Ultrasonic Cavitational Activation: A Simple and Feasible Route for the Direct Conversion of Zinc Acetate to Highly Monodispersed ZnO

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Highly monodispersed submicron structures of ZnO were successfully fabricated by a simple ultrasonic cavitational activation, which assists a direct conversion of zinc acetate to ZnO, without using any additives.

Monodispersed oxide fine particles have a wide variety of applications such as preparation of advanced ceramics, catalysts and their media, and packing materials for chromatography.[1] Out of the well established solution techniques, the emulsion process has been found to be more promising solution process in the preparation of fine, single, and multicomponent powder having a narrow sized distribution.[2,3] In general, so far reported conventional emulsification processes utilize reactant materials either in water or in ethanol; surfactant or a stabilizer; and kerosene or hexane as an oil phase[2,4] and homogenizer is applied to form the emulsion. After the formation of emulsion, gelling or precipitating agent is added to precipitate the materials which are then subjected to vigorous calcination conditions in order to obtain the materials. Even after all these rigorous stages, the obtained materials are not homogeneous.

Utilization of ultrasonic cavitation for the preparation of materials has become an active area of research in the last decade.[5] Many scientists and industrialists have started using different types of ultrasound devices (whistle, horn) to make emulsions.[6] Taking advantage of the application of ultrasonic cavitation in emulsification as well as in assisting chemical reactions, in this communication, we report a novel and a facile ultrasonic cavitation approach for the preparation of ZnO.

Our present approach is based on ultrasonical dispersing of an aqueous solution of Zn^{2+} cations into rapeseed oil to form well dispersed W/O emulsion droplets, without using a surfactant or an emulsifier. Here, ultrasound provides the mechanical energy to disperse the aqueous solution into the oil phase and its cavitation process leads to breaking the same into fine droplets. Again, by ultrasonic cavitation-mediated hydrolysis, zinc acetate present in the aqueous droplets is then directly converted to its oxide without using any precipitant and without subjecting it to any vigorous calcination conditions. In addition, rapeseed oil as an oil phase has been used, replacing the toxic and troublesome organic nonpolar solvents.

A typical experimental strategy was as follows: 4 mL of aqueous solution containing 0.2 M zinc acetate dihydrate was added to 100 mL of rapeseed oil taken in a sonoreactor. Ultrasound was applied for 20 min under atm pressure in order to preemulsify the W/O phase, maintaining the temperature between 25–30 °C, using a cooling bath. Ultrasound was applied using an ultrasonic probe with a 1/2 in. (ca. 1.27 cm) titanium tip (Branson Digital Sonifier, Model 450, Branson Ultrasonics Corporation, Danbury). The frequency and power applied were 20 kHz and 70 W, respectively. After 20 min of preemulsification, ultrasound dissipation was continued further for 30 min, but without cooling, in order to initiate the hydrolysis of zinc acetate. In the absence of cooling, the temperature increased rapidly due to the continuous dissipation of ultrasonic energy in the liquid. In both of the above cases sonication was carried out in a pulse mode (9 s on and 3 s off).

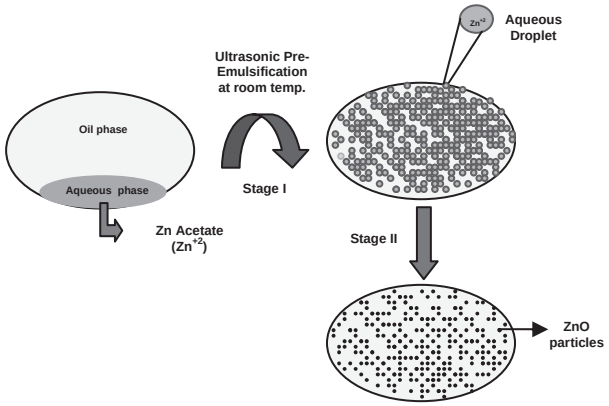

Figure 1. Schematic representation of ultrasonic cavitational activation for the direct conversion of zinc acetate to zinc oxide.

At the end of 30 min of sonication, the temperature of the reaction reached 125 °C so that all the water present in the internal aqueous droplets evaporates leaving behind the solid particles dispersed in the oil phase. Separation of the white solid particles from the oil phase was achieved by centrifuging the suspension at 5000 rpm for 1 h. After decanting the oil phase, the solid particles were then washed 3 times with ethanol in order to remove the small amounts of oil that present on the surface of the product which was then dried under vacuum at room temperature. The typical process followed has been depicted in Figure 1.

Figure 2 shows the comparison of XRD (RINT-2500/PC, Rigaku Co., Japan) pattern of zinc acetate precursor and zinc oxide obtained at different temperatures by the present method. Room temperature emulsification and hydrolysis does not result in the formation of ZnO. Hydrolysis occurs to a certain extent by carrying out the sonication at 98 °C, whereas complete conversion of zinc acetate to ZnO occurs when the sonication temperature reached 125 °C. The diffraction pattern of the product obtained at this temperature matches well to the hexagonal crystalline zincite phase (JCPDS No. 36-1451). No other impurity phases were found.

Figures 3A and 3B show representative TEM (JEOL JEM-2010) and FESEM (HITACHI S-4300) images of as-prepar ZnO. From these images, it was observed that the as-prepar

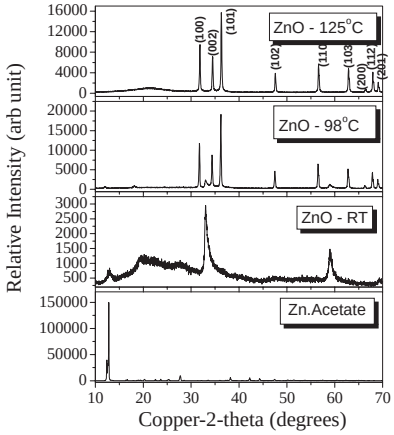

Figure 2. Comparison of XRD of zinc acetate and ZnO obtained at different temperatures by ultrasonic cavitation.

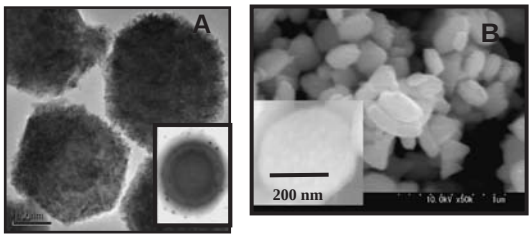

Figure 3. (A) TEM and (B) FESEM micrographs of ZnO fine powder. Inset of Figure 3A indicates electron diffraction pattern and B shows the hexagonal structure of ZnO obtained.

ZnO product is well-crystallized and uniform both in size and shape. The average size of ZnO estimated from Figures 3A and 3B is $0.25 \pm 0.02\,\mu m$. In addition, TEM image of Figure 3A and the inset of Figure 3B clearly reveals the hexagonal structure of the obtained ZnO. The electron diffraction dots shown in the inset of Figure 3A can be indexed as hexagonal structure of ZnO, which is very consistent with the analysis of XRD.

To confirm the chemical composition of the as-prepared product, EDS (NORAN (Vantage)) spectra (Figure 4A) were recorded at a number of positions of the product. The chemical signatures obtained are identical within experimental accuracy and essentially only Zn and O elements are observed with the expected elemental composition and atomic ratios (Zn and O with 50 atom %). The presence of Cu signal arises from the TEM grid.

The IR (FT-IR-8400 S, Shimadzu) spectrum in Figure 4B shows the presence of a large absorption band appeared at around $450\,cm^{-1}$. This band is characteristic of ZnO. Highly homogeneous and small sized particles obtained in this process should be due to the generation of efficient droplet size induced by ultrasound. Ultrasound itself generates sufficient and strong mechanical forces which can easily and evenly disperse the aqueous solution containing the zinc cations in the oil phase. In addition, the strong ultrasonic mechanical forces as well as the higher viscosity of the oil phase might also restrict the formed droplets from a higher mobility and thereby preventing them from coalescence. The aqueous droplets in the W/O emulsion act as microreactors in the bulk oil phase and must offer a unique environment for nucleation and crystal growth of the particles.

Figure 5A shows the micrograph of the emulsion droplets,

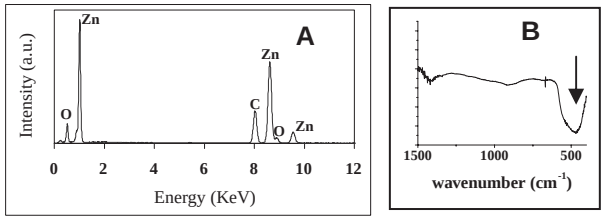

Figure 4. (A) Representative EDS spectrum and (B) FT-IR of ZnO prepared by the ultrasonic cavitation technique.

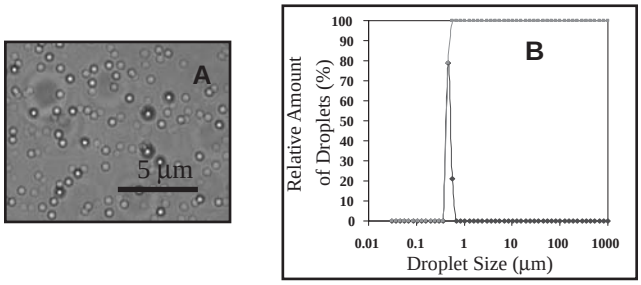

Figure 5. (A) Micrograph showing the emulsion droplets (B) Size distribution of the emulsion droplets.

whereas the Figure 5B reveals the size distribution of water droplets in W/O emulsion, measured using a laser particle size analyzer (Shimadzu, SALD-2000 J, Kyoto, Japan). The droplet size was measured soon after the emulsion was prepared and from these figures it can be seen that the size of the droplets is about $0.425\,\mu m$ in diameter. No detectable changes in the droplet diameter were observed for the emulsions even at high temperature. Looking at the droplet size and the actual particle size, it can be predicted that the individual zinc acetate emulsion droplets react to form particles with a size that can be correlated to the actual droplet size. A slight decrease in the actual particle size from the droplet size could be due to the release of the formed aqueous H^+ from the droplets to the outside.

In the fine water droplets, following is the likely reaction step that is possible for the ultrasonic cavitation-mediated hydrolysis of zinc acetate to give zinc oxide.

$$Zn\,(OCOCH_3)_2 + H_2O \xrightarrow{u/s} ZnO + 2\,CH_3COOH. \quad (1)$$

To conclude, the process demonstrated here is simple and avoids glimpse of outstanding problems that normally exists in conventional emulsion synthesis. Also, the method results in the formation of highly monodispersed ZnO. We also believe that, due to the ability of achieving the formation of ZnO by avoiding the usage of all of the additives and necessary conditions not only provide a simple route but also open a new avenue for the preparation of new and complex mixed oxide systems.

The authors thank the JSPS Postdoctoral Fellowship program for foreign researchers.

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Published on the web (Advance View) December 10, 2005; DOI 10.1246/cl.2006.60