

Hydrothermal synthesis of CuO Nanostructure and Their Characterizations

K.Kannaki, P.S.Ramesh and D. Geetha
Engineering Physics, Physics wing-DDE,
Department of Physics
Annamalai University, Annamalainagar.
E.mail:gee_d72@yahoo.co.in

Abstract

The CuO nano particles were synthesized from copper sulfate pentahydrate aqueous solution under the low hydrothermal condition at 80°C. The average crystallite size was calculated from De-Bye Scherrer's equation. SEM/EDS, XRD were used to characterize the structure features of the product. FTIR spectra confirmed the adsorption of ammonia on the surface of the CuO nanoparticles. In addition, UV-visible absorption spectra were employed to estimate the band gap energy of the CuO nanoparticles. This method may be suitable for large scale production of nano CuO particles for practical applications.

Keywords:

Copper oxide, Hydrothermal and Band gap energy.

INTRODUCTION

Metal oxides represent the most diverse class of materials with properties covering almost all aspects of materials science and physics. Copper oxide, an important p-type semiconductor with the band gap in the range of 1.8 – 2.5 eV [1] has obtained increasing interest because it has many potential applications in solar energy conversion, photocatalytic degradation of organic pollutants. Copper oxide is used in consumer products such as pillow cases [2] socks [3] due to its cosmetic and antimicrobial properties. In the present study nano CuO was prepared without any additive like ionic liquids, capping agents and used (CuSO₄. 5H₂O) as base. Here in, we report a hydrothermal synthetic method and physicochemical characterization of CuO nanostructures with spherical like shape, moreover, these type of CuO nanostructures show an excellent electrochemical behavior and good cycle stability.

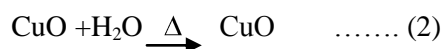
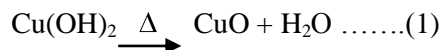
EXPERIMENTAL SECTION

Materials

Copper sulfate pentahydrate (CuSO₄.5H₂O) aqueous ammonia and Ethanol (CH₃ CH₂ OH) were used as chemicals in this research work, all were analytical grade and purchased from Merck and SISCO Pvt., Ltd., Chemicals company of India. They were used without further purification.

Synthesis of Copper Oxide Nanoparticles

Copper oxide nanoparticles (NPS) were prepared by hydrothermal route. The preparation scheme started with dissolving 0.1 mol% of CuSO₄.5H₂O in the combination (1:1) of distilled water and ethanol to obtain blue solution. 0.1 mol aqueous ammonia solution was added by dropwise while vigorous stirring to stabilize the pH level. A homogeneous mixture of precursors was formed. Cu(OH)₂ precipitate was yielded from the reaction. Then the precipitate was filtered out and washed with distilled water and Ethanol several times alternatively to remove the impurities. The resulting solution was kept in a hot-air-oven heated at 80°C for 3 hr and dried at required temperature for several hours. The formation of nano CuO from Cu(OH)₂ precipitant, the following reaction mechanism can be formulated in terms of equations as followed,



Heating the precipitates helps in better crystallization of materials. In order to study the characterization, the product was crushed into fine powder.

Characterization of Nano Copper Oxide powder

The prepared nano CuO particles were subjected to various characterization techniques like X-ray diffraction (XRD), ultraviolet-visible (UV-Vis), Fourier transform infrared (FTIR) and scanning Electron microscope with EDS (SEM/EDS). The XRD patterns of nano CuO were recorded on a (BRUKER AXS) diffractometer in the scanning range of 20-70° (2θ) using Cu Kα radiation having a wavelength of 1.54060Å at the scanning rate of 15.50sec with the measurement temperature 25°C. The optical UV-Visible absorption spectra of nano CuO were recorded using a (SHIMADZU, UV-1650 PC) Spectrophotometer in the region 220-400nm. The fourier transform infrared analysis was carried out by pelletized the synthesized

nano CuO with KBr were measured using (BRUKER OPTIC GmbH) in the range of 400-4000cm⁻¹. The surface morphology and phase purity were studied by scanning electron microscopy (JSM-5610,Version1.1) with an accelerating voltage 20Kv.

RESULTS AND DISCUSSIONS

Powder XRD analysis

Powder X-ray diffraction study was carried out on the prepared nano CuO. The copper oxide nanoparticles retained its monoclinic structure with lattice parameters a = 4.685Å, b= 3.423 Å, c=5.132 Å, β=99.52 and V=81.17 Å³. The crystallite of nano CuO was confirmed by the powder x-ray diffraction study and diffraction peaks are indexed (fig.1) from the crystal structure parameters obtained in the present study. All the diffraction peaks can be indexed with lattice planes and compared to the International center for diffraction data (ICDD) Card No: 41-0254. The d-spacing values of the present study were well matched with the reported values in the card. The grain sizes for different FWHM(β) values were calculated using Debye – scherrer’s equation $D=K\lambda / \beta \cos \theta$, where K is constant (shape factor, about 0.9), λ the x-ray wavelength used (1.54060Å), β the full width half maximum (FWHM) of the diffraction angle. Existence of CuO phase and the comparative studies between observed parameters and reported parameters (ICCD 41-0254) were listed in

Table 1. The observed full width half maximum (FWHM), calculated grain sizes, and reported atomic planes also given in the table. From the x-ray diffractograms the high intensity peaks located at 35.09° and 38.7° corresponds to the reflection from (022) and (111) atomic planes indicates CuO phase. These diffraction planes well matched with the literature data [4]. The average crystallite size found to be in the range 8nm-37nm.

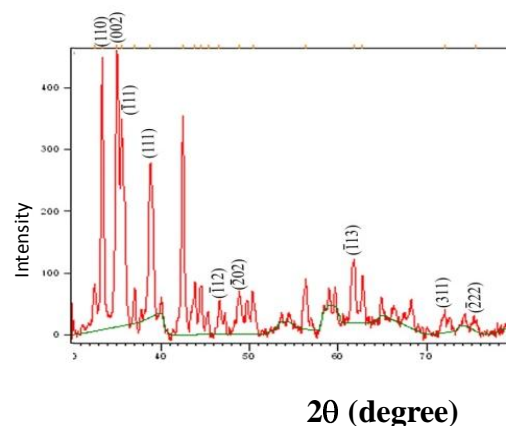


Fig.1. XRD spectra of CuO nanoparticles

Table.1. Presence of CuO phase in the synthesized sample and its comparative studies on diffraction angle, d-spacing between the observed and literature data from ICDD card No: (41-0254)

Diffraction angle (θ) [° 2 Th]		d-spacing Å		Atomic planes (h k l)	FWHM [°2Th]	Grain sizes nm
Observed	Reported	Observed	Reported	Observed	Observed	Calculated
32.555	32.508	2.7520	2.7505	(1 1 0)	0.2676	26.69
35.095	35.437	2.5570	2.5310	(0 0 2)	0.3011	26.38
35.619	35.538	2.5205	2.5240	($\bar{1}$ 1 1)	0.2676	26.69
38.779	38.730	2.3221	2.3230	(1 1 1)	0.5353	14.84
46.586	46.263	1.9496	1.9608	($\bar{1}$ 1 2)	0.5353	14.84
48.863	48.742	1.8939	1.8667	($\bar{2}$ 0 2)	0.4015	19.78
61.773	61.547	1.5017	1.5055	($\bar{1}$ 1 3)	0.4684	16.96
71.969	72.434	1.3120	1.3037	(3 1 1)	0.8026	09.90
75.429	75.260	1.2592	1.2616	($\bar{2}$ 2 2)	0.8160	09.73

UV-Visible analysis

The optical characterization of the sample was recorded on UV-Vis absorption spectrophotometer Fig (2) in order to determine the Band gap energy of nano CuO. The UV-Vis absorption spectroscopy of the

sample dissolved in absolute ethanol shows an absorption peak whose center is at about 270nm. In this study a simple UV-Vis – NIR technique was used to calculate the band gap energy of synthesized nano CuO and compared with value of bulk CuO. Eg value of nano CuO according to the following equation $E_g = h\nu_{\text{freq}}$.

The band gap energy was calculated in terms of eV. Eg is the band gap energy, h is plank’s constant and ν_{freq} is the frequency of the emitted radiation. The band gap of nano CuO is calculated to be 4.60eV, which is higher than the reported value of CuO in the range from 1.8-2.5 eV[1]. The increase in band gap may be due to the quantum size effect of the synthesized sample[5].

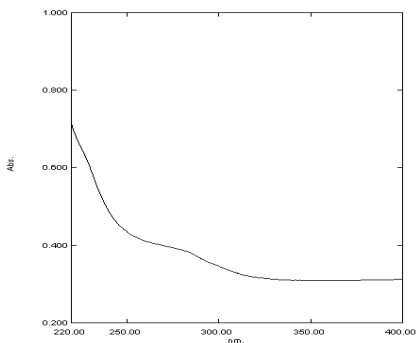


Fig.2 (a) UV-Vis spectra of CuO nanoparticles (b) FTIR Analysis

Fourier Transform Infrared spectroscopy is a technique used to measure the vibrational frequencies of bonds in the molecule. The FTIR spectra of CuO nano pellets is shown in Fig(3). The strong intensity peak at 3573 cm^{-1} assigned to alkyl (O-H) stretching for the deformation of diethylamine, 3486 cm^{-1} assigned to (N-H) vibration of amine group, weak band at 2361 cm^{-1} assigned to carboxylic group (COO^-) vibration. Peak at 1634 cm^{-1} assigned to amide (COO^-) while the very intense peak positioned at 1114 cm^{-1} revealed the presence of (O-H) stretching for alkyl. The characteristic peaks of CuO positioned from 984 cm^{-1} to 426 cm^{-1} . The peaks positioned at around 606 and 525 cm^{-1} observed due to cu-O stretching along the [-202] direction and 432 cm^{-1} from Cu-O stretching along the [202] direction [6].

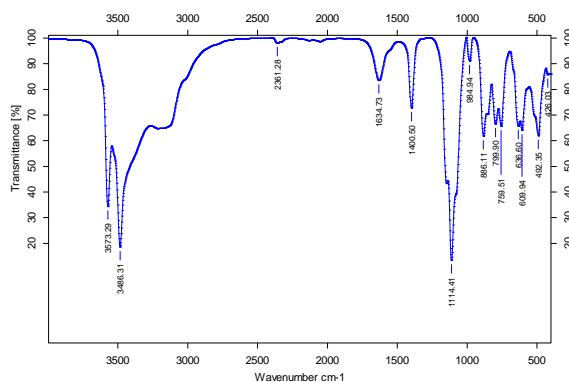


Fig.3 FTIR spectra of CuO nanoparticles

SEM Analysis

Fig (4) shows that how the CuO nanocrystals organized into spherical assemblies. With higher magnification on individual particle it appears like dandelion. In the present work $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was used to prepare spherical shaped nano CuO at mild reaction temperature. The same morphology was obtained when using $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ as reported by Anandan et al.[7].

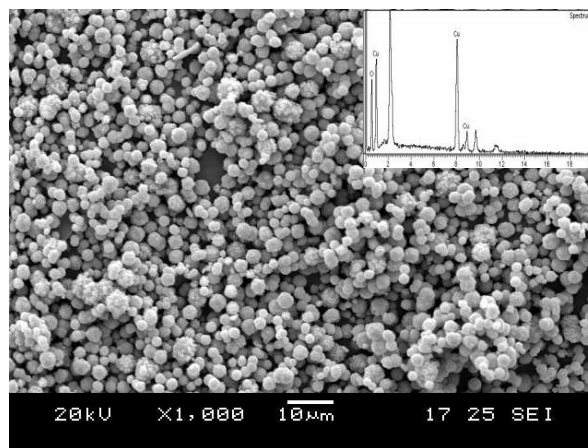


Fig.4 SEM / EDS images of CuO nanoparticles

CONCLUSIONS

Nano CuO particles are synthesized successfully by hydrothermal route. It is confirmed by XRD analysis. The UV-Visible study shows the radiation in red region can be applicable for fabrication of optoelectronic devices. The FTIR analysis reveals the characterization peaks for Cu-O stretching. The adsorption of ammonia is confirmed by FTIR spectra. The spherical Morphology is confirmed by SEM / EDS.

REFERENCES

- [1] Ning Wang, Hongcai He, Lit Han **2010**, “Room temperature preparation of cuprous oxide hollow microspheres by a facile wet-chemical approach,” *Applied Surface Science* 256:7335-7338
- [2] Borkow.G, J. Gabbay, A. Lyakhovitsky, M.Huszar, **2009**, “Improvement of facial skin characteristics using copper oxide containing pillowcases, a double – blind, placebo-controlled, parallel, randomized study”, *International Journal of Cosmetic Science*, Issue 6, P. 437 – 443.
- [3] Gadi Borkow, Richard C. Zatcoff, Jeffiery Gabbay, **2009**, Reducing the risk of skin pathologies in diabetics by using copper impregnated socks’, *Medical Hypotheses*, Vol.No. 73, Issue 6, p.883-886.
- [4] Ratish K, Bedi and Iqbal Singh **2010**, “Room Temperature Ammonia Sensor Based on Cationic Surfactant – Assisted nanocrystalline CuO”, *ACS Applied Materials & Interfaces*, Vol.2. N.5, p.1361-1368.
- [5] Swarnkar R.K, S.C. Singh and R.Gopal, **2009**, “Optical Characterizations of Copper oxide Nanomaterial,” *International conference on optics and photonics*’
- [6] Mushtag A.Das. Sang H.Nam, Youn S. Kim, Won Bal Kim, **2010** synthesis, Characterization and electrochemical properties of self-assembled leaf-like CuO nanostructures. *Journal of Solid State Electrochemical* 14: 1719-1726
- [7] Sambandam Anandan, Shine Yang, **2007** “Emergent Methods to Synthesize and Characterize Semiconductor CuO nano particles with various morphologies – an overview’, *Journal of Experimental Nanoscience*, Vol. 2, Nos. 1-2, p.23-56.