



# Optical Properties of Polyvinyl Alcohol (PVA) / Silver Sulfide Polymer Composites

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## Abstract

In this work silver sulfide ( $\text{Ag}_2\text{S}$ ) has been synthesized inside the PVA polymer by in situ chemical reduction method. The UV-Visible spectrophotometer was used to study the optical properties of the prepared composite samples. The absorption spectra reveal the influence of  $\text{Ag}_2\text{S}$  particles on optical behavior of PVA. There is an increase in refractive index of the samples contains  $\text{Ag}_2\text{S}$  filler, and exhibits a dispersion behavior. The extinction coefficients of the composite samples are higher than that of pure PVA. The linear relationship between the refractive index at high wavelength region and  $\text{Ag}_2\text{S}$  concentration was observed, indicating homogeneous dispersion of the filler in the PVA matrix. The absorption coefficient shifts to lower photon energy at higher  $\text{Ag}_2\text{S}$  concentration, in which the optical band gap will reduce.

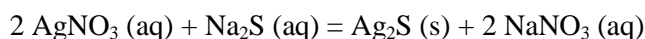
## 1. Introduction

The study of polymer composite materials by means of optical absorption provides simple methods for explaining some features concerning the band structure and optical energy band gap of materials [1], they have attracted much attention due to their enhanced optical and electronic properties [2,3]. PVA is used as glue and exhibits good emulsify and film forming properties, it is also resistant to grease, oil and solvents [3]. When a metal sulfide is doped on a transparent polymer like PVA, the resulting composites are expected to be used for electronic and optical device application [4,5]. Among the metal sulfides, Silver sulfide ( $\text{Ag}_2\text{S}$ ) is an important inorganic compound because of their technological applications [6]. In the past decade,  $\text{Ag}_2\text{S}$  has been studied for its numerous applications such as promising material for solar cell application [7]. There is a growing interest in  $\text{Ag}_2\text{S}$  films because of their unique electrical [8,9], optical [10], photovoltaic [11], and thermoelectric properties [12,13]. These unique properties suggest potentially broad application of  $\text{Ag}_2\text{S}$  films in various devices such as solar cells, superionic conductors and semiconductors, microwave shielding coating, photodetectors, photothermal conversion, electroconductive electrodes, gas sensors at room temperature and the polarizer of infrared radiation [14,15].

$\text{Ag}_2\text{S}$  semiconductor is a good prospective photoelectric and thermoelectric material, and many works have been done on it [16,17]. In the present investigation, we reported the fabrication of  $\text{Ag}_2\text{S}$  in an aqueous solution of PVA, using in situ chemical reduction method. The effect of synthesized  $\text{Ag}_2\text{S}$  on optical parameters of PVA polymer are also investigated using UV-Visible Spectrometer.

## 2. Experimental details

The raw materials utilized in the present work to synthesise the  $\text{Ag}_2\text{S}$  filler are silver nitrate ( $\text{AgNO}_3$ ) and sodium sulphide ( $\text{Na}_2\text{S}$ ) without further purification. In this work, PVA is used as a host polymer and as a capping material. For this purpose, 2 g of low molecular weight PVA (supplied by Alfa Aesar) was fixed and dissolved in 30 mL of distilled water at  $90^\circ\text{C}$  for one hour.  $\text{AgNO}_3$  and  $\text{Na}_2\text{S}$  as a source of  $\text{Ag}^{1+}$  and  $\text{S}^{2-}$  ions respectively, were dissolved in the 5 mL of distilled water separately at room temperature. Different molar concentrations of (0.01, 0.02, 0.03 and 0.04 M) has been used to prepare PVA-based polymer composites. To obtain the  $\text{Ag}_2\text{S}$  filler, the two solutions with ration 2:1 were incorporated into the homogeneous PVA solution at room temperature under stirring. The chemical reaction for the  $\text{Ag}_2\text{S}$  formation is given by:



The change of color of the solution from colorless to black demonstrates the formation of  $\text{Ag}_2\text{S}$  component. To get a homogenous dispersion, the mixture was further stirred continuously for 30 min without heating. The resulting solution was cast onto plastic Petri dish and allowed to dry slowly at room temperature for films to form. The optical absorption spectra of synthesized polymer composite films were recorded using the double beam UV-Visible-NIR spectrophotometer (Model: Lambda 25) in the wavelength range (190-1100) nm.

## 3. Results and Discussion

Figure (1) shows the optical absorbance spectra for pure PVA and PVA/ $\text{Ag}_2\text{S}$  composite films with different concentrations, which are measured at room temperature at the normal incident as a function of wavelength in the spectral range from 190 nm up to 1100 nm. It is clearly observable from the pure PVA curve that there is no remarkable absorption in the visible region with a wavelength above 400 nm, as compared to the UV region. The sharp decreases in the UV region can be observed in the absorption spectra in the range of (190 – 220) nm for pure PVA and is shifted to higher wavelength for the doped samples, which can be correlated with the optical band gap.

The optical absorbance of the pure PVA and PVA/ $\text{Ag}_2\text{S}$  composites near the fundamental absorption edge was found to be exponentially decreases with increase in wavelength. The sharp decrease observed in absorbance spectrum indicates the presence of the optical band gap of the material, which arises from the electronic transitions between the localized states, which have tailed off in the band gap [18,19].

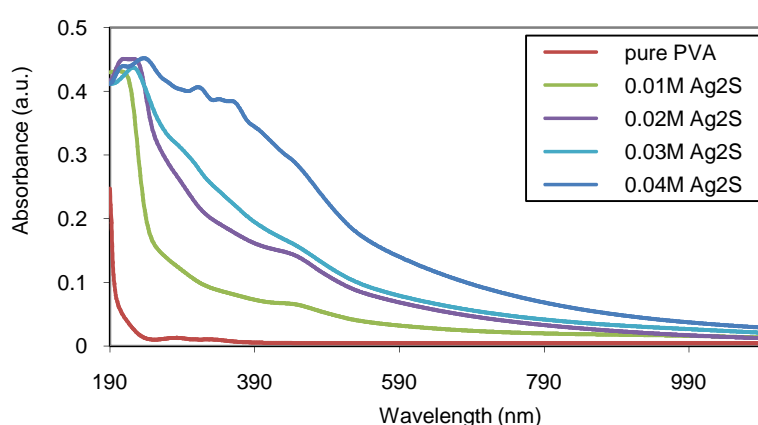


Figure (1): Absorbance versus wavelength for PVA/ $\text{Ag}_2\text{S}$  polymer composite.

The optical measurements constitute the most important means of determining the band structures. The optical behavior of materials is generally utilized to determine its optical constants. Both of the optical constants, refractive index ( $n$ ) and extinction coefficient ( $k$ ), represent fundamental properties of a material not only because of their relation to the electronic structure but also due to their applications in many

integrated optical devices [20]. The optical properties of composite materials can be expressed by using the concepts of refractive index ( $n$ ) and extinction coefficient ( $k$ ) through the following relations [18]:

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

$$k = \frac{\alpha\lambda}{4\pi} \quad (2)$$

where  $\lambda$  is the wavelength of incident photon,  $\alpha$  absorption coefficient, and  $R$  the reflectance, which calculated from the relation ( $R + A + T = 1$ ), where  $A$  represents absorption and  $T$  represent transmittance. In order to determine the extinction coefficient of the films, the absorption coefficient  $\alpha$  was determined based on the Lambert-Beer formula [21]:

$$\alpha = \frac{2.303A}{d} \quad (3)$$

where  $A$  is the absorbance and  $d$  is the film thickness.

Figure (2) shows the variation of refractive index ( $n$ ) as a function of wavelength for PVA/Ag<sub>2</sub>S polymer composite with different concentration of Ag<sub>2</sub>S. The refractive index gradually decreases with the increase in wavelength, whereas it increases with the increase in Ag<sub>2</sub>S concentration. It was also noticed that the highest value for the refractive index is 2.64 for 0.04M Ag<sub>2</sub>S. The peak value of refractive index move towards the higher wavelength values as the Ag<sub>2</sub>S concentration increases.

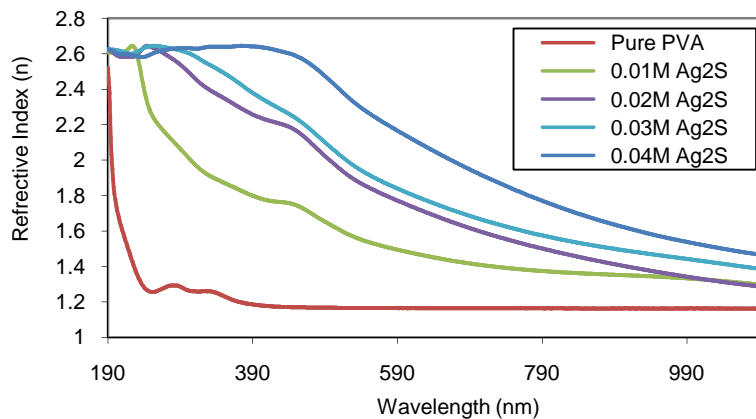


Figure (2): Refractive index versus wavelength for PVA/Ag<sub>2</sub>S polymer composite.

The extinction coefficient ( $k$ ) is a measure of the fraction of light lost due to scattering and absorption per unit distance of the penetration medium [22]. Figure (3) represents a variation in the extinction coefficient ( $k$ ) as a function of wavelength for PVA/Ag<sub>2</sub>S polymer composite with different concentration of Ag<sub>2</sub>S. It was observed that the value of the extinction coefficient have the same trends of absorbance spectra. This can be interpreted by saying that the increase in the value of the absorption coefficient directly affects the value of the extinction coefficient. The decrease in the extinction coefficient with an increase in wavelength of all samples shows that the fraction of light lost due to scattering [23].

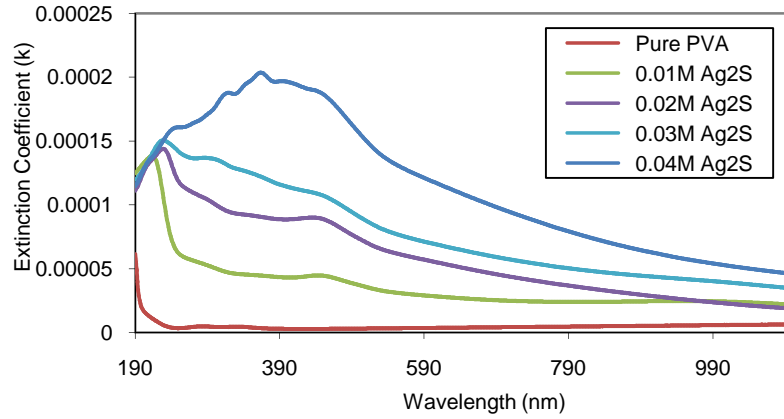


Figure (3): Extinction coefficient versus wavelength for PVA/Ag<sub>2</sub>S polymer composite.

Figure (4) represents the plot of the refractive index at high wavelength region against the Ag<sub>2</sub>S concentration. The values of refractive index of the samples are obtained from the intersection of the plateau (high wavelength region) of the figure (2) on the Y-axis (refractive index axis). It can be seen that the refractive index increased linearly with increasing the Ag<sub>2</sub>S concentration. It was reported that the linear behaviour between refractive index and volume fraction of filler can be attributable to the homogeneous dispersion of the filler inside the host polymer [24]. The linear dependence of the refractive index in polymeric composite materials with filler loading has been reported both from experimental measurements and theoretical modeling [25,26]. The regression value is (0.958) as exhibited in figure (4) indicates a well fitting between the data points.

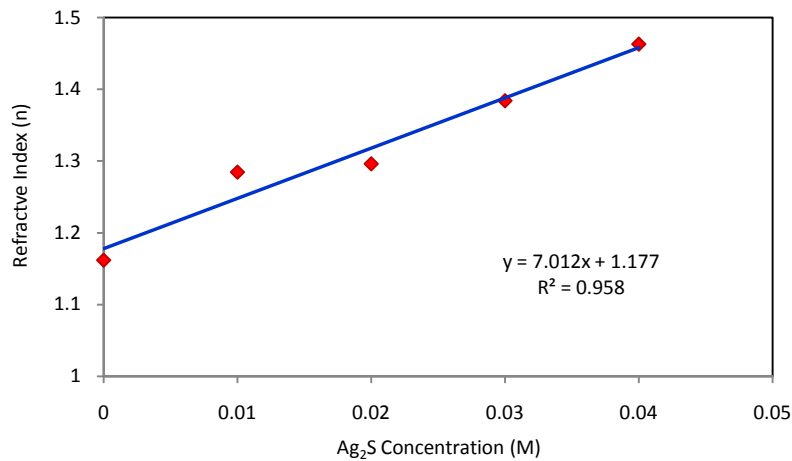


Figure (4): Refractive index (n) at high wavelength region as a function of Ag<sub>2</sub>S concentration.

One of the most important factors in developing the electronic band structure of composite film materials is a determination of their band gap energy [27]. The band gap energy of a material is defined as the energy distance between the valence band and conduction band and is one of the fundamental optical parameters that explain the optical absorption. The smaller the band gap, the more electrically conductive material will be [28]. According to the Davis and Mott model [29] near the fundamental band edge, the optical energy band gap  $E_g$  for the investigated films can be determined by using the Tauc's equation [30]:

$$\alpha h\nu = \beta(h\nu - E_g)^\gamma \quad (4)$$

where  $\beta$  is a constant,  $\gamma$  is an index, which take the values 1/2, 3/2, 2 or 3, depending on the nature of the electronic transition responsible for absorption mechanism of electron transition. The exponent value equal to 1/2, or 3/2 for allowed or forbidden direct transition in the quantum mechanical sense, and equal to 2, or 3 for allowed and forbidden indirect transition, respectively [31,32].

Figure (5) shows the relation between  $(\alpha h\nu)^2$  versus incident photon energy ( $h\nu$ ) (often referred to as a Tauc plot [18]) The value of direct optical energy band gap has been determined by the extrapolation of the best fit line to the intercept of the energy axis at  $(\alpha h\nu)^2 = 0$ .

The energy gap of pure PVA sample is equal to 6.27 eV, and with increasing the  $\text{Ag}_2\text{S}$  concentration in the PVA matrix, the band gap energy is decreased. The extracted band gap energy of PVA/ $\text{Ag}_2\text{S}$  samples are (4.83, 3.57, 3.12, and 2.43 eV) for composite samples with (0.01, 0.02, 0.03, 0.04 M)  $\text{Ag}_2\text{S}$  concentration, respectively.

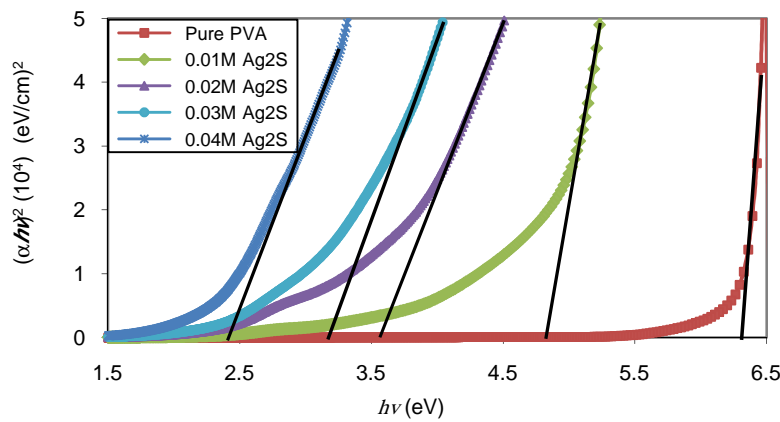


Figure (5): The value of  $(\alpha h\nu)^2$  versus  $(h\nu)$  for PVA/ $\text{Ag}_2\text{S}$  polymer composite.

The significant reduction of optical energy gap by increasing  $\text{Ag}_2\text{S}$  content was attributed to the interaction between polymer chains and  $\text{Ag}_2\text{S}$  particles which lowering the Fermi level and consequently affecting the energy gap [28]. Another reason was the increase in the degree of disorder in the network and broadening in the band tails in the localized electronic states [33].

Thus, the present work indicates that  $\text{Ag}_2\text{S}$  dispersion tunes the optical band gap of PVA significantly and consequently makes the PVA/ $\text{Ag}_2\text{S}$  composite film more useful in wide variety of optoelectronic device.

#### 4. Conclusion

We have introduced modified optical properties of PVA polymer by embedded  $\text{Ag}_2\text{S}$  inside it.  $\text{Ag}_2\text{S}$  particles cause a significant shift of absorption spectra to higher wavelengths. There was an increase in the absorption coefficient and refractive index of the composites as compared to pure PVA, in which the latter causes to increase the extinction coefficients and the former, can be ascribed to the increase in carrier density. The refractive index of the samples composite exhibits a dispersion behavior. The extinction coefficients of the composite samples are higher than that of pure PVA. The optical band gap of PVA significantly reduced from 6.27 to 2.43 eV.

## References

- [1] O.Gh. Abdullah, D.R. Saber, "Optical absorption of polyvinyl alcohol films doped with nickel chloride", *Applied Mechanics and Materials* Vol. 110-116, pp 177-182, (2012).
- [2] B.O. Dabbousi, M.G. Bawendi, O. Onitsuka, M.F. Rubner, "Electroluminescence from CdSequantumdot/polymer composites", *Appl. Phys. Lett.* Vol. 66, pp 1316-1318, (1995).
- [3] V.L. Colvin, M.C. Schlamp, A.P. Allvisatos, "Light-emitting diodes made from cadmium selenide nanocrystals and a semiconducting polymer", *Nature* 370, pp 354-357, (1994).
- [4] I. Grozdanov, M. Najdoski, "Optical and Electrical Properties of Copper Sulfide Films of Variable Composition", *Journal of Solid State Chemistry* Vol.114, pp 469-475, (1995).
- [5] S. Mizogami, H. Miyamoto, "Electrical and electromagnetic shielding properties of surface conducting polymer coated with Cu<sub>x</sub>S thin layer", *Synthetic Metals*, Vol, 57, pp 3661-3664, (1993).
- [6] R.V. Kumar, O. Palchik, Y. Koltypin, Y. Diamant, A. Gedanken, "Sonochemical synthesis and characterization of Ag<sub>2</sub>S/PVA and CuS/PVA nanocomposite", *Ultrasonics Sonochemistry* Vol.9, pp 65-70, (2002).
- [7] Xing-yuGuo, Shu-ying Cheng, Pei-min Lu, Hai-fang Zhou, "Preparation of Ag<sub>2</sub>S thin films by electro-deposition", *Materials Science Forum*, Vol. 663-665, pp 910-913, (2011).
- [8] S.S. Dhumure, C.D. Lokhande, "Studies on the preparation and characterization of chemically deposited Ag<sub>2</sub>S films from an acidic bath", *Thin Solid Films*, Vol. 240, pp 1-6, (1994).
- [9] B.R. Sankapal, R.S. Mane, C.D. Lokhande, "A new chemical method for the preparation of Ag<sub>2</sub>S thin films", *Materials Chemistry and Physics*, Vol.63, pp 226-229, (2000).
- [10] I.A. Ezenwa, N.A. Okereke, N.J. Egwunyenga, "Optical properties of chemical bath deposited Ag<sub>2</sub>S thin films", *International Journal of Science and Technology*, Vol.2, pp 101-106, (2012).
- [11] T.B. Nasrallah, H. Dlala, M. Amlouk, S. Belgacem, J.C. Bernede, "Some physical investigations on Ag<sub>2</sub>S thin films prepared by sequential thermal evaporation", *Synthetic Metals*, Vol. 151, pp 225-230, (2005).
- [12] M.C. Brelle, J.Z. Zhang, "Femtosecond study of photo-induced electron dynamics in AgI and core/shell structured AgI/Ag<sub>2</sub>S and AgBr/Ag<sub>2</sub>S colloidal nanoparticles", *Journal of Chemical Physics*, Vol.108, pp 3119-3126, (1998).
- [13] J.A. Munoz, C. Gomez, A. Ballester, M.L. Blazquez, F. Gonzalez, M. Figueroa, "Electrochemical behaviour of chalcopyrite in the presence of silver and Sulfolobus bacteria", *Journal of Applied Electrochemistry*, Vol. 28, pp 49-56, (1998).
- [14] A.P. Yadav, R.R. Pradhanang, "Preparation and characterization of silver sulphide/silver iodide ion selective electrodes for the determination of I<sup>-</sup>, S<sup>2-</sup> and Ag<sup>+</sup> ions", *Journal of Nepal Chemical Society*, Vol.15, pp 19-26, (1996).
- [15] Y. Umezawa, P. Buhlmann, K. Umezawa, K. Tohda, S. Amemiya, "Potentiometric selectivity coefficients of ion-selective electrodes part I. Inorganic Cations", *Pure and Applied Chemistry*, Vol.72, pp 1851-2082, (2000).
- [16] X.F. Qian, J. Yin, J.C. Huang, Y.F. Yang, X.X. Guo, Z.K. Zhu, "The preparation and characterization of PVA/Ag<sub>2</sub>S nanocomposite", *Materials Chemistry and Physics* Vol.68, pp 95-97, (2001).
- [17] C. Wang, X. Zhang, X. Qian, W. Wang, Y. Qian, "Ultrafine powder of silver sulfide semiconductor prepared in alcohol solution", *Materials Research Bulletin* Vol.33, pp 1083-1086, (1998).
- [18] O.Gh. Abdullah, S.B. Aziz, K.M. Omer, Y.M. Salih, "Reducing the optical band gap of polyvinyl alcohol (PVA) based nanocomposite", *Journal of Materials Science: Materials in Electronics*, Vol.26, pp 5303-5309, (2015).
- [19] A.N. Ananth, S. Umapathy, J. Sophia, T. Mathavan, D. Mangalaraj, "On the optical and thermal properties of in situ/ex situ reduced Ag NP's/PVA composites and its role as a simple SPR-based protein sensor", *Applied Nanoscience*, Vol.1, pp 87-96, (2011).
- [20] V. Pamukchieva, A. Szekeres, "Optical properties of GexSb<sub>20-x</sub>Te<sub>80</sub> thin films and their changes by light illumination", *Optical Materials* Vol. 30, pp 1088-1092, (2008).

- [21] O.Gh. Abdullah, S.A. Hussien, A. Alani, "Electrical characterization of polyvinyl alcohol films doped with sodium iodide", *Asian Transactions on Science & Technology*, Vol.1, pp 1-4, (2011).
- [22] O.Gh. Abdullah, D.A. Tahir, K. Kadir, "Optical and structural investigation of synthesized PVA/PbSnanocomposites", *Journal of Materials Science: Materials in Electronics*, Vol. 26, pp 6939-6944, (2015).
- [23] O.W. Guirguis, M.T.H. Moselhey, "Optical study of poly(vinyl alcohol)/ hydroxypropyl methylcellulose blends", *J Mater Sci* Vol.64, pp 5775-5789, (2011).
- [24] S.B. Aziz, H.M. Ahmed, A.M. Hussein, A.B. Fathulla, R.M. Wsw, R.T. Hussein, "Tuning the absorption of ultraviolet spectra and optical parameters of aluminum doped PVA based solid polymer composites", *J. Mater. Sci. Mater. Electron.* Vol. 26, pp 8022-8028, (2015).
- [25] J. Jin, R. Qi, Y. Su, M. Tong, J. Zhu, "Preparation of high-refractive-index PMMA/TiO<sub>2</sub> nanocomposites by one-step in situ solvothermal method", *Iran. Polym. J.* 22 (2013) 767-774.
- [26] Y.Q. Rao, S. Chen, "Molecular composites comprising TiO<sub>2</sub> and their optical properties", *Macromolecules* Vol.41, pp 4838-4844, (2008).
- [27] S.B. Aziz, R.T. Abdulwahid, H.A. Rsaul, H.M. Ahmed, "In situ synthesis of CuS nanoparticle with a distinguishable SPR peak in NIR region", *Journal of Materials Science: Materials in Electronics*, (2016), DOI: 10.1007/s10854-016-4278-y
- [28] J. Rozra, I. Saini, A. Sharma, N. Chandak, S. Aggarwal, R. Dhiman, P.K. Sharma, "Cu nanoparticles induced structural, optical and electrical modification in PVA", *Materials Chemistry and Physics*, Vol. 134, pp 1121-1126, (2012).
- [29] E.A. Davis, N.F. Mott, "Conduction in non-crystalline systems V. Conductivity, optical absorption and photoconductivity in amorphous semiconductors", *Philosophical Magazine* Vol.22, pp 903-922, (1970).
- [30] J. Tauc, "Amorphous and Liquid Semiconductors", Plenum Press, London and New York, (1974).
- [31] F. Urbach, "The Long-Wavelength Edge of Photographic Sensitivity and of the Electronic Absorption of Solids", *Journal of Physical Review*, Vol.92, pp 627-636, (1953).
- [32] S.F. Bdewi, O.Gh. Abdullah, B.K. Aziz, A.A.R. Mutar, "Synthesis, Structural and Optical Characterization of MgONanocrystalline Embedded in PVA Matrix", *Journal of Inorganic and Organometallic Polymers and Materials*, (2016), DOI: 10.1007/s10904-015-0321-3
- [33] M.K. El-Mansy, E.M. Sheha, K.R. Patel, G.D. Sharm, "Characterization of PVA/CuI polymer composites as electron donor for photovoltaic application", *Optik*, Vol. 124, pp 1624-1631, (2013).

