Electronic Supplementary Information

***In Situ* back-side illumination fluorescence XAFS (BI-FXAFS) studies on platinum nanoparticles deposited on a HOPG surface as a model fuel cell: A new approach to the Pt-HOPG electrode/electrolyte interface**

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Contents:

1. Estimation of number of Pt atoms on HOPG

TEM shows that the Pt nanocluster has a diameter of 1.6 ± 0.6 nm. EXAFS coordination number suggests the presence of Pt_{55} with 1.4 nm in diameter (shown below). If the Pt_{55} cluster is present, the ratio of surface to total atoms was 42/55. The surface atoms can be estimated from the cathodic charge between 0.35 to 0.07 V of stable CVs area (10.75×10^{-6} C) so that the total Pt loading was 0.9×10^{14} cm^{-2}.

$$\frac{10.75 \times 10^{-6} [C]}{96485 \ [C/mol]} \times \frac{55}{42} \times 6.02 \times 10^{23} = 0.9 \times 10^{14}$$

Independently we calculated the Pt loading from the density of clusters that was estimated from the AFM pictures as $(3 \pm 2) \times 10^{-2}$ nm^{-2}. If Pt_{55} was present, it provided $(1.7 \pm 1.1) \times 10^{14}$ cm^{-2} . Thus we estimated the Pt loading as 1×10^{14} cm$^{2.}$
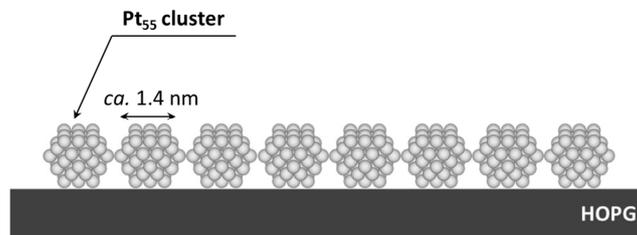

Fig. S1 Schematic illustration of PtNPs on HOPG.

2. Curve fitting result of as-syn. PtNPs

Fourier transform shows the two peaks. The first peak and second peak correspond to Pt-S and Pt-Pt, respectively. The second peak was Fourier flittered in the range of 0.22-0.32 nm and one shell curve fitting analysis provided the Pt-Pt distance at 0.274 nm.

We further carried out two shell fit for the inverse Fourier transformed data in the range of 0.13-0.33 nm with Pt-Pt and Pt-S. We obtained the results as shown in Table S1. The fitting results were well corresponding to the model of Pt_{55} fully covered with thiols. Pt_{55} cuboctahedral structure should have 1.4 nm in diameter with 7.8 in coordination number.

Table S1 Curve fitting results on as-syn. PtNPs.

scattering atom	coordination number	bond length / nm	DW / nm	Phase shift and amplitude references
Pt-Pt	7.5 ± 0.8	0.274 ± 0.003	0.01 ± 0.001	Pt foil
Pt-S	1.0 ± 0.3	0.225 ± 0.003	0.005 ± 0.001	FEFF

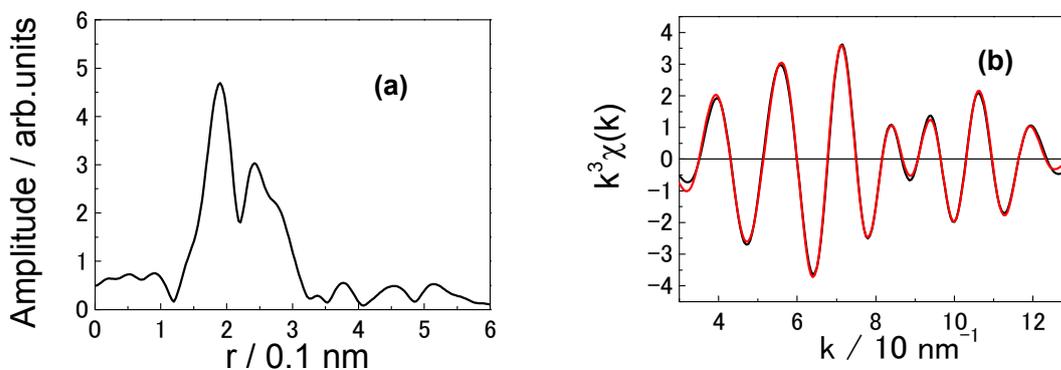K range: 30-130 nm^{-1}; Fourier Filtering: 0.13-0.33 nm; R-factor: 1.23%

Fig. S2 Fourier transform (a) and its best fitting results of inverse Fourier transform (b) of as syn. PtNPs. Red and black curves are calculated and observed $k^3\chi(k)$, respectively.

3. Preparation and morphology of conc. PtNPs/HOPG

The HOPG substrate was dipped in the PtNPs dispersed solution and then dried to obtain a sample with higher concentration. According to the AFM image, PtNPs were deposited as multilayers but one can still see the step and terrace structure of HOPG.
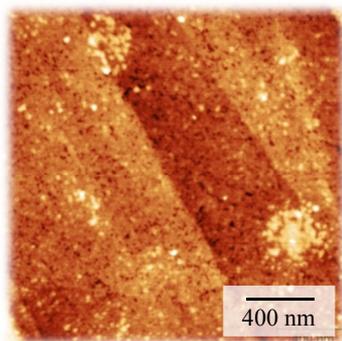

400 nm

Fig. S3 An AFM image of higher concentrated PtNPs on HOPG (conc. PtNPs/HOPG).

4. Throughput of BCLA

We briefly tested the throughput of the BCLA using a pixel-array detector and dilute PtO_2 as a test sample. Fig. S4 shows images obtained before and after the absorption edge. Before the absorption edge, the image was dark because there was no fluorescence, while some part of the pixels appeared brighter after the edge, as shown in Fig. S4c. The partial change of contrast before and after the absorption edge might be caused by the poor alignment of the BCLA crystal.
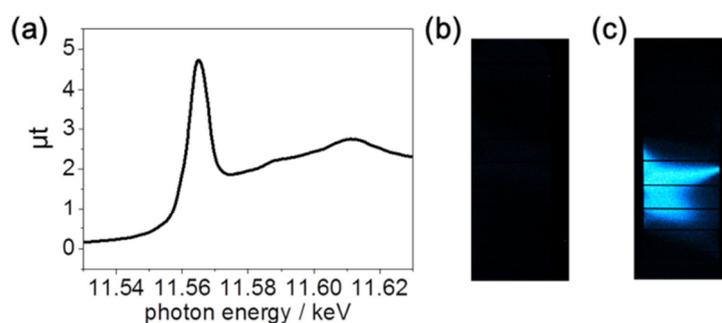

Fig. S4 (a) Fluorescent XANES spectrum of 0.1 mg PtO_2 diluted in 100 mg boron nitride obtained by a pixel-array detector (PILATUS 100K) with a BCLA. (b) Pixel-array detector image exposed at $E = 11540$ eV. Dwell time = 3 s. (c) Pixel-array detector image exposed at $E = 11565$ eV. Dwell time = 3 s. The beam size was 0.5×1 mm^2.

5. F-test of Fig. 8

The difference of XANES spectra in hydrogen adsorption/desorption reaction is very small both experimentally and theoretically. (Difference in normalized XANES spectra is less than 0.1). In order to claim the point definitely, we have applied F-test.

XANES spectra shown in Fig. 8a were averaged data of 29 spectra. Thus one can estimate regression sum of squares (SSR) (error in the average values) and error sum of squares (SSE) (data uncertainty in each file) as follows,

$$\text{SSR} = n_1(\mu_1 - \mu)^2 + n_2(\mu_2 - \mu)^2$$
$$\text{SSE} = \sum_{i=1}^{n_1}(y_i - \mu_1)^2 + \sum_{i=n_1+1}^{n}(y_i - \mu_2)^2$$

where n_x is a number of experiment ($n_1 = n_2 = 29$, $n = n_1 + n_2 = 58$), μ is average of all experiment, μ_x is the average of x each experimental group, y_i is data point of ith experiment, k is number of experimental group ($k = 2$).

The null hypothesis is "there is no difference between two spectra" or "SSE and SSR are equal". Thus the F is defined as

$$F_{\nu_1,\nu} = \frac{\text{SSR}/\nu_1}{\text{SSE}/\nu}$$

where ν and ν_1 are numbers of freedom ($\nu = n - k = 56$, $\nu_1 = k - 1 = 1$).

We can safely to say that the peaks in the difference spectrum around 11558 eV were meaningful with the confidence level more than 0.8 as shown in Fig.S5
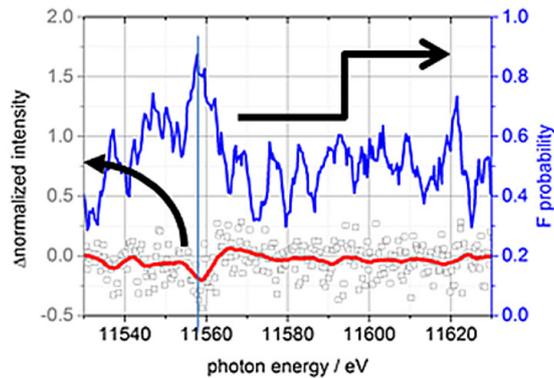

Fig. S5 Difference spectra (lower red line) and F values (upper blue line).