Synthesis and photoluminescence properties of CdS hollow nanospheres by chemical vapor deposition

MO Jia-qing(莫家庆)[1,2*], **FENG Zhi-qiang**(冯志强)[1], **HOU Jun-wei**(侯军伟)[3], **JIA Zhen-hong**(贾振红)[1], and **LV Xiao-yi**(吕小毅)[4]

1. College of Information Science & Engineering, Xinjiang University, Urumqi 830046, China

2. School of Electronic and Information Engineering, Xi'an Jiaotong University, Xi'an 710049, China

3. School of Materials Science and Engineering, Tongji University, Shanghai 200092, China

4. Postdoctoral Station of Computer Science and Technology, Xinjiang University, Urumqi 830046, China

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High-density CdS hollow nanospheres are successfully synthesized by a simple chemical vapor deposition technology. The crystal structure, compositional information, and morphological structure are characterized by X-ray diffraction (XRD), scanning electronic microscopy (SEM), transmission electronic microscopy (TEM), and energy-dispersive X-ray spectrometer (EDX). The results show that the as-prepared CdS hollow nanospheres have uniform size about 1−3 μm in diameter. The Kirkendall phenomenon is proposed for the formation of the CdS nanostructures. A strong emission located at 580 nm is observed.

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Hollow nanospheres are of great interest for a large number of applications, such as adsorbents, delivery carriers, catalysts, and biomedical uses[1-3]. As one of the most important group II-VI semiconductors, CdS has been extensively investigated during the past decades. It is a well-studied semiconductor with a direct band gap of 2.4 eV at room temperature, and it is now widely used for photoelectric conversion in solar cells, light-emitting diodes for flat-panel displays, and other optical devices based on its nonlinear properties[4-8]. The template approach has been widely used to grow hollow structures[9-13]; however, the capability of constructing complicated structure is limited by the availability of a template.

In this paper, we report a simple atmospheric pressure chemical vapor deposition method to synthesize self-assembled CdS hollow nanosphere structures on graphite substrate without the use of a catalyst. Studies find that the growth of CdS hollow nanospheres is governed by the Kirkendall phenomenon.

The CdS hollow nanospheres were synthesized in a horizontal quartz tube furnace by chemical vapor deposition technology. Source materials of high pure CdS (99.99%) and C powder (99.99% micro-powder) with a molar ratio of 10:1 in an alumina boat were placed in the heating center of a horizontal alumina tube furnace. Then a piece of graphite wafer was placed downstream to act as deposition substrate for material growth. The distance between the graphite substrate and the source material is 15 cm. Prior to heating, the system was evacuated and flushed with high pure Ar for 1 h to eliminate oxygen. The furnace was heated to 900 °C in 100 min and held at this temperature for 1 h, then cooled to 600°C and held at this temperature for 1 h again. At last, the furnace was cooled to room temperature under Ar with a constant flow rate of 300 sccm.

A Philips XL 30 FEG scanning electron microscope (SEM) with an energy-dispersive X-ray spectroscope (EDS) was used to observe the morphologies and elemental compositions of the samples. An X-ray diffraction (XRD) meter (Japan Mac Science) with Cu K_α radiation was used to obtain phase compositions of the samples. A JEOL 2010 transmission electron microscope (TEM) was used to analyze the morphology and microstructure. A Hitachi F-7000FL spectrophotometer was used to measure the room temperature photoluminescence (PL).

The phase and purity of the as-synthesized CdS hollow nanospheres have been determined by XRD pattern (shown in Fig.1). The position and intensity of the diffraction peaks are fitted well to JCPDS Card No.41-1049 (a = 0.4141 nm

* E-mail: xjqiushixinxi@sina.com

and c = 0.6720 nm), which indicates a high purity and good crystalline of these CdS hollow nanospheres. Roughly calculated on the basis of the Scherrer formula, the mean size of the sample is about 40 nm.

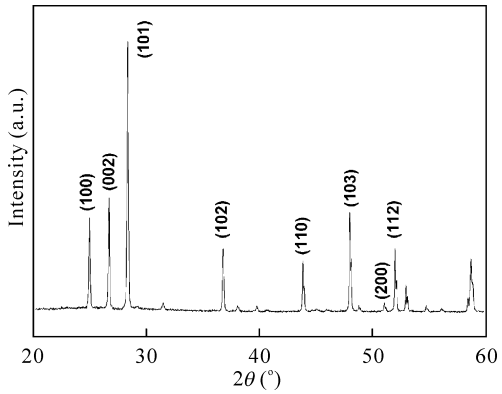

Fig.1 XRD pattern of the products

The morphology of the product was characterized by the scanning electron microscopy (SEM). Fig.2(a) shows a low-magnification SEM image of the as-grown sample, which indicates that the products are composed of a large number of microspheres with diameters of about 1−2 μm. Fig.2(b) and (c) are high-magnification SEM images of broken spheres, which further confirm the hollow nanostructure. Fig.2(d) shows the EDX pattern, which indicates that the microspheres are composed of pure CdS.

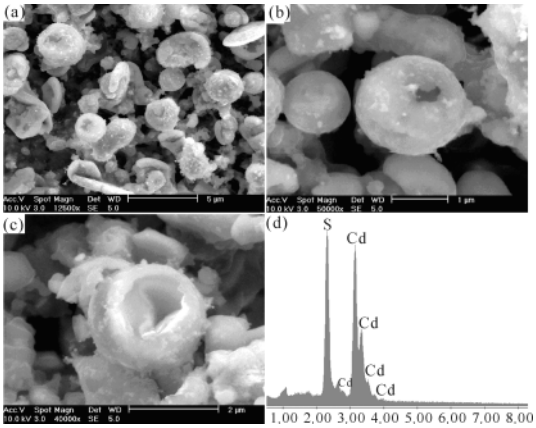

Fig.2 (a) Low- and (b, c) high-SEM images of the sample; (d) EDS spectrum

The microstructures of the hollow sphere were further investigated by TEM. Fig.3(a) and (b) are the low-magnified TEM images of as-grown sample. It can be clearly seen that the contrast between the dark edge and pale inner part provides a direct proof for its hollow nature. The diameters of these hollow spheres are approximately 1−2 μm, consistent with the SEM observation. The rough surface of the shell indicates that the shell consists of the assembly of primary nanoparticles. From the HRTEM image (Fig.3(c)), distinct lattice fringes can be observed. The interplanar spacing is calculated to be 0.36 nm, which matches well with the separation of the (100) plane of the standard wurtzite CdS.

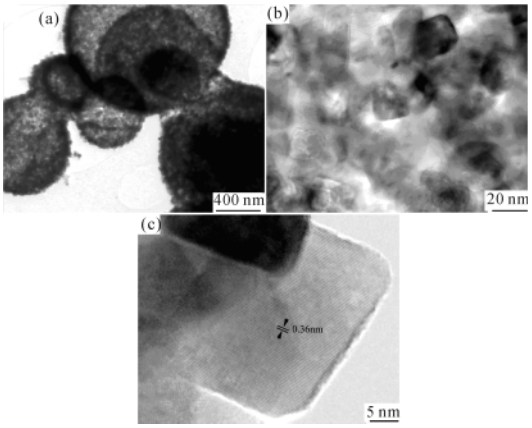

Fig.3 (a, b) TEM images and (c) HRTEM of the CdS hollow nanosphere

Therefore there are two main mechanisms for the hollowing process in template-free synthesis. One is the Kirkendall effect due to the difference of diffusion rates between two interdiffusion species across an interface[14]. The other one is the Ostwald ripening mechanism[15], which describes the process of dissolution-recrystallization in solid solutions or liquid sols. In our experiment, we believe that the Kirkendall effect is the key in the formation process of CdS hollow spheres. During the reactions, Cd and S_2 gases flow with the Ar carrier gas to the low temperature region. When the supersaturation increases to a level at which the nuclei forms, the S clusters aggregate into small amorphous noncrystalline particles. There is no preferential growth direction for S particles, so they are easy to form spheres. The S inside diffuses to the surface and reacts with Cd to form CdS. On the other hand, Cd also diffuses into the inside of CdS and reacts with S to form CdS. Because the size of S sphere is larger than that of CdS, the hollow structure is formed.

Room-temperature PL properties of the CdS hollow spheres were also investigated using a He–Cd laser line at 325 nm as the excitation source. Usually, two emissions are observed from semiconductor nanoparticles-excitonic and trapped luminescence[16,17]. The excitonic emission is sharp and located near the absorption edge of the particles, while the trapped emission is broad and Stokes-shifted. Fig.4 is the room-temperature PL spectrum of the as-grown sample. A strong yellow emission peak at 580 nm can be seen, which is far away from the CdS band edge (510 nm). So we believe that this peak is due to the trap of surface states.

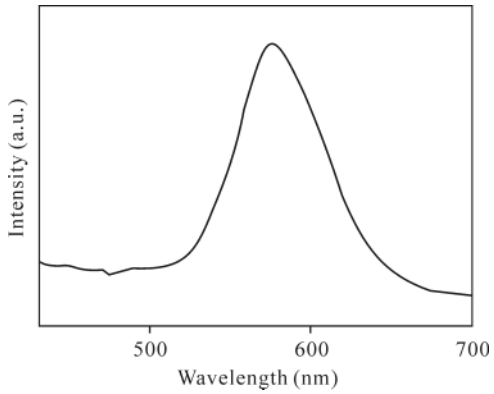

Fig.4 Photoluminescence (PL) spectrum of the products on substrate under room temperature

In summary, CdS hollow nanosphere structures have been successfully synthesized using a simple chemical vapor deposition technology. Studies find that the Kirkendall mechanism is proposed for the formation of CdS hollow structures. The simplicity and scalability of the chemical vapor deposition technology might provide a promising way for the synthesis of functional hollow nanomaterials for partical applications.

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