

Investigation of the Structural Parameters of Copper Oxide Nanoparticles using X-ray Diffraction

PIJUS KANTI SAMANTA

Department of Physics (PG & UG), Prabhat Kumar College, Contai-721404,
Purba Medinipur, West Bengal, India
E-mail: pijush.samanta@gmail.com

Abstract

We report here a simple and cost effective wet chemical synthesis of CuO nanoparticles. The formation of nanoparticles was observed using transmission electron microscopy (TEM). The nanoparticles of diameters ~ 8 nm were observed. Crystallinity of the nanoparticles was studied using X-ray diffraction (XRD). The XRD pattern also confirms the formation of pure CuO nanoparticles with monoclinic unit cell structure. The particle size as calculated from the XRD data matches well with that calculated from TEM. The average strain was calculated to be ~ 0.01 . Crystalline index calculation revealed that the nanoparticles are single crystalline in nature. We calculated the degree of orientation of different planes indicating the anisotropic growth of the nanocrystals. This study is very useful in understanding the structural properties of CuO nanoparticles.

Keywords: CuO; Nanoparticles; X-ray diffraction; Crystallinity; Strain; Anisotropy

1. INTRODUCTION

Researches on metal-oxide based nanostructures got considerable attention due to their enhanced multifunctional properties (optical, electrical, magnetic, and dielectric) exhibited in the nanoscale regime. These lead their unique applications in various optoelectronic, nano-electronic and sensor devices. Three metal-oxide nanostructures *viz* Zinc Oxide (ZnO), Titanium Oxide (TiO₂) and Copper Oxide (CuO and Cu₂O) are now in the forefront of research. CuO usually exists in two oxide forms-cuprous oxide (Cu₂O) and cupric oxide (CuO). During chemical growth at low temperature Cu₂O is formed, where as formation of CuO occurs at higher temperature. CuO is low band gap semiconductor of band gap $\sim 1.3 - 2.1$ eV [1]. It is non-toxic and has good catalytic property [2]. It is also quite useful in solar cells [3], sensor applications [4]. There are few reports of the formation of nanostructured CuO by low temperature wet chemical method. There are several methods such as chemical vapour deposition, oxidation, [5, 6] and potentiostatic electrodeposition, [7] to synthesize CuO nanostructures. However, Wet chemical method is a simple and cost effective route to grow varieties of nanostructures. There is a report on synthesis of CuO nanoparticles by a simple wet chemical route by Darezereshki *et al* [8]. Low temperature solution phase synthesis of CuO nanorods is also reported by Chen *et al*. [9]. Here, in this paper, we report a

simple wet chemical method to grow CuO nanoparticles. The fabricated material was further structurally characterized using transmission electron microscopy (TEM) and X-ray diffraction (XRD).

2. EXPERIMENTAL

2.1. Material preparation

All the chemicals used in this chemical growth process were of analytical grade (MERCK, 99.99% pure) and used without any further purification. In a typical synthesis process 4.9937 g of Copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) was dissolved in de-ionized water to prepare 0.2 M solution. 4.196 g of Lithium Hydroxide (LiOH) was dissolved in water to prepare 1 M LiOH solution. Now, under constant stirring of the LiOH solution, CuSO_4 solution was added drop wise for 5 minutes. The reaction as continued further for 30 min. At the end of the reaction a bluish white precipitate was deposited at the bottom of the flask. The solution was then aged for 24 hr. The precipitate was filtered and washed with de-ionized water 2-3 times and dried in a furnace at 200°C . The colour of the powder sample turned into black. The powder was then used for further characterization.

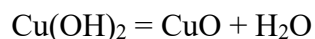
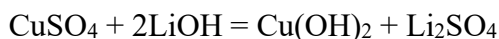
2.2. Material characterization

For TEM imaging, a small amount of sample and acetone together were taken in a beaker and undergo ultrasonication for 30 min. The articles were dispersed in the acetone. A drop of the acetone dispersed particles was put on a carbon coated copper grid. The grid was then dried in vacuum for TEM characterization. TEM imaging was performed in a JEOL-TEM operated at 200 kV. X-ray diffraction (XRD) experiment was performed in a RIGAKU X-ray diffractometer that uses $\text{Cu-K}\alpha$ radiation ($\lambda=1.54\text{\AA}$) and diffraction data were collected over an angular range of $30^\circ < 2\theta < 70^\circ$.

3. RESULTS AND DISCUSSIONS

3.1. Transmission Electron Microscopy and growth of the nanoparticles

A typical TEM image of the synthesized material is shown in Fig. 1. Spherical CuO nanoparticles are found to form. The diameters of the nanoparticles are in the range $\sim 6\text{-}12$ nm as measured from the TEM image. The size variation of the nanoparticles indicates the bottom up growth of the nanoparticles. In the chemical reaction of CuSO_4 with LiOH produces small sized $\text{Cu}(\text{OH})_2$ nuclei. These nuclei on thermal decomposition produce CuO nuclei. These CuO nuclei then grow further to form the CuO nanocrystals. The chemical reactions occurring during the growth process are shown below:



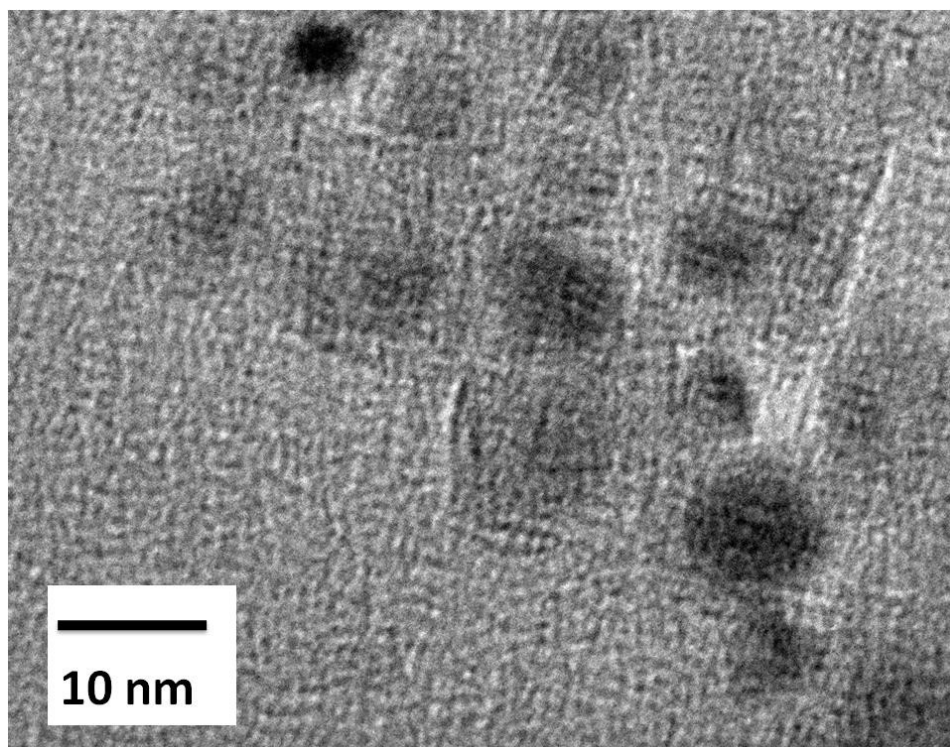


Fig. 1: TEM image of CuO nanoparticles.

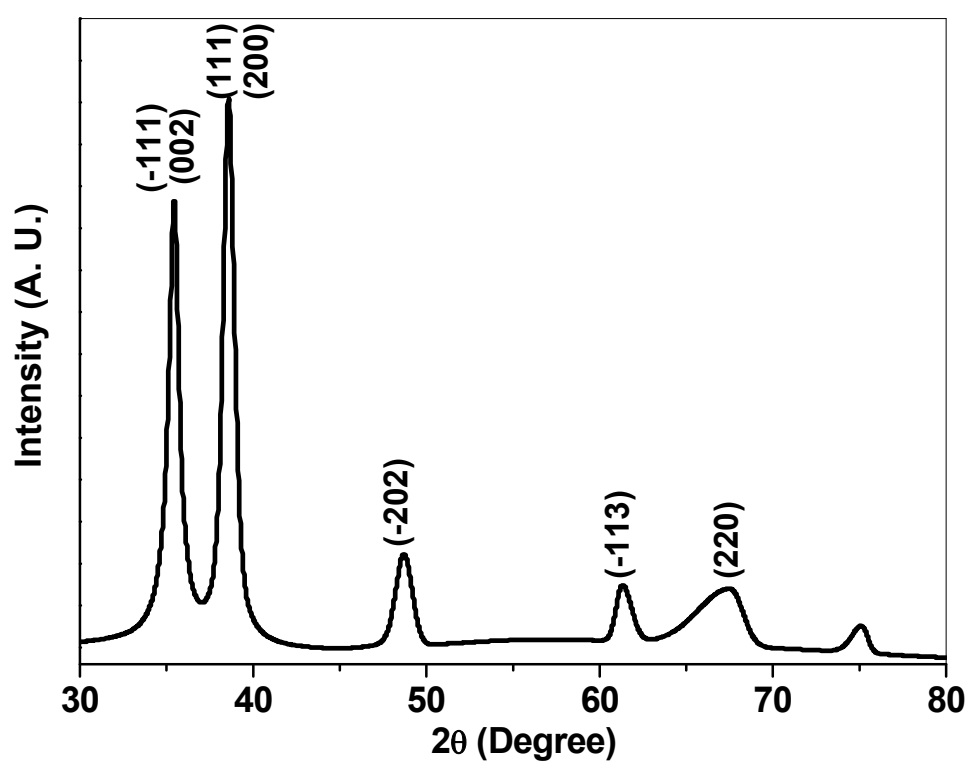


Fig. 2: XRD pattern of the CuO nanoparticles.

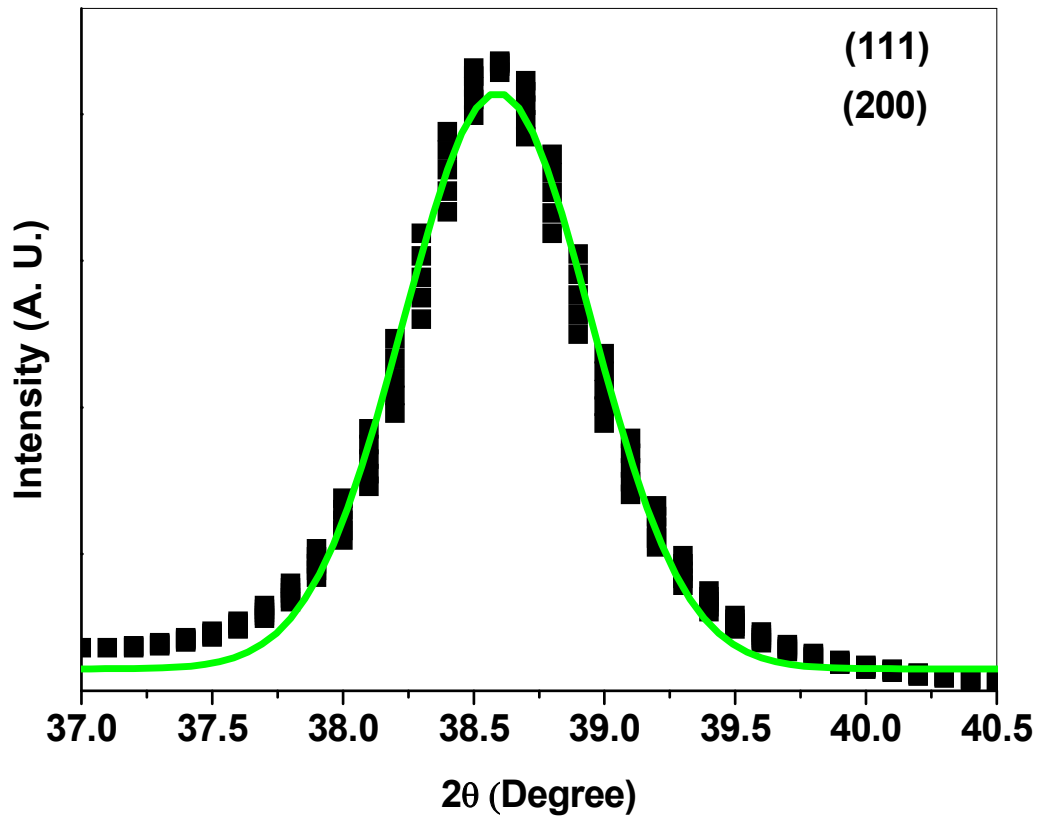


Fig. 3: Gaussian fitting of the (111) peak of the XRD pattern.

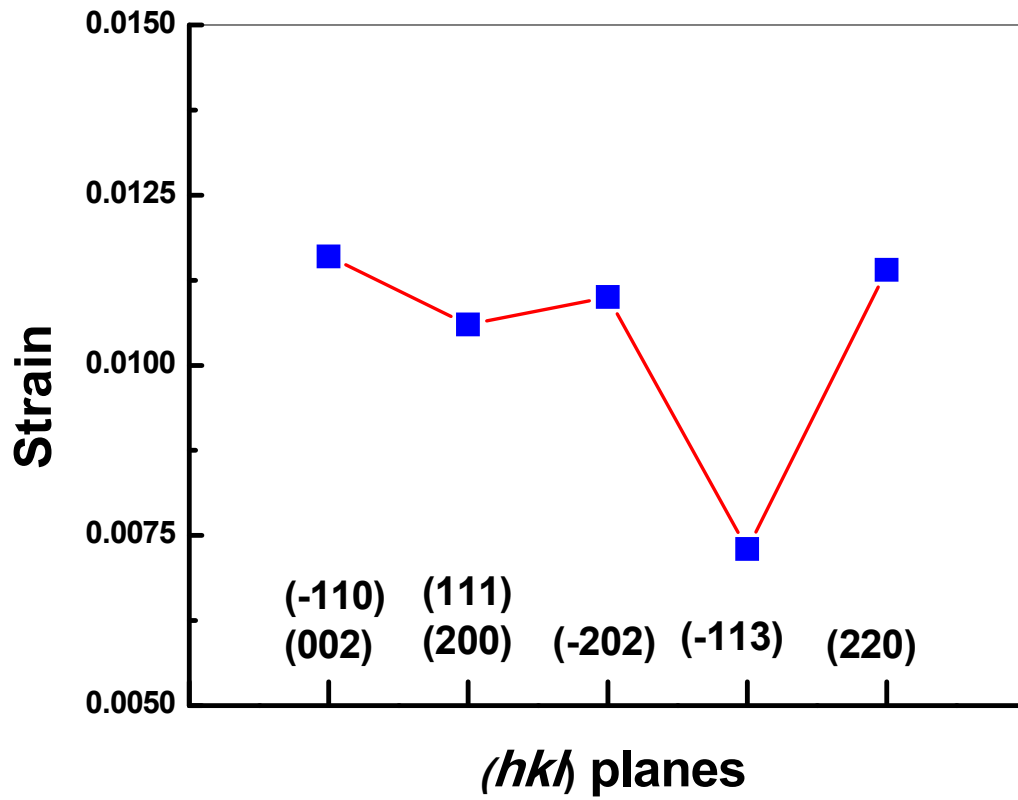


Fig. 4: Variation of strain for different (hkl) planes.

3.2. X-ray diffraction

3.2.1. Crystallite size

X-ray diffraction is an indigenous method for material characterization. A typical XRD pattern of the synthesized CuO nanoparticles is shown in Fig. 2. The XRD pattern was indexed using the standard JCPDS data card No 80-1917. It reveals that the unit cell of the synthesized CuO nanoparticles is monoclinic with the presence of the diffraction peaks ($\bar{1}10$) / (002), (111) / (200), ($\bar{2}02$), ($\bar{1}13$), (220). The different intensity of different diffraction peaks indicates that the growth rate is different along different crystallographic direction. Hence the growth of CuO nanocrystals is anisotropic. Besides no impurity peaks were detected indicating that the synthesized material is highly pure.

The crystallite size (R_{hkl}) and strain (ϵ) were calculated using the Scherer formula [10-12]:

$$R_{hkl} = \frac{0.89\lambda}{\beta \cos\theta}$$
$$\epsilon = \frac{\beta}{4 \tan\theta}$$

Here, λ is the wavelength of the X-ray used, θ is the angle of diffraction and β is the full width at half maxima. For this calculation, we have considered the highest intensity (111) / (002) peak and fitted the peak with Gaussian function (see Fig. 3) using Origin software version 8.0. The crystallite size as calculated from the fitting of the XRD peak is ~ 10.2 nm. This value is close to that observed from the TEM image (~ 8 nm).

The strain in the nanocrystals along different crystallographic plane is shown in Table-1 and also shown in Fig. 4. From table-1 it is evident that the strain is maximum along ($\bar{1}10$) / (002) direction ~ 0.116 and minimum along ($\bar{1}13$) having value ~ 0.0073 .

We calculated the d -values corresponding to different observed diffraction peaks using the well known Bragg's diffraction equation [10, 13-15]:

$$2d_{hkl} \sin\theta = \lambda$$

The calculated d -values are compared with that of the standard JCPDS data No. 80-1917 and are shown in Table-2. The result agreed well with the standard JCPDS data.

3.2.2. Crystallinity

We know that the broadening of the diffraction peak is related to the crystallite size of the material. Thus the “crystallinity” of a material is defined as the ratio of the crystallite size (particle size) as calculated from the morphological (SEM or TEM) study (R_s) and the crystallite size calculated from XRD pattern (R_{hkl}). It is expressed as [10, 16-18]:

$$I_{crys} = \frac{R_s}{R_{hkl}}$$

If the ratio I_{crys} is close to 1, then the particle is said to be monocrystalline. Larger value of I_{crys} represents the polycrystalline nature of the material. The average particle size as calculated from the TEM images is ~ 8 nm, and that calculated from XRD pattern is ~ 10.2 nm. Thus the value of I_{crys} is ~ 0.78 indicating that the synthesized CuO nanoparticles are monocrystalline in nature.

Table-1: Calculation of strain from XRD

(hkl)	$\beta(^{\circ})$	$\theta(^{\circ})$	ε
$(\bar{1}10) / (002)$	0.843	17.71	0.0116
$(111) / (200)$	0.844	19.29	0.0106
$(\bar{2}02)$	1.137	24.35	0.0110
$(\bar{1}13)$	0.996	30.7	0.0073
(220)	2.923	33.42	0.0114

Table-2: Comparison of d -values from XRD and that of JCPDS data

Diffraction peaks (hkl)	$d_{hkl}(\text{\AA})$ Calculated from XRD	$d_{hkl}(\text{\AA})$ from JCPDS (80-1917)
$(\bar{1}10) / (002)$	2.4461	2.5263
$(111) / (200)$	2.4251	2.3114
$(\bar{2}02)$	1.7935	1.8696
$(\bar{1}13)$	1.5034	1.5066
(220)	1.3791	1.3764

Table-3: Comparison of degree of orientation of various planes

Degree of orientation $\chi_{(hkl)}$	From XRD	From JCPDS (80-1917)
$(\bar{1}11)$	0.313	0.5125
$I_{(111)}$	0.365	0.1615
$I_{(\bar{2}02)}$	0.117	0.1528
$I_{(\bar{1}13)}$	0.103	0.1006
$I_{(220)}$	0.099	0.0723

3.2.3. Growth anisotropy and degree of orientation

As we have mentioned earlier that the difference in the intensities of different diffraction peaks indicates that the growth rates of the nanocrystals are different along different direction. If the growth rate of any particular plane is very large it will disappear very quickly in the experimentally observed diffraction pattern. To understand the anisotropic growth let us calculate the *degree of orientation* $\chi_{(hkl)}$ of different planes as defined below [19-21]:

$$\begin{aligned}\chi_{(\bar{1}11)} &= \frac{I_{(\bar{1}11)}}{I_{(\bar{1}11)} + I_{(111)} + I_{(\bar{2}02)} + I_{(\bar{1}13)} + I_{(220)}} \\ \chi_{(111)} &= \frac{I_{(111)}}{I_{(\bar{1}11)} + I_{(111)} + I_{(\bar{2}02)} + I_{(\bar{1}13)} + I_{(220)}} \\ \chi_{(\bar{2}02)} &= \frac{I_{(\bar{2}02)}}{I_{(\bar{1}11)} + I_{(111)} + I_{(\bar{2}02)} + I_{(\bar{1}13)} + I_{(220)}} \\ \chi_{(\bar{1}13)} &= \frac{I_{(\bar{1}13)}}{I_{(\bar{1}11)} + I_{(111)} + I_{(\bar{2}02)} + I_{(\bar{1}13)} + I_{(220)}} \\ \chi_{(220)} &= \frac{I_{(220)}}{I_{(\bar{1}11)} + I_{(111)} + I_{(\bar{2}02)} + I_{(\bar{1}13)} + I_{(220)}}\end{aligned}$$

Here, $I_{(hkl)}$ represents the intensity of the particular (hkl) planes. The results are shown in Table 3. The experimentally obtained result is different in some extent with the standard JCPDS data. This indicates that the growth of crystal prepared under different method and different experimental conditions are different.

CONCLUSIONS

In conclusion, we have synthesized CuO nanoparticles using simple and cost effective wet chemical method without using any surfactants. TEM images revealed the formation of nanoparticles. Extensive X-ray diffraction studies revealed the crystallinity of the synthesized material. The XRD study revealed that the growth of the CuO nanoparticles is anisotropic. It also revealed that the synthesized CuO nanoparticles are polycrystalline in nature. Thus this study is very useful in understanding the structural property of CuO nanostructures.

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