Available online at www.sciencedirect.com
SCIENCE DIRECT®
Inorganic Chemistry Communications 7 (2004) 572–575
INORGANIC CHEMISTRY COMMUNICATIONS
www.elsevier.com/locate/inoche

Shape controlled synthesis of PbS nanocrystals by a solvothermal–microemulsion approach

Junhua Xiang [a], Shu-Hong Yu [a,*], Bianhua Liu [a], Yang Xu [a], Xin Gen [a], Lei Ren [b]

[a] *Hefei National Laboratory for Physical Sciences at Microscale, Department of Materials Science and Engineering, University of Science and Technology of China, Hefei 230026, PR China*
[b] *Biomedical Engineering Research Center, Xiamen University, Xiamen 361005, PR China*

Received 9 February 2004; accepted 19 February 2004
Published online: 10 March 2004

Abstract

Shape controlled synthesis of PbS nanoparticles, cubes, and nanowires has been realized by a so-called solvothermal–microemulsion technique in a sodium dodecyl sulfate (SDS)/hexane/hexanol/water microemulsion system using different sulfur source. The effect of different sulfur source and temperature on the shape of PbS nanocrystallites was investigated. The results demonstrated that the combination of solvothermal process and microemulsion technique could provide a useful tool for the synthesis of other nanocrysals with unusual shape and structures.

Keywords: Solvothermal; Microemulsion; Synthesis; Shape control

Exploration of smart synthetic strategies for fabrication of various forms of low dimensional nanostructures such as nanowires, nanorods, and nanotubes has attracted a lot of attention [1,2]. Especially, shape control of semiconductor nanocrystallites has received a lot of concerns because of their unique electronic, optical properties, as well as important applications in single-electron transistors, nonlinear optics [3]. PbS is an important semiconductor with a narrow band gap of 0.41 eV and has applications in near-IR detector and optical switches [4].

Several kinds of solution methods have been explored for shape control of PbS nanocrystals. Equilateral-triangular, right-angle triangular and rectangularly shaped PbS nanocrystallites have been synthesized under control of monolayers [5]. PbS needles were synthesized in block copolymer polystyrene-*b*-polyvinylpyridine micelles [6]. Cubic- and star-shaped PbS nanocrystals have been synthesized by the thermolysis of single molecule precursor [7].

Recent advances in utilizing soft templates such as micelles, emulsions to control the shape of the inorganic nanocrystals have been reviewed by Pileni [8]. It has been demonstrated that reverse micelles and microemulsion are ideal nanoreactors for the synthesis of anisotropic nanoparticles, and even hollow tubes, which have been widely used for the preparation of various inorganic crystals. For example, nanotubes and nanowires of Cd, Cu, and Zn chalcogenides have been obtained from solutions containing a surfactant such as Triton 100-X [2,9]. Using reverse micelle and microemulsion nanoreactors for the preparation of PbS nanocrystals has also been reported [10–12]. Uniform PbS nanocubes have been synthesized by use of a surfactant [13]. Dendrite PbS structures have been synthesized by a surfactant-assisted hydrothermal growth method [14], or by use of lead acetate and acetic acid as precursors [15]. Closed PbS nanowires can be prepared by hydrothermal method which uses organic molecules as additive [16].

In recent years, the combination of microemulsion technique with hydrothermal process has been explored for the preparation of nanocrystals such as impurities-activated ZnS nanocrystallites [17], CdS nanoclusters

* Corresponding author. Tel./fax: +86-551-3603040.
E-mail address: shyu@ustc.edu.cn (S.-H. Yu).

1387-7003/$ - see front matter © 2004 Published by Elsevier B.V.
doi:10.1016/j.inoche.2004.02.023

and nanorods [18], Cu_2S flakes and nanodisks [19], and NiS nanosheets [20].

In this communication, we report the controlled synthesis of PbS nanocrystals with different shapes by a solvothermal–microemulsion technique. The effect of different sulfur source and temperature on the shape of PbS nanocrystallites was investigated.

Analytical grade hexane, hexanol, thiourea and $Pb(NO_3)_2$ were purchased from Shanghai Chemical Industrial Company. Sodium dodecyl sulfate (SDS) was purchased from Guangfu Chemical Engineering Institute of Tianjin and $Na_2S \cdot 9H_2O$ was purchased from Dongda Chemical Plant of Tianjin. All materials were used without further purification. The reaction was carried out in a 57 ml capacity Teflon-lined stainless steel autoclave, which was done in a digital type temperature controlled oven.

In a typical experiment, 0.01 mol SDS was dissolved in the mixed solution of 30 ml hexane and 9 ml hexanol that was cosurfactant. Then 7.2 ml 0.1 M $Pb(NO_3)_2$ aqueous solution was added to the mixture under stirring, which made the molar ratio of water and surfactant (w) 40 and the concentration of SDS was about 0.21 M based on overall volume of the microemulsion. After stirring for 5 min, a certain of amount $Na_2S \cdot 9H_2O$ (or thiourea) was added. The resulting microemulsion was held at room temperature for three days or transferred into a 57 ml capacity stainless Teflon-lined autoclave after stirring for 30 min at room temperature. The autoclave was sealed and maintained at 120 °C for 12 h, then allowed to cool to room temperature naturally. The obtained precipitates were centrifuged, washed several times using distilled water and absolute ethanol, and dried in vacuum at 60 °C for 6 h.

The products were characterized by X-ray diffraction pattern (XRD), recorded on a MAC Science Co. Ltd. MXP 18 AHF X-ray diffractometer with monochromatized Cu Kα radiation ($\lambda = 1.54056$ Å). Transmission electron microscopy analysis was performed on a Hitachi (Tokyo, Japan) H-800 transmission electron microscope (TEM) at an accelerating voltage of 200 kV.

Pure PbS phase was obtained using $Na_2S \cdot 9H_2O$ as sulfur source (Fig. 1). All reflection peaks of the product can be indexed as a pure face-centered cubic structure with cell parameter $a = 5.936$ Å, which is in good agreement with the previous literature (JCPDS Card No. 05-0592). The broadened diffraction peaks in Fig. 1(b) indicated that the particle sizes of the product that was prepared at room temperature after ageing for three days were very small. The calculated size based on the Scherrer's equation was 5–7 nm, which was consistent with that evaluated by TEM (Fig. 2(a)).

When the temperature was increased to 120 °C and the reaction time was 12 h, the fact that the diffraction peaks (Fig. 1(b)) became sharper implied that the particles had grown up. TEM image in Figs. 2(b) and (d)

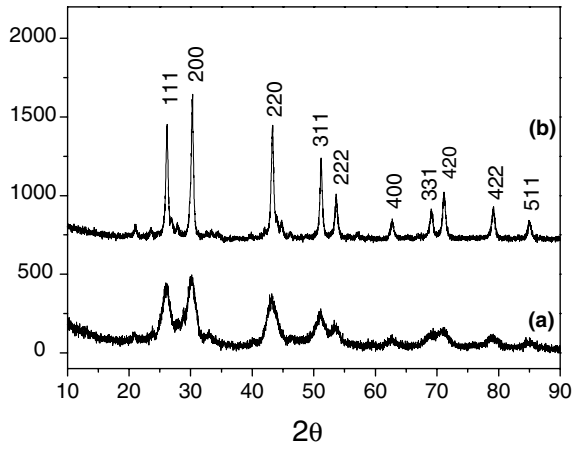

Fig. 1. XRD patterns of PbS nanocrystals prepared at room temperature (a) and 120 °C (b) using Na_2S as sulfur source.

showed that most of PbS nanoparticles grew into nanowires with an average diameter of 20–40 nm and length up to several micrometers. The electron diffraction pattern in Fig. 2(c) indicated that the product were polycrystalline, which can be readily indexed as cubic structure. An enlarged TEM image in Fig. 2(d) indicated that the surface of the nanowires is rough and also some aggregated nanoparticles were observed. It is obvious that the formation of nanowires were not directly due to the templating effects of the microemulsion, but resulted from a cooperative effect of the soft template effect and the anisotropic crystal growth at higher temperature. The detailed formation process of the nanowires is complicated and needs to be investigated further.

Cubic-shaped PbS nanocrystal with side length of 300–500 nm was synthesized when thiourea was used as sulfur source under identical conditions (Fig. 3(a)). A typical growing cube is shown in Fig. 3(b). The electron diffraction pattern (Fig. 3(c)) taken from $\langle 0\,0\,1 \rangle$ zone indicated that the PbS cubes were single crystal. The slow release S^{2-} anions due to the hydrolysis of thiourea can significantly affect the kinetic growth of PbS nanocrystals. In addition, the bonding of thiourea-to-Pb is stronger than the weak binding between PbS crystals and the SDS, resulting in the enhanced growth of PbS crystals, which could be similar to that argued by Cheon et al. [7a]. Since the formation of two dimensional nuclei on $\{1\,1\,1\}$ faces has a low activation energy in weakly binding capping molecules [21], the growth on $\{1\,1\,1\}$ faces will be favored, leading to the observed cubic shape (isotropic forms). This is consistent with that reported previously where weakly binding ligand such as dodecylamine for the synthesis of cubic PbS crystals [7a]. The results demonstrated that the choice of different sulfur sources will result in the PbS nanoparticles with different shapes in the same microemulsion system.

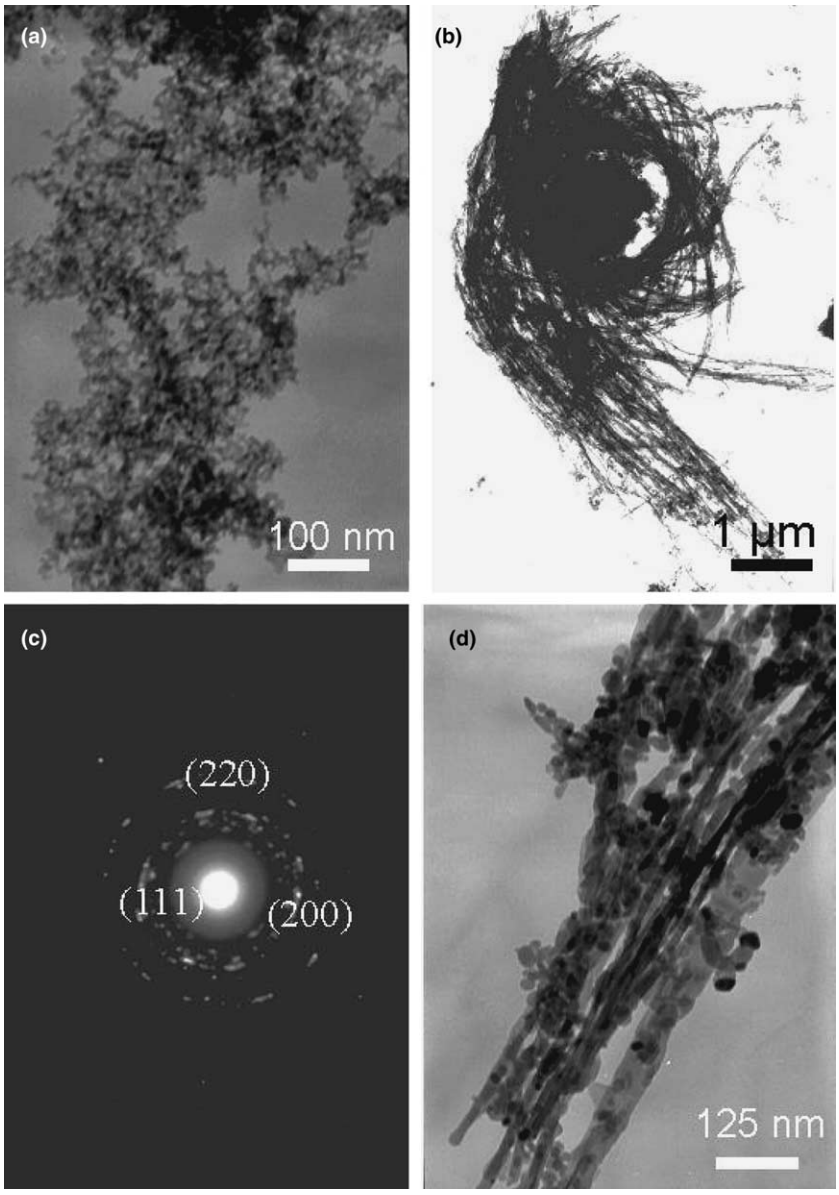

Fig. 2. TEM images of PbS nanocrystals synthesized using Na_2S as sulfur source: (a) at room temperature, 3 days; (b), (d) at 120 °C, 12 h. (c) Electron diffraction pattern of PbS nanowires shown in (b).

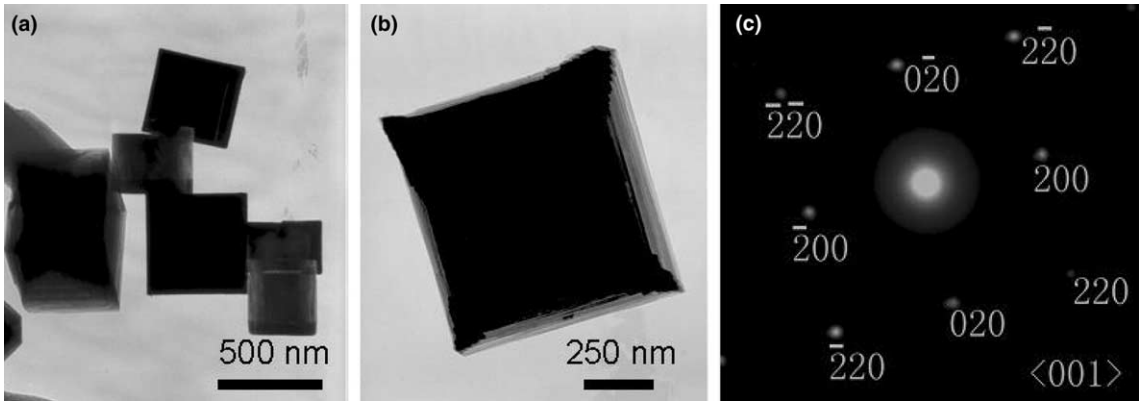

Fig. 3. TEM images of PbS cubes prepared using thiourea as sulfur source, 120 °C, 12 h: (a), (b) TEM images. (c) Selected area electron diffraction pattern of the cube shown in (b).

In summary, a solvothermal–microemulsion technique was applied for the shape controlled synthesis of PbS crystals in a sodium dodecyl sulfate (SDS)/hexane/hexanol/water microemulsion system. The results showed that the shape of the PbS crystals could be varied by using different sulfur source and controlling the reaction temperature in the same microemulsion system, underlying that the choice of suitable sulfur source could add another parameter for adjusting the shape of PbS nanocrystals. The further optimization of this synthesis route is still needed to further improve the quality of the PbS nanocrystals. The so-called solvothermal–microemulsion technique could provide a useful tool for the synthesis of other nanocrysals with different shape, structures, and crystallinity.

Acknowledgements

S.H. Yu thanks, for the special funding support from the Century Program of Chinese Academy of Sciences, the Distinguished Young Fund (Grant No. 20325104), and Project Grant No. 50372065, for the financial support from National Science Foundation of China (NSFC).

References

[1] Y.N. Xia, P.D. Yang, Y.G. Sun, Y.Y. Wu, B. Mayers, B. Gates, Y.D. Yin, F. Kim, Y.Q. Yan, Adv. Mater. 15 (2003) 353.
[2] C.N.R. Rao, F.L. Deepak, G. Gundiah, A. Govindaraj, Prog. Solid State Chem. 31 (2003) 5.
[3] (a) D.L. Klein, R. Roth, A.K.L. Lim, A.P. Alivisatos, P.L. Mceuen, Nature 389 (1997) 699;
(b) Y. Wang, Acc. Chem. Res. 24 (1991) 133.
[4] (a) P. Gadenne, Y. Yagil, G. Deutscher, J. Appl. Phys. 66 (1989) 3019;
(b) A.M. Malyarevich, V.G. Savitsky, I.A. Denisov, P.V. Prokoshin, K.V. Yumashev, E. Raaben, A.A. Zhilin, A.A. Lipovskii, Phys. Stat. Sol. b 224 (2001) 253.
[5] (a) X.K. Zhao, J. Yang, L.D. McCormick, J.H. Fendler, J. Phys. Chem. 96 (1992) 9933;
(b) J.P. Yang, J.H. Fendler, J. Phys. Chem. 99 (1995) 5505.
[6] T. Schneider, M. Haase, A. Kornowski, S. Naused, H. Weller, S. Forster, M. Antonitti, Ber. Bunsenges. Phys. Chem. 101 (1997) 1654.
[7] (a) S.M. Lee, Y.W. Jun, S.N. Cho, J. Cheon, J. Am. Chem. Soc. 124 (2002) 11,244;
(b) T. Trindade, P. O'Brien, X.M. Zhang, M. Motevalli, J. Mater. Chem. 7 (1997) 1011;
(c) G. Kraeuter, P. Favreau, W.S. Rees Jr., Chem. Mater. 6 (1994) 543.
[8] M.P. Pileni, Nature Mater. 2 (2003) 145.
[9] C.N.R. Rao, A. Govindaraj, F.L. Deepak, N.A. Gunari, M. Nath, Appl. Phys. Lett. 78 (2001) 1853.
[10] (a) P. Lianos, J.K. Thomas, Chem. Phys. Lett. 125 (1986) 299;
(b) P. Lianos, J.K. Thomas, J. Colloid. Interface Sci. 117 (1987) 505;
(c) P. Lianos, J.K. Thomas, Mater. Sci. Forum 369 (1988) 25.
[11] (a) J. Eastoe, A.R. Cox, Colloid Surface A 101 (1995) 63;
(b) R. Guo, T.Q. Liu, Colloid Surface A 587 (1997) 123;
(c) H. Wang, J.R. Wang, J.J. Zhu, J. Crystal Growth 246 (2002) 161;
(d) G. Lin, A.X. Cheng, Mater. Chem. Phys. 63 (2000) 30.
[12] B. Zhang, G.H. Li, J. Zhang, Y. Zhang, L.D. Zhang, Nanotechnology 14 (2003) 443.
[13] J. Joo, H.B. Na, T. Yu, J.H. Yu, Y.W. Kim, F.X. Wu, J.Z. Zhang, T. Hyeon, J. Am. Chem. Soc. 125 (2003) 11,100.
[14] D. Kuang, A. Xu, Y. Fang, H. Liu, C. Frommen, D. Fenske, Adv. Mater. 15 (2003) 1747.
[15] Y. Ma, L.M. Qi, J. Ma, H. Cheng, Cryst. Growth Des. 4 (2004) ASAP article.
[16] D.B. Yu, D.B. Wang, Z.Y. Meng, J. Lu, Y.T. Qian, J. Mater. Chem. 12 (2002) 403.
[17] S.J. Xu, S.J. Chua, Appl. Phys. Lett. 73 (1998) 478.
[18] (a) B. Liu, G.Q. Xu, L.M. Gan, C.H. Chew, J. Appl. Phys. 89 (2001) 1059;
(b) P. Zhang, L. Gao, Langmuir 19 (2003) 208.
[19] P. Zhang, L. Gao, J. Mater. Chem. 13 (2003) 2007.
[20] D. Chen, L. Gao, P. Zhang, Chem. Lett. 32 (2003) 996.
[21] T. Sugimoto, J. Colloid Interface Sci. 91 (1983) 51.