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The Solventless Syntheses of Unique PbS Nanowires of X-Shaped Cross Sections and the Cooperative Effects of Ethylenediamine and a Second Salt

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Unique PbS nanowires with x-shaped cross sections, with diameters in the range of 300–800 nm with an average of 598 nm ($\sigma = \pm 21.7\%$), and lengths of up to several tens of micrometers, have been made by a solventless method. Such nanowires show high adsorptivities of the PbS nanooctahedra, which can be washed off by ultrasound. The suitable precursor is obtained from a $Pb(NO_3)_2$/octanoate/ethylenediamine/dodecanethiol molar ratio of 1:2:1:1.6, and the PbS nanowires are produced by the thermolysis of such precursors at 280 °C for 1 hour. The X-ray diffraction, scanning electron microscopy, and transmission electron microscopy characterizations of the products and the keys of the morphological control have been reported. For the formation of such products, two cooperative effects are found to be crucial, the roles of ethylenediamine and a second salt, lead octanonate.

Introduction

Shape- and size-controlled syntheses of nano materials are highly desired, especially for semiconductor nanowires, which are considered promising candidates for many applications.[1,2] However, these demand controlled compositions, diameters, lengths, and morphologies, and diverse methodologies have been developed to achieve the controlled syntheses. The solventless method is an outstanding way to produce diverse metals and semiconductors over a wide range of morphologies.[3−9] Such a method has several advantages in that (i) the undesired interparticle collisions/aggregation rarely occur, which leads to size- and shape-monodisperse products, (ii) the solid-state precursor that separated from the solution can be analyzed by powerful methods, e.g., X-ray powder diffraction (XRD), IR spectra, and so forth, which enables one to establish its compositions and crystal structures, and (iii) the nanoproduct is produced from such a well-defined precursor, during which process, the negative effects of the solvent have not been involved, so the shape-control parameters are simplified and the formation mechanism might be relatively easier to access. For example, our previous studies have revealed layered-precursor-to-layered-nanoproduct conversions in a controlled manner by the solventless method.[5,6]

Lead sulfide is a semiconductor with a narrow band gap 0.41 eV (at 300 K) and a large Bohr excitonic radius (18 nm)[10] in the bulk. It exhibits a wide range of potential applications, such as near-IR communication, optical switches,

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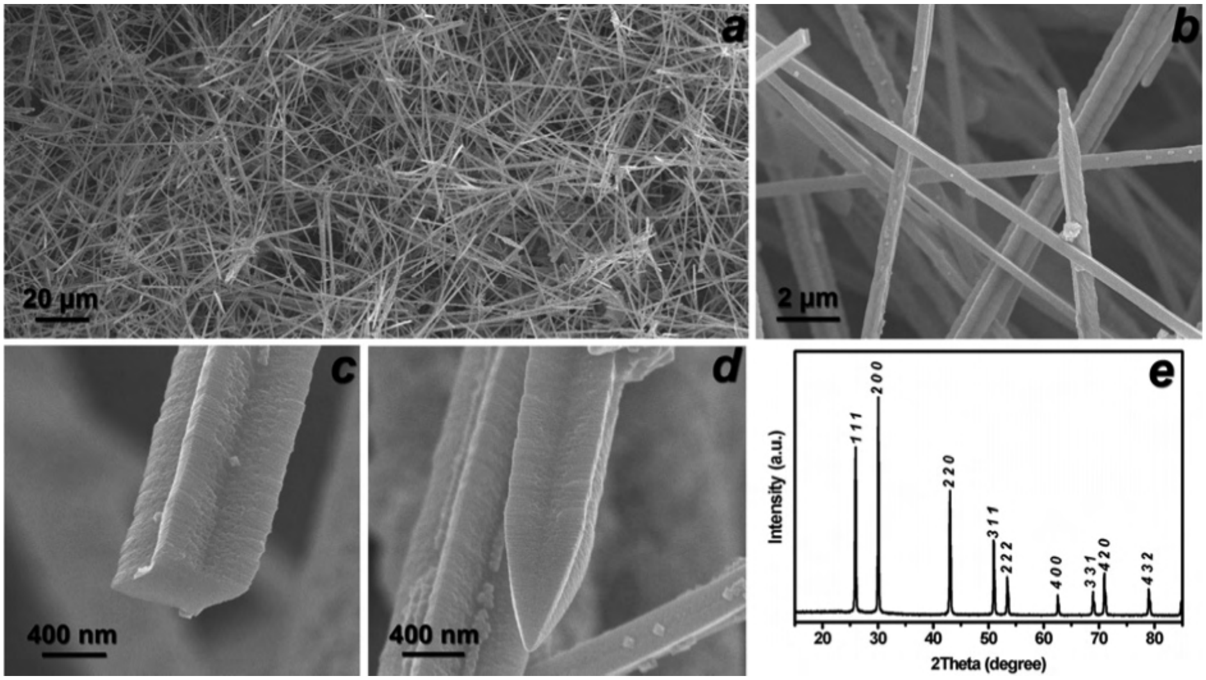

Figure 1. (a−d) SEM images of the x-shaped cross-sectional PbS wires produced at 280 °C for 1 h. (e) XRD pattern of the sample in panel a indexed as cubic PbS (ICSD No. 63095).

thermal and biological imaging, photovoltaics, and solar cells.[11,12] In this work, we report the synthesis of crystalline PbS nanowires with x-shaped cross sections, with diameters in the range of 300−800 nm with an average of 598 nm ($\sigma = \pm 21.7\%$), and lengths of up to several tens of micrometers. And several key parameters for the control of the wire morphology, e.g., reaction temperature, heating time, presence of the capping ligand, and the coexistence of a second salt, have been delineated.

Experimental Section

Chemicals. $C_{12}H_{25}SH$ (Lancaster, 98%), $C_{10}H_{21}SH$ and $C_{16}H_{33}SH$ (Alfa Aesar, 96%), octanoate (Lancaster, 98%), $Pb(NO_3)_2$ (A.R., >99.5%, Tianjin Chemical Co.), ethylenediamine (A.R., >99%, Shanghai Chemical Co.), ethanol (A.R., Shanghai Chemical Co.), and chloroform (A.R., Shanghai Chemical Co.) were used as purchased without further purification. N_2 gas (99.99%) was purchased from Fuzhou Xinhang Gas Co.

Synthesis of the PbS Nanowires. In a typical procedure, 1.5 mmol sodium octanoate in 25 mL of $CHCl_3$ is added to 32 mL of an aqueous solution of 0.75 mmol $Pb(NO_3)_2$ with stirring. After 30 min of stirring, the aqueous phase was discarded. A volume of 0.05 mL (0.75 mmol) of ethylenediamine was added to the chloroform phase to give a colorless solution, and after another 20 min of stirring, 0.22 mL of dodecanethiol ($C_{12}H_{25}SH$, DT) (1.2 mmol) was added, which caused a yellow color change and the precipitation. Continuous stirring for 40 min ensured the precipitation, and the evaporation of $CHCl_3$ resulted in the yellow powdered precursor. This was collected in a Pyrex boat and transferred into a long Pyrex tube (6 cm × 1 m), capped on both ends and purged with N_2 for 10 min, then heated to 280 °C for 1 h to produce a black solid. This black solid was washed in $CHCl_3$ and ethanol to remove byproducts and the possible adsorbed species and dried in air. The final black powder is the PbS nanowires in a yield of 74% based on $Pb(NO_3)_2$.

Characterization. The samples were characterized by XRD, energy-dispersive X-ray (EDX) spectroscopy, and scanning electron microscopy (SEM). The XRD pattern was measured on D-MAX-2500 instrument at room temperature. EDX analyses of nanocrystals were obtained on a Cu grid with the aid of a JEM 2010F transmission electron microscopy (TEM) device equipped with an Oxford INCA spectrometer. SEM was performed on a JSM-6700F scanning electron microscope on samples on electrical adhesive tape without any solvent.

Results and Discussion

Unique PbS Nanowires of X-Shaped Cross Sections. Such unique PbS nanowires have been achieved via a solventless method by the thermolysis of a selected precursor. The synthesis of a suitable precursor requires an optimal molar ratio of the starting reactants of $Pb(NO_3)_2$/octanoate/ethylenediamine (en)/dodecanethiol ($C_{12}H_{25}SH$, DT) to equal to 1:2:1:1.6, and the subsequent thermolysis condition is at 280 °C for 1 h. The low-magnification SEM image of the product in Figure 1a reveals strikingly unique wire morphology with diameters ranging from 300 to 800 nm, with an average diameter of 598 nm ($\sigma = \pm 21.7\%$) and lengths of up to several tens of micrometers (S-Figure 1 in the Supporting Information shows the diameter distribution). Note that each individual wire has a significantly uniform diameter except at the tip (Figure 1d). EDX analyses of single wires indicate only Pb and S (S-Figure 2, Supporting Information), and the single-phase purity is confirmed by the XRD pattern, which is well and completely indexed as

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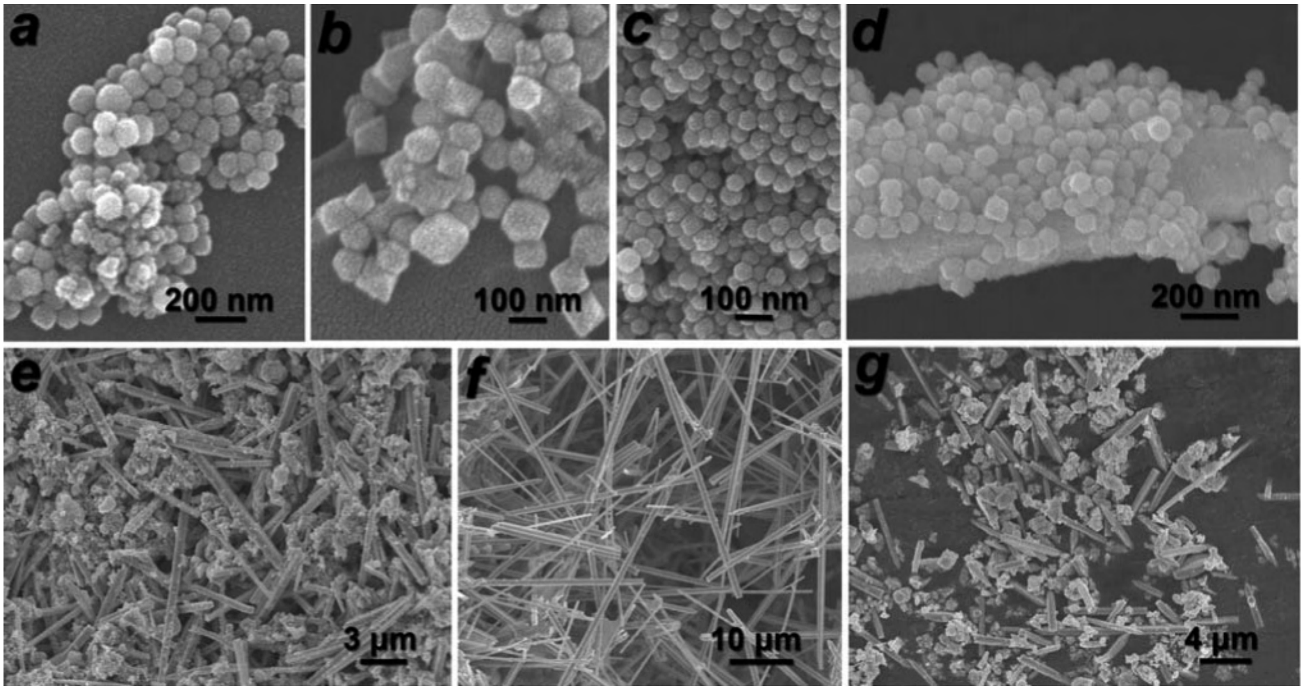

Figure 2. SEM images of samples produced at (a) 240 °C for 1 h; (b) 265 °C for 3 h; (c and d) 280 °C for 30 min; (e) 280 °C for 45 min; (f) 280 °C for 2 h; (g) 300 °C for 1 h.

fcc PbS (Figure 1e). The calculated lattice constant of a = 5.938 Å is consistent with that of ICSD No. 63095, $Fm\bar{3}m$, a = 5.934 Å. It is remarkable that a high-symmetry NaCl-type isotropic semiconducting PbS compound has been developed as a highly anisotropic one-dimensional (1D) nanostructure. Enlarged SEM images of individual wires consistently show a special x-shaped cross-sectional motif (Figure 1c). Such a nanostructure with very large aspect ratios (>several hundred) is markedly different from the cross-shaped discrete nanoparticles, e.g., tetrapod,[13] four-branched dendrites,[14] or flower-shaped particles.[15]

The Evolution of the PbS Nanowires. The evolution of the PbS nanowires was studied in several separate experiments with fixed precursors but varied growth temperature and time. When the temperature is lower than 240 °C, the product is mostly unreacted precursor, judging from the XRD pattern taken right after the firing. Heating at 240 °C for 1 h gives only small round particles with varied size and morphology (Figure 2a) Interparticle attachments and diffusion are obvious at temperatures in the range of 265 °C for 3 h (Figure 2b), 280 °C for 30 min (Figure 2c,d), and 280 °C for 1 h (Figure 3). Two simultaneous processes occurred with the increase of the temperature: (1) the individual PbS particles changed from round (Figure 2 parts a−c) to octahedral nanocrystals terminated by eight {111} facets (Figure 3); (2) the formation of a 1D wire first noted at 280 °C in 30 min (Figure 2d) is fully developed at 280 °C in 1 h (Figure 1) and ended at 300 °C in 1 h (Figure 2g) or at higher temperatures. Process 1 is typical for NaCl-type materials in the presence of the stabilizing agents[16] that bind to the {111} faces more than to the {100} facets and thereby block the growth of the {111} faces and lead to the formation of octahedra with well-defined {111} faces (Figure 3a,c). Process 2, the formation of the uniform PbS nanowires of x-shaped cross sections, is unique. Wires with x-shaped cross sections might initiate from star-shaped nanocrystals with six <100> branches, similar to that reported in PbSe,[16] and then develop via an oriented attachment along the [100] direction together with the relatively slow Ostwald ripening in the other four <010> directions. As shown in S-Figure 3 (Supporting Information), the oriented attachment has been supported by the PbS nanowires with “corrugated edges”, which are similar to those on the PbSe nanowires found by Cho et al..[16] It is very interesting that the PbS nanowires in the present work exhibit the tendencies for surface adsorption. For example, before washing, some wires are fully enwrapped by octahedral particles (Figure 3b,d) via a weak physical adsorption, most of which can be easily washed off in an EtOH solution by ultrasound (See Supporting Information, Section S1). Incompletely adsorbed nanowires are shown in Figure 3a,c, and the adsorption-free nanowires are shown in Figure 1a−d. This effect characterizes a pronounced difference between such PbS wires and those made with the Au seeds.[17] Note that, at the groove sites on the PbS wires, the majority of the octahedra are attached to each other at (111) faces in a very well-organized pattern (Figure 3a,c) along [100], similar to that found in the PbSe system in which the driving force is supposedly dipole−

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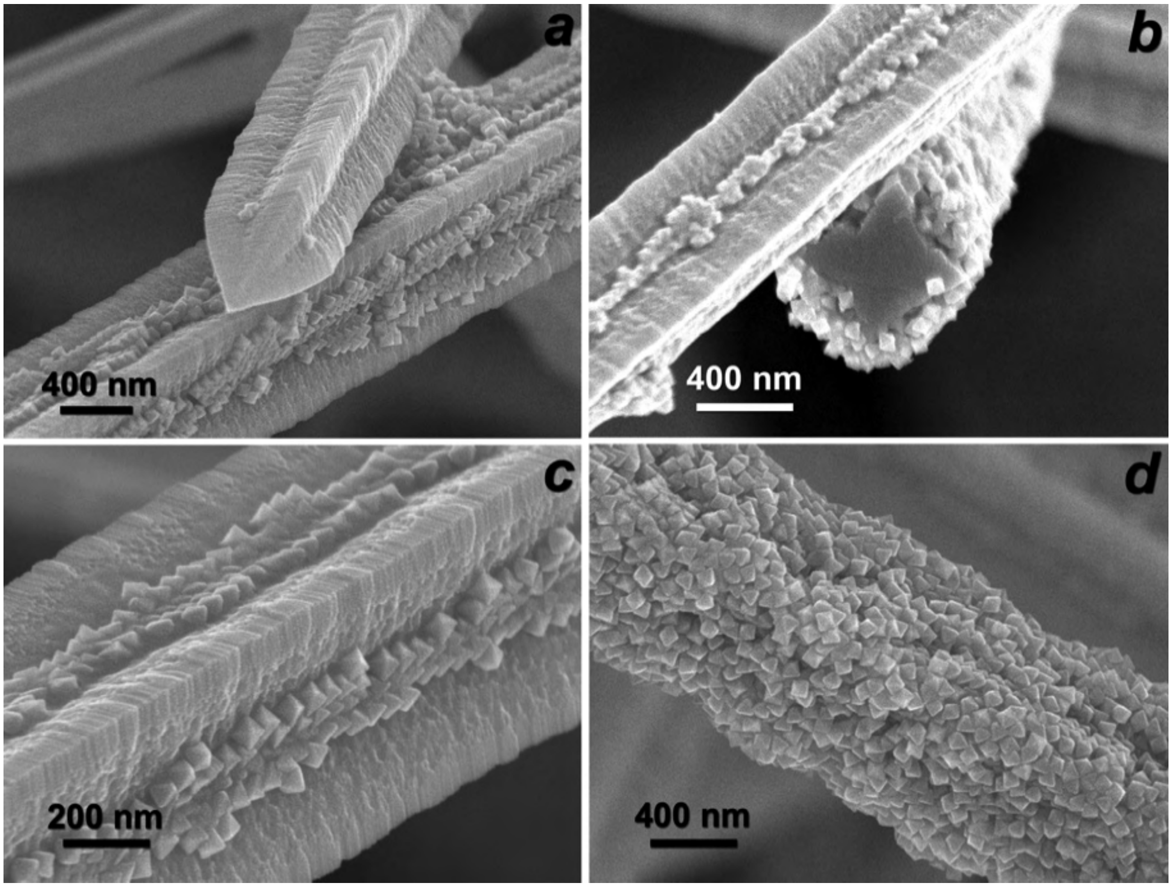

Figure 3. SEM images of PbS wires without complete washing. (a and c) Well-organized octahedra absorbed on the surface of the x-shaped cross-sectional wire. (b and d) Wires wrapped with the octahedra.

dipole interactions.[16] The observation in Figure 3a,c also suggests that the dipole−dipole interactions between the octahedra and the wires are relatively stronger at the groove sites; in this sense, the x-shape of the PbS wires is important for the adsorption. And Figure 3d suggests that a large number of PbS octahedra have nonzero dipole moments that drive the multiple orientated attachments of the octahedra, and as a result, the fully wrapped PbS wires are generated.

The Role of Ethylenediamine, a Switch Between PbS Wires and Cubes. To gain insight into the formation of the PbS nanowires, we have also investigated the role of each starting component employed in the synthesis of the precursor. Amine is known to be a capping ligand that highly influences the morphology of nanoproducts through interactions with the metal centers on the surface of nanocrystals, thus changing the growth rates of different faces. The formation of Fe_2O_3,[18a] MnO,[18b] and CdS[18c] are examples. In our case, ethylenediamine is intended to play a similar role. The {111} faces of fcc PbS have higher surface energies and faster growth rates, which result in their elimination as the nanocrystal size increases; thus, a cubic morphology is expected. We substantiated this postulate via parallel experiments in which ethylenediamine was not used. The precursor was synthesized as above except with a different molar ratio of $Pb(NO_3)_2$/octanoate/en/DT, namely, 1:2:0:2. In three parallel experiments, such a precursor was heated for 1 h at 240, 280, or 300 °C, respectively. The morphologies of these products were cubic or spherical, especially at 280 °C when uniform nanocubes of 30 nm were produced (Figure 4). This result seems to contradict at some degree to what Cheon and co-workers have concluded, that amine as a capping ligand was responsible for the formation of 90 nm PbS cubes,[13] but we made the 30 nm PbS cubes without amine. Note that their statement is that amine weakly bound to {111} facets favors cubes, whereas stronger ligands favor tetrahedral nanocrystals. In other words, with an effective/stronger {111}-capping ligand, they cannot produce PbS nanocubes. Therefore, their results in the phenyl ether solutions at 230 °C essentially agree with ours from solid-state thermolysis at ~280 °C. Moreover, we have demonstrated that amine as a capping ligand is not required, as they believed, to produce PbS nanocubes. This might be the intrinsic nature of the NaCl-type PbS, without external influences, that the higher energy {111} faces disappear as the size increases and nanocubes should be formed. However, under our experimental conditions, the presence of ethylenediamine might diminish the growth of {111} faces on PbS nanocrystals, leading to wires extending in [100] directions. (Figure 1) Also, the presence or absence of ethylenediamine in our precursors (made with different molar ratios of $Pb(NO_3)_2$/octanoate/en/DT, namely, 1:2:1:1.6 vs

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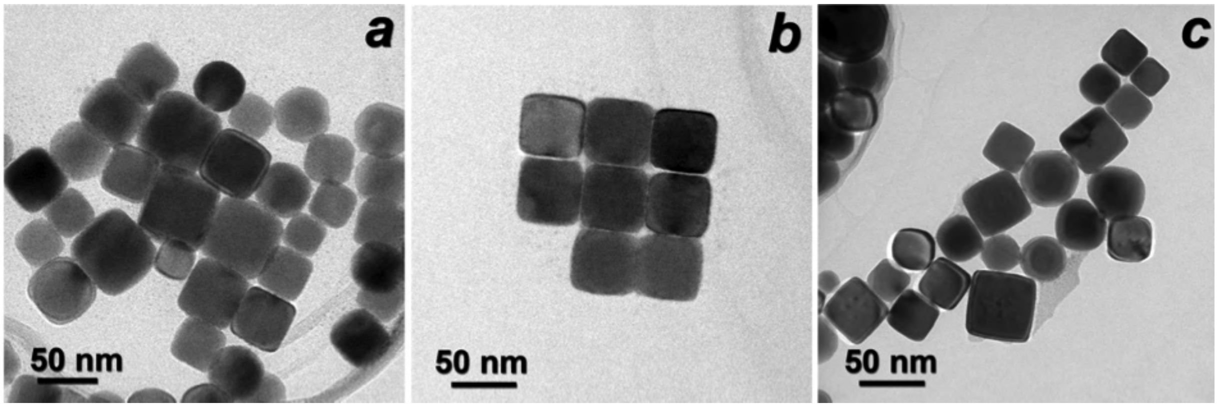

Figure 4. TEM images of PbS nanocubes produced from the precursor P_i (without ethylenediamine) under different conditions of (a) 240 °C for 1 h, (b) 280 °C for 1 h, and (c) 300 °C for 1 h.

1:2:0:2) has been detected by characteristic vibrations in their FTIR spectra (S-Figure 7, Supporting Information).

The Role of Dodecanethiolate. The dodecanethiol (DT) in our case is a coordination ligand that serves to generate $Pb(SR)_2$ complexes. Considering that 1 mol of Pb^{2+} would require 2 mol of DT, we also made the precursor at a molar ratio of $Pb(NO_3)_2$/octanoate/en/DT = 1:2:1:2. But in this case, a mixture of uneven 1D wires plus uneven particles was obtained as shown in S-Figure 4 (Supporting Information) after subsequent thermolysis of such precursor at 280 °C for 1 h. Heretofore, the optimal conditions to generate PbS nanowires were abstracted to involve a precursor with a molar ratio for $Pb(NO_3)_2$/octanoate/en/DT of 1:2:1:1.6 and heating of this precursor at 280 °C for 1 h. Note that the prescribed molar ratio of Pb^{2+}/DT is 1:1.6, so the Pb^{2+} ions are in excess, and interestingly, these conditions do not suggest the right stoichiometry for the sole formation of the PbS nanowires either. We thus carefully examined all of the starting materials. The ethylenediamine in our case has been proved to be a capping ligand that furthers the growth of 1D wires. The octanoate was previously found to be stable before and after the heating and served only as a surfactant in the formation of Cu_2S.[4] The DT is designated to precipitate Pb^{2+} so as to generate $Pb(SR)_2$ thiolate, which, at the subsequent heating stage, undergoes cleavage of the C−S bonds to give PbS as it does for Cu^{2+}.[4]

The Phase Identification of Layered Pb Dodecanethiolate with a 37.1 Å Spacing. Three precursors, namely, P_i, P_{ii}, and P_{iii}, were synthesized with similar procedures but with different molar ratios of $Pb(NO_3)_2$/octanoate/en/DT = 1:2:0:2, 1:2:1:2, and 1:2:1:1.6, respectively. Experimentally, these precursors under the same conditions produced different nanoproducts as follows: nanocubes (Figure 4); a mixture of uneven wires and uneven particles (S-Figure 4, Supporting Information); and 1D wires and well-organized octahedra (Figures 1 and 3). All of the nanoproducts are highly crystalline NaCl-type PbS as indicated by their corresponding XRD patterns (S-Figure 5, Supporting Information). To distinguish the differences among those three precursors, the XRD patterns of P_i−P_{iii} were examined before heating (Figure 5). The P_i and P_{ii} precursors are clearly layered structures with a large interlayer *d* spacing, exhibiting intense narrow reflections with all successive *0k0* orders from k = 3−17 (S-Tables 1 and 2, Supporting Information). The measured *kd* values of all reflections give an average *d* spacing of 37.1 Å for both P_i and P_{ii}. Such a layered motif is similar to that of Ag-containing[5] analogue with a spacing about twice the expected length of the alkyl chain. Therefore, this 37.1 Å spacing can be assigned as that of a layered lead thiolate. Differently, precursor P_{iii} exhibits two sets of successive *d* spacings, $kd_{(O)} = 25.7$ Å and $kd_{(T)} = 37.1$ Å (S-Table 3, Supporting Information). The $kd_{(T)}$ value is similar to that for P_i and P_{ii}, whereas the origin of $kd_{(O)}$ is more complicated because it is possible that this also comes from the $kd_{(T)}$-related phase with highly ordered intralayer information.

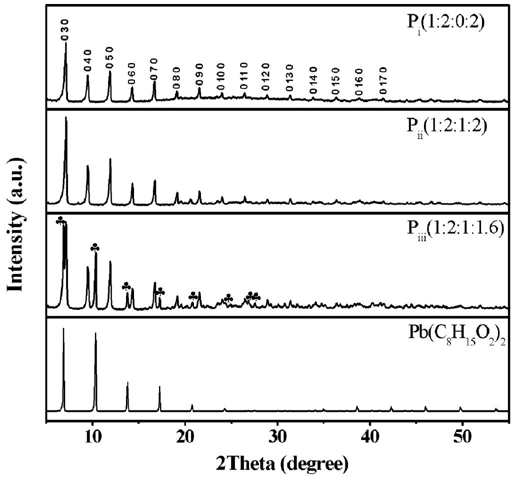

Figure 5. XRD patterns of the three precursors prepared with indicated molar ratios of $Pb(NO_3)_2$/octanoate/en/DT. (bottom) Lead octanoate, $Pb(O_2C_8H_{15})_2$. The marked peaks of the P_{iii} pattern are consistent with the $Pb(O_2C_8H_{15})_2$ pattern.

The Evidence of the Coexistence of Lead Thiolate and Lead Octanoate. Comparative reactions have been carried out to synthesize different precursors with fixed conditions except for the use of the longer ($C_{16}H_{33}SH$) or shorter thiol ($C_{10}H_{21}SH$) chains instead of $C_{12}H_{25}SH$. Both results show two sets of successive *d* spacings, respectively. For the longer thiol case, $kd_{(T)} = 47.5$ Å for $k = 3-10$ and $kd_{(O)} = 25.7$ Å for $k = 2-7$ (S-Table 4, Supporting Information), whereas for the shorter thiol case, $kd_{(T)} = 32.0$ Å for $k = 2-24$ and $kd_{(O)} = 25.6$ Å for k = 2, 3, 5 (S-Table 5, Supporting Information). It is clear that the $kd_{(O)}$ value is unchanged and $kd_{(T)}$ increases with the length of the alkyl chain of thiol RSH, R = $(CH_2)_nCH_3$ (n = 9, 11, 15). Previous studies indicate the $kd_{(T)}$ values for layered thiolates are roughly equal to the thickness of the central slab plus twice the length of the alkyl chain, so the contribution of each CH_2 group is about 1.2 Å.[5,6] Thus, the d spacing of the lead decanethiolate should be roughly 2 × (2 × 1.2 Å) = 4.8 Å less than that of dodecanethiolate, while that of hexadecanethiolate should be 2 × (4 × 1.2 Å) = 9.6 Å longer, and the observed differences, 5.1 and 10.4 Å, agree well with the respective estimated values. Thus the $kd_{(O)}$ and $kd_{(T)}$ phases are independent. And interestingly, the $kd_{(O)}$ phase is obtained only when the amount of dodecanethiol is insufficient to coordinate all the Pb^{2+} ions (molar ratio: Pb^{2+}/DT = 1:1.6), so the $kd_{(O)}$ phase is likely related to octanoate.

Finally, we have also made lead octanoate from $Pb(NO_3)_2$/octanoate in a stoichiometric 1:2 ratio in aqueous solution and recrystallized it from ethanol. The product exhibits a XRD pattern with a layered motif (Figure 5, bottom) that matches well with all the diffractions of the $kd_{(O)}$ phase. Taking all into account, we conclude that under the optimal conditions for the synthesis of the PbS nanowires with x-shaped cross sections, two salts coexist. The lead thiolate is the source of the PbS, and a second salt, lead octanonate, i.e., $Pb(O_2C_8H_{15})_2$, affords important assistance in the formation of the nanowire morphology. We also made the precursor with excess sodium octanoate; with a $Pb(NO_3)_2$/octanoate/en/DT ratio of 1:3:1:1.6 and heating of the thus-made precursor at 280 °C for 1 h, the X-shaped cross-sectional PbS nanowires are obtained (S-Figure 6, Supporting Information). So, excess sodium octanoate does not have a significant impact on the formation of PbS nanowires. Comparatively, with insufficient octanoate, i.e., a $Pb(NO_3)_2$/octanoate ratio of less than 1:2, the thus-obtained precursor only yielded a mixture of 1D structure and small particles as shown in S-Figure 4 (Supporting Information). Without sodium octanoate, no Pb^{2+} ions could be solved in the $CHCl_3$ phase; subsequently, no lead thiolate could be formed, and therefore, no PbS could be made. These experiments suggest that in our case, the octanoate is not serving as a surfactant as in the Cu_2S system[4] but as a phase-transfer agent via the generation of lead octanoate salt, which is important to the formation of PbS nanowires; the exact mechanism is worthy of further investigation.

Conclusion

In summary, unique x-shaped cross-sectional PbS nanowires have been made by a solventless method. Such nanowires show the adsorbing tendency of the octahedral PbS nanoparticles in the present work. The key parameters for morphology control are the stoichiometry of the starting reactants at the precursor-synthesis stage and the subsequent heating temperature and time in the thermolysis stage. The suitable precursor is obtained from a $Pb(NO_3)_2$/octanoate/ethylenediamine/dodecanethiol molar ratio of 1:2:1:1.6, and the PbS nanowire is produced by the thermolysis of the precursor at 280 °C for 1 h, evidently via the cleavage of the C−S bond of lead thiolate in the presence of ethylenediamine and a second salt of lead octanoate, i.e., $Pb(O_2C_8H_{15})_2$. The ethylenediamine functions as a capping ligand and blocks the growth of the {111} faces, favoring both the growth of octahedral PbS nanopolyhedra and the growth of the 1D x-shaped cross-sectional PbS nanowires. Octanoate serves as an organic−aqueous phase-transfer agent via the generation of the layered lead octanoate, the presence of which is crucial for the formation of the 1D PbS nanowires. The results of this paper provide some useful strategies for the shape control of nanostructures via a solventless method, taking advantage of the growth-blocking effect of a capping ligand and utilizing the cooperative effects of a second salt. These may lead to the achievement of further facile morphological control of some highly desired materials. Studies aimed at the morphology control of other important semiconductors, e.g., PbTe and Bi_2Te_3, are underway.

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Supporting Information Available: EDX analyses; SEM image; XRD patterns; FTIR spectra and their assignments; and interlayer spacings. This material is available free of charge via the Internet at http://pubs.acs.org.

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