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Atomic-Level Pd−Pt Alloying and Largely Enhanced Hydrogen-Storage Capacity in Bimetallic Nanoparticles Reconstructed from Core/Shell Structure by a Process of Hydrogen Absorption/Desorption

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Bimetallic nanomaterials have attracted much attention due to their potential applications in numerous fields of science and technology.[1] Controlling the structure, e.g. core/shell or alloy, size, and chemical composition of bimetallic nanomaterials is extremely important to modern materials chemistry because the intrinsic properties of bimetallic nanomaterials are strongly correlated with their structural parameters.[1,2] As the structure, size, and composition of bimetallic nanoparticles are simultaneously modified in response to changing reaction conditions, it is still challenging to precisely control a bimetallic nanostructure. Here we first report a method to alter only the atomic arrangement of a bimetallic nanostructure by a process of hydrogen absorption/desorption (PHAD), while the size and chemical composition are maintained.

Pd−Pt bimetallic nanoparticles are significant systems, and they play an important role as effective catalysts.[3−5] Due to the wide applications of these Pd−Pt catalysts, it is of great interest to study the structure of the bimetallic nanoparticles. Various phase-separated structures such as core−shell[3] or dendritic,[4] or alloy[5] structures have been reported. On the other hand, few reports exist on solid-solution structured alloy nanoparticles where Pd and Pt are homogeneously mixed at the atomic level.[6] The limited number of reports regarding the solid-solution nanoparticles may due to the fact that Pd and Pt intrinsically form a segregated domain structure.[7] Further development of a facile and effective synthesis method for the solid-solution Pd−Pt nanoparticles is, therefore, still required for technical applications with high efficiency and performance. In this report, we have achieved the creation of a solid-solution alloy where Pd and Pt are homogeneously mixed at the atomic level, by a process of PHAD as a trigger for core(Pd)/shell(Pt) nanoparticles. The Pd−Pt solid-solution nanoparticles with a Pt content of 8−21 atom % had a higher hydrogen-storage capacity than Pd nanoparticles. The hydrogen-storage capacity of Pd−Pt solid-solution nanoparticles can be tuned by changing the composition of Pd and Pt.

Pd/Pt core/shell nanoparticles constituted of a Pd core with a diameter of 6.1 ± 0.9 nm and a Pt shell with a thickness of ∼1.1 nm were used in this study.[8,9] The atomic percentage of Pt in the Pd/Pt nanoparticles was estimated to be 21% by inductively coupled plasma mass spectrometry (ICP-MS). From the results of in situ powder X-ray diffraction (XRD) patterns measured at the BL02B2[10] in SPring-8 for Pd/Pt core/shell nanoparticles during the PHAD at 373 K, it was found that the initial diffraction patterns consisting of Pd core and Pt shell portions changed dramatically to a single fcc lattice pattern following the PHAD at 373 K.[9] The high-resolution TEM and nanospot energy-dispersive X-ray spectroscopy (EDS) revealed that the obtained Pd−Pt nanoparticles form a homogeneous solid solution alloy, where Pd and Pt are mixing at the atomic level after the PHAD at 373 K.[9] Size growth of nanoparticles resulting from aggregation between nanoparticles was not observed because of the mildness of the PHAD. In fact, the initial diameters of the nanoparticles were unchanged after the PHAD.[9] This efficient method enables us to create a variety of precisely controlled solid solution nanoparticles by changing the size of the precursor core/shell nanoparticles.

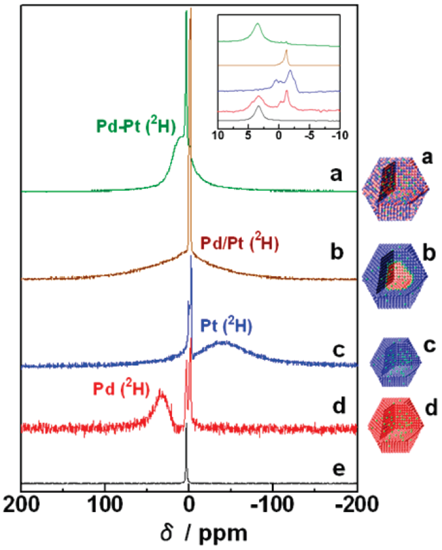

Figure 1. Solid-state ^{2}H NMR spectra for the samples of Pd/Pt nanoparticles after the PHAD (a) and as prepared (b). The samples of Pt (c) and Pd (d) nanoparticles and $^2H_2$ gas (e) were also measured for references. Inset shows expanded spectra. All the samples are measured under 86.7 kPa of $^2H_2$ gas at 303 K.

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10.1021/ja1013163

The temperature dependence of the XRD patterns for as-prepared Pd/Pt core/shell nanoparticles was examined.[9] The diffraction patterns do not change in the temperature range from 303 to 473 K, indicating that the core/shell structure is maintained during thermal treatment. It is also reported, in our previous study,[8] that the core/shell structure is maintained under the PHAD at 303 K. Therefore, we need both thermal energy and the PHAD to induce the structural change from core/shell to solid solution.

Solid-state ^{2}H NMR measurements were performed to investigate the states of ^{2}H in PdPt solid-solution nanoparticles. As shown in Figure 1a, two absorption lines with full widths at half-maximum (fwhm) of 1.9 and 29.3 ppm were observed at 3.6 and 8.3 ppm, respectively. In the spectrum for $^{2}H_2$ gas (Figure 1e), only a sharp line at 3.4 ppm was obtained. Upon comparison of these spectra, it is reasonable to attribute the sharp component in the PdPt solid-solution particle spectrum to free deuterium gas ($^{2}H_2$) (inset, Figure 1) and the broad component to deuterium atoms (^{2}H) absorbed in the particles. It is reported that the absorption lines of deuterium absorbed inside the lattices of Pd and Pt nanoparticles are observed at 34 and −36 ppm, respectively.[8] In the spectrum of Pd/Pt core/shell nanoparticles (Figure 1b), the resonance lines were 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.[8] The peak position of absorbed deuterium for PdPt solid-solution nanoparticles is the same as that for Pd/Pt core/shell nanoparticles (Figure 1a); i.e., the deuterium absorbed inside PdPt solid-solution nanoparticles lies in the space where Pd and Pt are in direct contact with each other. It should be noted that the absorption line for PdPt solid-solution nanoparticles is narrower than that for the core/shell nanoparticles; i.e., the FWHMs of the spectra for samples of PdPt solid solution and Pd/Pt core/shell nanoparticles are 29.3 and 103 ppm, respectively. A much narrower absorption line observed for the PdPt solid-solution nanoparticles indicates that deuterium exists within a random Pd−Pt lattice and experiences homogeneous potentials; i.e., the deuterium exists within a uniform solid-solution lattice composed of Pd and Pt.

Hydrogen-absorption properties of metal nanoparticles are strongly correlated with the structure and the electronic state.[8,11] In fact, we have observed the differences in hydrogen-absorption properties between Pd−Pt core/shell and solid solution nanoparticles.[9] Interestingly, the Pd−Pt solid-solution alloy nanoparticles had a higher hydrogen-storage capacity than the core/shell type nanoparticles.[9] To investigate the hydrogen-absorption properties of PdPt solid-solution nanoparticles in detail, we have prepared three kinds of solid-solution nanoparticles with different compositions of Pd and Pt from the precursor core/shell nanoparticles composed of a Pd core with a diameter of 6.1 ± 0.9 nm and different Pt shell thicknesses by a process of hydrogen absorption/desorption,[9] and their hydrogen pressure−composition (PC) isotherms were measured at 303 K (Figure 2). Although bulk Pt does not absorb hydrogen,[12] only 8 atom % replacement of Pd with Pt atom results in an increase in the amount of hydrogen absorption as shown in Figure 2. This largely enhanced hydrogen absorption in $Pd_{92}Pt_8$ nanoparticles indicates that the nanoparticles are not a phase-separation structure but a solid-solution one, where Pd and Pt atoms are homogeneously mixed at the atomic level. With further addition of Pt atoms, the hydrogen concentration decreases and the amount of the absorbed hydrogen for Pd_{50}-Pt_{50} solid-solution nanoparticles became smaller than that for Pd nanoparticles. These results demonstrate that the amount of absorbed hydrogen in Pd−Pt solid-solution nanoparticles can be tuned by controlling the Pt contents. In summary, we first demonstrate the existence of PdPt alloying at the atomic level resulting from the PHAD at 373 K. The hydrogen-storage capacities of the Pd−Pt solid solution alloy nanoparticles with a Pt content of 8−21 atom % were higher than that of Pd nanoparticles. Moreover, the amount of hydrogen absorption is controllable by altering the alloy compositions of Pd and Pt. These successfully obtained alloys are expected to show high activity or significant selectivity as a catalyst for organic synthesis or in various applications such as fuel cell electrodes, as a result of the mixing of Pd and Pt at the atomic level. Moreover, this efficient method allows us to further construct new nanostructured materials by changing the dimensionality or metal species.

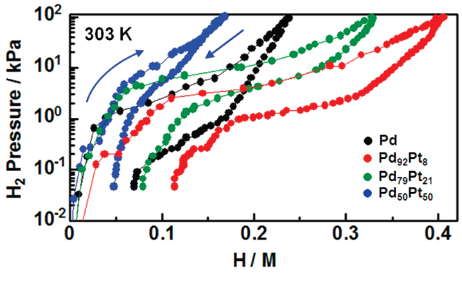

Figure 2. PC isotherms of Pd, Pd_{92}−Pt_8, Pd_{79}−Pt_{21}, and Pd_{50}−Pt_{50} solid solution nanoparticles. The atomic percentage of Pt in the Pd/Pt nanoparticles were estimated by ICP-MS. Isotherms were measured according to the direction of arrows. H/M shows the number of hydrogen atoms divided by the total number of metal atoms.

Acknowledgment. This work was partly supported by the Grants-in-Aid for the Global COE Program, “Science for Future Molecular Systems” and Elements Science and Technology Project from the MEXT, Japan. The synchrotron radiation experiments were performed at the BL02B2 in the SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2005A0244).

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

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JA1013163