Chinese Science Bulletin 2006 Vol. 51 No. 21 2576—2580

DOI: 10.1007/s11434-006-2169-y

Shape controllable preparations of PbS nanocrystals using cysteine as the precursor of S^{2-} ions

BAO Haobo, HAN Wei & GAO Mingyuan

Key Laboratory of Colloid, Interface Science and Chemical Thermodynamics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

Correspondence should be addressed to Gao Mingyuan (email: gaomy@iccas.ac.cn)

Received February 27, 2006; accepted June 12, 2006

Abstract Flowerlike, spherical and cubic PbS nanoparticles have been successfully synthesized by refluxing cysteine and lead nitrate in an alkaline solution. The influences of the cysteine to Pb^{2+} molar ratio, the pH value of the reaction mixture as well as the refluxing time on the shape of PbS nanoparticles were investigated. Detailed experimental results demonstrated that a higher molar ratio of cysteine to Pb^{2+} (5.2:1) and shorter refluxing time favor the formation of flowerlike PbS nanoparticles at pH 9.0. While lower pH value (8.0) favors the formation of spherical PbS nanoparticles, and higher pH value (10.0), however, favors the formation of cubic PbS nanoparticles. The mechanism for the shape control of PbS nanoparticles is discussed.

Keywords: shape control, PbS nanocrystals, cysteine.

More and more experimental results have demonstrated that the physical properties of nanocrystals (NCs) depend not only on their crystalline structure and particle size, but also on their shape[1,2]. Therefore, precise shape control has become another important parameter in the solution synthesis of nanocrystal materials for further turning their special physical properties. In the past few years, much effort has been devoted to the development of new synthetic routes with respect to the morphology control over various types of NCs.

PbS is an important direct bandgap semiconductor material with a small band gap (0.41 eV) and has potential applications in near-IR communication[3]. Moreover, due to the larger exciton Bohr radius of 18 nm, the third-order nonlinear optical response of PbS nanocrystals is expected to be huge, 30 times that of GaAs and 1000 times that of CdS particles with the same particle size, which makes PbS nanocrystals desirable for photonic and optical switching device applications[4,5]. Up to now, PbS nanowires[6,7], nanorods[8], nanotubes[9], star-shape[10] and dendrites consisting of nanorods[11] have successfully been prepared by various methods, although investigations on the synthesis of one- or multi-dimensional PbS nanocrystals began much later than that on spherical PbS nanocrystals. The shape controllable synthetic approaches for PbS nanocrystals mainly include solid-state template method[8], thermal decomposition of organometal compounds[10] and solvothermal synthetic routes[6,7,11]. In the solid-state template approach, Pb^{2+}-containing polymers are required as templates for PbS nanocrystals[8]. The stereospecificity characteristic makes this method suitable for preparing oriented nanoparticles. The thermal decomposition approach has however been proven to be one of the most successful methods for preparing high quality semiconductor nanocrystals. Up to now, PbS nanocrystals with different morphologies such as rod-based multipods, star-shaped nanocrystals and truncated octahedron have successfully been prepared by this method[10]. Nonetheless, the drawbacks of this method are quite evident, highly toxic metallorganic compounds and high reaction temperature are required for the synthesis[10]. By taking the advantage of high reaction temperature and pressure, solvothermal reaction is greatly in favor of anisotropic growth of PbS as well as many other types of nanocrystals[6,7,11]. But it is practically not so convenient to monitor the process of a solvothermal reaction

Recently, several facile syntheses based on aqueous routes have been developed for synthesizing PbS microcrystals with special shapes, for example, star-shape and flower-shape, by using thioacetamide and thiosulfate as sulfide ion precursors, respectively[12,13]. However, these methods are not applicable to producing PbS nanocrystals with smaller size. Herein, we report size-controllable synthesis of PbS nanocrystals in aqueous solution using cysteine as the precursor of sulfide ions. Different from thioacetamide and thiosulfate, cysteine can additionally serve as particle surface-capping agents due to the strong binding ability of its thiol group with Pb^{2+} ion, leading to nanometer-sized PbS nanocrystals. Flowerlike, cubic and spherical PbS nanocrystals were prepared simply by altering the cysteine to Pb^{2+} molar ratio, the pH value of reaction mixture and the refluxing time. The mechanism for shape control is discussed.

1 Experimental

1.1 Chemicals and reagents

All compounds used were analytically pure without further purification. L-cysteine was purchased from Adrich (product No. 168149, 97%); lead nitrate with a purity of 98% was purchased from Beijing Hongxing Chemical Co. Ltd.

1.2 Preparation of PbS nanoparticles

The synthesis of PbS nanocrystals was carried out by thermal decomposition of cysteine in the presence of lead nitrate in an aqueous solution. In a typical synthesis, a certain amount cysteine was dissolved completely in water and then lead nitrate was introduced. The concentration of Pb^{2+} was 1.5×10^{-3} mol/L and the cysteine to Pb^{2+} molar ratio was 5.2:1. The pH value of the solution was adjusted to alkaline range by using 2 mol/L NaOH before reflux. Black precipitates collected by centrifugation after a certain period of reflux were washed 3 times by water and subsequently dried in air before further characterizing. The influences of pH value, cysteine to Pb^{2+} ratio and refluxing time were investigated.

1.3 Characterizations

Transmission electron microscopy (TEM) measurements were performed with a JEM-100CX II microscope. Powder X-ray diffraction (XRD) was taken with the help of a Regaku D/Max-2500 diffractometer under Cu Kα radiation (λ = 1.54056 Å).

2 Results

2.1 Formation of PbS nanocrystals

Due to the acidity of α-C, cysteine is easily enolized and releases a S^{2-} ion by a 1,4-elimination reaction of the enolized intermediate in alkaline solution[14]. The elimination reaction as shown below can be catalyzed by base and accelerated by reflux. In addition, due to the strong binding ability of the thiol group from cysteine to Pb^{2+} ions, cysteine was chosen as both the S^{2-} precursor and the surface capping agent in the preparation of PbS nanoparticles.

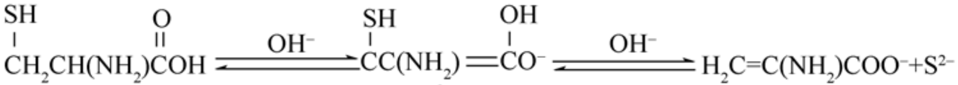
Fig. 1 shows the XRD pattern of a typical as-prepared PbS particle sample. All the diffraction peaks are indexed and labeled according to the face-center-cubic structured bulk PbS. The calculated lattice constant (5.945 Å) is close to the literature data (JCPDS No. 5-592). The appearance of strong and sharp diffraction peaks demonstrates that the as-prepared nanocrystals possess good crystallinity.

2.2 Influence of the refluxing time

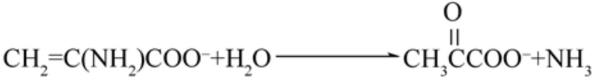
It was observed that refluxing process is necessary not only for generating PbS nanocrystals, but also for showing important impact on the shape of the resultant particles. In order to explore the shape evolution of the PbS nanocrystals during reflux, a series of PbS samples were prepared, under a cysteine to Pb^{2+} molar ratio of 5.2:1 at pH 9.0, by extracting a certain amount of reaction mixture after it was refluxed for 5, 15, 30, 60 min, respectively. TEM results shown in Fig. 2 reveal that during the early stage of reflux, 5 min, flowerlike PbS nanocrystals with a petal width of approximately 10 nm can be obtained. Their average size is of 80 nm. The SAED (selected are electron diffraction) patterns inserted in Fig. 2(a) indicate that the flowerlike PbS nanoparticle has a single crystalline structure. As the reflux is prolonged, the PbS particles change gradually in shape apart from a general increase in size. The interior structures of the PbS particles become more and more solid, meanwhile, the flower shape gradually vanishes in 15 min after reflux. Quasi spherical (Fig. 2(b)) and later polygonal (Fig. 2(c)) particles appear as reflux continued. Prolonged reflux demolished the embossment structure on the particle surface, and quasi cubic PbS particles of approximately 200 nm were formed after 60 min reflux (Fig. 2(d)).

2.3 Influence of the cysteine to Pb^{2+} ratio

Since cysteine has great coordinating ability to lead ions[15], the molar ratio between cysteine and Pb^{2+}



$$\overset{\mathrm{SH}}{\overset{|}{\mathrm{CH_2}}}\mathrm{CH(NH_2)}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OH} \overset{\mathrm{OH^-}}{\rightleftharpoons} \overset{\mathrm{SH}}{\overset{|}{\mathrm{C}}}\mathrm{C(NH_2)}{=}\overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}\mathrm{O^-} \overset{\mathrm{OH^-}}{\rightleftharpoons} \mathrm{H_2C{=}C(NH_2)COO^- + S^{2-}} \tag{1}$$



$$\mathrm{CH_2{=}C(NH_2)COO^- + H_2O} \longrightarrow \mathrm{CH_3}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{COO^- + NH_3} \tag{2}$$

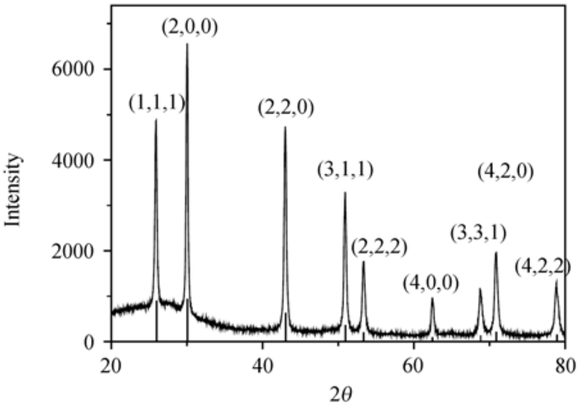


Fig. 1. XRD pattern of an as-synthesized PbS particle sample together with the standard stick pattern for cubic bulk PbS at the bottom.

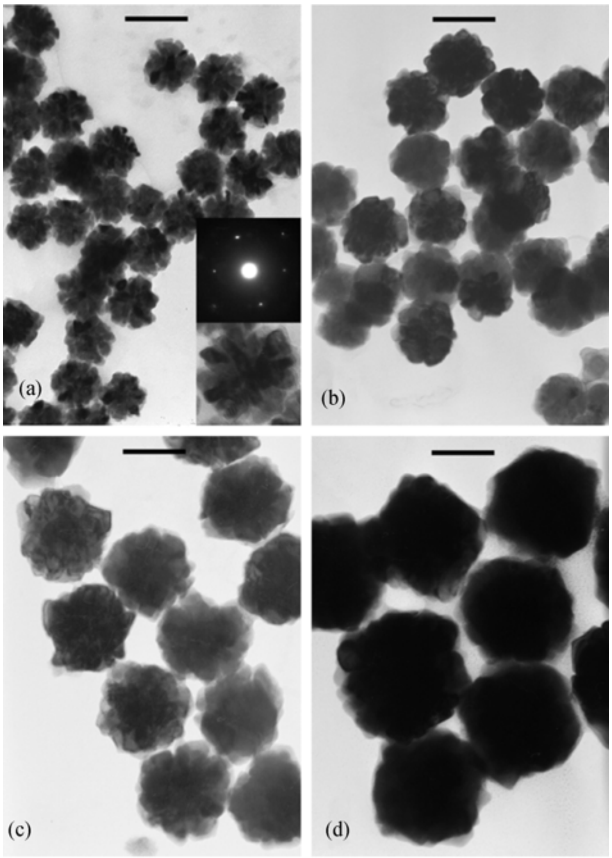


Fig. 2. TEM images of the PbS particle samples obtained by different refluxing time: (a) 5 min; (b) 15 min; (c) 30 min; (d) 60 min. These samples were prepared at pH 9.0 under a cysteine to Pb^{2+} ratio of 5.2:1. Insets: a typical flowerlike PbS particle by high magnification and its SAED pattern. Scale bar: 100 nm.

should affect the whole reaction process as well as the shape of the resultant PbS nanoparticles. To demonstrate this, two additional cysteine to Pb^{2+} ratios, 3.6:1 and 2.6:1, were chosen in preparation. When cysteine to Pb^{2+} ratio was set to 3.6:1 with the initial concentration of Pb^{2+} and pH value being unchanged, the PbS particles obtained after 5 min reflux (Fig. 3(a)) are much different from those shown in Fig. 2(a). In general, to decrease the molar raito of cysteine:Pb^{2+} from 5.2:1 to 3.6:1 leads to a dramatic decrease in PbS particle size. To further decrease the molar ratio to 2.6:1 greatly slowed down the generation of PbS particles. Nearly no color change with respect to the reaction mixture was observed after 5 min reflux. Nonetheless, 15 min reflux can generate PbS particles (Fig. 3(b)), which are very similar to those shown in Fig. 3(a). Apart from this, it is also quite evident that lowering the cysteine:Pb^{2+} ratio also helps to get quasi-cubic PbS particles.

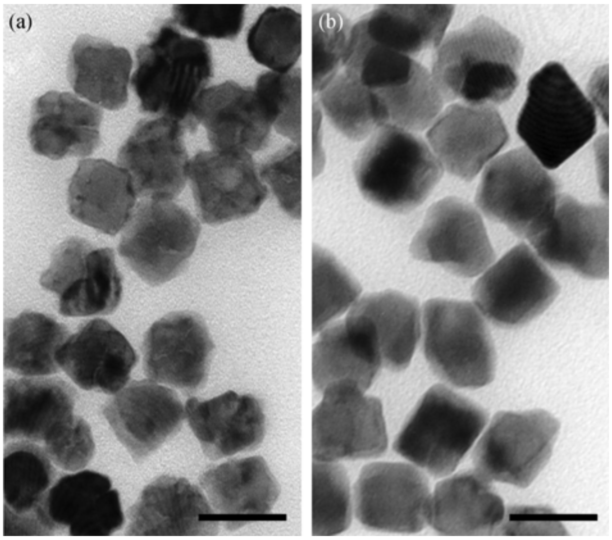


Fig. 3. TEM images of two PbS particle samples prepared at different cysteine to Pb^{2+} molar ratios: (a) 3.6:1; (b) 2.6:1. Samples were obtained after the reaction mixtures were refluxed for 5 min (a) and 15 min (b), respectively. The pH value of the reaction systems was 9.0. Scale bar: 100 nm.

2.4 *Influence of pH value of the reaction mixture*

As shown by reaction (1), the decomposition of cysteine is a base-catalyzing reaction[14], therefore the influence of pH value on the decomposition rate of cysteine and the growth kinetics of the PbS nanocrystals was investigated. To compare with the results mentioned in section 2, two additional preparations were performed under similar conditions except for the pH value of reaction systems. Different from the PbS particles obtained at pH 9.0 (Fig. 2(a)), the PbS particles prepared at pH 8.0 (Fig. 4(a)) present spherical shape with an average particle size of 70 nm. By contrast, the PbS particles prepared at pH 10.0 (Fig. 4(b)) present perfect cubic structure with the particle size of 110 nm; and those cubic particles were obtained only after 1 min reflux. The SAED patterns shown in the inset of Fig. 4(b) suggest that the cubic PbS nanoparticles possess a single crystalline structure.

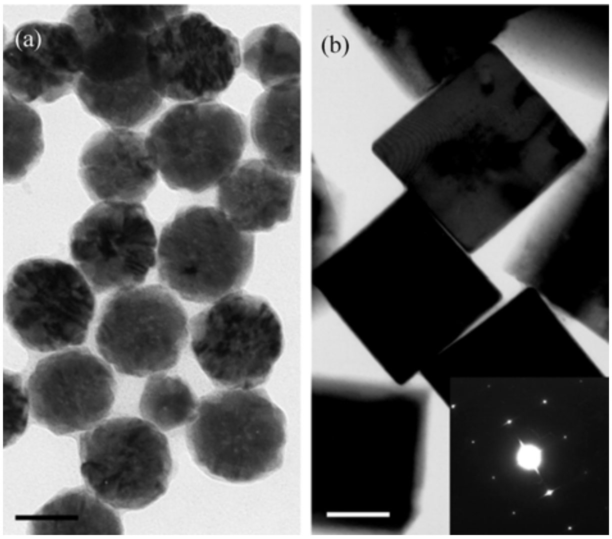


Fig. 4. TEM images of two PbS particle samples prepared at different pH values: (a) 8.0; (b) 10.0. The initial feed ratio of cysteine to Pb^{2+} was 5.2:1. Samples were obtained after the reaction mixtures were refluxed for 5 min (a) and 1 min (b), respectively. Inset: SAED pattern of the sample (b). Scale bar: 50 nm.

3 Discussion

In general, for a single-phase crystal with a small size, its surface should be a polyhedron since different crystal planes have different surface energy; the plane with higher energy exhibits a higher growth rate[16]. Therefore, the shape of an inorganic nanoparticle is determined by the growth rates of different crystal planes[17]. For a face-center-cubic (fcc) nanoparticle, its shape is mainly determined by the ratio (*R*) of the growth rates along 〈100〉 and 〈111〉 directions; and the (111) plane generally has a higher surface energy than (100) plane[16]. According to the theory of Wang[16] and the experiment results of Cheon[18], when *R* is approaching or smaller than 0.58, cubes bounded by (100) planes will be formed; when *R* is approaching 0.87, spherical nanoparticles will be formed. However, when *R* is above 1.73, one dimension rod-based single- and multi-pod structure nanoparticles are formed.

Since cysteine has great coordinating ability to Pb^{2+} forming a complex structure in aqueous solution[15], at the early stage of reflux there are more cysteine molecules binding on the PbS particle surface. Cysteine preferentially binds to (111) plane via the μ^3-Pb_3-SR bridging mode, which selectively lowers the surface energy of (111) plane in comparison with (100) plane[18]. The appearance of flowerlike nanoparticles as shown in Fig. 2(a) explains that under the molar ratio of 5.2:1 (cysteine:Pb^{2+}), the growth rate ratio between (100) and (111) may be near to or even larger than 1.73 at the beginning of reflux. Further reflux no doubt decreases the amount of cysteine in the system, simultaneously increases the growth rate on the (111) plane and therefore decreases the growth rate ratio *R*, which results in the transformation of particle shape from flowerlike to spherical. That quasi cubic PbS (Fig. 2(d)) appearing after the reaction mixture was refluxed for 60 min indicates that the growth rate ratio between (100) and (111) at this stage may be smaller than 0.87 and approaching 0.58 due to the further loss of cysteine in the reaction mixture. In general, the shape evolution shown in Fig. 2 indicates that lower concentration of cysteine favors the formation of cubic PbS particles. This was also supported by the fact that cube-like PbS particles, as presented in Fig. 3, were preferentially formed at low starting concentration of cysteine while the concentration of Pb^{2+} remained the same.

In addition, the maximum coordination number of cysteine to Pb^{2+} is 2[15], and all our experimental observations indicate that the sulfide ions are mainly contributed by the decomposition of free cysteine rather than cysteine-Pb^{2+} complex. At low cysteine to Pb^{2+} molar ratio, most of cysteine molecules in the solution exist in the form of cysteine-Pb^{2+} complex, greatly slowing down the growth rate of PbS particles due to the low production rate of S^{2-}, and consequently leading to the formation of smaller PbS nanoparticles as shown in Fig. 3.

According to decomposition reactions of cysteine shown above, the pH of the reaction mixture can be another important parameter determining the final shape of PbS nanoparticles. The TEM results shown in Fig. 4 demonstrate that spherical PbS and smaller PbS particles can be obtained at pH 8. The smaller particle size is mainly caused by slow decomposition rate of cysteine at pH 8 in comparison with that at pH 9 or 10. By contrast, much quicker appearance of bigger PbS particles at pH 10 demonstrates that the decomposition of cysteine at pH 10 is much faster than that at pH 9 or 8. Due to the fast consumption of cysteine, the amount of particle surface-binding cysteine is quickly reduced, thus the growth rate along 〈111〉 direction becomes dominant resulting in the formation of perfect PbS cubes.

4 Conclusions

By using cysteine as S^{2-} precursor and stabilizing agent, flowerlike, spherical and cubic PbS nanoparticles have successfully been prepared simply by refluxing the alkaline aqueous solution of cysteine and lead nitrate. Detailed results indicated that the cysteine to Pb^{2+} molar ratio, the pH value of reaction mixture as well as the refluxing time are important parameters determining the final morphologies of PbS nanoparticles since these parameters affect both decomposition rate of cysteine and its binding ability to the PbS particle surface. Effective balance between the growth rates along 〈100〉 and 〈111〉 directions gives rise to different morphologies of the resultant PbS nanoparticles. In conclusion, cysteine can act not only as sulfide ions precursor, but also as PbS particle surface capping agent, which makes the current synthetic approach into a very simple route for shape-controllable preparation of PbS nanoparticles.

Acknowledgements This work was supported by the National Natural Science Foundation of China (Grant Nos. 20225313, 90201006 and 90206024).

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