Structure, Microstructure and Optical Absorption Analysis of CuO Nanoparticles Synthesized by Sol-Gel Route

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Abstract We report the synthesis of CuO nanoparticles using different solvents by a low cost sol-gel route. Evolution of structure, microstructure and optical absorption analysis of these nanoparticles were studied using X-ray diffraction (XRD) and UV-Visible spectrophotometer. XRD analysis indicated that the crystallite size and strain are higher for the CuO nanoparticle synthesized using propanol as solvent. Optical absorption analysis indicated the red shift of indirect band gap and the blue shift of direct band gap. In the present case, red shift is associated with the formation of surface defects whereas the blue shift is due to the quantum confinement effect seen for nanoparticle systems.

Keywords Transition Metal Oxide, Sol-Gel Route, Nanoparticle, Cuo

1. Introduction

In recent years, nanoscale metal oxides have attracted a great deal of research interest because of both fundamental and technological point of view. Among all the metal oxides, cupric oxide (CuO) has attracted considerable attention because of its peculiar properties. CuO has been used as a basic material in cuprate High-T_C superconductors as the superconductivity in these classes of systems is associated with Cu-O bondings[1,2]. Apart from this, CuO has investigated as potential material for nanofluid in heat transfer applications[3], catalysts for the water-gas shift reaction[4], steam reforming[5], CO oxidation of automobile exhaust gases[6], photocathodes for photoelectrochemical water splitting application[7] etc. For technological applications the detailed understanding of size, morphology controlled emergence of different properties are important.

The synthesis procedure plays crucial role in controlling the size, shape of the nanostructure and hence detecting different properties of the material. CuO nanoparticles have been prepared by wet-chemistry route[8], sonochemical preparation[9], alkoxidebased preparation[10], hydrothermal process[11], solid-state reaction in the presence of a surfactant[12] etc.

In the present study, we have synthesized CuO nanoparticles using different solvent by a low cost sol-gel process. The aim of the present paper is to study the effect of different solvent on the structure, microstructure and optical band gap of CuO synthesized by sol-gel route.

2. Experimental Methods

For the synthesis of CuO nanoparticles in sol-gel process, 5 gm of $Cu(NO_3)_2.H_2O$ is dissolved into 20 ml of ethanol. In order to see the effect of solvent, we use propanol instead of ethanol for the synthesis of another CuO nanoparticles. $Cu(NO_3)_2.H_2O$ dissolved in two different solvents separately stirred for 1 hour to obtained for the homogenious solutions. These solutions kept for 1 day for gel formation. Then the gels were dried at 200℃ and calcined at 300℃ for 1 hour in each step. Then the obtained powders pressed into pellets. Finally these pellets were annealed at 500℃ for 1 hour.

The structural and optical properties of the CuO nanoparticles were studied by using Bruker X-ray diffractometer (D8 Advance) and UV-Visible spectrophotometer (Simadzu, UV-2450) respectively.

3. Results and Discussion

3.1. Structure and Microstructure of CuO Nanoparticles

Figure 1 shows the XRD pattern of CuO nanoparticles synthesized by sol-gel route using ethanol and propanol as solvent. In both solvent cases all the obtained peaks in the XRD pattern are well matched with the monoclinic phase of CuO bulk crystals and well consistent with the JCPDS card (card no: 048-1548). No impurity peak related to any other phases of Cu like $Cu(OH)_2$, Cu_2O or Cu are seen in the ob-

served XRD pattern. Our XRD results thus confirm synthesis of pure and well crystalline CuO nanoparticles without any impurity. The obtained results are well consistent with the previously reported literature[13,14]. The XRD peaks broaden and shift to higher angles for the CuO sample prepared when propanol used as solvent. The peak shift could be due to strain generation in the materials medium during synthesis. Since two different batches CuO nanoparticles were synthesized using ethanol and propanol as solvent. The solvent might be influencing the microstructure of resultant CuO nanoparticle.

In order to understand the peak shift for CuO nanoparticle synthesized by both solvent cases, we carried out Williamson–Hall (W–H) analysis[15] of the FWHM (β) of various Bragg peaks appeared in the XRD pattern (Fig. 1). The W–H plot of $\frac{\beta \cos\theta}{\lambda}$ versus $\frac{2\sin\theta}{\lambda}$ gives the value of microstrain from the slope and particle size from the ordinate intersection. For pure particle size broadening this plot is expected to be a horizontal line parallel to the $\sin\theta$ axis, whereas in the presence of strain, it has a non-zero slope. Figure 2 shows the W–H plot for CuO nanoparticle synthesized with two different solvents. The obtained values of crystallite size and microstrain for CuO nanoparticles synthesized under different solvent are given in Table 1. As indicated from the Table 1, the crystallite size and strain is higher for the CuO nanoparticle synthesized using propanol as solvent. The shifting of XRD peaks to higher angle may be a consequence of stain effect.
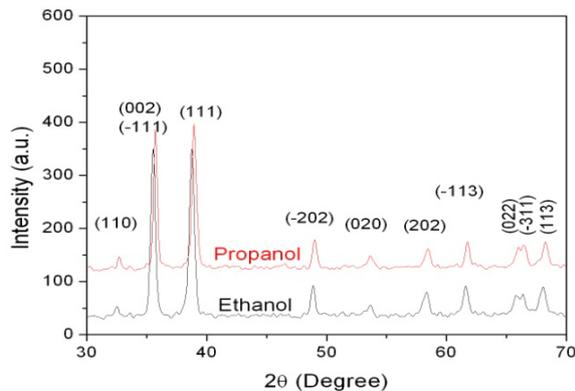
Figure 1. X-ray diffraction pattern of CuO nanoparticles synthesized by sol-gel route with different solvent as mentioned
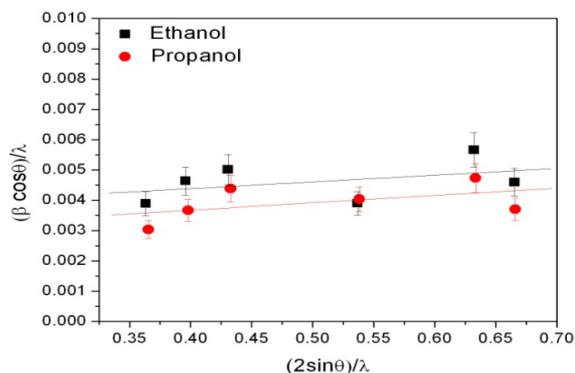

Figure 2. Williamson–Hall (W–H) plot for the CuO nanoparticles synthesized by sol-gel route with different solvent as mentioned

Table 1. Evolution of crystallite size and strain of CuO nanoparticles synthesized with different solvent as mentioned

Solvent	Crystallite Size (nm)	Strain (%)
Ethanol	28.57	0.22
Propanol	36.76	0.24

3.2. UV-Visible Characterization of CuO Nanoparticle

The variation of absorption coefficient, α of CuO nanoparticles as a function of wavelength is shown in Fig. 3. It is clearly seen from the figure that the absorption coefficient tends to decrease exponentially as the wavelength increases. This behaviour is typical for many semiconductors and can occur for a variety of reasons, such as internal electric fields within the crystal, deformation of lattice due to strain caused by imperfection and inelastic scattering of charge carriers by phonons[16-18]. The absorbance of CuO sample synthesized with propanol solvent shows faster exponential decrease indicating more strain generation in this case. The behaviour of absorbance shown in Fig. 3 is thus agreed with the strain analysis using W-H plot discussed above.
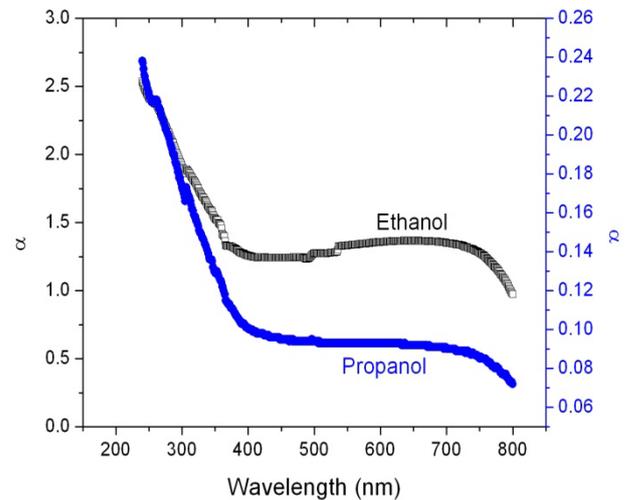

Figure 3. Variation of absorption coefficient of NiO nanoparticles as a function of wavelength

The optical band gap of CuO nanoparticles were extracted according to the following relation[19]:

$$\alpha = \frac{B(h\nu - E_g)^n}{h\nu} \tag{1}$$

where $h\nu$ is the incident photon energy, α is the absorption coefficient, B is a materials dependent constant and E_g is the optical band gap. The value of n depends on the nature of transition. Depending on whether the transition is direct allowed, direct forbidden, indirect allowed or indirect forbidden, n takes the value 1/2, 3/2, 2 or 3 respectively[20]. The usual method of determining E_g involves plotting $(\alpha h\nu)^{\frac{1}{n}}$ vs. photon energy, $h\nu$. Figure 4 and 5 show the variation of $(\alpha h\nu)^{\frac{1}{n}}$ vs. $h\nu$ for CuO nanoparticles with n values of 1/2 and 2 respectively. The values of direct and indirect band gap for CuO nanoparticles synthesized with different solvent are shown in Table 2. The indirect band gap of CuO nanoparticles synthesized using both

the solvents show similar values and the values red shifted ~ 0.24 to 0.27 eV as compared to bulk value (1.45 eV)[21]. The increasing red shift with decreasing particle size suggests that the defects responsible for the intra-gap states are primarily of surface defects[22-24]. Our results thus indicated that CuO nanoparticles prepared using ethanol as solvent show more surface defects as compared to the CuO nanoparticles prepared using propanol as solvent. Both the CuO samples show higher direct band gap as compared to bulk value (3.25 eV[24,25]). The blue shift in the direct band edges as seen in present case is due to the quantum confinement effect[24,26].
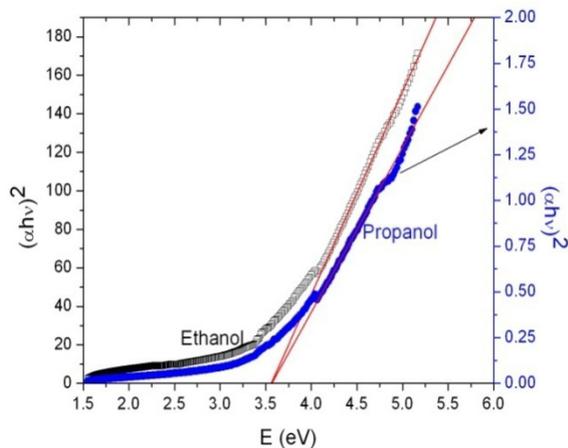
Figure 4. Variation of $(\alpha h\nu)^2$ vs. photon energy, $h\nu$ for CuO nanoparticles prepared sol-gel route with different solvent as mentioned
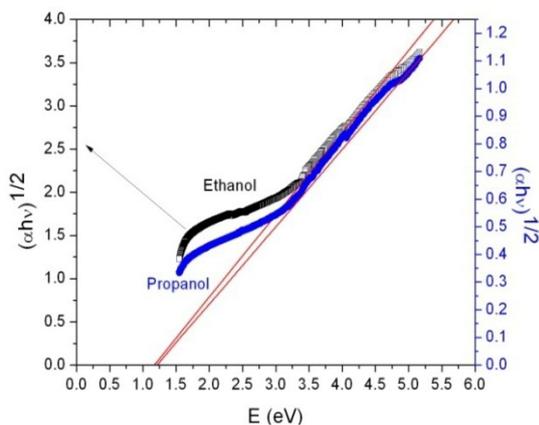
Figure 5. Variation of $(\alpha h\nu)^{1/2}$ vs. photon energy, $h\nu$ for CuO nanoparticles prepared sol-gel route with different solvent as mentioned

Table 2. Evolution of direct and indirect optical band gap of CuO nanoparticles synthesized with different solvent as mentioned

Solvent	Optical band gap (eV)	
	Direct	Indirect
Ethanol	3.57	1.18
Propanol	3.57	1.21

4. Conclusions

CuO nanoparticles were synthesized by a low cost sol-gel method. Effect of solvent on the structure, microstructure and optical absorption properties of CuO nanoparticles were studied. XRD analysis indicated that the crystallite size and strain are higher for the CuO nanoparticle synthesized using propanol as solvent. UV-Visible analysis also indicated the higher strain generation for CuO nanoparticle synthesized using propanol as solvent. Optical absorption analysis indicated that the both the CuO samples show red shift of indirect band gap due to the formation of surface defects. CuO nanoparticles on the other hand show higher direct band gap as compared to bulk value indicating blue shift of band gap due to the quantum confinement effect.

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