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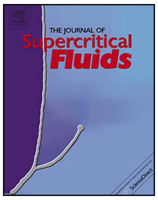

Hydrothermal growth of ZnO nanostructures in supercritical domain: Effect of the metal salt concentration ($Zn(NO_3)_2$) in alkali medium (KOH)

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ABSTRACT

The metal salt concentration effect on the size and morphology of ZnO NPs was highlighted through its synthesis thanks to a continuous one-step method at $401 \pm 15\,^{\circ}C$ and 306 ± 8 bar. Experiments were performed from $Zn(NO_3)_2$ and KOH as reactants in concentration ranges of 10–480 mM and 40–1920 mM, respectively. A constant $[KOH]/[Zn(NO_3)_2]$ ratio of 4 was fixed in order to maintain a constant pH value between 12.5 and 13.0. The as-prepared NPs were characterized by X-ray diffraction and (high-resolution) transmission electron microscopy. Based on Loüer's method, ZnO crystal exhibiting a hexagonal structure was considered as cylinder with a diameter *D* and a height *H*. The *D*/*H* parameter has already been used to observe the change of ZnO crystallite shape and correlated with (HR)TEM observations. The evolutions of crystal size and morphology according to $[Zn(NO_3)_2]$ in alkali medium are investigated and the particle growth mechanisms in supercritical water are discussed.

1. Introduction

The interest for producing metal oxides nanoparticles (NPs) with a perfectly controlled nanostructure is driven by the properties enhancement when the nanometric scale is reached [1,2]. Furthermore, getting a narrow size distribution of nanostructures greatly favors this improvement. Thus, the main challenge for powder elaboration processes is to control the particle nucleation and growth stages during the synthesis. Moreover, the development of large-scale, cheap synthesis routes of NPs, under favorable environmental conditions, is essential for nanotechnology to have acceptation on society [1]. One promising way is the continuous flow synthesis using supercritical fluids as reaction media. Especially, supercritical water (SCW) hydrothermal synthesis of metal oxides NPs has numerous advantages, such as environmental friendliness, catalyst free growth, low reaction times, well crystallized materials and ability to prepare doped materials. In supercritical domain, the decrease of the water dielectric constant and density leads to a modification of the solubility of inorganic compounds such as metal oxides. Thus, a higher supersaturation rate is achieved, allowing a faster nucleation kinetic to establish which results in the NPs formation. The reaction rate is enhanced more than 10^3 times compared to hydrothermal conditions owing to the low dielectric constant. However, if the SCW process is an interesting way to produce various nanopowders, the nucleation/growth mechanisms are still unknown [3]. Consequently, in order to improve the knowledge of these mechanisms in supercritical water domain, it was useful to select an uncomplicated reference material such as ZnO which is largely studied in SCW hydrothermal synthesis and also well documented in the literature [4–22]. Indeed, ZnO material crystallizes in a single stable wurtzite phase without secondary phases such as hydroxide in SCW domain compared to other metal oxides (TiO_2, Cu_xO, Ce_xO_y ...). Moreover, ZnO NPs find various applications in different fields such as optoelectronic transducers, chemical and gas sensors, photocatalyst, etc., because of a very wide range of morphologies as wires, flowers, rods, tubes, sheets, ribbons, plates, dumbbell, disks and springs [4–14]. The crystallite characteristics of ZnO NPs in terms of size and morphology can be tuned with experimental conditions such as the temperature [15–18], the nature and the concentration of the metallic precursor and the alkali solution [15,16,19–21]. For instance, the formation of spherical ZnO NPs can be favored by either an increase of temperature or an addition of alkali solution (KOH, NaOH). The addition of KOH and NaOH also tends to

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reduce the mean particle size. In the absence of this additional solution, rod-like particles are observed. The influence of the base concentration has also been demonstrated [16,20]. Sue et al. [15] have shown that increasing pH promotes the formation of spherical NPs by reducing the solubility of ZnO while Sondergaard et al. [16] observed such a morphology in a neutral medium. According to this last author, an acid or alkaline medium promotes the formation of rods and plates, respectively. About the effect of the metal precursor concentration, Ohara et al. [21] showed that the ZnO rods are smaller when Zn(II) concentration is increased without an addition of alkali solutions whereas other studies performed in alkali medium showed that spherical ZnO NPs are produced with reduced size when the Zn(II) concentration decreases [15,16,19,20]. However, it is very difficult to compare the size and the morphology of ZnO particles obtained from these studies [4–22] because of differences in residence time, ranges of pressure and temperature, type of reactor (batch or continuous process) and reactants, especially the counter-ion nature of the alkali solution (Na^+, K^+, Li^+) and the metallic precursor (nitrate, acetate and sulfate).

Our team has developed a continuous SCW synthesis process [22,23] with a production of 15 g h^{-1} of metal oxides NPs as simple oxides (ZnO, TiO_2...) and polycationic oxides ($Ce_xZr_{1-x}O_2$...) [24,25]. The morphology and the size can be tuned by changing experimental conditions such as temperature, pressure, reaction time, pH, nature and concentration of the metallic precursor and the alkali solution. The hydrothermal synthesis of ZnO crystals from room to supercritical conditions and also the effect of the pH in supercritical water domain were recently studied elsewhere [26,27]. The changes of size and morphology of ZnO crystals according to temperature and pressure and the [KOH]/[$Zn(NO_3)_2$] ratio were discussed and summarized by schematic synoptics [26,27].

In this study, the SCW process was employed to produce ZnO nanopowders in supercritical conditions from zinc nitrate ($Zn(NO_3)_2$) and potassium hydroxide (KOH) solutions as reactants in order to investigate the metal salt concentration effect on the ZnO crystallite characteristics. A constant [KOH]/[$Zn(NO_3)_2$] ratio of 4 was fixed in order to maintain a constant pH value between 12.5 and 13.0. The as-prepared NPs were characterized by X-ray diffraction (XRD) and (high-resolution) transmission electron microscopy ((HR)TEM). Based on the Loüer's method, ZnO crystal exhibiting a hexagonal structure was considered as cylinder with a diameter D and a height H [28]. The D/H parameter was used to observe the change of ZnO crystallite shape correlated with (HR)TEM observations.

2. Material and methods

2.1. Powder synthesis

ZnO powder was synthetized in supercritical domain ($T = 401 \pm 15\,°C$ and $P = 306 \pm 8$ bar) from a continuous hydrothermal process shown in Fig. 1 and accurately described elsewhere [22,23]. High-pressure pumps with a back-pressure regulator and tubular furnaces allow the desired temperature and pressure values inside the system to be set. Experiments were carried out from zinc nitrate hexahydrate (98% purity, Sigma–Aldrich) as aqueous metal salt precursor and potassium hydroxide (≥95% purity, Sigma–Aldrich) as alkali solution. To evaluate the effect of the metal salt concentration on the size and morphology of zinc oxide NPs, experiments were performed with different values of [$Zn(NO_3)_2$] from 10 to 480 mM in alkali basic medium with [KOH]/[$Zn(NO_3)_2$] = 4 (Table 1). Three thermocouples (type K) were placed inside the patented reactor [22] and, more specifically, in the reactant stream to monitor the temperature in the system. The temperature considered in the following sections is the one recorded at mid-reactor ($T_{\text{mid-reactor}}$). In the process, both aqueous metal salt precursor ($Zn(NO_3)_2$) (a) and alkali solutions (KOH) (b) were fed into the reactor and counter-currently mixed with preheated demineralized water (c). The geometry of the mixing zone inside the patented reactor is disclosed elsewhere [29]. The three solution flow rates were maintained at 20 mL min^{-1} which correspond to a residence time of 11 s inside the reactor in SCW domain. The measured pH (room conditions) at the outlet of the system (d) was in the range of 12.5–13.0. The resulted ZnO suspensions were centrifuged and washed with demineralized water under ultrasonication. Once suspensions were free of unreacted precursors (zinc salt and KOH in excess) and by-products (in this case, KNO_3), they were freeze-dried to produce well-dispersed powders.

2.2. Powder characterization

Dry powders were characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM) and X-ray diffraction (XRD). TEM and SEM observations were carried out on a Jeol JEM-2100 LaB6 operating at 200 kV and on a Jeol JSM-6400F operating at accelerating voltage in the range 0.5–30 kV, respectively. The TEM observations were performed in bright field mode and the micrographs were acquired and processed thanks to a Gatan US1000 CCD camera and DigitalMicrograph software (Gatan, Inc.). TEM Samples were prepared from freeze-dried powders dispersed in ethanol onto a 300-mesh carbon film coated copper grid, with a subsequent solvent evaporation in contact with ambient air at room temperature. SEM samples were prepared by disposing a sufficient amount of freeze-dried powders dispersed in ethanol onto a carbon film. XRD data were collected thanks to a D8 Advance diffractometer equipped with a Vantec linear detector using the $K\alpha_1$ and $K\alpha_2$ copper radiations. The $K\alpha_2$ contribution from the incident beam was stripped, a $K\alpha_2/K\alpha_1$ factor equal to 0.504 was used [30]. The XRD patterns were scanned over the angular range $20°–90°$ (2θ). The step size was selected to be constant over the whole angular range and equal to 0.025°. The counting time was chosen to be 2 s step^{-1}. In order to determine the ZnO crystallite size and, also their shape, a XRD pattern decomposition method was used in which each XRD peak is modeled by a Voigt function [31]. From the XRD pattern decomposition proposed by Langford, XRD peak position (2θ), integral breadth (β) and the shape factor (ϕ) are extracted. The instrumental resolution curve has been established from annealed BaF_2 powder [31]. Then, the Langford's method for which crystallites are considered as cylinder with a diameter D and an height H is applied, the broadening of each peak (hkl) are obtained and are sorted by groups as shown in Fig. 2. From this figure, some values of D and H may be obtained, allowing the aspect ratio D/H to be expressed which will be used to follow the change of crystallite shape versus the Zn(II) concentration.

3. Results and discussions

3.1. Crystallite size and shape of ZnO end-powders

The presented hydrothermal process allowed the synthesis of pure wurtzite ZnO powders in supercritical conditions ($T = 401 \pm 15\,°C$ and $P = 306 \pm 8$ bar) to be achieved whatever the $Zn(NO_3)_2$ concentration from 10 to 480 mM at constant pH value ([KOH]/[Zn(II)] = 4). An example of a XRD pattern of a pure ZnO powder is presented in Fig. 2. Only the size and morphology of synthesized particles change between experiments. Note that the experimental conditions have been selected in order to enhance the formation of NPs with smaller size and narrow size distribution ([KOH]/[$Zn(NO_3)_2$] = 4) [27]. The experimental conditions and