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Microwave-assisted Synthesis of Flower-like ZnO Nanosheet Aggregates in a Room-temperature Ionic Liquid

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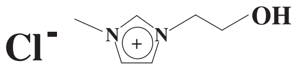
A fast and environment-friendly green microwave-heating route to synthesize flower-like ZnO nanosheet aggregates in a room-temperature ionic liquid has been reported. SEM images showed the nanosheets with uniform 50 nm in thickness. The PL spectrum of ZnO nanosheet aggregates exhibits a weak ultraviolet emission and a strong green emission at room temperature.

With growing concern over the environmental impact and health hazards of traditional volatile organic solvents, researchers continue to search for greener alternatives. Room-temperature ionic liquids (RTILs), a relatively new class of solvents, have been shown to be viable substitutes for organic solvents both in academia and industry because of their negligible vapor pressure, low melting points, 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 found wide application in the organic chemical reactions,[1] separations,[2] and electrochemical.[3] In contrast to their successful applications in organic and materials chemistry, the use of RTILs in inorganic synthesis is still in its infancy. These have been only a few reports on the formation hollow TiO_2 microspheres,[4] mesoporous TiO_2 nanosponges,[5] nanoparticles of palladium, platinum, iridium, and gold,[6] single-crystalline tellurium nanorods, and nanowires by using RTILs as solvents.[7]

Combining the advantages of RTILs with microwave heating opened a fast and environmentally friendly green route for the fabrication of nanomaterials.[7] However, to our knowledge, using microwave-assisted IL method have only synthesized Te nanorods and nanowires. There are no reports for the oxide material synthesis. ZnO is an important electronic and optical material because of its wide direct band gap of 3.37 eV. In recent years, in particular, ultraviolet lasing from ZnO nanostructures has been demonstrated at room temperature,[8] which triggers studying a wide range of the effects of morphology, dimensionality, and size on their physical and chemical properties. Up to now, many different morphological ZnO nanostructures, including rods,[9] wires,[8,10] ring,[11] flower-like,[12] etc., have been fabricated. However, most of the synthetic procedures involve high temperature, long reaction time and use of toxic template.[9–12] Herein, we report a fast, seedless, template-free, and environmentally benign green route for the production of flower-like ZnO nanosheet aggregates by microwave-assisted heating in a RTIL.

In a typical synthesis of flower-like ZnO nanostructure, we use 1-(2-hydroxylethyl)-3-methylimidazolium chloride, $[C_2OHmim]^+\ Cl^-$ (**1**), as solvent. The chemical structure of **1** is shown schematically below and which was synthesized according to the literature.[13]



1: 1-(2-hydroxyethyl)-3-methylimidazolium chloride

$Zn(CH_3COO)_2 \cdot 2H_2O$ (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 2 mL of **1**. 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, 30% of the output power of the microwave was used to irradiate the mixture for 10 min (on for 5 min, off for 30 s). The bulk temperature was found to be between 80 and 90 °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). The PL measurement was carried out on a Hitachi 850 fluorescence spectrophotometer using Xe lamp with an excitation wavelength of 325 nm at room temperature.

Typical SEM images of the synthesized ZnO are shown in Figures 1a–1c. It can be seen that flower-like ZnO spherical structures with diameters from 1 to 4 μm (Figure 1a) were

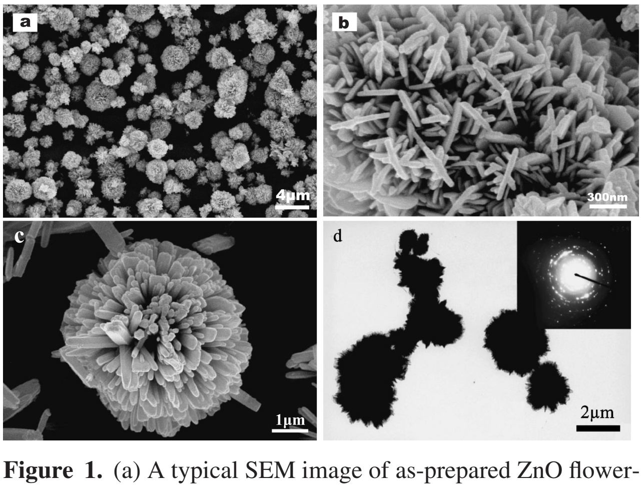


Figure 1. (a) A typical SEM image of as-prepared ZnO flower-like nanosheet aggregations by microwave heating for 10 min in a RTIL. (b) Typical high-magnification SEM image of the nanosheets. (c) SEM image of an individual spherical rod aggregate by microwave heating for 20 min. (d) TEM micrograph of an individual ZnO nanosheet sphere structure. Inset is the corresponding SAED pattern of nanosheets.

formed after microwave heating for 10 min. Figure 1b is the magnification image showing each spherical aggregate is composed of hundreds of individual small nanosheets with uniform thickness of about 50 nm and lengths of up to hundreds nanometers. And the nanosheets are cross-linked layer by layer to form a scaffold and the inner parts of the flower-like spheres are fused together. The TEM image (Figure 1d) shows that the nanosheets are radially aggregated into a ball-like morphology. The selected area electron-diffraction (SAED) pattern (inset in Figure 1d) reveals the crystalline features of the as-synthesized ZnO nanosheet aggregates. When the microwave heating is prolonged for 20 min, the sheetlike aggregates evolve into rodlike aggregates. Figure 1c clearly depicts an individual rodlike sphere composed of hundreds of rods with width from 100 to 300 nm growing homocentrically. XRD patterns from the as-prepared products show that all of the diffraction peaks can be indexed to the hexagonal structure of ZnO (JCPDS card No. 36-1451) with fine crystallinity. The energy-dispersive spectrometry (EDS) clearly shows only Zn and O elements in the product with an approximate atomic molar ratio of 1:0.95 (not 1:1), suggesting an oxygen deficiency in the sample.

Further experiments without RTIL **1** or substituted RTIL **1** with ethanol were done under the same conditions as the synthesis of flower-like ZnO nanosheet aggregates. However, no ZnO was obtained even if prolonged microwave-heating time to 30 min. This indicates that both the RTIL **1** and microwave heating play a crucial role in the formation of flower-like ZnO nanosheet aggregates. The RTIL $[C_2OHmim]^+Cl^-$ consists of cation C_2OHmim^+ and anion Cl^-. The high ionic conductivity and polarizability of C_2OHmim^+ make it an excellent microwave-absorbing agent, thus leading to a high heating rate and a significantly shorten reaction time.[7] The movement and polarization of ions under the rapidly changing electric field of the microwave result in transient, anisotropic microdomains for the reaction system, facilitating the anisotropic growth of flower-like ZnO nanostructure, and the morphology of ZnO evolved from sheetlike into rodlike when increased heating time.[12] Moreover, ZnO has fast growth directions of the type: $\langle 2\bar{1}\bar{1}0\rangle$; $\langle 01\bar{1}0\rangle$; and $\pm[0001]$.[14] Together with the polar surfaces due to atomic terminations, ZnO exhibits a wide range of novel structures that can be grown by tuning the growth rates along these directions. In our experiments, ZnO nanosheets grow along $[2\bar{1}\bar{1}0]$ or $[01\bar{1}0]$, with its top/bottom surfaces $\pm(0001)$ and the corresponding side surfaces $\pm(01\bar{1}0)$ or $\pm(2\bar{1}\bar{1}0)$. The outside face of the nanosheet aggregates is Zn-terminated (0001) surface and the inner of nanosheet aggregates is O-terminated $(000\bar{1})$ surface.[15] As time goes on, the sheetlike evolved to rodlike structure, the rods grow along [0001] with side surfaces of $\{2\bar{1}\bar{1}0\}$ or $\{01\bar{1}0\}$.

The PL spectrum in Figure 2 shows that the flower-like ZnO nanosheet aggregates display weak ultraviolet emission peaks centered at 395 nm and strong green light emission peaks centered at 530 nm. The emissions at 395 and 530 nm correspond to the near band-edge emission and the deep-level, respectively.[10,11] The strong green emission and relatively weak ultraviolet emission could be related with the special structure feature of the surface or subsurface oxygen vacancies under the present reaction condition.[16]

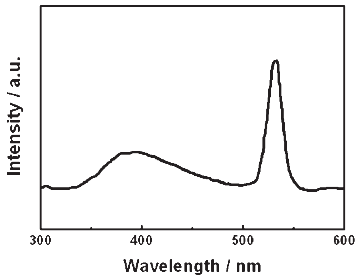


Figure 2. PL spectrum of ZnO nanosheet aggregates.

In summary, flower-like ZnO nanosheet aggregates have been successfully fabricated by microwave-assisted heating in a RTIL. This environmentally benign green method is a fast, seedless, and template-free route, which shortens reaction time and avoids the complicated synthetic procedures. It is expected that the present method can be easily extended to the similar nanostructures of other oxide materials, which is currently underway.

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