Optical Properties of the Synthesized Cr_2S_3 Nanoparticles Embedded in Polyvinyl Alcohol

Omed Gh. Abdullah, Dana A. Tahir and Dlear R. Saber

Department of Physics, Faculty of Science and Science Education, School of Science, University of Sulaimani
Sulaimani, Kurdistan Region - F.R. Iraq

***Abstract*—Polyvinyl alcohol (PVA) based nanocomposite, with different concentrations of chromium sulfide Cr_2S_3 nanoparticles, were prepared by reduction of $Cr(NO_3)_3$ and Na_2S in an aqueous PVA solution, using the chemical reduction rote, and casting technique. Effect of Cr_2S_3 nanoparticles on optical parameters such as absorbance, absorption coefficient, refractive index, and extinction coefficient have been investigated using UV-Visible spectroscopy. The study reveals that all these parameters are affected by the Cr_2S_3 nanoparticles concentration. The study has been also extended to investigate the changes in the optical band gap energies, the band tail width for the samples using Tauc and Urbach relations respectively. The optical energy band gap reduced from (6.17 eV) for pure PVA to (4.14 eV) for 0.04M Cr_2S_3; while the Urbach tail increased from (0.216 eV) for pure PVA to (0.523 eV) for 0.04M Cr_2S_3. The significant change of the optical properties of PVA with embedded Cr_2S_3 nanoparticles suggested their applicability in optical devices.**

***Index Terms*—Cr_2S_3 nanoparticles, filler effect, optical properties, polymer nanocomposite, solution cast technique.**

I. Introduction

In the past several years, considerable researches have been carried out focusing on the synthesis of the polymer nanocomposite materials with various nanoparticle filler to understanding their physical and chemical properties. By combining polymer and nanoparticle, the resulting composites can possess advantages of both organic polymers and inorganic nanoparticle (Jeon and Baek, 2010). Incorporating a small amount of nano-sized fillers into the polymer matrix, could lead to a significant change in optical, electrical, and mechanical properties (Ayandele, et al. 2012).

Optical properties of different polymers based nanocomposite have received considerable attention in recent literatures (Liu, et al. 2007; Luo, et al. 2007), it is still meaningful to extend the research on such materials as a promising material for sensors, rechargeable batteries, optoelectronics applications such as light emitting diodes LEDs, and electromagnetic interference shielding (Gurunathan, et al., 1999).

Due to their superior physical and chemical properties, polyvinyl alcohol (PVA) based nanocomposite, has attracted more attention among the other organic nanocomposite (Abdullah, et al., 2011). Major characteristics of PVA include excellent film forming capacity, good transparency, high tensile strength, tear and chemical resistance, and good insulating material which makes important for many applications in industry (Yang and Wu 2009; Gautam and Ram 2010; Ravi, et al., 2011).

The investigation of optical absorption, especially, the absorption edge, the band gap energy, and the band tail of localized state is importance for different applications (Deshmukh, et al., 2008; Abdullah, et al., 2011).

In the present work, an aqueous solution of PVA used as host matrix for $Cr(NO_3)_3$:Na_2S reaction to produce nano Cr_2S_3/polymer nanocomposite. The characterization and analysis focused on the influence of Cr_2S_3 nanoparticle concentration on the optical parameters of the PVA, to optimize the optical properties for desired applications.

II. Materials and Methods

The homogeneous and transparent solution of polyvinyl alcohol (PVA) was prepared by dissolving (2 gm) of low molecular PVA supplied by Alfa Aesar in 50 ml distilled water using a hot plate magnetic stirrer at 90°C for 1 hr. Chromium nitrate $Cr(NO_3)_3$ (molar mass=238.0108 g/Mol.) and Sodium sulfide Na_2S (molar mass=78.0445 g/Mol.) as Cr^{3+} and S^{2-} ion source respectively, were dissolved in the 5 mL distilled water separately with different molar concentrations (0.00, 0.01, 0.02, 0.03 and 0.04) at ambient temperature. Then $Cr(NO_3)_3$, and NaS solution with ration 2:3, prepared separately and then added drop by drop to the homogeneous solution of PVA at 40°C. For maximum dispersion, the solution was further stirred for 30 minutes without heating. The production process of Cr_2S_3 was according to the following reaction:

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Corresponding author's e-mail: omed.abdullah@univsul.edu.iq

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$$2Cr(NO_3)_3 + 3Na_2S \rightarrow Cr_2S_3\ (solid)\ + 6NaNO_3\ (aqueous)$$

The mixture of the prepared solution was casted onto a clean plastic Petri dish and allowed to evaporate slowly at room temperature for two weeks. For continuous drying with blue silica gel, the produced films transferred into desiccators. The prepared films have a uniform thickness in the range of (0.17-0.21) mm. The measurements of absorbance and transmittance spectra 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.

III. Results and Discussion

Fig. 1 shows the absorption spectra of the PVA films filled with different concentrations of Cr_2S_3. The pure PVA film exhibits a main peak at 284 nm as well as a shoulder at about 333 nm. The main peak attributed to the absorption of the carbonyl group, while the shoulder assigned to the -(CH=CH)3CO- structure (El-Khodary, 2010; Abdullah, et al. 2013).

The nanocomposite films with different contents of Cr_2S_3, showed two broad bands approximately centered at (415 and 570)nm in the visible region, which are related to surface plasmon resonance (SPR) that correlated to the Cr_2S_3 nanoparticle (Massoumi, et al. 2013). The SPR bands of the nanoparticle are sensitive to the shape and size of the particle size (Noguez 2007; El-Brolossy, et al. 2008). The intensity of these bands increases with increasing salt concentration providing evidence for the incorporation of the Cr_2S_3 into PVA matrix. The observed blue shift of the two bands comparing to the Cr(III) spectra (421 and 592) nm in reference (Subramaniam, et al. 2013), attribute to the quantum confinement effect (Seoudi, et al. 2012), Whereas the shift in onset of absorption spectra towards the higher wavelength upon increasing Cr_2S_3 confirm the increase of the average size of nanoparticles (Deshmukh, et al. 2012).

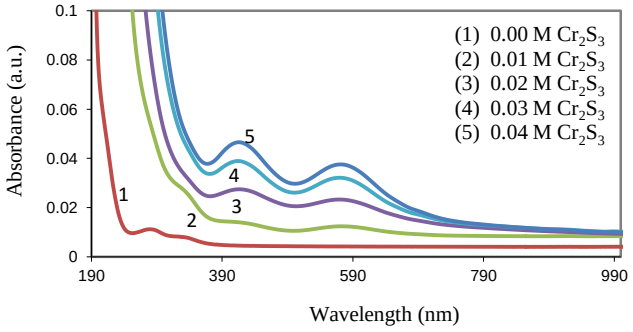

Fig. 1. The absorption spectra of pure PVA, and PVA/Cr_2S_3 nanocomposite.

The optical absorption coefficient α is defined as the ability of a material to absorb light of a given wavelength; it provides the most valuable optical information such as the electronic band structure and the optical energy band gap for material identification. The variation of optical absorption coefficient α with wavelength can be calculated from the optical absorption spectrum using the Beer-Lambert's relation (Abdullah, et al. 2013; Ballato, et al. 2003):

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

where, d is the sample thickness in (cm), and A is absorbance defined as $log(I_o/I)$ where I_o and I are the intensities of the incident and transmitted beam light respectively (El-Khodary, 2010).

Figure 2 shows the dependence of the absorption coefficient on the photon energy for pure PVA sample and the Cr_2S_3/PVA nanocomposite samples. The absorption coefficient increases with the increasing of Cr_2S_3 concentration.

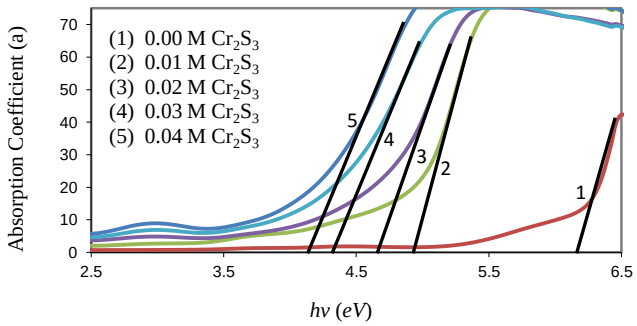

Fig.2. The optical absorption coefficient for pure PVA and PVA/Cr_2S_3 nanocomposite.

The refractive index is a fundamental characterization of the optical study, the values of refractive index (n) could be determined from the optical reflectance (R) of the investigated films, using the Fresnel formulae as follows (Yakuphanoglu, et al. 2007):

$$n = \left(\frac{1+R}{1-R}\right) + \left[\frac{4R}{(1-R)^2} - k^2\right]^{1/2} \quad (2)$$

where ($k = \alpha\lambda/4\pi$) is the extinction coefficient, λ is the incident photon wavelength.

Fig. 3 shows the variation of the refractive index of nanocomposites as the function of photon energy. The refractive index increases as a result of increasing the concentration of Cr_2S_3 nano-filler, this behavior can be attributed to the increasing of the packing density of nanocomposite as a result of filler content (Amma, et al., 2005).

The variation of the extinction coefficient (k) with photon energy for PVA/Cr2S3 nanocomposites is as shown in Fig.4. The extinction coefficient increases with increasing of Cr2S3 nanoparticles concentration. This behavior of extinction coefficient can be ascribed to the variation of the absorption coefficient since k directly proportional to α.

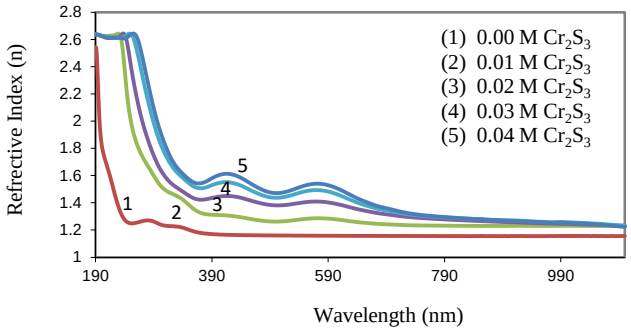

Fig. 3. The refraction index of PVA/Cr_2S_3 nanocomposite as a function wavelength.

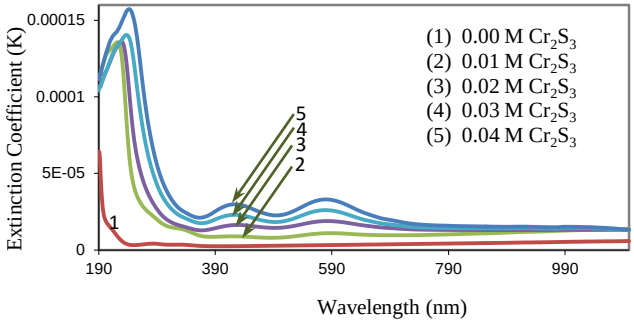

Fig. 4. The extinction coefficient for PVA/Cr_2S_3 nanocomposite as a function of wavelength.

The optical absorption spectra for the near absorption edge, can be used to determine the nature of the transition (direct or indirect), and the value of the optical energy band gap E_g. The present optical data can be investigated in view of the models proposed by Tauc (1970);

$$\alpha = B\frac{(h\nu - E_g)^r}{h\nu} \quad (3)$$

Where, B is a constant, $h\nu$ is the incident photon energy, and r is the power that characterizes the optical transition process. The exponent r determines the type of electronic transitions causing optical absorption, it can take values 1/2, 3/2, 2 or 3 for transitions designated as direct allowed, direct forbidden, indirect allowed, and indirect forbidden respectively (El-Khodary, 2010).

Figure 5 shows the plots of $(\alpha h\nu)^{1/2}$ versus the photon energy ($h\nu$) for the present experimental data near the absorption edge. The linearity of the data suggests the presence of indirect allowed transitions in the PVA and its composite. Extrapolation of the linear portion of the plots to the abscissa yields the indirect optical energy band gaps of PVA/Cr_2S_3 nanocomposite and Cr_2S_3 nanoparticles. The values of optical energy band gaps are given in Table 1. The obtained data revealed that the optical energy band gap decrease significantly with increasing nano Cr_2S_3 concentration, which may be explained on the basis of the fact that the incorporation of small amounts of dopant forms charge transfer complexes in the host matrix (Abdullah, et al. 2013). These charge transfer complexes increase the electrical conductivity by providing additional charges, this result in a decrease of the optical energy band gap, by facilitating the transfer of charge carrier between the localized states (Abdelrazek, et al., 2013; Sangawar, et al., 2007).

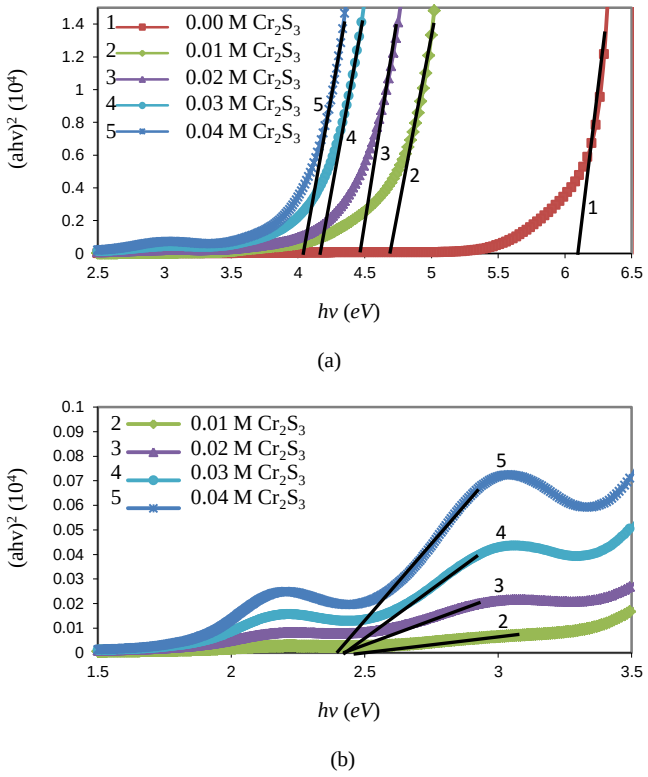

Fig. 5. $(\alpha h\nu)^{1/2}$ versus photon energy ($h\nu$) for; (a) PVA/Cr_2S_3 nanocomposite and (b) Cr_2S_3 nanoparticles.

The width of the localized tail states in the forbidden gap (Urbach tail), is an indicator of the defect levels in the forbidden band gap (El-Khodary, 2010).The absorption coefficients just below the fundamental gap can be used to calculate the Urbach energy using following relations (Urbach 1953):

$$\alpha = \alpha_o \exp\left(\frac{h\nu}{E_u}\right) \quad (4)$$

where α_o is a constant and E_u is the Urbach energy interpreted as the width of the tails of the localized state in the forbidden gap. The exponential dependence of α on the photon energy ($h\nu$) for the investigated samples indicates that it obeys Urbach's formula. The Urbach plot is presented in Fig.6, in which the natural logarithm of absorption coefficient α was plotted as a function of photon energy ($h\nu$). The magnitudes of the Urbach energy E_u were estimated, by taking the reciprocal of the slopes of the linear portion. The optical band gap and band tails of the localized state of the samples are summarized in Table I.

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The Urbach energy tail E_u was found to be proportional to the Cr_2S_3 concentration in PVA/Cr_2S_3 nanocomposites. Increasing Cr_2S_3 content may cause the localized states to overlap and extend into the mobility gap in the polymeric matrix (Reda, and Zahrani 2012; Abdelrazek, et al., 2013). The observed increase in the Urbach energy with increasing Cr_2S_3 concentration, correlated with the decrease of the energy gap, and absorption edge accordingly.

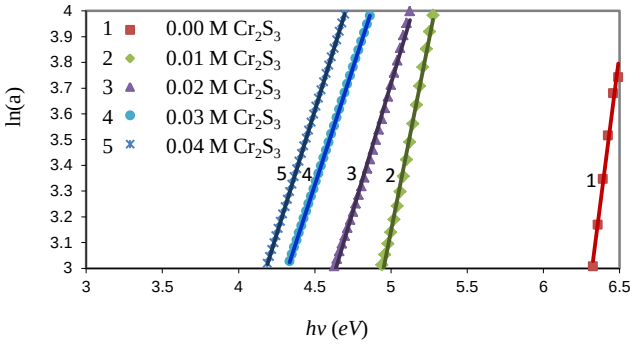

Fig. 6. The relation between *ln(α)* and photon energy (*hν*), for PVA at different Cr_2S_3 nanoparticles concentration.

TABLE I
VALUES OF THE ABSORPTION EDGE (E_E), DIRECT ENEGRGY GAP (E_C), FOR PVA/Cr_2S_3 NANOCOMPOSITE, ENERGY GAP OF Cr_2S_3 NANOPARTICLES (*EN*) AND BAND TAIL ENERGY (*EU*)

Cr_2S_3 (M)	E_e (eV)	E_d (eV)	E_n (eV)	E_u (eV)
0.00	6.17	6.10	-	0.216
0.01	4.93	4.69	2.50	0.336
0.02	4.67	4.47	2.44	0.503
0.03	4.33	4.17	2.43	0.550
0.04	4.13	4.04	2.40	0.523

IV. CONCLUSIONS

Chemical reduction rote and solution cast method and have been used to prepare polymer nanocomposite films of PVA with different concentrations of Cr_2S_3 nanoparticles, and their optical properties have been investigated. The absorbance, absorption coefficient, extinction coefficient, and refraction index of Cr_2S_3 doped PVA films increase with increasing of doping concentration. The decreasing trend of the optical band gap of nanocomposite, with increasing the Cr_2S_3 nanoparticles concentration, was attributed to formation charge transfer complexes, while the increase of Urbach energy suggests the presence of the deeps localized state in the band gaps. The decrease of the optical band gap of nanoparticle upon increasing Cr_2S_3 additions suggested the smaller Cr_2S_3 nanoparticles were synthesized in a small amount of Cr salt.

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