

INFLUENCE OF REACTION CONDITIONS ON MORPHOLOGY OF ZINC OXIDE MICRO- AND NANOPARTICLES

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Abstract

Zinc oxide is multifunctional material used for decades in industrial scale due to its unique physical properties. By appropriately chosen morphology of particles, we can get additional value from this “traditional” material. However, for optimal results, it is necessary to manage synthesis of different morphology. Here we report fast and economical method of ZnO synthesis by precipitation from aqueous solutions of zinc acetate by sodium hydroxide. We have studied, how concentration ratio $R = [\text{NaOH}] / [\text{Zn}^{2+}]$ and solution addition order can affect product morphology and composition. By this synthetic method we can selectively prepare different particle shapes (spheres, urchins, petals, rods) of pure ZnO with yield exceeding 75 %. By reverse addition of reactants, finely dispersed nanoparticles can be obtained by elimination of growth step during the synthesis. For product characterization XRD, SEM, TGA and Raman spectroscopy were used.

Keywords: Zinc oxide, nanoparticles, morphology, synthesis, precipitation

1. INTRODUCTION

Nanoparticles are in focus of many scientists in recent years [1,2]. This is due to their unique properties, which can be tailored by changing diameter and shape of particles (thus number of surface atoms) [3]. As an excellent example, ZnO should be mentioned - it can be used for UV protection, corrosion protection, sensors, white pigment, electronics, photo-catalysis, ceramics, etc. Zinc oxide offers wide range of the particle shapes, which gives us new application possibilities for this “traditional” material [4,5].

Zinc oxide is semiconductor from the group II-VI with band gap of ~ 3.4 eV, which cause transparency in visible light and absorption of UV light. Also, high piezoelectric coefficient makes it suitable for preparation of piezo ceramics and stress-strain sensors [4].

In the literature, there are many different synthetic methods of ZnO: gas-phase reactions, CVD, sol-gel, precipitation, hydro- and solvo-thermal synthesis, sonochemical, microwave, mechanochemical, etc. [6]. In this text, we will focus on wet chemical synthesis in aqueous environment.

For precipitation of ZnO, water-soluble salts of Zn^{2+} (e.g. acetate, nitrate, chloride or sulfate) are used. These salts are converted into insoluble precursors ($\text{Zn}(\text{OH})_2$, ZnCO_3) by reaction with base (NaOH , KOH , LiOH , NH_3 or $(\text{NH}_4)_2\text{CO}_3$). This precursor can be subsequently converted into ZnO directly in suspension or separated (e.g. by filtration) and calcined in furnace [7].

By different conditions of precipitation (concentration, pH, temperature, surfactant addition, rate of mixing, anion type) or calcination (temperature, gas type and its flow), different shapes and particle size can be obtained. Because of calcination step, it is hard to obtain well-dispersed nanoparticles and aggregated product must be milled. Thus, we decided for direct precipitation of ZnO from highly alkaline solutions.

2. EXPERIMENTAL

For synthesis by controlled precipitation, raw materials: NaOH and Zn(CH₃COO)₂ · 2 H₂O were purchased from Penta s.r.o. in analytical purity and were used without further treatment. Demineralized water was used for all experiments.

In a typical experiment 300 ml of aqueous solution of NaOH in the glass container was heated at 60 °C with vigorous stirring. To this solution 100 ml of aqueous solution of 0.2 M Zn(CH₃COO)₂ was added drop wise to create white suspension. After all solution was dropped, solution was mixed at 60 °C for additional 2 hours. After synthesis, solid product was separated from liquid and washed several times by water to remove byproducts and excess alkali. White product was dried overnight at 105 °C.

By this method 5 samples with different molar ratio $R = [\text{NaOH}] / [\text{Zn}^{2+}] = \{2.5, 5, 10, 15, 20\}$ were prepared. Also, one sample with $R = 10$ was prepared by reverse addition of solutions for synthesis at neutral pH and is noted as $R = 10 R$ through the text.

For characterization by XRD, TGA and Raman spectroscopy samples were used as dry powders. For SEM measurements, suspensions of samples in water were dip-coated onto electrically conductive substrate and dried at 60 °C.

3. RESULTS AND DISCUSSION

Aqueous solution of Zn(CH₃COO)₂ was used as precursor for synthesis. In the first step Zn(OH)₂ was precipitated as voluminous precipitate by NaOH as demonstrated in **Reaction 1** [8,9,10].



In the next step, Zn(OH)₂ is converted into soluble Zn(OH)₄²⁻ by excess amount of alkali according to **Reaction 2** [8,9]. This can be clearly observed as each new drop produce voluminous white precipitate, which immediately dissolves into clear solution. If the amount of hydroxide was low ($R = 2.5, 5, 10 R$), this precipitate dissolved only partially and thus colloid solution with smaller particles was formed.



From phase diagram (**Figure 1**) we can see, that supersaturation of Zn(OH)₄²⁻ species lead to direct precipitation of ZnO as is shown also in **Reaction 3**.



In the case of reverse „acidic“ route, we can consider value of R to be equal to zero, so the synthesis is from the beginning carried out at neutral pH (~ 7). These conditions can provide very fast local supersaturation for each drop and thus very fast nucleation of Zn(OH)₂ and ZnO nanoparticles. However, dissolution reaction (**Reaction 2**) is not favorable, because no more alkali is present in the surrounding solution. Thanks to that, also growth step (**Reaction 3**) is suppressed, so nanoparticles of Zn(OH)₂ and ZnO remain finely dispersed. When all Zn²⁺ species are converted into Zn(OH)₂, excess alkali increases rapidly pH, which causes conversion of all Zn(OH)₂ to ZnO. By this reverse process, growth step through dissolution-precipitation of Zn(OH)₄²⁻ species is successfully bypassed and small particles with narrow size distribution can be obtained.

Whereas for lower R values precipitate was formed immediately, for higher amount of alkali, it took longer time (30 min) for precipitate to be formed. In the case of $R = 20$, alkali amount is so high, that almost all Zn²⁺ remain in the soluble species Zn(OH)₄²⁻ and only very small amount of ZnO was formed (**Table 1**), because equilibrium solubility was not exceeded (**Figure 1**) [10].

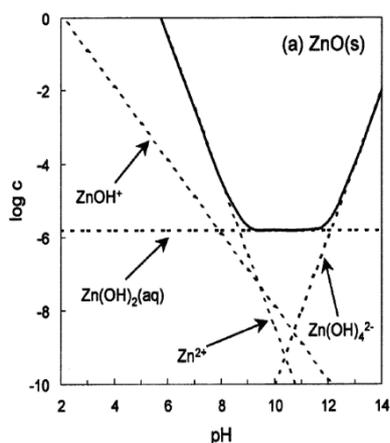


Figure 1 Phase diagram of Zn^{2+} species at different pH [9]

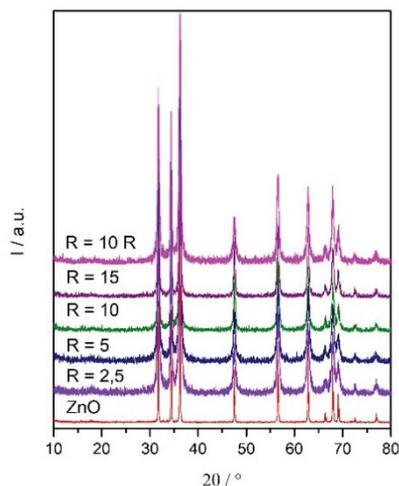


Figure 2 Diffractograms of ZnO and various R samples

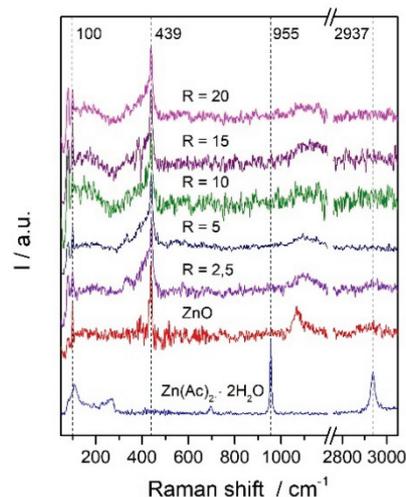


Figure 3 Raman spectra of ZnO, $Zn(Ac)_2 \cdot 2H_2O$ and various R samples

Based on XRD measurement (**Figure 2**), all prepared samples were identified as ZnO with wurtzite structure. No other phase or impurity was identified, which suggest to well washed crystalline sample. Sample R = 20 was not measured by XRD, because of low yield of the sample (**Table 1**).

Crystallite size and lattice parameters (**Table 1**) were determined from diffractograms by using Scherer method. It can be clearly seen, that with lower amount of alkali used, the lower crystallite size was. This observation was also confirmed by SEM measurements (**Figure 4**). Lattice parameters c/a are increasing with decreasing amount of alkali, which can be also contributed to lowering particle size and their structure expansion, which is typical for nanoparticles [11].

Table 1 Overview of prepared samples, yields, crystallite size and shape and lattice parameters

Sample name	ZnO	R = 20	R = 15	R = 10	R = 5	R = 2.5	R = 10 R
$R = [NaOH] / [Zn^{2+}]$	-	20	15	10	5	2.5	10 R
Yield (%)	-	4	77	79	87	75	82
Crystallite size by XRD (nm)	-	-	40	36	27	27	25
Lattice parameter c/a	1.6021	-	1.6019	1.6021	1.6022	1.6027	1.6031
Morphology		Rod	Urchin	Petal	Flower	Sphere	Sphere
Size of particles by SEM (nm)	$\sim 5 \mu m$	$1 \mu m \times 100 nm$	$2 \mu m$	300 nm	300 nm	50 nm aggregated	50 nm

Samples were also characterized by Raman spectroscopy (**Figure 3**). In spectra of all samples, we can see peaks at wavenumber of 100 cm^{-1} and 439 cm^{-1} , which confirm ZnO structure in agreement with XRD results. Absence of peaks at wavenumbers 955 cm^{-1} and 2937 cm^{-1} (which belongs to $Zn(CH_3COO)_2$) also confirm, that washing of the samples was sufficient.

Morphology of the samples was studied by SEM (**Figure 4**). Sample R = 20 is composed of nanorods with diameter about 90 nm and length in the order of hundreds of nanometers. This indicates (together with low yield), that nucleation step is completely suppressed and separated from the growth step, which takes place exclusively along c-axis as can be seen in diffractograms.

With lowering R value, particles tend to be more agglomerated into urchin-like particles ($R = 15$), flower-like particles ($R = 10$) with more pyramidal shape of individual beams. Also, number of beams is decreasing. It is more distinct at sample $R = 5$, and size of individual particles decrease below 100 nm in the sample $R = 2.5$ and they also tend to be more compact and agglomerated.

All these changes in morphology can be attributed to equilibrium between nucleation and growth of crystals and are dependent on super-saturation degree [12].

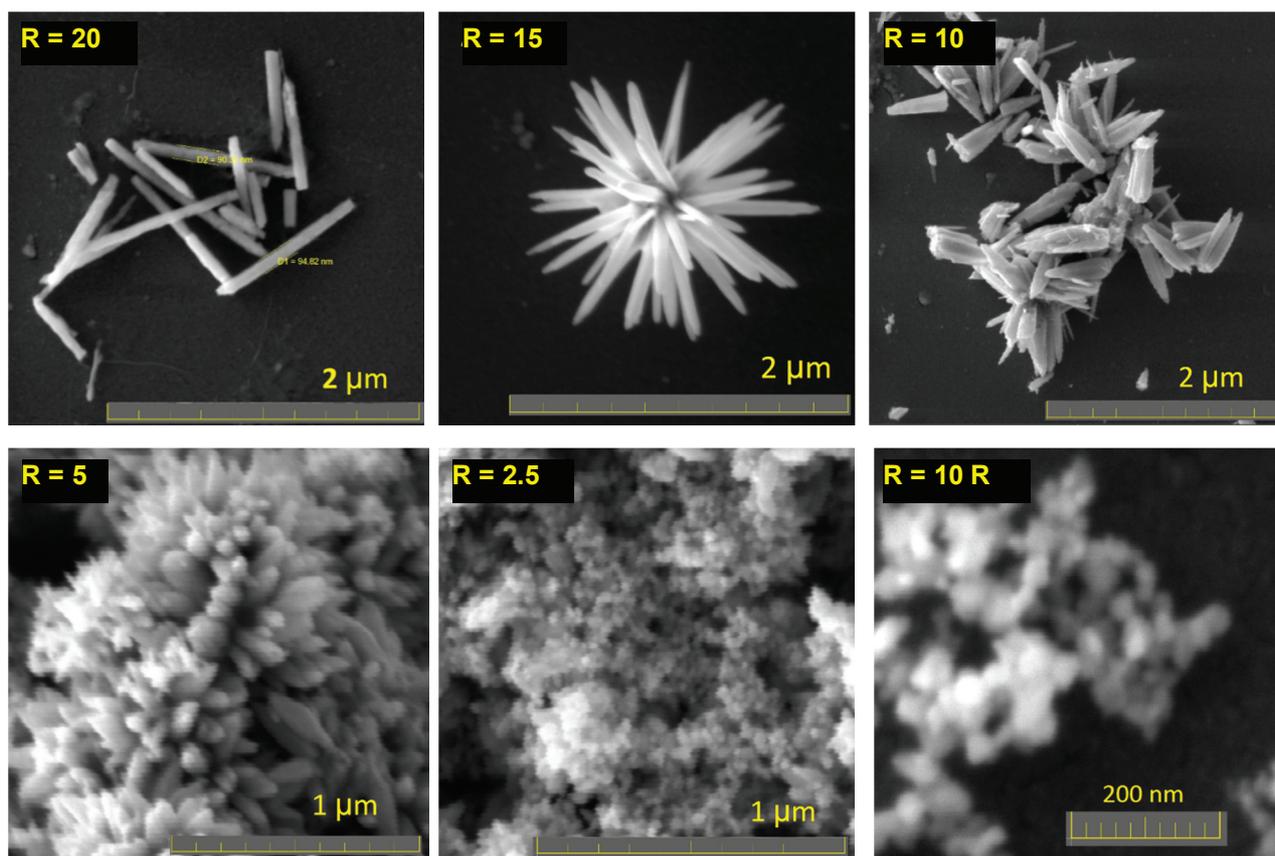


Figure 4 SEM images of prepared ZnO samples: $R = 20$, $R = 15$, $R = 10$, $R = 5$, $R = 2.5$, $R = 10 R$

CONCLUSION

Zinc oxide micro- and nanoparticles were prepared by wet chemical precipitation method. With decreasing amount of alkali, particle size decreases dramatically and morphology change from nanorods, urchin-like, petals to spheres. To confirm effect of alkali amount on nucleation and growth of nanoparticles, reverse addition of reactants was done. By reverse addition fast nucleation yields spherical nanoparticles with uniform size of about 50 nm and growth step was eliminated.

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