

Electronic Supplementary Information (ESI)

Evidence for Interfacial Geometric Interactions at Metal-Support Interfaces and Its Influence on the Electroactivity and Stability of Pt Nanoparticles

Xiao Zhao,^{a,f*} Takao Gunji,^{a,f} Takuma Kaneko,^{a,f} Shinobu Takao,^a Tomohiro Sakata,^a Kotaro Higashi,^a Yusuke Yoshida,^a Junjie Ge,^b Changpeng Liu,^b Wei Xing,^{b*}, Jianbing Zhu,^c Meiling Xiao,^c Tomoya Uruga,^e Franklin (Feng) Tao^d and Zhongwei Chen^{c*}

^a Innovation Research Center for Fuel Cells, The University of Electro-Communications, Chofugaoka, Chofu, Tokyo 182-8585, Japan

^b State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, Jilin 130022, China

^c Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario, Canada

^d Department of Chemical and Petroleum Engineering, University of Kansas, Lawrence, KS 66045, USA

^e Japan Synchrotron Radiation Research Institute, SPring-8, Sayo, Hyogo 679-5198, Japan

^f These authors contributed equally: X. Z., T. G., and T. K.

*e-mail: xiaozhao@uec.ac.jp, xingwei@ciac.ac.cn, and zhwchen@uwaterloo.ca

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Fig. S1-S12

Tables S1

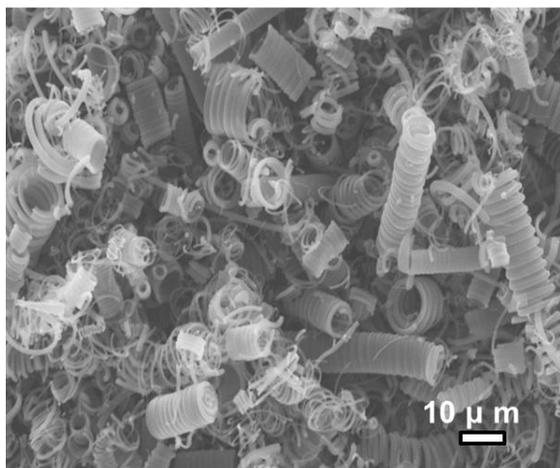
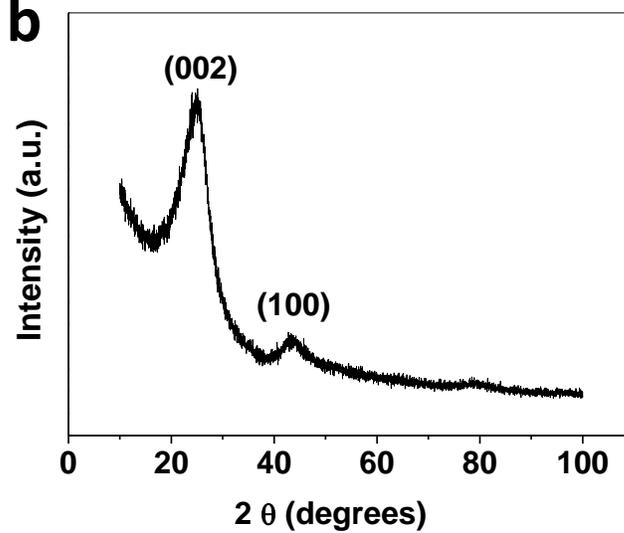
a**b**

Fig. S1. Basic properties of CMC. (a) SEM image of CMC. (b) X-ray diffraction pattern (2θ) of CMC.

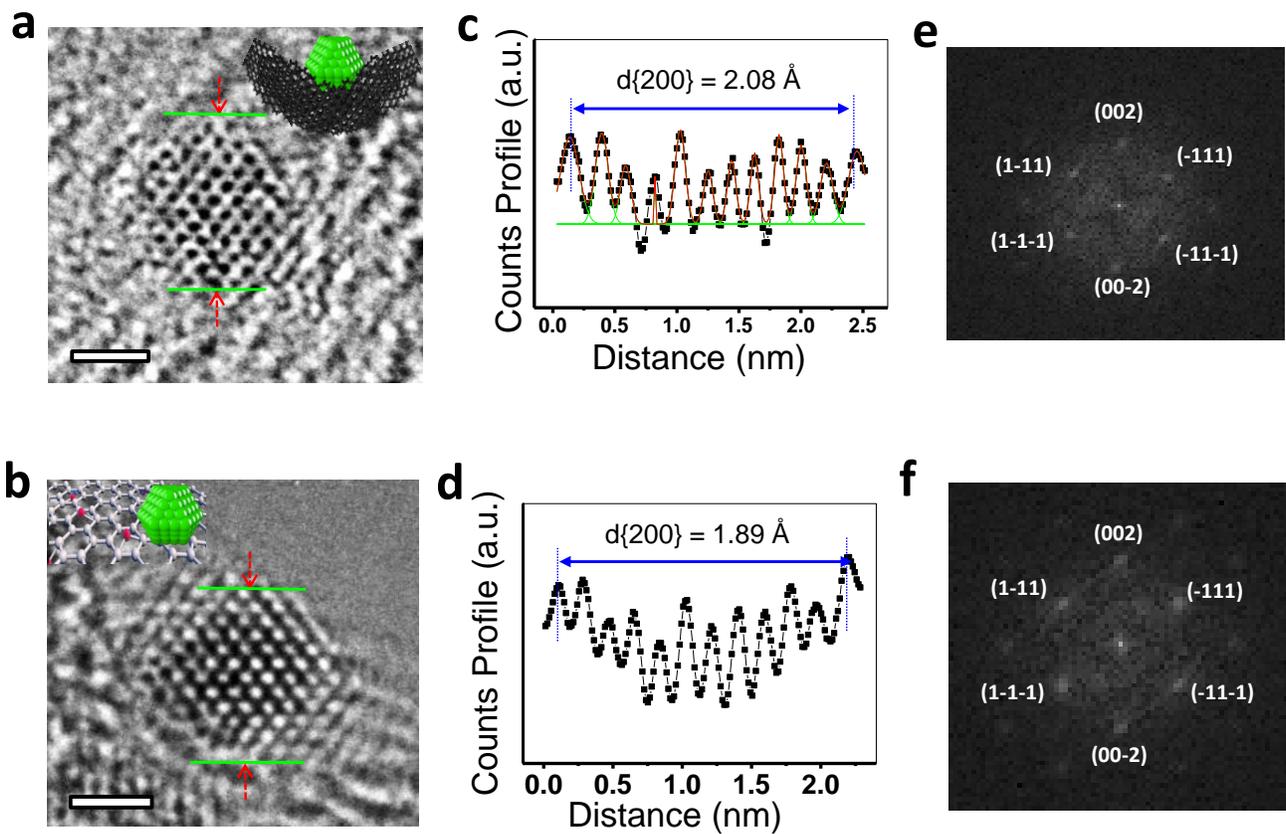


Fig. S2. (a, b) Atomically resolved ATEM images for the 2.1 nm Pt/KB (a) and the 2.1 nm Pt/CMC (b). (c, d) Single particle based analysis of {002} interplanar spacing analysis for the 2.1 nm Pt/KB (c) and the 2.1 nm Pt/CMC (d). (e, f) Fast Fourier Transform electron diffraction patterns for the 2.1 nm Pt/KB (e) and the 2.1 nm Pt/CMC (f).

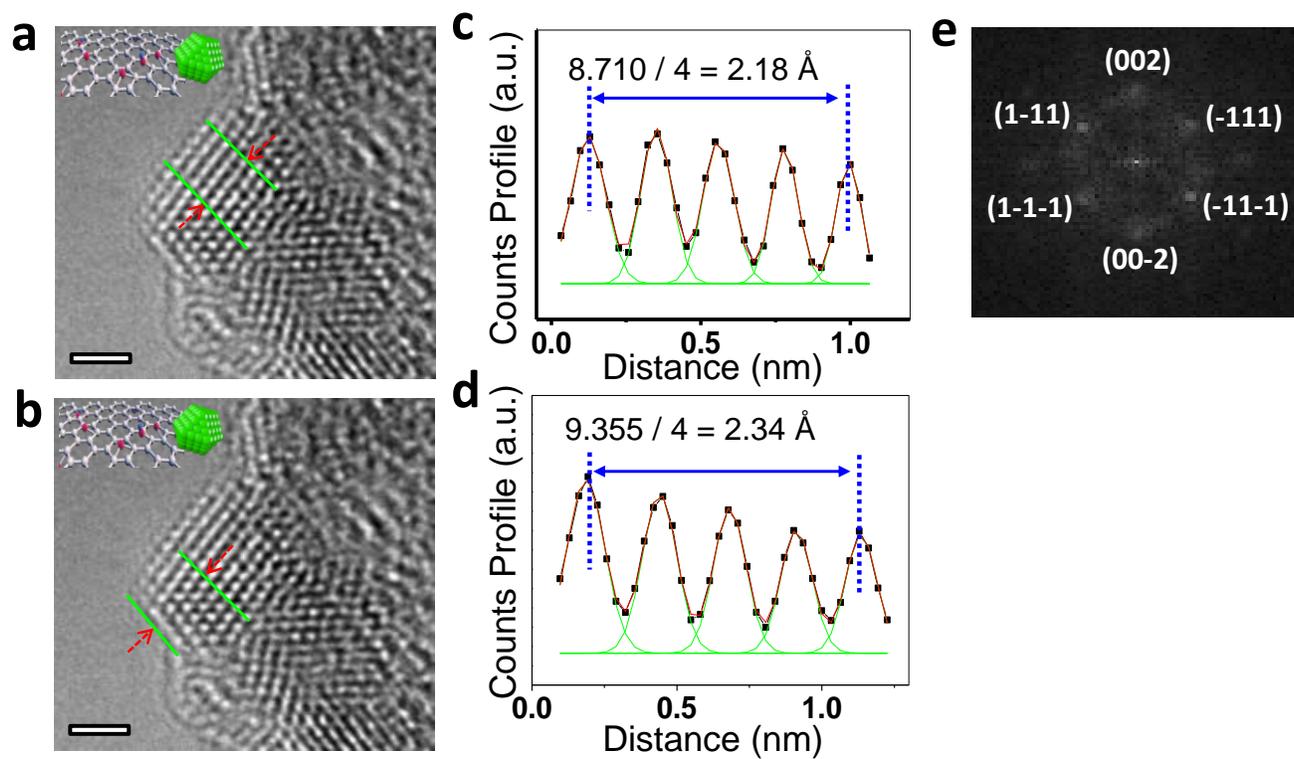


Fig. S3. (a, b) Atomically resolved ATEM images for the CMC-particle-3; (c, d) Single-particle based analysis of {111} interplanar spacing for supported (c) and unsupported regions (d). (e) Fast Fourier Transform electron diffraction patterns. Insets in (a, b) illustrate the geometry feature for the CMC-particle-3. Scale bars in (a, b) are 1 nm.

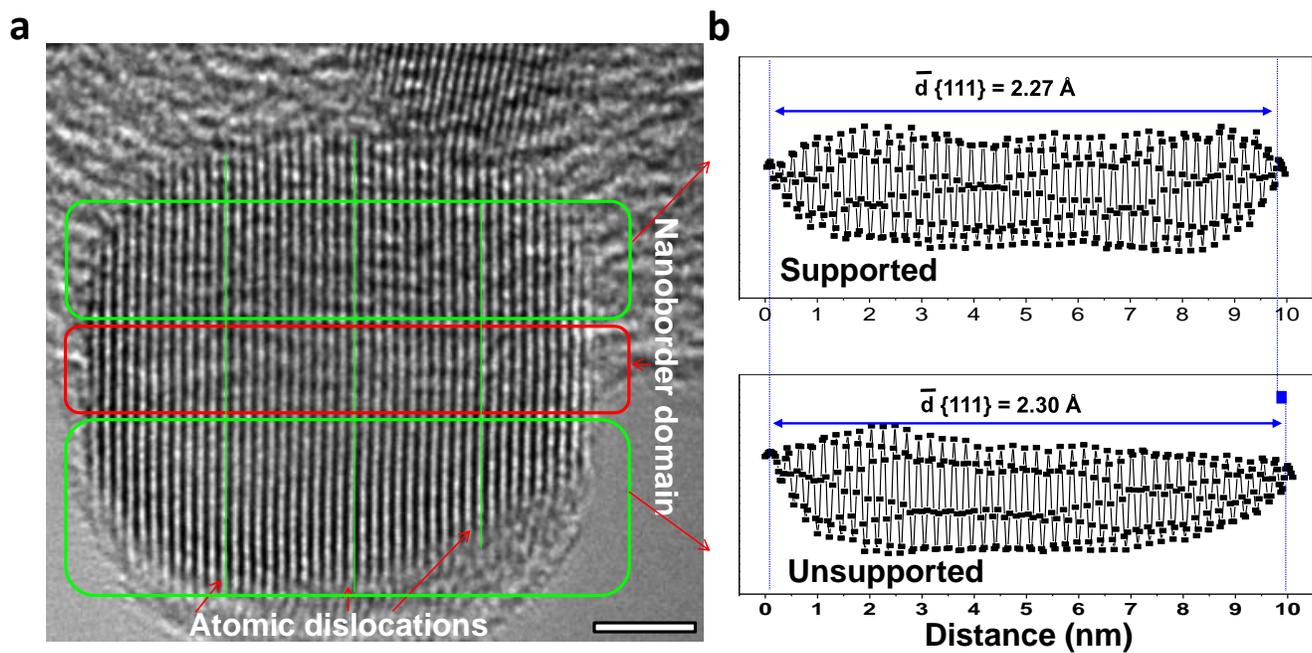


Fig. S4. (a) Atomically resolved ATEM image of a pended Pt/C from the commercial catalyst TEC10E50E-HT. (b) Single-particle based analysis of {111} interplanar spacing for the supported (upper) and the unsupported (lower) domains. The interplanar spacings differ between the unsupported and the supported region, accompanied by atomic dislocations. Scale bar in (a) is 2 nm.

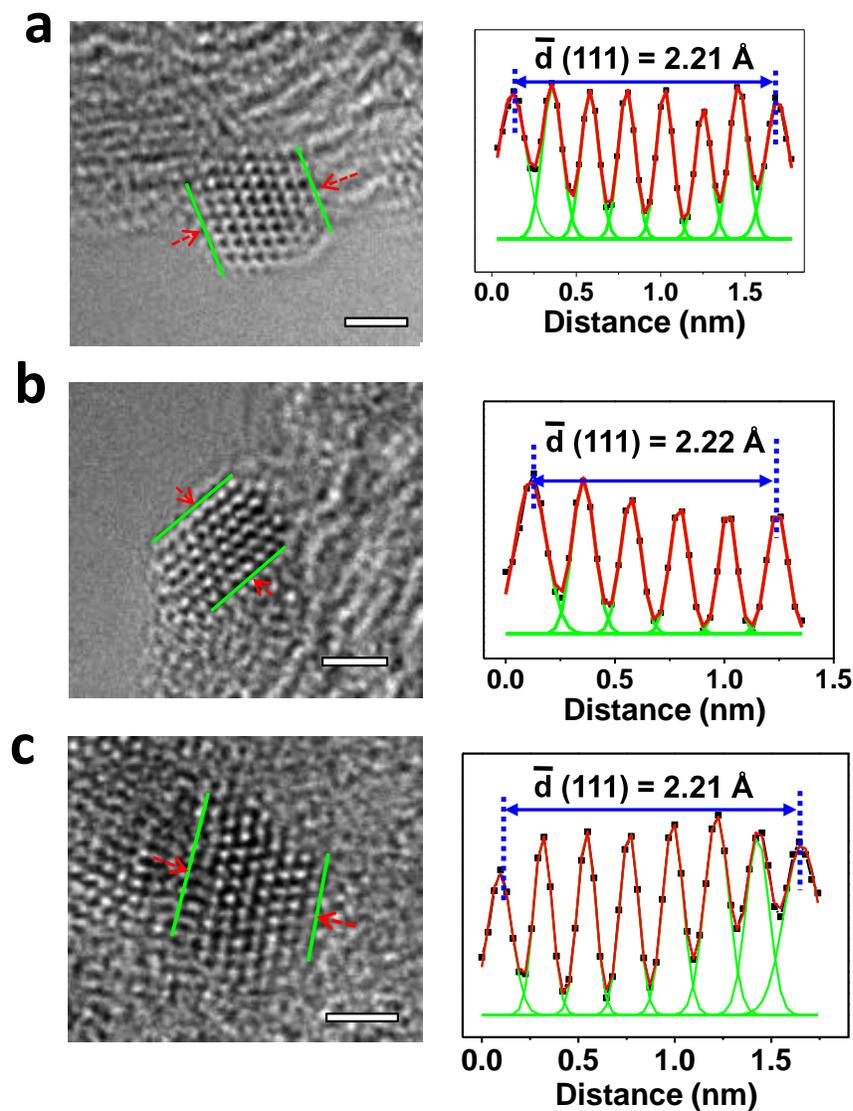


Fig. S5. Supplementary analysis of lattice strains for other Pt nanoparticles in 2.1 nm Pt/CMC catalyst. Scale bars in (a-c) are 1 nm. Notably, only statistically-limited information obtained from the atomic-scale structural analysis is an inherent characteristic of high-resolution TEM technique. Here, to make individual nanoparticles more representative for overall NPs, the main efforts were made in terms of controllable synthesis of shape- and size-uniform Pt nanoparticles. The in-situ XAFS and electrochemical measurements at a statistical level show consistent results with and thus provide supporting evidence for the observed compressive lattice strains in Pt nanoparticles for 2.1 nm Pt/CMC catalyst.

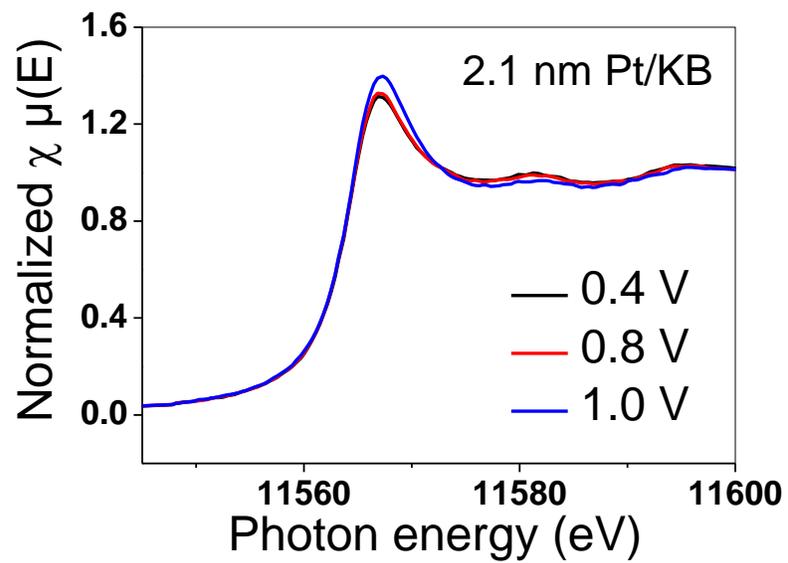


Fig. S6. In situ Pt-L₃ XANES spectra of the 2.1 nm Pt/KB as a function of applied electrode potentials.

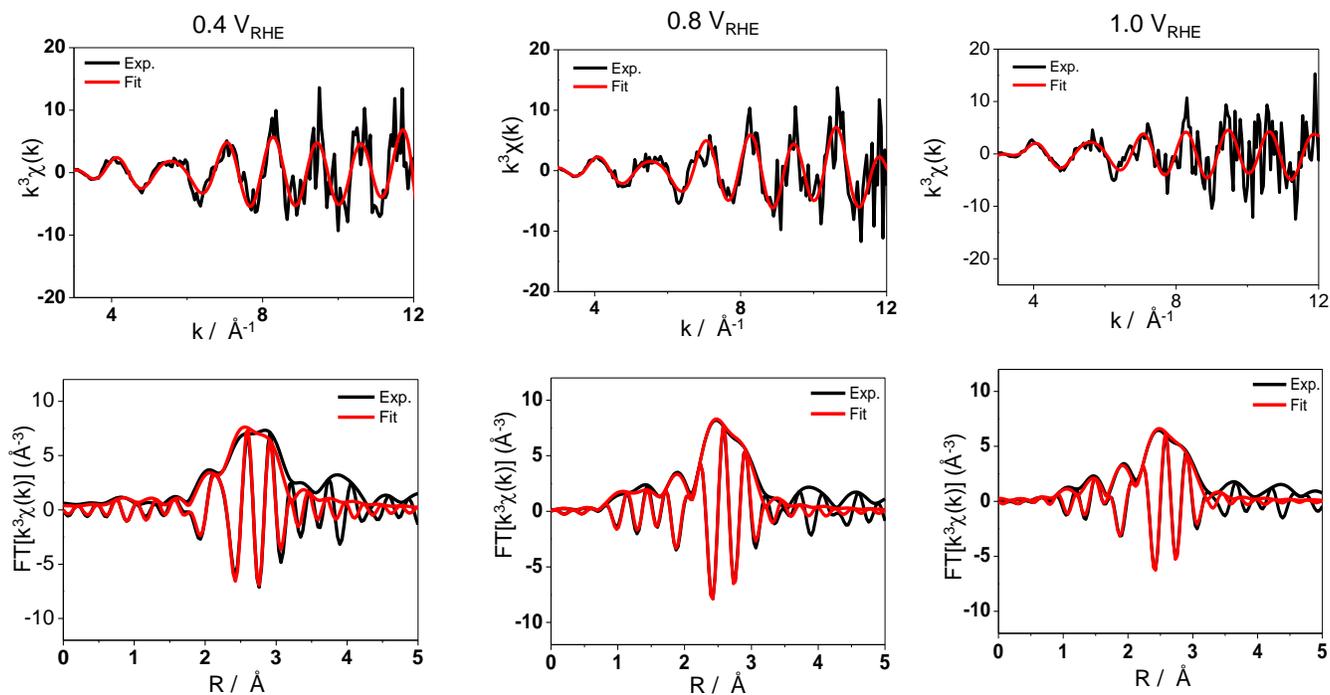


Fig. S7. k^3 -weighted Pt-L₃ edge EXAFS oscillations and associated Fourier transforms for the 2.1 nm Pt/KB at potentials of 0.4 → 0.8 → 1.0 V_{RHE}. Black: experiment curves; red: fitted curve. The curve fittings of k^3 -weighted EXAFS in R-space were carried out with Artemis; Δk : 3 - 12 \AA , ΔR : 1.4 - 3.0 \AA .

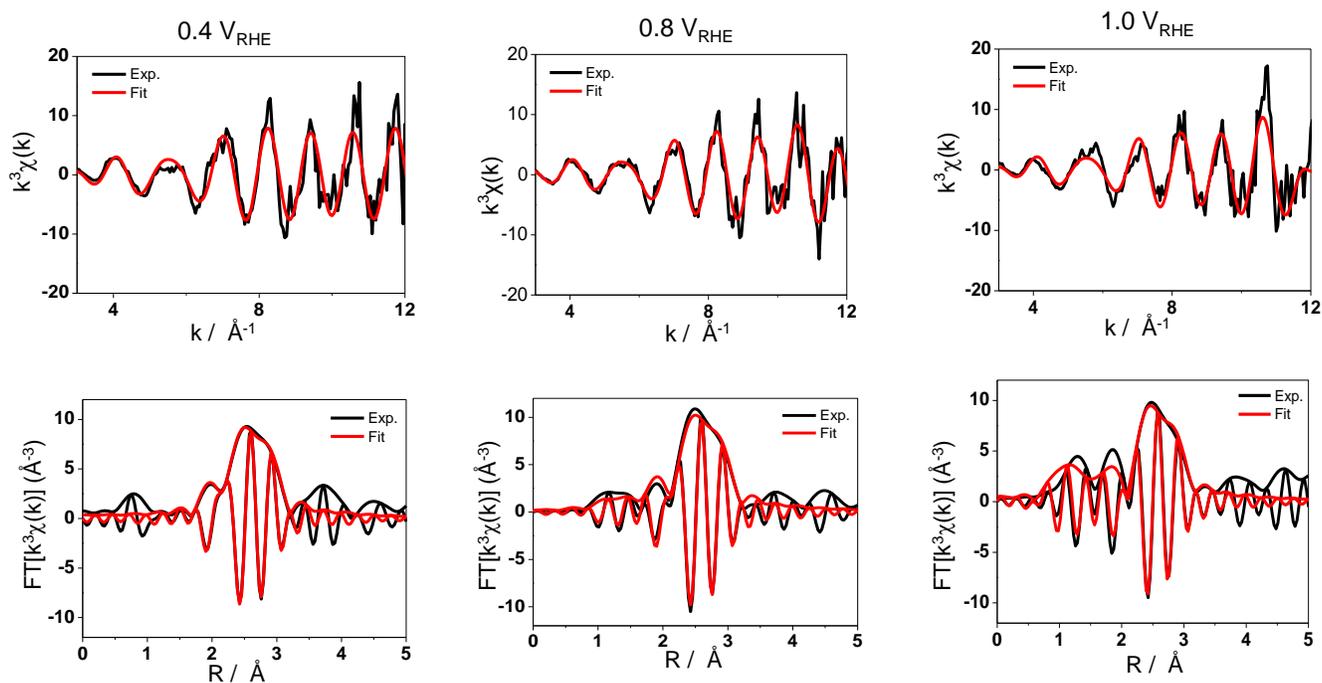


Fig. S8. κ^3 -weighted Pt-L₃ edge EXAFS oscillations and associated Fourier transforms for the 2.1 nm Pt/CMC at potentials of 0.4 → 0.8 → 1.0 V_{RHE}. Black: experiment curves; red: fitted curve. The curve fittings of κ^3 -weighted EXAFS in R-space were carried out with Artemis; Δk : 3 - 12 \AA^{-1} , ΔR : 1.4 - 3.0 \AA .

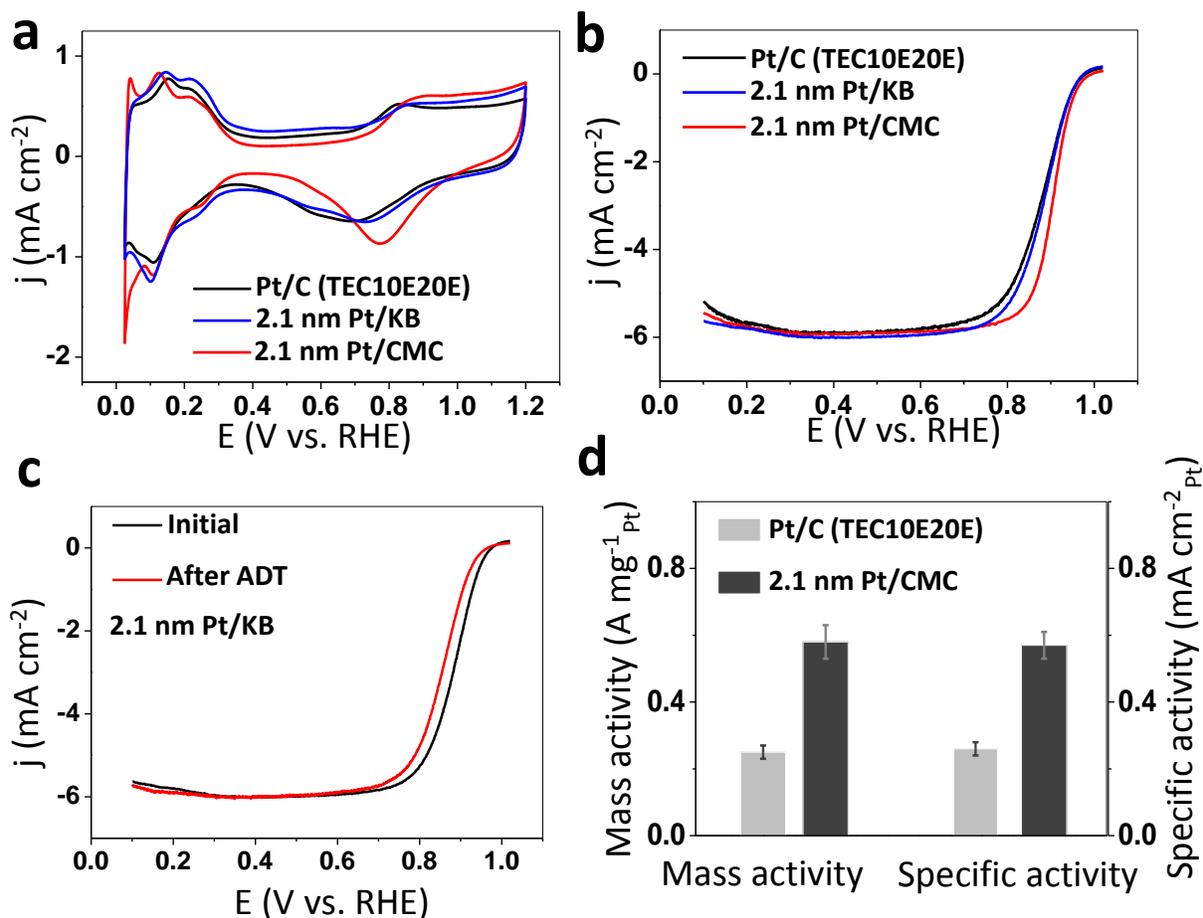


Fig. S9. (a) Cyclic voltammograms of a commercial Pt/C (from Tanaka Kikinzoku Kogyo (TKK) TEC10E20E), the 2.1 nm Pt/KB and the 2.1 nm Pt/CMC measured in N₂-saturated 0.1 M HClO₄ at 50 mVs⁻¹ at R.T.. (b) The ORR performance of catalysts evaluated by the anodic polarization curves in O₂-saturated 0.1 M HClO₄ solution at 1600 rpm with IR correction. (c) The durability of 2.1 nm Pt/KB after 30,000 potential cycles. (d) Comparison of mass activity and specific activity between a commercial Pt/C (TEC10E20E) and the 2.1 nm Pt/CMC.

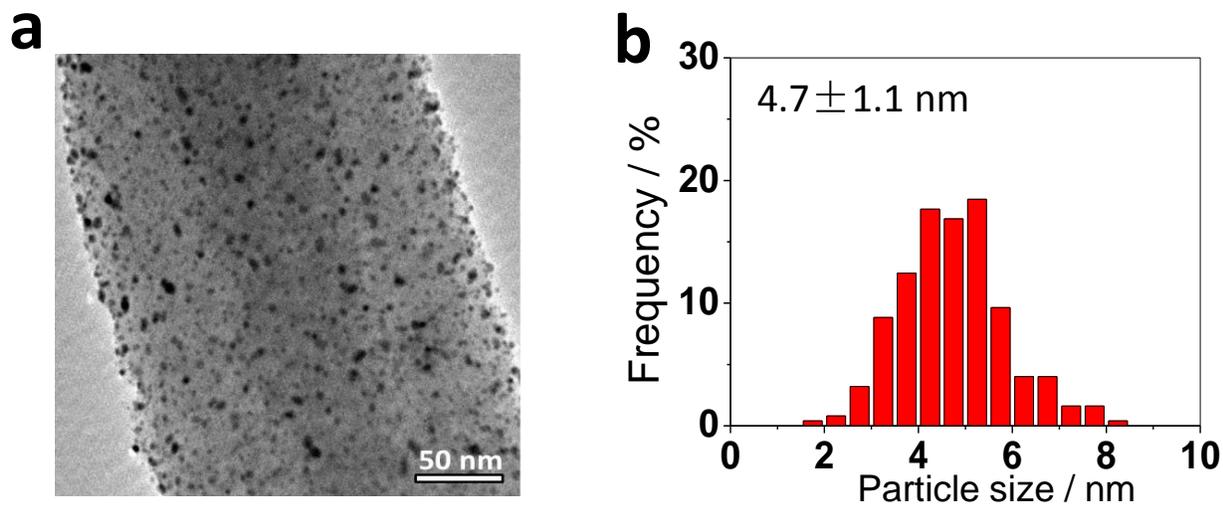


Fig. S10. (a) Bright-field STEM image for 4.7 nm Pt/CMC. (b) Corresponding histograms of particle size distribution.

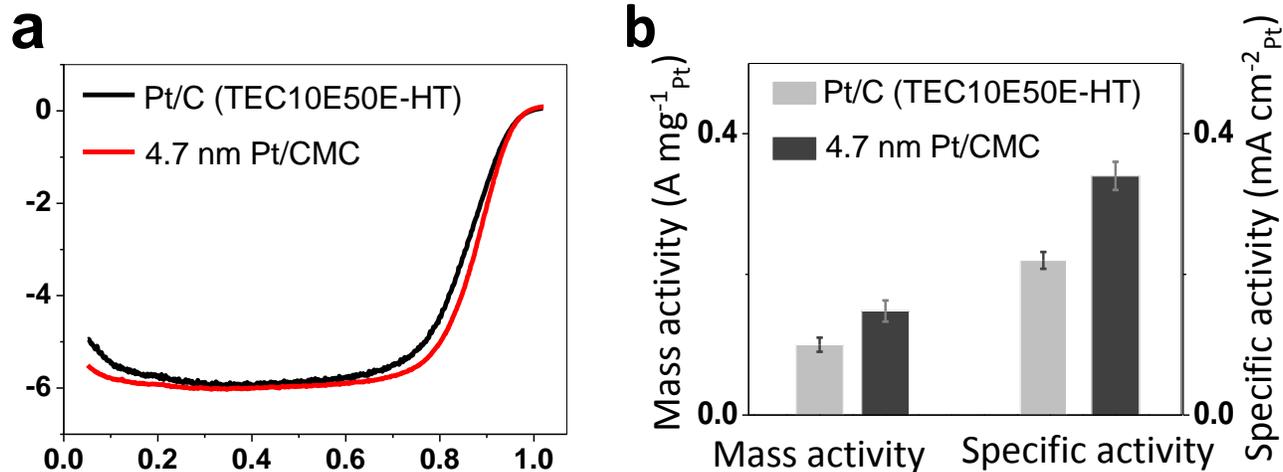


Fig. S11. (a) The ORR performance of a commercial Pt/C (from Tanaka Kikinzoku Kogyo (TKK) TEC10E50E-HT) and the 4.7 nm Pt/CMC evaluated by the anodic polarization curves tested in O₂-saturated 0.1 M HClO₄ solution at 1600 rpm with IR correction. (b) Comparison of mass activity and specific activity between a commercial Pt/C (TEC10E50E-HT) and the 4.7 nm Pt/CMC. The Pt loadings on those two electrodes are 18 μgcm⁻²

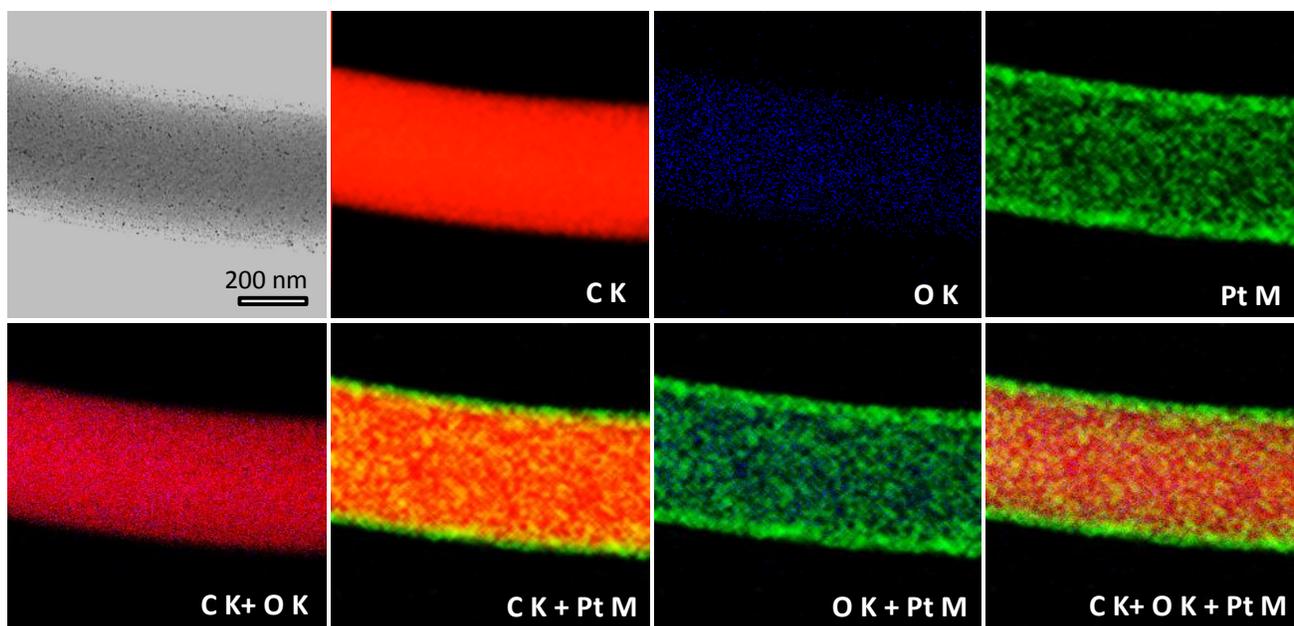


Fig. S12. Bright-field STEM image for the 2.1 nm Pt/CMC and corresponding EDS mappings for C- K, O-K, Pt-M, and associated element overlays. Platinum is highly overlapped with oxygen, suggesting the oxygenated defects on carbon surfaces may promote the interfacial combination of platinum with oxygen-functionalized carbon

Table S1. In situ EXAFS analysis results for 2.1 nm Pt/CMC and 2.1 nm Pt/KB-HT; Δk : 3 - 12 Å, ΔR : 1.4 - 3.0 Å.

Electrode-Potential	Pt-Pt scattering			Pt-O scattering			ΔE_0 / eV	R-factor (%)
	CN	R / Å	$\sigma^2/10^{-3}\text{Å}^2$	CN	R / Å	$\sigma^2/10^{-3}\text{Å}^2$		
2.1 nm Pt/KB-0.4 V	9.7 ± 1.7	2.749±0.012	7.2 ± 1.2				7.3±2.3	0.2
2.1 nm Pt/KB-0.8 V	8.0 ± 0.9	2.739±0.008	6.0± 0.7				5.3±1.6	0.07
2.1 nm Pt/KB-1.0 V	7.4 ± 2.9	2.741±0.030	6.8 ± 2.5	0.8± 1.6	2.02±0.09	6.4 ± 1.9	6.2±6.2	0.3
2.1 nm Pt/CMC-0.4 V	10.1 ± 0.8	2.741±0.004	6.4 ± 0.5				5.3±0.7	0.02
2.1 nm Pt/CMC-0.8 V	9.2 ± 2.6	2.746±0.018	5.7± 1.7				4.8±3.6	0.4
2.1 nm Pt/CMC-1.0 V	7.8 ± 4.1	2.733±0.048	3.8± 4.7	0.8± 1.0	2.04±0.15	2.0 [#]	3.4±8.4	1.9

* S_0^2 for Pt is set as 0.913 obtained by fitting Pt foil
[#] σ^2 were fixed to obtain each reasonable fitting after the first fitting with free parameters

Author contributions

X. Z., W. X., and ZW. C proposed and discussed the possible interfacial geometric interactions at metal-support interfaces. X. Z. synthesized electrocatalysts. X. Z., W. X., and ZW. C co-wrote the manuscript. X. Z., JB. Z, ML. X. JJ.G. and CP. L.conducted electrochemical experiments and discussed data. X. Z., T. K., Y. Y., T. S., K. H., and T. U. conducted in-situ RDE-XAFS tests. X. Z.and T. G. conducted high-resolution TEM, STEM and EDX measurement. Y. Y. and X. Z. conducted SEM measurements. S. T. measured partial STEM images. F.T. provided constructive suggestions. All authors read and commented the manuscript.