Subscriber access provided by ISTANBUL TEKNIK UNIV

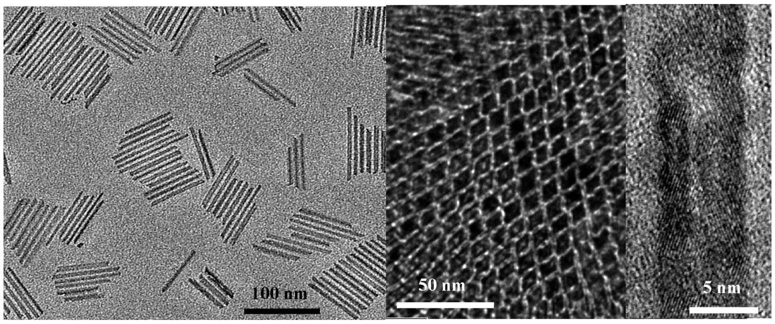
Communication

Synthesis of Uniform Goethite Nanotubes with Parallelogram Cross Section

Taekyung Yu, Jinkyung Park, Jaewon Moon, Kwangjin An, Yuanzhe Piao, and Taeghwan Hyeon

J. Am. Chem. Soc., **2007**, 129 (47), 14558-14559 • DOI: 10.1021/ja076176j

Downloaded from http://pubs.acs.org on February 9, 2009



More About This Article

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

- Supporting Information
- Links to the 4 articles that cite this article, as of the time of this article download
- 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

High quality. High impact.

Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
COMMUNICATIONS

Published on Web 11/06/2007

Synthesis of Uniform Goethite Nanotubes with Parallelogram Cross Section

Taekyung Yu, Jinkyung Park, Jaewon Moon, Kwangjin An, Yuanzhe Piao, and Taeghwan Hyeon*

National Creative Research Initiative Center for Oxide Nanocrystalline Materials and School of Chemical and Biological Engineering, Seoul National University, Seoul 151-744, Korea

Received August 16, 2007; E-mail: thyeon@snu.ac.kr

Since the first report on carbon nanotubes in 1991,[1] there has been a tremendous interest in inorganic nanotubes, due to their novel properties and potential applications in electronics, separation, catalysis, and biotechnology.[2] Recently, many oxide nanotubes have been synthesized using various synthetic procedures including the most popularly used template approaches.[3] However, the diameters of these oxide nanotubes are usually far larger than 10 nm and nonuniform. For many delicate applications such as biosensors and separation, it is necessary to develop a method of synthesizing uniform inorganic nanotubes with a diameter of less than 10 nm. Goethite (α-FeOOH), one of the iron oxide hydroxides, is known as a common constituent of soils and the atmospheric corrosion products of iron-based alloys.[4] Goethite plays an important role in environmental processes, as it possesses a strong affinity for a variety of contaminants such as heavy-metal ions and organic pollutants.[5] Herein, we report on the synthesis of uniform goethite nanotubes having a parallelogram-shaped cross section.

Goethite nanotubes were synthesized from the reaction of hydrazine[6] with Fe(III)-oleate complex immobilized in reverse micelles composed of oleic acid, water, and xylene. Previously, our group demonstrated the large-scale synthesis of monodisperse iron oxide nanocrystals from the thermolysis of Fe(III)-oleate complex.[7] In a typical synthesis, 4 mmol of Fe(III)-oleate (3.6 g) and 36 mmol of oleic acid (10.17 g) were dissolved in 15 mL of xylene, and subsequently 1 mL of DI water was added under vigorous stirring. The resulting mixture solution was stirred at room temperature for 2 h. The resulting reverse micelle solution was slowly heated to 90 °C and then 3 mL of hydrazine (11 wt % water solution) was injected. After aging at the same temperature for 3 h, 100 mL of ethanol was added to cause the precipitation of the goethite nanotubes. The precipitate was retrieved by centrifugation. The resulting precipitate was re-dispersible in many organic solvents such as *n*-hexane and chloroform. A typical transmission electron microscopic (TEM) image (Figure 1a) at low magnification showed that the nanotubes have a uniform cross-sectional dimension of 7 nm and length of about 80 nm. When the nanotube dispersion was slowly evaporated on a TEM grid, these nanotubes self-assembled to generate an extensive tetragonal close-packed superlattice, and the vertically aligned nanotubes showed a parallelogram-shaped cross section with a uniform edge dimension of 7 nm (Figure 1b). A tilting experiment in TEM confirmed the parallelogram-shaped cross section (Supporting Information). A high-resolution TEM image (HRTEM) and a TEM image of microtomed sample showed that the nanotube has a hollow interior and slightly wrinkled walls with a uniform thickness of 2 nm (Figure 1c and Supporting Information). The powder X-ray diffraction (XRD) and electron diffraction patterns revealed that the nanotubes have a goethite (α-FeOOH) structure. The magnetic property characterization using a superconducting quantum interference device (SQUID) showed that the nanotubes were antiferromagnetic with a Néel temperature of 320 K, which is lower than that of bulk goethite (400 K). This decrease in the Néel temperature seems to be a characteristic of nanostructured goethite.[8]

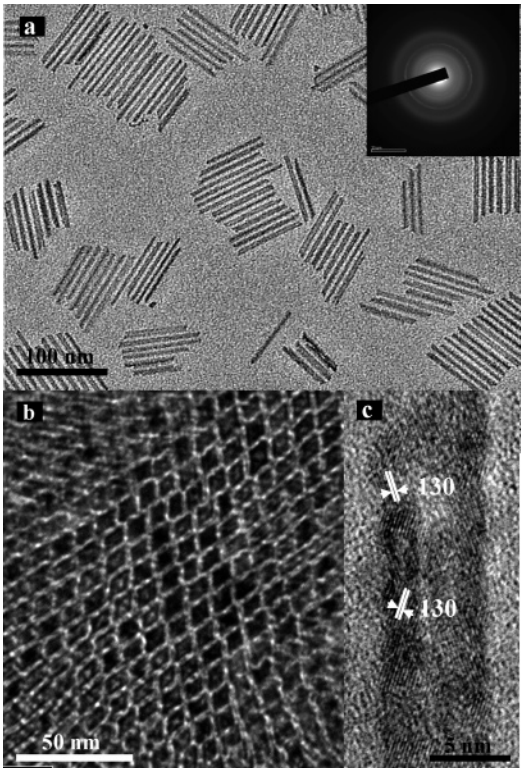


Figure 1. TEM (a) and HRTEM (c) images of goethite nanotubes; (b) TEM image of self-assembled goethite nanotubes.

In the current synthetic procedure, the reverse micelles generated by the mixing of oleic acid, xylene, and water seem to function as a template for the formation of the nanotubes. Temperature-dependent AC impedance measurements of the reaction mixture showed that reverse micelles were formed under the current synthesis condition of 90 °C (Supporting Information). Moreover, when we performed the synthesis without adding water to the reaction mixture while keeping the other experimental conditions unchanged, only polydisperse nanocrystals with an irregular shape were obtained. To investigate the growth process of the nanotubes, sampling experiments were performed by taking aliquots of the reaction mixture at regular time intervals after injecting hydrazine. The TEM image of the sample taken 30 min after the injection of hydrazine showed poorly crystalline pseudospherical nanocrystals with a size of about 2 nm. After conducting the reaction for 1 h, short nanotubes with an edge dimension of 7 nm and length of <20 nm were observed. Further aging at the same temperature of 90 °C for a longer time generated longer nanotubes with nearly the same edge dimension of 7 nm. For example, the TEM images of the samples taken after allowing the reaction to proceed for 2,

10.1021/ja076176j CCC: $37.00 © 2007 American Chemical Society

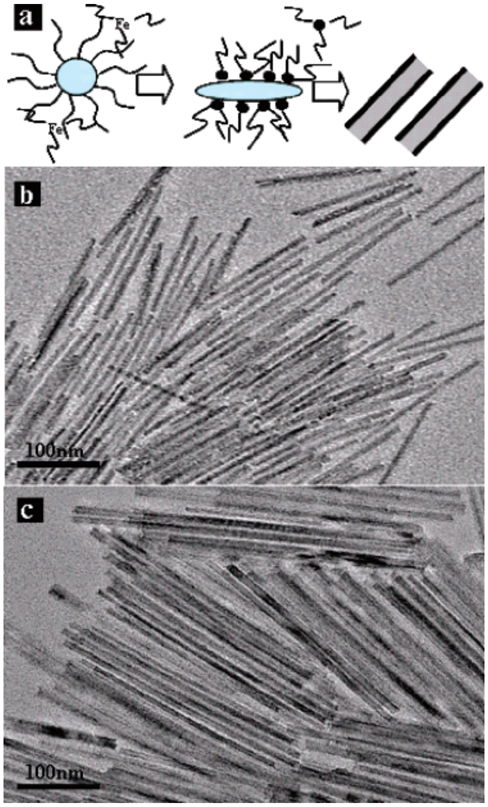


Figure 2. (a) Proposed growth mechanism of goethite nanotubes. TEM images of goethite nanotubes obtained after aging for 6 h (b) and 24 h (c).

3, and 6 h resulted in nanotubes with lengths of 60, 80, and 150 nm, respectively, while retaining nearly the same edge dimension of 7 nm. On the basis of these sampling experiments, we propose the following growth mechanism for the goethite nanotubes (Figure 2a). First, the Fe(III)-oleate complexes are immobilized (or interdigitated) in the outer hydrophobic part of the reverse micelles generated from oleic acid, xylene, and water. The addition of hydrazine induced the reaction with the Fe(III)-oleate complex and subsequent crystallization to form 2-nm-sized spherical nanoparticles of iron oxide or related iron-containing compounds. Further aging at 90 °C for a longer reaction time seems to induce the directional assembly of the 2-nm-sized nanoparticles onto the reverse micelle template (possibly rod-shaped), generating the nanotubes. As mentioned above, we were able to control the length of the nanotubes while keeping the edge dimension the same at 7 nm. When we performed the reaction for 6 and 24 h, goethite nanotubes with lengths of 150 nm (Figure 2b) and ∼400 nm (Figure 2c; HRTEM image in Supporting Information), respectively, were produced. By varying the types of iron−carboxylate complex and carboxylic acid, we were able to control the aspect ratios of the nanotubes. For example, when we used Fe(III)−octanoate and octanoic acid instead of Fe(III)−oleate and oleic acid in the synthesis and allowed the reaction to proceed for 6 h, goethite nanotubes with a thicker edge dimension of ∼30 nm and length of ∼80 nm were produced (Supporting Information). On the other hand, when we used octanoic acid instead of oleic acid and kept the other reaction conditions unchanged, nanotubes with an edge dimension of 12 nm and length of ∼150 nm were generated (Supporting Information).

In summary, we synthesized uniform iron oxide hydroxide (goethite) nanotubes having a parallelogram cross section from the reaction of hydrazine with Fe(III)−oleate complex immobilized in reverse micelles. The edge dimensions and lengths of the nanotubes were easily controlled by varying the reaction conditions, such as the kinds of Fe−carboxylate complex and carboxylic acid and the aging time. The current synthetic procedure is very simple and highly reproducible and, consequently, readily applicable to large-scale synthesis. For example, when we conducted the synthesis using 5 times more reagents than the amounts indicated above, we were able to synthesize as much as 7.2 g of the goethite nanotubes with a uniform edge dimension of 7 nm (Supporting Information).

Acknowledgment. This work was supported by the National Creative Research Initiative Program of the Korean Ministry of Science and Technology. We thank Dr. H. M. Park of the Korea Research Institute of Standards and Science for the XRD measurements and useful discussions.

Supporting Information Available: Experimental details, TEM, XRD, SQUID, photograph and DLS results of goethite nanotubes. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Iijima, S. *Nature* **1991**, *354*, 56.
(2) (a) Hu, J. T.; Odom, T. W.; Lieber, C. M. *Acc. Chem. Res.* **1999**, *32*, 435. b) Tenne, R. *Nat. Nanotechnol.* **2006**, *1*, 103. (c) Xiong, Y. J.; Mayers, B. T.; Xia, Y. N. *Chem. Commun.* **2005**, 5013. (d) Remskar, M. *Adv. Mater.* **2004**, *16*, 1497. (e) Steinhart, M.; Wehrspohn, R. B.; Gösele, U.; Wendorff, J. H. *Angew. Chem., Int. Ed.* **2004**, *43*, 1334. (f) Martin, C. R.; Kohli, P. *Nat. Rev. Drug Discovery* **2003**, *2*, 29. (g) Patzke, G. R.; Krumeich, F.; Nesper, R. *Angew. Chem., Int. Ed.* **2002**, *41*, 2446. (h) Lee, S. B.; Mitchell, D. T.; Trofin, L.; Nevanen, T. K.; Soderlund, H.; Martin, C. R. *Science* **2002**, *296*, 2198.
(3) (a) Mukherjee, S.; Kim, K.; Nair, S. *J. Am. Chem. Soc.* **2007**, *129*, 6820. (b) Tian, Z. R.; Voigt, J. A.; Liu, J.; Mckenzie, B.; Xu, H. *J. Am. Chem. Soc.* **2003**, *125*, 12384. (c) Elbaum, L. K.; Newns, D. M.; Zeng, H.; Derycke, V.; Sun, J. Z.; Sandstrom, R. *Nature* **2004**, *431*, 672. (d) Liu, Z.; Zhang, D.; Han, S.; Li, C.; Lei, B.; Lu, W.; Fang, J.; Zhou, C. *J. Am. Chem. Soc.* **2005**, *127*, 6. (e) Tokudome, H.; Miyauchi, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 1974. (f) Macák, J. M.; Tsuchiya, H.; Schmuki, P. *Angew. Chem., Int. Ed.* **2005**, *44*, 2100. (g) Son, S. J.; Reichel, J.; He, B.; Schuchman, M.; Lee, S. B. *J. Am. Chem. Soc.* **2005**, *127*, 7316. (h) Ye, C.; Bando, Y.; Shen, G.; Golberg, D. *Angew. Chem., Int. Ed.* **2006**, *45*, 4922. (i) Yue, L.; Gao, W.; Zhang, D.; Guo, X.; Ding, W.; Chen, Y. *J. Am. Chem. Soc.* **2006**, *128*, 11042. (j) Bachmann, J.; Jing, J.; Knez, M.; Barth, S.; Shen, H.; Mathur, S.; Gösele, U.; Nielsch, K. *J. Am. Chem. Soc.* **2007**, *129*, 9554.
(4) (a) Cornell, R. M.; Schwertmann, U. *The Iron Oxides*, 2nd ed.; Wiley-VCH; Weinheim, 2004. (b) Jolivet, J.-P.; Chanéac, C.; Tronc, E. *Chem. Commun.* **2004**, 481.
(5) (a) Parfitt, R. L.; Atkinson, R. J. *Nature* **1976**, *264*, 740. (b) Kosmulski, M.; Maczka, E. *Langmuir*, **2004**, *20*, 2320. (c) Mazeina, L.; Alexandra, N. *Chem. Mater.* **2007**, *19*, 825.
(6) Lee, Y.; Lee, J.; Bae, C. J.; Park, J.-G.; Noh, H.-J.; Park, J.-H.; Hyeon, T. *Adv. Funct. Mater.* **2005**, *15*, 503.
(7) Park, J.; An, K.; Hwang, Y.; Park, J.-G.; Noh, H.-J.; Kim, J.-Y.; Park, J.-H.; Hwang, N.-M.; Hyeon, T. *Nat. Mater.* 2**004**, *3*, 891.
(8) (a) Lemaire, B. J.; Davison, P.; Ferre, J.; Jamet, J. P.; Panine, P.; Dozov, I.; Jolivet, J. P. *Phys. Rev. Lett.* **2002**, *88*, 125507-1. (b) Bocquet, S.; Kennedy, S. J. *J. Magn. Magn. Mater.* **1992**, *109*, 260. (c) Bocquet, S.; Pollard, R. J.; Cashion, J. D. *Phys. Rev. B* **1992**, *46*, 11657.
(9) Alexandridis, P.; Holzwarth, J. F.; Hatton, T. A. *J. Phys. Chem.* **1995**, *99*, 8222.

JA076176J