

Synthesis of Zinc-Doped Copper Oxide Nanoparticles: Structural and Morphological Characterizations

T. Hemalatha¹ S. Akilandeswari²

^{1,2}Department of Physics

^{1,2}Annamalai University, Annamalai Nagar, Chidambaram 608 002, Tamilnadu, India

Abstract— Reported here is the various levels of Zn incorporated CuO nanocrystals derived from a simple chemical precipitation method. The prepared nanocrystals were studied for structural, functional and morphological analysis. The X-ray Diffraction (XRD) analysis of the prepared nanocrystals revealed the monoclinic crystal structure with the sizes in the range between 18 and 25 nm. The Fourier Transform Infrared Spectroscopy (FT-IR) of the prepared nanocrystals was recorded in the range of 4000-400 cm⁻¹ and its further supporting the formation of CuO nanocrystals. The morphology of the prepared products analyzed with Field Emission-Scanning Electron Microscopy (FE-SEM) and the results revealed the synthesized nanocrystals are well distributed and flaky nature in morphology.

Key words: FE-SEM, FT-IR, XRD

I. INTRODUCTION

Now a day, intensive research activities are being directed toward nanostructures, which are considered to be well-defined building blocks for the fabrication of diverse nanoscale devices. Further, with excellent physiochemical properties, nanostructured materials are employed in nanoelectronic devices [Singh 2011]. Lending even more credence, this hard fought technology also involves tailoring of materials at the atomic level to attain unique properties that can be suitably manipulated to get desired applications [Gleiter 2000]. Among the semiconductor metal oxides, copper oxide (CuO) has been extensively studied due to its important properties and applications in many fields [Wei-Tang Yao et al., 2005]. Copper Oxide (CuO), a p-type metal oxide semiconductor material has been majorly used for research and study as it associated with a narrow band gap ($E_g = 1.2$ eV). It constitutes some of the important properties such as it forms the basis for several high-temperature superconductors and several giant magnetoresistance materials [Zheng 2000]. CuO being photochemical and photoconductive material used for fabricating solar cells [Maruyama 1998]. To completely assess the potential of CuO, studies are conducted in lithium ion batteries [Lanza 1990] and gas sensors [Frietsch 2000] with CuO embedded in a variety of polymer materials. The study on synthesis and characterization of CuO nanoparticles is the least explored area compared to other transition metal oxides like ZnO, SnO₂, TiO₂ and Fe₂O₃, thus making it an interesting subject of investigation. Nanocrystals of copper oxide have attracted considerable interest due to their size and wide range of applications in branch of physics and biological fields [Djurisic et al., 2006; Djurisic et al., 2012; Brewster et al., 2012; Xing et al., 2011; Gulino et al., 2008]. Doping of CuO with transition metal ions alter the optical, electrical and morphological properties of CuO due to the exchange interaction between s and p

electrons of host CuO and d electron of transition metal ion [Zhang et al., 2010].

Different approaches have been suggested and investigated for the synthesis of copper oxide nanoparticles. Here, in the present work the pure and various levels of Zn ions (0.02, 0.04, 0.06, 0.08 and 0.1 M) doped CuO nanocrystals were synthesised through chemical precipitation method, because of its mild reaction conditions, low cost and good reproducibility. Nucleation and grain growth are involved in the preparation of CuO nanoparticles by such a precipitation method. The effects of Zn-doping on the structural, functional and morphological of the synthesized nanocrystals have been reported.

II. EXPERIMENTAL METHODS

A. Chemicals:

Copper acetate monohydrate ($\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$), sodium hydroxide (NaOH) pellet and Zinc acetate dihydrate [$\text{C}_4\text{H}_6\text{O}_4\text{Zn} \cdot 2\text{H}_2\text{O}$] were purchased from Merck, India with 99% purity. De-ionized water was used all the way through the synthesis and ethanol was used for the washing purpose.

B. Synthesis of Zn doped CuO nanocrystals:

For the synthesis of Zn doped CuO, 1.99 g (0.2 M) of copper acetate [$\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$] dissolved in 50 ml of deionised water was stirred vigorously by magnetic stirrer and Zinc acetate dihydrate [$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$], of preferred mole (0.02, 0.04, 0.06, 0.08 and 0.1 M) prepared in 20 ml aqueous solution were mixed drop by drop. Then, 1.2 g (0.6 M) of Sodium hydroxide (NaOH) in 50 ml of deionised water was added drop by drop to the former stirred mixture. The resulting solution was stirred magnetically at 60 °C until a black precipitate was formed. The obtained dispersions were purified by dialysis against deionised water and ethanol several times to remove impurities. The final products were dried in hot air oven at 80 °C to evaporate water and organic material to the maximum extent. Finally, the obtained product was annealed in a muffle furnace at 400 °C for 2 h. A similar method of preparation without the addition of Manganese was used to synthesize pristine CuO nanocrystals. Figure 1 shows the flow chart of the preparation process of Zn doped CuO nanoparticles.

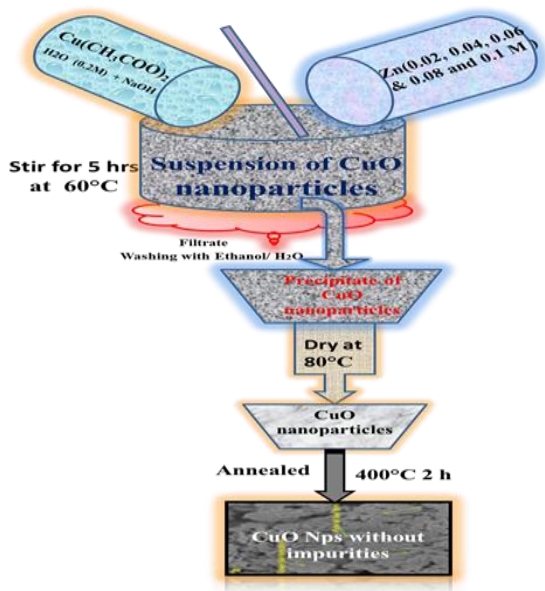


Fig. 1: Preparation Process of Zn Doped CuO Nanocrystals

C. Characterization:

The crystal structure and phase purity of the as synthesized products were investigated by X-ray diffractometer (X'PERT PRO) with CuK α radiation ($\lambda=1.5406 \text{ \AA}$). FT-IR has been employed to find the presence of functional groups in the range of 4000-400 cm^{-1} and it was recorded using SHIMADZU-8400 with a resolution of 4 cm^{-1} . Measurements were performed with pressed pellets which were made using KBr powder as diluents. The morphology of the products was examined using Philips Field Emission Scanning Electron microscopy (FE-SEM).

III. RESULT AND DISCUSSION

A. Crystal Structure and Phase Purity Analysis:

The typical X-ray diffraction patterns of pure and Zn-doped CuO compositions are shown in Fig. 2. The standard diffraction peaks confirmed the formation of the monoclinic CuO phase (space group C2/c) in accordance with the standard JCPDS card no. 89-2531. The strong and sharp diffraction peaks demonstrate that the products are well crystalline. Furthermore, it can be seen that at higher doping concentrations (from 0.06 M onwards) a secondary phase is noted and are specified by asterisks. The new phase corresponds to ZnO (JCPDS no: 36-1451). When the concentration of Zn is increased above 0.04, in addition to CuO peaks four weak diffractions peaks were also observed at $2\theta = 31.77^\circ, 34.41^\circ, 36.24^\circ,$ and 56.58° , which corresponds to hexagonal wurtzite structure of ZnO. Therefore, the doping concentration of 0.04 M may roughly be considered as the solubility limit of Zn in CuO. At higher doping concentration i.e. beyond the solubility limit a few of Zn ions get segregated in the form of secondary phase. The formation of secondary phase induces some kind of modifications in the prepared nanocrystals.

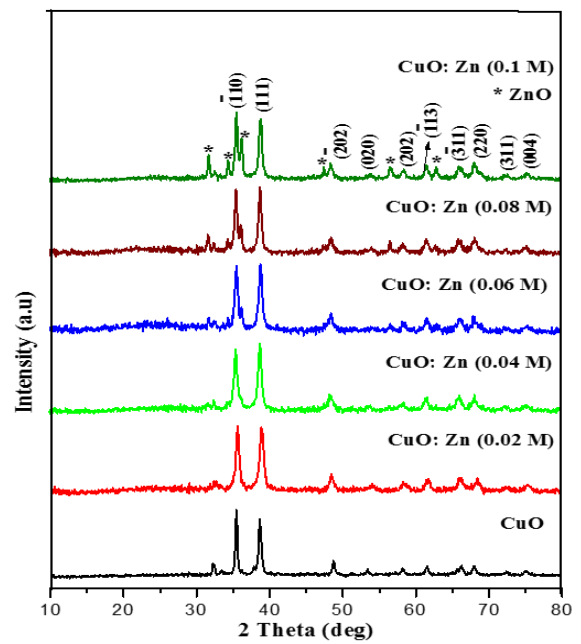


Fig. 2: XRD Pattern of Pure and Zn Doped CuO Nanocrystals

The intensity of peaks gets suppressed due to dopant addition, which confirms the incorporation of dopant in host lattice. The average crystallite size was calculated by using Debye-Scherer formula and it was found to be increase comparing pure, after the addition of 0.04 M of Zn into CuO and hence 0.04 M has been considered to be an optimum level of Zn doped CuO nanoparticles. Average size as estimated for undoped CuO Nano- crystals using the formula [Kannadasan et al., 2014] was found to be 21.63 nm and 18.03, 17.96, 23.75, 24.07 and 25.64 nm for 0.02, 0.04, 0.06, 0.08 and 0.1 M Zn doped CuO Nano crystals respectively. An increase in size is observed due to doping Zn in CuO Nano crystals. The incorporation of Zn at Cu site generates strain and hence it may lead to an increase in the lattice constant.

B. Fourier Transform Infrared Spectroscopy:

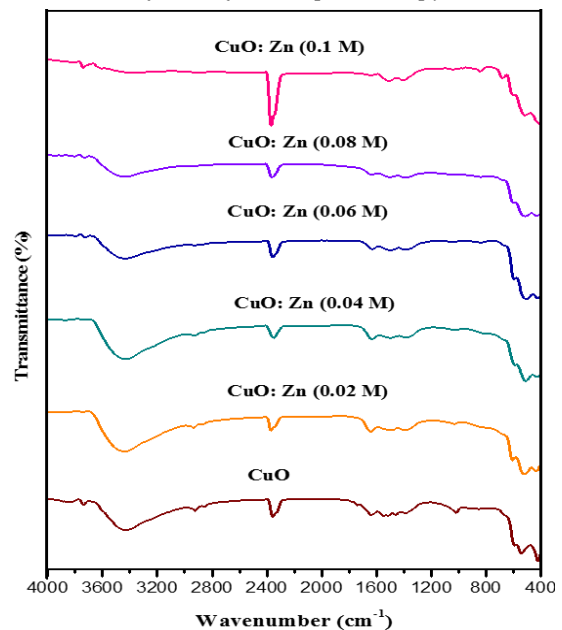


Fig. 3: FTIR Analysis of Pure and Various Concentrations Zn Doped CuO Nanoparticles

FT-IR spectra of pure and Zn doped CuO nanocrystals are shown in the Fig. 3. Broad band in the range of 3600–3250 cm⁻¹ is due to the O-H stretching of water molecules chemically associated with CuO. The sharp and broad transmittance peak at 3401 cm⁻¹ can be assigned as O-H stretching vibrations of hydroxyl group of CuO. The transmittance peaks at 2927 cm⁻¹ can be assigned as C-H asymmetric stretching vibration. The transmittance peaks around 2927 cm⁻¹ are assigned as O-H bending mode vibration of H₂O [Jiexiang Xia, et al. (2009)]. The transmittance peaks at 1392 cm⁻¹ indicate COO- stretching vibrations of carboxylic group elements. The peaks around at 425 cm⁻¹, 513 cm⁻¹ and 597 cm⁻¹ are assigned as Cu-O stretching mode vibration along (2 0 2) direction and confirms the monoclinic phase.

C. Morphological Analysis [FE-SEM]:

Figure 4 shows the FE-SEM image of the pure and 0.04 M Zn doped CuO nanorods and nanoflakes respectively. The image explains that the synthesized nanoparticles are well distributed and flaky nature in morphology. The two dimensional images of nanoflakes showed that they are agglomerated and flaky like shape as shown in Figure 4C. Therefore, the present study shows the clear variations and agglomerations in the pure and Zn doped CuO samples.

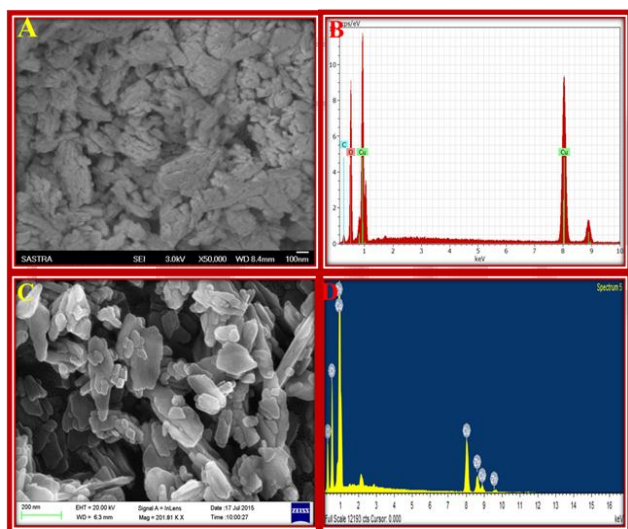


Fig. 4: FE-SEM images of a) pure and c) 0.04 M Zn doped CuO b) and d) corresponding EDAX patterns

The incorporation Zn has been confirmed by EDS analysis (Fig. 4 B and D). In addition to Cu and O, the prominent peaks of Zn are also noted in the EDS spectrum, indicating the successful incorporation of Zn in the host-material.

IV. CONCLUSION

Pure CuO and chemically precipitated Zn doped CuO with diverse concentrations of Zn (0.02, 0.04, 0.06, 0.08 and 0.1 M) have been successfully synthesized. X-ray diffraction studies show that the particles are monoclinic (crystalline) in nature without any impurity phases. The FT-IR study confirms the presence of Cu-O bonds. The influences of Zn and growth process on the morphology of CuO nanoparticles are discussed. FE-SEM images clearly shows the undoped CuO nanocrystals are in the formation of rod like structure and Zn doped CuO nanocrystals are flaky

nature in morphology. EDS analysis confirms the presence of elements in the prepared products. This precipitation method is demonstrated to be simple and potential for large scale production. This method may be extended to other metal oxide nanocrystals.

REFERENCES

- [1] Brewster M.M, Zhou X, Lu M.Y, Gradecak S (2012). *Nanoscale*, 4, 1455-1462.
- [2] Djuricic A.B, Chen X.Y, Leung Y.H, Ng A.M.C (2012). *J. Mater Chem*, 22, 6526-6535.
- [3] Djuricic B, Leung Y.H (2006). *Small*, 2, 944-961
- [4] Frietsch M, Zudock F, Goschnick J, Bruns M (2000). *Sensors Actuators B*, 65, 379-381.
- [5] Gleiter H (2000). *Acta Mater*, 48, 1-29
- [6] Gulino A, Lupo F, Fragala M.E (2008). *J. Phys Chem C*, 112, 13869-13872.
- [7] Jiexiang Xia, Huaming Li, Zhijun Luo, Hua Shi, Kun Wang, Huoming Shu, Yongsheng Yan (2009). *Journal of Physics and Chemistry of Solids*, 70(11), 1461-1464.
- [8] Lanza. F, Feduzi. R, Fuger J.J (1990). *J. Mater. Res*, 5, 1739-1744.
- [9] Maruyama T (1998). *Sol. Energy Mater. Sol. Cells*, 56, 85-92.
- [10] Shanmugam N, Cholan S, Kannadasan N, Sathishkumar K, Viruthagiri G (2014). *Spectrochim. Acta A*, 118, 557.
- [11] Singh I, Bedi R.K (2011). *J. Mater Sci*, 46:5568-5580.
- [12] Wei-Tang Yao, Shu-Hong Yu, Yong Zhou, Jun Jiang, Qing-Song Wu, Lin Zhang, and Jie Jiang (2005). *J. Phys. Chem. B*, 109, 14011-14016.
- [13] Xing G.Z, Xing G.C, Li M.J, Sie E.J, Wang D.D, Sulistio A, Ye Q.L, Huan C.H.A, Wu T, Sum T.C (2011). *Appl Phys Lett*, 98, 102105-3.
- [14] Zhang Y, Shi E.W, Chen Z.Z (2010). *Mater Sci Semicond Process*, 13, 132-136.
- [15] Zheng X.G, Xu C.N, Tomokiyo Y, Tanaka E, Yamada H, Soejima Y (2000). *Phys. Rev. Lett*, 85, 5170-5173.