IJASRM
International Journal of Advanced Scientific Research and Management, Special Issue 4, ICAMA-18, Apr 2019
www.ijasrm.com
ISSN 2455-6378

Composites of copper oxide and polyaniline for solar cell applications

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Abstract

A nanocomposite material of Polyaniline and Copper oxide was synthesized. The prepared nanocomposites were characterized by UV-Vis, FT-IR, AFM, SEM and electrochemical studies. The FT-IR spectral studies indicated the presence of metal oxide and polymer in nanocomposites. From the FT-IR spectra of nanocomposites, the peak around 512 cm^{-1} and 606 cm^{-1} indicated the bonding between Cu and O, the peak around 1571 cm^{-1} and 1502 cm^{-1} due to stretching vibrations of the quinonoid and benzenoid rings of polyaniline respectively. The surface morphology was characterized by AFM and SEM. Optical and electrochemical properties were determined using UV-visible spectroscopy and cyclic voltammetry respectively. These characterisations indicated that Polyaniline/CuO was a new semiconductor photoelectric material, and the solar cell prepared with Polyaniline/CuO performed well.

Keywords: ***Polyaniline, CuO, Nanocomposite material, Semiconductor, Solar cells***

1. Introduction

In recent years, researchers focused on synthesizing metal oxide nanoparticles and nanocomposites due to their unique electronic, optical, mechanical, magnetic, and chemical properties. Nanocomposites of metal oxide - polymer are important materials in the area of nanotechnology. These materials are especially important owing to their bridging role between the world of nanoparticles and that of conducting polymers. The polymers having poly-conjugated structures and possess poor electrical conductivity but the oxidized polymers exhibit appreciable electrical conductivity. Among conjugated polymers Polyaniline (PANI) is unique among the conducting and the most researched organic conducting polymer which is easy to synthesize, having fair good chemical stability and widely studied for electronic and optical applications [1-5]. This polymer can be used for the metallic parts in components like sensors, capacitors, displays, light-emitting diodes etc [6]. The oxides of transition metals are an important class of semiconductors having applications in multiple technical fields like solar energy transformation, magnetic storage media, electronics, and catalysis among the oxide of transition metals. Copper oxide (CuO) nanoparticles are of special interest because of their efficiency as semiconducting material with a narrow band gap and used for photoconductive and photothermal applications [7,8]. The oxides of copper are intrinsic p-type semiconductors with relatively small band gaps and show many attractive properties that can be utilized in a diversity of applications [9,10]. The present study aims to investigate PANI-CuO nanocomposites in order to obtain a new noble material which can be utilized for solar cell applications.

2. Experiments

2.1. Synthesis of CuO nanoparticles

In this synthesis 0.02M $CuSO_4.4H_2O$ and 0.5 g sodium hydroxide were added together at room temperature under constant stirring. The reaction lasted for 10 min forming a blue aqueous solution which was then continuous stirring. The resultant precipitates were washed with distilled water several times and dried at room temperature.

2.2. Synthesis of Polyaniline

Aniline hydrochloride (equimolar volume of aniline and hydrochloride acid) was dissolved in distilled water in a volumetric flask to 100mL of solution. Potassium perdisulphate (0.25M) was dissolved in water also to 100mL of solution. Both solutions were kept for 1 hour at room temperature, then mixed in a beaker, stirred with a magnetic stirrer and left at rest to polymerize. This was refrigerated for 24h for aging. The green precipitate obtained was filtered and washed with distilled water. The product was dried to get powder form of PANI.

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ISSN 2455-6378

2.3. Synthesis of PANI-CuO nanocomposites

Weighed amount of CuO was dispersed in 5mL of de-ionised water and 0.05g of PANI was added. Then the mixture was diffused for 1h using sonicator at room temperature. The obtained polymer composite was filtered and washed with de-ionised water. In this way, Polyaniline–Zinc oxide nanocomposite was synthesized.

2.4. Characterization

Fourier transformed infrared spectra of these composites and CuO nanoparticles were recorded on Thermo Fisher Scientific, USA, Model - Nicolet iS5, iD3 ATR spectrometer in the range 4000-400cm^{-1}. Computer controlled JASCO V-650 was used to the study the absorption characteristics. The morphology of the nano copper oxide and nanocomposites was investigated by Atomic Force Microscope (AFM) with Nanosurf Easyscan 2 AFM. The electrochemical analyzer CHI 650C (CH Instruments, USA) was employed for the electrochemical studies of nanoparticles and composites.

3. Results and Discussion

3.1. FT-IR analysis

FT-IR spectra of the CuO, PANI and the nanocomposites were recorded using KBr. Figures 1 and 2 show the IR spectrum of CuO, PANI and PANI-CuO nanocomposites, respectively. The band at 1573 cm−1 and 1503 cm−1 is attributed to C=N and C=C stretching mode of vibration for the quinonoid and benzenoid unit of PANI. The peaks around 1289 cm−1 are assigned to C-N stretching mode of benzenoid ring. [11,12]. The bands in the region 480-512 cm−1 are due to the presence of CuO in the nanocomposite. For the PANI-CuO composites, its IR-spectrum is almost identical to that of the pure PANI but all band shifts slightly towards the red side, and the intensity ratio of quinonoid band has also changed. These results indicate that some interactions exist between PAni and CuO.

3.2. UV analysis

UV-Visible spectra were recorded using DMF as the dispersing medium. The UV-vis spectrum of PANI (Fig.3(B)) shows bands at around 275 nm and 570 nm that attributed to π– π* transition of the benzenoid ring and n– π* transition of benzenoid to quinonoid respectively. From (Fig.2(C)), the UV-vis spectra of nanocomposities are similar to those of PANI and some shifting in the bands is noticed. In the case of nanocomposites, the peak around 520-655 nm is due to the interaction between CuO and quinonoid ring of polyaniline

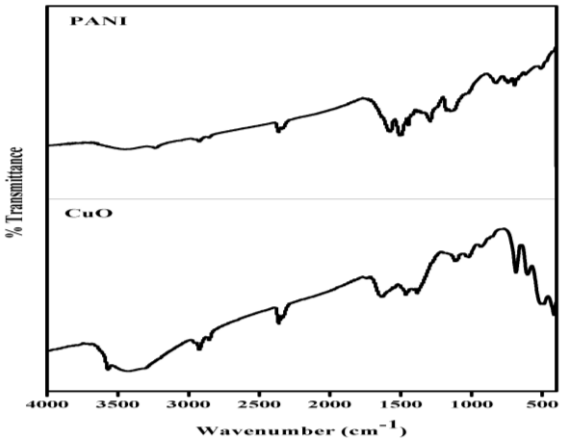

Fig1. (A) FTIR spectrum of CuO Nanoparticle and PANI

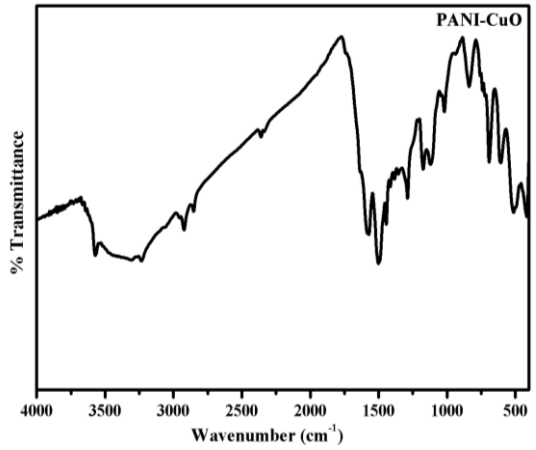

Fig1. (B) FTIR spectrum of PANI-CuO nanocomposites

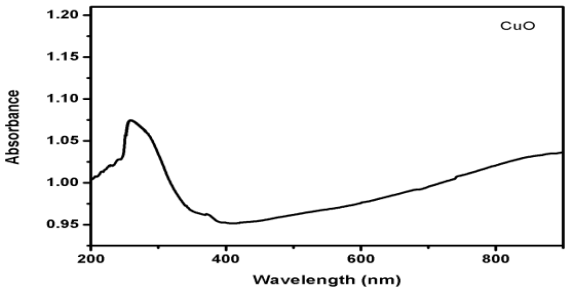

Fig.2 (A) UV-vis spectrum of CuO Nanoparticle

3.3. Optical absorption analysis

The absorption spectrum was used to study the optical properties of the synthesized nanoparticles and nanocomposites, from this the band gap and the type of electronic transitions were determined. The E_g value can be obtained by extrapolating the absorbance to the photon energy axis. The following table gives an optical band gap value which shows that, CuO addition decreases the

optical band gap of polyaniline from 2.4 eV to 2.1eV. The absorption spectrum reveals that the addition of CuO produces shift in the absorption peak and results in low band gap. The absorption increases and optical band gap decreases due to charge transfer transitions [13,14]. The prepared PANI-CuO nanocomposites in the present study expected to be more useful in photonic and electronic device applications.

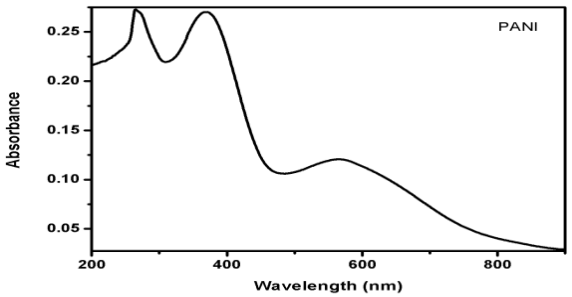

Fig.2 (B) UV-vis spectrum of PANI

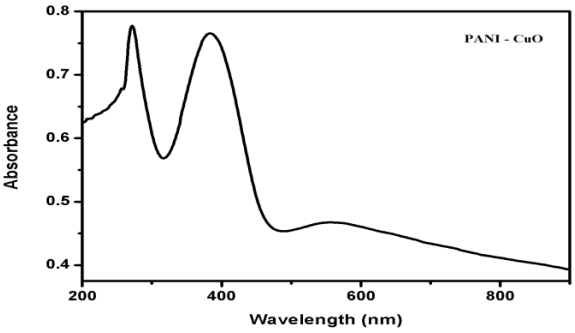

Fig.2 (C) UV-vis spectrum of PANI-CuO nanocomposites

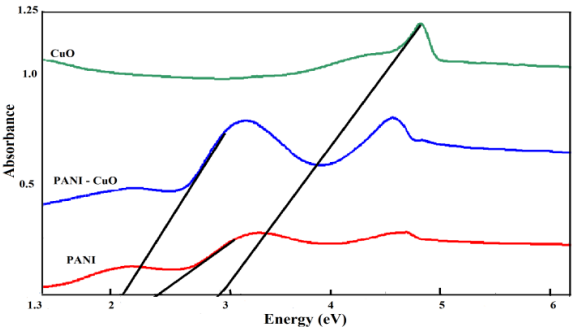

Fig. 3. UV Absorbtion spectra of CuO, PANI and PANI – CuO

Materials	Band gap (eV)
CuO	2.9
PANI	2.4
PANI - CuO	2.1

3.4. AFM analysis

Fig. 4 (A) shows the morphology of CuO nanoparticle. The scanning area is found to be 3.13 µm X 3.13 µm. The sample shows gravel like structure. Fig. 4 (B) shows the morphology of PANI. The scanning area is found to be 12.5 µm X 12.5 µm. The sample shows small gravel like structure.

Fig. 4 (C) shows the morphology of PANI-CuO nanocomposites and the composites show layer by layer structure.

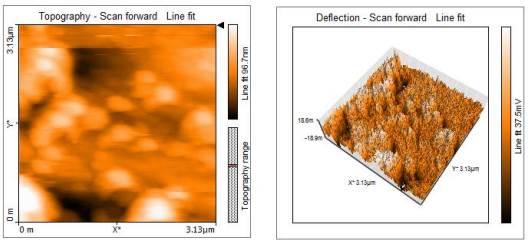

Fig4. (A) AFM image of CuO Nanoparticle

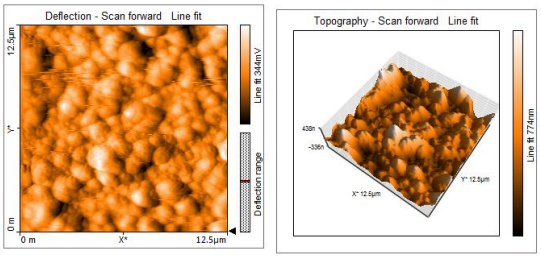

Fig4. (B) AFM image of PANI

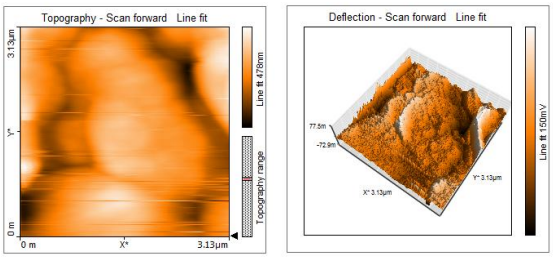

Fig4. (C) AFM image of PANI-CuO

3.5. SEM analysis

The surface morphology was examined by Scanning Electron Microscope (JEOL JSM-6390). SEM report of CuO nanoparticles, PANI and PANI-CuO was shown in Fig.5.(A-C). Fig.5.(A) shows that the powders are composed of non-agglomerated random shape particles which tends to built and aggregate to form a flower shape structure. SEM image of PANI showed crystaline structure. From the SEM image of PANI-CuO, it was observed that there was a higher tendency of agglomerations. It confirmed that the incorporation of metal oxide in the polymer matrix.

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ISSN 2455-6378

3.6. Electrochemical analysis

Cyclic voltammetric behaviour of CuO shows one oxidation peak at 0.3415 V and one reduction peak at -0.7190 V. For PANI the anodic peak appears at 0.4048 V and the reduction peak at 0.1415 V corresponding to the reduction of polyaniline.

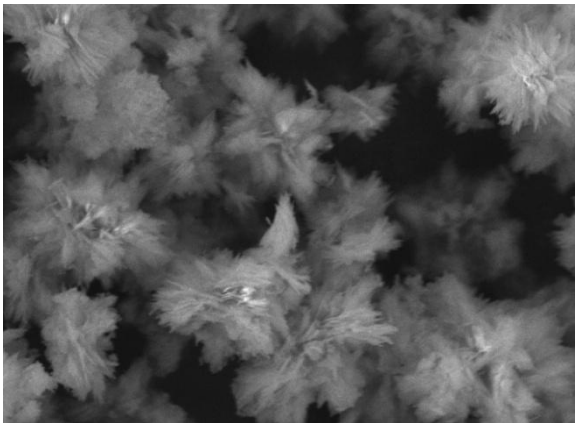

Fig5. (A) SEM image of CuO Nanoparticle

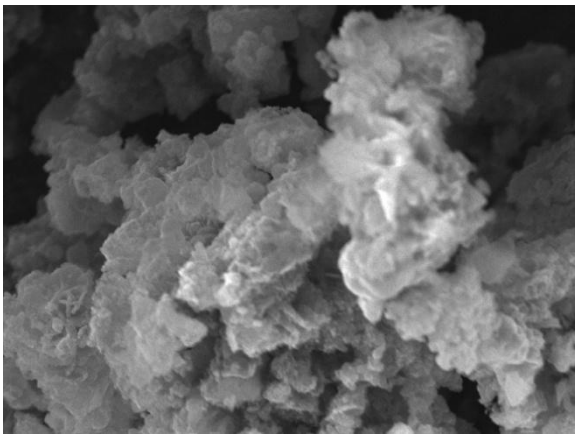

Fig5. (B) SEM image of PANI

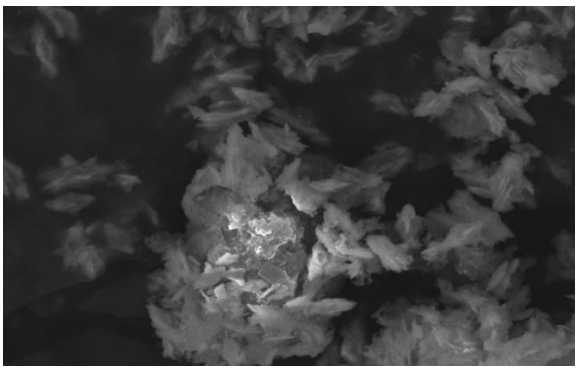

Fig5. (C) SEM image of PANI-CuO

Cyclic voltammetric behavior of polyaniline/CuO nanocomposite shows oxidation peak at 0.3502 V and reduction peak at -0.3672 V which indicate the interaction of polyaniline and ZnO nanoparticles.

The capacitance values calculated from the CV curves are presented in the following table. It is seen from the capacitance values that it increases with doping.

Materials	Average Current µA	Scan rate V	Capacitance µF
CuO	70	0.025	280
PANI	120	0.025	480
PANI - CuO	220	0.025	880

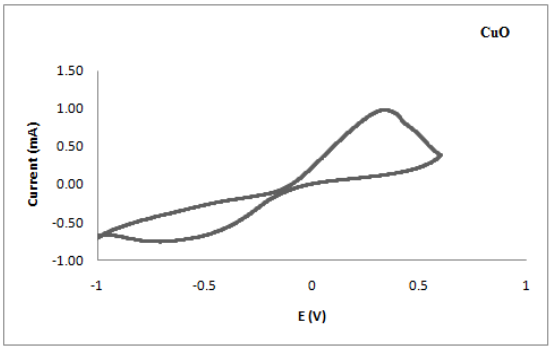

Fig6. (A) Cyclic Voltammogram of CuO Nanoparticle

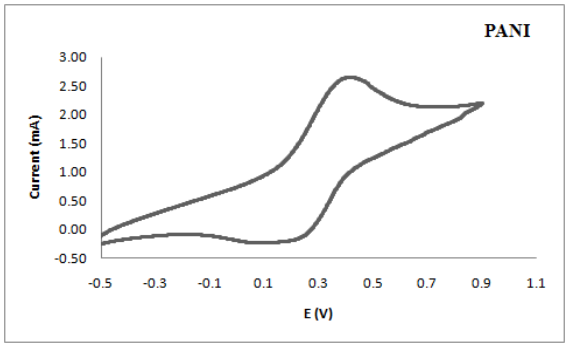

Fig6. (B) Cyclic Voltammogram of PANI

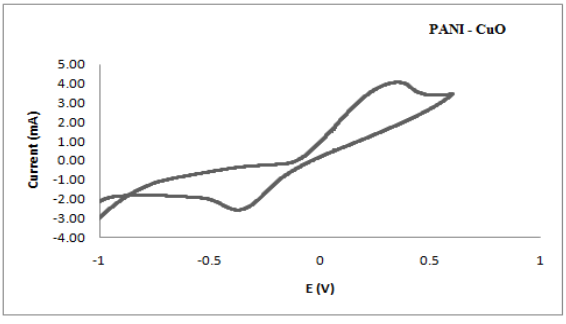

Fig6. (C) Cyclic Voltammogram of PANI-CuO nanocomposite

3.7. Device Fabrication and I-V Characterization

An efficient polymer-metal oxide solar cell can be fabricated with the device structure: ITO/CuO-PANI. To fabricate the cells, ITO-coated glass is cleaned with de-ionized water. A thin layer of CuO-PANI nanocomposite was coated manually onto ITO-coated glass. The device architecture is shown in Fig.7.(A). In the device, reasonable photovoltaic effect was observed with short-circuit current density (J_{SC}) of 0.7 μA/cm^2. However, open-circuit voltage (V_{OC}) and fill factor (FF) are 0.9 V and 72.2%, resulting in PCE of 65%

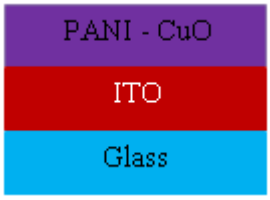

Fig7. (A) Device structure of polymer solar cell

Fig7. (B) J-V characteristics of PANI-CuO

4. Conclusion

CuO nanoparticles and PANI-CuO nanocomposites were successfully prepared. FTIR results show that interaction between CuO and PANI is based on the formation of hydrogen bonding and polyaniline plays a key role in the formation of the PANI–CuO nanocomposite. The developed method has potential for solar cell applications due to low-cost and simple processing. This highly efficient cell can be applied to design polymer solar cells, to improve the efficiency of polymer solar cells.

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