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ORIGINAL ARTICLE

Surfactant (PEG 400) effects on crystallinity of ZnO nanoparticles

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Abstract The surfactant effects on the size and crystallinity of ZnO powders prepared by Solid-state mechanochemical method. The present method is a simple and efficient method for the preparation of nanoparticles with high yield at low cost. The size and crystallinity of the nanoparticles were analyzed by X-ray diffraction, scanning electron microscopy and energy-dispersive spectrometer (SEM/EDAX). Optical properties and band gap were studied by UV–Vis spectroscopy. XRD shown that the lattice constants have been changed to some extent. These results showed that the band gap energy decreases with increase in lattice constants, which can be attributed to the improvement in crystallinity of the samples. The band gap of the ZnO can be tuned in the range of 3.37–3.33 eV respectively, by the use of PEG 400 surfactant.
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1. Introduction

The interest in nanomaterials has increased in recent years because of their unique physical and chemical properties (Ball and Li, 1992). 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. ZnO has also great potential in applications, such as solar cells, gas sensors, photocatalysis, photodetectors, photodiodes, optical modulator, chemical and bio-sensors, varistors, transparent thin film transistors, and so forth. Recently, extensive progress has been made on the research front of ZnO-based nanomaterials motivated by both basic sciences and potential advanced technologies (Zhou et al., 2008; Seema et al., 2008; Kim et al., 2005; Wang et al., 2010; Al-Hajry et al., 2009; Ian Bu, 2011). It also has interesting chemical, acoustic, optical, and electrical properties (Klingshirm, 1995). Various methods have been developed for the synthesis of ZnO nanoparticles, such as chemical vapor deposition onto Si substrates (Lee and Jeong, 2004), electrodeposition (Leprince-Wang et al., 2005), vapor–liquid–solid (VLS) process on a substrate (Fan et al., 2005) and hydrothermal or solvothermal treatment (Wang et al., 2004, 2005; Xu et al., 2004). A recent work reports on the use of zinc acetate in water; however, this synthesis comprises a multi-step process longer than a week

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(Maensiri et al., 2006). It is known that size of the nanoparticles can be controlled easily through the use of surfactants in the system (Sin et al., 2007). 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 (Tan et al., 2006). 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 termination of the nanoparticle growth is controlled by the diffusion and the attachment rates of surfactants on the nanoparticle surface, surfactant supported stabilization of the nanoparticles in aqueous solution has been demonstrated to be one of the most effectual method (Mehta et al., 2012; Kwon, 2009). Solid-state mechanochemical processing which is not only a physical size reduction process in conventional grinding but also a chemical reaction that is mechanically activated at the nanoscale. The rate of particle aggregation is a major factor that controls the morphology and crystallinity of the final product. By adjusting the amount of PEG we can modify the size and morphology of the product. Reducing the amount of surfactant results in the improving the crystallinity. 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. Polyethylene glycol 400 can be prepared by polymerization of ethylene oxide and are commercially available over a wide range of molecular weights from 300 g/mol to 10,000,000 g/mol. While PEG with different molecular weights find use in different applications and have different physical properties (viscosity). They are used in industry as surfactants, including food, cosmetics, toothpastes and pharmaceuticals; in biomedicine, as dispersing agents. Polyethylene glycol 400 is less toxic and soluble in water, acetone, alcohols and benzene (Vidyasagar et al., 2011). In this present work, to prepare low-cost advanced materials for photovoltaic energy production. We report a simple one-step, solid-state reaction in presence of PEG 400 [H–(O–CH_2–CH_2)*n*–OH] as size controlling agent for the preparation of ZnO nanoparticles. The process is carried out at room temperature. The method employed in the present study is surfactant-assisted technique. Surfactant assisted method is used for the production of high surface area nanoparticles as well as to prevent nanoparticle agglomeration.

2. Materials and methods

2.1. Materials

Zinc chloride and sodium hydroxide were procured from Merck (Mumbai, India). PEG 400 (Polyethylene glycol 400) was procured from s.d.fine-CHEM Ltd. (Mumbai, India). All the chemicals were of analytical grade and used as received for the experiments. Double distilled water was used for the experiments.

2.2. Characterization of nanoparticles

X-ray powder diffraction (XRD) patterns were recorded on a Philips X'Pert X-ray Diffractrometer using Cu Kα radiation. The size distribution and morphology of the samples were analyzed by field emission scanning electron microscope (FESEM) fitted with an Energy-dispersive X-ray spectrometer (EDAX) [Model: Nova Nano SEM600-FEI]. The absorbance of nano-ZnO samples was measured using UV–Vis spectrophotometer [Model: USB 4000, Ocean Optics, USA].

2.3. Synthesis of ZnO nanoparticles

In a typical synthesis, 5 g of $ZnCl_2$ and 3 g of NaOH were ground separately for 5 min in an agate mortar. Thus obtained fine powder of $ZnCl_2$ and NaOH were mixed with 6 mL PEG 400 and subjected to further grinding for 30 min. The resultant paste was washed in an ultrasonic bath three times with double distilled water and ethyl alcohol to remove the PEG 400. Finally, the product was dried at 70 °C in an oven and the resulting solid was subsequently annealed at 320 °C for 2 h (ZnO-A). The same procedure has been followed for the synthesis of ZnO without surfactant (ZnO-B).

3. Results and discussion

3.1. XRD analysis

The XRD patterns of ZnO nanoparticles are shown in Fig. 1. All the diffraction peaks could be indexed to hexagonal ZnO (JCPDS card no. 79-0208). The XRD results confirmed the purity of 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-B (Fig. 2A) were broadened and diffraction broadening was found to be dependent on Miller

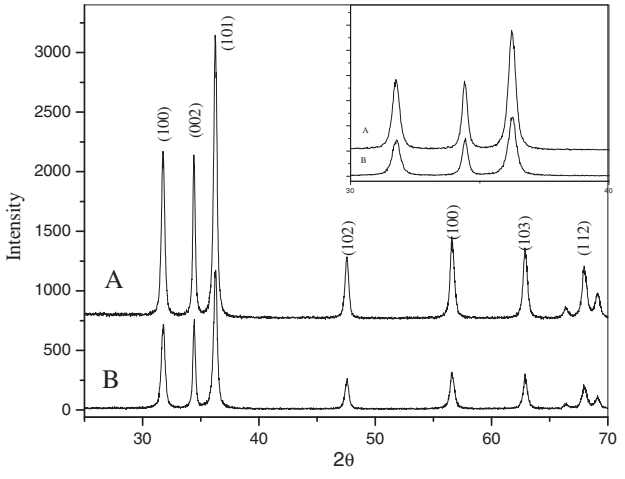

Figure 1 XRD pattern of powder sample annealed at 320 °C (A) ZnO with PEG (B) ZnO without PEG.

indices of the corresponding sets of crystal plane. The diffraction peak (002) was narrower than (100) peak, and in turn (100) peak was narrower than (101) peak. This clearly indicated the presence of asymmetry in the crystallite shape (Salavati-Niasari et al., 2008). The diffractogram of the sample obtained in Fig. 1A exhibits narrower peaks than those of the sample in Fig. 1B. Due to size affect the peaks narrower and then width becomes lesser as the particle becomes bigger. The intensity of peaks increases with decrease in the full width at half maximum (FWHM) of ZnO-A nanoparticles, which indicates a possible change in the grain size. This can be seen from the enlarged view of the inset Fig. 1. The lattice parameters for ZnO-B 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. As for ZnO-A, the lattice constant a increases to 0.32502 nm, and c increases to 0.52035 nm. The average sizes of the ZnO-A and ZnO-B nanoparticles were calculated from the Debye–Scherrer Equation $D = \frac{K\lambda}{\beta\cos\theta}$ and are found to be 250–280 nm and 120–150 nm, respectively. Where λ, θ and β are the X-ray wavelength (1.54056 Å), Bragg diffraction angle and full width at half maximum (FWHM), respectively. It reveals that the particle size as well as crystanility increases as the addition of the surfactant (Wang et al., 2010; Dhanam and Kavitha, 2009). It is found that the intensity of diffraction peak increases, which indicates that the crystallinity of powders is enhanced by the addition of surfactant.

4. SEM analysis

Fig. 2 shows SEM pictures, which indicate that the sample is composed of a large quantity of nanoparticle with uniform size and shape. Fig. 2B depicts some of ZnO particles obtained without the use of surfactant. It clearly showed that they have distinctive outlines such as triangle, circle, rectangle and square. This gives rise to different shaped particles and undistinguished geometries. Generally, the surfactant have 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. 2A). The variations in the morphology seemingly correlate with the variation in the crystallinity of the powders. Thus surfactants play a crucial role in protecting the particles from rapid flocculation, thus inhibiting

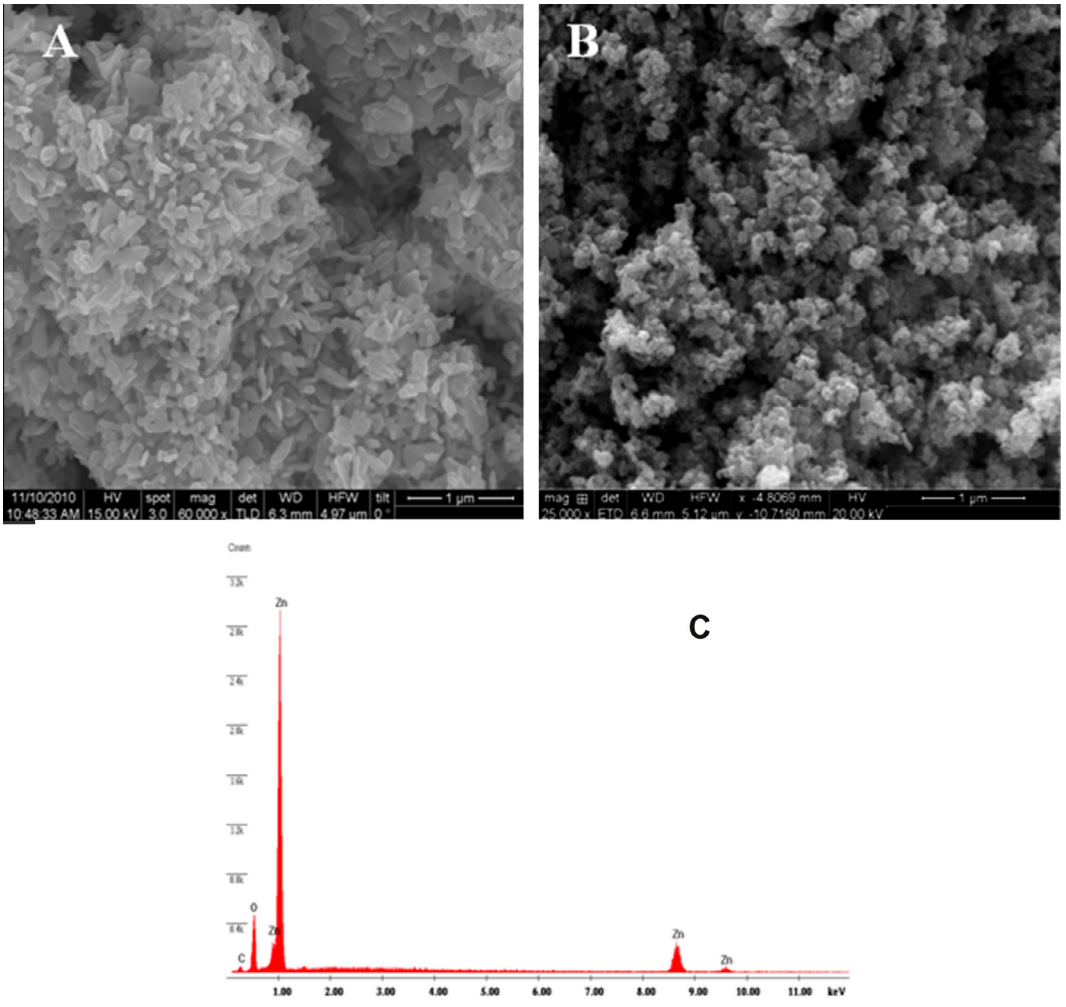

Figure 2 SEM images of pure samples as-prepared and annealed at 320 °C ((A) ZnO with PEG (B) ZnO without PEG (C) EDAX of ZnO particles.

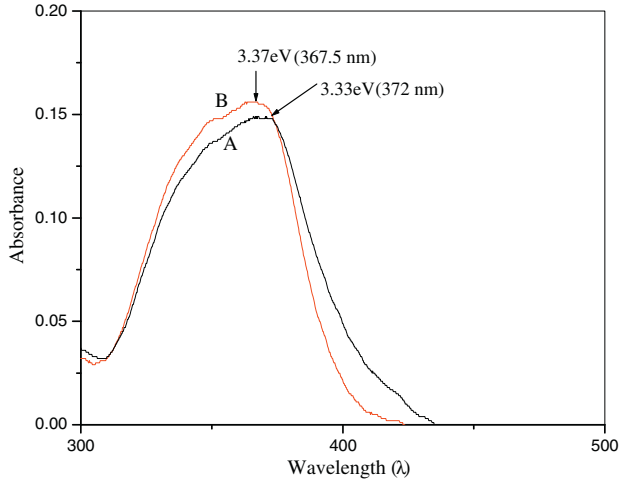

Figure 3 UV–Vis spectra of powder sample annealed at 320 °C (A) ZnO with PEG (B) ZnO without PEG.

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. 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 is controlled by the diffusion and the attachment rates of surfactants (PEG 400) on the nanoparticle surface. As shown in Fig. 2A, the ZnO particles appeared to be bigger and more crystallinity in nature. Fig. 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 (Tan et al., 2006; Dhanam and Kavitha, 2009; Lu et al., 2001).

5. UV–Vis spectroscopy analysis

To examine the crystallinity effect of the synthesized ZnO nanoparticles, UV–Vis absorption spectra were employed. 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 significant red shift in the optical absorption spectra (Fig. 3A). The shifts of the optical band gap edge towards longer wavelength may be pointed to the decreasing band gap and apparent increase in crystallinity is observed. By the addition of surfactant, the optical absorption edge slightly shifted towards longer wavelength (3.37–3.33 eV), which may be attributed to the increase in grain size. The optical band gap (E_g) of the ZnO-A and ZnO-B was determined by using the formula, $E_g = hc/\lambda$, where h is plank's constant, c is velocity of light, and λ is wavelength (Vidyasagar et al., 2011; Lu et al., 2001).

6. Conclusion

In summary, ZnO nanoparticles have been synthesized using a relatively simple, inexpensive, and rapid one-step solid state reaction method using PEG 400 as surfactant. This process not only significantly shortens the reaction time for preparing ZnO, but also increases the crystallinity of the ZnO particle to submicron order. The size, structure, crystallinity and to some extent the morphology of the as-formed ZnO nanoparticles are dependent on the nature of surfactants. The surfactant results in improving the crystallinity and slightly increasing the particle size of ZnO powders.

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