

Synthesis of cadmium-doped copper oxide nanoparticles: Optical and structural characterizations

S. G. Rejith^{a*} and C. Krishnan^b

^a*Department of Physics, St. Xavier's College, Palayamkottai, Tamilnadu, India*

^b*Department of Physics, Arignar Anna College, Aralvoymozhi, Tamilnadu, India*

ABSTRACT

Pure and cadmium-doped copper oxide nanoparticles have been successfully prepared by a microwave assisted solvothermal method using copper acetate as the starting material. The particle sizes have been obtained as, 10-14 nm for pure CuO and 42-87 nm for cadmium-doped CuO nanoparticles. The synthesized both pure and cadmium-doped copper oxide nanoparticles have been characterized by using XRD, SEM-EDAX and UV-Visible analysis techniques. From the XRD study, it is found that the prepared samples are in the monoclinic system. Scanning Electron Microscopy (SEM) pattern shows the spherical morphology of the prepared nanoparticles. The presence of dopant in the doped sample is found by using EDAX measurements. The optical property of cadmium-doped copper oxide nanoparticles are measured by UV-Visible spectroscopy.

Keywords: A. Nanostructure; B. Chemical synthesis; C. X-ray diffraction

INTRODUCTION

In chemical sciences, synthesis of transition metal and metal oxide nanoparticles is a growing research field. As the metal particles are reduced in size, bulk properties of the particles disappear to be substituted to that of quantum dot following quantum mechanical rules. It can thus be easily understood that metal nanoparticles chemistry differs from that of the bulk materials. Since with size reduction the high surface area to volume ratio lead to enhanced catalytic activity [1]. Among various metal nanoparticles, copper (Cu) and copper oxide (Cu₂O) nanoparticles have attracted considerable attention because copper is one of the most important in modern technologies and is readily available [2]. Considerable interest has been focused on copper nanoparticles due to their optical, catalytic, mechanical and electrical properties [3, 4].

In recent years, copper oxide has attracted increasingly interests for both fundamental and practical reasons. The oxides of transition metals are an important class of semiconductors, which have applications in magnetic storage media, solar energy transformation, electronics and catalysis [5-13]. Among the oxides of transition metals, copper oxide nanoparticles are of special interest because of their efficiency as nanofluids in heat transfer application. For example it has been reported that 4 % addition of CuO improves the thermal conductivity of water by 20 % [14].

CuO is a semiconducting compound with a narrow band gap and used for photoconductive and photo thermal applications [15]. Nano-copper oxide is a widely used material. It has been applied to the catalyst, superconducting materials, thermoelectric materials, sensing materials, glass, ceramics and other fields. In addition, the nano-copper oxide have been used as rocket propellant combustion catalyst and also more use such as: Ceramic resistors, gas

sensors, magnetic storage media, near-infrared filters, photoconductive and photo thermal applications, semiconductors, solar energy transformation, catalysts, high-tech superconductors[16]. The cuprous oxide (Cu_2O) and copper oxide (CuO) with different morphologies have also been prepared by several routes, such as thermal oxidation [17], simple solution [18], simple hydrolysis [19], template-based sol-gel [20], and electrochemical [21]. Besides, the hydrothermal [22-26], solvothermal [27, 28] and microwave-hydrothermal [29, 30] methods have also been employed to control the morphologies of these oxides. With the decrease in the crystal size, nanosized copper oxides may exhibit unique properties which can be significantly different from those of their bulk counterparts, for example, the large interfacial areas, homogeneity and highly reactive surfaces, unusual optical, electrical, and catalytic properties, etc. As a result, it is always desirable that physical and chemical characteristics can be controlled by tuning the grain size of the CuO particles in practical applications [31]. In the past decades, much effort has been made toward the synthesis and characterization of nanosized

Transition metal oxide particles. Among all transition metal oxides that have been investigated, Much less work has been devoted to the preparation and characterization of CuO nanoparticles. It is well known that copper oxides can be conventionally obtained by the thermal decomposition of copper salts in solid state [32].

The current work is devoted to the investigation of pure and cadmium -doped CuO nanoparticles formation from metal-organic compound, which have been prepared by using the solvothermal method and the prepared high purity CuO nanoparticles have been investigated using combined techniques of XRD, SEM-EDAX, and UV-Visible analysis. The results show that the formation of CuO nanoparticles from acetate precursors is complete and the particle sizes of the CuO nanoparticles can be controlled to be between 10 and 14 nm.

MATERIALS AND METHODS

2.1. Synthesis

Copper nanoparticles have been prepared by several methods ranging from thermal reduction, sonochemical method, sol-gel reaction, to gas phase process. Compared to the wet-phase sol-gel based method and the thermal reduction, both of which require inherent multistep processes, gas-phase methods are capable of continuous production of nanoparticles with a single step. Therefore, many modifications of the gas-phase method including inert gas condensation, sputtering, microwave synthesis, and spray pyrolysis have been developed for large-scale industrial production of nanoparticles. Among those, solvothermal process has been shown to be a powerful technique for generating novel materials with interesting properties. Particularly, the solvothermal technique provides the alternative approach that allows the economical synthesis of fundamentally important well-defined nanometer-sized materials at mild conditions. To our knowledge, this new synthetic technique has not been applied in the synthesis of transition metal oxides such as copper oxide. The present work is focused on the synthesis and characterization of nanometer-sized pure and cadmium-doped CuO particles by a simple microwave assisted solvothermal method. Analytical reagent (AR) grade copper acetate, urea, ethylene glycol (as solvent) are used as precursors. Copper acetate and urea are taken as solute in the molecular ratio 1:3 and dissolved in 100 ml ethylene glycol as individually. Then the two solutions are mixed together and the colour of the solution has turned to dark green. The prepared solution is kept in a domestic microwave oven (operated with frequency 2.45 GHz and power 800W). Microwave irradiation is carried out for about 20 minutes till the solvent is evaporated completely. The obtained colloidal precipitate is black in colour. In the end, the precipitate is washed several times with distilled water and acetone to remove the organic impurities. The prepared sample is dried in atmospheric air and annealed it for 30 minutes at 100°C to improve the ordering. For cadmium doping samples, cadmium acetate (2 wt %) are added with the above precursors and the same procedure was repeated.

2.2. Characterization

The powder XRD pattern of the prepared nanoparticles is recorded with automated X-ray diffractometer (X-PERT PRO Philips System) operating CuK_α at wavelength 1.54056 Å. The EDAX spectrum is obtained for the doped samples using JOEL / EO JSM-6390 scanning electron microscope. The UV-Vis absorption spectra are recorded for the powder specimen using a LAMBDA-35 spectrometer for all the samples which have been considered in the present study. The optical bandgap energy (E_g) is also estimated for all the samples.

UV-Visible absorption spectrum of synthesized nanoparticles shows the band edge-absorption peak is found to be at 350 nm. The optical band gap of the produced nanoparticles is calculated using the Tauc's relation [33]

$$\alpha h\nu = (h\nu - E_g)^\nu$$

Where $h\nu$ is the incident photon energy, n is the exponent that determines the type of electronic

Transition causing the absorption and can take the values 1/2 and 2 depending whether transition is direct or indirect respectively. Plots between $(\alpha h\nu)^2$ vs $h\nu$ for pure and doped samples are drawn and the best linear relationship indicating that the optical band gap of the pure and doped CuO nanoparticles is due to a direct allowed transition. The value of the band gap is determined from the intercepts of the straight line.

RESULTS AND DISCUSSION

3.1. Structural characterization

The XRD patterns which is obtained in the present study for both pure and cadmium -doped copper oxide nanoparticles are presented in Fig. A. All diffraction peaks can be indexed in the CuO monoclinic phase [34, 35]. The lattice parameters are calculated using the least square refinement from the UNITCELL-97 program [36]. The obtained parameters are $a= 4.682 \text{ \AA}$, $b= 3.424 \text{ \AA}$, $C=5.127 \text{ \AA}$ with volume cell of 81.52 \AA^3 . These values are consistent with the reported literatures [37, 38] and with the respective "JCPDS" (Joint Committee on Powder Diffraction Standards) card No.89-5895.

In the case of pure CuO spectrum the diffraction peaks are considerably broadened that is attributed to the small crystallite sizes. Small crystallites have relatively few lattice planes that contribute to the diffraction lines. Broadening the peak may also occur due to micro straining of the crystal structure arising from defects like dislocation and twinning etc. These defects are considerably negligible in the case of cadmium-doped CuO nanoparticles. In doped copper oxide nanoparticles spectrum the diffraction pattern peaks are considerably narrowed that are attributed to the change in crystallite sizes. The grain sizes which obtained are small enough to have the quantum confinement.

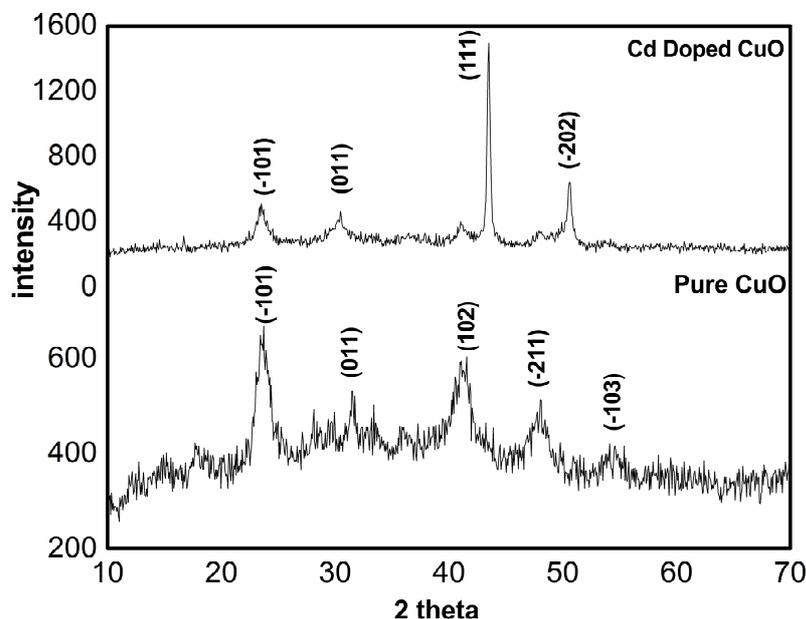


Fig. A : XRD spectrum of both pure and cadmium-doped CuO nanoparticles

The crystallite sizes can be estimated using Scherrer's formula

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

Where the constant K is taken to be 0.94, λ is the wavelength of X-ray used which is $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$), and β is the full width at half maximum of the diffraction peak corresponding to 2θ . Using above equation the crystallite sizes find to be in the range of nanometer. The particle sizes are measured by taking the average of three main line widths which are obtained from the XRD patterns as 10–14 nm for pure CuO and 42-87 nm for cadmium-doped CuO.

3.2. SEM-EDAX Analysis

The EDAX spectra of CuO doped nanoparticles are shown in Fig. B. This shows that Cd^+ impurity has entered in the crystal matrix of CuO. It is expected that the Cd^+ ions will be replacing the O^{2-} ions instead of occupying the interstitials. The doping levels and the bonding characteristics are determined by EDAX spectrum.

In order to obtain insight information about surface morphology and particle size of the samples, SEM analyses were performed. The product is agglomerated from few μm to a few tens of μm . The agglomeration was reduced with increase in grain growth. The agglomeration of particles is usually explained as a common way to minimize their surface free energy, and the SEM micrographies for pure and cadmium-doped CuO nanoparticles are shown in Fig. C.1 and Fig. C.2. SEM micrographies clearly show the surface features, by which it highlight that CuO nanoparticle was successfully prepared. From the SEM results, the prepared crystallites are nearly spherical in shape and it can be seen that the particles congregate together and the size of which is about 100 nm.

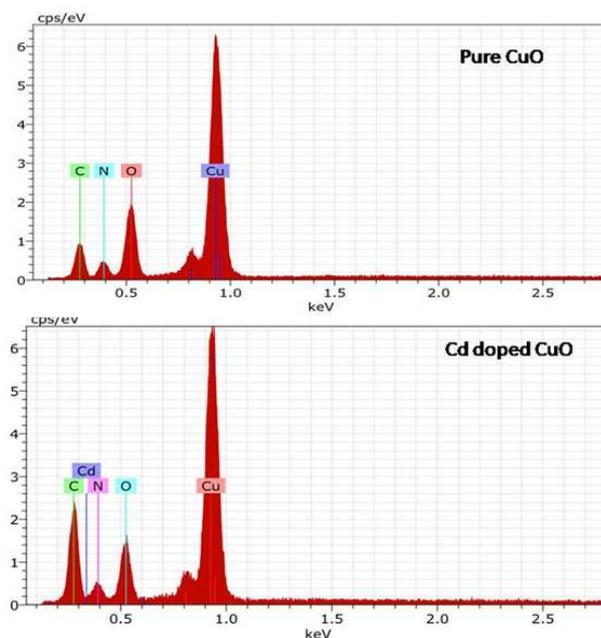


Fig. B : EDAX spectrum of pure and cadmium-doped CuO nanoparticles

3.3 Optical studies

UV-Visible absorption spectrum and direct bandgap spectrum for both pure and cadmium-doped CuO nanoparticles are shown in Fig. D and Fig. E. The spectrum shows the band edge-absorption peak which is found to be at 350 nm. In UV-Vis, high energy electromagnetic radiation in the wavelength range of 100-700nm is utilized to promote electrons to higher energy orbitals. Since orbitals have quantized energy, only certain transitions can occur in the UV-Vis energy range. The differences in the incident and transmitted beam give us information about the frequencies which are absorbed by the sample molecules. Based on absorbance data, the sample chemical structure can be analyzed.

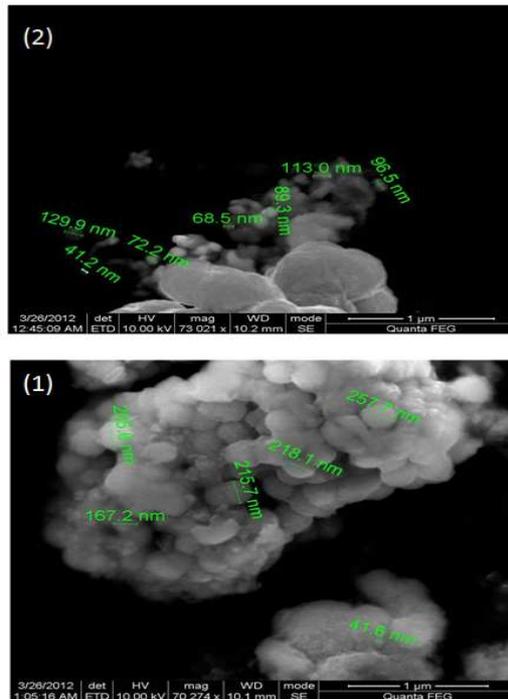


Fig. C.1: SEM micrographies of pure CuO nanoparticles
 Fig. C.2: SEM micrographies of cadmium-doped CuO nanoparticles

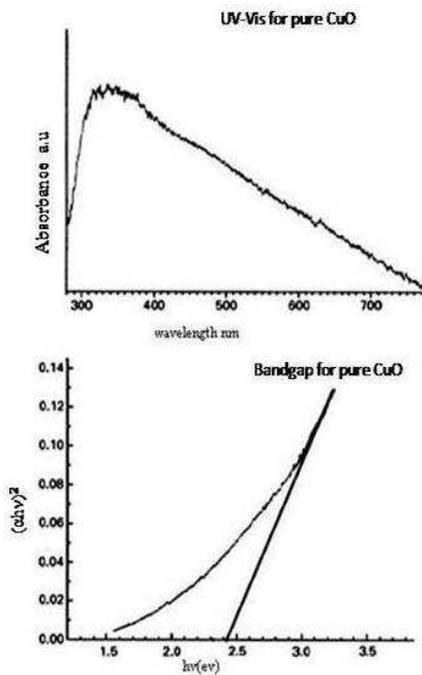


Fig. D : UV-Vis and band gap spectrum of pure CuO nanoparticles

The best linear relationship is obtained by plotting $(\alpha h\nu)^2$ against $h\nu$ indicating that the optical band gap of the pure and doped CuO nanoparticles is due to a direct allowed transition. The direct band gap is determined from the intercept of the straight line at $a = 0$, which is found to be 2.4 eV for pure CuO. In the case of cadmium-doped CuO

the band gap is decreases from 2.4 eV to 2.27 eV. Thus, it thus can be inferred that copper oxide can be activated by visible light [39].

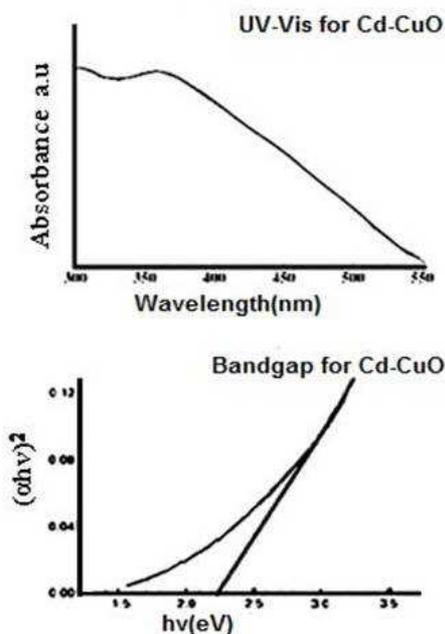


Fig. E: UV-Vis and band gap spectrum of Cadmium-doped CuO nanoparticles

CONCLUSION

Pure and cadmium-doped CuO nanoparticles with monoclinic structure have been synthesized successfully by microwave assisted solvothermal method. SEM micrographies clearly show the surface features, by which it pinpoints that CuO nanoparticle is successfully prepared. From the SEM micrographies, it can be understood that the crystallites prepared are of nearly spherical in shape so that the grain sizes determined by using the Scherrer formula can be considered as valid. The doping levels and the bonding characteristics have been determined by EDAX spectrum. This also shows that Cd^+ impurity has entered in the crystal matrix of CuO. UV-Visible absorption spectrum of synthesized nanoparticles shows the band edge-absorption peak and is found to be at 350 nm. The obtained band gap value is 2.4 eV for pure and 2.27 eV for cadmium-doped CuO nanoparticles.

REFERENCES

- [1] M. S. Niasari, F. Davar and N. Mir, *Polyhedron*, **2008**, 27, 3514-3518.
- [2] M. J. G. Pacheco, J. E Morales-Sanchez, J. Hernandez and F. Ruiz, *Material Letters*, **2010**, 64, 1361-1364.
- [3] Y. Xi, C. Hu, P. Gao, R. Yang, X. E., X. Wang and B Wan, *Material Science and Engineering B*, **2010**, 166, 113-117.
- [4] Y. He, *Material Research Bull.*, **2007**, 42, 190-195.
- [5] A.S. Lanje, R.S. Ningthoujam, S.J. Shrama, R.K. Vatsa, R.B. Pode, *Int. J. Nanotechnol.*, **2010**, 7, 979.
- [6] E.P. Wölfarth., *Ferromagnetic Materials*, Vol. II, North-Holland, Amsterdam, New York, Oxford, Tokyo, **1980**.
- [7] T. Mitsuyu, O. Yamakazi, K. Ohji, K. Wasa, *Ferroelectrics*, **1982**, 42, 233.
- [8] O. Regan, M. Gratzel, *Nature*, **1991**, 353, 737.
- [9] K. Naazeeruddin, A. Kay, M. Gratzel, *J. Am. Chem. Soc.*, **1993**, 115, 6832.
- [10] U. Bjoerksten, J. Moser, M. Gratzel, *Chem. Mater.*, **1994**, 6, 858.
- [11] W.P. Dow, T.J. Huang, *J. Catal.*, **1996**, 160, 171.
- [12] P.O. Larsson, A. Andersson, R.L. Wallengerg, B. Svensson, *J. Catal.*, **1996**, 163, 279.
- [13] Y. Jiang, S. Decker, C. Mohs, K.J. Klabunde, *J. Catal.*, **1998**, 180, 24.
- [14] S. Lee, U.S. Choi, S. Li, J.A. Eastman, *J. Heat Transfer*, **1999**, 121, 280.

- [15] A.E. Rakhshni, *Solid State Electron.* **1986**, 29, 7.
- [16] www.us-nano.com.us , 3063.
- [17] J.T. Chen, F. Zhang, J.Wang, G.A. Zhang, B.B. Miao, X.Y. Fan, D. Yan, P.X. Yan, *J. Alloys Compd.*, **2008**, 454, 268–273.
- [18] L. Yu, G. Zhang, Y. Wu, X. Bai, D. Guo, *J. Cryst. Growth*, 2008, 310, 3125–3130.
- [19] J. Zhu, H. Bi, Y. Wang, X. Wang, X. Yang, L. Lu, *Mater. Lett.*, **2007**, 61, 5236–5238.
- [20] Y.-K. Su, C.-M. Shen, H.-T. Yang, H.-L. Li, H.-J. Gao, *Trans. Nonferrous Met. Soc. China* , **2007**, 17, 783–786.
- [21] G.-Q. Yuan, H.-F. Jiang, C. Lin, S.-J. Liao, *J. Cryst. Growth*, **2007**, 303, 400–406.
- [22] H. Zhang, S. Li, X. Ma, D. Yang, *Mater. Res. Bull.*, **2008**, 43, 1291–1296.
- [23] M. Zhang, X. Xu, M. Zhang, *Mater. Lett.*, **2008**, 62, 385–388.
- [24] M.-G. Ma, Y.-J. Zhu, *J. Alloys Compd.*, **2008**, 455, L15–L18.
- [25] Z.-Z. Chen, E.-W. Shi, Y.-Q. Zheng, W.-J. Li, B. Xiao, J.-Y. Zhuang, *J. Cryst. Growth*, **2003**, 249, 294–300.
- [26] Y.C. Zhang, J.Y. Tang, G.L. Wang, M. Zhang, X.Y. Hu, *J. Cryst. Growth* , **2006**, 294, 278–282.
- [27] X.-L. Tang, L. Ren, L.-N. Sun, W.-G. Tian, M.-H. Cao, C.-W. Hu, *Chem. Res. Chin. Univ.*, **2006**, 22, 547–551.
- [28] X. Song, H. Yu, S. Sun, *J. Colloid Interf. Sci.*, **2005**, 289, 588–591.
- [29] D. Keyson, D.P. Volanti, L.S. Cavalcante, A.Z. Simões, J.A. Varela, E. Longo, *Mater. Res. Bull.*, **2008**, 43, 771–775.
- [30] X. Xu, M. Zhang, J. Feng, M. Zhang, *Mater. Lett.*, **2008**, 62, 2787–2790.
- [31] Zhong-shan Hong, Yong Cao, Jing-fa Deng, *Materials Letters* , **2002**, 52, 34–38.
- [32] C. Carel, M. Moullem-Bahout, J.C. Gaude, *Solid State Ionics*, **1999**, 117, 47.
- [33] A.M. Salem and M. Soliman selim, *J. Phys. Appl. Phys.*, **2001**, 34 ,12.
- [34] H. Wang, J. Zhang, J. J. Zhu, H. Y. Chen, *J. Cryst. Growth*, **2002**, 244, 88.
- [35] Amrut. S. Lanje, Satish J. Sharma, Ramchandara B. Pode, Raghumani S. Ningthoujam , *Advances in Applied Science Research*, **2010**, 1(2), 36-40.
- [36] T.J.B. Holland, S.A.T. Redfern, *Miner. Mag.*, **1997**, 61, 65.
- [37] Daqiang Gao, Jing Zhang, Jingyi Zhu , *Nanoscale Res Lett.*, **2010**, 5, 769–772.
- [38] D.P. Volanti, D. Keyson, L.S. Cavalcante et al, *Journal of Alloys and Compounds*, **2008**, 459, 537-542
- [39] Qingwei zhu, yihe Zhang, Jiajun Wang, *J. Mater. Sci. Technol.*, **2011**, 27, 289-295.