

# Enhancing the Optical Efficiency of ZnO–CuO Nanocomposites by Phycocyanin Inclusions for Solar Cell Applications

A.L. Subramaniyan<sup>1</sup>, P. Gopinath<sup>2</sup>, S. Sabari<sup>2</sup>, and M. Kathiresan<sup>2</sup>

<sup>1</sup>Department of Physics, Thiagarajar College of Engineering, Madurai, India

<sup>2</sup>Department of Mechanical Engineering, Thiagarajar College of Engineering, Madurai, India

## \*Correspondence to:

AL Subramaniyan  
Department of Physics, Thiagarajar College of  
Engineering, Madurai, India  
E-mail: [alsphy@tce.edu](mailto:alsphy@tce.edu)

Received: October 18, 2022

Accepted: December 20, 2022

Published: December 22, 2022

**Citation:** Subramaniyan AL, Gopinath G, Sabar S, Kathiresan M. 2022. Enhancing the Optical Efficiency of ZnO–CuO Nanocomposites by Phycocyanin Inclusions for Solar Cell Applications. *Nanoworld J* 8(4): 103-106.

**Copyright:** © 2022 Subramaniyan et al. This is an Open Access article distributed under the terms of the Creative Commons Attribution 4.0 International License (CC-BY) (<http://creativecommons.org/licenses/by/4.0/>) which permits commercial use, including reproduction, adaptation, and distribution of the article provided the original author and source are credited.

Published by United Scientific Group

## Abstract

This work was focussed on increasing optical transmittance of zinc oxide (ZnO) nano powders by doping it with copper oxide (CuO) and phycocyanin. ZnO–CuO nanocomposites were prepared by sol-gel assisted methods with zinc acetate and copper chloride as precursors. The prepared nanocomposites were characterised by X-ray diffraction (XRD) for structural features and scanning electron microscope (SEM) for morphology. The crystallite size from XRD pattern was found to be 24 nm. Phycocyanin was incorporated in the prepared ZnO–CuO nano powders by hand milling technique and optical absorption was analyzed with Ultraviolet-Visible (UV-Vis) spectroscopy studies. The absorbance of phycocyanin included ZnO–CuO nanocomposites was decreased in the range of 550 - 750 nm compared to pure ZnO–CuO nanocomposites indicating a rise in transmission. This was a successful attempt to increase the transmission from 500 nm for ZnO based solar cells against the previously reported low transmittance in visible range. The work recommends incorporation of Phycocyanin for cheap efficient higher transmission nanostructures-based metal oxide solar cells.

## Keywords

Solar cells, Nanocomposites

## Introduction

Non-materials have gained importance due to their unique size dependant properties. Discovering the novel unexplored properties at nanoscale has remained a challenge in nanotechnology. Among the various nanomaterials used, metal oxide nanostructures have been more widely used than metal nanostructures because of their easy method of preparation, large scale synthesis, low cost, and bio compatible nature. Metal oxides have been investigated to a greater extent in academic laboratories. Several nanostructure metal oxides like CuO, ZnO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, etc. have been investigated to a large extent. The main reason could be due to the possibility of preparation of above materials by sol-gel technique and the wide methods of synthesis like hydrothermal, solvothermal, CVD, and PVD techniques available. ZnO is researched widely in comparison to other metal oxides and is also the poor man's semiconductor. The major advantages of ZnO nanostructures include the multiple substrates options for growth, high electron mobility, good transparency, room temperature luminescence, bio compatibility, and bio safety [1]. ZnO has a tuneable wide band gap which is apt for solar cell materials. ZnO can be used in dye sensitised solar cells providing a cheap low-cost alternative to the conventional inorganic silicon (Si) solar cells. Each single Si cells can produce a maximum open circuit voltage of 0.5 - 0.6 V and power of 0.7 W. ZnO based dye sensitised solar cells (DSSC) have reported to have an open circuit voltage of 0.807 V [2]. However, the Si solar cells can yield an

efficiency of 4 times more than ZnO based DSSC. The major hindrance with DSSC is the low absorption of photons across the entire spectrum of sun light. Thus, improving the optical transmittance of ZnO can increase the efficiency of ZnO based DSSC. Doping ZnO with 1% to 3% and 6% to 30% Cu has shown to increase the transmittance of ZnO thin films [3, 4]. The scattering light in thin film ZnO based solar cells is harvested efficiently by modification in nanoparticle density through Al and Cu inclusions [5]. Doping ZnO with CuO can increase the surface area providing more reaction sites and increasing the electron transfer. CuO-ZnO nanocomposite based solar cells have reported to have a maximum conversion efficiency of 1.52% and an open circuit voltage of 0.41 [6]. The efficiency can be tuned with nanosized, nanoshape and composition variation of ZnO & CuO. ZnO can absorb only UV radiation whereas CuO can absorb the radiation till 1000 nm. Thus, a combination of ZnO-CuO can increase the absorption of sunlight over a broad range in comparison to pure ZnO. One of the main aims of this work was to enhance the optical transmission of ZnO and hence nanocomposites of ZnO-CuO have been investigated.

Phycocyanin is a pigment protein complex and is an accessory pigment to chlorophyll. It is generally used in medical and food applications and has a deep blue colour which can absorb radiations in the range of 600 nm. Hence inclusions of phycocyanin in the metal oxide based solar cells can increase the optical transmission. The present work was focussed on improving the optical transmission of ZnO-CuO Nanocomposites with phycocyanin inclusions for better transmittance by reduced absorbance.

If the transmittance of ZnO is improved in solar cell applications, it can potentially replace the ITO (Tin doped indium oxide layer). The ZnO conductive thin film has shown a high transmittance in the range of 800 nm - 1200 nm. The average transmittance in 300 - 1200 nm range is less and needs improvement [7]. It has been suggested that annealing or doping can enhance the optical performance of ZnO thin films. Annealing can change the grain size of the nanostructures and doping can produce interfacial defects which can alter the transmittance property. In the present work, ZnO has been investigated with CuO and phycocyanin inclusions, with an attempt to decrease the absorbance. ZnO - CuO nanocomposites with phycocyanin inclusions can also be coated on flexible substrates improving the usability of ZnO based electronics [8]. The present work aims to improve the transparency of ZnO based nanostructures. Though ITO are used extensively as transparent electrodes for various optoelectronic devices like LED, Solar cell, and OLED, they suffer from drawback of high cost. If the transmittance of ZnO based nanostructures can be enhanced, they can be a cheap substitute for ITO [9]. Previous research work was reported on increasing the transmittance of ZnO through Gallium dopants and by Chemical vapour deposition [10]. In this work an attempt to increase the transmittance of ZnO through low cost dopants (CuO, and phycocyanin) and low temperature synthesis methods was presented. Increasing the transparency of ZnO can also provide a high degree of protection against UV radiation [11]. Several works have also been reported with composites made from ZnO. Among all nanocomposites,

CuO-ZnO has attracted more interest in researchers. This is due to their tunable properties and nontoxic nature [12]. CuO can lower the band gap of ZnO and enhance its conductivity. It can also aid the photo catalytic and gas sensing properties of ZnO nanostructures. The complete interaction mechanism between CuO and ZnO is yet to be explored but researchers have demonstrated efficient solar cell applications for CuO-ZnO nanocomposites [13]. It has been reported that the transmittance and optical band gap of ZnO decreased with increasing concentration of CuO in the visible wavelength range [14]. In the present work phycocyanin, pigment protein complex was added in ZnO-CuO nanostructures with an attempt to increase the transmittance of ZnO for making more efficient ZnO-CuO nanostructure solar cell materials.

## Materials and Methods

0.1 M solution each of zinc acetate dihydrate and copper chloride with water are prepared individually by magnetic stirring for 1 hour each. The contents were then made into a single solution and suitable amount of NaOH was added so that the pH reaches 10.5 approximately. The contents were stirred for two hours and calcined at 500 °C for 2 hours. The product was hand milled to get nanocomposites of ZnO-CuO. The complete synthesis process for ZnO-CuO composites can be found in [15]. The prepared nanocomposites were characterised by XRD and SEM. Phycocyanin was added in the ratio 1:1 and the UV absorption of both the composites were investigated to analyse the optical absorption of phycocyanin included ZnO-CuO nanocomposites. The flow chart for the entire work was shown in Figure 1 and preparation of ZnO-CuO nanocomposites with phycocyanin was shown in Figure 2.

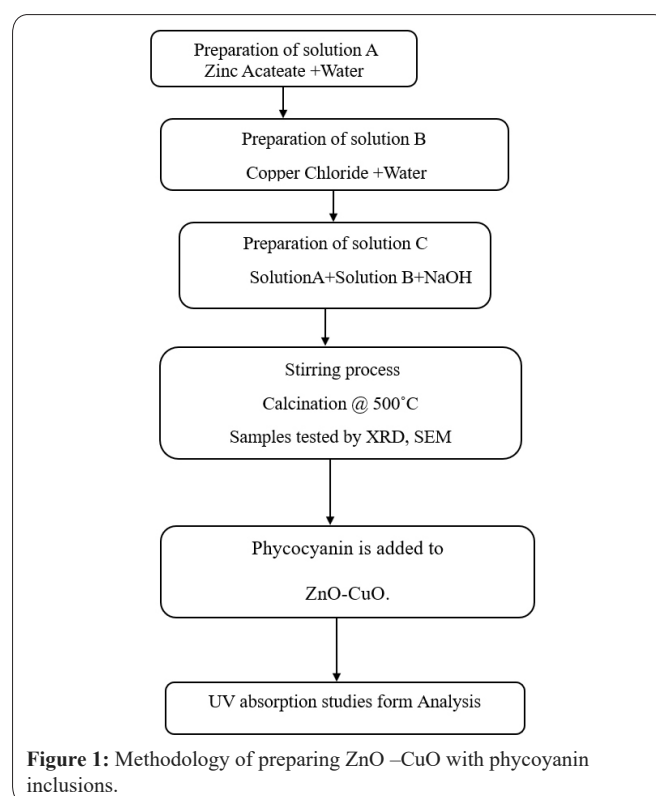


Figure 1: Methodology of preparing ZnO -CuO with phycocyanin inclusions.

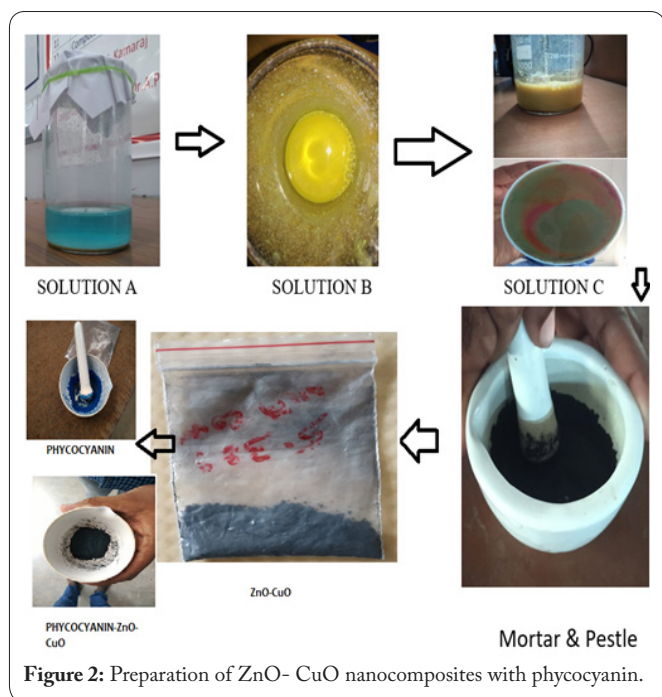


Figure 2: Preparation of ZnO- CuO nanocomposites with phycocyanin.

## Results and Discussion

XRD analysis was performed with PANalytical X'Pert PRO powder X-ray Diffractometer. XRD analysis is performing with X rays of Wavelength 1.54Å for diffraction angles from 20° to 80°. The scan size was 0.05 and scan step time was 10 seconds for 0.05° with a temperature of 25 °C. The start angle and end angle of scanning were 20° and 80°. The five peaks present between 2θ values of 30° to 40° indicate the presence of ZnO-CuO composites. The peaks corresponding to 32°, 34°, and 36° indicate the presence of ZnO and peaks close to 35° and 38° indicate the presence of CuO[8]. The XRD pattern was compared with JCPDS -48-1548 for CuO and JCPDS-036-1451 for ZnO. The peaks from 38° indicate reflection form (111) plane due to CuO phase and peak at 32° indicate reflection from (100) plane due to ZnO phase. By using Debye–Scherrer equation crystallite size calculated from

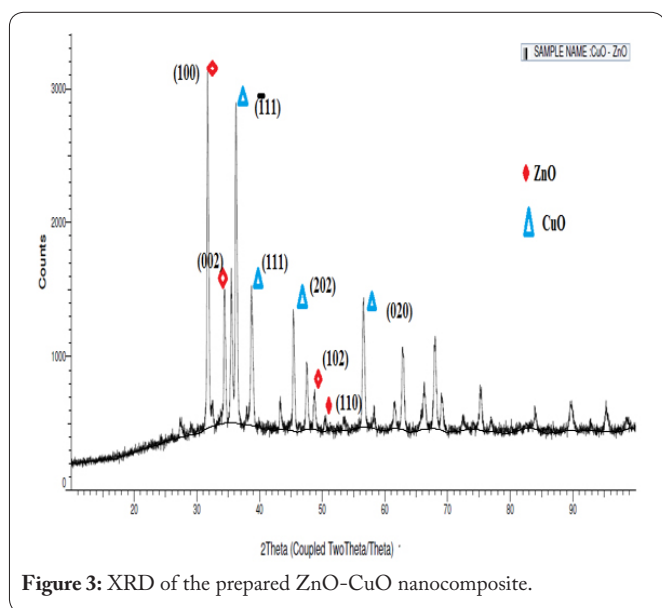


Figure 3: XRD of the prepared ZnO-CuO nanocomposite.

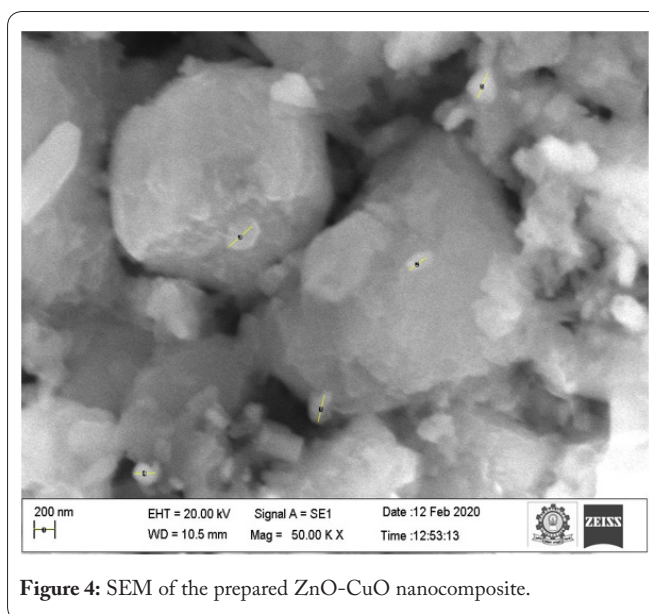


Figure 4: SEM of the prepared ZnO-CuO nanocomposite.

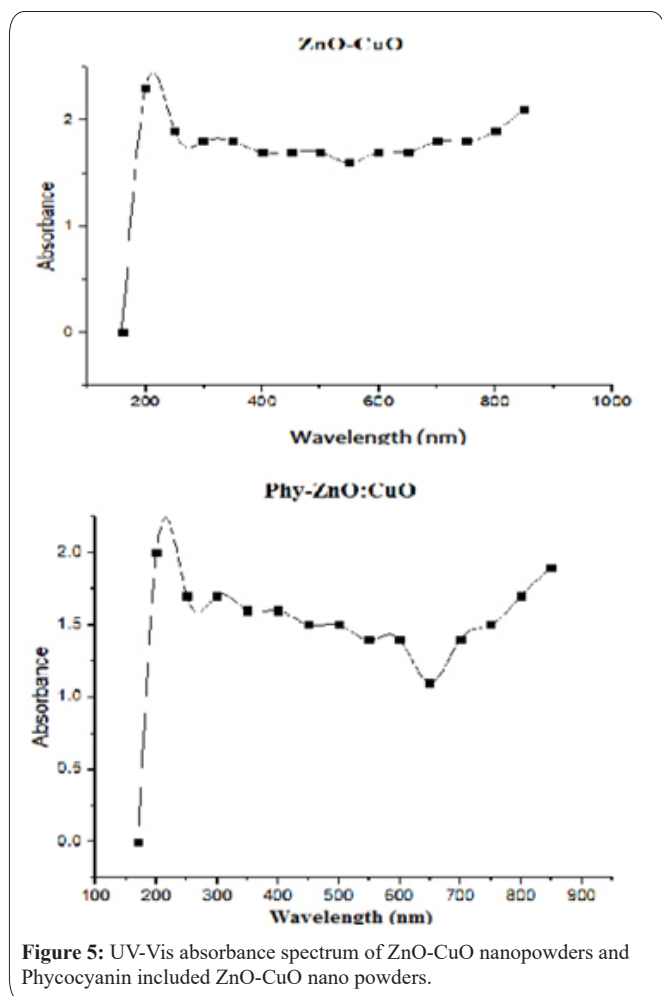
XRD was 24 nm. The XRD of the prepared ZnO-CuO nanocomposite was shown in Figure 3 The morphology of prepared sample was investigated by SEM. The Quanta FEG-250 SEM instrument was used for SEM analysis in which resolution of 1.5 nm can be obtained. The average particle size from SEM was found to be 100 nm. The SEM image in Figure 4 indicate a heterogeneous particle size mixture of ZnO –CuO nanocomposites.

The prepared ZnO-CuO nanocomposites and phycocyanin included ZnO-CuO nanocomposites were investigated for their optical absorption by UV-Vis spectroscopy studies. The UV-DRS-spectrophotometer (Thermofisher) was used for investigation within a wavelength range of 190 - 900 nm. Compared to ZnO-CuO nanocomposites, phycocyanin included ZnO-CuO nanocomposites showed a sharp decrease in absorption from 550 - 750 nm. Thus, the transmittance of the phycocyanin included ZnO-CuO nanopowders was better in comparison to pure metal oxide composite and is a better candidate for solar cell energy harvesting applications. Due to better transmittance, more efficient ZnO photo anodes can be implemented in DSSC.

## Conclusion

Nanocomposites of ZnO- CuO were prepared via sol-gel method. The structural properties were examined by XRD. Crystal sizes were calculated by Debye–Scherrer relation and found to be 24 nm. The morphology was investigated by SEM. Heterogeneous particle size was revealed from SEM. The average particle size was found to be 100 nm from SEM. Phycocyanin was added with ZnO-CuO nanocomposites in the ratio 1:1 and the UV-Vis absorption spectroscopy revealed a better transmittance of the phycocyanin inclusions within a range of 550 to 750 nm. This can provide an alternative to the existing drawback ZnO-CuO heterojunction solar cells with low transmission in visible range. Thus, phycocyanin based ZnO-CuO nanocomposites can be a better material in place of ZnO photo anodes or thin film ZnO-CuO solar cell materials. There is a future scope for research by varying the amount





of phycocyanin inclusions in ZnO-CuO nanocomposites.

## References

1. Shahzad S, Javed S, Usman M. 2021. A review on synthesis and optoelectronic applications of nanostructured ZnO. *Front Mater* 8: 613825. <https://doi.org/10.3389/fmats.2021.613825>
2. Tanaka E, Nurdiwijayanto L, Hagiwara M, Fujihara S. 2018. Structural improvement of ZnO electrodes through solution-processed routes for enhancing open-circuit voltage in dye-sensitized solar cells. *J Solid State Electrochem* 22: 3119–3127. <https://doi.org/10.1007/s10008-018-4024-x>
3. Mhamdi A, Mimouni R, Amlouk A, Belgacem S. 2014. Study of copper doping effects on structural, optical and electrical properties of sprayed ZnO thin films. *J Alloys Compd* 610: 250–257. <https://doi.org/10.1016/j.jallcom.2014.04.007>
4. Abass NK, Shanani ZJ, Mohammed TH, Abbas LK. 2018. Fabricated of Cu doped ZnO nanoparticles for solar cell application. *Baghdad Science Journal* 15(2): 198–203. <https://doi.org/10.21123/bsj.2018.15.2.0198>
5. Thankalekshmi RR, Dixit S, Rastogi AC. 2013. Doping sensitive optical scattering in zinc oxide nanostructured films for solar cells. *Adv Mater Lett* 4(1): 9–14. <https://doi.org/10.5185/amlett.2013.icnano.137>
6. Das S, Srivatsa VM. 2018. An overview of the synthesis of CuO-ZnO nanocomposites for environmental and other applications. *Nanotechnol Rev* 7(3): 267–282. <https://doi.org/10.1515/ntrev-2017-0144>
7. Chen Y. 2018. Review of ZnO transparent conducting oxides for solar applications. *IOP Conf Ser Mater Sci Eng* 423: 012170. <https://doi.org/10.1088/1757-899X/423/1/012170>
8. Liu Y, Li Y, Zeng H. 2013. ZnO-based transparent conductive thin films: doping, performance, and processing. *J Nanomater* 2013: 196521. <https://doi.org/10.1155/2013/196521>
9. Vyas S. 2020. A short review on properties and applications of zinc oxide based thin films and devices: ZnO as a promising material for applications in electronics, optoelectronics, biomedical and sensors. *Johnson Matthey Technology Review* 64(2): 202–218. <https://doi.org/10.1595/205651320X15694993568524>
10. Ponja SD, Sathasivam S, Parkin IP, Carmalt CJ. 2020. Highly conductive and transparent gallium doped zinc oxide thin films via chemical vapor deposition. *Sci Rep* 10: 638. <https://doi.org/10.1038/s41598-020-57532-7>
11. Cao Z, Zhang Z, Wang F, Wang G. 2009. Synthesis and UV shielding properties of zinc oxide ultrafine particles modified with silica and trimethyl siloxane. *Colloids Surf A Physicochem Eng Asp* 340(1-3): 161–167. <https://doi.org/10.1016/j.colsurfa.2009.03.024>
12. Das S, Srivastava VC. 2018. An overview of the synthesis of CuO-ZnO nanocomposite for environmental and other applications. *Nanotechnol Rev* 7(3): 267–282. <https://doi.org/10.1515/ntrev-2017-0144>
13. Minami T, Miyata T, Ihara K, Minamino Y, Tsukada S. 2006. Effect of ZnO film deposition methods on the photovoltaic properties of ZnO-Cu<sub>2</sub>O heterojunction devices. *Thin Solid Films* 494(1-2): 47–52. <https://doi.org/10.1016/j.tsf.2005.07.167>
14. Chang HT, Shih YH, Chen GJ. 2016. Influences of CuO doping on the properties of ZnO films by RF magnetron sputtering. 2016 International Conference on Applied System Innovation (ICASI). 2016: 1–4. <https://doi.org/10.1109/ICASI.2016.753991.1>
15. Subramaniyan AL, Thirupathi S, Sathath MM, Kannan M. 2019. Investigation on thermal properties of CuO-ZnO nanocomposites. *Natl Acad Sci Lett* 42: 81–85. <https://doi.org/10.1007/s40009-018-0723-1>