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CONTROLLED HYDROTHERMAL PROCESSING OF ZnO POWDERS IN THE PRESENCE OF PVP

A. Stanković, Z. Stojanović, Lj. Veselinović, S. Marković, D. Uskoković

Institute of Technical Sciences of the Serbian Academy of Sciences and Arts, Knez Mihailova 35/IV, Belgrade 11001, Serbia (ana.stankovic@itn.sanu.ac.rs)

Abstract

In this study low-temperature hydrothermal processing was used for synthesis of ZnO powders with controlled morphology, from micro-rods *via* hexagonal prism like to nano-spheres, by the varying of $[Zn^{2+}]/[OH^-]$ molar ratio. The synthesized powders were characterized using XRPD, FE-SEM, UV-Vis diffuse reflectance and Raman spectroscopy. It is noticed that the modification of the particle size and morphology from nanospheres to micro-rods resulted in increased visible light absorption. Besides, the band gap energy of the synthesized ZnO powders showed the red shift (~0.20 eV) compared to bulk ZnO. The enhanced visible light absorption of the ZnO powders is related to the existence of lattice defects and the particle surface sensitization by PVP.

Introduction

Since the functionality of materials are determined by the phase purity, homogeneity, particle size, morphology, as well as crystallinity, the possibility to control the synthesis process is of utmost importance. Several techniques such as precipitation, sol–gel process, spray pyrolysis, hydrothermal synthesis, and mechanochemical processing are used for the preparation of ZnO materials with controlled properties. Among them, hydrothermal synthesis is the most attractive due to the fact that it allows perfect control of purity, crystallinity, composition, size and morphology by simple tuning of the experimental variables: reaction temperature, time, reactant molar ratio and/or addition of the appropriate polymer surfactants [1,2]. Moreover, hydrothermal synthesis is environmentally safe and economical for large-scale production.

Here, we propose a low-temperature hydrothermal method for the synthesis of phase-pure ZnO powders with a controlled morphology and narrow particle size distribution. This simple and low-cost method allows to tailor the shape and size of ZnO particles, from micro-rods *via* hexagonal prism like to nano-spheres, by the varying of $[Zn^{2+}]/[OH^-]$ molar ratio. The synthesized powders were characterized by XRPD, FE-SEM, UV-Vis diffuse reflectance and Raman spectroscopy.

Experimental

ZnO powders were prepared by low-temperature hydrothermal processing. The reaction temperature and time were kept constant, while the $[Zn^{2+}]/[OH^-]$ molar ratio in the starting solution was changed in order to tailor the particle size and shape. The $[Zn^{2+}]/[OH^-]$ molar ratio was varied from 1:1, 1:3, 1:3.5, to 1:5,

resulting in the pH values of the reaction solution: 8, 10, 11, and 13, respectively. The starting materials were zinc acetate ($Zn(CH_3COO)_2 \cdot 2H_2O$), sodium hydroxide (NaOH) and polyvinylpyrrolidone (PVP), as a polymer surfactant. After the dissolution of zinc acetate dihydrate and PVP, an adequate amount of the aqueous solution of NaOH was added dropwise, resulting in a white precipitate. The as-prepared suspension was thermally treated in 2 l *Parr* stainless steel reactor up to 120 °C under constant stirring of 400 rpm. The reaction time was 72 h. The synthesized ZnO powders were designated as ZnO8, ZnO10, ZnO11 and ZnO13, where the number signifies the pH value of the reaction solution.

The crystal phases of synthesized powders were identified by XRPD analysis (Philips PW-1050). The morphology of ZnO particles was observed by FE-SEM (SUPRA 35 VP Carl Zeiss). The UV-Vis diffuse reflectance spectra were recorded in the wavelength range 300–800 nm (Evolution 600 UV-Vis spectrophotometer, Thermo Scientific). The μ-Raman spectra were recorded in the frequency interval of 50–3500 cm^{-1} (DXR Raman microscope, Thermo Scientific).

Results and Discussion

The results of XRPD analysis show that the synthesized ZnO powders are pure, highly crystalline, a wurtzite-type hexagonal structure with nanosized crystallites.

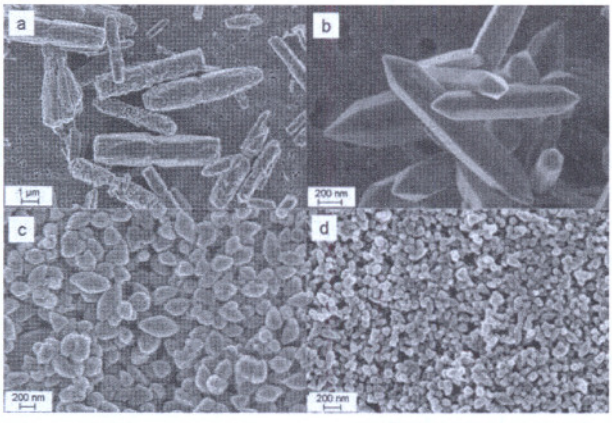

Figure 1. FE-SEM micrographs of: (a) ZnO8; (b) ZnO10; (c) ZnO11, and (d) ZnO13.

The morphologies of the synthesized ZnO powders, examined by FE-SEM, are shown in Fig. 1. The ZnO8 powder is consisted of the micro-rods with a rough particle surface and partially cracked edges with non-uniform particles size distribution; the particle lengths are between 1.4 and 7.1 μm, while the diameters are between 0.3 and 1.7 μm (Fig. 1a). ZnO10 powder, Fig 1b, is composed of the particles with a smooth hexagonal-faceted prismatic morphology with hexagonal pyramidal ends. The most of the rods have rather uniform diameters of about 200 nm and lengths of 1-2 μm. Powder ZnO11, Fig. 1c, is composed of ellipsoidal particles with an average diameter and length of about 200 nm and 500 nm,

respectively. Finally, ZnO13 powder consists of spherical nano-sized particles with uniform size distribution and average diameters of ~ 50 nm, Fig. 1d.

Influence of particles size and morphology on optical properties of ZnO was examined by UV-Vis diffuse reflectance spectroscopy (DRS). Using the recorded UV-Vis DRS and the Kubelka-Munk transformation method, the band gap energies (E_{bg}) were determined, and they are: ZnO8 — 3.16 eV, ZnO10 — 3.18 eV, ZnO11 — 3.19 eV, and ZnO13 — 3.22 eV. It is noticed that all the synthesized ZnO powders show increased absorption in the visible region at room temperature.

Raman spectroscopy was used to explain the improved optical properties of the synthesized ZnO powders (red shift of band gap). The modes that appear in the Raman spectra were assigned to wurtzite crystal structure, to the structural defects (impurities, oxygen vacancies and zinc interstitials) as well as to PVP. According to the Raman spectroscopy study, the red shift of the band gap (~ 0.20 eV) for the synthesized ZnO powders compared to bulk ZnO (E_{bg} = 3.37 eV) could be related to two phenomena: the introduction of lattice defects and surface sensitization by PVP, because PVP can improve visible light absorption. Detailed analysis of Raman spectra yields that nano-sized powder ZnO13 and ZnO11 has ordered wurtzite crystal structure with very few defects, while in micro-sized powders, ZnO10 and ZnO8, number of defects and impurities, as well as absorption of PVP at the surface increase.

Conclusion

The effect of the $[Zn^{2+}]/[OH^-]$ molar ratio i.e. pH of the reaction solution on the sizes and morphology of ZnO particles synthesized *via* low-temperature hydrothermal processing was examined. Varying the pH from almost neutral, pH=8, to a strong base solution, pH=13, ZnO particles from non-ordered micro-rods, hexagonal-faceted prismatic morphology with hexagonal pyramidal ends, sub-micron elipsoids to the nano-spheres were prepared. Therefore, it is possible to control morphology and sizes of the ZnO particles by adjusting the pH value of the reaction solution. The synthesized ZnO powders exhibit enhanced visible light absorption in comparison to bulk ZnO. Improved optical properties are related to two phenomena: introduction of lattice defects (impurities, oxygen vacancies and zinc interstitials), also, surface sensitization by PVP.

Proposed synthesis method provides simple, economic and low-temperature approach for a growth of ZnO particles with the different morphology and improved optical properties.

Acknowledgments

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