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SHORT COMMUNICATION

Controlled Solvothermal Synthesis of PbS Quasi-Nanorods by Calix[4]arene

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A new idea of the nanorods preparation and a novel application of calixarenes are presented. Calix[4]arene was introduced into solvothermal system to produce one-dimensional inorganic nanomaterial. The obtained product was characterized by XRD and TEM. Results of the XRD analysis showed that the product was pure cubic phase of PbS with high crystallinity. TEM images revealed that the diameter and length of the PbS nanorods were about 200 nm and up to 3.5 μm, respectively. Optical properties of the product were also studied. PL emission image showed that the product exhibited an emission peak at 308 nm in ultraviolet region showing a blue shift of 14 nm compared to the bulk material. The formation mechanism of PbS nanorods in the presence of calix[4]arene is discussed.

Keywords: calix[4]arene, PbS, nanorods, solvothermal

The calixarene is a special class of cyclophane capable of binding both neutral and charged guests [1, 2]. The first calixquinone series, calix[4]arenes, provides a prototypical example of electroactive calixarenes. These compounds are capable of undergoing two-electron reductions for each quinine moiety. Extraction of the first electron is generally reversible, while the subsequent elimination of the second one is typically quasi-reversible. The ability of calixarenes to bind alkali, alkaline earth, or transition metals ions, makes the calixarene systems suitable to control reaction speed in synthesis [3—5]. In recent decades, nanomaterials attracted interest of numerous researchers. Though there are a few reports on the cross of supermolecules with nanotechnology [6, 7], calixarene has not been employed for the controlled growth of lead sulfide nanorods.

PbS is a typical semiconductor with unique photoconductive properties [8]. PbS has potential application in production of devices with optical absorption and emission in red and near-infrared region of the electromagnetic spectrum for its especially small direct band gap energy [9]. Many methods have been used to prepare PbS nanomaterials, such as the precipitation method, metallorganic precursor method, solvothermal and hydrothermal methods [10]. Among these methods, solvothermal and hydrothermal methods are typically used for their simplicity, convenient equipment, and high yield [11]. The preparation of PbS nanorods using the solvothermal method has been reported in several papers [12—16]. However, the use of calix[4]arene for the hydrothermal preparation of PbS nanorods is first reported in this paper. It presents not only a new idea in the field of preparation of inorganic salts nanorods, but also a novel application of supermolecules.

Calix[4]arene (Fig. 1) used in this study was synthesized according to [17]. All other reagents were of analytical grade and used without any pretreatment.

During the preparation of PbS nanorods, 0.33 g of lead nitrate ($Pb(NO_3)_2$) and 0.01 g of calix[4]arene were dissolved in toluene at 80 ℃ for 1 h. Then, 0.076

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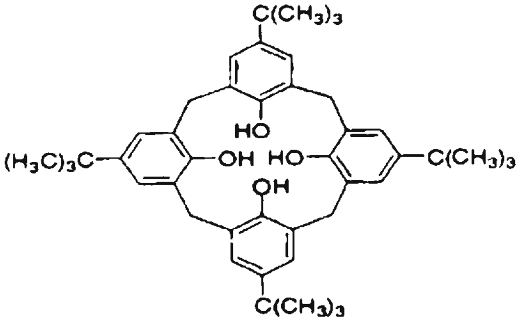

Fig. 1. Planar chemical structure of calix[4]arene.

g of thiourea ($CS(NH_2)_2$) was added into the solution. The mixture was transferred into Teflon-lined autoclave. The autoclave was sealed and heated at 170 ℃ for 24 h. The reaction system was cooled down to room temperature and the product was collected by centrifugation. A black powder was obtained after washing the raw product with deionized water and anhydrous ethanol.

X-Ray powder diffraction pattern (XRD) of the product was measured on a Philips PW1710 X-ray powder diffractometer with CuK_α radiation (λ = 1.5418 Å). The sample morphology was investigated on a JEOL JEM-1230 transmission electron microscope (TEM). The photoluminescence (PL) of the prepared sample was observed under excitation by UV light at 244 nm with a Perkin—Elmer LS-55 fluorescence spectrophotometer.

TEM images of the PbS samples are given in Fig. 2. Fig. 2*a* shows the image of the product prepared in the presence of calix[4]arene. Diameter of synthesized nanorods is about 200 nm and the length is up to 3.5 μm. ED picture inset in TEM image indicates that the product is cubic single crystal phase. Some nanoparticles observed in the image represent a direct reaction between Pb^{2+} and thiourea without the control of calix[4]arene. This assumption is confirmed by the image shown in Fig. 2*b* that presents the morphology of PbS obtained in the absence of calix[4]arene. The products are nanoparticles with diameter of about 70 nm. No one-dimensional nanomaterials were obtained using this procedure. Thus, it can be concluded that calix[4]arene controls the speed of Pb^{2+} reaction with thiourea and induces the formation of nanorods.

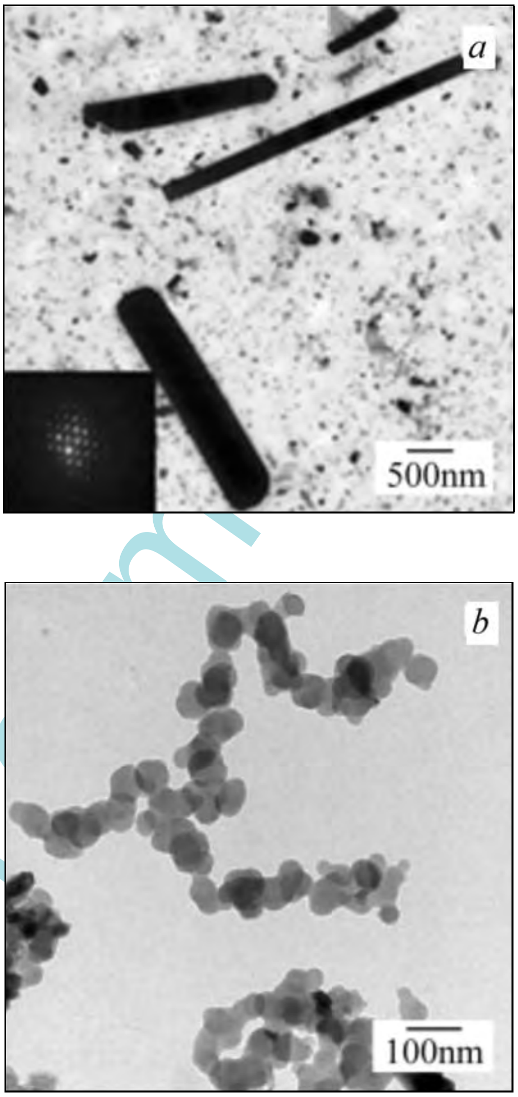

Fig. 2. TEM image of PbS prepared using calix[4]arene as template (*a*) and without calix[4]arene (*b*).

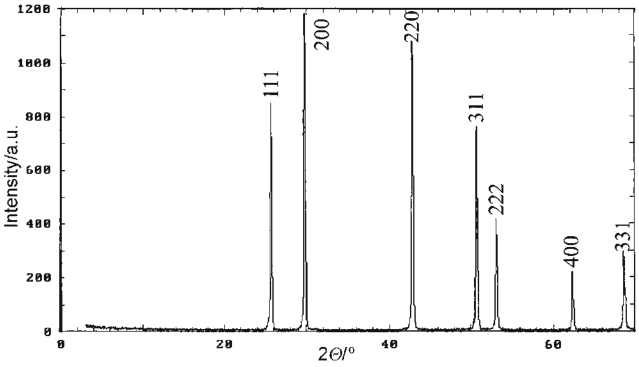

Fig. 3. XRD curve of the prepared PbS nanorods.

Fig. 3 shows the XRD pattern of the product. It can be observed that the product is cubic face-centered structure galena phase with high crystallinity, which corresponds with JCPDS card (No. 5-0592). Galena phase PbS is an important semiconductor with unique semiconducting and optical properties. The relative intensity of peak (220) is higher than that of PbS bulk material, which indicates orientation growth of nanorods in crystal face (220). The result is in accord with the image obtained by the TEM method.

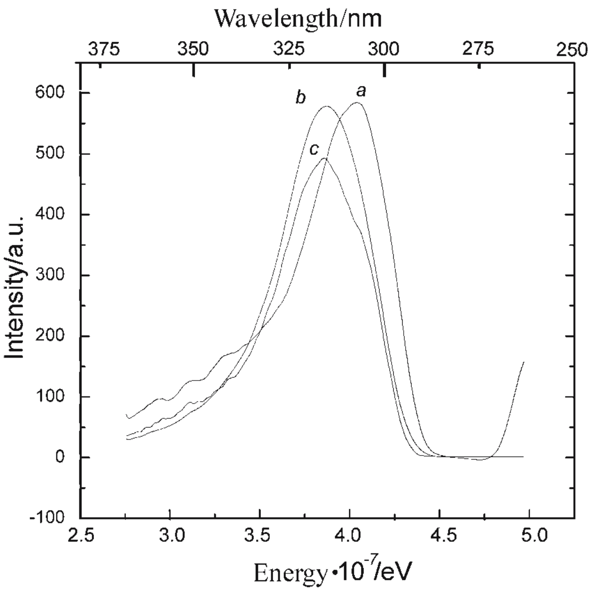

Fig. 4. PL emission curves of PbS nanorods (*a*), nanoparticles (*b*), and bulk PbS (*c*).

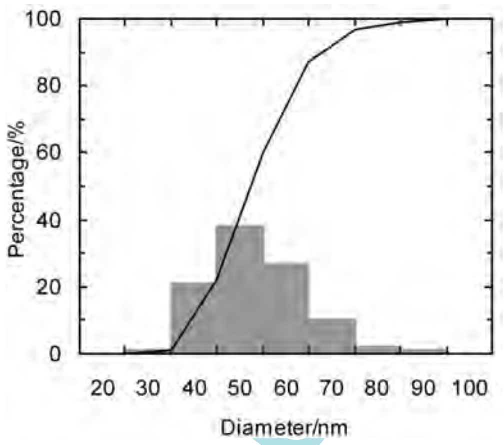

Fig. 5. PbS nanoparticles size distribution.

Fig. 4 shows the PL emission curves of PbS excited at 244 nm. Curve *a* represents emission spectral line of the prepared nanorods. Emission peak appears at 308 nm in ultraviolet region. Curve *b* shows a peak at 320 nm, which is the PL spectrum of PbS nanoparticles prepared without the presence of calix[4]arene. Curve *c* shows the PL emission spectrum of bulk PbS. It can be seen that the PL emission peak of the obtained PbS nanorods presents a blue shift of about 14 nm with respect to the emission peak of bulk PbS. This may be contributed to quantum-sized effect of nanorods. Moreover, PL emission peak of the obtained PbS nanorods is shifted by about 12 nm compared with the emission maxima found in the spectrum of nanoparticles prepared in the absence of calix[4]arene. This observation results from the fact that the thickness of PbS nanorods is smaller than the diameter of PbS nanoparticles.

Fig. 5 presents the size distribution of PbS nanoparticles showing that the length of the main portion of prepared particles is in the area of 40—60 nm,

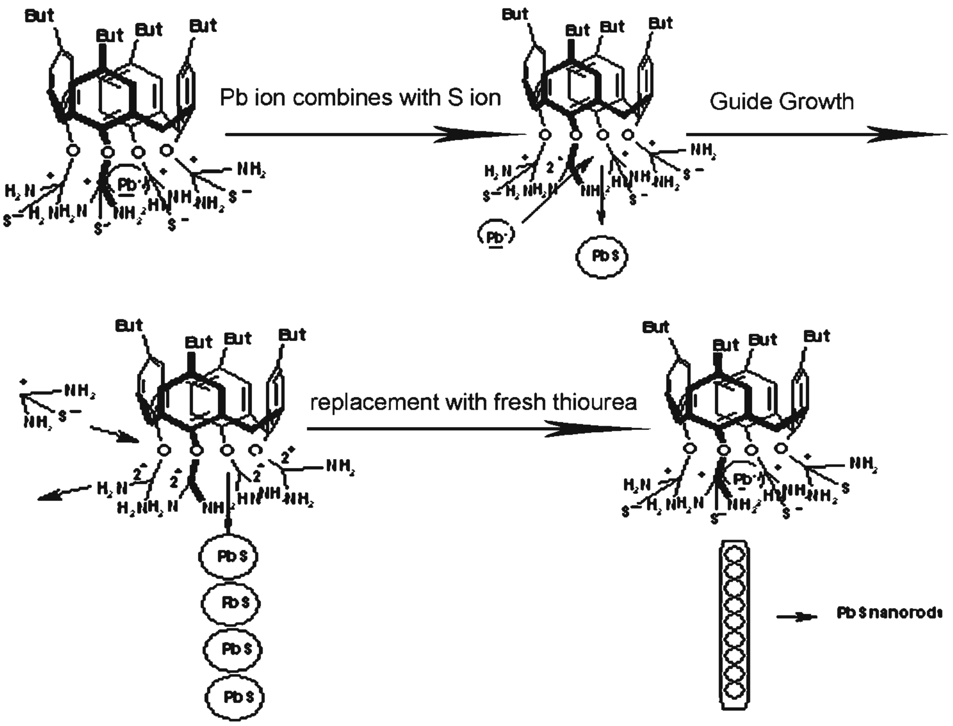

Fig. 6. Mechanism of the formation of PbS nanorods.

which agrees with TEM measurements. The results were obtained using Imager 4.00 software.

The mechanism of PbS nanorods formation was proposed as it is shown in Fig. 6. Firstly, thiourea interacts with hydroxyl groups of calix[4]arene forming a cavity. Pb^{2+} cation enters this cavity before being caught by S of the thiourea molecule. After the formation of PbS, fresh thiourea molecule combines with calix[4]arene replacing the spent one. Then, the formed PbS crystal nucleus is released from the cavity. Repeated interaction—reaction—exchange—release process causes that the PbS crystal nuclei are assembled into nanorods. According to the proposed mechanism, similar behavior of other calixarenes could be expected.

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REFERENCES

1. Liu, Z. L., Jiang, L., Liang, Z., and Gao, Y. H., *Tetrahedron 62*, 3214 (2006).
2. Ye, Z. F., He, W. J., Shi, X. F., and Zhu, L. G., *J. Coord. Chem. 54*, 105 (2001).
3. Rouis, A., Mlika, R., Dridi, C., Davenas, J., Ben Quada, H., Halouani, H., Bonnamour, I., and Jaffrezic, N., *Mater. Sci. Eng., C 26*, 247 (2006).
4. Turshatov, A. A., Melnikova, N. B., Semchikov, Yu. D., Ryzhkina, I. S., Pashirova, T. N., Möbius, D., and Zaitsev, S. Y., *Colloids Surf., A 240*, 101 (2004).
5. de Namor, A. F. D., Chahine, S., Kowalska, D., Castellano, E. E., and Piro, O. E., *J. Am. Chem. Soc. 124*, 12824 (2002).
6. Akola, J., Rytkönen, K., and Manninen, M., *J. Phys. Chem. B 110*, 5186 (2006).
7. Smith, D. K., *Chem. Commun. 1*, 34 (2006).
8. Zhao, X. K. and McCormick, L. D., *Appl. Phys. Lett. 61*, 849 (1992).
9. Machol, J. L., Wise, F. W., Patel, R. C., and Tanner, D. B., *Phys. Rev. B: Condens. Matter 48*, 2819 (1993).
10. Kuang, D. B., Xu, A. W., Fang, Y. P., Liu, H. Q., Frommen, C., and Fenske, D., *Adv. Mater. 15*, 1747 (2003).
11. Xu, J., Ge, J. P., and Li, Y. D., *J. Phys. Chem. B 110*, 2497 (2006).
12. Mo, M. S., Shao, M. W., Hu, H. M., Yang, L., Yu, W. C., and Qian, Y. T., *J. Cryst. Growth 244*, 364 (2002).
13. Saraidarov, T. and Reisfeld, R., in *NATO Science Series II: Mathematics, Physics, and Chemistry*, Vol. 204 (Vaseashta, A., Dimova-Malinovska, D., and Marshall, J. M., Editors), p. 375. Kluwer Academic Publishers, Dordrecht, 2005.
14. Zhang, C., Kang, Z. H., Shen, E. H., Wang, E. B., Gao, L., Luo, F., Tian, C. G., Wang, C. L., Lan, Y., Li, J. X., and Cao, X. J., *J. Phys. Chem. B 110*, 184 (2006).
15. Saraidarov, T., Reisfeld, R., Sashchiuk, A., and Lifshitz, E., *J. Non-Cryst. Solids 345*, 698 (2004).
16. Yu, D. B., Wang, D. B., Zhang, S. Y., Liu, X. M., and Qian, Y. T., *J. Cryst. Growth 249*, 195 (2003).
17. Gutsche, C. D., Dhawan, B., No, K. H., and Muthukrishnan, R., *J. Am. Chem. Soc. 103*, 3782 (1981).