

# The Electrical and Optical properties of Copper Oxide Nanostructures fabricated by Hot Deionized Water Copper Treatment

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## ABSTRACT

Surfaces with metal oxide nanostructures are becoming more popular for use in sensors, detectors, energy harvesting cells, and batteries. However, the limitations of conventional fabrication techniques impede the widespread and productive application of such surfaces. The majority of techniques for producing metal oxide nanostructures are pricey, complicated, hazardous to the environment, or restricted to a few particular material types. It is crucial to develop an easy way to make metal oxide nanostructures that can get beyond all of these limitations. This work used hot deionized water methods to prepare copper oxide nanostructures through thermal oxidation. A pure copper plate with two different surface roughness (0 grit and 80 grit) was subjected to four separate treatments with hot DI water at 100°C (0, 1, 5, 9 hours). The surface morphology of the nanostructures was studied using atomic force microscopy, and it was shown that the Root Mean Square roughness increased with treatment time. The semiconductor's characteristics were assessed using Hall effect measurements, and all test samples displayed p-type conductivity. UV-Vis spectroscopy was used to determine the optical properties; samples with 0 grit show an increase in UV absorption with longer treatment times, whereas samples with 80 grit show a decrease in UV absorption with longer treatment times.

### Keywords:

Copper oxide, DI-water, Surfaces roughness, Hall effect, Absorbation

## 1. Introduction

Nanotechnology is a specialized area of study that focuses on creating and structuring materials with novel characteristics and capabilities on the scale of a nanometer. The idea of restructuring materials at incredibly small sizes has been supported by significant innovative developments in the fields of physics, chemistry, and biology [1].

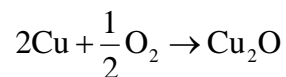
Metal oxide nanostructures are crucial in many fields of chemistry, physics, and materials science for the fabrication of fuel cells, microelectronic circuits, catalysts, surfaces' passivation against corrosion by coatings, sensors, and as piezoelectric devices. A wide variety of oxide compounds can be created using the metal elements. These elements have an electrical structure that can have a semiconductor, metallic, or insulator nature and can adopt a variety of structural shapes [2].

To manufacture metal oxide nanostructures, a variety of techniques have been employed, such as sol-gel [3], sputtering [4], Spray Pyrolysis [5], laser ablation [6], and atomic layer deposition (ALD) [7]. Each of these techniques includes difficult elements such as being constrained to a small number of materials, pricy processing, or requiring high temperatures, which have restricted their commercial use. To overcome the drawbacks of conventional techniques, fabricating Metal oxide nanostructure using a promising alternative method with useful properties such as applicability to a diverse range of materials, elevated fabrication, low-synthesis temperature, catalyst-free growth, low-cost equipment, and low toxicity is preferable [8].

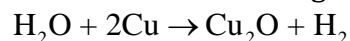
The p-type semiconductor copper oxide has three unique phases: CuO, Cu<sub>2</sub>O, and Cu<sub>4</sub>O<sub>3</sub>, each with its own morphologies and oxidation states of the metals [9].

By nature, copper is a noble metal that resists oxidation. It is thermodynamically stable and noble to hydrogen in the emf series, with no propensity to oxidize in water or nonoxidizing acids without dissolved oxygen [10].

There are two types of thermal oxidation: dry oxygen oxidation and wet oxygen oxidation. In the dry oxygen oxidation, pure oxygen is used as the oxidizing environment. The metal reacts with the surrounding oxygen during dry oxidation to produce a coating of metal dioxide on its surface [11]. According to Eriksen and his collaborators [12], ambient oxygen can cause oxidation in the containers based on the thermodynamically feasible reaction.



The metal and water molecules interact during the wet oxidation to produce the oxide. Wet oxygen oxidation has a substantially higher rate of oxidation than dry oxygen oxidation because the reaction components are a mixture of water and oxygen or air [11]. Hultquist [13] states that copper foil can oxidize in the following ways as a result of oxygen and hydrogen dissipation:



Depending on the rate of crystallization and formation, the oxidation can either be amorphous or crystalline. If the former is rate-determining, amorphous phases ought to develop. Colloid chemistry has shown that delayed solid-state transformation or the dissolution-precipitation process can cause amorphous phases to age or slowly evolve to the point where they change from amorphous to crystalline [10].

Researchers have recently become interested in a straightforward, cost-effective, environmentally benign, and scalable nanostructure growth technique of treatment in hot deionized water. To obtain metal oxide nanostructures, the approach merely involves heating a metallic substrate to between 70 and 100 °C in deionized water.

The design of metal oxide nanostructures using a straightforward, scalable, inexpensive, and environmentally friendly nanostructure development technique of treatment in hot deionized water will be discussed in this paper.

## 2. Experiment Details

A copper plate with a purity of 99.95 % and a thickness of 0.140 micrometer was purchased from a local store. The first set of samples was used without any surface modification (denoted as 0 grit), while the second set was mechanically sanded to create a micro roughness using coarse 80 grit sandpaper (denoted as 80 grit). Sanding the surface in one direction produces isotropy-sanded topography. To eliminate organic impurities from the Cu plate, it was cleaned using acetone and isopropanol alcohol (IPA). After that, the surface was etched with 0.3 M ammonium persulfite ( (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>3</sub> ) before being treated with hot water. The Cu plate was cut into 2cm×2cm specimens, which were then hot water treated at 100°C for 1, 5, and 9 hours without stirring using deionized water and dried at room temperature.

Atomic Force Microscope (NaioAFM) was used to determine the morphologies and micro, nanostructured roughness of the created Copper oxide nanostructures. Hall Effect tests were

performed on  $\text{Cu}_2\text{O}$  sheets measuring  $2\text{cm} \times 2\text{cm}$  with a 0.5 Tesla magnetic field applied. Using the HSR-25AC Hall Effect and Sheet Resistance Measurement System, the films' resistivity was determined

### 3. Results and Discussion

#### 3.1. Atomic Force Microscopy (AFM) Analysis

Figure 1 depicts the AFM images of the surface topography of both sets of samples (0 grit and 80 grit) as a function of treatment time variation. With increasing treatment time, the Root Mean Square roughness  $S_q$  of the hot water treated samples increases from 53.809 to 81.437 nm of 0 grit samples for 1 hour to 5 hours treatment time depicted in

The coalescence of neighboring nanostructure is attributed to the Ostwald ripening phenomena [16], where the small crystals or sol particles dissolve, and the dissolved species is redeposited on the surfaces of bigger crystals or sol particles [17]. Due to Ostwald ripening phenomena and

dissolution redeposition process,  $S_q$  for 80 grit samples decreases from 141.43 to 40.455 nm and then increases to 985.18 nm, as show in **Error! Not a valid bookmark self-reference..**

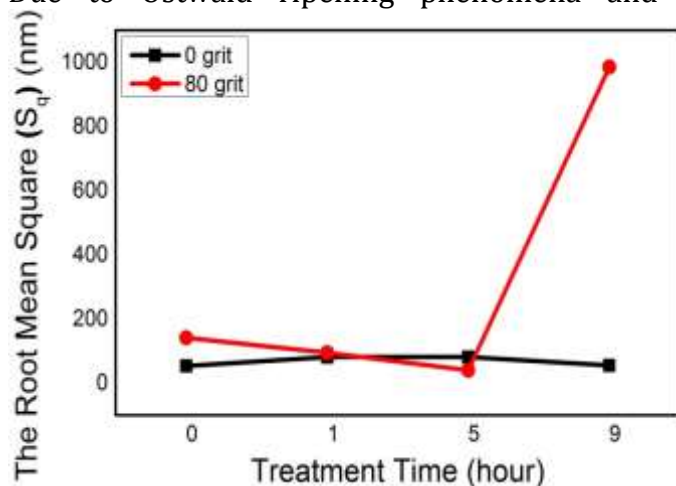


Figure 2. The increase in surface area roughness may be as a result of dissolution of Copper oxide to form Cu ions, followed by subsequent redeposition of Cu ions as Copper oxide ( $\text{Cu}_2\text{O}$ )[14, 15] as shown in Figure 1a, b, and c. However, after 9 hours of hot water treatment, the surface area roughness decreased to 55.206 nm due to neighboring nanostructure coalescence as shown in Figure 1d.

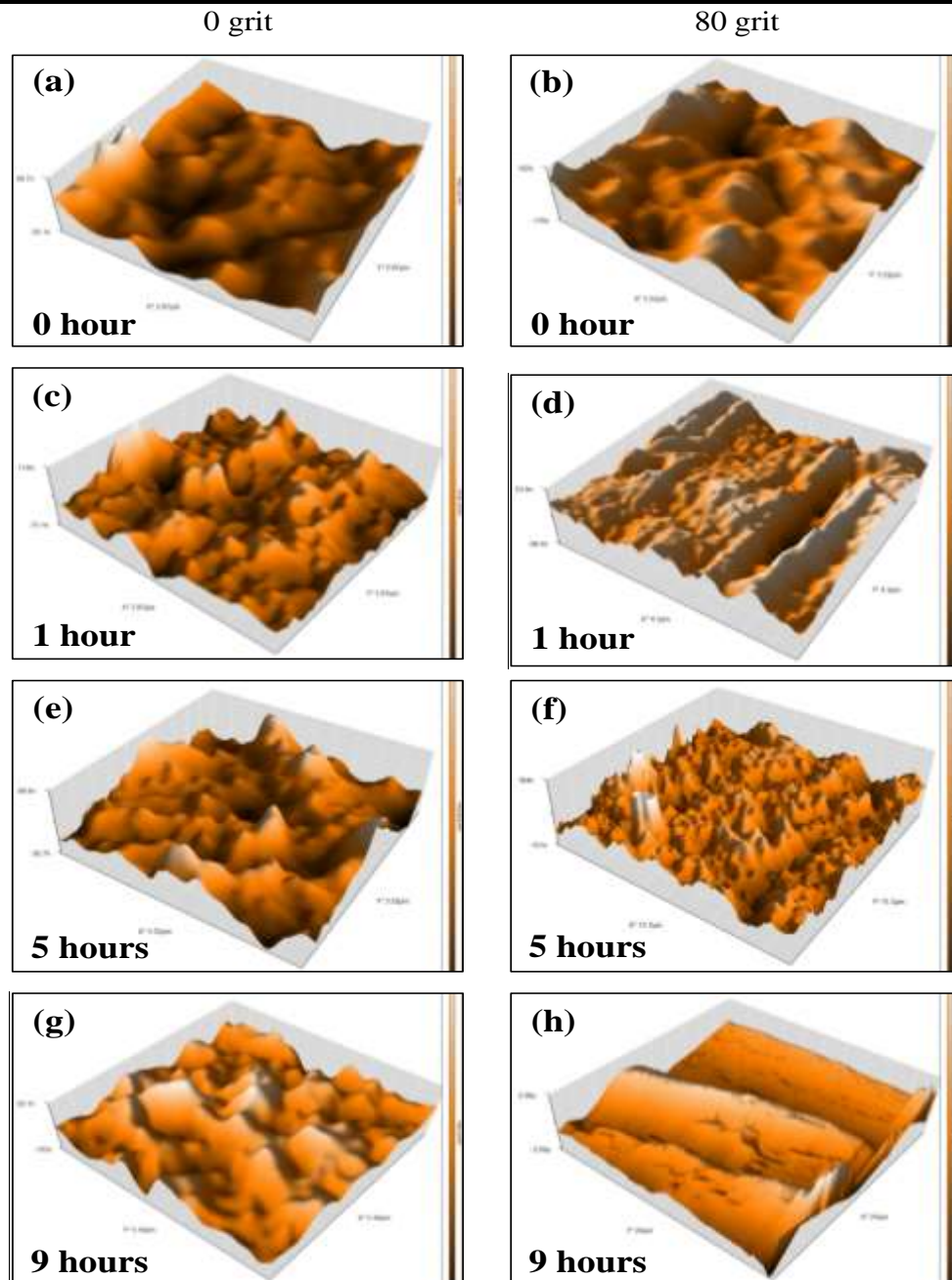


Figure 1. AFM images of Cu plate for various hot water treatment time.

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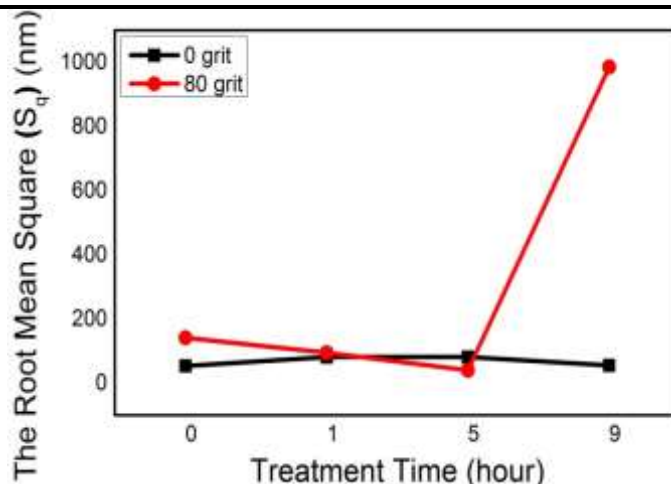


Figure 2. The variation of Root Mean Square with treatment time.

### 3.2. Electrical properties Analysis

The conductivity ( $\sigma$ ), hall mobility ( $\mu_H$ ), carrier concentration ( $n$ ), Hall coefficient ( $R_H$ ), and type of charge carriers in copper oxide are all estimated using the Hall effect technique, where p-type conductivity was

present in all samples. After one hour of hot water treatment, Figure 3 depicts an increase in conductivity caused by oxidation of the Cu plat surface. Copper grain is reduced as a result of cuprous oxide production [18], which also raises the conductivity.

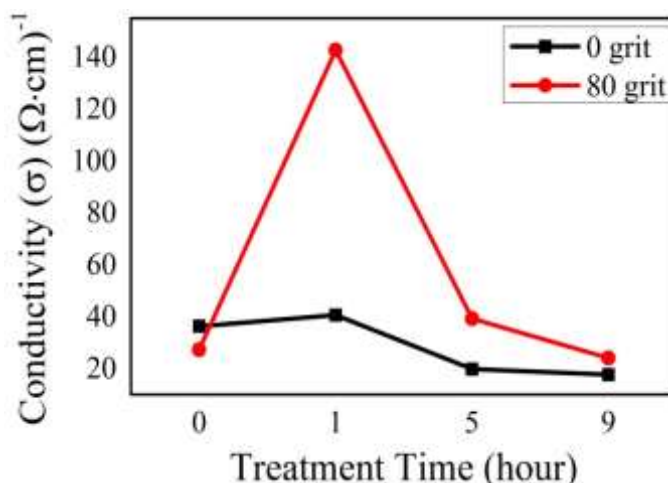


Figure 3. The conductivity of fabricated copper oxide nanostructures for various hot water treatment time.

The improvement in hall mobility and carrier concentration is due to the reduction in copper grain, as seen in Figure 4 and Figure 5, respectively. Conduction electrons scatter across the surface and interface [19], causing conductivity to drop substantially during longer treatment times (5 hours), as a result of increased surface roughness. Figure 4 demonstrates clearly that after 9 hours of treatment, the hall mobility of the 0 grit and 80 grit samples begins to increase and decrease alternately. Smoothing the sidewall of the

grooves causes an increase in hall mobility [11], whereas carrier scattering from ionized centers causes a decrease [20] as it can be seen from AFM image (Figure 1g, h) for 9 hours treatment time. The stoichiometric  $\text{Cu}_2\text{O}$  structure, which is made up of an appropriate number of Cu and O atoms, could be the reason for the increased carrier concentration that was seen at 1 hour of treatment time for the 80 grit sample as shown in Figure 5. Table 1 lists the parameters of the Hall effect for 0 grit and 80 grit samples.



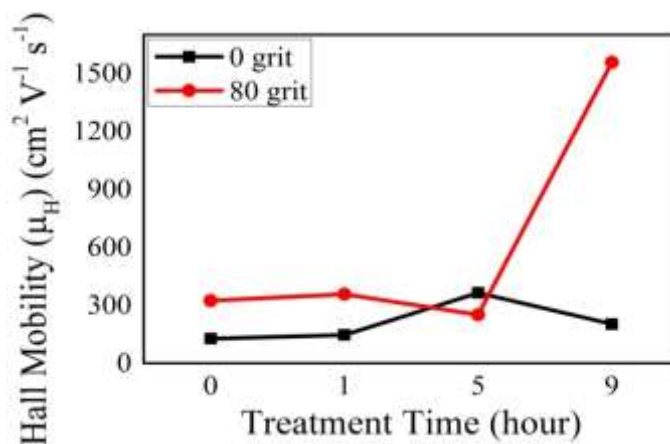


Figure 4. Hall Mobility of fabricated copper oxide nanostructures for various hot water treatment time.

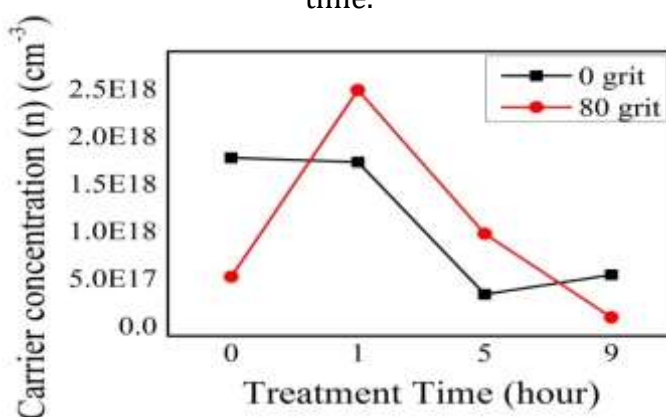


Figure 5. Carrier concentration of fabricated copper oxide nanostructures for various hot water treatment time.

Table 1. Hall effect parameters of copper oxide films fabricated for 0 grit and 80 grit samples throughout a range of hot water treatment times, including 0, 1, 5, and 9 hours.

samples	Treatment Time (hour)	$\sigma(\Omega \cdot \text{cm})^{-1}$	$\mu_H (\text{cm}^2 \text{V}^{-1} \text{s}^{-1})$	$n(\text{cm}^{-3})$	$R_H(\text{cm}^3 \text{C}^{-1})$
0 grit	0	36	127	1.8E18	3.5
	1	41	146	1.7E18	3.6
	5	20	364	3.4E17	18.4
	9	18	203	5.4E17	11.5
80 grit	0	27	324	5.2E17	11.9
	1	143	357	2.5E18	2.5
	5	39	251	9.8E17	6.4
	9	24	1558	9.6E16	64.7

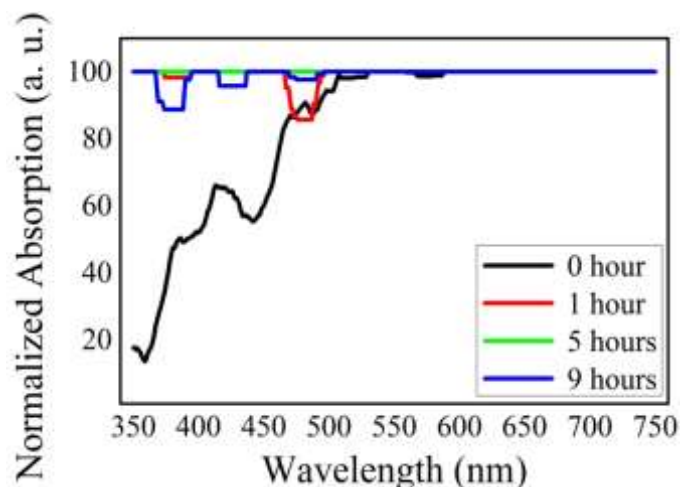
### 3.3. UV-Vis Spectroscopy Analysis

Figure 6 displays the variation in absorption that was determined for both 0 grit and 80 grit samples at varied hot water treatment times spanning a wavelength spectrum from 350 nm to 800 nm. For 0 grit

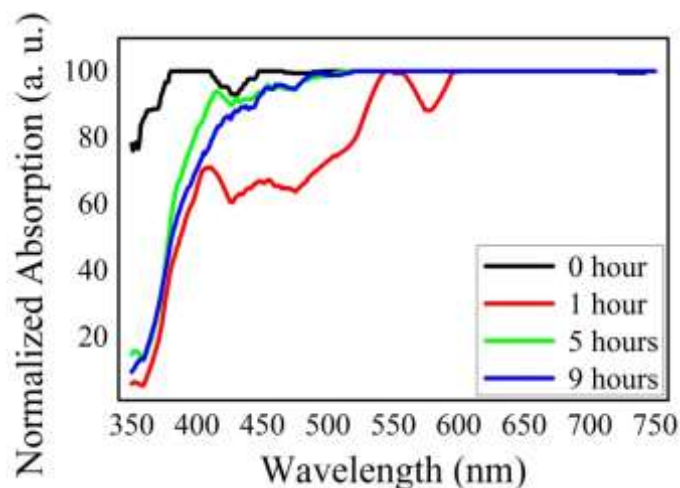
samples (Figure 6a), it is feasible to see an increase in absorption with longer treatment times at the visible range, which is caused by light absorption. It is observable to see a decrease in absorption for 80 grit samples (Figure 6b) with longer treatment times at the visible range, which is caused by light

reflection from the surface. It is obvious from the results of the absorption measurements on both sets of samples that adding a microstructure to the surface will not increase

light absorption. The fabricated nanostructure can be used for solar cells [21], and Metal oxide semiconductor-based Schottky diodes[22].



(a)



(b)

Figure 6. Optical absorption spectra of copper oxide nanostructure for (a) 0 grit and (b) 80 grit samples throughout a range of hot water treatment times (0, 1, 5, and 9 hours)

#### 4. Conclusion

Copper oxides have a promising future as sensors or in solar cells. In this study, thermal oxidation was employed to produce copper oxide nanostructures in hot deionized water. A pure copper plate was given four independent treatments with hot DI water at 100°C and two different levels of surface roughness (0 grit and 80 grit) (0, 1, 5, 9 hours). AFM was used to examine the surface morphology of the nanostructures, and it was revealed that

treatment duration had an impact on the Root Mean Square roughness. Hall effect measurements were used to evaluate the characteristics of the semiconductor, and all test samples revealed p-type conductivity. Using UV-Vis spectroscopy, the optical characteristics were determined. Samples with 0 grit exhibit an increase in UV absorption with prolonged treatment, whereas samples with 80 grit exhibit a decrease in UV absorption with prolonged treatment.

## References

- [1] R.B. Abdulrahman, A.S. Alagoz, and T. Karabacak, "**Enhanced Light Trapping in Periodic Aluminum Nanorod Arrays as Cavity Resonator**", MRS Proceedings, 1566 (1), mrss13-1566-ii09-06 (2013).
- [2] J. Singh and M. Rawat, "**A Brief Review on Synthesis and Characterization of Copper Oxide Nanoparticles and its Applications**", Journal of Bioelectronics and Nanotechnology, 1 (1), 1–9 (2016).
- [3] M. Dhaouadi, M. Jlassi, I. Sta, I. Ben Miled, G. Mousdis, M. Kompitsas, and W. Dimassi, "**Physical properties of copper oxide thin films prepared by sol-gel spin-coating method**", American Journal of Physics and Applications, 6 (2), 43–50 (2018).
- [4] A.H. Shukor, H.A. Alhattab, and I. Takano, "**Electrical and Optical Properties of Copper Oxide Thin Films Prepared by DC Magnetron Sputtering**", Journal of Vacuum Science & Technology B, 38 (1), 012803 (2020).
- [5] R.D. Prabu, S. Valanarasu, V. Ganesh, M. Shkir, S. AlFaify, A. Kathalingam, S.R. Srikumar, and R. Chandramohan, "**An Effect of Temperature on Structural, Optical, Photoluminescence and Electrical Properties of Copper Oxide Thin Films Deposited by Nebulizer Spray Pyrolysis Technique**", Materials Science in Semiconductor Processing, 74 129–135 (2018).
- [6] M. Fernández-Arias, M. Boutinguiza, J. del Val, A. Riveiro, D. Rodríguez, F. Arias-González, J. Gil, and J. Pou, "**Fabrication and Deposition of Copper and Copper Oxide Nanoparticles by Laser Ablation in Open Air**", Nanomaterials, 10 (2), 300 (2020).
- [7] J.D. Lenef, J. Jo, O. Trejo, D.J. Mandia, R.L. Peterson, and N.P. Dasgupta, "**Plasma-enhanced atomic layer deposition of p-type copper oxide semiconductors with tunable phase, oxidation state, and morphology**", The Journal of Physical Chemistry C, 125 (17), 9383–9390 (2021).
- [8] K.R. Khedir, Z.S. Saifaldeen, T. Demirkan, R.B. Abdulrahman, and T. Karabacak, "**Growth of zinc oxide nanorod and nanoflower structures by facile treatment of zinc thin films in boiling de-ionized water**", Journal of Nanoscience and Nanotechnology, 17 (7), 4842–4850 (2017).
- [9] M. Heinemann, B. Eifert, and C. Heiliger, "**Band structure and phase stability of the copper oxides Cu<sub>2</sub>O, CuO, and Cu<sub>4</sub>O<sub>3</sub>**", Physical Review B, 87 (11), 115111 (2013).
- [10] P.A. Schweitzer, "**Fundamentals of metallic corrosion: atmospheric and media corrosion of metals.**" CRC Press, (2006).
- [11] Z. Shi, S. Shao, and Y. Wang, "**Improved the Surface Roughness of Silicon Nanophotonic Devices by Thermal Oxidation Method**", Journal of Physics: Conference Series, 276 (1), 012087 (2011).
- [12] T.E. Eriksen, P. Ndalamba, and I. Grenthe, "**On the corrosion of copper in pure water**", Corrosion Science, 29 (10), 1241–1250 (1989).
- [13] G. Hultquist, "**Hydrogen evolution in corrosion of copper in pure water**", Corrosion Science, 26 (2), 173–177 (1986).
- [14] W.K. Tan, K. Abdul Razak, Z. Lockman, G. Kawamura, H. Muto, and A. Matsuda, "**Formation of highly crystallized ZnO nanostructures by hot-water treatment of etched Zn foils**", Materials Letters, 91 111–114 (2013).
- [15] Z. Liu, C. Wang, J. Hou, P. Wang, L. Miao, B. Lv, Y. Yang, G. You, Y. Xu, M. Zhang, and H. Ci, "**Aggregation, Sedimentation, and Dissolution of CuO and ZnO Nanoparticles in Five Waters**", Environmental Science and Pollution Research, 25 (31), 31240–31249 (2018).
- [16] B. Liu and X. Hu, "**Hollow Micro- and Nanomaterials: Synthesis and Applications**", In: Q. Zhao, Ed. *Advanced Nanomaterials for Pollutant Sensing and Environmental Catalysis*. 1–38. Elsevier (2020).



- [17] J. V Alemán, A. V Chadwick, J. He, M. Hess, K. Horie, R.G. Jones, P. Kratochvíl, I. Meisel, I. Mita, G. Moad, S. Penczek, and R.F.T. Stepto, "**Definitions of Terms Relating to The Structure and Processing of Sols, Gels, Networks, and Inorganic-Organic Hybrid Materials**", Pure and Applied Chemistry, 79 (10), 1801–1829 (2007).
- [18] M.J. Balart, J.B. Patel, F. Gao, and Z. Fan, "**Grain Refinement of Deoxidized Copper**", Metallurgical and Materials Transactions A: Physical Metallurgy and Materials Science, 47 (10), 4988–5011 (2016).
- [19] J.W. Lim, K. Mimura, and M. Isshiki, "**Thickness dependence of resistivity for Cu films deposited by ion beam deposition**", Applied Surface Science, 217 (1–4), 95–99 (2003).
- [20] Y.S. Lee, M.T. Winkler, S.C. Siah, R. Brandt, and T. Buonassisi, "**Hall mobility of cuprous oxide thin films deposited by reactive direct-current magnetron sputtering**", Applied Physics Letters, 98 (19), 1–4 (2011).
- [21] P. Sawicka-Chudy, M. Sibiński, E. Rybak-Wilusz, M. Cholewa, G. Wisz, and R. Yavorskyi, "**Review of the development of copper oxides with titanium dioxide thin-film solar cells**", AIP Advances, 10 (1), 10701 (2020).
- [22] N.A. Al-Ahmadi, "**Metal oxide semiconductor-based Schottky diodes: a review of recent advances**", Materials Research Express, 7 (3), 32001 (2020).