Research Article

Structural, Optical and Morphological characteristics of In Doped CuO Nano Particles Prepared by Precipitation Method

K. Rajaram, E. Savarimuthu and S. Arumugam*
Department of Physics, Gandhigram Rural Institute-Deemed University, Gandhigram 624 302. Tamil Nadu. India

Abstract
The structural, optical and morphological characterization of In doped CuO nanoparticles for different molar concentration of In at 3, 5 and 7 wt% has been investigated. The XRD analysis confirms that all the particles are polycrystalline in nature. The FT-IR spectrum explores the presence of functional groups of Copper oxide and Indium in the prepared system. The doping concentration of Indium chloride has an influence on the optical properties of Copper oxide. The SEM analysis revealed that the particles were to spherical shape in undoped CuO and doping of Indium chloride into CuO, the cauliflower structure nanoparticles could be obtained by aggregation of tetragonal shaped nanoparticles.

***Corresponding Authors**
S. Arumugam,
E-mail: *****rajaramkram@gmail.com,
sarumugam_gri@yahoo.co.in,
Tel.: +91 9787150870; fax: +91 451 2454466.

Keywords: Doping Concentration, In doped CuO, Nano particle, Precipitation method.

Introduction

Copper oxides (Cu_2O and CuO) are important *p*-type multifunctional semiconductors that have attracted much technological and scientific attention as a result of their interesting size-dependent chemical and physical properties and wide applications in electronics, magnetism, optics, field emission devices, batteries, solar energy conversion, photovoltaic materials and gas sensors[1,2]. CuO has been widely used as the basis in high temperature superconductors, lithium ion electrode materials and giant magneto resistance materials. CuO was evaluated as a possible alternative to precious metal catalysts such as Platinum, Palladium and Rhodium for reactions [3]. Cu_2O nanoparticles with different sizes and morphologies have been prepared by using various methods, such as, precipitation, solvothermal, hydrothermal, chemical vapor deposition and electrodeposition [4].In the present study the characteristic behavior of In doped CuO nano particle has been studied by varying doping concentration of indium chloride.

Experimental procedure

Indium doped Copper oxide nano particles have been synthesized by precipitation method with 3, 5 and 7 wt% of indium chloride. 1M of copper (II) chloride dehydrate salt ($CuCl_2.H_2O$), 5 wt% (0.17048g) capping agent of Di ammonium Citrate and Indium chloride are dissolved in 100ml of double distilled water. The solution is stirred at room temperature for 15 minutes. After stirring, liquid ammonia hydroxide is added drop wise into the solution till the solution attains a pH value of 10. Precipitation may occur when an insoluble copper indium hydroxide is formed in the solution. The solution has been stirred for additional 2 hours at room temperature using the magnetic stirrer apparatus. Later it was cooled to room temperature and then the precipitate was centrifuged and separated by successive repeated washing with double distilled water. After, the precipitation, the collected solid particle was dried at 60 $^{\circ}$C for 16 hours and calcinated at 500 $^{\circ}$C for 1 hour. Finally the dried indium doped copper oxide nano particles were obtained. The X-ray differaction pattern of the prepared indium doped copper oxide nano particles have recorded by using pan analytical XPERT-PRO X-ray diffractometer. The FTIR spectrum was recorded by using Perkin Elmer SPECTRUM BX II spectrometer, The optical properties of the films have been studied using PERKIN ELMER Lambda35 UV/Vis absorption spectrometer and The study of surface morphology have been carried out using VEGA3 TESCAN scanning electron microscope.

Results and Discussion
Structural Analysis

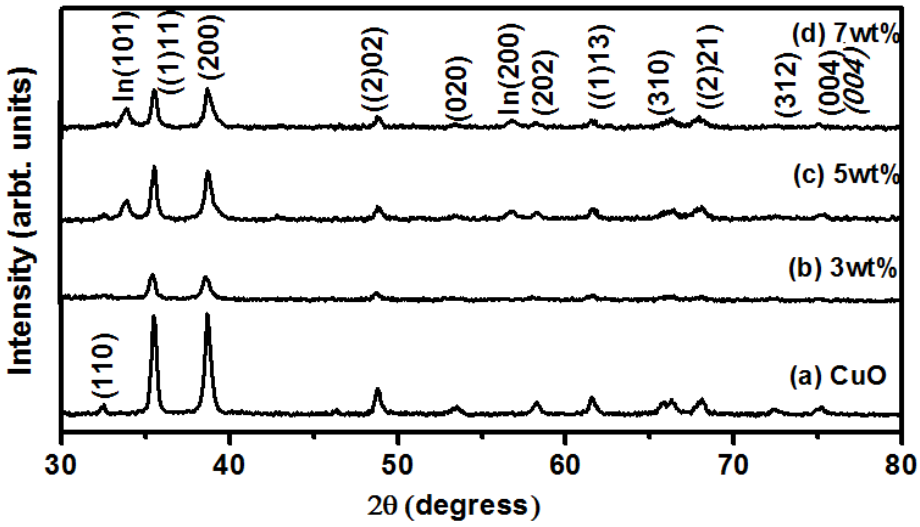

Fig.1 XRD patterns of (a) undoped CuO and (b) 3 (c) 5 and (d) 7 wt% of Indium chloride doped with CuO

In order to investigate the effect of In doping on the crystal structure of doped CuO nano particles XRD measurements are recorded. The curves a,b,c and d in Fig.1 represent the XRD patterns for the undoped CuO and CuO doped with 3, 5 and 7 wt% of Indium chloride respectively . From the XRD curves it is inferred that the particles are polycrystalline in nature and their 2θ values are 32.3 °, 35.5 °, 38.5 °, 48.74 °, 52.66 °, 58.53 °, 61.40 °, 66.07 °, 68.18 °, 72.40° and 75.2° which are corresponding to the reflections from (110), ($\bar{1}11$), (200),(202),(020),(202),($\bar{1}13$),(310)(221),(312) and (004) planes respectively and of monoclinic in nature. Referring fig.1 (b–d), the intensities of the indium doped CuO's preferred orientations are found to have a initial decrease for 3wt% and the intensity rose to a maximum for 5wt% doping and further increase to 7wt% doping resulted with decrease in intensity compared with the undoped CuO orientations recorded as curve a. Reflections corresponding to the crystallinity of indium have been detected for doping level of 3, 5, 7 wt% and 2θ values of 33.81° and 56.75° corresponding to the reflections from (101) and (200) planes of indium particles, which are of tetragonal in nature. For 3wt% the presence of indium peak was hardly noticed. For 5wt% the indium peak corresponding to 2θ of 33.8° and 56.75° were found to be prominently appearing. For 7wt% the indium peak intensity almost remains the same as well as for 5wt%. Hence it could be concluded that an optimum doping of 5wt% of indium chloride doping provides a better crystallinity character for the nano particle systems.

FT-IR spectroscopy

The FTIR spectrum for undoped CuO and indium doped CuO (b-d) have been observed to be in identical band positions and the only change notices is in their observed intensities. The absorption peak around 532 cm^{-1} is mainly attributed to the presence of CuO stretching vibration in the nanoparticles. The absorption at 592 cm^{-1} could be attributed to the Cu–O vibration stretching of the prepared nanoparticles systems [6]. With addition of Indium in the CuO nano particles, the intensity corresponding to the CuO stretching bond is increased upto 5 wt% of Indium chloride and then the intensity gets decreased, which reveals that structural modifications due to the presence of indium. The absence of peak at 610 cm^{-1} reveal the there is negligible formation of Cu_2O nano particles in the present investigations. The observed stretching vibrations in the region 1000–1200 cm^{-1} is may be assigned due to the presence of C=O stretching. The intense absorption peak around 1500–1600 cm^{-1} is could be assigned to the second generation of OH^- groups in the prepared systems. The peak around 2893 and 2931 cm^{-1} are ascribed due to the hydrogen bonding. The intense peak about 3402 cm^{-1} is mainly attributed the presence of OH stretching vibrations in the present investigated nano particles. Hence it is conclude that the 5wt% indium chloride doping is found to be an optimum doping level, in the making of indium doped copper oxide nanoparticles. A similar conclusion has been arrived at in the XRD analysis also.

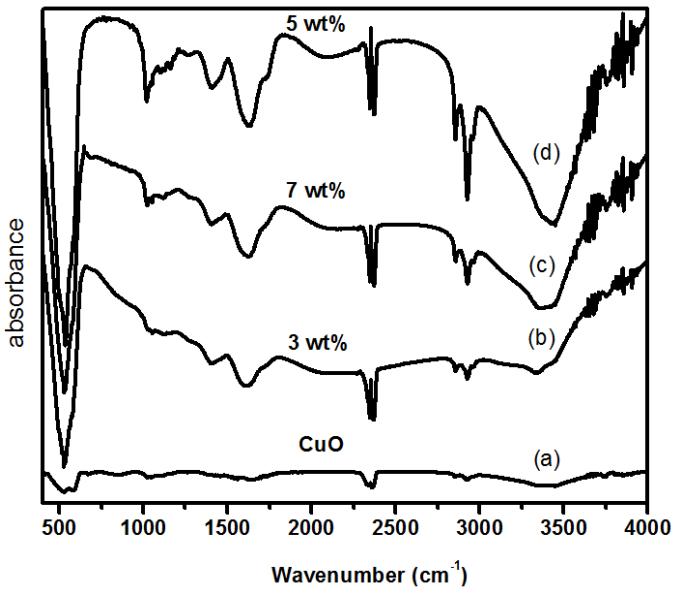

Figure. 2 FT-IR spectrum of undoped (a) CuO and (b) 3 (c) 7 and (d) 5 wt% of Indium doped with CuO.

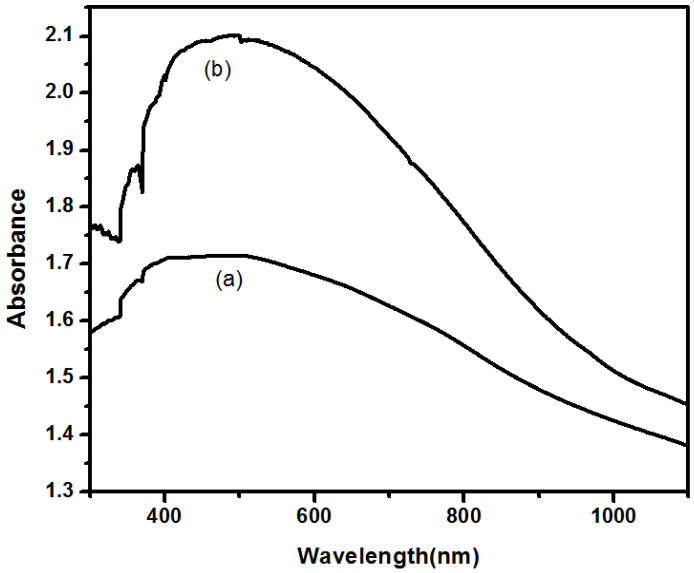

Fig 3. UV–Visible spectra of a) CuO and b) In doped CuO nanoparticles.

Optical and Surface Studies

The optical absorption in solid or liquid occurs by two mechanisms the photon energy can be absorbed by either lattice or by electrons where the transferred energy is conserved. Figure 3 depicts optical absorption spectrum of undoped CuO and 5 wt% of In doped CuO nanoparticles. As prepared CuO nano particle and In doped CuO nano particle exhibit an optical absorption band in the visible region. The sharp absorption edges of the as prepared CuO and In doped are found to be 440 and 480 nm, respectively. Furthermore these sharp absorption edges of the prepared samples are due to crystalline nature of the nano systems. It is observed that the fundamental absorption edges are shift back and forth with the addition of In in the CuO nano particles which is the evident of structure rearrangement of CuO nanoparticles. Resulting, it is observed that the doping concentration of indium chloride has a influence on the optical properties of undoped copper oxide for the particular doping level of 5wt%.

Figure 4 a shows the surface morphology images of undoped CuO and In doped CuO nanoparticles synthesized at the doping level 5wt% of Indium chloride. The micrographs reveal that the undoped CuO nano particles were found in orderly form with aggregated fine grains of Spherical and ellipsoidal shape of size about 50 nm (fig.4a). The concentration of 5 wt% indium doped to CuO has an impact on the particle size and the shape of the particles which is formed to tetragonal shape of size about 100 nm (Fig 4b). At 2μm scale the tetragonal particles are aggregated which is look like that cauliflower shape.

Conclusions

In summary, a precipitation method for the preparation of In doped CuO nanoparticles has been successfully synthesized. The XRD analysis reveals that the particles are polycrystalline in nature. The FTIR spectrum explores the presence of CuO stretching vibration in the nanoparticles. SEM analysis reveals that the size of undoped CuO and In doped CuO nanoparticles were found to be about 50 nm and 100nm respectively. The undoped CuO nano particle Spherical and ellipsoidal shapes can be obtained. By doping 5wt% of Indium chloride into CuO, the cauliflower structure nanoparticles synthesized by aggregation of tetragonal shaped nanoparticles. It could be obtained by easily preparation of precipitation method.

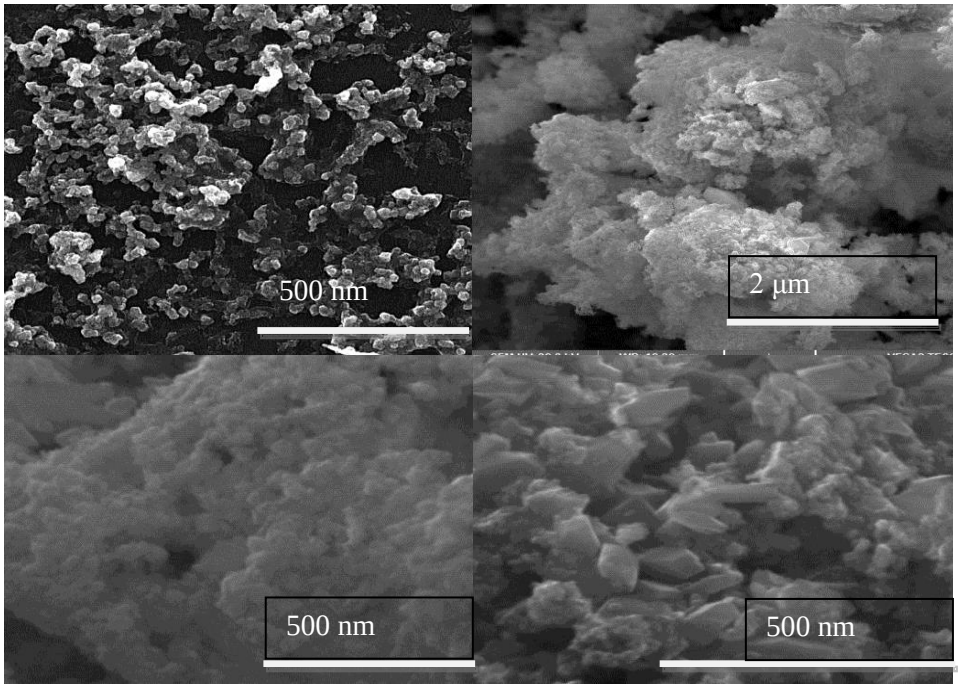

Figure 4. SEM images of (a) undoped CuO and b, c and d of 5 wt% Indium doped with CuO

References

[1] X. Wang, F. Zhang, B. Xia, X. Zhu, J. Chen, S. Qiu, P. Zhang, J. Li, Solid State Sci 11, 655–659 (2009).
[2] S. Kose, E. Ketenci, V. Bilgin, F. Atay, I. Akyuz, Curr Appl; Phy 1, 6 (2012).
[3] J. Pike, S. W. Chan, F. Zhang, X. Wang, J. Hanson, Appl Catalysis A: General 303 (2006) 273–277.
[4] R. Wu, Z. Ma, Z. Gua, Y. Yang, J. Alloys and Compounds 504, 45–49 (2010).
[5] Johan, M. R.; Suan, M. S. M.; Hawari, N.L.; Ching, H. A. Int J Electrochem Sci, 6, 6094 (2011).
[6] J. Zhu, D. Li, H. Chen, X. Yang, L. Lu, X. Wang, Mater Lett 58, 3324–3327 (2004)

Publication History
Received 25th Nov 2013
Revised 08th Feb 2014
Accepted 10th Mar 2014
Online 29th Apr 2014