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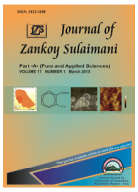

Synthesis and optical band gap investigation of PVA/CdS nanocomposite films

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Abstract

The nanocomposites of polyvinyl alcohol PVA with different concentration of cadmium sulfide nanoparticles CdS-NPs were obtained using chemical reduction route and casting technique. The effects of CdS concentrations on the optical properties of the PVA films were studied in the regions near-infrared, ultraviolet, and visible wavelength, (190-1100) nm. The obtained optical parameters were found to be strongly affected by CdS contents. From the derivation of Tauc's relation, it was found that the direct allowed transition was more probable in both CdS/PVA nanocomposite and CdS-NP. The results indicate that the obtained values of optical absorption edge and energies band gap decreases with increasing salt contents, as well as the reduction of the width of the tail localized states was observed. The study has been also extended to include the estimating of CdS particle size from the energies band gap for the investigated nanocomposite films.

Introduction

In the last few decades, numerous nanocomposites have been synthesized by various methods and characterized using different techniques for a wide range of applications. Various polar polymers such as polyvinyl alcohol (PVA), polyethylene oxide (PEO), polyvinyl chloride (PVC), polycarbonate (PC); and non-polar polymers such as polyethylene (PE), polystyrene (PS) and polypropylene (PP), have been extensively used for formulating composites [1-5]. The different fillers or dopants like various transition metal salts, metal sulphides, metal oxides, and different types of carbon nanotubes in the nanoscale, have been used for the preparation of nanocomposites as reported in the literatures [6-9]. The nanocomposites materials find a wide number of applications in many diverse fields such as UV shields, microwave absorbents, optoelectronics, gas sensors, fuel cells, and batteries of higher specific energy [8]. Among the various polymers mentioned above, PVA has been used extensively due to some associated unique properties such as excellent film forming, non-toxicity, high-performance hydrophilic, processability, biodegradability, and biocompatibility; moreover PVA have a carbon chain backbone with hydroxyl groups (OH) attached to methane carbon, which can be a source of hydrogen bonding and trap the ions and nanoparticles to form complexes [10]. The physical and chemical properties of PVA depend to a great extent on its method of preparation.

Polyvinyl alcohol (PVA) based nanocomposite materials were prepared and characterized by many researchers, The effect of different nanoparticle fillers such as ZnO [11], TiO_2 [12], Al_2O_3 [13], ZnS [14] and Ag_2S [15], on some physical properties of PVA are investigated and described. Among these, especially CdS-NPs embedded in the PVA polymer, have attracted considerable interest because of their potential applicability for various optoelectronic devices in the visible range of the electromagnetic spectrum [16, 17]. Different techniques have been reported in the literature describing the synthesis PVA/CdS nanocomposite. Khanna et al. [18] synthesized CdS-NPs embedded in PVA using cadmium acetate ($Cd(CH_3COO)_2.2H_2O$) and cadmium chloride ($CdCl_2$) for cadmium source and carbon disulphide (CS_2) and hydrogen sulfide (H_2S) as sulfur source. El-Tantawy et al. [19], studied the physical properties of PVA/CdS nanoconducting composite prepared by organosols techniques using CdI_2 solution. Wang et al. [20], reported the synthesis of the PVA/CdS nanocomposite films by means of the in-situ synthesis method via reaction of Cd^{2+}-dispersed PVA with H_2S. Saikia et al. [21], used the in-situ thermolysis of precursors dispersed in PVA to deposited the PVA/CdS nanocomposite thin films on the glass substrates.

The production and characterization of the PVA/CdS nanocomposite in the present work have been carried out, using chemical reduction route and casting technique. The analysis will focus on the influence of concentration of synthesis CdS-NP on the optical energy band gap of the PVA films, using UV/Vis analysis, which gives an evidence of understanding the effect of synthesis nanoparticle on the optical parameters and energy band diagram of the host polymer.

Materials and sample preparation:

Low molecular Polyvinyl alcohol (PVA) was used as a basic nanocomposite material, Cadmium nitrate $Cd(NO_3)_2$ (molar mass=236.4208 g/Mol.) and Sodium sulfide Na_2S (molar mass=78.0445 g/Mol.) were supplied by Alfa Aesar, are used as Cd^{2+} and S^{2-} ion source respectively. All chemicals were used as received without any purification. Aqueous solution of PVA was prepared by dissolving 2 gm of PVA in the 40 mL distilled water at 90°C. Solutions of $Cd(NO_3)_2$ and Na_2S were prepared separately at different concentrations ranging from (0.03-0.12) M in the 5 mL distilled water at ambient temperature. Equal volumes of salt and PVA solution prepared earlier were mixed drop by drop at 40 °C with continuously stirred for 20 minutes at room temperature. The immediate change in color after adding salts solution from colorless to yellow and orange light indicates the formation of the CdS-NPs. The additional stirring was allowed for 10 minutes, it was then the final solution transferred to Petri dishes and kept at room temperature (about 27 °C) in dust free chamber for 7 days until the solvent completely evaporated. Dried samples were obtained in the form of films. The optical characterization of the prepared films were carried out at room temperature using double beam Ultraviolet-visible spectrophotometer (Lambda-25) in the wavelength region of (190-1100) nm.

Theoretical background

The absorption coefficient (α) is related to the optical absorbance and thickness of the film d, based on the Lambert Beer's law [22, 23] that is:

$$\alpha = \frac{2.303}{d} A \qquad (1)$$

The optical energy gap (E_g) of the films has been determined from absorption coefficient data as a function of photon energy ($h\nu$ in eV). According to the generally accepted model proposed by Tauc for higher values of absorption coefficient, the optical absorption of non-crystalline materials are given by the Tauc [24] and Mott-Davis model [25]:

$$\alpha h\nu = \beta\left(h\nu - E_g\right)^{\gamma} \qquad (2)$$

where β is a constant called the band tail parameter and γ is the exponential constant index which determine the type of electronic transition responsible for the absorption mechanism of electron transition. There are four types of transition in amorphous materials that can be represented with γ. The values of γ are commonly 1/2, 3/2, 2, and 3 for direct allowed, direct forbidden, indirect allowed, and indirect forbidden transitions, respectively [10].

In the low absorption region ($\alpha < 10^4\ cm^{-1}$), the absorption coefficient (α) shows an exponential dependence on photon energy ($h\nu$) and obeys an empirical relation due to Urbach [26]:

$$\alpha = \alpha_o\, exp(h\nu/E_u) \qquad (3)$$

where α_o is a constant and E_u corresponds to the Urbach energy, interpreted as the width of the band tail of the localized states in the band gap energy, which associated with the amorphous nature of materials. In general largest value of E_u, related to great disorder in the structure. The dependence of $ln(\alpha)$ versus photon energy ($h\nu$), is a straight line, from which the inverse of the slope, gives the width of the tails of the localized states.

Results and discussions

The study of optical absorption spectra provides essential information about the band structure and the energy gap in crystalline and non-crystalline materials. Analysis of the absorption spectra in the lower energy part gives information about atomic vibrations, while the high energy part of the spectrum gives knowledge about electronic state in atoms [27].

Figure 1 shows the absorption spectra of both pure PVA and PVA/CdS nanocomposites in the wavelength range (190-1100 nm). It is evident from the figure that there is a significant change between pure and doped spectrum. The pure PVA spectra show a lower absorbance comparison to the nanocomposite samples over the investigated wavelength range, and it was almost constant at higher wavelength. The spectrum of pure PVA show the sharp drops in the absorbance values in the UV region (190-250 nm), as well as exhibits a shoulder like a band absorbance peak around 200 nm which are related to high energy absorbance [28].

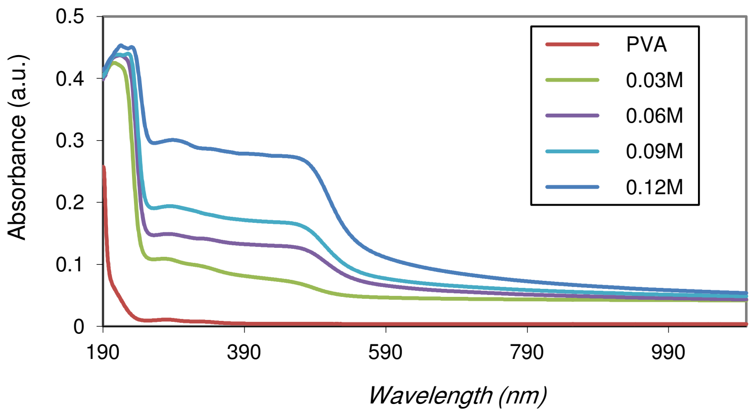

Fig. 1 The absorption spectra of PVA/CdS nanocomposites.

The absorption spectra of nanocomposite shows the additional absorption shoulder around 500 nm that characteristic of CdS-NPs. By comparing this absorption band with the absorption band of CdS bulk (515 nm), the blue shift can be noticed, which may be due to the quantum confinement effect [29]. The significant changes in absorption spectra may be correlated with the interface adhesion and network structure of PVA/CdS nanocomposite [19]. The increase in the absorbance values of the samples with increasing the concentration of CdS may be attributed to the fact that increasing the dopant concentration decreases the transparency of the sample, and also due to the formation of complex charge transformation.

The fundamental absorption edge is one of the most important features of the absorption spectra of crystalline and non-crystalline materials. The increased optical absorption near the edge is caused by the transition of electrons from the valence band to the conduction band [30]. Figure 2 illustrates the relation between the absorption coefficients (α) as a function of photon energy for investigated samples. It is clear that the absorption coefficient α increases gradually with increasing photon energy, and CdS content. The increase in α with the increase in the CdS content may be attributed to the change of the molecular configuration which indicates to the formation of charge transfer complexes.

The intercept of extrapolation to zero absorption with photon energy axis was taken as the value of absorption edge (E_e). The values obtained are listed in Table 1. It is clear that the values E_e for nanocomposite are lower than that for pure PVA. The decrease in E_e on adding CdS may be explained on the basis of the fact that the incorporation of dopant form charge transfer complexes in the polymer matrix [31]. These charge transfer complexes increase the optical conductivity by providing additional charges, this results in a decrease of E_e.

Figure 3 shows the relation between $ln(\alpha)$ and hv for all samples. The straight lines obtained suggest that the absorption follows the quadratic relation for interband transitions and obey the Urbach rule [25]. The values of band tail energy (E_u) were determined from the reciprocal of the slopes of the straight lines and are listed in Table 1. The increase of band tail energy E_u values with increasing the CdS contain lead to increase in electronic transitions between localized states [22].

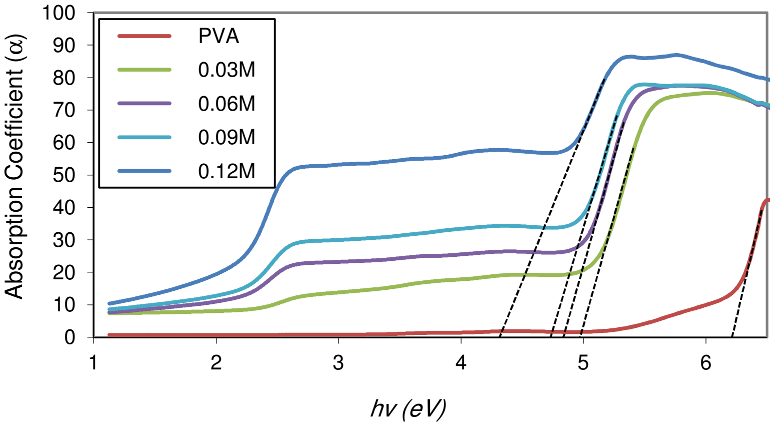

Fig. 2 The absorption coefficient (α) of PVA/CdS nanocomposites as a function of photon energy (hv).

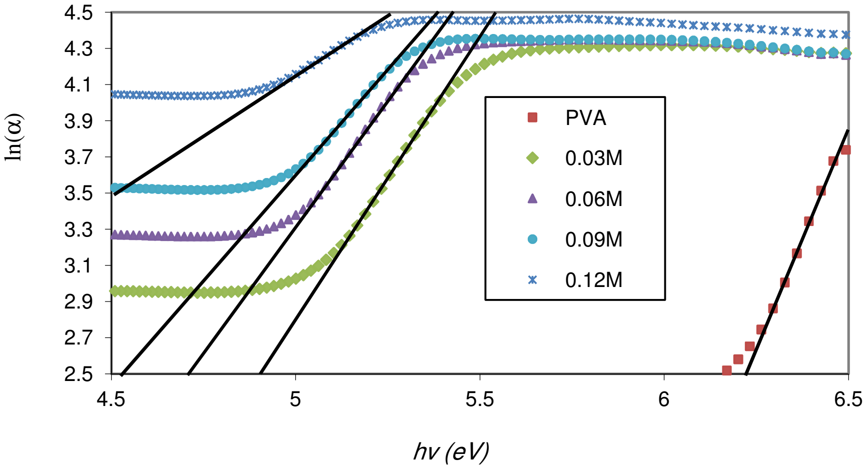

Fig. 3 Urbach law plots for PVA/CdS nanocomposites.

The accurate values of optical band gaps for PVA/CdS nanocomposite, and CdS-NP have been calculated by taking the natural logarithm and the derivation of Eq (2) as [32]:

$$\frac{d\,ln(\alpha hv)}{d\,hv} = \frac{\gamma}{hv - E_g} \qquad (4)$$

According to this equation, a peak in the curve of $(d\,ln(\alpha h\nu)\,/d\,h\nu)$ versus $(h\nu)$ should be observed at about a point of energy gaps. Fig.4 shows the plot of $(d\,ln(\alpha h\nu)\,/d\,h\nu)$ versus $(h\nu)$ for nanocomposite samples. The appeared two peaks at a particular energy value provides the approximate value of energy gaps of CdS nanopaticles (E_{g1}), and PVA/CdS nanocomposite (E_{g2}). This initial value of energy gaps was used to estimate the value of γ. Figures (5a and 5b) illustrate the graph of $ln(\alpha h\nu)$ versus $ln(h\nu - E_g)$ for both nanocomposite and nanoparticle respectively. From the slope of the graphs, γ was determined to be in the range (0.79-0.88). Interestingly, this estimation provides evidence for the presence of a direct gap as a more probable transition between the energy bands in the investigated samples.

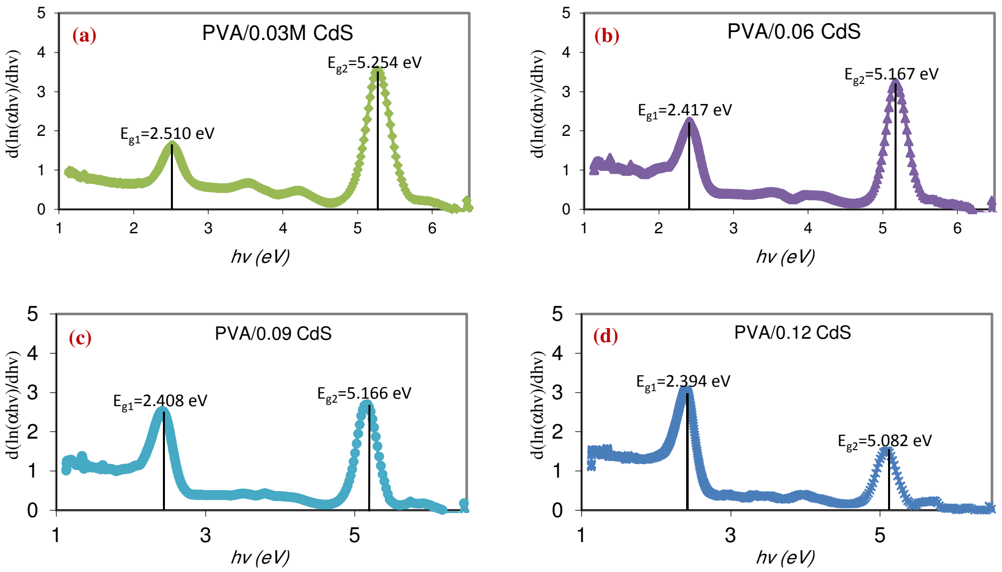

Fig. 4 Plot of $(d\,\ln(\alpha h\nu)\,/d\,h\nu)$ versus $(h\nu)$, to estimate the values of energy gaps.

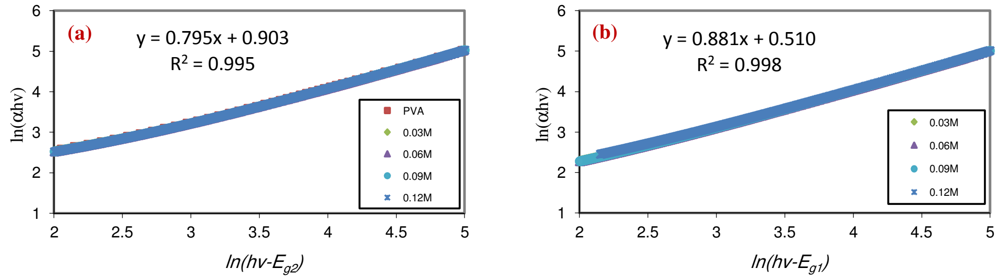

Fig. 5 Plot of $\ln(\alpha h\nu)$ versus $\ln(h\nu - E_g)$ to determine the value of γ, of (a) PVA/CdS nanocomposite, (b) CdS-NPs.

The direct optical band gaps for PVA/CdS nanocomposite samples, and CdS-NP was obtained by plotting $(\alpha h\nu)^2$ against energy $(h\nu)$ as shown in Fig. 6. The allowed direct energy gap for PVA/CdS nanocomposite (E_d), and CdS-NP (E_{np}), was determined by extrapolating the linear parts of the curves to zero absorption and the values are given in Table 1. The significant decrease of energy band gap E_d for nanocomposite samples compared to the pure PVA sample, reveals the presence of deeper localized state into nanocomposite samples [19], whereas the decrease of the band gap of CdS-NPs (E_{np}) with salt concentration can be attributed to the increase of the particle size of CdS-NPs.

It is evident that the values of E_e, E_d and E_{np} decreases with increasing the concentration of CdS, which indicate the fact that multiple states were introduced between the valence and conduction bands, i.e. an increase in the density of defect states [25]. Also the decrease in the optical energy gap of nanocomposite on adding CdS, may be explained on the basis that CdS-induced structural changes in the system. Furthermore, it was recognized that dopant plays a dominant role in morphological and microstructure changes occurring in the polymer matrix [28, 33], which responsible for the presence of localized state in the band gap.

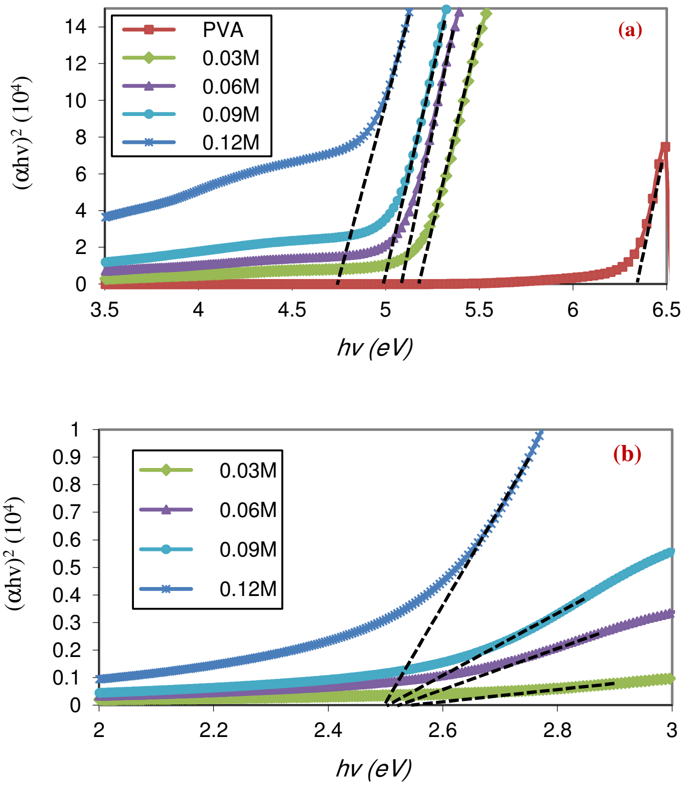

Fig. 6 The variation of $(\alpha hv)^2$ as a function of photon energy (hv): for (a) PVA/CdS nanocomposites; (b) CdS-NP.

Table 1. Values of the E_e, E_u, E_d, and E_{np} as a function of CdS concentration.

CdS (M)	E_e(eV)	E_u(eV)	E_d(eV)	E_{np}(eV)
0.00	6.22	0.206	6.35	-
0.05	4.98	0.323	5.17	2.62
0.10	4.83	0.360	5.08	2.57
0.15	4.73	0.433	4.98	2.53
0.20	4.31	0.806	4.74	2.51

It is seen that the energy gap of CdS semiconductor is blue shifted as compared to the absorption edge of the bulk value (2.42 eV), thus proving formation of nanometer-sized CdS in the samples [34]. The average size of CdS-NPs were calculated according to the Brus equation for quantum dot [35], the band gap of nanoparticles (E_{np}) is related to the radius of the particle (R) as:

$$E_{np} = E_g + \frac{\hbar^2\pi^2}{2R^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) - \frac{1.8\,e^2}{4\pi\epsilon R} \qquad (5)$$

to get a rough estimation of the size of CdS particles in the composite, the pure values of CdS are used, the band gap of bulk CdS (E_g=2.42 eV), effective mass of an electron (0.19 m_e), effective mass of a hole (0.8

m_e), and dielectric constant of CdS (ϵ=5.7) [34]. The calculated average radius of the particles using Eq(5) are (3.5, 4.0, 4.7, and 5.2) nm for Cd^{2+} concentration of (0.03, 0.06, 0.09, 0.12) M respectively.

This is suggested that the small CdS-NPs were synthesized in a small amount of Cd salt, so the size of the nanoparticles in the composite could be controlled in the nanometer range by adjusting the salt concentration used in synthesis of CdS-NPs.

V. Conclusions:

The influence of salt concentration on the optical energy band gap of PVA/CdS nanocomposite synthesized via chemical reduction route, and casting technique has been carried out. The UV-Visible spectroscopy illustrates that the estimated values of the absorption edge, and energy gaps of nanocomposite decrease with increasing the CdS content, due to the formation of charge transfer complexes, and the crystalline defect. The decrease in the CdS-NPs energy gap with increasing salt concentration, indicate the formation of larger nano-sized CdS in the samples, whereas the blue shift of Nps energy gap from that of CdS bulk attributed to the quantum confinement effect.

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