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Synthesis of Nanosized Copper Oxide by Assimilating Microwave Radiation and its Characterizations

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ABSTRACT

Copper oxide (CuO) nanoparticles have been successfully synthesized by microwave assisted - precipitation technique. In terms of advanced nanostructure synthesis, microwave method in which copper hydroxide nanostructures are produced in the precursor solution and sequentially transformed by microwave into CuO may be considered as a promising method. To explore, the blend of two methods adopted was very simple and reliable. This gives a large scale production of CuO nanoparticles easily with a brilliant band gap of 1.55 eV. This method produces not only large quantities of nano yield in a short reaction time but also high-quality materials with advanced properties. The structural, morphological, and optical properties of CuO nanoparticles have been studied and reported.

Key words: *Nanoparticles, Band gap, Morphology, Metal oxides nanostructures, Microwave assimilation.*

1. INTRODUCTION

The metal oxides are major class of semiconductors. Copper oxide (CuO), is a well-known p-type semiconducting metal oxide among them, having narrow band gap. The results of earlier works focused on the synthesis and applications of this nanomaterial in several fields [1-6], in various morphologies [7-10], and different preparation methods [11-14]. Along with these methods, microwave-assisted synthesis is typically quite fast, simple, and energy-efficient. The power, heating time, and irradiation cycles are the key parameters of a microwave oven and each of them may have a strong effect on the structure and properties of the products. To the best of our knowledge, there have been few reports on the synthesis of CuO nanopowder which have considered the potential relations between the microwave power and the morphology of materials [15]. In this work, feather-like morphologies of CuO nanopowder were obtained by microwave-assisted synthetic route, using copper sulfate as the precursor without any surfactant and sodium hydroxide as stabilizing agent. The phase, structures, and morphologies of the as-prepared products were investigated by X-ray diffraction (XRD) analysis and scanning electron microscopy (SEM). Optical properties have been studied by ultraviolet-visible (UV-Vis) spectrophotometer.

2. EXPERIMENTAL

2.1. Synthesis of CuO Nanopowder

Analytical grade of cupric sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) and sodium hydroxide (NaOH) were purchased from Loba Chemie Pvt. Ltd., Mumbai, India. It has been used as precursors and stabilizing agent, respectively. Double distilled water was used as solvent. In a typical reaction, 0.5 M sodium hydroxide solution was added dropwise to 0.1 M of copper sulfate aqueous solution in the ratio of 1:3 and stirred for 15 min. The resulting solution is kept in a domestic microwave oven (operated with frequency 2.45 GHz and power 800 W) for 10 min and cooled down to room temperature. The obtained colloidal precipitate is black in color. The final product was separated by centrifugation, washed with distilled water, and absolute ethanol 4-5 times. In the end, acetone washing is used to remove the organic impurities and then dried at 40°C for 24 h.

3. RESULTS AND DISCUSSION

3.1. XRD Analysis

XRD pattern of synthesized CuO nanoparticles is shown in Figure 1. It gives a single-phase monoclinic structure. The obtained parameters are a = 4.683 Å, b = 3.473 Å, and C = 5.122 Å with volume cell of 82.14 Å. 10 distinct diffraction peaks can be seen at 2θ values of 32.56, 35.59, 38.82, 48.24, 53.50,

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58.41, 61.56, 68.1, 72.42, and 75.28. These values are consistent with the values reported in literatures [16] and with the respective Joint Committee on Powder Diffraction Standards No.45-0937. No peaks of impurities are found in XRD pattern. The average crystallite size of CuO nanoparticles is found to be 12-14 nm using Scherrer formula.

3.2. Structural Studies

Figure 2 shows the SEM image of the prepared CuO nanoparticles. The size and morphology CuO nanoparticles have been examined by SEM. It shows that the CuO nanoparticles are in feather shape. SEM micrographs clearly show the surface features, by which it highlights that CuO nanoparticle was successfully prepared and it can be seen that the particles congregate together and the size of which is within 50 nm.

3.3. Fourier Transform Infrared (FTIR) Analysis

The prepared CuO nanomaterials were examined by FTIR analysis and FTIR spectra are shown in Figure 3. There are two absorbance bands which appear at around 650 and 3600-3100 cm^{-1}. Sharp absorption band at 650 cm^{-1} is associated with Cu-O stretching mode. A broad band in the range of 3600-3100 cm^{-1} is due to the stretching in water molecules associated with CuO. Thus, FTIR result suggests the presence of Cu-O bonds and some constitutional water is incorporated in the CuO structure. Thus, the formation of CuO is confirmed from the FTIR study.

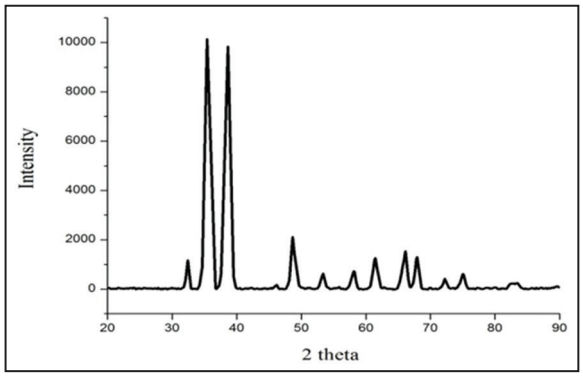

Figure 1: Powder X-ray diffraction spectrum for pure copper oxide nanoparticles.

3.4. Optical Studies

UV-vis absorption spectrum for pure CuO nanoparticles is shown in Figure 4. In UV-vis, high energy electromagnetic radiation in the wavelength range of 190-800 nm is utilized to promote electrons to higher energy orbitals. From the UV spectra, it is clear that the absorbance decreases with increase in wavelength. This decrease in the absorption indicates the presence of optical band gap in the material.

To study the optical properties of the synthesized CuO nanoparticles, the band gap and the type of electronic transitions were determined. When a semiconductor absorbs photons of energy larger than the gap of the semiconductor, an electron is transferred from the valence band to the conduction band there occurs an abrupt increase in the absorbency of the material to the wavelength corresponding to the band gap energy. The relation of the absorption coefficient (α) to the incidental photon energy depends on the type of electronic transitions. When in this transition, the electron momentum is conserved, the transition is direct, but if the momentum does not conserve in this transition it must be attended by a photon this is an indirect electronic transition. To analyze the electronic properties of the synthesized CuO, we have used Tauc's plot relation (Figures 5 and 6) [17].

The indirect band gap of synthesized CuO nanoparticles (1.55 eV) shows slight higher values of already reported CuO nanoparticles (1.2 eV) and the values are red shifted compared to bulk value (1.8 eV) due to the formation of surface defects. The direct band gap (1.75 eV) is higher as compared to bulk values; this blue shift in the direct band gap is due to the quantum confinement effect. Optical absorption shows that the direct band gap versus indirect band gap permits the determination of the crystallinity of material. If the direct band gap is higher as compared to indirect band gap the materials will be crystalline in nature. Therefore, the CuO nanoparticles prepared in this study are crystalline in nature [18].

4. CONCLUSION

We have successfully synthesized CuO nanoparticles using microwave assisted- precipitation technique.

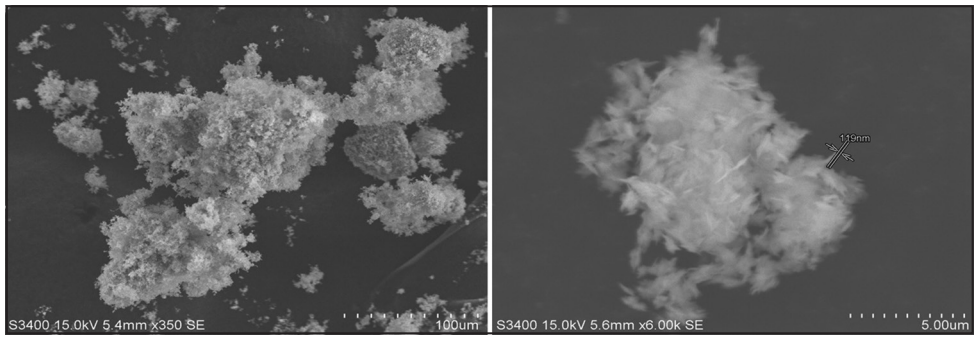

Figure 2: Scanning electron microscopy images for pure copper oxide nanoparticles.

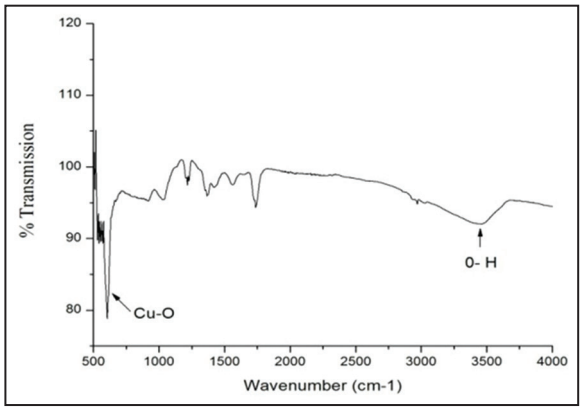

Figure 3: Fourier transform infrared spectra of the prepared copper oxide nanomaterial.

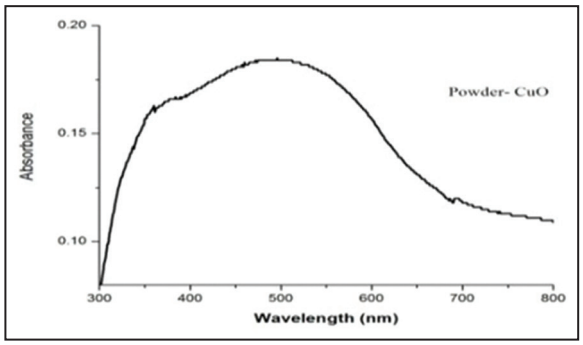

Figure 4: Ultraviolet-visible spectra of copper oxide nanoparticles.

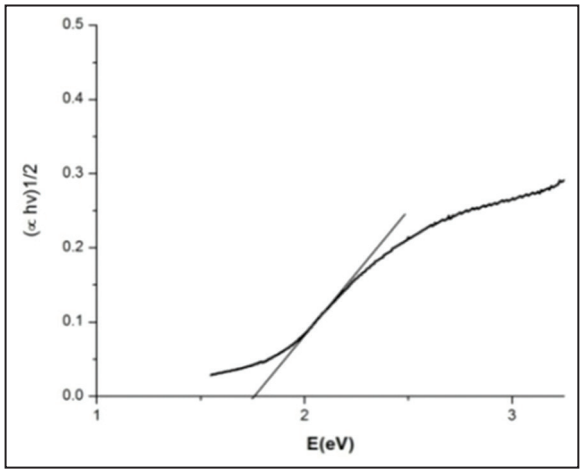

Figure 5: Tauc's plot of direct transitions.

XRD spectra confirmed the formation of single phase CuO nanoparticles. Crystallite size was found that 12-14 nm. SEM results support well with XRD results. FTIR spectra also validated the purity of CuO nanoparticles. Finally, we have accomplished with highly crystalline feather-like CuO nanoparticles in minimum band gap energy.

5. ACKNOWLEDGMENTS

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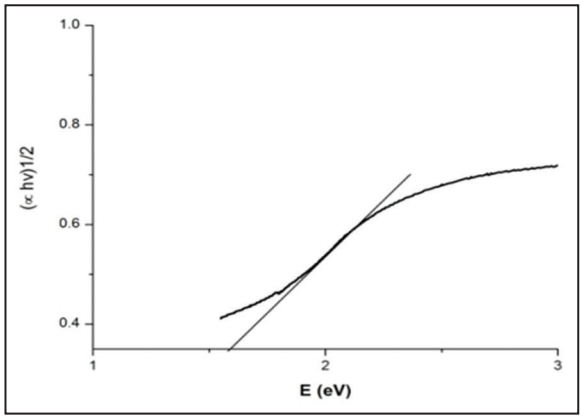

Figure 6: Tauc's plot of indirect transitions.

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6. REFERENCES

1. Y. M. Li, J. Liang, Z. L. Tao, J. Chen, (2008) CuO particles and plates: Synthesis and gas-sensor application, ***Materials Research Bulletin***, **43:** 2380-2885.
2. H. X. Zhang, M. L. Zhang, (2008) Synthesis of CuO nanocrystalline and their application as electrode materials for capacitors, ***Materials Chemistry and Physics,*** **108:** 184-187.
3. T. I. Arbuzova, B. A. Gizhevskii, S. V. Naumov, A. V. Korolev, V. L. Arbuzov, K. V. Shal'nov, A. P. Druzhkov, (2003) Temporal changes in magnetic properties of high-density CuO nanoceramics, ***Journal of Magnetism and Magnetic Materials*****, 258-259:** 342-344.
4. P. Gao, Y. J. Chen, H. J. Lu, X. F. Li, Y. Wang, Q. Zhang, (2009) Synthesis of CuO nanoribbon arrays with noticeable electrochemical hydrogen storage ability by a simple precursor dehydration route at lower temperature, ***International Journal of Hydrogen Energy,*** **34:** 3065-3069.
5. T. Maruyama, (1998) Copper oxide thin films prepared by chemical vapor deposition from copper dipivaloylmethanate, ***Solar Energy Materials and Solar Cells,*** **56:** 85-92.
6. D. Barreca, P. Fornasiero, A. Gasparotto, V. Gombac, C. Maccato, T. Montini, E. Tondello, (2009) The potential of supported Cu_2O and CuO nanosystems in photo catalytic H2 production, ***ChemSusChem***, **2:** 230-233.
7. W. Jisen, Y. Jinkai, S. Jinquan, B. Ying, (2004) Synthesis of copper oxide nanomaterial's and the growth mechanism of copper oxide nanorods, ***Materials and Design,*** **25:** 625-629.
8. M. Kaur, K. P. Muthe, S. K. Despande, S. Choudhury, J. B. Singh, N. Verma, S. K. Gupta, J. V. Yakhmi, (2006) Growth and branching of CuO nanowires by thermal oxidation of copper, ***Journal of Crystal Growth,*** **289:** 670-675.
9. C. L. Zhu, C. N. Chen, L. Y. Hao, Y. Hu,

Z. Y. Chen, (2004) Template - free synthesis of Cu2Cl(OH)3 nanoribbons and use as sacrificial template for CuO nanoribbon, ***Journal of Crystal Growth,* 263:** 473-479.

10. X. Song, H. Yu, S. Sun, (2005) Single-crystalline CuO nanobelts fabricated by a convenient route, ***Journal of Colloid and Interface Science,* 289:** 588-591.
11. Z. Liu, Y. Yang, J. Liang, Z. Hu, S. Li, S. Peng, Y. J. Qian, (2003) Synthesis of copper nanowires via a complex-surfactant- assisted hydrothermal reduction process, ***The Journal of Physical Chemistry B,* 107:** 12658-12661.
12. R. V. Kumar, Y. Mastai, Y. Diamant, A. Gedanken, (2001) Sonochemical synthesis of amorphous Cu and nanocrystalline Cu2O embedded in a polyaniline matrix, ***Journal of Materials Chemistry,* 11:** 1209-1213.
13. G. G. Condorelli, L. L. Costanzo, I. L. Fragala, S. Giuffrida, G. Ventimiglia, (2003) A single photochemical route for the formation of both copper nanoparticles and patterned nanostructured films, ***Journal of Materials Chemistry,* 13:** 2409-2411.
14. S. Kapoor, T. Mukherjee, (2003) Photochemical formation of copper nanoparticles in poly (N-vinylpyrrolidone), ***Chemical Physics Letters,* 370:** 83-87.
15. Y. L. Min, T. Wang, Y. C. Chen, (2010) Microwave-assistant synthesis of ordered Cuo micro-structures on Cu substrate, ***Applied Surface Science,* 257:** 132-137.
16. D. P. Volanti, D. Keyson, L. S. Cavalcante, A. Z. Simoes, M. R. Joya, E. Longo, J. A. Varela, P. S. Pizani, A. G. Souza, (2008) Synthesis and characterization of CuO flower nanostructure processing by a domestic hydrothermal microwave, ***Journal of Alloys and Compounds,* 459:** 537-542.
17. J. K. Rao1, A. Raizada, D. Ganguly, M. M. Mankad, S. V. Satayanarayana, G. M. Madhu, (2015) Investigation of structural and electrical properties of novel CuO-PVA nanocomposite films, ***Journal of Materials Science,* 50:** 7064-7074.
18. A.A. Radhakrishnan, B.B. Beena, (2014) Structural and optical adsorption analysis of CuO nano particles, ***Indian Journal of Advances in Chemical Science,* 2 (2):** 158-161.

***Bibliographical Sketch**

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