

Synthesis and optical property of PbSe nanocubes via a facile organic solvent route

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Abstract: Lead selenide nanocubes were successfully prepared on a large scale via a facile solvothermal route using formamide as both solvent and complexing agent. The obtained nanocubes were characterized by a variety of techniques, such as powder X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectra (XPS) and fourier-transformed infrared (FT-IR). The average particle size of the nanocubes is about 20 nm. A higher growth rate in the [111] direction compared to that in the [100] direction results in the formation of nanocubes. And a possible growth mechanism was proposed. The optical property of the resulting PbSe nanocubes was examined. The blue-shift phenomenon might be ascribed to the quantum effect of the nanocubes.

Key words: lead selenide; nanostructured; growth mechanism; optical property

CLC number: O611.4 **Document code:** A

有机溶剂法合成 PbSe 纳米立方块及其光学性质研究

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摘要: 用甲酰胺作溶剂和配位剂, 通过温和的溶剂热路线成功地大量合成了 PbSe 纳米立方块。运用一系列技术手段, 如粉末 X 光衍射 (XRD)、透射电子显微术 (TEM)、X 光电子能谱 (XPS) 和傅立叶变换红外光谱等对所合成的 PbSe 立方块进行表征。纳米立方块的平均颗粒尺寸约为 20 nm。相对于 [100], [111] 方向较快的生长速率导致了纳米立方块的形成, 并提出了可能的生长机理。同时, 对所得产物的光学性质进行研究, 可能由于纳米颗粒的量子效应, 吸收光谱出现蓝移现象。

关键词: PbSe; 纳米结构; 生长机理; 光学性质

0 Introduction

Lead selenide nanocrystals have attracted

considerable attention because they are expected to have the fundamental electronic and optical properties and potential application in both

Received: 2007-06-15; Revised: 2007-10-18

Foundation item: Supported by NNSFC (20431021).

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mesoscopic research and development of nanodevices.^[1~3] PbSe has a wide variety of applications in IR detectors, photographic plates, selective and photovoltaic absorber, etc.^[4~6] A bulk PbSe has a cubic rock salt crystal structure and a narrow direct band gap (0.28 eV at 300 K) at the L point in the Brillouin zone. Its effective Bohr radius ($a_B = 46$ nm) is eight times larger than that of CdSe, indicating strongly pronounced size quantization effects for PbSe nanocrystals^[7]. During the past two decades, nanosized PbSe have been prepared by various methods, including chemical bath deposition, sonochemical and photochemical synthesis, and organometallic precursor thermolysis.^[8~13]

Herein, we report a facile organic route to synthesize PbSe nanocubes with an average particle-size of about 20 nm using formamide as both solvent and complexing agent. The morphology of PbSe nanocrystals was controlled by the coordination between the organic solvent and the metal ions. And the optical property of the nanocubes was examined.

1 Experimental

All the chemicals were of analytical grade and were used as received without further purification. In a typical procedure, 1 mmol of PbCl_2 was added to a 40 mL of formamide solution. The mixture was stirred vigorously to form homogeneous solutions at room temperature. Then, 3 mmol of Se powder was added to the mixture, which was stirred for 5 min. The mixture was subsequently transferred into a 60 mL Teflon-lined stainless autoclave, sealed and heated at 160 °C for 20 h. The autoclave was then allowed to cool to room temperature. The precipitate was filtered and washed several times with distilled water and absolute ethanol to remove impurities, and dried at 60 °C in a vacuum.

The crystalline phase was identified by powder X-ray diffraction (XRD) using a Philips X'Pert Pro Super diffractometer with graphite

monochromatized $\text{Cu } K_\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$). The morphology of PbSe nanocrystals was studied by transmission electron microscopy (TEM) and was recorded on a JEOL-2010 transmission electron microscope at an acceleration voltage of 200 kV. X-ray photoelectron spectrum (XPS) analysis was performed on an ESCALab MKII X-ray photoelectron spectrometer using nonmonochromatized $\text{Mg } K_\alpha$ ($h\nu = 1253.6 \text{ eV}$) as the exciting source. Fourier-transformed infrared (FT-IR) spectra were measured with a spectral resolution of 1 cm^{-1} on a Nicolet FT-IR spectrophotometer (Nexus670) using KBr pellets at room temperature. The absorption spectrum was recorded using a Shimadzu UV-vis spectrometer and a UVvis-NIR spectrometer.

2 Results and discussion

Fig. 1 shows the XRD pattern of the resulting product. All the diffraction peaks can be indexed as face-centered cubic PbSe with the lattice parameter $a = 6.122 \text{ \AA}$ (Space group; Fm-3m [225]), in good agreement with that of the reported values ($a = 6.124 \text{ \AA}$, ICDD-JCPDS card No. 06-0354). No obvious peaks for other impurities were detected.

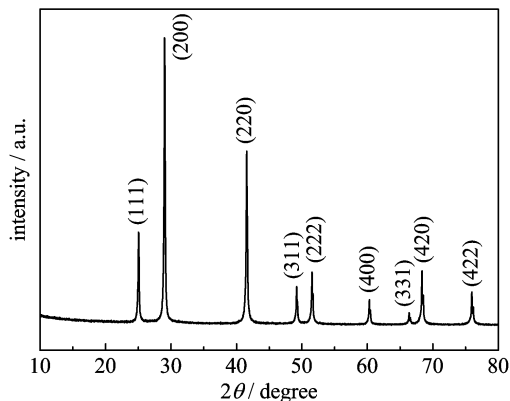
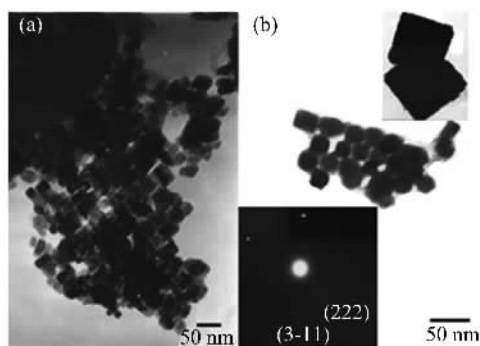


Fig. 1 XRD pattern of the resulting PbSe nanoparticles

The morphology of PbSe nanocrystals was observed by TEM. In Fig. 2 (a), a cubic morphology of the product can be clearly observed and the size distribution is fairly narrow. Fig. 2(b)

shows a bright-field TEM image of the sample, exhibiting the nanocrystals with an average particle-size of about 20 nm. The inset (the top) shows a typical magnified TEM image of the product, indicating a regular cubic morphology. The single-crystal nature of the nanostructures is revealed by the corresponding electron diffraction (ED) pattern (the bottom of Fig. 2(b)).



Inset: the magnified image (top);
the corresponding ED pattern (bottom)

Fig. 2 TEM image (a) and of the resulting nanocrystals;
the bright-field TEM image (b)

The binding energies obtained in the XPS analysis were standardized for specimen charging using C 1s as the reference at 284.5 eV. The peaks at 137.4 and 142.2 eV corresponded to Pb 4f of PbSe (Fig. 3(a))^[14], and the peak at 54.1 eV corresponded to Se 3d of PbSe (Fig. 3(b))^[15]. These results are close to those of the bulk PbSe. No impurity peaks were detected, such as Pb 4f of PbO (138.2 eV)^[16], or Se 3d of SeO₂ (59.8 eV)^[17]. The contents of Pb and Se were estimated from the area under the peaks of Pb 4f and Se 3d, respectively, and an average composition of PbSe_{0.92} was given. The XPS results further confirmed the XRD analysis, indicating that the obtained nanocubes were pure lead selenide.

During the solvothermal process, formamide played an important role in the formation process of the nanocubes as both solvent and complexing agent to form (HCONH₂)₂PbSO₄, which remarkably decreased the concentration of free Pb²⁺ ions in the system, and sequentially reduced the reaction speed for the formation of PbSe

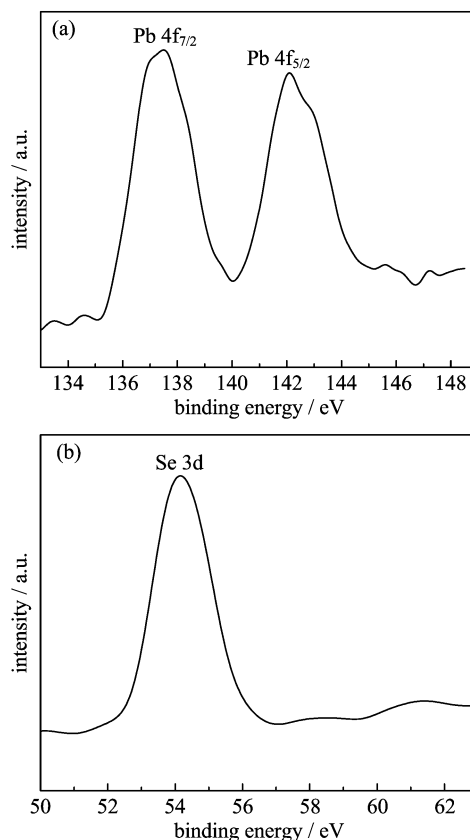


Fig. 3 XPS core spectra of the resulting PbSe
nanocubes for Pb 4f (a) and Se 3d (b)

crystals. Fig. 4 shows the FT-IR spectra of the solvent before and after the reaction, respectively. The N-H absorption peak at 1 607 cm⁻¹ in pure formamide is shifted to 1 595 cm⁻¹ with a slight broadening. This shift in the N-H absorption peak implies a weak coordinative chemical bonding of N-H to metal ions, and similar phenomena were also observed in other researches^[18,19]. For other non-coordinative solvents, such as water, ethanol, or toluene, no pure PbSe nanocubes could be obtained.

In the kinetically-controlled organic system, the crystal morphology of the fcc of PbSe nanocrystals is dependent on the growth ratio between the {111} and {100} facets^[20,21]. As the higher energy site, the faster growth of high index {111} facets results in their elimination as the nanocrystalline size increases, and ultimately the nanocubes were formed. Fig. 5 exhibits the evolution of the shape of PbSe nanocrystals from

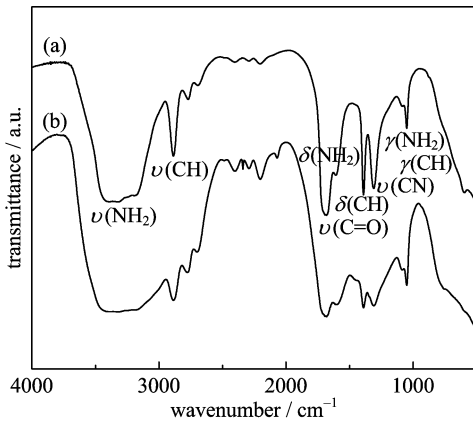


Fig. 4 FT-IR spectra of the solvent before (a) and after (b) the reaction, respectively

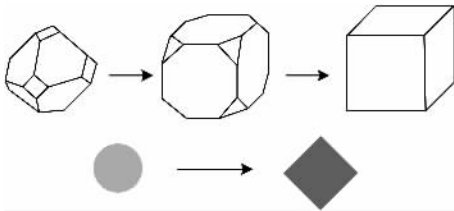


Fig. 5 A schematic illustration of the growth process of PbSe nanocubes

quasi-spherical to cubic.

The optical property of the resulting PbSe nanocubes was examined. The absorbance curve is shown in Fig. 6. The curve exhibits two pronounced exciton bands between 1 000 and 1 600 nm (corresponding to band gap of 0.775~1.240 eV). Comparing PbSe nanocrystals with the bulk

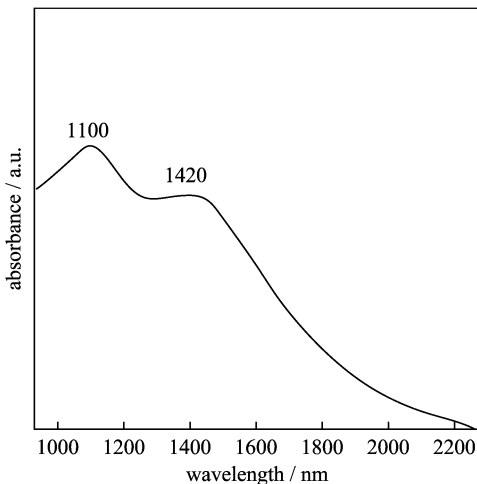


Fig. 6 Optical absorption curve of the resulting PbSe nanocubes

PbSe (0.28 eV), blue-shift phenomenon was observed, which might be ascribed to the quantum effect of the nanocubes.

3 Conclusion

In summary, PbSe nanocubes with an average particle-size of about 20 nm were successfully prepared via a facile solvothermal method. Formamide, as both solvent and complexing agent, played an important role in the growth process of the nanocubes. The optical property of the resulting PbSe nanocubes was examined. The blue-shift phenomenon was observed, which might be ascribed to the quantum effect of the nanocubes. Similar synthetic routes could be adopted for the preparation of other metal chalcogenide semiconductor nanocrystals.

References

- [1] Sirota M, Minkin E, Lifshitz E, et al. Spectroscopic properties of molecular-wire/semiconductor nanocrystalline superstructures[J]. The Journal of Physical Chemistry B, 2001,105: 6 792-6 797.
- [2] Cho K S, Talapin D V, Gaschler W, et al. Designing PbSe nanowires and nanorings through oriented attachment of nanoparticles [J]. Journal of the American Chemical Society, 2005, 127: 7 140-7 147.
- [3] Pietryga J M, Schaller R D, Werder D, et al. Pushing the band gap envelope: Mid-infrared emitting colloidal PbSe quantum dots [J]. Journal of the American Chemical Society, 2004, 126: 11 752-11 753.
- [4] Bakueva L, Gorelikov I, Musikhin S, et al. PbS quantum dots with stable efficient luminescence in the near-IR spectral range[J]. Advanced Materials, 2004, 16: 926-929.
- [5] Harman T C, Taylor P J, Walsh M P, et al. Quantum dot superlattice thermoelectric materials and devices [J]. Science, 2002, 297: 2 229-2 232.
- [6] Murray C B, Sun S, Gaschler W, et al. Colloidal synthesis of nanocrystals and nanocrystal superlattices [J]. IBM Journal of Research and Development, 2001, 45 (1): 47-56.
- [7] Santoni A, Paolucci G, Santoro G, et al. Band structure of lead sulphide [J]. Journal of Physics: Condensed Matter, 1992, 4(32): 6 759-6 768.
- [8] Gorer S, Albu-Yaron A, Hodes G. Chemical solution deposition of lead selenide films; A mechanistic and

- structural study[J]. *Chemistry of Materials*, 1995, 7: 1 243-1 256.
- [9] Brumer M, Kigel A, Amirav L, et al. PbSe/PbS and PbSe/PbSe_xS_{1-x} core/shell nanocrystals[J]. *Advanced Functional Materials*, 2005, 15: 1 111-1 116.
- [10] Chen M, Xie Y, Lu J, et al. A novel two-step radiation route to PbSe crystalline nanorods [J]. *Journal of Materials Chemistry*, 2001, 11: 518-520.
- [11] Lifshitz E, Bashouti M, Kloper V, et al. Synthesis and characterization of PbSe quantum wires, multipods, quantum rods, and cubes [J]. *Nano Letters*, 2003, 3: 857-862.
- [12] Lu W, Fang J. Formation of PbSe nanocrystals: A growth toward nanocubes[J]. *The Journal of Physical Chemistry B*, 2005, 109: 19 219-19 222.
- [13] Wang W, Geng Y, Qian Y, et al. A novel pathway to PbSe nanowires at room temperature [J]. *Advanced Materials*, 1998, 10: 1 479-1 481.
- [14] Shalvoy R B, Fisher G B, Stiles P J. Bond ionicity and structural stability of some average-valence-five materials studied by X-ray photoemission[J]. *Physical Review B*, 1977, 15: 1 680-1 697.
- [15] Weser U, Sokolowski G, Pilz W. Reaction of selenite with biochemically active thiols: An X-ray photoelectron spectroscopic study [J]. *Journal of Electron Spectrosc Relat Phenom*, 1977, 10: 429-439.
- [16] Morgan W E, Van Wazer J R. Binding energy shifts in the x-ray photoelectron spectra of a series of related Group IVa compounds[J]. *The Journal of Physical Chemistry B*, 1973, 77: 964-969.
- [17] Malmsten G, Thoren I, Hogberg S, et al. Selenium compounds studied by means of ESCA[J]. *Physica Scripta*, 1971, 3: 96-100.
- [18] Wang F, Yang Z, Zhang L, et al. FT-IR study of the interaction between phosphatidylcholine and bovine serum albumin [J]. *Acta Physico-Chimica Sinica*, 2004, 20 (10): 1 186-1 190.
- [19] Priyam A, Chatterjee A, Das S K, et al. Synthesis and spectral studies of cysteine-capped CdS nanoparticles [J]. *Research on Chemical Intermediates*, 2005, 31(7-8): 691-702.
- [20] Wang Z L. Transmission electron microscopy of shape-controlled nanocrystals and their assemblies [J]. *The Journal of Physical Chemistry B*, 2000, 104: 1 153-1 175.
- [21] Petroski J M, Wang Z L, Green T C, et al. Kinetically controlled growth and shape formation mechanism of platinum nanoparticles [J]. *The Journal of Physical Chemistry B*, 1998, 102: 3 316-3 320.