

Synthesis and optical characterization of copper oxide nanoparticles

Amrut. S. Lanje^{1*}, Satish J. Sharma², Ramchandara B. Pode³, Raghumani S. Ningthoujam⁴

¹Department of Electronics, Dr. Ambedkar College, Chandrapur- 442 401, India

²Department of Electronics, R.T. M. Nagpur University, Nagpur- 440 033, India

³Department of Physics, Kyung Hee University, Seoul- 130 701, Korea

⁴Chemistry Division, Bhabha Atomic Research Center, Mumbai- 400 085, India

ABSTRACT

Copper oxide (CuO) nanoparticles are synthesized by aqueous precipitation method using copper acetate as a precursor and NaOH as a stabilizing agent. This gives a large scale production of CuO nanoparticles easily. X-ray diffraction pattern (XRD) reveals single phase monoclinic structure. Scanning electron microscopy (SEM) showed the rectangular morphology of as prepared CuO nanoparticles. The transmission electron microscopy (TEM) showed 5-6 nm size of as prepared CuO nanoparticles. Photoluminescence (PL) showed band edge emission at 398 nm and green emission at 527 nm. The band edge-absorption peak is found to be at 355 nm.

Keywords: Nanoparticles, Precipitation, Copper oxide, Photoluminescence.

INTRODUCTION

The oxides of transition metals are an important class of semiconductors, which have applications in magnetic storage media, solar energy transformation, electronics and catalysis [1-9]. 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 % [10]. CuO is a semiconducting compound with a narrow band gap and used for photoconductive and photothermal applications [11]. However, the reports on the preparation and characterization of nanocrystalline CuO are relatively few to some other transition metal oxides such as zinc oxide, titanium dioxide, tin dioxide and iron oxide. Some methods for the preparation of nanocrystalline CuO have been reported recently such as the sonochemical method [12], sol-gel technique [13], one-step solid state reaction method at room temperature [14], electrochemical method [15], thermal decomposition of precursors [16] and co-implantation of metal and oxygen ions [17] and so on.

In this paper, we have synthesized CuO nanoparticles by simple aqueous precipitation method with size 5-6 nm. The synthesized nanoparticles were characterized by XRD, SEM, TEM and PL spectrometer.

METHODS AND MATERIALS

2.1 Chemicals

All chemicals used in the experiment are analytic reagent grade. Copper acetate monohydrate $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ and acetic acid glacial were purchased from Merck, India. Sodium hydroxide NaOH (pellets) was purchased from Lobha Chemie. Deionized water was used throughout the experiment.

2.2 Synthesis

Aqueous solution of copper acetate (0.02 mol) is prepared in round bottom flask. 1 ml glacial acetic acid is added to above aqueous solution and heated to 100°C with constant stirring. About 0.4 g of NaOH is added to above heated solution till pH reaches to 6-7. The large amount of black precipitate is formed immediately. It is centrifuged and washed 3-4 times with deionized water. The obtained precipitate was dried in air for 24 h.

2.3 Characterization

The powder X-ray diffraction (XRD) was performed using Philips Holland, XRD system PW 1710 with nickel filtered CuK_α ($\lambda = 1.5405 \text{ \AA}$) radiation. The average crystallite size (t) has been calculated from the line broadening using Scherrer's relation: $t = 0.9\lambda / B\cos\theta$, where λ is the wavelength of X-ray and B is full width of half maximum (FWHM). Photoluminescence (PL) measurements were performed by F-4500 FL spectrophotometer with 150 W xenon lamp at room temperature. Powder samples are spread over a glass slide and mounted inside the sample holder. The morphology of CuO nanoparticles was studied using scanning electron microscope (JEOL JSM 5600). The transmission electron microscopy (TEM) was performed with Tecnai 20 G² under 200 KV. Samples are prepared by dispersing drop of colloid on copper grid, covered with the carbon film and the solvent is evaporated.

RESULTS AND DISCUSSION

3.1 XRD study

XRD pattern of as prepared CuO nanoparticles is shown in figure 1. It gives a single-phase with a monoclinic structure. Lattice parameters are $a = 4.84 \text{ \AA}$, $b = 3.47 \text{ \AA}$, $c = 5.33 \text{ \AA}$. The intensities and positions of peaks are in good agreement with the reported values (JCPDS file No. 05-661).

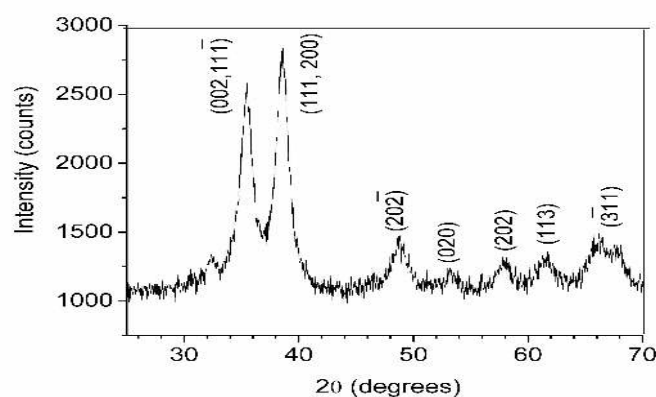


Fig. 1: XRD of CuO nanoparticles

No peaks of impurities are found in XRD pattern. The peaks are broad due to the nano-size Effect. The average crystallite size of CuO nanoparticles is found to be 8 nm using Scherrer formula.

3.2 SEM and TEM study

Figure 2 shows the SEM image of as prepared CuO nanoparticles. It shows that the CuO nanoparticles are in rectangular shape. Figure 3 (a) shows the TEM image of as prepared nanoparticles. The size of particle observed in TEM image is in the range of 5-6 nm which is in good agreement with calculated by Scherrer formula using XRD. Figure 3 (b) shows the selected area diffraction pattern (SAED) of as prepared CuO nanoparticles. It shows that the particles are well crystallized. The diffraction rings on SAED image matches with the peaks in XRD pattern which also proves the monoclinic structure of as prepared CuO nanoparticles [18].

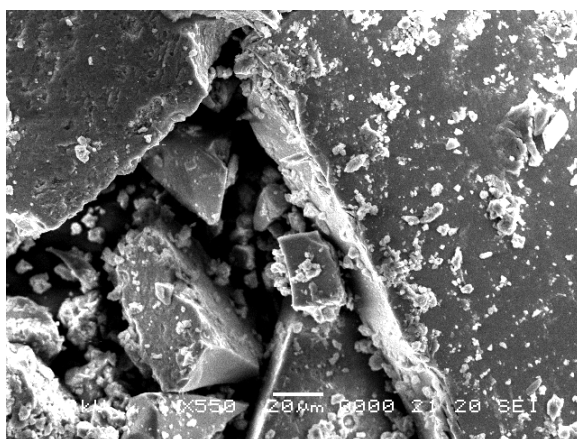


Fig. 2: SEM image of as prepared CuO nanoparticles.

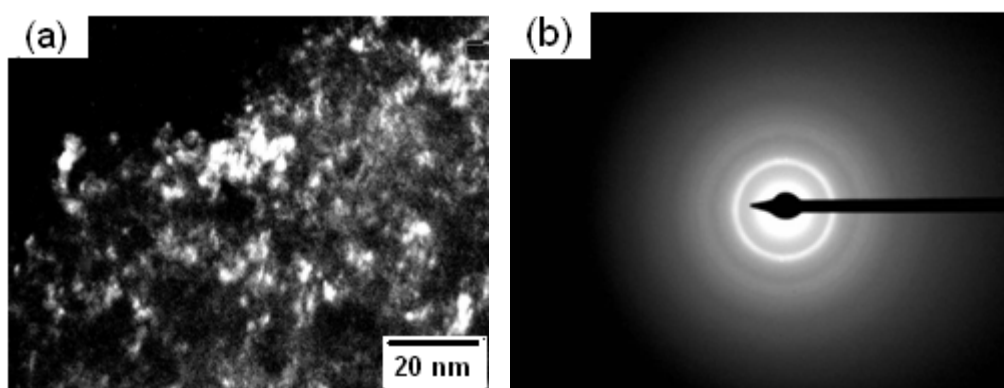


Fig.3: (a) TEM image, (b) SAED pattern of as prepared CuO Nanoparticles.

3.3 PL study

The room temperature photoluminescence spectra of as prepared CuO nanoparticles are shown in figure 4 after excitation at 330 nm. Three emission peaks are observed at 398 nm (violet), 470 nm (blue) and 527 nm (green) for CuO. The first one corresponds to the band-edge emission [19-21]. The second one is due to artifact. The third one arises from the singly ionized oxygen vacancy resulting in green emission of CuO materials because of recombination of a photo generated hole with a singly ionized electron in valence band [19, 22-24]. Figure 5 shows excitation spectra of CuO nanoparticles monitored at 470 nm. It is clearly observed that the

band-edge absorption is found at 355 nm. The band gap is found to be 3.5 eV which is higher than the reported values [21].

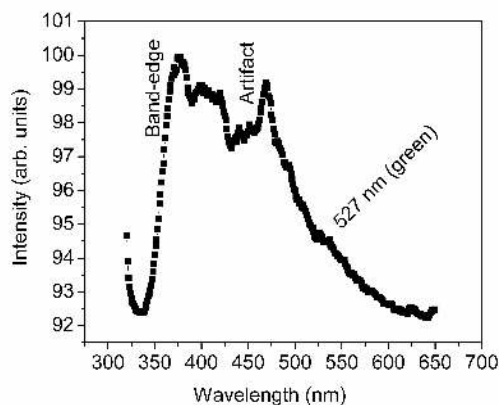


Fig. 4: Emission spectrum at 320 nm

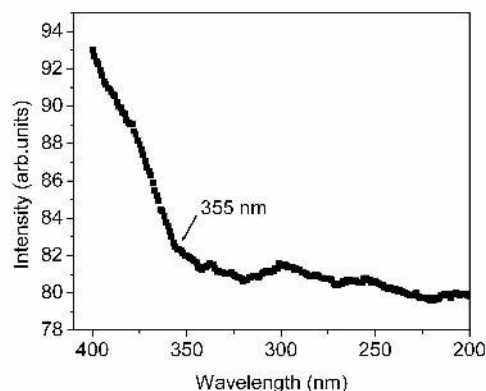


Fig. 5: Excitation spectrum at 470 nm

CONCLUSIONS

CuO nanoparticles with monoclinic structure are synthesized successfully by aqueous precipitation method. From SEM and TEM study, it is found that particles are rectangular in shape with average size of 5-6 nm. The band-edge emission peak is found at 398 nm and green emission peak is found at 527 nm. Green emission peak arises from the singly ionized oxygen vacancy of CuO materials because of recombination of a photo generated hole with a singly ionized electron in valence band. The band-edge absorption is found to be at 355 nm.

Acknowledgments

The authors wish to acknowledge financial support from UGC, New Delhi, for present research work. The authors are also grateful to Dr. Ajay Gupta, Center Director, Dr. N. P. Lalla and Dr. D. M. Phase, UGC-DAE Consortium for Scientific Research Center, Indore for facilitating the use of SEM and TEM. The author thanks to Dr. D. Das, Chemistry division, Bhabha Atomic Research Center, Mumbai for facilitating the use of photoluminescence equipments and Dr. R. R. Dahegaonkar, Principal, Dr. Ambedkar College, Chandrapur for providing laboratory facilities.

REFERENCES

- [1] A.S. Lanje, R.S. Ningthoujam, S.J. Shrama, R.K. Vatsa, R.B. Pode, *Int. J. Nanotechnol.*, **2010**, 7, 979.
- [2] E.P. Woltharth; *Ferromagnetic Materials*, Vol. II, North-Holland, Amsterdam, New York, Oxford, Tokyo, **1980**.
- [3] T. Mitsuyu, O. Yamakazi, K. Ohji, K. Wasa, *Ferroelectrics*, **1982**, 42, 233.
- [4] O. Regan, M. Gratzel, *Nature*, **1991**, 353, 737.
- [5] K. Naazeeruddin, A. Kay, M. Gratzel, *J. Am. Chem. Soc.*, **1993**, 115, 6832.
- [6] U. Bjoerksten, J. Moser, M. Gratzel, *Chem. Mater.* **1994**, 6, 858.
- [7] W.P. Dow, T.J. Huang, *J. Catal.*, **1996**, 160, 171.
- [8] P.O. Larsson, A. Andersson, R.L. Wallengerg, B. Svensson, *J. Catal.*, **1996**, 163, 279.
- [9] Y. Jiang, S. Decker, C. Mohs, K.J. Klabunde, *J. Catal.* **1998**, 180, 24.
- [10] S. Lee, U.S. Choi, S. Li, J.A. Eastman, *J. Heat Transfer*, **1999**, 121, 280.
- [11] A.E. Rakhshni, *Solid State Electron.*, **1986**, 29, 7.
- [12] R.V. Kumar, Y. Diamant, A. Gedanken, *Chem. Mater.*, **2000**, 12, 2301.

- [13] A. A. Eliseev, A.V. Lukashin, A. A. Vertegel, L.I. Heifets, A. I. Zhirov, Y. D. Tretyakov, *Mater. Res. Innov.*, **2000**, 3, 308.
- [14] J.F. Xu, W. Ji, Z.X. Shen, S.H. Tang, X.R. Ye, D.Z. Jia, X.Q. Xin, *J. Solid State Chem.*, **2000**, 147, 516.
- [15] K. Borgohain, J.B. Singh, M.V. Rama Rao, T. Shripathi, S. Mahamuni, *Phys. Rev.*, **2000**, 61, 11093.
- [16] J.Q. Yu, Z. Xu, D.Z. Jia, Chin. J., *Func. Mater. Instrum.*, **1999**, 5, 267.
- [17] S. Nakao, M. Ikeyama, T. Mizota, P. Jin, M. Tazawa, Y. Miyagawa, S. Miyagawa, S. Wang, L. Wang, *Rep. Res. Cent. Ion Beam Technol.*, Hosei Univ. Suppl., **2000**, 18, 153.
- [18] H. Wang, J. Zhang, J. J. Zhu, H. Y. Chen, *J. Cryst. Growth*, **2002**, 244, 88.
- [19] R. S. Ningthoujam, N. S. Gajbhiye, A. Ahmed, S. S. Umre, S. J. Sharma, *J. Nanosci. Nanotech.*, **2008**, 8, 3059.
- [20] L. R. Singh, R. S. Ningthoujam, V. Sudarsan, S. D. Singh, S. K. Kulshreshtha, *J. Lumin.*, **2008**, 128, 1544.
- [21] R. S. Ningthoujam, V. Sudarsan, S. K. Kulshreshtha, *J. Lumin.* **2007**, 127, 747.
- [22] K. Vanheusden, W. L. Warren, C. H. Seager, D. R. Tallant, J. A. Voigt, B. E. Gnade, *J. Appl. Phys.*, **1996**, 79, 7983.
- [23] A.S. Lanje, S.J. Shrama, R.B. Pode, R.S. Ningthoujam, *Arch. Appl. Sci. Res.*, **2010**, 2, 127.
- [24] A.S. Lanje, S.J. Shrama, R.B. Pode, *Arch. Phy. Res.*, **2010**, 1 (1), 49.