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A novel processing route for the production of nanoparticulate zinc oxide using an isophthalate precursor

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Abstract

Zinc oxide nanoparticles have been processed from a novel isophthalate precursor. In contrast to those processed from an oxalate precursor, this material exhibits three-dimensional, non-directional aggregation behaviour. Such non-directional aggregation of uniaxial crystallites may allow for the production of structures with a higher proportion of catalytically active surfaces than can be prepared through conventional sol–gel methods. XRD, FTIR, TEM and SEM were used to characterize the synthesized materials. Zinc oxide particles synthesized by using isophthalic acid ($C_6H_4-1,3-(COOH)_2$) are found to be slightly smaller than the previously reported materials prepared through chelation with oxalic acid ($H_2C_2O_2 \cdot 2H_2O$).

1. Introduction

Zinc oxide is a wide, direct bandgap semiconductor which has been used in areas such as catalysis [1, 2], gas sensing [3], varistors [4, 5], as a piezoelectric actuator [6], and as a transparent conducting oxide layer for solar cell applications [7, 8]. While numerous methods of synthesis of zinc oxide films and structures have been investigated, the sol–gel route is favourable because of its low cost and the non-destructive nature of the processing conditions involved. The number of synthesis methods reported illustrates the ease with which zinc oxide can be made, and controlling the size and shape presents a challenge. Sol–gel methods [4, 5, 9], especially those involving polymeric precursors [10, 11], are of interest in the present work. We have examined the structure and morphology of zinc oxide nanoparticles produced by the calcination of a zinc isophthalate precursor, synthesized in a simple, low temperature reaction. The effect of the chelating agent and solvent have been investigated for this route [12, 13], and indeed previous authors have reported on the characterization of a zinc isophthalate precursor [14]. However, as far as we are aware, the use of isophthalic acid

for the production of zinc oxide nanoparticles has not been reported. The solution-phase reaction of zinc acetate and isophthalic acid, in ratios of 1:1 and 1:2, was examined. After a brief ageing period, during which gelation occurred, the precursor powders were calcined to 500, and 800 °C, and their structure and morphology examined using XRD, FT-IR, SEM and TEM. The product powders were found to be composed of single crystalline aggregates, with a characteristic structure.

2. Experimental details

Zinc acetate dihydrate ($Zn(CH_3CO_2)_2 \cdot 2H_2O$, $\geq 98\%$, Sigma-Aldrich), isophthalic acid ($C_6H_4-1,3-(COOH)_2$, 98%, Fluka) and absolute ethanol (C_2H_5OH , spectroscopic grade, $>99.5\%$, Sigma) were used without further purification. Stock solutions containing 1 mmol zinc acetate dihydrate, and the required quantity of isophthalic acid, in 10 ml ethanol, were rapidly combined under stirring. The resultant solution was stirred at room temperature for a further 30 min, then dried in an oven at 100 °C for 1 h. The powders were then ground and calcined in a muffle furnace at a ramp rate of $10^\circ C \text{ min}^{-1}$ and dwell time of 2 h. Powder diffraction measurements were undertaken

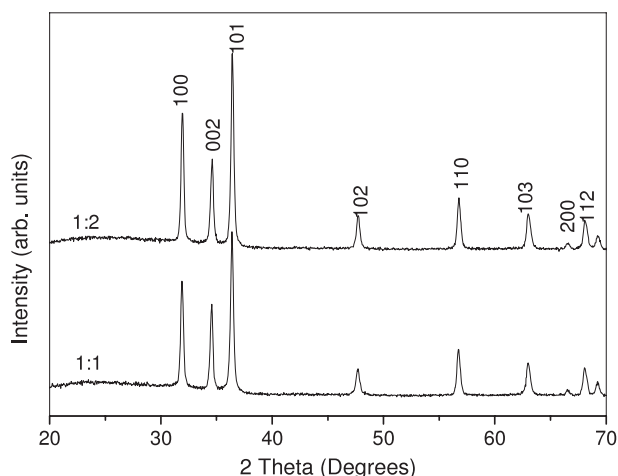


Figure 1. X-ray diffractograms for powders synthesized from 1:1 (lower) and 1:2 ratios of $\text{Zn}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}:\text{C}_6\text{H}_4-1,3-(\text{COOH})_2$, calcined to 500°C .

on a Siemens D500 XRD, operating at 40 kV and 30 mA, at 25°C , using $\text{Cu K}\alpha$ radiation. A Jeol J100CX TEM, operating at an accelerating voltage of 100 kV, and a Jeol 8600 SEM, operating accelerating voltages of 15 kV and 7.5 kV, were used to image the powders. FT-IR spectra of the solid samples were undertaken in transmission mode between 4000 and 400 cm^{-1} using a Perkin-Elmer Spectrum GX microscope and potassium bromide diluent.

3. Results and discussion

Powder x-ray diffraction (XRD) patterns for powders synthesized in a ratio of zinc acetate to isophthalic acid of

1:1 and 1:2, and calcined to 500°C , are shown in figure 1. These diffraction patterns correspond to the ICSD reference for polycrystalline zinc oxide [15], with no unidentified phases detected. XRD studies of the material synthesized reveals wurtzite ZnO has been produced in all cases. The domain sizes of the powders calcined to 500°C was estimated from the (100) and (002) peaks to be $40 \pm 1\text{ nm}$ for powders synthesized in a 1:1 ratio of reagents, and $41 \pm 2\text{ nm}$ for the 1:2 powders. Equivalent studies for powders synthesized from an oxalic acid precursor showed domain sizes of the same or a slightly larger diameter [4, 5]. The growth of domain sizes, indicated by peak sharpening, was observed for powders sintered to 800°C ; analysis of these samples revealed average domain diameters of $103 \pm 8\text{ nm}$ for powders synthesized in a 1:1 ratio, and $105 \pm 12\text{ nm}$ for particles synthesized in a 1:2 ratio.

Investigation of the powder morphology via electron microscopy revealed an unconventional aggregation, which can be seen in figure 2. Figures 2(a), (b) and (c) show SEM images of powders synthesized in a 1:1 and 1:2 ratio of reagents and calcined at 500°C , and in a 1:1 ratio calcined to 800°C , respectively, at a magnification of $5000\times$. It can be seen from these images that the decomposition of a precursor synthesized in a 1:1 ratio of reagents results in the production of micron scale aggregates, of uniform composition, while for the powders synthesized using twice the stoichiometric amount of isophthalic acid, some surfaces are smoother and brighter, possibly indicating the presence of an insulating material. Figure 2(d) shows a single grain, of the powder synthesized in a 1:1 ratio, calcined to 800°C ; a number of curved surfaces may be identified in this image. Figures 2(e)–(g) show TEM images of powders synthesized at a magnification of $20000\times$. The planar aggregation of particles is visible in these images, as is the dramatic difference in morphology between particles sintered to 500°C and to 800°C . While single flakes of

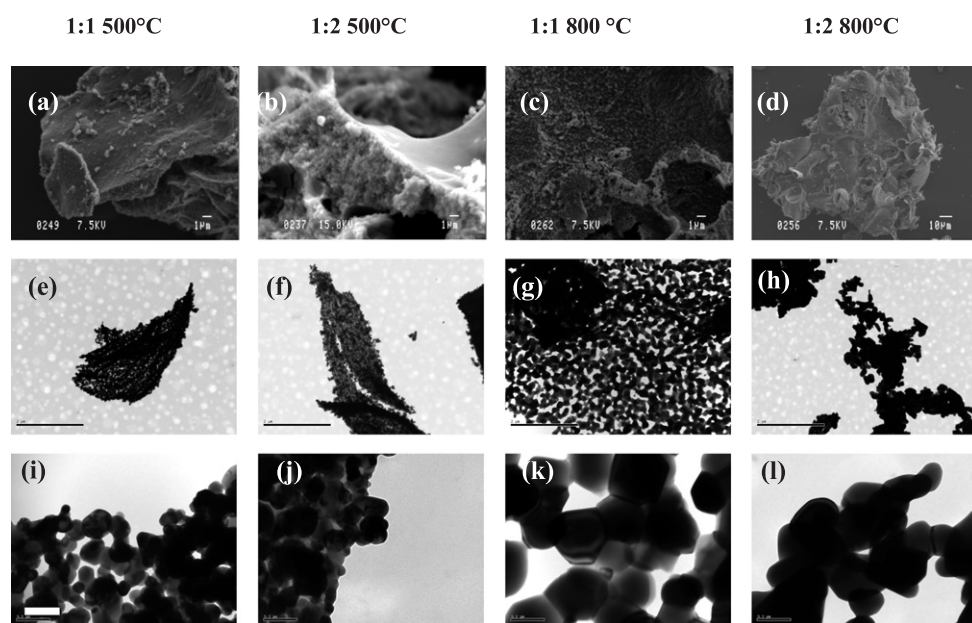


Figure 2. SEM (a)–(d) and TEM (e)–(l) images of product powders. Images (a), (e) and (i) show powders synthesized in a ratio of $\text{Zn}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}:\text{C}_6\text{H}_4-1,3-(\text{COOH})_2$ of 1:1, and calcined to 500°C ; (b), (f) and (j), a precursor synthesized in the ratio 1:2, and calcined to 500°C ; (c), (d), (g) and (k), 1:1 ratio, calcined to 800°C ; (h) and (l), a 1:2 ratio, calcined to 800°C . Scale bars show: (a)–(c) $1\text{ }\mu\text{m}$; (d) $10\text{ }\mu\text{m}$; (e)–(h) $2\text{ }\mu\text{m}$; (i)–(l) 200 nm .

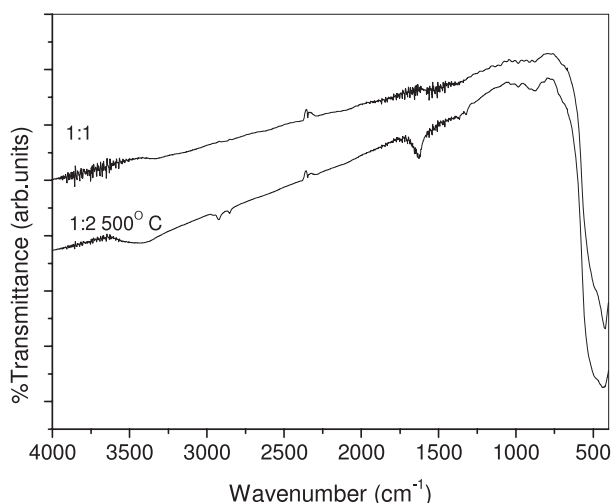


Figure 3. FT-IR spectra of powders synthesized in ratios of zinc acetate to isophthalic acid of 1:1 and 1:2 calcined to 500 °C.

the product material show a variation in contrast, and several small pores, the aggregate shown in figure 2(g) is much larger, and contains pores of a greater size. This may be considered as the result of sintering of particles from a small number of planes to form a single flake, or an artefact of the preparation of TEM samples. For the material shown in figure 2(h), no planar structures were found in this sample, although a three-dimensional aggregation was also observed here. TEM images of these powders at a magnification of 100 000 \times are shown in figures 2(i)–(l). For particles sintered to 500 °C, the random aggregation of polydisperse particles is observed; those sintered to 800 °C are shown to be less polydisperse but much larger, and less closely spaced. No grain boundaries are observed within discrete particles, indicating that the powders are composed of single crystal aggregates. Some variation on contrast is found for particles calcined to 500 °C, this may be attributed to surface impurities also noted for figure 2(b), since particles sintered to 800 °C show much less contrast variation. It is possible that the decomposition of surface ligands is not complete after calcination at the lower temperature. Particles synthesized in a 1:2 ratio of reagents are shown by TEM to be more closely packed than those synthesized in equimolar combinations; this could be a result of the number of singly bound surface ligands in this case, and their stronger interaction.

In order to identify the possible impurities in this material, FT-IR spectroscopy was performed on the samples; spectra of the powders calcined to 500 °C are shown in figure 3. All three spectra shown here exhibit a strong, broad absorbance between 400 and 600 cm^{-1} , as expected for a material that indexes so readily to zinc oxide. A number of weak absorbances are found at 875 cm^{-1} ; these are present in increasing strength as the amount of isophthalic acid used is increased above a stoichiometric ratio, and may thus indicate the increasing presence of a small amount of surface bound carboxyl groups here. Studies of an equivalent system, namely chelation with oxalic acid, have shown that the decomposition of organic

ligands and production of zinc oxide occurs below the sintering temperature of zinc oxide; for the system investigated above, we have found that decomposition continues to occur to much higher temperatures, although a large amount of zinc oxide has formed at 500 °C. Thus, while particles made from an isophthalate precursor are in close proximity, the organic residue present may prevent the contact of crystallite faces. On the removal of this residual layer, crystallites are in immediate contact at a temperature at which they can sinter. This may hinder the oriented aggregation expected for zinc oxide, and lead to the three-dimensional structure found in this case. The sintering of small particles may also account for the change in morphology found in these materials when calcined to 800 °C; since the aggregation structure of many of the larger particles will be fixed while the thermal energy allows the smaller ones to sinter, a porous network such as those seen in figure 2(g) may be expected.

4. Conclusions

In conclusion, we have demonstrated the use of a dicarboxylic acid, namely isophthalic acid, for the processing of a porous zinc oxide network. Particles synthesized at 500 °C are found to be slightly smaller than those synthesized through chelation with oxalic acid, and of a striking morphology. We have associated this characteristic structure with the presence of surface contaminants above the sintering temperature of zinc oxide when the isophthalate precursor is calcined. The non-directional aggregation behaviour found may result in the presence of a higher number of exposed *c* faces in the material, allowing greater catalytic and sensing activity for this material. Further investigation of the relationship between particle size and surface contamination, and calcination may yield the optimum conditions for such uses.

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