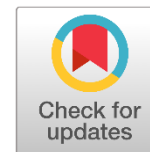




Content lists available at:  
[www.journals.irapa.org/index.php/BCS/issue/view/26](http://www.journals.irapa.org/index.php/BCS/issue/view/26)

# Biomedicine and Chemical Sciences

Journal homepage: <https://www.journals.irapa.org/index.php/BCS>



## Synthesis Nanoparticles of Copper and Dicopper Oxide via Change Atmosphere of Copper Ablation

Ahmed Hussein Mohammed Al-Antaki\*

Department of Chemistry, Faculty of Science, University of Kufa, Najaf – Iraq

### ARTICLE INFO

#### Article history:

Received on: March 31, 2023  
 Revised on: April 12, 2023  
 Accepted on: April 12, 2023  
 Published on: July 01, 2023

#### Keywords:

Cu<sub>2</sub>ONPs  
 CuNPs  
 Green chemistry  
 Pulsed laser ablation  
 Pure copper rod

### ABSTRACT

The fabrication technique to synthesis dicopper oxide nanoparticles (Cu<sub>2</sub>ONPs) and copper nanoparticles (CuNPs) is laser ablation by a pure copper rod. To save the environmental system, we converted setup of device to develop the clean technology. In addition, the solvent using in both systems is water (green chemistry) without agent or surfactant. The average size of Cu<sub>2</sub>ONPs is 20 nm via enclosed platform of air under 600 mJ of laser power for 1h. However, the average size is 12 nm to generate CuNPs under N<sub>2</sub> gas and 600 mJ of laser power for 1h. The morphology and the shape of the particles explain by Scanning Electron Microscope (SEM) images and Transmission Electron Microscopy (TEM) images. Also, the average size of the nanoparticles proved by measuring of 100 particles by using TEM image. In addition, The High-Resolution Transmission Electron Microscopy (HRTEM) image explains the distance between the layers in CuNPs which is 0.21 nm. The X-ray diffraction (XRD) and Attenuated Total Reflection-Fourier Transform Infrared (ATR-FTIR) of the product show the type of nanoparticles' structure.

Copyright © 2023 Biomedicine and Chemical Sciences. Published by International Research and Publishing Academy – Pakistan, Co-published by Al-Furat Al-Awsat Technical University – Iraq. This is an open access article licensed under CC BY:

(<https://creativecommons.org/licenses/by/4.0>)

## 1. Introduction

Various methods to create of dicopper oxide nanoparticles (cuprous oxide nanoparticles (Cu<sub>2</sub>ONPs)) and copper nanoparticles employing chemical, physical and biological techniques considering top-down methods synthesis have been studied. The properties of dicopper oxide nanoparticles and copper nanoparticles depend largely on their synthesis procedures. The product from many investigations outright by different scientists using these experiments have been summarized (Umer et al., 2012). They used many characterization techniques to mention the advantage and

disadvantages to use each synthesis method with some applications on the other via discussion. Batch processing is one of methods used in the fabrication of dicopper oxide nanoparticles and copper nanoparticles. The one of study details to product is the Pulsed laser ablation methods which is more suitable to synthesis dicopper oxide nanoparticles and copper nanoparticles (Sadrolhosseini et al., 2016). Pulsed laser ablation (PLA) involves ablating a pure metal target in a liquid phase or in gas phase, which has several advantages such as no high vacuum, high yielding, high purity, and avoiding harsh chemicals to be high impact for sustainable processing for the future as green chemistry. Furthermore, the experimental parameters could control the types and size of the nanoparticles (Haram & Ahmad, 2013).

The metal surface will absorption the laser radiation to make interaction zone which will transform of kinetic energy into thermal energy. Also, when the laser power is sufficiently high, a local plasma plume with high temperatures and pressures is formed (Vitta et al., 2011), and this can lead to synthesis of metal oxide particles under presence of oxygen or metal particles under Nobel gas

\***Corresponding author:** Ahmed Hussein Mohammed Al-Antaki, Department of Chemistry, Faculty of Science, University of Kufa, Najaf – Iraq

E-mail: [ahmed.alantaki@uokufa.edu.iq](mailto:ahmed.alantaki@uokufa.edu.iq)

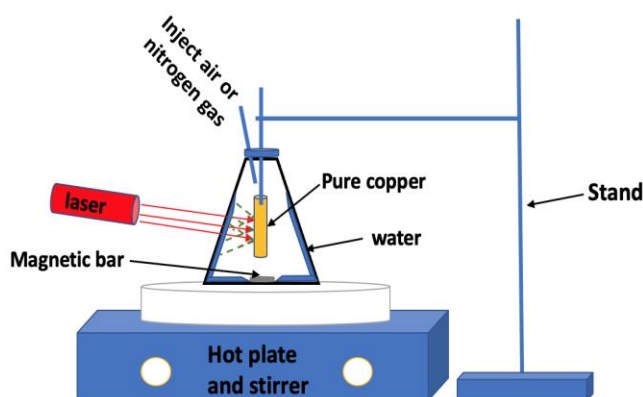
#### How to cite:

Al-Antaki, A. H. M. (2023). Synthesis Nanoparticles of Copper and Dicopper Oxide via Change Atmosphere of Copper Ablation. *Biomedicine and Chemical Sciences*, 2(3), 227–232.

DOI: <https://doi.org/10.48112/bcs.v2i3.488>

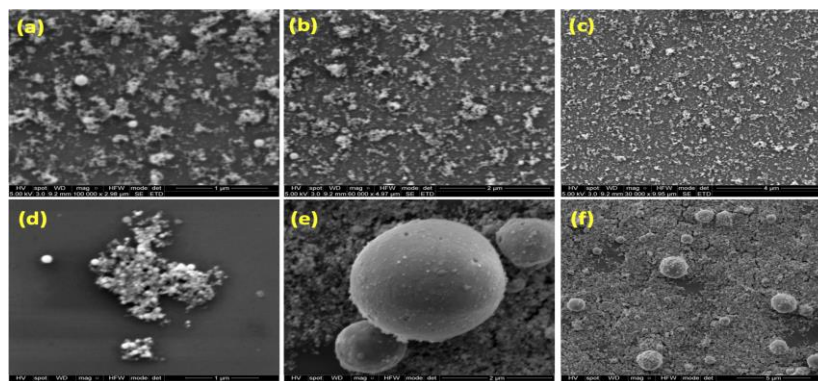
or  $N_2$  gas (Al-Antaki et al., 2019). These types of nanoparticles have many applications such as catalytic organic, electrocatalysis, and photocatalysis (Allen et al., 2013; Poreddy et al., 2015; Yin et al., 2015). Moreover, copper nanoparticles are good applications with sensitivity to oxygen, water, and different reagents (Gawande et al., 2016).

The research uses a simple setup of pure copper rod as a target in the conical flask and the pulsed laser hits it under air or  $N_2$  gas and a magnetic bar to stir water on the wall of a conical flask with avoid touching the pure copper rod, Figure 1. The experiment with air could synthesise dicopper oxide nanoparticles ( $Cu_2ONPs$ ). On the other hand, using  $N_2$  gas to collect copper nanoparticles (CuNPs). We used 600 mJ of laser energy to ablate the nanoparticles from pure copper rod during 15 mins. The lower power of the laser is not enough to ablate nanoparticles from the surface of pure copper rod. In contrast, the high yield of the nanoparticles during the same time is high power of the laser. Thus, the 600 mJ is the best power of the laser to collect high yield from nanoparticles. To determine the end of the experiment as other conditions, we used high power laser (600 mJ) with 15min, 30min, 45min, 1h, and 1.5h. we found 1h is enough time to end the experiment with a high yield and less agglomeration of nanoparticles. In addition that, the concentration of the yield in the solvent (water) will reduce the effect of the laser power on the surface of the pure copper rod to ablate nanoparticles.



**Fig. 1.** The Experiments under Air or Nitrogen Gas with High Speed of Starrier

## 2. Materials and Methods



**Fig. 2.** SEM images for nanoparticles via 600 mJ of laser power for 1h (a-c) dicopper oxide nanoparticles ( $Cu_2ONPs$ ) under air, (d-f) copper nanoparticles (CuNPs) under  $N_2$  gas

## Materials

Milli-Q water was used. A high purity (>99.998%) of copper metal rod of 8 mm in diameter (Colnbrook Bucks, England) was used for all the processing.

## Synthesis of $Cu_2ONPs$ and CuNPs

The power laser used to synthesis dicopper oxide nanoparticles ( $Cu_2ONPs$ ) and copper nanoparticles (CuNPs) was 600 mJ/pulse by 1064 nm as a wavelength of the source operating which was generated from a Nd:YAG source, and the solvent of both the experiments was Milli-Q water. The  $Cu_2ONPs$  are synthesised by the flowing of air inside the conical flask when the magnetic bar stirrer water for 1h. On the other hand, to synthesis CuNPs are by the flowing of  $N_2$  gas inside a conical flask to avoid oxidation of copper when the magnetic bar stirrer water for 1h.

## Characterization

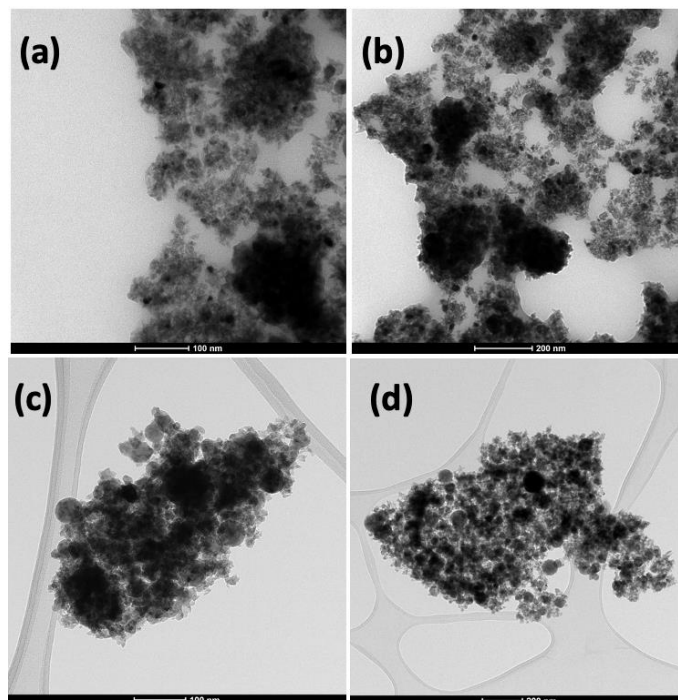
To character the dicopper oxide nanoparticles and copper nanoparticles used scanning electron microscopy (SEM, Inspect FEI F50), XRD (Bruker D8 ADVANCE ECO, Co K $\alpha$ ,  $\lambda = 1.7889$  Å), ATR-FTIR (Perkin Elmer Frontier), and HR-TEM (Tecnai\_G2\_Spirit).

## 3. Results and Discussion

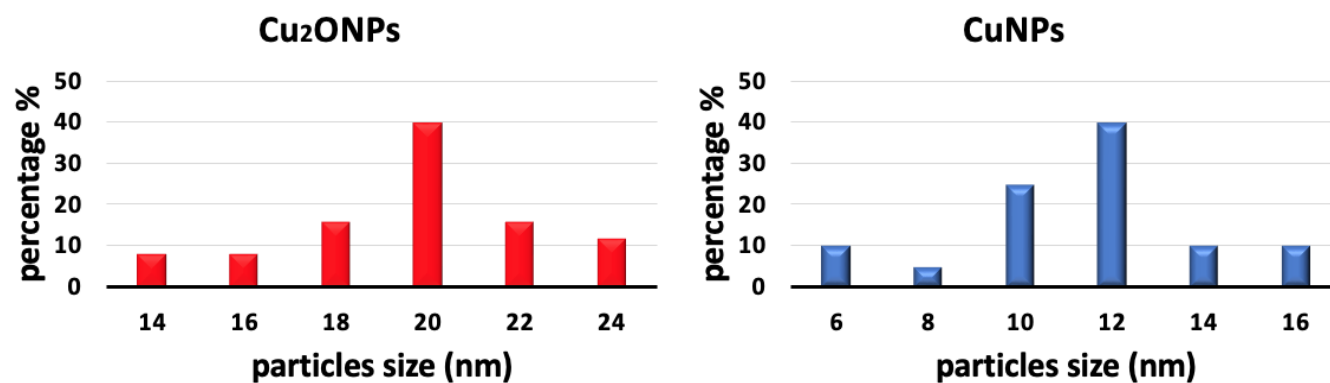
The method to synthesis  $Cu_2ONPs$  or CuNPs by using simple setup of the pure copper rod inside the conical flask under air or  $N_2$  gas respectively, which is useful to collect nanosize structure of the copper. Furthermore, the solvent is water without using an agent or surfactant to stabilize the particles as nanosize is a big deal for green chemistry and clean technology. The SEM images of our results show the morphology and the shape of nanoparticles, figure 2. The images (a-c) of  $Cu_2ONPs$  explain the size of the particles after the experiment which are nanosize and less agglomeration of the nanoparticles. In contrast, the images (d-f) show the morphology and nanosize of copper with some agglomeration as spherical shape.

To understand more details about the shape and the morphology of the nanoparticles we used HRTEM. The images (a, b) in figure 3 prove the nanosize of  $\text{Cu}_2\text{ONPs}$  and less aggregation. However, the images (c, d) from figure 3 show the nanosize of the  $\text{CuNPs}$  with some aggregation of nanoparticles as spherical shape. By using TEM images, the size estimations of hundred particles from  $\text{Cu}_2\text{ONPs}$  and  $\text{CuNPs}$  show high percent with average 20 nm and 12 nm

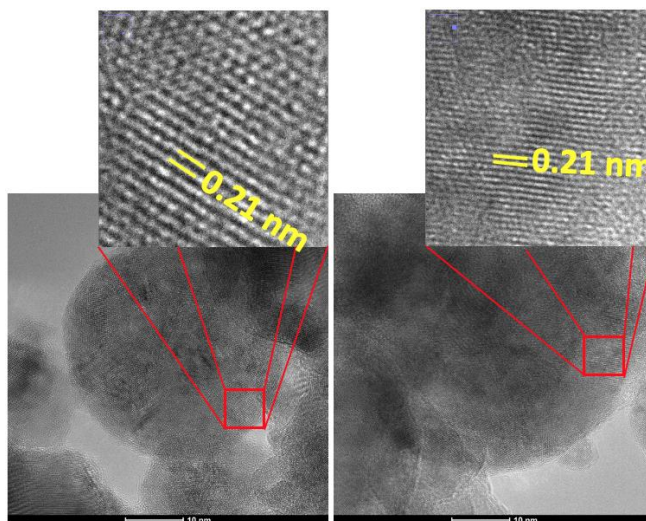
respectively, figure 4. From that, we could prove the nanosize of both particle's structures which are prepared in the same conditions but different atmospheres. Furthermore, the figure 5 is HRTEM for  $\text{CuNPs}$  which shows the distance between the layers 0.21 nm by zoom in of HRTEM image (Cheng & Hight Walker, 2010; Zhang et al., 2015; Fernández-Arias et al., 2020).



**Fig. 3.** TEM images for nanoparticles via 600 mJ of laser power for 1h (a, b) dicopper oxide nanoparticles ( $\text{Cu}_2\text{ONPs}$ ) under air, (c, d) copper nanoparticles ( $\text{CuNPs}$ ) under  $\text{N}_2$  gas



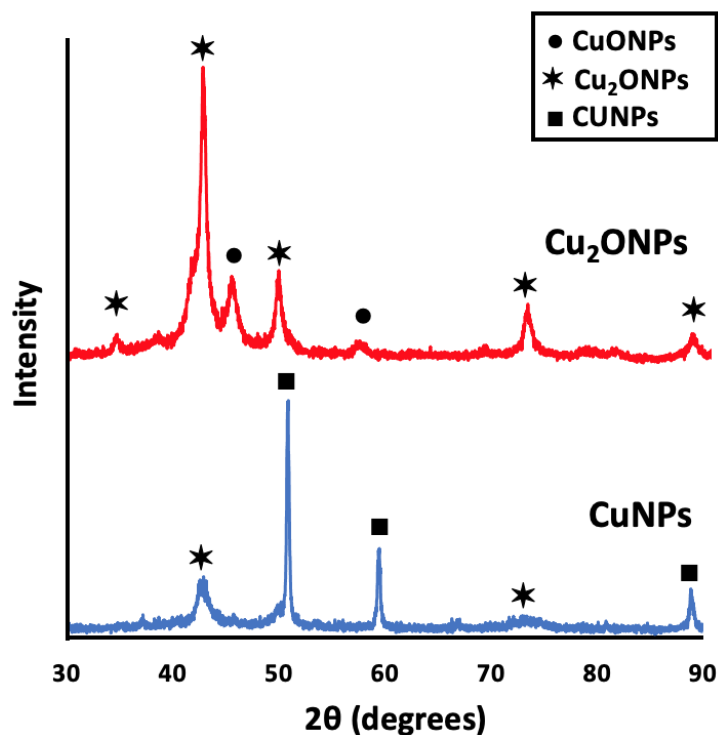
**Fig. 4.** Particles size of dicopper oxide nanoparticles and copper nanoparticles by using TEM images.



**Fig. 5.** HRTEM images with zoom in to measure the layers of copper nanoparticles (CuNPs) collected via 600 mJ of laser power for 1h under N<sub>2</sub> gas.

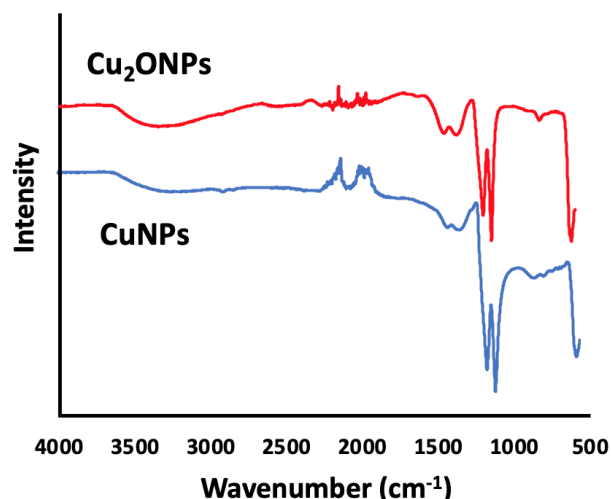
The X-ray diffraction (Co K $\alpha$ ,  $\lambda = 1.7889$  Å) of Cu<sub>2</sub>ONPs shows 2 $\theta$  peaks at 34.7°, 42.6°, 49.5°, 72.8° and 88.2° which are corresponding to (110), (111), (200), (220), and (311) for cubic cuprite, respectively (Salavati-Niasari & Davar, 2009; Gondal et al., 2013; Zhao et al., 2014; Bergum et al., 2018). Moreover, the diffraction pattern presents small peaks of some CuO by oxidation of Cu<sub>2</sub>ONPs during the experiment (Lupan et al., 2020). On the other hand, the X-ray diffraction pattern of CuNPs shows 2 $\theta$  peaks at 50.9°, 59.5° and 89.1° which correspond to a cubic crystal structure of (111), (200) and (220) respectively (Betancourt-Galindo et al., 2014; Ji et al., 2014; Fernández-Arias et al.,

2020; Lupan et al., 2020), and small peaks of Cu<sub>2</sub>ONPs by oxidation of CuNPs during the workup, Figure 6. The Scherrer equation via XRD presents the average nanosize 20 nm and 12 nm of Cu<sub>2</sub>ONPs and CuNPs respectively which are match the result of TEM images in figure 4.



**Fig. 6.** X-ray diffraction (XRD) for dicopper oxide nanoparticles (Cu<sub>2</sub>ONPs) under air and copper nanoparticles (CuNPs) under N<sub>2</sub> gas via 600 mJ of laser power for 1h

The Figure 7 is ATR-FTIR spectra to present of Cu<sub>2</sub>ONPs and CuNPs, with a broad peak at 3389 cm<sup>-1</sup> corresponding to H-O-H stretching vibration band and two peaks in the fingerprint region for surface-bound hydroxyl of water at 1460 cm<sup>-1</sup> and 1375 cm<sup>-1</sup> (Zhang et al., 2013; Tadjarodi & Roshani, 2014; Ullah et al., 2020). The peak at 597 cm<sup>-1</sup> is corresponded to Cu-O vibrations in dicopper oxide nanoparticles (Zhang et al., 2006; Basu et al., 2012; Guo et al., 2015). However, the main stretch peak of copper nanoparticles is at 621 cm<sup>-1</sup> (Ullah et al., 2020).



**Fig. 7.** ATR-FTIR for dicopper oxide nanoparticles (Cu<sub>2</sub>ONPs) under air and copper nanoparticles (CuNPs) under N<sub>2</sub> gas via 600 mJ of laser power for 1h

#### 4. CONCLUSION

In the present study, we could synthesis dicopper oxide nanoparticles (Cu<sub>2</sub>ONPs) and copper nanoparticles (CuNPs) by laser ablation technique. To develop the clean technology and green chemistry, we used water as solvent and 600 mJ laser power for 1 h under air to collect Cu<sub>2</sub>ONPs or N<sub>2</sub> gas to create CuNPs without agent or surfactant. Because of the setup of device, the average size of Cu<sub>2</sub>ONPs and CuNPs are 20 nm and 12 nm respectively. The characterisations used to evident the size and the morphology of the two types of nanoparticles are SEM images and TEM images. Also, HRTEM use to measure the distains between the layers in CuNPs which is 0.21 nm. Moreover, the XRD and ATR-FTIR prove the structure of nanoparticles.

#### Competing Interests

The authors had no competing interests.

#### References

Al-Antaki, A. H. M., Luo, X., Duan, X., Lamb, R. N., Hutchison, W. D., Lawrance, W., & Raston, C. L. (2019). Continuous flow copper laser ablation synthesis of copper (I and II) oxide nanoparticles in water. *ACS omega*, 4(8), 13577-13584. <https://doi.org/10.1021/acsomega.9b01983>

Allen, S. E., Walvoord, R. R., Padilla-Salinas, R., & Kozlowski, M. C. (2013). Aerobic copper-catalyzed organic reactions. *Chemical reviews*, 113(8), 6234-6458. <https://doi.org/10.1021/cr300527g>

Basu, M., Sinha, A. K., Pradhan, M., Sarkar, S., Pal, A., Mondal, C., & Pal, T. (2012). Methylene Blue-Cu<sub>2</sub>O reaction made easy in acidic medium. *The Journal of Physical Chemistry C*, 116(49), 25741-25747. <https://doi.org/10.1021/jp308095h>

Bergum, K., Riise, H. N., Gorantla, S., Lindberg, P. F., Jensen, I. J., Gunnæs, A. E., ... & Monakhov, E. (2018). Improving carrier transport in Cu<sub>2</sub>O thin films by rapid thermal annealing. *Journal of Physics: Condensed Matter*, 30(7), 075702. <https://doi.org/10.1088/1361-648x/aaa5f4>

Betancourt-Galindo, R., Reyes-Rodríguez, P. Y., Puente-Urbina, B. A., Avila-Orta, C. A., Rodríguez-Fernández, O. S., Cadenas-Pliego, G., ... & García-Cerda, L. A. (2014). Synthesis of copper nanoparticles by thermal decomposition and their antimicrobial properties. *Journal of Nanomaterials*, 2014, 10-10. <https://doi.org/10.1155/2014/980545>

Cheng, G., & Hight Walker, A. R. (2010). Transmission electron microscopy characterization of colloidal copper nanoparticles and their chemical reactivity. *Analytical and bioanalytical chemistry*, 396, 1057-1069. <https://doi.org/10.1007/s00216-009-3203-0>

Fernández-Arias, M., Boutinguiza, M., del Val, J., Riveiro, A., Rodríguez, D., Arias-González, F., ... & Pou, J. (2020). Fabrication and deposition of copper and copper oxide nanoparticles by laser ablation in open air. *Nanomaterials*, 10(2), 300. <https://doi.org/10.3390/nano10020300>

Gawande, M. B., Goswami, A., Felpin, F. X., Asefa, T., Huang, X., Silva, R., ... & Varma, R. S. (2016). Cu and Cu-based nanoparticles: synthesis and applications in catalysis. *Chemical reviews*, 116(6), 3722-3811. <https://doi.org/10.1021/acs.chemrev.5b00482>

Gondal, M. A., Qahtan, T. F., Dastageer, M. A., Maganda, Y., & Anjum, D. H. (2013). Synthesis of Cu/Cu<sub>2</sub>O nanoparticles by laser ablation in deionized water and their annealing transformation into CuO nanoparticles. *Journal of nanoscience and nanotechnology*, 13(8), 5759-5766. <https://doi.org/10.1166/jnn.2013.7465>

Guo, D., Wang, L., Du, Y., Ma, Z., & Shen, L. (2015). Preparation of octahedral Cu<sub>2</sub>O nanoparticles by a green route. *Materials Letters*, 160, 541-543. <https://doi.org/10.1016/j.matlet.2015.08.055>

Haram, N., & Ahmad, N. (2013). Effect of laser fluence on the size of copper oxide nanoparticles produced by the ablation of Cu target in double distilled water. *Applied Physics A*, 111, 1131-1137. <https://doi.org/10.1007/s00339-012-7329-0>

Ji, R., Sun, W., & Chu, Y. (2014). One-step hydrothermal synthesis of Ag/Cu<sub>2</sub>O heterogeneous nanostructures over Cu foil and their SERS applications. *RSC Advances*, 4(12), 6055-6059. <https://doi.org/10.1039/C3RA44281K>

Lupan, O., Ababii, N., Mishra, A. K., Gronenberg, O., Vahl, A., Schürmann, U., ... & Hansen, S. (2020). Single CuO/Cu<sub>2</sub>O/Cu microwire covered by a nanowire network as a gas sensor for the detection of battery hazards. *ACS*

- Applied Materials & Interfaces*, 12(37), 42248-42263.  
<https://doi.org/10.1021/acsami.0c09879>
- Poreddy, R., Engelbrekt, C., & Riisager, A. (2015). Copper oxide as efficient catalyst for oxidative dehydrogenation of alcohols with air. *Catalysis Science & Technology*, 5(4), 2467-2477. <https://doi.org/10.1039/C4CY01622J>
- Sadrolhosseini, A. R., Abdul Rashid, S., Zakaria, A., & Shameli, K. (2016). Green fabrication of copper nanoparticles dispersed in walnut oil using laser ablation technique. *Journal of Nanomaterials*, 2016. <https://doi.org/10.1155/2016/8069685>
- Salavati-Niasari, M., & Davar, F. (2009). Synthesis of copper and copper (II) oxide nanoparticles by thermal decomposition of a new precursor. *Materials Letters*, 63(3-4), 441-443. <https://doi.org/10.1016/j.matlet.2008.11.023>
- Tadjarodi, A., & Roshani, R. (2014). A green synthesis of copper oxide nanoparticles by mechanochemical method. *Current Chemistry Letters*, 3(4), 215-220.
- Ullah, N., Ullah, A., & Rasheed, S. (2020). Green synthesis of copper nanoparticles using extract of *Dicliptera Roxburghiana*, their characterization and photocatalytic activity against methylene blue degradation. *Letters in Applied NanoBioScience*, 9, 897-901.
- Umer, A., Naveed, S., Ramzan, N., & Rafique, M. S. (2012). Selection of a suitable method for the synthesis of copper nanoparticles. *Nano*, 7(05), 1230005. <https://doi.org/10.1142/S1793292012300058>
- Vitta, Y., Piscitelli, V., Fernandez, A., Gonzalez-Jimenez, F., & Castillo, J. (2011).  $\alpha$ -Fe nanoparticles produced by laser ablation: Optical and magnetic properties. *Chemical Physics Letters*, 512(1-3), 96-98. <https://doi.org/10.1016/j.cplett.2011.07.020>
- Yin, G., Nishikawa, M., Nosaka, Y., Srinivasan, N., Atarashi, D., Sakai, E., & Miyauchi, M. (2015). Photocatalytic carbon dioxide reduction by copper oxide nanocluster-grafted niobate nanosheets. *ACS Nano*, 9(2), 2111-2119. <https://doi.org/10.1021/nn507429e>
- Zhang, Y. C., Tang, J. Y., Wang, G. L., Zhang, M., & Hu, X. Y. (2006). Facile synthesis of submicron Cu<sub>2</sub>O and CuO crystallites from a solid metallorganic molecular precursor. *Journal of Crystal Growth*, 294(2), 278-282. <https://doi.org/10.1016/j.jcrysgro.2006.06.038>
- Zhang, Y. X., Huang, M., Li, F., & Wen, Z. Q. (2013). Controlled synthesis of hierarchical CuO nanostructures for electrochemical capacitor electrodes. *International Journal of Electrochemical Science*, 8(6), 8645-8661. [https://doi.org/10.1016/S1452-3981\(23\)12916-6](https://doi.org/10.1016/S1452-3981(23)12916-6)
- Zhang, Z., Ji, Y., Li, J., Zhong, Z., & Su, F. (2015). Synergistic effect in bimetallic copper-silver (Cu x Ag) nanoparticles enhances silicon conversion in Rochow reaction. *Rsc Advances*, 5(67), 54364-54371. <https://doi.org/10.1039/C5RA04575D>
- Zhao, Y. F., Yang, Z. Y., Zhang, Y. X., Jing, L., Guo, X., Ke, Z., ... & Sun, K. N. (2014). Cu<sub>2</sub>O decorated with cocatalyst MoS<sub>2</sub> for solar hydrogen production with enhanced efficiency under visible light. *The Journal of Physical*