



EXPLOITATION OF POLYANILINE NANOCOMPOSITE FOR PHOTOVOLTAIC SOLAR CELL APPLICATION

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ABSTRACT

Nanocomposites of conducting polyaniline with CdS nanoparticles have been synthesized by insitu polymerization method. A series of the nanocomposites have been synthesized by varying the weight percentage of CdS (5, 10, 15, 20, 25 %) with the polymerization of aniline (monomer). PANI-CdS 5 % nanocomposite was optimized sample for high conductivity. Polycrystalline nature and particlesize have been analyzed by X-ray diffraction study. The particle size was found to be in the range of 53 to 400 nm. which has been confirmed from SEM images. The agglomeration of crystallites is observed. FTIR spectra of CdS, polyaniline and PANI-CdS nanocomposite are displayed from 500 to 4000 cm^{-1} . The PANI-CdS composite based thin film solar cell device structure consists of glass/ITO/PANI-CdS/Ag. The I-V characteristics is studied to calculate efficiency of the solar cell, including the maximum power (P_{max}), the energy conversion efficiency (η) and the fill factor (FF).

Keywords: Nanocomposites, Polyaniline (PANI), Doped polyaniline Synthesis, SEM, XRD, FTIR Photovoltaic cell

1. Introduction

Recently, conductive polymer composites have attracted much attention because of their variety of properties and functionalities, such as mechanical strength, processibility, ease of preparation, etc. (Lu *et al* 2005, Yan *et al* 2010, Nagrajan *et al* 2001). Among conducting polymers, polyaniline (PANI) is probably the

most widely studied due to its several unique properties (Li *et al* 2007, Mathur *et al* 2001). Its ease of preparation, light weight, low cost, better electronic and optical properties, highly stable in air and soluble in various solvents and good processibility (Li *et al* 2008, MacDiarmid *et al* 1995, Apesteguy *et al* 2004), and reversible control of conductivity both by charge-transfer doping and protonation (Heeger 2001, MacDiarmid *et al* 1997) are the important one and responsible for the exploitation of various applications. Also inorganic semiconductors CdS, ZnS and PbS in nanoparticles form are equally important materials used in various applications like sensors, optoelectronic devices and in solar cells. Polymeric nanocomposites consisting of organic polymer and inorganic nanoparticles in a nanoscale regime represent a novel class of materials that have motivated considerable interest in recent years. These composites exhibit new advantageous properties and can be very different from those of their individual counterparts. It is therefore expected that this type of materials will play increasingly important role in research and in numerous applications. They frequently have special properties and are significant for many technological applications, ranging from microelectronics to catalysis, optoelectronic devices, and synthesis of lubricant and preparation of electrolytes for rechargeable batteries (Honma *et al* 1999, Trindade *et al* 2000, Chen *et al* 1998, Krawiec *et al* 1995). The conductive polymer photovoltaic is the present day solution to the increasing demand of energy. The conversion of light energy into electrical energy is a challenging task. To fulfill

this demand conductive polymer photovoltaic cell plays an important role. In such types of cell one electron accepting layer and another electron donating layers are used. Most of the light falls on the PV cell is absorbed by the electron donating layer creates excitons. With this basic principle the nanocomposites are exploited to fabricate the heterojunction photovoltaic solar cell. Another reason is that these two different semiconductors (ITO and PANI) allows the band gap to be tuned to desire value because of its flexibility in composition of conducting polymer especially polyaniline. The main aim of this work is to study the glass/ITO/PANI-CdS/Ag heterojunction solar cell by using the PANI-CdS as active organic material.

2. Experimental

2.1 Materials used

The Aniline Hydrochloride (AR), Ammonium Persulphate (AR) and Cadmium Nitrate Tetrahydrate (AR) obtained from Loba Chem. Mumbai, (India). Ammonium Sulphide was received from National Chemicals, Vadodara, Gujarat (India). All the chemicals were used as received.

2.2 Synthesis of nano CdS

Aqueous solution of $\text{Cd}(\text{NO}_3)_2$ (0.085M) was taken in a beaker and aqueous solution of $(\text{NH}_4)_2\text{S}$ (0.1M) was in another beaker. Both have 100 ml quantity. Now aqueous Solution of $\text{Cd}(\text{NO}_3)_2$ (0.085M) was added drop wise to 100 ml aqueous solution of $(\text{NH}_4)_2\text{S}$ (0.1M) with vigorous stirring for 5h. The dark yellow precipitate of CdS nanoparticles was obtained. Left the precipitate overnight then filtered with Distilled water and acetone. Then dry in air and kept at 80°C in oven for 5 h.

2.3 Synthesis of PANI

The synthesis was based on mixing aqueous solutions of aniline hydrochloride (0.2M) and ammonium persulfate (APS) (0.25M) at room temperature, followed by the separation of PANI hydrochloride precipitate by filtration and drying. More precisely, 2.59 g of aniline hydrochloride was dissolved in distilled water in a volumetric flask to 50 mL of solution. 5.71 g of ammonium persulfate (APS) was dissolved in water to make 50 ml solution. Both solutions were kept for 1 h at room temperature ($\sim 18\text{--}24^\circ\text{C}$), then mixed in a beaker, briefly

stirred, and left at rest to polymerize. Next day, the resulting dark green PANI precipitate was collected on a filter, washed with three 100 ml portions of 0.2 M HCl, and similarly with acetone.

2.4 Synthesis of PANI-CdS Nanocomposite

In the Present work polymer composite film of Polyaniline (PANI)-CdS was prepared for different weight percent of Cadmium Sulphide (CdS). Synthesis steps of PANI/CdS nanocomposite are similar to the synthesis method of PANI. Different amount of CdS were dispersed into the APS solution and stirred for 1 hour prior to the addition of aniline. Aniline (0.4 mol) stirred with 0.4M H_2SO_4 in 100 ml of distilled water were added drop wise using burette into the APS-CdS solution and stirred vigorously to form homogeneous dispersion. For convenience, PANI Composites were prepared with different weight percentages of CdS (Bompilwar *et al* 2010). Same synthesis conditions were maintained for all composites as that of pure PANI.

3. Characterization

3.1 Scanning Electron Microscopy (SEM)

For the present work Field Emission Gun-Scanning Electron Microscope (Model number JSM-7600F) was used. The resolution of the instrument was 1.0 nm at 15KV and 1.5 nm at 1KV. The accelerating voltage was in the range of 0.1 to 30KV and magnification was about 25 times to 1,000,000 times.

3.2 X-Ray Diffraction Technique

XRD is an indispensable method used for materials characterization. The MiniFlex 600 X-ray diffractometer (XRD) is used for the characterization. Characterization was carried out at Department of Physics and Electronics, Government Vidarbha Institute of Science and Humanities, Amravati.

3.3 FTIR

The FTIR study of, Pure PANI, CdSand PANI-CdS Nanocomposites was studied on a BRUKER FTIR IR spectrophotometer in the range 500 to 4000 cm^{-1} at room temperature (303 K) at Department of Physics and Electronics, Government Vidarbha Institute of Science and Humanities, Amravati.

4. Results and discussion

4.1 SEM

The surface morphology of PANI, CdS and PANI-CdS nanocomposite was studied by scanning electron microscope (SEM). The photographs of microstructure of respective samples are shown in figures 1 (a,b,c). The fine microspheroidal surface was observed with poor matrix. Nanoparticles formed are not of homogenous size. These materials are polycrystalline in nature. Particle sizes of PANI, CdS and PANI-CdS nanocomposite are found to be in the range between 200-550 nm, 75-400 nm and 25-340 nm respectively. There is agglomeration of crystallites which is clearly seen from the figure 1(b).

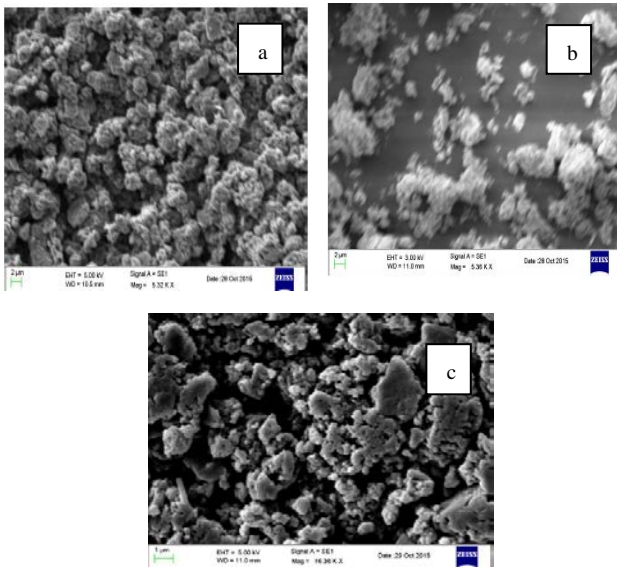


Fig 1- (a)SEM of Pure PANI, (b) Pure CdS and (c)PANI-CdSNanocomposite

Fig. 1(b) shows the crystalline nature where small crystallites of CdS are seen. The same type of structure can be observed from XRD also. PANI is completely amorphous in nature whereas PANI-CdS composite shows partly crystalline as well as amorphous phase.

4.2 XRD

The degree of crystallinity increased in PANI-CdS nanocomposite than pure PANI and CdS, clearly indicated the homogeneous distribution of nanoparticles in the polymer matrix. The crystallite size of can be determined using Debye Scherrer formula $[(0.9 \lambda) / (\beta \cos \theta)]$ and it is found that the crystallite size of PANI-CdS nanocomposite is 75 nm. The XRD pattern of PANI shows the three broad peaks at $2\theta = 15.13^\circ, 20.34^\circ, 25.20^\circ$. The CdS has strong peak at $2\theta = 25.20^\circ$ which is

attributed to the (100) plane of CdS in hexagonal structure having lattice parameter $a = 4.119 \text{ \AA}$ and $c = 6.728 \text{ \AA}$. The SEM analysis shows that the particles are held together by a porous irregular network for CdS (Elilarassi *et al* 2010).

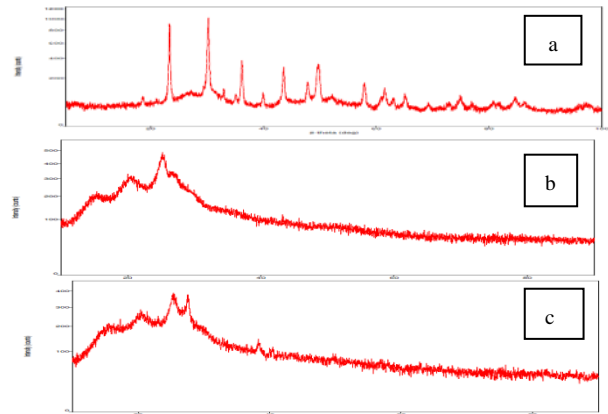


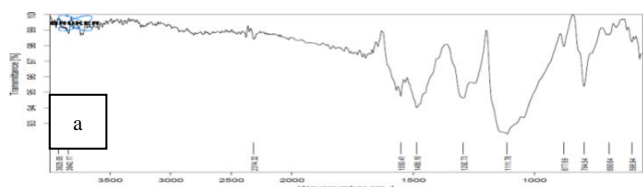
Fig 2- (a) XRD of Pure CdS, (b) XRD of Pure PANI, (c) XRD of PANI-CdSNanocomposite

We can observe broad diffraction peaks for all composites indicating the presence of very small size crystallites. Again, it can be seen that the nanocomposites show crystalline as compared to that of pure PANI due to uniform dispersion of the nanoparticles in the polymer matrix. The crystallinity of the nanocomposites is dominated by polymer matrix.

PANI showed two broad hallowes at $2\theta = 20.34^\circ$ and 25.20° . The entire sample has an amorphous nature (Trindade *et al* 2000). A nanocomposite show the greater crystallinity due to the addition of CdS in PANI matrix as compared to pure PANI and shows the peaks related to CdS with increasing concentration in PANI matrix as seen from figure 2(a,b,c).

FTIR

FTIR spectra of CdS, polyaniline and PANI-CdS nanocomposite are displayed in Fig.3(a,b,c) in the range of 500 to 4000 cm^{-1} . The peaks of PANI-CdS nanocomposite are the modification of the spectrum of the polyaniline due to embedding CdS. This approves the CdS polymerization and formation of core-shell model.



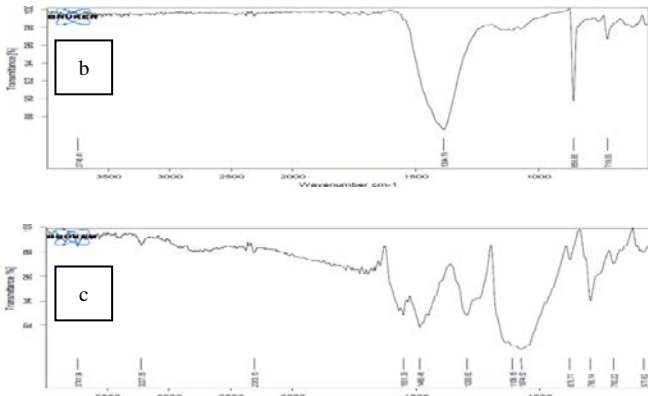


Fig 3- (a) FTIR of Pure PANI, (b) Pure CdS and(c) FTIR of PANI-CdSNanocomposite

In PANI-CdS composite various peaks are observed (Fig. 3a,b,c). The peaks at 876 and 877 cm^{-1} are attributed to the out of plane benzene of C-H; 1109, 1110, 1111, 1113, 1112 cm^{-1} are attributed to the in-plane bending vibration of C-H; 1291 to 1294 cm^{-1} are attributed to the C=N of quinone ring; 1485 to 1486 cm^{-1} and 1550 to 1551 cm^{-1} are attributed to the C=C stretching of the benzenoid/quinoid rings and peaks at 3122, 3227, 3234, 3236, 3224 cm^{-1} are attributed to the aliphatic C-H stretching of PANI-CdS Composite respectively. The peaks at 3733, 3741, 3742, 3743 cm^{-1} attributed to N-H stretching of PANI-CdS composite. Peak at 719 and 856 cm^{-1} is assign to Cd-S Stretch medium and strong respectively and peaks around 3842 cm^{-1} are assigned to N-H vibration of PANI.

The FTIR spectra shows the characteristic peak for CdS at 405 cm^{-1} (Malliket al 2008, Ramkrishnan et al 2012, Salmiet al 2012). The incorporation of CdS nanoparticles caused the shift of some peaks of PANI. The main characteristic peaks of PANI can be assigned as follows: the band at 3460 cm^{-1} and 3230 cm^{-1} can be attributed to the free (non hydrogen bonded) N-H stretching vibration and hydrogen bonded N-H bond between amine and imine sites (MacDiarmid 1997, Honma et al 1999, Trindade et al 2000). The strong band at 1173 cm^{-1} was considered to be a measure of the degree of electron delocalization and thus it is a characteristic peak of PANI conductivity. The out-of plane deformations of C-H in the 1,4-disubstituted benzene ring were located at 870 cm^{-1} .

PV Cell

The PANI-CdS composite based thin film solar cell device structure consists of glass/ITO/PANI-CdS/Ag is shown in figure 4. The I-V characteristic is studied to investigate the solar cell parameters.

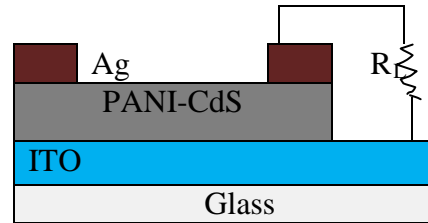


Fig. 4-Schematic diagram of solar cell device with PANI-CdS nanocomposite

Few parameters are used to characterize the efficiency of the solar cell, including the maximum power (P_{max}), energy conversion efficiency (η) and the fill factor (FF). These points are illustrated in Figure 5, which shows a typical forward bias I-V curve of an illuminated PV cell. The maximum power (P_{max}) is the product of the maximum cell current (I_{max}) and the voltage (V_{max}) where the power output of the cell is maximum. This point is located at the “knee” of the curve. The fill factor (FF) is a measure of how far the I-V characteristics of an actual PV cell differ from those of an ideal cell. I-V response of fabricated PV Cell was done using incandescent light bulb (60W) radiating light power of 3.49 mW/m^2 , measured using Lux meter. The bulb and Photovoltaic cell separation was 30 cm.

The fill factor is defined as (Ramkrishnan et al 2012, Giannelis 1995)

$$FF = \frac{I_{\text{max}} V_{\text{max}}}{I_{\text{sc}} V_{\text{oc}}}$$

Where

I_{max} is the current at the maximum power output (A), V_{max} is the voltage at the maximum power output (V), I_{sc} is the short-circuit current (A) and V_{oc} is the open-circuit voltage (V).

As defined, the fill factor is the ratio of the maximum power ($P_{\text{max}} = I_{\text{max}} V_{\text{max}}$) to the product of the short circuit current (I_{sc}) and the open circuit voltage (V_{oc}). The ideal solar cell has a FF=1 but losses from series and shunt resistance decrease the efficiency. Another important parameter is the conversion

efficiency (η), which is defined as the ratio of the maximum power output to the power input to the cell.

$$\eta = \frac{P_{max}}{P_{in}}$$

Where

P_{max} is the maximum power output (W) and P_{in} is the power input to the cell defined as the total radiant energy incident on the surface of the cell (W).

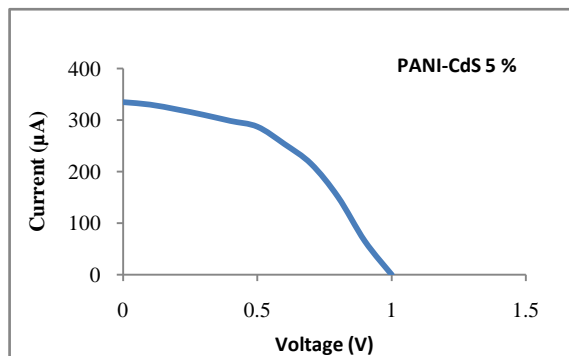


Fig. 5- I-V characteristics of PANI-CdS nanocomposite

The maximum value of short circuit current (I_{sc}) was found to be 334.8 μ A for optimized PANI-CdS nanocomposite. Similarly the maximum value of open circuit voltage V_{oc} is 1000 mV. The value of Maximum current and maximum voltage is 287.1 μ A and 500 mV respectively. The power conversion efficiency (η) of PANI-CdS composite is 4.1 %. The less efficiency of the PV cell is due to the poor surface morphology of the PANI-CdS composite which absorbs less light limits the electron hopping transport.

5. Conclusion

PANI-CdS nanocomposite was fabricated and characterized using the co-precipitation and polymerization and usual techniques. It is seen from the XRD spectra shows crystalline nature of CdS and each highly agglomerated irregular shape which reflects the amorphous state of the obtained PANI. The PANI-CdS nanocomposite shows amorphous nature. FTIR spectroscopic analysis proved that the bonds of PANI are modified due to the addition of CdS nanoparticles. PV Cell of PANI-CdS nanocomposite has less efficiency and fill factor value. The efficiency of PANI-CdS is found to be 4.1 % under light illumination 3.49

mW/m². The less efficiency caused due to poor absorber morphology which limits the electron hopping transport. The low value of FF is associated with the high value of series and shunt resistances.

6. References

- Lu X., Yu Y., Chen L., Mao H., Wang L., Zhang W. & Wei Y., (2005) Poly(acrylic acid) guided synthesis of helical polyaniline microwires. *Polymer*, 46 (14), 5329-5333.
- Yan Y., Wang R., Qiu X. & Wei Z., (2010) Hexagonal Superlattice of Chiral Conducting Polymers Self-Assembled by Mimicking Sheet Proteins with Anisotropic Electrical Transport, *J Am. Chem. Soc.*, 132 (34) 12006-12012.
- Nagarajan R., Liu W., Kumar J., Tripathy S. K., Bruno F. F. & Samuelson L. A.(2001) Manipulating DNA conformation using intertwined conducting polymer chains, *Macromolecules*, 34(12), 3921-3927.
- Li L., Jiang J.& Xu F., (2007) Materials Letters 61 1091–1096.
- Mathur R., Sharma D. R., Vadera S. R., Kumar N.,(2001) Acta Mater. 49, 181–187.
- Li L., Liu H., Wang Y., Jiang J. & Xu F., Preparation and magnetic properties of Zn-Cu-Cr-La ferrite and its nanocomposites with polyaniline. *J Coll. Inter.Sc.321*, 2008, 265– 271.
- MacDiarmid A.G. & Epstein A.J., Synthesis and Properties of Polyaniline/Ferrites Nanocomposites. *Synthetic Metals* 69 (1995) 86-92.
- Apesteguy J.C. & Jacobo S.E., Composite of Polyaniline containing iron oxides. *Physica B* 354 (2004) 224–227.
- Heeger J., Semiconducting and metallic Polymers. *J. Phys. Chem. B* 105, (2001) 8475.
- MacDiarmid G., *Synthetic Metals* 84, (1997) 27.
- Hirakawa S., Honma I., Yamada K. & Bae J.M., *Solid State Ionics* 118 (1999) 29.
- Trindade T., Neves M.C. & Barros A.M.V., Synthesis and Characterization of Polyaniline/Lead Oxide

- Nanocomposite. *Scr. Mater.* 43 (2000) 567.
- Chen S., Liu W.M. & Yu L.G., Preparation of DDP-Coated PbS nanoparticles and investigation of the antiwear ability of the prepared nanoparticles as additive in liquid paraffin. *Wear* 218 (1998) 153.
 - Krawiec Jr. W., Scanlon J.G., Fellner J.P., Vaia R.A., Vasudevan S. & Giannelis E.P., Polymer nanocomposite a new strategy for synthesizing solid electrolytes for rechargeable lithium batteries. *J. Power Sources* 54 (1995) 310.
 - Bompilwara Shubhangi D., Kondawar Subhash B., Tabhanec Vilas A., Kargirward Snehal R., R. Elilarassi, S. Maheshwari & G. Chandrashekharan (2010) *Optoelectronics Adv Mater* .RC ,4(3)309-312., *Pelagia Research Library*, 1 (1): 166-173,2010.
 - Karim M. R., Yeum, J.H., Lee M.S. & Lim K.T. Preparation of conducting polyaniline/TiO₂ composite Submicron-rod by the γ radiolysis oxidative polymerization method. *Reactive Functional Polymers*, 68, 2008,1371-1376.
 - Witcomb Mallick, K., Scurrall M. J. & Strydom M. S. ,In-situ chemical synthesis route for a fibre shaped gold-polyaniline nanocomposite. *A. M. Gold Bulletin*, 41, 2008, 246-250.
 - Ramakrishnan Rajaraman, Sudha Janardhanan D & Viswan L R. Nanostructured polyaniline-polytitanate-clay composite for polycatalytic applications. *RSC Advances*, 2, 2012, 6228-6236.
 - Salmi T., Bouzguenda M., Gastli A. & Masmoudi A., Matlab/simulink based modelling of photovoltaic cell. *Int. J. Renew. Energy Res.* 2, 213(2012).