

# Green Synthesis of CuO Nanoparticles using *Ziziphus Mauritiana* L. Extract and Its Characterizations

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## ABSTRACT

Copper oxide nanoparticles (CuONPs) synthesized by a completely environmentally safe and facile process using *Ziziphus mauritiana* L. aqueous plant extract as an effective stabilizing agent. Phytochemical screening of the fresh aqueous leaves extract showed the presence of coumarins, tannins, saponins, flavonoids, and glycosides. The synthesized CuO nanomaterial was characterized by XRD, SEM, EDX, TEM and surface area. This green synthesis route indicates that, it is efficient method than chemical method.

**Keywords:** Nanotechnology, *Ziziphus mauritiana* L., CuONPs, Phytochemical screening.

## I. INTRODUCTION

Nowadays CuONPs have generated a great deal of interest, especially in the field of gas sensing [1], catalysis [2] and biomedical [3] because of their remarkable applications. These CuONPs fabricated using different synthetic routes such as ionic liquid assisted, microwave irradiation, sonochemical, electrochemical, sol-gel technique and thermal treatment [4-9] have been reported. Nevertheless, these routes have some drawbacks like the use of toxic chemical, use of acrimonious synthesis conditions like high temperature and requirement of external additives during the reaction time. Hence there is limited scope for the development of efficient, environmentally safe and additive free synthesis of CuONPs. Currently plant extract mediated nonmaterial synthesis is getting lot of attention with several advantages offered by chemical methods [10-12]. The scrutiny of the literature revealed some notable plant extract used for facile synthesis of CuO-NPs. For example, *Rauvolfia serpentina* [13], *Leucaena leucocephala* [14], *Calotropis gigantea* [15], *Aloe barbadensis* [16], *Ficus religiosa* [17], *Albizia lebbek* [18] and *Acanthospermum hispidum* [19] have been reported.

*Ziziphus mauritiana* L. (Figure 1) belongs to family Rhamnaceae is an annual plant which grows in tropical and sub-tropical regions of world. Different parts of this

plant have been used in the traditional medicine for the treatment of different ailments. In this study, we report the use of *Ziziphus mauritiana* L. as stabilizing and reducing agent in the ecofriendly synthesis of CuONPs.



Figure 1. Leaves of *Ziziphus mauritiana* L.

## II. MATERIALS AND METHODS

### 2. 1. Materials

Copper acetate monohydrate was used as a precursor. The fresh leaves of *Ziziphus mauritiana* L. were sourced from Sangamner college campus, Maharashtra, India. The collected leaves were washed with deionized water, cut into small pieces. All glassware's are washed with distilled water and acetone and dried in oven before use.

## 2.2. Biogenic synthesis of CuONPs

5g chopped leaves of *Ziziphus mauritiana* L. were transferred into 500 mL beaker containing 100 mL deionized water. The mixture were refluxed at 80 °C for 30 minutes and cooled at room temperature and resultant filtrate was filtered through Whatmann No. 1. The filtered extract is stored in refrigerator at 5 °C and used for synthesis of CuONPs. The aqueous solution of 1 mM copper sulphate monohydrate was prepared in deionized water. *Ziziphus mauritiana* L. leaf extract was mixed to 1 mM aqueous copper acetate solution in 1:9 ratios in a 250 ml beaker with constant stirring on magnetic stirrer. After time of period the color of solution turns to dark yellow. The mixture was kept in a muffle furnace at 250 °C. A fine black colored material was obtained and this was carefully collected and packed for characterization purposes.

## 2.3. Characterization techniques

The morphology and composition of the synthesized CuONPs were examined by field emission scanning electron microscopy (FESEM, FEI, Nova Nano SEM 450), FESEM coupled energy-dispersive X-ray spectroscopy (EDX, Bruker, XFlash 6I30). Find the exact morphological structures and size of the CuONPs using transmission electron microscopic (TEM) analysis is done by using a PHILIPS-CM200. The crystallinity and crystal phases were characterized by X-ray diffraction (XRD, Bruker, D8-Advanced Diffractometer) pattern measured with Cu- K $\alpha$  Radiation ( $\lambda= 1.5406 \text{ \AA}$ ) in the range of 5–90°.

## 2.4. Phytochemical Screening

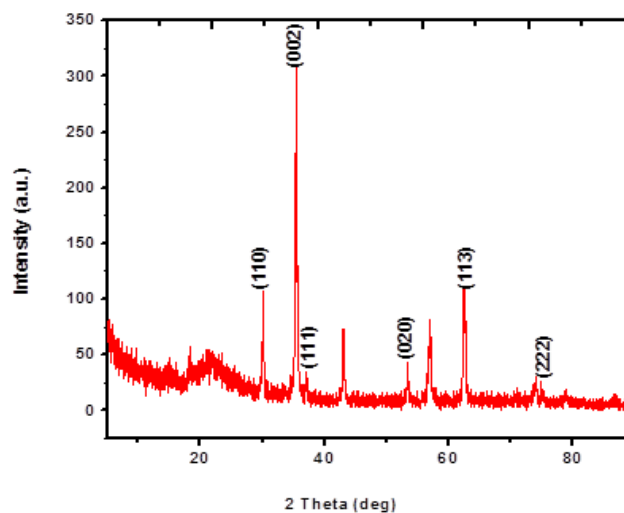
The fresh aqueous extract of *Ziziphus mauritiana* L. leaves were investigated for the presence of phytochemicals viz. coumarins, saponins, tannin, flavonoids, and glycosides by standard biochemical method [20].

# III. RESULTS AND DISCUSSION

## 3.1. Structural & crystallographic analysis

The CuONPs fabricated from *Ziziphus mauritiana* L. leaves extract were confirmed by the characteristic peaks observed in the XRD patterns, as shown in Fig. 2. XRD analysis evinced prominent diffraction peaks at 32.59°, 35.47°, 38.69°, 53.41°, 61.45° and 75.19°

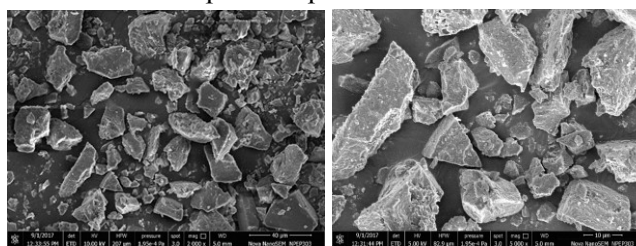
corresponding to (110), (002), (111), (020), (113) and (222) of face-centered-cubic structure of copper oxide nanoparticles with a monoclinic phase (JCPDS No. 45-0937). The XRD pattern exposed that synthesized copper oxide nanoparticles are crystalline in nature [30].



**Figure 2.** X-Ray diffraction pattern of synthesized CuO-NPs at room temperature

## 3.2. FE-SEM microphotographs

From the FESEM image as shown in Fig. 3 the synthesized CuONPs present uniform and define spherical morphology. Each CuONPs possesses the average particles size of 20-45 nm. It is noticed that green synthesis of CuONPs produces the small and uniform size of spherical particles.

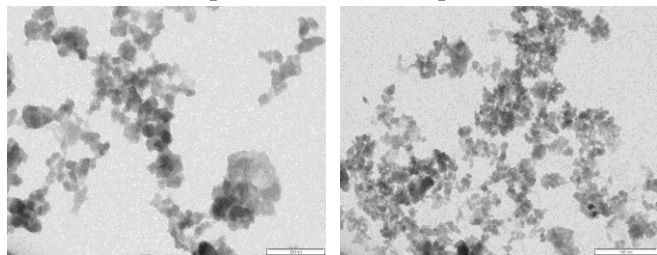


**Figure 3.** FE-SEM microphotographs of CuO-NPs deposited on a carbon strip.

## 3.3. TEM images

Figure 4 shows the TEM images of synthesized CuONPs. The low magnification TEM image reveals almost similar spherical morphology of CuONPs as seen in FESEM image. From TEM images, the average particle size is estimated to be 20-45 nm spherical particles, which is consistent with the FESEM results.. Therefore, the morphological characterizations confirm the

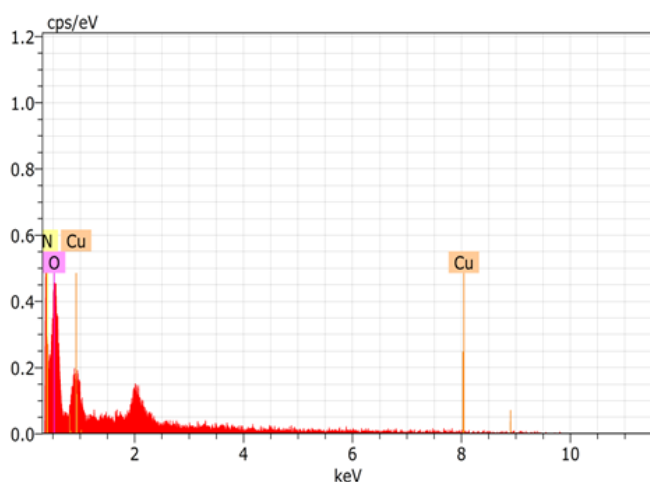
spherical morphology of CuONPs biosynthesized from the leaves of *Ziziphus mauritiana* L. plant.



**Figure 4.** TEM images indicating the presence of spherical CuO-NPs recorded at various magnifications.

### 3. 4. EDS studies

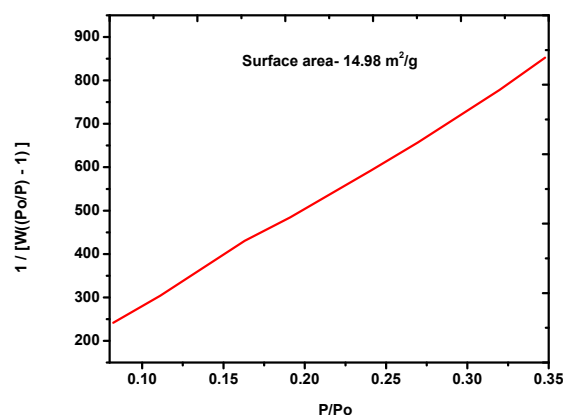
The composition of synthesized CuONPs has been analyzed by investigating the energy-dispersive X-ray spectroscopy (EDS), as shown in Fig. 5. EDS spectrum displays the Cu and O peaks. The quantitative data confirms the formation of CuO instead of other copper oxide in the synthesized materials by green synthesis of *Ziziphus mauritiana* L. plant.



**Figure 5.** EDS spectrum of synthesized CuO-NPs.

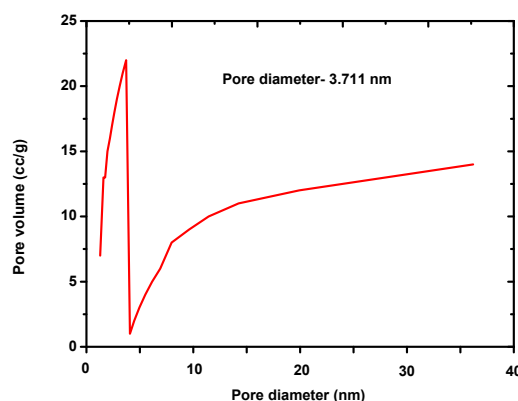
### 3. 5. Specific surface area and porosity studies

The considerable parameters such as particle size, shape and density are related to the specific surface area measurements ( $\text{m}^2\cdot\text{g}^{-1}$ ) Fig. 6 exhibit BET plots of CuONPs. The specific surface area of CuONPs calculated using the multipoint BET-equation is  $14.98 \text{ m}^2/\text{g}$ . Assuming that the particles have solid, spherical shape with smooth surface.



**Figure 6.** BET plots of CuONPs.

Figure 7 shows the typical BJH desorption pore size distribution curves of CuONPs. From the curves, we can see that most of the micropores with a size smaller than  $36.19 \text{ nm}$ , the pore size of which estimated from the peak position are about  $3.711 \text{ nm}$  possesses a relatively narrow pore size distribution. Therefore, these particles are actually grain clusters and small polycrystalline in nature.



**Figure 7.** BJH desorption pore size distribution curves of CuONPs

### 3. 6. Phytochemical screening

The results of qualitative phytoconstituents analysis of aqueous leaf extract of *Ziziphus mauritiana* L. are shown in table 1. Phytochemical analysis of *Ziziphus mauritiana* L. leaves revealed and highlighted the presence of tannins, saponins, coumarins, flavonoids, and glycosides which may be responsible for the efficient stabilizing agent of nanoparticles.

**Table 1.** Phytochemical screening of aqueous leaves extract of *Ziziphus mauritiana* L.

Phytoconstituents	Test	Phytoconstituents	Test
Tannin	+	Saponins	+
Coumarins	+	Emodins	-
Proteins	-	Flavonoid	+
Glycosides	+	Anthraquinone	-
Anthocyanosides	-	Phytosterols	-

#### IV. CONCLUSION

In present work a new green protocol for the synthesis of CuONPs using aqueous extract of *Ziziphus mauritiana* L. leaves is developed, which is ecofriendly method and a promising, low cost & without using any toxic chemicals. Average size of synthesized CuONPs is 5-40 nm.

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#### VI. DISCLOSURE

The authors declare no conflicts of interest in this work.

#### VII. REFERENCES

- [1]. Frietsch M, Zudock F, Goschnick J, Bruns M. CuO catalytic membrane as selectivity trimmer for metal oxide gas sensors. *Sens. Actuators B.* 2000; 65(1): 379-381.
- [2]. Gawande M B, Goswami A, Felpin F-X, Asefa T, Huang X, Silva R, Zou X, Zboril R, Varma R S. Cu and Cu-based nanoparticles: synthesis and application in catalysis. *Chem. Rev.* 2016; 116: 3722-3811.
- [3]. Rehana D, Mahediran D, Senthil Kumar R, Kalilur Rahiman A. Evaluation of antioxidant and anticancer activity of copper oxide nanoparticles synthesized using medicinally important plant extracts. *Biomed. & Pharmaco.* 2017; 89: 1067-1077.
- [4]. Kessler M T, Robke S, Sahler S, Prechtel M H G. Ligand-Free copper (I) oxide nanoparticle-catalysed amination of aryl halides in ionic liquids. *Catal. Sci. Technol.* 2014; 4: 102-108.
- [5]. Wang H, Xu J Z, Zhu J J, Chen H Y. Preparation of CuO nanoparticles by microwave irradiation. *J. Cryst. Growth.* 2002; 244: 88-94.
- [6]. Kumar R V, Diamant Y, Gedanken A. Sonochemical synthesis and characterization of nanometer-size transition metal oxides from metal acetates. *Chem. Mater.* 2002; 12: 2301-2305.
- [7]. Borgohain k, Singh J B, Rama Rao M V, Shripathi T, Mahamuni S. Quantum size effects in CuO nanoparticles. *Phys. Rev.* 2000; 61: 11093-11096.
- [8]. Eliseev A A, Lukashin A V, Vertegel A A, Heifets L I, Zhirov A I, Tretyakov Y D. Complexes of Cu (II) with polyvinyl alcohol as precursor for the preparation of CuO/SiO<sub>2</sub> nanocomposites. *Mater. Res. Innov.* 2000; 3: 308-312.
- [9]. Salavati-Niasari M, Davar F. Synthesis of copper and copper (I) oxide nanoparticles by thermal decomposition of a new precursor. *Mater. Lett.* 2009; 63: 441-443.
- [10]. Savale A, Ghotekar S, Pansambal S, Pardeshi O. Green synthesis of fluorescent CdO nanoparticles using *Leucaena leucocephala* L. extract and their biological activities. *J Bacteriol Mycol open access.* 2017; 5: 00148.
- [11]. Ghotekar S K, Pande S N, Pansambal S S, Sanap D S, Mahale K M, Sonawane B. Biosynthesis of silver nanoparticles by using *Annona reticulata* L. And its characterization. *Wor. Jou. Pha. & Pha. Sci.* 2015; 11: 1304-1312.
- [12]. Pande S N, Bharati K T, Wakchure S K, Ghotekar S K, Gujrathi D B, Phatangare N D. Green synthesis of silver nanoparticles by *Carallia fimbriata* L. and its characterization. *Ind. Jou. App. Res.* 2015; 5: 749-750.
- [13]. Lingaraju K, Raja Naika K, Manjunath K, Nagaraju G, Suresh D, Nahabhushna H. Rauvolfia serpentine-mediated green synthesis of CuO nanoparticles and its multidisciplinary studies. *Acta Metall. Sin.* 2015; 18: 1134-1140.
- [14]. Aher Y B, Jain G H, Patil G E, Savale A R, Ghotekar S K, Pore D M, Pansambal S S, Deshmukh K K. Biosynthesis of copper oxide nanoparticles using leaves extract of *Leucaena leucocephala* L. and their promising upshot against the selected human pathogen. *Int. Jou. Mol. Clin. Micro.* 2017; 7: 776-786.

- [15]. Sharma J, Akhtar J K, Ameen M S, Srivastava S, Singh P G. Green synthesis of CuO nanoparticles with leaf extract of *Calotropis gigantea* and its dye-sensitized solar cells applications. *J. Alloys Compd.* 2015; 632: 321.
- [16]. Gunalan S, Sivaraj R, Venckatesh R. Aloe barbadensis Miller mediated green synthesis of mono-disperse copper oxide nanoparticles: optical properties. *Spectrochim. Acta A.* 2012; 97: 1140.
- [17]. Sankar R, Manikandan P, Malarvizhi V, Fathima T, Shivashangari K S, Ravikumar V. Anticancer activity of *Ficus religiosa* engineered copper oxide nanoparticles. *Spectrochim. Acta A.* 2014; 121: 746.
- [18]. Jayakumarai G, Gokulpriya C, Sudhapriya R, Sharmila G, Muthukumaran C. Phytofabrication and characterization of monodisperse copper oxide nanoparticles using *Albizia lebbek* leaf extract. *Appl. Nanosci.* 2015; 5: 1017-1021.
- [19]. Pansambal S, Deshmukh K, Savale A, Ghotekar S, Pardeshi O, Jain G, Aher Y, Pore D. Phytosynthesis and biological activities of fluorescent CuO nanoparticles using *Acanthospermum hispidum* L. extract. *J. Nanostruct.* 2017; 7: 165-174.
- [20]. Fransworth N R. Biological and phytochemical screening of plants. *Jou. of Pharma. Sci.* 1996; 55: 225-227.