ZnO Nanoparticles Synthesised by mechanochemical processing

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Abstract. Some characterization and microstructural features of mechanochemicaly milled ZnO powders are presented in this study. It is shown that the application of mechanochemical ZnO nanoparticles is a simple technique for preparation of nanocrystalline powders. Synthesised powders are analyzed by X-ray diffraction, scanning electron microscopy (SEM), transmission electron microscope (TEM) and Brunauer-Emmett-Teller (BET).

1. Introduction

Powders with particles of uniform shape and narrow size distribution lying in the nanometer range have been shown to possess interesting properties. Nanoscale oxide particles are gaining increasing technical importance for classic areas of application such as catalysts, passive electronic components, or ceramic materials [1,2]. Metal oxide nanoparticles are also widely used in industrial applications as catalysts, ceramic, pigments and so on. Many methods for the fabrication of nanoparticles have been developed, ranging from lithographic technologies to chemical methods [2,3]. Mechanochemical processing is a novel method for the production of nanosized materials, where separated nanoparticles can be prepared. The method has been widely applied to synthesise a large variety of nanoparticles, including ZnS, CdS, ZnO, LiMn2O4, SiO2 and CeO2 [4-8]. Milling of precursor powders leads to the formation of a nanoscale composite structure of the starting materials that react during milling or subsequent heat treatment to form a mixture of separated nanocrystals of the desired phase within a soluble salt matrix. The separation of the nanoparticles will occur due to existence of NaCl that prevents the subsequent agglomeration ZnO nanoparticles during calcination. Removal of the salt matrix is usually carried out through simple washing. For example, ultrafine ZnO powder was synthesized by the milling and subsequent heat treatment of a ZnCl2, NaCl and Na2CO3 powder mixture. Removal of the NaCl with a simple washing process resulted in separated ZnO particles [8,9,10].
2. Experimental Procedure
The starting materials were anhydrous ZnCl₂ granules (Merck, 99.5%), Na₂CO₃ powder (Merck, 99%) and NaCl (Merck, 99%). All the starting materials were dried in air at 150°C. The NaCl was used as an inert diluent and added to the starting powders. The mixture of starting powders was milled in a ball mill with zirconia balls of 10mm in diameter and 250 rpm. The precursor was calcined at 400°C in air in a porcelain crucible for 0.5h to prepare the ZnO nanoparticles. Since the mechanochemically formed ZnCO₃ nanoparticles were isolated in the NaCl matrix, sintering of the ZnO powder did not occur during heat treatment. Removal of the salt by-product was carried out by washing the powder with de-ionised water. The washed powder was dried in a spray drier. Powder characterization was carried out using XRD (Cu-Kα radiation), SEM, TEM and BET.

3. Results and Discussion
A stoichiometric mixture of the starting materials was milled corresponding to the following reaction equation:

\[
\text{ZnCl}_2 + \text{Na}_2\text{CO}_3 + 8\text{NaCl} \rightarrow \text{ZnCO}_3 + 10\text{NaCl}
\]

NaCl was added to the reactants so that the volume ratio of the ZnCO₃: NaCl in the product phase was 1:10.

![Figure 1. Shows the XRD patterns of the ZnCl₂, Na₂CO₃ and NaCl milled powders: (a) the starting mixture; (b) milled for 1 h; (c) after calcination at 400°C for 0.5 h; and (d) after washing with water three times.](image)

Figure 1 shows the XRD patterns of the ZnCl₂, Na₂CO₃ and NaCl milled powders: (a) the starting mixture; (b) milled for 1 h; (c) after calcination at 400°C for 0.5 h; and (d) after washing with water three times. Only the peaks associated with NaCl, ZnCO₃ and Na₂CO₃ were observed in the patterns of the starting materials (Fig. 1a). After 1 h milling of the mixture, only typical NaCl peaks were detected (Fig. 1b). A new peak associated with ZnO was observed in the pattern of the sample after thermal treatment of the as-milled powder. As shown in Fig. 1c, the pattern of the powder heated at 400°C...
consisted of peaks corresponding to ZnO and NaCl after washing, only those peaks of ZnO remained, indicating the complete removal of the NaCl by-product phase (Fig. 1d).

The mean crystallite size estimated from the XRD peak width at $2\theta = 36^\circ$ using the Scherrer equation [11] was 28.5 nm.

Figures 2 and 3 respectively show a typical TEM and SEM micrograph of the ZnO powder heat treated and subsequently washed. It can be observed that the particles are almost 20–30 nm which is in good agreement with XRD crystal sizes.

The BET surface area of the ZnO powder heated at 400°C was 23.28 m$^2$/g, which corresponds to a spherical particle size of 51 nm. This difference can be due to agglomeration of nanoparticles during drying.

4. Conclusions

Zinc oxide (ZnO) nanoparticles can be successfully prepared by heat treatment of the milled powder obtained synthesized by mechanochemical reaction of ZnCl$_2$ and Na$_2$CO$_3$ with NaCl as a diluent. Heat treatment of the as-milled powders at 400°C led to the thermal decomposition of ZnCO$_3$, leaving ZnO nanoparticles embedded in the NaCl matrix. Since the mechanochemically formed ZnCO$_3$ nanoparticles were isolated in the NaCl matrix, sintering of the ZnO powder did not occur during heat treatment.

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