

MICROWAVE ASSISTED HYDROTHERMAL SYNTHESIS OF Ag-ZnO NANO-MICRO STRUCTURES: COMPARISON OF CLOSED AND OPEN VESSEL REACTOR INFLUENCE ON NITRATE SOLUTION PREPARATION ROUTE

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Abstract

Various Ag-ZnO nanostructures were synthesized by open vessel microwave system MWG1K-10 with reflux system and by pressurized microwave system CEM MARS 5. The material was prepared by microwave synthesis using soluble silver and zinc salts as source materials and hexamethylenetetramine as precipitating agent for ZnO and reducing agent for Ag. Influence of Ag⁺ ions, reaction condition and pressure by the pressurized microwave system on formation of particle microstructure was investigated. Scanning electron microscopy (SEM), Energy dispersive X-ray analyse (EDX) and powder X-ray diffractometry (XRD) was used in order to investigate the morphology, phase composition and crystalline structure.

Keywords: microwave synthesis, Ag-ZnO nanostructures, ZnO microstructures

1. Introduction

Zinc oxide is a versatile, multifunctional material with unique properties. It has been extensively used in several industrial products such as ceramics, rubber additives, pigments, personal cares, medicines [1, 2]. Furthermore, ZnO as a wide-band gap ($E_g = 3.37$ eV at 300 K) semiconductor with a large excitation binding energy (about 60 meV) has gained wide attention for its potential applications in light emitting diodes, data storages, gas sensors, or catalyst supports [3, 4, 5]. Electrical and thermal transport, optical and mechanical properties can be varied with respect to particle size, shape, orientation and aspect ratio. Hence, size and morphology controlled growth of zinc oxide has become a challenging topic in order to design novel functional devices. [6]

The well-known semiconductor ZnO and metal Ag still offers unexplored opportunities for the development of novel hybrid nanocomposite systems. It is expected that the addition of metal Ag to ZnO nanomaterials allows constructing Ag-ZnO nanocomposites with novel optical, electrical and microbiological properties. [7] For example, Koga et al. synthesized Ag nanoparticles on ZnO whiskers through selective ion-exchange, and incorporated Ag-ZnO into a paper-like bioactive material to assure its antibacterial activity. [8] Ye et al. obtained Ag-ZnO composites via a facile conventional synthesis method by using glucose as the reductant [9]. Xu et al. prepared Ag-ZnO composites by a simple hydrothermal approach and found that the addition of AgNO₃ to the reaction system reduced the concentration of vacancies and surface hydroxyl of ZnO [10]. Microwave irradiation plays an important role in chemical synthesis in aqueous media, reducing the time, decreasing particle size with narrow size distribution, increasing the product yield rate, and producing high purity products in comparison with conventional methods. [11, 12, 13]

Herein, we report a study on a simple and fast solvothermal microwave assisted preparation of Ag-ZnO micro/nanostructures by open and pressurized microwave system. In comparison with the hydrothermal process which is used extensively in the recent years, the presented approach requires very mild reaction conditions under normal atmospheric or slightly elevated pressure in open and closed reaction system,

respectively. The effect of reactor choice on controlled growth of microstructures of ZnO with addition of AgNO₃ was investigated. Hexamethylenetetramine (HMT) was selected as precipitation and reduction agent.

2. Experimental

Zinc nitrate hexahydrate Zn(NO₃)₂·6H₂O, silver nitrate AgNO₃ and hexamethylenetetramine (CH₂)₆N₄ were purchased from PENTA (Czech Republic). All chemicals were of analytical grade and used as received without further purification. Demineralised water was used throughout experiments.

Microwave open vessel system MWG1K-10 (Radan, Czech Republic) operating at 2.45 GHz was used for open vessel microwave solvothermal synthesis. Pressurized system MARS 5 (CEM Corporation, USA) was chosen for microwave solvothermal synthesis under high pressure.

Standard synthesis procedure was as follows:

Synthesis route 1: Reaction mixture was prepared by mixing the equal volumes of aqueous solutions of zinc nitrate hexahydrate (0.1M) and HMT (0.1M) so that the total volume was 60mL.

Synthesis route 2: Equal volumes of aqueous solutions of zinc nitrate hexahydrate (0.1M), HMT (0.1M) and silver nitrate (0.05 M) were mixed together so that the total volume was 60mL.

In the case of open system, the solution was heated for 10 minutes by MW in quasi-continuous mode at full power of 800 W. The solution reaches boiling point very fast within one minute. In the case of pressurized synthesis, the solution was transferred into a Teflon-lined vessel of capacity 100 mL and heated at 100°C for 10 minutes. The temperature was regulated by MW power control in the closed system. Similarly, the maximum temperature was reached within one minute. The reaction mixture was always left to cool naturally and then the product was collected by microfiltration and washed by water. Obtained powders were dried in a laboratory oven until constant weight at 40°C. Process conditions and sample codes are summarized in Table 1.

Tab. 1 Process conditions of MW synthesis and sample codes

Synthesis	Sample code	Precursors	Precipitation agent	MW exposure Time [min]	Pressure [KPa]
Open vessel MW	D1	Zn(NO ₃) ₂ ·6H ₂ O	HMT	10	n.a.
	D2	AgNO ₃ , Zn(NO ₃) ₂ ·6H ₂ O	HMT	10	n.a.
Pressurized MW	P1	Zn(NO ₃) ₂ ·6H ₂ O	HMT	10	230
	P2	AgNO ₃ , Zn(NO ₃) ₂ ·6H ₂ O	HMT	10	260

3. Characterization

The crystalline phase structure of obtained powders was characterized by X-ray diffractometer PANalytical X'Pert PRO (PANalytical, The Netherlands) using Cu Kα1 radiation (λ = 0.1542 nm) operating at 40 kV and 30 mA with detector PIXcel. Both materials were measured in transmission mode with fixed setting and screen of range angle 25-85° (2θ) and step 0.0263°. The phase composition was evaluated by the software PANalytical X'Pert High Score using normalized RIR (Reference Intensity Ratios) method. The RIR is the ratio between the integrated intensities of the peak of interest and that of a known standard [14]. The morphology of the products was investigated by scanning electron microscope Vega II LMU (Tescan, Czech Republic) with beam acceleration voltage set at 10 kV, after coating with gold/palladium by a high-resolution SEM sputter coater SC 7640 (Quorum Technologies Ltd, UK). SEM equipment includes Energy dispersive X-ray analyser (Oxford INCA) used for elemental analysis.

4. Results and discussion

Figure 1 shows XRD pattern of crystalline phases of Ag-ZnO nano-microparticles. The positions and relative intensities of peaks observed at $2\theta = 31.7^\circ, 34.4^\circ, 36.2^\circ, 47.5^\circ, 56.6^\circ, 62.8^\circ, 67.8^\circ, 68.9^\circ$ and 72.47° matches perfectly to ZnO with the hexagonal wurtzite crystal structure according to JCPDS 01-079-0207 card. Diffraction peaks at $2\theta = 38.8^\circ, 44.4^\circ, 64.6^\circ, 77.6^\circ$ and 81.8° correspond well with fcc crystal structure of silver to JCPDS 01-087-0720 card. No other crystalline impurities are observed. The diffractograms of samples D2 and P2 are dominated by silver diffraction lines, while ZnO phase yields much lower signal. Only ZnO diffraction lines are manifested for samples D1 and P1 where no silver is present in reaction batch.

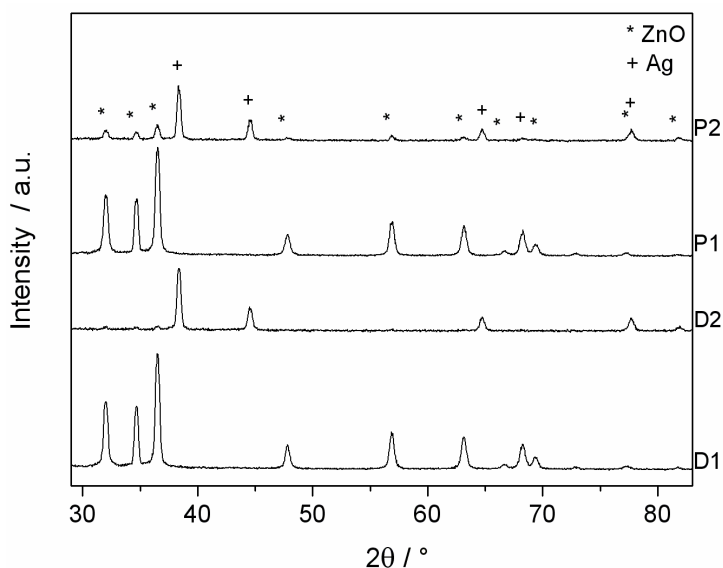


Fig. 1 XRD diffraction analysis of crystalline phases of prepared powders

The SEM images shown in Figure 2 manifest changes of ZnO morphology with the addition of a small quantity of the silver nitrate solution to the reaction system. Left panel images show pure ZnO system while Ag-ZnO particles are presented in the right panel. The influence of the pressure, i.e. of the choice between the microwave open and pressurized system on morphology of ZnO can be understood with the aid of comparison between the upper and lower rows of images in Figure 2. Twinned hexagonal rods of ZnO microparticles with length up to $5\ \mu\text{m}$ and diameter more than $0.5\ \mu\text{m}$ are observed in image of sample D1. In the case of D2, hexagonal rods of ZnO microparticles are up to $2\ \mu\text{m}$ in length and diameter of several hundreds nm. Silver nanoparticles have globular shape and their diameter is up to $100\ \text{nm}$. The particles can be identified due to the material contrast as bright points between light grey ZnO microstructures. In pressurized MW system, star or flower-like pure ZnO were prepared with an average size about $2\ \mu\text{m}$ of the ZnO conical microrods which create the points or petals of the star-like or flower-like particles as can be seen in Figure 2 for material P1. The stars in P2 sample are slightly smaller with much thinner points. The number of microrods aggregated into stars seems to be bigger also. Moreover, strong aggregation of silver particles is observed for P2 sample in Figure 2, while almost no small silver particles similar to the material P1 can be found for the material P2. The comparison of upper and lower row in matrix of images in Figure 2 indicates that the

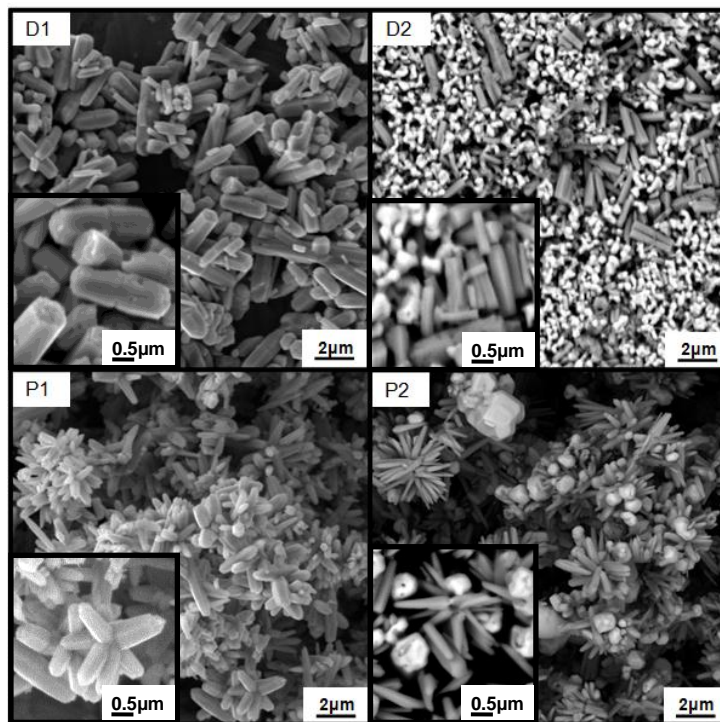
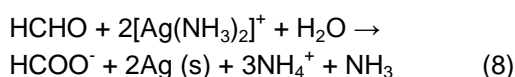
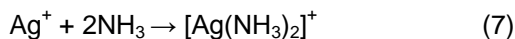
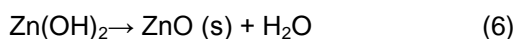
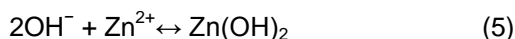
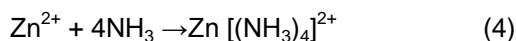
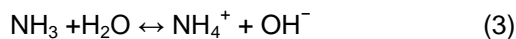
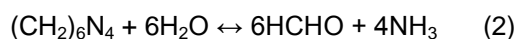


Fig. 2 SEM microphotographs of Ag-ZnO microparticles

increase of pressure during the synthesis causes formation of star-like and flower-like structures together with aggregation of silver into relatively large microparticles.

Figure 3 gives typical EDX spectra recorded for the obtained powders. The EDX spectrum indicates that samples are composed of Ag, Zn, C and O, where oxygen or carbon can be obtained from adsorbed H_2O , CO_2 , CH_2O (or paraformaldehyde) and possible rests of HMT. Presence of zinc cation is observed in all samples, however silver is present in samples in which $AgNO_3$ was added to the reaction mixture. Atomic ratio of silver and Zn in prepared samples is summarised in table 2, where the results of XRD and EDX analysis are compared. XRD results were recalculated from weight % to atomic or molar %. Excellent agreement between these two different methods was found. Content of silver was reasonably higher for D2 than for P2.

Chemical mechanism for precipitation of ZnO microstructures and silver nanoparticles caused by relatively mild reduction agent HMT was already proposed in literature and can be adopted for investigated system as well. HMT is converted into ammonia and formaldehyde through microwave heat treatment. In the presence of ammonia, $Zn(OH)_2$ and $[Ag(NH_3)_2]^+$ complexes are formed and Ag-ZnO particles can be obtained by their subsequent reactions. The chemical reaction process in aqueous solutions of zinc nitrate, silver nitrate and HMT can be formulated by following chemical reactions [15, 16]:



CONCLUSION

Microwave assisted syntheses of Ag-ZnO and ZnO powders by open and pressurized microwave systems were investigated. The product can be obtained within a few minutes without any template, catalyst, and surfactant or stabilisation agent. It was observed that addition of $AgNO_3$ reduced size and changed slightly the shape of ZnO microparticles in comparison to silver less reaction mixture. Moreover, the product obtained at atmospheric pressure contains well developed population of silver nanoparticles besides typical ZnO microparticles. Pressure generated during microwave synthesis influences aggregation of ZnO

Tab. 2 Composition of samples by EDX analysis and XRD powders diffraction

Sample code	EDX analysis (atomic %)		XRD analysis of (atomic or molar %)	
	Ag	Zn	Ag	ZnO
D1	n.a	100	n.a	100
D2	78	22	82	18
P1	n.a	100	n.a	100
P2	49	51	47	53

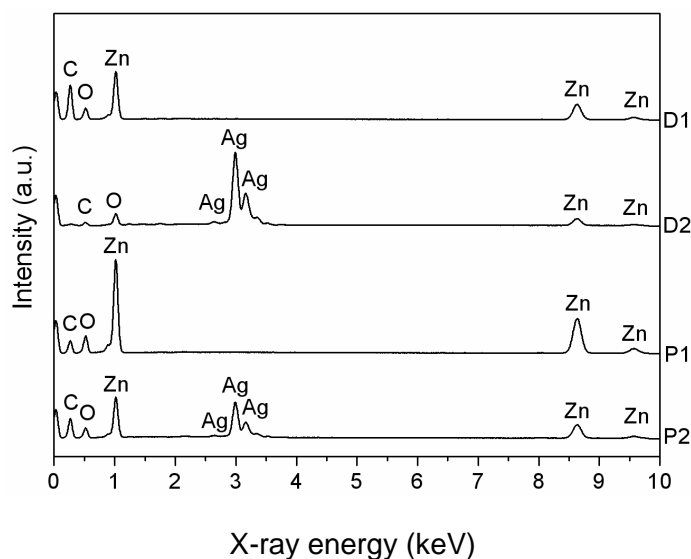


Fig. 3 EDX spectrum of Ag-ZnO powders

microparticles by nucleation of centres for star-like or flower-like particles and results in formation of such assemblies. In next, the pressure elevation causes increase of the ZnO to Ag concentration ratio in obtained product. As the third effect, elevated pressure causes aggregation of silver into relatively big microparticles in comparison with globular nanoparticles obtained from open vessel system. The results gained in this paper can be exploited to investigate any other material systems, which offer promising opportunities for design and fabrication of new hybrid Ag-ZnO materials utilizing external pressure control during synthesis.

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REFERENCES

- [1] HENDRIKSE, K. G., MCGILL, W. J., REEDIJK, J., NIEUWENHUIZEN, P. J. Vulcanization of Chlorobutyl Rubber. I. the Identification of Crosslink Precursors in Compounds Containing ZnO/ZnCl₂. *Journal of Applied Polymer Science*, 2000, vol. 78, no. 13 p. 2290-2301.
- [2] PILLAI, S. C., KELLY, J.M., MCCORMACK, D.E., O'BRIEN, P., RAMESH, R. The Effect of Processing Conditions on Varistors Prepared from Nanocrystalline ZnO. *Journal of Materials Chemistry*, 2003, vol. 13, no. 10 p. 2586-2590.
- [3] GUO, H. G., ZHOU, J. Z., LIN, Z. G. ZnO Nanorod Light-emitting Diodes Fabricated by Electrochemical Approaches. *Electrochemistry Communications*, 2008, vol. 10, no. 1 p. 146-150.
- [4] CALESTANI, D., ZHA, M., MOSCA, R., ZAPPETTINI, A., CAROTTA, M. C., DI NATALE, V., ZANOTTI, L. Growth of ZnO tetrapods for nanostructure-based gas sensors. *Sensors and Actuators B: Chemical*. Vol. 144, No. 2, p. 472-478
- [5] SHAHEEN, W. M., DERAZ, N.-A.M., SELIM, M., M. Effect of ZnO doping on surface and catalytic properties of manganese oxides supported on alumina. *Materials Letters*, 2002. Vol. 52, No. 1-2, p. 130-139.
- [6] KRISHNAN, D., PRADEEP, T. Precursor-controlled Synthesis of Hierarchical ZnO Nanostructures, Using Oligoaniline-coated Au Nanoparticle Seeds. *Journal of Crystal Growth*, 2009, vol. 311, no. 15 p. 3889-3897.
- [7] LI, F., LIU, X.Q., QIN, Q.H., WU, J.F., LI, Z., HUANG, X.T. Sonochemical Synthesis and Characterization of ZnO Nanorod/Ag Nanoparticle Composites. *Crystal Research and Technology*, 2009, vol. 44, no. 11 p. 1249-1254.
- [8] KOGA, H., KITAOKA, T., WARIISHI, H. In Situ Synthesis of Silver Nanoparticles on Zinc Oxide Whiskers Incorporated in a Paper Matrix for Antibacterial Applications. *Journal of Materials Chemistry*, 2009, vol. 19, no. 15 p. 2135-2140.
- [9] YE, X., ZHOU, Y. M., SUN, Y. Q., CHEN, J., WANG, Z. Q. Preparation and Characterization of Ag/ZnO Composites Via a Simple Hydrothermal Route. *Journal of Nanoparticle Research*, 2009, vol. 11, no. 5 p. 1159-1166.
- [10] XU, J., CHANG, Y. G., ZHANG, Y.Y., MA, S.Y., QU, Y., XU, C. T. Effect of Silver Ions on the Structure of ZnO and Photocatalytic Performance of Ag/ZnO Composites. *Applied Surface Science*, 2008, vol. 255, no. 5 p. 1996-1999.

- [11] CHO, S., JUNG, S.-H., LEE, K.-H. Morphology-controlled Growth of ZnO Nanostructures Using Microwave Irradiation: From Basic to Complex Structures. *Journal of Physical Chemistry C*. 2008, vol. 112, no. 33 p. 12769-12776.
- [12] AL-GAASHANI, R., AL-GAASHANI, R., RADIMAN, S., TABET, N., DAUD, A. Razak. Effect of Microwave Power on the Morphology and Optical Property of Zinc Oxide Nano-structures Prepared Via a Microwave-assisted Aqueous Solution Method (Report). *Materials Chemistry & Physics*, 2011, vol. 125, no. 3846.
- [13] LORENTZEN, E.M.L., KINGSTON, H.M. Comparison of Microwave-assisted and Conventional Leaching Using EPA Method 3050B. *Analytical Chemistry*, 1996, vol. 68, no. 24 p. 4316-4320.
- [14] Chung, F.H., Quantitative interpretation of x-ray-diffraction patterns of mixtures .1 [Matrix-flushing method for quantitative multicomponent analysis, *Journal of Applied Crystallography*, 1974, vol. 7, p. 519-525.
- [15] ZHANG, Y., MU, J. One-pot Synthesis, Photoluminescence, and Photocatalysis of Ag/ZnO Composites. *Journal of Colloid and Interface Science*, 2007, vol. 309, no. 2 p. 478-484.
- [16] POLSONGKRAM, D., CHAMNINOK, P., PUKIRD, S., CHOW, L., LUPAN, O., CHAI, G., KHALLAF, H., PARK, S., SCHULTE, A. Effect of Synthesis Conditions on the Growth of ZnO Nanorods Via Hydrothermal Method. *Physica B: Condensed Matter*. 2008, vol. 403, no. 19-20 p. 3713-3717.