

MICROWAVE-ASSISTED HYDROTHERMAL SYNTHESIS OF Ag/ZnO SUB-MICROPARTICLES

HIDROTERMIČNA SINTEZA PODMIKROMETRSKIH DELCEV Ag/ZnO Z MIKROVALOVI

Lukáš Münster^{1,2}, Pavel Bažant^{1,2}, Michal Machovský², Ivo Kuřitka^{1,2}

¹Polymer Centre, Faculty of Technology, Tomas Bata University in Zlin, Nam. T. G. Masaryka 275, 762 72 Zlin, Czech Republic
²Centre of Polymer Systems, University Institute, Tomas Bata University in Zlin, Nad Ovcirnou 3685, 760 01 Zlin, Czech Republic
l_munster@ft.utb.cz

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A fast and environmentally friendly, microwave-assisted, hydrothermal synthesis was utilized for the preparation of a Ag/ZnO hybrid system by using zinc acetate dihydrate and silver nitrate as the sources of Zn²⁺ and Ag⁺, and hexamethylenetetramine as the reducing and precipitating agent. The influence of the concentration was investigated by X-ray diffraction analysis, scanning electron microscopy and energy-dispersive analysis. It was found that the concentration has a strong effect on the morphology and proportion between the Ag and ZnO components of the prepared particulate materials. With a decreasing concentration, the morphology of the ZnO changed from twinned or single frustums to rod-like microparticles, whereas the silver morphology changed from large polygon-shaped microparticles to very small, spherical nanoparticles.

Keywords: zinc oxide, silver, nanoparticle, hydrothermal, microwave synthesis

Uporabljena je bila hitra in okolju prijazna mikrovalovna hidrotermična sinteza hibridnega sistema Ag/ZnO z uporabo cink-acetat dihidrata in srebrovega nitrata kot vira Zn²⁺ in Ag⁺ ter heksametilentetramina kot reducenta in sredstva za izločanje. Z rentgensko difrakcijo, vrstično elektronsko mikroskopijo in energijsko disperzijsko analizo je bil preučevan vpliv koncentracije. Ugotovljeno je bilo, da ima koncentracija močan vpliv na morfologijo in razmerje med komponentama Ag in ZnO pripravljene zrnatega materiala. Z zmanjšanjem koncentracije se je morfologija ZnO spremenila iz dvojčičnih ali stožčastih mikrodelcev v paličaste, medtem ko se je morfologija srebra iz velikih poligonalnih mikrodelcev spremenila v majhne sferične nanodelce.

Ključne besede: cinkov oksid, srebro, nanodelec, hidrotermičen, sinteza z mikrovalovi

1 INTRODUCTION

Various metals (Au, Ag) and metal oxides (ZnO, TiO₂, SnO₂, CuO) have been the subjects of investigation for a long time because of their unique optical, electrical, and mechanical properties that can be modulated by varying the size and the morphology of the particles on the nano- and sub-micro scales^{1,2}. Recently, hybrid metal-semiconductor materials have attracted great attention because their metal and semiconductor interface possesses a unique electronic band structure resulting in a specific chemical activity³. Therefore, great efforts have been devoted to the synthesis of hybrid materials by combining various metals and semiconductors such as Ag/TiO₂, Ag/SiO₂, Pt/SnO₂ and Ag/ZnO.⁴⁻⁷ Among them, Ag/ZnO is of great interest because of potential applications in many fields, such as catalysis and medicine.^{7,8} This particulate material has been successfully demonstrated as a suitable filler for an inorganic antibacterial polymer system⁹. ZnO is an important semiconducting material because of its unique optoelectronic and piezoelectric properties.^{10,11} Moreover, it possesses strong antibacterial activity towards gram-negative bacteria and it is both non-toxic and biocompatible¹⁰. Metallic silver, its salts and complexes

have been exploited for their antibacterial properties for millennia before the realization that bacteria are the agents of the infection². Silver nanoparticles are commercially available on the antibacterial-additives market, exhibiting a broad spectrum of antibacterial activity against gram-positive, gram-negative bacteria, fungi, certain viruses, including antibacterial-resistant strains.¹²⁻¹⁴ Therefore, with the combination of Ag and ZnO in a hybrid material on the nano- or sub-micro scales could achieve a synergic effect of antibacterial and photocatalytic activity, biosensing, electrochemical properties, etc.¹⁵⁻¹⁷

Hence, we developed a simple, fast and efficient preparation of a Ag/ZnO hybrid via a microwave (MW) assisted hydrothermal synthesis using a modified open-vessel laboratory microwave-oven system¹⁸. Introducing microwaves instead of the conventional heating allowed us to shorten the reaction time to 12 min, compared to hours reported in references for conventional heating¹⁷. The concentration of reactants is one of the key factors affecting the properties of the prepared hybrid material. Therefore, a study of the influence of the reactants' concentrations on the morphology and particles size was performed.

Table 1: Sets of samples and amounts of precursors and reducing/precipitating agent used in MW synthesis and yields of the powder product
Tabela 1: Sklopi vzorcev in količina predhodnikov in reducirnega/izločevalnega sredstva, uporabljenih v MW-sintezi, in izkoristki proizvodov v obliki prahu

Set	Sample	Zn(Ac) ₂ ·2H ₂ O mol	AgNO ₃ mol	HMTA mol	Yield g	Theoretical Yield g
I	I-ZnO	0.0500	–	0.0500	0.740	4.070
	I-Ag	–	0.0050	0.0500	0.501	0.539
	I-AgZnO	0.0500	0.0050	0.0500	1.160	4.609
II	II-ZnO	0.0050	–	0.0050	0.190	0.407
	II-Ag	–	0.0005	0.0050	0.048	0.054
	II-AgZnO	0.0050	0.0005	0.0050	0.182	0.461
III	III-ZnO	0.0010	–	0.0010	0.025	0.041
	III-Ag	–	0.0001	0.0010	0.003	0.005
	III-AgZnO	0.0010	0.0001	0.0010	0.026	0.046

2 EXPERIMENTAL WORK

2.1 Sample preparation

Zinc acetate dihydrate Zn(Ac)₂ · 2H₂O (PENTA) and silver nitrate AgNO₃ (PENTA) were used as the sources of Zn²⁺ and Ag⁺, respectively. Hexamethylenetetramine (HMTA), (CH₂)₆N₄ (LACHNER) was used as the source of OH⁻, acting as a precipitating agent and CH₂O as a reducing agent. All the chemicals were of analytical grade and used as received without any further purification. Demineralised water with a conductivity 0.1 μS cm⁻¹ was used throughout the experiment.

The synthesis was carried out using an open-vessel microwave-oven laboratory system MWG1K-10 operated at 800 W and 2.45 GHz (RADAN) with an external reflux cooler. In a typical experimental procedure a given amount of precursor (Zn²⁺, Ag⁺ or both) and reducing/precipitating agent were dissolved in 100 mL and 50 mL of demineralised water, respectively. The precursor solutions were first preheated in the microwave oven for 2 min, then the solution of HMTA was added via a dropping funnel, and then microwave heating continued for another 10 min. Hence, the total time of the microwave synthesis was 12 min for each prepared sample. The reaction mixture was always left to cool to approximately 50 °C and then the material was collected and washed by microfiltration. Samples were dried at 40 °C in a laboratory oven until a constant weight was achieved. In all the experiments, the molar ratio of Zn²⁺/Ag⁺ was set to 10/1. In order to investigate the influence of concentration, the initial solution mixture concentration, which is close to the saturation limit for zinc acetate (set I), was lowered ten (set II) and fifty times (set III), giving rise to three sets of samples. The concentration of HMTA was kept at a constant ratio to the precursors as well. For the reaction-mixture compositions (Table 1).

2.2 Characterization methods

Crystal-phase structure identification was conducted using the multifunctional X-ray diffractometer PANalytical X'Pert Pro MPD (PANalytical) and Cu-K_α X-ray source (λ = 0.15418 nm), at 40 kV and 30 mA and the 2θ

diffraction angle range 10–90 °. The morphology was observed in a scanning electron microscope (SEM) Vega II LMU (TECSAN) at an acceleration voltage of 10 kV. Semi-quantitative elemental analysis was performed with the energy-dispersive X-ray (EDX) analyzer (Oxford Instruments, INCA, UK) mounted on the microscope.

3 RESULTS AND DISCUSSION

All the samples were examined by powder X-ray diffraction (XRD) analyses. As an example of the crystal-phase structure investigation, X-ray patterns of the samples prepared at the lowest concentration, i.e., pure ZnO, Ag and hybrid Ag-ZnO (set III) are shown in Figure 1. Other sets of the experiment with higher concentrations of precursors and reducing/precipitating agents (set I and II) showed similar XRD patterns. Specific diffraction lines (labeled by #) were observed at approximately 2θ = (31.7, 34.4, 36.2, 47.5, 56.5, 62.8, 66.2, 67.8, 72.5, 76.8, 81.3 and 89.7) °. According to the

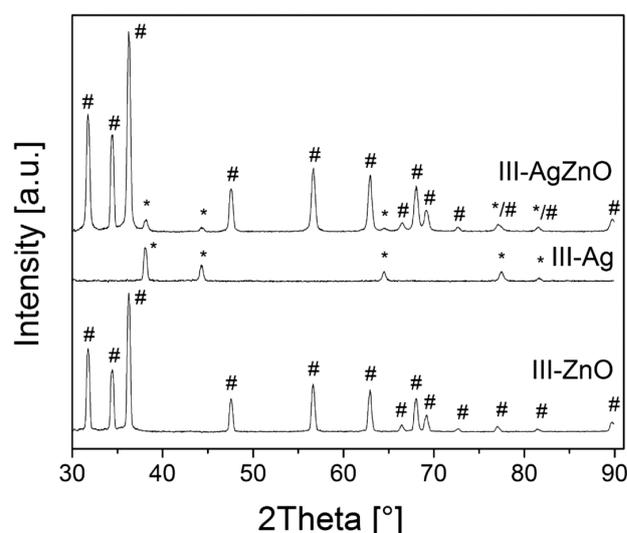


Figure 1: X-ray diffractogram of samples from set III, the 2θ range is cropped at lower values in the graph as no peaks were detected between 10 ° and 30 °

Slika 1: Rentgenski difraktogram vzorcev iz sklopa III, področje 2θ je odrezano pri nižjih vrednostih, ker v območju 10–30 ° ni bilo vrhov

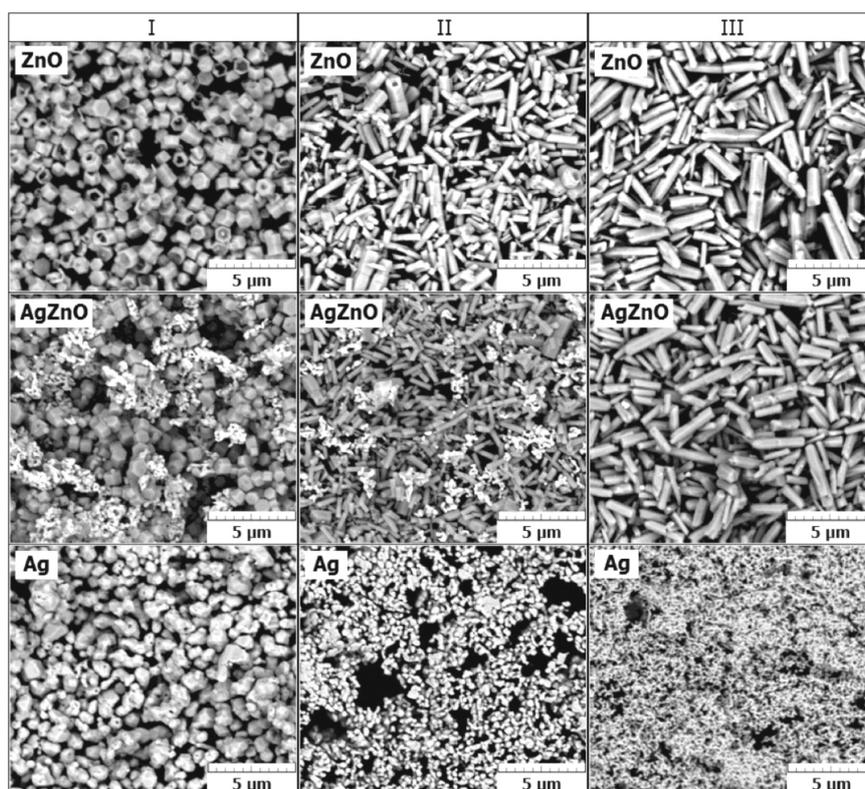


Figure 2: SEM micrographs of prepared samples of ZnO, Ag and AgZnO particles arranged in dependence of the concentration of precursors and HMTA in the reaction mixture

Slika 2: SEM-posnetki pripravljenih vzorcev ZnO, Ag in AgZnO delcev, razvrščenih v odvisnosti od koncentracije predhodnikov in HMTA v reakcijski zmesi

JCDD PDF-2 entry 01-079-0207, these peaks can be unambiguously assigned to the ZnO wurtzite hexagonal crystal phase. Other observed diffraction peaks (labeled by *) at approximately $2\theta = (38.2, 44.4, 64.6, 77.6$ and $81.8)^\circ$ were assigned to a metallic silver cubic crystal phase according to JCDD PDF-2 entry 01-087-0720. Moreover, the sharpness and the narrowness of the diffraction peaks imply well-developed crystalline structures for both the Ag and ZnO, with no level traces of crystalline impurities.

The morphology of the prepared particles is shown in **Figure 2**. A back-scattered electron (BSE) detector was utilized to enhance the contrast between the Ag and ZnO particles. It is clear that the concentration strongly influenced the particles size and the morphology. For pure ZnO synthesized at the highest concentration (set I), the particles form typical twinned frustums joined by their apical bases, in many cases hollow if single frustums. The dimensions of these particles are diameter up to $1.5 \mu\text{m}$ and in length up to $2 \mu\text{m}$. The particles with a hollow core have a wall thickness starting from tens of nanometers. Lowering the concentration to one tenth of the ZnO precursor (set II) resulted in an increased aspect ratio from approximately $1 : 1$ observed for pure ZnO at the highest concentration (set I) to $6 : 1$. The approximate diameter and length were 500 nm and $3 \mu\text{m}$. At the lowest concentration (set III), rod-shaped ZnO particles have the same aspect ratio; however, there is observable

a slight increase of the particles' length and diameter. The morphology of the Ag particles prepared by using the highest concentration of the precursor (set I), displayed polygon-shaped particles with a diameter up to $1.5 \mu\text{m}$. The lowering of the concentration of the Ag precursor (set II) results in spherically shaped Ag particles with an approximate diameter of 250 nm . The lowest concentration of Ag (set III) displayed the smallest particles with a size in the range of tens of

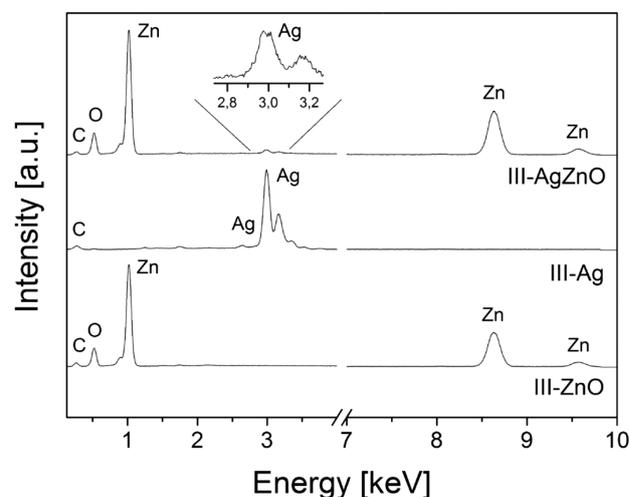


Figure 3: EDX spectra of samples from set III

Slika 3: EDX-spektri vzorcev iz sklopa III

nanometers. For the hybrid Ag/ZnO system, the trend is very similar as that observed for the pure Ag and ZnO components in the prepared material.

Figure 3 shows typical spectra obtained from the EDX analyses. For the sake of brevity, only spectra for the lowest concentration (set III) are presented. The presence of elemental zinc (peaks at 1.0, 8.6 and 9.5 keV) and oxygen (peak at 0.5 keV) from the ZnO particles was confirmed in the samples ZnO, Ag/ZnO. Elemental silver (peaks at 2.6 keV and 3.0 keV) was confirmed even within the lowest concentration used in the samples Ag and Ag/ZnO. Elemental carbon with a peak at 0.3 keV can be assigned to the carbon tape used for fixation of the sample to the holder inside the microscope chamber or to other organic impurities. The semi-quantitative results from the EDX in the weight percentage of Ag, Zn and O content are listed in **Table 2**. It is clear that the weight percentage of Zn increases with lowering of the concentration, whereas the content of Ag decreases with lowering the concentration, which is in accordance with observations based on the SEM micrographs. The large observed content of O points towards the presence of water adsorbed at the surface or in the pores of the particles.

Table 2: EDX results of prepared samples, content of Zn, Ag and O in mass fractions, w/%

Tabela 2: EDX-rezultati pripravljenih vzorcev, vsebnost Zn, Ag in O v masnih deležih, w/%

Set	EDX (w/%)		
	ZnO	Ag	AgZnO
I	Zn: 59.1; O: 40.9	Ag: 100	Ag: 39.5; Zn: 31.7; O: 28.8
II	Zn: 60.9; O: 39.1	Ag: 100	Ag: 28.2; Zn: 36.4; O: 35.5
III	Zn: 65.2; O: 34.8	Ag: 100	Ag: 3.3; Zn: 62.2; O: 34.4

4 CONCLUSION

A simple one-pot open-vessel microwave-assisted hydrothermal synthesis of a ZnO, Ag and Ag/ZnO hybrid combination of both types of particles was introduced. The influence of the concentration of precursors and the precipitating/reducing agent on the properties and on the morphology was investigated. Powder XRD analysis showed wurtzite crystalline phases of zinc oxide in all the samples prepared using $Zn(Ac)_2 \cdot 2H_2O$ as a precursor and cubic crystalline phases of silver prepared using the precursor $AgNO_3$, even at the lowest concentrations. The alternation of the concentration has a marked effect on the particle morphology: (i) the decrease of the concentration of the zinc precursor results in prolongation and an increased size of the ZnO particles, whereas (ii) the size of the silver particles decreases directly with the concentration decrease, from micrometer down to tens of nanometers, and the highest percentage yield was almost 93 % of pure silver particles.

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