JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

COMMUNICATION

pubs.acs.org/JACS

Fabrication of Nanopeapods: Scrolling of Niobate Nanosheets for Magnetic Nanoparticle Chain Encapsulation

Yuan Yao, Girija S. Chaubey, and John B. Wiley*

Department of Chemistry and Advanced Materials Research Institute, University of New Orleans, New Orleans, Louisiana 70148, United States

S Supporting Information

ABSTRACT: Scrolling of niobate nanosheets (NSs) in the presence of magnetic nanoparticle (NP) chains can lead to peapodlike structures. Surface functional groups on both the NSs and NPs are important in directing the assembly and subsequent NS convolution. The dimensions of the peapods are typically dictated by the diameters of the NPs and the length of the NP chains.

Nanopeapod structures, where spherical molecules or nanoparticles (NPs) are contained within nanotubes (NTs), have been extensively studied because of their potential applications in electronics, magnetics, optics, and sensors.[1−10] Among the first peapod structures reported were those based on C_{60} and carbon nanotubes (CNTs), where C_{60} molecules were simply inserted into the CNTs.[1,2] More recently, peapods containing metal[3−8,10] and metal oxide[9] NPs have been produced; a diverse set of preparation methods has been utilized to create the metal-sphere component (pea), such as Rayleigh instability, single-displacement reactions, and controlled electrodeposition. Fabrication of the outer component (pod) has also been extensively studied, leading to the production of a variety of NTs[3−9] including SiO_2,[3] Ga_2O_3,[4] MgO,[5] TiO_2,[6] Al_2O_3,[6] $CoAl_2O_4$,[7] Ni_3S_2[8] and carbon NTs.[9] The NT components are typically made by template methods within porous membranes[6a,7,10] or via chemical routes involving core−shell nanostructures.[3−5,6b,8,9] While most of the peapod synthetic routes involve the formation of the NP components within an existing tube structure, one exception involves a displacement reaction where a Te sheath forms as cobalt is displaced from Au/Co superlattice wires.[10]

Tubular-like structures can also be formed via the scrolling of lamella. Convolved nanosheets (nanoscrolls) have been reported for a number of layered materials, including those based on graphite, oxides, sulfides, hydroxides, nitrides, and metals.[11] Similar behavior occurs naturally in the mineral halloysite.[12] Among the oxides, the layered niobate $K_4Nb_6O_{17}$ is especially notable because of its use in photocatalysts;[13] scrolling of exfoliated nanosheets (NSs) of the acid form of this compound can be readily achieved by reacting it with tetrabutylammonium hydroxide (TBAOH).[14] Herein we report an alternative approach to the synthesis of nanopeapod structures that exploits the convolution of oxide layers. Co NPs are generated in the presence of exfoliated niobate NSs, and the resulting magnetic chain structures are captured within scrolled lamella.

To fabricate the peapod structures, initially the layered oxide $K_4Nb_6O_{17}$ was exfoliated by acid treatment to give $H_xK_{4-x}Nb_6O_{17}$ NSs.[14] Following a drying step, the NSs were suspended in octyl ether and combined with TBAOH, oleylamine, and oleic acid under a nitrogen atmosphere. TBAOH is known to promote nanoscroll formation, and the oleylamine and oleic acid serve as NP surface groups. Cobalt NPs were then generated in situ by decomposition of cobalt carbonyl, $Co_2(CO)_8$. [**Caution:** *Cobalt carbonyl should be handled with extreme caution because of its high toxicity.*] The cobalt carbonyl was added after the mixture was heated to various temperatures; lower temperatures (100−130 °C) produced a wider particle size distribution (2−45 nm), while higher ones (140−150 °C) produced a narrower range (>80% 10−20 nm). The crude product was washed repeatedly with ethanol and hexane to remove excess surfactant and free Co NPs. In some cases, a centrifugation step and/or magnet separation step was carried out to separate peapods from unscrolled and empty scrolled NSs. The final products were redispersed in hexane for characterization by transmission electron microscopy (TEM) [see the Supporting Information (SI) for details concerning synthesis, characterization, and particle size distributions].

Figure 1 presents TEM images of a series of Co@niobate nanopeapod structures. As-prepared samples were found to contain peapods as well as some free NPs, NSs, and nanoscrolls (Figure 1a). Additional processing steps (centrifugation and magnetic separation) could be used to minimize unwanted byproducts (Figure 1b−d). Peapods of different lengths with various numbers of aligned NPs were obtained. In some cases, peapods well over 1 μm in length were seen, containing 15 or more NPs depending on the NP sizes. Both single-walled (Figure 1c) and multiwalled (Figure 1d) structures were observed; the thickness of the tube walls was found to be ∼10 Å, in agreement with the known thickness of single niobate NSs.[14c] The outer diameters of the empty niobate nanoscrolls (Figure S2 in the SI) averaged ∼20 nm,[14c] while those of the peapods were dictated by the resident NP sizes. Interestingly, single-walled structures undulated along the length of the peapod to conform to the NP chains (Figure 1c). In contrast, the diameters of the multiwalled peapods were more constant, likely being influenced by strong interactions with the additional oxide layers (Figure 1d).

The magnetic alignment of the Co NPs is believed to be essential in the formation of these peapod structures. Such magnetic chains have been reported in a number of systems,[15] and it is typically required that NP diameters exceed 8 nm for the chains to form.[16] This is consistent with our results in that we observed nanopeapod structures containing NPs with diameters of ∼10 nm and greater.

Received: July 5, 2011
Published: September 21, 2011

dx.doi.org/10.1021/ja206237v | J. Am. Chem. Soc. 2012, 134, 2450–2452

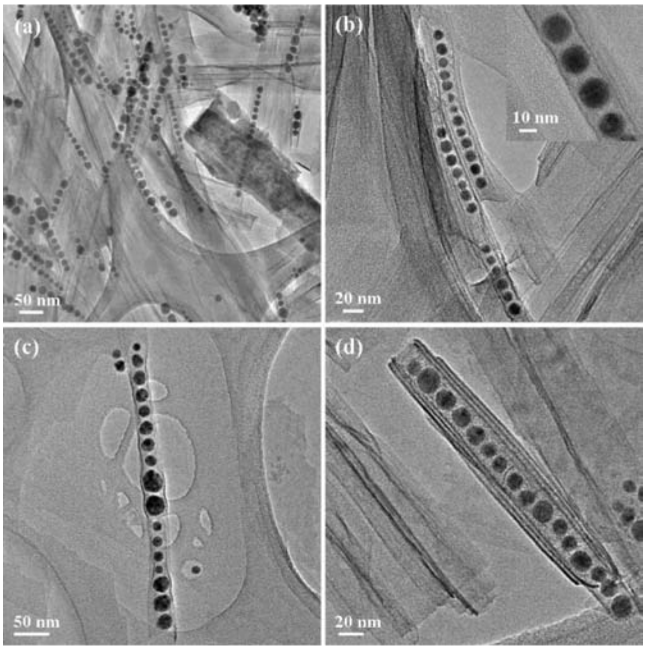

Figure 1. TEM images of Co@niobate nanopeapods: (a) as-prepared product containing peapods, NSs, empty nanoscrolls, and free Co NPs; (b−d) product after separation steps. The inset of (b) shows an enlarged image of a peapod; (c) and (d) show single-walled and multiwalled peapods, respectively. In (c), cobalt carbonyl was introduced at a lower temperature.

While most of the above nanopeapod structures were obtained after successive washing steps to remove free NPs and NSs, if one examines samples prior to this work up, some insight into a possible reaction mechanism may be gleaned. TEM images suggest that NPs can align on the surface of thin multilayer NSs (Figure 2a, white ovals); here we expect that exfoliated multilayer niobate crystals are better than single layers in the formation of nanopeapod structures since the multilayered structures allow for more rigid reaction platforms in solution. Because of the asymmetry of the niobate layers, the sheets can curl in only one orientation.[14] This is likely important in determining whether the top layer of a rigid NS can scroll up to encase the NPs (Figure 2b, white arrows) before detaching from the surface. Figure 2c shows an isolated peapod structure in which the NS appears to be curling from two sides to encase two adjacent NP chains. The chains may have aligned simultaneously on the same NS and were encased as scrolling occurred from opposite sides. This series of images (Figure 2a−c) suggests a possible mechanism for the formation of the nanopeapods: initially, NPs align in a chain on top of a multilayered NS; next, the top NS curls to encase the chain; and finally, the resulting peapod is detached from the surface. Figure 3 illustrates this proposed mechanism. It should be noted that this is not the only plausible mechanism for peapod formation. Structures could certainly form by a similar mechanism from individual NSs or through the insertion of NPs into rolled NSs, although the latter may be less effective for larger NPs because of the relatively small average outer diameter (∼20 nm) available in these structures.

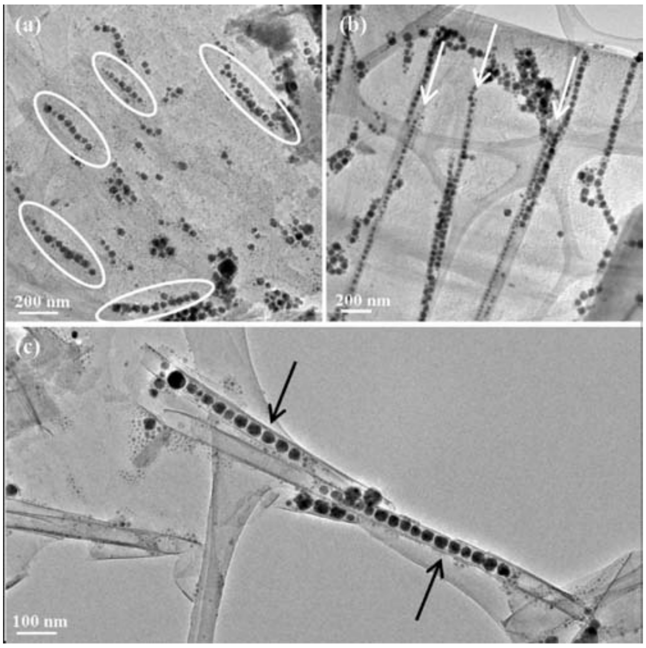

Figure 2. (a) Free Co NP chains on a nanosheet (circled in white). (b) Aligned peapods on a nanosheet (indicated by white arrows). (c) Free peapod structure in which the nanosheet appears to be curling from two sides to encase two adjacent NP chains; black arrows indicate the two NP chains.

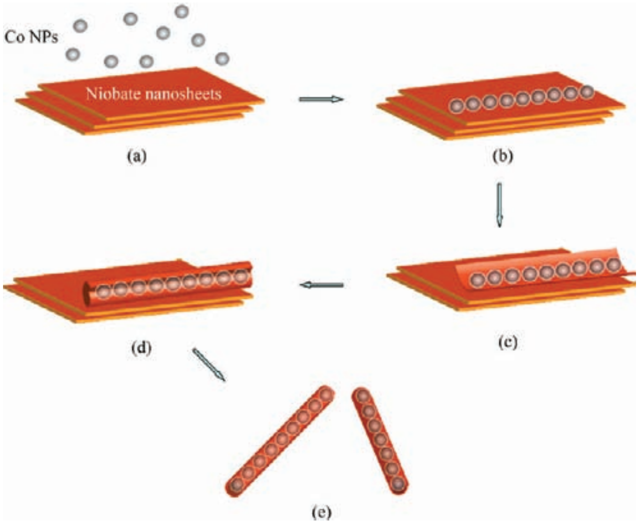

Figure 3. Proposed mechanism for the formation of a nanopeapod. (a) Co NPs nucleate and grow in solution. (b) NPs assemble and form a chain on the surface of a niobate NS. (c, d) The niobate NS scrolls around the chain. (e) Nanopeapods form and separate from the niobate NSs.

Nanopeapods can be readily prepared via scrolling of niobate nanosheets around magnetically aligned chains of Co nanoparticles. This approach is unique among peapod fabrication methods in that it involves NP chain assembly and NS scrolling. While our approach has focused on niobate NSs, a number of other layered materials (see above) might also be utilized.[11] Similarly, a variety of NP chain components could also be incorporated, since other magnetic NPs are known to form chains,[15] as do some nonmagnetic nanostructures such as those based on functionalized NPs or fullerene molecules.[17,18] Furthermore, shapes should not be limited to spherical NPs; cubes, rods, or nanowire structures may also be amenable to NS encapsulation.[19] The availability of such a wide variety of components could offer important flexibility in the design of technologically significant materials, including those with applications in catalysis, magnetics, and sensing.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Detailed experimental procedures; TEM images of NSs, nanoscrolls, and nanopeapods; NP size distributions; and high-resolution TEM, energy-dispersive spectroscopy, and X-ray powder diffraction results. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

jwiley@uno.edu

■ ACKNOWLEDGMENT

Thanks are given to the Louisiana Board of Regents for financial support through the Post-Katrina Support Fund Initiative [LEQSF-(2007-12)-ENH-PKSFI-PRS-04]. We also thank Dr. B. Cao for assistance with TEM and Dr. K. Ranmohotti, Dr. E. Josepha, and D. Montasserasadi for assistance with X-ray powder diffraction. Special thanks to Dr. X. Wei for assistance with the cover design.

■ REFERENCES

(1) Smith, B. W.; Monthioux, M.; Luzzi, D. E. *Nature* **1998**, *396*, 323–324.

(2) (a) Chiu, P. W.; Gu, G.; Kim, G. T.; Philipp, G.; Roth, S.; Yang, S. F.; Yang, S. *Appl. Phys. Lett.* **2001**, *79*, 3845–3847. (b) Yoon, Y. G.; Mazzoni, M. S. C.; Louie, S. G. *Appl. Phys. Lett.* **2003**, *83*, 5217–5219. (c) Sun, B. Y.; Sato, Y.; Suenaga, K.; Okazaki, T.; Kishi, N.; Sugai, T.; Bandow, S.; Iijima, S.; Shinohara, H. *J. Am. Chem. Soc.* **2005**, *127*, 17972–17973.

(3) (a) Wu, J. S.; Dhara, S.; Wu, C. T.; Chen, K. H.; Chen, Y. F.; Chen, L. C. *Adv. Mater.* **2002**, *14*, 1847–1850. (b) Hu, M. S.; Chen, H. L.; Shen, C. H.; Hong, L. S.; Huang, B. R.; Chen, K. H.; Chen, L. C. *Nat. Mater.* **2006**, *5*, 102–106. (c) Kolb, F. M.; Berger, A.; Hofmeister, H.; Pippel, E.; Gosele, U.; Zacharias, M. *Appl. Phys. Lett.* **2006**, *89*, No. 173111. (d) Park, G. S.; Kwon, H.; Lee, E. K.; Kim, S. K.; Lee, J. H.; Li, X. S.; Chung, J. G.; Heo, S.; Song, I. Y.; Lee, J. H.; Choi, B. L.; Kim, J. M. *Adv. Mater.* **2010**, *22*, 2421–2425. (e) Hunyadi, S. E.; Murphy, C. J. *J. Phys. Chem. B* **2006**, *110*, 7226–7231.

(4) (a) Hsieh, C. H.; Chou, L. J.; Lin, G. R.; Bando, Y.; Golberg, D. *Nano Lett.* **2008**, *8*, 3081–3085. (b) Chen, P. H.; Hsieh, C. H.; Chen, S. Y.; Wu, C. H.; Wu, Y. J.; Chou, L. J.; Chen, L. J. *Nano Lett.* **2010**, *10*, 3267–3271.

(5) (a) Lai, Y. F.; Chaudouet, P.; Charlot, F.; Matko, I.; Dubourdieu, C. *Appl. Phys. Lett.* **2009**, *94*, No. 022904. (b) Zhou, W. W.; Sun, L.; Yu, T.; Zhang, J. X.; Gong, H.; Fan, H. J. *Nanotechnology* **2009**, *20*, No. 455603.

(6) (a) Qin, Y.; Liu, L. F.; Yang, R. B.; Gosele, U.; Knez, M. *Nano Lett.* **2008**, *8*, 3221–3225. (b) Qin, Y.; Lee, S. M.; Pan, A. L.; Gosele, U.; Knez, M. *Nano Lett.* **2008**, *8*, 114–118.

(7) (a) Liu, L. F.; Lee, W.; Scholz, R.; Pippel, E.; Gosele, U. *Angew. Chem., Int. Ed.* **2008**, *47*, 7004–7008. (b) Sioss, J. A.; Keating, C. D. *Nano Lett.* **2005**, *5*, 1779–1783. (c) Zhu, W.; Wang, G. Z.; Hong, X.; Shen, X. S.; Li, D. P.; Xie, X. *Electrochim. Acta* **2009**, *55*, 480–484.

(8) Zhou, W.; Chen, W. M.; Nai, J. W.; Yin, P. G.; Chen, C. P.; Guo, L. *Adv. Funct. Mater.* **2010**, *20*, 3678–3683.

(9) Wang, Y.; Zhang, H. J.; Lu, L.; Stubbs, L. P.; Wong, C. C.; Lin, J. Y. *ACS Nano* **2010**, *4*, 4753–4761.

(10) Hangarter, C. M.; Lee, Y. I.; Hernandez, S. C.; Choa, Y. H.; Myung, N. V. *Angew. Chem., Int. Ed.* **2010**, *49*, 7081–7085.

(11) (a) Feldman, Y.; Wasserman, E.; Srolovitz, D. J.; Tenne, R. *Science* **1995**, *267*, 222–225. (b) Remskar, M. *Adv. Mater.* **2004**, *16*, 1497–1504. (c) Schaak, R. E.; Mallouk, T. E. *Chem. Mater.* **2000**, *12*, 3427–3434. (d) Schaak, R. E.; Mallouk, T. E. *Chem. Mater.* **2002**, *14*, 1455–1471. (e) Sidorov, A.; Mudd, D.; Sumanasekera, G.; Ouseph, P. J.; Jayanthi, C. S.; Wu, S. Y. *Nanotechnology* **2009**, *20*, No. 055611.

(12) Joussein, E.; Petit, S.; Churchman, J.; Theng, B.; Righi, D.; Delvaux, B. *Clay Miner.* **2005**, *40*, 383–426.

(13) (a) Gasperin, M.; Bihan, M. T. L. *J. Solid State Chem.* **1982**, *43*, 346–353. (b) Nassau, K.; Shiever, J. W.; Bernstein, J. L. *J. Electrochem. Soc.* **1969**, *116*, 348–353. (c) Domen, K.; Kudo, A.; Shibata, M.; Tanaka, A.; Maruya, K.; Onishi, T. *J. Chem. Soc., Chem. Commun.* **1986**, 1706–1707. (d) Maeda, K.; Eguchi, M.; Youngblood, W. J.; Mallouk, T. E. *Chem. Mater.* **2008**, *20*, 6770–6778.

(14) (a) Saupe, G. B.; Waraksa, C. C.; Kim, H. N.; Han, Y. J.; Kaschak, D. M.; Skinner, D. M.; Mallouk, T. E. *Chem. Mater.* **2000**, *12*, 1556–1562. (b) Kobayashi, Y.; Hata, H.; Salama, M.; Mallouk, T. E. *Nano Lett.* **2007**, *7*, 2142–2145. (c) Du, G. H.; Chen, Q.; Yu, Y.; Zhang, S.; Zhou, W. Z.; Peng, L. M. *J. Mater. Chem.* **2004**, *14*, 1437–1442. (d) Du, G. H.; Peng, L. M.; Chen, Q.; Zhang, S.; Zhou, W. Z. *Appl. Phys. Lett.* **2003**, *83*, 1638–1640.

(15) Wang, H.; Yu, Y. F.; Sun, Y. B.; Chen, Q. W. *NANO* **2011**, *6*, 1–17.

(16) Punnakitikashem, P.; Chang, S. H.; Huang, C. W.; Liu, J. P.; Hao, Y. W. *J. Nanopart. Res.* **2010**, *12*, 1101–1106.

(17) Xiao, W. D.; Ruffieux, P.; Ait-Mansour, K.; Groning, O.; Palotas, K.; Hofer, W. A.; Groning, P.; Fasel, R. *J. Phys. Chem. B* **2006**, *110*, 21394–21398.

(18) Wang, M. H.; Li, Y. J.; Xie, Z. X.; Liu, C.; Yeung, E. S. *Mater. Chem. Phys.* **2010**, *119*, 153–157.

(19) (a) Chen, M.; Kim, J.; Liu, J. P.; Fan, H. Y.; Sun, S. H. *J. Am. Chem. Soc.* **2006**, *128*, 7132–7133. (b) Ahmed, W.; Laarman, R. P. B.; Hellenthal, C.; Kooij, E. S.; Silfhout, A. V.; Poelsema, B. *Chem. Commun.* **2010**, *46*, 6711–6713. (c) Salem, A. K.; Chao, J.; Leong, K. W.; Searson, P. C. *Adv. Mater.* **2004**, *16*, 268–271.