

A Complex-Based Soft Template Route to PbSe Nanowires

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PbSe nanowires with an average size of 8×350 nm were synthesized by the reaction of $\text{Pb}(\text{NO}_3)_2$ and Se powder at 60°C under ambient pressure. A mixture of arachidic acid (AA, $n\text{-C}_{19}\text{H}_{39}\text{COOH}$) and octadecylamine (ODA), which could form a complex with Pb^{2+} , was employed as a soft template to control the morphology of the resultant PbSe nanowires.

The products were characterized by X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy. The photoluminescence (PL) spectrum of the PbSe nanowires is presented.

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Introduction

Nanomaterials often display optical, electronic, and structural properties different from those of their bulk counterparts. Nanoparticles may adopt various shapes, which play a critical role in determining their basic properties.^[1] To obtain a nanomaterial of a particular shape a variety of synthetic methods are needed not only to prepare the starting material but also to manipulate such materials to give desirable nanostructures.

One-dimensional (1D) nanostructures, such as nanorods, nanowires, and nanotubes, which serve as building blocks for many novel functional materials, are currently the focus of considerable interest.^[2] So far, several significant synthetic methods, which include hard templates^[3] (such as porous anodic alumina and carbon nanotubes), soft templates^[4] (such as liquids and polymers), and hydrothermal routes^[5] have been employed to prepare 1D nanostructures.

The study of PbSe 1D nanostructures is meaningful since PbSe can be used in IR sensors,^[6] solar cells and infrared detectors,^[7] and chemical sensors,^[8] and is an important semiconductor owing to its large Bohr exciton radius, which can result in a strong confinement of the electron-hole pair.^[9] However, there are only a few examples of the preparation of 1D PbSe nanostructures. These include: (i) synthesis of PbSe nanowires with an average size of $18\text{ nm} \times 3\text{ }\mu\text{m}$ by the reaction of PbCl_2 and Se in ethylenediamine

with KBH_4 as the reducing agent,^[10] (ii) preparation in a monolayer of rod-like PbSe nanocrystals with a size of $10 \times 100\text{ nm}$,^[3] and (iii) synthesis of PbSe nanorods with an average size of $60 \times 700\text{ nm}$ through ultrasonic and γ -irradiation techniques in ethylenediamine.^[11]

Soft templates have been demonstrated to be a very effective method for controlling the shapes of materials. Soft templates include liquid crystals,^[12] monolayers,^[13] polymers,^[1] and surfactants.^[14]

In this work, we obtained PbSe nanowires with an average size of $8 \times 350\text{ nm}$ from a CHCl_3 solution of the surfactants arachidic acid (AA, $n\text{-C}_{19}\text{H}_{39}\text{COOH}$) and octadecylamine (ODA).

Results and Discussion

The XRD pattern of the PbSe nanowires isolated is shown in Figure 1. All peaks in Figure 1 could be indexed

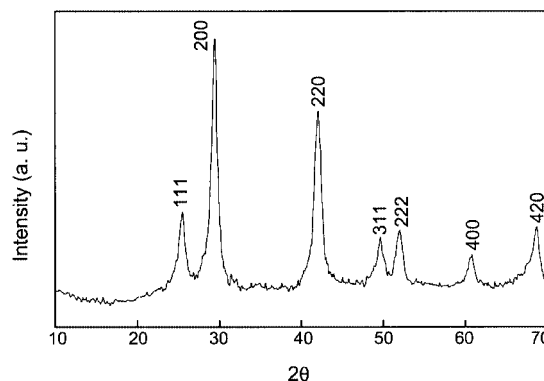


Figure 1. XRD pattern of prepared PbSe nanowires from AA/ODA (1:2)

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as cubic PbSe. The calculated cell constant, $a = 6.128 \text{ \AA}$, is consistent with the reported value ($a = 6.124 \text{ \AA}$, JCPDS Card No.6-354). No peaks characteristic of impurities were observed. Given that the Debye–Scherrer calculations are approximate and more accurate for spherical particles, and that the PbSe has a curved nanowire morphology, the calculated average size of PbSe nanowires relies only on the TEM results.

XPS was further applied to determine the purity and composition of the product. The survey spectrum of PbSe nanowires is typical, and higher-resolution spectra of the Pb and Se regions of PbSe are shown in Figure 2. The survey spectrum of PbSe shows the presence of Pb and Se from the nanowires, and C and O from the surface of the material and from absorbed gaseous molecules. The strong peak observed in the Pb region at 137.2 eV is assigned to the (4f) Pb binding energy; the peak in the Se energy region is detected at 53.2 eV and is attributed to (3d) Se. No other

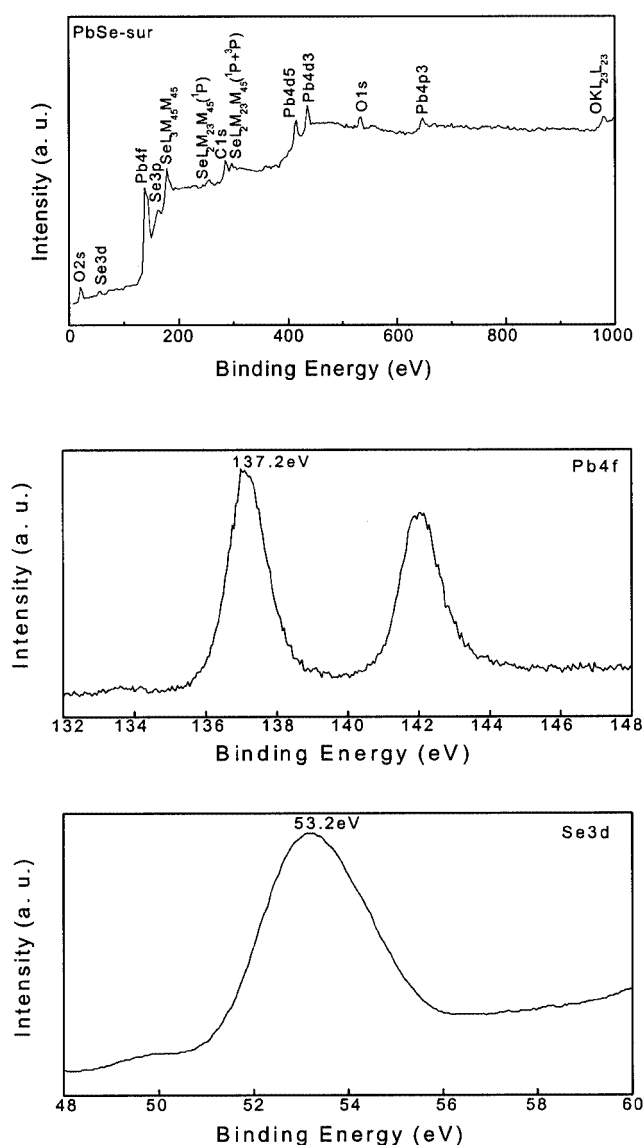


Figure 2. XPS analysis of as prepared PbSe nanowires from AA/ODA (1:2)

peaks in the survey spectrum of PbSe were obvious. The (4f) Pb and (3d) Se peak areas quantified the content of Pb and Se and gave the atomic ratio of Pb to Se as 1:0.92, which is close to the literature value of 1:0.91.^[10] Elemental analysis shows the atomic ratio of Pb/Se to be 1.003. This value is close to the stoichiometric ratio of PbSe (1) and the XRD results but is slightly different from that obtained by XPS. This is because XRD and elemental analysis are bulk-phase analyses while XPS gives only surface composition analysis. For nanoparticles, it is a common phenomenon, that surface composition is different from the corresponding bulk material, which is caused by the dangling bonds existing on the surface and segregation of a particular element to the surface of nanoparticles.^[15,16]

The morphology and size of the PbSe product were investigated by TEM, and the results are shown in Figure 3. The curved PbSe nanowires cross and overlap each other to form a net-like structure, and their average size is $8 \times 350 \text{ nm}$ (Figure 3, a). ED images of PbSe nanowires, shown in Figure 3, b, confirmed that the product is highly crystalline.

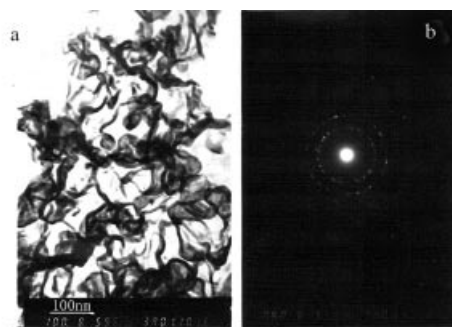


Figure 3. TEM and ED images of as prepared product from AA/ODA (1:2); (a) TEM of PbSe nanowires, (b) ED image of PbSe nanowires

To examine the quantum-confined effect of the product, the room-temperature photoluminescence (PL) spectrum of the PbSe nanowires, which were dispersed in alcohol, was recorded. To avoid the possible interference of trace AA and ODA, an alcohol solution of AA and ODA in a 2:1 ratio was used as reference. Figure 4 depicts the photoluminescence (PL) emission spectrum of the PbSe nanowires. Under photoluminescence excitation at 280 nm, the emitting peak is located at 359 nm with a 40 nm blue-shift compared with Guha's report.^[9] The characteristic blue-shift of the PL spectrum of PbSe nanowires is attributed to their small diameter and larger aspect ratio.^[17]

During formation of the PbSe nanowires, surfactants AA and ODA, in their various ratios, play an important role. When there is no surfactant and other conditions are identical, the PbSe obtained is a spherical nanoparticle. Mixtures of AA and ODA in varying ratios (0:1, 1:5, 1:1, 2:1, 5:1, and 1:0) were applied successively as a soft template keeping other conditions identical with those when AA/ODA = 1:2. The XRD patterns of the resultant products indicated that PbSe could indeed be formed in the mixtures of AA

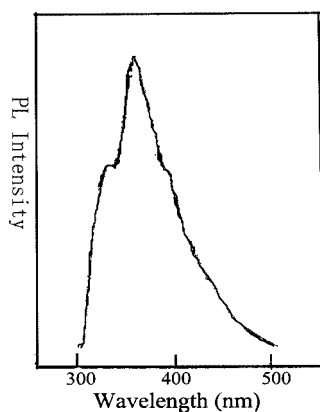


Figure 4. Photoluminescence (PL) spectrum of PbSe nanowires from AA/ODA (1:2)

and ODA. TEM images show the product yield of nanowires is clearly affected by the ratios of AA and ODA. When AA/ODA = 0:1, 1:5, 1:1, 2:1, or 5:1, nanorods and nanoparticles or hollow spheres consisting of nanoparticles are produced instead of nanowires. When the ratio of AA/ODA = 1:0, PbSe nanowires and a small amount of nanorods and nanoparticles are formed.

As regards the shape formation mechanism of PbSe nanowires, mixtures of AA and ODA have been employed before to prepare monolayers, which acted as a soft template to control the morphology of PbS and PbSe.^[13] The shape of the PbS obtained is equilateral-triangular while that of PbSe is equilateral-triangular and rod-like. These results differ from those obtained in our experiments; presumably due to the different behavior and structure of AA/ODA as a solid-state monolayer compared to those of AA/ODA as a solution. In our experiment, the basicity of ODA which could promote conversion of RCOOH (AA) to RCOO⁻.

It has been reported that Pb²⁺ can react with RCOO⁻ to form lead carboxylate complexes with, for example, a three-dimensional polymer structure, a chain structure, or as monomers and dimers.^[18,19] It can be concluded, therefore, that RCOO⁻ in AA may act as a bidentate ligand to react with Pb²⁺ to form relatively stable complexes. According to the following experimental results, a three-dimensional polymer or chain structure was formed when Pb(CH₃COO)₂ reacted with AA in the presence of ODA. Lead carboxylate complexes of general formula [Pb(C₁₉H₃₉COO)₂]_n were prepared as described in the Exp. Sect. IR spectroscopy indicates that the product has a similar IR spectrum to that of AA, except that the peaks at 1707.4 cm⁻¹ [ν(C=O)], 2917.2 cm⁻¹, and 2848.8 cm⁻¹ [ν(OH)] disappear, and new peaks at 1598.7 cm⁻¹ [ν_{asym}(COO⁻)] and 1361 cm⁻¹ [ν_{sym}(COO⁻)] appear. The values of ν_{asym}(COO⁻) and ν_{sym}(COO⁻) in the Pb²⁺-AA complex are close to those in the Pb²⁺-citric acid complex, which has a chain structure and bidentate carboxylic groups.^[20] However, MALDI-TOF-MS results indicate no polymer was formed when the AA/ODA ratio was 0:1, 1:5, 1:1, 2:1, or 5:1. The MS of the Pb²⁺ complex formed

when AA/ODA = 1:2, is as follows: calcd. for {[Pb(C₁₉H₃₉COO)₂]₃₉₅Na₂}²⁺ 327738, found 327736.7; additional peaks: calcd. for {[Pb(C₁₉H₃₉COO)₂]₁₀Na₂}²⁺ 8342, found 8344; calcd. for [Pb(C₁₉H₃₉COO)₂Na₂]²⁺ 875.6, found 877.5.

All the above results confirm the formation of polymers of the Pb²⁺-AA complex. From both literature reports^[18,19] and these results, such [Pb(C₁₉H₃₉COO)₂]_n systems may have a three-dimensional polymeric structure or a curved chain structure. In solution, Se²⁻, which is produced in hydrazine,^[21] attacks the complex. This attack can disrupt the bonds between the Pb and O atoms and promote gradual bond formation between Pb and Se. In the event of Pb-O bond cleavage, the Pb centre is ligated to Se and net-like PbSe nanowires are formed. Clearly, other carboxylic acids may be used as a soft template to prepare 1D nanomaterials. For example, Jiang et al.^[2] prepared Ag nanowires with oleic acid as a soft template; Brase et al.^[22] observed BaSO₄ nanowires in aqueous polymer solution, and pointed out that for nanowire formation, the polymer must have a high percentage of carboxy groups; Benton et al.^[23] produced BaSO₄ nanofibers from polymaleate-based macromolecules with a high content of maleic acid as a modifier. All these results agree with our soft-template mechanism.

Efforts have also been made to prepare PbS 1D nanostructures with S replacing Se under identical conditions to those for the PbSe nanowires. The product obtained is a PbS nanorod. However, the nanorods are short and product yield is low. This result may be due to the different radii and coordination properties of S²⁻ and Se²⁻.

Conclusion

In summary, a complex-based soft-template method has been developed to prepare PbSe nanowires in a mixture of AA and ODA at 60 °C under ambient atmosphere. The ratio of surfactants has a crucial influence on the rate of production of the PbSe nanowires. The optimum ratio of AA and ODA for preparing PbSe nanowires is 1:2. PbSe nanowires are formed because Pb²⁺ can react with AA to produce polymers of a Pb²⁺-AA complex, which acts as a soft template. The soft-template mechanism provides a good example of the use of surfactants in the synthesis of 1D nanostructures. It is possible to replace AA by other carboxylic acid as a soft template for certain inorganic systems. The PL spectra of the PbSe nanowires show a strong confinement effect.

Experimental Section

General: Elemental analyses were carried out by gravimetric analysis combined with atomic emission spectroscopy using a Perkin-Elmer/6500 ICP-AES instrument. Microanalysis of C and H was carried out with a Perkin-Elmer 240C elemental analyzer. ¹H NMR spectra were recorded with a Bruker AM-200 spectrometer. MALDI-TOF-MS was performed with a Bruker Biflex III

mass spectrometer equipped with 1.25-m linear and 2.7-m reflection flight tubes and a 337-nm nitrogen laser. Angiotensin I (1269.5 Da) and adrenocorticotrophic hormone (2466.7 Da) were used as external standards. The experiment was done at an accelerating potential of 20 kV. Sample solutions were prepared by dissolution of polymer, matrix (5-chlorosalicylic acid), and cationizing agent (CF_3COONa) in acetone. Typically, mixtures of 1.0 mL of a polymer solution (10 mg/mL) and 9.0 mL of a matrix solution (8.89 mg/mL) containing a cationizing agent (1.11 mg/mL) were prepared. Immediately after mixing, 1.0 μL portions of solution were deposited with a calibrated pipette onto the dimples of the sample slide and gently dried under air at room temperature. The plate was inserted into the apparatus under high vacuum (about 10^{-5} Pa). The X-ray powder diffraction (XRD) analysis was carried out with a Japan Rigaku D/max- γA X-ray diffractometer with graphite-monochromatized $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$). X-ray photoelectron spectra (XPS) were collected with an ESCALAB MK II X-ray photoelectron spectrometer, using a monochromatized $\text{Mg-K}\alpha$ radiation as the X-ray excitation source. The binding energies are referenced to the (1s) C binding energy (284.6 eV) of the carbonaceous contaminant of the sample. Transmission electron microscopy (TEM) images were taken with a Hitachi H-800 transmission electron microscope. Infrared analyses were performed with KBr discs with a Magna IR-750 FT spectrometer in the range $400\text{--}4000 \text{ cm}^{-1}$ at room temperature. Luminescence spectra were recorded with a Hitachi 850-fluorescence spectrophotometer.

Synthesis of PbSe Nanowires: In a typical procedure, AA and ODA in a 1:2 molar ratio (0.001 mol of AA and 0.002 mol of ODA) were dissolved in 100 mL of chloroform to form colloidal solutions of surfactants whilst stirring at 60°C . A solution of 20 mL of absolute ethanol solution and 0.002 mol of $\text{Pb}(\text{OAc})_2$ was added to the surfactants. A red solution of 0.002 mol of Se, 10 mL of 85% hydrazine, and 40 mL of absolute alcohol was added to the surfactant/metal salt mixture drop by drop to give an immediate black precipitate. After stirring at 60°C for 0.5 h and standing for 1 h, the precipitate was filtered, and then washed successively with chloroform, absolute ethanol, and distilled water. Finally, the black product was dried under vacuum at 60°C for 4 h.

Synthesis of the Lead Carboxylate Polymer: Similar to the preparation of PbSe nanowires, 0.001 mol of AA and 0.002 mol of ODA were dissolved in 100 mL of chloroform stirred at 60°C to form a colloidal solution. A solution of 20 mL of absolute ethanol solution and 0.002 mol of $\text{Pb}(\text{OAc})_2$ was added and after stirring at 60°C for 0.5 h and standing for 1 h, the resultant white precipitate was filtered, then washed with chloroform, absolute ethanol, and distilled water. Finally, the white product was dried under vacuum at 60°C for 4 h. ICP-AES for $[\text{Pb}(\text{C}_{19}\text{H}_{39}\text{COO})_2]_n$: calcd. C 57.91, H 9.40, Pb 24.98; found C 57.58, H 9.82, Pb 24.88. ^1H NMR (C_6D_6): $\delta = 0.9$ [3 H, $\text{CH}_3(\text{CH}_2)_{18}\text{COO}^-$], 1.27 [32 H, $\text{CH}_3-(\text{CH}_2)_{16}\text{CH}_2\text{CH}_2\text{COO}^-$], 1.65 [2 H, $\text{CH}_3(\text{CH}_2)_{16}\text{CH}_2\text{CH}_2\text{COO}^-$],

2.35 [2 H, $\text{CH}_3(\text{CH}_2)_{16}\text{CH}_2\text{CH}_2\text{COO}^-$] ppm. MALDI-TOF-MS: $m/z = 344332.5$, calcd. for $[\text{Pb}(\text{C}_{19}\text{H}_{39}\text{COO})_2]_{415}\text{Na}_2^{2+}$ 344330; additional peaks at $m/z = 322762.5$, calcd. for $[\text{Pb}(\text{C}_{19}\text{H}_{39}\text{COO})_2]_{389}\text{Na}_2^{2+}$ 322760.4 and $m/z = 8344$, calcd. for $[\text{Pb}(\text{C}_{19}\text{H}_{39}\text{COO})_2]_{10}\text{Na}_2^{2+} = 8342$.

Acknowledgments

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- [1] J. H. Zhan, X. G. Yang, D. W. Wang, S. D. Li, Y. Xie, Y. N. Xia, Y. T. Qian, *Adv. Mater.* **2000**, *12*, 1348–1351.
- [2] P. D. Yang, C. M. Lieber, *Science* **1996**, *273*, 1836–1840.
- [3] H. Dai, W. Wong, E. Y. Z. Lu, S. S. Fan, C. M. Lieber, *Nature* **1995**, *375*, 769–772.
- [4] X. C. Jiang, Y. Xie, J. Lu, L. Y. Zhu, W. He, Y. T. Qian, *Chem. Mater.* **2001**, *13*, 1213–1218.
- [5] Y. F. Liu, J. H. Zeng, W. X. Zhang, W. C. Yu, Y. T. Qian, J. B. Cao, W. Q. Zhang, *J. Mater. Res.* **2001**, *16*, 3361–3365.
- [6] X. F. Liu, M. D. Zhang, *Int. J. Infrared Millimeter Waves* **2000**, *21*, 1697–1701.
- [7] P. A. Kondas, *Report ARFSD-TD-92024*, **1993**.
- [8] J. N. Zemel, *J. Franklin Inst.* **1973**, *296*, 475–483.
- [9] S. Guha, V. J. Leppert, S. H. Risbud, I. Kang, *Solid State Commun.* **1998**, *105*, 695–699.
- [10] W. Z. Wang, Y. Gen, Y. T. Qian, M. R. Ji, X. M. Liu, *Adv. Mater.* **1998**, *10*, 1479–1481.
- [11] M. Chen, Y. Xie, J. C. Lu, L. J. Zhu, Y. T. Qian, *J. Mater. Chem.* **2001**, *11*, 518–520.
- [12] X. C. Jiang, Y. Xie, J. Lu, L. Y. Zhu, W. He, Y. T. Qian, *J. Mater. Chem.* **2001**, *11*, 1775–1777.
- [13] [13a] J. Yang, J. H. Fender, T. C. Jao, T. Laurion, *Microsc. Res. Tech.* **1994**, *27*, 402–411. [13b] J. Yang, J. H. Fender, *J. Phys. Chem.* **1995**, *99*, 5505–5511.
- [14] N. W. Zheng, Q. S. Wu, Y. P. Ding, Y. D. Li, *Chem. Lett.* **2000**, 638–639.
- [15] C. J. Lu, A. X. Kuang, G. Guang, *J. Appl. Phys.* **1996**, *81*, 202–206.
- [16] H. Y. Lee, N. H. Goo, W. T. Jeong, K. S. Lee, *J. Alloys Compd.* **2000**, *313*, 258–262.
- [17] B. M. I. van der Zande, L. Pages, R. A. M. Hikmet, A. van Blaaderen, *J. Phys. Chem. B* **1999**, *103*, 5761–5767.
- [18] R. G. Bryant, V. P. Chacko, M. C. Etter, *Inorg. Chem.* **1984**, *23*, 3580–3584.
- [19] P. G. Harrison, A. T. Steel, *J. Organomet. Chem.* **1982**, *239*, 105–113.
- [20] M. Kourgiantakis, M. Matzapetakis, C. P. Raptopoulou, A. Terzis, A. Salifoglou, *Inorg. Chim. Acta* **2000**, *297*, 134–138.
- [21] Y. F. Liu, J. H. Zeng, C. Li, J. B. Cao, Y. Y. Wang, Y. T. Qian, *Mater. Res. Bull.*, in press.
- [22] I. E. Brase, United States Patent, no. 4,898,677, **1990**.
- [23] W. J. Benton, I. R. Collins, I. M. Grimsey, G. M. Parkinson, S. A. Roger, *Faraday Discuss.* **1993**, *95*, 281–297.

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