Electronic Supplementary Information for

Relation between crystalline disorder and electronic structure of Pd nanoparticles and their hydrogen storage properties

Okkyun Seo^{1,2,†}, Jaemyung Kim^{1,2†}, Akhil Tayal¹, Chulho Song^{1,§}, L. S. R. Kumara^{1,£}, Shun Dekura^{3,¶}, Hirokazu Kobayashi³, Hiroshi Kitagawa³, and Osami Sakata^{1,2,4,*}

¹Synchrotron X-ray Station at SPring-8, Research Network and Facility Services Division, National Institute for Materials Science (NIMS), 1-1-1 Kouto, Sayo, Hyogo 679-5148, Japan

²Synchrotron X-ray Group, Research Center for Advanced Measurement and Characterization, NIMS, 1-1-1 Kouto, Sayo, Hyogo 679-5148, Japan

³Division of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan

⁴Department of Innovative and Engineered Materials, Interdisciplinary Graduate School of Science and Engineering Tokyo Institute of Technology, Nagatsuta, Midori-Ku, Yokohama, Kanagawa, 226-8502, Japan

[†] These authors contributed equally to this work

§ Present address: NISSAN ARC, LTD., 1 Natsushima-cho, Yokosuka, Kanagawa 237-0061, Japan.

[£] Present address: Research & Utilization Division, Japan Synchrotron Radiation Research Institute (JASRI), 1-1-1 Kouto, Sayo, Hyogo 679-5198, Japan.

[¶]*Present address: The Institute for Solid State Physics, The University of Tokyo, Kashiwanoha* 5-1-5, Kashiwa, Chiba, 277-8581, Japan

* Corresponding author. E-mail: SAKATA.Osami@nims.go.jp

Reverse Monte carlo (RMC) modeling

The 3D RMC modeling of Pd NPs was performed by RMC_POT software for non-periodic boundary conditions.¹⁾ Structure factor results were extracted from HE-XRD data of Pd NPs. We have conducted RMC modeling for Pd 2.0 and 4.6 nm-diameter NPs, because Pd 7.6 nm-diameter NPs is too large to perform the 3D RMC modeling.



Fig. S1. Experimental and RMC modeling of Pd NPs with 2.0 and 4.6 nm-diameter using the hard sphere model were performed on 277 and 3447 atoms, respectively. Hollow black circle, red line, and blue line were experimental results, RMC modeling results, and difference, respectively.

Bond orientational order parameters

The bond orientational order (BOO) parameter was introduced by Steinhardt et al.,²⁾ and is a characteristic of the liquid and the atomic arrangement of the RMC modeling. The BOO parameter near the atom k is defined as

$$q_{l}^{k} = \sqrt{\frac{4\pi}{2l+1} \sum_{m=-l}^{l} |q_{lm}^{k}|^{2}}$$

$$q_{lm}^{k} = \frac{1}{n_{b}^{k}} \sum_{j=1}^{n_{b}^{k}} Y_{lm}(r_{kj})$$
(S1)
(S2)

where $Y_{lm}(\mathbf{r}_{kj})$ is a spherical harmonic function of degree *l* and order *m* and n_b^k is the number of neighboring atoms around atom *k*. The q_4 and q_6 plane are represented by the spherical harmonic function of atoms in the nearest neighbor, which included the bond angles and the numbers of nearest neighbors.^{3,4)} We evaluated the degree of disordering by comparing how much it deviates from the ideal ordered structure. (fcc case, $q_4 : 0.190 q_6 : 0.575$)

P_{BOO} parameters

The P_{BOO} value is a structural parameter describing the local structural deviation of the metal nanoparticles from an ideal crystal structure.⁵⁾

$$P_{BOO} = \sqrt{\left(\frac{\overline{q_4}}{q_{4,ideal}} - 1\right)^2 + \left(\frac{\overline{q_6}}{q_{6,ideal}} - 1\right)^2}$$
(S3)

The $\overline{q_4}$ and $\overline{q_6}$ is the average BOO values of Pd nanoparticles along the q_4 and q_6 planes. We evaluated the mean value of the $\overline{q_4}$ and $\overline{q_6}$ for the core and surface sections using the distribution of BOO parameters.

Fitted profiles and metrical parameters of XAFS results

Figure S4 represents the fitted profiles of (a) Fourier transform (FT) moduli and (b) $\chi(k) \times k^3$ EXAFS spectra at Pd *K*-edge. Red line is data profiles and blue line is fitted profiles of EXAFS spectra.



Fig. S2. (a) Fitted profiles of the Fourier transform moduli of Pd NPs and reference Pd foils. (b) Fitted profiles of the Pd k-edge XAFS spectra of $\chi(k) \times k^3$. (1: Pd reference, 2: 7.6 nm, 3: 4.6 nm, 4: 2.0 nm, respectively.)

Although a reduction in the amplitude of $\chi(k)$ EXAFS spectrum is generally attributed to either reduce in the coordination number or increase in the structural disorder. If the structural disorder is dominantly increasing in the series of samples, the $\chi(k)$ amplitude falls rapidly relatively in the higher *k*-region. The metrical parameters from the EXAFS data are derived by performing a non-linear least square fits and listed in Table S1.

Shell	Pd-ref	Pd 7.6 nm	Pd 4.6 nm	Pd 2.0 nm
First shell				
<i>R</i> (Å)	2.73±0.01	2.73±0.01	2.72±0.01	2.72±0.01
Ν	12.0	6.8±1.5	6.3±1.4	5.0±1.2
σ	0.08 ± 0.01	0.08 ± 0.01	0.09±0.01	0.10±0.01
ΔE_0	1.7±2.8	2.3±2.7	2.5±2.5	3.9±2.6
Second shell				
R (Å)	3.84±0.02	3.83 ± 0.02	3.81±0.02	3.78±0.02
Ν	6.0	3.1±1.0	3.4±1.5	3.0±0.8
σ	0.09 ± 0.01	0.09 ± 0.01	0.10±0.01	0.10±0.01
ΔE_0	0.7 ± 2.2	1.6 ± 2.1	2.9±1.9	4.9 ± 2.5

Table S1. Metrical parameters such as shell distance (*R*), coordination number (N), and root mean square deviation in the shell distance (σ) derived from EXAFS.

Photon energy calibration using the Au reference sample

The photon energy was calibrated by Au reference sample. Figure S3 shows the Fermi level of au samples at a kinetic energy of 5948.284 eV.



Fig. S3. Fermi edge of Au measured using HAXPES. The red line indicates the fitting of the position of the Fermi level.

Reference

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