ZnO nanoparticles obtained by mechanochemical technique and the optical properties

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Abstract

Crystalline ZnO nanoparticles were synthesized by mechanochemical method. Mechanochemical processing involves the mechanical activation of solid-state displacement reactions at low temperatures in a ball mill. Statistical design was used to investigate the effect of main parameters (i.e. time, milling rate and calcination temperature) on ZnO crystallite size and morphology. After annealing at 400 °C in air, zinc oxide (ZnO) nanoparticles were obtained. The milled powders are analyzed by X-ray diffraction (XRD), TG/DTA and transmission electron microscope (TEM).

The crystallite size of ZnO samples calculated from XRD is consistent with the TEM images and estimated to be less than 20 nm. The optical properties of the samples were studied by UV–vis spectrophotometer.

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1. Introduction

Zinc oxide (ZnO) nanoparticles recently have received much attention due to a various applications such as UV absorption, NO_x decomposition, deodorization, and anti-bacterial treatment [1–3]. Various techniques have been used to synthesize ZnO nanoparticles and can be categorized into either chemical or physical methods [4]. For example, the former includes mechanical processing [5–10], thermal hydrolysis technique [11], hydrothermal processing [12], and sol–gel method [13–15] while the latter methods are vapor condensation [16], spary pyrolysis [17–19], and thermochemical/flame decomposition of metal-organic precursors [20,21].

The optical measurements show that the band gap of the n-type semiconductor crystal of ZnO micron-powders is

3.37 eV at the room temperature but ZnO nanoparticles display a shift of absorption edge and a variation of the optical band gap [26,27], which increases with decreasing the size of the nanoparticles [22,23,28,29].

ZnO is a notable inorganic material closely related to UV light. The electrical conductivity of ZnO is extremely sensitive to UV light and hence it has been assumed that ZnO nanowires would serve as highly sensitive UV-light detectors and optically switching devices [24,25].

In this paper, the MCP method was used to prepare ZnO nanoparticles with variable fine particle sizes. Investigation of the effects of calcination temperature on particle size and structural properties of ZnO nanoparticles was carried out using TGA, DTA, XRD and TEM methods.

Transparent ZnO/ethanol nanocomposites were prepared by incorporating ZnO nanoparticles with various particle sizes into a transparent ethanol (95%) matrix. The optical properties of the nanocomposites were characterized by an ultraviolet–visible (UV–vis) spectrophotometer. The effects of ZnO particle size on the optical properties of the nanocomposites were studied.

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According to the results of the experiments, it seems that ZnO is an excellent candidate for a various practical applications, such as precision optical device components, and windows for automobiles, and transparent high-UV light shielding [30].

2. Experimental procedure

2.1. Preparation of ZnO nanoparticles

The starting materials were anhydrous ZnCl_2 , anhydrous Na_2CO_3 and NaCl. The NaCl was used as a dilute additive to the starting powder. The stoichiometric mixture of the starting powders was milled, corresponding to the following reaction:

The diameter of balls was 10 mm and the ratio of ball to powder mass was 10:1. Mechanochemical milling was carried out with planetary mill for 9 h at 250 rpm. Powder were calcined in air at 300, 350, 400 and 450 °C for 30 min, respectively (Table 1).

The samples were washed with distilled water three times. Finally, ZnO nanoparticles were obtained from drying of washed powders.

2.2. Preparation of ZnO/ethanol nanocomposites

Colloidal solution of zinc oxide in ethanol has been prepared with Ultrasonic (Elma T780/H) for 15 min. It is

Table 1
Preparation of ZnO nanoparticles by calcination of precursor at different temperatures for 30 min

Sample code	a1	a2	a3	a4
Calcination temperature (°C)	300	350	400	450

interesting to note that nanocomposite containing an extremely low content (1×10^{-3} M) of ZnO nanoparticles with an average particle size of 20–45 nm.

2.3. Characterization

Powder characterization was carried out using X-ray diffraction (Philips, Xpert). XRD technique was also used to determine particle diameters according to Scherrer's formula [31]:

$$d_e = K\lambda/\beta \cos \theta \quad (1)$$

where d , K , λ , β and θ are related to particle diameter, equivalent constant, wave length of applied X-ray, peak broadening and Bragg angle, respectively.

Transmission electron microscopy (Philips, CM200), simultaneous differential thermal analysis (DTA) and thermogravimetric analysis (TGA) measurement used to determine particle characterizations (Netzsch STA 409 PC).

The optical properties of the transparent ethanol/ZnO nanocomposites were studied by using a UV–vis spectrophotometer (Cary Bio 100). The absorbance and transmittance spectra were scanned in the range of 200–800 nm.

3. Results

3.1. The morphology and structure of ZnO

Fig. 1 shows the TGA/DTA curves of the precursor in the air. The endothermic peak occurs at 239.8 °C, indicating the transformation at the precursor to ZnO. TGA curve shows that the weight loss occurs in the temperature range 190–300 °C. Also, it is clearly shown from the TGA curve that the precursor can be completely decomposed to ZnO after calcination at about 300 °C or above [34].

Fig. 2 shows the XRD patterns of the washed powders after calcination. As it shows pure ZnO powder has obtained in this step. The ZnO crystallite sizes are calculated

Fig. 1. TG/DTA of the precursor heat treated at 10 °C/min.

Fig. 2. XRD pattern of a1 sample of the washed powders.

Table 2

Crystallite size of ZnO nanoparticles estimated using the XRD technique and Scherrer's equation

Sample code	a1	a2	a3	a4
Mean particle size (nm)	27.7	38.5	42.5	56.3

using Scherrer's formula and the results are given in Table 2. Clearly, an increase in calcination temperature brings about a corresponding increase on crystallite size and leading to sharper diffraction peaks. The applicability of Scherrer's formula is restricted to small particles (usually smaller than 100 nm) and the above observed large differences reflect the inapplicability of Scherrer's equation to large ZnO crystallites.

Fig. 3 shows TEM micrographs of the precursor and the ZnO nanoparticles prepared at 350 °C calcination temperature. After calcination of the precursor at different temperature, the ZnO nanoparticles with variable fine particle sizes are obtained and the particle size increases with calcination temperature. As the TEM figure shows, the average size of particles resulted from this method is approximately 20–30 nm. The particle sizes obtained from TEM are in good agreement with XRD measurement.

3.2. The optical properties of the ZnO nanoparticles

Transparent ZnO/ethanol nanocomposites were prepared from transparent ethanol (95%). The UV–vis transmittance spectra of ZnO nanoparticles (1×10^{-3} M) are shown in Fig. 4. As the calcination temperature increases, the transmittance of UV light generally increases.

Moreover, Fig. 5 shows that UV light absorbance of the nanocomposites decreases generally with increasing calcination temperature. This agrees with the transmittance result (Fig. 4).

3.3. Effects of size on optical properties

The UV–vis absorption of the ZnO nanoparticles is related to their size. As we know that the interface and surface play a key role in the light absorption of materials

Fig. 3. TEM micrographs of ZnO nanoparticles of heat treated at 300 °C.

[32]. The smaller size of ZnO nanoparticles have larger ratio of surface to volume. Their surfaces are composed of crystal faces $\{10\bar{1}0\}$ and $\{10\bar{1}1\}$, the atoms on these faces can easily vibrate to transform the light energy [33].

Fig. 4. Transmittance of ZnO/ethanol nanocomposites containing (1×10^{-3} M) ZnO nanoparticles.

Fig. 5. Absorbance of ZnO/ethanol nanocomposites containing (1×10^{-3} M) ZnO nanoparticles.

4. Conclusion

ZnO nanoparticles were synthesized through Mechano-chemical method by using ZnCl_2 , NaCl and Na_2CO_3 as raw materials. According to the XRD and TEM results the main particle size increase with increasing the calcination temperature.

According to TG results, the temperature, 300 °C is a proper one for calcination which confirms theoretical value of CO_2 extracted from ZnCO_3 and then nanoparticles of ZnO can be obtained.

The dependence of the optical properties of the ZnO nanoparticles on particles size shows that UV light absorbance of the ZnO nanoparticles increases generally with decreasing particles size and also the particle size increases with increasing calcination temperature. So the optical properties get better with increasing ratio of surface to volume in Zinc oxide nanoparticles.

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