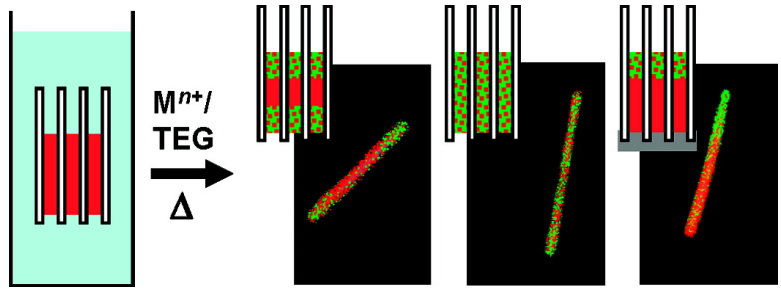
Communication

On-Wire Conversion Chemistry: Engineering Solid-State Complexity into Striped Metal Nanowires using Solution Chemistry Reactions

Mary E. Anderson, Matthew R. Buck, Ian T. Sines, Karl D. Oyler, and Raymond E. Schaak

J. Am. Chem. Soc., **2008**, 130 (43), 14042-14043 • DOI: 10.1021/ja804743b • Publication Date (Web): 07 October 2008



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

J|A|C|S
COMMUNICATIONS

Published on Web 10/07/2008

On-Wire Conversion Chemistry: Engineering Solid-State Complexity into Striped Metal Nanowires using Solution Chemistry Reactions

Mary E. Anderson, Matthew R. Buck, Ian T. Sines, Karl D. Oyler, and Raymond E. Schaak*

Department of Chemistry and Materials Research Institute, The Pennsylvania State University, University Park, Pennsylvania 16802

Received June 20, 2008; E-mail: schaak@chem.psu.edu

Template-grown metal nanowires represent an important class of one-dimensional nanomaterials that can be fabricated with multiple segments to include arbitrary sequences and thicknesses of different metals.[1] The electronic,[2] magnetic,[3] optical,[4] and catalytic[5] properties that result from their dimensionality and multisegment nature, coupled with their ability to be integrated with device architectures via self- and directed-assembly,[6] make them useful for a wide range of applications that include sensors, microelectronic devices, nanoscale motors, and platforms for biological detection and diagnosis.[1−6] Metal nanowires with uniform lengths and widths and single or multiple segments are typically fabricated by electrodeposition into porous membranes, such as anodic aluminum oxide (AAO).[1] This technique is applicable to a range of metals, alloys, and semiconductors that are amenable to electrodeposition from solution.[1−6]

We and others have been developing solution chemistry reactions that convert preformed metal nanoparticles into multimetal nanoparticle products.[7] These reactions directly transform metal nanostructures into multielement shape-controlled nanostructures that are otherwise challenging or impossible to prepare. Here we show that these "conversion chemistry" reactions are directly applicable to template-grown metal nanowires, which have dimensions that are 1−2 orders of magnitude larger than the nanoparticles typically used as precursors for these chemical transformations. This provides a single unified strategy for spatially controlled incorporation of a diverse library of compositionally and structurally complex components into template-grown nanowires. As such, it represents a simple robust alternative to incorporating multielement segments into nanowires using electrochemical codeposition,[8] which often requires significant system-specific optimization for stoichiometry control.

Figure 1 shows the process for transforming single-component metal nanowires into multisegment nanowires with multimetal components. Metal nanowires are first grown by galvanostatic electrodeposition into Ag-backed AAO membranes.[1] The nanowire-containing membrane is then immersed into a tetraethylene glycol (TEG) metal salt solution, either with the Ag backing intact to selectively react one end of the nanowire or with the Ag backing removed to react both ends. Upon heating, the metal salt reduces and diffuses into the exposed ends of the nanowires. The AAO membrane can then be dissolved to release the nanowires.

For proof-of-concept purposes, we focused initially on introducing intermetallic Pt−M (M = Pb, Bi, Sb, Co) segments into Pt nanowires, since reaction conditions are available for these systems and their successful formation requires careful control over composition. They also include a range of properties that may be useful to incorporate into striped metal nanowires, including catalytic activity (PtPb, PtBi),[7d,9] superconductivity (PtSb, PtBi),[10] and ferromagnetism (PtCo).[11]

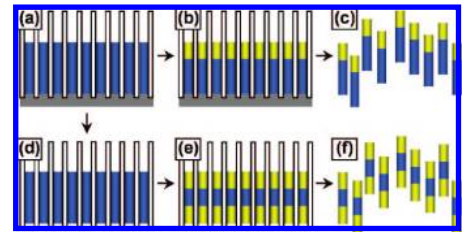


Figure 1. Metal nanowires in AAO membrane reacted either before (a−c) or after (d−f) Ag backing removed. Nanowires undergo site-specific modifications (b,e) and then are released from the membrane (c,f).

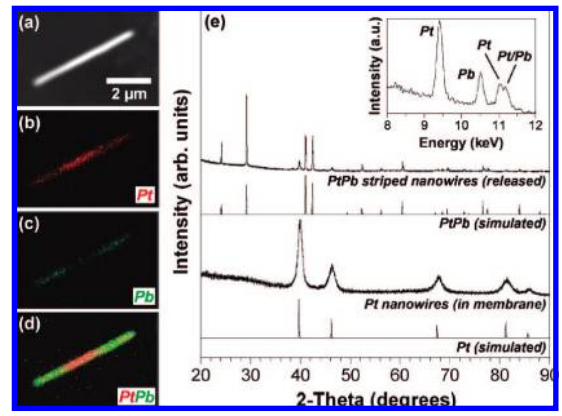


Figure 2. (a) SEM micrograph with element maps for (b) Pt, (c) Pb, and (d) SEM image with Pt and Pb overlay. (e) XRD data for as-grown Pt nanowires in the AAO membrane and released PtPb/Pt/PtPb nanowires after conversion. Inset: EDS spectrum for PtPb/Pt/PtPb nanowires.

Figure 2 shows a scanning electron microscope (SEM) image, along with energy dispersive X-ray spectroscopy (EDS) element mapping data, for a PtPb/Pt/PtPb nanowire formed by immersing an AAO membrane (Ag backing removed) containing 300 nm × 4 μm Pt nanowires into a 30 mM solution of $Pb(C_2H_3O_2)_2 \cdot 3H_2O$ at 300 °C for 1 h. Element mapping clearly shows the presence of Pt throughout the entire nanowire, with a higher concentration in the center (Figure 2b). In contrast, Pb is present primarily at the ends of the nanowire (Figure 2c).

Powder X-ray diffraction (XRD) data, shown in Figure 2e, confirm that the nanowire templates consist of Pt and the chemically converted products contain a mixture of Pt and NiAs-type PtPb, along with a small impurity of a Pt_3Pb alloy phase. It is worth noting that the Pt XRD peaks in the PtPb/Pt/PtPb nanowire are sharper than in the Pt nanowire template, implying that the crystallinity of the wire was improved during the solution-phase annealing. EDS spectra taken on an ensemble of nanowires show that both Pt and Pb are present exclusively (Figures 2e and Supporting Information, S1), with more Pt than Pb as expected.

10.1021/ja804743b CCC: $40.75

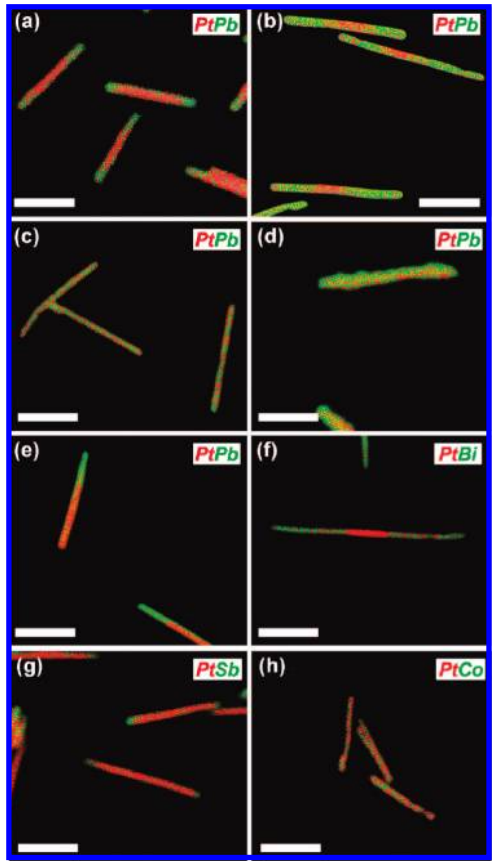


Figure 3. Element maps for (a,b) PtPb/Pt/PtPb nanowires; PtPb nanowires reacted (c) in the membrane and (d) after release; (e) PtPb/Pt nanowires reacted in the membrane with the Ag backing intact; (f) PtBi/Pt/PtBi, (g) PtSb/Pt/PtSb, and (h) Pt_3Co nanowires formed in the membrane. Red, Pt; green, Pb, Bi, Sb, or Co. All scale bars are 2 μm.

Ensemble XRD and EDS data, coupled with single-wire imaging, provide good evidence that the nanowires consist of a Pt center with intermetallic PtPb ends (rather than a compositionally variable $Pt_{1-x}Pb_x$ alloy). Spatially resolved EDS spectra confirm this (Figure S3).

The on-wire chemical conversion reactions are diffusion-mediated, so temperature and concentration affect the diffusion process and provide control over the segment lengths. Compared to the nanowires in Figure 2 and 3b, it is possible to fabricate Pt nanowires with shorter PtPb tips (Figure 3a; 10 mM, 220 °C, 1 h), as well as convert the entire Pt nanowire to PtPb using reactions that occur either in the membrane (Figure 3c; 60 mM, 300 °C, 1 h) or after releasing from the membrane (Figure 3d). The former produces PtPb nanowires with surface roughness close to that of the Pt nanowire template, while the latter generates significantly rougher nanowires since they are not spatially confined within the template (Figure S7). When the Ag backing is left on during the conversion reaction, the Pb diffuses only into the exposed end of the Pt nanowire, forming anisotropic PtPb/Pt two-segment nanowires (Figure 3e). The general nanowire conversion process can be extended to other metal systems as well, including PtBi (Figure 3f), PtSb (Figure 3g), and Pt_3Co (Figure 3h).

The solution chemistry conversion reactions developed for metal nanoparticles are directly applicable to on-wire transformations while maintaining interfacial stability, providing a convenient toolkit for engineering complex solid-state components into template-grown metal nanowires. Reaction parameters permit control over segment length and composition, as well as site-specific reactivity. Intermetallic compounds were chosen as proof-of-concept targets, but similar reactions convert metal nanoparticles to oxides,[12] chalcogenides,[7g−j] phosphides,[7e,f] alloys,[13] etc. Preliminary data suggests that metal phosphides can indeed be incorporated into the metal nanowires via reaction with trioctylphosphine (e.g., Rh_2P, Figure S8). Related reactions such as galvanic replacement[14] and ion exchange[7i,j] work under similar conditions, and collectively these tools should provide facile solution-mediated access to a wide range of solid-state nanowire components, as well as compositional gradients, dopants, and nonconducting segments.

Acknowledgment. This work was supported by NSF (DMR-0748943), a Beckman Young Investigator Award, a Sloan Research Fellowship, a DuPont Young Professor Grant, and a Camille Dreyfus Teacher-Scholar Award. SEM was performed at the Materials Characterization Facility at the Penn State Materials Research Institute and at the Huck Institutes of the Life Sciences. The authors thank Dr. Christine Keating and her group for help with nanowire electrodeposition. The authors also acknowledge use of facilities at the PSU site of the NSF NNIN.

Supporting Information Available: Experimental details, additional EDS, XRD, and SEM data. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Mieszawska, A. J.; Jalilian, R.; Sumanasekera, G. U.; Zamborini, F. P. *Small* **2007**, *3*, 722. (b) Kline, T. R.; Tian, M.; Wang, J.; Sen, A.; Chan, M.; Mallouk, T. E. *Inorg. Chem.* **2006**, *45*, 7555. (c) Hust, S. J.; Payne, E. K.; Qin, L.; Mirkin, C. A. *Angew.Chem. Int. Ed.* **2006**, *45*, 2672.
(2) (a) Wang, J.-G.; Tian, M.-L.; Mallouk, T. E.; Chang, M. H. W. *Nano Lett.* **2004**, *4*, 1313. (b) Tian, M.; Wang, J.; Kumar, N.; Han, T.; Kobayashi, Y.; Liu, Y.; Mallouk, T. E.; Chan, M. H. W. *Nano Lett.* **2006**, *6*, 2773. (c) Chen, X.; Jeon, Y.-M.; Jang, J.-W.; Qin, L.; Huo, F.; Wei, W.; Mirkin, C. A. *J. Am. Chem. Soc.* **2008**, *130*, 8166. (d) Wu, Y.; Xiang, J.; Yang, C.; Lu, W.; Lieber, C. M. *Nature* **2004**, *430*, 61.
(3) (a) Oh, B.-K.; Park, S.; Millstone, J. E.; Lee, S. W.; Lee, K.-B.; Mirkin, C. A. *J. Am. Chem. Soc.* **2006**, *128*, 11825. (b) Piraux, L.; George, J. M.; Despres, J. F.; Leroy, C.; Ferain, E.; Legras, R.; Ounadjela, K.; Fert, A. *Appl. Phys. Lett.* **1994**, *65*, 2484. (c) Urbach, A. R.; Love, J. C.; Prentiss, M. G.; Whitesides, G. M. *J. Am. Chem. Soc.* **2003**, *125*, 12704.
(4) (a) Nicewarner-Pena, S. R.; Freeman, R. G.; Reiss, B. D.; He, L.; Pena, D. J.; Walton, I. D.; Cromer, R.; Keating, C. D.; Natan, M. J. *Science* **2001**, *294*, 137. (b) Hornyak, G. L.; Patrissi, C. J.; Martin, C. R. *J. Phys. Chem. B* **1997**, *101*, 1548.
(5) (a) Kline, T. R.; Paxton, W. F.; Wang, Y.; Velegol, D.; Mallouk, T. E.; Sen, A. *J. Am. Chem. Soc.* **2005**, *127*, 17150. (b) Qin, L.; Banholzer, M. J.; Xu, X.; Huang, L.; Mirkin, C. A. *J. Am. Chem. Soc.* **2007**, *129*, 14870.
(6) (a) Li, M.; Bhiladvala, R. B.; Morrow, T. J.; Sioss, J. A.; Lew, K.-K.; Redwing, J. M.; Keating, C. D.; Mayer, T. S. *Nature Nanotechnol.* **2008**, *3*, 88. (b) Smith, P. A.; Nordquist, C. D.; Jackson, T. N.; Mayer, T. S.; Martin, B. R.; Mbindyo, J.; Mallouk, T. E. *Appl. Phys. Lett.* **2000**, *77*, 1399.
(7) (a) Vasquez, Y.; Henkes, A. E.; Bauer, J. C.; Schaak, R. E. *J. Solid State Chem.* **2008**, *181*, 1509. (b) Chou, N. H.; Schaak, R. E. *J. Am. Chem. Soc.* **2007**, *129*, 7339. (c) Cable, R. E.; Schaak, R. E. *Chem. Mater.* **2007**, *19*, 4098. (d) Bauer, J. C.; Chen, X.; Liu, Q.; Phan, T.-H.; Schaak, R. E. *J. Mater. Chem.* **2008**, *18*, 275. (e) Henkes, A. E.; Vasquez, Y.; Schaak, R. E. *J. Am. Chem. Soc.* **2007**, *129*, 1896. (f) Henkes, A. E.; Schaak, R. E. *Inorg. Chem.* **2008**, *47*, 671. (g) Jeong, U.; Camargo, P. H. C.; Lee, Y. H.; Xia, Y. *J. Mater. Chem.* **2006**, *16*, 3893. (h) Yin, Y.; Rioux, R. M.; Erdonmez, C. K.; Hughes, S.; Somorjai, G. A.; Alivisatos, A. P. *Science* **2004**, *304*, 711. (i) Son, D. H.; Hughes, S. M.; Yin, Y.; Alivisatos, A. P. *Science* **2004**, *306*, 1009. (j) Camargo, P. H. C.; Lee, Y. H.; Jeong, U.; Zou, Z.; Xia, Y. *Langmuir* **2007**, *23*, 2985.
(8) (a) Huang, Y. H.; Okumura, H.; Hadjipanayis, G. C.; Weller, D. *J. Appl. Phys.* **2002**, *91*, 6869. (b) Singh, K. V.; Martinez-Morales, A. A.; avan, G. T. S.; Bozhilov, K. N.; Ozkan, M. *Chem. Mater.* **2007**, *19*, 2446. (c) Mosby, J. M. A.; Prieto, A. L. *J. Am. Chem. Soc.* **2008**, *130*, 10656.
(9) Alden, L. R.; Roychowdhury, C.; Matsumoto, F.; Han, D. K.; Zeldovich, V. B.; Abruna, H. D.; Disalvo, F. J. *Langmuir* **2006**, *22*, 10465.
(10) Matthias, B. T. *Phys. Rev.* **1953**, *92*, 874.
(11) Weller, D.; Doerner, M. F. *Annu. Rev. Mater. Sci.* **2000**, *30*, 611.
(12) Hyeon, T.; Lee, S. S.; Park, J.; Chung, Y.; Na, H. B. *J. Am. Chem. Soc.* **2001**, *123*, 12798.
(13) (a) Chen, J.; Wiley, B.; McLellan, J.; Xiong, Y.; Li, Z.-Y.; Xia, Y. *Nano Lett.* **2005**, *5*, 2058. (b) Vasquez, Y.; Sra, A. K.; Schaak, R. E. *J. Am. Chem. Soc.* **2005**, *127*, 12504.
(14) Sun, Y.; Xia, Y. *J. Am. Chem. Soc.* **2004**, *126*, 3892.

JA804743B