Facile Microwave-Assisted Synthesis of Zinc Oxide and Characterization

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The physical and chemical properties of inorganic nanomaterials can be tailored to meet the requirements of the intended application by varying the particle size and shape, which in turn depend upon many parameters including synthesis route. This work presents rapid facile synthesis of ZnO using microwave-assisted method. The microwave synthesis offers several advantages over conventional heating methods. The structure, size, morphology and thermal properties of the sample are characterized using several techniques such as by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Transmission electron microscopy (TEM), Energy Dispersive Spectroscopy (EDS), Fourier-Transform Infrared spectroscopy (FT-IR), Thermogravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC). The results confirm the successful synthesis of ZnO, possessing characteristic hexagonal wurtzite structure. The size of particles is wide over a range of tens of nm to over a micron.

Keywords: Zinc Oxide, Microwave Synthesis, Structural Properties, Thermal Behavior

Introduction

The control of particle size and shape of inorganic nanomaterials is a challenging task and depends upon many parameters including synthesis route1. In this regard, microwave synthesis offers several advantages over conventional heating method, which is generally employed in the most of the current synthesis techniques for developing nanomaterials2-5. Hence, the present work involves microwave assisted synthesis of zinc oxide (ZnO), a multifunctional material6 and its characterization using different analytical techniques.

Materials and methods

All the chemicals used in the experiment were of analytical grade. Zinc nitrate hexahydrate (ZnNO3 6H2O), Urea, and Ethylene glycol were purchased from Fischer Scientific International, Inc. The ultrapure water of Type 1 obtained from Milli-Q was used throughout the study.

Synthesis of ZnO

The ZnO powder was obtained by a microwave-assisted homogeneous precipitation reaction using dedicated single-mode sealed-vessel MW reactor (Anton Paar, Monowave 200). The instrument features built-in magnetic stirrer, Infra-red (IR) temperature measurement, and programmed temperature and pressure control by regulation of MW power output. In order to obtain 0.1 M stock solution of zinc nitrate, the zinc nitrate and urea with a molar ratio of 1:5 were dissolved in a mixture of water and ethylene glycol taken in 1:3 volume ratios. About 20 cm³ of this solution was filled into a G30 glass vial with a magnetic stir bar and the sealed vial was placed inside the reactor. A target temperature of 150 °C was set using heat in time option with 15 min hold time. After the reaction time elapsed, the vial was allowed to cool under compressed air condition. The precipitate was centrifuged at 7000 rpm for 5 min and washed with water. This process of washing and centrifugation repeated several times. Finally, the ZnO particles were obtained after drying the precipitate at 50 °C overnight.

Characterization techniques

The surface morphology of samples was investigated using scanning electron microscopy (Carl Zeiss, Neon 40 coupled with an energy dispersive spectroscopy) (INCA, Oxford). Transmission electron microscopy (TEM) studies were carried out in a 200 keV JEOL 2010 machine. The ZnO powder was dispersed in deionized water. A few drops were put on a clean Si substrate and let it for air drying. This was used as a SEM specimen.
A drop of the dispersion was put on a 300 mesh carbon coated copper grid for TEM measurements. The Powder X-ray diffraction (PXRD) patterns were obtained using a Bruker D8 ADVANCE ECO X-ray diffractometer equipped with a Cu Kα radiation source (0.154 nm). The samples were also characterized by Fourier transform infrared (FTIR) analysis (Perkin Elmer FTIR spectrum 2). The spectra were recorded in the range of 400 – 4000 cm⁻¹, with a resolution of 4 cm⁻¹. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed under N₂ atmosphere (flow rate; 50 cm³ min⁻¹) in the temperature range of 30 °C to 900 °C with a temperature ramp of 10 °C min⁻¹, by using Shimadzu thermal instrument (DTG-60). Differential scanning calorimetry (DSC) studies were performed using Shimadzu differential scanning calorimeter (DSC-60). The measurements were made under N₂ atmosphere with a flow rate of 100 ml min⁻¹, with the temperature ramped up to 600 °C at a rate of 10 °C min⁻¹.

Results and Discussion

Figure 1 shows the electron microscopy images of the synthesized ZnO. At first glance, the morphology (Figure 1(a), SEM image) appears to be an assortment of microstructures of different sizes. Some of them show a flower-like pattern. The length of these structures varies from sub microns to a few microns, while the breadth is anywhere between 10s of nm to over a micron, indicating a wide size distribution. The more detailed inspection reveals the presence of numerous tiny flake-like structures covering the surface (Figure 1(b)). Figure 1(c) shows the chemical composition of the sample determined by EDX, which reveals the presence of Zinc and Oxygen (Silicon peak comes from the substrate used for dispersion of sample). The surface morphology shown by SEM studies is evidenced by TEM studies (Figure 1(d), (e), and (f)). The core (middle part) appears darker as it is not electron transparent due to larger thickness (Figure 1(d)). The one on the right side shows the exposed portion of the core without flakes. Figure 1(e) shows the electron transparent flake-like surface structures. The varying contrast can be attributed to changing electron densities (mass thickness contrast). Interestingly, the electron diffraction (Figure 1(f)) shows two major reflections (002) and (102), corresponding to hexagonal wurtzite.

Fig. — 1 (a) Scanning electron micrograph of microwave synthesized ZnO; (b) Representative image of a couple of microstructures showing surface morphology; (c) Corresponding EDX spectrum; (d) Bright field image of two representative microstructures; (e) Flake like structures on the thick hard core and (f) Corresponding SAED pattern.
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ZnO structure (PCPDF 00-036-1451). This reveals near single crystalline nature of individual microstructures with (002) being predominant orientation. Additionally, a weak amorphous ring corresponding to (110) is also visible. The XRD diffraction pattern of synthesized ZnO is shown in Figure 2(a). All diffraction peaks of sample correspond to the characteristic hexagonal wurtzite structure of ZnO (PCPDF 00-036-1451) and are in good agreement with those reported in literature. However, in contrast to TEM results, the XRD pattern shows the polycrystalline nature of the sample due to much larger sampling size. As X-ray beam hits thousands of grains, oriented in all possible directions, the resultant multiple peaks represent the polycrystalline nature of the powder as a whole. On the other hand, when only one microstructure is analyzed using an e-beam, near-single crystalline nature of the individual structures is revealed. Further, no extra peaks corresponding to any other impurity or secondary phase were observed within the sensitivity limit of XRD. It confirms single phase, hexagonal wurtzite structure of pure ZnO sample. This is corroborated by FTIR spectral analysis (Figure 2(b)).

In general, metal oxides show absorption bands in the fingerprint region (below 1000 cm⁻¹) due to interatomic vibrations. Here, the spectra shows a single prominent sharp peak at 414 cm⁻¹, which can be attributed to Zn-O stretching vibrations. The remaining spectrum was relatively smooth with few weak diffused peaks corresponding to stretching vibrations of C=O group due to Lewis acidity. Figure 3(a) shows the curves of thermo gravimetric and differential thermal analyses for ZnO. The total weight loss over the temperature range of 30 °C to 900 °C was 6.5%. The major weight loss of about 5% was observed in the temperature range of 180 °C to 450 °C, with a corresponding DTA peak at 252 °C. This weight loss step can be attributed to decomposition of hydroxide groups. No considerable weight loss is observed after this up to 900 °C, indicating the thermal stability as well as purity of synthesized sample. This is further corroborated by DSC analysis as depicted in the Figure 3(b). A sharp single endothermic peak centered around 252 °C was observed in the DSC curve.

Fig. — 2 (a) XRD diffraction pattern and (b) FTIR spectra of microwave synthesized ZnO

Fig. — 3 (a) TGA/DTA and (b) DSC analyses of microwave synthesized ZnO
Conclusion
Herein, zinc oxide was successfully synthesized using microwave-assisted homogeneous precipitation technique. The structural and thermal properties of sample were studied by different characterization techniques. XRD analysis confirmed the wurtzite structure of ZnO. All elements expected in the sample were observed through EDX. FTIR spectrum exhibited the bands corresponding to Zn-O stretching. SEM showed an assortment of microstructures with a wide size distribution in the range of 10s of nm to over a micron. These findings were further evidenced by TEM study. The thermal stability and purity of sample were ascertained by TGA and DSC studies.

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References