CHAPTER-8
Nanostructured materials have gained growing attention because of their special chemical and physical properties compared to their bulk or microsized counterparts. One-dimensional (1D) nanomaterials such as nanowires, nanobelts, nanotubes, and nanorods have become the focus of intensive research due to their unique properties and their potential for fabrication into high density nanoscale devices [1]. The oxides of transition metals are an important class of semiconductors. Among various semiconductors, Cu and its oxides have attracted a great deal of attention in both fundamental research and technical application because of their catalytic, optical, and electrical conducting properties [2, 3]. Copper is an important material because of its high electrical and thermal conductivities. CuO is known as p-type semiconductor exhibiting narrow band gaps ($E_g = 1.4$ eV) which makes it a promising material for gas sensors, magnetic storage media, solar energy transformation, electronics, semiconductors, varistors, and catalysis [4]. The experimental conditions used in the preparation of these materials play an important role in the particle size of the product. For this reason, a great variety of experimental methods have been used in the production of nanoparticles, such as hydrothermal method, sol-gel technique, gas-phase oxidation, micro-emulsion, and so forth, as the solution process presents an easy, low energy, low-temperature, and cost-effective approach to obtain the products with good yield. Therefore, until now, a variety
of CuO nanostructures by solution method have also been reported in literature such as nanorods, nanowires, nanotubes, nanosheets, nanoribbons [5-7]. Recently, various methods have been developed for obtaining CuO nanoparticles, including alcohol thermal route, in which large amounts of organic solvents are used in the preparation process [8]. Solid-state techniques are among the simplest ones and are much utilized nowadays. Conventional methods for the preparation of CuO powders include one step solid-state reaction at room temperature, thermal decomposition of copper salts and mechanical milling of commercial powders [9, 10, 11]. Solid-state mechanochemical processing is an effective, useful and simple processing technique widely applied to the synthesis of quasicrystalline, nanocrystalline and crystalline materials, which is not only a physical size reduction process in conventional milling but also a chemical reaction that is mechanically activated at the nanoscale during grinding with PEG. Thus, there is a renewed interest in understanding the fundamental physical properties of CuO, as well as for upgrading its performance in applications [12, 13]. In this chapter, synthesis and characterization of nanocrystalline CuO by simple mechanochemical process at different temperatures has been carried out.

8.1 RESULTS AND DISCUSSIONS

8.1.1 XRD ANALYSIS

X-ray diffraction measurements were carried out to study the crystal structure and crystalline quality. Fig. 8.1.1 represents the X-ray diffraction pattern of synthesized CuO nanoparticle calcined at 400 °C, 600 °C and 800 °C. All the diffraction peaks could be indexed to crystalline monoclinic structure. The major peaks located at 2θ values correspond to the characteristic diffraction of monoclinic phase of CuO, (JCPDS NO-80-
No other peaks were observed belonging to any impurity such as Cu(OH)$_2$ and Cu$_2$O, which indicates the high purity of CuO nanoparticles. Fig. 8.1.1a, 8.1.1b and 8.1.1c depicts XRD patterns of CuO annealed at 400 °C, 600 °C and 800 °C respectively. CuO particles annealed at higher temperature shows shift in (1 1 0), (0 0 2) and (2 0 0) plane compared to those annealed at lower temperature. As the annealing temperature increases, the peak intensity of CuO nanoparticles increases with a decrease in the full width at half maximum (FWHM), which indicates a possible change in the grain size of CuO [14-16]. The diffraction peak (1 1 0) was narrower than (0 0 2) peak, and in turn (0 0 2) peak was narrower than (2 0 0) peak. This evidently point out the presence of asymmetry in the crystallite shape. The height of c-axis of the crystal is bigger than the basal diameter (crystal axis, a$_1$, a$_2$) [17]. The intensity of (1 1 0), (0 0 2) and (2 0 0) peaks gradually increases with increase in annealing temperature. However, the peak intensity of the annealed samples at 800 °C was found to be increased. The lattice parameters for CuO nanoparticles were calculated from the XRD data. The lattice constants $a$, $b$ and $c$ for CuO annealed at 400 °C were found to be 0.47153 nm, 0.33774 nm and 0.51247 nm, respectively. As for CuO annealed at 600 °C, the lattice constant $a$ decreases to 0.47141 nm, $b$ increases to 0.34206 nm and $c$ increases to 0.51264 nm. These crystal planes play an important role in growth process. For CuO annealed at 800 °C $a$ decreases to 0.46392 nm, $b$ decreases to 0.33934 nm and $c$ decreases to 0.50409 nm. The decrease in lattice parameters at 800 °C shows temperature plays significant role in crystallinity at higher temperature. Fig. 8.1 illustrate the changes in (0 0 2) and (2 0 0) peaks position of the nano powders. As shown in this Fig. 8.1.1, when the calcinations temperature changes from 400-600 °C, the peaks slight shift towards lower angles have been observed.
other hand the strongest shift towards higher angles has been observed in the sample annealed at 800 °C. This can be seen from the enlarged view of the inset in Fig. 8.1.1. These shifts depend directly on the changes of the lattice constants [24]. It can be seen that the shift of the peak was detected as the lattice constants changed, which resulted in the changes of lattice constant along \( a \), \( b \) and \( c \)-axis. As the peaks shifted towards lower angle, the lattice constants increased and as it shifted towards higher angle, the lattice constants decreased [22]. The increase in peak intensity at higher annealing temperature is attributed to the increase in crystallinity.

![XRD pattern](image)

**Figure 8.1.1** XRD pattern of powder sample prepared at room temperature (a) CuO annealed at 400 °C, (b) CuO annealed at 600 °C and (c) CuO annealed at 800 °C.
8.1.2 FESEM/EDAX ANALYSIS

Figure 8.1.2 shows the FESEM micrographs of all annealed samples and EDAX patterns of CuO. It was clearly seen that the samples annealed at 800 °C revealed the uniform and plate-like particles. From Fig. 8.1.2a it can be seen that size of CuO nanoparticles annealed at 400 °C are in the range of 21-25 nm. As the annealing temperature increases (400 to 800 °C) the crystal size of CuO was also found to be increased (65 to 454 nm) (Fig. 8.1.2b, 8.1.2c). With increase in the annealing temperatures, the nucleation rate of the particles increases more rapidly. This is because of the increase in supersaturation of the reaction products, which accelerates the crystal core forming reaction within a short time. Under these conditions the controlling step of the reaction is transferred from grain growth to crystal nucleus formation. With the temperature continuing to rise, the phenomenon of “nuclear-aggregation” caused by the rapid formation of crystal nucleus is obvious which results in forming aggregate among the crystal nucleus [14, 18, 19]. The rate of particle aggregation is a major factor that controls the morphology and structure (crystalline) of the final product [20]. With increasing the calcination temperature particle agglomeration was observed in FESEM images. Literature also indicates that with increase in calcination temperature the crystallinity of the particle increases as well as the surface area decreases. Variation in calcination temperature brought about changes in the crystallinity [23]. The micrographs clearly indicated that the crystallinity has increased with an increase in annealing temperature, which is in agreement with XRD results. EDAX spectra of CuO particles at different temperature are shown in Fig. 8.1.2d, 8.1.2e and 8.1.2f which indicate the high purity of the synthesized material where only Copper and Oxygen are present. Carbon signal are due to the Gold
coating and carbon film supporting the specimen in FESEM observation [12]. Various surfactants (PEG 400) can alter nanoparticle's shape, size and other surface properties to different extent depending upon their molecular structure i.e. nature of head group, length of hydrophobic tail and type of counter ions. The termination of the nanoparticle growth and size is controlled by the diffusion and the attachment rates of surfactants (PEG 400) on the nanoparticle surface [25, 26].

8.1.3 UV-VIS SPECTRAL STUDIES

Figure 8.1.3 shows the UV-visible absorption spectra of the samples annealed at different temperatures. The exciton absorption is at about 650-900 nm. The CuO particles obtained at higher annealing temperature exhibits the relatively lower absorption in the visible range. As shown in Fig. 8.1.3 we consider the increasing annealing temperature of CuO particles are the main factor for the intense decrease in absorption [21]. The crystallinity of the particles in our experiment improved when the substrate temperatures increased from 400 °C to 800 °C (Fig. 8.1.3a, 8.1.3b and 8.1.3c). With increase in the annealing temperature from 400 °C to 800 °C, the optical absorption edge slightly shifted towards longer wavelength, which may be attributed to the increased in grain size at higher annealing temperature. The optical band gap ($E_g$) of the CuO was determined by using the formula, $E_g = \frac{hc}{\lambda}$, where $h$ is planck's constant, $c$ is velocity of light, and $\lambda$ is wavelength [14]. The crystallinity of the CuO improved when the temperature increased from 400 °C to 800 °C. It is obvious that the conduction type of CuO was dependent on the temperature. From UV-Vis results, the shift in the band gap is attributed to the effect of temperature on the crystallinity of CuO samples.
Results and Discussions

Figure 8.1.2 FESEM images of pure samples as-prepared and annealed (a) CuO annealed at 400 °C, (b) CuO at 600 °C, (c) CuO at 800 °C and EDAX spectra of pure samples as-prepared, (d) CuO annealed at 400 °C, (e) CuO annealed at 600 °C and (f) CuO annealed at 800 °C.
On the other hand, the crystallinity became better as the $E_g$ value red-shifted from 1.72 to 1.58 eV. The changes in the optical band gap of CuO samples upon increase in temperature were due to the change of crystallinity at higher temperature. The observed results show that the annealing temperature influence is very important in the band gap assignment.

![Graph showing UV-Vis spectra of as-prepare nanoparticles annealed at different temperatures](image)

**Figure 8.1.3** UV-Vis spectra of as-prepare nanoparticles annealed at different temperatures (a) CuO annealed at 400 °C, (b) CuO at 600 °C, (c) CuO at 800 °C.

**8.1.4 CONCLUSION**

- In summary, nanocrystalline CuO particles with a monoclinic structure have been synthesized through a relatively simple, method using PEG 400 as surfactant.
The effect of annealing temperature on the structure and optical properties of CuO particles were studied. The improved crystallinity was observed in the particles annealed at higher temperatures than the other samples.

The grain (crystalline) sizes of CuO particles observed by FESEM vary between 21-450 nm. The intensity of peaks have been increased with increase in annealing temperature, as well as the optical band gap edge shifts towards longer wavelength region which may be attributed to the decreasing band gap of the CuO nanoparticles at higher temperature.
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Effect of Surfactant on The Synthesis and Optical Properties of ZnO Nanoparticles

Recently, nanostructured materials have attracted great attention due to their intriguing physiochemical properties. Immense amount of efforts have been conducted to study the effect of structural properties on their functional behavior [1]. The experimental conditions used in the preparation of these materials play an important role in the particle size of the product. For this reason, a great variety of experimental methods have been used in the production of nanoparticles. ZnO is one of the most important and versatile inorganic semiconductor with a direct wide band gap of 3.37 eV at room temperature. Its strong exciton binding energy of 60 MeV makes it very attractive for exciton-based lasing applications. Recently, extensive progress has been made on the research front of ZnO-based nanomaterials motivated by both basic sciences and potential advanced technologies [27]. It also has interesting chemical, acoustic, optical, and electrical properties [8, 9]. Various methods have been developed for the synthesis of ZnO nanoparticles, such as chemical vapour deposition onto Si substrates [10], electrodeposition [11], vapour–liquid–solid (VLS) process on a substrate [12] and hydrothermal or solvothermal treatment [13–15]. A recent work reports on the use of zinc acetate in water; however, this synthesis comprises a multi-step process longer than a week [16]. It is known that size of the nanoparticles can be controlled easily through the use of surfactants in the system [17]. The term surfactant (short for surface-active-agent) designates a substance which exhibits some superficial or interfacial activity. The past two decades have seen the introduction of a new class of surface active substance,
so-called polymeric surfactants or surface active polymers, which result from the association of one or several macromolecular structures exhibiting hydrophilic and lipophilic characters, either as separated blocks or as grafts. They are now very commonly used in formulating products as different as cosmetics, paints, foodstuffs, and petroleum production additives. Many surfactants are known to have long hydrocarbon chain structures with hydrophobic ends. It is believed that this structure is critical in manipulating particle sizes [18]. Various surfactants can alter nanoparticle’s shape, size and other surface properties to different extent depending upon their molecular structure i.e. nature of head group, length of hydrophobic tail and type of counter ions. The annihilation of the nanoparticle growth is controlled by the diffusion and the attachment rates of surfactants on the nanoparticle surface [19, 20]. Nonionic surfactants do not produce ions in aqueous solution. As a consequence, they are compatible with other types and are excellent candidates to enter complex mixtures, as found in many commercial products. They are much less sensitive to electrolytes, particularly divalent cations, than ionic surfactants, and can be used with high salinity or hard water. Nonionic surfactants are good detergents, wetting agents and emulsifiers. Some of them have good foaming properties. Some categories exhibit a very low toxicity level and are used in pharmaceuticals, cosmetics and food products. Non-ionic surfactants are found today in a large variety of domestic and industrial products, such as powdered or liquid formulations. However the market is dominated by polyethoxylated products, i.e., those whose hydrophilic group is a polyethylenglycol chain produced by the polycondensation of ethylen oxide on a hydroxyl or amine group
Results and Discussions

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8.2 RESULTS AND DISCUSSION

8.2.1 XRD ANALYSIS

The XRD patterns of ZnO nanoparticles are shown in Fig. 8.2.1. All the diffraction peaks could be indexed to hexagonal ZnO (JCPDS card no. 79-0208). The XRD results confirmed the purity of the products via the absence of other phases of zinc oxide. Although the peak positions in the above two patterns are identical, the intensities of diffraction peaks are different. Diffraction lines of ZnO (Fig. 8.2.1B) were broadened and diffraction broadening was found to be dependent on Miller indices of the corresponding sets of crystal plane. The diffraction peak (0 0 2) was narrower than (1 0 0) peak, and in turn (1 0 0) peak was narrower than (1 0 1) peak. This clearly indicated the presence of asymmetry in the crystallite shape [22]. The diffractogram of the sample obtained in presence of surfactant (Fig. 8.2.1A) exhibits narrower peaks than those of the sample obtained in absence of surfactant (Fig. 8.2.1B). The intensity of peaks increases with decrease in the full width at half maximum (FWHM), which indicates a possible change in the grain size. This can be seen from the enlarged view of the inset Fig. 8.2.1. The lattice parameters for ZnO nanoparticles were calculated from the XRD data. The lattice constants $a$ and $c$ were found to be 0.32490 nm and 0.52009 nm, respectively in case of ZnO obtained in presence of surfactant. As for ZnO obtained in absence of surfactant, the lattice constant $a$ increases to 0.32502 nm, and $c$ increases to 0.52035 nm. The average sizes of the ZnO nanoparticles were calculated from the Debye-Scherrer Equation and are found to be 250-280 nm and 120-150 nm, respectively, for ZnO nanoparticles obtained in presence and absence of surfactant. It reveals that the particle size as well as crystallinity
increases as the addition of the surfactant [23, 24]. It is found that the intensity of diffraction peak increases, which indicates that the crystallinity of ZnO nanoparticles is enhanced by the addition of surfactant.

Figure 8.2.1 XRD pattern of powder sample annealed at 320 °C (A) ZnO with PEG, (B) ZnO without PEG.

8.2.2 FESEM ANALYSIS

Figure 8.2.2 shows FESEM pictures which indicate that the sample is composed of a large quantity of nanoparticle with uniform size and shape. Fig. 8.2.2B depicts some of ZnO particles obtained without the use of surfactant. It clearly showed that, the ZnO particles in absence of surfactant are in irregular shape. This gives rise to different shaped particles and indistinguished geometries. Generally, the surfactant has a significant influence on the size and structure of resultant products. Without any surfactants, the as-synthesized ZnO particles were a mixture of small individual particles and aggregates.
When surfactant was used, the prepared sample exhibited well developed facet planes (as shown in Fig. 8.2.2A). The variation in the morphology seemingly correlates with the variation in the crystallinity of the powders. It has been reported that PEG with uniform and ordered chain structure is easily absorbed at the surface of metal oxide colloid. When the surface of the colloid adsorbs PEG, the colloidal activities will greatly decrease and the growth rate of the colloids in some certain facet will be confined. Therefore the addition of PEG in the reaction system will modify the kinetics of the growing process, which is attributed to that the addition of PEG cause the rapid growth of nucleation and cause the aggregation of nanoparticles. Therefore, the addition of PEG can elevate the crystallinity of samples and change the product morphology. However, it also increases the size of product, which is accord with other reports. Thus surfactants play a crucial role in protecting the particles from rapid flocculation, thus inhibiting the agglomeration of particles. Surfactants act as capping agents and can exert a strong influence on the shape of as-formed particles by governing the growth rate of various crystallographic surfaces and create orientations in crystals formation. As shown in Fig. 8.2.2A, the ZnO particles appeared to be bigger and more crystalline in nature. Fig. 8.2.2C shows the EDAX spectrum of ZnO. The pattern shows the presence of only zinc and oxygen and hence indicates the purity of ZnO nanostructures [18, 24, 25].

8.2.3 UV-VIS SPECTRAL STUDIES

To examine the effect of surfactant on the optical properties of ZnO nanoparticles, UV-Vis absorption studies were undertaken. The peak in the UV absorption is indicative of the band gap of the ZnO nanoparticles. As the particle size and crystallinity are increased there is a shift in the optical absorption spectra. The shifts of the optical band gap edge
Figure 8.2.2 SEM images of pure samples as-prepared and annealed at 320 °C (A) ZnO with PEG, (B) ZnO without PEG, (C) EDAX of ZnO particles.

towards longer wavelength region may be pointed to the decreasing band gap and apparent increase in crystallinity. By the addition of surfactant, the optical absorption edge slightly shifted towards longer wavelength (3.37 to 3.33eV), which may be attributed to the increase in grain size. The optical band gap ($E_g$) of the ZnO was calculated by using the formula, $E_g = \frac{hc}{\lambda}$ [21, 25].
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0.20 300 3.37eV 3.33eV 400 Wavelength (Å)

Figure 8.2.3 UV-Vis spectra of powder sample annealed at 320 °C (A) ZnO with PEG, (B) ZnO without PEG.

8.2.4 CONCLUSION

➢ ZnO nanoparticles have been synthesized using a relatively simple, inexpensive, and rapid one-step solid state reaction using PEG 400 as surfactant.

➢ The size and crystallinity of ZnO nanoparticles were found to be dependent on surfactant.

➢ The band gaps of ZnO obtained in presence and absence of surfactant were found to be 3.37 and 3.33 eV, respectively.
REFERENCES


