



ELECTROCHEMICALLY SYNTHESIZED COPPER OXIDE NANOSTRUCTURES AND THEIR MORPHOLOGY

AND SIZE

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ABSTRACT

By maintaining other parameters constant, such as current (100mA), electrolyte (sodium hydroxide), time (2 hrs), and solvent (pure water, water-methanol, or water-acetonitrile), an easy, straightforward electrochemical method to fabricate morphologically different copper oxide nanoparticles (CuO NPs) has been developed. An undivided cell with a sacrificed copper anode and an inert platinum cathode was used to conduct the electrolysis, which was done at ambient temperature and under amperostatic conditions. Systematic FTIR, XRD, SEM, and TEM characterization of CuO NPs isolated after electrolysis and calcinations at 900°C has been completed. When water, water-methanol, and water-acetonitrile (water-ACN) were utilised as the solvents, respectively, the SEM micrograph showed that morphologies such as snow white particles, spherical potato form particles, and clusters of

spherical ball shape bee hives had been obtained. In the presence of water-acetonitrile solvent, an average grain size ranging from 2-36 nm was achieved, according to a TEM image. The size of CuO NPs with smaller size has been achieved using water-acetonitrile mix solvent as compared to water or water-methanol mix solvent.

KEYWORDS: Electrochemical methods, CuO NPs, Water-CAN

INTRODUCTION

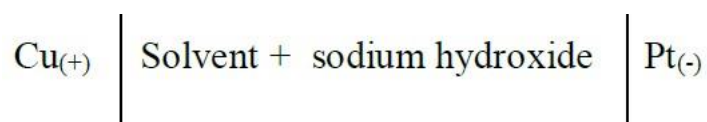
Among numerous metal oxides, copper oxide nanoparticles have attracted much attention because of their catalytic, optical properties, high electrical and heat conductivity. CuO with a narrow bandgap of 1.2 eV and it has potential applications in solar cells¹, nano-magnetic devices², Li ion battery³, biosensors⁴ and photovoltaic devices⁵. All these properties depend up on size, morphology and surface area of CuO NPs. Thus it is necessary to develop a method to prepare nano CuO particles with enriched fundamental properties that increase its application scope. In past few years numerous methods have been developed for the synthesis of CuO nano structures like such as sol–gel method⁶, solid–liquid phase arc discharge process⁷, hydrothermal decomposition route⁸, solid-state reaction process⁹, sonochemical method¹⁰, direct oxidation of copper substrates in air at elevated temperature¹¹ etc. Among all these methods electrochemical method has got much attention due to its unique advantages like simplicity, direct route, low-temperature operation process, high current efficiency and is a keen step toward green methods. A number of papers have been reported in electrochemical synthesis of metal oxide¹²⁻¹⁶. Reetz et al.¹⁷⁻²⁰ proposed a sacrificial anode electrochemical route to synthesize metal nanoclusters. Mahamuni and co-workers further developed Reetz et al. route to synthesize ZnO and CuO nanocrystals using (Zn, Cu) as a sacrificial anode in the electrochemical bath.²¹⁻²²

Thus in the present work, we report the synthesis and characterization of CuO NPs and the effect of reaction media on the size and shape of product. The morphology and size of CuO NPs could be easily controlled by changing solvent.

MATERIAL AND METHODS

Conductivity water and its mixture with acetonitrile or methanol have been used as solvent in all these reaction. Sodium hydroxide has been used as electrolyte in different electrolytic reactions. Electrolysis of aqueous solution containing conductivity water or (12:1) water-methanol, (12:1) water-ACN and 1.25 mM of electrolyte have been conducted at sacrificial

copper ($3 \times 2 \text{ cm}^2$) anode and inert platinum ($1 \times 1 \text{ cm}^2$) cathode in individual cell. The potential across the electrodes was adjusted so that a current of 100 mA passed through the cell. The electrolysis has been conducted for two hours with continuous stirring. After the electrolysis, the products were collected by centrifugation and washed three times with ethanol then finally dried. The resulting particles have been calcined at 900°C temperature for 1 hour. The electrolytic cell can be represented as:



Where, solvent represents water or water-methanol or water-acetonitrile.

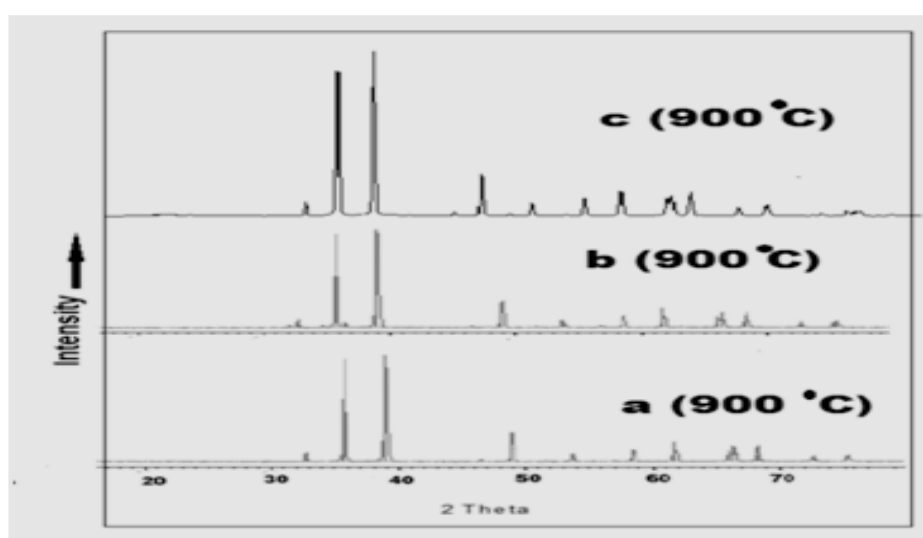
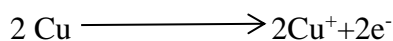


Fig 1: XRD patterns of as-prepared CuO NPs samples using different solvents (a) water (b) water-methanol (c) water-ACN

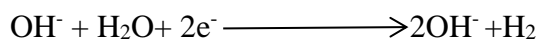
Growth Mechanism of Electrodeposition

The morphology, size and purity of CuO NPs can be achieved by complete understanding of growth mechanism of electrodeposition. Based on XRD results and the mechanism of electrodeposition of ZnO thin films in aqueous zinc nitrate bath²³⁻²⁵, a possible mechanism of as prepared CuO NPs has been proposed via the electrochemical route in sodium hydroxide electrolyte and three solvents (water, water-methanol, water-acetonitrile).

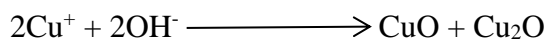
Anode:



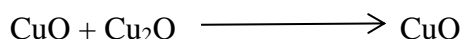
Cathode:



Electrolyte Solution:



Calcined:



When current passes through the electrochemical cell, Cu^+ and OH^- ions are generated on anode and cathode surface. Cu^+ ion react with OH^- ions to produce CuO_2 and Cu_2O precipitates, followed by hydration at 900°C to give CuO .

Crystal structure of the CuO NPs has been determined by a powder X-ray diffractometer (XRD) (PANalytical X'Pert), employing $\text{Cu-K}\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$) at 50 kV and 200 mA in the 2θ range from 10° to 90° and the composition has been characterized by the Fourier transform infrared (FTIR) spectroscopy in the range of $4000\text{-}450 \text{ cm}^{-1}$ using KBr pellets. Growth orientation of the CuO NPs has been further characterized by a high resolution transmission electron microscopy HRTEM/STEM (Philips FEI TECNAI F30) at 200 kV. TEM samples have been prepared by dropping diluted solution of copper oxide nanoparticles on copper grids covered with a thin amorphous carbon film. HRTEM characterization has been performed using TEM at 200 KeV X1150. The average crystallite sizes were calculated by using the Debye–Scherrer equation.

$$D = K\lambda / \beta \cos \theta$$

where D is the diameter of the crystallite size, K is the shape factor (the typical value is 0.9), λ is the wavelength of incident beam, β is the broadening of the diffraction line measured in radians at half of its maximum intensity (FWHM) and θ is the Bragg's angle.

RESULTS AND DISCUSSION

XRD analysis

The powder XRD pattern for CuO NPs prepared in the presence of water, water-methanol and water-ACN as solvent were shown in (Fig 1).

All the obtained peaks in the XRD pattern are well matched with the monoclinic phase of CuO bulk crystals with lattice parameters $a = 4.685 \text{ \AA}$, $b = 3.423 \text{ \AA}$, $c = 5.132 \text{ \AA}$. All the diffraction peaks can be indexed with lattice planes and compared to the International center for diffraction data (ICDD) Card No: 41-0254. No impurity peak related to any other phases of Cu like $\text{Cu}(\text{OH})_2$, Cu_2O or Cu are seen in the observed XRD pattern.

The average crystallite size of CuO nanoparticles is found to be using Scherrer formula²⁶. XRD calculation shows that the particles prepared in the presence of water-ACN solvent have smallest average particle size among the others. From the XRD data, the average crystallite sizes were found to be 40-80, 42-70 and 11-36nm respectively shown in (Table 1, 2, 3).

SEM/ TEM Analysis

Scanning electron micrographs of CuO NPs obtained from 100 mA shown in Fig 2. The different morphologies of CuO NPs (prepared in the presence of water, water-methanol, and water-ACN solvents). Fig 2 reveals that the morphology of copper oxide nanoparticles has been greatly influenced by solvents used for synthesis. The obtained results show that the average particles size which were obtained from the analysis of scanning electron microscope micrographs are in a good agreement with the values obtained from the Scherrer's formula. Among three samples, the particles size of sample (2c) (11-40 nm) is the smallest one in comparison with sample (2b) (42-70 nm) and sample (2a) (40-80 nm).

Table 1: Crystallite size at different 2 theta values for as prepared sample in water solvent calcined at 900 °C

Diffraction angle [$^{\circ} 2 \text{ Th}$]		Atomic planes (h k l)	FWHM [$^{\circ} 2 \text{ Th}$]	Grain sizes [nm]
Observed	Reported	Observed	Observed	Calculated
32.7	32.5	(1 1 0)	0.118	70
35.6	35.4	(0 0 2)	0.143	58
35.7	35.5	(T 1 1)	0.102	81
38.9	38.7	(1 1 1)	0.195	43
46.4	46.2	(T 1 2)	0.113	78
48.9	48.7	(Z 0 2)	0.142	61

61.7	61.5	(1 1 3)	0.145	48
72.5	72.4	(3 1 1)	0.187	52
75.1	75.2	(2 2 2)	0.148	67

Table 2: Crystallite size at different 2 theta values for as prepared sample in water-methanol solvent calcined at 900 °C

Diffraction angle [$^{\circ}$ 2 Th]		Atomic planes (h k l)	FWHM [$^{\circ}$ 2Th]	Grain sizes [nm]
Observed	Reported	Observed	Observed	Calculated
32.7	32.5	(1 1 0)	0.121	68
35.7	35.4	(0 0 2)	0.173	48
35.8	35.5	(1 1 1)	0.106	78
38.9	38.7	(1 1 1)	0.198	42
46.4	46.2	(1 1 2)	0.116	78
48.9	48.7	(2 0 2)	0.135	64
61.7	61.5	(1 1 3)	0.129	71
72.5	72.4	(3 1 1)	0.149	66
75.1	75.2	(2 2 2)	0.141	71

Table 3: Crystallite size at different 2 theta values for as prepared sample in water-acetonitrile solvent calcined at 900 °C

Diffraction angle [$^{\circ}$ 2 Th]		Atomic planes (h k l)	FWHM [$^{\circ}$ 2Th]	Grain sizes [nm]
Observed	Reported	Observed	Observed	Calculated
32.6	32.5	(1 1 0)	0.225	36
35.6	35.4	(0 0 2)	0.229	35
38.7	38.7	(1 1 1)	0.259	31

46.3	46.2	(1 1 2)	0.214	40
48.7	48.7	(2 0 2)	0.294	29
61.6	61.5	(1 1 3)	0.300	30
72.5	72.4	(3 1 1)	0.230	42
75.1	75.2	(2 2 2)	0.630	11

(Fig 2a) shows the SEM micrograph of CuO nanoparticles prepared in the presence of water. It can be seen that the particles are snow white particles in cluster form, whereas the CuO nanoparticles prepared in the presence of water-methanol solvent has spherical potato shape particle (Fig 2b). (Fig 2c) shows the cluster of spherical ball shape bee hive prepared in the presence of water-ACN solvent. The micrographs show that the nature of solvent affects the shape of nanoparticles. (Fig 3) the TEM micrograph of CuO NPs obtained in the presence of water- acetonitrile solvent calcined at 300 °C shows that particle size vary from 5-30 and when CuO calcined at 900 °C size varied from 2 - 36 nm which is in good agreement with XRD results.

Fig 3a reveals that when sample calcined at 300°C, we observed the particles were agglomerated. At high temperature i. e. 900°C the particle were well defined and each bigger particle surrounded by smaller particles clearly shown in Fig 3b.

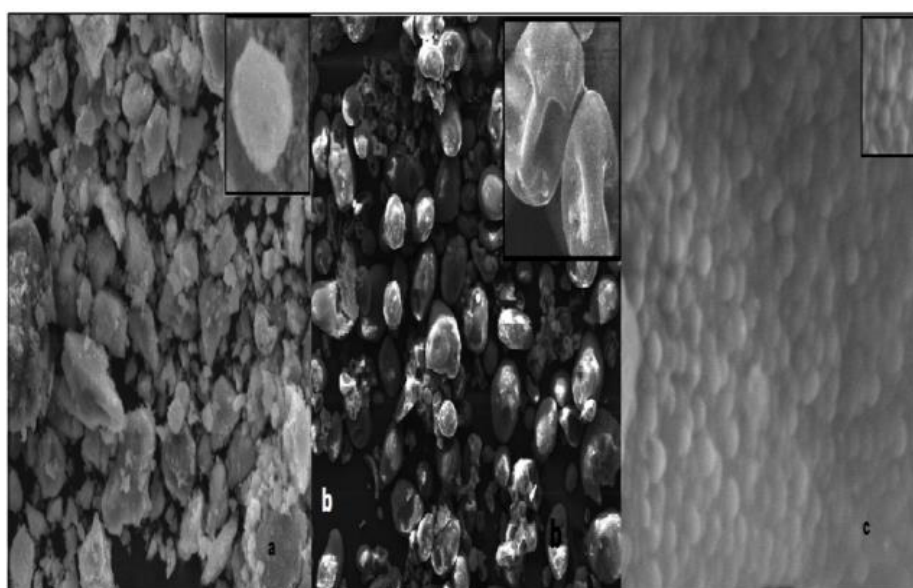


Fig 2: SEM micrograph of copper oxide nanoparticles (a) water (b) water-methanol (c) water-CAN

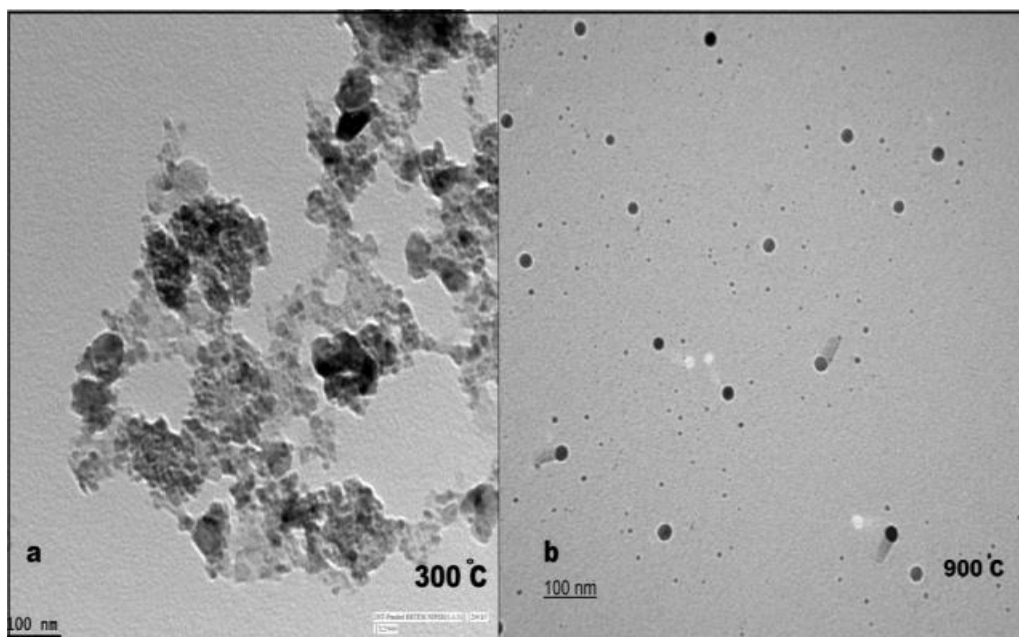


Figure 3: TEM micrographs of prepared CuO nanoparticles in water-acetonitrile solvent

FT-IR Spectroscopy

Infrared spectra have been scanned in the region of 4000 - 450 cm^{-1} . Infrared spectra of copper oxide (calcined at 900 $^{\circ}\text{C}$) consist of characteristic peaks at 3398 cm^{-1} , 3737 cm^{-1} , 2332 cm^{-1} , 2348 cm^{-1} , 2318 cm^{-1} , 1627 cm^{-1} , 1566 cm^{-1} , 1384 cm^{-1} , 1337 cm^{-1} , 1050 cm^{-1} , 1019 cm^{-1} , 617 cm^{-1} , 602 cm^{-1} , 587 cm^{-1} , 536 cm^{-1} , 510 cm^{-1} and 507 cm^{-1} .

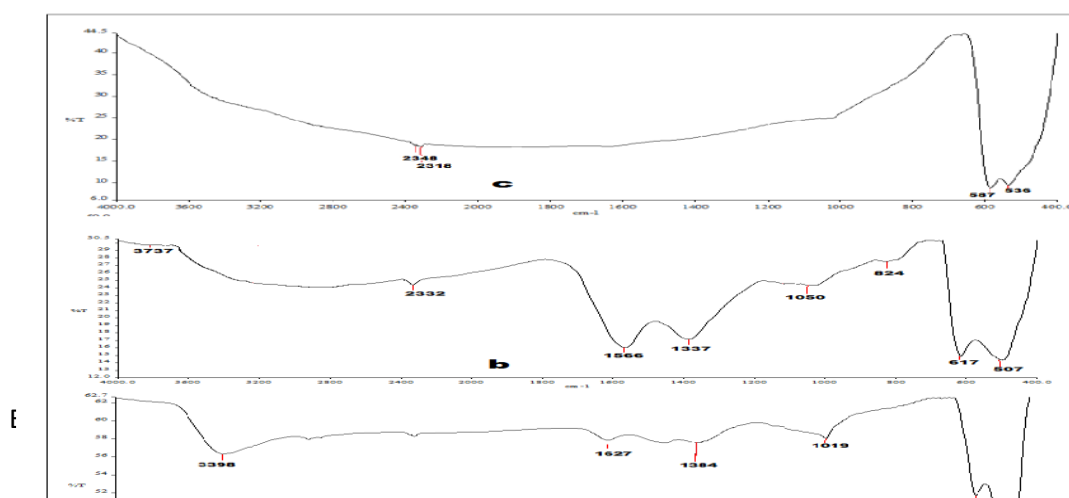


Fig 4: FTIR spectra of CuO NPs in presence of solvents (a) water (b) water-methanol (c) water-CAN

(Fig 4) shows that the band presents in the region of 3400 - 3300 cm^{-1} may be assigned to stretching vibration of OH bond. The weak band in the region 2348 – 2318 cm^{-1} may be assigned²⁷ to carboxylic group (COO-) and the peaks at 1627 cm^{-1} may corresponds to H-O-H bending vibration and peaks at 1384 cm^{-1} and 1337 cm^{-1} may be assigned to alkyl group. Peaks at 1050 cm^{-1} and 1019 cm^{-1} may be assigned to (-OH) stretching. The absorption peaks in the region of 587 - 507 cm^{-1} may be assigned²⁸ to stretching vibration of the Cu-O bond²⁹. Whereas infrared spectra of copper oxide shows sharp peaks in the region of 617 cm^{-1} and 602 cm^{-1} . The results are well in agreement with the XRD patterns.

CONCLUSION

CuO nanoparticles were synthesized by a low cost electrochemical method. Effect of solvents on the shape and size of CuO NPs were studied. XRD analysis indicated that the crystallite size is small for the CuO NPs synthesized using water-acetonitrile as solvent. SEM results revealed that snow white NPs were prepared in presence of water, potato shaped NPs in presence of water-methanol and bee hive shaped NPs due to presence of water-ACN.

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