

# STRUCTURAL AND OPTICAL STUDIES OF CONDUCTING PANI/CuS NANOCOMPOSITES ON NANOCRYSTALLINE ZINC-OXIDE THIN FILM

<sup>1</sup>Sangamesha, M.A., <sup>1</sup>K. Pushpalatha and <sup>2</sup>G.L. Shekar

<sup>1</sup>Department of Chemistry, The National Institute of Engineering, Mysore, India

<sup>2</sup>Department of Industrial Production and Engineering, The National Institute of Engineering, Mysore, India

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## ABSTRACT

In this article, a p-n heterostructure diode was developed by incorporating the synthesised nanocomposite of CuS/PANI into the hallow network of ZnO thin film deposited on the glass substrate, which hitherto not reported. Analyses of the obtained heterostructure were carried out using XRD, FT-IR, UV-Visible and SEM. The penetration, bonding and the interaction of the nanocomposite with ZnO was investigated by the morphological, structural and optical studies. The obtained new hybrid material was found to have very good absorption in near IR region and results obtained supports that it may be used for different nanoelectronic devices.

**Keywords:** Polyaniline, Thin Films, Nanocomposite, Conducting Polymer

## 1. INTRODUCTION

For a polymer to become electrically conductive, it must imitate the metal, which means that electrons in polymers must be free to move. The electrical property of polymeric materials has become an increasingly interesting area of research because these materials possess a great potential for solid state devices (Xiao *et al.*, 2011; Dong *et al.*, 2011; MacDiarmid, 2001). Conducting polymers (Reda and Al-Ghannam, 2013) are semiconductors and their band gaps could be tuned by altering the chemical nature of either the polymer backbone or the side groups present in the polymeric chain. The overlapping of the molecular orbital for the formation of the delocalized molecular wave functions and the partially filled molecular orbital for a free movement of electrons throughout the polymeric structure are the basic requirements for the polymers to become conductors. Conducting polymers have a great interest due to high mobility of the charge carriers and as excellent hosts for the trapping of metals and semiconducting

nanoparticles. The development of conducting polymers such as polyaniline, polypyrrole, polythiophene, polyphenylene etc, has increased tremendously during the last decade, among them, polyaniline is one of the most important conducting polymer because of its flexibility, light weight, easy preparation and doping process, environmental stability, its potential application in electrochromic devices, sensors, anticorrosion coatings, photochemical devices (Chang *et al.*, 2010) etc. PANI is a stable conducting polymer with unique electronic properties which can be controlled by protonation as well as by varying the oxidation state of the main chain. These properties turned PANI as more attractive to use in various applications. The investigations have showed that it can be an excellent matrix for forming polymer-nanomaterials composites (Kong *et al.*, 2008). The properties of PANI largely depend on the structure of the polymeric backbone and the packing of the polymer chains. Furthermore, it is reported elsewhere that conductivity of PANI also depends on the chain length morphology (Zhang *et al.*, 2002), texture and degree of

\*Corresponding Author: Pushpalatha, K., Department of Chemistry, The National Institute of Engineering, Mysore-570008, Karnataka, India

crystallization of the polymer film. In the recent past, the conducting polymer based nanocomposites have drawn attention in many applications, also organic semiconductor solar cells are the 3rd generation of photovoltaic devices finds much importance in the field of research. Since, PANI/CuS nanocomposite is a p-type semiconductor (Ramesan, 2014), it can be used as a multifunctional material for nano electronic devices (Ameen *et al.*, 2009). Herein to fabricate hybrid materials, the inorganic components are dispersed in the organic matrix. Further, the Transparent Conducting Oxides (TCO's) have long been a subject of various investigations due to its unique physical properties and applications in commercial devices. These transparent metallic oxides include in part, Indium-oxide, Tin oxide, Indium Tin Oxide (ITO), Cadmium Tin Oxide, Zinc-Oxide (ZnO) etc. Among these, ZnO belongs to a member of hexagonal Wurtzite class and an n-type semi conducting material due to oxygen vacancies and/or interstitial Zinc, which involves in the formation of a charge depletion layer on the surface due to electron trapping at adsorbed oxygen species (Law and Thong, 2008; Franke *et al.*, 2006). This has potential application in solar cells because of well crystallized high transmittance. Due to wide-band gap, this can absorb only a small part of visible light. Therefore it is necessary to sensitize the ZnO nanoparticles deposited as thin film on glass substrate.

In the present work, attempts have been made to synthesize a nanocomposite using CuS and PANI, later it is inserted in the hallow network of ZnO thin film deposited on glass substrate which is hitherto not reported. The characterization of the hybrid structure was carried out by X-ray diffraction, Fourier Transform Infrared Spectroscopy, UV-Visible Spectroscopy and Scanning Electron Microscopy (SEM).

## 2. EXPERIMENTAL

### 2.1. Materials

Copper Chloride ( $\text{CuCl}_2 \cdot \text{H}_2\text{O}$ ), Sodium thiosulphate ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ), HCl, Sodium Dodecyl Sulphate (SDS) ( $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$ ), Hexa Methyl Tetramine (HMT) ( $(\text{CH}_2)_6\text{N}_4$ ), Ammonium Persulphate (APS) ( $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ) and Zinc Nitrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) were used as they received from the market. Aniline ( $\text{C}_6\text{H}_5\text{NH}_2$ ) supplied by Rankem was doubled distilled before use.

### 2.2. Synthesis of Nanocrystalline Copper Sulphide

Copper Sulphide nanoparticles were prepared by a simple Sol-Gel method (Sangamesha *et al.*, 2013a). The reactants such as copper chloride and sodium thiosulphate are mixed in the presence of SDS, which acts as a capping agent, avoids the agglomeration and helps to maintain the uniform size of the nanoparticles. Since, concentration of the reactants also affects the quality of the CuS nanoparticles (Sangamesha *et al.*, 2013b; Kassim *et al.*, 2011), equi volumes of  $\text{CuCl}_2$  (0.2 M) and sodium thiosulphate (0.2 M) are used for the synthesis. SDS was added slowly with constant stirring to the  $\text{CuCl}_2$  (0.2 M) solution taken in a 250 mL beaker and stirred for 2 h using magnetic stirrer. Subsequently, Sodium thiosulphate solution was added drop wise for the formation of nanocrystalline copper sulphide. The resultant solution was stirred for 13-14 h, then filtered and washed several times with distilled water, followed by acetone and dried at  $60^\circ\text{C}$ .

### 2.3. Synthesis of PANI (Polyaniline)

Polyaniline was synthesized by chemical oxidative polymerization of aniline in the presence of hydrochloric acid and ammonium persulphate (Pawar *et al.*, 2010). For the synthesis of PANI 50 mL of 1N HCl was taken in a 250 mL beaker and 2 mL aniline was added at room temperature with constant stirring. Ammonium persulphate solution (5 g in 50 mL of 1N HCl) and the aniline solution were cooled separately to  $\sim 0^\circ\text{C}$  using ice. The persulphate solution was then slowly added drop wise to the aniline with constant stirring. The mixture was stirred continuously for 5 h to complete the polymerization reaction. The precipitate obtained was filtered and washed successively by 1 M HCl and distilled water, later by acetone, then dried in vacuum at  $60^\circ\text{C}$  for 24 h.

### 2.4. Synthesis of PANI/CuS

The CuS nanocrystals prepared as mentioned above, were dispersed in the mixture of HCl (50 mL, 1 M) and aniline (2 mL) and kept agitated for 15-20 min (Ramesan, 2014). APS solution was later added drop wise to the above solution till it turned black colour which indicates the initiation of polymerization reaction. The stirring was continued for 6 h in order to complete the polymerization reaction. Then obtained precipitate of PANI-CuS nanocomposite was filtered and washed repeatedly with water and ethanol then dried in an oven at  $60^\circ\text{C}$  for 1 h.

## 2.5. Synthesis of ZnO/PANI-CuS thin Film

For the preparation of ZnO thin film on glass substrate, 0.01 M Zinc nitrate solution was mixed with HMT slowly with constant stirring until it dissolved completely. Glass substrate was dipped in the above solution maintained at 80°C without stirring (Polsongkram *et al.*, 2008) for 30 min. A thin transparent film formed on the substrate indicates the thin film formation of ZnO (Lee *et al.*, 2014). Later, the reaction bath was cooled to the room temperature, then washed using distilled water and annealed at 150°C for 5 min. CuS doped PANI nanocomposite crystals were dispersed in m-cresol at room temperature and coated using spin coater with 1000 rpm for 60 sec and then annealed in vacuum at 120°C for 1.

## 3. RESULTS

### 3.1. Structural Characterization by X-Ray Diffractometer

X-Ray Diffraction (XRD) analyses of undoped PANI, copper sulphide, ZnO, PANI: CuS nano composite and ZnO/PANI: CuS thin film were carried out using a Bruker powder X-ray diffractometer (Model: D2 phaser), are depicted in **Fig. 1a-e**. The XRD pattern was recorded in the  $2\theta$  range of 20-90° using  $\text{CuK}_\alpha$  radiation ( $\lambda = 1.5406\text{Å}$ ). The observed patterns were in good agreement with the previously reported pattern by other authors (Pawar *et al.*, 2010; Polsongkram *et al.*, 2008; Wanga *et al.*, 2010; Ramesan, 2014). The XRD pattern of PANI (**Fig. 1a**) shows a broad peak at  $2\theta = 25^\circ$  which corresponds to (110) plane (Pawar *et al.*, 2009) and it is the characteristic peak of PANI which is ascribed due to the periodicity in parallel and perpendicular directions of the polymer chains. The sharp and well-defined peaks (**Fig. 1b**) indicate the crystallinity of the synthesized copper sulphide nanoparticles. The observed  $2\theta$  values in **Table 1** indicate the formation of copper sulphide nanoparticles (Wang *et al.*, 2009). The several XRD peaks for ZnO thin film shown in **Fig. 1c**, indicates the random orientation of the crystallites. This nanocomposite exhibits a characteristic peak of PANI along with the crystalline peaks of CuS (**Fig. 1d**), owing to the systematic alignment of the polymer chain. The **Fig. 1e** indicates the obtained hybrid structure of the nano composite in ZnO matrix.

The average particle size was calculated from the Full Width of Half Maximum (FWHM) values of the diffraction peaks using Debye-Scherrer formula (Sangamesha *et al.*, 2013a):

$$D = \frac{0.94\lambda}{\beta \cos \theta} \quad (1)$$

Where:

$D$  = The average crystallite size,

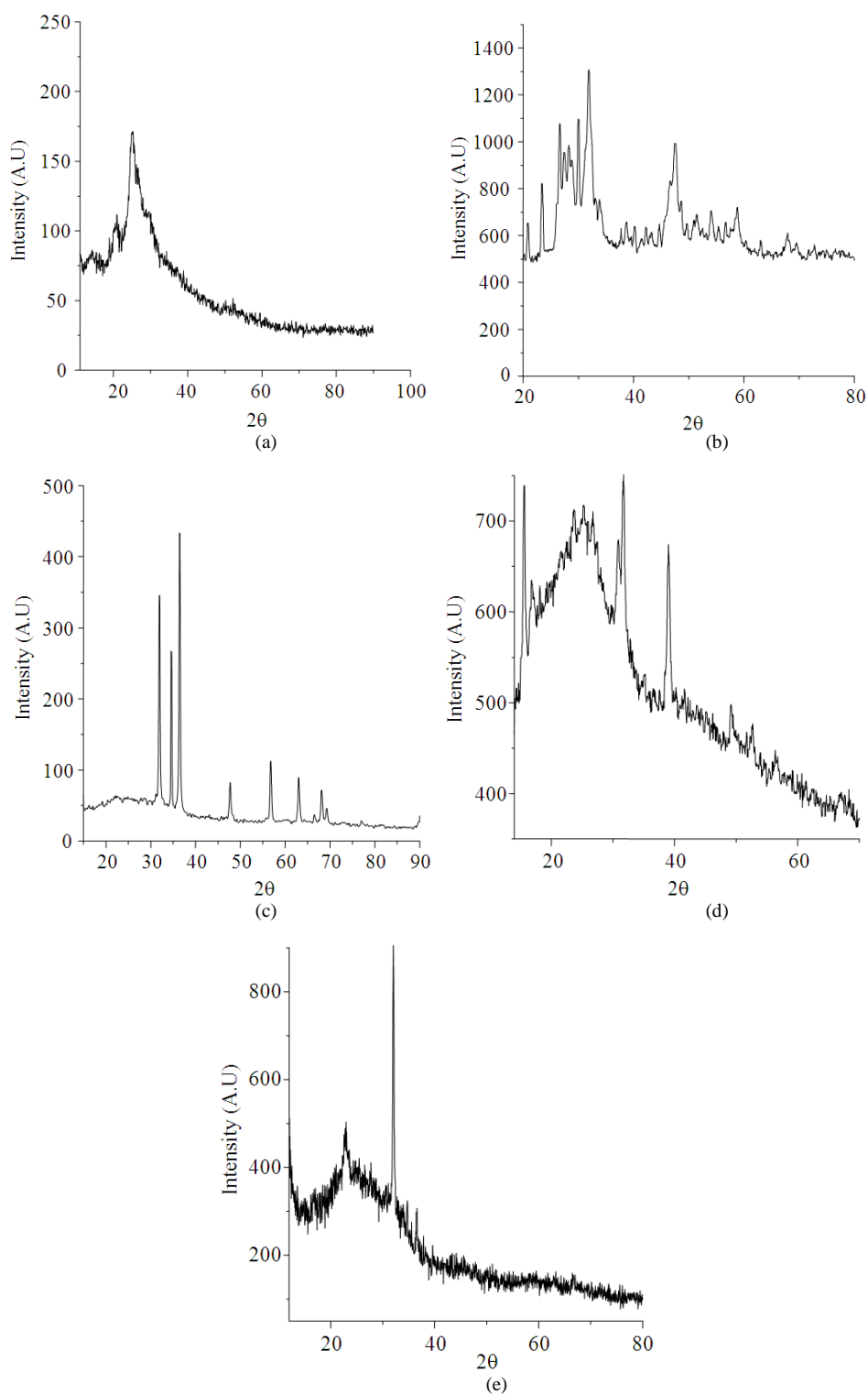
$\lambda$  = The x-ray wavelength of  $\text{CuK}_\alpha$  radiation (0.154 nm),

$\theta$  = The diffraction angle and  $\beta$  the FWHM.

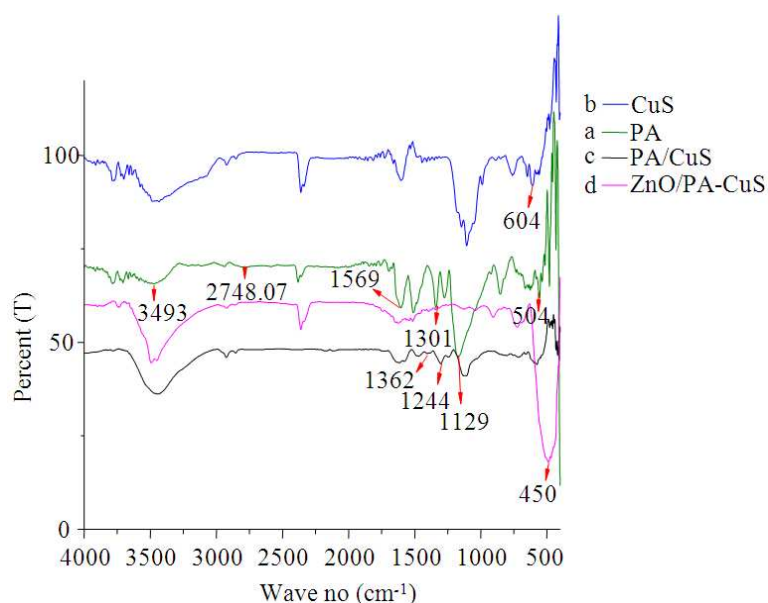
**Table 1** illustrates the size of the nanoparticle calculated from Equation 1. Further, very small crystallite size and strain on the nanoparticles results the appreciable broadening in x-ray diffraction pattern (Sangamesha *et al.*, 2013b).

### 3.2. Structural Studies by FT-IR Spectrometer

Molecular structure of the synthesized samples and composites were obtained by the FT-IR spectroscopy (Agilent technologies, Model: Carry 660) and the graphs obtained are as shown in **Fig. 2a-d**. FT-IR spectroscopy helps to ascertain the type and nature of the bond in the synthesized samples. Formation of the polymers, presence of a functional group on the backbone or change in the protonation or deprotonation equilibrium of emeraldine can be deduced from the corresponding bands in the FT-IR spectrum. Generally metal oxides show the absorption bands below  $1000\text{ cm}^{-1}$  which arise from inter atomic vibrations. In **Fig. 2a**, the peak observed at  $1129.12\text{ cm}^{-1}$  is due to the  $\text{B-NH}^+ = \text{Q}$  vibration, indicates that the PANI is conductive and is in the form of Emeraldine Salt (ES). The absorption bands at 809, 1237, 1301 and  $1569\text{ cm}^{-1}$  are the characteristic peaks of the ES form of PANI. The peak at  $879.38\text{ cm}^{-1}$  shows the evidence of formation of polyaniline with 1,4 substituted phenyl rings. The absorption band at  $1237.11\text{ cm}^{-1}$  refers to quinonoid unit arises due to protonation of PANI (Pawar *et al.*, 2010). The characteristic peaks appearing at 1301.72 and  $1237.11\text{ cm}^{-1}$  is C-N stretching mode of the benzenoid ring and C = N stretching of quinoid units of polyaniline. The peak at 1569.77 and  $1475.28\text{ cm}^{-1}$  corresponds to quinonoid and benzenoid structure of PANI respectively. The polymer shows the absorption around  $2748.07\text{ cm}^{-1}$  is for the aromatic C-H stretching. The C-H out of plane bending mode vibration at  $504\text{ cm}^{-1}$  indicates for the substituted benzene and the peak at  $3493.42\text{ cm}^{-1}$  is due to NH stretching vibrations of aromatic amines. In **Fig. 2b** the prominent sharp and intense spectral band at  $609\text{ cm}^{-1}$  indicates the typical absorption of CuS. The FT-IR spectrum for CuS/PANI is as shown in **Fig. 2c**, in which the peak at  $1129.12\text{ cm}^{-1}$  corresponds to C-H bending and  $807.06\text{ cm}^{-1}$  for C-H stretching are comparable with the reported value (Ramesan, 2014).



**Fig. 1.** X-ray diffraction of (a) PANI (b), CuS, (c) ZnO, (d) PANI:CuS composite, (e) ZnO/PANI: CuS thin film



**Fig. 2.** FT-IR Spectrum of (a) PANI, (b) CuS, (c) PANI/CuS and (d) ZnO/PANI-CuS thin film

The incorporation of CuS nanoparticles to PANI causes changes in the spectrum of the composite. The broad band located at  $1244\text{ cm}^{-1}$  indicates the intermolecular interaction between CuS nanoparticle and electronegative nitrogen of PANI. The characteristic absorption peaks of N-H band of nanocomposite shifted to higher frequency region with a sharp peak. The ordering of nano structured molecular chains results in an ordered regularity in polymer composite that leads to shifting and sharpening of spectral bands (Ramesan, 2014). The FT-IR spectrum of the synthesized ZnO/PANI-CuS, is as shown in **Fig. 2d**, the band around  $450\text{ cm}^{-1}$  due to inter atomic vibrations of ZnO. On comparison with shifted characteristic peaks at around  $1569$  and  $1362\text{ cm}^{-1}$  of PANI and peak around  $600\text{ cm}^{-1}$  of CuS confirms the bonding between the oxide and sulphide groups with imine groups of PANI molecules in ZnO/PANI-CuS. This confirms the PANI-CuS is having strong bonding with the ZnO and the same is also reflected in XRD and SEM results. The peak assignment revealed that the product is of hybrid structure and it contains the doped PANI in the ZnO interface.

### 3.3. Absorption Study by UV-VIS Spectrometer

Ultra Violet-Visible Spectroscopy (UV/VIS) is a powerful technique to characterise the interfacial interaction between the particles and also to study the

optical properties. It involves the spectroscopy of photons in the UV-visible region. It uses light in the Visible, Ultraviolet (UV) and Near Infrared (NIR) ranges. In this region of the electromagnetic spectrum, molecules undergo electronic transitions. The optical studies of PANI, PANI/CuS nanocomposite and ZnO doped with PANI-CuS nanocomposite thin films was carried out using Shimadzu, Model: UV-1800 and the spectra obtained are as shown in the **Fig. 3a-c**. The spectrum of PANI (**Fig. 3a**) shows three distinctive peaks at  $\sim 323\text{ nm}$  which are attributed to the  $\pi\text{-}\pi^*$  transition of the benzenoid ring, shoulder at  $\sim 427\text{ nm}$  is attributed to the transition from valence band to the antibonding polaron state (polaron- $\pi^*$ ) and peak at  $\sim 843\text{ nm}$  indicates the  $\pi$ -polaron transitions (Xia and Wang, 2002; Wu *et al.*, 2008). The spectrum of PANI/CuS composite (**Fig. 3b**) the characteristic of  $\pi\text{-}\pi^*$ , polaron- $\pi^*$  and  $\pi$ -polaron are shows red shift in comparison with pure PANI. It indicates the insertion of nanoparticles with PANI affects the polymer chain interactions. But after the insertion of PANI/CuS composites to ZnO thin films the  $\pi\text{-}\pi^*$  transition shows red shift but  $\pi$ -polaron shows the blue shift. However it can be noted that the peaks of PANI and PANI-CuS appears in ZnO/PANI/CuS thin films (**Fig. 3c**). Further, the absorption is increased after incorporation of CuS/PANI nanoparticles to ZnO hollow network and also resulted in the shift of the

absorption edge towards lower wave length. This may be due to the size effect in the nanostructures.

### 3.4. Surface Analysis

The surface morphology of ZnO and ZnO/PANI-CuS composite thin films were analysed by using Phenom desktop model Scanning Electron Microscope (SEM) and the images obtained are depicted in **Fig. 4a and b** respectively. The pure ZnO thin film shows the network like structure with uniform pores between the networks. ZnO thin film is compact homogeneous and uniformly covered all over the substrate. The hybrid of ZnO/PANI-CuS nano composite (**Fig. 4b**), shows a uniform distribution of the nanocomposite in the ZnO matrix without any agglomeration.

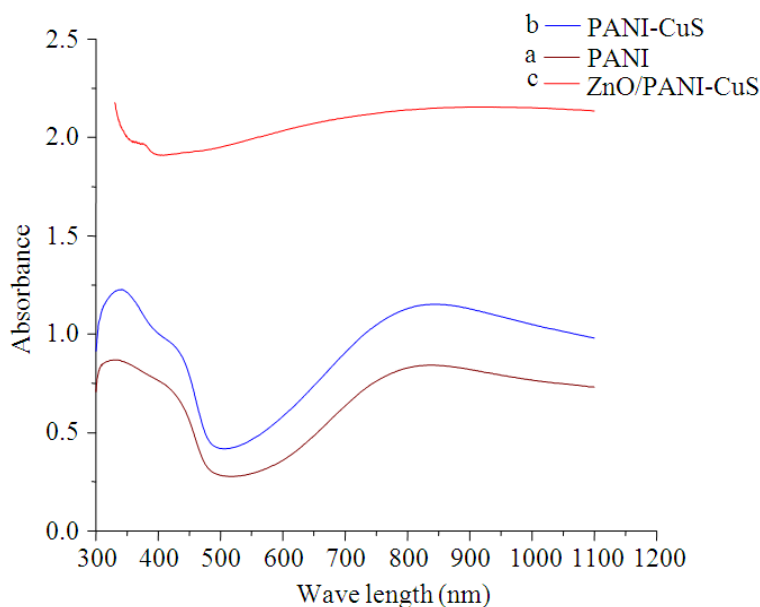
## 4. DISCUSSION

The formation of CuS/PANI composite and its systematic alignments of polymer were confirmed by X-ray diffraction studies. The  $2\theta$  value in **Table 1** also indicates the presence of ZnO (Raoufi and Raoufi, 2009). The mesh like structure so obtained for ZnO (Bdullah *et al.*, 2009) helps for easy insertion the fine tuned particle size of CuS/PANI composite in to its hollow region. The systematic alignment of the polymer chain confirms the strong interaction of PANI with the CuS nanoparticles and results the respective

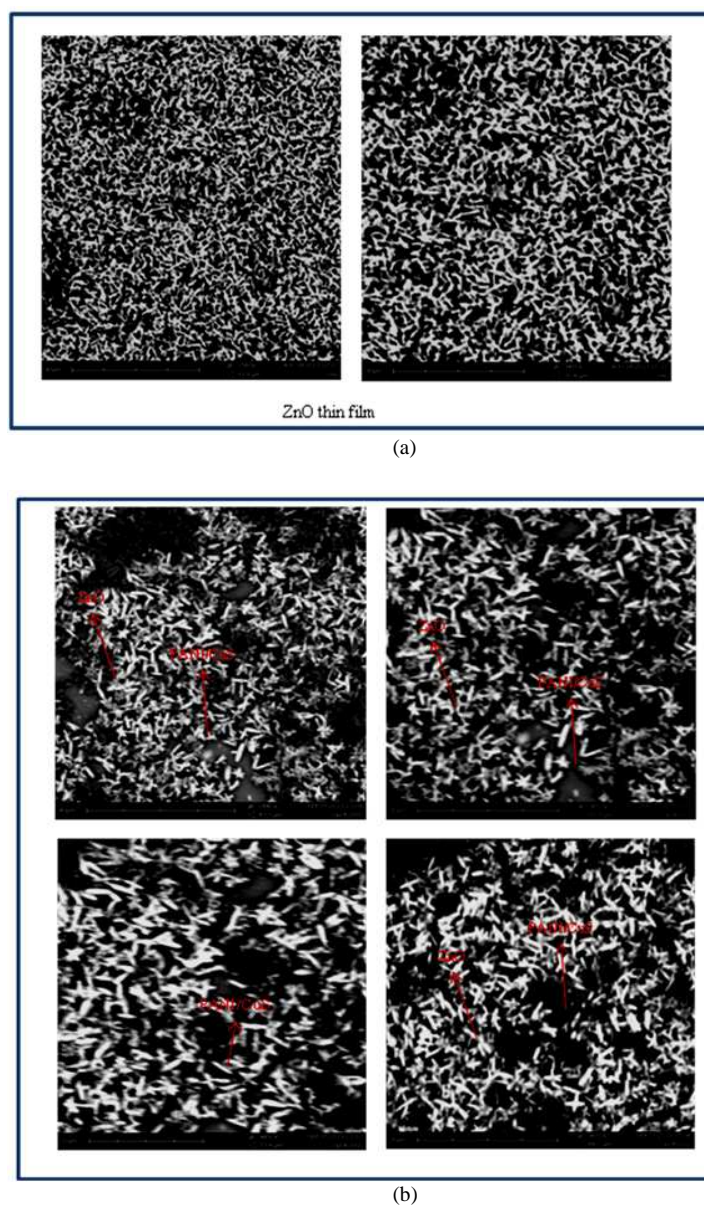
nanocomposite. After the insertion of nanocomposite to the hallow ZnO matrix, it forms the strong interaction with the base metal oxide and forms the hybrid structure, this were supported with X-ray studies. The increase in degree of regularity in arrangement or ordering of conducting polymer nanocomposites is of much interest, because more highly ordered polymer matrix could display a conductive property. The so formed hybrid structured thin film may be used in solar cells.

The strong interaction of CuS nanomaterial with the polymer matrix is observed by FT-IR studies. The incorporation of PANI-CuS composites in ZnO thin film leads to small shift of the peaks and also decrease in the intensity of peaks, which indicates the structural change of polymer, occurs with the incorporation of PANI-CuS nanoparticles.

An optical characteristic of hybrid material supports the formation of composite and hybrid structure. The formation of new hybrid material having good absorption of light in near IR region, this intern causes the increase in the efficiency of solar cells. The  $\pi$ - $\pi^*$  transition shows red shift and  $\pi$ -polaron displays blue shift (**Fig. 3**). It is observed from the SEM image (**Fig. 4b**), that the nanostructured PANI-CuS nano particles are embedded within the porous structure build by ZnO thin film having strong bonding with it, which is reflected also in the XRD and FT-IR results.



**Fig. 3.** UV-Vis spectra of PANI, PANI/CuS and nanocomposite/ZnO thin film



**Fig. 4.** Surface view SEM images of (a) ZnO nanoparticles and (b) PANI-CuS/ZnO thinfilm

**Table 1.** The average crystalline size of the CuS, ZnO, PANI/CuS and ZnO/PANI-CuS thin films

Thin films	2θ						Average particle size (nm)
	24.17	29.01	31.91	32.52	38.17	44.11	
CuS	24.17	29.01	31.91	32.52	38.17	44.11	30.09
ZnO	48.08	52.82	59.08	68.56	73.59	78.01	66.33
PANI/CuS	31.98	34.67	36.41	47.87	56.52	62.71	30.81
ZnO/PANI/CuS	39.19	32.03		31.72			46.96

## 5. CONCLUSION

A PANI/CuS nanocomposite was successfully obtained by in-situ polymerization of aniline. The nanocomposite is successfully inserted in the hallow network of ZnO thin film obtained on the glass substrate. The resulting thin film of the nanocomposite were analysed using XRD, FT-IR, UV-Visible and SEM, which confirmed the presence of nanocomposite in the network of ZnO. This results in a p-n hetero structure diode of PANI/CuS and ZnO on the glass substrate. The nanocomposite in ZnO exhibits the significant blue shift. The hybridization of inorganic nanoparticles and polymer has various advantages viz. long-term stability, good optical, electrical properties etc. These results reveal that prepared hybrid material are ideally suited for the fabrication of opto-electronic devices in the near IR region and could be used to photo-voltaic applications. Furthermore, the obtained results are also potentially useful for the preparation of other semiconductor-based composites with varied properties. These results will to meet diverse applications in chemical sensors, solar cells, etc. Hence, polymer-based inorganic nanocomposites are emerging as new materials; provide new opportunities and rewards for creating a novel world of interest. Further work in this direction will be highly useful in the field of nano electronic devices. However, properties and morphology of the hybrid structure of a nanocomposite strongly depends on the preparation conditions and the coating technique.

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## 7. REFERENCES

- MacDiarmid, A.G., 2001. Synthetic metals a novel role for organic polymers. *Current Applied Phys.*, 1: 269-279. DOI: 10.1016/S1567-1739(01)00051-7
- Bdullah, H., N.P. Ariyanto, S. Shaari, B. Yulianto and S. Junaidi, 2009. Study of porous nanoflake ZnO for dye-sensitized solar cell application. *Am. J. Eng. Applied Sci.*, 2: 236-240. DOI: 10.3844/ajeassp.2009.236.240
- Chang, H., M.J. Kao, T.L. Chen, C.G. Kuo and K.C. Cho *et al.*, 2010. Natural sensitizer for dye-sensitized solar cells using three layers of photoelectrode thin films with a schottky barrier. *Am. J. Nanotechnol.*, 1: 13-22. DOI: 10.3844/ajnsp.2010.13.22
- Wu, C.G., C.H. Chiang and U.S. Jeng, 2008. Phenol assisted deaggregation of polyaniline chains: Simple route to high quality polyaniline film. *J. Phys. Chem. B*, 112: 6772-6778. DOI: 10.1021/jp800932y
- Raoufi, D. and T. Raoufi, 2009. The effect of heat treatment on the physical properties of sol-gel derived ZnO thin films. *Applied Surface Sci.*, 255: 5812-5817. DOI:10.1016/j.apsusc.2009.01.010
- Dong, F., L. Wu, Y. Sun, M. Fu and Z. Wu *et al.*, 2011. Efficient synthesis of polymeric g-C<sub>3</sub>N<sub>4</sub> layered materials as novel efficient visible light driven photocatalysts. *J. Mater. Chem.*, 21: 15171-15174. DOI: 10.1039/C1JM12844B
- Franke, M.E., T.J. Koplín and U. Simon, 2006. Metal and metal oxide nanoparticles in chemiresistors: Does the nanoscale matter? *Small*, 2: 36-50. DOI: 10.1002/sml.200500261
- Kassim, A., H.S. Min, T.W. Tee and N.C. Fei, 2011. Influence of triethanolamine on the chemical bath deposited NiS thin films. *Am. J. Applied Sci.*, 8: 359-361. DOI: 10.3844/ajassp.2011.359.361
- Law, J.B.K. and J.T.L. Thong, 2008. Improving the NH<sub>3</sub> gas sensitivity of ZnO nanowire sensors by reducing the carrier concentration. *Nanotechnology*, 19: 205-502 DOI: 10.1088/0957-4484/19/20/205502
- Lee, K., Z.A. Saipolbahri, B.H. Guan and H. Soleimani, 2014, Organic sol-gel method in the synthesis and characterization of zinc oxide nanoparticles. *Am. J. Applied Sci.*, 11: 959-962. DOI: 10.3844/ajassp.2014.959.962
- Kong, L., X. Lu and W. Zhang, 2008. Facile synthesis of multifunctional multiwalled carbon nanotubes/Fe<sub>3</sub>O<sub>4</sub> nanoparticles/polyaniline composite nanotubes. *J. Solid State Chem.*, 181: 628-636. DOI: 10.1016/j.jssc.2008.01.006
- Pawar, S.G., S.L. Patil, M.A. Chougule, S.N. Achary and V.B. Patil, 2010. Microstructural and optoelectronic studies on polyaniline: TiO<sub>2</sub> Nanocomposites. *Int. J. Polymeric Materials*, 60: 244-254. DOI: 10.1080/00914037.2010.504175



- Pawar, S.G., S.L. Patil, M.A. Chougule, S.N. Achary and V.B. Patil, 2009. Growth, characterization and gas sensing properties of polyaniline thin films. *Arc. Applied Sci. Res.*, 1: 109-114.
- Polsongkram, D., P. Chamninok, S. Pukird, L. Chow and O. Lupan *et al.*, 2008. Effect of synthesis conditions on the growth of ZnO nanorods via hydrothermal method. *Physica B*, 403: 3713-3717. DOI: 10.1016/j.physb.2008.06.020
- Ramesan, M.T., 2014. Synthesis, characterization and properties of new conducting polyaniline/copper sulfide nanocomposites. *Polymer Eng. Sci.*, 54: 438-445. DOI: 10.1002/pen.23572
- Reda, S.M. and S.M. Al-Ghannam, 2013. Enhanced dielectric properties of polyaniline/silver/carbon nanotubes nanocomposite. *Am. J. Nanotechnol.*, 4: 16-22. DOI: 10.3844/ajns.2013.16.22
- Ameen, S., M.S. Akhtar, S.G. Ansari, O.B. Yang and H.S. Shina, 2009. Electrophoretically deposited polyaniline/ZnO nanoparticles for p-n heterostructure diodes. *Superlattices Microstructures*, 46: 872-880. DOI: 10.1016/j.spmi.2009.09.007
- Sangamesha, M.A., K. Pushpalatha, G.L. Shekar and S. Shamsundar, 2013a. Preparation and characterization of nanocrystalline CuS thin films for dye-sensitized solar cells. *ISRN Nanomaterials*, 2013: 8-8. DOI: 10.1155/2013/829430
- Sangamesha, M.A., K. Pushpalatha and G.L. Shekar, 2013b. Effect of concentration on structural and optical properties of CuS thin films. *Int. J. Res. Eng. Technol.*
- Wanga, S., J. Ning, L. Zhao, B. Liu and B. Zou, 2010. Facile synthesis and assembly of CuS nano-flakes to novel hexagonal prism structures. *J. Crystal Growth*, 312: 2060-2064. DOI: 10.1016/j.jcrysgro.2010.03.040
- Wang, W., Q. Li, H. Lin, Z. Chen and M. Ye *et al.*, 2009. Deposition of copper sulfide hollow nanospheres in aqueous solution at room temperature. *Materials Sci. Eng. B*, 156: 52-56. DOI: 10.1016/j.mseb.2008.11.005
- Xiao, J., D. Mei, X. Li, W. Xu and D. Wang *et al.*, 2011. Hierarchically porous graphene as a lithium-air battery electrode. *Nano. Lett.*, 9: 5071-5078. DOI: 10.1021/nl203332e
- Xia, H.S. and Q. Wang, 2002. Ultrasonic irradiation: A novel approach to prepare conductive polyaniline/nanocrystalline titanium oxide composites. *Chem. Mater.*, 14: 2158-2165. DOI: 10.1021/cm0109591
- Zhang, Z., Z. Wei and M. Wan, 2002. Nanostructures of polyaniline doped with inorganic acids. *Macromolecules*, 35: 5937-5942. DOI: 10.1021/ma020199v