Rapid Microwave-assisted Synthesis of Twinned Hexagonal ZnO Microparticles

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Abstract: In the present work, we report on successful preparation of twinned hexagonal ZnO microparticles in modified domestic microwave oven using zinc acetate dehydrate and hexamethylenetetramine. While no surfactants or capping agents were used, fully developed twinned hexagonal microparticles were synthesized in 7 minutes. The morphology was studied by scanning electron microscopy and the crystal phase structure was verified by X-ray diffractometry. Short synthesis time, high reproducibility and environment benign starting chemicals make this method suitable candidate for large-scale production.

Key-Words: ZnO, Microwave synthesis

1 Introduction

Zinc oxide (ZnO) has been extensively used for a long time in several industrial products such as ceramics, rubber additives, pigments, personal cares, and medicine, as well as other metallic compounds. Besides this, ZnO as an important semiconducting and piezoelectric material has gained wide attention in recent years for its potential novel applications in light emitting diodes [1], gas sensors [2], piezoelectric devices [3], solar cells [4], etc. As the size, morphology, and dimensionality of ZnO particles have great impact on the physico-chemical properties, a large effort has been devoted to the synthesis and characterization of ZnO structures. A large variety of ZnO nano- and microstructures have been successfully prepared. [5-8]. This abundance of various shapes made ZnO probably the richest family of structures among all materials. Many methods have been developed for synthesis of ZnO particles. Solid-state methods of growth include vapor-liquid-solid (VLS) [9], vapor phase transport (VPT) [10], molecular beam epitaxy (MBE) [11] and many others. However, these processes often demand special equipments and stringent reaction condition such as high temperature, and low or high pressure. Compared to the solid-state methods, liquid-based routes such as sol-gel method [12], precipitation [13] electrochemical deposition [14], hydrolysis [15] or hydrothermal method [16] require only mild reaction condition under normal atmospheric pressure and no sophisticated equipments are needed. Unfortunately, these advantages are usually achieved at the expense of long reaction time. This can be improved by introducing microwave heating in the hydrothermal method. Microwave techniques were successfully applied for the synthesis of various metal oxide of diverse morphologies and size in the recent years [17, 18]. This radiation has unique properties like homogenous volumetric heating, which causes heating directly inside the sample, high reaction rate, selectivity and increased product yield. Moreover, it can be integrated into industrial processes to save energy and time [19].

Here we report on rapid and efficient microwave assisted hydrothermal synthesis of ZnO twinned hexagonal ZnO microparticles utilizing open vessel reaction system and simple chemicals. Similar particles have been already reported. Surfactants [20, 21] or capping agents [22] were used for the control of ZnO crystals morphology. In addition,

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synthesis time in above mentioned reports was in the range of hours. According to our best knowledge, only Yu et. al. prepared similar particles without growth modifying agents, during 2 hours [23]. With the aid of microwave radiation, fully developed particles can obtained after seven minutes of synthesis in the case of our method.

2 Experimental

2.1 Materials

Zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$) and hexamethylenetetramine ($(CH_2)_6N_4$, HMTA) were purchased from PENTA (Czech Republic). The chemicals of analytical grade were used as received without further purification. Demineralised water with a conductivity of 15.0 μScm^{-1} was used.

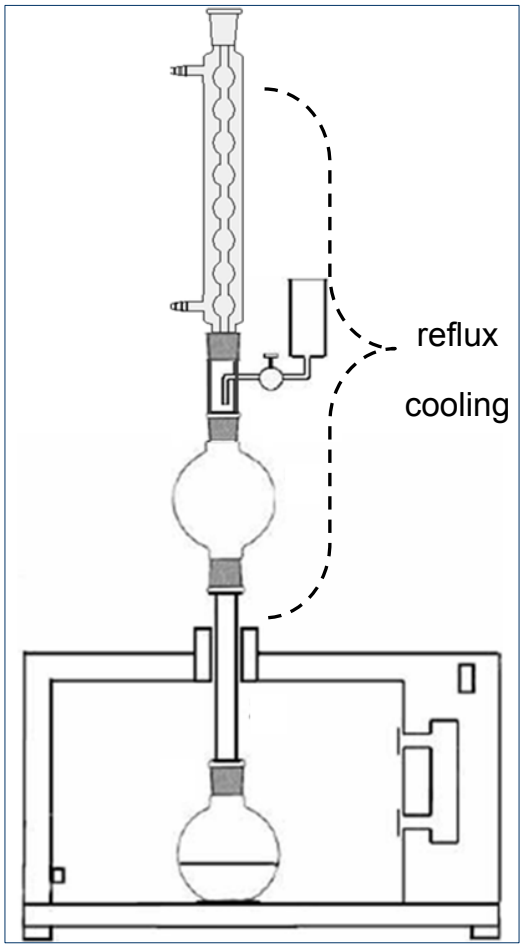

Fig. 1 Schematic of modified MW oven.

2.2 Synthesis

A domestic microwave oven (CWR-TECH, 1150W/230V-50Hz) was modified by drilling a hole on the ceiling for open vessel hydrothermal synthesis with external cooler (Figure 1). In a typical synthesis, 10.8 g of ($Zn(CH_3COO)_2.2H_2O$) and 6.9 g of HMTA were dissolved in 100 ml and 50 ml of water, respectively. Obtained solutions were mixed together in a reaction bottle and placed into the microwave oven cavity. Solutions were irradiated for 2 (sample A) and 7 (sample B) minutes. After that, the system was left to cool down naturally. Resulting white precipitate were separated by filtration (0,23µm pore size membrane)

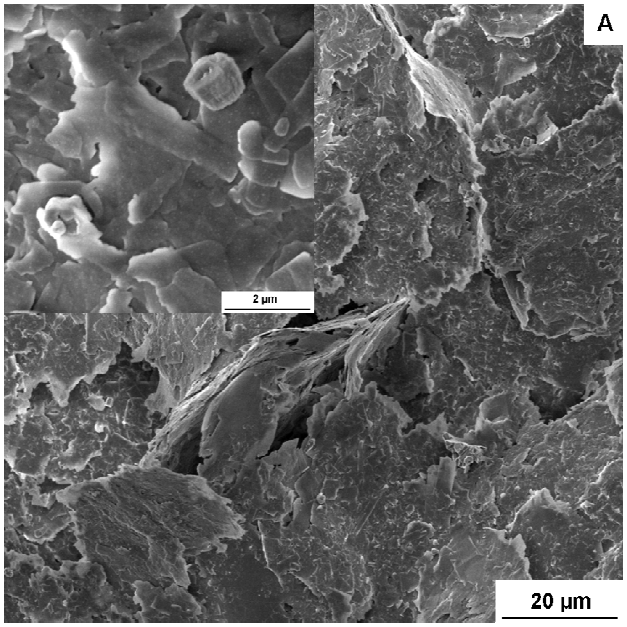

Fig. 2 SEM image of sample A.

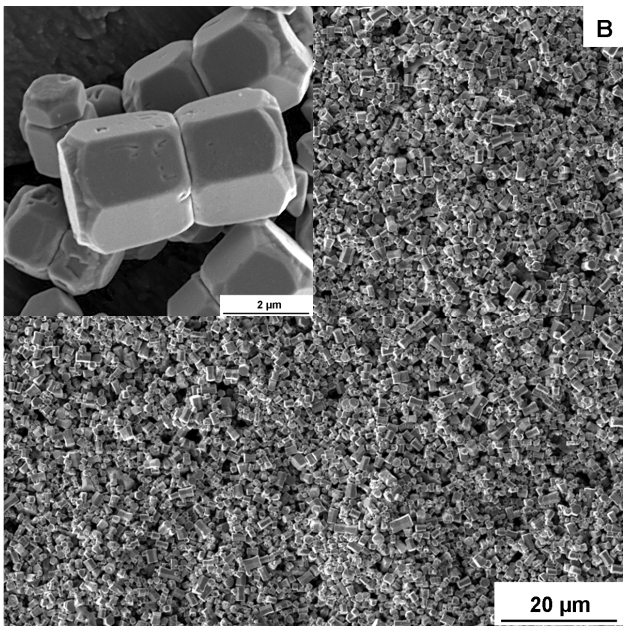

Fig. 3 SEM image of sample B.

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and washed thoroughly several times by demineralised water. Collected powders were dried in an oven at 37°C overnight.

2.3 Characterization

The morphology of as-obtained samples was investigated by scanning electron microscope Vega II/LMU (Tescan, Czech Republic) operating at acceleration voltage 5 kV. X-ray diffraction (XRD) for crystal phase identification was performed using a PANalytical X´Pert PRO X-ray diffractometer (PANalytical, The Netherlands) in the diffraction angle range 2θ 10-85° with Cu Kα1 radiation (λ = 1.540598 Å).

3 Results and discussion

The morphologies of synthesized samples are shown in Figures 2 and 3. The low-resolution image of sample A (synthesis time 2 minutes) reveals plates with one dimension being in the range of several tens of nanometers tangled together. It can be clearly seen in Figure 3 showing sample B (synthesis time 7 minutes) that additional 5 minutes of MW irradiation results in transformation of nano-plates into ZnO particles with uniform particle size distribution. High resolution image inserted in Figure 3 shows detail of typical twinned hexagonal prisms with the length of about 4 μm and diameter of 2 μm. Probable seed of these ZnO particles is captured in the detail image shown in the upper left corner of Figure 2. Such seeds were scattered randomly and infrequently over all sample A. The mechanism of seeds creation may be rolling up of one or more plates into themselves thus forming a three dimensional hexagonal structure.

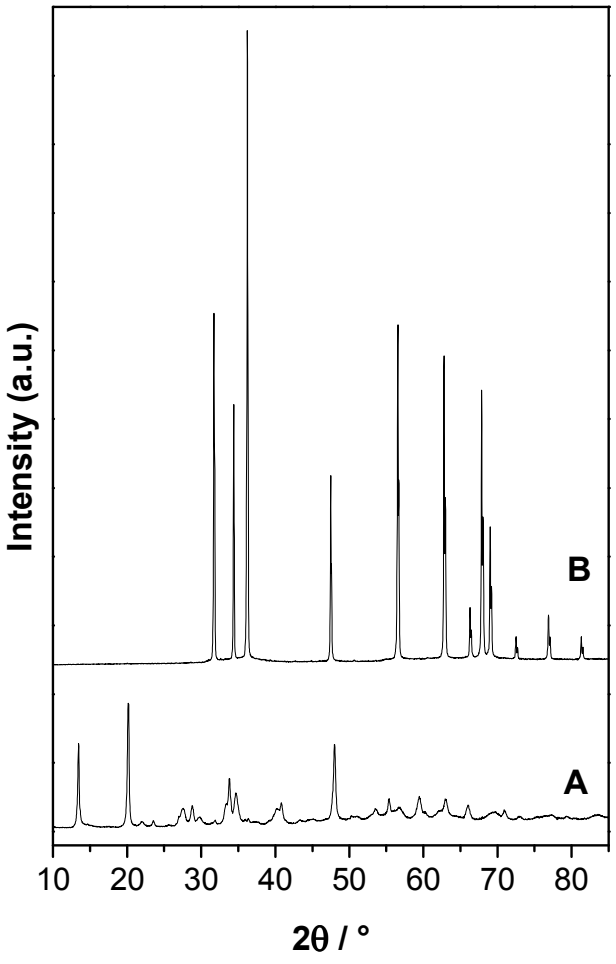

Fig. 4 XRD patterns of sample A, B.

The formation of prisms co-occurs with crystal phase transformation and change of composition of obtained material which can be explained with the aid of XRD patterns shown in Figure 4 for samples A and B. Low intensities and broadness of diffraction lines of sample A indicate small (nano)size of particles with relatively imperfect crystalline structure. Interpretation of this poorly developed diffractogram is not unambiguous, however, according to literature, available databases and knowledge of original materials composition possible assignments can be found. Significant peak observed below the diffraction angle 20° can be assigned to the tetragonal form of zinc hydroxide (reference code: 00-038-0356). Other peaks can be assigned to zinc acetate hydrate (reference code: 00-001-0215), zinc carbonate hydroxide (reference code: 00-019-1458), and zinc acetate hydroxide hydrate (reference code: 00-056-0569). On the other hand, all diffraction peaks of sample B display a standard pattern of wurtzite hexagonal ZnO structure (reference code: 01-079-0207). In this sense, XRD measurements confirm complete transformation of precursor to ZnO twinned hexagonal particles observed by SEM.

4 Conclusion

Twinned hexagonal ZnO microparticles were successfully prepared by microwave-assisted hydrothermal synthesis using zinc acetate dihydrate and hexamethylenetetramine. Without any surfactant and/or capping agents, fully developed ZnO microparticles were obtained after seven minutes of microwave irradiation. Plausible transformation mechanism of precursors to ZnO microparticles was suggested. Due to demonstrated easiness, time and energy saving ability and general simplicity of the method, this system can serve as model candidate for scaling-up studies of microwave-assisted hydrothermal synthesis aimed on industrial production.

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