

The influence of light and heat on the degradation of Cu₂O nanoparticles under humid conditions

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1. ABSTRACT

The Cu₂O is an oxide semiconductor with the potential for many applications. This study focused on changes in the structural and chemical properties of Cu₂O under different environmental conditions. The samples were stored under six different environmental conditions, for one month, to study the changes in Cu₂O surface morphology. The different environmental conditions are Dark-low humid, Dark-high humid, Illuminated-low humid, Illuminated-high humid, Illuminated - low humid under heat and Illuminated - high humid under heat. Cu₂O samples were prepared using electrolyte cell method and chemical bath heating method under same conditions. The sample characterization method of Scanning Electron Microscope (SEM) was used to study the surface morphology and X-ray Diffraction (XRD) was used to study the structural changes of Cu₂O under different environmental conditions compared to Cu₂O initial sample. The results revealed that, if the environment is high humid the Cu₂O nanoparticles will degrade whether it is at dark, illuminated, heated or at room temperature. The morphological feature of the Cu₂O particle can controlled or slowdown by applying the heat under low humidity.

2. INTRODUCTION

Copper oxide (Cu₂O) is a very important semiconductor for optoelectronics and photovoltaic applications; it is a promising candidate for technological applications due to its nontoxicity, and its wide and direct band gap in the order of 1.9-2.2 eV [1]. When thin films of copper oxide are forming, the copper atoms in Cu₂O are organized into a face-centered cubic (*fcc*) sublattice and the oxygen atoms into a body-centered cubic (*bcc*) sublattice as it crystallizes[2]. The lattice constant of this structure is 4.2696Å, and one sublattice is displaced by one-fourth of the body diagonal. Each copper atom in the lattice is linearly coordinated by two nearby oxygen atoms, and each oxygen atom is surrounded by four copper atoms [2].

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As it is designated a low-cost semiconductor material, cuprous oxide (Cu_2O) has been researched for use in low cost, environmentally friendly material for solar cells and other optoelectronic devices [3]. A recent study by Madusanka et al [4] have attempted to grow Cu_2O thin films on conducting glass substrate. And an extension of this study (not reported), to fabricate a solar cell; have revealed a rapid degradation in IV characteristics under illumination.

One of the challenges in Cu_2O nanoparticle research is the issue of stability and oxidation. Cu_2O nanoparticles are easily oxidized in presence of water and their nanostructure can be destroyed under certain external conditions such as pH. Therefore, finding ways to enhance the stability of Cu_2O nanoparticles and protect them from oxidation is a crucial direction for future research [5].

In application of solar cells, the devices are exposed to environmental conditions mainly heat, moisture and sun light. Therefore, the effects of environmental factors on Cu_2O nanoparticle stability and oxidation are an area that requires further investigation. Understanding how environmental factors such as pH, temperature, and light intensity affect the stability and oxidation of Cu_2O nanoparticles is important for their practical applications [6]. This study is focused on identifying the influences of heat and light on Cu_2O nanoparticles on a thin film under low and high humid condition.

3. METHODOLOGY

3.1 Sample preparation

A thin layer of Cu_2O was deposited on a ITO glass plate using electrodeposition and thermal oxidation. The ITO glass plate was cut into small pieces ($1\text{cm}\times 3\text{cm}$) to use as an electrode (cathode) to deposit a thin metallic copper layer. A piece of copper metal of purity 99%, ($2\text{cm}\times 3\text{cm}$) is used as the anode of the electrodeposition cell. First, ITO conductive glass and copper pieces were cleaned and the pieces were dried at room temperature [7]. The electrolyte solution was prepared with 0.3 mol dm^{-3} of copper sulfate pentahydrate (pure) and 0.5 mol dm^{-3} of sulfuric acid, mixed in 1:1 ratio by volume. Also, added a small amount of 0.05 mol dm^{-3} PEG400 and 0.002 mol dm^{-3} Sodium Chloride were added to the electrolyte solution [8]. The copper electrodeposition was performed by applying 2V potential between the electrodes using a KEITHLY 2400 source meter for 40 minutes [4]. After deposition of the metallic copper layer, the ITO glass was cleaned with distilled water and methanol [4].

The next step is to thermally oxidize copper into Cu_2O by using a chemical bath heating method [9]. The Cu-deposited ITO glass was dipped in a 0.1 mol dm^{-3} CuSO_4 bath at temperature between 70°C and 80°C , with continuous slow stirring, using a magnetic stirrer. In the final step of sample preparation, the sample was cleaned using deionized water.

3.2. Exposure to different environmental conditions

Samples (Cu_2O films) were exposed to four different environmental conditions: (i) Dark & low humid, (ii) Dark & high humid (iii) Illuminated & low humid, (iv) Illuminated & high humid. The dark condition is maintained by covering the samples under fully covered black substance. The illuminated area was created using a 11W compact fluorescent lamp (CFL, Philips) [10].

Furthermore, the low moisture content of the environment was maintained by placing desiccant surrounding the sample in a closed sealed capsule. The high humidity condition was applied to the samples by supplying water droplets into the closed capsule, surrounding the sample area with water droplets but without been contact with the samples. Several samples were prepared and stored under these four different environmental conditions. The desiccant in the low humidity environment condition was replaced once a week to maintain the humidity level. The humidity level and the average temperature of each environment condition were measured using a humidity meter. Further to understand any effects due to heat and the illumination (e.g. in a solar cell application the device gets heated under the sun), a set of separate samples were placed under tungsten lamp as the source (heat - illuminated) under low humidity and under high humidity conditions.

Samples were analyzed using SEM and XRD after continues 30 days of exposure to different environmental conditions. A fresh sample was used as the control. A Zeiss EVO model SEM was used to characterize the surface morphology of the Cu_2O nanoparticles, and ImageJ software was used to analyze the micrographs obtained. A Rigaku Ultima IV model X-Ray power diffractometer with $\text{Cu K}\alpha$ monochromatic source was used to analyze the chemical composition of the samples.

4. RESULTS AND DISCUSSION

4.1 Initial Cu_2O characterization

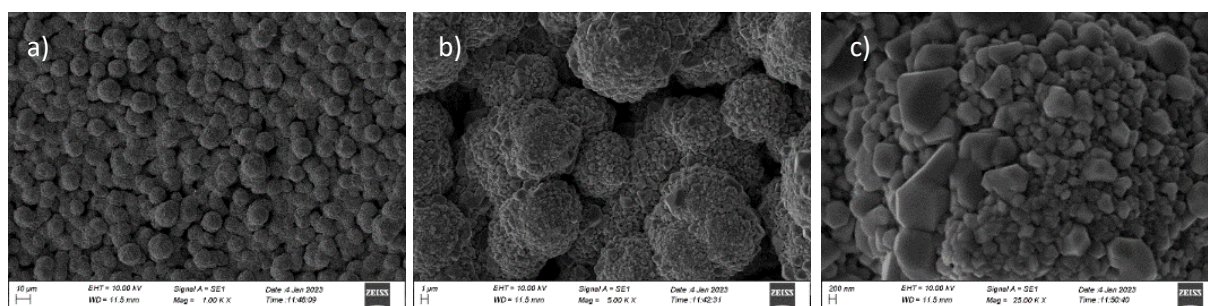


Figure 1 - a) 1k \times magnification SEM image of Cu_2O layer. b) 5k \times magnification SEM image of Cu_2O , c) 25k \times magnification SEM image of Cu_2O layer

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SEM is used to study the surface morphology of the Cu_2O layer, grain size, and surface features. The SEM images of the prepared Cu_2O nanoparticles (fresh sample) are shown in Figure 1. In the absence of the exposure to any environmental conditions, the products were large and showed a typical agglomeration feature [11], as suggested in Figure 1-a) and b). The Cu_2O particles were agglomerated into a spherical shape with an average diameter of $\sim 10.1 \mu\text{m}$. From the high SEM image in Figure 1 c), samples composed of numerous nanoparticles with an average diameter of $\sim 426.9 \text{ nm}$ were observed. Shape of these Cu_2O nanoparticles are truncated octahedron and octahedral [12].

XRD analysis shows that the peaks of Cu_2O at $2\theta = 35.8^\circ, 41.8^\circ, 60.8^\circ$ correspond to planes (1 1 1), (2 0 0) and (2 2 0), and well suited with ICDD[13]. In addition to the peaks of Cu_2O , the peaks of Cu also appeared at $2\theta = 42.7^\circ, 49.85^\circ, \text{ and } 73.6^\circ$; correspond to planes (1 1 1), (2 0 0), and (2 2 0), and also well suited with ICDD[13]. There are no signatures of byproducts (such as CuO) or residual products ($\text{Cu}(\text{OH})_2$) remaining in the Cu_2O sample.

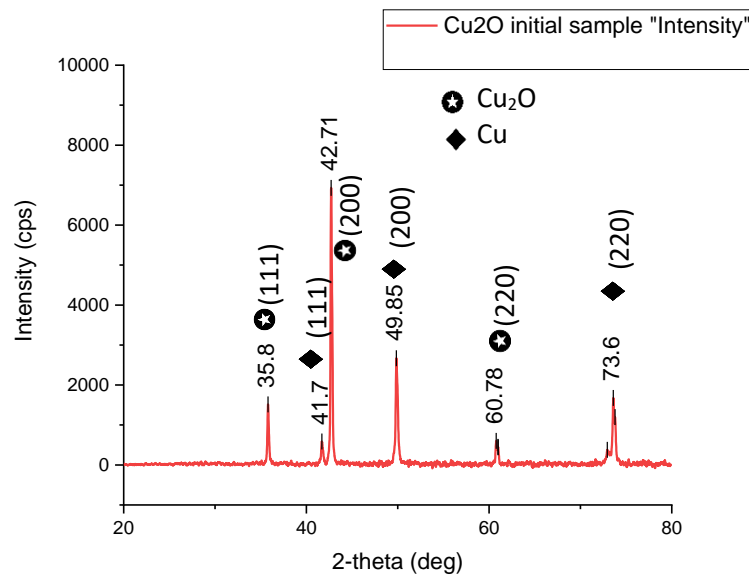


Figure 2 - XRD pattern of Initial Cu_2O sample. Cu_2O at $2\theta = 35.8^\circ, 41.8^\circ, 60.8^\circ$ correspond to planes (1 1 1), (2 0 0) and (2 2 0), and the peaks of of Cu also appeared at $2\theta = 42.7^\circ, 49.85^\circ, \text{ and } 73.6^\circ$; correspond to planes (1 1 1), (2 0 0), and (2 2 0)

4.2 XRD analysis of Cu₂O under different environment conditions

The XRD analyses for samples at four different environment conditions were compared with the initial condition to identify whether the new components were produced in the Cu₂O sample area. But there are no byproducts (such as CuO) created on the one month aged Cu₂O sample under any environment condition when compared with the initial sample peak positions. All the Cu₂O peak positions were appeared in the aged sample compared with the initial sample. Only the intensity of the Cu₂O peaks were decreased.

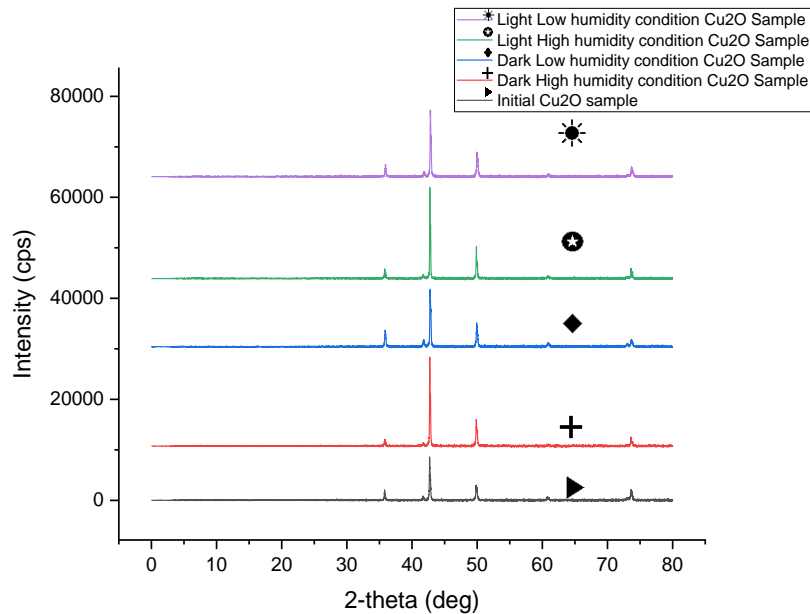


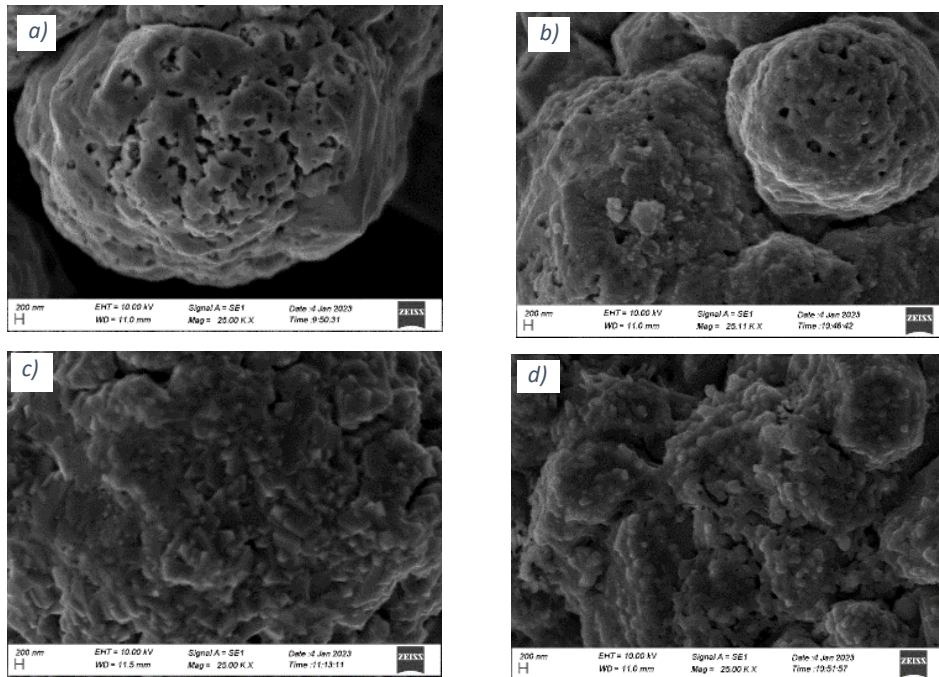
Figure 3 – XRD analysis of an initial Cu₂O sample, under Dark-high humidity Cu₂O sample, Dark-low humidity Cu₂O sample, Light-high humidity Cu₂O sample and Light- low humidity Cu₂O sample.

Figure 3 shows that the peaks of Cu₂O at $2\theta = 35.8^\circ$, 41.8° , 60.8° correspond to planes (1 1 1), (2 0 0) and (2 2 0) respectively and matched well with ICDD. In addition to the peaks of Cu₂O, the peaks for metallic Cu are also appeared at $2\theta = 42.7^\circ$, 49.85° , and 73.6° ; correspond to planes (1 1 1), (2 0 0), and (2 2 0), respectively. After 5 months aging there is neither shift no new peaks occur. Only the intensities of Cu₂O peaks at $2\theta = 35.8^\circ$, 41.8° , 60.8° were changed. Also, similar results were observed for Cu peaks at $2\theta = 42.7^\circ$, 49.85° , and 73.6° . The Figure 3 illustrate that there is no shift occur in peak positions due to aging or environmental conditions. The Cu₂O and Cu can identify after aging.

4.3 SEM analysis of Cu₂O under different environment conditions

The figure 4 illustrates the 25kx magnification SEM image of 1-month aged Cu₂O sample under different environmental conditions. All the environment conditions maintain while

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the ambient humidity is in between 62.5%RH – 74.7%RH and average ambient room temperature is closer to 30 °C.

Figure 4 – 25k× magnification Cu₂O nanoparticle SEM image under, a) dark low humidity condition (28.5%RH – 51.7%RH), b) illuminated low humidity condition (26%RH – 50.6%RH), c) dark high humidity condition (92.2%RH – 94.1%RH), d) illuminated high humidity condition (94.1%RH - 95.7%RH)

Figure 4.a) displays a 25kx magnification SEM image of a one month-old Cu₂O sample that was exposed to low humidity and darkness. The humidity of dark and low humid environmental condition is in between 28.5%RH – 51.7%RH. The average temperature of the dark and low humid environmental condition is 30.2 °C. The nanoscale particles (observed in Figure 1.c)) are not visible in this sample. The surface morphology implies erosion (melting like effect) in the topology.

Figure 4.b) shows a SEM picture of a one month-old Cu₂O sample that had been exposed to low humidity and light conditions. The humidity of the light and low humid environmental condition is in between 26%RH – 50.6%RH. The average temperature of the light and low humid environmental condition is 30.7 °C. The nanoscale particles (observed in Figure 1.c)) are not clearly visible in this sample. The surface morphology implies erosion in the topology, but signatures of nanoparticles on the topology with a lower density compared to Figure 1.c) is observed.

Figure 4.c) displays a 25kx magnification SEM image of a Cu₂O sample exposed to high humidity and darkness for a month. The Humidity of Dark and High humidity

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environmental condition is in between 92.2%RH – 94.1%RH. The average temperature of the Dark and High humidity Environmental condition is 29.8 °C. The nanoscale particles (observed in Figure 1.c)) are not visible in this sample and the surface morphology implies erosion in the topology.

Cu₂O sample that exposed to the high humidity and light for a month is shown in Figure 4.d) as a SEM image. The humidity of light and high humid environmental conditions were in between 94.1%RH - 95.7%RH. The average temperature of the illuminated and high humid environmental conditions is 29.8°C. Here too, features are similar to Figure. 4.c) the nanoscale particles (observed in Figure 1.c) are not clearly visible in this sample. The surface morphology implies erosion in the topology, but a signature of nanoparticles appears on the topology with a lower density compared to Figure 1.c).

Summarizing the above observations, it clearly shows degradation in the surface morphology and topology under variations in environmental condition. It was interesting to note irrespective of the lighting condition, the samples kept at low humidity environments have degraded in similar proportions. Similarities in the degraded surface morphologies were observed for the samples kept at high humidity, irrespective of lighting condition. In ability to lower the humidity further downwards was a disadvantage in the study. Since the samples under low humidity, have exposed to fair amount of humidity, it can be concluded that the humidity has played a major role in the degradation.

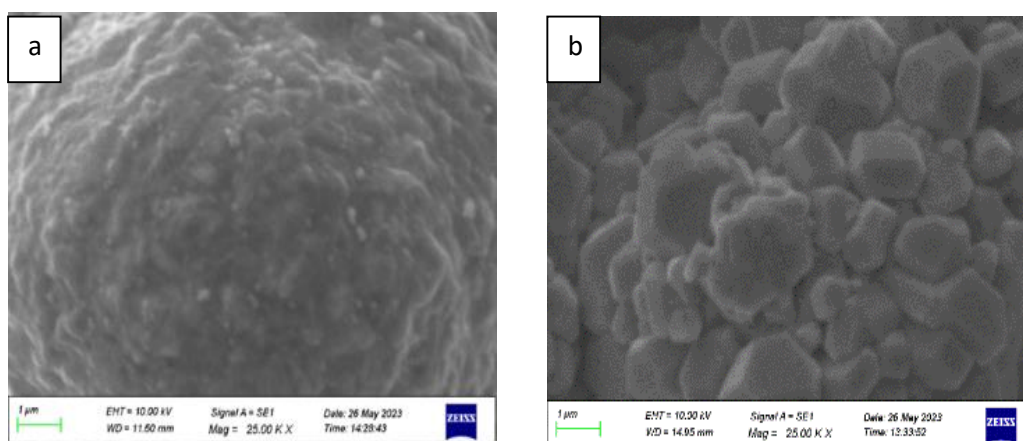


Figure 5 - 25k× SEM image of a) light - high humidity under heat condition, b) light – low humidity under heat condition

Analyzing the results under dark and illuminate condition, it implies the high humidity have enforced a delay or have retarded the degradation process. Both samples kept at high humidity have not fully eroded/melted compared to the samples kept in low humidity. Further study of the sample kept heating (~45 °C) under a continues heat source (tungsten lamp) at high and low humid conditions, shown in Figure.5, revealed the degradation is

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suppressed in the low humid heating sample compared to the high humid heating sample. This is attributable to vaporizing samples more easily or efficiently due to absorbance on the Cu_2O surface compared to the samples at room temperature ($\sim 30^\circ\text{C}$). Further, the sample kept at high humidity was in a water vapor saturated environment, so the contact of water vapor and the Cu_2O are constant. So, there can be a constant thin water-layer present on the Cu_2O surface enforcing the degradation. In the previous samples, even under the low humid conditions, there were comparatively considerable amount of water vapor present in its environment. Hence it can be assumed that a thin water layer can still be formed on the surface of samples. The reason for slowness in degradation of the sample kept at high humidity is not clear at this moment and needs substantial future work. It is interesting that, all three sample kept at high humidity have shown a similar surface morphology / topology despite other conditions (dark, light, and heat). Further studies will require for a better understanding of this situation as well.

This observation implies that the heating of the Cu_2O is retarding the degradation process of the Cu_2O crystals, under low humidity, and this is an encouraging observation especially regarding the photovoltaic applications of Cu_2O . As the photovoltaic cell is heated with the exposure to the sun, it can easily maintain a low humid condition by sealing the devices. In general, solar cells are planted in dry regions that are typically low in humidity. Therefore, these natural environmental conditions, themselves will slow the degradation of the Cu_2O film and hence the device too.

5. CONCLUSION

According to the observe results it can be concluded that there is an effect from the high humidity condition greater than 90% RH for the stability of Cu_2O . There are morphological differences identified in the Cu_2O particles under light area, dark area as well as under heat condition. Therefore, if the environment is high humid the Cu_2O nanoparticles will degrade at dark, illuminated, heated or at room temperature.

Under low humidity condition, the illumination and dark condition, the surface morphology of Cu_2O samples was changed after one month. When applying heat condition, and the temperature was increased up to 45°C average temperature, there are no drastic changes in the surface morphology was identified after one month exposure. Therefore, it can be concluded that the morphological feature of the Cu_2O particle can control by applying the heat (45°C average temperature) under low humidity.

Further studies are required to understand the effects of heat itself without light radiation and effects of solvents used when fabricating the hole conductors and any influences by the ITO or FTO glass substrate.

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7. REFERENCES

- [1] M. D. Susman, Y. Feldman, A. Vaskevich, and I. Rubinstein, “*Chemical deposition of Cu₂O nanocrystals with precise morphology control*,” ACS Nano, vol. 8, no. 1, pp. 162–174, (2014), doi: 10.1021/nm405891g.
- [2] S. M. Shahrestani, “*Electrodeposition Of Cuprous Oxide For Thin Film Solar Cell Applications*,” UNIVERSITÉ DE MONTRÉAL ELECTRO, (2013).
- [3] W. Siripala, K. M. D. C. Jayathileka, and J. K. D. S. Jayanetti, “*Low Cost Solar Cells with Electrodeposited Cuprous Oxide*,” J. Bionanoscience, vol. 3, no. 2, pp. 118–123, (Dec. 2009), doi: 10.1166/jbns.2009.1018.
- [4] M. Madusanka, D. Pitigala, and C. Karunarathna, “*Fabrication of Copper (I) Oxide (Cu₂O) thin films on Transparent Conductive glass substrate Fabrication of Copper (I) Oxide (Cu₂O) thin films on Transparent Conductive glass substrate*,” Proc. Tech. Sess. Inst. Physics, Sri Lanka, vol. 39 (2023), no. March, pp. 46–53, (2023).
- [5] M. Boussaid, A. Belghachi, K. Agroui, M. Abdelaoui, and M. Otmani, “*Solar cell degradation under open circuit condition in out-doors-in desert region*,” Results Phys., vol. 6, pp. 837–842, (2016), doi: 10.1016/j.rinp.2016.09.013.
- [6] A. Moncmanová, “*Environmental factors that influence the deterioration of materials*,” Environ. Deterior. Mater., vol. 28, pp. 1–25, (2007), doi: 10.2495/978-1-84564-032-3/01.
- [7] Z. Xu, Z. Bi, and C. Shen, “*A facile fabrication of Cu₂O nanowire arrays on Cu substrates*,” Cent. Eur. J. Eng., vol. 2, no. 3, pp. 364–368, (2012), doi: 10.2478/s13531-012-0007-3.
- [8] I. S. Jayalath, W. R. Nisansa, and D. P. Pitigala, “*Growing n-Cu₂O Thin Films on Transparent ITO Substrate to Replace the Opaque Copper Metal Substrate for Dye-Sensitized Solar Cells*,” Proc. Tech. Sess., vol. 36, pp. 30–35, (2020).
- [9] F. H. Alsultany, “*One-step chemical bath deposition of Cu₂O flowers grown on ITO seed layer coated glass substrate*,” IOP Conf. Ser. Mater. Sci. Eng., vol. 557, no. 1, pp. 6–11, (2019), doi: 10.1088/1757-899X/557/1/012081.

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- [10] N. T. T. Mai *et al.*, “*Cu₂O Nanoparticles: A simple synthesis, characterization and its photocatalytic performance toward methylene blue,*” *Mater. Trans.*, vol. 61, no. 9, pp. 1868–1873, (2020), doi: 10.2320/matertrans.MT-MN2019039.
- [11] M. Tahir *et al.*, “*Cuprous Oxide Nanoparticles: Synthesis, Characterization, and Their Application for Enhancing the Humidity-Sensing Properties of Poly(dioctylfluorene),*” *Polymers (Basel)*, vol. 14, no. 8, (2022), doi: 10.3390/polym14081503.
- [12] Y. H. Won and L. A. Stanciu, “*Cu₂O and Au/Cu₂O particles: Surface properties and applications in glucose sensing,*” *Sensors (Switzerland)*, vol. 12, no. 10, pp. 13019–13033, (2012), doi: 10.3390/s121013019.
- [13] N. H. Lam *et al.*, “*Evaluation of the Structural Deviation of Cu/Cu₂O Nanocomposite Using the X-ray Diffraction Analysis Methods,*” *Crystals*, vol. 12, no. 4, (Apr. 2022), doi: 10.3390/cryst12040566.