

## Structural and Morphological Characterization of CuO Nanostructure Precipitated by Water-soluble Copper (II) Nitrate Hemi(pentahydrate) and NaOH as Reactants

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In the present work, for the first time, a homogeneous sponge-like porous CuO nanostructure was successfully developed via an eco-friendly precipitation route. The product was obtained using copper (II) nitrate hemi(pentahydrate) and NaOH as reactants without thermal treatment or use of any additives and surfactants. The crystallographic structure, functional group and surface morphology of the samples were characterized by X-ray diffractometry (XRD), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). XRD analysis reveals the formation of a pure and highly crystalline CuO monoclinic structure with an average grain size of around 23.8 nm. Besides, the FTIR result indicates that the characteristic vibrational bands appeared in the 400-650  $\text{cm}^{-1}$  range can be ascribed to the stretching vibration of the Cu-O bond. Moreover, SEM images of the CuO sample clearly demonstrate a uniform sponge-like nanoporous structure with fiber growth on the surface with pore sizes ranging from 70 to 90 nm. Hence, this fascinating structure could potentially serve as a catalyst for the destruction of pollutants as well as a solar absorber for capturing sunlight energy.

**Keywords:** CuO, Nanostructure, Precipitation, SEM, XRD.

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### 1. INTRODUCTION

Nanostructured materials with particle dimension below 100 nm provide useful applications in the fields of medicine, pharmaceuticals, environment, energy, and materials [1, 2]. Tenorite or copper oxide (CuO) nanostructure is a black transition metal oxide with a monoclinic crystal structure. It is also a *p*-type semiconductor with a narrow optical band gap of 1.2 eV [3-6]. Owing to its special features, such as stable structure with high optical absorbance, environmental friendliness, relatively non-toxicity, low cost and natural abundance [4, 5], it becomes a promising material and is widely utilized in heterogeneous catalysis or photocatalysis for purification and wastewater treatment, electrochemical and solar cells for lithium-ion batteries and energy storage applications, high temperature superconductors, gas sensors, biomedical agents for antimicrobial activity and anticancer drugs and optoelectronic devices such as optical switches [4, 7-12].

Up to this moment, CuO nanomaterials have been formulated by different techniques such as laser ablation, hydrothermal synthesis, sol-gel method, precipitation, green synthesis, microwave-assisted irradiation, spray pyrolysis, thermal evaporation, electrodeposition etc. [3, 4, 7, 9, 13, 14]. As a result, the synthesized CuO nanostructures exist in many different forms like nanocrystals, nanospheres, nanocubes, nanorods and nanoparticles [3]. However, some of these synthesis techniques involve high cost, low output and lack of crystallinity in the resulting product. Precipitation synthesis is a well-defined method due to its non-toxic and safe approach with high yield and better crystallinity, cost-effective as it needs a lower produc-

tion temperature and less expensive starting materials for large-scale production, which is mainly used in the industry [3, 4, 9, 15]. Thus, in the present work, CuO nanostructures have been prepared in alkaline medium using precipitation method near the boiling point, and the crystal structure, functional groups and surface morphology were instantly characterized by XRD, FTIR and SEM.

### 2. MATERIALS AND METHODS

Copper (II) nitrate hemi(pentahydrate) ( $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ ) was purchased from HmbG Chemicals (Germany), while sodium hydroxide (NaOH) pallets were procured from Merck. All the reagents were of analytical grade and used without any further refinement. CuO nanomaterials were prepared by precipitation route from  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$  in alkaline medium. Distilled water was used to prepare solutions and remove any possible impurities in the solution. In a typical procedure, appropriate amount of  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$  was dissolved in 20 ml of distilled water and constantly stirred for 10 min to form a blue aqueous solution (0.3 M). Thereafter, NaOH was slowly added dropwise to  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$  solution. The solution was then stirred and gently heated at 90 °C for 2 h until a black precipitate is formed. Afterwards, the black precipitate formed was separated by filtration and rinsed 5 times with distilled water to remove any unwanted ions or impurities from the product. Eventually, the collected precipitate was dried in air at room temperature for 24 h prior to subsequent characterizations. The synthesized CuO nanomaterials were stable at room temperature and thus were dried to obtain smaller particles.

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The structural properties of the samples were investigated using XRD (Rigaku Miniflex-TM II) with monochromatic Cu-K $\alpha$  radiation ( $\lambda = 1.541 \text{ \AA}$ ) generated at an operating voltage of 40 kV and a current of 40 mA. The diffraction pattern was recorded at room temperature in the  $2\theta = 20\text{-}80^\circ$  scanning range with a scan step size of  $0.04^\circ$ . The average crystallite sizes of the samples were then calculated by Debye-Scherrer method. The surface morphology and particle size of the samples were monitored through a scanning electron microscope (SEM) of model JSM JEOL-6360 at an operating voltage of  $\sim 15 \text{ kV}$ . A Fourier transform infrared spectrometer (FTIR-Thermo Nicolet Alvarar 380) was utilized to identify functional groups present in the samples. The FTIR spectra were recorded at room temperature in the mid-infrared spectral range from  $4000$  to  $400 \text{ cm}^{-1}$  with a resolution of  $2 \text{ cm}^{-1}$ .

### 3. RESULTS AND DISCUSSION

XRD analysis was initially performed by a Rigaku Miniflex-TM X-ray diffractometer in order to elucidate the crystal structure and crystallite size of as-prepared CuO nanostructures. The result of the wide-angle XRD diffractogram recorded for the CuO nanostructure synthesized by chemical precipitation route is displayed in Fig. 1. The diffractogram shows that the peaks are visible in the studied  $2\theta$  value range. First of all, the sample exhibits a pure polycrystalline nature, and no amorphous states are tracked by XRD. Also, all peaks can be exactly matched to the pure phase of the desired materials. As can be visualized from the figure, the XRD pattern shows twelve distinguishable diffraction peaks positioned at  $2\theta$  values of  $32.34^\circ$ ,  $35.50^\circ$ ,  $35.65^\circ$ ,  $38.63^\circ$ ,  $48.91^\circ$ ,  $53.63^\circ$ ,  $58.22^\circ$ ,  $61.39^\circ$ ,  $66.41^\circ$ ,  $68.13^\circ$ ,  $72.30^\circ$  and  $74.98^\circ$ . Accordingly, these peaks correlate well with the crystallographic lattice planes (110), (002)/(-111), (111)/(200), (-202), (020), (202), (-113), (022)/(-311), (220)/(113), (311), and (004)/(-222). All the defined XRD peaks are well matched to the JCPDS card no. 00-48-1548 and further indicate the formation of pure single-phase CuO in the crystalline monoclinic tenorite structure that belongs to C2/c symmetry space group. Kannan et al. [16] and Daira et al. [7] discovered a similar CuO structure using, respectively, facile microwave-assisted synthesis and spray pyrolysis. Moreover, sharp and prominent peaks with a narrow width located at  $35.50^\circ$ ,  $35.65^\circ$  and  $38.63^\circ$  reveal that the crystalline nature of CuO is relatively high in related planes. No peaks corresponding to impurities or other compounds such as  $\text{Cu}(\text{OH})_2$  and  $\text{Cu}_2\text{O}$  were detected in the XRD diffractogram, indicating a high purity phase of the CuO nanostructure. Furthermore, the crystallite size was computed applying the Debye-Scherrer relation [17, 18]:  $D = 0.9\lambda/\beta\cos\theta$ , where  $D$  is the average crystallite size,  $\lambda$  is the wavelength of applied X-ray radiation,  $\beta$  represents the full width at half maximum (FWHM) value, and  $\theta$  is the Bragg's diffraction angle. The average crystallite size of CuO is estimated to be  $23.8 \text{ nm}$ , implying the nano dimension of CuO. The lattice parameters  $a$ ,  $b$  and  $c$  for the present structure are represented by the following formula [7]:

$$\frac{1}{d^2} = \frac{1}{\sin^2\beta} \left( \frac{h^2}{a^2} + \frac{k^2 \sin^2\beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl \cos\beta}{ac} \right), \quad (1)$$

where  $h$ ,  $k$  and  $l$  are the Miller indices,  $d$  is the lattice spacing and  $\beta = 99.45^\circ$ . Hence, the mean lattice parameters and unit cell volume of the synthesized CuO are obtained to be  $a = 4.685 \text{ \AA}$ ,  $b = 3.423 \text{ \AA}$ ,  $c = 5.135 \text{ \AA}$  and  $V = 80.875 (\text{ \AA})^3$  under the restriction  $\alpha = \gamma = 90^\circ \neq \beta$ . The obtained lattice parameters values agree well with the previously reported works [9, 12]. The degree of crystallinity is dependent on the arrangement and periodicity of the crystals structure [15], and widening of the XRD diffraction peak is usually correlated with the crystallite size and lattice strain [9]. Even though CuO was synthesized at a temperature close to the boiling point by one-step precipitation without undergoing any thermal treatment, nevertheless, the crystallinity of the as-prepared CuO is quite comparable with the one reported in literature [7, 16]. Therefore, based on the XRD analysis, it can be considered that, the present method is appropriate to fabricate highly crystalline and purified CuO.

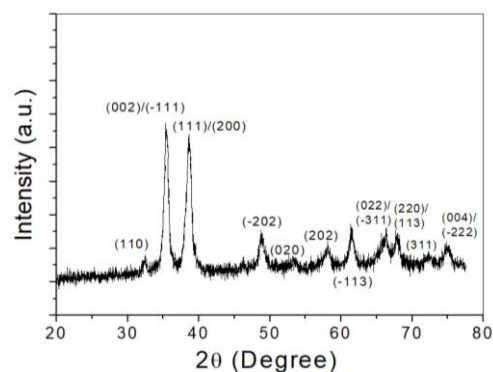


Fig. 1 – XRD pattern of CuO nanostructure

The FTIR analysis was carried out to examine the presence of various functional groups on the surface of the synthesized materials [10, 19, 20]. Fig. 2 depicts the typical FTIR spectra of CuO in the spectral region from  $400$  to  $4000 \text{ cm}^{-1}$ . The band appeared in the range between  $400$  and  $650 \text{ cm}^{-1}$  can be assigned to the bond formation of Cu–O stretching vibration [4, 21, 22]. In the present case, precipitated CuO exhibits the characteristic vibrational modes at  $453$  and  $569 \text{ cm}^{-1}$ , whereby a sharp and a very strong peak is observed centered at  $453 \text{ cm}^{-1}$ , which corresponds to the characteristic vibrational modes of Cu–O stretching along the (002) direction [9, 14]. Meanwhile, a small hump emerged at  $569 \text{ cm}^{-1}$  might be ascribed to the Cu–O stretching vibration along the (220) direction. On the one hand, there is a point of view based on the group theory proposed by Dolai et al. [6], in which the peaks located at  $453$  and  $569 \text{ cm}^{-1}$  may be due to Eu and A $_{2u}$  modes, respectively, as for the unique characteristic of pure tenorite CuO phase. Therefore, the samples produced were affirmed to be CuO. Furthermore, on the other hand, several IR bands observed in the range of  $700$  to  $1700 \text{ cm}^{-1}$  are related to carbonyl groups [4, 16]. The band located at  $759 \text{ cm}^{-1}$  can be attributed to aromatic bending vibration of the C–H group, while a small band at  $1122 \text{ cm}^{-1}$  is due to the stretching vibration of the

C–O group. The band occurred at  $1355\text{ cm}^{-1}$  can be ascribed to the deformation vibration of the C–H band of alkane ( $\text{CH}_3$  and  $\text{CH}_2$ ) group [6, 9]. Moreover, a sharp peak centered at around  $1620\text{ cm}^{-1}$  corresponds to aromatic bending of alkene group ( $\text{C}=\text{C}$ ) [9]. Thus, it is worth to deduce that these residues or intermittent functional groups are more likely to induce and stabilize the formation of CuO. A broad band at around  $3213\text{ cm}^{-1}$  is related to the O–H stretching vibration of hydroxyl groups of physical adsorbed water molecules on the sample surface [23–25]. Also, the existence of asymmetric stretching vibration of  $\text{CO}_2$  molecules attached to the particle surface can be detected as small peaks located at  $2341$ ,  $2104$  and  $1907\text{ cm}^{-1}$  [16]. Additionally, the bands of  $\text{Cu}_2\text{O}$  and other impurities cannot be detected in the spectra, hence assuring the formulation of a high purity CuO crystal.

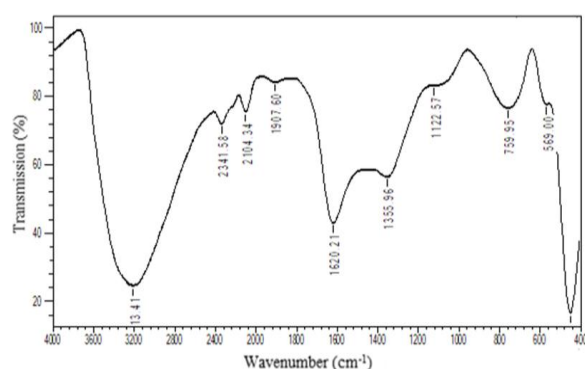


Fig. 2 – FTIR spectra of the CuO nanostructure

SEM imaging is conducted to characterize the nanostructure morphology. The morphology of the nanostructure depends on the stoichiometric ratio, nature of stabilizers, and reaction conditions, such as temperature, reaction time, solvent etc. [14]. Fig. 3 displays the SEM images of CuO surface morphology with two different magnifications ( $\times 5,000$  and  $\times 10,000$ ). The as-grown CuO sample exhibits a uniform, well-defined sponge-like structure with a size ranging between 200 and 350 nm along its porous surface. The spongy structure consists of many small pores, which are evenly distributed throughout the surface with an average pore size of 70 to 90 nm. Moreover, there are also nanofibers that are attached to the surface, and some are even outgrow through the sponge surface. The presence of nano-sized pores can increase the surface area of the particles and, hence, improve the photocatalytic and sensing ability of the materials. Also, alkaline based liquid media present in the process cause self-assembly growth and enhance non-classical formation of grains

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[9]. Therefore, it is worth to note that the sponge-like, fibrous porous CuO nanostructure can be produced through precipitation method near the boiling point without using any surfactants.

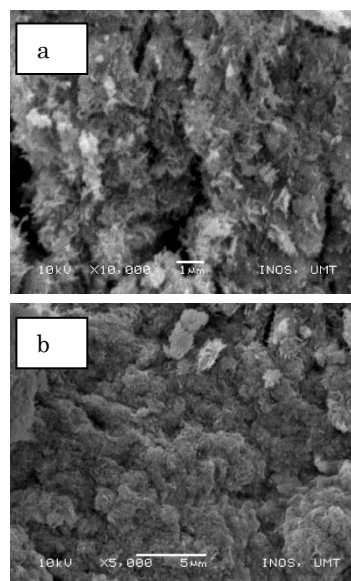


Fig. 3 – SEM images of CuO nanostructure at magnifications: (a)  $\times 10,000$ ; (b)  $\times 5,000$

## 4. CONCLUSIONS

In summary, the CuO nanostructure has been effectively fabricated by employing a low-cost and environmentally friendly precipitation route. The physical characterizations have been carried out using XRD, FTIR and SEM. The XRD result indicates the presence of a pure and highly crystalline monoclinic CuO tenorite with a crystallite size of 23.8 nm. FTIR study suggests that the characteristic bands appeared at 453 and  $569\text{ cm}^{-1}$  can be associated with the Cu–O stretching vibrational mode. SEM images reveal a uniform, sponge-like nanoporous structure with fiber growth on the surface in nano dimension. Based on the results obtained in the study, it is worth to propose that the present CuO nanostructure can potentially be used for wastewater treatment and also as a solar collector.

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### Структурне та морфологічне дослідження наноструктури CuO, яка осаджується водорозчинним нітрат-гемі(пентагідратом) міді (II) та NaOH як реагентами

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У роботі вперше вдало була розроблена однорідна губчаста пориста наноструктура CuO шляхом екологічно чистого осадження. Продукт був отриманий з використанням нітрат-гемі(пентагідрату) міді (II) та NaOH як реагентів без термічної обробки або використання будь-яких домішок та поверхнево-активних речовин. Кристалографічна структура, функціональна група та морфологія поверхні зразків характеризувалися рентгенівською дифракцією (XRD), інфрачервоною спектроскопією з перетворенням Фур'є (FTIR) та скануючою електронною мікроскопією (SEM). XRD аналіз показує утворення чистої і висококристалічної моноклінної структури CuO із середнім розміром зерна близько 23,8 нм. Результат FTIR вказує на те, що характерні смуги коливань, які з'явилися в діапазоні 400-650 см<sup>-1</sup>, можна приписати коливанням розтягування зв'язку Cu-O. Крім того, SEM зображення зразка CuO чітко демонструють однорідну губчасту нанопористу структуру з ростом волокон на поверхні з розміром пор від 70 до 90 нм. Отже, ця незвичайна структура потенційно може служити каталізатором знищення забруднюючих речовин, а також поглиначем сонячної енергії світла.

**Ключові слова:** CuO, Наноструктура, Осадження, SEM, XRD.