



Controlled Synthesis of Self-Assembled CdS Hierarchical Microspheres Through a Mixed-Solvothermal Route†

CHONGHAI DENG^{1,*}, HANMEI HU², PENG DU², CHENGLIANG HAN¹, CHANGAN TIAN¹ and BENHONG YANG¹

¹Department of Chemical and Materials Engineering, Hefei University, Hefei 230022, P.R. China

²School of Materials and Chemical Engineering, Anhui University of Architecture, Hefei, P.R. China

*Corresponding author: Tel: +86 551 2158436; E-mail: chdeng@hfuu.edu.cn

AJC-11325

Three kinds of hierarchical three-dimensional (3D) hexagonal CdS microspheres with different building blocks (nanoparticle-based microspheres, nanosheet-based microspheres and nanorod-based microspheres) were fabricated using $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ and NH_2CSNH_2 as starting materials through a facile mixed-solvothermal route. Various techniques have been used to characterize the prepared products, such as XRD, FESEM, TEM and UV-visible absorption spectroscopy. The experimental results indicated that the morphologies of CdS microcrystals were greatly affected by the volume ratio of two different solvent. When the volume ratio of ethylenediamine and ethanol were changed from 2:1, through 1:1 to 1:2, the building units of CdS microspheres could be changed from nanoparticles, through nanosheets to nanorods. UV-Vis absorption spectra confirmed that as-obtained three kinds of microspheres all have obvious quantum-confinement effect.

Key Words: CdS, Microstructures, Solvothermal technique, Nanomaterials.

INTRODUCTION

In recent years, many efforts have been developed to shape-controllable hierarchical architectures because that hierarchical assembly of nanoscale building blocks is a crucial step toward the realization of functional nanosystems and represents a significant challenge in the field of nanoscience¹⁻³. As an important II-VI semiconductor with a direct band gap of 2.53 eV, CdS has received considerable attention because of its potential applications in solar cell⁴, laser light-emitting diodes⁵, photodetectors⁶ and photocatalytic materials⁷.

Over the past decades, considerable efforts have been focused on synthesizing CdS hierarchical architectures. Xiong *et al.*⁸ fabricated CdS with various novel hierarchical nanostructures assembled from nanobelts/nanowires *via* a hydrothermal technique. Gao *et al.*⁹ prepared CdS hierarchical spindles by a hydrothermal process. Guo *et al.*¹⁰ synthesized CdS spheres composed of hexagon-based pyramids through a facile solution-phase reaction. Zhang *et al.*¹¹ prepared novel CdS dendritic nanoarchitectures *via* a facile template-free hydrothermal process. Xu *et al.*¹² fabricated CdS hollow nanospheres consisting of nanoparticles through hydrothermal route. Ao *et al.*¹³ synthesized CdS mesospheres composed of

radially arranged nanorods by hydrothermal method without any surfactant. Wang *et al.*¹⁴ prepared CdS hierarchical microspheres constructed of nanosheets through hydrothermal reaction using sodium dodecylbenzenesulfonate (SDBS) as structure directing reagent.

Herein, we developed a mixed-solvothermal process to synthesize hierarchical 3D CdS microstructures by the reaction of $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ and NH_2CSNH_2 at 160 °C for 12 h. The morphologies of CdS microstructures could be manipulated from nanoparticle-based microsphere, through nanosheet-based microsphere to nanorod-based microsphere by only changing the volume ratio of ethylenediamine and ethanol from 2:1, through 1:1 to 1:2 while maintaining other conditions constant.

EXPERIMENTAL

All chemicals (analytical grade reagents) were purchased from Shanghai Chemical Reagents Co. and used without further purification.

General procedure: In a typical experimental procedure, 1 mmol $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ and 2 mmol NH_2CSNH_2 were respectively dissolved in three beakers containing 40 mL mixed solvent of ethylenediamine and ethanol (the volume ratio of

†Presented to The 5th Korea-China International Conference on Multi-Functional Materials and Application.

ethylenediamine and ethanol is 2:1, 1:1 and 1:2). After stirring for 20 min, the obtained solutions were respectively transferred into three 60 mL Teflon-lined autoclaves. These autoclaves were sealed and maintained at 160 °C for 12 h. After the reaction was completed, the resulting solid products were filtered off, washed with absolute ethanol and distilled water for several times and then finally dried in a vacuum at 60 °C for 4 h. The collected CdS powders were signed as Sample A, Sample B and Sample C, respectively.

Detection method: The phase purity of the as-synthesized products was examined by X-ray diffraction (XRD) using a Dandong Y-2000 X-ray diffractometer equipped with graphite monochromatized $\text{CuK}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$). Field-emission scanning electron microscope (FESEM) images of the samples were taken on a field-emission microscope (Sirion 200, 15kV). The transmission electron microscope (TEM) images of the samples were performed on a JEOL-2010 transmission electron microscope with an accelerating voltage of 200 kV. The optical properties of the samples were studied using a UV-Vis spectrophotometer (UV-2550).

RESULTS AND DISCUSSION

The typical XRD patterns of the as-prepared CdS products (Sample A: $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2:\text{C}_2\text{H}_5\text{OH} = 2:1$, Sample B: $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2:\text{C}_2\text{H}_5\text{OH} = 1:1$ and Sample C: $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2:\text{C}_2\text{H}_5\text{OH} = 1:2$) are shown in Fig. 1. All diffraction peaks can be indexed as CdS hexagonal structure with cell constants $a = 4.12 \text{ \AA}$ and $c = 6.72 \text{ \AA}$, which was in good agreement with the reported data (JCPDS File, 41-1049, $a = 4.140 \text{ \AA}$, $c = 6.719 \text{ \AA}$). No characteristic peaks related with CdO, $\text{Cd}(\text{OH})_2$ and other cadmium compound were detected.

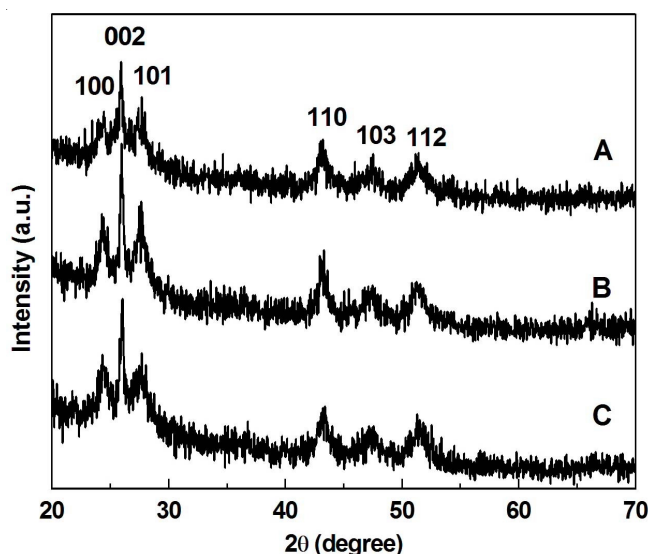


Fig. 1. XRD pattern of the as-prepared sample

The morphologies and structures were detected by FESEM and TEM. The as-prepared CdS products (Sample A, Sample B and Sample C) take on different morphologies, which are shown in Figs. 2. Fig. 2(a) and (b) give the pictures of Sample A obtained in the mixed solvent of $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ and $\text{C}_2\text{H}_5\text{OH}$ with the volume ratio of 2:1, which indicates that the CdS products are sphere-like microstructures with diameters ranging from 0.5 to 1.5 μm . The enlarged image (inserted at the upper right corner of Fig. 2(b)) shows that these CdS microspheres with considerably rough surfaces are assembled from plenty of small nanoparticles with average diameter of 15 nm. The TEM image of a single microsphere

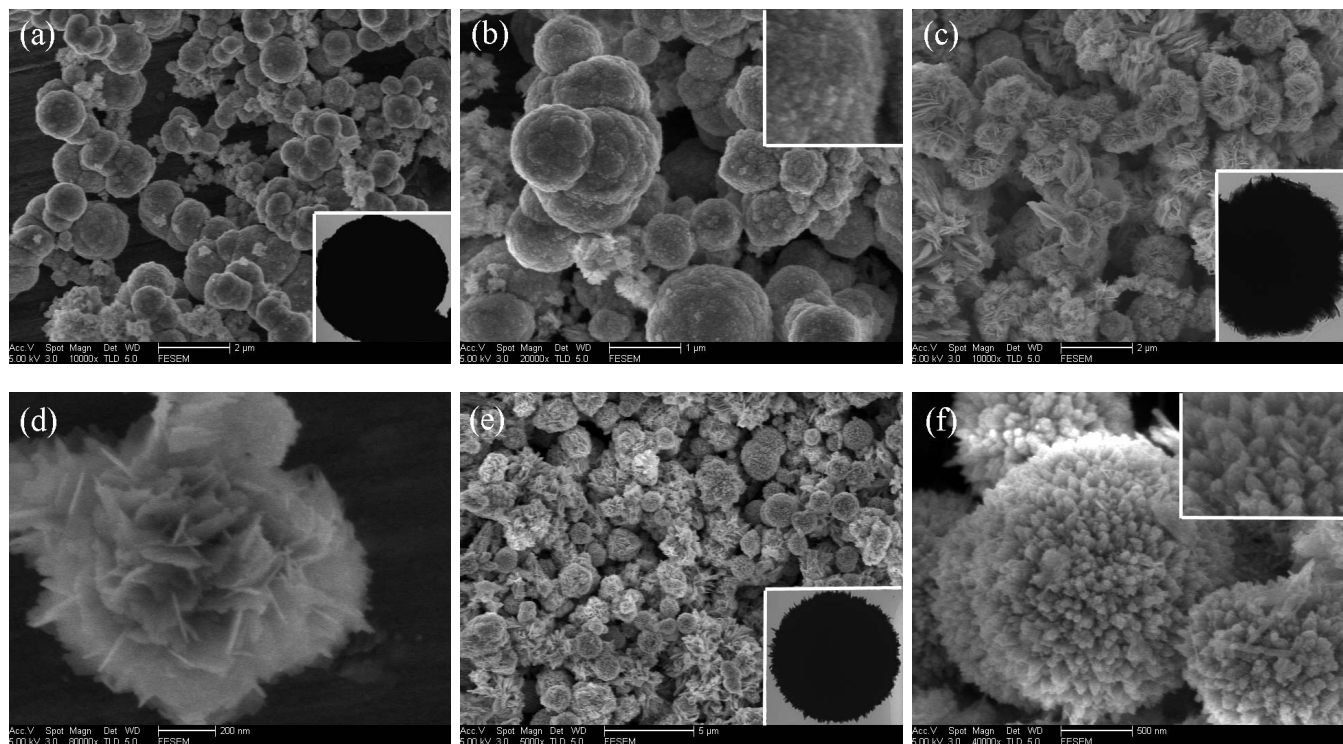


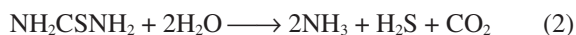
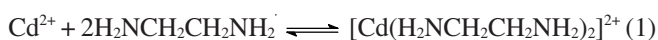
Fig. 2. Morphology of CdS products prepared in mixed solvent of ethanediamine and ethanol: (a,b) $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2:\text{C}_2\text{H}_5\text{OH} = 2:1$, (c,d) $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2:\text{C}_2\text{H}_5\text{OH} = 1:1$, (e,f) $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2:\text{C}_2\text{H}_5\text{OH} = 1:2$

(inserted at the lower right corner of Fig. 2(a)) clearly demonstrates that the prepared CdS microspheres are compact and solid, which agrees with the FESEM results.

Fig. 2(c) and (d) show the morphologies of Sample B obtained in the mixed solvent of $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ and $\text{C}_2\text{H}_5\text{OH}$ with the ratio of 1:1, which reveals that the CdS products mainly take on the morphology of flower-like microspheres. These microspheres are loose and the size is about in the range of 1-2 μm . By closely observing, we discover that these microspheres are build up by tens to hundreds of nanosheets with average thicknesses of 20 nm. Fig. 2(d) is the FESEM image of a beautiful flower-like microsphere with diameter of 1 μm , which displays that the building blocks of nanosheets grow from the same nuclei center and intersect with each other. The picture inserted in Fig. 2(c) is the representative TEM image of a single microsphere, which agrees with the FESEM results.

Fig. 2(e) and (f) present the morphologies of Sample C obtained in the mixed solvent of $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ and $\text{C}_2\text{H}_5\text{OH}$ with the ratio of 1:2, which shows that the CdS products are microspheres consisting of nanorods. The size of these microspheres is 1-2 μm . Fig. 2(f) is a high-magnification FESEM image, which further reveals that the microspheres are constructed by hundreds of nanorods with average diameters of 30 nm radiating from the same nuclei center. The enlarged image inserted in Fig. 2(f) displays that there exist many pores among adjacent nanorods. The picture inserted in Fig. 2(e) is the representative TEM image of a single microsphere composed of nanorods, which agrees with the FESEM results.

In the present reaction system, as a complexing reagent, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ can react with metal Cd^{2+} to form $[\text{Cd}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2]^{2+}$ complexes at low temperature. Under solvothermal (elevated temperature and pressure) conditions, the preformed $[\text{Cd}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2]^{2+}$ complexes decompose to release dissociative meta ion Cd^{2+} . Meanwhile, as a alkaline reagent, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ can hydrolyze and produce alkaline solution (OH^-). Then, meta ion Cd^{2+} combine with H_2S which comes from the hydrolyzation of thiourea to form CdS products in the alkaline solution. The whole reaction process can be described as follows:



With respect to the exact formation mechanism of as-prepared nanoparticle-based, nanosheet-based and nanorod-based microspheres, more in-depth studies are underway. But we think that the morphology of CdS products were greatly influenced by solvent effect produced by mixed solvent of ethanediamine and ethanol. Under the mixed-solvothermal condition, the volume ration of ethanediamine and ethanol would affect the nuclei and growth of CdS building blocks and further determine its orientated aggregation growth to form particular hierarchical microstructures. In addition, comparative experiments were also performed by only using single solvent and simultaneously keeping other conditions unchanged. Fig. 3(a) and (b) are the FESEM images of CdS obtained in pure

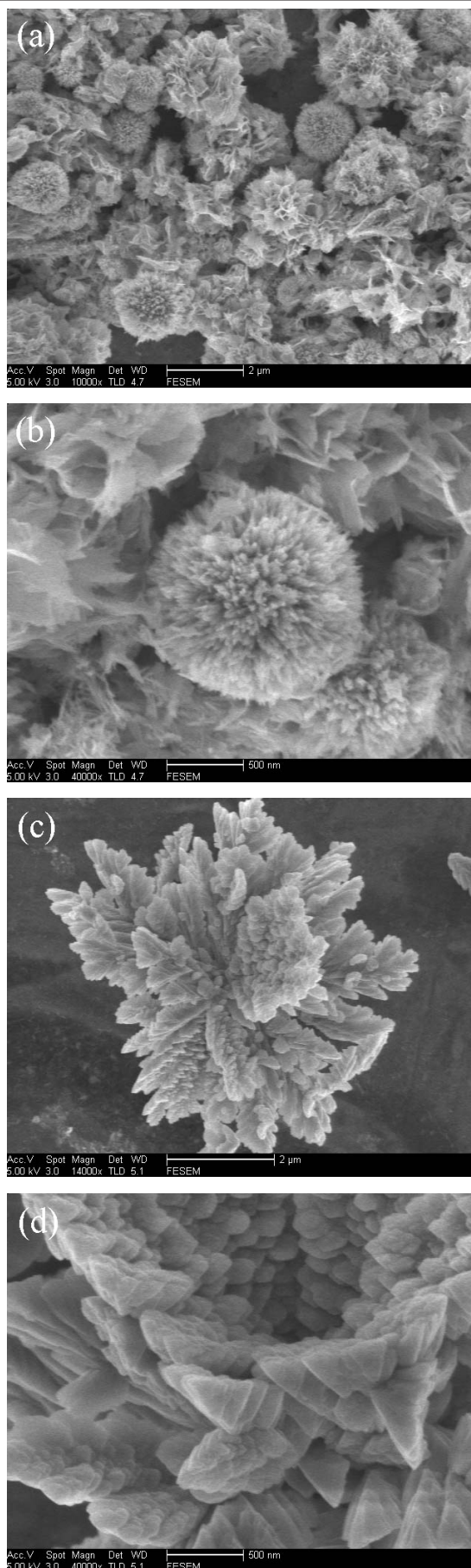


Fig. 3. FESEM images of CdS products obtained using single solvent: (a,b) $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$, (c,d) $\text{C}_2\text{H}_5\text{OH}$

ethanediamine, which show that there exist the mixture of nanosheet-based and nanorod-based microspheres in the products. When using pure ethanol as solvent, the CdS products take on dendritic microstructures which were made up of triangular nanoparticles (Fig. 3(c) and (d)).

Fig. 4 shows UV-vis absorption spectra of the synthesized three different kinds of CdS microspheres. The blue shifted absorption at 491 nm (Sample A), 497 nm (Sample B), 475 nm (Sample C) were observed compared with the bandgap of bulk CdS¹⁵, which can be attributed to the excitonic absorbance due to the quantum confinement. It is noted that nanorod-based microspheres (Sample C) have much more quantum-confinement effect.

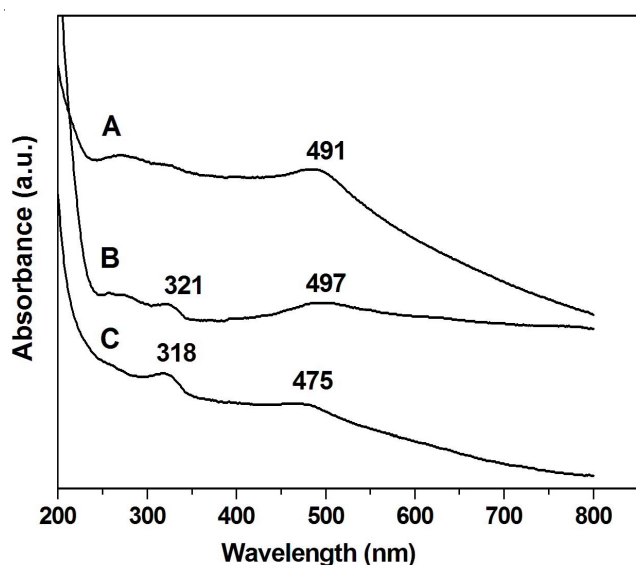


Fig. 4. UV-Vis absorption spectra of the synthesized CdS microspheres

Conclusion

In conclusion, by employing a simple mix-solvothermal method, various CdS hierarchical microstructures (nanoparticle-based microsphere, nanosheet-based microsphere and nanorod-based microsphere) have been successfully synthesized. The experimental results have indicated that as-prepared

CdS products are single phase with hexagonal structure. The volume ratio of two different solvent (ethanediamine and ethanol) is a key factor influencing the morphology of CdS products. UV-Vis absorption spectra confirmed that as-obtained three kinds of microspheres all have obvious quantum-confinement effect, which may make them have potential applications in future optoelectronic nanodevices.

ACKNOWLEDGEMENTS

This work was supported by the Science and Research Foundation for Development of Hefei University (Grant No. 11KY01ZD), the Fifth Science and Technology Foundation of Outstanding Youth of Anhui Province (Grant No. 10040606Y25), the Natural Science Foundation of Anhui Educational Committee (Grant No. KJ2011A247) and the National Natural Science Foundation of China (Grant No.51102073).

REFERENCES

1. I.A. Aksay, M. Trau, S. Manne, I. Honma, N. Yao, L. Zhou, P. Fenter, P.M. Eisenberger and S.M. Gruner, *Science*, **273**, 892 (1996).
2. F. Caruso, *Adv. Mater.*, **13**, 11 (2001).
3. H.Q. Yan, R.R. He, J. Johnson, M. Law, R.J. Saykally and P.D. Yang, *J. Am. Chem. Soc.*, **125**, 4728 (2003).
4. M.A. Arturo, *Sol. Energy*, **80**, 675 (2006).
5. O. Hayden, A.B. Greytak and D.C. Bell, *Adv. Mater.*, **17**, 701 (2005).
6. N. Kouklin, L. Menon, A.Z. Wong, D.W. Thompson, J.A. Woollam, P.F. Williams and S. Bandyopadhyay, *Appl. Phys. Lett.*, **79**, 4423 (2001).
7. A. Mills and G. Williams, *J. Chem. Soc. Farad. Trans. I*, **85**, 503 (1989).
8. S.L. Xiong, X.G. Zhang and Y.T. Qian, *Cryst. Growth Des.*, **9**, 5259 (2009).
9. X.B. He and L. Gao, *Mater. Lett.*, **63**, 995 (2009).
10. L. Fan and R. Guo, *Cryst. Growth Des.*, **9**, 1677 (2009).
11. D.J. Wang, D.S. Li, L. Guo, F. Fu, Z.P. Zhang and Q.T. Wei, *J. Phys. Chem. C*, **113**, 5984 (2009).
12. G.F. Lin, J.W. Zheng and R. Xu, *J. Phys. Chem. C*, **112**, 7363 (2008).
13. C. Wang, Y.H. Ao, P.F. Wang, J. Hou, J. Qian and S.H. Zhang, *Mater. Lett.*, **64**, 439 (2010).
14. Y.H. Xu, C. X. Song, Y.W. Sun and D.B. Wang, *Mater. Lett.*, **65**, 1762 (2011).
15. P. Thangadurai, S. Balaji and P.T. Manoharan, *Mater. Chem. Phys.*, **114**, 420 (2009).