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TUNING THE STRUCTURE, OPTICAL AND PHOTOLUMINESCENCE PROPERTIES OF POLYVINYLIDENE FLUORIDE AND CdS/ZnS-based NANOCOMPOSITES

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ABSTRACT

Have been developed a hybrid nanomaterials for applications in solar cells. Using ultraviolet spectroscopy, the optical absorption edges of the polymer nanocomposites have been determined, establishing that as the concentration of nanoparticles in the polyvinylidene fluoride matrix increases, the band gap decreases. Scanning electron microscope and X-diffraction analysis indicate that the cadmium and zinc sulphide nanoparticles are distributed in the polyvinylidene fluoride polymer as a separate phase and do not form a solid solution within the polymer matrix. Photoluminescence analysis reveals that for polymer nanocomposites with a hybrid combination of quantum dots, luminescence is observed over a wide range of wavelengths.

1. Introduction

The study of semiconductor quantum dots (QDs) of AIIBVI type has drawn a great deal of attention due to the widespread use of these materials. Already today, these nanoparticles and the composites based on them are used to create a new generation of LEDs, including white light sources with a very high (up to 90) color rendering index (CRI), as highly efficient luminescent bio labels, as well as active media for laser generation. Semiconductor nanoparticles possess several unique properties and successfully compete with traditional organic dyes. They have a higher molar extinction coefficient than dyes and a much higher photostability that is retained at excitation power densities up to 10^6 W/cm^2. One of the most vividly manifested trends in recent years is the use of polymers as a matrix for NPs since the nature of these polymers- the chemistry of functional groups, their structure allows regulating the production of the composite. An important point is that the polymers not only serve as a medium for dispersing NPs and facilitating the processing of the material as a whole, but can also contribute, leading to the synergism of the properties of the components. In particular, we are talking about both a possible increase in the filling limits of the material with NPs without their uncontrolled aggregation and the optimization of the optical properties of materials containing NPs. The optical properties of such materials serve as the basis for such current and future practical applications as optical absorption in a wide spectral range and photoluminescence (PL).

Recently, interest has increased in hybrid polymer nanocomposites, where several quantum dots are introduced into an optically transparent polymer matrix simultaneously. This is because such materials lead to an improvement in the efficiency of solar energy conversion by solar cells due to the creation of luminescent layers on their surface. Such hybrid layers based on QDs can convert UV radiation to a longer wavelength region, which is optimal for widely used solar cells. In this case, layers based on quantum dots can, in principle, divide the solar spectrum into several spectral bands, optimized for various types of photocells. Surface luminescent layers for solar cells must have a transparent matrix that is optimal for the introduction of quantum dots into it, which in turn must have absorption bands in the UV region, the required red shift of the luminescence, a high quantum yield, and stable characteristics. Among semiconductor nanoparticles, ZnS and CdS are of huge interest because of their different optoelectronic applications. Quantum dots based on CdS and ZnS, which have weak degradation and the ability to select absorption and luminescence characteristics by varying their sizes, are very promising. A combination of materials from different kinds of semiconductor nanoparticles shows very distinctive properties that have never been observed in composite systems consisting of only one of the types of semiconductors [1-5].

In the literature analysis, the synthesis and characterization of polymer nanocomposites based on hybrid quantum dots have been rarely studied. Therefore, the purpose of this article is to study hybrid nanomaterials based on an optically transparent PVDF polymer and nanoparticles of cadmium and zinc sulfides.

2. Experimental part

Materials:

All chemical reagents were used without preliminary purification: polyvinylidene fluoride (PVDF, Solvay 6020/1001), cadmium chloride ($CdCl_2{\times}5H_2O$, Sigma Aldrich C3141), sodium sulfide (Na_2Sx9H_2O, PLC 141687), CTABr (cetyltrimethylammonium bromide % chemically pure), zinc chloride ($ZnCl_2$, PLC 141779), dimethylformamide (DaejungCAS No. 68-12-2).

Synthesis of polymer nanocomposites:

CdS and ZnS nanoparticles were synthesized and stabilized in the presence of the surface-active substance CTABr according to the works [6]. Polymer nanocomposite materials were synthesized using solution casting method. PVDF polymer was dissolved in dimethylformamide at a room temperature. Nanopowders of CdS and ZnS were added into PVDF solution at 1, 3, 5, and 10% contents and stirred until a homogeneous mixture was prepared. The solution was dried in air until the DMF solvent completely evaporated. To completely remove the solvent from the volume of the PVDF, the films were dried in a vacuum oven for a hour. Then, using hot pressing method at the melting temperature of polymer (180^0C) thin nanocomposite films were obtained.

Characterization of nanocomposites:

XRD analysis was performed on a diffractometer Rigaku Mini Flex 600 equipped with Cu K α radiation at room temperature. The structure of the nanocompositions was studied using Integra-Prima atomic force microscopy (AFM, NT-MDT, Zelenograd) and scanning electron microscopy (SEM, Jeol JSM-7600 F). The photoluminescence properties of nanomaterials were studied using a Varian CaryEclipse spectrofluorimeter. UV analysis have been realized using spectrophotometer Specord 250 Plus.

3. Results and discussion:

Figure 1 shows the diffraction patterns of PVDF+CdS/ZnS-based nanocomposites depending on the content of CdS and ZnS nanoparticles in the PVDF matrix. As seen from XRD patterns with the introduction of CdS and ZnS nanoparticles into the matrix, the intensity of the peaks belonging to the α-phase of PVDF polymer (18.83°; 26,8^0; 35.43° and 41.19°) and for the β-phase

(20.6^0) decreases. It was also found that an increase in the content of nanoparticles, appearing peaks characterize both CdS and ZnS nanoparticles with the wurtzite crystal structure. While peaks at 24.9^0 (002) and 43.9^0 (103) belong to cadmium sulfide nanoparticles, peaks at 30.5^0 (101) and 51.5^0 (103) correspond to zinc sulfide nanoparticles in the diffraction pattern of PVDF+5%CdS/ZnS nanocomposite [7,8].

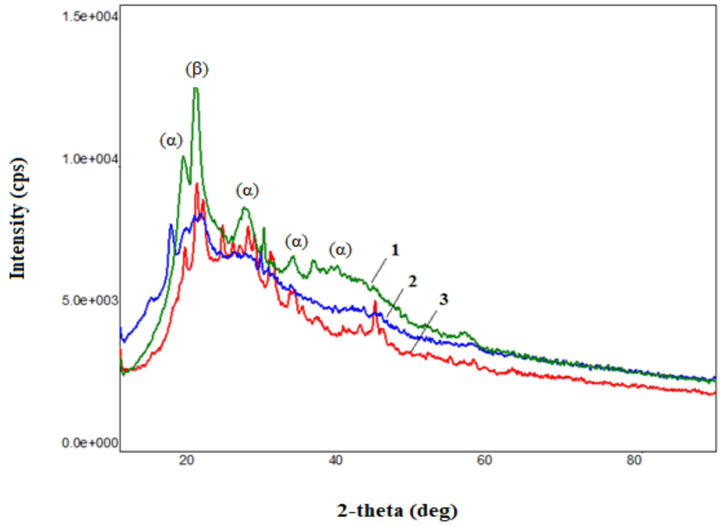

Fig.1 XRD patterns of PVDF+CdS/ZnS based nanocomposites: 1.PVDF+1%CdS/ZnS; 2.PVDF+3%CdS/ZnS; 3.PVDF+5%CdS/ZnS.

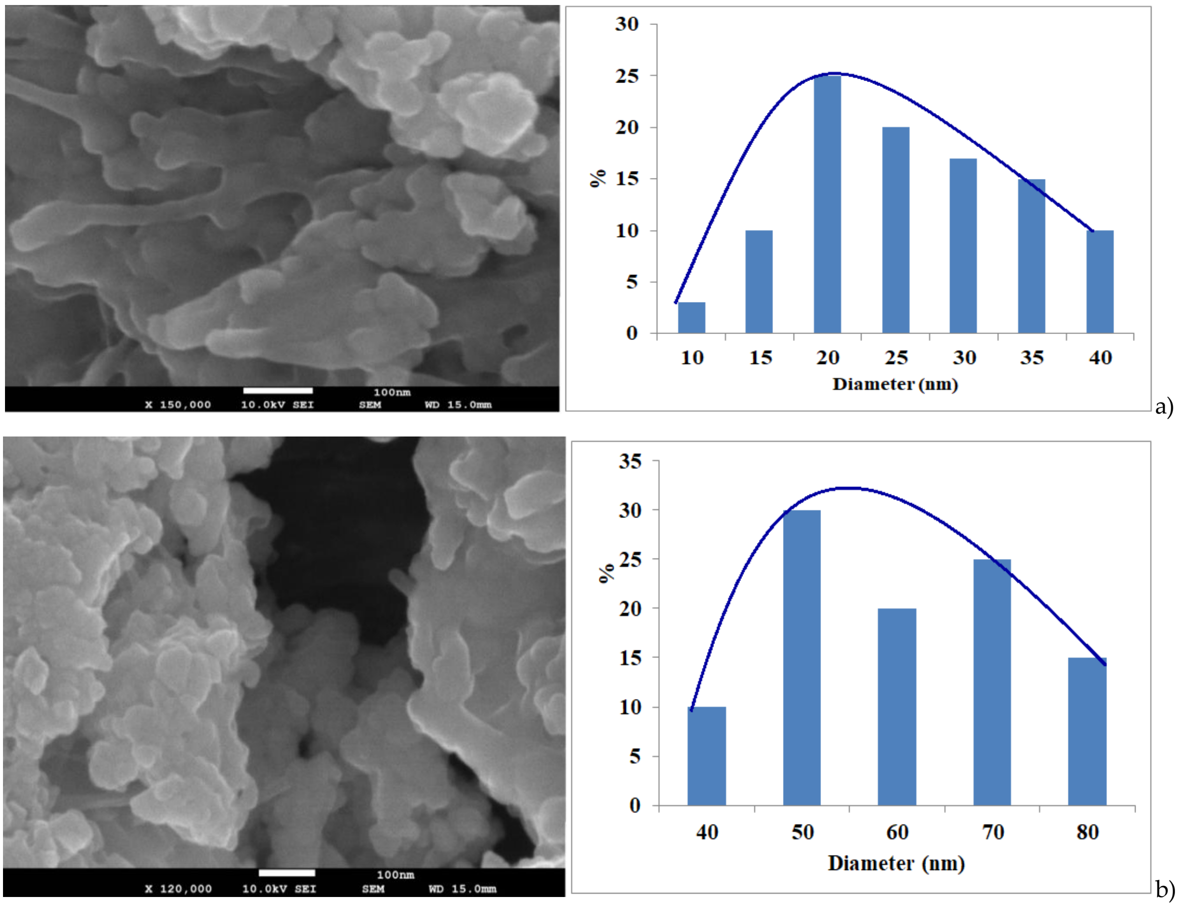

Fig. 2 SEM images and particle size distribution of CdS and ZnS nanoparticles in PVDF matrix:
a) PVDF+1%CdS/ZnS; b) PVDF+10%CdS/ZnS.

Figure 2 shows SEM images and particle size distribution of CdS and ZnS nanoparticles in PVDF matrix for PVDF+1%CdS/ZnS and PVDF+10%CdS/ZnS nanocomposite. According to SEM images, CdS and ZnS nanoparticles are uniformly distributed and the nanoparticle size for PVDF+1%CdS/ZnS and PVDF+10%CdS/ZnS is 10-40 nm, and 40-80 nm, respectively. XRD and SEM analysis of nanocomposites showed that CdS and ZnS nanoparticles don't form a solid solution in the PVDF matrix, but are distributed in the polymer as a separate dispersed phase [9,10.11].

Figures 3 and 4 show 3D AFM images and a histogram of the root-mean-square roughness of PVDF+CdS/ZnS based nanocomposites. It was found that with an increase in the content of CdS and ZnS nanoparticles, the supramolecular structure of polymer nanocomposites changes. Thus, the average roughness of a nanocomposite based on PVDF+1%CdS/ZnS is 10-70 nm, and for PVDF+10%CdS/ZnS is 20-140 nm. AFM analysis of nanocomposites shows that at low concentrations of nanoparticles, in contrast to high concentrations, a relatively smooth and ordered structure is formed.

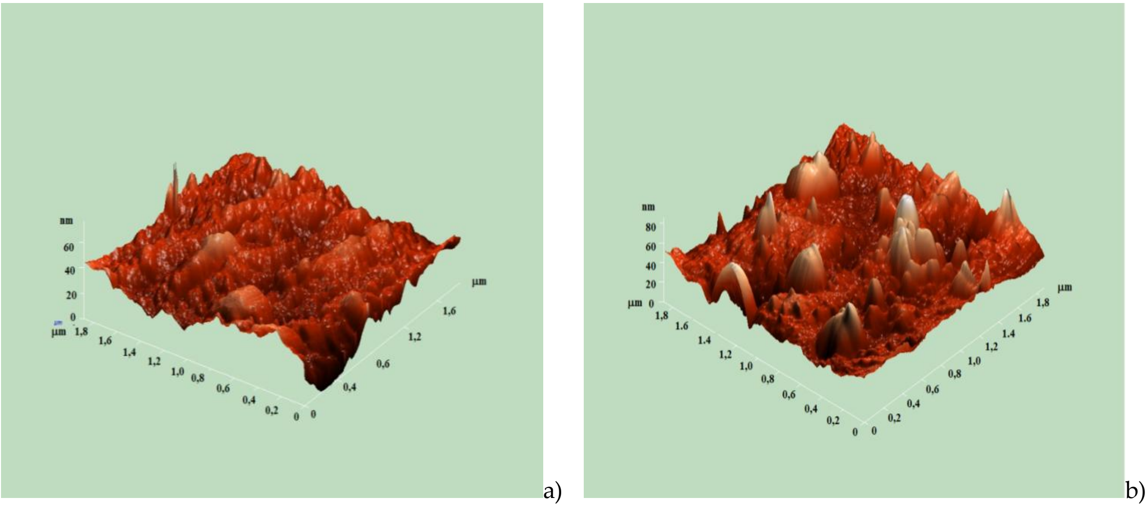

Fig.3 AFM 3D images of PVDF+CdS/ZnS based nanocomposites: a) PVDF+1%CdS/ZnS; b) PVDF+10%CdS/ZnS.

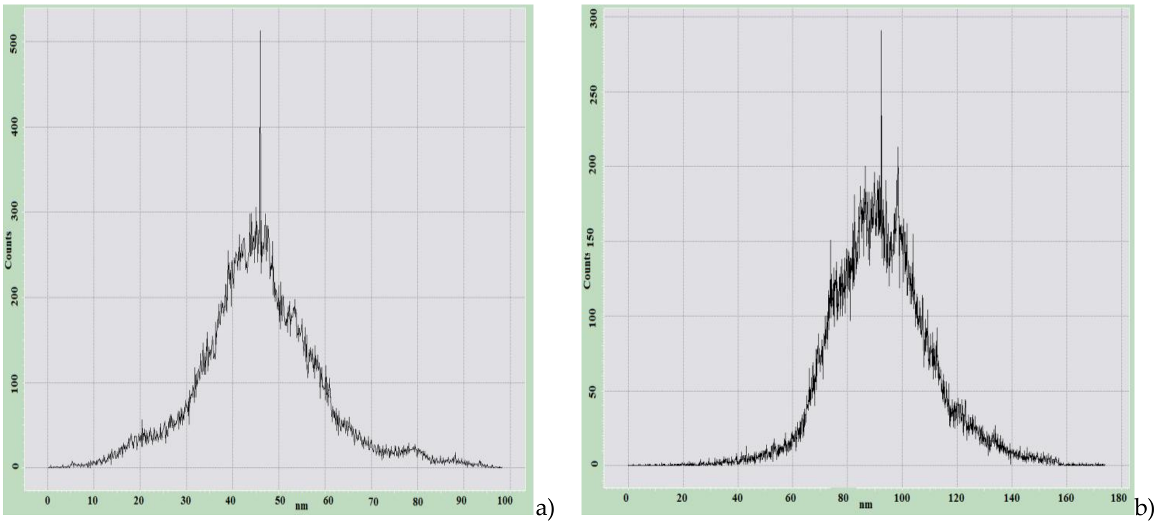

Fig.4 Histogram of the root-mean-square roughness of PVDF+CdS/ZnS based nanocomposites: a) PVDF+1%CdS/ZnS; b) PVDF+10%CdS/ZnS.

Figure 5 (a) shows the optical absorption edge of PVDF+ZnS, PVDF+CdS and PVDF+CdS/ZnS based nanocomposites. From the literature data it is known that a decrease of the size of semiconductor nanoparticles leads to a shift in the edge of the UV spectrum to the blue part of the spectrum (T.Serrano, et.al, 2014) [12]. It was found that for nanocomposites based on PVDF+ZnS, the band gap is 3.6 eV, for PVDF+CdS, 3.0 eV, and PVDF+CdS/ZnS nanocomposite- 4.5 eV. We should note that for bulk cadmium sulfide with a wurtzite crystal structure, the band gap is 2.4 eV and for bulk zinc sulfide with a wurtzite crystal structure- 3.4 eV. Figure 5 (b) shows the optical absorption edge for nanocomposites based on PVDF+ CdS/ZnS depending on the concentration of ZnS and CdS nanoparticles. It was found that the band gap for hybrid nanocomposites based on PVDF+CdS/ZnS decreases with an increase in the content of ZnS and CdS nanoparticles. Thus, for a nanocomposite based on PVDF+1% CdS/ZnS, the band gap is 5.3 eV; for PVDF+3%CdS/ZnS- 5.0 eV, for PVDF+5%CdS/ZnS- 4.3 eV, for PVDF+10%CdS/ZnS- 3.1 eV. The decrease in the band gap can be explained with an increase in the particle size by an increase in the content of CdS and ZnS nanoparticles in the PVDF matrix. Chunchun and et.al in work [13] have developed epoxy-ZnO/CdS based hybrid nanocomposites and determined that these materials exhibit strong absorption in the wavelength range from UV to blue light in compare of ZnO nanoparticles, that absorb one part of the UV radiation.

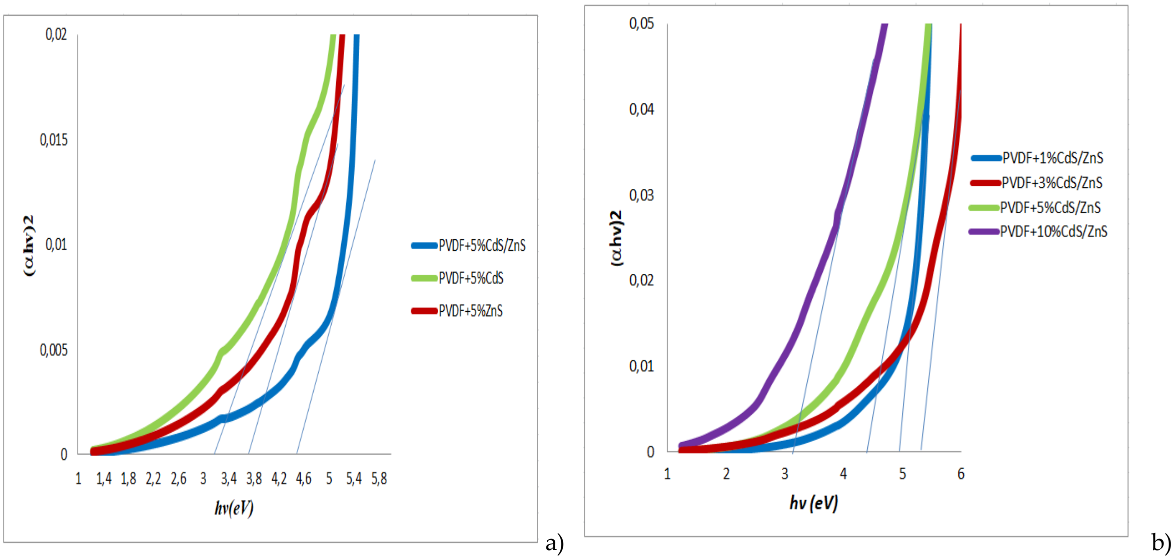

Fig.5 Optical absorption edge for nanocomposites based on PVDF+CdS, PVDF+ZnS and PVDF+CdS/ZnS.

Figure 6 shows the PL spectra of PVDF+CdS/ZnS nanocomposites depending on the content of CdS and ZnS nanoparticles. PL spectra were obtained upon excitation of nanocomposite films with light with a wavelength of λ=260 nm. It was found that the main peaks at 356 nm, 421 nm, 446 nm, 458 nm, 495 nm, 530 nm, 547 nm, 563 nm, 647 nm are luminescent peaks belonging to the hybrid PVDF+CdS/ZnS nanocomposite. As can be seen from the Figure 6, with an increase in the concentration of CdS and ZnS nanoparticles in the PVDF matrix to 3% of the content of nanoparticles, the PL intensity increases, and with a further increase in the content of nanoparticles, the PL intensity decreases. This is explained by the fact that with an increase in the concentration of CdS and ZnS nanoparticles, their size increases and the specific surface decreases, and this leads to a decrease in the contact area between the polymer and the nanoparticle.

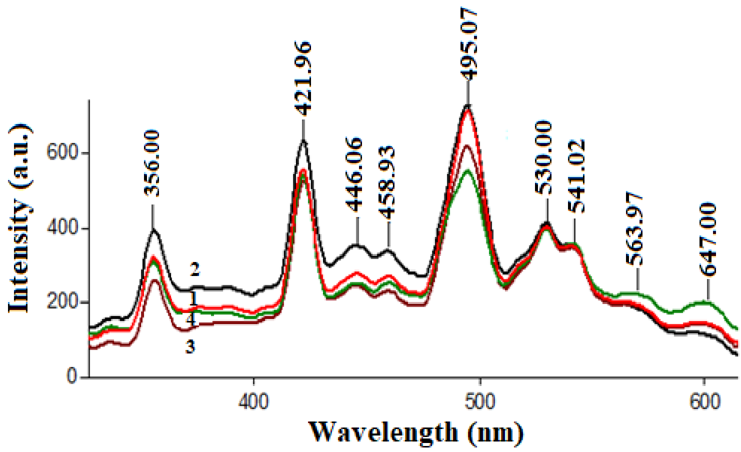

Fig. 6 PL spectra of polymer nanocomposites.

1. PVDF+1%CdS/ZnS; 2. PVDF+3%CdS/ZnS; 3.PVDF+5%CdS/ZnS; 4. PVDF+10%CdS/ZnS.

A decrease in the interfacial boundary leads to a decrease in interfacial interactions, and this, in turn, to a change in the PL intensity. It has been determined that the combined combination of photosemiconductor CdS and ZnS nanoparticles leads to a broadening of the spectral sensitivity. Photoluminescence analysis shows that for nanocomposites with a hybrid combination of quantum dots, luminescence is observed over a wide range of wavelengths [13-17]. Ramazanov and et.al in work [18] studied of hybrid polymer nanocomposites based on PP+PbS/CdS and observed that these nanocomposites exhibit intensive photoluminescence in the near infrared range at 680 nm and 715 nm [19-21].

Therefore, it has been established that hybrid nanocomposites can emit the light at a wide wavelength range, which makes it possible to use these nanocomposites in various fields: displays, converters, as active elements for solar cells applications, etc.

4. Conclusion

In the paper have been developed hybrid nanomaterials for solar cells applications. By UV spectroscopy, the optical absorption edges of the polymer nanocomposites have been determined and established that with an increase in the concentration of nanoparticles in the PVDF matrix, the band gap decreases. SEM and X-ray analysis showed that the nanoparticles are distributed in the polymer as a separate phase and do not form a solid solution in the polymer. Photoluminescence analysis shows that for nanocomposites with a hybrid combination of quantum dots, luminescence is observed over a wide range of wavelengths.

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