

Recent Findings on Metal Nanoparticles as New-Type Hydrogen-Storage Materials

The search for materials enabling efficient storage and safe transport of fuel gases, particularly hydrogen gas, has focused on hydrogen-storage alloys, metal-organic frameworks, carbon materials and many more. Hydrogen-storage alloys provide the best way to store hydrogen compactly and safely under mild condition as a consequence of the stability of their hydride. Most recently, metal nanoparticles have attracted much attention as advanced materials of new hydrogen-storage alloys [1-4]. It is well known that metal nanoparticles exhibit characteristic chemical and physical properties that are quite different from those in bulk metals owing to high surface-to-volume ratios and unique electronic states. Since the hydrogen-storage properties of metals are strongly related to their electronic states, novel hydrogen-storage properties are expected in metal nanoparticles. Here we report the recent findings about hydrogen-absorption properties of Pd and core (Pd)/shell (Pt) nanoparticles.

As shown in Fig. 1, Pd nanoparticles having 6.1 nm diameter absorb hydrogen, and the hydrogen composition under 101.3 kPa of hydrogen pressure at 303 K is 0.22 H/Pd. In the desorption process the curve does not completely return to the starting point in the case of Pd nanoparticles [2,3], while for bulk Pd, it is completely reversible [2]. The origin of this phenomenon has been a puzzle so far. In order to clarify the location of hydrogen, the surface or the

body, and its chemical form, molecular, atomic or hydride, we carried out *in situ* powder X-ray diffraction (XRD) measurement using synchrotron radiation with a 51.148 pm wavelength at beamline BL02B2.

Pd nanoparticles showed a diffraction pattern corresponding to the metallic face-centered-cubic (fcc) lattice under different hydrogen pressures (Fig. 2(a)). The positions of the diffraction peaks were shifted continuously to the lower-angle side in response to hydrogen pressure. The hydrogen-pressure dependences of the lattice constants at 303 K were determined by Le Bail via fitting to the diffraction patterns, and are shown in Fig. 2(b). It can be seen that the lattice constants increase with hydrogen pressure, indicating that Pd atoms within the lattice are forced apart; this can only be a consequence of hydrogen atoms essentially penetrating the inside of the Pd lattice and expanding it. The lattice constant decreases with hydrogen desorption, and the lattice constant at 0 kPa is larger by 0.006 Å than that of the pristine sample, indicating that the lattice constant does not completely return to the same value as in the pristine sample, i.e., the lattice constant shows hysteresis in the course of hydrogen absorption/desorption. Surprisingly, this hysteresis behavior is exactly the same as that observed in the PC hydrogen adsorption isotherm at 303 K. The present results reveal that hydrogen atoms are strongly trapped and highly stabilized in the lattice of Pd nanoparticles, compared with bulk Pd, resulting in the incomplete recovery of the PC isotherm observed at 303 K [2].

We also applied core/shell-type nanoparticles as hydrogen-storage materials for the first time, and their hydrogen-storage properties were investigated [1]. Pd/Pt core/shell nanoparticles comprising a Pd-core with a diameter of 6.1 ± 0.9 nm and a Pt-shell with a thickness of about 1.1 nm were used as the target material. The solid-state ^2H NMR measurement of 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 (Fig. 3(b)). In the ^2H NMR spectra for Pd and Pt nanoparticles having a diameter of 5.1 nm under 86.7 kPa of $^2\text{H}_2$ gas, we could see absorptions at 34 and -36 ppm [4], respectively, indicating the existence of deuterium absorbed inside the lattice of the Pd or Pt nanoparticles. 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.

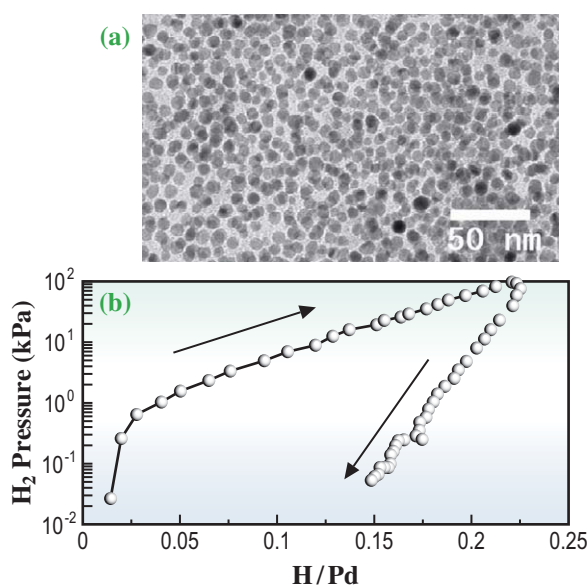


Fig. 1. (a) TEM images and (b) PC isotherms of Pd nanoparticles at 303 K. Isotherm was measured along directions of arrows.

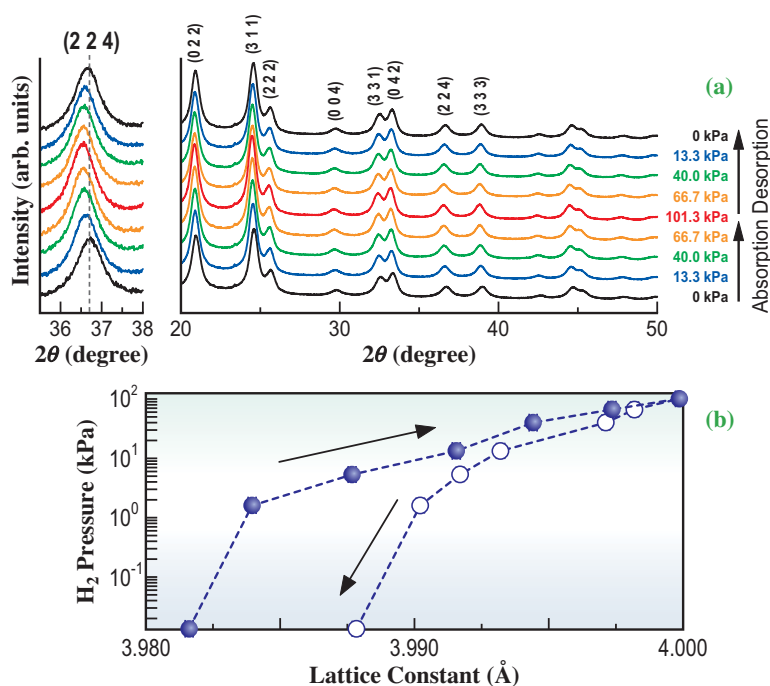


Fig. 2. (a) *In situ* synchrotron XRD patterns of Pd nanoparticles with hydrogen absorption/desorption at 303 K. (b) Lattice constants of Pd nanoparticles obtained by fitting of XRD patterns (● absorption; ○ desorption). Lattice constants were plotted following the directions of the arrows.

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. These results mean 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 a

hetero-interface provides a favorable environment for metal-hydride formation (Fig. 3(a)) [1]. We gained a new revelation 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 new findings obtained in this research will provide a clue to the development of practical hydrogen-storage materials.

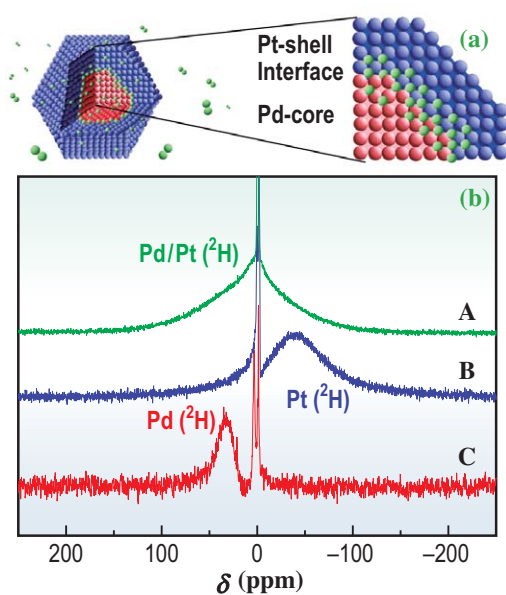


Fig. 3. (a) Image of hydrogen storage of Pd/Pt nanoparticles (green=hydrogen, red=Pd, blue=Pt). (b) Solid-state ^2H NMR spectra for the samples of (A) Pd/Pt, (B) Pt, and (C) Pd nanoparticles under 86.7 kPa of deuterium gas at 303 K.

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