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Varying the microstructural properties of ZnO particles using different synthesis routes

Ankica Šarić, Svetozar Musić *, Mile Ivanda

Ruđer Bošković Institute, P. O. Box 180, Bijenička cesta 54, HR-10002 Zagreb, Croatia

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ABSTRACT

The hydrolysis at 90 °C of zinc acetylacetonate [$Zn(acac)_2$] in solutions containing sodium hydroxide and trisodium citrate was monitored using Raman and FT-IR spectroscopies and field emission scanning electron microscopy. The size and shape of the precipitated particles depended on the initial mole ratio [$Zn(acac)_2$]/[Na_3-citrate] and initial NaOH concentration. The conditions for precipitation of square plate-like particles or thin foils were determined. Nanosize ZnO particles of good uniformity were obtained by heating square plate-like particles or thin foils at 300 °C. With additional heating at 600 °C larger particles were obtained. These particles showed the Raman bands at 332, 384, 413, 438, 540 and 583 cm^{-1}, which were assigned to wurtzite-type ZnO. For the initial mole ratio [$Zn(acac)_2$]/[Na_3-citrate] = 1:0.5 and at concentration of 1×10^{-2} M NaOH the ZnO particles of different shapes were obtained which consisted of primary nanosize particles with chemically bonded citrate groups.

1. Introduction

In the last decade a rapid increase in the number of publications dealing with the synthesis of ZnO particles and thin films and their properties has been noted [1]. This is understandable in view of very important applications of ZnO materials. For example, ZnO materials have found use in both traditional technologies (paints, catalysts, rubber and cosmetics), and in advanced technologies (mechanical actuators, piezoelectric and gas sensors, photodetectors, LED's, transistors, etc.) It should be mentioned that many applications of ZnO depend on the nanostructure of ZnO particles or thin films. Generally, it is possible to change the size and shape, as well as other properties of ZnO particles by varying the synthesis procedures.

Musić et al. [2] investigated the influence of synthesis procedure on the formation and properties of ZnO. ZnO failed to crystallize through the hydrothermal treatment of the $Zn(NO_3)_2$ aqueous solution in decomposing urea at 160 °C; hydrozincite was formed instead. On the other hand, nanosize ZnO particles were instantaneously precipitated by the addition of tetramethylammonium hydroxide (TMAH) to the ethanolic solution of zinc acetate dihydrate at pH ~ 14. The precipitates obtained by an abrupt addition of the concentrated NH_4OH solution to the $Zn(NO_3)_2$ solution consisted of a complex compound of the general formula $Zn_5(OH)_8(NO_3)_2(H_2O)_{2-x}(NH_3)_x$ which on additional autoclaving transformed to ZnO [3]. The aqueous suspensions produced from the zinc acetate solution with varying amounts of the NH_4OH solution were hydrothermally aged at 160 °C and the precipitates obtained were characterized by XRD, Raman, B.E.T. and TEM [4]. ZnO particles in the micron range were precipitated by dissolution/recrystallization of the starting precipitate and the rate of this transformation increased with an increase in pH from 7 to 10. Ageing of the starting aqueous suspension for 7 months at pH 10 and room temperature yielded aggregates consisting of nanosize ZnO particles (~20 to ~60 nm). These works [2–4] were continued with the investigation [5] of the formation of ZnO particles by mixing concentrated aqueous $Zn(NO_3)_2$ and NaOH solutions. At 160 °C and pH ~ 6, plate-like $Zn_5(OH)_8(NO_3)_2(H_2O)_2$ were obtained which quickly transformed into ZnO via a dissolution/recrystallization process yielding particles of different shapes based on the hexagonal prism. $Zn_5(OH)_8(NO_3)_2(H_2O)_2$ particles precipitated at pH ~ 6 were stable up to 6 months of ageing at 20 °C. Only ZnO particles precipitated at 160 or 20 °C at pH ~ 13. All ZnO particles thus obtained were plate-like and their size depended on the time of ageing. Musić et al. [6] precipitated the $Zn_5(CO_3)_2(OH)_6$ precursor and then the precursor was converted to nanosize ZnO particles at 300 °C. The size of these ZnO particles increased to ~100 nm upon additional heating at 600 °C. The obtained ZnO particles showed a pseudospherical shape; however, their basic structure was based on the hexagonal space group. Precipitation of Zn^{2+} ions in the decomposing HMTA (hexamethylenetetramine) at 90 °C yielded ZnO particles in the micron range and these particles were strongly elongated in the direction of the crystallographic *c*-axis. Nanosize ZnO particles were prepared by rapid hydrolysis of zinc 2-ethylhexanoate dissolved in 2-propanol by adding the TMAH aqueous solution [7]. XRD showed an

* Corresponding author. Tel.: +385 1 45 61 094; fax: +385 1 46 80 098.
E-mail address: music@irb.hr (S. Musić).

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average value of 25–35 nm for the basal diameter of supposed cylinder (prism)-shaped crystallites, whereas the height of these crystallites was 35–45 nm. TEM showed that the majority of ZnO particles were 20–50 nm in size, thus indicating that the crystallite and particle sizes were approximately equal. The conditions for the formation of nanosize ZnO particles by thermal decomposition of zinc acetylacetonate monohydrate were also investigated [8].

As a follow-up to our previous investigations [2–8] we present some novel results obtained by the hydrolysis of zinc acetylacetonate in the presence of citrates. The conditions for the preparation of nanosize ZnO particles have been identified. Samples were characterized with Raman and FT-IR spectroscopies, as well as field emission scanning electron microscopy.

2. Experimental

2.1. Sample preparation

All the chemicals used in the experiments were of analytical purity. Zinc acetylacetonate monohydrate ($Zn(C_5H_7O_2)_2\cdot H_2O$) supplied by *Alfa Aeser*®; trisodium citrate ($Na_3C_6H_5O_7\cdot 5½H_2O$) supplied by *Merck*, and C_2H_5OH and NaOH supplied by *Kemika* were used. Twice distilled water was prepared in own laboratory.

The experimental conditions for sample preparation are given in Table 1. Different amounts of trisodium citrate were dissolved in 200 ml of 2×10^{-3} M NaOH solution (samples S1–S3) or 1×10^{-2} M NaOH solution (sample S4) at room temperature. Then 2.00 g Zn $(acac)_2\cdot H_2O$ was added to each of the above transparent solutions. The formed milky suspensions were vigorously shaken for ~15 min, then heated at 90 °C for 1–7 days. After a proper ageing time, the isolated precipitates were washed several times with ethanol and twice distilled water using ultracentrifuge, then dried for 48 h at 110 °C. The precipitation systems for mole ratio $[Zn(acac)_2]/[Na_3\text{-citrate}]$ = 1:0.6 to 1:1 and at concentration of 2×10^{-3} M NaOH were also prepared. However, for mole ratios 1:0.6 and 1:0.75 the precipitation was delayed for more than 1 day and for mole ratio 1:1 the precipitation was absent. Selected samples were thermally treated at 300 °C for 4 h and additionally at 600 °C for 4 h.

2.2. Instrumentation

The Raman spectra were recorded at room temperature using the double subtractive configuration of a *Horiba Jobin Yvon* T64000 triple monochromator. The 514.5 nm laser excitation line beam of the *Coherent* argon ion laser was used.

The FT-IR spectra were recorded using a *Perkin Elmer* spectrometer, model 2000. The FT-IR spectrometer was coupled to a personal computer loaded with the IRDM (IR Data Manager) program. The specimens were pressed into the pellets using spectroscopically pure KBr as a matrix.

The FE-SEM images were taken using the *JEOL* field emission scanning electron microscope JSM-7000F. Specimens were not coated with a conductive layer.

The representative results of these measurements are shown below.

Table 1
Experimental conditions for the preparation of samples.[a]

Sample	$[Zn(acac)_2]/[Na_3\text{-citrate}]$	[NaOH]/M	t_{ageing}/days	pH_{final}
S1	1:0.5	2×10^{-3}	1	6.91
S2	1:0.5	2×10^{-3}	7	5.81
S3	1:0.1	2×10^{-3}	1	6.08
S4	1:0.5	1×10^{-2}	1	7.51

[a] Each precipitation system was prepared in 200 ml volume and contained 2.00 g of zinc acetylacetonate monohydrate.

3. Results and discussion

3.1. Raman and FT-IR spectroscopies

Raman spectroscopy is a useful technique in studying ZnO particles and thin ZnO films. It is useful not only in the identification of ZnO phase but also in the investigation of some effects originating from particle size and shape, crystal disorder, doping, etc. Damen et al. [9] investigated the Raman effect on ZnO crystals in the mm size range. The authors measured two E_2 vibrations at 101 and 437 cm^{-1}; one transverse A_1 at 381 cm^{-1}, the other transverse E_1 at 407 cm^{-1}, with one longitudinal E_1 at 583 cm^{-1}. Calleja and Cardona [10] also investigated the Raman effect on a ZnO single crystal. The resonance effect of the Raman scattering by E_2, A_{1T}, E_{1L} and E_{1T} phonons and several second-order features have been investigated for ZnO with photon energies between 1.6 and 3 eV. Raman spectroscopy was used by Exarhos and Sharma [11] in the investigation of wurtzite (ZnO) films. It was concluded that these films exhibited a certain degree of residual tensile stress, as inferred from the E_2 Raman shift relative to the single crystal position of this mode.

The Raman spectra of selected samples, prepared in the present work, are shown in Figs. 1 and 2. Fig. 1 shows the Raman spectrum

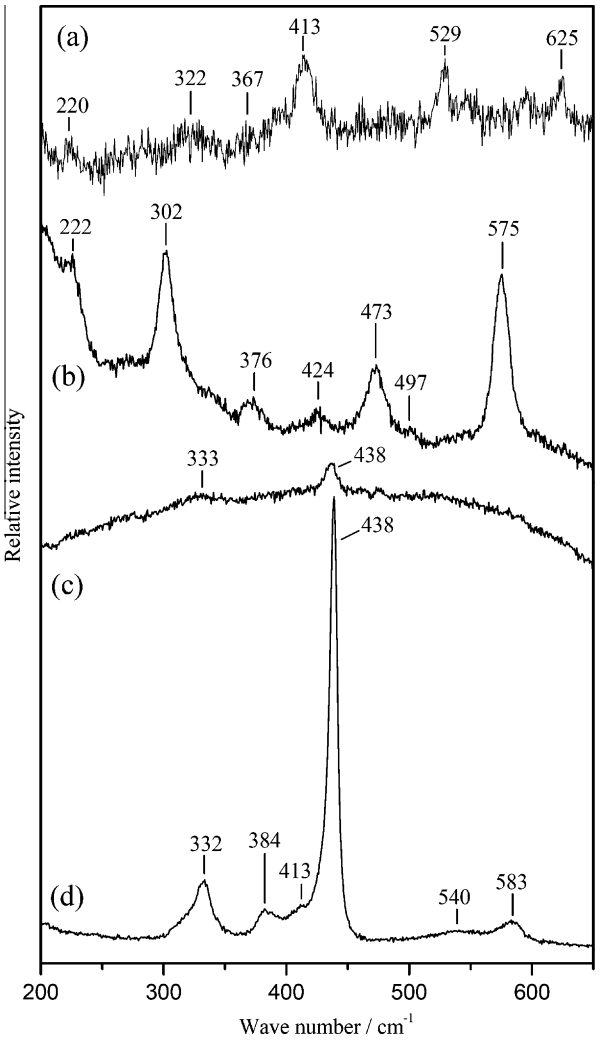

Fig. 1. Characteristic parts of the Raman spectra of (a) trisodium citrate ($Na_3C_6H_5O_7\cdot 5½H_2O$), (b) sample S2, (c) sample S2 upon heating at 300 °C, and (d) sample S2 upon heating at 600 °C.