Available online at www.sciencedirect.com
SCIENCE DIRECT®
Materials Letters 57 (2003) 3137–3139
MATERIALS LETTERS
www.elsevier.com/locate/matlet

A novel route to prepare CdSe hollow structures

Yong Hu[a,b,*], Wenming Chen[b], JiaFu Chen[b], Shuyuan Zhang[a]

[a] Structure Research Laboratory, University of Science and Technology of China, Hefei, Anhui, PR China
[b] Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei, Anhui, PR China

Received 12 August 2002; accepted 26 December 2002

Abstract

Cadmium selenide hollow structures have been successfully synthesized in a polymer solvent system by γ-irradiation at room temperature. The product is characterized by electron diffraction (ED), transmission electron microscope (TEM), high-resolution transmission electron microscope (HRTEM) and UV-Vis, respectively. It was found that CdSe hollow structures (with 25–180 nm in pore diameter, 3–7 nm in wall thickness) could be obtained directly in solution and the size of CdSe nanoparticles is about 3 nm. The influence on the size and morphology of the product was also studied.

Keywords: Hollow structures; γ-Irradiation; Polyvinyl pyrrolidone

1. Introduction

In recent years, there has been growing interest in materials with specific nanomorphologies because of the expectation of novel properties in electrical or biological fields [1–8]. Materials chemists try to construct novel material architectures on nano- or mesoscale. Considerable efforts have been made to fabricate inorganic materials with three-dimensional nano- or mesoscale structures. Of particular interest are hollow structures because of their potential for encapsulation of large quantities of guest molecules or large-sized guests within the empty core domain.

We have been interested in wet chemical fabrication of II–VI semiconductor nanostructures because of their technical importance [9,10]. A handful of examples of such compounds with interesting morphologies or specific structures have been reported in the literature, including nanorods, nanowires, nanocables and nanospheres [11–14]. In this paper, we reported a simple and clean method of producing cadmium selenide hollow structures by γ-irradiating polyvinyl pyrrolidone (PVP) aqueous solution at room temperature.

2. Experimental

All compounds used in the experiments were analytically pure and were used without further purification. Water was used after distillation throughout the experiments. Solution were prepared by dissolving an appropriate amount of analytically pure $CdCl{\cdot}2H_2O$

* Corresponding author. Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, PR China.
E-mail addresses: huyong@mail.ustc.edu.cn (Y. Hu), wchen@ustc.edu.cn (W. Chen).

0167-577X/03/$ - see front matter
doi:10.1016/S0167-577X(03)00010-7

(1.15 g), PVP (2.5 g), $(CH_3)_2CHOH$ (20 ml) and Na_2SeO_3 solution (10 ml) in distilled water. Sodium selenosulfate (Na_2SeO_3) can be synthesized by refluxing selenium powders in a sodium sulfite solution [15]. The solution were deaerated by bubbling with pure nitrogen for 20 min to remove oxygen, and then irradiated in the field of 2.59×10^{15} Bq ^{60}Co γ-ray source at the dose rate of 20.3 Gy/min for 16 h. After γ-irradiation, red and transparent products were obtained. The product was dried in vacuum at room temperature, ground to powder and then washed with distilled water to remove the by-products. The final products were dried in vacuum, again at room temperature.

The size and morphology of CdSe hollow structures were investigated by X-ray energy dispersive spectrum (EDS), transmission electron microscope (TEM) and high-resolution transmission electron microscope (HRTEM). EDS, TEM, ED and HRTEM images of as-prepared hollow structures were taken on a JEOL-2010 transmission electron microscope with accelerating voltage 200 kV.

3. Results and discussion

X-ray energy dispersive spectrum (EDS) shown in Fig. 1 reveals that the wall of hollow structures is composed of Cd and Se, and quantitative analysis result indicates that the atomic ratio of Cd/Se is 53.47:46.53.

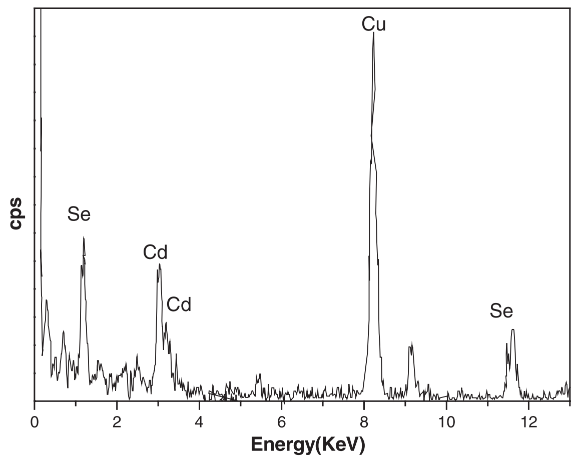

Fig. 1. EDS spectrum revealing that the wall of hollow structures is composed of Se and Cd.

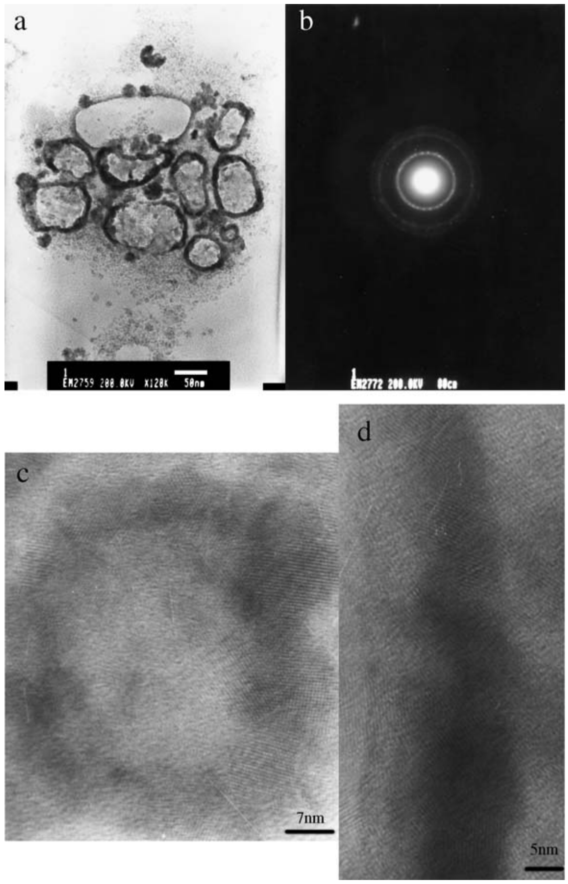

Fig. 2. HRTEM images and ED pattern of as prepared samples. (a) TEM image of CdSe hollow structures. (b) ED pattern of CdSe hollow structures. (c) HRTEM image of an integral hollow structure. (d) HRTEM images of a section of wall fabrication.

Fig. 2 shows TEM image, ED pattern and HRTEM images of the products. The morphology of hollow structures, which are 25–180 nm in pore diameter and 3–7 nm in wall thickness, can be clearly seen in the Fig. 2a. The ED pattern in Fig. 2b shows the diffraction rings of CdSe, which can be characterized as 111, 220 and 311 diffraction from inner to outer, respectively, by calculating the ratio of the corresponding radii. The HRTEM images (Fig. 2c and d) reveal the fabrication of the hollow structures wall. The wall is shown to be composed of CdSe nanoparticles, which the size is about 3 nm. From Fig. 2c, one could clearly see an integral hollow structure that the inner is hollow and the surrounding is composed of the wall of CdSe. Fig. 2d shows a section of wall of CdSe hollow structures.

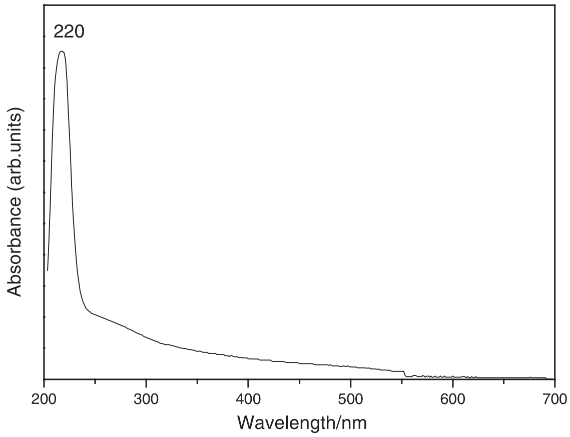

Fig. 3. Absorption spectrum of a CdSe hollow structures sample dispersed in C_2H_5OH.

Fig. 3 shows the room-temperature UV-Vis absorption spectrum of a CdSe hollow structures sample dispersed in C_2H_5OH. UV-Vis absorption spectrum was recorded using a Shimadzu UV-240 UV-Vis spectrometer at room temperature. The maximum at 220 nm is assigned to the optical transition of the first excitation state.

We think, a possible reason to form CdSe hollow structures could be divided two steps as follows: first, Se^{2-} can be released homogeneously from the composition SeO_3^{2-} under γ-irradiation. In an aqueous solution with the existence of Cd^{2+}, CdSe seed formation occurs by the reaction of Cd^{2+} with free Se^{2-}:

$$Cd^{2+} + Se^{2-} \rightarrow CdSe$$

The growth of the seeds occurs whether the CdSe grows on the seeds (growth from a supersaturated solution) or by the process of Ostwald ripening, whereby larger seeds grow at expense of the smaller ones:

$$n\mathrm{CdSe} \rightarrow (\mathrm{CdSe})_n \downarrow$$

In this experiment, oxidative radicals (·OH) were scavenged by isopropyl alcohol [16]. Second, the choice of proper water-soluble polymer is the key to the successful synthesis of CdSe hollow structures. Organic molecules can alter inorganic microstructures, offering a very powerful tool for the design of novel materials [17]. PVP monolayers around the CdSe nanocrystals prevent the formation of disordered structures, and self-organization of the quantum dots occurs in a controlled fashion as the solubilizing power of the solvent is decreased. Along with the formation of these two- and three-dimensional networks, CdSe quantum dots can also be joined with specific chemical linkers and formation [18]. However, at the same condition, we could not acquire CdSe hollow structures in other water-soluble polymer solution.

4. Conclusion

In summary, CdSe hollow structures were prepared with a simple and novel method. Compared with the conventional routes, this method is simpler and more convenient. It may stimulate technological interest and see many applications in materials fields. In the end, the authors acknowledge Prof. Shu-yuan Zhang for his assistance with HRTEM.

References

[1] S. Lijima, Nature 56 (1991) 354.
[2] N.G. Chopra, R.J. Luyken, K. Cherrey, V.H. Crespi, M.L. Cohen, S.G. Louie, A. Zettl, Science 269 (1995) 966.
[3] P.V. Braun, P. Osenar, S.I. Stupp, Nature 325 (1996) 380.
[4] P.C. Ohara, J.R. Heath, W.M. Gelbart, Angew. Chem., Int. Ed. Engl. 36 (1997) 1078.
[5] G. Oldfield, T. Ung, P. Mulvaney, Adv. Mater. 12 (2000) 1519.
[6] W. Schart, Adv. Mater. 12 (2000) 1899.
[7] O. Siiman, A. Burshteyn, J. Phys. Chem., B 104 (2000) 9795.
[8] S.L. Westcott, S.J. Oldenburg, T.R. Lee, N.J. Halas, Langmuir 14 (1998) 5396.
[9] Y. Xie, Z.P. Qiao, M. Chen, X.M. Liu, Y.T. Qian, Adv. Mater. 11 (1999) 1512.
[10] P. Yan, Y. Xie, Y. Qian, X. Liu, Chem. Commun. (1999) 1293.
[11] P. Yang, C.M. Lieber, Science 273 (1996) 1836.
[12] S.H. Yu, Y.S. Wu, J. Yang, et al., Chem. Mater. 10 (1998) 2309.
[13] J.F. Xu, W. Ji, J.Y. Lin, et al., Appl. Phys., A Mater. Sci. Process. 66 (6) (1998) 639.
[14] R.N. Barnett, U. Landman, Nature 387 (1997) 788.
[15] P. Pramanick, R.N. Bhattacharye, J. Solid State Chem. 44 (1982) 425.
[16] H.Y. Ni, X.W. Ge, H.R. Liu, Z.C. Zhang, et al., Chem. Lett., (2001) 458.
[17] S.L. Stupp, P.V. Braun, Science 277 (1997) 1242.
[18] X. Peng, T.E. Wilson, A.P. Alivisatos, P.G. Schultz, Angew. Chem., Int. Ed. Engl. 36 (1997) 145.