

Supercritical CO₂ assisted synthesis of flower – like ZnO nanoparticles

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In the last decade the synthesis and design of nanoscale ZnO materials gain significant interest due to the variety of possible applications. The present work describes a novel method to obtain flower-like ZnO nanocrystals using a simple solvothermal synthesis assisted by supercritical CO₂. The effect of various parameters on the morphology and optical properties of the nanoparticles was investigated. The solid material obtained was investigated for structural information using SEM, XRD. In optimal conditions chrysanthemum like aggregates of ZnO nanorods were obtained as 3D highly ordered structures.

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1. Introduction

From the end of '90 years, nanostructured semiconductor materials have attracted remarkable attention since they possess specific electronic and optical properties, tunable in large range, closely related to their size and morphology.

Zinc oxide is an n-type semiconductor material with application in many industrial fields, such as photovoltaics [1], chemical sensing, photocatalysis [2], anticorrosion and self-cleaning coatings [3], UV absorbing materials [4], solar cells [5], acoustic wave resonators, bioimaging [6], optoelectronics [7].

Usually ZnO is a white powder (with slight color changes in yellow or green if impurities are present) obtained either in cubic zinc blende or hexagonal wurtzite structure [8]. In normal conditions wurtzite is the thermodynamic stable phase, the one also considered to show the best photocatalytic activity. Zinc oxide generates oxidative species when is exposed to UV light, which is the main mechanism of its oxidative effect on organic pollutants [9]. The main properties, and consequently the application of ZnO nanostructures, are influenced by some important factors that include: the crystalline structure, degree of crystallinity, size and shape of the particles and surface area [10].

In the last two decades various ZnO nanostructures were synthesized, with a large variety of sizes, morphologies and superior 2D or 3D architectures, such as spherical nanoparticles, hollow nanoparticles, nanorods, nanowires grown on solid support, helices, cones, bipods and tetrapods, nanotubes [11].

Flower-like nanostructures are highly ordered 3D architectures with significantly modified properties compared to isolated nanoparticles.

For the preparation of ZnO nanopowders several methods are employed, such as sol-gel combustion, chemical precipitation in various conditions [12], chemical vapor deposition, solar physical vapor deposition (SPVD) [13], sonochemical synthesis [14], thermal oxidation [15]. The most used methods to prepare ZnO nanostructures are various hydrothermal or solvothermal syntheses, sometimes using structuring additives to modify the shape of the nanoparticles [16].

The ZnO nanoparticles preparation is based on the dissolution of various Zn²⁺ precursors (zinc perchlorate, zinc nitrate, zinc acetate dihydrate, zinc acetylacetonate monohydrate) in water or organic solvents (alcohols, diols, etc.) and the addition of an OH⁻ aqueous solution (NaOH, NH₄OH, LiOH) to ensure a basic environment [17]. It was found that the molar ratio of hydroxide/Zn²⁺ precursor is the most important parameter governing the ZnO particle size, while the presence of surfactants generates anisotropic particles.

Most of these methods have limitations in terms of the quality of the product obtained (polydisperse, poor crystallinity) or high energy and time consuming.

In this work, a simple method is proposed based on a solvothermal synthesis assisted by supercritical CO₂ to obtain ZnO nanoflowers.

2. Experimental

The ZnO nanoparticles were prepared using a Zn (NO₃)₂ hexahydrate as Zn²⁺ precursor (99.99% purity, Aldrich reagent) and NaOH pellets (98% purity, reagent purchased from Sigma). Cetyltrimethylammonium bromide (CTABr) was employed as surfactant for growth control of nanoparticles, and was purchased from Sigma,

as reagent with 99% purity. For the supercritical synthesis CO₂ (99.999% purity) from Techigaz Romania was used.

2.1. Nanoparticles preparation

The ZnO nanomaterials were prepared by a facile solvothermal synthesis modified in our laboratory. Briefly, Zn²⁺ precursor solution was prepared by dissolving appropriate amount of Zn (NO₃)₂ hexahydrate in a solvent containing 4:1 molar ratio ethanol-water in order to obtain 1M concentration. The solution is magnetically stirred at 80^o C for 1 hour. A volume of 10 mL of 2M NaOH in ethanol was added under vigorous stirring and the system was further reacted in various conditions. For the sample prepared in the presence of surfactant 0.75 g of cetyl trimethylammonium bromide (CTABr) was added in the Zn nitrate solution and stirred for 1 hour until complete dissolution.

The unmodified solvothermal synthesis is conducted at 90^o C for at least 12 hours (typically 24 hours to obtain ZnO nanoparticles with high degree of crystallization).

For the synthesis in high pressure and elevated temperature conditions, the above white cloudy dispersion was transferred in a stainless steel autoclave with Teflon coating (Parr model 4370), and the cell was filled up to 70% of the total volume. The autoclave was kept at 180^oC for 12 h and then left to cool to room temperature.

The supercritical CO₂ assisted synthesis was performed using a laboratory installation consisting in a high pressure copper vessel (internal volume 25 mL) with Teflon coating. The pressure of gas supply was controlled by a Bourdon manometer (precision class 0.6), and the whole synthesis cell was suspended in a thermostat bath (model Lauda K4R with PTR Regler R20K) for temperature regulation. The cell was filled with carbon dioxide at certain temperature (40^oC or 60^oC) and pressure (60 bar or 75 bar) values and remained at these conditions for the various period of time. After the system was cooled at -10^oC was slowly depressurized at a constant rate of 1 bar/min.

The white precipitates obtained in various methods were collected, filtered and washed several times with distilled water and ethanol. The powders were dried in a vacuum at 40^o C for 12 h, and the white final product was further analyzed.

2.2. Instrumentation

The solid product obtained according to the above section was investigated for size, size distribution, crystallinity, morphology and optical properties. The crystallinity of the nanopowder was evaluated using an X-ray diffractometer Bruker-AXS D8-ADVANCE. For the measurements, K_α radiation of copper was used.

IR spectra of the ZnO nanoparticles were obtained at room temperature with a Nicolet (Bruker) FTIR spectrometer with the range of 3500~500 cm⁻¹. The Raman

spectra were determined using a Jasco V670 instrument equipped with 535 nm laser source. The size and size distribution of nanoparticles were determined by using DLS method on a Malvern instrument model NanoZetasizer (Malvern, UK). The morphology was evaluated using scanning electron microscopy (SEM) method and the images were obtained on a Quanta 200 FEI instrument.

3. Results and discussion

ZnO nanopowders were prepared according to the procedure described in the previous section. Various time periods for maturation were tested, and for normal conditions (temperature 90^o C, with stirring and high temperature synthesis in autoclave without stirring) best products were obtained after at least 18-24 hours. No flower-like 3D morphology was obtained without structuring agent CTABr.

In order to study the possibility to fabricate ZnO nanopowders with good crystallinity and 3D morphology using a less time consuming and temperature saving method, a modification of the solvothermal synthesis in the presence of the supercritical CO₂ was performed.

For the synthesis in supercritical CO₂ samples were collected at 6, 12, 18 and 24 hours. Nanopowders with flower-like morphology and good crystallinity were obtained starting with 12 hours.

In Fig. 1 the XRD spectra of ZnO nanopowder obtained using the modified solvothermal synthesis in the presence of supercritical CO₂ (temperature 60^oC and pressure 75 bar) is shown.

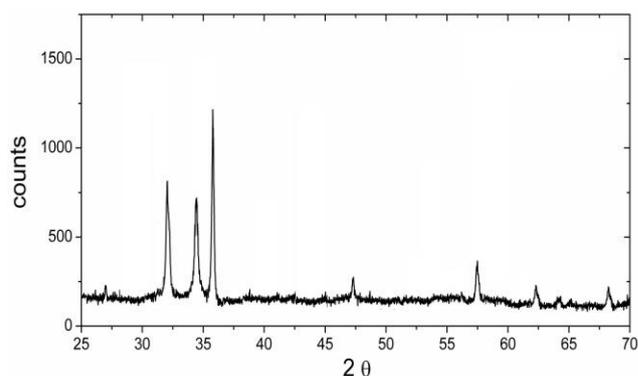


Fig. 1. XRD diffractogram of ZnO nanopowder synthesized by supercritical CO₂ assisted solvothermal method in the presence of CTABr

The spectra exhibit the peaks corresponding to the hexagonal phase of ZnO (ICDD-PDF # 89-0511 file) without the presence of signals for other phases. The diffraction patterns consists in sharp peaks that indicate that solid product obtained have good crystalline quality. The rather high relative intensity of (002) Bragg reflection is consistent with the specific XRD pattern of nanorods.

Similar XRD spectra were obtained for samples prepared using supercritical CO₂ assisted solvothermal

synthesis (temperature 40°C and pressure 60 bar) and also for the samples prepared in autoclave (high pressure, high temperature).

Raman spectroscopy was used to confirm the crystal phase and to reveal the defects in the ZnO crystals. The Raman spectra collected from the ZnO powder obtained in various experimental conditions are presented in Fig. 2. The peaks in the region 300 – 400 (at ~430 and ~380 cm⁻¹) are attributed to the Raman vibration modes of the wurtzite phase ZnO, that agree with the XRD data.

Characteristic peaks of ZnO at the approximately 335, 430 and 550 cm⁻¹ are present in the spectra of all samples prepared in various conditions, in some cases more attenuated. The peak at ~335 cm⁻¹, assigned to the bending vibration according to the literature, appears as significantly reduced, while the peak at ~430 cm⁻¹, related to the stretching vibrations is sharp and clear.

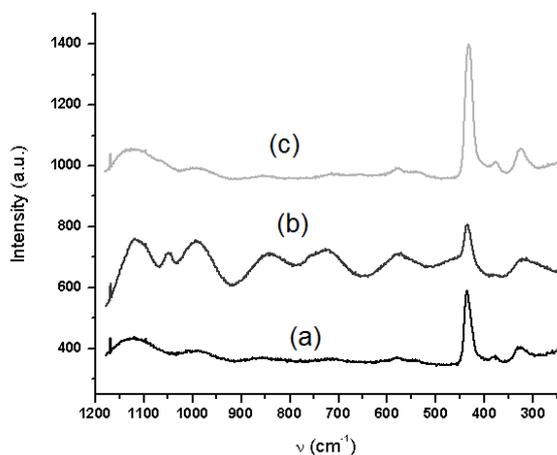


Fig. 2. Raman spectra of ZnO nanopowders synthesized in various conditions (a – normal solvothermal synthesis, b- solvothermal synthesis in autoclave, c- supercritical CO₂ assisted solvothermal method).

The peaks at 550 cm⁻¹, which are related to the presence of ZnO nanoparticles, are more or less evidenced in the samples prepared in various conditions.

The FTIR analysis is complementary with the Raman spectroscopy. In Fig. 3, the FTIR spectra of the ZnO samples prepared using solvothermal method in autoclave and in supercritical CO₂.

In both cases the reaction was conducted in the presence of CTABr as structuring surfactant.

The absorption band in the region 410–430 cm⁻¹ (reported in literature to correspond to the stretching vibration of ZnO) confirms the ZnO formation.

The samples analyzed exhibit a shift of this specific band to higher frequencies that indicates the existence of an extended ZnO structure.

For both the samples prepared in the presence of CTABr as structuring agent, in autoclave and in supercritical CO₂ respectively, the FTIR spectrum is very complex, due to the presence of the specific bands of hydroxyl from ZnO surface, and also of multiple signals from the surfactant.

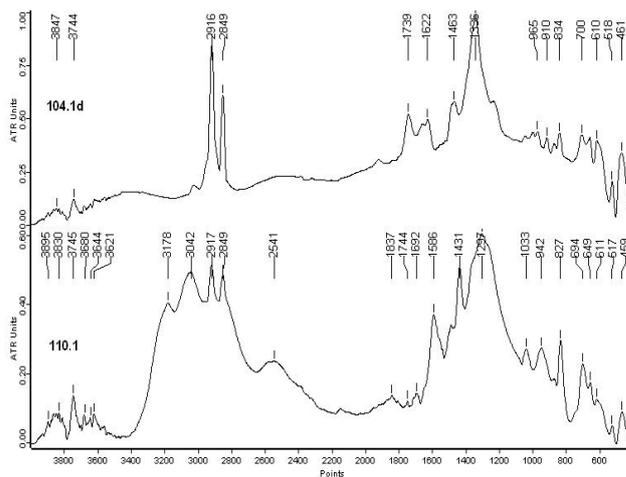


Fig. 3. FTIR spectra of ZnO nanopowders synthesized in various conditions (104- solvothermal synthesis in autoclave, 110- supercritical CO₂ assisted solvothermal method)

The functionalization of the ZnO nanoparticles surface with the long hydrocarbon chains of CTABr molecules is supported by the changes in FTIR spectra.

The peak present approximately at 3300 cm⁻¹, assigned for -OH group, has a decreased intensity and is shifted to smaller wave number. The two notable peaks in the regions 2900 and 2850 cm⁻¹ are related to the presence of -CH₂ group of CTABr. The other peaks in the region 1480-1490 cm⁻¹ and 1390 cm⁻¹ (for the asymmetric and symmetric CH₃-N⁺ group deformation mode) are reduced in intensity and shifted to longer wave numbers.

The UV-VIS spectra of ZnO nanoparticles prepared in various experimental conditions were measured and specific shift of maximum absorbance compared to bulk material was recorded in each case.

In the Fig. 4 the optical properties of ZnO nanoparticles prepared in the supercritical CO₂ assisted solvothermal synthesis is shown, for the other samples the spectra are similar in shape and maximum absorbance position.

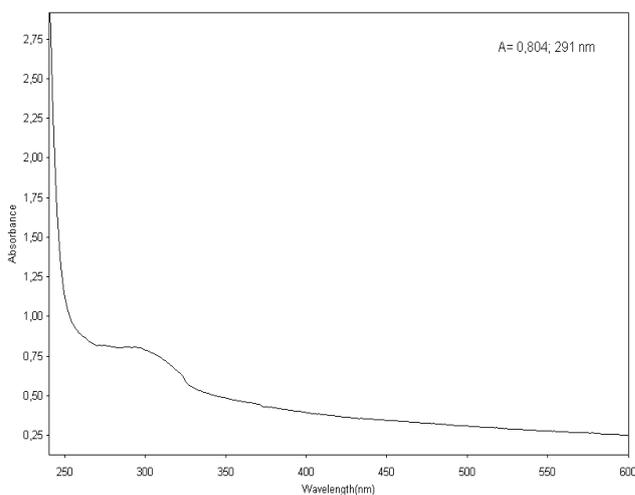


Fig. 4. UV-VIS spectra of ZnO nanopowders synthesized in supercritical CO₂ assisted solvothermal method

The absorption peak is broad, indicating large and irregular aggregates rather than spherical nanoparticles.

The size and size distribution of the nanopowders prepared as described before were measured by using DLS method. In Fig. 5 DLS diagrams for the samples prepared in the presence of CTABr surfactant in various synthesis conditions were shown.

The surfactant is used both to promote the formation of flower-like aggregates from ZnO nanorods and to orient the growth of the nanocrystals, resulting in elongated shaped ZnO particles. Also the main role of the CTABr in this kind of the synthesis is to limit the size of the ZnO nanoparticles formed during the maturation period.

The solvothermal synthesis of ZnO nanopowders performed in autoclave (high temperature and high pressure conditions) and in supercritical CO₂ assisted variation lead in both cases to the formation of aggregates with sizes ranging in the domain of 700-900 nm.

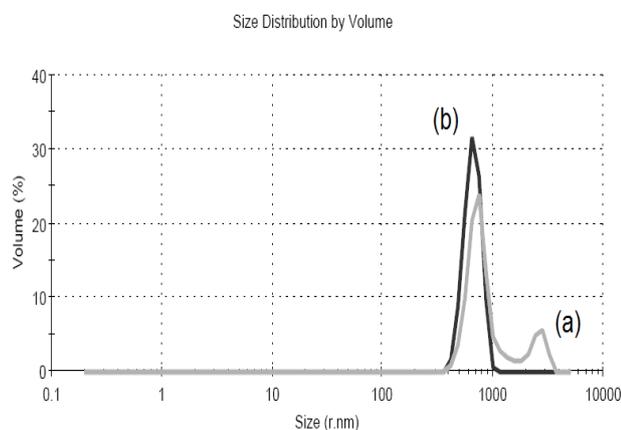


Fig. 5. DLS diagrams for the ZnO nanopowders obtained in the presence of CTABr: (a) = solvothermal synthesis in autoclave; (b) = supercritical CO₂ assisted solvothermal synthesis. (Aging time 12 hours)

For the synthesis performed in supercritical CO₂ a monomodal representation is obtained, that indicates the presence of a single population of particles, with a good polydispersity index (PDI with a value of 0.189). The CTABr is probably better distributed on the ZnO nanorods during the 3D morphology formation in the more hydrophobic environment provided by the supercritical carbon dioxide. The sample prepared also in the presence of surfactant but in autoclave exhibits a more obvious tendency of aggregation, since on the DLS diagram a second signal is recorded, a larger value of size (at approximately 3000 nm).

The zeta potential values of the samples mentioned before are presented in the Fig. 6.

For all the samples prepared in the presence of surfactant CTABr, a positive value for the electrokinetic potential is obtained, ranging to 25 to 65 mV, according to the experimental method. As it is expected from the size and size distribution diagrams, for the sample prepared using supercritical CO₂ assisted solvothermal method the value is higher (55-65 mV) than the values obtained for the samples prepared in autoclave.

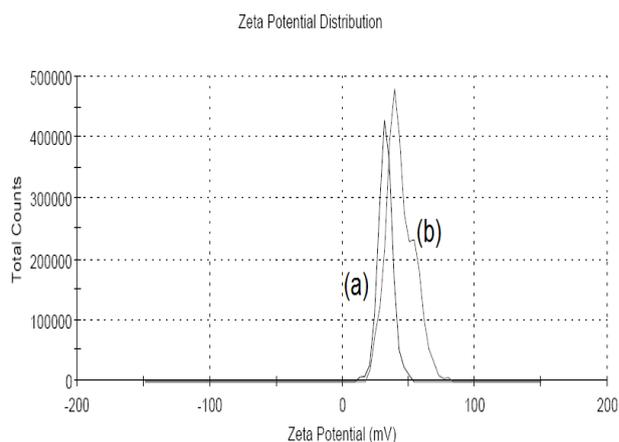


Fig. 6. Zeta potential for the ZnO nanopowders obtained in the presence of CTABr. (a) = solvothermal synthesis in autoclave; (b) = supercritical CO₂ assisted solvothermal synthesis

The morphology of ZnO nanopowders obtained was shown in Fig. 7.

In the Fig 7 (A) the typical morphology of spherical ZnO nanoparticles aggregated in large irregular clusters is present, for the product obtained in normal conditions (temperature of 90⁰ C, 24 hours of aging), without surfactant. In many hydrothermal and solvothermal synthesis proposed in the literature, using various Zn²⁺ precursors, Zn/OH molar ratios or temperature and aging conditions similar nanoparticles were obtained. The presence of the structuring agents, such as CTABr results in the formation of nanorods, as one could observe in Fig. 7 (B and C) for the samples prepared using solvothermal methods.

No flower-like morphology was obtained for the ZnO powders prepared using zinc nitrate and sodium hydroxide in the absence of surfactant, in either solvothermal method with aging in high temperature – high pressure conditions (autoclave) or in the variation of the method using supercritical carbon dioxide.

For the sample prepared with the aid of CTABr as structuring agent aged in autoclave in high temperature and high pressure conditions (Fig. 7 B) a 3D morphology with the aspect of chrysanthemum is present. The SEM images for the samples prepared in those conditions and aged for 12, 18 and 24 hours exhibit good crystallinity, confirmed by the XRD spectra. The native nanocrystals are rods with 100-300 nm diameter and hundred of nm length for the samples matured for a period of 12 hours. For samples let to react longer time the nanorods obtained are longer, and thus the “flowers” aggregates are bigger in size, up to 2-5 micrometers.

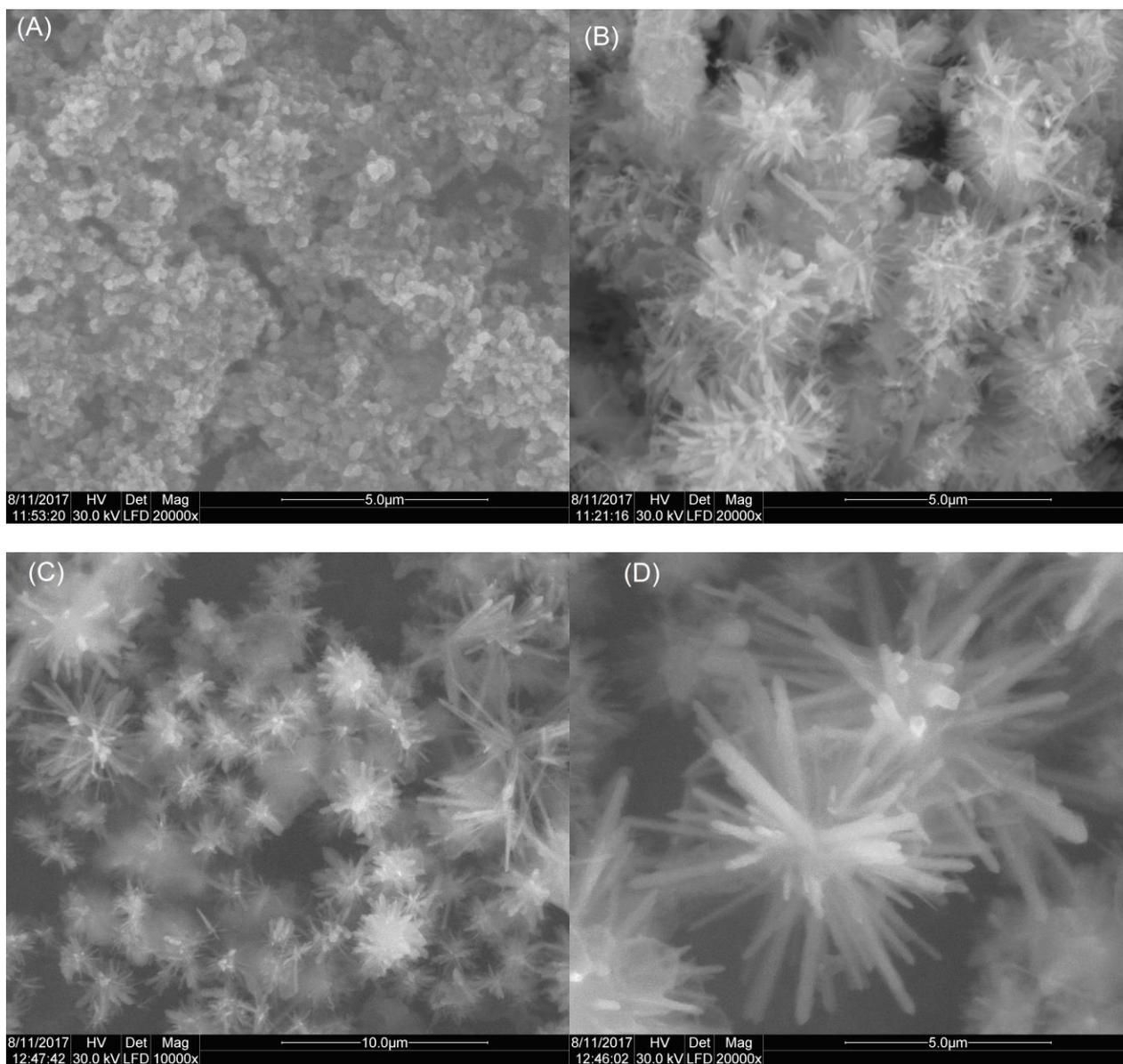


Fig. 7. SEM images of the ZnO nanopowders obtained in various experimental conditions: (A) solvothermal synthesis in normal conditions, without surfactant; (B) solvothermal synthesis in autoclave, in the presence of surfactant CTABr; (C) supercritical CO₂ assisted solvothermal synthesis, in the presence of surfactant CTABr (low magnification); (D) high magnification of sample C.

Similar 3D nanostructured (flower-like aggregates made from long nanorods) products were obtained in a more convenient experimental conditions using supercritical CO₂ assisted solvothermal method. In Fig. 7 C the same crysanthemum structure is present, recorded for the sample prepared in CO₂ at 60⁰ C and 75 bar, time of maturation 18 hours. The sample show high degree of crystallinity (see details in Fig. 7 D at high magnification), that confirm the XRD data, and defined 3D structure.

4. Conclusions

ZnO nanomaterials with flower-like morphology were successfully synthesized by using a novel solvothermal

method assisted by supercritical carbon dioxide. Zinc nitrate and sodium hydroxide were used as reactants and CTABr was used as the structuring agent. The XRD spectra demonstrated that the synthesized materials were crystalline in nature. The quality of the ZnO nanopowders obtained in the above mentioned synthesis were comparable to those of product obtained in solvothermal synthesis conducted in more drastic conditions (high temperature). Raman and FTIR spectroscopic studies confirmed the presence of ZnO nanorods and functionalization of the ZnO nanoparticle surface with CTABr molecules. SEM images show that the flower-like 3D morphology is obtained in both cases of solvothermal synthesis performed in high temperature –high pressure conditions (autoclave) and in more “mild” conditions

using supercritical carbon dioxide. The method proposed exhibits advantages, such as use of less toxic reagents, reduced energy consumption, decreased reaction time, leading to similar results in term of quality of the ZnO nanopowder produced.

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References

- [1] S. H. Kim, U. Ahmad, O. R. Kumar, H. Algarni, G. Kumar, *J. Nanosci. Nanotechnol.* **15**(9), 6807 (2015).
- [2] C. B. Ong, L. Y. Ng, A. W. Mohammad, *Renew. Sustain. Energy Rev.* **81**, 536 (2018).
- [3] B. Stieberova, M. Zilka, M. Ticha, F. Freiberg, P. Caramazana - Gonzalez, J. McKechnie, E. Lester, *ACS Sustain. Chem. Eng.* **5**(3), 2493 (2017).
- [4] A. Becheri, M. Dürr, P. Lo Nostro, P. Baglioni, *J. Nanoparticle Res.* **10**(4), 679 (2008).
- [5] Z. L. S. Seow, A. S. W. Wong, V. Thavasi, R. Jose, S. Ramakrishna, G.W. Ho, *Nanotechnology* **20**(4), 045604 (2009).
- [6] H. Mirzaei, M. Darroudi, *Ceram. Int.* **43**(1), 907 (2017).
- [7] T. Ganetsos, J. Kovac, J. Kovac Jr., L. Bousiakou, R. Qindeel, A. Farook, O. Aldossary, *Optoelectron. Adv. Mat.* **10**(9-10), 716, (2016).
- [8] M. Willander, O. Nur, J. R. Sadaf, M. I. Quadir, S. Zaman, A. Zainelabdin, N. Bano, I. Hussain, *Materials* **3**(4), 2643 (2010).
- [9] W. He, H. Jia, J. Cai, X. Han, Z. Zheng, W. G. Wamer, J-J. Yin, *J. Phys. Chem. C.* **120**(6), 3187 (2016).
- [10] C.W. Nan, A. Tschöpe, S. Holten, H. Kliem, R. Birringer, *J. Appl. Phys.* **85**(11), 7735 (1999)
- [11] A. Kołodziejczak-Radzimska, T. Jesionowski, *Materials*, **7**(4), 2833 (2014).
- [12] L. E. Shi, Z. H. Li, W. Zheng, Y. F. Zhao, Y. F. Jin, Z. X. Tang, *Food Addit. Contam. Part A* **31**(2), 173 (2014).
- [13] A. G. Plaiășu, M. Abrudeanu, M. M. Dicu, C. Monty, *J. Optoelectron. Adv. M.* **16**(9–10), 1116 (2014).
- [14] E. Luévano-Hipólito, L.M. Torres-Martínez, *Mater. Sci. Eng. B*, **226**, 223 (2017).
- [15] S. Duman, B. Ozkal, *J. Optoelectron. Adv. M.* **18**(7–8), 705 (2016).
- [16] B. Shouli, C. Liangyuan, L. Dianqing, Y. Wensheng, Y. Pengcheng, L. Zhiyong, C. Aifan, C.C. Liu, *Sens. Actuators B Chem.* **146**(1), 129 (2010).
- [17] X. Bai, L. Li, H. Liu, L. Tan, T. Liu, X. Meng, *ACS Appl. Mater. Interfaces* **7**(2), 1308 (2015).

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