Electronic Supplementary Information

Hydrogen absorption and desorption on Rh nanoparticles revealed by *in-situ* dispersive X-ray absorption fine structure spectroscopy

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SUPPORTING NOTE 1. Particle size distributions of Rh NPs

Supplementary Figure 1 shows the particle size distribution of Rh NPs. The mean diameters of the nanoparticles were determined from the TEM images to be **a)** 4.0 ± 0.7 and **b)** 10.5 ± 0.8, respectively. Numbers that follow the ± sign represent estimated standard deviations.
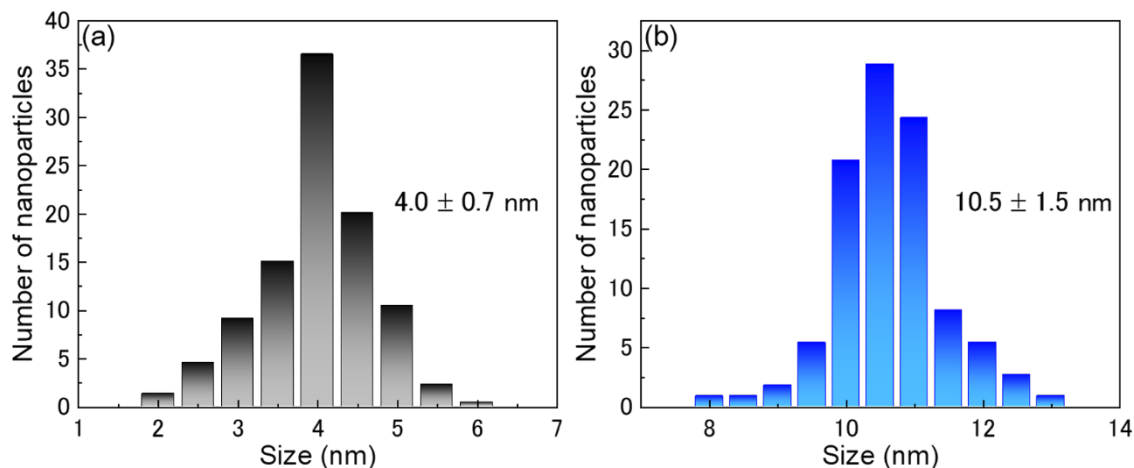

Figure S1. Particle size distributions of Rh NPs: **a**, 4.0 nm; **b**, 10.5 nm.

SUPPORTING NOTE 2. Hydrogen pressure-composition (PC) isotherms for Rh NPs

Hydrogen pressure-composition (PC) isotherms for the Rh NPs were measured with a volumetric technique using a pressure-composition temperature (PCT) apparatus (Suzuki Shokan Co., Ltd. Japan). The pressure sensor was a INFICON SKY Model CR090 and its range was from 1.33 to 133000 Pa. The purity of the hydrogen was 99.999 %, oxygen < 1 ppm. The weights of the measured samples were more than 100 mg as the amount of the metal. As a pre-treatment before the absorption process, a volume measurement of the NPs was performed with helium. Because the amount of hydrogen absorption tends to be overestimated from the 1st PC isotherm owing to reduction of the particle surface, we measured each PC isotherm more than three times. After confirming whether the 2nd and 3rd measurements exhibited reproducibility, we used the 2nd PC isotherm dataset. For absorption measurements, the pressure during the introduction of the hydrogen was raised in 23 steps (50, 100, 200, 300, 400, 500, 600, 700, 800, 900, 1000, 1500, 2000, 3000, 4000, 5000, 6000, 7000, 8000, 9000, 10000, 15000, 20000 Pa). The next step was not initiated until the differential pressure had settled within 15 Pa after 5 min of hydrogen introduction and the PC isotherm data had been collected. Above 2×10^{-2} MPa, the pressure was automatically set and the measurements were performed using the same conditions. During desorption measurements, the next step was initiated after the differential pressure had settled to the same conditions as the corresponding absorption measurements by automatic control. The PC isotherms of Rh NPs are described in Supplementary Ref. 1.

SUPPORTING NOTE 3. XANES and FT spectra of the Rh bulk:

Figure S2(a) and S2(b) show the XANES and interatomic distance spectra of the bulk Rh at 300 K. We were investigated the XAFS spectra of the bulk Rh sample before the *in-situ* XAFS spectra during the hydrogen absorption and desorption of the Rh NPs.
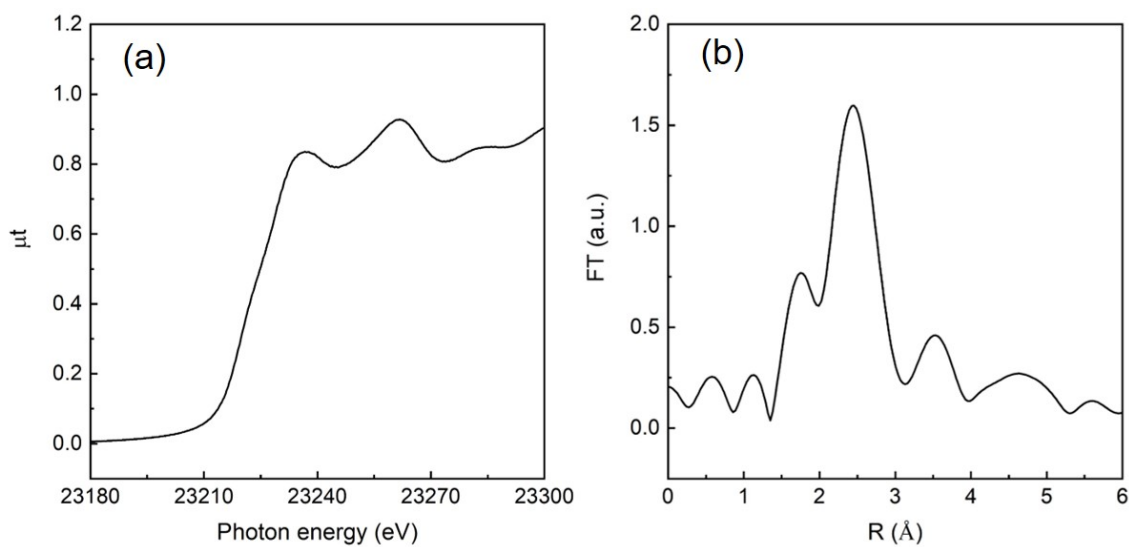

Figure S2. (a) XANES and (b) interatomic distance spectra of bulk Rh at the Rh K edge

SUPPORTING NOTE 4. Enlarge part of *in-situ* Rh K-edge XAFS spectra during the hydrogen absorption and desorption of the Rh NPs:
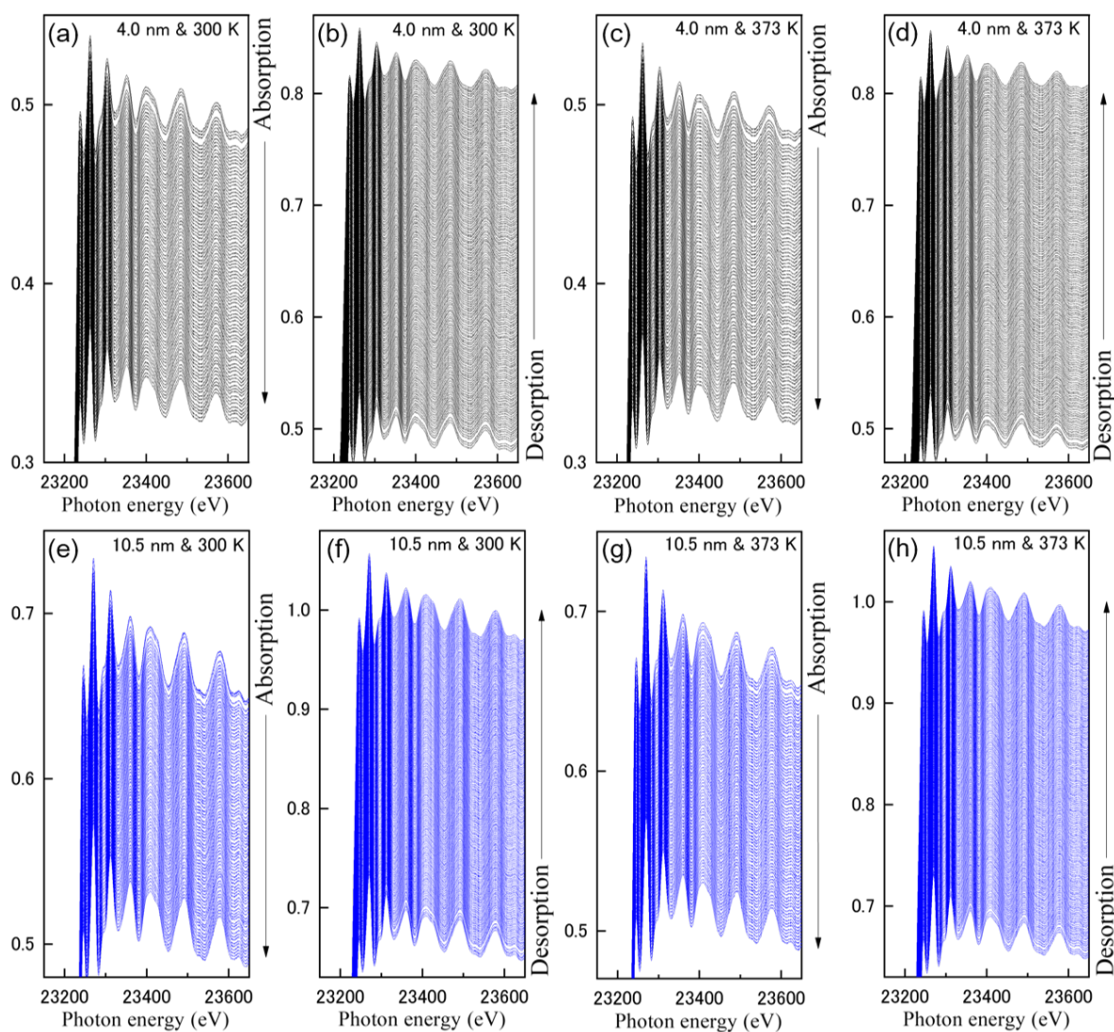

Figure S3. Enlarge part of real-time-resolved Rh K-edge XAFS spectra during the hydrogen absorption and desorption of the Rh NPs: (a) absorption, (b) desorption at 300 K and (c) absorption, (b) desorption at 373 K for Rh NPs with a size of 4.0 nm. (e) absorption, (f) desorption at 300 K and (g) absorption, (h) desorption at 373 K for Rh NPs with a size of 10.5 nm.

SUPPORTING NOTE 5. Activation energy of hydrogen absorption/ desorption for Rh NPs using Arrhenius equation:

The Arrhenius equation is expressed as follow:

$$\frac{1}{t_{1/2}} = Ae^{-Ea/RT} \quad (Eq. S1)$$

where, A: pre-exponential factor or Frequency factor for the reaction, Ea: activation energy (J/mol), R: molar gas constant (8.314472 J/mol•K), and T: temperature in Kelvin. The equation (S1) can be expressed in another form as follows.

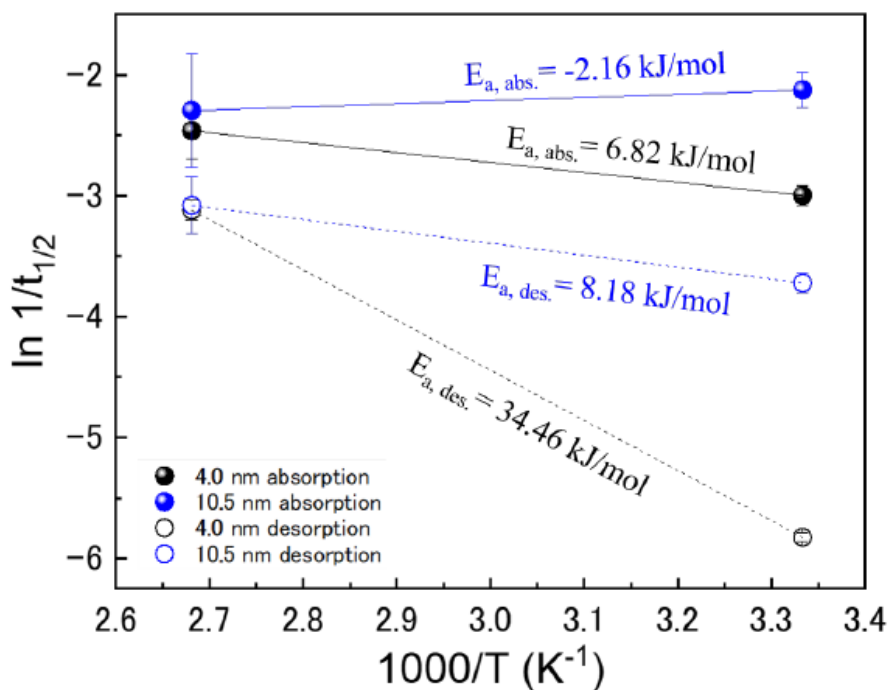$$\ln \frac{1}{t_{1/2}} = \ln A - \frac{E_a}{RT} \quad (Eq. S2)$$

Figure S4. Arrhenius plots for determining the activation energy of hydrogen adsorption/desorption for Rh NPs. The black and blue circles are for Rh NPs with a size of 4.0 and 10.5 nm, respectively.

References

[1] K. Kusada et al., Chem. Lett. **42** (2013) 55-56