

Short communication

Formation of hollow ZnO particles by simple hydrolysis of zinc acetylacetonate

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Abstract

Formation of hollow ZnO particles by simple hydrolysis of zinc acetylacetonate [Zn(acac)₂] at 90 °C was monitored. Isolated precipitates were characterized with XRD, FT-IR and FE-SEM. Different amounts of Zn(acac)₂ underwent the hydrolysis in 1 × 10⁻³ M NaOH for 24 h. The conditions for the formation of hollow ZnO particles were determined and the process was explained by the aggregation mechanism.

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1. Introduction

The precipitation chemistry of zinc oxide (ZnO) is in the focus of many investigations, primarily because ZnO has found important applications, both in the traditional technologies such as paints, catalysts, rubbers, cosmetics, and in advanced technologies of sensors, photodetectors, LEDs, and transistors. The microstructure of ZnO powders or films is an important property for their specific applications. ZnO can be prepared to display various microstructures by varying the chemistry and physical parameters in a corresponding synthesis. Musić et al. [1–5] investigated the influence of a type of Zn(II)-salt, a type of precipitating agent, the temperature and time of precipitation in ZnO synthesis. In dependence on these factors different shapes and sizes of ZnO particles were obtained. The type of Zn(II)-salt and precipitation agent also influenced the chemical state of the ZnO precursor. Nanosize ZnO particles were prepared by a rapid hydrolysis of zinc 2-ethylhexanoate in 2-propanol by adding the TMAH aqueous solution [6]. The formation of nanosize ZnO particles by thermal decomposition of zinc acetylacetonate monohydrate was likewise investigated [7]. Hydrolysis at 90 °C of zinc(acac)₂ in a solution containing sodium hydroxide and trisodium citrate yielded square plate-like particles or thin ZnO foils, depending on the initial mole

ratio [Zn(acac)₂]/[Na₃-citrate] and the initial NaOH concentration [8]. Upon heating of so obtained particles or thin foils at 300 °C nanosize particles of good uniformity were produced. ZnO nanoparticles were also produced from Zn(acac)₂ in organic media [9,10]. ZnO nanorods [11] or ZnO nanowires [12] were produced starting from the Zn(acac)₂ precursor. Zn(acac)₂ was also used to produce gold and ruthenium colloids [13] in thin ZnO films or to incorporate indium [14] into thin ZnO films.

Within the frame of a systematic investigation of the relationship between the precipitation conditions and the microstructural properties of ZnO in the present work we report novel data on the conditions for the formation of hollow ZnO particles by simple hydrolysis of Zn(acac)₂.

2. Experimental

Chemicals of analytical purity were used. Zinc acetylacetonate monohydrate (Zn(C₅H₇O₂)₂·H₂O) was supplied by *Alfa Aeser*[®] and C₂H₅OH and NaOH by *Kemika*. Twice-distilled water was prepared in our own laboratory. The experimental conditions for the preparation of samples are given in Table 1. The Zn(acac)₂·H₂O powder of a proper weight was vigorously mixed with H₂O or aqueous NaOH solution for 15 min and then heated at 90 °C. After 24 h heating the precipitated solid phase was separated from the mother liquor by ultracentrifugation and the precipitate was washed several times with ethanol and twice-distilled water, then dried for 48 h at 110 °C.

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Table 1
Experimental data for the preparation of samples.

Sample	Zn(acac) ₂ ·H ₂ O ^a (g)	H ₂ O (ml)	1 × 10 ⁻³ M NaOH (ml)	T (°C)	Time (h) ^b	Heating of isolated precipitate at 300 °C (h)
S0	2	200		90	24	
S0-300						4
S1	1		200	90	24	
S1-300						4
S2	2		200	90	24	
S2-300						4
S3	3		200	90	24	
S3-300						4

^a Zinc acetylacetonate monohydrate.

^b Hour.

The samples were characterized with *Italstructures* X-ray powder diffractometer (APD 2000), *Perkin-Elmer* FT-IR spectrometer (model 2000), and scanning electron microscope (FE-SEM; JSM-7000F) manufactured by *Jeol Ltd.*

3. Results and discussion

XRD measurements showed that in all samples ZnO was present as a single phase. ZnO crystallized in the space group *P6₃mc* (186, hexagonal system, wurtzite-type structure). Figs. 1 and 2 show characteristic XRD patterns of samples S0, S1, S2 and S3. XRD pattern of reference sample S0 (Fig. 1) shows that ZnO prepared upon 24 h of ageing at 90 °C is relatively well crystallized (small broadening of XRD lines). The relative intensities between the XRD lines 100, 002 and 101 of samples S1, S2 and S3 changed, which can be related with preferential growth changes in crystallite domains.

The FT-IR spectra of ZnO samples are shown in Fig. 3. The FT-IR spectrum of reference sample S0 is characterized by IR bands located at 505 and 399 cm⁻¹, as well as a shoulder at 541 cm⁻¹. Sample S3 showed one very broad IR band at 520 cm⁻¹ and one intensive band at 390 cm⁻¹. Upon heating samples S0 and S1 to S3 at 300 °C, no significant changes

occurred in the features of the corresponding spectra in relation to the reference samples. The relative intensities of the IR bands at 510 and 521 cm⁻¹ were increased and the IR band at 401 cm⁻¹ for sample S0-300 was located at 378 cm⁻¹ for sample S3-300. The nature of the IR spectrum of ZnO was investigated by Hayashi et al. [15]. According to the authors ZnO shows three distinct absorption peaks located between the bulk TO-phonon frequency ($\omega_{T\parallel}$) and the LO-phonon frequency ($\omega_{L\perp}$). The absorption peaks shifted towards lower

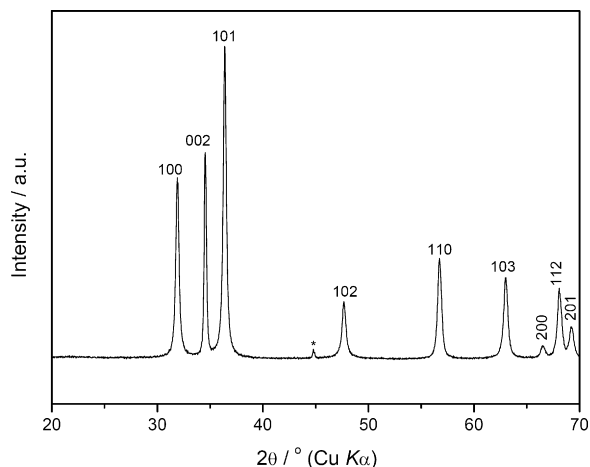


Fig. 1. Characteristic parts of XRD pattern of sample S0 (*, parasitic line due to Al-holder), recorded at 20 °C.

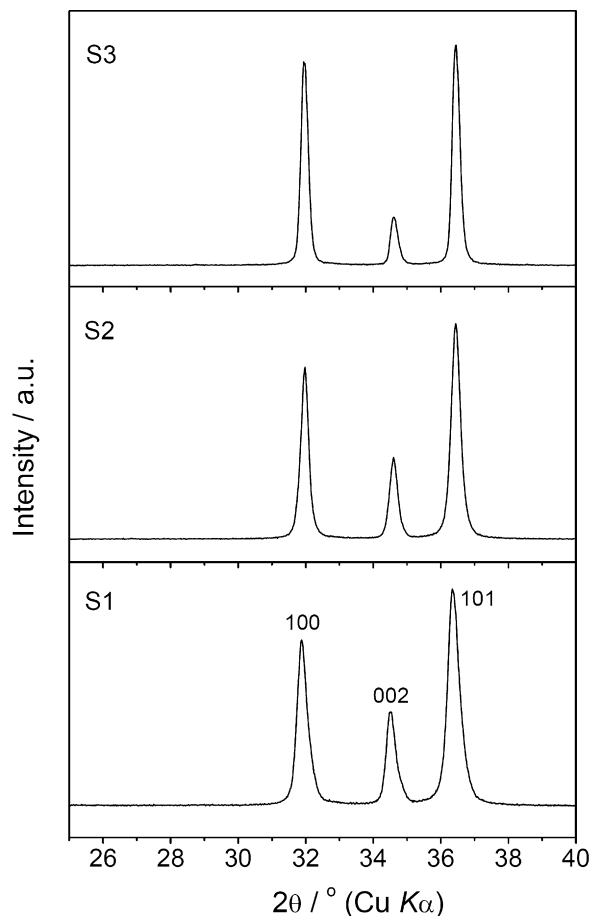


Fig. 2. Characteristic parts of XRD patterns of samples S1, S2 and S3, recorded at 20 °C.

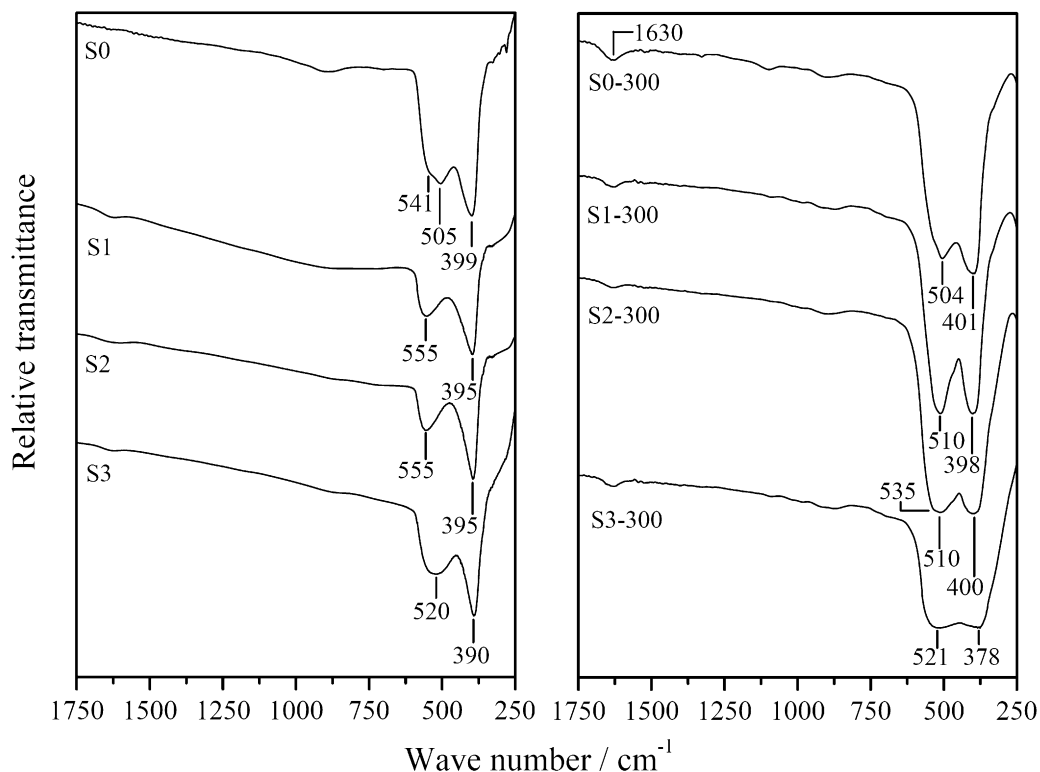


Fig. 3. Characteristic parts of FT-IR spectra of samples S0, S1, S2, S3 and the spectra of these samples heated at 300 °C, recorded at RT.

frequencies when the permittivity of the surrounding medium was increased. Generally, the IR spectrum of ZnO particles may vary from a very broad single band, over a doublet up to a three-band superposition [16]. The geometrical shape of particles influences the corresponding ZnO IR spectrum [17]. Cubic and hexagonal ZnO particles, as well as tetrapod-shaped ZnO particles showed differences in their IR spectra [18]. Fig. 4 shows characteristic part of FT-IR spectrum of zinc

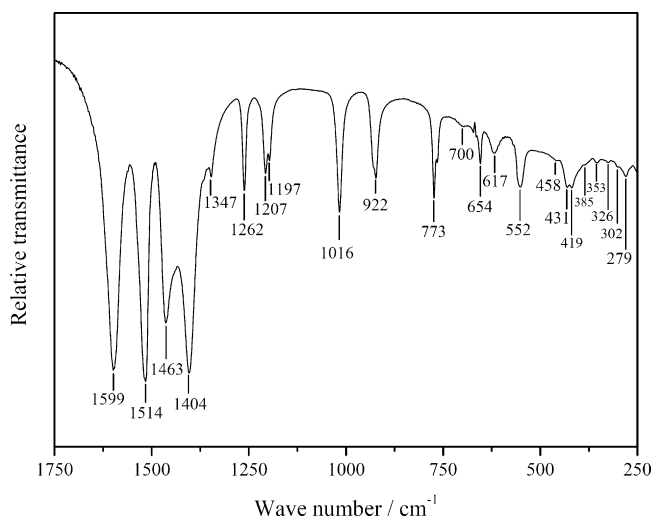


Fig. 4. Characteristic parts of FT-IR spectrum of zinc acetylacetonate mono-hydrate, recorded at RT.

acetylacetonate. Taking into account this spectrum in samples S0–S3 is not possible to conclude about the organic contamination adsorbed, originating from acetylacetonate. The IR band at $\sim 1630 \text{ cm}^{-1}$ noticed in samples S0–S3 and S0-300 to S3-300 corresponds to bending vibration due to adsorbed H_2O (moisture) on ZnO particles.

The FE-SEM images of the prepared samples are summarized in Figs. 5 and 6. Fig. 5a shows two shapes of ZnO particles present in a sample. The presence of elongated ZnO laths and less elongated ZnO particles laterally arrayed similar to sunflower seeds were noticed. The addition of $\text{Zn}(\text{acac})_2 \cdot \text{H}_2\text{O}$ to $1 \times 10^{-3} \text{ M}$ NaOH solution caused radical changes in the shape of ZnO particles. Very elongated and hollow ZnO particles were formed, as shown in Fig. 5b and c. For a higher content (3 g) of added $\text{Zn}(\text{acac})_2 \cdot \text{H}_2\text{O}$, large ZnO particles were formed along with thin and elongated ZnO particles (Fig. 5d). Obviously, at a higher starting concentration of $\text{Zn}(\text{acac})_2$ a process of dissolution of one kind of ZnO particles and the corresponding growth of larger ZnO particles occur. The basis of larger ZnO particles (bullet-type), obtained by hydrolysis of 3 g of $\text{Zn}(\text{acac})_2$, shows that these particles are formed as aggregates of ZnO nanoparticles. Heating of samples S0 and S1–S3 at 300 °C did not cause any significant changes in ZnO shapes, as shown in Fig. 6. Fig. 6a shows two shapes of ZnO particles as in reference sample. Fig. 6b clearly demonstrates a hierarchic crystal growth by the aggregation of ZnO particles in the form of a hollow hexagon as a stable geometrical shape. The diameter, $\sim 350\text{--}400 \text{ nm}$ at the top of these hollow particles, the wall thickness $\sim 80\text{--}85 \text{ nm}$ and the

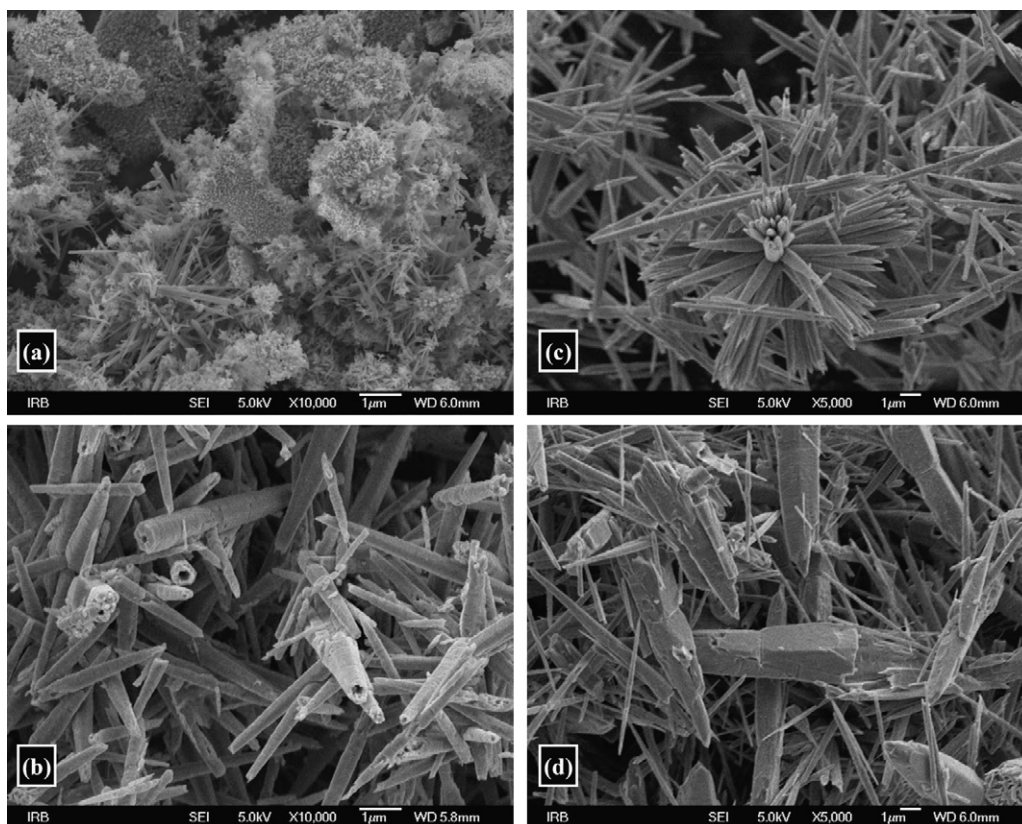


Fig. 5. FE-SEM images of samples: (a) S0, (b) S1, (c) S2 and (d) S3.

length of layer $\sim 85\text{--}90$ nm in hierarchic crystal microstructure are measured. This aggregation mechanism in the formation of hollow particle is also present in sample S2-300 (Fig. 6c). The hollow ZnO particles, shown in Fig. 6c, are $\sim 3\text{--}3.5$ μm in length, average diameter at the top of these particles is $250\text{--}300$ nm and the wall thickness is $\sim 50\text{--}55$ nm. The length of hierarchic layers in the crystal microstructure of the same particles is $75\text{--}80$ nm. The shapes of ZnO particles S3-300 (Fig. 6d) practically did not change in relation to their reference sample S3 either.

The hydrolysis of $\text{Zn}(\text{acac})_2$ in 1×10^{-3} M NaOH solutions obviously plays a key role in the formation of hollow ZnO particles. Moreover, hollow ZnO particles are also formed at a higher concentration of NaOH solution. In the presence of NaOH the hydrolysis of $\text{Zn}(\text{acac})_2$ proceeds much faster than in H_2O , thus producing fine primary ZnO particles which aggregate in stable hexagons and then hierarchically grow with time. In very early stage of zinc acetylacetonate hydrolysis without NaOH addition OH^- ions are obtained by the deprotonation reaction of H_2O molecules. On the other hand, in the presence of NaOH the zinc acetylacetonate molecules are directly attacked with OH^- ions in two steps giving $\text{Zn}(\text{OH})_2$, which in the following step produces ZnO and H_2O . It can be suggested that in this process of hydrolysis acetylacetonate has a templating role giving the hexagonal arrangement of primary ZnO particles. The formation of hollow ZnO particles is also dependent on the starting concentration of zinc acetylacetonate.

The formation mechanism of tubular ZnO is also discussed in reference literature by other researchers due to importance of this morphology for practice. Yan et al. [19] reviewed the tube formation in nanoscale materials. Shen et al. [20] obtained the ZnO microtubes and nanotubes by hydrothermal synthesis in the presence of cetyltrimethylammonium bromide (CTAB) or neutral tri-block copolymer of poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (P123). The formation of tubular ZnO was explained by rolling the ZnO precursor sheets. Wei et al. [21] investigated the formation of ZnO microtubes by hydrothermal treatment at 95°C of the precipitates formed by mixing ZnCl_2 and NH_4OH solutions. The formation of ZnO tubular microstructure was proposed by the preferential dissolution of ZnO rods and the corresponding Zn^{2+} extraction. The inner dissolution of ZnO rods along the c -axis was also proposed by Wang et al. [22]. Further proposed was a protective role of CTAB by its lateral adsorption on ZnO rods. ZnO nanotubes were grown on glass substrate using a two-step procedure [23]. A solution of $\text{Zn}(\text{NO}_3)_2$ and polyethylene glycol (PEG-2000) was mixed with the NH_4OH solution, then the mixture was refluxed at 80°C . The precipitate thus formed was washed, then in the corresponding suspension a glass plate added and hydrothermally treated. It was suggested that the PEG-2000 addition assisted in the one-direction growth of ZnO nanotubes.

The results of the present work and those reported in reference literature [19–23] show that the formation of hollow

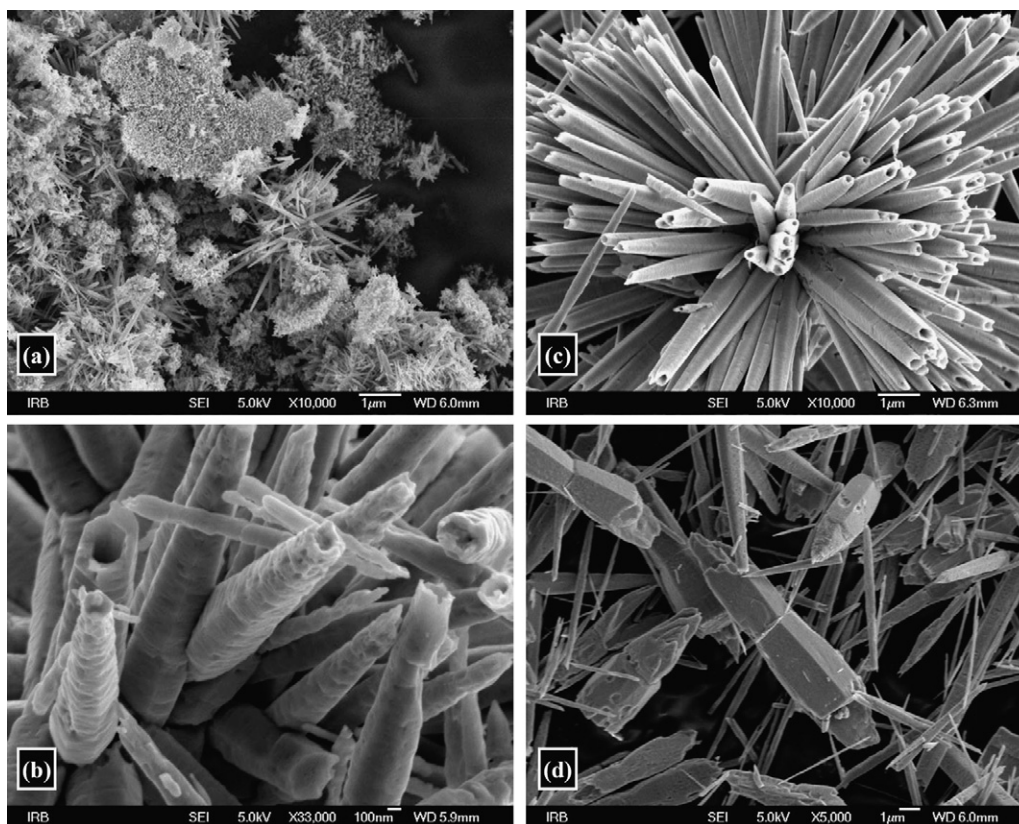


Fig. 6. FE-SEM images of samples: (a) S0, (b) S1, (c) S2 and (d) S3 after their heating at 300 °C.

(tubular) ZnO particles is of a complex origin. From the present research it is evident that flask chemistry and the conducting of chemical reactions determine the formation mechanism of hollow (tubular) ZnO particles.

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