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Low temperature synthesis of ZnO nanoparticles using mechanochemical route : A green chemistry approach

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ABSTRACT : This paper reports study on the synthesis and characterization of ZnO nanoparticles by a two-step synthesis procedure. The first step is the solution-free mechanochemical synthesis of zinc tartarate by grinding of zinc acetate and tartaric acid at room temperature for 30 minutes. The second step is the thermal decomposition of zinc tartarate at 450°C for 30 minutes to form ZnO nanoparticles. Synthesized ZnO nanoparticles have been characterized by XRD, FT-IR, and TGA/DTA. X-ray diffraction pattern shows a wurtzite structure (hexagonal phase) with high crystallinity. The lattice parameters calculated from XRD pattern are a = 3.278 Å and c = 5.268Å. The average grain size of the synthesized nanoparticles was found to be ~ 15 nm.

Keywords : ZnO, Infrared Spectroscopy, X-ray Techniques, Mechanochemical

INTRODUCTION

The development of nanocrystalline materials is a recent thrust area of research. ZnO is an important semiconductor, which has a direct band gap (3.3 eVat room temperature), large bond strength, large excitation binding energy (Eb = 60 meV) and high melting temperature (2248 K) [1], has been widely used in many applications such as transparent conductive films, varistors, solar cell windows, bulk acoustic wave devices, lasers and diodes [2, 3]. ZnO nanomaterials, in comparison to the bulk form ZnO, have shown novel properties for some special applications in the fields of nanoelectronics, ultraviolet lasing, frequency conversion, nanoscale optical circuitry and so on [4–8]. The characteristics of ZnO powder depend on its size and methods of preparation. ZnO nanoparticles can be prepared on a large scale at low cost by simple solution-based synthesis methods, such as chemical precipitation [9–11], sol–gel synthesis [12, 13] and solvothermal/hydrothermal reaction [14–17]. However, agglomeration and secondary growth often occur in these ZnO nanoparticles when we dry the wet particles separated from the reaction solution. This is because large numbers of hydroxyl groups exist on the wet particle surface.

Grinding processing has been routinely used as a scalable physical technique to directly break bulk materials to form fine particles, but it is unsuitable for preparing nanoparticles.

Mechanochemical or solid-state reactions are particularly suitable for the large-scale production of nanoparticles because of their simplicity and low cost. Since such reactions do not involve organic solvents, therefore, for controlling the nucleation and growth of nanoparticles, they are attractive from an environmental point of view.

In the present study, we use a simple, economical and moderately low temperature (450°C). The intermediate (zinc tartarate) phase was obtained by grinding the solid reactants zinc acetate and tartaric acid. The ZnO nanoparticles were then prepared by thermal decomposition of the tartarate phase. The process reported here is potentially cheaper, simple and useful for large-scale production without use of any organic solvents.

EXPERIMENTAL

Sample Preparation

The AR-grade reactants, $Zn(CH_3COO)_2$ and $C_4H_6O_6$, were purchased from Thomas Baker. A typical synthesis was as follows : 0.1 mol of $Zn(CH_3COO)_2$ and 0.12 mol of $C_4H_6O_6$ were mixed by grinding in an agate mortar for 30 min at room temperature, forming the zinc tartarate. ZnO nanoparticles were then prepared by thermal decomposition of the obtained zinc tartarate at 450°C for 30 min. The X-ray diffraction (XRD) pattern of the final ZnO nanoparticles was obtained with Cu Kα radiation (λ = 1.5418 Å) on a Rigaku (Miniflex-II) X-ray Powder Diffractometer and the mean grain size (*D*) of the particles was determined from the XRD line-broadening measurement from the Scherrer equation [18] :

$$D = 0.89\lambda/(\beta \cos\theta)$$

Where λ is the wavelength (Cu Kα), β is the full width at the half-maximum of the ZnO (101) line and¸ is the diffraction angle.

Characterization

The thermal study of the synthesized zinc tartarate was carried out using thermo gravimetric analyzer (TGA-DTA; SCHIMADZU; DTG – 60H; C305743 00134) upto 1000°C in

air at the heating rate of 10°C /min, after purging N_2 gas. Data acquisition was performed on-line, and the data were exported as images. ZnO prepared by decomposition of zinc tartarate at 450°C was employed for the powder XRD studies. FTIR (Interspec-2020, SPECTROLAB U.K) was used to observe the stretching of metal oxygen bond.

RESULTS AND DISCUSSION

Fig. 1 shows the X-ray diffraction pattern of ZnO nanoparticles. It shows a hexagonal wurtzite structure and the lattice constant values obtained from the XRD pattern of zinc oxide powders were in good agreement with the reported values [19]. Moreover, all diffraction peaks of the product show stronger peak intensities, indicating that the obtained ZnO nanoparticles have high crystallinity. The ZnO nanoparticles have an average grain size of about 15 nm calculated by using the Scherrer formula.

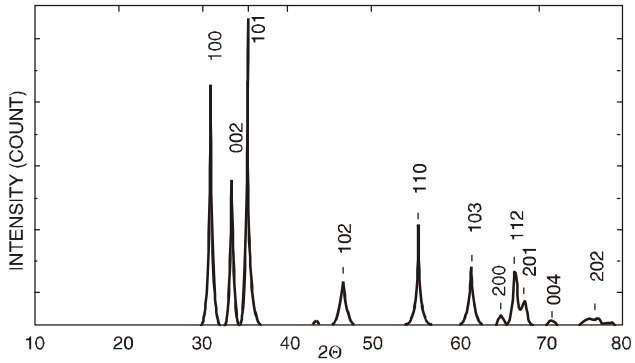

Fig.1. XRD patterns of nanocrystalline ZnO powder calcined in air at 450°C for 30 min.

Fig.2. depicts the TGA/DTA curves for decomposition of synthesized zinc tartarate. TGA showed a weight loss in two steps at 120 and 400°C and corresponding DTA showed two endothermic peaks at these temperatures. The endothermic peak at 120°C was due to removal of water and the peak at 400°C was due to decomposition of zinc tartarate to form ZnO. Dehydration (excess water removal) of zinc tartarate at 120°C is endothermic in nature. Further decomposition of anhydrous zinc tartarate at 400°C is also an endothermic process, which also confirms the purity and phase of Zinc oxide. Using TGA/DTA data, the zinc tartarate obtained was decomposed at 450°C and used for further study.

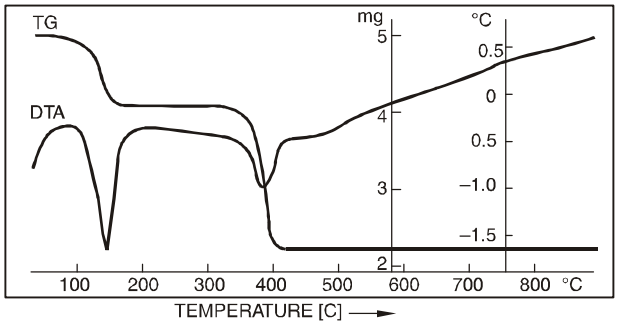

Fig.2. TG/DTA curves of thermal decomposition of nanocrystalline ZnO powder precursor at a heating rate of 10°C /min.

The formation of ZnO wurtzite structure in the synthesized ZnO powders was further supported by FTIR spectra as shown in Fig.3. The FTIR spectra show main absorption bands at ~3400, ~1300, and ~1600 cm^{-1}, which correspond to the O–H mode, and asymmetric and symmetric C = O stretching modes of zinc acetate, respectively. The absorption band at ~457cm^{-1} is the stretching mode of Zn-O.

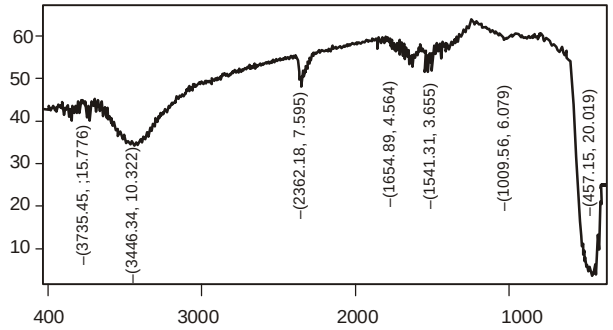

Fig.3. FT-IR spectra of nanocrystalline ZnO powder calcined in air at 450°C for 30 min.

The particle size in a reaction depends on the rates of nucleation and growth of the product. Nanoparticles are formed only if the growth of product clusters stops or the nucleation rate is faster than the growth of product clusters; otherwise, bulk materials will be generated. The present solution-free mechanochemical reaction by grinding is maintained at the nucleation stage of the product because the reaction occurs only at the contacting surface of solid reactant particles and the amount of reactants involved in the reaction is far smaller than in traditional solution synthesis. During the grinding, a self-initiated and self-sustained reaction starts with the CH_3COOH release immediately after grinding the mixture of Zn $(CH_3COO)_2$ and $C_4H_6O_6$ for 5 min.

CONCLUSION

The ZnO nanoparticles were obtained from zinc acetate through tartarate route. The XRD results and FTIR spectra confirmed the hexagonal crystal structure of nano size ZnO after calcinations the precursor at 450°C for 30 min. The particle size calculated from Scherrer formula was found to be 15 nm. Thermal studies showed the complete conversion of zinc tartarate into zinc oxide at 400°C.

In contrast to most other synthesis methods involving high temperatures or complex reaction conditions, the present method is a simple and efficient method of preparing ZnO nanoparticles with high yield at low cost and low temperature.

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