

Structural and Optical Properties of CuO Nanocubes Prepared Through Simple Hydrothermal Route

Hafsa Siddiqui, M. S. Qureshi, F. Z. Haque

Abstract— A simple hydrothermal route have been developed for the fabricating cupric oxide (CuO) nanocubes with excellent reproducibility. Copper acetate monohydrate, polyvinylpyrrolidone and sodium hydroxide were used as copper precursor, structural direction agent and accelerator, respectively. The prepared sample was calcined at 500 °C for 3 hours. The growth mechanism of CuO nanocubes was analyzed on the basis of the experimental results. The nanocrystalline CuO powder was characterized by X-ray diffraction (XRD) which result indicates that the obtained nanocubes were well crystalline single phase CuO with (~33nm crystallite size) monoclinic crystal structure. The Williamson–Hall plot was used to distinguish the effect of crystalline size-induced broadening and strain-induced broadening at Full Width Half Maximum (FWHM) of the XRD profile. Scanning Electron Microscopy (SEM) result indicates that the synthesized products are cubic shaped. Fourier Transform Infrared (FTIR) spectra confirmed composition and formation of single phase CuO wherein the characteristic vibrational modes of Cu–O were identified. The optical analysis by UV–vis diffuse reflectance (DRS) spectroscopy showed that these CuO nanocubes have considerable blue shift in the optical band gap energy ($E_g = 1.42\text{eV}$) due to quantum confinement effect. The high absorbance of synthesized nanocrystalline CuO powder indicates the applicability of using it as an absorbing material in solar cells. This method is low cost, fast, mild and environmental friendly rout to produce high-quality CuO nanoparticle.

Keywords: CuO Nanoparticles, Hydrothermal, Polyvinylpyrrolidone, capping agent, Calcined, Williamson–Hall plot

1 INTRODUCTION

Cupric Oxide (CuO), is a P-type semiconductor material with a monoclinic crystal structure and indirect band gap Eg. 1.2 eV [1]. It is an important transitional metal oxide. It has excellent thermal stability, good electrical and optical properties and many practical applications such as an antimicrobial [2] photothermal and photoconductive [3], chemical and biological sensing [4], catalysis [5] application in lithium ion batteries [6] solar cell [7], dye-sensitized solar cells [8], field emission emitters [9] etc. It also forms the basis of several interesting high temperature T_c- superconductors and giant magnetoresistance materials [10]. Nanostructured CuO offers highly reactive surfaces, and improves optical, electrical, and catalytic properties compared to bulk crystals. Most of the properties of CuO strongly depend on its structures, including the morphology, size and aspect ratio. These structural characteristics have an important role in many optoelectronic applications

tion-phase route[15], quick-precipitation method[16], thermal oxidation[17], and hydrothermal method [18]. Among these methods, hydrothermal method has been developed to synthesize CuO nanoparticles. This technique has drawn much more attention because it provides high surface stability and also has significant influence on the morphology and optical properties of CuO nanoparticles [19]. Moreover, compared with the aforementioned methods, it also has several other advantages, such as facile process and gentle reaction conditions.

In the present work, we report the synthesis of CuO nanoparticles through a simple hydrothermal process. By the surface modification using PVP chemically stable and monodisperse CuO cubes-like nanoparticles was prepared. It also minimizes the surface defects, enhances the optical properties and the size confinement of CuO nanoparticles. Moreover the morphological features of the nanoparticles are also dependent on the pH level and the calcination (500°C) temperature. It was found that this method is low cost, fast, mild and environmental friendly route to produce high-quality CuO nanoparticles.

2 EXPERIMENTAL DETAILS

2.1 Synthesis of CuO nanocubes

So far, many efforts have been directed towards the preparation of CuO nanostructures to enhance its performance in currently existing applications. Well defined CuO nanostructures with different dimensionalities have been obtained successfully, synthesized via different routes like solid-state reaction[11], surfactant templating method [12], electrochemical method [13], thermal annealing of copper thin films [14], solu-

The procedure for the synthesis is briefly summarized in Fig. 1. Key step in our method was the introduction of PVP as capping molecules for the preparation of CuO. Copper acetate monohydrate [(CH₃COO)₂.H₂O] and sodium hydroxide [NaOH] were used as precursor materials. Two separate solutions of copper acetate (0.2mol/L) and NaOH (0.2M) with deionized (DI) water as solvent were prepared. Aqueous copper

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acetate and NaOH solutions were referred to as solution A and solution B, respectively. PVP (0.05 mol/L) is slowly added to solution A, and is stirred for 10 minutes at 60°C, followed by the dropwise addition of Solution B and stirred for 15 minutes. A dark blue precipitate of Cu(OH)₂ was formed, pH level of the final solution was maintained at 8. The precipitate was collected by the centrifugation process after the overnight stay and dried in hot air oven at 100°C for 7 hours to obtain black powder. Finally, powder was obtained after calcination at 500°C for 3 hour in furnace.

photometer (Perkin Elmer, lambda 950) in region 200nm-1300.

3 RESULTS AND DISCUSSION

3.1 X-ray diffraction analysis

Fig. 2(a) shows the X-ray diffraction pattern of PVP modified CuO nanoparticles calcined at 500°C. All diffraction peaks are well indexed to the single phase of CuO monoclinic crystals structure (JCPDS: 80-0076 card ICSD#: 067850). No peaks of impurity are detected in the XRD pattern. The well-defined peaks in the XRD spectrum of CuO nanoparticles show the high crystalline nature. The broadening of the peaks indicates the formation of nanometric particle size. In this case, this was found to be about 33 nm, as calculated using the Scherrer equation:

$$D = k\lambda / \beta_{hkl} \cos \theta \dots\dots\dots(1)$$

where D is the crystallite size (nm), k is a constant equal to 0.94, λ is the wavelength of X-ray radiation (1.5406 Å), β is the full-width at half-maximum (FWHM) of the peak (in radians) and 2θ is the Bragg angle (degree).

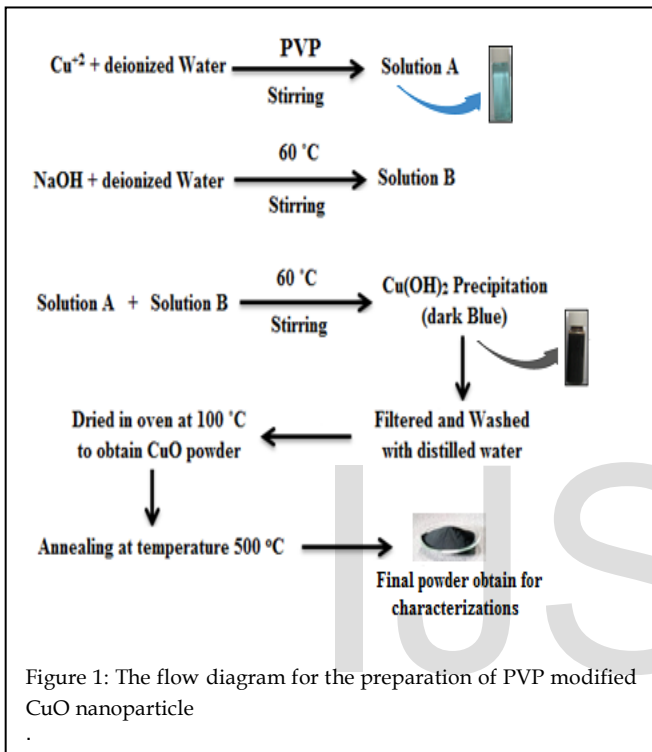


Figure 1: The flow diagram for the preparation of PVP modified CuO nanoparticle

2.2 Characterizations

The as-synthesized powder was characterized by various techniques like X-Ray Diffraction, Scanning Electron Microscope, FT-IR, and UV-Vis-IR spectroscopies. The crystallinity and phase identification of powder was investigated using X-ray powder diffraction, (X-ray powder diffractometer D8 Advance) in the scanning range of 20-80° 2θ using Cu Kα radiation having a wavelength of 1.54060Å at the scanning rate of 15.50sec with the measurement temperature 25°C, operating at 40 kV and 40 mA. The phase was identified using the standard (JCPDS: 80-0076 card ICSD#: 067850) data files. X-ray peak broadening analysis was used to evaluate the lattice strain by Williamson-Hall (W-H) analysis. The surface morphology was studied by scanning electron microscopy (JEOL-JSM-6390) with an accelerating voltage 10Kv, at operating potential of 15 kv. The composition of the sample was characterized by the Fourier Transform Infrared (FT-IR) spectroscopy; spectrum was obtained on KBr pellets using a Bruker (Model Vertex 70). Each FTIR spectrum was collected after 40 scans at a resolution of 0.5 cm⁻¹ from 400 to 4000 cm⁻¹. Optical analysis was determined from UV-vis-NIR Spectro-

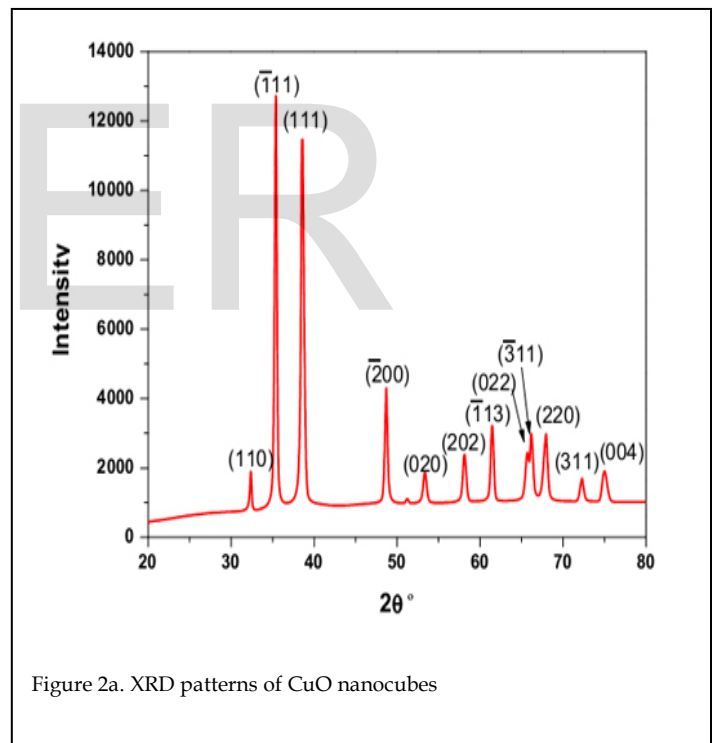


Figure 2a. XRD patterns of CuO nanocubes

3.2 Williamson-Hall (W-H) analysis

In order to understand the strain associated with the sample due to lattice deformation and line broadening analysis were carried out by Williamson-Hall (W-H) method [20]. Williamson and Hall proposed a good method for separation of strain and size effects on broadening by looking at the peak width as a function of diffracting angle. Addition of the Scherrer equation and the volume-weighted average strain ε_{str} = β_{hkl} / 4 tan θ results in the following equations:

$$\beta_{hkl} \cos \theta = (K\lambda / D) + (4\epsilon \sin \theta) \dots\dots\dots(2).$$

Eq.(2) represents Uniform Deformation Model (UDM), where the strain was assumed to be uniform in all crystallographic directions, thus considering the isotropic nature of the crystal, where all the material properties are independent of the direction along which they are measured [21].

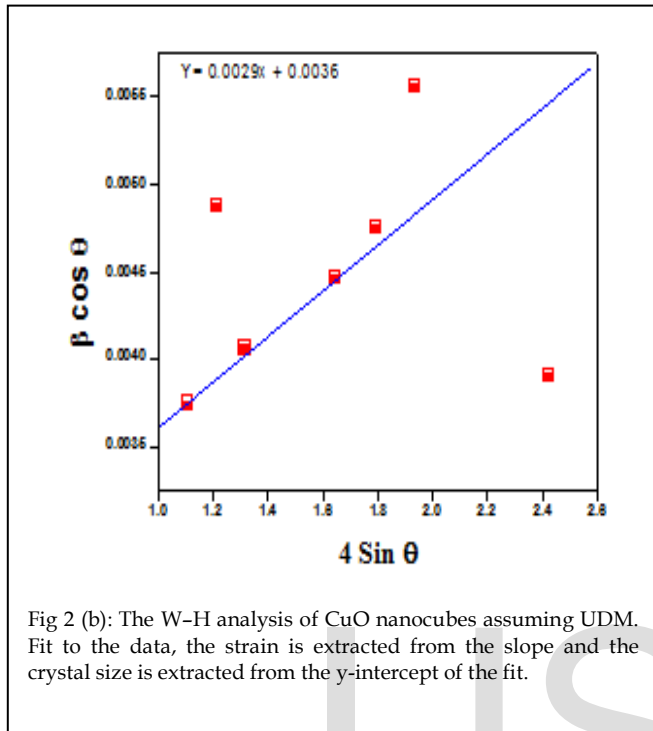


Fig 2 (b): The W-H analysis of CuO nanocubes assuming UDM. Fit to the data, the strain is extracted from the slope and the crystal size is extracted from the y-intercept of the fit.

The term $\beta \cos\theta$ was plotted with respect to $4 \sin\theta$ for the preferred orientation peaks of as prepared sample. Accordingly, the slope and y-intersect of the fitted line represent strain and particle size, respectively. The volume weightage average crystallite size of the sample was found to be around 42 nm by this method. The plot showed a positive strain and is found to have the value 0.00297. However, the strain arising from W-H model is very small and has negligible effect on peak broadening. The results of UDM analysis for sample are shown in Fig. 2b.

3.3 MORPHOLOGY ANALYSIS

SEM analysis

Fig.3 (a-b) shows SEM micrographs of as prepared CuO nanoparticles. These images reveal that the most of the nanoparticles with uniform morphology. The nanoparticles grown under hydrothermal treatments along with the capping molecules (PVP) can influence the morphology. The features of nanocubes may vary significantly depending on the interaction between the surface of the CuO particle and PVP molecule during synthesis clearly shows the formation of nanocubes, and has demonstrate.

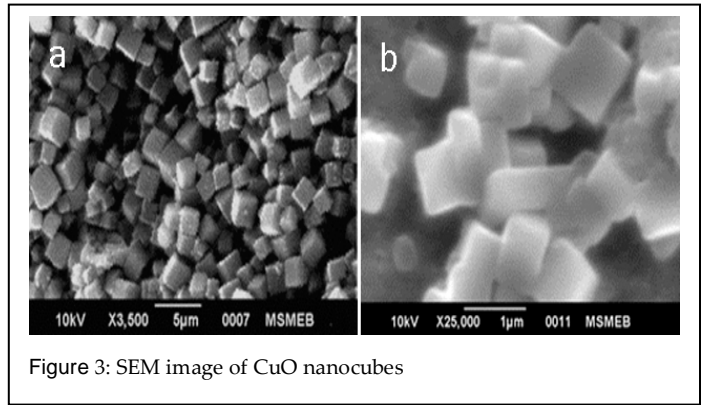


Figure 3: SEM image of CuO nanocubes

3.4 Possible growth mechanism nanocubes:

Figure 4 shows the schematic evolution of major stages and possible growth process of the nanocubes. The presence of poly-vinylpyrrolidone seems beneficial to the growth of CuO. It is reported that PVP has selective adsorption properties to specific crystal planes, and could be used to kinetically control the growth of single-crystalline nanocubes [22]. The concentration of capping agent (0.2g) used in the solution is playing a significant role for the formation of nanocubes.

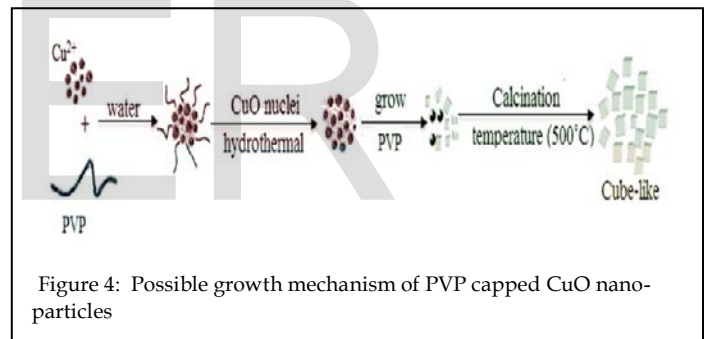


Figure 4: Possible growth mechanism of PVP capped CuO nanoparticles

PVP a large polymer molecule ($M_w = 58,000 \text{ g/mol}$) was employed in the current synthesis. It has long chain of repeated units that could form a sort of capping on the surface of CuO. On the other hand, PVP can form a shell surrounding the particles to prevent them from agglomeration to larger particles as a result of its steric or electrostatic repulsion effect. As a result, the selective interaction between PVP and various crystallographic planes of CuO could reduce the growth rate along the (111) direction and accordingly enhance the growth rate along $(\bar{1}\bar{1}\bar{1})$ direction and lead to controller nanosized particles. Feather the overnight aging of material could reduce surface roughness and provide more uniform grains size. Thus, PVP, overnight aging and pH values significantly affects the morphology of CuO nanostructures under hydrothermal treatment.

3.5 FTIR ANALYSIS

Figure 5 shows the FTIR spectrum of sample at room-temperature. Various well-defined peaks at 489.7, 520.4, 604.5, 1330.3, 2352.5, 2910.1 and 3447 cm^{-1} were observed in the spec-

trum.

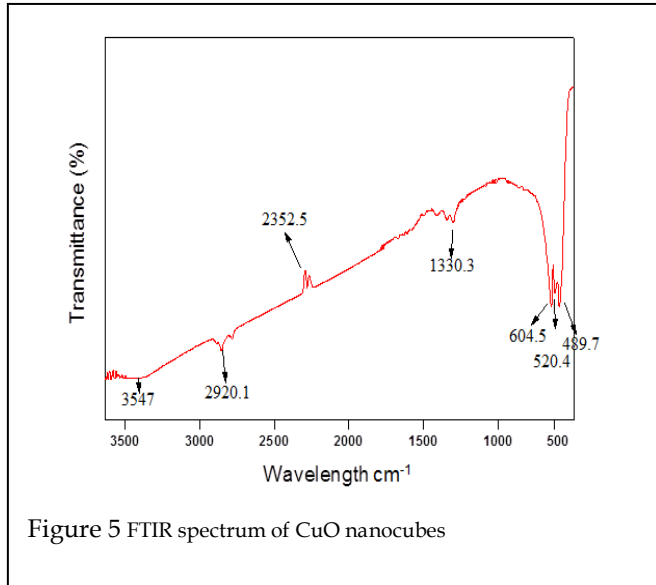


Figure 5 FTIR spectrum of CuO nanocubes

The Appearance of three peaks at 489.7, 520.4 and 604.5 cm^{-1} corresponds to the characteristic stretching vibrations of Cu-O bond in the monoclinic crystal structure of CuO [23]. Origin of two well-defined absorption bands at 1330.3 cm^{-1} and 2910 cm^{-1} were due to the CH_3 group and CH_3 asymmetrical stretching mode present on the surface of CuO nanostructures. The absorption peak around 2352.5 cm^{-1} is due to the existence of CO_2 molecules in air, and the peak around 3447 cm^{-1} were due to the bending vibration of absorbed water and surface hydroxyl and O-H stretching mode. No infrared active modes from Cu_2O were detected [24]. Moreover, no absorption band of PVP can be detected as they are completely washed out at the time of synthesis.

3.5 Optical properties

Fig 6a shows the reflectance (R %) versus wavelength λ (nm) trace of the CuO nanoparticle calcined at 500°C.

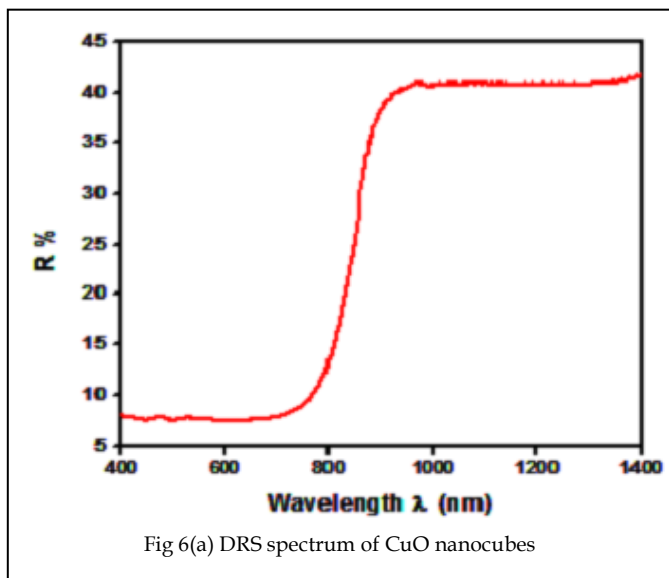


Fig 6(a) DRS spectrum of CuO nanocubes

The reflectance spectrum of CuO nanoparticle shows 42% of

reflectivity in the visible and also in near infrared region. The high absorbance of light in the visible region ranging from 400 nm to 800 nm indicates the applicability of using CuO as an absorbing material in solar cells. The optical band gap and the nature of transition in CuO sample were determined by using the relationship to the Kubelka-Munk function:

$$F(R) = \frac{(1-R)^2}{2R} \dots \dots \dots (3)$$

Here (R) is the absolute value of reflectance and F(R) is equivalent to the absorption coefficient.

The indirect band gap of CuO was calculated by plotting $[F(R) \cdot h\nu]^{0.5}$ vs. the energy is presented in the figure 6b.

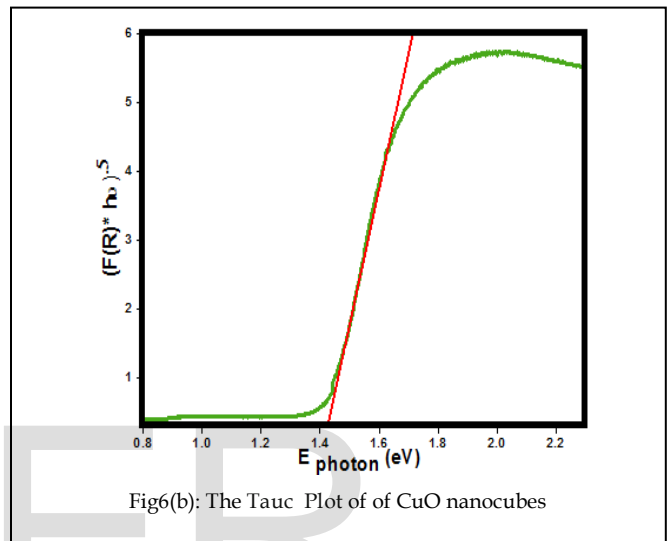


Fig6(b): The Tauc Plot of CuO nanocubes

The liner part of the tauc curve was extrapolated to $[F(R) \cdot h\nu]^{0.5} = 0$ to get the indirect energy band gap. The obtained band-gap energy (E_g) value is 1.42eV. Compared with the reported value of E_g for bulk CuO ($E_g=1.2$ eV) [25] blue-shift in band gap energy by an amount of 0.22 eV is evident here, which is due to the quantum confinement effect exerted by the nanosize crystals.

Conclusion

The present study demonstrates that the hydrothermal method is one of the successful routes for obtaining good quality CuO nanoparticles. The structural analysis clearly indicated the single crystalline nature of CuO monoclinic phase with an $\sim 35\text{nm}$ crystallite size was obtained. A very small strain ($\sim 29 \times 10^{-3}$) associated with the CuO cubes due to lattice deformation has negligible effect on peak broadening at Full Width Half Maximum (FWHM) of the XRD profile. The SEM morphology of the product revealed that the CuO nanoparticles with a high aspect ratio and have a uniform distribution of cubic shapes were grown under moderate conditions. Furthermore, the formation of pure CuO cubes has been supported by the FT-IR spectra. The quantum confinement effect exerted by such nanocrystals found to bring a significant blue-shift in the band gap energy (1.42 eV). It was found that this method is low cost, mild and environmental friendly rout to produce high quality CuO nanoparticle. It is expected that the CuO nanocubes may offer some exciting opportunities for potential applications as absorbing material in solar cells.

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