PREPARATION OF FLOWER-LIKE ZNO MICROPARTICLES BY MICROWAVE ASSISTED SYNTHESIS

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Abstract

Flower-like ZnO microparticles were prepared by microwave assisted hydrothermal synthesis. Zinc acetate dihydrate was used as starting material, polyethylene glycol, cetyltrimethylammonium bromide and crystal violet were chosen as growth modification and stabilization agents, ammonia was chosen as precipitation agent. Synthesis mechanism and influence of selected modificators on particle microstructure were investigated. ZnO microparticles were characterized by X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM).

Key words: Zinc oxide, flower-like, microwave, synthesis

1. INTRODUCTION

Zinc oxide (ZnO) is well known semiconducting material with wide direct band gap of 3.37 eV at room temperature and a large exciton binding energy of about 60 meV [1; 2]. Besides, ZnO posses excellent thermal and chemical stability, a large piezoelectric constant [3] and antibacterial properties.[4] Therefore, ZnO has found a lot of applications in solar cells [5; 6; 7], protection against UV radiation [8], optoelectronic and piezoelectric device [9; 10], UV photodiode [11] and etc. Moreover, it has been shown as promising material for photocatalysis and photoelectrical water splitting [12]. According to all aforementioned sources, the properties of ZnO material and its possible applications depend on morphology, shape and size of ZnO particles. Modern synthesis methods enable preparation of a large variety of ZnO morphologies [13], among them can be found rods, combs [14], pyramids, cabbages, flowers [15], dumbbells [16], donuts, stars and other types of particles [13]. In this paper we report a facile and fast route of ZnO flower-like microstructure preparation by microwave hydrothermal synthesis in open microwave system. Within the synthesis, zinc acetate was used as a precursor, aqueous NH_3 as precipitation agent and polyethylene glycol, cetyltrimethylammonium bromide and crystal violet as growth modifying agent. Moreover, the mechanism of particles growth and effects of the stabilizers are discussed.

2. EXPERIMENTAL

2.1 Materials

Zinc acetate dihydrate $Zn(CH_3COO)_2 \cdot 2H_2O$ (ZAD), crystal violet $C_{25}N_3H_{30}Cl$ (CV) and aqueous ammonia (25-29%wt; NH_3 aq.) were purchased from PENTA (Czech Republic). Polyethylene glycol (PEG; M_r = 400) and cetyltrimethylammonium bromide $C_{19}H_{42}BrN$ (CTAB) were purchased from Sigma-Aldrich (Czech Republic). All chemicals were of analytical grade and used as received without further purification. Demineralized water was used within all of these experiments.

2.2 Synthesis of ZnO particles

Microwave open vessel system MWG1K-10 (Radan, Czech Republic) operating at 2.45 GHz was used for open vessel microwave solvothermal synthesis with an external cooler. In the typical procedure, the starting materials were dissolved in water as follows: the solution A was prepared by dissolution of 10.8 g ZAD in 80 mL of water, solution B was prepared by dilution of 14,2 mL of NH_3 aq. by in 40 mL of water, 0.35 g CTAB (C1), 5.142g PEG (C2) and 0.039g CV (C3) were used for preparation of solution CX (X = 0, 1, 2 or 3) which was prepared by dissolution or mixing of the respective amount of the modifier in 20 mL of water. C0 code denotes 20 mL of pure water, i.e. addition of no modifier. Reaction mixture was prepared by mixing of solution A and C, followed by addition of solution B thus the total amount of added water was always kept 140 mL in each synthesis. The solutions were poured in to 250 mL reaction bottle and placed into the microwave oven cavity immediately, connected to an external condenser and exposed to MW irradiation for 10 minutes. Four syntheses that differ in the used solution C0, C1, C2 and C3 were performed. Each reaction mixture was left to cool naturally after heating. Finally, prepared particles were collected by microfiltration and several times washed by demineralized water. Obtained powders were dried in a laboratory oven overnight. Sample codes and product yields are summarized in Table 1.

Tab. 1 Samples codes and product yields

Sample code	Precursor	Precipitation agent	Modifying agent	Product yield (g)
S0	ZAD	NH_3	-	2.994
S1			CTAB	3.243
S2			PEG	2.918
S3			CV	3.057

2.3 Characterization

Powder X-Ray diffraction analysis (XRD) for crystal phase identification was performed on PANalytical X´Pert PRO X-ray diffractometer (PANalytical, The Netherlands) in the diffraction 2θ angle range 5-95°, using Cu Kα1 radiation. The morphological and structural observation was made on scanning electron microscope (SEM) Vega II/LMU (Tescan, Czech Republic) equipped with a SE detector.

3. RESULTS AND DISSCUSION

Prepared ZnO powders were characterized by XRD as shown in Fig. (1). The position and relative intensities of characteristic peaks for ZnO were observed at 2θ = 31.79°, 34.39°, 36.24°, 47.50°, 56.55°, 62.79°, 66.32°, 67.88°, 69.03°, 72.51°, 76.88°, 81.30° and 89.49° that perfectly fits to ZnO with the hexagonal wurtzite crystal structure according to JCPDS 01-079-0207 card. No further peaks were observed.

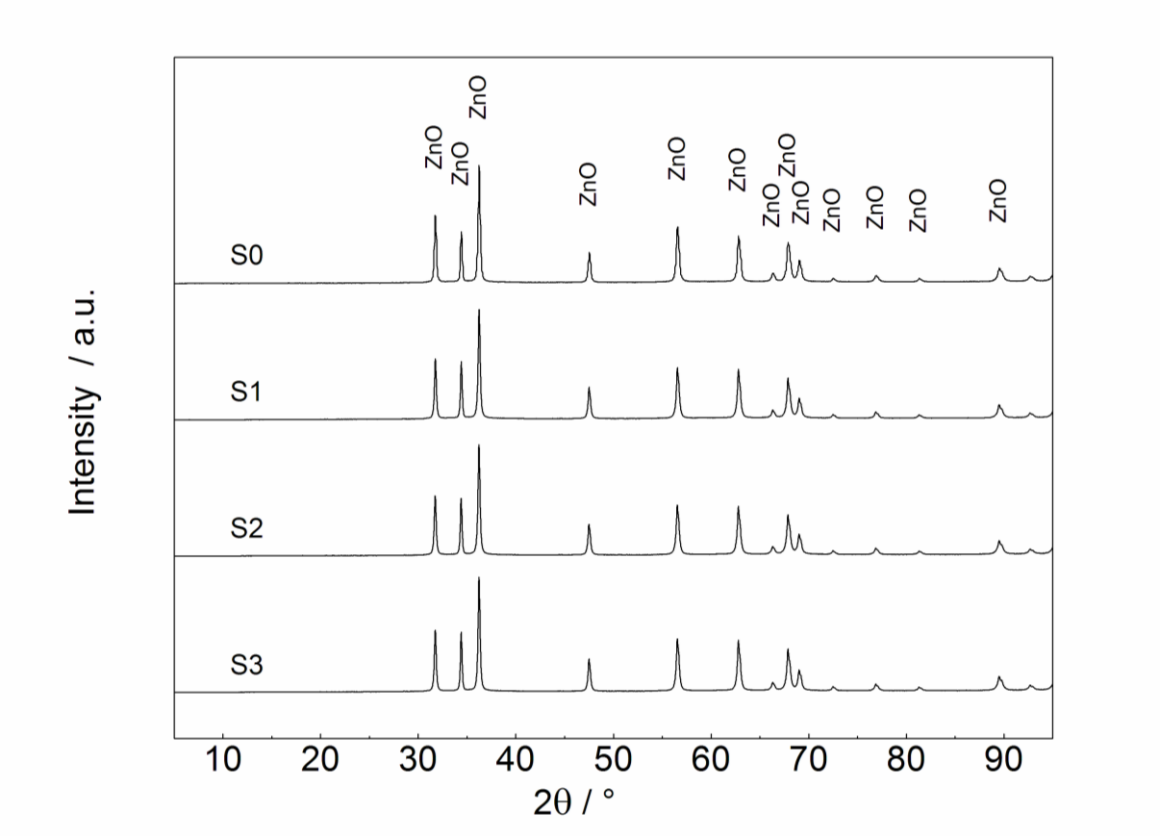

Fig. 1 X-Ray diffraction patterns of prepared materials.

Figure 2 show SEM images of prepared ZnO microparticles. Sample S0 is composed of hexagonal ZnO rod-like particles with the length up to 2 μm and average diameter 0.5 μm. Rarely, it is possible to observe wide rods which are composed from several laterally stacking rod-like particles of ZnO. Sample S1, is based on geometrically regular hexagonal ZnO rods assembled into star-like ZnO particles (right lower corner of the image) and flower-like particles, where the constituting rods resemble flower petals rather than hexagonal prisms (see the particle agglomerate in the centre of the image). The length of all observed rods or petals is up to 2 μm. The sample S2 is mainly composed from star-like particle aggregates of ear of corn resembling ZnO rods connected in the centre of the particle aggregate by their tips. The sample S3 is composed from star-like ZnO aggregated particles where it is possible to observe small cap buttons on the top of rods. The diameter of these buttons is up to 0.5 μm. To summarize, NH_3 aq. causes precipitation of hexagonal rod-like particles which is in accordance with previous observations [17]. Following chemical reactions are generally accepted to be involved in the synthesis of ZnO structures with the use of ammonia as precipitation agent [18].

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \quad (1)$$

$$Zn^{2+} + 4OH^- \rightarrow [Zn(OH)_4]^{2-} \quad (2)$$

$$Zn^{2+} + 4NH_3 \rightarrow [Zn(NH_3)_4]^{2+} \quad (3)$$

$$[Zn(OH)_4]^{2-} \rightarrow ZnO + H_2O + 2OH^- \quad (4)$$

$$[Zn(NH_3)_4]^{2+} + 2OH^- \rightarrow ZnO + 4NH_3 + H_2O \quad (5)$$

It is evident that used amount (concentration) of ammonia is not sufficient to induce formation of star-like particles, although it was reported for stronger reaction conditions [19]. Addition of modifying agents causes formation of star- or flower-like particles aggregated from rod-like components united at a common centre. Collected powders have a tendency to agglomerate due to the clustering by their wedged points. All used modifiers strongly influence the initial stage of ZnO nucleation and support formations of defects in the initial

ZnO crystal undergoes non-regular fourling formation and therefore obtains many polar (0001) surfaces which serve as a base for preferential growth along the [0001] direction hence the particle from star-like shape during the growth stage of the synthesis process. Moreover, the addition of different ionic and non-ionic agents controls the shape development of the star spines by selective adsorption on different crystal surfaces.

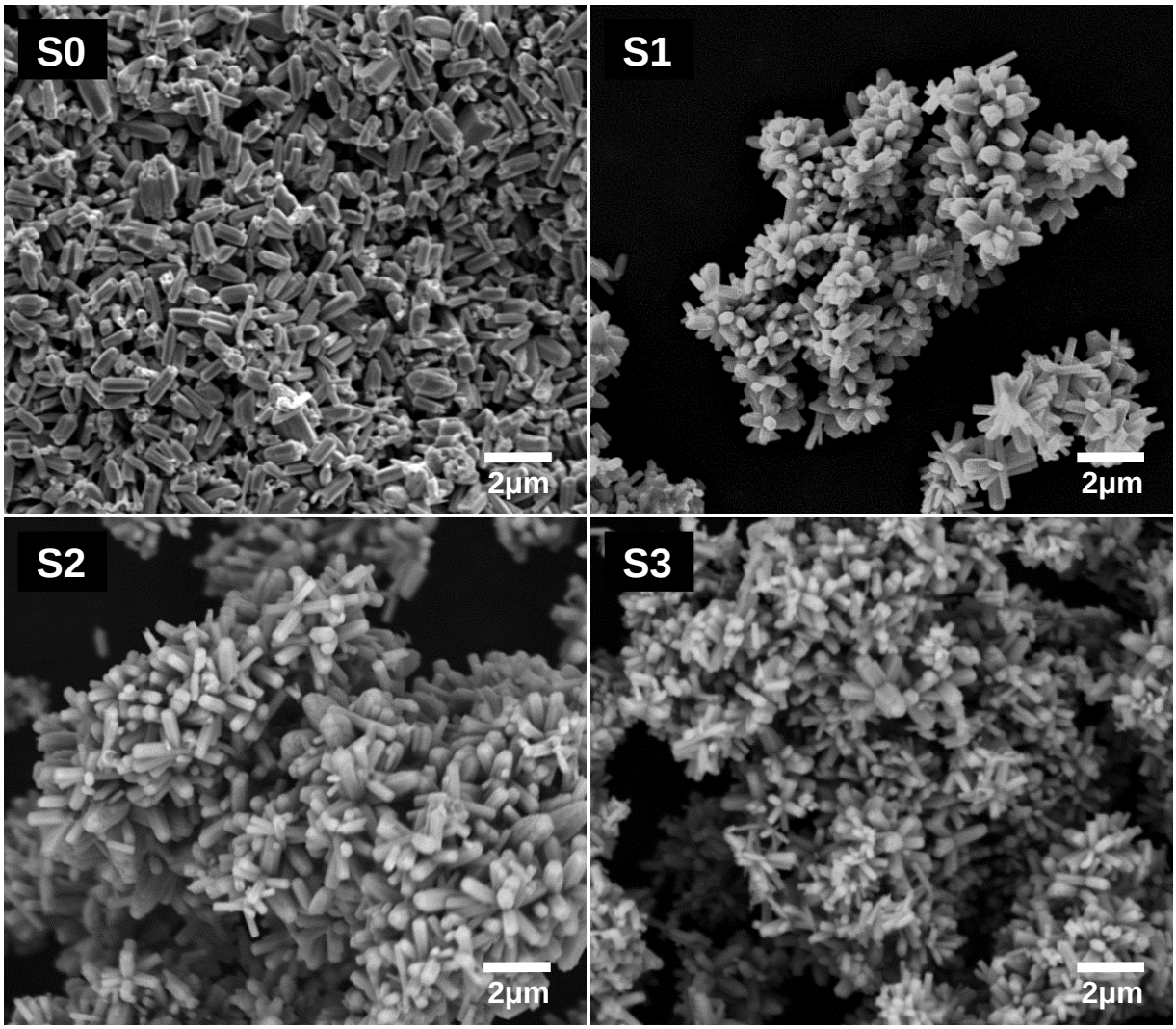

Fig. 2 SEM image of prepared ZnO microstructures.

4. CONCLUSIONS

A simple and fast synthesis method for preparation of nanostructured ZnO microparticles was demonstrated. The yields were about 75 % with respect to the initial amount of raw ZnO precursor (zinc acetate dihydrate) which together with short reaction time testifies for the efficiency of microwave assisted hydrothermal synthesis.

Common process of ZnO precipitation from concentrated solution of zinc acetate by aqueous ammonia was successfully adapted and modified by non-usual capping agents of both ionic and non-ionic character. The addition of these agents resulted in dramatic changes of products morphology from hexagonal rods to star-like and flower-like microparticles even with the use of relatively diluted aqueous ammonia. The second and relatively subtle growth directing role of used agents was manifested in the shape variation of spines of obtained particles from regular hexagonal prisms to ear of corn and flower petal-like shapes. Moreover, no adverse effect of application of investigated agents on reaction yield was observed.

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