / h\nu \qquad (1)$$

where A is a constant, a is the light absorption coefficient, Eg is the energy gap and h is the Planck's constant. The exponent n is 1/2 for direct allowed transitions, 2.0 for indirect allowed transitions, 3.0 for forbidden transitions. We have assumed for the examined film a direct transition, that is n =1/2.

As can be seen from the graphs, the optical band gap for PVDF+(1%,3%,5%,10%,15%) PbS/CdS nanocomposites is changed as follows:

Table.1. Optical band gap of PVDF+(1%,3%,5%,10%,15%)PbS/CdS nanocomposites

Sample	Optical band gap(eV)
PVDF+1%PbS/CdS	3
PVDF+3%PbS/CdS	3,6
PVDF+5%PbS/CdS	2,2
PVDF+10%PbS/CdS	2,3
PVDF+15%PbS/CdS	1,9

As can be seen as the nanocomposites concentration increase, the optical band gap is decrease. The optical band gap decreasing is explained by the increasing of particle sizes (Table.1).

The morphology of nanocomposites and the distribution of nanoparticles in a polymer matrix were also studied by means of scanning electron microscopy. Fig. 3 shows SEM images of nanocomposites with various volume content of PbS/CdS. SEM

images of nanocomposites PVDF+3%PbS/CdS, PVDF+5%PbS/CdS, PVDF+10% PbS/CdS in the fig. 3 show average sizes of nanoparticles in the PVDF matrix in the range of 48-83nm, 73-88 nm and 79-90 nm in respectively.

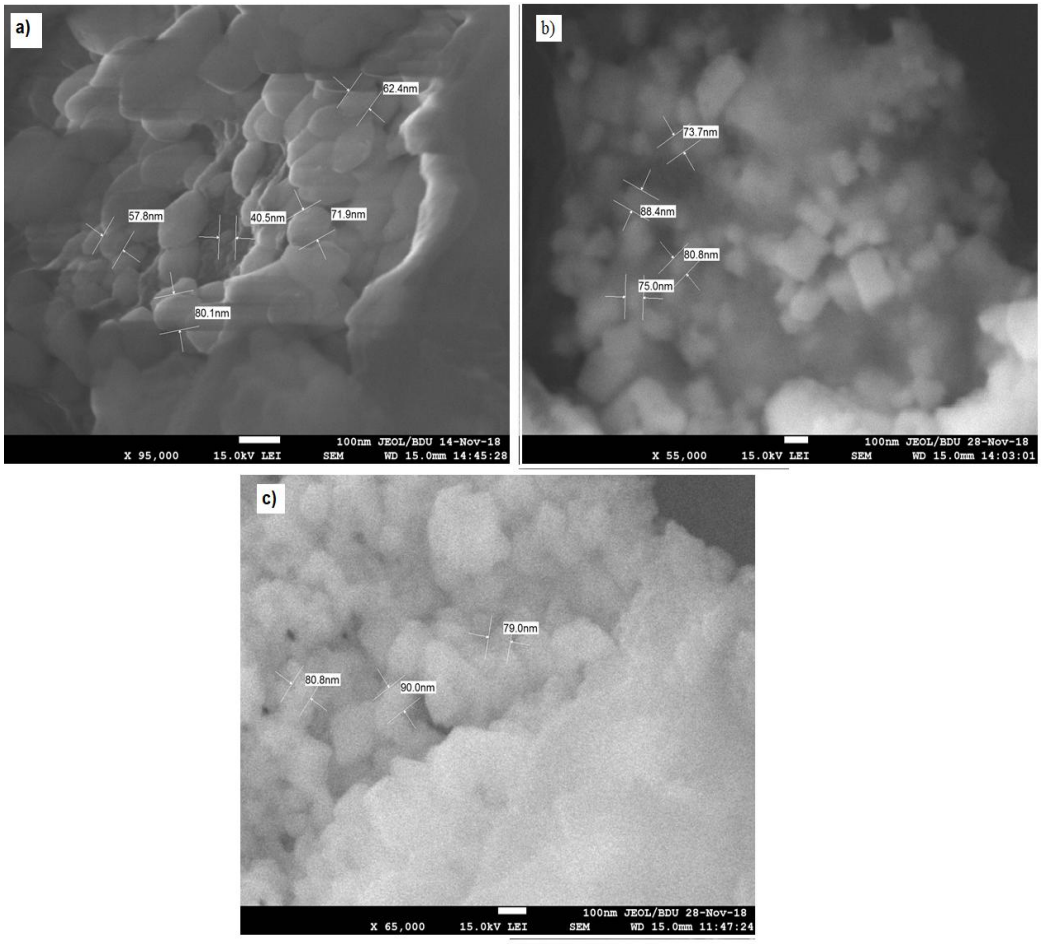

Fig. 3. SEM images of PVDF+3%PbS/CdS *(a)* ,PVDF+5%PbS/CdS *(b)* and PVDF+10%PbS/CdS *(c)* based nanocomposites

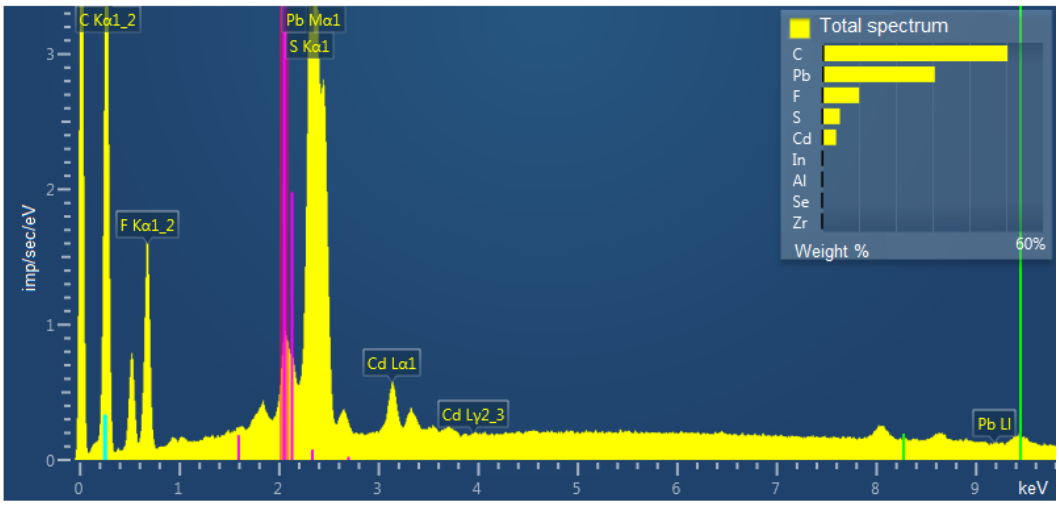

Fig. 4. EDS spectra of PVDF+PbS/CdS base nanocomposite

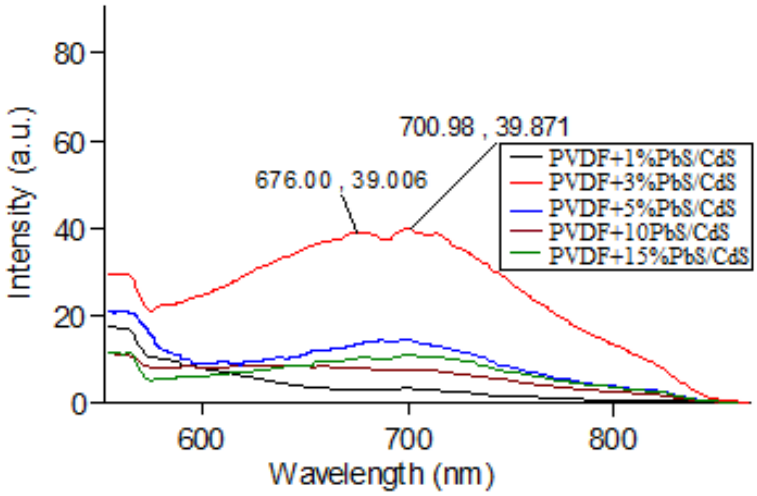

Fig. 5. Photoluminescence spectrum of PVDF+(1%,3%,5%,10%,15%)PbS/CdS nanocomposites

Fig. 4 reports the EDS spectrum of nanocomposites PVDF+PbS/CdS with various volume content of PbS and CdS nanoparticles. Fig. 4 shows that nanoparticles PbS, CdS in nanocomposites PVDF+PbS/CdS have been obtained cleanly.

Fig. 5 shows the luminescent spectra of the PVDF+(1%,3%,5%,10%,15%) PbS/CdS nanocomposites with different concentrations. Various concentrated nanocomposites were excited 300 nm wavelength. As can be seen from the graph , depending on the concentration, the maximum wavelengths are observed for nanocomposites in the range of 676.00 nm-700.98nm. As seen, the highest luminescence intensity was observed in nanocomposite PVDF+3%PbS/ CdS. This can be explained by the fact that in this concentration the luminescent centers are more active and more optimal structures are formed. It is known that bulk lead sulfide PbS produces photoluminescence in the infrared region in the wavelength range 1000-1200 nm. With a decrease in the size of PbS nanoparticles, due to quantum size effects, the photoluminescence peak for the PVDF+PbS/CdS nanocomposite shifts from the far infrared to the near infrared and is observed at the range of 676.00 nm-700.98nm. Hence such hybrid nanocomposites can luminesce at a wide range of wavelengths, which makes it possible to use these nanocomposites in various fields, including as active elements of solar cells, displays, converters, etc. (Chaudhuri & Paria, 2012; Das & Pal, 2018; Priya & Jog, 2002; Martins *et al*., 2012).

4. Conclusion

In given paper, were studied structure and optical properties of nanocomposites obtained on base of PVDF +PbS/CdS with different concentration. The optical band gap was calculated on the basis of the spectra of UV absorbtion and it was shown that the with increasing of concentration of semiconductor nanoparticles inside the polymer decreases the optical band gap of nanocomposites. This can be explained by increasing of size of nanoparticles due to agglomeration of nanoparticles with increasing of concentration. SEM analysis of PVDF+PbS/CdS based nanocomposites showed that particle size in PVDF+3%PbS/CdS, PVDF+5%PbS/CdS, PVDF+10%PbS/CdS nanocomposites was the range of 48-83nm, 73-88nm and 79-90nm in respectively. At

the same time, were investigated luminescence spectra of nanocomposites with different concentrations obtained on the base of PVDF + PbS/CdS. It has been established that the highest luminescence intensity is observed in nanocomposites PVD + 3% PbS/CdS. This can be explained by the fact that in this concentration the luminescent centers are more active and more optimal structures are formed.

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