

A Sinter-Resistant Catalytic System Based on Platinum Nanoparticles Supported on TiO₂ Nanofibers and Covered by Porous Silica**

Yunqian Dai, Byungkwon Lim, Yong Yang, Claire M. Cobley, Weiyang Li, Eun Chul Cho, Benjamin Grayson, Paul T. Fanson, Charles T. Campbell, Yueming Sun, and Younan Xia*

Platinum is a key catalyst that is invaluable in many important industrial processes such as CO oxidation in catalytic converters, oxidation and reduction reactions in fuel cells, nitric acid production, and petroleum cracking.^[1] Many of these applications utilize Pt nanoparticles supported on oxides or porous carbon.^[2] However, in practical applications that involve high temperatures (typically higher than 300 °C), the Pt nanoparticles tend to lose their specific surface area and thus catalytic activity during operation because of sintering. Recent studies have shown that a porous oxide shell can act as a physical barrier to prevent sintering of unsupported metal nanoparticles and, at the same time, provide channels for chemical species to reach the surface of the nanoparticles, thus allowing the catalytic reaction to occur. This concept has been demonstrated in several systems, including Pt@SiO₂,^[3] Pt@CoO,^[4] Pt/CeO₂@SiO₂,^[5] Pd@SiO₂,^[6] Au@SiO₂,^[7] Au@SnO₂,^[8] and Au@ZrO₂^[9] core-shell nanostructures. Despite these results, a sinter-resistant system has not been realized in supported Pt nanoparticle catalysts.

Improved catalytic or photocatalytic properties are often achieved when metal nanoparticles are supported on oxides such as TiO₂ and CeO₂ that interact strongly with late

transition metals.^[2f,5] Herein, we demonstrate a thermally stable catalytic system consisting of Pt nanoparticles that are supported on a TiO₂ nanofiber and coated with a porous SiO₂ sheath. In this system, the porous SiO₂ coating offers an energy barrier to prevent the migration of individual Pt atoms or nanoparticles because of its weak interaction with late transition metals, including Pt. The porous-SiO₂/Pt/TiO₂ catalytic system was prepared in three steps (Figure 1):

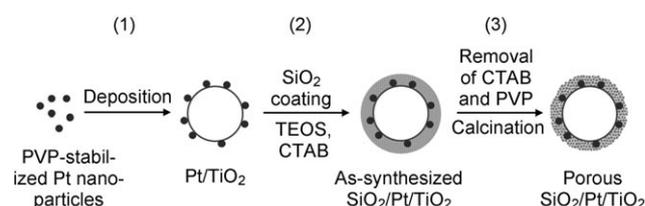


Figure 1. Preparation of the catalytic system based on Pt nanoparticles that are supported on TiO₂ nanofibers and then covered by porous sheaths of SiO₂: 1) deposition of PVP-stabilized Pt nanoparticles onto the surface of TiO₂ nanofibers; 2) formation of SiO₂ coating by the Stober method; and 3) removal of CTAB and PVP by calcination in air to generate a porous sheath of SiO₂.

1) deposition of Pt nanoparticles onto the surface of TiO₂ nanofibers; 2) coating of SiO₂ with cetyltrimethylammonium bromide (CTAB) as a pore-generating agent; and 3) calcination in air to generate a porous sheath of SiO₂. By using this approach, we were able to produce a platinum-based catalytic system that can resist sintering up to 750 °C in air, while retaining the catalytic activity of the Pt nanoparticles.

The TiO₂ nanofibers were prepared by electrospinning and subsequent calcination in air at 750 °C for 2 hours.^[10] The as-prepared nanofibers had a rough surface and a polycrystalline structure that contained both anatase and rutile phases (69% anatase and 31% rutile; Figure S1 in the Supporting Information). Poly(vinyl pyrrolidone) (PVP) stabilized Pt nanoparticles were prepared by using the polyol method.^[11] The as-synthesized Pt nanoparticles were uniform in size, with an average size of (3.1 ± 0.5) nm (Figure 2a,b). These Pt nanoparticles were deposited onto the TiO₂ nanofibers by immersing the sample in a suspension of the Pt nanoparticles, which was prepared by a 10-fold dilution of the as-prepared Pt sample with ethanol. As shown in Figure 2c, the Pt nanoparticles were well dispersed on the surface of each TiO₂ nanofiber, without significant aggregation. The Pt loading in the Pt/TiO₂ nanofibers was 1.3 wt%, as determined by inductively coupled plasma mass spectrometry (ICP-MS) measurements. Figure 2d shows a high-resolution TEM

[*] Y. Dai, Dr. B. Lim, C. M. Cobley, W. Li, Dr. E. C. Cho, Prof. Y. Xia
Department of Biomedical Engineering
Washington University, St. Louis, MO 63130 (USA)
E-mail: xia@biomed.wustl.edu

Y. Dai, Prof. Y. Sun
School of Chemistry and Chemical Engineering
Southeast University, Nanjing, Jiangsu 211189 (P. R. China)

Dr. Y. Yang, Prof. C. T. Campbell
Department of Chemistry, University of Washington
Seattle, WA 98195 (USA)

Dr. B. Grayson, Dr. P. T. Fanson
Toyota Motor Engineering & Manufacturing North America, Inc.
Ann Arbor, MI 48105 (USA)

[**] This work was supported by the Toyota Motor Engineering & Manufacturing North America, Inc. Part of the research was performed at the Nano Research Facility (NRF), a member of the National Nanotechnology Infrastructure Network (NNIN) that is funded by the National Science Foundation under award no. ECS-0335765. As a visiting graduate student from Southeast University, Y.D. was also partially supported by the National Basic Research Program (973 program, 2007CB936300), the Innovation Program for Graduate Students in Jiangsu Province (CX08B-051Z), and the China Scholarship Council. We thank Prof. Jimmy Liu at the University of Missouri (St. Louis) for helping us with the sintering experiments under hydrogen gas.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201001839>.

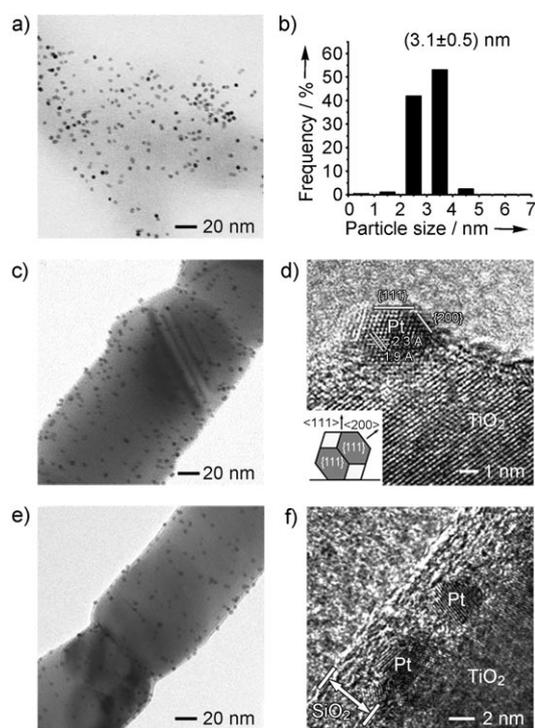


Figure 2. a) TEM image of PVP-stabilized Pt nanoparticles synthesized using the polyol method and b) the corresponding particle size distribution obtained by counting 150 particles in the TEM images. c) TEM and d) HRTEM images taken from the Pt/TiO₂ nanofiber sample prepared by immersing the calcined TiO₂ nanofibers in a suspension of the Pt nanoparticles. The inset in (d) shows a schematic model of a Pt truncated octahedron on the TiO₂ surface. e) TEM and f) HRTEM images taken from the sample that was obtained by coating the Pt/TiO₂ nanofibers shown in (c) with SiO₂ sheaths 4–6 nm thick.

each Pt/TiO₂ nanofiber (Figure 2 e). The HRTEM image in Figure 2 f clearly shows that the thin SiO₂ sheath covered both the TiO₂ nanofiber and the Pt nanoparticles and that its thickness was uniform. We did not observe the formation of isolated SiO₂ particles in the product in both TEM and HRTEM analyses.

The as-prepared SiO₂/Pt/TiO₂ sample contains CTAB within the SiO₂ sheaths and the Pt nanoparticles are surrounded by PVP. These organic species can be removed from the SiO₂/Pt/TiO₂ nanofibers by calcination in air at 350 °C to generate porous SiO₂ sheaths.^[2g,13] The TEM image and particle size analyses of the calcined porous-SiO₂/Pt/TiO₂ nanofibers revealed that the Pt nanoparticles did not form aggregates and retained small sizes with an average size of (3.5 ± 0.8) nm (Figure 3 a). We also proved that the Pt surface in these materials was accessible to reactants by measuring the Pt surface area using selective chemisorption (CO titration of O adatoms; reference [14]). For several samples before (Figure 2 c) and after (Figure 3 a) silica coating, the average Pt dispersions were measured to be 42 % and 29 %, respectively. These dispersions are very close to the value of 39 %, which was estimated using the average diameter of 3.5 nm from TEM, assuming that the spherical particles have the same surface packing density as Pt(111), that is, 1.5 × 10¹⁵ Pt atoms per cm² (representative titration curves and surface areas are shown in Figure S2 in the Supporting Information).

Notably, the Pt nanoparticles did not exhibit a morphological change upon calcination at temperatures up to 750 °C (Figure 3 b,c). However, in sharp contrast, the Pt nanoparticles were observed to aggregate in the absence of SiO₂ sheaths at all temperatures in the range 350–750 °C (Figure 3 d–f). At 750 °C, the Pt nanoparticles aggregated extensively to form particles larger than 20 nm in size (Figure 3 f). These results

(HRTEM) image of a single Pt nanoparticle on a TiO₂ nanofiber recorded along the [011] zone axis. The Pt nanoparticle exhibited a truncated octahedral shape with exposed {111} and {100} facets. The fringe spacing of 1.9 Å and 2.3 Å correspond to the {200} and {111} planes of face-centered cubic Pt, respectively.^[1b] The Pt/TiO₂ nanofibers were then coated with SiO₂ sheaths by using a modified Stöber method,^[12] in which CTAB was used as a pore-generating agent. The TEM analysis showed that a uniform SiO₂ coating with a thickness of 4–6 nm was formed on the surface of

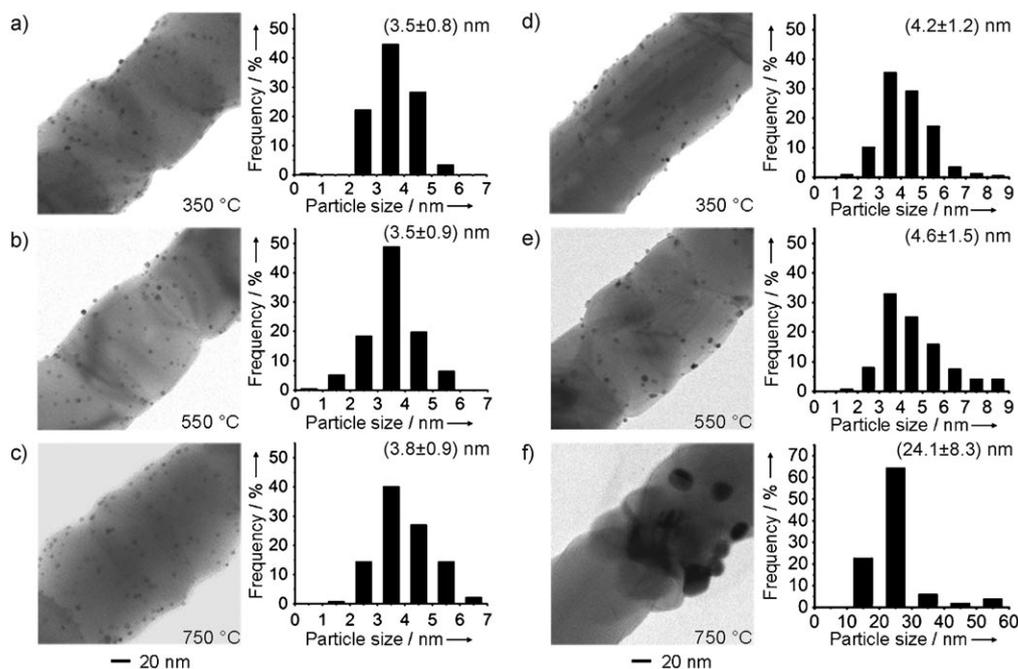


Figure 3. Comparison of thermal stability of the SiO₂/Pt/TiO₂ nanofibers (a–c) and Pt/TiO₂ nanofibers without SiO₂ coating (d–f) at three different calcination temperatures in air for 2 h.

demonstrate that the porous SiO₂ sheath could serve as an effective barrier to prevent the migration of Pt atoms and/or nanoparticles during calcination, thus enabling the Pt nanoparticles to become sinter-resistant. This new catalytic system also exhibited good resistance against sintering in a reducing gas environment such as hydrogen gas (Figure S3 in the Supporting Information).

The effect of Pt loading on the sinter resistance of the porous-SiO₂/Pt/TiO₂ nanofibers was also investigated. In this case, the Pt/TiO₂ nanofibers with a relatively higher Pt loading (ca. 3.6 wt %) were prepared by immersing the calcined TiO₂ nanofibers in the as-prepared suspension of Pt nanoparticles (Figure S4a in the Supporting Information). These nanofibers were coated with porous SiO₂ sheaths using the same procedure as in Figure 2e (Figure S4b in the Supporting Information). This sample exhibited good sinter resistance upon calcination in air up to 550 °C, but sintering started to occur at 750 °C (Figure S5 in the Supporting Information). In this case, sintering could be facilitated by the significant reduction in the nearest-neighbor distance between the Pt nanoparticles.

We also investigated the catalytic property of the Pt nanoparticles embedded in the porous SiO₂ sheaths by employing the hydrogenation of methyl red (an azo dye) as a model reaction (Figure 4a). The hydrogenation of the N=N

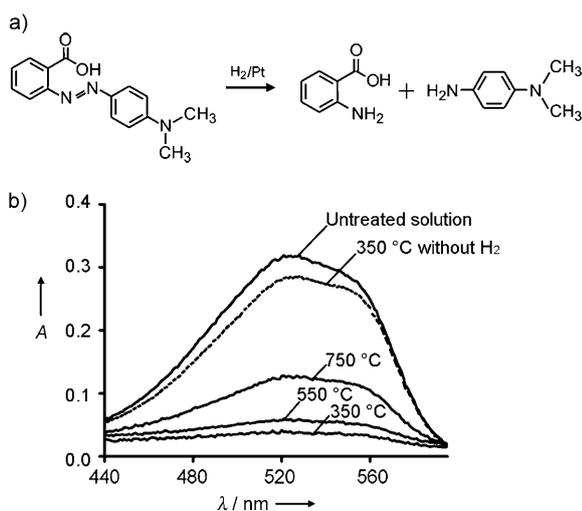


Figure 4. a) Hydrogenation of methyl red. b) UV/Vis spectra of a methyl red solution before and after the hydrogenation reaction with porous-SiO₂/Pt/TiO₂ nanofibers. The conversions were 87%, 81%, and 61% for the porous-SiO₂/Pt/TiO₂ nanofibers obtained by calcination in air for 2 h at 350, 550, and 750 °C, respectively.

bond of methyl red breaks the π conjugation of the molecule, thus resulting in a loss of the red color, which can be readily monitored by UV/Vis spectroscopy.^[2b,15] Figure 4b shows absorption spectra of a methyl red solution (which was bubbled with H₂ in advance) before and after passing through the porous-SiO₂/Pt/TiO₂ nanofibers. A high conversion was achieved with all the three porous-SiO₂/Pt/TiO₂ nanofiber catalysts prepared by calcination at different temperatures from 350 to 750 °C, thus indicating that both methyl red and

hydrogen molecules were able to diffuse through the porous SiO₂ sheaths to the surface of the embedded Pt nanoparticles. The highest catalytic activity was achieved from the porous-SiO₂/Pt/TiO₂ nanofiber catalyst prepared by calcination at 350 °C, with a conversion of 87%. The conversion dropped slightly to 81% for the sample calcined at 550 °C and to 61% for the sample calcined at 750 °C. These reductions in catalytic activity with increasing calcination temperature might also be caused by surface reconstruction of the Pt nanoparticles,^[3] as well as densification of the silica coating.^[16] We also confirmed the absence of homogeneous catalysis that might arise from partial dissolution of the Pt into the solution by conducting a control experiment in which the methyl red solution was not bubbled with H₂ gas until it was stirred with the catalyst for 2 minutes and then separated from the catalyst by centrifugation. In these experiments, there was essentially no change to the absorption peak (Figure S6 in the Supporting Information). Taken together, these results clearly show that the porous SiO₂ coating was permeable toward chemical species, and that the porous-SiO₂/Pt/TiO₂ nanofibers retained their catalytic properties.

In summary, we have demonstrated a sinter-resistant catalytic system based on TiO₂-supported Pt nanoparticles coated by a porous sheath of SiO₂. The porous-SiO₂/Pt/TiO₂ system could resist sintering up to a temperature of 750 °C in air, thus demonstrating the excellent sinter resistance of the catalyst. The porous SiO₂ sheath provides a physical barrier to slow down surface migration for the Pt atoms and/or nanoparticles and thus effectively prevent sintering. Significantly, the porous-SiO₂/Pt/TiO₂ nanofibers were still catalytically active towards hydrogenation of methyl red even after high-temperature calcination, thus demonstrating accessibility of the Pt nanoparticle's surface because of the porous nature of the SiO₂ sheath. The synthetic strategy presented herein should be extendible to other catalytic systems with different compositions.

Received: March 29, 2010

Revised: August 24, 2010

Published online: September 24, 2010

Keywords: nanostructures · platinum · silica · sinter resistance · supported catalysts

- [1] a) J. Chen, B. Lim, E. P. Lee, Y. Xia, *Nano Today* **2009**, *4*, 81; b) B. Lim, M. Jiang, P. H. C. Camargo, E. C. Cho, J. Tao, X. Lu, Y. Zhu, Y. Xia, *Science* **2009**, *324*, 1302; c) B. Lim, M. Jiang, J. Tao, P. H. C. Camargo, Y. Zhu, Y. Xia, *Adv. Funct. Mater.* **2009**, *19*, 189; d) B. Lim, X. Lu, M. Jiang, P. H. C. Camargo, E. C. Cho, E. P. Lee, Y. Xia, *Nano Lett.* **2008**, *8*, 4043; e) Y. Xia, Y. Xiong, B. Lim, S. E. Skrabalak, *Angew. Chem.* **2009**, *121*, 62; *Angew. Chem. Int. Ed.* **2009**, *48*, 60.
- [2] a) E. Formo, P. H. C. Camargo, B. Lim, M. Jiang, Y. Xia, *Chem. Phys. Lett.* **2009**, *476*, 56; b) E. Formo, E. Lee, D. Campbell, Y. Xia, *Nano Lett.* **2008**, *8*, 668; c) E. Formo, Z. M. Peng, E. Lee, X. M. Lu, H. Yang, Y. Xia, *J. Phys. Chem. C* **2008**, *112*, 9970; d) E. Formo, M. S. Yavuz, E. P. Lee, L. Lane, Y. Xia, *J. Mater. Chem.* **2009**, *19*, 3878; e) L. Yang, W. Yang, Q. Cai, *J. Phys. Chem. C* **2007**, *111*, 16613; f) L. Jiang, G. Sun, Z. Zhou, S. Sun, Q. Wang, S. Yan, H. Li, J. Tian, J. Guo, B. Zhou, Q. Xin, *J. Phys.*

- Chem. B* **2005**, *109*, 8774; g) H. Song, R. M. Rioux, J. D. Hoefelmeyer, R. Komor, K. Niesz, M. Grass, P. Yang, G. A. Somorjai, *J. Am. Chem. Soc.* **2006**, *128*, 3027; h) W. Huang, J. N. Kuhn, C. K. Tsung, Y. Zhang, S. E. Habas, P. Yang, G. A. Somorjai, *Nano Lett.* **2008**, *8*, 2027.
- [3] S. H. Joo, J. Y. Park, C. K. Tsung, Y. Yamada, P. Yang, G. A. Somorjai, *Nat. Mater.* **2009**, *8*, 126.
- [4] S. Kim, Y. Yin, A. P. Alivisatos, G. A. Somorjai, J. T. Yates, *J. Am. Chem. Soc.* **2007**, *129*, 9510.
- [5] H. P. Zhou, H. S. Wu, J. Shen, A. X. Yin, L. D. Sun, C. H. Yan, *J. Am. Chem. Soc.* **2010**, *132*, 4998.
- [6] K. T. Li, M. H. Hsu, I. Wang, *Catal. Commun.* **2008**, *9*, 2257.
- [7] Q. Zhang, T. Zhang, J. Ge, Y. Yin, *Nano Lett.* **2008**, *8*, 2867.
- [8] K. Yu, Z. Wu, Q. Zhao, B. Li, Y. Xie, *J. Phys. Chem. C* **2008**, *112*, 2244.
- [9] P. M. Arnal, M. Comotti, F. Schüth, *Angew. Chem.* **2006**, *118*, 8404; *Angew. Chem. Int. Ed.* **2006**, *45*, 8224.
- [10] D. Li, Y. Xia, *Nano Lett.* **2003**, *3*, 555.
- [11] J. Chen, T. Herricks, M. Geissler, Y. Xia, *J. Am. Chem. Soc.* **2004**, *126*, 10854.
- [12] a) Y. Lu, Y. Yin, Z. Y. Li, Y. Xia, *Nano Lett.* **2002**, *2*, 785; b) Y. Yin, Y. Lu, Y. Sun, Y. Xia, *Nano Lett.* **2002**, *2*, 427; c) W. Stöber, A. Fink, E. Bohn, *J. Colloid Interface Sci.* **1968**, *26*, 62.
- [13] Y. Borodko, L. Jones, H. Lee, H. Frei, G. Somorjai, *Langmuir* **2009**, *25*, 6665.
- [14] M. H. Kim, J. R. Ebner, R. M. Friedman, M. A. Vannice, *J. Catal.* **2001**, *204*, 348.
- [15] C. M. Copley, D. J. Campbell, Y. Xia, *Adv. Mater.* **2008**, *20*, 748.
- [16] a) J. Gallardo, P. Galliano, A. Durán, *J. Sol-Gel Sci. Technol.* **2000**, *19*, 393; b) H. Saito, M. Higuchi, K. Katayama, Y. Azuma, *J. Mater. Sci. Lett.* **2003**, *22*, 1419.