Fabrication and Photoluminescence of Urchin-like ZnO/MgO Hierarchical Structures

Li-rong Qin,*[1] Jian-wei Zhao,[2] Li-de Zhang,[2] and Xian-wu Zou[1]
[1]*Department of Physics, Wuhan University, Wuhan 430072, P. R. China*
[2]*Institute of Solid State Physics, Chinese Academy of Sciences, Hefei, Anhui 230031, P. R. China*

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A novel hollow urchin-like hierarchical structure of ZnO nanorods grown on hollow MgO microspheres has been prepared through a simple one-step chemical vapor deposition method. Photoluminescence property and possible growth mechanism of the ZnO/MgO hierarchical structures have also been discussed.

Recently, many efforts have focused on the integration of one-dimensional nanoscale building blocks into two- and three-dimensionally ordered superstructures or complex functional architectures, which is a crucial step toward the realization of functional nanosystems.[1] Self-assembly nanostructures of multiple dimensionality and/or hierarchy are highly desirable and provide an attractive alternative method in terms of realizing mesoscopic assembly of nanodevices.[2] They can be prepared directly by growing nanoscale structures of materials with different dimensions. In addition to common hierarchical architectures, composite nanomaterials based on different material systems are expected to have complex device functionalities owing to their diverse properties. In this regards, some hierarchical complex structures, such as SiO_2/Si,[3] ZnO/In_2O_3,[4] and SnO_2/Fe_2O_3,[5] have been studied.

As important fundamental materials, ZnO and MgO have attracted great interest. Many kinds of ZnO[6] and MgO[7] nano- and microstructures have been widely investigated. However, studies on the fabrication of hierarchical architectures assembled from low-dimensional ZnO and MgO structures have been relatively limited. In this paper, we report a successful self-assembled fabrication of the ZnO/MgO hierarchical structures by a simple one-step thermal evaporation route without use of additive or catalysts, which would be helpful in designing and preparing many other novel hierarchical structures.

The hierarchical structure was prepared using a previously reported reaction chamber setup for hollow MgO microsphere preparation.[8] Briefly, metal Mg and Zn powders mixed in the weight ratio of 1:10 were used as the sources, similar to our previous reported experiment,[8] and other ratio would bring about MgO- or ZnO-type impurity. The powders were placed in a ceramic boat and covered with a quartz plate. The boat was placed in the center of an alumina tube. High purity argon (80 sccm) was introduced into the tube furnace to purge for 25 min, and the residual oxygen in the tube was available to oxidize the metal powders. Under a constant flow of Ar (20 sccm), the furnace was rapidly heated to 650 °C in 5 min, and after 1 min of deposition, the quartz tube was taken out of the furnace to allow rapid cooling. After the quartz tube was cooled to room temperature, gray-white product was obtained in the rear of the source region.

The as-synthesized product was characterized by X-ray diffraction [(XRD) PW1710 instrument with Cu Kα radiation], scanning electron microscopy [(SEM) Sirion 200 FEG], and transmission electron microscopy [(TEM) JEOL 2010, operated at 200 kV]. Photoluminescence (PL) spectrum was obtained using an Edinburgh FLS 920 fluorescence spectrophotometer (Xe 900 lamp) at room temperature.

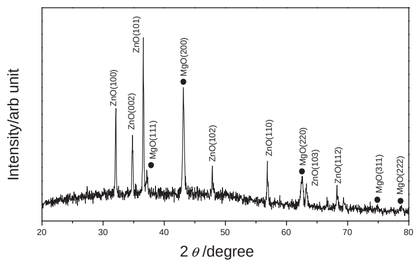

Figure 1. XRD pattern of as-synthesized product.

The as-obtained product was firstly characterized by XRD, and the result is presented in Figure 1, clearly evidencing that the structure is composed of two crystalline phases. One set of peaks can be indexed as the hexagonal structured ZnO with lattice constants $a = 3.256$ and $c = 5.214$ Å, and the other set of peaks marked with solid circle can be identified as the cubic MgO with the lattice constant $a = 5.4$ Å. Figure 2a is the typical SEM image of product, which shows a novel urchin-like assembly is obtained. Some broken assemblies indicate that the structure consists of the hollow microsphere with many nanorods growing on both outside and inside of the spherical shell, which has a mean thickness of about 100 nm. The diameters of these assemblies are mostly in a range of 7–11 µm. In Figure 2a, some small-size assemblies were also shown, which could reveal clearly the whole hierarchical structure. The local SEM images of the outside and inside surfaces for the assemblies are shown in Figures 2b and 2c. The insets are the corresponding enlarged pictures of the nanorods. From the inset in Figure 2b, the nanorod having a well-faceted hexagonal head and a uniform diametrical stem with smooth surface is easily noticed outside of the spherical shell. The hexagonal tip is similar to the reported morphology about ZnO,[9] manifesting that the nanorods grow along the [0001] direction. The diameters of the nanorods range from 40 to 100 nm, and the lengths reach up to 1 µm. The inset in Figure 2c indicates that in the inside surface the nanorods have sharp tips. The diameter of the nanorods decreases from the root to the tip; the typical length is about 140–650 nm.

Further insight into the detailed structures of the hollow

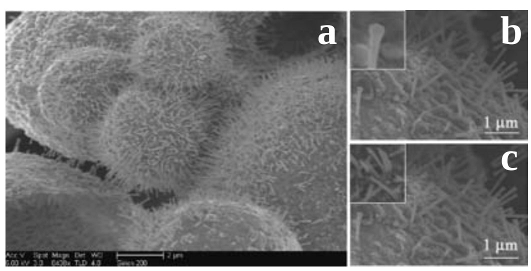

Figure 2. (a) A typical SEM image of the urchin-like assembly. (b) and (c) show the local images of the outside surface and the inside surface, respectively. The insets are the corresponding enlarged pictures of the nanorods.

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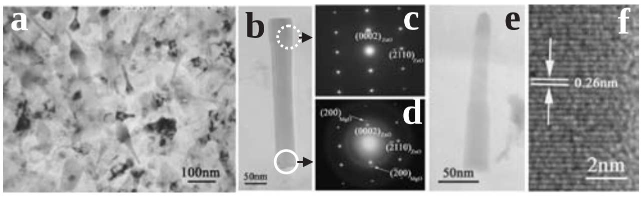

Figure 3. TEM images of (a) a patch of the urchin-like assembly, (b) individual ZnO nanorod with the uniform diametrical stem, and (c) and (d) the corresponding SAED patterns of the head and the root of the nanorod, (e) another TEM image of the ZnO nanorod with the sharp tip, and (f) the corresponding HRTEM image.

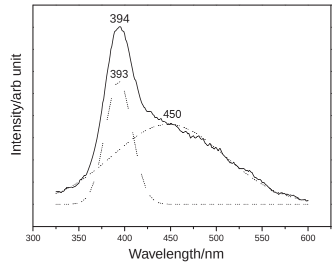

Figure 4. Room-temperature PL spectrum of the assembly. The Gaussian fit band drawn by the dot line.

urchin-like hierarchical structures has been taken by TEM and SAED. However, because of the considerable weight of the assembly with lots of nanorods grown on the sphere shell, it is difficult to obtain relatively intact sphere-like morphology in TEM observation. We just observe some patches of the assembly, as shown typically in Figure 3a, which may be broken from the sphere shell because of the ultrasonic vibrations, and it clearly reveals that many small nanorods extend outward from the spherical shell. The spherical shell is polycrystalline and composed of numerous nanoparticles, as consistant with the structure characteristics of the MgO sphere in our former report.[8] Figure 3b is a typical TEM image of nanorod. It can be seen that this nanorod has a smooth side face and a uniform diametrical stem along the length. Thus, it can be classified as the nanorod on the outside surface. However, with a careful examination, we can find that the root of the nanorod is relatively rough by comparison with other part. Moreover, Figures 3c and 3d show that the SAED pattern of the head of this nanorod is different from that of the root. The diffraction pattern of the head indicates the hexagonal ZnO single crystalline structure with preferred orientation in the [0001] direction, but the diffraction pattern of the root shows that except ZnO diffraction pattern, two other diffraction spots indexed with arrow are found also. These two spots can be assigned to be (200) zone axis of cubic MgO and come from the spherical shell. Figure 3e shows the TEM image of the sharp-tip nanorod. It can be seen that its diameter decreases gradually from bottom to tip. Corresponding high-resolution TEM image is shown in Figure 3f. The lattice fringes can be clearly observed, and the spacing of the two neighbouring planes is about 0.26 nm, which is consistent with the interplanar separation of the (0002) plane of wurtzite ZnO. This result confirms that the sharp-tip nanorod is also single crystalline ZnO structure with preferential growth orientation in the *c* axis direction. The analyses described above prove that the product presented here is an urchin-like hierarchical structure with ZnO nanorods grown on hollow MgO microspheres.

On the basis of our previous study,[8] the melting Zn droplets can act as an interim template to assist the formation of the MgO hollow sphere. Considering the structure feature of the hierarchical assembly, we could reasonably separate the growth process into two stages by looking into the growth conditions. Firstly, the hollow MgO sphere formed assisted by melted Zn droplet, while the inner Zn core was vaporized and oxidized into ZnO_x by the residual oxygen. However, different from the previous experiment,[8] in this work the quartz tube was taken out of the furnace to allow rapid cooling to room temperature after 1 min of evaporation. In this case, the ZnO_x vapor could nucleate in situ on the pregrowing MgO spherical shell. As a result, ZnO nanorods sprout out epitaxially from the sphere surface via a self-catalytic mechanism,[10] and finally ZnO/MgO hierarchical structure is formed. As for the different morphologies of the nanorods grown on the outside and inside surface, it is caused by the different concentration of ZnO_x due to the obstruction effect of the MgO spherical shell.

The room-temperature PL spectrum of the assembly is obtained with the excitation wavelength of 266 nm. The result is shown in Figure 4, which reveals besides a sharp and strong UV emission band located at 394 nm, a shoulder peak at higher energy is also observed. Through Gaussian fitting, the PL spectrum can be well fitted into two peaks at 393 and 450 nm, as shown by the dot line in Figure 4. According to the literature, the UV emission corresponds to the near band-edge transition of wide band gap ZnO due to the annihilation of excitons.[11] Additionally, the PL spectrum of MgO always shows a weak blue peak located at 450 nm, which is responsible for various structural defects.[12] From the above analysis, it can be predicted that the ZnO phase in the structure results in the UV emission, while the blue emission arises from the MgO phase. Compared with previous PL report about MgO sphere,[8] the intensity of emission from MgO in the assembly changes not much, but the peak position shifts much. We suppose that it could be attributed to the different defect states in MgO caused by the different experiment conditions. Consequently, the urchin-like ZnO/MgO assembly exhibits a specific luminescence property quite different from that of the hollow MgO spheres.[8]

In summary, novel hollow urchin-like ZnO/MgO hierarchical structures have been successfully prepared via one-step thermal evaporation. The PL spectrum of the structures shows a sharp, strong band located at 394 nm and a shoulder peak at higher energy. Importantly, here the hollow ZnO/MgO hierarchical structure might fulfill some special demands unattained by the individual MgO microsphere unit.

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