Systematic Study of Hydrothermal Synthesis of Zinc Oxide (ZnO) Nanosized Powders with Superior UV Absorption

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Abstract

Zinc oxide (ZnO) powders were synthesized by the hydrothermal method at 160-280ºC for 6-24 hours, under 90-930 psi pressure, from concentrated precursors without stirring. The precursors were formed by mixing aqueous solutions of zinc acetate, chloride, sulphate, or nitrate with KOH (aq) under either controlled or rapid precipitation conditions. The precursor quantities were chosen to yield zinc concentration of 0.3-4.0 m, KOH concentration of 0.6-8.0 m, and pH between 4 and 14 after precipitation has been completed. Most of the synthesized powders exhibited equiaxed morphology, low aggregation levels and narrow crystallite size distributions in the range of 60-200 nm. Some of the ZnO powders consisted of nanosized equiaxed crystallites mixed with large, mostly elongated crystals, 0.5-4.0 μm in size. Based upon this systematic study encompassing a wide range of synthesis conditions, temperature-controlled growth rate and Ostwald ripening were found to dominate the hydrothermal crystallization of ZnO powders. Comparison with several commercially available ZnO powders revealed superior purity, particle size distributions, defect structure, and ultimately UV absorption, in selected powders synthesized hydrothermally. Results of this study enable the use of hydrothermally made ZnO powders in sunscreens or other UV absorption applications and make their hydrothermal production commercially feasible.
Introduction

Zinc oxide (ZnO) is a wide-band semiconductor, with a variety of applications in photonic, photovoltaic, and electronic devices, such as blue light emitting diodes (LEDs), lasers, UV detectors, transistors, and solar cells \(^1\text{-}^4\). In addition, ZnO exhibits attractive piezoelectric properties, which enable its applications as transducers, SAW, and BAW devices \(^5\). Among other major uses of ZnO, particularly in powder form, are pigments \(^6\text{-}^7\), photocatalysts \(^8\text{-}^9\), and UV absorbers.

Zinc oxide is one of only two inorganic UV filters in sunscreens approved for use in Europe and in the USA \(^10\). Advantages of ZnO in this application include broad absorption of the UV radiation both in UVA and UVB range, much better than in the case of TiO\(_2\) \(^11\text{-}^12\), combined with high transparency, and biocompatibility superior to the widely used organic UV filters, such as benzophenone or others \(^13\text{-}^14\). Excellent UV absorption of ZnO can be also utilized in cosmetics, paints, varnishes, and plastics \(^15\text{-}^16\). Performance of ZnO in the UV absorption applications is determined primarily by such properties of the ZnO powders as particle size, morphology, agglomeration level, defect structure, and chemical composition (purity, dopants). The UV filters must exhibit sufficiently low agglomeration level, low crystallite size, and high dispersability to provide transparent layers. At the same time, they should possess high UV absorption, which is determined by the crystallographic and chemical properties. Achieving synergy between all of these features requires highly engineered ZnO powder thus necessitates use of advanced synthesis techniques.

ZnO powders can be synthesized by several well-established synthesis methods, for example oxidation of metallic zinc vapor from zinc metal (French process) or ore (American process) \(^17\), decomposition of zinc-containing salts \(^18\), or spray pyrolysis \(^8\text{-}^19\). All of these methods use high temperatures up to 1,000\(^\circ\)C in order to crystallize the ZnO phase. In most cases, the high synthesis temperatures lead to the formation of strong aggregates in the ZnO powders, which subsequently have to be excessively milled resulting in poor control of particle morphology and size distribution.

Hydrothermal synthesis is a low-temperature alternative to the methods described above and crystallizes anhydrous materials in a variety of forms directly from aqueous solutions at elevated temperatures and pressures, for fine powders usually up to 200-300\(^\circ\)C under corresponding saturated vapor pressure of water \(^20\text{-}^26\). This technology offers several advantages over
conventional powder synthetic methods, such as one-step synthesis without high temperature calcination and milling, low aggregation levels and narrow crystallite size distributions, in addition to excellent control of particle morphology and size\textsuperscript{20-26}. The purity of hydrothermally synthesized powders usually significantly exceeds purity of the starting materials, because the growing crystallites tend to reject impurities present in the growth environment, which are subsequently removed from the system with together the crystallizing solution\textsuperscript{27}. In addition, low synthesis temperatures can result in unique chemical defect structures, which cannot be achieved at very high temperatures required by the classical synthesis methods, thus may result in unique materials properties in particular applications.

The hydrothermal synthesis of ZnO powders has been relatively well described in the literature\textsuperscript{28-62}. The hydrothermal synthesis conditions of ZnO powders encompass a very broad range of temperatures (20-400°C), pressures (0-4,000 psi), durations at peak temperature (0.1 second – 21 days), types of precursors, reactants concentrations (0.001 – 1.5 M), pH (5-14), additives, precursor preparation methods, and types of autoclaves, i.e. both batch and continuous flow. The synthesized ZnO powders exhibit a broad variety of sizes (20 nm – tens of microns), morphologies (equiaxed, needles/whiskers, rods, fibers, sheets, flakes plates, polyhedra, ellipsoid), and aggregation levels as well. Unfortunately, most of these papers report only a few experimental points, often not well characterized, i.e. without specified reactants concentration and/or temperature and/or pH etc. While some trends can be noticed in individual papers, there is no consistency between them, which will be discussed in detail later. Moreover, none of the published reports on ZnO shows well documented and characterized hydrothermal synthesis of nanosized ZnO powders from concentrated precursors, with equiaxed morphology, low aggregation level, and properties superior to the ZnO powders made by classical techniques.

In the present work, we have synthesized a wide range of ZnO powders by the hydrothermal technique from concentrated precursors without stirring. It is a systematic study encompassing a wide range of synthesis conditions including temperature, reactants concentration, pH, types of precursors and chemical additives, based upon which the growth mechanism can be elucidated. In selected ZnO powders we observed unique combination of equiaxed morphology, low aggregation level, and narrow particle size distribution, with high chemical purity and unique defect structure, which resulted in superior UV absorption. Results of this study enable the use of
hydrothermally made ZnO powders in sunscreens or other UV absorption applications and make their hydrothermal production commercially feasible.

**Experimental Procedure**

**Preparation of precursors for ZnO hydrothermal synthesis.** Hydrothermal syntheses of 4-35 g of ZnO powders were performed as follows. Appropriate weight of zinc chloride (ZnCl₂, USP grade or technical grade), zinc acetate (Zn(Ac)₂·2H₂O, USP grade), zinc sulphate (ZnSO₄·7H₂O, USP grade), or zinc nitrate (Zn(NO₃)₂·6H₂O, reagent grade, all Spectrum Chemical, New Brunswick, NJ) was dissolved in 28.3-233.2 mL of DI water in a glass beaker. Several drops of 37% HCl were added to prevent formation of gel-like precipitates in some cases. In a separate glass beaker, appropriate weight of potassium hydroxide (KOH, 85%, reagent grade, Spectrum Chemical, New Brunswick, NJ) was dissolved in 20.0-160 mL of DI water. Both types of solutions were cooled down to room temperature. The quantities of the starting materials were selected to yield 0.3-4.0 m ZnCl₂, Zn(Ac)₂, Zn(NO₃)₂, or ZnSO₄ and 0.6-8.0 m KOH (aq) after mixing (see Table I for details). Subsequently, the zinc salt solution and KOH solution were mixed using two different methods, denoted hereafter “controlled precipitation” or “rapid precipitation”. During the controlled precipitation, the Zn-salt solution was placed on a Cimarec® digital stirring hot plate (Model No. SP131325, Barnstead/Thermolyne, Dubuque, IO) and the KOH solution was slowly poured into it using a pipette, under intensive stirring by Teflon-coated magnetic stirrer. The stirring rate was adjusted depending on the viscosity of the aqueous slurry in such a way that vortexing was always visible. During the KOH addition, formation of white precipitates of zinc hydroxide was observed. Starting pH was 2.42-5.54, temperature slightly increased to about 30-45°C during the course of the precipitation process. The precipitation was carried out until the desired temperature-compensated pH of about 9-14 was achieved (see Table I for detailed pH values). The temperature-compensated pH was being monitored with high accuracy using an Accumet® Excel dual channel pH/ion meter (Model No. XL25, Fisher Scientific, Hampton, NH) equipped with a universal Accumet® glass electrode and temperature probe. Prior to the measurements, the pH meter was checked against 3 standard buffers (measurement results in brackets): 7.00 (7.03), 10.00 (10.01), and 12.43 (12.43). The total precipitation time was about 15-30 min. The slurry was subsequently agitated for another 10 min in order to stabilize pH. In the case of
reagent mixing by “rapid precipitation” (i.e. ZOP-15, ZOP-30), the Zn salt solution was rapidly poured into the KOH solution and the mixture was stirred with a pipette for only 1 minute, while the final pH was measured using pH paper. The precursor slurries were then transferred to one or several clean 120 mL Teflon containers.

**Hydrothermal synthesis of ZnO powders.** The containers were closed with a screw caps, placed in a special steel holder and put into cleaned autoclave (13”Dia x 120”H, Autoclave Engineers, Erie, PA), together with several other small containers with loads targeting different types of ZnO powders. About 60 L of DI water were then placed in the bottom of the autoclave. The autoclave was sealed using a special plate closure with an O-ring. Calibrated pressure gauge and two J-type thermocouples were attached. A few hours after closing the autoclave, the heating cycle of the hydrothermal treatment was initiated as follows: from room temperature to 160-280°C with heating rate of 29.0°C/hr, followed by holding at 160-280°C for 6-24 hours, with temperature stability of a few °C, with pressure of 90-920 psi, which were saturated vapor pressures of water at 160-280°C. After completing soaking at the maximum temperature, the autoclave was shut down and cooled in an uncontrolled manner. The cooling to room temperature took approximately 48 hours. After unloading, pH of the aqueous slurry was again measured precisely using the pH meter (see Table I for detailed pH values). In some cases (i.e. ZOP-15, ZOP-30), the pH after the synthesis was measured using pH paper. Subsequently, content of the Teflon containers in form of aqueous slurries was placed on a 0.45 μm Supor®-450 (Pall Gelman Laboratory, Ann Arbor, MI) membrane filter with 47 mm diameter inside a porcelain Büchner funnel, and vacuum filtrated using a laboratory vacuum/pressure pump (Model No. 2522B-01, Welch Rietschle Thomas, Skokie, IL). After filtering off the initial aqueous solution (mother liquor), the powders were washed several times using DI water while being filtrated under vacuum. After using at least 250 mL of DI water for washing, all water was filtered off and the remaining powder cake was placed on a hot plate and dried overnight at 120°C. Subsequently, the dried powder was collected and analyzed by different methods. Estimated ZnO powder yield was measured only for one composition (ZOP-52) and was 91.6%. Compositions ZOP-52 and ZOP-46 were successfully reproduced and scaled-up, in order to manufacture kilogram quantities from a single batch.

**Materials Characterization.** Phase composition of all powders after hydrothermal synthesis was characterized by X-ray diffraction using Advanced Diffraction System X1 diffractometer.
(XRD, Scintag Inc.) using Cu K$_\alpha$ radiation, in the 2\(\Theta\) range between 10-70° with a 0.05° step size and 0.1-0.3 s count time. The chemical identity of the powders was determined by comparing the experimental XRD patterns to standards compiled by the Joint Committee on Powder Diffraction and Standards (JCPDS), i.e. card # 01-1136 for ZnO (zincite).

The morphology and phase purity of all synthesized ZnO powders were examined using scanning electron microscope (SEM, Model S-4500, Hitachi, Japan) at 5 kV accelerating voltage. The powders were attached to the aluminum holders using a conductive carbon tape. All samples were sputtered with thin conductive layers of palladium prior to the SEM examination.

Chemical moieties present on the surface of the ZnO powders were determined using X-ray photoelectron spectroscopy (XPS) using the Phi 5000 VersaProbe Scanning ESCA Microprobe (Ulvac-Phi, Inc., Minneapolis, MN), utilizing Al K$_\alpha$ radiation with energy of 1,486.6 eV. The ZnO powders were attached to the holders using conductive carbon tape. The XPS spectra were acquired from the surface areas with diameters of approximately 0.3 mm on each sample. Only one spot on each sample was analyzed by this technique. In a typical XPS measurement, a 20-60 min. overview scans were performed in the binding energy range of 0-1,100 eV with 0.4 eV step. High-resolution XPS analysis of the O1s peaks was performed in the range of 523-543 eV for 30 min, with a step of 0.1 eV. Standard software was subsequently used for peak deconvolution using Gaussian-Lorenzian curve fits.

Selected ZnO powders and starting materials were subjected to chemical analysis at NSL Analytical (Cleveland, OH). The powders were analyzed for the following elements (analytical technique in brackets): Pb, Cd, Cu, Mn, Fe, and As (inductively-coupled plasma-mass spectrometry, i.e. ICP/MS), SO$_4$ (Parr/IC), and CO$_3$ (wet chem.).

Particle size distributions of selected ZnO powders were measured using X-ray Disc Centrifuge Sedimentation method (XDC, Brookhaven X-ray Disc Centrifuge Particle Size Analyzer Ver. 3.69). In order to prepare sample for analysis, 2 g of ZnO powder was dispersed in 0.1% aqueous solution of NaHMP at pH=10. Disc speed was 1,500 rpm in all cases. Particle density, spin fluid density, and spin fluid viscosity were 5.6 g/cm$^3$, 0.997 g/cm$^3$, and 0.890 cP, respectively. Average crystallite sizes were calculated from SEM images based upon averaging data for at least 100 randomly selected crystallites.

UV attenuation of selected ZnO powders was measured using the following methodology. First, the test sunscreen formulation was prepared, which was a non-water resistant oil-in-water
emulsion with the following constituents: 7.5% octyl methoxycinnamate, 3.0% Arlacel 165, 1.0% DC345 fluid, 1.5% ceteryl alcohol, 1.5% Ceteareth-20, 0.5% Trivasperse NH, 0.1% Crodaphos N3N, 10.0% isopropyl myristate, 15.0% of Xanthan Gum (2% solution), 1.5% propylene glycol, 0.1% tetrasodium EDTA. The formulation contained 5.0% of ZnO powder, which is concentration that should produce in-vitro SPF number of about 15-20. The rest of the formulation was water. Subsequently, in-vitro SPF measurements were performed using Labsphere UV Transmittance Analyzer. The substrate used was Transpore Tape® (3M) and the test sunscreen formulation was applied at 2 mg/cm² (as per the FDA in-vivo methodology). The SPF value was calculated from the difference in transmission of UV radiation (from 290 nm to 400 nm) between the substrate with and without applied sunscreen. The mean SPF values were based on averaging 6 measurements.

Results and Discussion

Properties of ZnO powders synthesized hydrothermally. Typical synthesis conditions and properties of selected ZnO powders prepared in this work are summarized in Tables I-III.

Powder XRD analysis revealed high level of crystallinity and 100% phase purity of the ZnO powders shown in Fig. 1 and Tables I-III. Only XRD peaks derived from the ZnO (zincite) phase were observed.

SEM photographs in Fig. 1 reveal two types of morphologies of the ZnO powders. Fig. 1(a)-(c) show mostly nanosized ZnO powders consisting of very well defined, equiaxed, weakly agglomerated, and round crystals with narrow size distributions (as shown are powders with primary particle size ranging between 60 nm and 200 nm). Conversely, powders shown in Fig. 1(d)-(h) exhibit significantly high level of agglomeration, aspect ratio higher than 1 (Fig. 1(d)), and clearly bi-modal crystallite size distribution, consisting of micron-sized mostly elongated particles mixed with submicron equiaxed particles (Fig. 1(e)-(h)). It is apparent from the pictures in Fig. 1 that the level of the aggregation and crystallite size distributions of the hydrothermally synthesized ZnO powders could be controlled in wide ranges by changing the processing parameters, thus the powders could be used for a wide range of applications. The nanosized ZnO powders with narrow particle size distributions may be utilized as pigments, photocatalysts, or UV absorbers. Such powders should also exhibit high sinterability due to the small crystallite size and very narrow crystallite size distributions. The ZnO powders with
bimodal size distributions could be used to fabricate textured ceramics with quasi-single crystal-like properties, if the large elongated particles could be oriented, for example by tape casting or hot pressing.

Chemical analysis of the bulk of the ZnO powders (Table II) and XPS analysis of the surface (will be discussed in detail in the last sections of this paper) confirmed high purity of the hydrothermally synthesized ZnO powders. The major impurity was carbonate, detected by the chemical analysis on the level of 400ppm-0.1%. XPS confirmed high purity of the ZnO powders surfaces. Except for traces of chlorine detected in one case, no other major impurities were detected either in the bulk or on the surface of the hydrothermally synthesized ZnO powders.

Chemical analysis data shown in Table II for both starting ZnCl₂ (technical grade, column 5) and hydrothermally synthesized ZnO powder (ZOP-52, column 3) additionally confirmed effect of hydrothermal purification, i.e. synthesized crystals having higher purity than the starting materials, because the growing crystals tend to reject impurities under hydrothermal conditions. Concentrations of all analyzed elements/ions shown in Table II, except for carbonate and copper, were either reduced in the synthesized ZnO powder vs. starting ZnCl₂ or at least at comparable level. Particularly strong reduction was observed for sulphate, iron, and arsenic. Increase of Cu concentration cannot be explained at this time. Increase in carbonate content is most likely related to the additional presence of dissolved CO₂ in water used in hydrothermal synthesis of ZnO, as all precursor preparation and synthesis work was conducted in air.

**Effects of the synthesis variables on properties of the ZnO powders.** Hydrothermal synthesis of the ZnO powders was performed in a wide range of synthesis conditions, such as temperature/pressure, type and concentrations of the starting materials, pH, and methodology of precursor preparation. A schematic map, which summarizes the experimental conditions of the hydrothermal synthesis of ZnO, is shown in Fig. 2. All these synthesis factors were found to affect in various degrees properties of the ZnO powders synthesized in this work, as described below.

**Effects of the precursor (chemical composition, concentration, pH, preparation method).** Both concentration of the starting materials and pH of the precursor were found to be very important parameters in synthesis of ZnO, as demonstrated in Fig. 2. Formation conditions of pure ZnO phase were primarily determined by the combination of these two parameters. When pH of the ZnO precursor was between 4 and 7, and zinc concentration (denoted hereafter [Zn])
between 0.0 and 2.0 m, no pure ZnO phase was observed to form, even at 250°C. In the temperature range of 200-280°C, pH in excess of 9-10 (preferably 12-14) was required to obtain pure ZnO phase when [Zn] was below 2.0 m. In the same temperature range, [Zn]=2.0 m at pH=9 resulted in the formation of pure ZnO phase. However, at temperatures under 200°C, pH of 9 did not produce pure ZnO phase even at [Zn]=2.0 m. In the investigated temperature range (160-280°C), the optimum combination of pH and [Zn] to obtain pure-phase ZnO powders appears to be 9-14 and 1-4 m, respectively. All findings of this systematic study were summarized in Fig. 2, which is an experimentally generated phase diagram for the hydrothermal synthesis of ZnO powders from concentrated precursors.

Effect of pH and [Zn] on size, morphology, and aggregation level of ZnO crystallites were difficult to elucidate (see also Fig. 3). Nevertheless, ZnO powders with the smallest crystallites, most narrow particle size distributions and lowest aggregation levels, were synthesized at [Zn]=1-2 m, pH=9-12, 160-200°C for 12-24 hours. High [Zn]=4.0 m combined with rapid precipitation resulted in bi-modal crystallite size distributions, i.e. mixtures of micron size crystals surrounded by submicron crystallites (ZOP-30). Base concentration was typically twice as high as [Zn] (see Table I), thus it is considered a dependent variable and its effect was not studied.

The investigated starting materials containing zinc were aqueous solution of the following zinc-containing salts: ZnCl₂, ZnSO₄·7H₂O, Zn(NO₃)₂·6H₂O, and Zn(Ac)₂·2H₂O. Only aqueous solution of KOH as a base was investigated. It was found that zinc chloride and acetate produced comparable phase composition, crystallite size, morphology, and aggregation level of the ZnO powders, although the use of ZnCl₂ appears to produce slightly superior results. Different grades of ZnCl₂ [USP grade, technical grade] produced more or less comparable results as well. However, use of zinc nitrate or sulfate resulted in the formation of bi-modal crystallite size distributions even at low synthesis temperature of 200°C (ZOP-63, ZOP-66).

Controlled precipitation with controlled pH appears to produce better results than quick mixing of the starting materials during “rapid precipitation”, although the second method could also produce ZnO powders with low aggregation level and uniform particle size distribution of the primary ZnO crystallites, bracketing the size range of 100-200 nm (ZOP-15).

It is worth mentioning that zinc concentrations in excess of 1 m guarantee high production yields in case of commercialization, while significantly lower concentrations do not. Several
papers report hydrothermal synthesis of equiaxed ZnO crystallites with sizes under 100 nm \cite{29,34,43-46,53}. However, all of them use diluted precursors with concentrations well below 1 m, sometimes even as low as 0.001 m. Only Li et al. report hydrothermal synthesis of ZnO with crystallite size of 70 nm from 1 M-zinc acetate-based precursor \cite{35,36}. However, these ZnO powders do not have as uniform particle size distributions as ZnO powders synthesized in this work. The results obtained in the present work at zinc concentrations of 1.0-2.0 m demonstrated commercial potential for the hydrothermal synthesis of ZnO powders in batch autoclaves without stirring. Subsequently, experiments ZOP-52, ZOP-46, and ZOP-43 were reproducibly scaled-up to produce kilogram quantities of ZnO powders from a single batch.

Conditions of the of the hydrothermal synthesis. In the investigated temperature range, most of the synthesis conditions yielded pure phase ZnO powders. However, other requirements also had to be met in order to obtain pure ZnO phase, particularly appropriate pH of the precursor slurry and concentrations of starting materials (see Fig. 2). As clearly demonstrated in Fig. 3, increasing synthesis temperature facilitated formation of larger ZnO crystallites. This trend was applied to all precursor concentrations at pH between 9.6 and 12.

The hydrothermal synthesis of ZnO powders described in this work was carried out under saturated vapor pressures of water at the syntheses temperatures, thus the pressure is here a temperature-dependent variable and will not be discussed separately. Time is here also a temperature-dependent variable and its effects were not investigated in detail. However, it is believed that formation of ZnO requires time in the order of minutes to hours in the investigated temperature range of 160-280°C. The higher the synthesis temperature, the lower the time required to complete the synthesis. The heating rate of 29°C/hr was used in all syntheses of ZnO powders in this work. Heating rate may impact size, morphology, and aggregation of ZnO crystallites, however its effects were not investigated in this work.

Growth mechanism of the ZnO powders under hydrothermal conditions. The balance between nucleation and growth rates determines crystallite size during the hydrothermal crystallization \cite{20}. With increasing supersaturation (controlled by temperature, reactants concentration, pH), both growth rate and nucleation rate increase. Consequently, when the growth rate dominates over the nucleation rate, crystallite sizes increase, while in the case of nucleation rate domination, crystallite size decreases \cite{63}. The results of the present work are summarized in Fig. 3 and show strong relationship between the synthesis temperature and the
crystallite size, i.e. increasing crystallite size with increasing synthesis temperature on all investigated levels of precursor concentration and pH. Such behavior is consistent with the growth rate-dominated crystallization. Effects of the pH and concentration are difficult to elucidate probably because the solution supersaturation during hydrothermal synthesis of ZnO reaches maximum at different combinations of pH and [Zn] for different Zn salts $^{64,65}$. Thus the temperature effect at constant [Zn] and pH is the only clearly visible effect during hydrothermal synthesis of ZnO, unless a very detailed study of varying [Zn] or pH with all other parameters kept constant could be performed.

The bi-modal crystallite size distributions (Fig. 1e-h) were observed in both “rapid precipitation” and “controlled precipitation” cases thus the uniformity of the precursor, which is lower in the earlier case, does not seem to have played any role in creating such large particles. The large micron-sized ZnO particles were formed mostly from precursors prepared by “rapid precipitation”, all of which where prepared at had pH of about 14 and also during “controlled precipitation” at pH of about 12 but at high temperatures of 250-280°C. Most of the bi-modal crystallites forming conditions do not correspond to maximum supersaturation, which occurs at pH below 14 in hydrothermal ZnO synthesis $^{64,65}$. Uniform crystallite size distributions were obtained under intermediate conditions, i.e. [Zn]=1-2 m, pH=9-12, 160-200°C, which appear to be close to maximum supersaturation, at least from the point of view of pH. All this is pointing out towards Ostwald ripening effects, i.e. dissolution of fine particles and re-precipitation on large particles, which occurs in batch systems due to supersaturation decrease $^{66}$. During the hydrothermal synthesis of powders, the supersaturation gradually decreases as the crystallization progresses, and at certain point small particles start dissolving, resulting in constant supersaturation, which favors growth of only large crystallites $^{66}$. This may occur when the synthesis time is too long with respect to the synthesis temperature or when the initial supersaturation is already low. It seems, that the Ostwald ripening effects were responsible for bi-modal size distributions in some batches of the hydrothermally synthesized ZnO powders.

Literature data for ZnO hydrothermal synthesis is summarized in Fig. 4. No clear relationship between crystallite size and synthesis temperature or precursor concentration could be observed. There are trends in individual papers $^{30,36,37,40}$, which however are not consistent with other works. The present work is thus the first systematic report studying effects of various synthesis parameters and their combinations in wide ranges, establishing experimentally stability phase
diagram for ZnO under hydrothermal conditions and elucidating the synthesis temperature as the most essential parameter in control of size of ZnO crystallites.

Comparison of the hydrothermally synthesized ZnO powders with commercial ZnO powders. For comparison with the hydrothermally prepared powders, several commercially available ZnO powders used as UV filters in sunscreens are shown in Fig. 5: NyasorbUV (Nyacol Nano Technologies, Ashland, MA) synthesized by decomposition of Zn-containing salts, ZCote, and SunSmart (both Nanophase Technologies Co., Romeoville, IL) both synthesized by oxidation of Zn metal. It is obvious that the commercial ZnO powders exhibit much higher agglomeration levels, non-uniformly sized crystallites, and broader particle size distributions than the ZnO powders from this work, although all of them are highly-crystalline, phase-pure ZnO, as revealed by powder XRD patterns shown in Fig. 6. As estimated using the Scherrer’s equation, broad peaks of the NyasorbUV powder shown in Fig. 6a are related to the small size of the primary crystallites rather than to the lattice disorder. Properties of commercially available ZnO powders are also summarized in Table III.

Typical particle size distributions of selected ZnO powders synthesized hydrothermally and the commercially available ZnO powders are compared in Fig. 7 and Table III. The particle size distributions data are consistent with the SEM observations: ZnO powders from this work exhibit much more narrow particle size distributions than the other commercial ZnO powders, due to very uniform crystallite size and low aggregation levels. The differences are particularly strongly pronounced for particle sizes greater than 150-200 nm. Nyasorb UV exhibits narrow particle size distribution and reasonable median/mode particle sizes, but this is due to high aggregation level of 10-30 nm primarily crystallites.

Crystallite size and aggregation levels are important features of ZnO powders designated for UV filter applications in sunscreens. Size of primary particles should not be lower than 50 nm, like in the case of the Nyasorb UV powder, because particles smaller than 50 nm may penetrate through the skin pores and cause adverse health effects. High level of aggregation can result in broader particle size distribution and larger median/average particle sizes, which may result in whitening of the sunscreen composition applied on skin (particularly above 150 nm). Thus the optimum size of ZnO particles for UV filter applications in sunscreens is around 50-80 nm, with low aggregation level and high particle uniformity. It is clear from Fig. 5 and Table III that the hydrothermally synthesized ZnO powders are most close to this requirement.
Survey XPS spectra of both hydrothermal and commercial ZnO powders (Fig. 8) did not reveal significant differences between the powders, although NyasorbUV had substantial magnesium contamination and ZOP-46 had traces of chlorine adsorbed on the surface. Otherwise, all four powders exhibited XPS spectra typical for ZnO, showing strong Zn- and O-derived bands. However, high resolution XPS analysis of the O1s band of the ZnO powders revealed significant differences between the commercial and hydrothermally synthesized ZnO powders. As shown in Fig. 9, the hydrothermally synthesized ZnO powders had much smaller shoulders of the O1s band, located at about 1.5 eV higher binding energy than the main component of the O1s peak, than the commercial ZnO powders synthesized by the high-temperature methods. The low binding energy component of the O1s peak, located at 530.0 eV is ascribed in the literature to the O\(^{2-}\) ions in stoichiometric ZnO, while the higher binding energy shoulder located 1.0-1.5 eV higher is derived from O\(^{2-}\) ions in oxygen-deficient ZnO. Presence of oxygen vacancies with effective positive charge can also explain shift of the O1s peaks towards higher energies in both commercial ZnO powders (Fig. 9c-d). The third component of the O1s peak with the highest binding energy is derived from adsorbed or chemisorbed O\(_2\) or OH\(^-\) groups on the ZnO surface. In all investigated powders, the Zn 2p\(_{3/2}\) peak was highly symmetrical and positioned around 1,022 eV, which should be assigned to the Zn\(^{2+}\) ions in ZnO. These high-resolution XPS data indicate significantly lower level of oxygen deficiency, i.e. higher stoichiometry, in hydrothermal ZnO powders than in the commercial ZnO powders, which were synthesized by the high-temperature methods. It is not surprising, as the hydrothermal synthesis of ZnO takes place under strongly oxidizing conditions. All these XPS data demonstrate superior defect structure and higher purity of the hydrothermally synthesized ZnO powders over the commercial powders synthesized at high temperature.

UV absorption comparison. UV absorbance of selected ZnO powders (both this work and commercial) is shown in Fig. 10 and Table III. The ZnO powder from this work exhibits high SPF factor of 23, high critical wavelength of 372 nm, and high UVA ratio of 0.49. The combination of all three parameters is superior to the corresponding properties of commercial ZnO powders. SPF number reflects mostly UVB radiation protection, whereas the critical wavelength corresponds to UVA protection. High critical wavelength is particularly important, because the long UVA radiation is responsible for occurrence of melanoma and premature aging of the skin, while the UVB radiation causes erythema (sunburn) and non-malignant skin
cancer\textsuperscript{11,12}. While the ZnO powders synthesized in this work were tested as UV filters in sunscreens, other potential UV filters applications are possible, such as in paints, plastics, etc.

One of possible explanations of superior UV absorption of the hydrothermally synthesized ZnO powders could be different defect structures and/or impurity contents, which was demonstrated using the XPS analysis. However, despite of finding empirical correlation in the present work, such conclusion appears to be speculative without further, more detailed understanding of the UV attenuation mechanism in ZnO.

\textbf{Summary}

Zinc oxide (ZnO) powders were hydrothermally synthesized from highly concentrated precursors without stirring, demonstrating good potential for commercial production. The hydrothermal method was found to be useful to produce a range of phase-pure ZnO powders with varying level of agglomeration and crystallite size distribution, including nanosized ZnO powders with very narrow crystallite size distributions and a range of bimodal size distributions. Systematic study of the hydrothermal crystallization of ZnO in a very broad range of synthesis conditions allowed identifying the growth rate and Ostwald ripening as the dominant factors governing size of the ZnO crystallites and the synthesis temperature as the most important size controlling parameter. The hydrothermally synthesized ZnO powders exhibited much more uniform crystallite size distributions and significantly higher level of lattice perfection than the commercially available ZnO powders synthesized by classical high-temperature methods. Their UV absorption was superior to the commercial ZnO particularly in the UVA range, making them attractive as UV filters in sunscreens or other applications.

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References


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Table 1. Synthesis conditions and properties of hydrothermally synthesized ZnO powders (selected examples)

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Zn Salt</th>
<th>[Zn] (m)</th>
<th>[KOH] (m)</th>
<th>pH*</th>
<th>Synthesis Conditions</th>
<th>Phase Composition</th>
<th>Powder size, and morphology by SEM</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZOP-43</td>
<td>ZnCl$_2$ (USP grade)</td>
<td>1.0</td>
<td>2.0</td>
<td>12.14 /12.65</td>
<td>Controlled precept.: 200°C (225 psi), 12 hours</td>
<td>100% ZnO (zincite)</td>
<td>Equiaxed, low aggregation, narrow crystallite size distribution (60-150 nm)</td>
</tr>
<tr>
<td>ZOP-46</td>
<td>ZnCl$_2$ (USP grade)</td>
<td>2.0</td>
<td>4.0</td>
<td>9.65 /11.21</td>
<td>Controlled precept.: 200°C (225 psi), 12 hours</td>
<td>100% ZnO (zincite)</td>
<td>Equiaxed, low aggregation, narrow crystallite size distribution (60-150 nm)</td>
</tr>
<tr>
<td>ZOP-52</td>
<td>ZnCl$_2$ (USP grade)</td>
<td>1.0</td>
<td>2.0</td>
<td>12.53 /12.25</td>
<td>Controlled precept.: 160°C (90 psi), 24 hours</td>
<td>100% ZnO (zincite)</td>
<td>Equiaxed, low aggregation, narrow crystallite size distribution (60-120 nm)</td>
</tr>
<tr>
<td>ZOP-58</td>
<td>Zn($\text{Ac}_2$)$_2$·2H$_2$O (USP grade)</td>
<td>1.0</td>
<td>2.0</td>
<td>12.39 /12.81</td>
<td>Controlled precept.: 160°C (90 psi), 24 hours</td>
<td>100% ZnO (zincite)</td>
<td>Equiaxed, low aggregation, narrow crystallite size distribution (60-200 nm)</td>
</tr>
<tr>
<td>ZOP-60</td>
<td>Zn($\text{Ac}_2$)$_2$·2H$_2$O (USP grade)</td>
<td>1.0</td>
<td>2.0</td>
<td>12</td>
<td>Controlled precept.: 200°C (225 psi), 12 hours</td>
<td>100% ZnO (zincite)</td>
<td>Equiaxed, low aggregation, narrow crystallite size distribution (80-200 nm)</td>
</tr>
<tr>
<td>ZOP-15</td>
<td>ZnCl$_2$ (USP grade)</td>
<td>2.0</td>
<td>4.0</td>
<td>14/8-9 (by paper)</td>
<td>Rapid precept.: 250°C (577 psi), 7 hours</td>
<td>100% ZnO (zincite)</td>
<td>Equiaxed, low aggregation, narrow crystallite size distribution (100-200 nm)</td>
</tr>
<tr>
<td>ZOP-30</td>
<td>ZnCl$_2$ (USP grade)</td>
<td>4.0</td>
<td>8.0</td>
<td>14 (by paper)</td>
<td>Rapid precept.: 250°C (577 psi), 7 hours</td>
<td>100% ZnO (zincite)</td>
<td>Low aggregation, 2 fractions: equiaxed (100-200 nm) and large equiaxed/elongated (0.5-2.0 μm)</td>
</tr>
<tr>
<td>ZOP-51</td>
<td>ZnCl$_2$ (USP grade)</td>
<td>2.0</td>
<td>4.0</td>
<td>12.15/12.87</td>
<td>Controlled precept.: 280°C (930 psi), 6 hours</td>
<td>100% ZnO (zincite)</td>
<td>Low aggregation, 2 fractions: equiaxed (100-200 nm) and large equiaxed/elongated (0.5-4 μm)</td>
</tr>
<tr>
<td>ZOP-63</td>
<td>Zn(NO$_3$)$_2$·6H$_2$O (reagent grade)</td>
<td>1.0</td>
<td>2.0</td>
<td>12.05/12.18</td>
<td>Controlled precept.: 200°C (225 psi), 14 hours</td>
<td>100% ZnO (zincite)</td>
<td>Low aggregation, 2 fractions: equiaxed (60-120 nm) and elongated (0.5-1.0 μm)</td>
</tr>
<tr>
<td>ZOP-66</td>
<td>Zn(NO$_3$)$_2$·6H$_2$O (reagent grade)</td>
<td>2.0</td>
<td>4.0</td>
<td>12.12/12.56</td>
<td>Controlled precept.: 200°C (225 psi), 14 hours</td>
<td>100% ZnO (zincite)</td>
<td>High aggregation, 2 fractions: elongated (300-500 nm) and equiaxed (60-120 nm)</td>
</tr>
</tbody>
</table>

* temperature-compensated pH values before/after hydrothermal synthesis
### Table II. Chemical analysis of selected ZnO powders synthesized hydrothermally and selected starting materials.

<table>
<thead>
<tr>
<th>Element/ion</th>
<th>USP requirements for ZnO</th>
<th>ZnO from technical grade ZnCl₂ (ZOP-52-TG)</th>
<th>ZnO from USP grade ZnCl₂ (ZOP-54)</th>
<th>Technical grade ZnCl₂ as starting materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>&lt;4.6 ppm</td>
<td>0.2 ppm</td>
<td>0.14 ppm</td>
<td>0.16 ppm</td>
</tr>
<tr>
<td>As</td>
<td>&lt;0.23 ppm</td>
<td>0.008 ppm</td>
<td>0.16 ppm</td>
<td>0.83 ppm</td>
</tr>
<tr>
<td>Cd</td>
<td>&lt;4.4 ppm</td>
<td>0.75 ppm</td>
<td>0.006 ppm</td>
<td>0.46 ppm</td>
</tr>
<tr>
<td>Cu</td>
<td>&lt;4.0 ppm</td>
<td>1.2 ppm</td>
<td>1.6 ppm</td>
<td>0.42 ppm</td>
</tr>
<tr>
<td>Mn</td>
<td>&lt;3.9 ppm</td>
<td>4.9 ppm</td>
<td>4.7 ppm</td>
<td>4.0 ppm</td>
</tr>
<tr>
<td>Fe</td>
<td>&lt;3.5 ppm</td>
<td>&lt;5 ppm</td>
<td>3.0 ppm</td>
<td>7.2 ppm</td>
</tr>
<tr>
<td>SO₄</td>
<td>&lt;10 ppm</td>
<td>&lt;10 ppm</td>
<td>4 ppm</td>
<td>32 ppm</td>
</tr>
<tr>
<td>CO₃</td>
<td>-</td>
<td>0.10%</td>
<td>440 ppm</td>
<td>280 ppm</td>
</tr>
</tbody>
</table>
Table III. Particle size distributions and UV absorption properties of selected ZnO powders, synthesized in this work by the hydrothermal method and commercially available powders.

<table>
<thead>
<tr>
<th>Powder ID</th>
<th>Synthesis Conditions</th>
<th>Phase Purity</th>
<th>Morphology/ particle size by SEM</th>
<th>Particle Size Distribution</th>
<th>UV absorption in-vitro</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>D&lt;sub&gt;10&lt;/sub&gt; (nm)</td>
<td>D&lt;sub&gt;50&lt;/sub&gt; (nm)</td>
</tr>
<tr>
<td>ZOP-46 (present work)</td>
<td>Hydrothermal</td>
<td>100%</td>
<td>Equiaxed (60-150nm) primary particles, narrow psd, low aggregation</td>
<td>68</td>
<td>94</td>
</tr>
<tr>
<td>ZOP-52 (present work)</td>
<td>Hydrothermal</td>
<td>100%</td>
<td>Equiaxed (60-120nm) primary particles, narrow psd, low aggregation</td>
<td>74</td>
<td>106</td>
</tr>
<tr>
<td>ZOP-43 (present work)</td>
<td>Hydrothermal</td>
<td>100%</td>
<td>Equiaxed (60-150nm) primary particles, narrow psd, low aggregation</td>
<td>83</td>
<td>118</td>
</tr>
<tr>
<td>ZCote (commercial, Nanophase)</td>
<td>Oxidation of Zn</td>
<td>100%</td>
<td>Both equiaxed &amp; elongated (60-250nm) primary particles, broad psd, moderate aggregation</td>
<td>78</td>
<td>116</td>
</tr>
<tr>
<td>SunSmart (commercial, Nanophase)</td>
<td>Oxidation of Zn</td>
<td>100%</td>
<td>Equiaxed (30-250nm) primary particles, broad psd, highly aggregated</td>
<td>84</td>
<td>123</td>
</tr>
<tr>
<td>NyasorbUV (commercial, Nyacol)</td>
<td>Decomposition of Zn salts</td>
<td>100%</td>
<td>Equiaxed (10-30nm) primary particles, uniform psd, highly aggregated</td>
<td>52</td>
<td>71</td>
</tr>
</tbody>
</table>

“psd” stands for particle size distribution
Figure 1. SEM photographs of hydrothermally synthesized ZnO powders: (a) ZOP-43, (b) ZOP-46, (c) ZOP-60, (d) ZOP-51, (e) and (g) ZOP-66, (f) and (h) ZOP-30. Synthesis conditions details are given in Table I. Note varying level of aggregation and crystallite size distributions from (a) through (h).
Figure 2. Experimentally generated phase diagram for the hydrothermal synthesis of ZnO powders from concentrated precursors. Open symbols represent experimental points with no ZnO formation; solid symbols represent experimental points with formation of ZnO (mostly 100% pure phase zincite). Dotted area is the pH vs. concentration region where the ZnO precursor was precipitated under stirring under controlled pH conditions (i.e. precipitation was carried out slowly to reach desired pH value). Dashed areas are pH vs. concentration regions where the base was added rapidly without pH control (i.e. pH was determined by the quantity of added base). The dashed line separates region of pure phase ZnO formation (on the right) from the region where no pure phase ZnO could be obtained (on the left).
Figure 3. Average crystallite size of ZnO powders as function of the temperature of their hydrothermal synthesis for various sources of Zn and various concentration of Zn in the precursor. All experimental points correspond to controlled precipitation conditions, most of them with targeted pH of 12.0 (real pH variation is between 12.05-12.40), some with pH of 9.6.
Figure 4. Literature data analysis of hydrothermal synthesis of ZnO without organic additives. (a) and (b) show effects of the concentration of Zn at various synthesis temperatures on ZnO crystallite size; (c) and (d) show effects of the synthesis temperature at various concentration levels of Zn on average ZnO crystallite size. Graphs (a) and (c) emphasizes lower particles sizes than (b) and (d), respectively. The experimental points encompass a broad variety of other synthesis variables, such as pH and type of Zn-containing salts, mineralizers (bases), if any, and their concentrations.
Figure 5. SEM photographs revealing morphologies of selected ZnO powders: (a) powder from this work (ZOP-52) synthesized under hydrothermal conditions, (b) commercially available powder NyasorbUV (manufactured by Nyacol Nano Technologies, Ashland, MA), (c) commercially available powder SunSmart (manufactured by Nanophase Technologies Co., Romeoville, IL), and commercially available powder ZCote (Nanophase). Magnifications are the same in all cases.
Figure 6. Powder X-ray diffraction patterns of selected ZnO powders: (a) commercially available powder NyasorbUV (manufactured by Nyacol Nano Technologies, Ashland, MA), (b) commercially available powder SunSmart (manufactured by Nanophase Technologies Co., Romeoville, IL), (c) commercially available powder ZCote (Nanophase), and powders from this work synthesized under hydrothermal conditions (d) ZOP-52, and (e) ZOP-46.
Figure 7. Particle size distributions of selected ZnO powders: (a) ZOP-43, (b) ZOP-46, (c) ZOP-52, (d) commercial powder NyasorbUV (Nyacol), (e) commercial powder SunSmart (Nanophase), and commercial powder ZCote (Nanophase).
Figure 8. XPS spectra of selected ZnO powders: (a) ZOP-52 synthesized hydrothermally in this work, (b) ZOP-46 synthesized hydrothermally in this work, (c) commercial powder ZCote (Nanophase), and (d) commercial powder NyasorbUV (Nyacol). Unmarked bands are Auger peaks derived from Zn.
Figure 9. High-resolution XPS spectra with Gaussian-Lorenzian curve fits, showing details of the O1s peak for selected ZnO powders: (a) ZOP-46 synthesized hydrothermally in this work, (b) ZOP-52 synthesized hydrothermally in this work, (c) commercial powder NyasorbUV (Nyacol), and (d) commercial powder ZCote (Nanophase). The spectra were charge-corrected with respect to the carbon C1s peak at 284.5 eV.
Figure 10. UV absorbance spectra of selected ZnO powders: (a) ZOP-46 synthesized hydrothermally in this work, (b) commercial powder NyasorbUV (Nyacol), and (c) commercial powder ZCote (Nanophase).