

## Synthesis of Copper Oxide nano-rods by Microwave-assisted combustion route and Their Characterization studies

Yathisha R O<sup>a</sup>, Y. Arthoba Nayaka<sup>a\*</sup>.

<sup>a</sup>Department of Chemistry, School of Chemical Sciences, Kuvempu University, Jnanasahyadri, Shankaraghatta-577 451, Karnataka, India

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### ABSTRACT

The present study demonstrates the petal-shaped copper oxide (CuO) nano-rod structures were fabricated by microwave-assisted combustion method. The prepared material was annealed at temperature 500°C and characterized by means of optical absorption spectroscopy (UV–Vis), X-ray diffraction (XRD), Field emission scanning electron microscopy (FE-SEM) and Photo-conductivity technique (I-V characteristics). The optical energy gap of CuO nano-rods was analyzed through UV–Vis NIR spectroscopic technique and the result illustrated that the energy gap of synthesized CuO nano-rods is found to be 1.44 eV. The XRD of the synthesized sample confirms copper oxide nano-rods are in pure monoclinic phase with lattice parameters  $x=4.675 \text{ \AA}$ ,  $y=3.343 \text{ \AA}$ ,  $z=5.183 \text{ \AA}$ . Energy dispersive analysis using X-rays confirms the existence of copper and oxygen atoms in synthesized CuO nanocrystals. FE-SEM micrographs specified that the synthesized material contains nanostructured nano-rods with a small amount of agglomeration in the product. The electrical properties of CuO film were studied by I-V characterization and the results depict that the conductance of CuO film is found to be superior in UV- light compared to the dark.

**Keywords:** Crystalline size, Energy gap, Morphology, Petal shaped rods, Tenorite

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\*Corresponding author, Tel.: +91 9448855078; Fax: +91 8282 256255

E-mail address: [drarthoba@yahoo.co.in](mailto:drarthoba@yahoo.co.in), [yathisharo@yahoo.com](mailto:yathisharo@yahoo.com)

## 1. INTRODUCTION

Synthesis of metal-oxide and transition metal doped semiconducting nanomaterial give opportunities for the improved applications in different areas of science and technology due to their unique physical and chemical properties, caused by their nano-sized dimension and large surface/volume ratio [1]. One-dimensional nanomaterial such as nano-ribbons, nano-belts, nano-cubes and nano-prisms have become the concentrates of intensive research due to their distinctive properties and their significance for fabrication into high-density nanoscale devices [2]. The transition metal oxides such as copper sulphide (CuS), cerium oxide (CeO<sub>2</sub>), nickel oxide (NiO), ferrous oxide (Fe<sub>2</sub>O<sub>3</sub>) and Titania (TiO<sub>2</sub>) are an important class of semiconductors. Among these metal-oxides, Copper (I) oxide (Cu<sub>2</sub>O) and copper (II) oxide (CuO) are gained more popularity in recent years is due to the properties of excellent thermal stability, easily available reactant materials, non-toxic and exhibits good optical and electrical properties [3]. Due to these properties, recently most of the research works is mainly focussed on the synthesis of different CuO nanostructures, such as nano-flowers, nano-flakes, nano-pyramid, nano-plates, nano-bats [4]. Therefore, a number of CuO nanostructures have been prepared in different morphologies by a variety of methods like precipitation [5], solvothermal [6], hydrothermal [7], thermal evaporation [8], electrochemical [9] and combustion [10], solid-state [11] methods. Generally, the above methods faces certain following drawbacks: (i) need more complicated equipment, (ii) require more additional solvent (iii) require very high temperature and pressure (iv) take more time for the reaction and (v) more steps are required for the synthesis of CuO nanoparticles [11]. Hence to resolve the above problems, a simple and low-cost method is necessary for the preparation of CuO nanocrystals. Out of the various methods, microwave heating process has recently popular and most usual process compared to other combustion methods. In this route, the microwave

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has got more penetrating power and it penetrates into the materials at the molecular level. This leads to the conversion of microwave energy into heat throughout the materials by either ionic conduction or dipole rotation. This shows acceleration in reaction rate, the yield of homogeneous product within a few minutes, well size distribution and excellent control of stoichiometry [12]. By means of this method, a number of functional materials and composites with novel structures are obtained such as  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nano-rings [13], NiS<sub>2</sub> nano-cubes [14], CuS nano-prisms [15], rose like ZnO [16] with their excellent properties.

CuO is known as potential *P*-type semiconductor materials with narrow optical energy gap varying between 1.2- 1.4 eV [17]. When comparing the CuO nanoparticles to commercially available CuO powder, CuO nanoparticles have attracted a lot of potential applications and uses due to nanocrystals have advanced selectivity and photo catalytic activity [18]. Due to its unconventional band structure, CuO nanoparticles has a wide range of potential applications in the fields of superconductors[19], lithium-ion batteries [20], electrochemical gas sensors [21], dye-sensitized solar cells (DSSC) [22] and electro-chemiluminescence. Therefore, it is of fundamental interest to the synthesis of high-purity, single phase CuO nanocrystals to study their structure and characterize their optical and electrical properties [23].

Here, we have synthesized the high purity CuO nano-rods through microwave irradiation method where as the solution of copper sulphate, sodium hydroxide and urea have been used. The diffraction pattern of CuO was recorded on X-ray diffractometer. The band gap was calculated using UV-Vis absorption studies. I-V characteristics were measured on Keithley source meter. The rod-like structure of CuO was investigated through FE-SEM.

## **2. EXPERIMENTAL DETAILS**

### **2.1. Chemicals Used**

Copper sulphate pentahydrate ( $\text{Cu}(\text{SO})_4 \cdot 5\text{H}_2\text{O}$ ), Sodium hydroxide ( $\text{NaOH}$ ) and Urea ( $\text{NH}_2\text{CONH}_2$ ) were procured from Himedia Laboratories Pvt. Ltd., Acetone ( $\text{CH}_3\text{COCH}_3$ ) was purchased from Merck. All the chemicals were of analytical grade and were used as received without further purification. Double distilled water was used for the preparation of solutions. The synthesis of nanosized CuO rods was carried out in a domestic microwave oven (Onida power solo 17D) operating at 100% power of 700 W.

### **2.2. Synthesis of CuO nano-rods**

To prepare CuO nanoparticles, 100 mL of 0.4 M sodium hydroxide was added drop-wise into a beaker containing 100 mL of 0.8 M copper sulphate and 0.8 M urea solution under constant stirring. When blue coloured homogenous reaction mixture turned in to partial green colour, the resulting solution was kept in a microwave oven and the reaction mixture was irradiated with 60% power (175 °C) of microwave energy for 15 minutes. Then so obtained dark green precipitate of copper hydroxide was centrifuged, washed several times with distilled water and then with alcohol, acetone and dried at 80 °C in an oven for 5 hours. The obtained samples were calcinated (500 °C) in the air for 1 hour to get the desired dark brown coloured CuO nanocrystal.

### **2.3. Characterization details**

The crystallinity of nanoparticles was carried out on an X-Ray diffractometer using  $\text{Cu-K}_\alpha$  radiation ( $\lambda=0.15406$  nm). The patterns were recorded in the range of  $10^\circ$  to  $80^\circ$  ( $2\theta$ ). The crystallite size and structure of the samples were studied through Field emission scanning

electron microscope (FESEM) fitted with an Energy-dispersive X-ray spectroscopy (EDAX) [Model: FE-SEM Carl Zeiss AG-ULTRA 55]. The absorbance for CuO nanomaterial was measured through UV-Vis spectrophotometer (Model: USB 4000, Ocean Optics, USA). Photoconductivity properties were analyzed by Keithley low voltage source meter and measured voltage in between 0-20V [Model: Keithley 2401].

### 3. RESULTS AND DISCUSSION

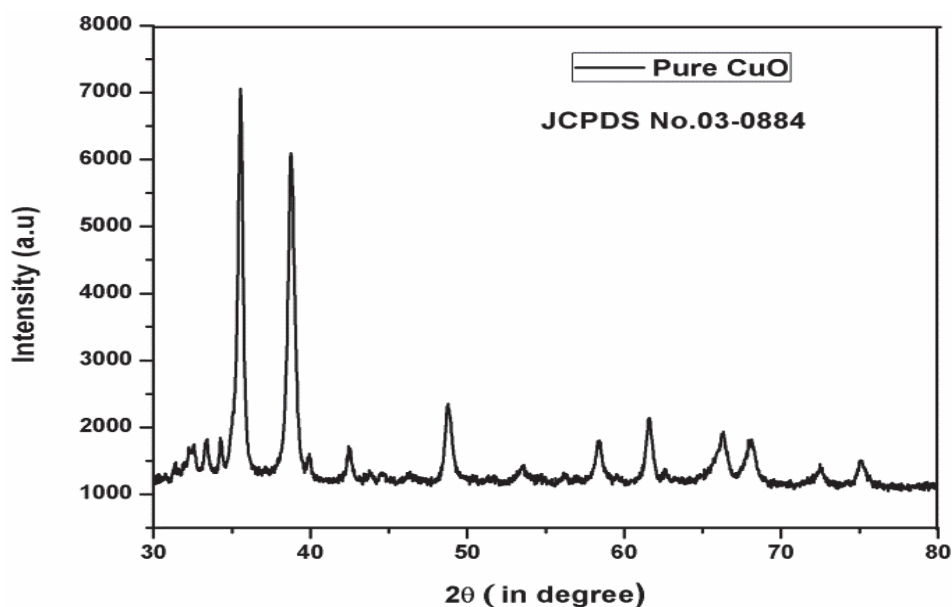
#### 3.1. XRD Analysis

Fig. 1 shows the XRD pattern of CuO nanoparticles prepared by microwave heating method. As can be seen from Fig. 1, all the diffraction peaks are assigned well to the monoclinic structure of tenorite system. The major peaks observed at  $2\theta$  values  $32.55^\circ$ ,  $35.50^\circ$ ,  $38.69^\circ$ ,  $48.70^\circ$ ,  $53.53^\circ$ ,  $58.57^\circ$ ,  $61.67^\circ$ ,  $66.24^\circ$ ,  $68.04^\circ$ ,  $72.24^\circ$ ,  $75.10^\circ$  [24]. Further, no other impurity peaks of copper hydroxide were observed in the XRD pattern, showing single phase CuO formation. Which are in agreement with JCPDS card No: 03-0884. The measured values of spacing and FWHM of synthesizing CuO nanocrystals are well matched with the JCPDS card no. In addition, the peak of XRD shows broader due to obtained materials contains nanorange of particles. The crystalline size of synthesized CuO nanoparticles was calculated using Scherrer's formula [25];

$$\text{Average crystalline size (D)} = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

where  $\lambda$  the wavelength of  $\text{CuK}\alpha$  radiation,  $\beta$  is the FWHM with Bragg's reflection angle  $\theta$

. The average crystalline size of CuO found to be in the range of  $\sim 21$ – $54$  nm.

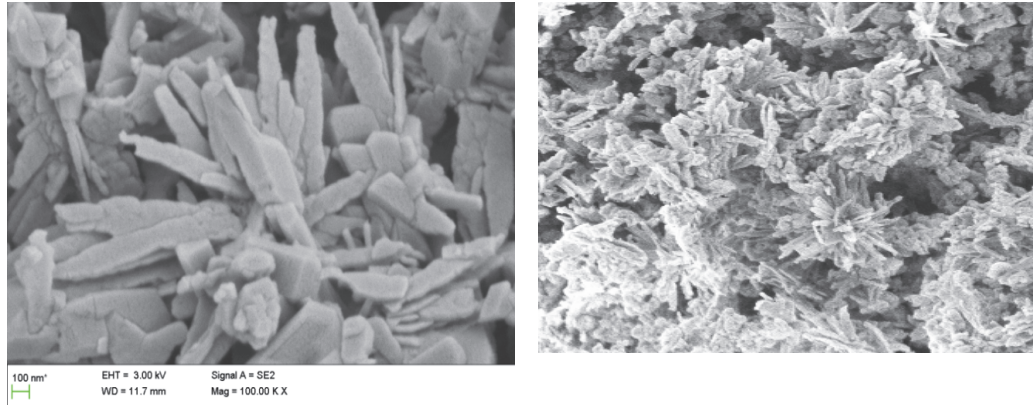


**Fig.1:** XRD pattern of petal-shaped rod-like CuO nanoparticle

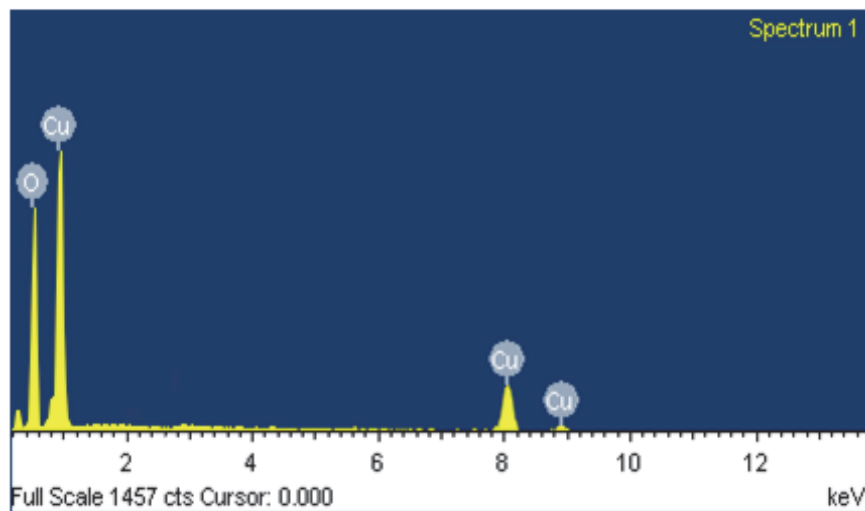
### 3.2. Structural and Elemental Analysis

Fig.2 shows FE-SEM images of synthesized pure CuO nanoparticles. The FE-SEM micrograph of samples shows that the CuO structures prepared at 60% of power consist of petal-shaped rod-like CuO nanocrystals and low resolution (2  $\mu\text{m}$ ) images shows the minority of flower shaped particles. The particle aggregation is a major factor that controls the morphology and structure of the final product. Even though it is not yet understood, it is evident that NaOH plays an important role in the formation of the flower-like structure. Microwave irradiation has also got an influence on the surface morphology of CuO nanostructures due to its volumetric heating effect. Moreover, vibrational frequency of the atoms during different reaction conditions plays an important role in deciding the size of the nanoparticles [26]. EDAX spectra were used to analysis of the composition of CuO particles at 500°C is shown in Fig.3. Based on the determination of elemental composition of CuO nanorods (Cu=59.03% and O=40.97%) the weight percent of Cu/O ratio is found to be 1.45 and EDAX spectrum obtained from CuO nanoparticles shows peaks confirming the presence

of Cu and O only. Which confirms the synthesized CuO was single phase and high purity material. [27].



**Fig.2:** FE-SEM images of pure CuO nanoparticles (a) petal shape of rods (b) flower-like particles.

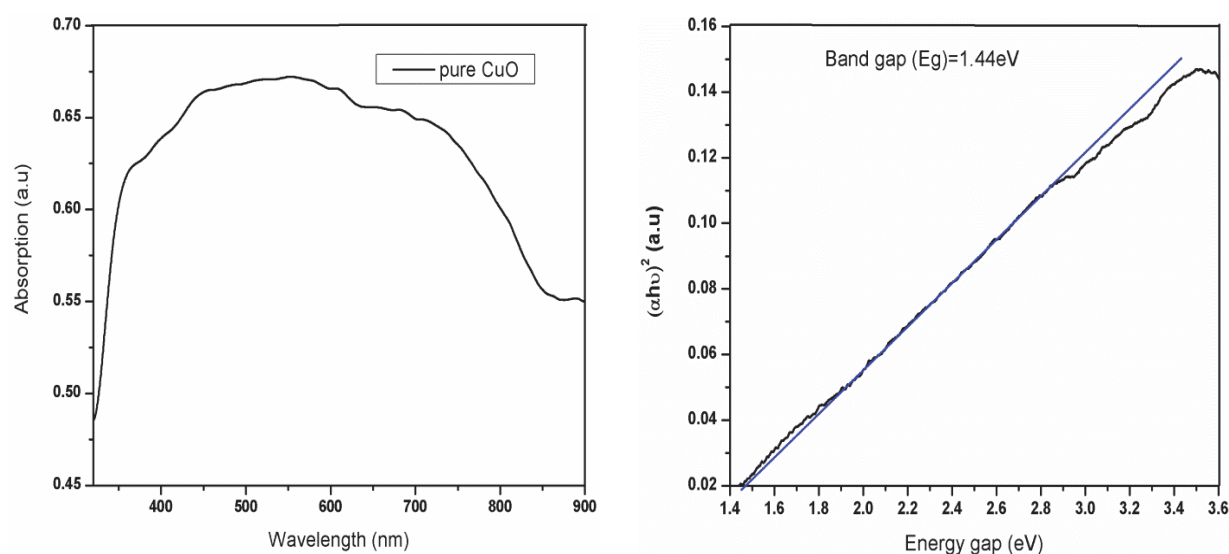


**Fig.3:** EDAX spectra of synthesized pure CuO nanoparticles.

### 3.3. UV-Visible Spectral Analysis

Fig.4 shows the optical absorption spectra of the sample annealed at 500°C temperature. A UV-Vis spectrum was measured in the range between 300 and 900nm wavelength region at room temperature. The measured energy gap of CuO is to be 1.44 eV, which is calculated from Tauc's relation,  $(\alpha h\nu)^{1/r} = B(h\nu - E_g)$  where  $h$  is the planks constant,  $B$  is a constant,  $\alpha$

is the absorption coefficient,  $\nu$  is the frequency of the incident radiation,  $r$  is determined by the type of optical transition of a semiconductor. Energy band gap ( $E_g$ ) can be obtained by plotting the graph  $(h\nu)$  against  $(\alpha h\nu)^{1/r}$  for various values of  $r$ , it becomes possible to determine the nature of transitions involved and the intercepts of the straight line portion of the respective plots (at  $h\nu > E_g$ ) corresponding to zero absorption on energy axis gives values of energy gaps[28].



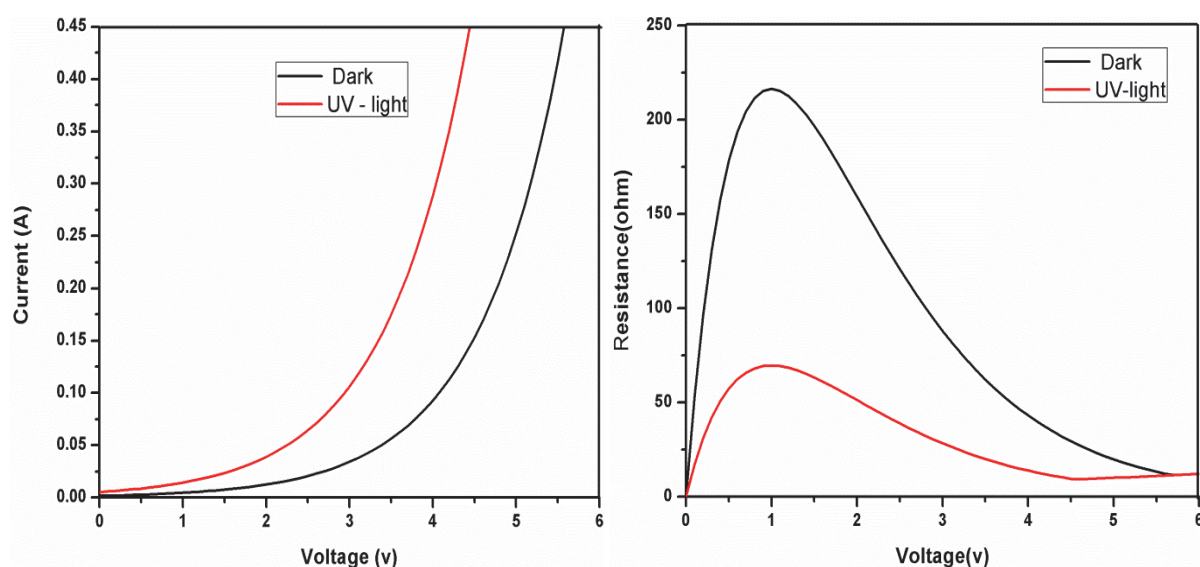
**Fig.4.** UV-Vis absorption spectra and Tauc's plot of pure CuO nanoparticles

### 3.4.I-V Characterization

The Current-Voltage (I-V) characteristics of CuO film was studied under dark as well as a light condition to check nature of contact of CuO with silver paste using two probe methods. The typical current-voltage curves of CuO film under as shown in Fig.5. Area of used samples is  $2 \times 2 \text{ cm}^2$ . As seen in Fig 5, the conductivity of CuO thick film was extremely small in the dark condition. It is due to the slowdown motion of electrons present in the grain boundaries. These boundaries operate as diffusion sites and impending walls which direct to an in the electron movement by reducing the resistance and enhance the conductivity.



Further, the improvement of conductance under the UV-light condition is may be the reason of activation of charge carrier like electrons and enhance the mobility of charge carriers [29]. Fig. 5 shows the measured current of CuO films at 5V is 0.45A (dark condition), but the same photo-current was observed at low voltage (4V) in UV-light condition. Consequently the measured optical energy gap, conductivity, and resistivity are very valuable for the application of fabrication of optical devices [30].



**Fig. 5:** I-V characteristics of CuO nanoparticles under dark as well as UV-light conditions.

#### 4. CONCLUSIONS

In summary, rod-like CuO nanoparticles with a monoclinic structure have been synthesized by microwave combustion method, urea used as a fuel. XRD studies showed that the synthesized CuO nanoparticles are of monoclinic structure and show the average size of the particle. A FESEM observation displayed the surface morphology of rod-shaped CuO particles in nano-meter dimension. UV-Vis spectra showed that the optical bandgap of CuO

is 1.45eV and which is calculated from Tauc's relation. I-V indicated the photo-current conversion efficiency for CuO nanoparticles.

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