

MICROWAVE ASSISTED MODIFICATION OF BIO-TEMPLATE BY Ag-ZnO SUB-MICROPARTICLES

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Abstract

One-pot microwave assisted modification of a bio-carrier wood dust with Ag-ZnO sub-microparticles is presented. Prepared materials were synthesized by hydrothermal route in an open vessel system in microwave oven with an external reflux cooling system. Zinc acetate dihydrate and silver nitrate were used as sources of zinc and silver ions, HMTA and aqueous ammonia were chosen as reduction and precipitation agents. X-ray diffraction (XRD), Energy dispersive X-ray analysis (EDX) and scanning electron microscopy (SEM) were used for structure and morphology characterization.

Keywords: wood dust, zinc oxide, silver, hydrothermal route, microwave, sub-microparticles

1. INTRODUCTION

Nowadays, development of new polymers does not grow as fast as development of new additives and fillers, especially in nano and micro scale, which enhance specific properties of already known and economically feasible plastics. Modification of properties with filler imparts potential application of polymer in praxis, usually it is health safety, ability to improve mechanical and thermal properties or certain level of biodegradability of final material. Recently, plastics used in medical sector and hygiene in every day usage should possess antibacterial properties. Positive influence of wood based filler on mechanical, thermal properties and biodegradability of plastics has been reported in [1], hence if the surface of this kind of filler is treated with other species, i.e. zinc oxide and silver (Ag-ZnO) sub-microparticles, it could lead to fabrication of multifunctional system with other specific properties. Zinc oxide is a wide band gap semiconductor (3.37 eV) with a large exciton binding energy (60 meV) [2], depending on its size and shape. It can be utilized in pigment applications due to its high refractive index (1.95-2.10), in opto-electronics, used as electrical conductor when suitably doped [3] and as photocatalytic oxidant [4]. It is categorized as non-toxic and has no evidence of carcinogenicity, genotoxicity or reproduction toxicity [5-7] and is a bactericide inhibiting both Gram-positive and Gram-negative bacteria [8; 9]. In addition, metallic silver possess many similar properties, i.e. antibacterial effects [10], electrical conductivity [11] and oxidative catalysis [12]. Combination of these two compounds in Ag-ZnO nanocomposite material results in synergic effect of above mentioned properties [13].

Hence, we present a simple method of wood dust modification by Ag-ZnO sub-microparticles. Microwave (MW) assisted solvothermal modification in open vessel system using modified domestic microwave oven and external reflux cooler was adopted towards this purpose.

2. EXPERIMENTAL

Wood dust with size of the particles in range 300-500 μm , bulk density 170-230 g/l (BK 40 – 90, J. RETTENMAIER & SÖHNE, Austria) was used as a bio-template for microwave assisted solvothermal modification. Zinc acetate dihydrate $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (PENTA, Czech Republic) and silver nitrate AgNO_3 (PENTA, Czech Republic) were used as precursors, hexamethylenetetramine (HMTA), $(\text{CH}_2)_6\text{N}_4$, (LACHNER, Czech Republic) and aqueous ammonia 25-29 wt%. (PENTA, Czech Republic) were used as

precipitation agents. All chemicals were of analytical grade and used without further purification. Demineralised water was used throughout the experiment.

Microwave assisted solvothermal synthesis were carried out (see Table 1) in an open vessel system using modified domestic microwave oven laboratory system MWG1K-10 operated at 800 W and 2.45 GHz (Radan, Czech Republic) with an external reflux cooler. At first, 1 g of wood dust was soaked and stirred vigorously in 30 mL of water for 30 minutes at laboratory temperature, followed by addition of zinc acetate dihydrate (10.800 g dissolved in 60 mL of water) and silver nitrate (0.699 g dissolved in 10 mL of water) mixture. After another 30 minutes of stirring in dark, prepared reaction dispersion was preheated in microwave oven for 10 minutes. In next, HMTA (6.928 g in 50 mL of water) was added via dropping funnel and the mixture heating continued for 10 minutes. The second material was prepared in the same way but with addition of aqueous ammonia (14.2 mL via dropping funnel) after 20 minutes of MW exposure and prolongation of heating for another 10 minutes. Hence, the total time of microwave synthesis differ with the type of sample, 30 minutes for the material precipitated with aqueous ammonia (DM_A) and 20 minutes for the sample without the second precipitation agent (DM_B). 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 laboratory oven until constant weight. Table 1 summarizes sample codes, reaction conditions and yields of products.

Tab. 1 List of used precursors and reduction/precipitation agents along with MW exposure time and yield of each sample

Sample code	Precursors	Reduction/precipitation agents	MW exposure time	Yield
			[min]	[g]
DM_A	Zn(Ac) ₂ ·2H ₂ O, AgNO ₃	HMTA, NH ₃	30	4.564
DM_B	Zn(Ac) ₂ ·2H ₂ O, AgNO ₃	HMTA	20	1.928

Synthesized materials were characterized by powder X-ray diffraction analysis using PANalytical X'Pert PRO X-ray diffractometer (PANalytical, Netherlands) in diffraction range 25 – 85 2θ angle utilizing Cu Kα1 radiation, scanning electron microscopy (SEM) carried on Vega II/LMU device (Tescan, Czech Republic) equipped with a backscattered electron detector (BSE) and energy dispersive X-ray analysis (EDX).

3. RESULTS AND DISCUSSION

Wood dust with Ag-ZnO sub-microparticles was examined by powder X-ray diffraction analysis (XRD) (see Fig. 1). Diffraction lines observed at 2θ = 31.7°, 34.4°, 36.2°, 47.5°, 56.5°, 62.8°, 66.3°, 67.9°, 69.0° and 72.5° can be unambiguously assigned to ZnO wurtzite hexagonal crystal structure according to the JCPDS 01-079-0207 card. Other observed diffraction peaks at 2θ = 38.1°, 44.3°, 64.5°, 76.9° and 81.3° in the diffractogram were assigned to metallic silver crystal structures according to JCPDS 01-087-0720 card.

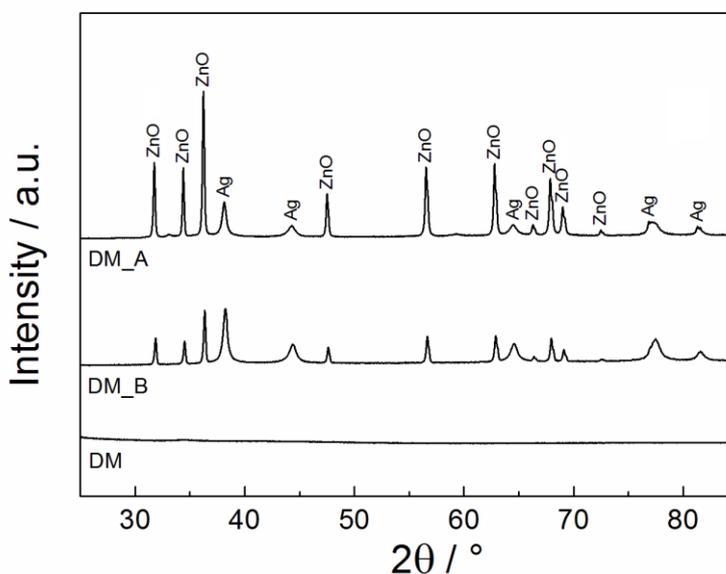


Fig. 1 Powder XRD patterns of synthesized materials

Also, pure wood dust (DM) was examined in search for powder XRD patterns, although no significant peaks were found in the diffractogram. As it can be seen in Fig. 1, peaks for ZnO in the diffractogram for DM_A material are bigger when compared to DM_B material. This was caused by precipitation of residual Zn^{II} cations by aqueous ammonium in the second step of the synthesis. This signalizes higher content of crystalline ZnO phase in prepared powder as well. DM_A composition was 93 wt% of ZnO and 7 wt% of Ag, whereas DM_B 93 showed 74 wt% of ZnO and 26 wt% of Ag. Results are listed in Table 2 along with results from EDX analysis.

Tab. 2 Composition of synthesized materials by XRD and EDX analysis

Sample code	XRD analysis		EDX analysis	
	[wt%]		[at%]	
	Ag	ZnO	Ag	Zn
DM_A	7	93	5.32	5.36
DM_B	26	74	4.52	3.37

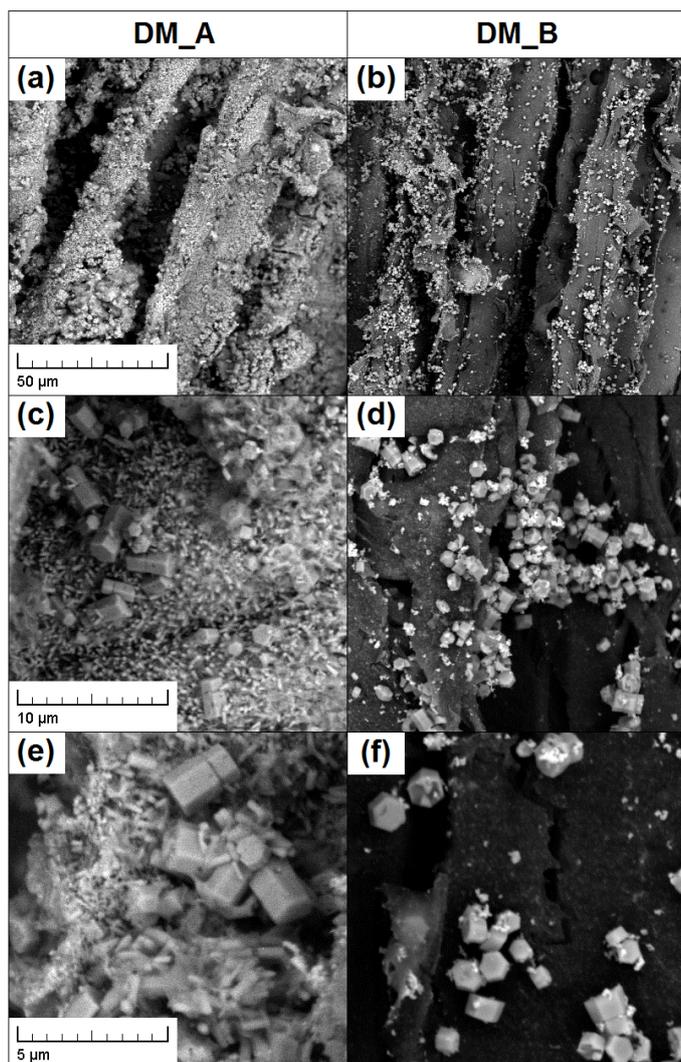


Fig. 2 SEM micrographs of wood dust modified by Ag-ZnO sub-microparticles

The morphology of wood dust decorated with Ag-ZnO sub-microparticles was examined under scanning electron microscope using BSE detector. Fig. 2 shows synthesized materials at three different magnifications and allows comparison between products of different routes of microwave assisted solvothermal synthesis. As it can be seen on Fig. 2a, modified bio-template material DM_A prepared by utilizing HMTA and aqueous ammonia as reduction/precipitation agents of zinc acetate dihydrate and silver nitrate was entirely cloaked with zinc oxide and silver sub-microparticles, whereas Fig. 2b shows DM_B sample treated just with HMTA agent where vacant spots and uncovered substrate surface area can be seen.

Concerning the sub-microstructures, observed zinc oxide formed on surface of wood dust hexagonal prisms joined by their bases in both cases of preparation routes A and B. Difference between two synthesized materials can be seen in size of evolved hexagonal prisms. Material DM_A contains particles with diameter up to 2 μm while the size of hexagonal prisms in material DM_B was up to 1.5 μm. Furthermore, the DM_A material featured secondary epitaxial growth of hexagonal rod shaped particles (Fig. 2c, 2e) as a result of precipitation induced by aqueous ammonia addition in the second reaction step.

Formation of both hexagonal prisms and rod shaped ZnO sub-microparticles were reported for single generation systems in previous literature, e.g. in [14; 15]. Two generations system is used for ZnO yield increase originally in this case (see Table 1). Silver globular shaped sub-microparticles can be seen on Fig. 2 as light dots with diameter up to 100 nm. Growth or change of these particles showed no association with additional increase of reaction mixture basicity due to secondary addition of aqueous ammonia.

In Fig. 3, energy dispersive X-ray analysis EDX typical spectrum was recorded on 200 μm x 200 μm surface area of the examined material. Presence of elemental zinc and silver was confirmed. Peak at 0.5 keV was assigned to elemental oxygen from ZnO sub-microparticles, wood dust or residual water or other impurities on template surface. Elemental carbon manifested by a peak at 0.3 keV can be assigned to wooden dust or organic impurities.

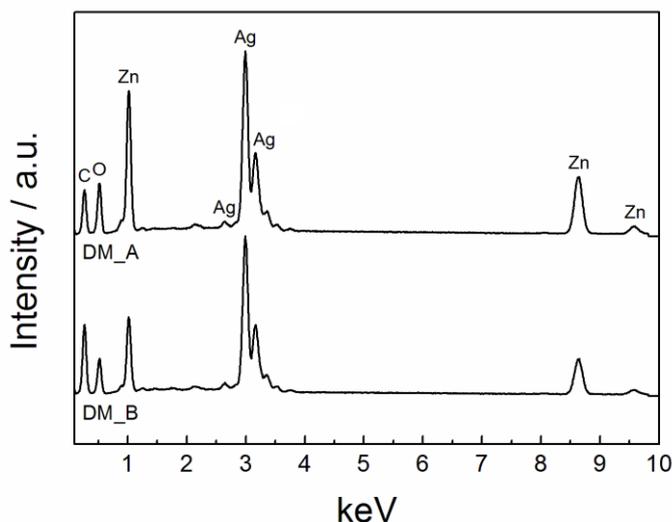


Fig. 3 EDX spectrum of synthesized materials

Semi-quantitative analysis of DM_A material showed zinc content 5.36 at% and silver content 5.32 at%, whereas DM_B material exhibited zinc content 3.37 at% and silver content 4.52 at%. These results (Table 2) confirmed higher content of zinc in DM_A material compared to DM_B material, although EDX results showed higher content of silver than zinc which is virtually in contradiction to the results of powder XRD crystalline phase quantification (see Table 2). This may be caused by possible adsorption of silver cations all over the surface of wood dust, whereas zinc oxide formed distinguishable clusters of sub-microstructures. It means, that silver is present not only in form of metallic silver sub-microparticles but also in form of Ag^+ bonded on template surface in reasonable

amounts. Visual observation of color change of the wood dust turning from yellowish white to dark grey during the 30 minutes of stirring in dark prior MW exposure supports this explanation.

4. CONCLUSION

A simple one-pot microwave assisted solvothermal synthesis of Ag-ZnO modified bio-template in open vessel system was introduced. Zinc oxide sub-microparticles and silver globular sub-microparticles were synthesized successfully on the template surface. Powder XRD analysis showed crystalline phases of zinc oxide and silver in both prepared material. The yield of zinc oxide surface decorations can be increased by addition of aqueous ammonia in the second reaction step. The secondary ammonia addition has two effects: (i) increase of size of primary twinned ZnO prisms and (ii) growth of secondary generation of significantly smaller ZnO hexagonal rods which increases the degree of template surface coverage. Silver spherical sub-microparticles growth was unaffected by addition of aqueous ammonia and prolongation of heating period. Reasonable amount of silver was observed to be present in form of Ag^+ adsorbates on the template surface for both synthesis routes.

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