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Synthesis and optical characteristics of ZnO nanocrystals

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Abstract. Zinc oxide nanomaterials with an average particle size of 20–30 nm are readily synthesized by the reaction of zinc acetate and oxalic acid under hydrothermal conditions. The samples are characterized by XRD, SEM, TEM, UV and photoluminescence (PL) studies. The average crystal size of the as prepared ZnO nanopowder is determined by XRD and the values are in good agreement with the TEM analysis. UV absorption spectra revealed the absorption at wavelength < 370 nm indicating the smaller size of ZnO nanoparticles. The quality and purity of ZnO nanomaterial crystalline samples are confirmed by photoluminescence spectra.

Keywords. Nanomaterials; optical materials; properties; ZnO.

1. Introduction

ZnO is a wide bandgap semiconductor with optoelectronic properties that make it an attractive candidate for a variety of device applications. Zinc oxide is a versatile material that has achieved applications in photocatalysts, solar cells, chemical sensors, piezoelectric transducers, transparent electrodes (Bauer *et al* 2001; Duran *et al* 2002), electro luminescent devices, and ultraviolet laser diodes (Johnson *et al* 2001; Zhang *et al* 2002). Compared to other semiconductors, ZnO has wide bandgap of 3·37 eV and other large excitation binding energy, which makes excitation stable even at room temperature. There are various methods in order to synthesize ZnO nanomaterials viz. solvothermal synthesis, sol–gel (Li and Kanbunde 1992; Mondelaers *et al* 2002), combustion synthesis (Vorkakpic and Matsaukas 1998; Hwang *et al* 2004), spray analysis (Ko *et al* 2006), thermal hydrolysis (Kodas 1989), hydrothermal synthesis etc. Hydrothermal synthesis is one of the most extensively used and cost effective methods for the preparation of nanomaterials. In this study, we have synthesized ZnO nanomaterials and their optical and surface morphological properties are investigated.

2. Experimental

Zinc oxide is synthesized in aqueous solutions by taking zinc acetate and oxalic acid under hydrothermal conditions. 0·1 M solution of zinc acetate (AR) is taken in a beaker containing 0·1 M solution of oxalic acid (AR) and stirred for about 12 h. The white precipitates thus obtained are filtered and washed with acetone and distilled water to remove impurities and dried over 120°C for 6 h in order to remove water molecules.

$$Zn(CH_3COO)_2{\cdot}2H_2O + H_2C_2O_4{\cdot}2H_2O \xrightarrow{H_2O} ZnC_2O_4.XH_2O + CH_3COOH + 2H_2O$$

$$ZnC_2O_4{\cdot}XH_2O \rightarrow ZnO + CO + CO_2 + XH_2O.$$

The calcination process is carried out over a temperature of 400–450°C in order to remove CO and CO_2 from the compound.

Thus obtained samples are characterized by powder X-ray diffractometer XPERT PRO with CuK_α X-ray radiation ($\lambda = 0{\cdot}15496$ nm). The crystalline nature of ZnO samples is confirmed by sharp intense peaks. The surface morphology of the sample is observed by scanning electron microscopy (SEM, JEOL, JSM-67001) and high-resolution transmission electron microscopy (HRTEM, HITACHI model H-800). The composition of elements like Zn, O is confirmed by energy dispersive X-ray spectra (EDX). Optical absorption spectrum is taken with SHIMA DZU UV-310PC, UV scanning spectrophotometer. The room temperature photoluminescence (PL) spectrum of ZnO is recorded with fluorescence spectrometer (FLS920) using Xe lamp as the excitation source at excitation wavelength ($\lambda_{ex} = 325$ nm). The luminescence is dispersed with a monochromator and recorded.

3. Results and discussion

Figure 1(a) shows the XRD patterns of ZnO nanocrystalline powder. The sharp intense peaks of ZnO confirms the good crystalline nature of ZnO and the peaks originated from (100), (002), (101), (102), (110), (103), (200),

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(112) and (201) reflections of hexagonal ZnO (Yang *et al* 2005). The size of the particles is calculated by Debye Scherrer's formula. The average crystal size is calculated by the formula

$$D = k(\lambda/\beta\cos\theta),$$

K is a constant equal to 0·89, λ the X-ray wavelength (0·154095 nm), β the full wavelength at half maximum and θ the half diffraction angle.

The crystal size of the ZnO nanoparticles calculated from FWHM was tabulated in table 1.

Energy dispersive X-ray spectra displayed in figure 1(b) and table 2 furnish the composition of various elements in the prepared sample.

Figure 2 represents the scanning electron micrographs of ZnO nanomaterials synthesized under aqueous medium. The orientation growth of ZnO crystal in water is higher (Kwon *et al* 2002). And the spherical shaped morphology is observed in the micrograph as shown in figure 2. The SEM pictures show distinguished spherical morphology with a self-aligned prismatic nanoparticles. The transmission electron micrograph of the ZnO sample is given in figure 3. The figure clearly indicates the morphology of the particles to be roughly spherical and homogeneous. Some of the particles are agglomerates. The distribution of particles obtained from the TEM image is given in figure 4.

Figure 5 shows the optical absorption spectrum of ZnO nanopowder prepared under aqueous conditions. The UV visible spectra for ZnO nanoparticles synthesized in aqueous media displayed excitonic absorption peak at 363 nm which implies the lower particle size ZnO. The

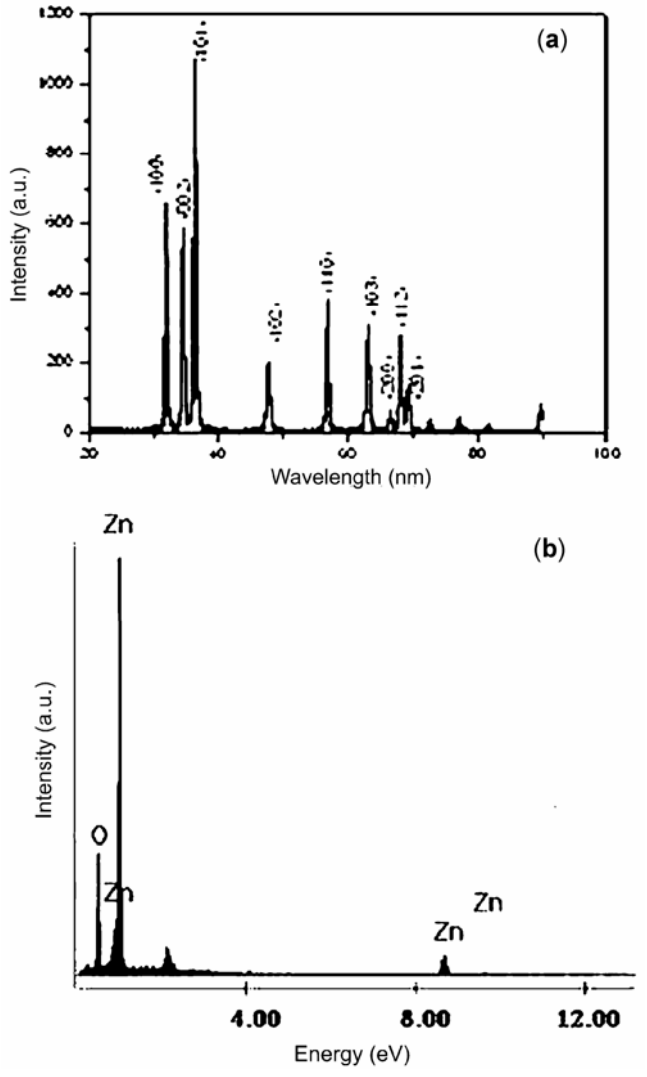

Figure 1. (**a**) XRD pattern of ZnO nanoparticles after calcination at 450°C and (**b**) EDX spectrum of ZnO nanoparticles.

Table 1. Particle size estimated from the diffraction spectrum in figure 1 by using half maximum widths.

Phase	Width	2θ (deg)	(*hkl*)	Particle size (nm)
ZnO	0·42	31·750	100	21
	0·37	34·380	002	24
	0·39	36·180	101	25
	0·39	47·500	102	24
	0·40	56·540	110	24
	0·35	62·780	103	32
	0·30	66·310	200	29
	0·41	67·840	112	26
	0·29	68·910	201	35

Table 2. Composition of elements in ZnO sample.

Element	Wt%	At%
OK	24·44	56·93
ZnK	75·56	43·07
Total	100·00	100·00

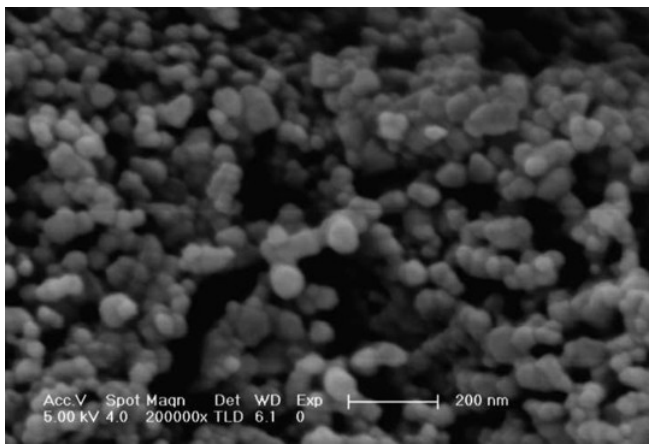

Figure 2. SEM image of ZnO nanocrystals.

bandgap calculated from the UV cut-off is found to be 3·41 eV ZnO nanoparticle. These band gap values blue shifted relative to the bulk zinc oxide of 3·37 eV (Huang *et al* 2001).

Figure 6 depicts the photoluminescence spectrum of nanosize ZnO synthesized in aqueous medium. Strong emission peak centred at 397 nm was observed in ZnO. The ZnO sample exhibits only UV bandgap luminescence but no oxygen defects luminescence was observed. (In general, it is observed around 530 nm, i.e. green–yellow emission). Generally, a green–yellow emission is observed in PL spectra, due to recombination of photo generated holes with singly ionized charge state of specific defect (Hsieh *et al* 2003). However, absence of the green yellow emission in our samples indicates the potential of our synthetic strategy to produce a low concentration of oxygen defects and high optical quality of single crystal ZnO (Zu *et al* 1997; Gao *et al* 2005).

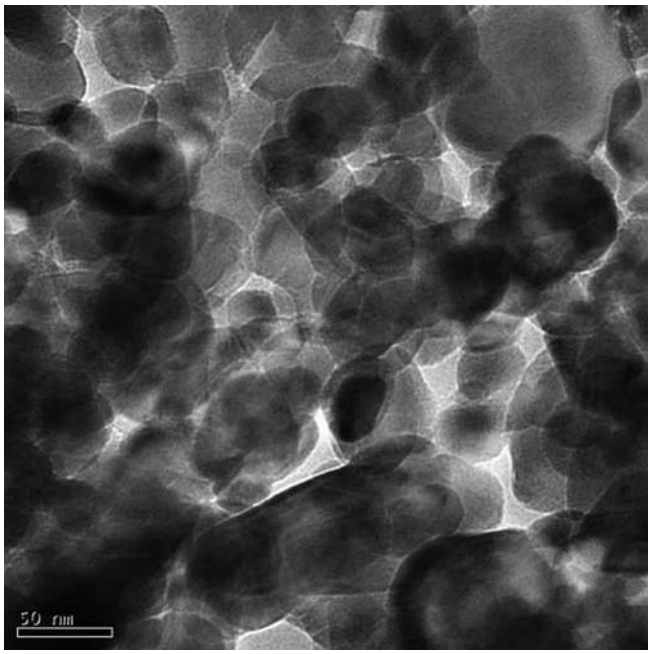

Figure 3. TEM image of ZnO nanocrystals.

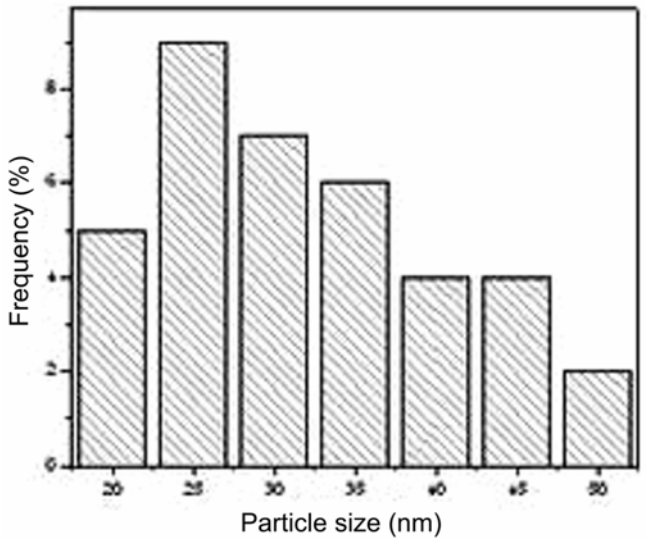

Figure 4. Particle distribution obtained from TEM image.

4. Conclusions

ZnO nanomaterials have been successfully synthesized by hydrothermal method using zinc acetate and oxalic acid as the reactants. The XRD pattern reveals that the synthesized materials are crystalline in nature. The size of the particles determined by XRD is in good agreement with TEM analysis. The optical properties of ZnO nanomaterials are studied by absorption and photoluminescence spectra.

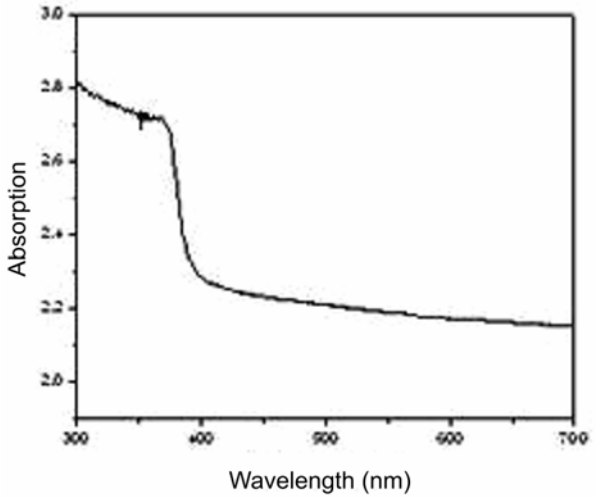

Figure 5. UV absorption spectrum of obtained sample.

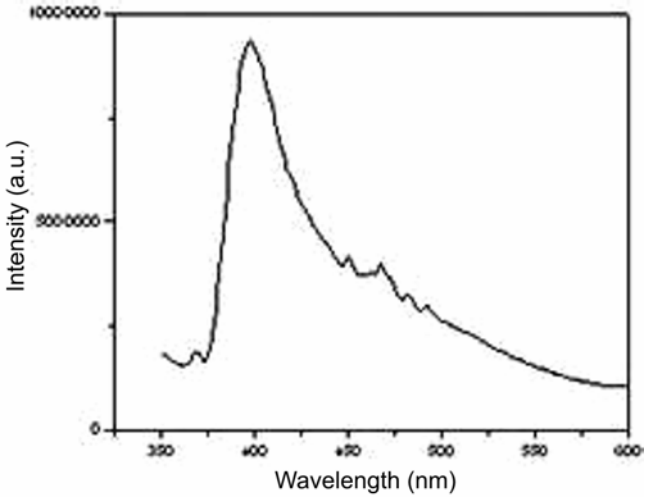

Figure 6. PL spectrum of obtained sample.

The high crystalline and purity of the ZnO nanomaterials are confirmed by photoluminescence spectra.

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