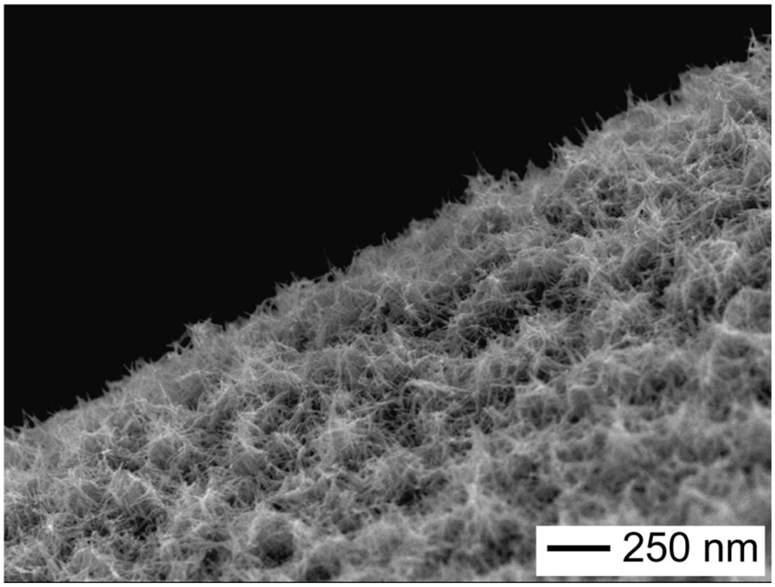
J|A|C|S
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

Growing Pt Nanowires as a Densely Packed Array on Metal Gauze

Eric P. Lee, Zhenmeng Peng, David M. Cate, Hong Yang, Charles T. Campbell, and Younan Xia

J. Am. Chem. Soc., **2007**, 129 (35), 10634-10635• DOI: 10.1021/ja074312e • Publication Date (Web): 09 August 2007



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

Growing Pt Nanowires as a Densely Packed Array on Metal Gauze

Eric P. Lee,† Zhenmeng Peng,‡ David M. Cate,† Hong Yang,‡ Charles T. Campbell,† and Younan Xia*,†

Department of Chemistry, University of Washington, Seattle, Washington 98195-1700, and Department of Chemical Engineering, University of Rochester, Rochester, New York 14627-0166

Received June 13, 2007; E-mail: xia@chem.washington.edu

Platinum is a major catalyst in many industrial applications, including fuel-cell technology, hydrogenation reaction, three-way automobile catalytic conversion, and gas sensing.[1] All of these applications require the use of Pt as fine particles, not only because of the enhanced surface area, but also because of the peculiar surface properties different from those of a bulk material.[2] Thus, a great deal of research has been devoted to the chemical synthesis of Pt nanostructures.[3] Some of these nanostructures have been further explored as catalysts. There are two major types of catalysts: the homogeneous type with catalysis occurring in a colloidal solution and the heterogeneous type in which the reaction is catalyzed by nanoparticles supported on a solid substrate.[4] Most work in the heterogeneous field involve deposition of metal nanoparticles by evaporation in a high vacuum system, or via electrochemical deposition.[5] It is also common to deposit presynthesized nanoparticles on a solid surface by encapsulation or use of Langmuir−Blodgett technique.[6] However, with respect to the procedures and materials used, production of Pt catalysts with high surface areas for great catalytic performance and utilization efficiency is still costly and far from being trivial.

Recently,[7] we demonstrated a practical and affordable method for growing Pt nanostructures on polymeric or ceramic particles. This template-directed synthesis has proven to be straightforward and remarkably versatile, especially for the facile growth of Pt nanowires. By modifying this template-directed synthesis, we have demonstrated a more attractive approach for the growth of Pt nanowires on functional solid supports. Herein, we report the synthesis of single-crystal Pt nanowires directly on the surface of metal gauze. By simply adding the metal gauze to the polyol reduction of Pt(IV), large quantities of Pt nanowires could be directly grown on the gauze as a densely packed array.[8]

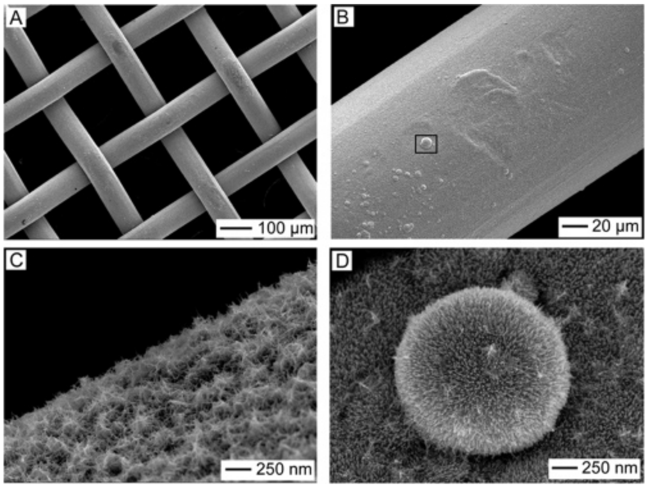


Figure 1. SEM images of hierarchically structured Pt nanowires grown directly on the surface of a Pt gauze without any surface modification: (A−C) An overview of the sample at different magnifications with panel C showing an edge view of the Pt nanowires growing outward from the surface of the gauze; (D) a high magnification image of the structure boxed in panel B, showing the formation of Pt nanowires on the surface of a raised island that exists on the surface of the pristine Pt gauze (Figure S1).

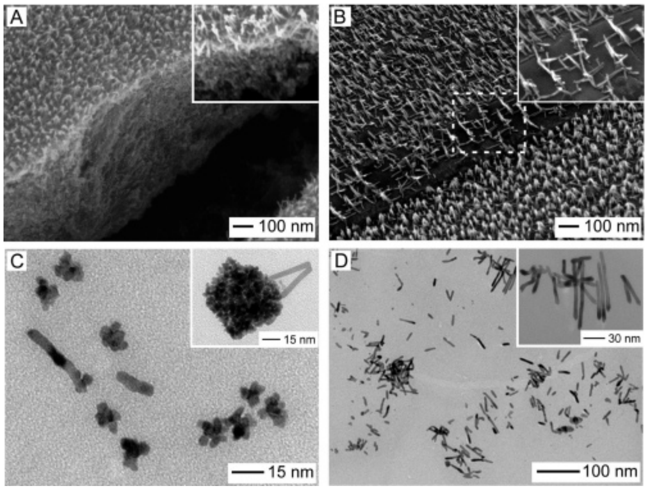


Figure 2. (A) Cross-sectional SEM image of a typical sample showing Pt nanowires growing from a relatively thick layer of Pt nanoparticles that was formed on the surface of the Pt gauze in the early stage of synthesis; (B) SEM image of a different sample that was prepared with a reduced Pt precursor concentration. Note that the nanowires directly nucleated and grew on the surface of the Pt gauze, as clearly seen in the inset. (C) TEM images of Pt nanoparticle agglomerates that were separated from the sample shown in panel A via sonication; (D) TEM images of well-dispersed Pt nanowires that were released from the Pt gauze by brief sonication.

Figure 1 shows SEM images of a typical product at different magnifications. A dense array of Pt nanowires was formed on the surface of a fine Pt gauze (Figure 1, A and B) by following the iron-mediated polyol process, in which ethylene glycol (EG) serves as both reducing agent and solvent.[9] In this synthesis, Pt(II) species were formed by reducing H_2PtCl_6 with EG at 110 °C in the presence of poly(vinyl pyrrolidone) (PVP). By adding 20 mM of $FeCl_3$ or $FeCl_2$, the Pt(II) species were reduced at an extremely slow rate and the resulting Pt atoms began to nucleate and grow into uniform nanowires as seen in Figure 1C. Raised islands covered by Pt nanowires also formed on the surface, which we attribute to the existence of small bumps on the surface of the pristine Pt gauze (Figure S1 in Supporting Information). Figure 1D shows an example of such a structure, which is an enlarged image of the portion indicated by the box in Figure 1B. Figures 2A and 2B show SEM images of dense arrays of Pt nanowires grown at two different concentrations of H_2PtCl_6. The sample in Figure 2A was prepared with 80 mM of H_2PtCl_6. In this case, the Pt atoms resulting from the reduction of the Pt(II) species initially nucleated and grew into

---

† University of Washington.
‡ University of Rochester.

10.1021/ja074312e CCC: $37.00

Pt nanoparticles at the surface of the Pt gauze, which further evolved into agglomerates and larger features. When the concentration of Pt atoms dropped below a critical value, the addition of Pt atoms was switched to a highly anisotropic mode owing to the higher growth rates at areas of high curvatures.[9a] Thus, uniform Pt nanowires were grown on the surface of the agglomeration layer.[9b] As shown in Figure S1, the nanowires are single crystalline with the growth direction along the $\langle 111 \rangle$ axis. To bypass the formation of Pt nanoparticles and thus maximize the effective use of Pt, the concentration of H_2PtCl_6 was reduced by half to 40 mM, resulting in the nucleation and growth of Pt atoms into nanowires directly on the surface of the Pt gauze (Figure 2B). The inset in Figure 2B shows a closer view of the sample in Figure 2B, verifying that the Pt nanowires grew from the Pt gauze without a thick layer of Pt nanoparticles.

It is not yet known whether these Pt nanowires mainly nucleate at defect sites on the Pt gauze surface (see Figure S2) or if they arise from homogeneous nucleation. However, it is often proposed that highly irregular and rough surfaces serve as primary nucleation sites for the growth of metal nanostructures because of the higher surface energies associated with irregularities such as indentions, step edges, or protrusions which significantly lower the barrier for heterogeneous nucleation.[10] This same synthesis has also been demonstrated with a fine-tungsten gauze, where Pt nanoparticles and nanowires directly grew on the surface of a W gauze (Figure S3). It seems that this procedure can be applied to any metal gauze that is stable under the polyol reducing conditions. The fact that our earlier study showed that these could be grown on polymeric and ceramic substrates as well suggests that this technique can also be applied to a variety of other solid substrates including semiconductors, insulators, and polymers.

To observe the growth mechanics of the Pt nanowires more closely, we released the Pt nanoparticle agglomerates and Pt nanowires from the sample shown in Figure 2A via sonication (Branson 1510, for 90 min) and obtained TEM images of the resulting sample. Figure 2C and the inset clearly show that Pt nanoparticles, with a diameter of ~5 nm, agglomerate into larger structures and act as supports for the nucleation and growth of Pt atoms into nanowires. Figure 2D and the inset show well dispersed Pt nanowires with lengths of up to 50 nm. Although the as-grown nanowires could have a length up to ~200 nm, those released from the substrate surface are rarely as long owing to their breaking during the sonication process. After the wires had been released from the Pt gauze, the substrate could be reused to grow new batches of Pt nanowires.

The electrochemically active surface area of such Pt nanowire-coated gauze was studied based on hydrogen adsorption using cyclic voltammetry (CV). We found that the nanowire-coated gauze had an active surface area of about two to three orders in magnitude higher than the pristine Pt gauze (Figure S4). Note that the nanowire-coated gauze was only washed with chloroform, ethanol, and distilled water and was without any heat treatment that is typically used for carbon-supported Pt catalysts.

In summary, we have demonstrated a simple yet versatile procedure for directly growing a high density of single crystalline Pt $\langle 111 \rangle$ nanowires on gauze made of Pt or W. The growth mechanism of the nanowires is related to the concentration of the Pt precursor and the surface roughness of the substrate. At high precursor concentrations, a Pt nanostructured bilayer forms, with the initial growth of Pt nanoparticle agglomerates followed by a densely packed array of Pt nanowires. By reducing the precursor concentration, the layer of nanoparticle agglomerates can be substantially reduced and even completely eliminated, resulting in a rich surface coverage of Pt nanowires, which nucleate at the defective sites of the substrate. The results described in the present report demonstrate a new type of conductive support that can be used as active components for high-power density fuel cell applications. The resulting Pt nanowire/support is also expected to be an ideal 3D model catalyst as a result of their high surface area and structural uniformity of the metal nanocrystals. Catalytic studies and surface analysis are currently in progress.

Acknowledgment. This work was supported in part by a research grant from the NSF (Grant DMR-0451788, Y.X.) and the DOE-OBES Chemical Sciences Division (CTC), and by an NSF CAREER Award (DMR-0449849, H.Y.) and ACS-PRF (42446-G10, H.Y.). Y.X. is a Camille Dreyfus Teacher Scholar (2002−2007).

Supporting Information Available: Experimental procedure; HR-TEM image of a Pt nanowire; SEM images of pristine Pt gauze and additional samples prepared on W gauze; and electrochemical measurements on pristine and nanowire-coated Pt gauzes. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) See, for example: (a) Chen, W.; Kim, J.; Sun, S.; Chen. S. *Phys. Chem. Chem. Phys.* **2006**, *8*, 2779. (b) Jun, C. H.; Park, Y. J.; Yeon, Y. R.; Choi, J. R.; Lee, W. R.; Ko, S. J.; Cheon, J. *Chem. Comm.* **2006**, 1619. (c) Wartnaby, C. E.; Stuck, A.; Yeo, Y. Y.; King, D. A. *J. Phys. Chem.* **1996**, *100*, 12483.

(2) (a) Schuster, R.; Ertl, G. In *Catalysis and Electrocatalysis at Nanoparticle Surfaces*; Wieckowski, A., Savinova, E. R., Vayenas, C. G., Eds.; Marcel Dekker: New York, 2003; p 212. (b) Baranova, E. A.; Bock, C.; Ilin, D.; Wang, D.; MacDougall, B. *Surf. Sci.* **2006**, *600*, 3502.

(3) See, for example: (a) Chen, J.; Herricks, T.; Xia, Y. *Angew. Chem., Int. Ed.* **2005**, *44*, 2589. (b) Teng, X.; Yang, H. *Nano Lett.* **2005**, *5*, 885. (c) Chen, Z.; Waje, M.; Li, W.; Yan, Y. *Angew. Chem., Int. Ed.* **2007**, *46*, 4060. (d) Sun, S.; Murray, C. B.; Weller, D.; Folks, L.; Moser, A. *Science* **2000**, *287*, 1989. (e) Ahmadi, T. S.; Wang, Z. L.; Green, T. C.; Henglein, A.; El-Sayed, M. A. *Science* **1996**, *272*, 1924.

(4) Narayanan, R.; El-Sayed, M. A. *Nano Lett.* **2004**, *4*, 1343.

(5) See, for example: (a) Guo, Y. G.; Hu, J. S.; Zhang, H. M.; Liang, H. P.; Wan, L. J.; Bai, C. L. *Adv. Mater.* **2005**, *17*, 746. (b) Li, F.; Zhu, M.; Liu, C.; Zhou, W. L.; Wiley, J. B. *J. Am. Chem. Soc.* **2006**, *128*, 13342.

(6) See, for example: (a) Zhu, J.; Kónya, Z.; Puntes, V. F.; Kiricsi, I.; Miao, C. X.; Ager, J. W.; Alivisatos, A. P.; Somorjai, G. A. *Langmuir* **2003**, *19*, 4396. (b) Yoo, J. W.; Hathcock, D.; El-Sayed, M. A. *J. Phys. Chem. A* **2002**, *106*, 2049. (c) Teng, X.; Liang, X.; Rahman, S.; Yang, H. *Adv. Mater.* **2005**, *17*, 2237. (d) Song, H.; Kim, F.; Conner, S.; Somorjai, G. A.; Yang, P. *J. Phys. Chem. B* **2005**, *109*, 188. (e) Wei, Z.; Mieszawska, A.; Zamborni, F. P. *Langmuir* **2004**, *20*, 4322.

(7) Lee, E. P.; Chen, J.; Yin, Y. Y.; Campbell, C. T.; Xia, Y. *Adv. Mater.* **2006**, *18*, 3271.

(8) See Supporting Information for full experimental description.

(9) (a) Herricks, T.; Chen, J.; Xia, Y. *Nano Lett.* **2004**, *4*, 2367. (b) Chen, J.; Herricks, T.; Geissler, M.; Xia, Y. *J. Am. Chem. Soc.* **2004**, *126*, 10854. (c) Chen, J.; Xiong, Y.; Yin, Y.; Xia, Y. *Small* **2006**, *2*, 1340.

(10) (a) Gouldstone, A.; Van Vliet, K. J.; Suresh, S. *Nature* **2001**, *411*, 656. (b) Brune, H. *Surf. Sci. Rep.* **1998**, *31*, 121.

JA074312E