JOURNAL OF
Materials
CHEMISTRY

Growth of well-defined ZnO microparticles by hydroxide ion hydrolysis of zinc salts†

Ruth A. McBride,[a] John M. Kelly*[a] and Declan E. McCormack*[b]

[a]*Department of Chemistry, University of Dublin, Trinity College, Dublin 2, Republic of Ireland. E-mail: jmkelly@tcd.ie; Fax: +353-1-6712826; Tel: +353-1-6081947*
[b]*School of Chemistry, Dublin Institute of Technology, Kevin Street, Dublin 8, Republic of Ireland. E-mail: declan.mccormack@dit.ie; Fax: +353-1-4024989; Tel: +353-1-4024778*

Received 25th November 2002, Accepted 21st February 2003
First published as an Advance Article on the web

The morphology of the microcrystalline zinc oxide formed by reaction of zinc salts with sodium hydroxide depends critically on the reaction conditions. To understand this, the nature of the solid product has been probed by scanning electron microcopy (SEM) and X-ray diffraction (XRD) and the concentration of zinc remaining in the solution has been determined at regular intervals throughout the reaction. Two general preparative procedures have been followed. The first, which involves simply heating an aqueous solution containing $Zn(NO_3)_2$ (0.025 M) and sodium hydroxide (0.375 M) to 101 °C and maintaining it at that temperature for periods of up to 8 hours, produces star-like microcrystals. The star-like morphology is apparently caused by multiple crystal twinning at the onset of growth, and the size and shape of the microcrystals have been found to be affected by both the reaction stoichiometry and the type of zinc salt
1 counterion. In the second method, which produces needles of zinc oxide (lengths up to 6 µm—aspect ratio >6), the reagents are stirred at room temperature for two hours before heating the mixture to 101 °C and maintaining it at that temperature for up to 24 hours. Pre-stirring allows the formation of $Zn(OH)_2$, which is shown by XRD and SEM to transform to ZnO upon heating.

Introduction

Controlling the morphology and size is a matter of considerable importance for the manufacture of microcrystalline powders, as for many applications both the size and shape of the particles determine the usefulness of the product. However the mechanism for the formation and transformation of these different forms is often still poorly understood. One such material is ZnO, which is extensively used in industries ranging from the health care sector to the manufacture of electronic components. For example, it is the base material for a number of electronic applications, including varistor-electronic devices, which serve as voltage surge limiters. The effectiveness of such devices is determined by the number of grain boundaries and therefore depends on the size and shape of the constituent particles, which are normally in the micron range.[1,2]

ZnO has been prepared by a number of methods such as the reaction of zinc salts with base,[3–6] chemical bath deposition,[7–9] thermal decomposition,[10] hydrothermal synthesis,[11] sol–gel methods,[12–14] template methods including the use of alumina membranes,[15] and vapour phase transport,[16] giving rise to particles of various shapes and sizes. A particularly striking recent observation is that of lasing action in micron-sized rods.[16,17]

Some of these methods only produce ZnO material in small amounts, restricting their application for many industrial purposes. The method studied here (reaction of zinc salts and sodium hydroxide) uses aqueous solutions with high concentrations of zinc salts and sodium hydroxide, so that large quantities of the oxide can readily be produced in high yield. The size and shape of the microcrystals, which are determined by conditions such as stirring the solution prior to heating, reaction stoichiometry and the nature of the counterion, have been monitored regularly throughout the reaction.

Results and discussion

The zinc oxide is produced by the reaction of aqueous solutions of zinc nitrate and NaOH. Two methods are used, which differ principally by the inclusion of a stirring step in Method B. As illustrated in Fig. 1, Method A yields star-like materials whereas Method B yields microcrystalline needles.

Initial precipitate

In both procedures it was found that the initial addition of a small amount of base produced a precipitate, which subsequently dissolved as the remaining base was added. This initial precipitate was characterised by SEM (see ESI, Fig. I†) and XRD and identified as aggregates of semi-crystalline ZnO. This is in agreement with the early observation of Dirske,[18] who showed that in aqueous solutions at room temperature, an increase in pH results in an increase of ZnO solubility. More recently O'Brien and co-workers[4] also reported the formation of this initial precipitate and noted that it dissolved at pH > 13.5. They postulated that the poorly defined solid was a hydrated zinc oxide on the basis of its IR spectrum.

After addition of all of the base, the two routes outlined in Fig. 1 were followed.

Method A—Star-like particles

Star-like particle growth. In this procedure, heating of the alkaline aqueous zinc nitrate solution commenced immediately after mixing, reaching its boiling point after *ca.* 30 min and was maintained there for several hours. It was observed that precipitation took place *ca.* 10 minutes after mixing (at 55–60 °C). Samples were withdrawn from the mixture at regular intervals and the growth of these particles was followed by

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†Electronic supplementary information (ESI) available: SEM images of precipitates and particles formed by the reaction of zinc nitrate with sodium hydroxide. See http://www.rsc.org/suppdata/jm/b2/b211723c/

DOI: 10.1039/b211723c

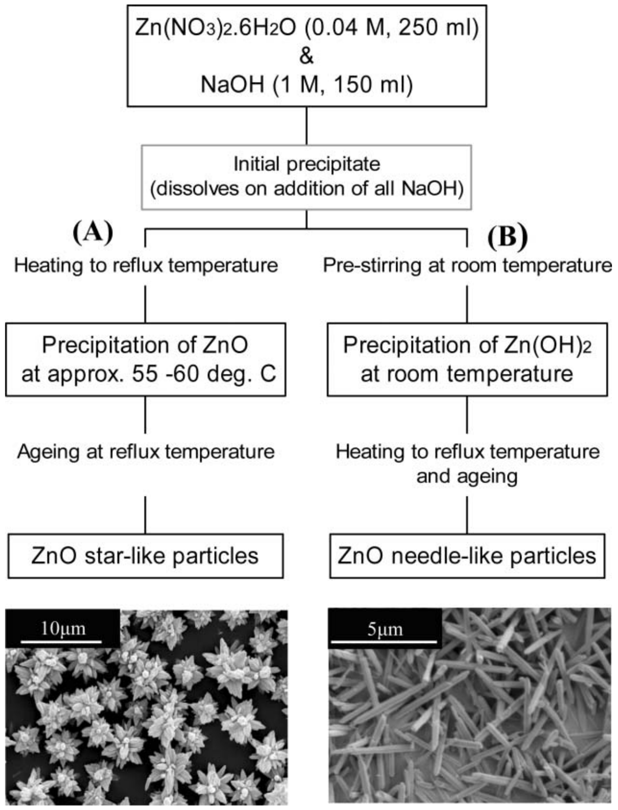

Fig. 1 Flow chart of experimental procedure for the production of ZnO particles with differing morphologies.

XRD and microscopy. All samples showed XRD patterns consistent with ZnO (zincite JCPDS 36-1451). Peak sharpening, indicating an increase in the sample crystallinity was observed as the heating time increased.

The star-like morphology is already observed at the onset of precipitation/turbidity and SEM measurements show that the particles increase in size during the ageing process (see ESI, Fig II†). The precipitated particles removed at the first appearance of turbidity have a diameter of *ca.* 3.5 μm. After a further 5 minutes the size distribution broadens, with the particle diameters ranging from 3.5 to 8 μm (average *ca.* 6 μm). 30 minutes after precipitation, the average particle diameter is still *ca.* 6 μm, although the distribution of particle diameters has narrowed slightly (4–8 μm). In all cases the morphology is similar with the spines originating at a single point. The peaks in the XRD sharpen substantially up to 30 minutes, indicating an increase in crystallite size. No notable change in the average particle size, sample crystallinity or the number of particles occurs on ageing for 2 hours [particle diameter 4.5–8.5 μm (average 6.3 μm)]. However when ageing is extended up to 8 hours, a slight increase in the average particle size is observed (from 6.3 to 7.7 μm).

The observation that turbidity-sized particles (*ca.* 3.5 μm) are in existence for heating times up to 30 minutes after precipitation possibly suggests that nucleation is taking place up to that point. As there is no reservoir for any component of the reaction and the concentration is well above the critical concentration, a number of nucleation events are expected to take place. The formation of stars may be explained by the coalescence of several nuclei.

After the microcrystalline samples had been removed from the reaction mixture, the hot filtrate was neutralised with nitric acid (1 M) and analysed by EDTA titration (Fig. 2). On examining the curve, it is evident that the concentration of Zn^{2+} in solution decreases rapidly (0.025 M to 0.006 M) during the first 30 minutes heating and after 40 minutes heating, the concentration of Zn^{2+} in solution has levelled off at approximately 0.0044 M (consistent with the solubility expected under the reaction conditions[18]). This result correlates with the observed changes in particle size, as it appears that while nucleation is taking place, the concentration of Zn^{2+} drops rapidly. However, when the rate of particle growth is small, the change in $[Zn^{2+}]$ is almost zero.

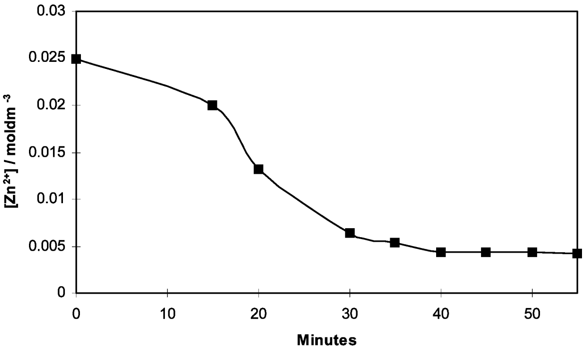

Fig. 2 $[Zn^{2+}]$ in solution at various times during reaction of $Zn(NO_3)_2$ with NaOH (Method A).

The growth of these star-like ZnO particles does not follow the simple LaMer theory,[19] as it appears that there are several nucleation events. Den Ouden and Thompson[20] have shown that monodisperse populations can form even though nucleation extends over a period of time, if the particle growth is low relative to nucleation. After the first nucleation, the particles begin to grow by diffusion of the reactants through the solution to the surface of the growing particles. While this is taking place, further nucleations also occur. However, when a level below critical concentration is achieved, nucleation no longer takes place and the existing particles continue to grow until the point of solubility is reached. The low concentration of Zn^{2+} ions available after 30 min reaction necessitates that for particles to significantly increase in size, dissolution–reprecipitation must occur and consequently growth of the particles is slow.

ZnO has a hexagonal lattice, with an $a:c$ axial ratio of $1:1.6$.[21] The most common morphologies observed are either rod-like or needle-like crystals, elongated in the *c*-axis direction and with hexagonal prismatic faces. However, crystal twinning is common. While many crystalline compounds exhibit twinning consisting of two lattices growing from a common junction, zinc oxide is unusual in readily forming fourlings.[22] These fourlings consist of four acicular spines united at a common base and approximately tetrahedral to each other. Star-like ZnO particles were previously observed using hydrothermal methods, forced hydrolysis of zinc nitrate using hexamethylenetriamine,[23] 1,2-diaminoethane,[4,24] and ammonium hydroxide[25] and also by the decomposition of hydrozincite.[26]

Star-like particles were also observed in ZnO smoke[27] and their morphology was studied in detail by Fuller.[28] He deduced that the ZnO particles twinned along the $(11\bar{2}2)$ planes to produce these so-called fourlings. Each spine of the fourling is a ZnO crystal, elongated along the *c*-axis. It is believed that thin sheets (approximately 50 to 500 Å) can form between spines, with each sheet lying in the plane of two spines, similar to webbing. These sheets can then act as nuclei for further spines to grow. Fourlings can also grow together, binding along two spines and hence ideally having seven spines. An example of this structure can be seen in Fig. 3. However, many deviations from this ideal structure can occur. For example, only one sheet may be well developed resulting in missing spines or others can have a large portion of complex groups, resulting in many spines and sheets radiating from a central nucleus. It would appear from the results obtained, that the latter case is evident in this study.

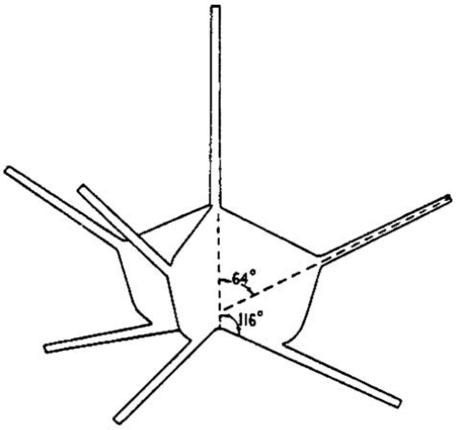

Fig. 3 Idealized group of three sheets and seven spines related by $(11\bar{2}2)$ twinning.[29]

Concentration and zinc counter-ion effects. The concentrations of $Zn(NO_3)_2$ and NaOH were varied so as to examine the effect of each on the samples produced by Method A. In all cases although the XRD patterns were consistent with the ZnO (zincite) structure, the morphology was dramatically changed. When the $Zn(NO_3)_2$ concentration is doubled (0.05 M after mixing) spherical type particles are observed (Fig. 4A) These are probably caused by dendritic growth, with the twinned particles forming re-entrant corners that are favourable to further nucleation and growth.[29] Between the spines of the star-like particles new growth sites are encouraged, which causes this 'filling in', resulting in the formation of the almost spherical particles.

Fig. 4B shows particles prepared when the sodium hydroxide concentration is halved (0.19 M after mixing). This decreased OH^- concentration also gave large spherical type particles. However, the particles do not show the spines expected for star-like particles, but rather aggregated platelet type particles. In this case the initial precipitate of ZnO, which forms when a small amount of NaOH is added to the zinc solution, never re-dissolves, as the final concentration of OH^- is never sufficient for this to happen. Hence, the final particles are a result of continued growth of this initially-formed material, so that the original morphology is largely retained.

In other experiments it was found that either doubling the hydroxide concentration (to 0.75 M after mixing) or halving the zinc nitrate concentration (to 0.0125 M in the final mixture) yielded no microcrystalline precipitate.

Changing the zinc salt counter-ion has a noticeable effect on the morphology of the particles produced. The particles do not take on the star-like morphology when zinc sulfate or chloride is used in place of the nitrate salt, rather they form aggregates of non-uniform particles, similar to spines of the star-like particles. The particles also show a lower degree of crystallinity (seen as XRD peak broadening) when compared to the zinc nitrate product. It can therefore be assumed that the nitrate ion plays an important role in the formation of the star-like particles. Counter-ion effects on crystal habit have been explained by the preferential adsorption of certain anions onto some faces of the growing crystals,[30,31] inhibiting growth on that face. It is presumed that this is happening with the nitrate ion, giving rise to the observed particle shape. The different behaviour of SO_4^{2-} and Cl^- suggests that neither of these ions show such preferential adsorption.

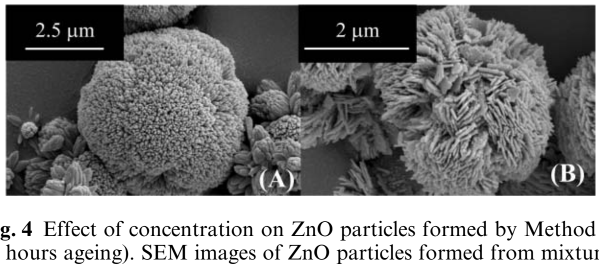

Fig. 4 Effect of concentration on ZnO particles formed by Method A (5 hours ageing). SEM images of ZnO particles formed from mixtures of (A) 0.05 M $Zn(NO_3)_2$ and 0.375 M NaOH and (B) 0.025 M $Zn(NO_3)_2$ and 0.19 M NaOH.

Method B—Needle-like particles

The second reaction procedure used (Method B, Fig. 1) results in the formation of needle-like ZnO. This method differs from Method A in that the basic zinc nitrate solution was stirred at room temperature for 2 hours prior to heating to its boiling point.

Pre-stirring step. It was observed that 10–15 minutes after the dissolution of the initial precipitate, a new precipitate formed. The XRD patterns obtained for the samples withdrawn at regular intervals for up to 2 hours after this were all consistent with the compound being $Zn(OH)_2$ (wulfingite JCPDS 38-385). Up to 30 minutes stirring, a sharpening of peaks was recorded, indicating that the particles were becoming more crystalline, but no significant change was observed after that time. Fig. 5 presents SEMs of particles withdrawn from the dispersion immediately after precipitation and after a further 2 hours stirring. The particles are seen to precipitate with a rhombic morphology, gradually getting larger and more uniform with time. This morphology reflects the orthorhombic lattice structure of the $Zn(OH)_2$ crystal.[21] Upon initial precipitation the particles range in size from 1 to 5 μm. After 30 minutes, the particles have increased in size, with the largest now *ca.* 7 μm and they reach a maximum size of *ca.* 10 μm after the mixture is stirred for 60 minutes. No further increase in size is observed, although they become considerably more uniform, in the range 6–10 μm (Fig. 5B). Prolonged stirring, up to 24 hours, showed no further change in particle crystallinity, morphology, or size distribution.

In the first 30 minutes of this room temperature reaction, the $[Zn^{2+}]$ drops from 0.025 M to 0.01 M (Fig. 5C), subsequently decreasing much more slowly (to 0.008 M at 45 minutes) and remaining almost constant at approximately 0.0076 M after 1 hour. This presumably represents the solubility of $Zn(OH)_2$ in the reaction mixture.[32]

Previous workers,[4,5] who studied zinc nitrate–sodium hydroxide systems, did not stir the solution at room temperature prior to high temperature ageing and hence did

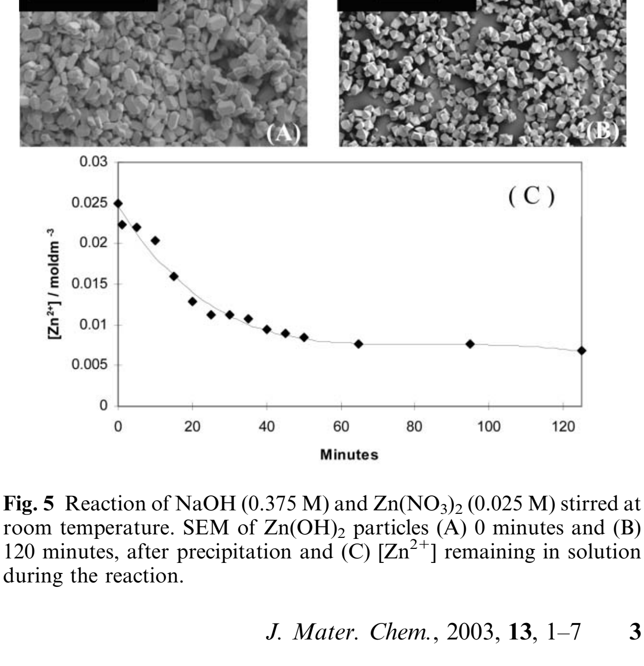

Fig. 5 Reaction of NaOH (0.375 M) and $Zn(NO_3)_2$ (0.025 M) stirred at room temperature. SEM of $Zn(OH)_2$ particles (A) 0 minutes and (B) 120 minutes, after precipitation and (C) $[Zn^{2+}]$ remaining in solution during the reaction.

not report the formation of $Zn(OH)_2$ particles. Indeed in many of the cases where inorganic base hydrolysis is carried out on metal ions, organic bases are added as complexing agents to prevent the formation of the $Zn(OH)_2$ phase.[30] It is interesting to note that when the mixture is not stirred the microparticles of $Zn(OH)_2$ are much less uniform (as are the ZnO microcrystals formed upon subsequent heating). This effect of stirring results presumably from changes to the rate of nucleation.[33]

Needle-like particle growth. The reaction suspension containing the $Zn(OH)_2$ particles was heated to 101 °C and aged for various times. Samples were withdrawn at intervals during the reaction to study the growth of the particles and their XRD patterns were recorded (Fig. 6). It was observed that after 30 minutes only $Zn(OH)_2$ was present while after 60 minutes the solid was composed solely of ZnO (zincite). SEM measurements show that between 35–40 minutes (when the mixture is at 101 °C) small particles start to grow on the surface of the rhombic hydroxide microcrystals (Fig. 7C and 7D) and after 45 minutes, it is evident that these particles have a needle-like morphology. Concurrent with this growth the XRD shows the pattern for ZnO beginning to appear and by 50 minutes, the ZnO pattern is predominant. By 55 minutes, SEM shows only needle-like particles and the XRD shows the pattern for ZnO alone. Raman microscopy was also used to distinguish between ZnO and $Zn(OH)_2$ in the mixed samples.

By titration of the filtrate it was shown that the concentration of Zn^{2+} remaining in solution drops from 0.0076 M (corresponding to the solubility of $Zn(OH)_2$ under the conditions of the experiment) to 0.0046 M (the solubility of ZnO *vide supra*) over the period when the transformation is taking place (Fig. 8). Such transformations may take place either by dissolution–reprecipitation[34] or by solid phase transformation[35]

The thermal transformation of zinc salts to ZnO has been studied in the solid state by Louër and co-workers.[10] They investigated the decomposition of $Zn_3(OH)_4(NO_3)_2$, $Zn_5(OH)_6(CO_3)_2$, $Zn(C_2O_4)\cdot 2H_2O$ and $Zn(CH_3CO_2)_2\cdot 2H_2O$ using XRD and SEM methods. It was found that despite the varying crystal structures of these zinc 'precursor' compounds, the crystallite shape of the ZnO formed was independent of the zinc salt used, although the aspect ratio was strongly 'precursor' dependent. It is possible therefore that the growth of ZnO needle-like particles from rhombic $Zn(OH)_2$ is a solid state thermal decomposition. It may be noted that the thermal decompositions of the zinc salts studied by Louër and co-workers occurred at a higher temperature than is observed in the decomposition of $Zn(OH)_2$ under our conditions. However the formation of ZnO from $Zn(OH)_2$ might be a particularly 'soft' process (*i.e.* loss of water from the lattice) and therefore proceed at a lower temperature.

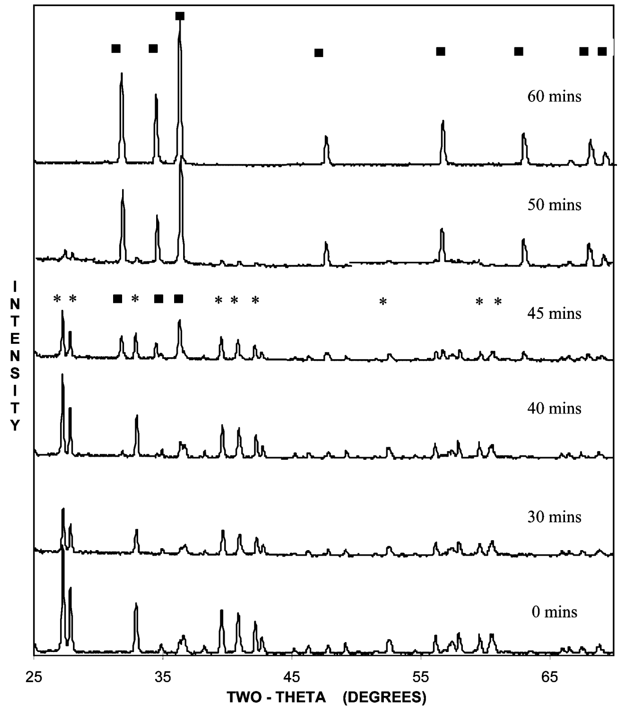

Fig. 6 XRD patterns showing growth of ZnO needle-like particles by thermal decomposition of $Zn(OH)_2$ rhombic particles (* wulfingite; ■ zincite).

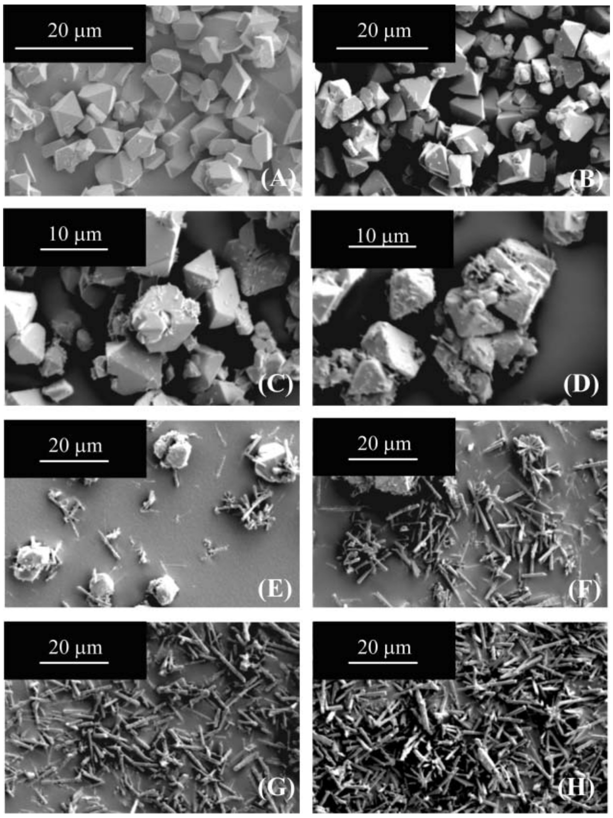

Fig. 7 Growth of needle-like ZnO by thermal decomposition of $Zn(OH)_2$ (Method B) stirred for two hours followed by heating for (A) 0 minutes, (B) 30 minutes, (C) 35 minutes, (D) 40 minutes, (E) 45 minutes, (F) 50 minutes, (G) 55 minutes and (H) 60 minutes.

Alternatively the process may involve dissolution of the $Zn(OH)_2$ and formation of the ZnO by precipitation from solution. Sugimoto and Matijevic have proposed that this is the mechanism for the formation of microcrystalline hematite (Fe_2O_3) from $Fe(OH)_3$.[35] The SEM micrographs (Fig. 7) appear to show that the ZnO forms primarily on the $Zn(OH)_2$ microcrystals. The subsequent growth then takes

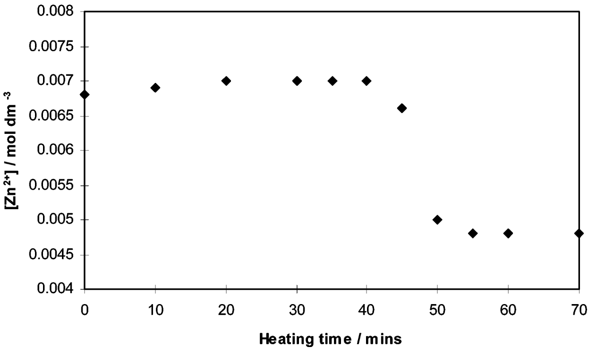

Fig. 8 Variation of $[Zn^{2+}]$ with heating time upon heating $Zn(OH)_2$ rhombic particles in the reaction mixture (Method B).

place in a regular well-controlled fashion. The absence of star-like particles is consistent with the fact that the $Zn(OH)_2$ is acting as a reservoir, maintaining the $[Zn^{2+}]$ concentration well below that where nucleation can occur.

The needle-like morphology reflects the structure of the ZnO lattice. The hexagonal structure can be seen by the prismatic shape of the needles and the $a:c$ axial ratio of 1 : 1.6 is expressed by the elongation in the c-axis direction. As the aspect ratio of the particles is far greater than 1.6, the growth appears favoured in this direction. The net polarization of the ZnO c-axis has been previously put forward as an explanation 2 for the directional growth in ZnO from zinc nitrate–HMT solutions.[23] The growth mechanism may also be similar to that proposed by Ocana *et al.*[31] where the formation of spindle-shaped Fe_2O_3 is believed to involve aggregation of smaller primary particles, which is accompanied by the desorption of the adsorbing anions.

Varying the time over which the ageing step is carried out between 5 and 24 hours alters the dimensions of the needle-like particles formed. The width of the needle-like particles does not change significantly with time (*ca.* 0.6 to 1.3 μm). In contrast, the length of the needle-like particles is seen to be affected by ageing time [range 2.5–7.5 μm (average = 4.5 μm) after 5 hours; range 2.5–9.5 μm (average = 6.4 μm) after 24 hours. As the ZnO needle-like particles are formed from the decomposition of $Zn(OH)_2$ within 60 minutes heating, any subsequent growth of the particles must result from a dissolution and reprecipitation of the existing ZnO particles. The results suggest that this is a slow process, as significant changes in the particle dimensions are only seen after 24 hours ageing.

Concentration and zinc counter-ion effects. The concentrations of both the initial concentrations of the zinc nitrate and the NaOH solutions were altered from the standard concentrations as used above [$Zn(NO_3)_2$ (0.025 M) and NaOH (0.375 M)]. On doubling the zinc nitrate concentration (0.05 M), no effect on the particles is observed. However, although halving the zinc nitrate concentration (0.0125 M) still resulted in needle-like particles, they were no longer uniform and the size distribution was seen to broaden greatly.

When double the hydroxide ion concentration is used (0.75 M), a very low yield ($\sim$7%) is obtained and the particles are needle-like in morphology. The solubility of both the $Zn(OH)_2$ and ZnO is reported to increase with pH,[32] which results in a low yield. When half the hydroxide concentration is used (0.19 M NaOH), spherical platelet particles are formed, similar to those obtained for Method A (Fig. 4B). This can again be accounted for by the fact that the solution pH never reaches a level at which the initial ZnO precipitate becomes fully soluble. Instead, continued growth of these particles takes place, resulting in spherical platelet aggregation.

Changing the counter-ion does not have an obvious effect on the ZnO particles formed. Zinc chloride gave needle-like particles with a similar size distribution to those produced by using the nitrate salt. Zinc sulfate also gives needle-like particles, however, in this case the particles are non-uniform.

Conclusion

The experiments reported here confirm that the morphology of zinc oxide formed by the reaction of zinc salts and hydroxide ion is very dependent on the route taken and the precise reagent concentrations used. The pre-stirring step is especially important as it yields the orthorhombic form of zinc hydroxide, which converts to zinc oxide on heating. The advantage of this approach is that the zinc oxide produced is in the form of hexagonal rods of high aspect ratio. It appears that the ZnO is formed from the $Zn(OH)_2$ by a solid phase transformation process, which occurs over a relatively short time period. Because of this the twinning process, which leads to the stars formed by direct reaction of $Zn(NO_3)_2$ and hydroxide, does not take place.

Experimental

Reagents

Zinc nitrate hexahydrate (Aldrich 98%), zinc sulfate heptahydrate (M&B 98%), zinc chloride (BDH 97%); sodium hydroxide (Wardle Chemicals Ltd. 96%) were used without further purification.

Synthesis

Sodium hydroxide (1 M, 150 cm^3) was added with stirring to aqueous zinc nitrate hexahydrate (0.04 M, 250 cm^3) in a round-bottomed flask. After addition of approximately 20 cm^3 of NaOH, an initial white precipitate formed, which dissolved on the addition of the remainder of the base. After this point in the reaction, two different methods were investigated.

The first method (A) involved heating the reaction mixture to reflux temperature (101 °C) over a silicone oil bath and holding the temperature constant for given times. Approx. 10–15 minutes after mixing, when the temperature is *ca.* 55–60 °C, a second precipitate forms. This second precipitate was identified as star-like ZnO. After the ageing time has elapsed, the white solid was filtered from the hot solution through a 0.45 μm pore filter (Millipore) and dried in air to constant weight (typical yield 85%).

In the second method (B), the reaction mixture was stirred for 2 hours at room temperature prior to heating. After *ca.* 10–15 minutes, a white precipitate formed, identified as rhombic $Zn(OH)_2$. After the stirring time had elapsed, the mixture was then heated to reflux (101 °C, reached after *ca.* 30–35 minutes) and aged at that temperature for a given time period. The hot solution was filtered through a 0.45 μm pore size filter and the white powder, now needle-like ZnO, was dried in air to constant weight. The effect of both the stirring time and the heating time was investigated (typical yield 85%).

The growth patterns of the $Zn(OH)_2$ and the ZnO particle morphologies were studied by removing samples (approx. 30 cm^3) at regular intervals using a pipette and filtering through 0.45 μm pore size filters. The filtrate taken from the reaction at various stages was neutralised by nitric acid (1 M), then buffered at pH 10 using an ammonia–ammonium chloride buffer, (4% w/w ammonium hydrate, 1% w/w ammonium chloride) and titrated against EDTA using a solochrome black indicator.[36]

For both methods the reactions with zinc sulfate heptahydrate or zinc chloride were also studied under essentially identical conditions by adding sodium hydroxide (1 M, 150 cm^3) with stirring to aqueous solutions of the zinc salt (0.04 M, 250 cm^3).

Instrumentation

Particle morphology was determined using a Hitachi S-3500N scanning electron microscope (SEM). Crystal structure data was collected using a Siemens Diffrac500 powder X-ray diffractometer (XRD) with a copper filament and patterns matched to those in the JCPDS data library. Size distributions of samples were determined using an Olympus BX60 B201 light microscope using transmitted light and connected to a Vantage CCD colour camera, MVD plug-in digitizer, running through a MAC 5300.

Raman microscopy was carried out using an ISA Dilor-JobinYvon-Spex Labram spectrometer. The exciting 20 mW He–Ne laser (632.8 mm) was focussed using a 100× objective lens and focussing was confirmed using a CCD camera in imaging mode. A spectral resolution of 1.5 cm^{-1} per pixel was achieved using 1800 lines mm^{-1} grating.

Acknowledgements

This work was funded by the Enterprise Ireland (ST/96/208). We thank the Centre for Microscopy and Analysis (Trinity College Dublin) for their help with SEM studies and Dr Tia Keyes for Raman microscopy studies.

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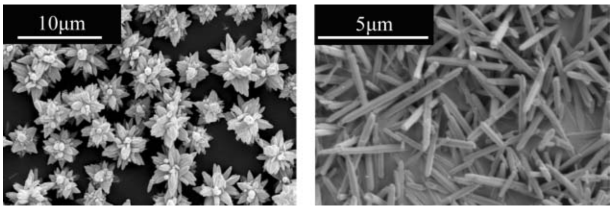
0000 **Growth of well-defined ZnO microparticles by hydroxide ion hydrolysis of zinc salts**

Ruth A. McBride, John M. Kelly and Declan E. McCormack



The morphology of the microcrystalline zinc oxide formed depends critically on the reaction conditions.

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