DOI: 10.1002/ange.200602952

Lead Chalcogenide Nanotubes Synthesized by Biomolecule-Assisted Self-Assembly of Nanocrystals at Room Temperature**

Hua Tong, Ying-Jie Zhu, Li-Xia Yang, Liang Li, and Ling Zhang*

Since the discovery of carbon nanotubes in 1991,[1] extensive research has been carried out on one-dimensional nanostructures because of their unique properties.[2–6] Various methods have been developed for the synthesis of nanotubes.[7] In general, it is relatively easy for layered materials to form nanotubes directly under the appropriate experimental conditions.[8] For materials that do not have a layered structure, nanotubes may be synthesized by a variety of methods, such as decomposition of the precursor,[9] template-assisted growth,[8,10–14] self-assembly,[15,16] and vapor deposition.[17,18] However, these methods are still limited to the synthesis of specific kinds of nanotubes.

Lead chalcogenides (PbE, E = S, Se, Te) are important semiconductors with narrow band gaps that are showing great promise in the field of IR photoelectronic and thermoelectric devices.[19–21] Various nanostructures of lead chalcogenides, such as quantum dots,[22–24] nanorods,[25,26] nanowires,[27,28] and nanotubes,[14,15,29,30] have been reported over the past decade. However, to the our knowledge, little work has been reported on polycrystalline nanotubes of lead chalcogenides assembled from nanocrystals, although one key example is the formation of composite nanotubes consisting of PbS nanoparticles, sodium dodecyl sulfate, and poly(ethylene oxide).[15]

Herein we report a novel biomolecule-assisted route to the synthesis of lead chalcogenide polycrystalline nanotubes by the self-assembly of nanocrystals at room temperature. Cysteine ($HSCH_2CH(NH_2)COOH$, including L-cysteine, L-cysteine hydrochloride monohydrate, and DL-cysteine hydro-

---

[*] H. Tong, Prof. Y.-J. Zhu, L.-X. Yang, L. Li, L. Zhang
State Key Laboratory of High Performance Ceramics and Superfine Microstructure
Shanghai Institute of Ceramics
Chinese Academy of Sciences
Shanghai 200050 (P.R. China)
and
Graduate School of Chinese Academy of Sciences
Shanghai 200050 (P.R. China)
Fax: (+86) 215-241-3122
E-mail: y.j.zhu@mail.sic.ac.cn

[**] Financial support from the National Natural Science Foundation of China (50472014) and the Chinese Academy of Sciences under the Program for Recruiting Outstanding Overseas Chinese (Hundred Talents Program) is gratefully acknowledged. We also thank the Fund for Innovation Research of the Shanghai Institute of Ceramics and financial support from the National Basic Science Research Program of China (973 Program) (grant no. 2005CB522700).

Supporting Information for this article is available on the WWW under http://www.angewandte.org or from the author.

chloride monohydrate) biomolecules, lead nitrate, and ethanolamine (or ethanediamine or ammonia) are used to prepare nanowires of a precursor at room temperature. These nanowires, which self-assemble from nanocrystals, act as both lead source and template for the subsequent preparation of lead chalcogenide nanotubes. Note that the precursor nanowires are transformed into lead chalcogenide nanotubes by our synthetic route, and that L-cysteine was recently used in the synthesis of sulfide nanostructures, such as Bi_2S_3[31] and Sb_2S_3.[32]

The precursor nanowires were characterized by powder X-ray diffraction (XRD; Figure 1a), which showed that they are well crystallized. On the basis of energy-dispersive spectroscopy (EDS) (see Supporting Information, Figure S1) and FTIR spectroscopy (Supporting Information, Figure S2), the likely chemical structure of the precursor nanowires is $HSCH_2CH(NH_2)COO{-}Pb{-}OH$. We chose cysteine for the synthesis because of its three functional groups (SH, NH_2, COOH). In the presence of a weakly basic additive, such as ethanolamine, which provides OH^- ions, the proton of the COOH group is removed and Pb^{2+} ions can react with cysteine to form the precursor.

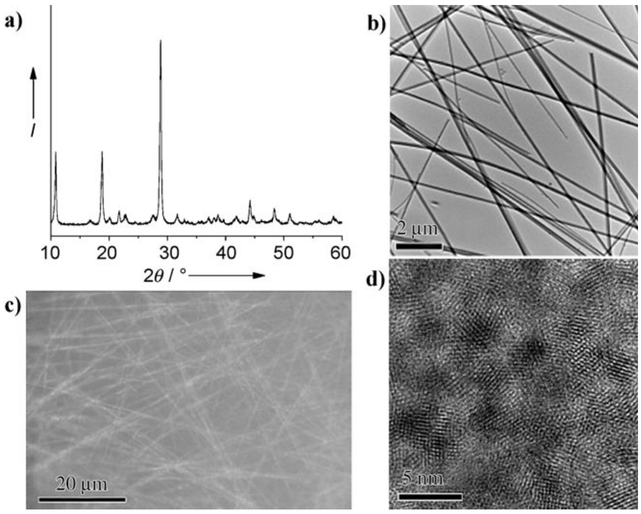

Figure 1. Characterization of the precursor nanowires prepared from $Pb(NO_3)_2$, L-cysteine, and ethanolamine: a) XRD pattern; b) TEM image; c) optical microscopy image; d) HRTEM image.

TEM revealed that the precursor has a wirelike morphology. These precursor nanowires have a typical diameter of around 200 nm (Figure 1b) and a length of around 100 µm (Figure 1c). The high-resolution TEM (HRTEM) image in Figure 1d shows that the nanowires are formed by the self-assembly of nanocrystals smaller than 5 nm. The precursor nanowires can also be obtained by using L-cysteine hydrochloride monohydrate or DL-cysteine hydrochloride monohydrate instead of L-cysteine.

In addition to ethanolamine, we also tried other weakly basic additives, such as ethanediamine or ammonia with quite similar results (see Supporting Information, Figure S3 and Figure S4). However, no precursor nanowires were obtained in the absence of base, in the presence of a strong base such as NaOH, or in the presence of an acid.

A simple replacement route was designed to synthesize lead chalcogenide nanotubes using the precursor nanowires as both the lead source and the template. Figure 2 schematically outlines the synthetic route and the proposed mechanism for the formation of lead chalcogenide nanotubes. It includes three key points: a) PbE nanocrystals are formed on the surface of the precursor nanowire by an anion-replacement reaction that is the result of the lower solubility of PbE in solution; b) the wall of the PbE nanotube is built up on the surface of the precursor nanowire by the self-assembly of PbE nanocrystals; c) the tubular structure forms at the expense of the precursor nanowire. Herein we demonstrate the synthesis of PbS, PbSe, and PbTe nanotubes by using this simple synthetic route.

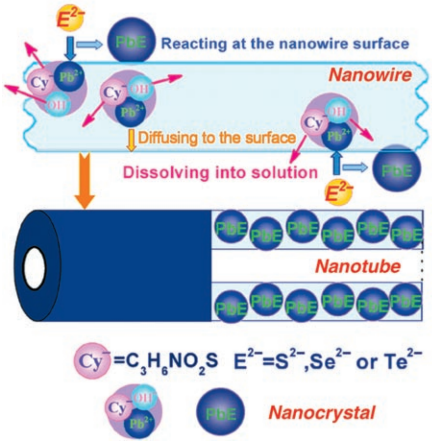

Figure 2. Schematic diagram of the synthetic route and proposed mechanism for the formation of PbE (E = S, Se, Te) nanotubes self-assembled from nanocrystals.

The XRD patterns (Figure 3) of the synthesized samples confirmed the formation of crystalline PbS (JCPDS no. 78-1901, Figure 3a), PbSe (JCPDS no. 78-1903, Figure 3b), and

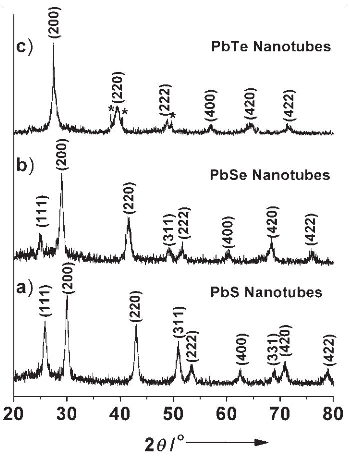

Figure 3. XRD patterns of synthesized lead chalcogenide nanotubes: a) PbS; b) PbSe; c) PbTe (* indicates peaks arising from Te).

PbTe (JCPDS no. 78-1905, Figure 3c), all of which have a face-centered cubic structure. No diffraction peaks from the precursor nanowires were observed, thus indicating that the precursor nanowires are completely transformed into lead chalcogenide nanotubes. The total yields of lead chalcogenides were higher than 90%. The broadening of the diffraction peaks implies that the lead chalcogenide nanotubes consist of very small nanocrystals.

The TEM and SEM images (Figure 4) show that all the synthesized samples of PbS (Figure 4a–e), PbSe (Figure 4f–j), and PbTe (Figure 4k–o) consist of nanotubes. These nanotubes have similar sizes in terms of both diameter and length. The typical diameter is about 200 nm. They are several micrometers long—much shorter than the precursor nanowires—possibly because of breaking of the nanotubes by sonication during preparation. PbE nanotubes could also be obtained without using sonication, although it was frequently observed that several nanotubes grew together. From Figure 4 it can be seen that the PbE nanotubes are formed by the self-assembly of nanocrystals. The electron diffraction (ED) patterns (insets in Figure 4d, i, and n) show that the nanotubes are polycrystalline in nature. The HRTEM images (Figure 4e, j, and o) reveal that the PbE nanocrystals in the nanotubes are smaller than 10 nm.

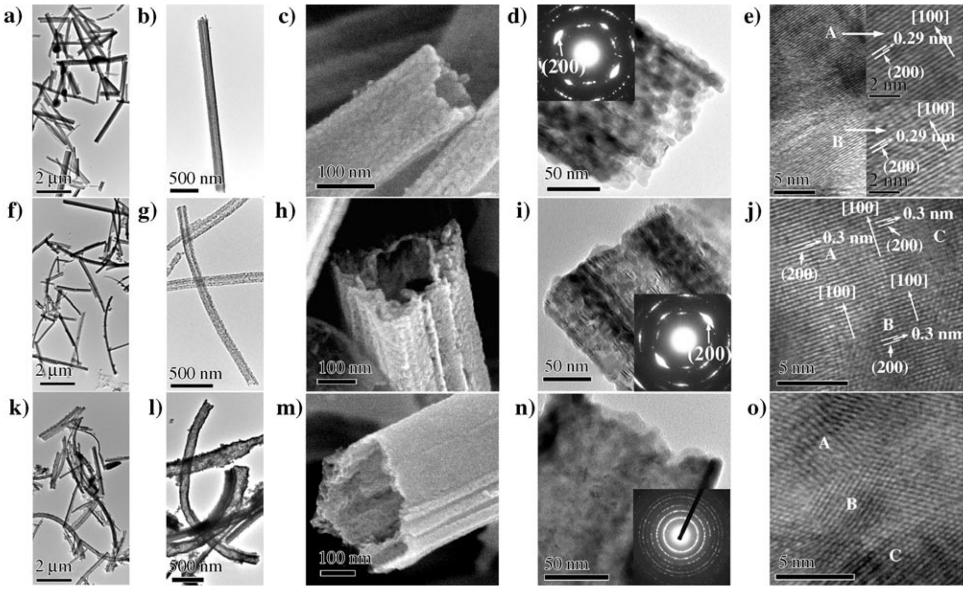

Figure 4. Characterization of PbE nanotubes: TEM (a,b,d,f,g,i,k,l,n; insets in d,i,n: ED pattern of a single nanotube), SEM (c,h,m), and HRTEM (e,j,o) of PbS (top), PbSe (middle), and PbTe (bottom), respectively.

The ED patterns of the PbS (inset in Figure 4d) and PbSe nanotubes (inset in Figure 4i) show discrete elongated bright dots for the (200) planes, unlike the usual polycrystalline diffraction rings, thus indicating that the nanocrystals aggregate into nanotubes with a highly oriented [100] crystallographic axis. This observation was supported by HRTEM. Figure 4e shows that two neighboring nanocrystals (A and B) in a PbS nanotube have the same orientation of the crystallographic axis along [100]. In Figure 4j, three nanocrystals (A, B, and C) in close contact in a PbSe nanotube have the same orientation along the [100] crystallographic axis.

No surfactant is used in our synthesis therefore the nanocrystals may aggregate together preferentially along a certain axis corresponding to a lower atom-density plane[33] and attach spontaneously through dipole–dipole attractions.[34,35] For face-centered cubic lead chalcogenides, a crystal unit has six equivalent [100] crystallographic axes and the (100) plane has the lowest atom density, thus making it more probable for nanocrystals to aggregate with their [100] crystallographic axis oriented in one direction. In contrast, the ED pattern (inset in Figure 4n) and HRTEM image (Figure 4o) of the PbTe nanotube clearly show a disorderly aggregation of the nanocrystals. The Pb/S and Pb/Se atomic ratios of the nanotubes were found to be about 1 by chemical composition analysis using EDS, whereas the Pb/Te atomic ratio was about 0.6. This excess of Te is due to the oxidation of Te^{2-} to elemental Te (Figure 3c, JCPDS no. 79-0736), which is responsible for the disordered aggregation of the PbTe nanocrystals.

The lead chalcogenide nanotubes described herein, which consist of nanocrystals smaller than 10 nm, in contrast to the Bohr exciton radii (bigger than 20 nm[23]) for bulk materials, exhibit a significant quantum confinement effect, as shown by the room-temperature absorption spectra (Figure 5). At the beginning of the absorption, a steep linear transition (absorption edge) can be seen, which is characteristic of direct band gap semiconductors. Based on the absorption edges,[36] the band gaps of the PbS, PbSe, and PbTe nanotubes were calculated to be 1.35, 1.13, and 0.75 eV, respectively, much larger than those of the bulk materials (0.2–0.4 eV[22]). These lead chalcogenide nanotubes, which are self-assembled from nanocrystals that display a quantum confinement effect as strong as that

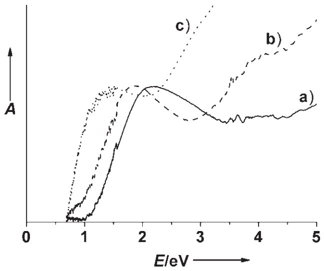

Figure 5. Absorption spectra of PbE nanotubes: a) PbS; b) PbSe; c) PbTe.

reported for quantum dots,[22–24] are presumed to be remarkably different from single-crystalline lead chalcogenide nanotubes.

In summary, lead chalcogenide nanotubes self-assembled from nanocrystals have been synthesized by a novel biomolecule-assisted method at room temperature. Polycrystalline precursor nanowires self-assembled from nanocrystals synthesized using cysteine play crucial roles as both the lead source and the template in the formation of lead chalcogenide nanotubes. These lead chalcogenide polycrystalline nanotubes display a definite quantum confinement effect. The biomolecule-assisted synthetic method demonstrated herein may also be extended to synthesize a variety of nanostructures assembled from nanocrystals.

Experimental Section

In a typical synthetic procedure for the precursor nanowires, a source solution was prepared by dissolving $Pb(NO_3)_2$ (0.033 g) and L-cysteine (0.012 g) in deionized water (30 mL) under magnetic stirring at room temperature. The reaction started when ethanolamine (0.2 mL) was quickly injected into the source solution at room temperature. A white product (precursor nanowires) formed immediately, and the solution was stirred for 20 min at room temperature. The product was separated by centrifugation and washed three times with deionized water and absolute ethanol. The precursor nanowires were then dispersed in ethanol (30 mL) to act as the lead source for the subsequent synthesis of lead chalcogenide nanotubes.

For the synthesis of the nanotubes, the chalcogenide source solution was prepared by dissolving $Na_2S\cdot 9H_2O$ (0.050 g) or Se powder (0.015 g) and $NaBH_4$ (0.020 g) or TeO_2 powder (0.032 g) and $NaBH_4$ (0.050 g) in deionized water (5 mL). The reaction started and was allowed to proceed for 5 min by mixing the chalcogenide source solution and the precursor nanowire solution at room temperature whilst sonicating to ensure a homogeneous dispersion. The product was collected by centrifugation and washed three times with deionized water and absolute ethanol.

TEM was performed with a JEM-2100F field-emission transmission electron microscope (JEOL). SEM was carried out with a JSM-6700F field-emission scanning electron microscope (JEOL). X-ray powder diffraction patterns were recorded with a D/MAX 2200 (Rigaku) X-ray diffractometer with $Cu_{K\alpha}$ radiation ($\lambda = 1.54178$ Å) and a graphite monochromator. Absorption spectra were measured with a Cary-500 spectrophotometer (Cary).

Received: July 22, 2006

Keywords: chalcogens · lead · nanostructures · nanotubes · self-assembly

---

[1] S. Iijima, *Nature* **1991**, *354*, 56.
[2] L. Sun, F. Banhart, A. V. Krasheninnikov, J. A. Rodriguez-Manzo, M. Terrones, P. M. Ajayan, *Science* **2006**, *312*, 1199.
[3] A. B. Panda, G. Glaspell, M. S. El-Shall, *J. Am. Chem. Soc.* **2006**, *128*, 2790.
[4] D. Normile, *Science* **1999**, *286*, 2056.
[5] T. Hasobe, S. Fukuzumi, P. V. Kamat, *Angew. Chem.* **2006**, *118*, 769; *Angew. Chem. Int. Ed.* **2006**, *45*, 755.
[6] H. Tokudome, M. Miyauchi, *Angew. Chem.* **2005**, *117*, 2010; *Angew. Chem. Int. Ed.* **2005**, *44*, 1974.
[7] M. Remskar, *Adv. Mater.* **2004**, *16*, 1497.
[8] Y. G. Sun, Y. N. Xia, *Adv. Mater.* **2004**, *16*, 264.
[9] C. C. Tang, Y. Bando, B. D. Liu, D. Golberg, *Adv. Mater.* **2005**, *17*, 3005.
[10] Z. Y. Sun, H. Q. Yuan, Z. M. Liu, B. X. Han, X. R. Zhang, *Adv. Mater.* **2005**, *17*, 2993.
[11] K. S. Mayya, D. I. Gittins, A. M. Dibaj, F. Caruso, *Nano Lett.* **2001**, *1*, 727.
[12] W. Lee, R. Scholz, K. Niesch, U. Gosele, *Angew. Chem.* **2005**, *117*, 6204; *Angew. Chem. Int. Ed.* **2005**, *44*, 6050.
[13] T. Kijima, T. Yoshimura, M. Uota, T. Ikeda, D. Fujikawa, S. Mouri, S. Uoyama, *Angew. Chem.* **2004**, *116*, 230; *Angew. Chem. Int. Ed.* **2004**, *43*, 228.
[14] L. Li, Q. S. Wu, Y. P. Ding, *Nanotechnology* **2004**, *15*, 1877.
[15] E. Leontidis, M. Orphanou, T. Kyprianidou-Leodidou, F. Krumeich, W. Caseri, *Nano Lett.* **2003**, *3*, 569.
[16] N. Diaz, F. X. Simon, M. Schmutz, M. Rawiso, G. Decher, J. Jestin, P. J. Mesini, *Angew. Chem.* **2005**, *117*, 3324; *Angew. Chem. Int. Ed.* **2005**, *44*, 3260.
[17] E. Bakkers, M. A. Verheijen, *J. Am. Chem. Soc.* **2003**, *125*, 3440.
[18] X. G. Wen, Y. P. Fang, S. H. Yang, *Angew. Chem.* **2005**, *117*, 3628; *Angew. Chem. Int. Ed.* **2005**, *44*, 3562.
[19] H. Zogg, K. Kellermann, K. Alchalabi, D. Zimin, *Infrared Phys. Technol.* **2004**, *46*, 155.
[20] V. V. Shchennikov, S. V. Ovsyannikov, *Solid State Commun.* **2003**, *126*, 373.
[21] T. C. Harman, R. E. Reeder, M. P. Walsh, B. E. LaForge, C. D. Hoyt, G. W. Turner, *Appl. Phys. Lett.* **2006**, *88*, 243504.
[22] E. H. Sargent, *Adv. Mater.* **2005**, *17*, 515.
[23] F. W. Wise, *Acc. Chem. Res.* **2000**, *33*, 773.
[24] W. G. Lu, J. Y. Fang, K. L. Stokes, J. Lin, *J. Am. Chem. Soc.* **2004**, *126*, 11798.
[25] M. Chen, Y. Xie, J. C. Lu, Y. J. Zhu, Y. T. Qian, *J. Mater. Chem.* **2001**, *11*, 518.
[26] X. F. Qiu, Y. B. Lou, A. C. S. Samia, A. Devadoss, J. D. Burgess, S. Dayal, C. Burda, *Angew. Chem.* **2005**, *117*, 6005; *Angew. Chem. Int. Ed.* **2005**, *44*, 5855.
[27] W. H. Wang, Y. Geng, Y. Qian, M. R. Ji, X. M. Liu, *Adv. Mater.* **1998**, *10*, 1479.
[28] K. S. Cho, D. V. Talapin, W. Gaschler, C. B. Murray, *J. Am. Chem. Soc.* **2005**, *127*, 7140.
[29] G. F. Zou, Z. P. Liu, D. B. Wang, C. L. Jiang, Y. T. Qian, *Eur. J. Inorg. Chem.* **2004**, 4521.
[30] S. F. Wang, F. Gu, M. K. Lu, G. J. Zhou, A. Y. Zhang, *J. Cryst. Growth* **2006**, *289*, 621.
[31] B. Zhang, X. H. Ye, W. Y. Hou, Y. Xie, *J. Phys. Chem. B* **2006**, *110*, 8978.
[32] X. Y. Chen, X. F. Zhang, C. W. Shi, X. L. Lia, Y. T. Qian, *Solid State Commun.* **2005**, *134*, 613.
[33] Z. P. Zhang, H. P. Sun, X. Q. Shao, D. F. Li, H. D. Yu, M. Y. Han, *Adv. Mater.* **2005**, *17*, 42.
[34] Z. Y. Tang, N. A. Kotov, M. Giersig, *Science* **2002**, *297*, 237.
[35] C. Pacholski, A. Kornowski, H. Weller, *Angew. Chem.* **2002**, *114*, 1234; *Angew. Chem. Int. Ed.* **2002**, *41*, 1188.
[36] N. S. Pesika, K. J. Stebe, P. C. Searson, *Adv. Mater.* **2003**, *15*, 1289.