

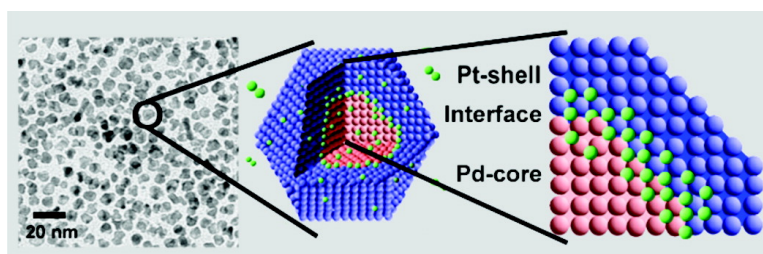
Communication

## Hydrogen Absorption in the Core/Shell Interface of Pd/Pt Nanoparticles

Hirokazu Kobayashi, Miho Yamauchi, Hiroshi Kitagawa, Yoshiki Kubota, Kenichi Kato, and Masaki Takata

*J. Am. Chem. Soc.*, **2008**, 130 (6), 1818-1819 • DOI: 10.1021/ja078126k

Downloaded from <http://pubs.acs.org> on February 8, 2009



### More About This Article

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

- Supporting Information
- Links to the 1 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](#)

## Hydrogen Absorption in the Core/Shell Interface of Pd/Pt Nanoparticles

Hirokazu Kobayashi,<sup>†</sup> Miho Yamauchi,<sup>†,‡</sup> Hiroshi Kitagawa,<sup>\*,†,‡</sup> Yoshiki Kubota,<sup>§</sup> Kenichi Kato,<sup>¶</sup> and Masaki Takata<sup>¶</sup>

Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Fukuoka 812-8581, Japan, JST PRESTO, Sanbancho 5, Chiyoda-ku, Tokyo 102-0075, Japan, JST CREST, Sanbancho 5, Chiyoda-ku, Tokyo 102-0075, Japan, Department of Physical Science, Graduate School of Science, Osaka Prefecture University, Sakai, Osaka 599-8531, Japan, and RIKEN SPring-8 Center, Sayo-gun, Hyogo 679-5148, Japan

Received October 23, 2007; E-mail: hiroshiscc@mbox.nc.kyushu-u.ac.jp

Recently, metal nanoparticles have attracted much attention as a new type of hydrogen storage alloy.<sup>1,2</sup> Because hydrogen storage properties of metals are strongly related to their electronic states,<sup>3</sup> the hydrogen storage properties of metal nanoparticles are quite different from those in bulk metals.<sup>1,2</sup> In previous reports, the hydrogen solubility as the hydride (Pd–H) phase in Pd nanoparticles having a diameter of 2–3 nm was observed to be smaller than that of bulk Pd, which has a high hydrogen storage ability.<sup>1a–c</sup> On the other hand, Pt nanoparticles with a diameter of 3.2 nm exhibit hydrogen storage ability, although bulk Pt never does so.<sup>1d</sup> This striking difference prompted us to look for possible exploitation of these nanoparticles. We, therefore, prepared core/shell (Pt) nanoparticles for a study of their absorption properties.

The core/shell nanoparticles can be regarded as a kind of phase separation of an alloy into a core surrounded by the shell composed of a metal. The core/shell boundary has been observed to bring about interesting physical and chemical properties that have important technological applications.<sup>4–6</sup> Due to the modification of the structure and electronic states, such as atomic arrangements and chemical potentials of the interfacial region, we anticipate, therefore, that the hydrogen absorption properties can be quite different to the pure metals nanoparticles. With the lack of any published results on the hydrogen absorption properties of core/shell-type nanoparticles, it is difficult to predict what kinds of hydrogen absorption properties can be expected.

Here, we study Pd/Pt bimetallic nanoparticles (Pd/Pt nanoparticles) with a Pd core/Pt shell structure. In this case, do the Pd/Pt nanoparticles absorb hydrogen, as expected? Where is the hydrogen trapped inside the core/shell-type nanoparticles, that is, the Pd core, the Pt shell, or the interface between the Pd core and Pt shell? In this work, in order to clarify the hydrogen absorption behavior of Pd/Pt nanoparticles, we obtained the hydrogen pressure–composition (PC) isotherms and performed solid-state <sup>2</sup>H NMR measurements of Pd/Pt nanoparticles. As a result, we found that the Pd/Pt nanoparticles can absorb hydrogen, and the absorbed hydrogen lies at the interface between the Pd core and the Pt shell, as illustrated in Figure 1. This report gives the first information about hydrogen absorption properties of core/shell-type nanostructured materials.

Poly(*N*-vinyl-2-pyrrolidone) (PVP)-protected Pd nanoparticles were prepared by stepwise growth.<sup>7</sup> The coating of these nanoparticles was performed by an improved variation of the reported hydrogen sacrificial protective method.<sup>8</sup> From the results of transmission electron microscopy (TEM) measurements, the mean diameters of the Pd and Pd/Pt nanoparticles were determined to be

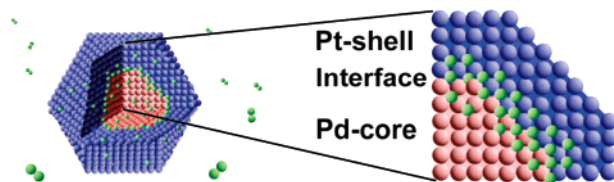


Figure 1. Image of hydrogen storage of Pd/Pt nanoparticles. (green = hydrogen, red = Pd, blue = Pt).

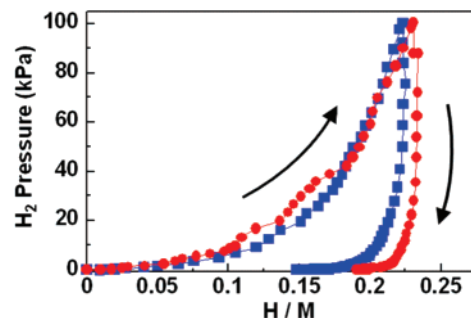


Figure 2. PC isotherms of Pd (blue) and Pd/Pt nanoparticles (red) at 303 K. Isotherm was measured according to the direction of the arrows.

6.1 ± 0.8 and 8.1 ± 0.9 nm, respectively (Figure S1). From the difference of the mean diameters between the Pd and the Pd/Pt nanoparticles, it was found that the Pt shell part of the Pd/Pt nanoparticles is composed of ca. four atomic layers. We also confirmed the core/shell structure by means of high-resolution transmission electron microscopy (HRTEM) and nanoscale energy-dispersive X-ray spectroscopy (EDS) (Figure S2). The atomic percentage of Pt in the Pd/Pt nanoparticles was estimated to be 21% by ICP–MS spectrometry. The powder X-ray diffraction (XRD) pattern measured at the BL02B2 in SPring-8 for Pd/Pt nanoparticles consisted of two kinds of face-centered-cubic (fcc) patterns (Figure S3), indicating that core Pd and shell Pt portions retain their original structures.

The PC isotherm for Pd/Pt nanoparticles measured at 303 K is shown in Figure 2. We evaluated the number of hydrogen atoms per M atom, H/M ( $M = \text{Pd}_{0.79}\text{Pt}_{0.21}$ ). The hydrogen concentration in the Pd/Pt nanoparticles was found to increase with hydrogen pressure, as was the case for Pd nanoparticles, and the total amount of hydrogen absorption at ca. 101.3 kPa was 0.23 H/M, compared with 0.22 H/Pd in Pd nanoparticles. It was, therefore, determined that the Pd/Pt nanoparticles can absorb almost same amount of hydrogen to Pd nanoparticles.

The solid-state <sup>2</sup>H NMR measurement for Pd/Pt nanoparticles under 86.7 kPa of deuterium gas at 303 K was performed to investigate the absorption site of deuterium inside the nanoparticles.<sup>9</sup> As shown in Figure 3a, a broad absorption line with a full width at

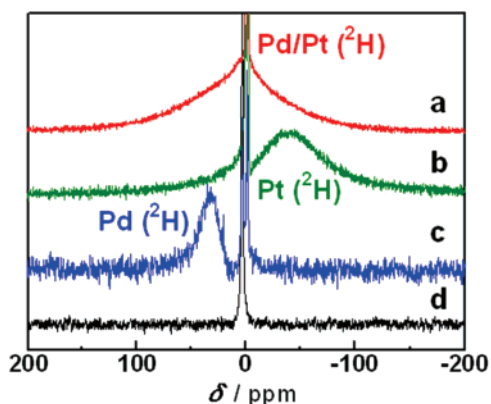
<sup>†</sup> Kyushu University.

<sup>‡</sup> JST PRESTO.

<sup>§</sup> JST CREST.

<sup>¶</sup> Osaka Prefecture University.

<sup>¶</sup> RIKEN SPring-8 Center.



**Figure 3.** Solid-state  $^2\text{H}$  NMR spectra for the samples of (a) Pd/Pt, (b) Pt, and (c) Pd nanoparticles under 86.7 kPa of deuterium gas at 303 K and (d)  $^2\text{H}_2$  gas at 303 K.

half-maximum (fwhm) of 107 ppm and a sharp line around 0 ppm were observed. In the spectrum for  $^2\text{H}_2$  gas (Figure 3d), only a sharp line at 3.35 ppm was obtained. By comparison of these spectra, it is reasonable to attribute the sharp component in the spectrum of the Pd/Pt particle to free deuterium gas ( $^2\text{H}_2$ ) and the broad component to absorbed deuterium atoms ( $^2\text{H}$ ) in the particles. In the  $^2\text{H}$  NMR spectra for Pd and Pt nanoparticles having a diameter of 5.1 nm under 86.7 kPa of  $^2\text{H}_2$  gas,<sup>10</sup> we could see absorptions at 34 and  $-36$  ppm, respectively, with a sharp component around 0 ppm, indicating the existence of deuterium absorbed inside the lattice of the Pd or Pt nanoparticles.<sup>10,11</sup> These absorption lines are narrower than that for the core/shell particle; that is, the fwhm values of the spectra for Pd and Pt nanoparticles are 20 and 95 ppm, respectively. It is characteristic that the shifts of the absorption lines for Pd and Pt have opposite signs to each other relative to the position of the deuterium gas peak. The wide absorption for Pd/Pt particles covers the range containing peaks for Pd and Pd nanoparticle samples. This result indicates that the deuterium disperses inside both Pd and Pt lattices. However, the highest intensity was observed between the peak positions for Pd and Pt samples, implying that most of the deuterium is concentrated in the interfacial region between the Pd core and the Pt shell in Pd/Pt nanoparticles. From these results, it can be concluded that the atomic arrangements or chemical potential around the core/shell interface boundary is different from those of Pd or Pt nanoparticles, which implies that such the hetero-interface provides favorable environment for metal-hydride formation. As a result, hydrogen atoms gather particularly around the hetero-interface in the Pd/Pt nanoparticle.

Bearing in mind that the XRD patterns of the Pd/Pt nanoparticles were hardly dependent on hydrogen pressure, the interfacial region between the Pd core and the Pt shell can absorb hydrogen without lattice expansion, in contrast to that of the core portion of Pd (Figure S3).

In summary, we have investigated the hydrogen absorption behavior of Pd/Pt nanoparticles with a core/shell-type structure. It was revealed that most of the absorbed hydrogen atoms are situated around the interfacial region between the Pd core and the Pt shell of the Pd/Pt nanoparticles, indicating that the core/shell boundary plays an important role in the formation of the hydride phase of the Pd/Pt nanoparticles. It is hoped that the results obtained in this study will provide a clue for the creation of highly concentrated hydrogen storage materials.

**Acknowledgment.** This work was partly supported by a Grant-in-Aid for Scientific Research on Priority Areas (Chemistry of Coordination Space, No. 16074212), the Joint Project for Chemical

Synthesis Core Research Institutions, and the Grants-in-Aid for the Global COE Program, "Science for Future Molecular Systems" and the 21st Century COE Program, "Integration Technology of Mechanical Systems for Hydrogen Utilization" and Elements Science and Technology Project from the MEXT, Japan, and by a Grant-in-Aid for Scientific Researches for Encouraged Areas (B) No. 17750056 and Research Fellowships for Young Scientists No. 1852932 from the JSPS.

**Supporting Information Available:** Experimental details, TEM and HRTEM images, EDS spectra, and XRD patterns. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) (a) Yamauchi, M.; Kitagawa, H. *Synth. Met.* **2005**, *153*, 353–356. (b) Pundt, A.; Sachs, C.; Winter, M.; Reetz, M. T.; Fritsch, D.; Kirchheim, R. *J. Alloys Compd.* **1999**, *293–295*, 480–483. (c) Sachs, C.; Pundt, A.; Kirchheim, R. *Phys. Rev. B* **2001**, *64*, 075408. (d) Isobe, Y.; Yamauchi, M.; Ikeda, R.; Kitagawa, H. *Synth. Met.* **2003**, *135–136*, 757. (e) Eastman, J. A.; Thompson, L. J.; Kestel, B. J. *Phys. Rev. B* **1993**, *48*, 84. (f) Züttel, A.; Nützel, C.; Schmid, G.; Chartouni, D.; Schlapbach, L. *J. Alloys Compd.* **1999**, *293–295*, 472–475. (g) Hanneken, J. W.; Baker, D. B.; Conradi, M. S.; Eastman, J. A. *J. Alloys Compd.* **2002**, *330–332*, 714–717. (h) Suleiman, M.; Jisrawi, N. M.; Dankert, O.; Reetz, M. T.; Bahtz, C.; Kirchheim, R.; Pundt, A. *J. Alloys Compd.* **2003**, *356–357*, 644–648. (i) Wolf, R. J.; Lee, M. W. *Phys. Rev. Lett.* **1994**, *73*, 557. (j) Mütschele, T.; Kirchheim, R. *Scr. Metall.* **1987**, *21*, 1101. (k) Sibirteev, D. S.; Skripov, A. V.; Natter, N.; Hempelmann, R. *Solid State Commun.* **1998**, *108*, 583–586. (l) Natter, H.; Wettmann, B.; Heisel, B.; Hempelmann, R. *J. Alloys Compd.* **1997**, *253–254*, 84–86. (m) Kishore, S.; Nelson, J. A.; Adair, J. H.; Eklund, P. C. *J. Alloys Compd.* **2005**, *389*, 234–242. (n) Horinouchi, S.; Yamanoi, Y.; Yonezawa, T.; Mouri, T.; Nishihara, H. *Langmuir* **2006**, *22*, 1880–1884. (o) Stuhr, U.; Wipf, H.; Udovic, T. J.; Weissmüller, J.; Gleiter, H. *J. Phys.: Condens. Matter* **1995**, *7*, 219. (p) Shao, H.; Xu, H.; Wang, Y.; Li, X. *J. Solid State Chem.* **2004**, *177*, 3626.
- (2) (a) Callejas, M. A.; Anson, A.; Benito, A. M.; Maser, W.; Fierro, J. L. G.; Sanjuán, M. L.; Martínez, M. T. *Mater. Sci. Eng. B* **2004**, *108*, 120. (b) Sun, Y.; Tao, Z.; Chen, J.; Herricks, T.; Xia, Y. *J. Am. Chem. Soc.* **2004**, *126*, 5940. (c) Yavari, A. R.; LeMoulec, A.; de Castro, F. R.; Deledda, S.; Friedrichs, O.; Botta, V. J.; Vaughan, G.; Klassen, T.; Fernandez, A.; Kvick, A. *Scr. Mater.* **2005**, *52*, 719. (d) Janot, R.; Rougier, A.; Aymard, L.; Lenain, C.; Herrera-Urbina, R.; Nazri, G. A.; Tarascon, J. M. *J. Alloys Compd.* **2003**, *356–357*, 438. (e) Bogdanovic, B.; Felderhoff, M.; Kaskel, S.; Pommerin, A.; Schlichte, K.; Schüth, F. *Adv. Mater.* **2003**, *15*, 1012. (f) Shao, H.; Wang, Y.; Xu, H.; Li, X. *J. Solid State Chem.* **2005**, *178*, 2211.
- (3) (a) Lewis, F. A. *The Palladium Hydrogen System*; Academic Press: London, 1967. (b) Alefeld, G.; Völkl, J., Eds. *Hydrogen in Metals II*; Springer: Berlin, Heidelberg, 1978.
- (4) (a) Lee, W.-r.; Kim, M. G.; Choi, J.-r.; Park, J.-I.; Ko, S. J.; Oh, S. J.; Cheon, J. *J. Am. Chem. Soc.* **2005**, *127*, 16090. (b) Zhao, W.; Gu, J.; Zhang, L.; Chen, H.; Shi, J. *J. Am. Chem. Soc.* **2005**, *127*, 8916. (c) Masala, O.; Seshadri, R. *J. Am. Chem. Soc.* **2005**, *127*, 9354. (d) Wang, L. Y.; Luo, J.; Fan, Q.; Suzuki, M.; Suzuki, I. S.; Engelhard, M. H.; Lin, Y.; Kim, N.; Wang, J. Q.; Zhong, C. J. *J. Phys. Chem. B* **2005**, *109*, 21593. (e) Skumryev, V.; Stoyanov, S.; Zhang, Y.; Hadjipanayis, G.; Givord, D.; Nogués, J. *Nature* **2003**, *423*, 850. (f) Zeng, H.; Li, J.; Wang, Z. L.; Liu, J. P.; Sun, S. *Nano Lett.* **2004**, *4*, 187.
- (5) (a) Gerion, D.; Pinaud, F.; Williams, S. C.; Parak, W. J.; Zanchet, D.; Weiss, S.; Alivisatos, A. P. *J. Phys. Chem. B* **2001**, *105*, 8861–8871. (b) Mandal, S.; Selvakannan, P. R.; Pasricha, R.; Sastry, M. *J. Am. Chem. Soc.* **2003**, *125*, 8440. (c) Dabbousi, B. O.; Rodriguez-Viejo, J.; Mikulec, F. V.; Heine, J. R.; Mattoussi, H.; Ober, R.; Jensen, K. F.; Bawendi, M. G. *J. Phys. Chem. B* **1997**, *101*, 9463–9475. (d) Danek, M.; Jensen, K. F.; Murray, C. B.; Bawendi, M. G. *Chem. Mater.* **1996**, *8*, 173–180. (e) Peng, X.; Schlamp, M. C.; Kadavanich, A. V.; Alivisatos, A. P. *J. Am. Chem. Soc.* **1997**, *119*, 7019–7029.
- (6) (a) Toshima, N.; Shiraishi, Y.; Shiotsuki, A.; Ikenaga, D.; Wang, Y. *Eur. Phys. J. D* **2001**, *16*, 209–212. (b) Zeng, J.; Yang, J.; Lee, J. Y.; Zhou, W. *J. Phys. Chem. B* **2006**, *110*, 24606–24611. (c) Zhang, J.; Lima, F. H. B.; Shao, M. H.; Sasaki, K.; Wang, J. X.; Hanson, J.; Adzic, R. R. *J. Phys. Chem. B* **2005**, *109*, 22701–22704. (d) Scott, R. W. J.; Wilson, O. M.; Oh, S. K.; Kenik, E. A.; Crooks, R. M. *J. Am. Chem. Soc.* **2004**, *126*, 15583–15591. (e) Zhou, S.; Varughese, B.; Eichhorn, B.; Jackson, G.; McIlwraith, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 4539–4543.
- (7) Teranishi, T.; Miyake, M. *Chem. Mater.* **1998**, *10*, 594–600.
- (8) Wang, Y.; Toshima, N. *J. Phys. Chem. B* **1997**, *101*, 5301–5306.
- (9) Solid-state  $^2\text{H}$  NMR spectra were measured at 303 K with 61.36 MHz frequency by using APOLLO NMR spectroscope (Tecmag). Samples of Pd and Pd/Pt nanoparticles were evacuated in vacuo at 373 K for 30–60 min. After evacuation, the samples were sealed into glass capillaries with 86.7 kPa of  $^2\text{H}_2$  gas.  $^2\text{H}_2$  gas into glass capillary was also prepared for reference.
- (10) Yamauchi, M.; Kitagawa, H. *Chem. Eng. Trans.* **2005**, *8*, 159–163.
- (11) Manuscript in preparation for publication.

JA078126K