Preparation of Bowl-like Hexagonal ZnO Nanostructures by a Template-assisted Solvent-thermal Route

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Bowl-like ZnO nanostructures with hexagonal shape have been fabricated by a solvent-thermal synthesis route with the assistance of ultrathin anodic aluminum oxide (AAO) template. Transmission electron microscopy and high-resolution transmission electron microscopy investigations confirm that the bowl-like ZnO structures are single-crystalline. The room temperature photoluminescence investigation shows that the products have a sharp near band-edge emission and another broad green emission band centered at 386 nm and around 525 nm, respectively.

Synthesis of inorganic materials with controlled size and defined morphology have stimulated great interest in the nanotechnology fields because of their great potential for fundamental studies and application.[1,2] On the other hand, the rapid development of micro/nanodevices is placing increasing demands on various new functional nanostructures. ZnO, with a wide band gap (3.37 eV) and a large exciton binding energy (60 meV), is one of the most ideal candidates for applications in electronics, photoelectronics, and sensors.[3,4] The researches on ZnO-related nanostructures are forefront in nanotechnology owing to their unique properties. Up to now, different ZnO nanostructures with various morphologies, such as nanorods, nanobelts, nanocombs, and nanorings,[5,6] have been prepared via various methods, including physical thermal evaporation, chemical vapor deposition, electrodeposition, and hydrothermal method.[7,8] Among these the general preparation routes, anodic aluminum oxide (AAO) template-assisted method has been proved to be efficient to fabricate 1D ZnO nanorod arrays or nanotube arrays.[9,10] In this letter, we report a newly found nanostructure of ZnO, i.e. bowl-like hexagonal ZnO nanostructure, which was prepared by a solvent-thermal route. Combined with a modified ultrathin AAO template-assisted approach, bowl-like ZnO nanostructures with hexagonal shape can be assembled under solvent-thermal conditions. Interestingly, shape and size of the products are not confined by the AAO template. The solvent-thermal treatment process is crucial for the formation of the bowl-like ZnO structures.

Our strategies to fabricate the hexagonal bowl-like ZnO nanostructures are summarized in Figure 1. Firstly, the metallic Zn was evaporated on the AAO membrane supported by a Si wafer. The AAO membrane was prepared by a two-step anodization process as described previously.[11] Subsequently, the template was heated for 3 h under an oxygen atmosphere at 450 °C. The Zn predeposited in the holes of AAO membrane by evaporation was oxidized enough. Subsequently, the template and 40 mL of glycerol were loaded into a Teflon-lined stainless steel autoclave of 50-mL capacity (pH 8.5). The autoclave was maintained at 180 °C for 24 h. After quenching the autoclave with cold water, the samples were washed with dilute hydrochloric acid and distilled water for several times. The as-obtained white products, which were found on the Si substrate, were heat-treated at 500 °C for 5 h in a nitrogen atmosphere. The final product was a white powder.

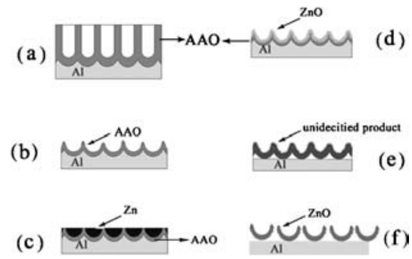

Figure 1. Schematic illustration of the experimental procedure. (a) The empty AAO membrane, (b) decrease of the thickness and enlarging of the diameters of the pores of AAO membrane, (c) evaporation of the Zn on the surface of AAO membrane, (d) the Zn was oxidized during the thermal treatment in an oxygen atmosphere, (e) formation of unidentified inorganic–organic material and the shape evolution of a bowl-like nanostructure, (f) the bowl-like ZnO nanostructure obtained by heat decomposition.

Figure 2 shows typical field emission scanning electron microscopy (FESEM) images of final as-produced ZnO products dispersed on Si substrate. Low-magnification FESEM image (Figure 2a) shows the hexagonally shaped ZnO particles, uniform in size and shape, which are dispersed on the whole substrate. The higher-magnification FESEM image (Figure 2b) further confirms that there are hollow concave on the surface of these hexagonal ZnO particles, which look like a bowl with hexagonal frame. These bowls are 300–350 nm in outside diameters. And the edge wall thickness is about 30–40 nm. The highness of the bowls, estimated from the titled particles, is about 100 nm.

It is notable that the outside diameter of the bowls is larger than the inside diameter of AAO membrane (200 nm), and the

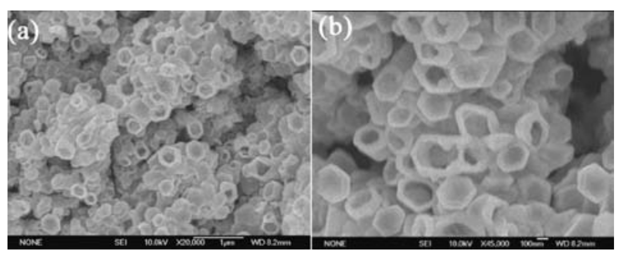

Figure 2. (a) Low-magnification FESEM image of bowl-like ZnO nanoparticles dispersed on the whole substrate, (b) higher-magnification FESEM image of bowl-like ZnO structures.

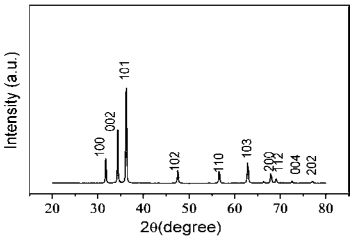

Figure 3. XRD pattern of the final white product.

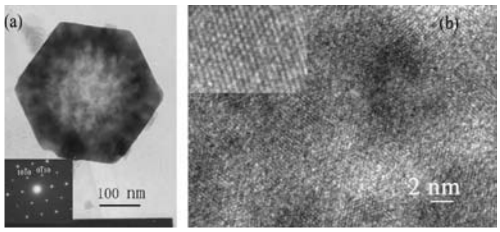

Figure 4. (a) TEM image of bowl-like ZnO nanostructure and its SAED pattern (inset), (b) high-resolution TEM of bowl-like ZnO nanostructures recorded along [0001].

shape of these particles are not confined by the hole of the template, which indicates that there is somewhat deformation process during the solvent-thermal process. We believe that the ZnO and glycerol combine to produce a kind of unidentified inorganic–organic intermediate and undergo a dissolution–recrystallization process during the solvent-thermal treatment. And the dissolution–recrystallization process confined in the AAO template is responsible for the formation of bowl-like ZnO structures.

The phase of the final product was examined by powder X-ray diffraction measurements. Figure 3 is the XRD patterns taken from the final white product after heated at 500 °C in nitrogen atmosphere. All the diffraction peaks can be indexed as hexagonal ZnO (JCPDS 36-1451).

The structures of the bowl-like ZnO were further investigated by transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM). Figure 4a shows a typical TEM image of the bowl-like ZnO structures. The light contrast in the center of the particle reveals that the thickness of central portion is smaller than the brim. The corresponding selected area electron diffraction (SAED) pattern recorded from the center can be indexed as a hexagonal wurtzite ZnO. And the sixfold symmetry of SAED patterns indicates that the bowl-like ZnO structure is single-crystal and that the direction of electron beam is along [0001] zone axis. The HRTEM image taken from the central portion is shown in Figure 4b. The lattice spacing is about 0.28 nm, which is in accordance with the (100) plane distance. The inset of it clearly shows the sixfold symmetric lattice image. The TEM, SAED, and HRTEM measurements all prove that the bowl-like ZnO structures are single-crystalline.

Figure 5 shows the room temperature photoluminescence spectrum of the resulted bowl-like ZnO nanostructures. The ultraviolet (UV) emission band at about 386 nm are found, which is originated from excitonic recombination corresponding to the band-edge emission of ZnO.[12] The broad and strong visible band at around 525 nm is also found in the spectrum, which is attributed to different intrinsic defects in ZnO.[13]

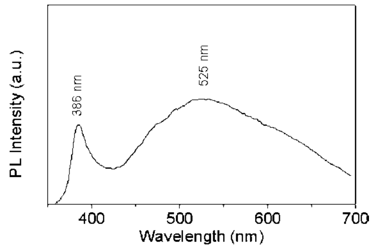

Figure 5. PL spectrum of the final white product at room temperature.

In summary, bowl-like hexagonal ZnO nanostructures were prepared by a solvent-thermal method assisted with AAO membrane. The bowl-like ZnO nanostructures are single crystalline. A possible growth mechanism is proposed to be a process following oxidation of the Zn in the hole of AAO, a dissolution–recrystallization process of the ZnO under solvent-thermal conditions, Final the pure bowl-like ZnO was obtained by heat treatment. The PL spectrum of the bowl-like ZnO shows a sharp and relatively intense UV emission at 386 nm and a broad and strong green emission at 525 nm. These ZnO nanostructures are expected to be useful for designing nanodevices as building blocks. This work may further expand a wide usage of the AAO template method in morphology- and size-controlled material preparation.

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