materials proceedings

MDPI

Proceeding Paper

Study of the Influence of Process Parameters on the Morphology of ZnO Nanostructures †

Alina Matei *, Oana Brincoveanu, Cosmin Romanitan and Vasilica Tucureanu *

National Institute for Research and Development in Microtechnologies—IMT Bucharest, 126A Erou Iancu Nicolae, 077190 Bucharest, Romania; email1@email.com (O.B.); email2@email.com (C.R.)

* Correspondence: alina.matei@imt.ro (A.M.); vasilica.tucureanu@imt.ro (V.T.)

† Presented at the 4th International Online Conference on Nanomaterials; Available online: https://iocn2023.sciforum.net.

Abstract: Zinc oxide nanostructures are considered materials with real potential in different scientific fields. In the case of these nanostructures, it was found that the morphology of ZnO plays an essential role in the development of further applications, but it is necessary a rigorous control of the main factors that influence the size, shape, agglomeration tendency, uniformity, and orientation of the nanostructures. In the present paper, our efforts are oriented to synthesize different types of ZnO nanostructures by chemical method, and an optimization was achieved varying parameters, such as the concentration of precursors, types of solvents, pH, time or temperature, as well as the parameters required for thermal treatment. To obtain the characteristic structural and morphological information, ZnO nanostructures were investigated using Fourier transform infrared spectrometry (FTIR), scanning electron microscopy (SEM), and X-ray diffraction (XRD). SEM analysis confirms that the morphology and size of the ZnO nanostructures depend on the process parameters. The XRD results reveal that the synthesized samples have a wurtzite crystalline structure, and FTIR spectra show the presence of Zn-O bonding. The wetting capacity of continuous ZnO surfaces with different morphologies was studied by measuring the contact angle, indicating that the wetting and percolation capacity, depend by the orientation of the synthesized nanostructures.

Keywords: Zinc oxide; chemical synthesis; nanostructures; morphology

Citation: Matei, A.; Brincoveanu, O.; Romanitan, C.; Tucureanu, V. Study of the Influence of Process Parameters on the Morphology of ZnO Nanostructures. *Mater. Proc.* **2023**, *14*, x. https://doi.org/10.3390/xxxxx

Published: 5 May 2023

1. Introduction

Current efforts in the field of nanotechnology have led to the orientation of research towards transition metal oxide nanostructures, due to their characteristics, such as: composition, size, shape, high surface-to-volume ratio, thermal and chemical stability, low toxicity and the ability to be modified with specific sensitive elements [1].

Among transition oxides, zinc oxide is a versatile material with unique properties due to its advantages, such as special properties, cost efficiency, low toxicity, good biocompatibility and biodegradability, adjustable band-gap, different shapes and a broad size distribution range, many other features, making it applicable in a wide range of scientific fields (e.g., optoelectronic devices, textile industry, food packaging, luminescent materials, drug delivery, bioimaging, medical device, cancer diagnostics, agriculture, cosmetic etc.). Also, it is well known that the morphological diversity and particle size distribution of the nanoparticles have a great influence on properties and technological applications, and therefore a rigorous control over the process parameters for the synthesis of ZnO particles, become necessary [2,3].

Depending on the approached method, chemical intermediates and the variety of conditions involved in the synthesis process, ZnO nanostructures can be obtained in different shapes and sizes, which determines various physico-chemical properties. The synthesis methods for ZnO nanostructures have been widely developed in recent years,

through the sol-gel method, direct precipitation, solid-state method, mechano-chemical process, hydrothermal and solvothermal techniques, thermal decomposition of organic precursor, biological approach etc. [4–6].

By using known methods, ZnO can be synthesized as nanoparticles, nanoflowers, nanorods, nanowires, nanobelts, nanorings, nanotubes, nanoplates or quantum dots and it oxide provides one of the greatest selections of varied structures with special properties among all known materials. Therefore, many researches have focused on the investigation of the main factors, which influence the particle size, morphology, phase, and surface area of the ZnO. Among the factors that influence the final structure can be mentioned: the type of raw materials (zinc acetate dehydrate (zinc acetate dehydrate ($Zn(C_2H_3O_2)_2{\cdot}2H_2O$)), zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$), zinc sulphate heptahydrate ($Zn(SO_4)_2{\cdot}7H_2O$), zinc chloride ($ZnCl_2$)), the concentration of raw materials, molar ratio, pH of the reaction mixture, time and temperature reaction, types of solvent, nature of additives dopants, capping agents or other parameters used during the steps of thermal treatment etc. The use of varying precursors implies the development of materials with different morphological, textural and optical properties. The pH value has a significant influence on the properties, morphology and the crystallite size of the ZnO. Capping agents and surfactants are responsible for the control of growth rate, particle size, and prevention of particle aggregation. Moreover, sintering temperature also significantly influences the morphology, structures and photoluminescence properties of ZnO nanostructures [7–12].

In the present paper, we obtained ZnO nanostructures by the sonochemical method, using different zinc precursors (such as zinc acetate dihydrate and zinc sulphate heptahydrate), and establish the optimum thermal treatment temperature at 550 °C. The synthesized ZnO nanostructures have been investigated by using Fourier transform infrared spectrometry (FTIR), scanning electron microscopy (SEM), and X-ray diffraction (XRD). The wetting and percolation capacity of ZnO surfaces with different morphologies was studied by measuring the contact angle. Therefore, with the final goal to tailor the properties of ZnO structures according to a specific application, it is necessary to understand the steps and the parameters of the process, and the relationship between the physico-chemical properties of the synthesized materials.

2. Experimental Detail

2.1. Synthesis of ZnO Nanostructures

For the synthesis of ZnO, zinc salt such as Zinc acetate dihydrate [$Zn(CH_3COO_2)_2$ $2H_2O$] and zinc sulphate heptahydrate [$ZnSO_4$ $7H_2O$], was used as the source for Zn^{2+} cations, and sodium hydroxide [NaOH] as precipitator material. Sodium hydroxide solution [NaOH] (0.5 M) was added to the aqueous solution of zinc acetate [$Zn(CH_3COO_2)_2$ $2H_2O$] (0.05 M), respectively the solution of zinc sulphate heptahydrate [$ZnSO_4$ $7H_2O$] (0.05 M), drop by drop under continuous stirring, until the formation of white precipitates. The vessels with the formed precipitations were sealed and left under magnetic stirring for 2 h, after that the solutions were ultrasonication for 1 h, at a temperature of 40 °C, with a frequency of 45 kHz. After ultrasonication, the formed precipitates were filtered and washed with deionized water and ethanol, at least 3 times to remove impurities and other unreacted compounds. The samples were left overnight in the desiccator, under vacuum, followed by heat treatment at 550 °C, with an oven heating rate of 7 °C/min and maintained for 3 h.

2.2. Characterization

The ZnO samples were characterized by Fourier transform infrared spectroscopy (FTIR) using a Tensor 27 FTIR spectrometer (Bruker Optics, Germany), in the spectral range 4000–370 cm^{-1}, by averaging 64 scans and with a resolution of 4 cm^{-1} at room temperature, using an ATR Platinum holder.

The morphology and particle size of the ZnO samples were investigated by a Field Emission Scanning electron microscope (FEI Company, Hillsboro, OR, USA) with operating voltage at 10 kV. The as-synthesized ZnO samples were analyzed using a Rigaku Smartlab diffractometer, operating at 75 mA and 40 kV with Cu-Kα radiation. The diffraction spectra were recorded 2θ in the range between 20° and 90°.

Contact angles were estimated with a goniometer (Theta Optical Tensiometer, KSV Instruments, Monroe, CT, USA) equipped with the CAM 101 camera, light source, lens, and the 1394 firewire interface for fast image acquisition. The mean contact angle was determined with the help of Attension Theta software, using polar liquid water with the volume of the drop varied between 1 and 1.5 µL.

3. Results and Discussion

3.1. FTIR Analysis

Figure 1 shows the comparative ATR-FTIR spectra drawn for ZnO nanoparticles obtained from precursors of (a) acetate and (b) sulfate (Figure 1A), but also the detail of the main bands characteristic of the Zn-O bond (Figure 1B). The spectra of the oxide are characterized by absorption bands of high intensity below 500 cm^{-1}. The absorption bands centered at about 385 cm^{-1} can be attributed to the vibrational mode of the Zn-O bond in the wurtzite structure of ZnO. In the case of the obtained oxide from the sulfate precursor, the existence of the second peak at 410 nm, associated with the Zn-O bond, indicates the coexistence of an oxide with different morphologies.

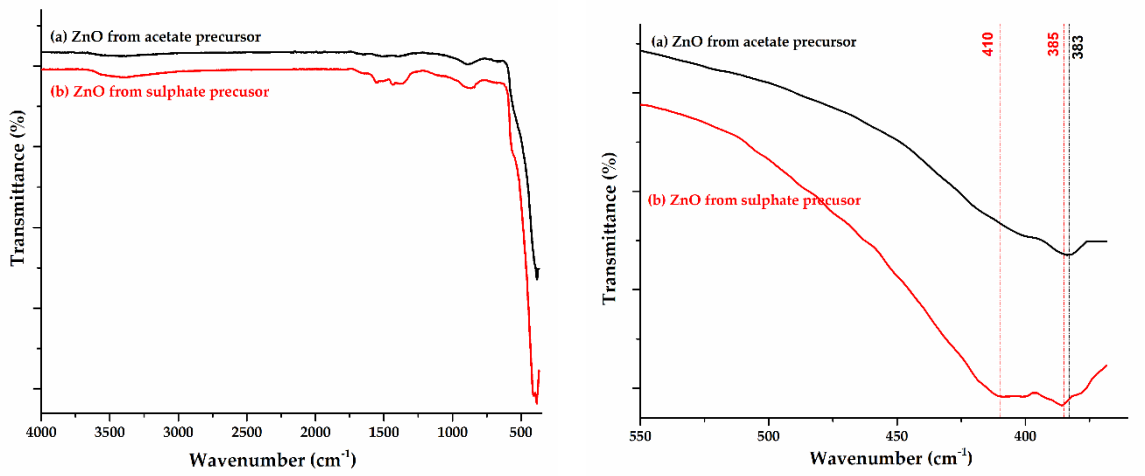
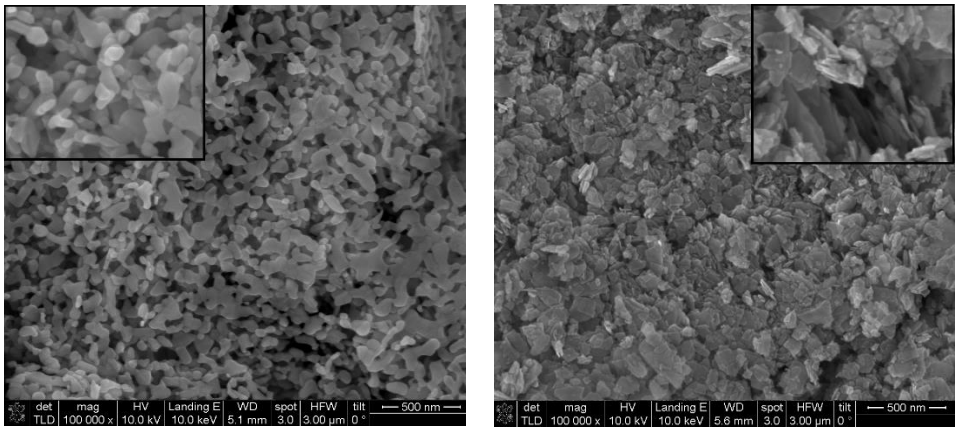


Figure 1. ATR-FTIR spectra for ZnO samples obtained from (a) Zinc Acetate; (b) Zinc sulphate (**A**); detail of Zn-O bands (**B**).

3.2. SEM Analysis

Figure 2 shows the morphology of ZnO samples obtained from (A) zinc acetate and (B) zinc sulphate. From the examination of the SEM micrograph in Figure 2A it can be seen that the particles have spherical formations, with a slight tendency to agglomerate, and with sizes varying between 25–70 nm. Figure 2B of the ZnO sample obtained from zinc sulfate shows irregular morphologies with different shapes, spherical nanoparticles with a tendency to aggregate, but also of the type of sheets/plates of various sizes maintained in the nanometric range. As can be seen, the morphology of the samples depend strongly by the nature of the used precursors.



(**A**) (**B**)

Figure 2. SEM images for ZnO samples obtained from (**A**) Zinc Acetate; (**B**) Zinc Sulphate.

3.3. XRD Analysis

The XRD patterns of the ZnO samples synthesized using the two precursors (zinc acetate and zinc sulphate) are shown in Figure 3 (a and b). For both samples it was found that the diffraction peaks correspond to the wurtzite phase of ZnO, that belongs to the space group P63mc, according to the International Center for Diffraction Data (ICDD), card no. 36-1451 and other data that exist in the literature [12].

No peaks characteristic of other phases of ZnO or corresponding to any impurity were detected, which confirmed the high purity of the synthesized samples. The sharp and narrow diffraction peaks revealed the high crystallinity of the ZnO nanostructures. Based on the diffraction peak positions and their Full Width at Half Maximum (FWHM) the values of the unit cell (a and c) and the mean crystallite size were calculated (Table 1). From the analysis of the parameters, it was found that the value of the lattice constant shows a negligible variation, and the average size of the crystallites calculated using the Debye-Scherer equation varies between 16–32 nm, depending on the type of used precursor.

Table 1. XRD data analysis and crystallite size of ZnO samples obtained from different zinc precursors.

Precurors	Lattice Parameters			Strain [%]	Avearege Crystallite Size [nm]
	A = b (A)	c (A)	c/a Ratio		
$Zn(CH_3COO)_2$	3.2512	5.2084	1.6019	0.11	16.2
$ZnSO_4$	3.2482	5.2028	1.6017	0.02	31.6

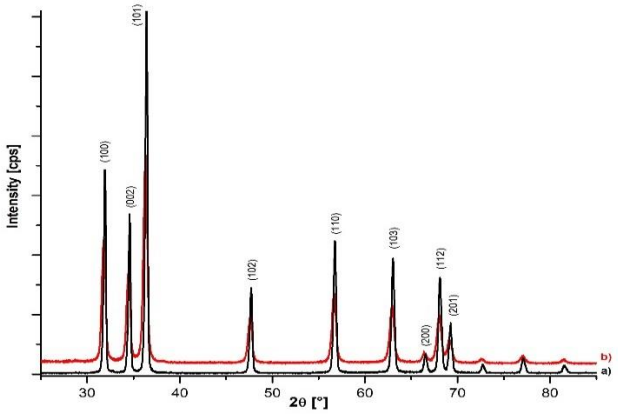


Figure 3. XRD diffraction patterns for ZnO samples obtained from (a) Zinc Acetate; (b) Zinc Sulphate.

3.4. Wetting Capacity (Contact Angle)

Water contact angle (WCA) measurements were performed to investigate the surface wettability of ZnO nanostructures. Figure 4 shows the value of the contact angle (WCA) of the water drop in contact with the surface of the ZnO nanostructures deposited on the Si substrate, observing a hydropholic character regardless of the type of precursor used in the synthesis. The contact angle for the ZnO samples indicates a high hydrophilicity with a value of 52° (in the case of using zinc acetate) and 82° (in the case of using zinc sulphate). The decrease in the hydrophilic character of the ZnO obtained from sulphate can be associated with the existence of sheets/plates. The surface of nanostructured ZnO exhibits hydrophilic wetting behaviour and good percolation capacity, character which can be attributed to the surface morphology, size, and structure form.

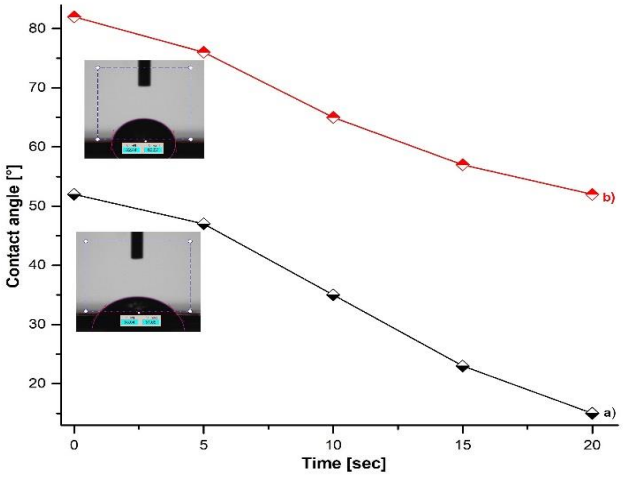


Figure 4. The variation of contact angle depending on time at the contact of the water droplet with surface of ZnO samples obtained from (a) Zinc Acetate; (b) Zinc Sulphate.

4. Conclusions

ZnO nanostructures with two types of zinc precursors have synthesized by the sonochemical method. The FTIR spectra of ZnO nanostructures showed the characteristic absorption of Zn–O bond, regardless of the type of precursor used in their synthesis. The FESEM morphology of the analyzed samples indicates the formation of some spherical particles in the case of using acetate and the coexistence of different morphologies for sulfate oxide, with a tendency to agglomerate and keeping the dimensions in the nanometric range. The XRD results show that the synthesized powders possess crystalline, wurtzite hexagonal phases of ZnO for both samples, and the crystallite size is strongly influenced by morphology, and respectively by the type of precursor used. According to the water contact angle measurements, ZnO nanostructures exhibit hydrophilic wetting character and good percolation properties, better for ZnO synthetised from in acetate precursor than sulphate. Based on the obtained results, ZnO could be considered a functional material with applicability in multidisciplinary fields.

Author Contributions: A.M. conceived, planned, carried out the experiments for the synthesis of ZnO nanostructures; FTIR characterization, V.T.; XRD characterization, C.R.; SEM characterization, O.T.; wettability studies, A.M.; writing—original draft preparation, A.M.; writing—review and editing, A.M., V.T., C.R., O.T. All authors have read and agreed to the published version of the manuscript.

Acknowledgments: This work was supported by Core Program within the National Research Development and Innovation Plan 2022-2027, carried out with the support of MCID, project no. 2307 (μNanoEl).

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Hedlund Orbeck, J.K.; Hamers, R.J. Surface properties and interactions of transition metal oxide nanoparticles: A perspective on sustainability. *J. Vac. Sci. Technol.* **2020**, *38*, 031001-1-6.
2. Borysiewicz, M.A. ZnO as a Functional Material, a Review. *Crystal* **2019**, *9*, 505.
3. Matei, A.; Tucureanu, V.; Dumitrescu, L. Aspects regarding synthesis and applications of ZnO nanomaterials. *Bull. Transilv. Univ. Brasov. Ser. I: Eng. Sci.* **2014**, *7*, 45–52.
4. Raha, S.; Ahmaruzzaman, M. ZnO nanostructured materials and their potential applications: Progress, challenges and perspectives. *Nanoscale Adv*. **2022**, *4*, 1868–1925.
5. Jiang, J.; Pi, J.; Cai, J. The advancing of zinc oxide nanoparticles for biomedical applications. *Bioinorg. Chem. Appl.* **2018**, *2018*, 1062562.
6. Matei, A.; Dumitrescu, L.; Cernica, I.; Tucureanu, V.; Mihalache, I.; Bita, B.; Danila, M.; Manciulea, I. Study of the influence of capping agents on the structural and optical properties of ZnO nanostructures. *J. Optoelectron. Adv. Mater.* **2015**, *17*, 952–957.
7. Mousavi, S.M.; Behbudi, G.; Gholami, A.; Hashemi, S.A.; Nejad, Z.M.; Bahrani, S.; Chiang, W.H.; Wei, L.C.; Omidifar, N. Shape-controlled synthesis of zinc nanostructures mediating macromolecules for biomedical applications. *Biomater. Res.* **2022**, *26*, 4.
8. Gatou, M.A.; Lagopati, N.; Vagena, I.A.; Gazouli, M.; Pavlatou, E.A. ZnO Nanoparticles from Different Precursors and Their Photocatalytic Potential for Biomedical Use. *Nanomaterials* **2023**, *13*, 122.
9. Shaba, E.Y.; Jacob, J.O.; Tijani, J.O.; Suleiman, M.A.T. Critical review of synthesis parameters affecting the properties of zinc oxide nanoparticle and its application in wastewater treatment. *Appl. Water Sci.* **2021**, *11*, 48.
10. Sambath, K.; Saroja, M.; Rajendran, K.; Muthukumarasamy, N. Morphology controlled synthesis of ZnO nanostructures by varying pH. *J. Mater. Sci. Mater. Electron*. **2012**, *23*, 431–436.
11. Rathnasekara, R.; Hari, P. Impedance spectroscopy of nanostructured ZnO morphologies. *J. Mater. Res.* **2021**, *36*, 1937–1947.
12. Matei, A.; Tucureanu, V.; Popescu, C.M.; Romanitan, C.; Mihalache, I. Influence of Cu dopant on the morpho-structural and optical properties ZnO nanoparticles. *Ceram. Int.* **2019**, *45*, 10826–10833.