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Annealing effects on crystallite size and band gap of CuO nanoparticles

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Abstract

Annealing effects on particle size of the prepared CuO nanoparticles studied successfully. The prepared samples were annealed at different temperatures and analyzed using X-ray diffraction and UV-Vis absorption spectroscopy. The morphology of the as prepared product was analyzed using Scanning Electron microscopy(SEM). It was found that an increase in particle size with the increase in annealing temperature. The band gap of CuO nanoparticles determined with the help of Tauc plot and was cleared that band gap decreases with the increase of annealing temperature.

Keywords: CuO nanoparticles, Quantum confinement, XRD, SEM

1. INTRODUCTION

The study of nanomaterials is of great interest in science. It is great challenge to the researchers that the synthesis of uniform nanomaterials by simple procedures. Metal oxides nanoparticles such as CuO, ZnO, TiO_2 etc have attracts much interests due to their potential and technological applications [1, 2]. They exhibit properties that differ strongly from those of their bulk phases. CuO nanoparticles attracted much more attention than any other metal oxide nanoparticles because copper oxide is the simplest member of the family of copper compounds. It has excellent catalytic activity and is used in environmental catalysis [3, 4]. Copper oxide nanoparticles are used in wide range of applications which includes optoelectronic devices, microelecrochemical systems, field effect transistors, electrochemical cells, gas sensors, magnetic storage media, solar cells, field emitters and nanodevices for catalysis[5-11].

The reduced crystallite size of nanostructures influence the structural properties such as lattice symmetry and cell parameters. The quantum confinement effect in nanostructures are also the effect of their small size. By decreasing size particles change the colour, semiconducting materials exhibit metallic properties and nonmagnetic particles become magnetic [12]. Nanomaterials show high surface to volume ratio and quantum size effect due to their size [13]. CuO is a p-type semiconductor which exhibits a narrow band gap(1.2 eV). Monoclinic CuO belongs to a particular class of materials known as Mott insulator and their electronic structures cannot be explained using conventional theory [14, 15]. CuO composites such as CuO/ZnO, CuO/Cu_2O and CuO/SnO_2 could be employed in humidity and gas-sensors applications [16, 17]. Also copper oxide systems also attracted much interest due to their superconducting properties [18,19].

With the miniaturization of crystallite size, the fraction of suface atoms dominated and hence many features of the material were no longer constant and can be tunable with size [20]. The band gap of nanostructures can be tuned, which is of intense importance due its application in optical devices such as light emitters and laser diodes. Thermal annealing is one of the best methods to tune the band gap and grain size of nanostructures. The main objective of the present study is to investigate correlation of annealing temperature-grain size-bandgap of CuO nanoparticles.

2. EXPERIMENTAL

2.1. Materials

All the reagents were of of analytical grade and were used without further purification. All the solutions were prepared using double distilled water.

2.2. Characterization

The crystalline structure of the synthesized CuO was determined by Bruker AXS D8 Advance X-ray diffractometer employing Cu-Kα radiation.The UV-Visible absorption spectrum of CuO has been recorded by using double beam spectro photometer. The morphology of the prepared CuO nanoparticles was studied using the Quanta 200 FEG Scanning Electron Microscope.

2.3. Synthesis of CuO nanoparticles

CuO nanoparticles were synthesized by a precipitation method. In this method first, 300 mL of copper acetate aqueous solution was mixed with glacial acetic acid. The obtained solution was heated with vigorous stirring, and then suitable amount of solid NaOH was added into the above boiling solution till the pH reached about 8. Large amount of black precipitate was produced. After being cooled to room temperature the precipitate was centrifuged, washed once with distilled water and then with ethanol and dried in air at room temperature.

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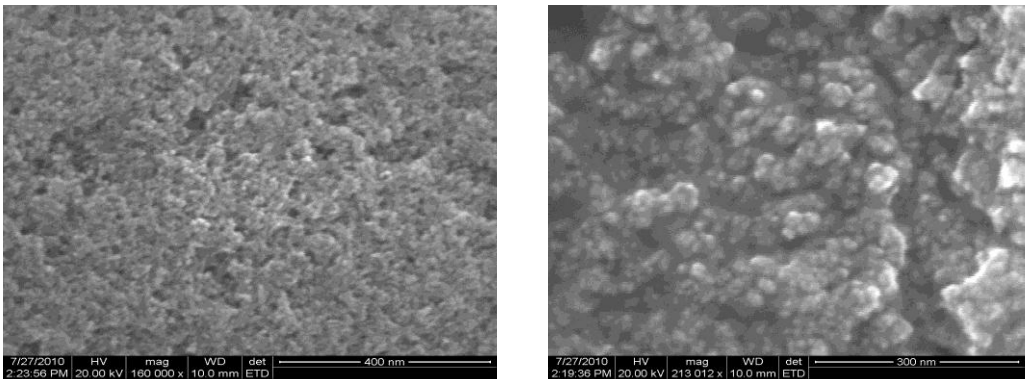
3. RESULTS AND DISCUSSIONS

The morphology of the as prepared sample can be analyzed by scanning electron microscopy (SEM). SEM image of the as prepared sample in both low resolution and high resolution is shown in Figure 1 (a) and (b) respectively. The images confirm that the prepared CuO is in the nano regime with spherical morphology. The high resolution SEM shows that the particle size is 7-8 nm.



(a) **(b)**

Figure 1: SEM image of the as prepared CuO nanoparticles

The x-ray diffraction studies were carried out to determine the structure and size of the CuO nanoparticle. Figure 2 represents the XRD pattern of the as prepared CuO nanoparticles. The diffraction data are in good agreement with JCPDS card of CuO (JCPDS 80-1268). The data shows that CuO nanoparticles have monoclinic structure. No peak of impurity is observed in the XRD pattern. The broadening of the peak indicates the small size of the product. The crystallite size is calculated using Scherer's formula $L = \frac{0.9\lambda}{\beta Cos\theta}$, where L is the crystallite size, λ is the wave length of X-ray used and θ is the Bragg angles of diffraction peak [21]. The crystallite size calculated for CuO nanoparticle is 8 nm. The crystallite size obtained from SEM and XRD are complementing each other.

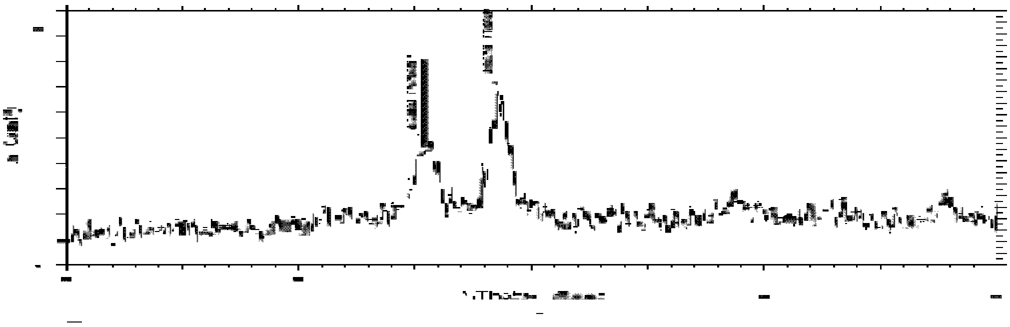


Figure 2: XRD pattern of the as prepared CuO nanoparticle

Annealing effect on CuO nanoparticles were studied. The obtained product is annealed at 300 °C and 600 °C. The following figures show the XRD pattern of the annealed samples.

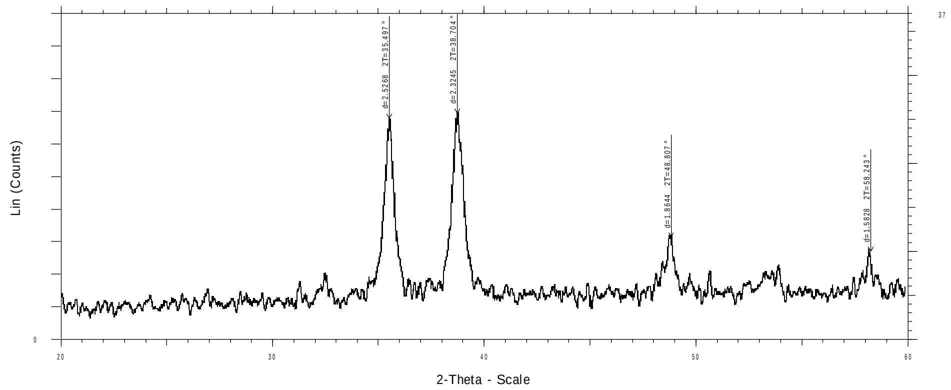


Figure 3: XRD pattern of the as prepared CuO nanoparticle annealed at 300°C

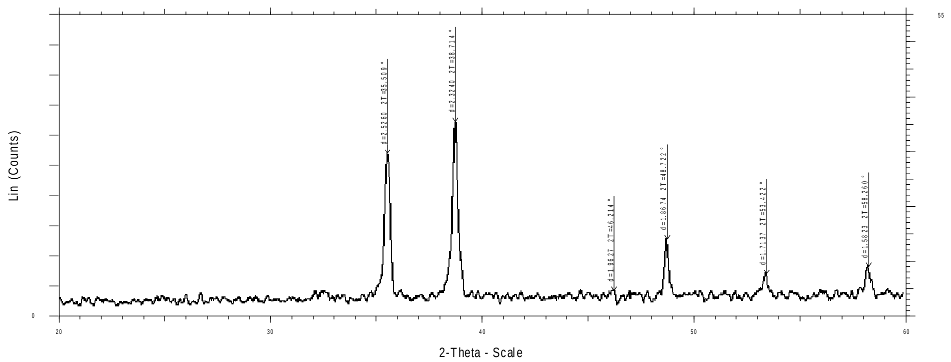


Figure 4: XRD pattern of the as prepared CuO nanoparticle annealed at 600°C

From these figures we can infer that CuO nanoparticles annealed at these temperatures maintain the monoclinic structure. The width of the peak decreases and more sharp peaks are obtained with increasing temperature which indicates the crystalline nature of the CuO nanoparticle increases with temperature. This is due to the fact that the diffusion of atoms from grain to grain boundary. Average particle size obtained for the particles annealed at 300 °C and 600 °C is 14.73 nm and 20.51 nm respectively. Figure 5 represents the variation of particle size with temperature. From the figure we can easily notice that the particle size increases with the increasing temperature.

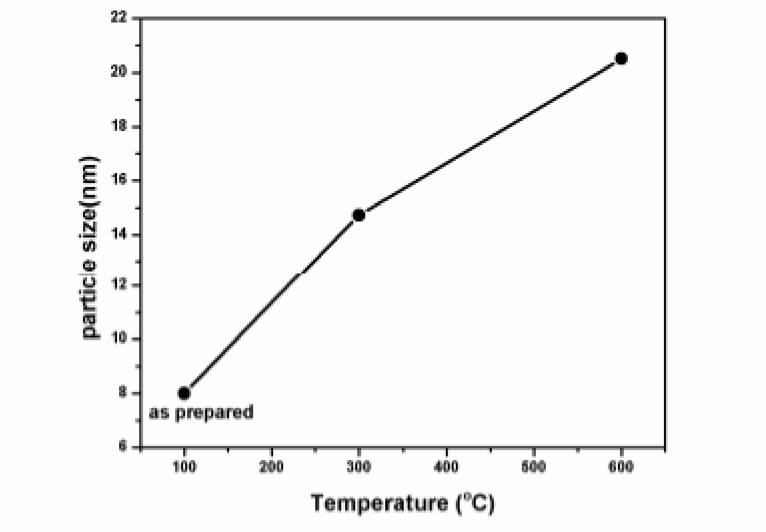


Figure 5: Variation of particle size with annealing temperature

In CuO nanoparticle, there are large numbers of vacancies of oxygen, vacancy cluster and local lattice disorder. When temperature increases, there is a rapid decrease in the density of vacant lattice sites and local lattice disorder. The volume of the unit cell coming towards the normal value hence the grain begins to grew [22]. Also during annealing, the powder sample fuse together under the influence of surface tension and therefore it shrinks as much as 30% in volume. These small particles agglomerate together and form large clusters.

Optical properties of CuO nanoparticles were calculated using UV-Vis absorption spectroscopy. The optical band gap of the as prepared CuO nanoparticle is calculated using the Tauc's relation $\alpha h\upsilon = (h\upsilon\text{-}Eg)^n$ where hυ is the incident photon energy, n is the exponent that determines the type of electronic transition causing the absorption and can take the values 1/2 and 2 depending whether transition is direct or indirect respectively. Figure 6 shows $(\alpha h\upsilon)^2$ versus hυ plot of absorption spectrum of CuO nanoparticles. The best linear relationship is obtained by plotting $(\alpha h\upsilon)^2$ against hυ indicating that the optical band gap of these CuO nanoparticle is due to a direct allowed transition. The value of the band gap is determined from the intercept of the straight line at a = 0, which is found to be 3 eV. This value is much higher than tha of bulk CuO(1.2 eV). Band gap energy increases with decreasing particle size due to quantum confinement effects. When photons are incident on the semiconductor material they will be absorbed only when the minimum energy of photons is enough to excite an electron from the valence band to conduction band or when the photon energy equal to the energy gap of the material. The prepared nanoparticles are highly confined and the absorption spectrum of it becomes more structured because its electronic band structure changes to molecular level with non vanishing energy spacing. So the material needs more energy for electronic transition from valence band to conduction band. Hence the band gap energy of CuO nanoparticles is more than that of the bulk.

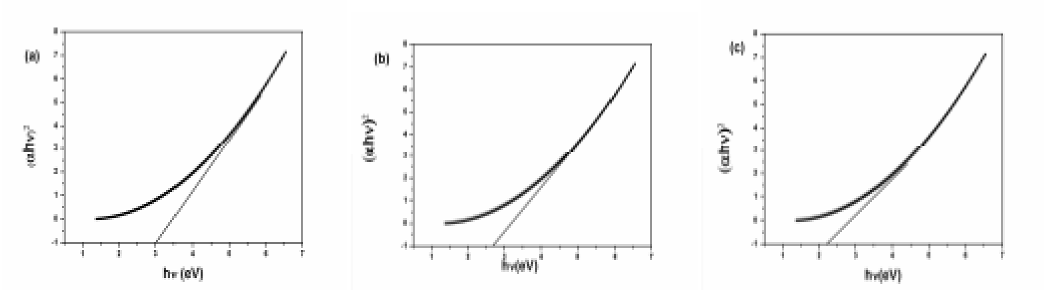


Figure 6: Tauc plots of (a) as prepared CuO nanoparticles, (b) CuO nanoparticles annealed at 300 ^{0}C, (c) CuO nanoparticles annealed at 600 ^{0}C

Figure 6 represents the tauc plots of as prepared and annealed samples. The band gap energy of each sample is depicted in table 1. From the table we can easily notice the relationship of the annealing temperature with the changes in band gap and particle size. The band gap decreases while particle size increases with increase in annealing temperature.

CuO	Particle size(nm)	Band Gap (eV)
As prepared	8	3
Annealed at 300 ºC	14	2.6
Annealed at 600 ºC	20	2.2

The band gap energy of CuO nano particle decreases with increasing particle size. Also energy gap decreases with annealing temperature. Energy gap of bulk CuO is 1.2eV. Here there is an increase in the band gap energy. So we can say that this increase in band gap energy is due to the reduction in particle size.

CONCLUSION

Copper oxide nanoparticle was prepared by precipitation method. The morphology of the as prepared sample was analysed by scanning electron microscopy (SEM).The size and crystal structure of CuO nanoparticle was studied using XRD. From the XRD pattern we get the size as about 8nm with narrow size distribution and with monoclinic structure. UV–visible absorption spectrum was used to find the band gap of CuO nanoparticles. UV-Visible absorption spectrum studies showed that the band gap of CuO nanoparticle is much larger than bulk CuO. Band gap of CuO nanoparticles was 3 eV which is very larger than that of bulk CuO. Particle size and absorption wavelength of CuO nanoparticle was increases with annealing temperature.

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