Nanostructures

DOI: 10.1002/anie.200701591

Superconducting and Oxidation-Resistant Coaxial Lead–Polymer Nanocables**

*Xiaoli Lu, Genqiang Zhang, Wei Wang, and Xiaoguang Li**

Recent advances in nanotechnology have stimulated the study of mesoscopic superconductors for both fundamental interest[1–3] and potential applications in cryoelectronics.[4,5] Although superconducting nanowires of metals[6] and cuprates[7] have been fabricated, their high surface-to-volume ratios often cause high chemical reactivity or low toughness, leading to degradation of the structure, morphology, and properties.[8] The cablelike coaxial configuration creates a large and close interface between the sheathing layer and the core, which can induce an enhanced photoconductive response[9] or chemical stability,[8] for example. However, to our knowledge, the fabrication of superconducting nanocables has not been reported. Herein, an in situ templating strategy to fabricate well-defined superconducting nanocables with lead cores and polymer shells is described. The oxidation resistance of these nanocables is also discussed.

Generally, core–shell structures can be obtained through either a coating process (such as laser ablation,[10] a deposition procedure,[11] or a sol–gel reaction[12]) or an encapsulation process in a tubular structure (such as carbon nanotubes[13] or mesoporous silica[14]). In our previous study on the synthesis of lead nanowires,[15] sheetlike polymer structures were found at the early stages of the hydrothermal reaction in the presence of poly(vinylpyrrolidone) (PVP). If these sheets could be rolled up into tubular structures, they could act as both in situ templates and microreactors[16] for the subsequent growth of lead cores, resulting in core–shell architectures. However, no bending of the sheets was detected, probably because of poor interaction among the functional groups. Thus, increased interaction may drive the rolling of the microsheets to produce tubular structures.[9,17]

In accordance with this strategy, an appropriate amount of poly(vinyl alcohol) (PVA) was introduced into the hydrothermal reaction system, which contained PVP, ethylene glycol (EG), and $Pb(Ac)_2{\cdot}3H_2O$ (Ac = acetate). PVA can increase the interaction between functional groups on the PVP and PVA backbones through hydrogen bonds and cross-links (Figures S1 and S2 in the Supporting Information).[18] After reaction at 185 °C for 4 h, some tubular structures with higher contrast along the edges are obtained (Figure 1 a). Many metallic lead nanoparticles adhere to the inner tube surfaces (Figure 1 a, inset), as confirmed by energy-dispersive X-ray (EDX) spectroscopy and selected-area electron diffraction (SAED; Figure S3). The polymer tubes confine nanoparticle growth, leading to discontinuous rodlike blocks inside the tubes (Figure 1 b). The SAED pattern of these structures indicates that the blocks are polycrystalline; it can be indexed to face-centered cubic (fcc) lead (space group *Fm*3*m*; Joint Committee on Powder Diffraction Standards (JCPDS) 4-686). When the nanorods grow big enough, they merge with one another in a crystallographically oriented manner to form uniform nanowires (Figure 1 c,d).[19] In the transmission electron microscopy (TEM) image in Figure 1 d, there is a clear contrast between the lead cores with diameters of 80–100 nm and the polymer sheaths.

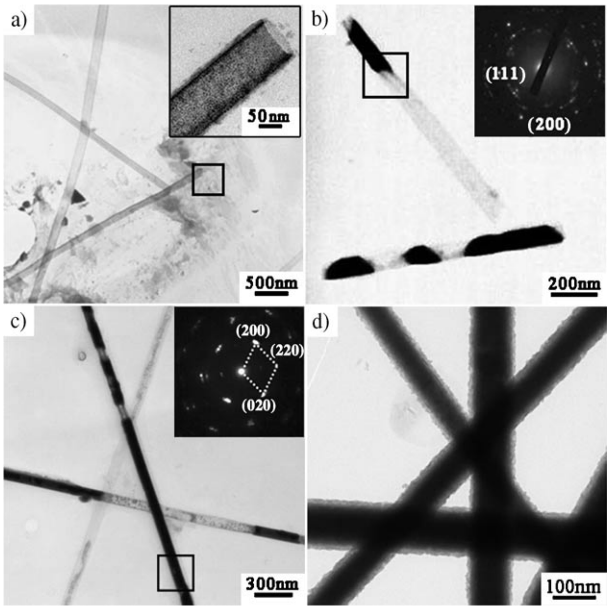


Figure 1. TEM images of the coaxial lead–polymer nanocables produced by reaction at 185 °C for time periods of: a) 4 h (inset: higher-magnification image of the indicated area); b) 8 h (inset: SAED pattern of the indicated area); c) 12 h (inset: SAED pattern of the indicated area); d) 24 h. See text for details.

---

[*] Dr. X. L. Lu, G. Q. Zhang, W. Wang, Prof. X. G. Li
Hefei National Laboratory for Physical Sciences at the Microscale
Department of Physics
University of Science and Technology of China
Hefei, 230026 (China)
Fax: (+86) 551-360-3408
E-mail: lixg@ustc.edu.cn
and
Hefei High Magnetic Field Laboratory
Hefei, 230031 (China)

[**] This work was supported by the National Natural Science Foundation of China (50421201 and 10334090) and the National Basic Research Program of China (2006CB601003 and 2006CB922005).

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

High-resolution (HR) TEM images of a single nanocable reveal lattice fringes with an interval of about 0.29 nm (assigned to the $(1\bar{1}1)$ planes), and the corresponding SAED pattern can be indexed to fcc lead (Figure 2 a,b). HRTEM also indicates that the nanowires are single-crystalline along their entire length (Figure S4). Local microstructure analysis gave no indication of PbO or Pb_2O layers on the wire surfaces. This result is consistent with the X-ray diffraction (XRD) pattern, in which no phases other than fcc lead are detected (Figure 2 c). The core–shell structure is further confirmed by an EDX line scan, in which the signals of lead (from the core) and carbon (from the polymer sheath) have different distributions (Figure 2 d).

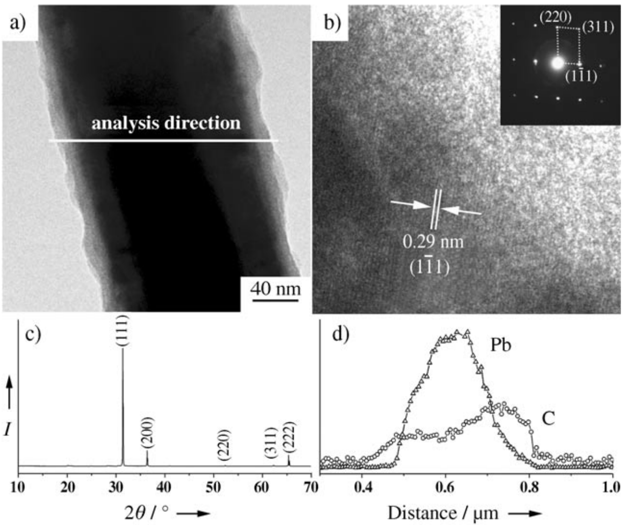
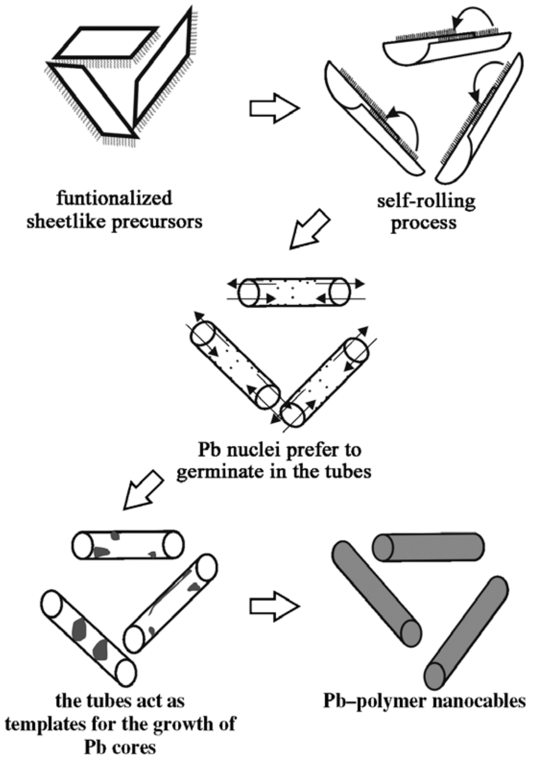


Figure 2. a) HRTEM image of a randomly selected coaxial lead–polymer nanocable. b) Higher-magnification image of the nanocable (inset: SAED pattern). c) XRD pattern of the nanocables. d) EDX line scan of the nanocable in (a); the lines are the guide to eyes. See text for details.

A self-rolling in situ templating mechanism is proposed to explain the growth process of the nanocables (Scheme 1). At the early stages of growth, sheetlike precursors, which are functionalized with PVA, are present. Interactions involving the PVA chains drive the sheets to roll up into tubular structures. The role of PVA in this process is similar to those of ultraviolet photocrosslinking[20] and bridging-type coordination[16] in other tube-forming reactions. Meanwhile, lead nuclei form in the solution through the reversible thermal decomposition of $Pb(Ac)_2{\cdot}3\,H_2O$.[21] The polymer tubes limit the migration of the reaction species and protect the nuclei from dissolving.[22] Thus, the concentration of lead nuclei inside the tubes is higher than that outside the tubes. At an appropriate temperature, the crystal nuclei germinate and grow preferentially inside the tubes. The polymer tubes act as microreactors generating lead structures with one-dimensional morphologies. Finally, lead nanowires fill the tubes, and coaxial lead–polymer nanocables are formed.



Scheme 1. Proposed growth process of the coaxial lead–polymer nanocables.

Bare lead nanowires exposed to air have been reported to react with both O_2 and CO_2 to form basic lead salts, leading to a dramatic decrease in the superconducting volume fraction (V_S).[21] To investigate the stability of our coaxial lead–polymer structures, the as-prepared nanocables and, for comparison, bare lead nanowires were both left in air at ambient temperature for 3 days. The bare nanowires (with diameters of 80–200 nm and lengths up to tens of micrometers) were prepared by a hydrothermal reaction, as described in our previous work.[15] The zero-field-cooled (ZFC) magnetization (M)–temperature curves of the aged nanocables and bare nanowires and of their as-prepared counterparts, measured on warming from 4 K in a field of 10 Oe, are shown in Figure 3. The curves exhibit a diamagnetic transition temperature (T_C) of about 7.2 K, which is consistent with that of bulk lead. The curve of the aged nanocables nearly overlaps with that of the as-prepared nanocables, which implies that there is no change in the superconducting volume fraction (estimated from the diamagnetic signal at 4 K) upon aging. However, the superconducting volume fraction in the aged bare nanowires is reduced to about 3 % of that in the as-prepared nanowires, which means that 97 % of the bare lead nanowires corroded during the aging process. These results indicate that the polymer sheath can efficiently protect the lead core from oxidation.

In conclusion, we have successfully prepared superconducting coaxial lead–polymer nanocables by a mild solution method. The use of PVA induced the growth of polymer tubes, consistent with a roll-up mechanism of nanotube formation. This method provides a simple one-step route to polymer-sheathed metal nanowires with good oxidation

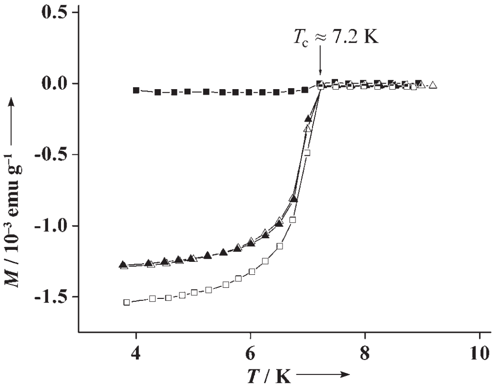


Figure 3. ZFC magnetization–temperature curves of the as-prepared coaxial lead–polymer nanocables (△) and bare lead nanowires (□) and of the nanocables (▲) and nanowires (■) after aging in air at ambient temperature for 3 days; the lines are the guide to eyes. See text for details.

resistance, which could have many applications in nanodevices.

Experimental Section

All chemicals were of analytical grade and were used without further purification. In a typical synthesis, $Pb(Ac)_2 \cdot 3H_2O$ (0.21 g), PVP (K 30, $M_w \approx 40000$; 0.21 g), PVA ($M_w \approx 1750$; 0.042 g), and EG (14 mL) were mixed in a teflon-lined autoclave and were magnetically stirred to give a solution. The sealed autoclave was heated at a rate of 1 °C min^{-1} to 185 °C and maintained at that temperature for different reaction times. Then the product was collected by centrifugation, washed with ethanol several times, and dried in vacuum at 60 °C. The XRD, SEM, TEM, HRTEM, FTIR, and magnetization measurements are described in the Supporting Information.

Received: April 11, 2007
Published online: June 25, 2007

Keywords: lead · nanostructures · oxidation · polymers · superconductors

---

[1] A. Bezryadin, C. N. Lau, M. Tinkham, *Nature* **2000**, *404*, 971–974.
[2] D. S. Hopkins, D. Pekker, P. M. Goldbart, A. Bezryadin, *Science* **2005**, *308*, 1762–1765.
[3] J. M. Blatt, C. J. Thompson, *Phys. Rev. Lett.* **1963**, *10*, 332–334.
[4] L. Chirolli and G. Burkard, *Phys. Rev. B* **2006**, *74*, 174510.
[5] J. P. Cleuziou, W. Wernsdorfer, V. Bouchiat, T. Ondarcuhu, M. Monthioux, *Nat. Nanotechnol.* **2006**, *1*, 53–59.
[6] J. G. Wang, M. L. Tian, N. Kumar, T. E. Mallouk, *Nano Lett.* **2005**, *5*, 1247–1253.
[7] a) X. L. Lu, T. Zhang, J. F. Qu, C. G. Jin, X. G. Li, *Adv. Funct. Mater.* **2006**, *16*, 1754–1758; b) G. Q. Zhang, X. L. Lu, T. Zhang, J. F. Qu, W. Wang, X. G. Li, S. H. Yu, *Nanotechnology* **2006**, *17*, 4252–4256.
[8] Y. C. Zhu, Y. Bando, D. F. Xue, F. F. Xu, D. Golberg, *J. Am. Chem. Soc.* **2003**, *125*, 14226–14227.
[9] Y. Yamamoto, T. Fukushima, Y. Suna, N. Ishii, A. Saeki, S. Seki, S. Tagawa, M. Taniguchi, T. Kawai, T. Aida, *Science* **2006**, *314*, 1761–1764.
[10] Y. Zhang, K. Suenaga, C. Colliex, S. Iijima, *Science* **1998**, *281*, 973–975.
[11] a) J. Goldberger, R. R. He, Y. F. Zhang, S. K. Lee, H. Q. Yan, H. J. Choi, P. D. Yang, *Nature* **2003**, *422*, 599–602; b) J. R. Ku, R. Vidu, R. Talroze, P. Stroeve, *J. Am. Chem. Soc.* **2004**, *126*, 15022–15023.
[12] D. L. Ma, J. W. Guan, F. Normandin, S. Dénommée, G. Enright, T. Veres, B. Simard, *Chem. Mater.* **2006**, *18*, 1920–1927.
[13] D. Ugarte, A. Châtelain, W. A. de Heer, *Science* **1996**, *274*, 1897–1899.
[14] Y. F. Zhu, J. L. Shi, W. H. Shen, X. P. Dong, J. W. Feng, M. L. Ruan, Y. S. Li, *Angew. Chem.* **2005**, *117*, 5213–5217; *Angew. Chem. Int. Ed.* **2005**, *44*, 5083–5087.
[15] X. L. Lu, W. Wang, G. Q. Zhang, X. G. Li, *Adv. Funct. Mater.* **2007**, DOI: 10.1002/adfm.200700011.
[16] O. Weichold, S. C. Hsu, M. Möller, *J. Mater. Chem.* **2006**, *16*, 4475–4479.
[17] a) C. N. R. Rao, M. Nath, *Dalton Trans.* **2003**, 1–24; b) M. Kogiso, Y. Zhou, T. Shimizu, *Adv. Mater.* **2007**, *19*, 242–246.
[18] Y. Wang, H. F. Liu, Y. X. Huang, *Polym. Adv. Technol.* **1996**, *7*, 634–638.
[19] S. H. Yu, X. J. Cui, L. L. Li, K. Li, B. Yu, M. Antonietti, H. Colfen, *Adv. Mater.* **2004**, *16*, 1636–1640.
[20] T. Ren, S. Xu, W. B. Zhao, J. J. Zhu, *J. Photochem. Photobiol. A* **2005**, *173*, 93–98.
[21] Y. Wang, X. Jiang, T. Herricks, Y. Xia, *J. Phys. Chem. B* **2004**, *108*, 8631–8640.
[22] M. Ryo, Y. Wada, T. Okubo, T. Nakazawa, Y. Hasegawa, S. Yanagida, *J. Mater. Chem.* **2002**, *12*, 1748–1753.