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SYNTHESIS AND CHARACTERIZATION OF LARGE-SCALE HIERARCHICAL CdS MICROFLOWERS

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The synthesis of three-dimensional semiconductor superstructures with specific size and shape is a crucial issue due to their size- and shape-dependent properties and significant applications. Using polyvinylpyrrolidone (PVP) as a capping agent, we employed a facile hydrothermal process to synthesize large-scale hierarchical CdS microflowers. X-ray diffraction, X-ray photoelectron spectroscopy and field-emission scanning electron microscopy were used to characterize the as-prepared products. The contrast experiment indicated that PVP played a great role on formation of CdS microflowers. By varying the reaction time, the morphologies of CdS crystals can be easily controlled. The absorption spectra of CdS crystal at the different growth stage were also examined.

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Keywords: CdS; microflowers; hydrothermal synthesis; electronic materials; microstructure.

1. Introduction

The synthesis of inorganic semiconductor materials with specific size and shape has been a crucial issue due to their fundamental size- and shape-dependent properties and significant applications [1-4]. In past decades, much improvement has been achieved on the shape-controlled synthesis of inorganic crystals. Besides many simple shapes (spheres, wires, tubes, etc.), the self-assembly of three-dimensional (3D) superstructure with higher complexity, such as multipods, combs, urchins and dendrites has been obtained, which opens new pathways for more applications in advanced devices [5-8]. The synthesis of 1D, 2D and 3D structures of CdS, one of important II-VI group semiconductor materials, has received tremendous attention because of its versatility in the range of applications, including solar cells, nonlinear optical materials, lightemitting diodes, optoelectronic devices, biological labeling, etc [9-13].

To date, various methods have been employed for the morphology control of CdS. For example, Zhai et al. [14] synthesized single-crystalline rocketlike tetrapodal CdS nanorods thought one-step seed-epitaxial MOCVD approach. Wang et al. [15] reported the crystalline CdS nanorods synthesized by a solid-state process. Gao et al. [16] obtained the multi-armed CdS nanorods-based materials via a one-step surfactant-ligand co-assisted solvlthermal technique. Saunders et al. [17] successfully prepared high aspect ratio quantum-size CdS nanorods with hot colloidal method.

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Among the various reported methods, the hydrothermal method is one of the ideal industrial methods due to its low cost and controllability.

In the present work, we synthesized well-defined hierarchical CdS microflower in high yield by hydrothermal reaction with appropriate surfactant at suitable temperature. To study the effect of polyvinylpyrrolidone (PVP) addition on the CdS crystal morphology, the contrast reactions were carried out. We also examined the products under different reaction time to study the growth history of CdS microflower.

2. Experimental details

1mmol $Cd(NO_3)_2.4H_2O$, 3 mmol thiourea and 0.2 g PVP were dissolved in 32 ml distilled water and sealed in the Teflon-lined stainless steel autoclave. Subsequently, the autoclave was put into electronic oven and maintained at 230 °C for 0.5~8 h. After cooling, the product was collected by centrifuging, washed with water and dried at 70 °C. X-ray diffraction (XRD) measurement was carried out using an X-Ray Diffractometer (D-MAX 2200 VPC) with Cu Kα1 radiation. The X-ray photoelectron spectroscopy (XPS) was measured with Al Ka radiation. The morphology of sample was observed by field-emission scanning electron microscopy (FESEM, JSM-6330F) equipped with an energy-dispersive X-ray (EDS) detector. Absorption spectra of samples were recorded using a spectrophotometer (Hitachi U-4100).

3. Results and Discussion

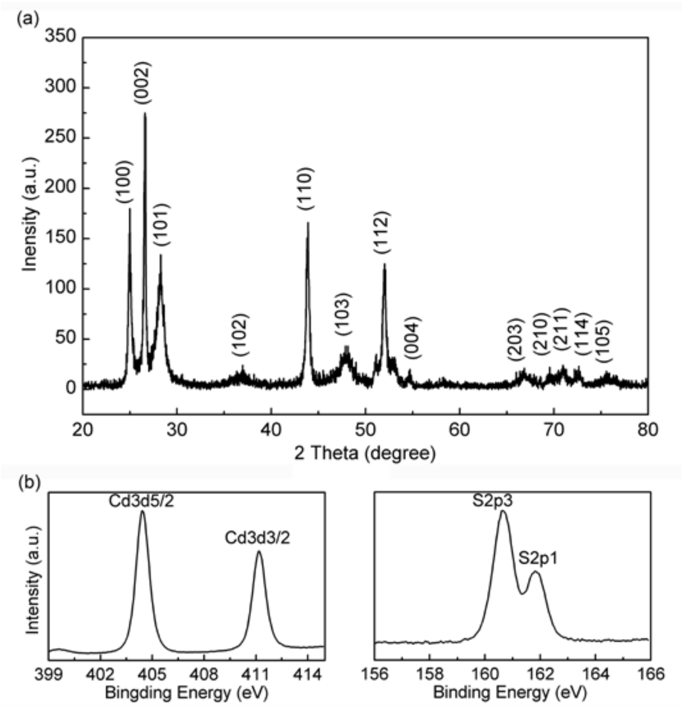

Fig.1 XRD and XPS patterns of product prepared with 0.2 g PVP in reaction system at 230□for 8 h.

The phase composition of the sample was examined by XRD. As shown in Fig.1a, the sample was of good crystalline nature and all diffraction peaks can be conclusively indexed as hexagonal structure with the lattice constants of a=4.132 Å and c=6.734 Å, which were consistent with the values in the standard card (JCPDS 65-3414). No characteristic peaks from other crystalline impurities were observed. These indicated that an addition of PVP had no effect on the crystal phase of the products and CdS was the only product after hydrothermal reaction. Compared with the standard reflection, the XRD pattern shows a relatively strong and narrow (002) diffraction peak, as previous reports have mentioned that CdS crystals with short rod-like morphology would lead to this phenomenon due to a preferred growth direction of the [001] axis [18-19]. The XPS measurement was also carried out to investigate the compositional information of the as-prepared products. As shown in Fig.1b, the peaks of XPS spectra appeared at 404.44, 411.17, 160.66 and 161.82 eV, which corresponded to Cd3d5/2, Cd3d3/2, S2p3 and S2p1, respectively. It was evident that the product was CdS.

The effect of the PVP addition on the morphology of resultant CdS was investigated. Figure 2 shows the morphologies of final CdS products without and with PVP in the hydrothermal system. Without the addition of PVP, the obtained product has brush-like morphology. The SEM image (Fig.2a) shows that the product consists almost entirely of such brush structures. The individual CdS brush is composed of a long central trunk with a mean length of 2-3 μm and several rows of branches. The rows of branches arrange in a symmetry array, separated by ~90°. The branches in the same row are parallel to each other, which emerge at about 90° with respect to the central trunk. When 0.2 g PVP was introduced into the solution, flower-like structures with mean scales of 3 μm were formed (Fig. 2b). The individual CdS microflower is composed of many relatively long petals with a mean length of 1-2 μm and several rows of branches. The petals of microflower have the similar structure to the CdS brushes obtained without PVP in hydrothermal system except the shorter branches and diverse angles of branches to trunk. The stoichiometric relation between Cd and S elemensts on petals and cores of microflower was confirmed by EDS analysis, suggesting there were no organic compounds such as PVP residual in the complex structures. From the contrast experiment, it was found that PVP played a great role in the formation of CdS microflower structure.

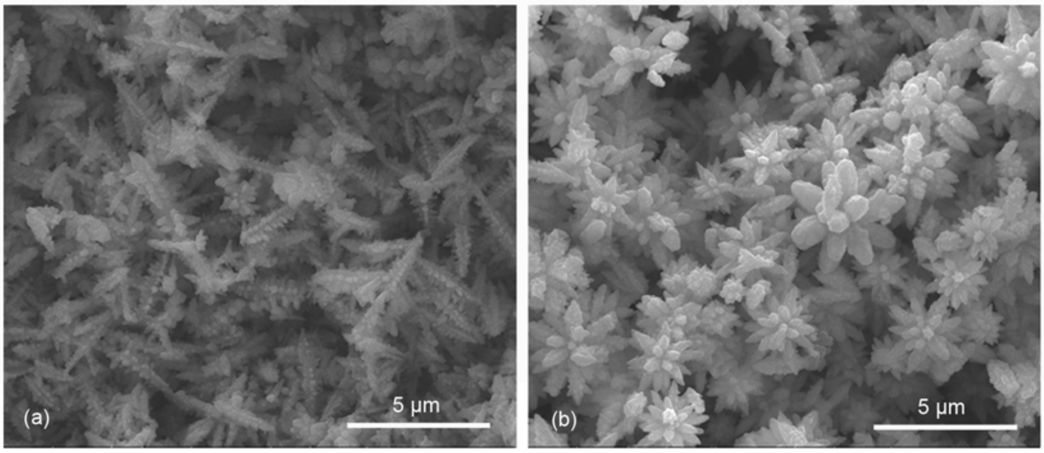

Fig.2 SEM images of CdS crystals obtained (a) without PVP and (b) with 0.2 g PVP in hydrothermal system at 230℃ for 8 h.

We performed the synthesis under different reaction time to investigate the morphology evolution of the CdS microflower and the corresponding SEM images of the as-prepared samples were illustrated in Fig.3. The obtained product was composed of highly uniform spherical particles at the very early stage of 0.5 h (Fig.3a).These spherical particles possessed rough surfaces and the diameter was ca. 350 nm. When reaction time increased from 0.5 to 1.0 h, the spherical particles changed into star-like particles with the diameter of ca. 750 nm (Fig.3b). Some short petals grew out of the original spherical core extending towards several directions. After 1.5 h reaction, the flower-like product with the mean diameter of 2 μm was formed (Fig.3c). The surface of the petals was smooth as shown in inset of Fig.3c. When the reaction time was further prolonged to 8 h, the mean size of microflower increased to 4 μm (Fig.3d). The petals further extended and the branches emerged from the petals. Then the CdS microflowers with hierarchical petals were obtained (inset of Fig.3d).

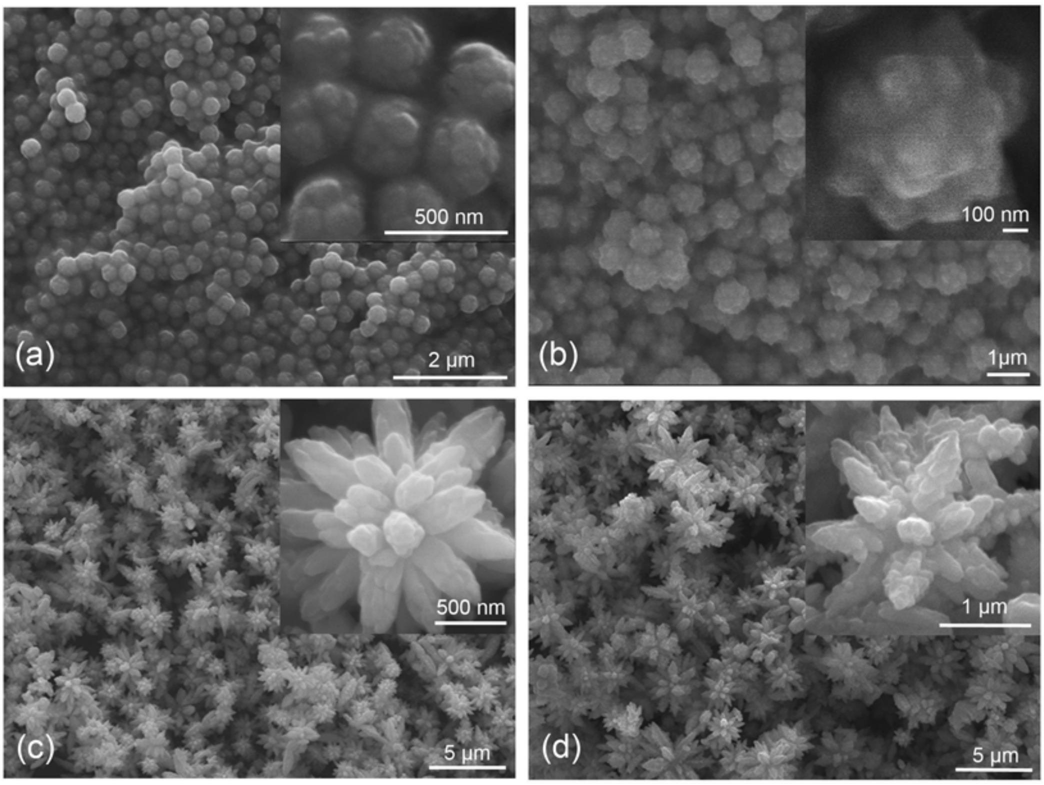

Fig.3 SEM images of CdS crystals obtained with 0.2 g PVP in reaction system at different reaction times: (a) 0.5 h, (b) 1 h, (c) 1.5 h and (d) 8h.

It was known that thiourea can act as not only the sulfur source but also functional groups in crystalline frameworks which contributed to the formation of brush-like CdS [20]. In the reaction process, thiourea was selectively adsorbed on a specific facet of initially formed CdS particles, which decreased surface energy of this face and leaded to its preferential growth. So when there was no PVP in reaction system, the trunks of CdS brushes grew at one direction. At the same time, the adsorption of thiourea on the side surface made it possible to form well-assembled branches to the central trunk. When PVP was added, the different selectively adherence of thiourea and PVP on CdS made the multi-direction growth of petals and further formed diverse angles of branches to the central trunk of petals.

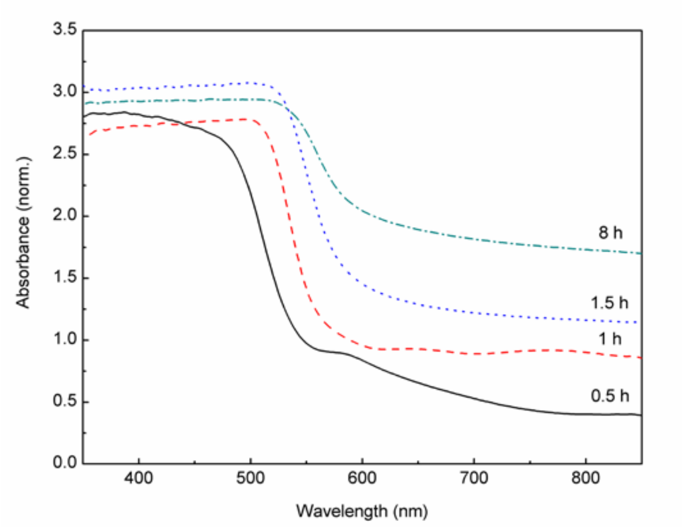

Fig.4 UV-vis absorption spectra of samples obtained at different reaction time.

UV-vis absorption spectra data which is related to the band gap can be used to assert structural variation of material. Figure 4 presents the UV-vis absorption spectra of samples obtained at different reaction time. The star-like CdS shows a slightly red-shifted absorption spectrum from that of the spherical CdS, and the absorption spectrum for the CdS microflower is further red-shifted, which can attribute to the increasing size of the products. The corresponding absorption edges for products obtained at reaction time of 0.5-8 h are around 560, 570, 580, and 610 nm, respectively. Generally, the band gap value can be calculated via the equation of Eg =1240/λ, where λ is the wavelength of the absorption edge. Then, the band gap values of the samples for different reaction time are 2.21, 2.18, 2.14 and 2.03 eV, respectively. These results confirm the size and shape-dependent properties of CdS.

4. Conclusions

We have demonstrated the preparation of CdS microflowers via a facile hydrothermal process. The product was in a pure hexagonal phase. The addition of PVP was found to be responsible for the formation of the hierarchical CdS microflowers. The spheres, star-like particles and microflowers with different petals can be obtained by easily changing the reaction time. The band gap of CdS changed according to the morphology. This controllable hydrothermal process provides a simple way to fabricate the inorganic materials with specific morphology and properties.

Acknowledgments

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References

[1] S.K. Poznyak, D.V. Talapin, E.V. Shevchenko, H. Weller, Nano Lett **4**, 693(2004).

[2] C. Burda, X. Chen, R. Narayanan, M.A. El-Sayed, Chem.Rev. **105**, 1025(2005).

[3] A.P. Alivisatos, Science **271**, 933(1996).

[4] H. Yang, N. Coombs, G.A. Ozin, Nature **386**, 692(1997).

[5] H. Chu, X. Li, G. Chen, W. Zhou, Z. Jin, J. Xu, Y. Li, Crystal Growth & Design **5**, 1801(2005).

[6] H. Yan, R. He, J. Johnson, M. Law, R.J. Saykally, P. Yang,. J. Am. Chem. Soc. **125**, 4728(2003).

[7] H.X. Bai, L.X. Zhang, Y.C. Zhang, Materials Letters 63, 823(2009).

[8] G. Sun, B. Dong, M. Cao, B. Wei, C. Hu, Chem. Mater DOI: 10.1021/cm103441u.

[9] T. Zhai, X. Fang, Y. Bando, Q. Liao, X. Xu, H. Zeng, Y. Ma, J. Yao, D. Golberg, Acs Nano **3**, 949(2009).

[10] T. Gao, T. Wang, Crystal Growth & Design **10**, 4995(2010)..

[11] L. Fan, R. Guo, Crystal Growth & Design **9**, 1677(2009).

[12] L.L. Beecroft, C.K. Ober, Chem. Mater **6**, 1302(1997).

[13] M. Bruchez, M. Moronne, P. Gin, S. Weiss , A.P. Alivisatos, Science 281, 2013(1998).

[14] T. Zhai, Z. Gu, H. Zhong, Y. Dong, Y. Ma, H. Fu, Y. Li, J. Yao, Crystal Growth & Design **7**, 488(2007).

[15] W. Wang, L. Ao, G. He, G. Zhang, Mater Lett **62**, 1014(2008).

[16] F. Gao, Q. Lu, S. Xie, D. Zhao, Advanced Materials **14**, 1537(2002).

[17] A.E. Saunders, A. Ghezelbash, P. Sood, B.A. Korgel, Langmuir **24**, 9043(2008).

[18] J. Yang, J.H. Zeng, S.H. Yu, L.Yang, G.E. Zhou, Y.T. Qian, Chem. Mater. **12**, 3259(2000).

[19] Y. Li, D. Xu, Q. Zhang, D. Chen, F. Huang, Y. Xu, G. Guo, Z. Gu, Chem. Mater. **11**, 3433(1999).

[20] R. Custelcean, Chem. Commun. **21**, 295(2008).