Optical Properties of the Synthesized Cr$_2$S$_3$ Nanoparticles Embedded in Polyvinyl Alcohol

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Abstract—Polyvinyl alcohol (PVA) based nanocomposite, with different concentrations of chromium sulfide Cr$_2$S$_3$ nanoparticles, were prepared by reduction of Cr(NO$_3$)$_3$ and Na$_2$S in an aqueous PVA solution, using the chemical reduction route, and casting technique. Effect of Cr$_2$S$_3$ 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$_2$S$_3$ 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$_2$S$_3$; while the Urbach tail increased from (0.216 eV) for pure PVA to (0.523 eV) for 0.04M Cr$_2$S$_3$. The significant change of the optical properties of PVA with embedded Cr$_2$S$_3$ nanoparticles suggested their applicability in optical devices.

Index Terms—Cr$_2$S$_3$ 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$_2$S reaction to produce nano Cr$_2$S$_3$/polymer nanocomposite. The characterization and analysis focused on the influence of Cr$_2$S$_3$ 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$_2$S (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$_2$S$_3$ was according to the following reaction:

\[\text{Cr}^{3+} + 3 \text{S}^{2-} \rightarrow \text{Cr}_2\text{S}_3\]
2Cr(NO₃)₃ + 3Na₂S → Cr₂S₃ (solid) + 6NaNO₃ (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 Cr₂S₃. 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 Cr₂S₃, 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 Cr₂S₃ nanoparticles (Massoumi, et al. 2013). The SPR bands of the nanoparticle are sensitive to the shape and size of the particle (Noguez 2007; El-Broloosy, et al. 2008). The intensity of these bands increases with increasing salt concentration providing evidence for the incorporation of the Cr₂S₃ 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 Cr₂S₃ confirm the increase of the average size of nanoparticles (Deshmukh, et al. 2012).

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):

\[ \alpha = \frac{2.303A}{d} \]

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 Cr₂S₃/PVA nanocomposite samples. The absorption coefficient increases with the increasing of Cr₂S₃ concentration.

![Fig. 2. The optical absorption coefficient for pure PVA and PVA/Cr₂S₃ nanocomposite.](image)

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):

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

where \( k = \alpha \lambda/4\pi \) is the extinction coefficient, \( \lambda \) 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 Cr₂S₃ 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.
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):

\[
\alpha = B \left( \frac{h\nu - E_g}{h\nu} \right)^r
\]

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 \((ah\nu)^{1/2}\) versus 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\(_2\)S\(_3\) nanocomposite and Cr\(_2\)S\(_3\) nanoparticles. The values of optical energy band gaps are given in Table I. The obtained data revealed that the optical energy band gap decrease significantly with increasing nano Cr\(_2\)S\(_3\) 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).

\[
\alpha = \alpha_o \exp \left( \frac{h\nu}{E_u} \right)
\]

where \( \alpha_o \) 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 \( \alpha \) 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 \( \alpha \) 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.
The Urbach energy tail $E_u$ was found to be proportional to the Cr$_2$S$_3$ concentration in PVA/Cr$_2$S$_3$ nanocomposites. Increasing Cr$_2$S$_3$ 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$_2$S$_3$ concentration, correlated with the decrease of the energy gap, and absorption edge accordingly.

![Graph](http://dx.doi.org/10.14500/aro.10067)

Fig. 6. The relation between $ln(a)$ and photon energy ($hν$), for PVA at different Cr$_2$S$_3$ nanoparticles concentration.

### Table I

<table>
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<tr>
<th>Cr$_2$S$_3$ (M)</th>
<th>$E_g$ (eV)</th>
<th>$E_x$ (eV)</th>
<th>$E_u$ (eV)</th>
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### IV. Conclusions

Chemical reduction route and solution cast method have been used to prepare polymer nanocomposite films of PVA with different concentrations of Cr$_2$S$_3$ nanoparticles, and their optical properties have been investigated. The absorbance, absorption coefficient, extinction coefficient, and refraction index of Cr$_2$S$_3$ doped PVA films increase with increasing of doping concentration. The decreasing trend of the optical band gap of nanocomposite, with increasing the Cr$_2$S$_3$ nanoparticles concentration, was attributed to formation charge transfer complexes, while the increase of Urbach energy suggests the presence of the deep localized state in the band gaps. The decrease of the optical band gap of nanoparticle upon increasing Cr$_2$S$_3$ additions suggested the smaller Cr$_2$S$_3$ nanoparticles were synthesized in a small amount of Cr salt.

### Acknowledgment

The authors express their gratefulness to the School of Science, University of Sulaimani, for the facilities and financial support.

### References


