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Control of ZnO Morhpology by Solution Route

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ABSTRACT

In this paper, ZnO with a rich variety of well-defined morphologies have been achieved by solution route using different kind of precursors, which can prepare particles by only one step without calcination. The influences of solvent, and temperature on the particle size and morphology of ZnO were investigated. It was revealed by the scanning electron microscope (SEM) and transmission electron microscope (TEM) images that the morphological feature of ZnO can be controlled as rod-, polyhedron-, fluffy sphere-, snowflake- and flower-like, etc. XRD measurement showed that all of the ZnO samples with different morphologies has the same hexagonal structure, which is well consistent with electron diffraction (ED) characterization. This communication not only provides promising candidates for materials science due to the importance of shape in relationship with materials, but also presents an effective route to synthesize the well-defined inorganic materials.

INTRODUCTION

More attentions nowadays are paid on studies of the morphology control of inorganic materials, because the properties are liable to be tailored for diversified morphologies [1]. Except for focusing on sulfide or selenide nanocrystals [2-6], the studies on diversity of oxides, especially ZnO, are going on.

ZnO, as a wide band gap semiconductor, has been investigated both in fundamental and application studies [7-9]. The reports of ZnO with controlled size and morphology emerged endlessly in order to fine-tune the properties for practical applications, especially to realize the novel lasing effect [10]. Hydrothermal synthesis [3,11], as a mild reaction route, can be performed at a relatively lower temperature to produce the sufficiently crystallized products without further calcination. Previous works were extremely focused on the influence of the reaction condition on size of as-prepared ZnO, or on the simple morphologies, such as sphere- or rod-like ZnO particles [12].

In this communication, hexagonal structured ZnO with a rich variety of well-defined morphologies, have been obtained by solution routes. Some of the morphologies shown the fractal patterns and may have the potential applications for strong light scattering and localization, which are important for lasing [13]. The influences of temperature, and solvent on the particle size and morphology of ZnO were investigated.

EXPERIMENTAL DETAILS

The zinc precursor solution containing $Zn(OH)_4^{2-}$ or $Zn(NH_3)_4^{2+}$ was prepared by adjusting the pH of zinc acetate solution ($ZnAc_2$, 0.50 mol/L) with NaOH or ammonia to 14 and 10, respectively. The precursor was transferred into a 25 mL teflon-lined autoclave and heated to a certain temperature for a given time to form ZnO. After cooled to room temperature, the white precipitate was collected, and then washed with absolute ethanol and distilled water several times. Finally, ZnO samples was obtained by centrifugation and drying in a vacuum at 60-70 °C. In order to control the morphology, different kinds of solvent media can be selected.

The structure of all ZnO samples is wurtzite (hexagonal phase, space group $P6_3mc$) determined by XRD and ED. All of the diffraction peaks are well indexed to the hexagonal phased ZnO reported in JCPDS card (No. 36-0145).

DISCUSSION

Based on the decomposition of soluble $Zn(OH)_4^{2-}$ or $Zn(NH_3)_4^{2+}$, by adjusting the reaction condition in different processes, a rich variety of ZnO with certain morphology can be obtained. For this solution route synthesis, the solvent is polarity tempered from water, ethanol to n-heptane. Polyhedron, short rod, and fluffy nanocomposite ZnO were obtained (Fig. 1) by ethanol solvent. Reacted at 100 °C for 13 h, ZnO from decomposition of the two kinds of $Zn(NH_3)_4^{2}$ or $Zn(OH)_4^{2-}$ precursors, have distinct morphologies, polyhedron and fluffy nanocomposite (Fig. 1a and 1b, respectively). The uniform fluffy nanocomposite was composed of needle-like rods with several tens of nanometers in width. Increased the reaction temperature to 180 °C, fluffy sphere evolved to uniform rod-like ZnO (Fig. 1c). The diameter of the rod is about 100 nm and the aspect ratio is about 5. The ED patterns proved the preferred growth direction is along the *C*-axis for the rod like ZnO crystals, which is the same as other one-dimensional ZnO materials [7]. The hexaganol like ZnO microcrystals have been reported and its growth mechanism is deduced . It is quite interesting that the nanorods can not be grow into microcrystals even with prolonged growth time.

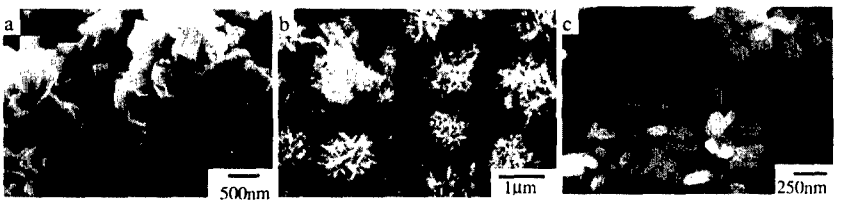

Figure 1 SEM images of ZnO prepared by using ethanol as reaction media (a) polyhedron-like ZnO (pH~10, 100 °C, 13 h), (b) fluffy sphere-like ZnO (pH~14, 100 °C, 13 h). (c) short rod-like ZnO (pH~14, 180 °C, 13 h).

The flower- and snowflake-like ZnO, shown in Fig. 2, were synthesized by using $Zn(OH)_4^{2-}$ (pH~14) as precursors and H_2O or n-heptane as solvent, respectively. There are two kinds of flower-like ZnO as the two magnified images shown in the insets of Fig. 2a. It seems like they grow from a center nucleus. The different polarity of solvents, H_2O and n-heptane, sensitively determines the nucleation and shape evolution, what is the main reason caused the diversified morphology is still under active investigation.

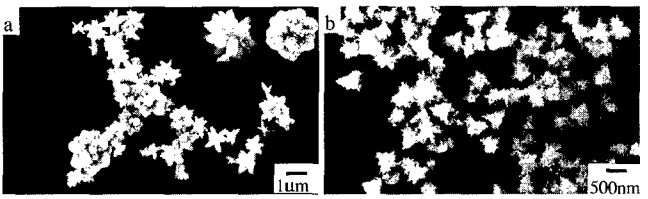

Figure 2 SEM images of ZnO prepared by using H_2O and n-heptane as reaction media, respectively. (a) flower-like ZnO using H_2O as solvent (pH~14, 180 °C, 13 h), the magnified images are the two kinds of particle patterns, (b) snow flake-like ZnO formed using n-heptane as solvent (pH~14, 180 °C, 13 h).

CONCLUSIONS

The diversiformed ZnO have been achieved by solution routes. The reaction temperature and solvent was studied for the influence on the particle size and morphology. This communication not only obtained ZnO with unusual and well-defined morphologies, which can be used as the potential candidates for the fabrication of the new application devices, but also afforded an effective way to synthesize inorganic materials with diverse morphology.

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