Synthesis and characterization of octahedral PbS nanocrystals assisted with mixed cationic/anionic surfactants

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Abstract. Octahedral PbS nanocrystals were synthesized in aqueous solution assisted with mixed cationic/anionic surfactants. X-ray diffraction, transmission electron microscopy were used to characterize the products. The formation mechanism of octahedral PbS nanocrystals was also studied. The study result would be a huge contribution to the terahertz research.

1. Introduction

In recent years, many efforts have devoted to the morphology control of semiconductor materials, because the shape and size of inorganic nanocrystals control their widely varying optical and electric properties [1]. Among the familiar semiconductor materials, PbS is an important binary IV–VI semiconductor material which have novel semiconducting and optical properties [2]. It has attracted considerable attention in the field of materials science due to its specially small direct band-gap energy (0.41 eV, for bulk at room temperature) and a large exciton Bohr radius (18 nm) [3-6]. PbS nanostructures may be one of the most potential candidates for optical devices such as light-emitting diodes and optical switches due to its exceptional third-order nonlinear optical properties [7, 8]. Up to now, various shapes of PbS nanocrystals such as nanospheres, nanobelts, nanorods, nanotubes, nanowires, dendritic nanostructures, star-shapes and flower-shapes have been prepared [9-17]. Moreover, many methods have been developed to fabricate PbS nanostructures. Among them, the hydrothermal method and thermal decomposition provides a more promising way for the synthesis of crystals due to its low cost, high efficiency and potential for large-scale production [18].

Qian et al. reported a one-step route to crystalline PbS by a solvothermal reaction between lead oxalates and elemental sulfur in organic solvents such as ethylenediamine and pyridine [19]. Cheon et al. have synthesized PbS nanocrystals with various rod-based structures including highly faceted star shapes, truncated octahedrons and cubes from the thermal decomposition of a molecursor [16]. Zou et al. have synthesized PbS microcrystals including dendrites, flowers, multipods and cubes from the reaction of dissoluble lead salt (lead nitrate or lead acetate) and thiourea through a simple
hydrothermal process [5]. Warner has synthesized PbS nanorods by lead acetate, elemental sulfur and oleic acid as surfactant [20].

On the other hand, the surfactant-assisted synthesis of nanostructured materials has attracted considerable attention for its soft-template effect, reproducibility and simple maneuverability [21, 22]. Additional, it is to be noted that mixtures of various surfactants, including alkyl amines, alkyl acids, alkylphosphonic acids, and trioctyl phosphine oxide, are frequently used as capping agents to tailor the crystal shape in high-temperature solution-phase synthesis. The mixed cationic/anionic surfactants reverse-micelle solutions were also used to synthesis of morphology-controlled one-dimensional nanostructures and hierarchical architectures at low temperature [23-25]. Herein, we synthesize octahedral PbS nanocrystals in aqueous solution assisted with mixed cationic/anionic surfactants.

2. Experimental section

2.1. Synthesis of PbS nanocrystals with octahedral morphology

All of the chemical reagents used in this experiment were analytical grade. PbS nanocrystals were synthesized as follows: 3.0 mL of water, 0.5 mL of 0.05 M Cetyltrimethylammonium bromide (CTAB), 0.1 mL of 0.05 M dodecyl sulfonic acid sodium salt (SDSA), and 0.4 mL of 1 M acetic acid were mixed at room temperature, followed by the addition of 0.2 mL of 0.5 M Pb(OAc) and 0.2 mL of 0.5 M TAA under stirring, giving concentrations of 5.7 mM and 1.1 mM for CTAB and SDSA, respectively. The resultant solution was thermo-stated at 80°C for 6 h. The resultant colloidal particles were collected by centrifugation, washed with water, and dried in air.

2.2. Characterizations

The X-ray diffraction (XRD) patterns were recorded using a Shimadzhu XRD 6000 X-ray diffractometer. Transmission electron microscopic (TEM) image were recorded using a HITACHI H-8100 electron microscope. For TEM characterization, the products were ultrasonically dispersed in ethanol, and then a drop of the resulting suspension was placed on a Cu grid coated with carbon film.

3. Results and discussion

3.1. XRD pattern

![Figure 1](image)

Figure 1. The XRD pattern of the octahedral PbS nanocrystal.

Figure 1 shows an XRD pattern of the octahedral PbS nanocrystal. The XRD pattern of the octahedral PbS nanocrystal contains eight peaks that are clearly distinguishable. All the diffraction peaks can be indexed according to the cubic rock-salt structured PbS, which is in agreement with the value in the literature (JCPDS card No. 5-592). The peaks with 2θ values of 26.03°, 30.18°, 43.12°, 51.03°, 53.55°,
62.61°, 68.91° and 71.04° correspond to the crystal planes of 111, 200, 220, 222, 400, 311 and 420 of crystalline PbS, respectively. The strong and sharp peaks indicate that PbS nanocrystals are highly crystalline.

3.2. TEM image

Figure 2. TEM image of the octahedral PbS nanocrystals. The inset shows the electron diffraction (ED) pattern of the octahedral PbS nanocrystals.

Figure 2 shows a typical TEM image of the octahedral PbS nanocrystals. The products exhibit high uniform, regular octahedra with an average edge length of 70 nm. The selected area electron diffraction (SAED) pattern indicates that the octahedral nanocrystal is a single crystal of PbS.

3.3. Mechanical analysis

The presence of the cationic/ anionic mixture in the reaction system plays a key role in the formation of octahedral PbS nanocrystals. Cetyltrimethylammonium bromide (CTAB), the cationic surfactant and dodecyl sulfonic acid sodium salt (SDSA), the anionic surfactant were used in the system. As we known, CTAB is often used as “capping reagent” in nanomaterial fabrication because it can bond to solid surface and selectively adsorb on some specific facets of crystals to control crystal growth direction consequently. The presence of CTAB will bring an increase in the growth rate of \{100\} faces, which favors the formation of octahedrons with eight \{111\} faces. In the present case, when CTAB was used in reaction system, it maybe preferentially adsorb on the faces parallel to (100) axis direction of PbS nanocrystals, leading to preferential growth along the (100) direction, resulting in the formation of octahedral morphology.

We expect that the formation of these octahedral nanocrystals should be generally applicable to many other metal or semiconductor systems. When the amount of surfactant used exceeded a certain value, it probably not only limited the diameter but also the length, in other words, under the condition of too much CTAB in reaction system, a small part of CTAB maybe adsorb on (100) crystal face, resulting in the decrease of length with the increment of surfactant. At the same time, we found the obtained octahedral PbS nanocrystals will form a 3D well-packed octahedral PbS nanocrystal arrays when the reaction time was prolonged. We think that it may be probably determined by the assistant of SDSA.

4. Conclusion

In summary, we demonstrated a novel method for the synthesis of octahedral PbS nanocrystals. This octahedral PbS nanocrystal may become an advanced material for its special optical and electric properties determined by its special structure. And it will play an important applying role in the optical
and electrical fields in the future. Meantime, this study result would be a huge contribution to the terahertz research.

References
[1] Yang P D and Lieber C M 1996 Science 273 1836
[2] Qin A M, Fang Y P, Zhao W X, Liu H Q and Su C Y 2005 J. Cryst. Growth 283 230
[3] Xu L, Zhang W, Ding Y, Yu W, Xing J, Li F and Qian Y T 2004 J. Cryst. Growth 273 213
[4] Zhang Y C, Qiao T, Hu X Y, Wang G Y and Wu X 2005 J. Cryst. Growth 277 518
[5] Wang S, Pan A, Yin H, He Y, Lei Y, Xu Z and Zou B 2006 Mater. Lett. 60 1242
[6] Zhou S, Feng Y and Zhang L 2003 J. Mater. Res. 18 1188
[7] Colvin V L, Schlamp M C and Alivisatos A P 1994 Nature 370 354
[8] Dementjev A, Gulbinas V and Valkunas L 2004 Phys. Stat. Sol. B 241 945
[9] O’Brien P 1997 J. Mater. Chem. 7 1011
[10] Wang S and Yang S 2000 Langmuir 16 389
[11] Liveri V T, Rossi M D, Arrigo G, Manno D and Micocci G 1999 Appl. Phys. A 69 369
[12] Wang S F, Gu F, Lü M K, Zhou G J and Zhang A Y 2006 J. Cryst. Growth 289 621
[13] Yu D, Wang D, Meng Z, Lu J and Qian Y 2002 J. Mater. Chem. 12 403
[14] Kuang D, Xu A, Fang Y, Liu H, Frommen C and Fenske D 2003 Adv. Mater. 15 1747
[15] Ma Y, Qi L, Ma J and Cheng H 2004 Cryst. Growth Des. 4 351
[16] Lee S M, Jun Y W, Cho S N and Cheon J W 2002 J. Am. Chem. Soc. 124 11244
[17] Ni Y, Liu H, Wang F, Liang Y, Hong J, Ma X and Xu Z 2004 Cryst. Growth Des. 4 759
[18] Jana S, Goswami S, Nandy S and Chattopadhyay K K 2009 J. Alloy. Compd. 481 806
[19] Yu S H, Yang J, Wu Y S, Han Z H, Lu J, Xie Y and Qian Y T 1998 J. Mater. Chem. 8 1949
[20] Warner J H 2008 Adv. Mater. 20 784
[21] Liu Y, Hou D and Wang G 2003 Chem. Phys. Lett. 379 67
[22] Yu Y, Du F P, Yu J C, Zhuang Y and Wong P K 2004 J. Solid State Chem. 177 4640
[23] Shi H, Qi L, Ma J and Cheng H 2003 J. Am. Chem. Soc. 125 3450
[24] Shi H, Qi L, Ma J, Cheng H and Zhu B 2003 Adv. Mater. 15 1647
[25] Shi H, Qi L, Ma J and Wu N 2005 Adv. Funct. Mater. 15 442