NANOSTRUCTURED ZINC OXIDE MICROPARTICLES WITH VARIOUS MORPHOLOGIES

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Abstract

In this paper we present a simple two stage preparation method of nanostructured zinc oxide microparticles by using microwave-assisted solvothermal synthesis. Zinc acetate dihydrate and sodium carbonate were used as starting materials, ethyleneglycol (EG), diethyleneglycol (DEG) and demineralised water were used as solvents and polyethylene glycol (PEG) was used as a surface stabilising agent. Obtained powders show various morphology which is influenced by the time duration of microwave assisted reaction and particularly by selection of suitable solvent. According to their morphology, prepared particles are categorised as needle-like structure, platelet structures and urchins-like structures and other shapes, which demonstrates a great potential of this synthesis route. Prepared materials were characterized by Scanning Electron Microscopy (SEM), X-ray diffraction (XRD) and Ultraviolet-visible diffusion reflectance spectroscopy (UV-VIS-DRS).

Keywords: microwave synthesis, ZnO, microparticles, nanoparticles

1. INTRODUCTION

Nanosized ZnO is very attractive II-VI semiconductor material because of its unique properties such as wide band gap (3.37 eV) and large exciton binding energy (60 meV) at room temperature [1]. ZnO nanocrystals have found many applications including solar cells, gas sensors, UV - protection, light emitting diodes etc [2-5]. Up to now, numerous different methods have been developed to synthesize nanocrystalline ZnO powders, e.g. mechanochemical [6], precipitation [7-9], hydrothermal [10-12], thermal decomposition [13,14], sol-gel [15], solvothermal [16] and microwave assisted [17,18]. Microwave radiation is an efficient heating method, which can significantly decrease reaction time and it has been already used for successful preparation of different materials [4,16,17]. Here we adopted and further developed a fast and easy method for preparation of ZnO nanoparticles in two stages. First step is mechanochemical preparation of a precursor in the form of a nanopowder, from which are prepared particles by solvothermal reaction in microwave apparatus with open vessel reflux system in the second preparation step. This method offers short reaction time and saving of energy consumption.

2. EXPERIMENTAL

All of the chemical reagents used in the experiment were of analytical grade. Zinc acetate dihydrate, p.a., (Purity 99 %, Penta, Czech Republic), Sodium carbonate anhydrous, p.a., (Purity 99 %, Penta, Czech Republic), Ethylene glycol, p.a., (Purity 99 %, Penta, Czech Republic), Polyethylene glycol 400, p.a. (Fluka, Germany). Microwave reaction was performed in a modified domestic microwave oven (CRW-TECH, frequency 2.45 GHz, maximum power 1150 W). Products number 2 and 3 were heated at maximum heating power (1150 W), product number 1 was heated at variable heating powers. Energy consumption was measured during every synthesis. Preparation of precursor started by grinding of 8.8g Zn(CH₃COO)₂·2H₂O for 5 min before it was mixed with 16 ml of PEG and then 4.24 g of Na₂CO₃ was added. After 20 min of grinding, the mixture was firstly washed by demineralised water and secondly by alcohol to remove possible
by-product or rests of starting chemicals. After that, the mixture was left to dry on the air naturally. In the second step a 0.5 g of a precursor was moved to the boiling flask together with 10 ml of PEG and 80 ml of EG or demineralised water was added. The mixture was sonicated in ultrasound bath for 10 min (Elma S 80, Ultrasonic) to achieve better dispersion of the precursor in the liquid medium. The mixture was then irradiated for 20 or 40 minutes by microwaves. The product was collected by suction filtration, washed with demineralised water followed by alcohol and finally dried in air. Detailed description of preparation of individual products is summarized in a Table 1.

Table 1 List of prepared products

<table>
<thead>
<tr>
<th>Product number</th>
<th>Composition</th>
<th>Microwave synthesis time</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>0.5 g precursor 10 ml PEG 400 80 ml demineralised water</td>
<td>20 min</td>
</tr>
<tr>
<td>2</td>
<td>0.5 g precursor 10 ml PEG 400 80 ml EG</td>
<td>20 min</td>
</tr>
<tr>
<td>3</td>
<td>0.5 g precursor 10 ml PEG 400 80 ml EG</td>
<td>40 min</td>
</tr>
</tbody>
</table>

The powders were characterized by X-ray powder diffraction (XRD) using PANalytical X’Pert PRO X-ray diffractometer with Cu Kα radiation (λ = 1.540598 Å). Scanning electron microscope Tescan Vega II was used for obtaining micrographs and UV-VIS spectrometer Avaspec Avantes with source type AvaLight-DHSV-UV and integrating sphere (BaSO₄ coated) was used for diffuse reflectance (DR) spectrometry in UV-VIS.

3. RESULTS AND DISCUSSION

Fig. 1 (a) shows XRD pattern of the precursor. Compared with the JCPDS cards (reference code: 00-003-0787), diffraction peaks fits well with that of Zn₄CO₃(OH)·6H₂O (Zinc Carbonate Hydroxide Hydrate). Fig. 1(b) shows UV-VIS DR spectrum of the precursor, which confirms that no ZnO absorbing near 400 nm is present.

![Fig. 1](image)

Fig. 1 (a) XRD pattern of the precursor and (b) UV-VIS DR spectrum of the precursor.

Fig. 2 (a) shows the SEM image of the precursor that do not reveal any specific shape, just irregular pointed particles of submicrometric size. Fig. 2(b) shows the SEM image of product 1 made with PEG and demineralised water for 20 minutes. As can be seen, this product is needle-like in shape. Needles are
approximately from 4 to 6 µm length and less than 1 µm width. Residuals of very fine nanofibres resembling snow or dust in the image are most likely the constituents of the growing needles. Fig. 2(c) presents SEM image of product 2 made with PEG and EG for 20 minutes. Product 2 was obtained exclusively in form of thin curtain-like platelets with very fine nanoporous structure. With the aid of the last picture Fig. 2(d) can be demonstrated the influence of reaction time on final structure of the particles. Product 3 is made as well as product 2 from dispersion with PEG and EG, with the only difference that is longer reaction time i.e. 40 minutes. The assembling of platelets into urchin-like microstructures is supported by longer synthesis time.

Fig. 2 SEM image of the precursor (a) and SEM images of the final products 1, 2, 3, (b), (c), (d) respectively.

Fig. 3 (a), (b) and (c) shows XRD patterns of final products 1, 2, 3 respectively. Compared with the JCPDS cards, diffraction peaks labelled as (100), (002), (101), (102), (110), (103), (200), (112), (201), (004), (202), (104) and (203) fits well with hexagonal ZnO wurtzite structure (reference code: 01-079-0207) and diffraction peaks labelled with symbol * with that of Zn(CH₃COO)₂·2H₂O (reference code: 00-001-0215), which stayed in the final products as a certain impurity. Fig. 3(d) shows UV-VIS optical DR spectra of the final products testifying the presence of ZnO by pronounced decrease of relative reflectance in spectral range below 400 nm.
CONCLUSION

In summary, needle, urchin- and platelet-shaped nanostructured ZnO microparticles were successfully prepared by simple two stage method, based on combination of mechanochemical preparation of the precursor and solvothermal microwave-assisted reaction with open reflux system. The size of prepared particles ranges from hundreds of nanometers to micrometers.

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LITERATURE