Electronic Supplementary Information

Simultaneous fast XAS/SAXS measurements in an energy-dispersive mode

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Contents

SAXS intensity calculation for Pt@Pd and Pt nanoparticles

The SAXS intensity of the Pt@Pd nanoparticle for an X-ray energy E and scattering vector $\boldsymbol{q}$ was calculated based on the following equation:[1,2]

$$I_{\text{SAXS}}(E, q) = \Phi(E)[Bq^{-d} + \int D(r)A_{\text{sph}}(E, q, r)A_{\text{sph}}^*(E, q, r)dr], \qquad (\text{S1})$$

where $q = |\boldsymbol{q}|$, $\Phi(E)$ is the flux of the incident X-ray component, the power law factor Bq^{-d} with free parameters of B and d describes the scattering from the polydispersive carbon support and boron nitride particles, and $A_{\text{sph}}(E, q, r)$ and $A_{\text{sph}}^*(E, q, r)$ are the scattering amplitude of the spherical nanoparticle and its complex conjugate, respectively. r is the particle radius and $D(r)$ is the Schultz-Zimm distribution function

$$D(r) = \frac{(\frac{z+1}{r_0})^{z+1}r^z}{\Gamma(z+1)} \exp\left(-\frac{z+1}{r_0}r\right), \qquad (\text{S2})$$

where $z = (r_0/\sigma)^2$-1 and r_0 and σ are the average radius and root mean square (RMS) deviation of the size distribution, respectively. The scattering amplitude of the core-shell particle is

$$A_{\text{sph}}(E, q, r) = V(r)n_{\text{Pt}}f_{\text{Pt}}(E, q)[F(q, r) - F(q, r - t_{\text{shell}})]$$
$$+ V(r)n_{\text{Pd}}f_{\text{Pd}}(q)F(q, r - t_{\text{shell}}), \qquad (\text{S3})$$

where $V(r) = 4\pi r^3/3$ is the volume of the spherical particle and n_{Pt} (n_{Pd}) and f_{Pt} (f_{Pd}) are the number density and scattering factor of Pt (Pd) atom, respectively. In the analysis, $n_{\text{Pt}} = 4/(0.392)^3$ nm^{-3} and $n_{\text{Pd}} = 4/(0.389)^3$ nm^{-3} were used according to the Pt and Pd bulk crystals. t_{shell} is the shell thickness and thus $r - t_{\text{shell}}$ corresponds to the core radius r_{core}. $F(q, r)$ is the form factor of a spherical structure,

$$F(q, r) = \frac{3[\sin(qr) - qr\cos(qr)]}{(qr)^3}. \qquad (\text{S4})$$

In equation S3, the first term denotes the energy-dependent scattering amplitude from Pt constituting the shell and the second term denotes the non-resonant scattering amplitude from Pd constituting the core. The overall intensity recorded at a detector position P is the sum of SAXS intensities from all the X-ray components, $I_P = \sum_j T(E_j) I_{\text{SAXS}}(E_j, \boldsymbol{q}_{Pj})$, where $T(E_j)$ is the transmittance for an X-ray energy of E_j, as mentioned in the main text. The intensities at the detector pixels were calculated to reproduce the experimental ED-SAXS image, using the anomalous scattering factors of Pt obtained from the ED-XAS data and the incident flux and the direction of each X-ray component obtained from the incident X-ray spectrum measurements. For the analysis of the Pt nanoparticles, the scattering amplitude of an uniform Pt sphere was used ($r = t_{\text{shell}}$ in eq. S3). The fits to the ED-SAXS and SAXS data were performed using a least-squares method with a homemade software. Optimized values of the fitting parameters of the Pt@Pd and Pt nano particles are shown in Tables 2 and S2, respectively.

EXAFS analysis for Pt@Pd and Pt nanoparticles

The EXAFS analysis was performed using Athena/Artemis software of the Demeter package.[3] For the analysis, k^2-weighted EXAFS spectra were Fourier transformed to R-space with Hanning window functions, where the k-ranges were 3.0–10.0 Å^{-1} and 3.0–10.5 Å^{-1} for the Pt@Pd and Pt nanoparticles, respectively. The FEFF 6.0 was used for the calculation of scattering paths. In addition to Pt–Pt or Pt–Pd paths, we assumed a Pt–O path taking account of a possible oxidation of Pt, because the measurements were performed more than 6 months after the sample synthesis and no oxide reduction treatment was performed before the experiments. For the Pt@Pd nanoparticles, the nearest neighbor Pt–Pt and Pt–Pd derived from a Pt crystal structure and the nearest neighbor Pt–O derived from an α-PtO$_2$ crystal were used as the scattering paths. For the Pt nanoparticles, the nearest neighbor Pt–Pt derived from the Pt crystal and the nearest neighbor Pt–O and Pt–Pt in the α-PtO$_2$ crystal were used as the scattering paths, referring to a previous EXAFS analysis for an ini-

tial oxidation of Pt nanoparticles.[4] The bond distances d, the coordination numbers (CN), and mean square variation in the scattering path length σ^2 were used as the fitting parameters. We used a common σ^2 for all the scattering paths in order to reduce the number of fitting parameters. The fits were done in R-space, and the ranges of R-space were 1.3–3.1 Å and 1.3–3.5 Å for the Pt@Pd and Pt nanoparticles, respectively.
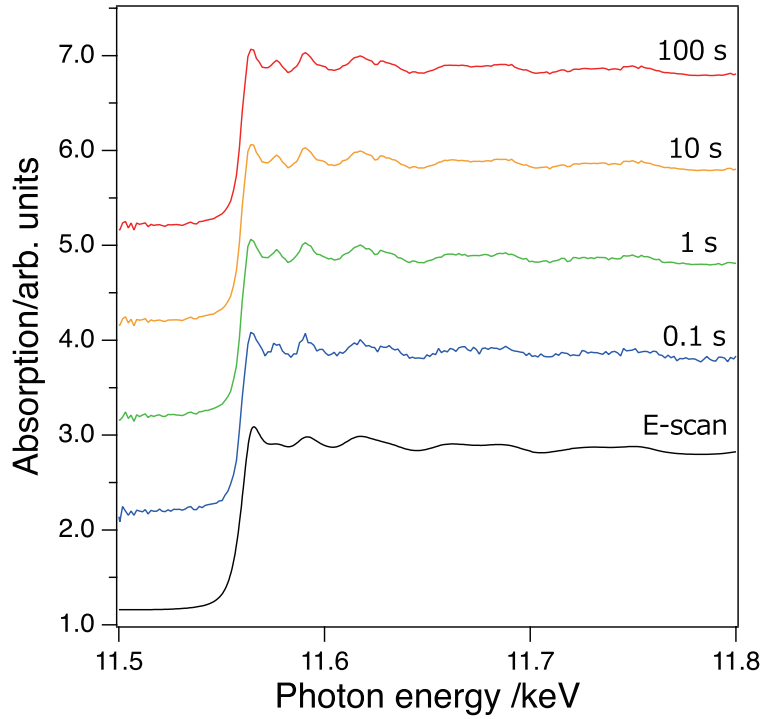
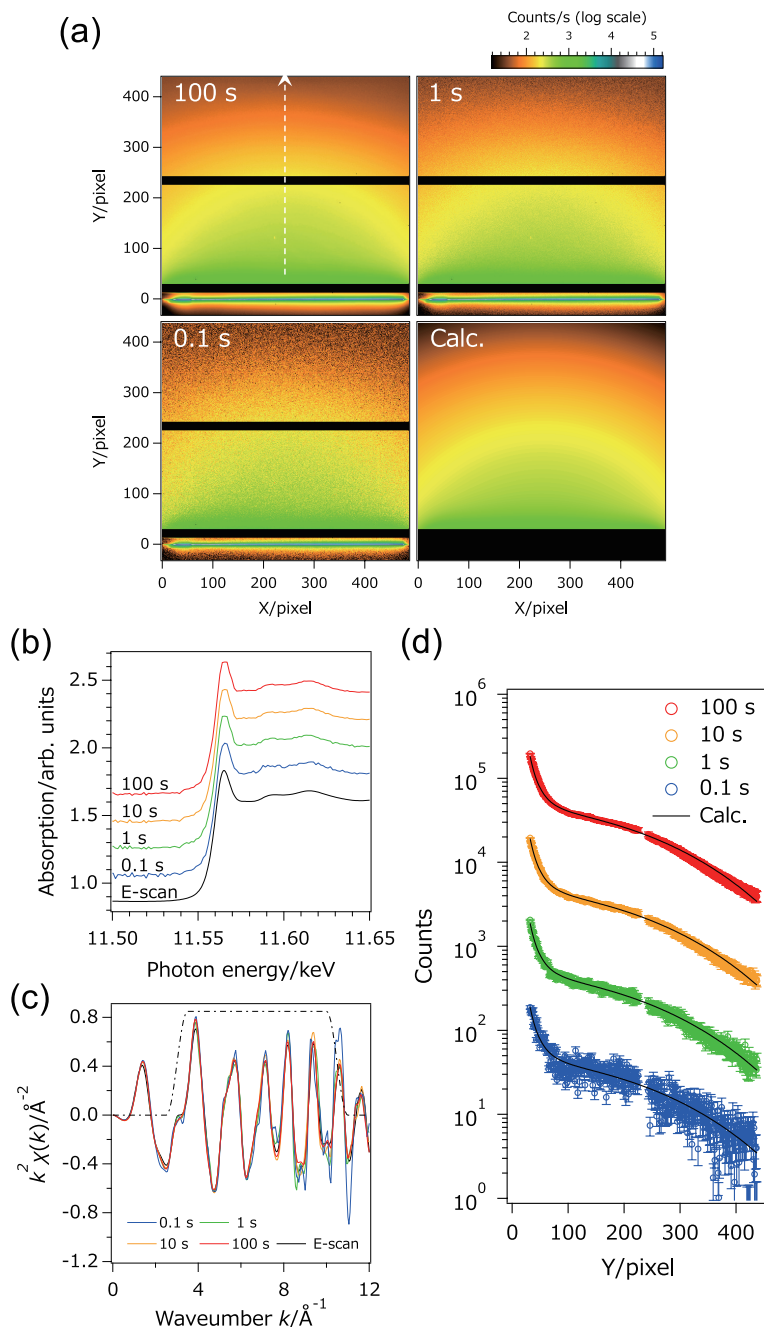Figure S1: ED-XAS and energy-scan XAS spectra of a Pt foil reference sample (thickness: 7.5 μm).

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Figure S2: ED-XAS/SAXS data of Pt nanoparticles. The Pt nanoparicles (8.3 wt.% Pt) were supported by carbon black (8.3 wt.%) and mixed with boron nitride powder (83.4 wt.%, particle size $\sim 1~\mu$m) to be shaped into a pellet (diameter: 7 mm and thickness: 0.5 mm). (a) The ED-XAS/SAXS images with data acquisition times of 100 s, 1 s, and 0.1 s and the calculated ED-SAXS image fitted to the experimental data of 0.1 s. (b) XANES spectra and (c) k^2-weighted EXAFS spectra of the Pt nanoparticles, obtained by the ED-XAS measurements with different exposure times and the conventional energy-scan measurements. Dashed-dotted line in (c) represents a Hanning window function used for the Fourier transform of the EXAFS spectra into R-space (see Fig. S4(b)). (d) The ED-SAXS intensities along the dashed arrow in (a) and calculated ones for the structure parameters obtained from a monochromatic SAXS data (see Table S2).
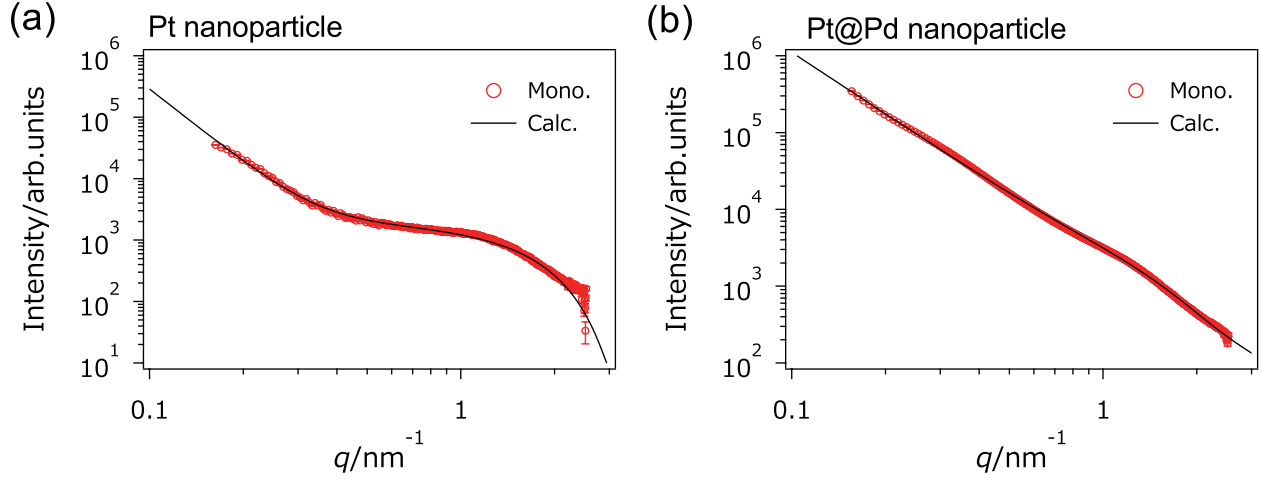
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Figure S3: Monochromatic SAXS data of (a) Pt nanoparticles and (b) Pt@Pd nanoparticles.

Table S1: Best-fit structure parameters of the Pt nanoparticles obtained from the EXAFS analysis for the ED-XAS data with different exposure times and for the energy-scan XAS data.

data	$d_{\mathrm{Pt-Pt}}$/Å	$d_{\mathrm{Pt-Pt(PtO_2)}}$/Å	$d_{\mathrm{Pt-O}}$/Å	$CN_{\mathrm{Pt-Pt}}$	$CN_{\mathrm{Pt-Pt(PtO_2)}}$	$CN_{\mathrm{Pt-O}}$	σ^2/Å^2
E-scan	$2.76_{\pm 0.02}$	$3.11_{\pm 0.05}$	$1.99_{\pm 0.02}$	$7.0_{\pm 1.4}$	$0.9_{\pm 0.5}$	$1.9_{\pm 0.4}$	$0.005_{\pm 0.002}$
100 s	$2.75_{\pm 0.02}$	$3.10_{\pm 0.05}$	$1.99_{\pm 0.02}$	$7.4_{\pm 1.6}$	$1.0_{\pm 0.6}$	$2.0_{\pm 0.5}$	$0.005_{\pm 0.002}$
10 s	$2.76_{\pm 0.02}$	$3.11_{\pm 0.04}$	$1.99_{\pm 0.02}$	$7.2_{\pm 1.6}$	$1.1_{\pm 0.6}$	$2.1_{\pm 0.6}$	$0.005_{\pm 0.003}$
1 s	$2.76_{\pm 0.01}$	$3.08_{\pm 0.05}$	$1.99_{\pm 0.02}$	$6.7_{\pm 1.5}$	$0.8_{\pm 0.5}$	$1.8_{\pm 0.4}$	$0.004_{\pm 0.002}$
0.1 s	$2.76_{\pm 0.01}$	$3.09_{\pm 0.04}$	$1.99_{\pm 0.02}$	$6.7_{\pm 1.3}$	$0.9_{\pm 0.5}$	$2.0_{\pm 0.4}$	$0.004_{\pm 0.002}$

Table S2: Best-fit structure parameters of the Pt nanoparticles obtained from the ED-SAXS and monochromatic SAXS data.

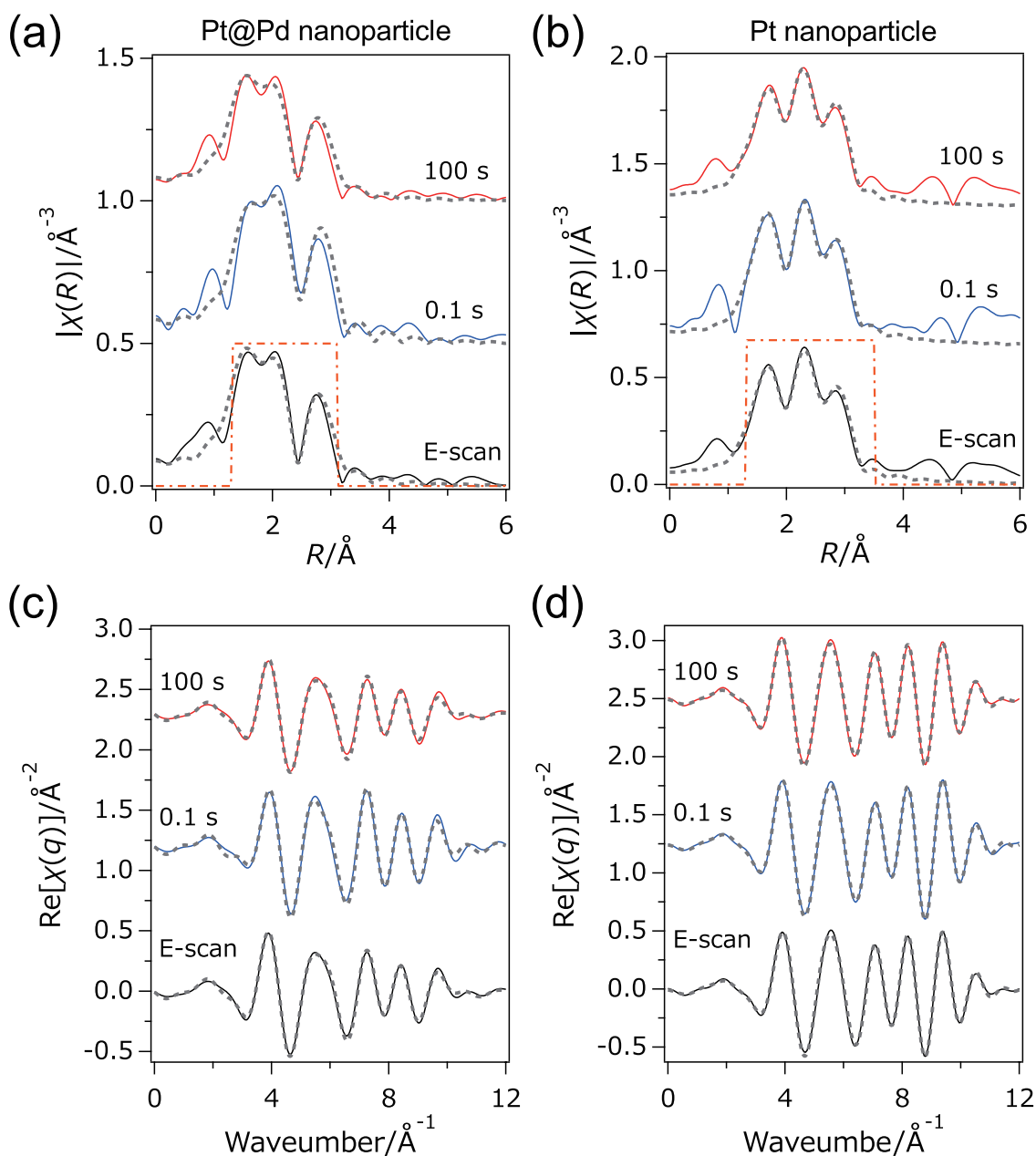| data	r/nm	σ_{RMS}/nm
Mono.	$1.40_{\pm 0.02}$	$0.12_{\pm 0.02}$
100 s	$1.40_{\pm 0.02}$	$0.13_{\pm 0.03}$
10 s	$1.40_{\pm 0.02}$	$0.13_{\pm 0.03}$
1 s	$1.40_{\pm 0.03}$	$0.14_{\pm 0.03}$
0.1 s	$1.40_{\pm 0.05}$	$0.12_{\pm 0.03}$

Figure S4: (a) and (b) Amplitudes of the Fourier transform of the k^2-weighted EXAFS spectra of the Pt@Pd and Pt nanoparticles, respectively. Dashed lines are the calculated amplitudes. Dashed-dotted windows represent the data range used in the EXAFS fitting. (c) and (d) Real part of the inverse Fourier transform of the window ranges of (a) and (b), respectively.

References

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