Journal of Population Therapeutics & Clinical Pharmacology

RESEARCH ARTICLE
DOI: 10.47750/jptcp.2023.30.09.040

Electrolytic synthesis of CuO/SnO2 Nanocomposites for Dye-Sensitized Solar Cells Applications

Aqeel Mahdi Alduhaidahawi[1*], Hanaa Kadtem Egzar[2]
[1,2]Faculty of Science, University of Kufa, Iraq
***Corresponding author:** Aqeel Mahdi Alduhaidahawi, Faculty of Science, University of Kufa, Iraq, Email: aqeelm.alduhaidahawi@uokufa.edu.iq

Submitted: 28 February 2023; Accepted: 19 March 2023; Published: 07 April 2023

ABSTRACT
In this study, CuO/SnO2 nanocomposites were synthesized by an easy, low cost and short time electrolytic method for fabrication dye-sensitized solar cells (DSSCs). The characterization of the prepared CuO/SnO2 NCs were studied by several techniques. The FE-SEM images of CuO/SnO2-PVA and CuO/SnO2-PVP NCs were both rectangle and regular cube shapes respectively. HRTEM images of synthesized CuO/SnO2 NCs show homogeneous cubic shapes had an average size of 30-40 nm. The XRD results show the monoclinic-tenorite phase of CuO crystal structure and the SnO2 crystal structure is in rutile tetragonal SnO2. The optical properties of the prepared CuO/SnO2- PVA and CuO/SnO2-PVP NCs were studied through UV / VIS spectroscopy. The optical bandgap was found to be 3.15 eV and 3.18 eV respectively. Dye-sensitized solar cells were fabricated using CuO/SnO2- PVA and CuO/SnO2-PVP NCs as anode electrodes (front electrode) and graphite as cathode (back electrode) in the presence of two kinds of natural dyes, these are pomegranate and parsley dyes, and iodine / iodate electrolyte solution. The photovoltaic parameters were determined from I-V plots of the DSSCs indicated that the DSSCs prepared from parsley dye were more efficient. The reason may be attributed to the fact that parsley chlorophyll dye contains an abundance of electrons capable to providing the DSSCs with these electrons better than the anthocyanin dye found in pomegranate

Keywords: *Electrolytic synthesis, CuO/SnO2 nanocomposites, dye-sensitized solar cells; SEM; TEM*

1.INTRODUCTION
In the recent period, the renewable forms of energy has been focus of interest by many researchers around the world. The most common form of renewable energy is solar cells. Dye-sensitized solar cells (DSSCs) are the most future alternative to all familiar silicon cells for conversion sunlight into electrical energy (1). DSSCs are among the various photovoltaic devices of the modern generation, which have attracted researchers' interest because of their easy fabrication, low toxicity, and ease of production. DSSCs typically consist of a photo-anode, a dye sensitizer, an electrolyte and a cathode. The part that plays the biggest role of DSSCs is the dye, which is the main generator of the photo-excited electrons (2). Nanocomposites are the most widely used materials in various applications such as batteries, fuel cells, photovoltaic cells, flexible cells and photo-degradation catalysis (3). It has recently been largely employed to improve the photovoltaic efficiency of DSSCs in general

and for dye-based solar cells in particular (4), as it enhances the efficiency of the solar cell better than if it used pure single semiconductors (5). Copper oxide nanoparticles are normally the chosen substance in the solar cell industry, as a result of being an enhancer of the photocurrent density, which increases the efficiency of energy conversion (6,7). Although tin dioxide is commonly used as a carrier of electrons as a result of being an n-type semiconductor and having a wide bandgap energy but its efficiency is limited, so it is resorted to dopping or forming nanocomposites with other materials to improve its properties (8,9).

The electrolytic techniques are methods that deals with electro-chemical reactions were carried out as result to passing electrical current through electrolytic cell solution .The electrolytic methods of nanoparticles preparation are specializes in several advantages over other methods such as; production a high purity nanoparticles , possibility to control on morphology and size of nanoparticles by regulating the electrical and chemical parameters, low cost , shortened time to production of product ,high efficiency , don't causes any pollution troubles, and tremendously selective methods (10,11).

2. EXPERIMENTAL

2.1 Electrolytic Preparation of CuO/SnO2 Nanocomposites

The electrolytic system for the preparation of CuO/SnO2 Nanocomposites powders. A 250 ml glassy beaker, pure copper and tin foils as positive anode electrode, graphite plate as negative cathode electrode, D.C-regulated power supply (30 volts–maximum voltage and 5000 milli-ampere maximum currents), stirrer plate, and magnetic stirrer bar were used for providing and measuring the electrolytic system for the preparation of CuO/SnO2 nanocomposites. Prior to electrolysis, both the two electrodes were washed by ethanol and then deionized water is used to clean the two electrodes surfaces from any organic materials. In a typical electrolytic procedure; the electrolytic cell is filled with 200 millileters solution which contains: 5 millileters of 10 g/100 ml of KCl as the electrolyte, 10 mL of 1 g/100 mL of the stabilizer (Polyvinyl alcohol (PVA), Polyvinyl pyrrolidone (PVP)) and deionized water. A pure foil of copper-tin (2 cm x 4cm x 0.25mm) and inert graphite electrode (2 cm x 4 cm) were used as anode and cathode respectively, being vertically placed face to face in the electrolytic cell solution with 2 cm apart. The electrolysis reaction was carried out for one hour in electrolytic cell and stirred at a temperature of (50-60) °C. The voltage is at a range of (6-10) volt. After (10-15) minutes of starting electrolysis, an orange suspended solution is produced of Cu(OH)2 / Sn(OH)4 nanocomposites(NCs). The resulted precipitates orange Cu(OH)2 / Sn(OH)4 NCs were centrifuged, rinsed with deionized water(D.W) and ethanol many times and dried at 60℃ for 1 hour , then calcinated at 700 °C for 1 hour for formation navy colored precipitate from CuO/SnO2 Nanocomposites.

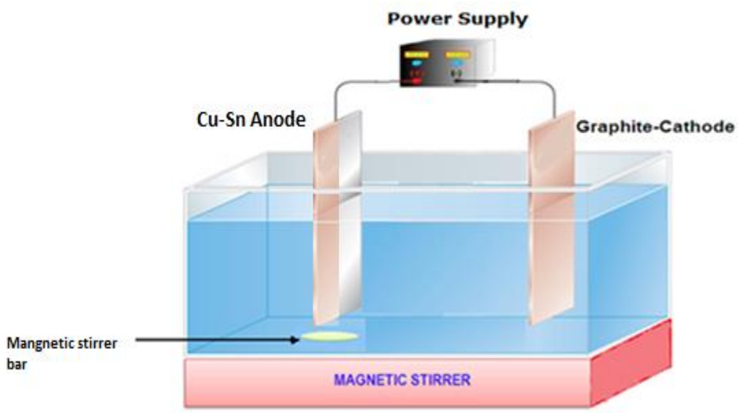


FIGURE 1: The electrolytic system of CuO/SnO2 Nanocomposites preparation.

2.2 Extraction of the Natural Dyes

The dye was extracted from parsley leaves according to similar states (12): 20g of parsley leaves were weighted, washed well with deionized water, then leave to dry. After that, it is immersed in 25 ml of ethanol, and left for one day. Then the solution was filtered and kept in a bottle darkened light in a temperature less than 8 °C .The pomegranate dye was extracted from pomegranate juice by filtering and then concentrating.

2.3 Redox Electrolyte between Two Electrodes

A solution of iodine (0.1 M) was prepared, 10 g of potassium iodide (KI) was dissolved in 25 ml of DW , and 3.175 g of iodine (I2) liquid is added, until it dissolves and then the solution is kept. After that a working electrode is putted on the counter pole and an adhesive tape is placed between the electrodes, provided that the solution does not leak from the area

2.4 Working Electrodes

ITO glass substrates was utilized as an electrical contact for preparation the optical anode. The glass substrates were washed in ethanol and air dried. Then, ITO is coated with pre-prepared CuO/SnO2 Nanocomposites paste by doctor blade technique. The membranes were put in an electric oven at 450 °C after 15 minutes. Through heat treatment, the optical anodes are ready. After that immerse in a dye solution for 12 hours and then washed in ethanol and distilled water to remove excess dye particles. Graphite was utilized as an anti-electrode after the DSSCs was fabricated by two electrodes with a separator. Finally, an iodine /iodate electrolyte was utilized between the two electrodes to complete the solar cell architecture (13).

3.CHARACTERIZATION

X-ray diffractometric (XRD) study was used Cu-Kα1 radiation line analysis of the crystal structure of the prepared CuO/SnO2 Nanocomposites samples. The morphology and size of nanoparticles were observed by scanning electron microscopy (SEM) and high resolution transmission electron microscopy (HR-TEM). Energy dispersive X-ray spectroscopy(EDS) was used to determine the purity and chemical compositions. Eg was calculated by using UV-visible technology. The solar cell I-V is measured with a Keithley device.

3.1 Characterization of CuO/SnO2 Nanocomposites

The XRD patterns were used for study the purity and phases of two prepared CuO/SnO2 Nanocomposites powders. The XRD patterns of two CuO/SnO2 Nanocomposites which prepared by PVA and PVP show that the CuO crystal structure is in monoclinic-tenorite phase (JCPDS Card-No: 48-1548) and the SnO2 crystal structure is in rutile tetragonal SnO2 (JCPDS Card No: 41-1445).The CuO peaks are appeared at the 2θ of around 32.563 , 35.567 , 38.7801, 48.833, 53.517, 58.241, 61.601 ,66.075 68.023 and 72.367 values were match with (110), (002), (111), (202), (020), (202), (113), (311), (220) and (311) lattice plane of CuO respectively. The SnO2 peaks are appeared at the 2θ of around 26.80 , 34.16 , 38.20, 39.02, 42.84, 52.02, 55.04 ,58.02, 61.80, 64.96 , 66.20 , 71.64 and 78.88 values were corresponding to (110), (101), (200), (111), (210), (211), (220), (002), (310) , (112) , (301) , (202) and (321) lattice plane of CuO respectively.The average diameter of prepared crystals were determined by Scherrer's method and it found to be 18.8 nm and 22.4 nm for CuO/SnO2-PVA and CuO/SnO2-PVP crystals respectively.

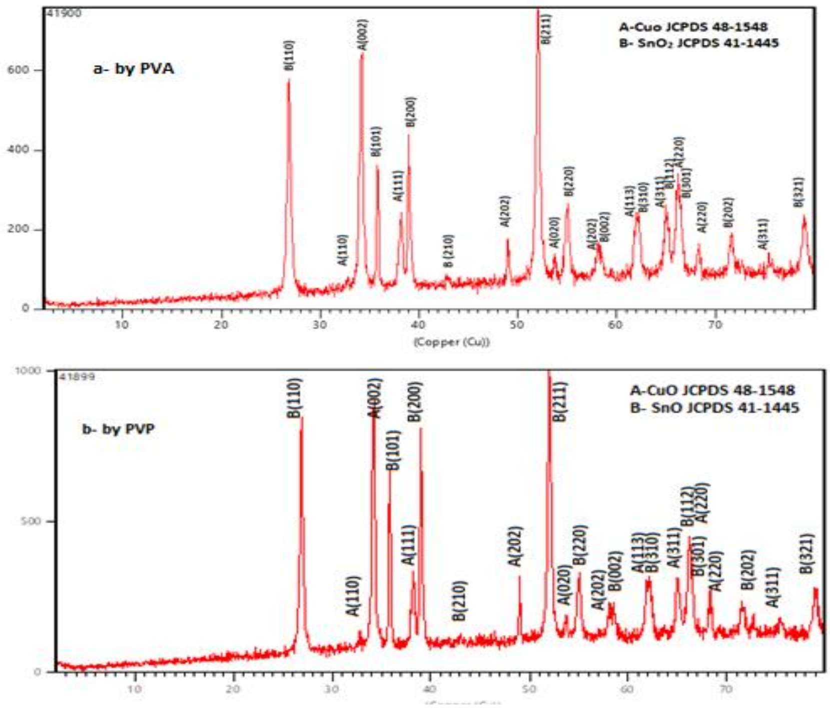
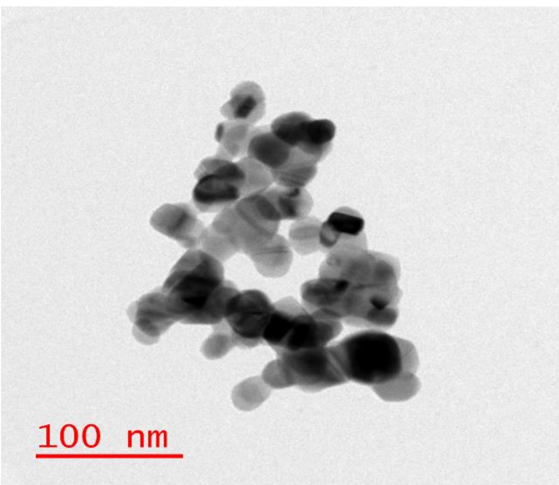
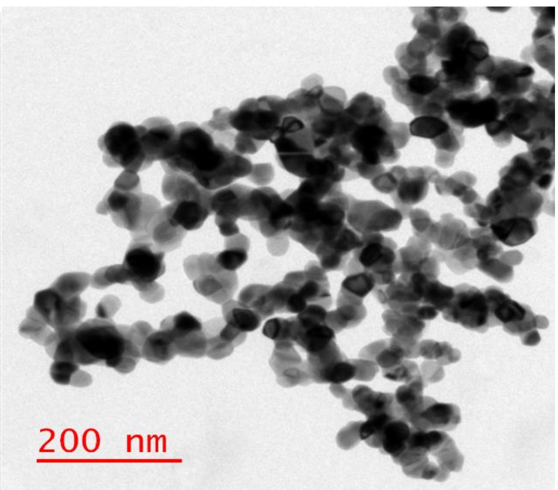


FIGURE 2: X-Ray Diffraction pattern of CuO/SnO2 Nanocomposites were prepared by (a- PVA and b- PVP)

3.2 High Resolution Transmission Electron Microscopy (HRTEM) Analysis

The morphological and structural information were studied by HRTEM. Figure (3 and 4) of HRTEM images of CuO/SnO2 Nanocomposites were prepared by PVA and PVP at a different magnification shows the HRTEM micrographs of CuO/SnO2 Nanocomposites have nanostructured regular and homogeneous rectangular and cubic shapes, with mean particle sizes is approximately 30nm. Figure (3) shows the HRTEM micrograph of CuO/SnO2 Nanocomposites were prepared by PVA and Figure (4)CuO/SnO2 Nanocomposites were prepared by PVP .





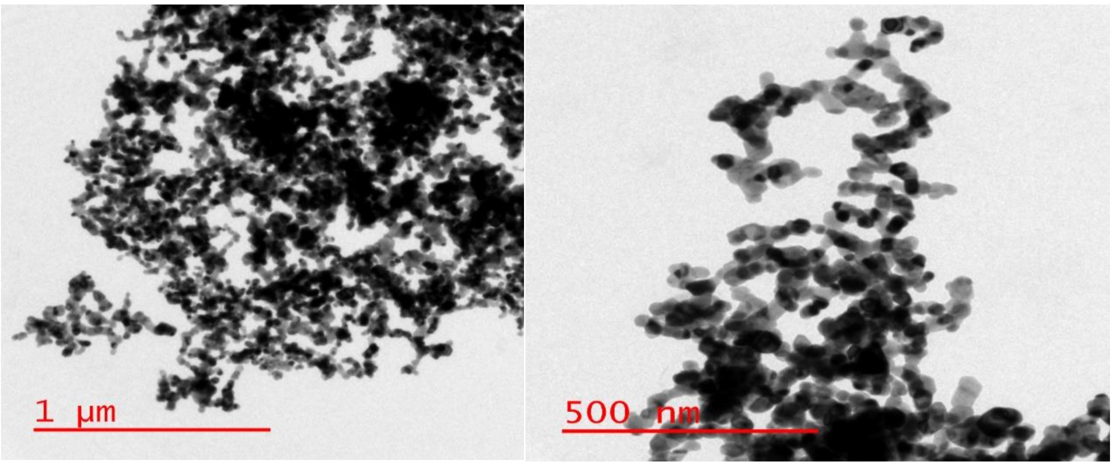


FIGURE 3: HRTEM micrographs of CuO/SnO2 Nanocomposites were prepared by PVA as stabilizer.

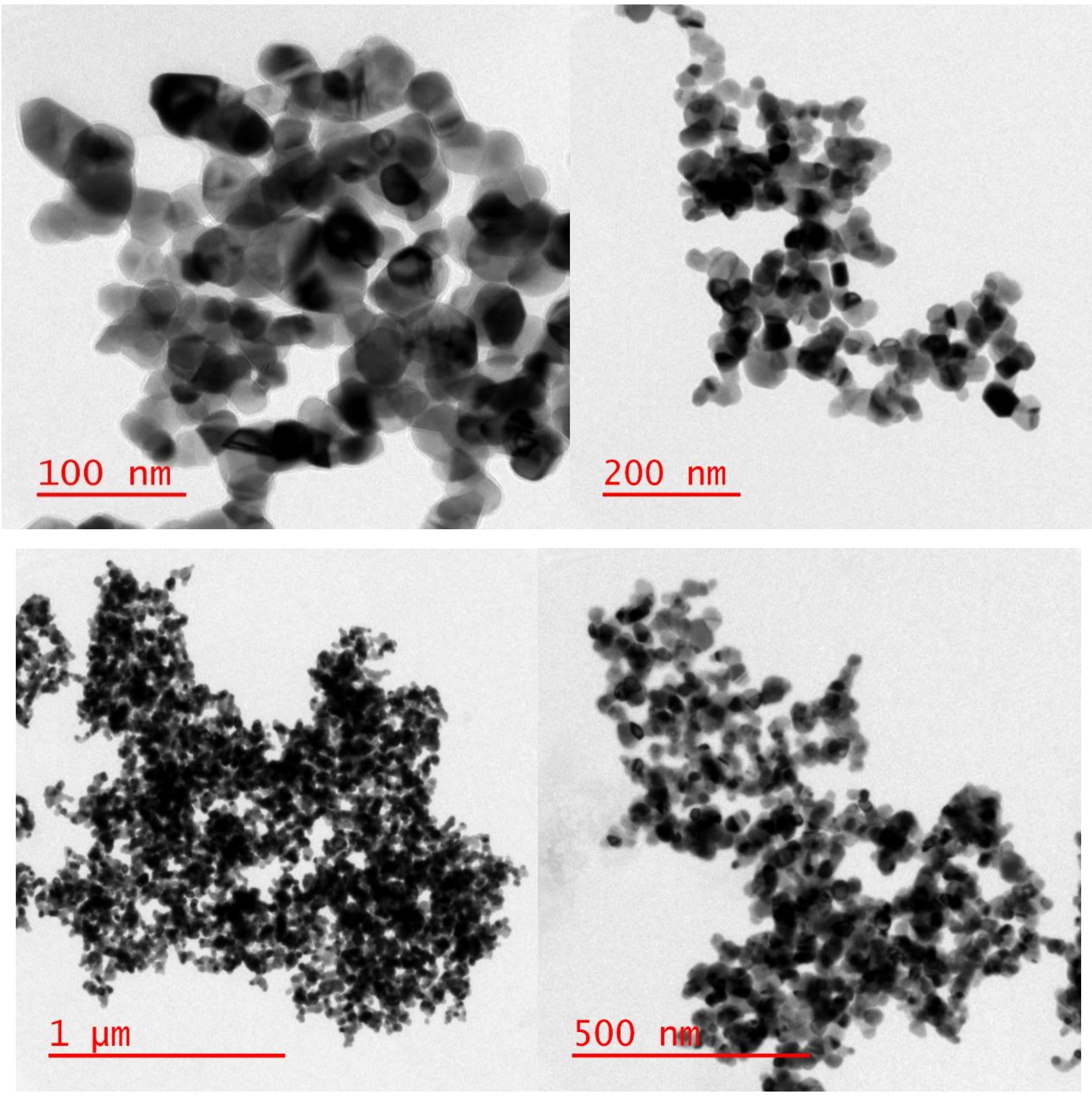


FIGURE 4: TEM micrographs of CuO/SnO2 Nanocomposites were prepared by PVP as stabilizer

3.3 The Field Emission Scanning Electron Microscope (FESEM)

The surface morphology and particle size were studied by two – dimensional micrograph FESEM analysis. Figure (5) shows that the FE-SEM micrographs of CuO/SnO2 Nanocomposites were prepared by PVA as stabilizer have a homogeneous regular cubic with size range about 45 nm. The FE-SEM micrographs with a different magnification CuO/SnO2 Nanocomposites were prepared by PVP as stabilizer are shown in figure (6) and have spherical shape with average size about 35 nm and nanotubes with average diameter about 41.8 nm with a flower-like structure overall appearance.

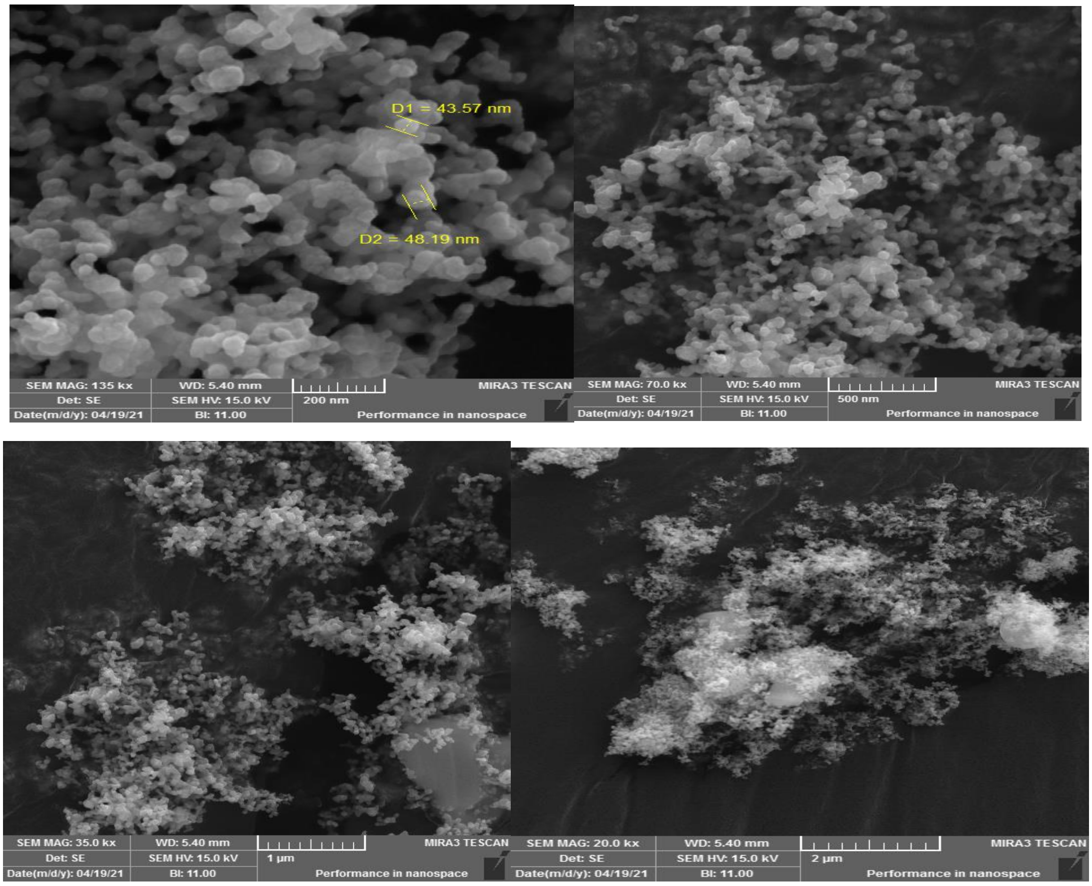
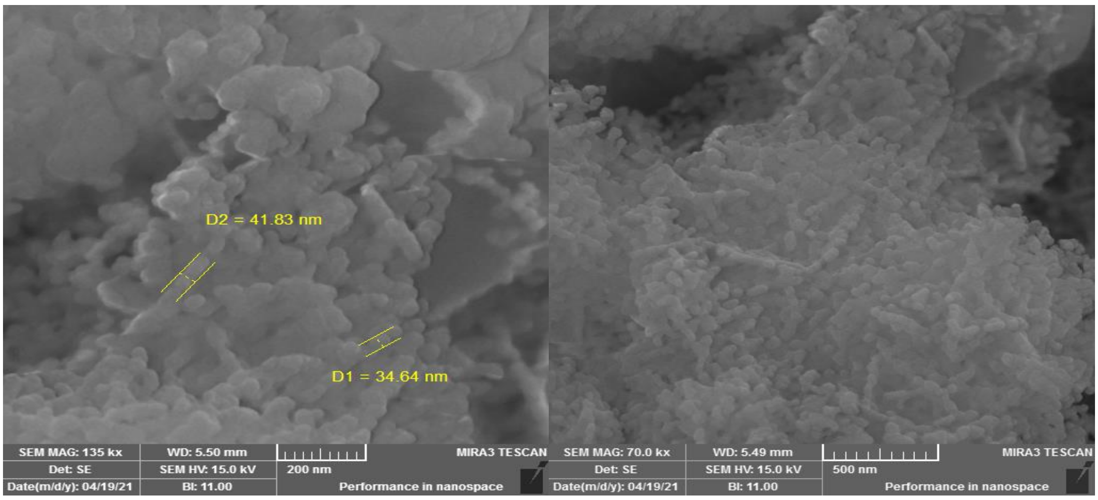


FIGURE 5: FE-SEM micrographs of CuO/SnO2 Nanocomposites were prepared by PVA as stabilizer



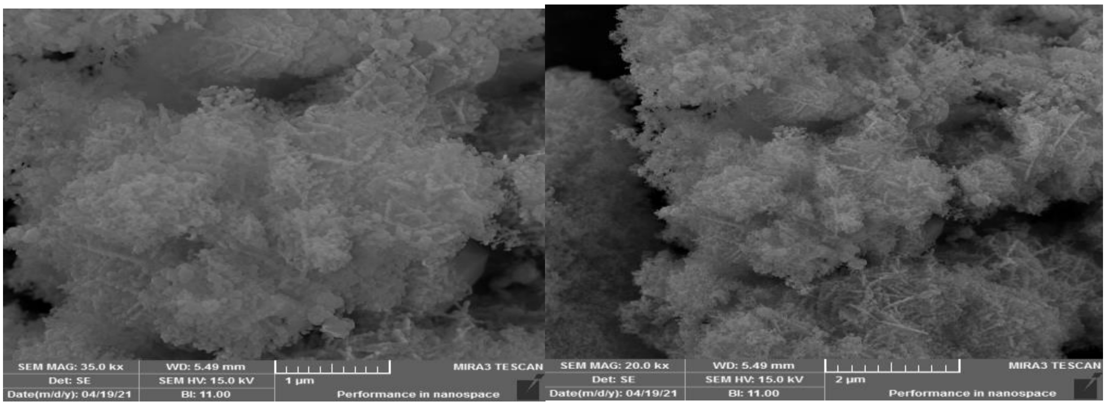


FIGURE 6: FE-SEM micrographs of CuO/SnO2 Nanocomposites were prepared by PVP as stabilizer

3.4 Energy Dispersive X-Ray Spectroscopy (EDX)

The EDX technique was utilized to study of elemental analysis or chemical characterization and purity of prepared samples. Figures (7 and 8) The EDX spectra of CuO/SnO2 Nanocomposites were prepared by PVA as stabilizer and CuO/SnO2 Nanocomposites were prepared by PVP as stabilizer are indicated that the high purity of the prepared nanoparticles, and the ratio of Cu:O /Sn:O were found to be around 1:1 /1:2 for the two samples.

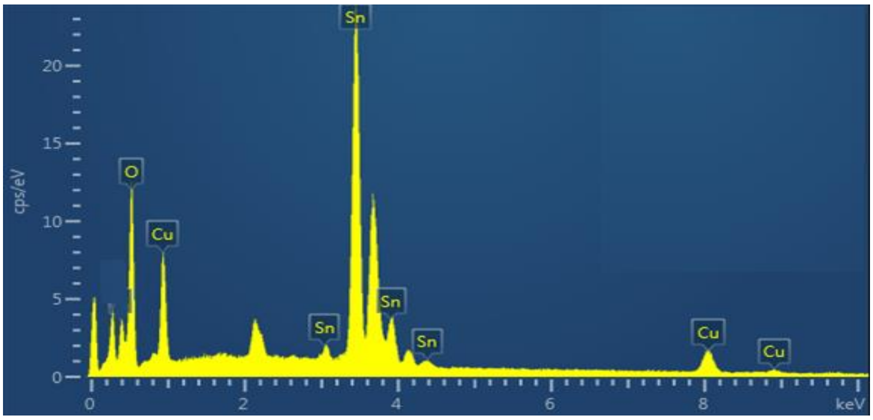


FIGURE 7: EDX spectrum of CuO/SnO2 Nanocomposites were prepared by PVA as stabilizer

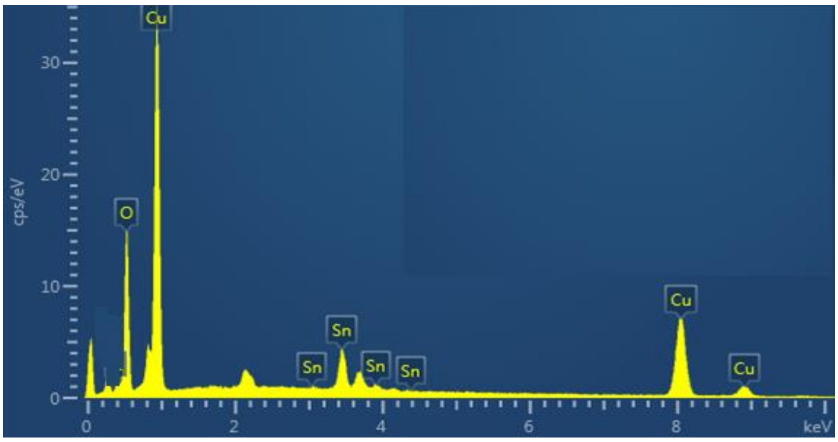


FIGURE 8: EDX spectrum of CuO/SnO2 Nanocomposites were prepared by PVP as stabilizer

3.5 UV-Visible Microscopy Analysis

The optical energy band-gap (Eg) of the CuO/SnO2 Nanocomposites were prepared by PVA and PVP as stabilizers were determined by tauc method which used the UV-Visible spectrum data. The Eg were found to be about 3.15 eV and 3.18 eV respectively.

4.Electrical Characteristics

The photocurrent density was observed under illumination, and the performance of DSSCs is measured by current density (mA/cm2) - voltage (mV) (I_V) measurements, characteristic curves with short-circuit current (Isc) and open-circuit voltage (VOC) were shown in figure (9) .The fill factor (FF) and photo-conversion efficiency (η) of the fabricated DSSCs were illustrated in table 1 .

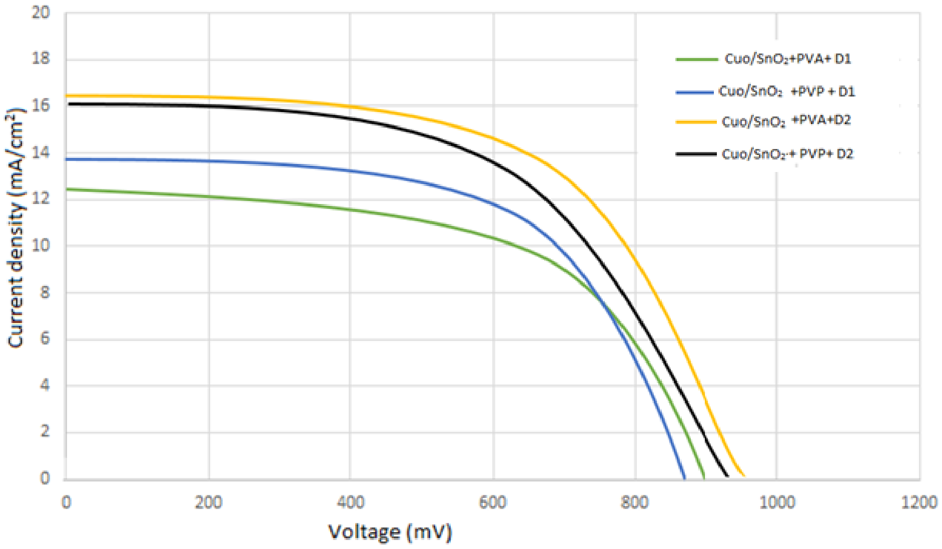


FIGURE 9: I-V characteristics of fabricated DSSCs ; CuO/ SnO2+ PVA + pomegranate dye (D1) , CuO/ SnO2+PVP+pomegranate dye (D1), CuO/ SnO2 + PVA + parsley dye (D2) and CuO/ SnO2 + PVP+ parsley dye(D2).

TABLE 1: Photovoltaic properties of fabricated DSSCs

Catalyst+stabilizer+ dye	Isc (mA/cm2)	Voc(V)	Im (mA/cm2)	Vm (V)	FF	η%
Cuo/SnO2+PVA+D1	12.60	0.901	9.60	0.63	0.5333	0.9163
Cuo/ SnO2+PVP+D1	13.8	0.88	11.2	0.638	0.5884	1.082
Cuo/ SnO2+PVA+D2	16.2	0.97	11.8	0.66	0.4956	1.18
Cuo/ SnO2+PVP+D2	16.01	0.94	11.2	0.64	0.4766	1.086

5 CONCLUSIONS

Cuo/SnO2 nanocomposites(NCs) were synthesized by the electrodeposition method using PVA and PVP as stabilization agents.

Cuo/SnO2 nanocomposites(NCs) with parsley dye are given higher efficiency as the photoelectric anode in DSSCs than pomegranate dye natural dyes.

That means the chemical structure of dye has a very important role in enhancement the efficiency of the DSSCs, as the DSSCs manufactured from the parsley dye a much higher efficiency than the DSSCs manufactured from pomegranate dye in all cases. That may be attributed to the fact that parsley chlorophyll dye contains an abundance of electrons capable to provide the DSSCs with these electrons better than the anthocyanin dye found in pomegranate .

REFERENCES

1. Daiyaan K. , etal," Dye-sensitized solar cell with plasmonic gold nanoparticles modified photoanode", Nano-Structures & Nano-Objects, Volume 26, April 2021, 100698.
2. S Bera, D Sengupta, S Roy and K Mukherjee," Research into dye-sensitized solar cells: a review highlighting progress in India", J. Phys. Energy 3 (2021) 032013.
3. B. Kurc , M. Pigłowska , Ł. Rymaniak and P. Fu´," Modern Nanocomposites and Hybrids as Electrode Materials Used in Energy Carriers", Nanomaterials ,2021, 11, 538.
4. F. Ziaeifar, A. Alizadeh and Z. Shariatinia," Dye sensitized solar cells fabricated based on nanocomposite photoanodes of TiO2 and AlMo0.5O3 perovskite nanoparticles", Solar Energy 218 (2021) 435–444.
5. R.Sekar,etal, " Ultrasonically synthesized TiO2/ZnS nanocomposites to improve the efficiency of dye sensitized solar cells" , Materials Science in Semiconductor Processing, Volume 132, September 2021, 105917.
6. H. Siddiqui , etal.," Utility of copper oxide nanoparticles (CuO-NPs) as efficient electron donor material in bulk-heterojunction solar cells with enhanced power conversion efficiency", Journal of Science: Advanced Materials and Devices, Volume 5, Issue 1, March 2020, Pages 104-110
7. Prerna M.A., Singh S.A.," Improved performance of solution processed organic solar cells with an additive layer of sol-gel synthesized ZnO/CuO core/shell nanoparticles" , Journal of Alloys and Compounds,Volume 814, 25(2020), 152292
8. Young W.N.,etal." Tailored electronic properties of Zr-doped SnO2 nanoparticles for efficient planar perovskite solar cells with marginal hysteresis" , Nano Energy,Volume 65, (2019), 104014
9. Hafiz M. A.J.,etal." Investigation on the surface modification of TiO2 nano hexagon arrays based photo anode with SnO2 nanoparticles for highly-efficient dye-sensitized solar cells", Materials Research Bulletin,Volume 109, (2019), Pages 21-28.
10. P. D Shelke and A. S Rajbhoj ; " Electrolytic Synthesis and their Photocatalytic Application of Mesoporous γ-Al2O3 Nanoparticles" Der Chemica Sinica, 8(2017)5:482-486.
11. F. J.Sheini, M. Cheraghizade, R. Yousefi," Electrolyticly synthesis and optoelectronic properties of Pb- and Zn-doped nanostructured SnSe films", Applied Surface Science, 443(2018) : 345-353.
12. S.S.Ishwar ,C.M.Shubham, S.S. Prakash, S.K.Pankaj and S.L.Bahadur ," Application of new natural dyes extracted from Nasturtium flowers (Tropaeolum majus) as photosensitizer in dye-sensitized solar cells", Optik ,Volume 243 (2021): 167331
13. Rahul,S.Singh,P. K.Singh,S.Kakroo,D. M.Hachim,P. S. Dhapola, Z. H. Khana," Eco-friendly dye sensitized solar cell using natural dye with solid polymer electrolyte as hole transport material",Materialstoday, 34(2021) 3: Pages 760-766