Synthesis and Characterization of Hollow Porous MgO Microspheres

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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The hollow porous MgO microspheres have been synthesized through a simple in situ chemical vapor deposition method, and the investigations reveal that Zn in raw source is key and possibly acts as an interim template in the formation of MgO hollow-sphere morphology.

It is well known that the shape and size of inorganic materials have an important influence on their electrical and optical properties. As a special class of materials, metal oxide hollow spheres with nano- and microsizes, because of their unique properties including low density, high specific surface area and good permeation, have attracted great investigative interests and show various potential applications such as catalysis, delivery of drugs, development of artificial cells, protection of biologically active agents, and so on.[1–7] Especially, hollow spheres with porous shells would exhibit more advantages in mass diffusion and transportation compared with conventional hollow spheres with solid shells. Usually, the template synthetic route is employed to fabricate hollow spheres. The templates are classified as hard-core templates such as colloid particles[8] and soft-core templates such as large molecule aggregates.[9] However, owing to the complication, the application is limited for reported template methods. So it is still important to explore a simple and cheap access to preparing inorganic hollow spheres.

MgO is an important metal oxide and has potential applications such as catalysts, additives in refractory, paint and superconductor products, and substrates for thin film growth.[10] Recently, considerable attention has been focused on the fabrication of MgO structures and investigation of their potential applications. Although various morphologies of MgO have been synthesized, the studies on the fabrication of the MgO hollow spheres are very few. Herein, we report a one-step and reproducible synthesis route of hollow porous MgO microspheres in bulk quantities; that is, a simple in situ chemical vapor deposition method. Our results show that Zn in raw source is key and possibly acts as an interim template in the formation of MgO hollow-sphere morphology. The potential growth mechanism and the optical characterization will be presented.

The apparatus used to prepare MgO hollow spheres was a conventional horizontal tube furnace with a 2-cm-inner-diameter and 75-cm-length alumina tube mounted inside. The raw material was a mixture of Mg and Zn metal powders at a weight ratio of 1:10. The powders were placed in a ceramic boat covered with a quartz plate. The boat was located in the center of the alumina tube. Under a constant flow of high-purity Ar (80 sccm), the tube furnace was purged for 30 min, and the residual oxygen in the tube was used to oxidize the metal powders. Then, the furnace was rapidly heated to 1050 °C in 7 min with the Ar flow rate of 20 sccm and kept at this temperature for 30 min. After the system was cooled down to room temperature, a soft white product was collected in the boat. The as-synthesized products were characterized and analyzed by scanning electron microscopy [(SEM) JEOL JSM 6700F], X-ray diffraction [(XRD) PW1710 instrument with Cu Kα radiation], and transmission electron microscopy [(TEM) JEOL 2010, operated at 200 kV]. Photoluminescence (PL) spectra were obtained using an Edinburgh FLS 920 fluorescence spectrophotometer (Xe 900 lamp) at room temperature.

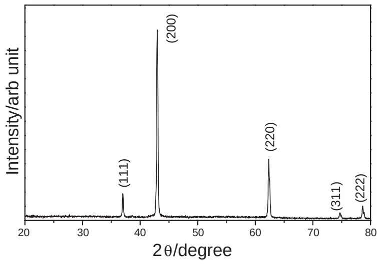

Figure 1. XRD pattern of as-synthesized products.

The as-prepared product was characterized by XRD and the pattern was shown in Figure 1. All peaks can be indexed to a cubic structure of MgO with lattice constant of $a = 4.204\,\text{Å}$, within experimental error. The clear peaks reveal the product with high purity and crystallinity. The morphology of products was examined using SEM. Figure 2a is a low-magnification SEM image. It can be seen that the as-prepared product possesses of sphere structures with a diameter size distributed within 3–6 µm. Both broken and relatively intact spheres exist. As shown in the higher magnification SEM image (Figure 2b), a broken sphere reveals the hollow structure with thin sphere shell. Careful examination of many sphere shells indicates that the thickness is in a range of 60–90 nm. Regarding many pores in the shell, we considered the spheres to be porous. Because of lack of equipments, we could not measure the surface area and pore volume, so we could not draw a confirmed conclusion.

To get more details of the sphere structure, TEM and SAED were applied. In Figure 3a, a representative TEM image reveals that the produced MgO spheres are not orbicular single crystal structure. The strong contrast between the dark edge and the pale

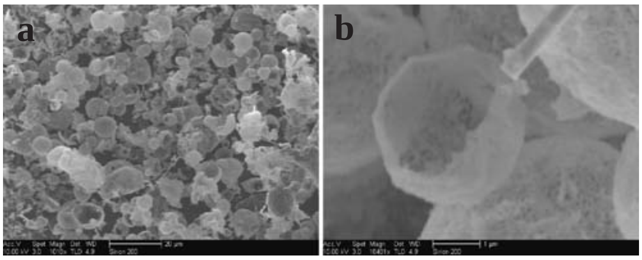

Figure 2. (a) A low-magnification and (b) a high-magnification SEM images of the as-prepared MgO hollow spheres.

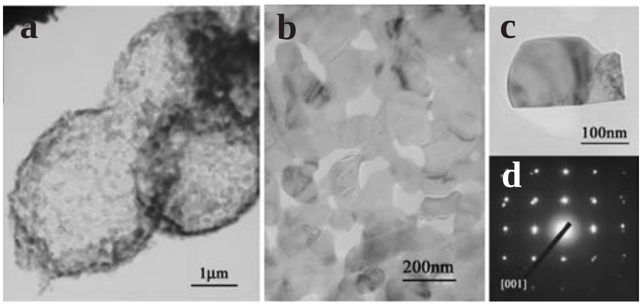

Figure 3. (a) TEM image of the MgO hollow spheres and (b) a high-magnification TEM image showing the sphere shell, (c) TEM image of a sheetlike unit, and (d) the corresponding SAED pattern.

centre of the spheres is the characteristic of hollow spheres.[11] The higher magnification TEM image of the sphere (Figure 3b) illustrates that there are many anomalous pores on the shell and that it looks as if the shell is constructed by the disordered assembled sheetlike units. The dimensions of these units are mostly from tens of nanometers to several hundred nanometers. Figure 3c shows an example of the single unit, and it may be broken from the sphere shell because of the ultrasonic vibrations. Corresponding SAED pattern of the unit (Figure 3d) can be indexed for the [001] zone axis of single crystalline MgO with a face-centered cubic structure.

The room-temperature PL spectra of these hollow spheres are shown in Figure 4a and the excitation wavelength is 325 nm. A broad yellow-green emission band at about 570 nm and a weak red emission band at 667 nm are observed. The measured PL spectrum of cubic MgO has an emission peak at 470 nm. It is similar to the work finished by our group before and the peak is attributed to the structural defects.[12] For other MgO structures, Rosenblatt et al. have reported the 390- and 530-nm bands in time-resolved PL spectra of bulk materials with different defect densities.[13] Chao has reported a red band with peak at about 700 nm and assigned the band to impurity.[14] In our experiment, rapid calefaction, incomplete crystallization, and trace of Zn impurity may generate various structural defects, such as oxygen vacancy and Mg interstitials. Therefore, the two bands in the PL of the MgO hollow spheres in our study can be attributed to these defects and impurities with different densities from the mentioned reports.

In order to explore the formation mechanism of the MgO hollow spheres, another growth experiment was performed without Zn powder in the source and with other parameters essentially the same. In this case the obtained products were the three-dimensional cube-shaped MgO entities, as shown in Figure 4b. So it can be concluded that the Zn powders in the original source materials played a crucial role in the formation process of the MgO spheres.

Although the details of the process involved in the formation of MgO hollow sphere are not very clear, the following mechanism can be proposed on the basis of the existing information. When the system temperature rose above the melting point of Zn (419 °C), the melted Zn grains were closely attached to each other to form liquid droplets, and the Zn atoms on the droplets surface were gradually oxidized. With the increasing temperature, Mg also began to melt (the melting point of Mg is 649 °C) and became mineralized around the droplet, forming a porous MgO shell with the Zn core. The possible formation mechanism of MgO could be explained as follows:

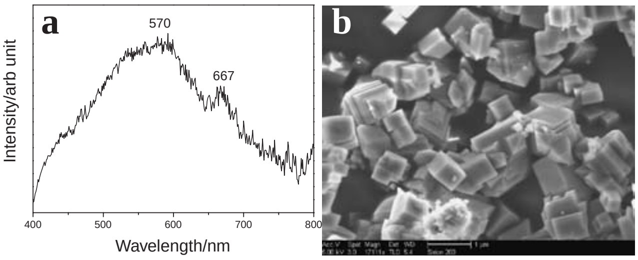

Figure 4. (a) Room-temperature photoluminescence spectrum of the MgO spheres, (b) SEM image of the MgO cubic entities produced by another growth experiment without any Zn powders in the source.

$$2Zn + O_2 = 2ZnO, \tag{1}$$

$$Mg + ZnO = MgO + Zn, \tag{2}$$

$$2Mg + O_2 = 2MgO. \tag{3}$$

In reactions (1) and (3), oxidation of Zn and Mg was induced by the residual of oxygen in our furnace system. Without this oxygen, we speculate that the melted Mg should not be mineralized and then not achieve the hollow spheres. As the surrounding temperature rose above the boiling point of Zn (907 °C), the Zn cores vaporized from the unique pore channel arrangement in the shells, the vaporous Zn was carried away by the flowing argon and the MgO shells were left, thus the MgO hollow spheres formed. In a word, the melted Zn droplets possibly acted as an interim template to assist the formation of the MgO hollow spheres.

In summary, porous hollow MgO spheres with micrometer scale have been successfully synthesized by an in situ chemical vapor deposition method. Compared with previous methods of preparing hollow spheres, our approach is simpler and more effective. In this experimental system, Zn acting as an interim template is essential. The synthetic pathway here is promising for use to fabricate other oxide hollow spheres.

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