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Nanopowder synthesis of zinc oxide via solochemical processing

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Abstract

Zinc oxide is used in functional devices, catalysts, pigments, optical materials and many other important applications. ZnO nanopowders can be produced mechanochemically or solochemically. The synthesis of ZnO nanopowder has been carried out via solochemical processing from an aqueous solution of a zinc containing complex in this research. This is the newest economic method for synthesis of ZnO nanopowder. The results obtained from XRD and TEM show that the nanoparticles are single crystals and the mean particle size is 45.3 nm. TEM micrographs of ZnO nanopowder reveal that the particles have elongated particulate shape with a narrow size distribution. Solochemical processing can thus be an attractive method for industrial production of the nanopowders.

Keywords: Solochemical processing; Nanopowder; Complex; Aqueous solution

1. Introduction

Zinc oxide has a wide range of applications in the functional devices, catalysts, pigments, optical materials, cosmetics, nanostructure varistors, UV absorbers, gas sensors and industrial additives [1–3]. Different methods for production of ZnO nanopowders have been investigated before [1–5]. Mechanochemical processing is an example [6–12]. But it needs milling. It cannot, therefore, be economically feasible to be applied in a nanopowder mass production process.

Solochemical (SC) processing is a new zinc oxide nanopowder production method that involves preparation of a solution containing zinc complex and subsequent decomposition of the complex into the zinc oxide nanopowder. Another name for this method is two-stage solochemical (TSSC) method. TSSC method can also be used for production of other oxides such as Mn_2O_3 and NiO. Pouring of a limpid chemical (containing zinc complex) onto a second chemical leads to the formation of a nanoscale powder.

The solochemically formed nanopowder can further be doped with other oxides. The product can be nanocomposite. Nanocomposite particles are usually used as varistores with nanostructure morphology. Results of the most recent studies carried out in our laboratory on synthesis of ZnO nanopowders via two-stage solochemical reaction $(NH_4)_2ZnO_2 + H_2O \rightarrow ZnO + 2NH_4OH$ is reported in this paper.

2. Experimental procedure

Anhydrous $ZnCl_2$ powder (Merk, 99.5%), ammonia and an appropriate additive were used to produce the initial zinc containing solution. $ZnCl_2$ powder was dried in air at 150 °C overnight prior to use and milled simply in a ceramic mortar. It was then added to a beaker containing NH_4OH aqueous solution to produce the complex.

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Concentrated NH_4OH was gradually poured into the beaker until a white precipitate of zinc hydroxide was formed. Further addition of NH_4OH resulted in dissolution of the precipitate indicating the time for addition of the additives. The solution, which was transparent, was diluted with de-ionized water. It was then dropped into the second solution containing the additive at 100 °C to produce zinc oxide nanopowder.

Nanopowders were then washed with ethanol and saved into a glass case. The powder was subsequently dried at 60 °C in an oven holding the sample for several hours. The powder was then characterized by X-ray diffraction (XRD) (Cu Kα radiation), transmission electron microscopy (TEM), simultaneous differential thermal analysis (DTA) and thermogravimetric analysis (TGA).

3. Results and discussion

3.1. X-ray diffraction

Fig. 1 depicts the X-ray diffraction spectrum of the nanopowder sample produced by SC method. The experimental values obtained for the lattice parameter *d* of the powder were comparable with those given by ASTM (card no. 3-0888). These values indicated a hexagonal crystal system with Wurzite structure of ZnO having the prominent diffraction peaks from crystal planes such as (1 0 0), (0 0 2) and (1 0 1). A mean particle size of 35 nm was calculated for (1 0 1) crystal planes by Scherrer's formula. This value agreed well with TEM micrograph of the ZnO powders.

3.2. Transmission electron microscopy (TEM)

A typical TEM micrograph of the ZnO powder processed by SC method at different magnifications is shown in Fig. 2. The powder consisted of 20–60 nm particles having two morphologies: (a) equiaxed particulates and (b) elongated grains. These morphologies are related to the SC processing nature.

The particles appeared to be well separated from each other. Fig. 3 shows the diffraction pattern (DP) imaging of the produced nanopowder. Sharp diffraction rings appear in the diffraction pattern and strong diffraction spots exist in these rings. The diffraction pattern corresponds with zinc oxide. As shown in Fig. 3, no amorphous phase can be detected in the diffraction pattern. Dark field imaging revealed that each particle was a single crystal. As is shown in Fig. 2, each elongated particle contained some porosity. This was related to the nature of the SC processing. Due to the difference between the temperatures of the two chemical solutions, the formation of ZnO nanopowder was accompanied with a thermal shock, which resulted in production and increasing of porosity in powders, especially the elongated and the large particles that sensed greater shock effects.

TEM studies indicated a mean particle size of 45.3 nm with a standard deviation of 9.8 nm. This was as good as the nanopowders produced by the mechanochemical method measured by TEM analysis [13]. The nanopowders produced in this research can be used in gas sensors devised for air pollutants detection. These nanopowders incorporate innovative specifications obtained for the first time.

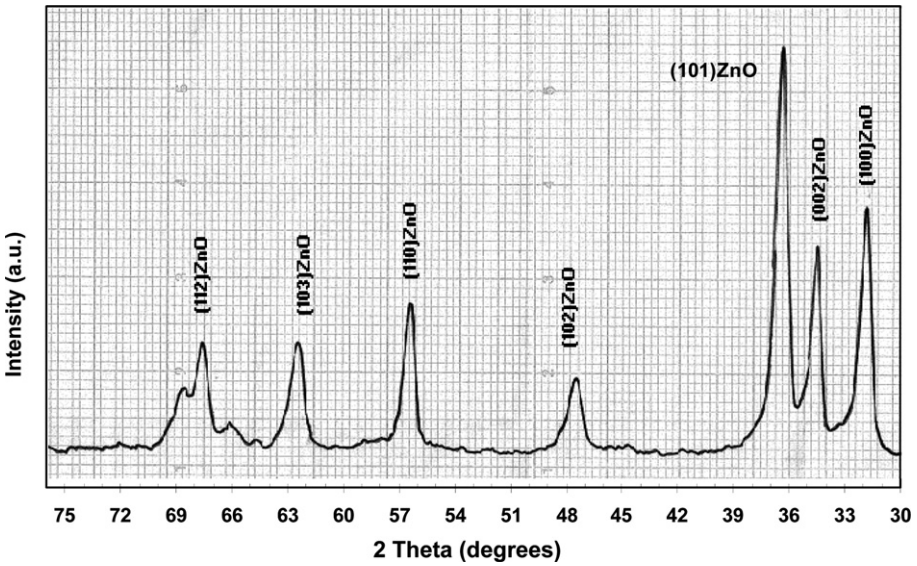

Fig. 1. The diffractogram of ZnO nanopowder produced by SC processing.

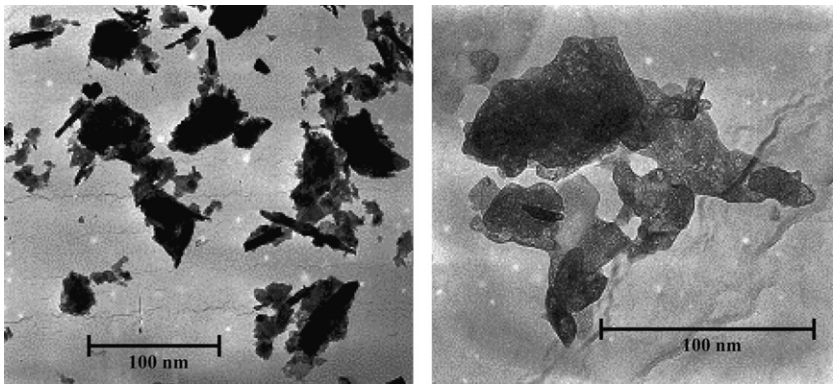

Fig. 2. TEM micrographs of ZnO nanopowder obtained from SC processing.

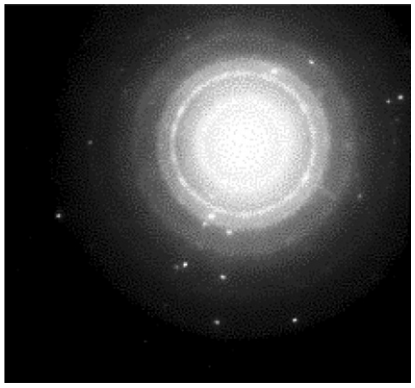

Fig. 3. The diffraction pattern imaging of ZnO nanopowder.

3.3. Fourier transform infrared spectroscopy (FTIR)

Infrared spectrum is an important record, which provides information about the structure of a compound. Almost all functional groups in a molecule characteristically absorb within a definite range of frequency in this technique [14]. Transmission of IR radiation in this technique causes the various bonds in a molecule to stretch and bend with respect to one another. In the present study, infrared transmission spectrum of the solochemically synthesized zinc oxide nanopowder was recorded to be in the range of 4000–400 cm^{-1}. The result is a transmittance infrared spectrum, which is shown in Fig. 4.

The aim of the present IR spectral analysis on the synthesized ZnO nanopowder includes: (a) assessment of the formation of the material and (b) the absence of un-reacted starting materials in the synthesized ZnO nanopowder. A systematic interpretation of the IR spectrum can be of great help to determine whether a reaction occurs and to give the possible products. The absorption region from 650 to 1500 cm^{-1} represents generally the finger print region of the materials, which are unique in characteristic. As reported in the literature [14], Zn–H vibrations (both symmetric and asymmetric) are indexed around 150 cm^{-1} and O–H stretching is observed around 3500 cm^{-1}. The presence of Zn–H vibration may be attributed to the adsorption of hydrogen during SC processing, while the presence of O–H vibration may be probably attributed to the residual $Zn(OH)_2$ present in the powder.

3.4. TG/DT analysis

Figs. 5 and 6 show TG/DTA curves of the nanopowder produced by SC method. The TGA curve shows that the weight loss occurs in three stages:

(a) A weight loss of 6.411 occurs in the temperature range 21.7–402 °C. This weight loss attributes to the adsorption of humidity on the exterior surface of the nanopowders, which can be desorbed from the surface during heating the sample by the TG analyzer.
(b) The second stage occurs in the temperature range of 402.1–563 °C corresponding to a weight loss of 10.01% attributed to the adsorption of humidity in the interior pores of the nanopowder desorbed from the pores during the TGA processing.
(c) The third stage is related to evolution of the additional humidity from pores, which cannot exit during heating of the sample. No appropriate exothermic or endothermic peaks are evident in the DTA curve.

4. Economic aspects

The proposed method, i.e., solochemical processing for the preparation of ZnO nanopowder, is very economic because the method described is very simple

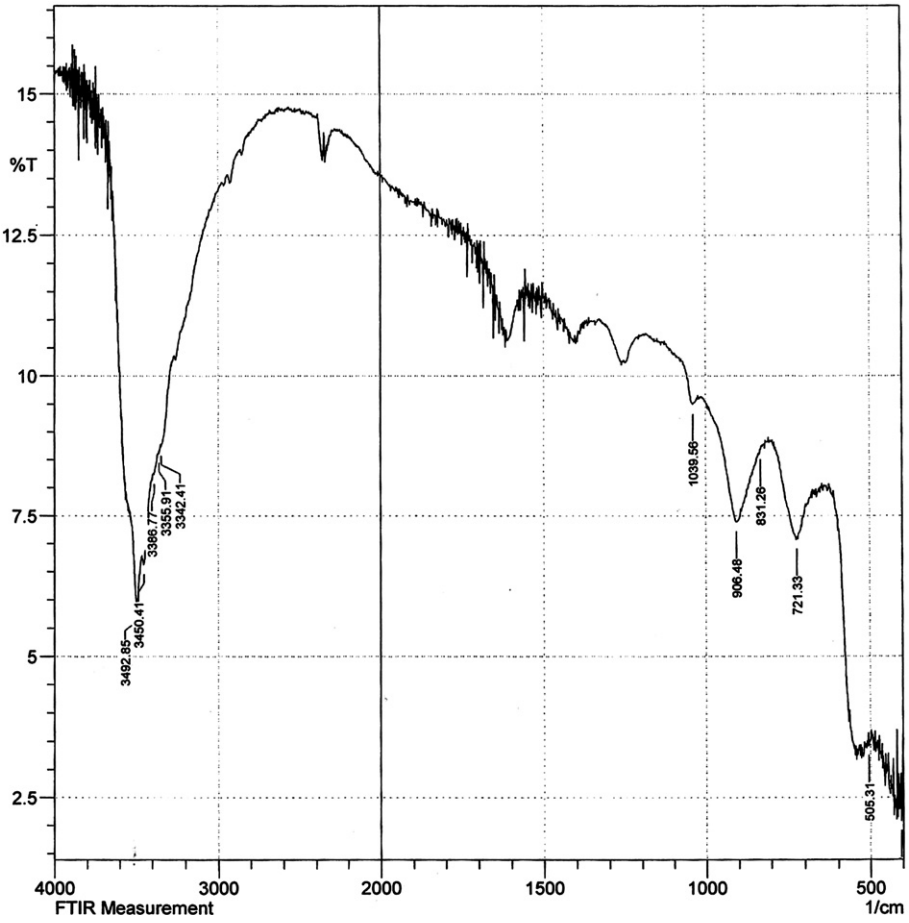

Fig. 4. FTIR spectrum of ZnO nanopowder.

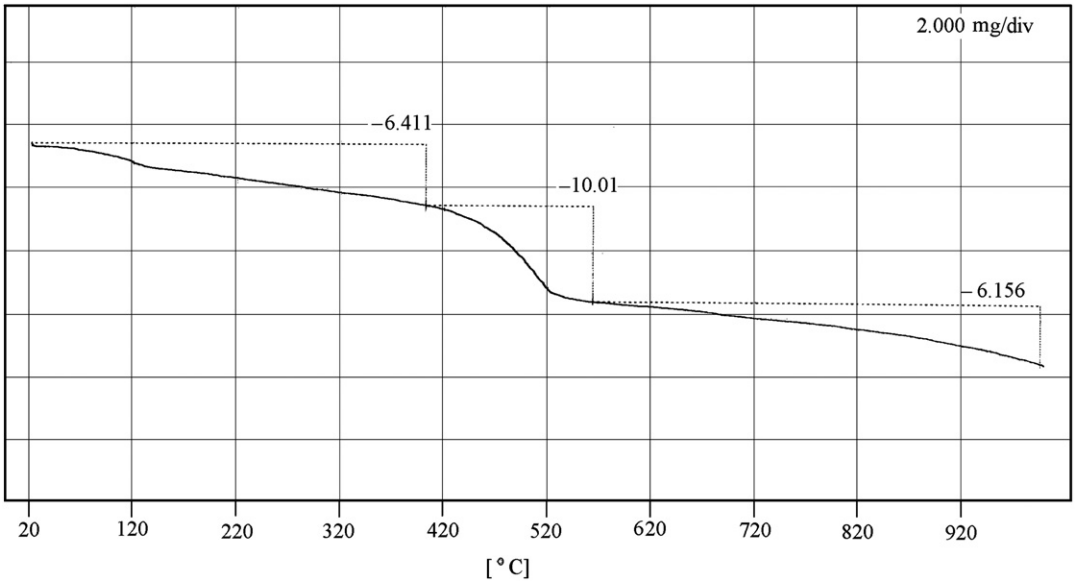

Fig. 5. TGA curve of ZnO nanopowder obtained from SC processing.

and no milling procedure is used in the SC processing. Also, the chemicals used are inexpensive and non-toxic. Therefore, the SC processing for the production of zinc oxide nanopowder could be attractive for industrial production and is particularly suitable for a large scale production of ZnO.

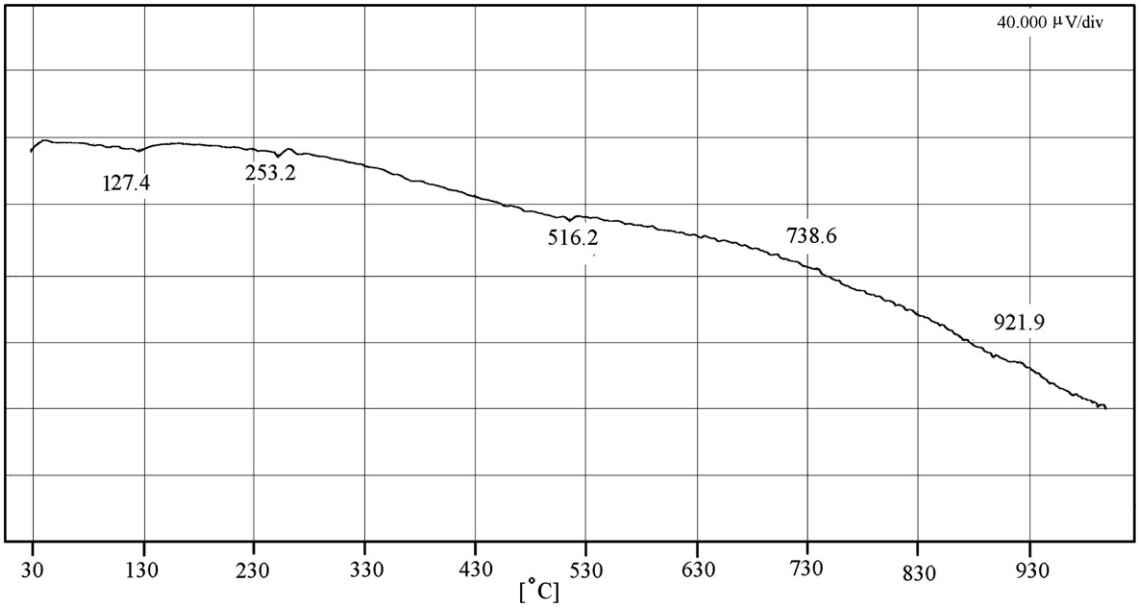

Fig. 6. DTA curve of ZnO nanopowder obtained from SC processing.

5. Conclusion

High quality nanopowders can easily be obtained by solochemical method. After preparation of a transparent solution containing zinc complex and gradual pouring of the solution into hot water, formation of ZnO nanopowder starts to take place. The mean particle size is 45.3 nm. This value agrees well with the result of the mechanochemical processing studied by other investigators before. Elongated particles have a particulate morphology characteristic of the SC process with a noticeable amount of porosity. SC processing seems particularly suitable for a large scale production of ZnO.

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