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Synthesis and characterization of multipod, flower-like, and shuttle-like ZnO frameworks in ionic liquids

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Abstract

A fast and environment-friendly microwave-heating route to synthesize multipod, flower-like and shuttle-like ZnO nano-/microstructures in room-temperature ionic liquids has been reported. The products were characterized by X-ray diffraction (XRD), scanning electron microcopy (SEM) and transmission electron microscopy (TEM). These ZnO frameworks are composed of needle-like, cone-like and shuttle-like rods growing homocentrically, respectively.

Keywords: Ionic liquids; ZnO; Multipod; Flower-like

1. Introduction

One-dimensional nanometer-sized semiconductor materials, i.e., nanowires and nanorods, have attracted considerable attention due to their great potential for fundamental studies of the roles of dimensionality and size in their physical properties as well as for their application in optoelectronic nanodevices [1]. Zinc oxide (ZnO), a semiconductor with a direct wide band gap (3.37 eV at room temperature) and large exciton binding energy (60 meV), is one of the most promising materials for the fabrication of optoelectronic devices operating in the blue and ultraviolet (UV) region and for gas sensing applications [2]. The synthesis, characterization and application of various 1D ZnO nanostructures including the rods/wires [3], belts/ribbons [4], rings [5], tetrapods [6], combs [7], sheets [8] and complex structures [9] are presently the subject of intense research. However, most of the synthetic procedures involve high temperature, long reaction time and toxic template.

Recently, a new solvent system, room-temperature ionic liquids (RTILs), has developed to a focal point of interest in both academia and industry [10]. RTILs are salts that are liquid at low temperatures (<100 °C) with low melting points, negligible vapor pressure, wide range of liquidus temperatures (up to 400 °C), low toxicity, nonflammability, large electrochemical window, good solvents for many organic and inorganic materials and high ionic conductively and thermal stability, making them attractive novel environmentally friendly solvents for organic chemical reactions [10], separations [11] and electrochemistry [12]. In contrast to their successful applications in organic and materials chemistry, the use of RTILs in inorganic synthesis is still in its infancy. There have been only a few reports on the formation hollow TiO_2 microspheres [13], mesoporous TiO_2 nanosponges [14], super-microporous silica [15], nanoparticles of palladium [16], platinum [17], iridium [18] and gold [19], single-crystalline tellurium nanorods and nanowires by using RTILs as solvents [20]. Recently, We synthesized ZnO nanosheet aggregates by microwave heating in a RTIL $[C_2OHmim]^+Cl^-$ [21]. Herein, we extend this fast, seedless, template-free and environmentally benign

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green route for the production of multipod, flower-like and shuttle-like ZnO nano-/microstructures by microwave heating in RTILs $[Bmim]^+Cl^-$ and $[Bmim]^+BF_4^-$.

2. Experimental

In a typical synthesis of ZnO nano-/microstructure, we use 1-butyl-3-methylimidazolium chloride, $[Bmim]^+Cl^-$ and 1-butyl-3-methylimidazolium tetrafluoroborate, $[Bmim]^+BF_4^-$ as solvent, which were synthesized according to the literature [11]. $Zn(CH_3COO)_2 \cdot 2H_2O$ (5.5 g) was dissolved in 50 mL of distilled water, and then solid NaOH (16 g) was slowly added into the solution and stirred for about 15 min and formed a transparent $Zn(OH)_4^{2-}$ solution. Then 2 mL of the above solution was loaded into a 30 mL Teflon tube, which was then filled with 1 mL of RTILs $[Bmim]^+Cl^-$ or $[Bmim]^+BF_4^-$. After homogenization of the mixture, the suspension was put into a domestic microwave oven (LG, MS-2079 T, 2.45 GHz, 700 W) in air, 50% of the output power of the microwave was used to irradiate the mixture for 7–12 min (on for 21 s, off for 7 s). The bulk temperature was found to be between 110 and 120 °C. The products were separated by centrifugation, washed with absolute ethanol and distilled water twice, respectively, and dried at 40 °C in vacuum. The morphology of the as-prepared products was characterized and analyzed using scanning electron microscopy (SEM) (LEO1530), X-ray diffraction (XRD) (Bruker D8 advance) and transmission electron microscopy (TEM) (JEOL, JEM-200CX, at 200 kV).

3. Results and discussion

A typical XRD pattern of the as-prepared sample is shown in Fig. 1. All of the diffraction peaks can be indexed to the hexagonal structure of ZnO (JCPDS card no. 36-1451) with fine crystallinity. Compared with the standard diffraction patterns, the intensity of ZnO (002) peak is higher than the results of bulk ZnO, revealing high [0001] growth orientation of the ZnO rods. The overall reaction may be simplified as follows.

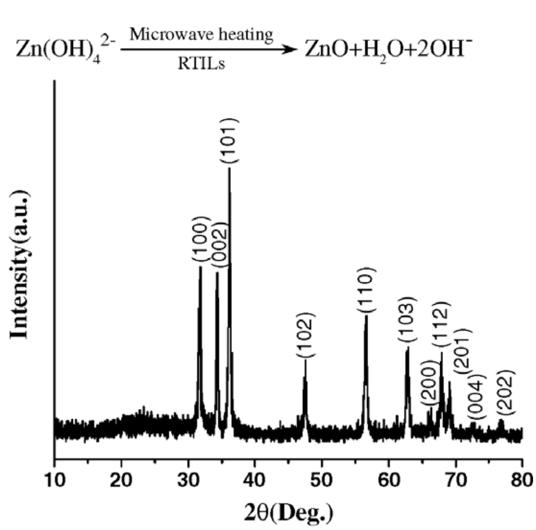

Fig. 1. A typical XRD pattern of as-prepared sample.

SEM morphologies of ZnO nano-/microstructures synthesized by microwave heating in RTILs are shown in Fig. 2. Fig. 2a and b shows the ZnO nanostructures by microwave heating for 7 min in RTIL $[Bmim]^+Cl^-$. It can be seen that the multipod framework has smooth surface and each multipod is composed of needle-like nanorods with 80–200 nm in diameters and ~500 nm in lengths growing homocentrically. When prolonging heating time to 12 min, the ZnO multipod framework evolves to flower-like structure, the diameters and the average length of rods increase to 200–400 nm and 1.5 μm, respectively (see Fig. 2c and d). We find some small ZnO nanoparticles appear on the surface of rods. When the RTIL was changed to $[Bmim]^+BF_4^-$ and the heating time was 12 min, shuttle-like ZnO rod aggregates were achieved. Fig. 2e shows the SEM image of the as-obtained ZnO spheres composed of shuttle-like ZnO rod with diameters ranging from 4 to 10 μm. A magnified SEM image of the spherical ZnO microstructure is shown in Fig. 2f. It can be seen that many novel shuttle-like ZnO rods with diameters of 300–500 nm grew along the direction perpendicular to the center of sphere in the well-distributed mode, and their morphologies are irregular. Each rod similar to the morphology of shuttle becomes gradually thinner and forms a hexagonal or near hexagonal shape showing impressive layered structure. More interestingly, there are some small nanorods, which perpendicularly grew on the surface of these shuttle-like rods, thus forming the ZnO hierarchical structure.

Further structural characterization of the ZnO flower-like and shuttle-like rod aggregates were performed by TEM. Fig. 3a shows the typical morphology of ZnO flower-like structure. It can be seen that flower-like ZnO is not a simple aggregation of small crystallites, but is composed of cone-like ZnO rods growing homocentrically. A similar morphology of ZnO was previously observed by Zhang [22]. The TEM image of shuttle-like ZnO hierarchical framework is shown in Fig. 3b, which depicts the end planes of the ZnO rods are smooth, corresponding to the ZnO (0001) plane and revealing good crystal quality of the rods.

Further experiments without RTILs or substituted RTILs with ethanol were done under the same conditions as the synthesis of ZnO nano-/microstructures. However, no ZnO was obtained even if prolonging microwave-heating time to 20 min. This indicates that both the RTILs and microwave heating play a crucial role in the formation of various morphologies of ZnO. The RTILs $[Bmim]^+Cl^-$ or $[Bmim]^+BF_4^-$ consist of cation $Bmim^+$ and anion Cl^- or BF_4^-. The high ionic conductivity and polarizability of $Bmim^+$ make it an excellent microwave absorbing agent, thus leading to a high heating rate and a significantly shorten