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Supporting Information

Changes in the Oxidation State of Pt Single-Atom Catalysts Upon Removal of Chloride Ligands and Their Effect for Electrochemical Reactions

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Experimental Section

Catalyst Syntheses

TiC (NanoAmor, 99%) were acid-treated to remove oxides on the surface. The TiC powder 500 mg was added to 20 mL of hydrochloric acid (Samchun, 35.0-37.0%) and the mixture was sonicated for 15 min, then heated for 1 h at 45 ˚C. The acid-treated TiC powder was separated by centrifugation and washed several time with deionized water (18.3 cm, Human power II$^+$ scholar). Then, the TiC powder was dried in a vacuum oven at 50 ˚C for 4 h and uniformly ground. Pt was deposited on the acid-treated TiC at 0.2 wt% and 0.5 wt% by incipient wetness impregnation (IWI) method or at 5 wt% by wetness impregnation (WI) method. $H_2PtCl_6 \cdot 6H_2O$ (Sigma−Aldrich) 0.267 mg and 0.667 mg were dissolved in 20 μL of anhydrous ethanol (Sigma-Aldrich) for 0.2 wt% and 0.5 wt% Pt/TiC, respectively. The Pt precursor solution and 50 mg of acid-treated TiC powder were mixed well and dried in a vacuum oven at 50 ˚C for 4 h. Then, the resulting powder was put on an alumina boat and reduced at 100, 300, 500, and 700 ˚C for 1 h under 10 vol% H_2 flow with balance N_2. $H_2PtCl_6 \cdot 6H_2O$ (Sigma−Aldrich) 13.34 mg was dissolved in 1 mL of anhydrous ethanol (Sigma-Aldrich) for 5 wt% Pt/TiC. The acid-treated TiC 100 mg was added to 5 mL of anhydrous ethanol (Sigma-Aldrich) and sonicated for 15 min. The Pt precursor solution 1 mL was added to the TiC nanoparticles in ethanol and the mixture was stirred for 9 h at 60 ˚C. After all the ethanol was dried, the remaining powder was collected and dried further for 4 h at 50 ˚C in a vacuum oven. Then, the powder was put on an alumina boat and reduced at 100 ˚C for 1 h under a 10 vol% H_2 flow with balance N_2. The powders were stored in a vacuum desiccator.

Electrochemical Reactions

Electrochemical oxygen reduction reaction (ORR), methanol oxidation reaction (MOR), formic acid oxidation reaction (FAOR) were performed. A three-electrode electrochemical cell composing of a rotating ring disk electrode (glassy-carbon disk, platinum ring, PINE), a 3 M NaCl Ag/AgCl (RE-5B, BASi) reference electrode, and a Pt wire counter electrode, was used for all the electrochemical measurements. The potential was measured with a bipotentiostat (CHI 760E, CH Instruments, Inc). The reversible hydrogen electrode (RHE) was measured prior to each measurement by performing cyclic voltammetry in H_2-purged 0.1 M $HClO_4$ (Sigma-Aldrich) solution with a rotating Pt electrode as a working electrode. The reaction temperature maintained at 25 ˚C using a water bath. The catalyst 5 mg and carbon black (XC72R, Vulcan) 2.5 mg were mixed with 17 μL of nafion solution (5 wt %, Sigma-Aldrich) in 5 mL of anhydrous ethanol (Sigma-Aldrich), and sonicated for 10 min. The catalyst solution

15 μL was deposited on the polished glassy-carbon disk. The ORR was performed by anodic linear scan voltammetry (LSV) in an O_2-saturated 0.1 M $HClO_4$ solution with a scan rate of 0.01 V s^{-1} and a rotating rate of 1600 rpm. The potential of the Pt ring electrode was held at 1.2 V during the ORR to measure the H_2O_2 oxidation current. The iR compensation was performed using the CHI software. H_2O_2 selectivity was calculated by the Equation (1), where i_R is the ring current, i_D is the disk current, and N is the collection efficiency (0.3826 for the specific rotating ring disk electrode that we have used).

$$H_2O_2\ selectivity\ (\%) = \frac{2_{iR}/N}{(i_R/N + i_D)} \times 100 \qquad (1)$$

The MOR or FAOR was performed by cyclic voltammetry (CV) in an Ar-saturated 0.5 M methanol or formic acid in 0.1 M $HClO_4$ solution with a scan rate of 0.05 V s^{-1} and a rotating rate of 1600 rpm.

Characterizations

Transmission electron microscopy (TEM) images were collected using F30 S-Twin (Tencai) instruments. High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images were collected using a Titan cubed G2 60-300 with an accelerating voltage of 300 kV. X-ray photoelectron spectroscopy (XPS) were conducted using a K-alpha (Thermo Scientific) instrument. Al K-alpha 1488.6 eV beam was used. The atomic concentration was calculated using Thermo Abantange v5.964 software. High resolution X-ray photoelectron spectroscopy (HR-XPS) was conducted using 10A2 HR-PES beamline of the Pohang Light Source (PLS). 650 eV beam was used and the beam was calibrated so that the peak position of $4f_{7/2}$ of Au metal was 84.0 eV. X-ray absorption spectroscopy (XAS) was conducted using 8C Nano XAFS beamline of the Pohang Light Source (PLS). A fluorescence spectra of Pt L3 edge was obtained and a reference Pt foil was concurrently measured to calibrate each sample. The XAS data were processed and fitted with ATHENA and ARTEMIS software programs. The coordination number was estimated based on the fitted S_0^2 value of the reference Pt foil. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) was conducted using Nicolet iS50 FTIR spectrometer (Thermo scientific) equipped with a Collector II diffuse reflectance accessory (DRIFT cell). The catalyst 3 mg and KBr powder 97 mg were grinded well and put into a sample cup in a DRIFT cell. Before measuring the CO adsorption spectrum, the sample was heated at 100 ˚C for 1 h under Ar flow. All spectra were measured in room temperature. CO gas was flowed for 10 min, the DRIFT cell was purged by flowing Ar with vacuum pumping for 5 min, then the spectra was collected.

Additional Data

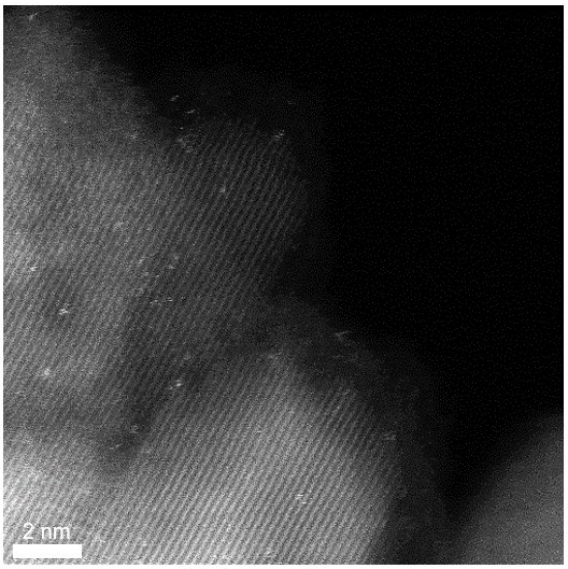

Figure S1. HAADF-STEM images of 0.2 wt% Pt/TiC catalyst reduced at 100 ˚C.

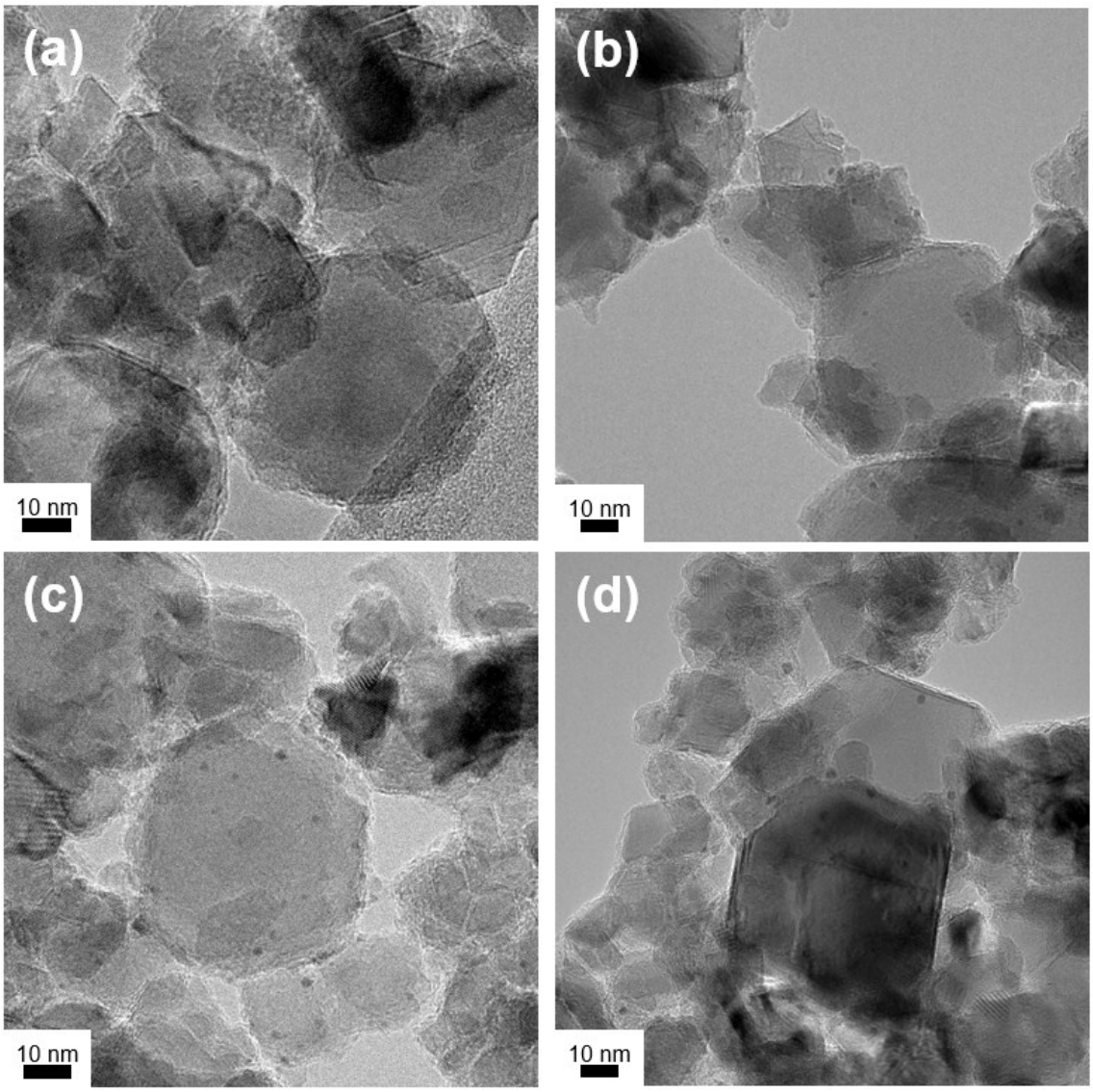

Figure S2. TEM images of 0.2 wt% Pt/TiC catalysts reduced at a) 100 ˚C, b) 300 ˚C, c) 500 ˚C and d) 700 ˚C.

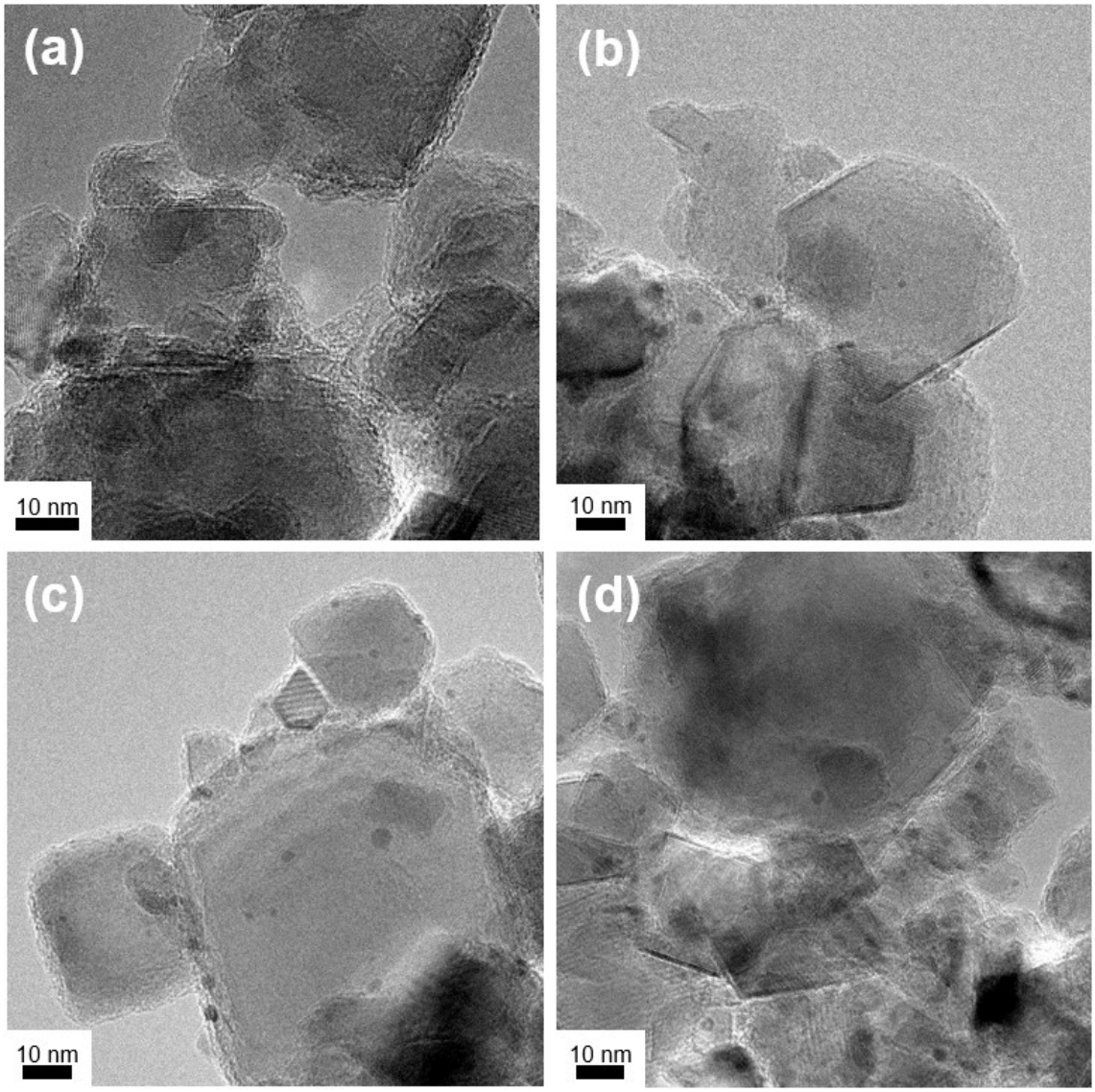

Figure S3. TEM images of 0.5 wt% Pt/TiC catalysts reduced at a) 100 ˚C, b) 300 ˚C, c) 500 ˚C and d) 700 ˚C.

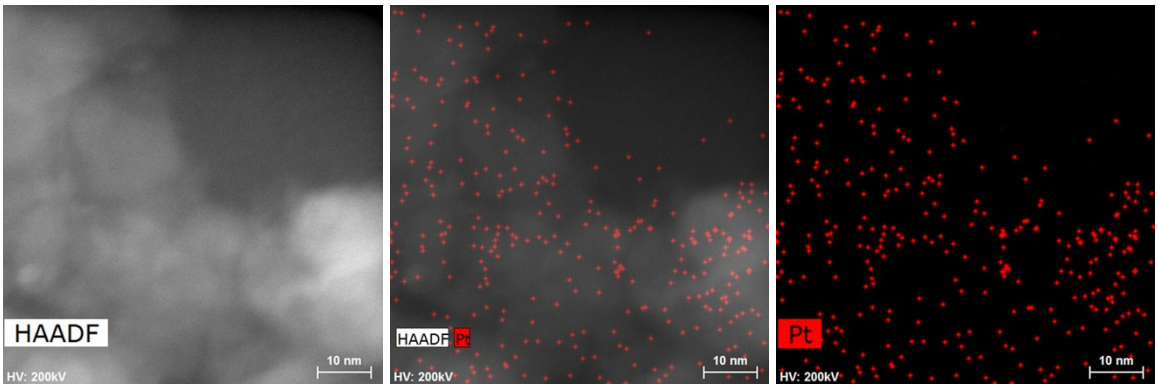

Figure S4. HAADF-STEM image and the corresponding STEM-EDX elemental mapping images of 0.2 wt% Pt/TiC reduced at 100 ˚C. These HAADF-STEM images and elemental mapping data were collected using a Talos F200X (FEI) with an accelerating voltage of 200 kV.

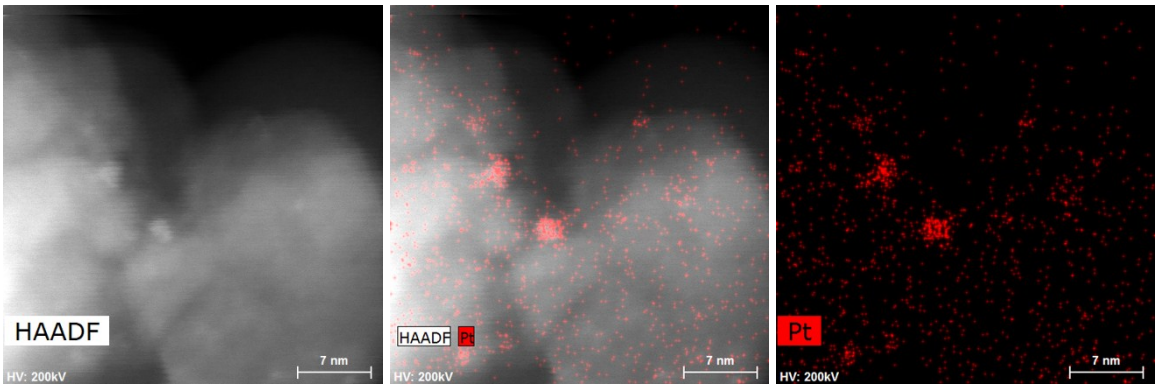

Figure S5. HAADF-STEM image and the corresponding STEM-EDX elemental mapping images of 0.2 wt% Pt/TiC reduced at 300 ˚C. These HAADF-STEM images and elemental mapping data were collected using a Talos F200X (FEI) with an accelerating voltage of 200 kV.

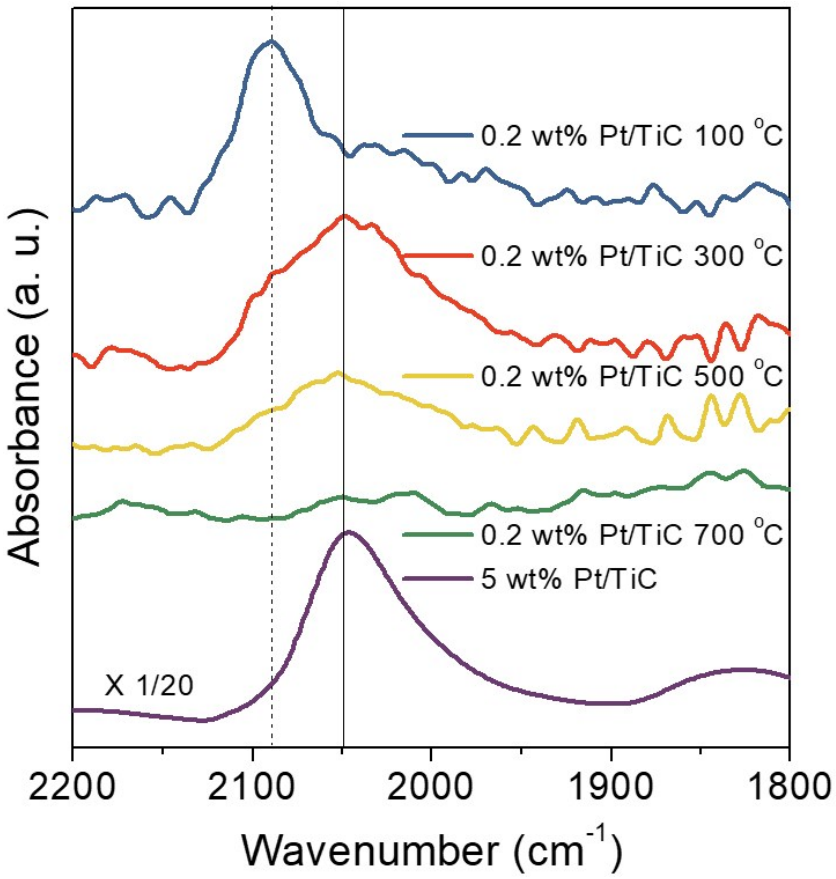

Figure S6. Diffuse reflectance infrared Fourier transform (DRIFT) spectra of CO adsorbed on 0.2 wt% Pt/TiC catalysts reduced at various temperatures and 5 wt% Pt/TiC catalyst. The dashed line indicates a CO peak attached to the single atomic Pt, and the solid line indicates a CO peak attached to the Pt nanoparticles.

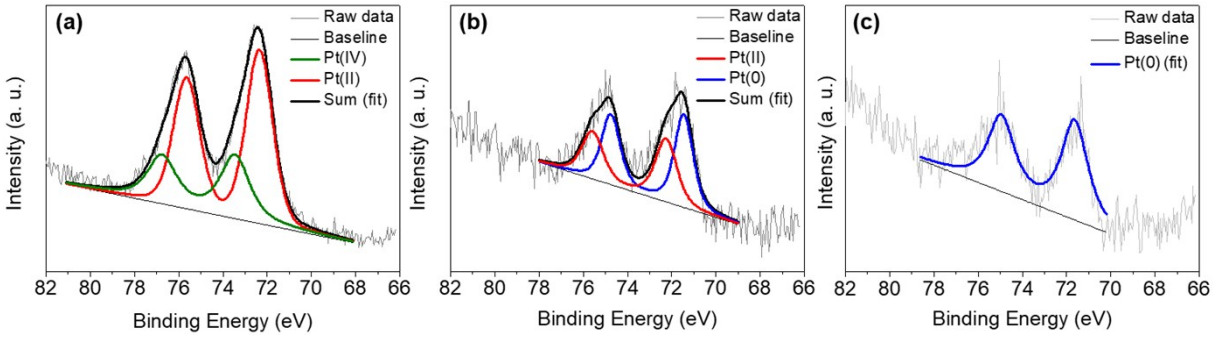

Figure S7. Peak fitting of high resolution XPS spectra (Pt 4f region) of 0.2 wt% Pt/TiC catalysts reduced at a) 100 ˚C, b) 300 ˚C and c) 700 ˚C. The green line indicates Pt(IV), the red line Pt(II) and the blue line Pt (0).

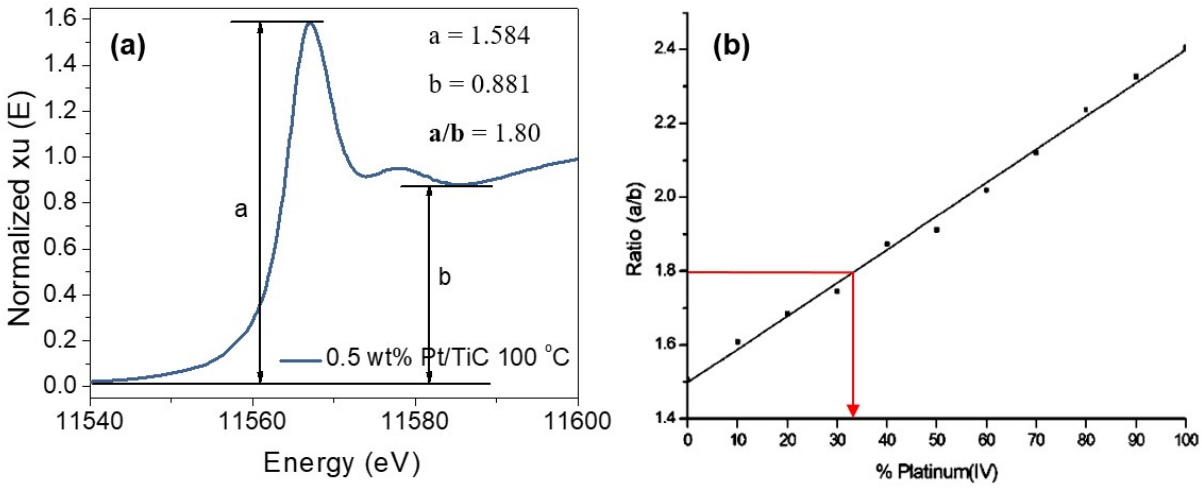

Figure S8. a) White line height ratio (a/b) of XANES spectra at Pt L3 edge of 0.5 wt% Pt/TiC catalyst reduced at 100 ˚C. b) The ratio of Pt(IV) to Pt(II) estimated from the white line height ratio. The white line height ratio of 1.80 corresponds to Pt(IV) ratio of ~33% (Pt(IV) : Pt(II) = 1 : 2) from the calibration curve made by Hambley et al.; Adopted with permission.[S1]

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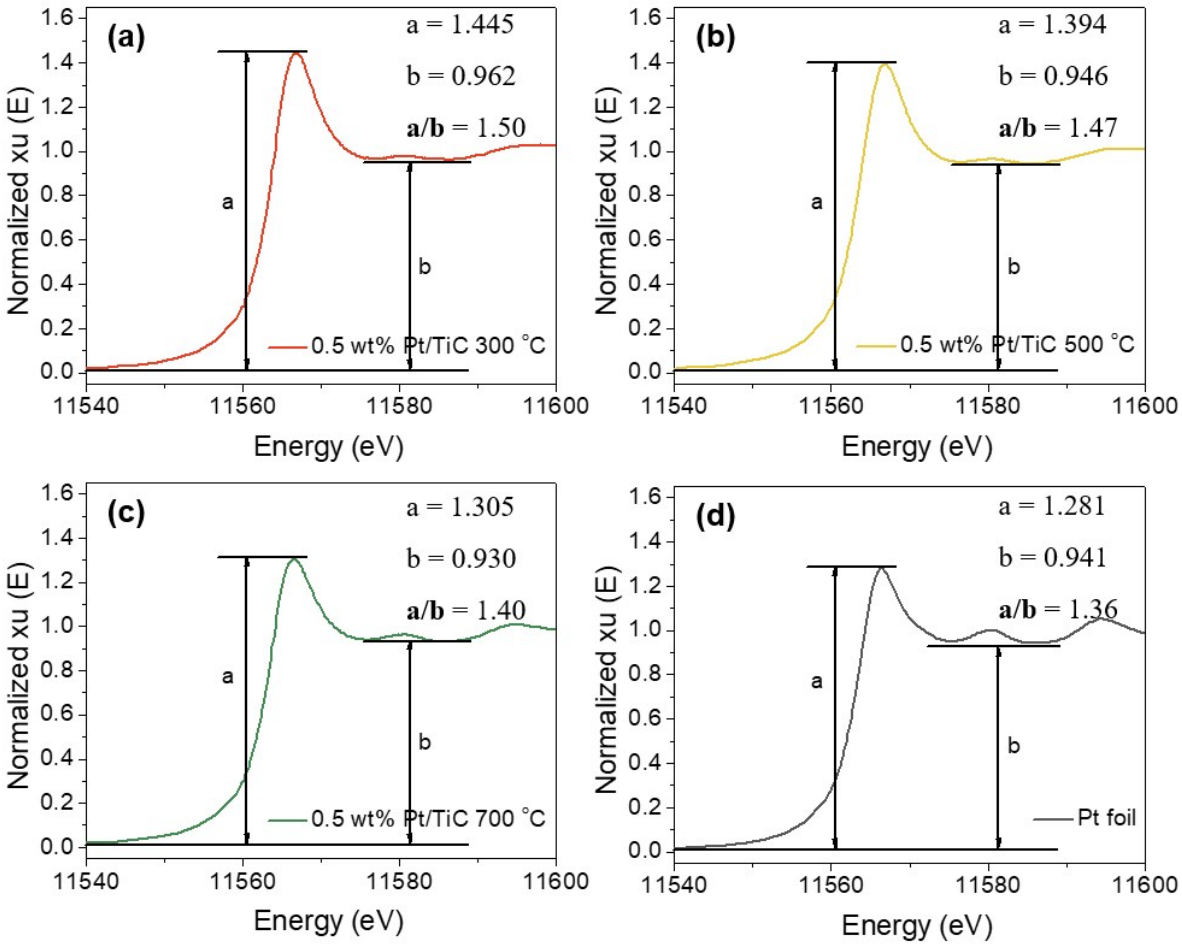

Figure S9. White line height ratio (a/b) of XANES spectra at Pt L3 edge of 0.5 wt% Pt/TiC catalysts reduced at a) 300 ˚C, b) 500 ˚C, c) 700 ˚C, and d) Pt foil.

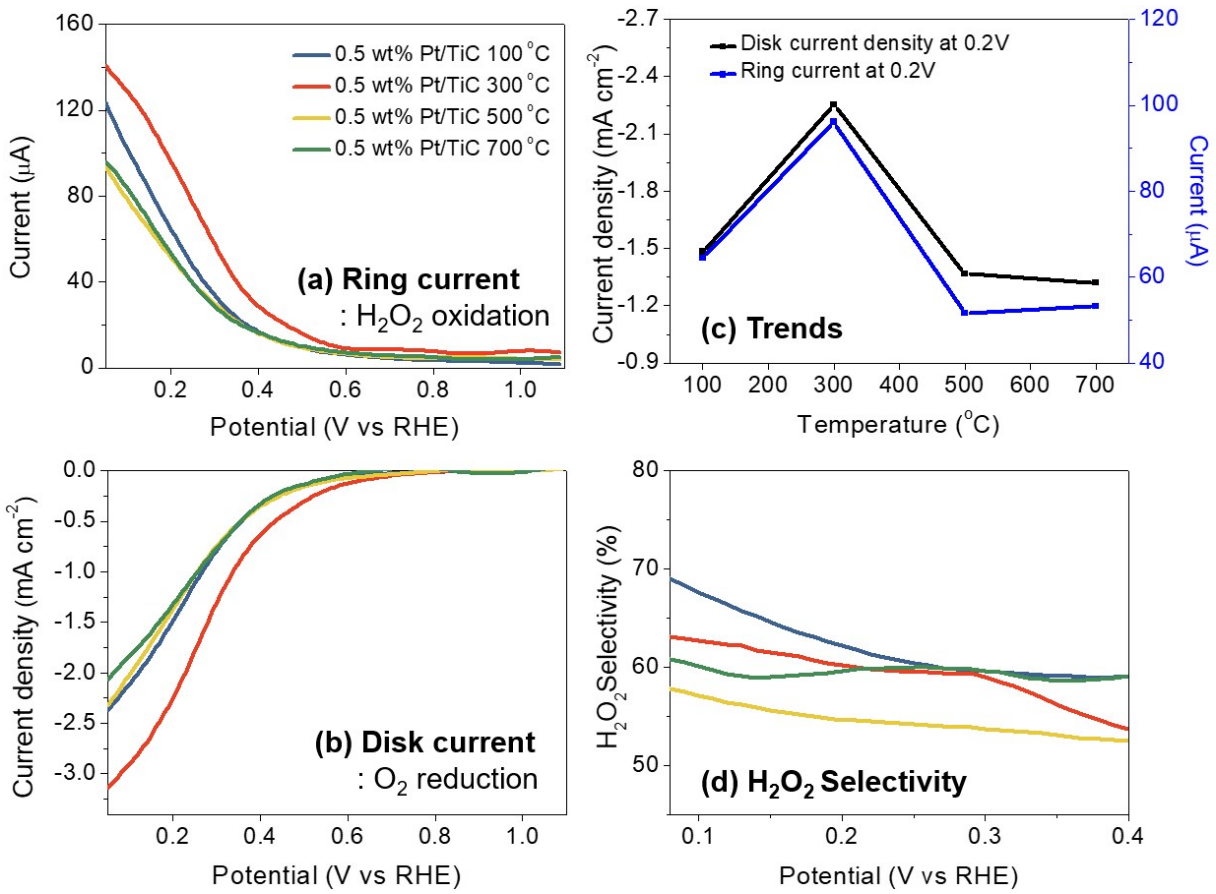

Figure S10. Oxygen reduction reaction polarization curves of 0.5 wt% Pt/TiC reduced at 100 ˚C (blue), 300 ˚C (red), 500 ˚C (yellow), and 700 ˚C (green). a) Ring currents measured concurrently during the ORR with a ring potential held at 1.2 V (vs RHE). b) Disk currents measured in O_2-saturated 0.1 M $HClO_4$ solution with a scan rate of 0.01 V s^{-1}. c) Trends of disk current density and ring current at 0.2 V (vs RHE) for various reduction temperatures. d) H_2O_2 selectivity calculated from the disk and ring currents.

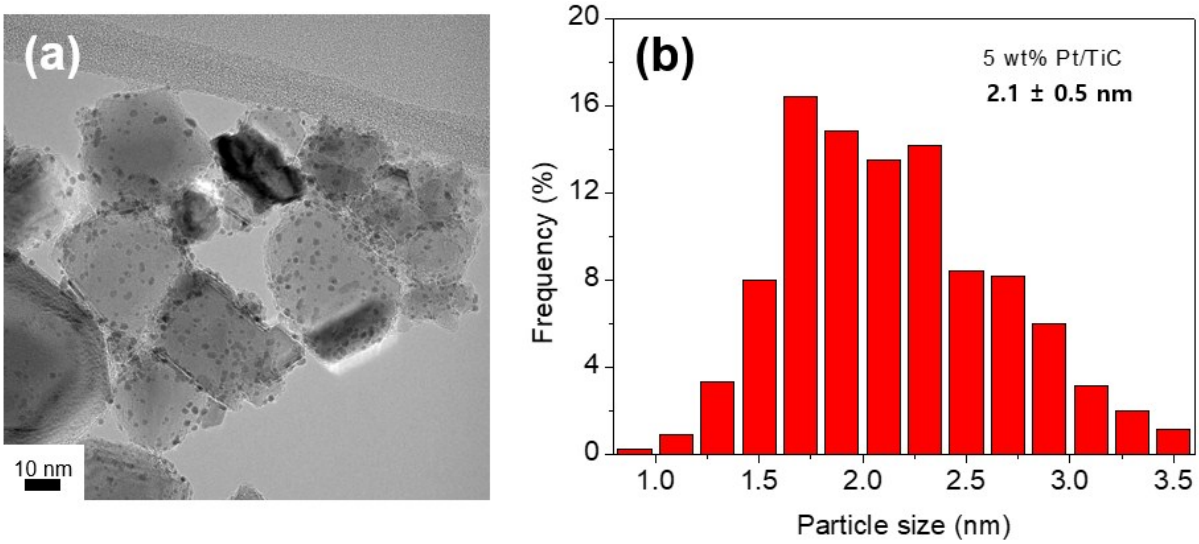

Figure S11. a) TEM image and b) nanoparticle size distribution of 5 wt% Pt/TiC catalyst.

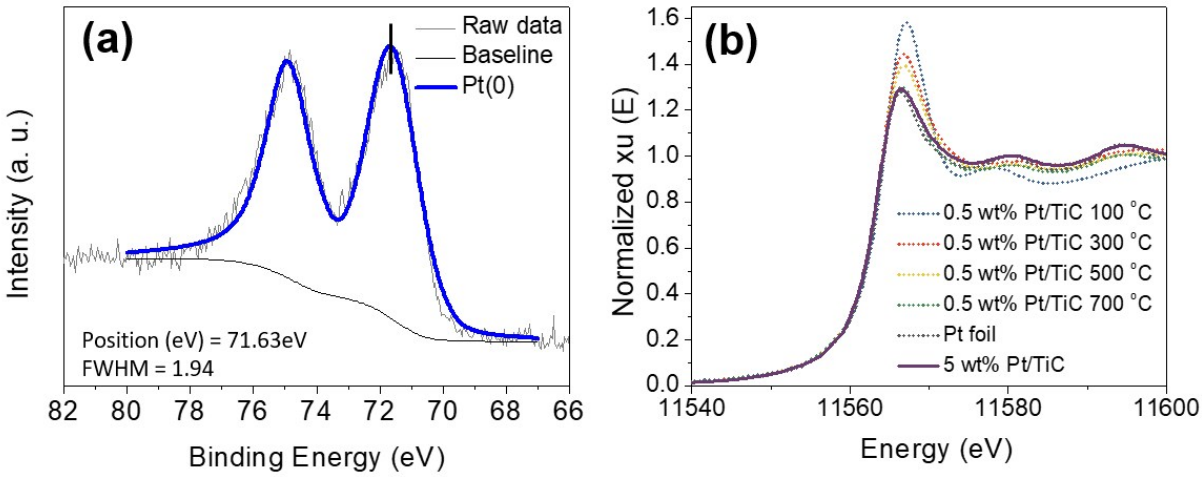

Figure S12. a) Peak fitting of XPS spectrum (Pt 4f region) of 5 wt% Pt/TiC catalyst. b) Normalized XANES spectra at Pt L3 edge of 0.5 wt% Pt/TiC catalysts reduced at various temperatures, Pt foil, and 5 wt% Pt/TiC.

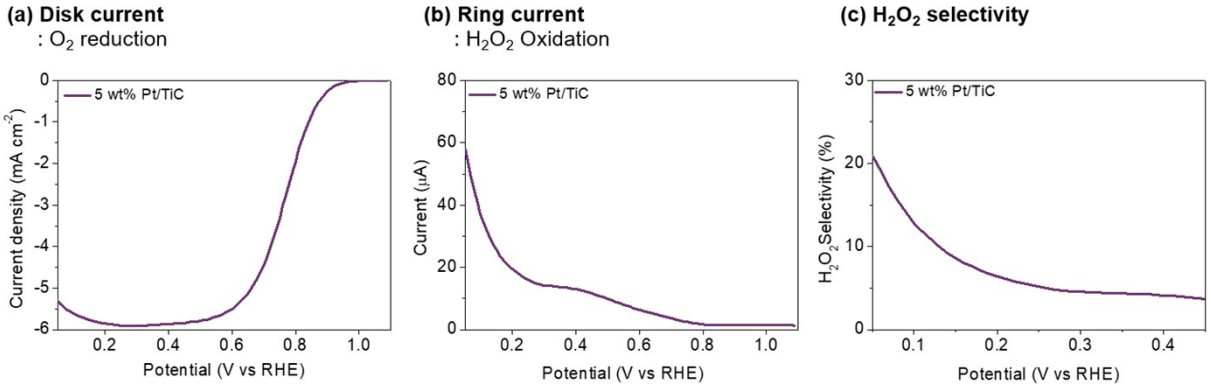

Figure S13. Oxygen reduction reaction polarization curves of 5 wt% Pt/TiC. a) Disk currents measured in O_2-saturated 0.1 M $HClO_4$ solution with a scan rate of 0.01 V s^{-1}. b) Ring currents measured concurrently during the ORR with a potential held at 1.2 V (vs RHE). c) H_2O_2 selectivity calculated from disk and ring currents.

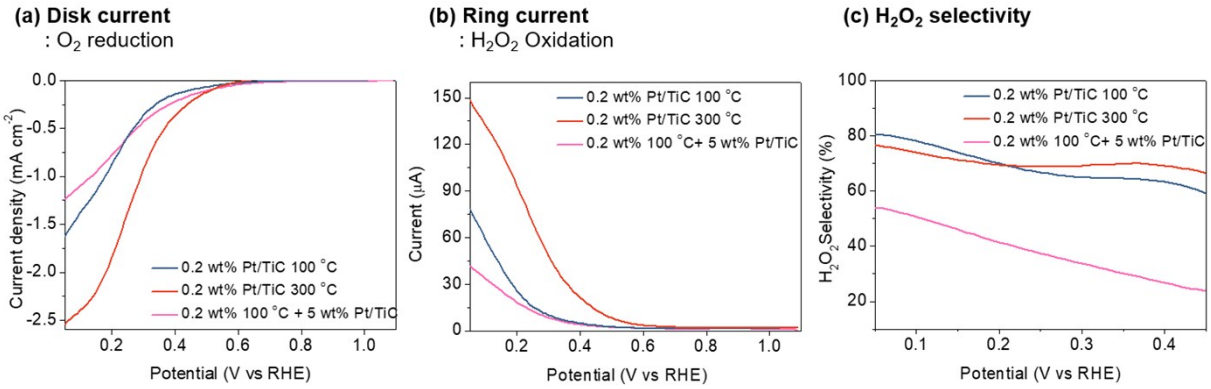

Figure S14. Oxygen reduction reaction polarization curves of 0.2 wt% Pt/TiC reduced at 100 ˚C (blue), 0.2 wt% Pt/TiC reduced at 300 ˚C (red), and a physical mixture of 5 wt% Pt/TiC with 0.2 wt% Pt/TiC reduced at 100 ˚C (pink) with the same Pt loading. a) Disk currents measured in O_2-saturated 0.1 M $HClO_4$ solution with a scan rate of 0.01 V s^{-1}. b) Ring currents measured concurrently during ORR with a potential held at 1.2 V (vs RHE). c) H_2O_2 selectivity calculated from disk and ring currents.

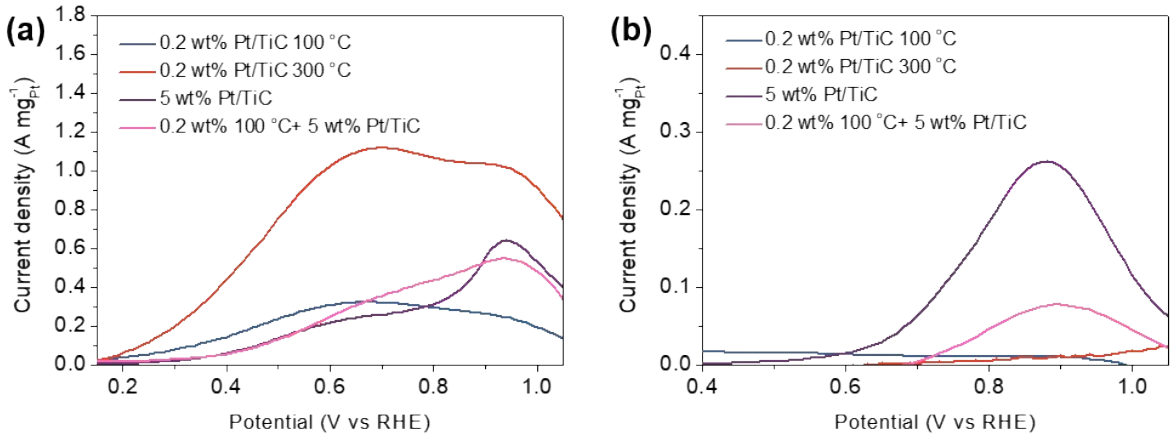

Figure S15. Forward scans of cyclic voltammetry of 0.2 wt% Pt/TiC reduced at 100 °C (blue), 300 °C (red), 5wt% Pt/TiC (purple) and physical mixture of 5 wt% Pt/TiC and 0.2 wt% Pt/TiC 100 °C (pink). (a) Formic acid oxidation reaction performed in Ar-saturated 0.5 M HCOOH + 0.1 M $HClO_4$ solution. (b) Methanol oxidation reaction performed in Ar-saturated 0.5 M CH_3OH + 0.1 M $HClO_4$ solution.

Table S1. Surface elemental composition (% atomic concentration) of 0.2 wt% Pt/TiC catalysts reduced at various temperatures determined by high resolution XPS analyses (using synchrotron X-ray source).

0.2 wt% Pt/TiC	Reduced Temperature		
Elements	100 ˚C	300 ˚C	700 ˚C
C	81.54	87.73	78.83
Ti	9.39	4.84	12.49
O	5.34	6.45	8.57
Pt	0.39	0.17	0.08
Cl	3.35	0.82	0.03
Cl/Pt ratio	8.6	4.8	0.4
Pt/Ti ratio	0.042	0.035	0.006

Table S2. Surface elemental composition (% atomic concentration) of 0.5 wt% Pt/TiC catalysts reduced at various temperatures determined by XPS analyses.

0.5 wt% Pt/TiC	Reduced Temperature			
Elements	100 ˚C	300 ˚C	500 ˚C	700 ˚C
C	78.57	77.61	76.16	68.91
Ti	9.21	9.89	11.49	13.82
O	11.12	11.93	11.86	17.11
Pt	0.15	0.11	0.11	0.08
Cl	0.95	0.46	0.37	0.07
Cl/Pt ratio	6.3	4.2	3.4	0.9
Pt/Ti ratio	0.016	0.011	0.010	0.006

Table S3. Best-fit values for the EXAFS data of 0.5 wt% Pt/TiC catalysts reduced at 100 ˚C, 300 ˚C, 500 ˚C, and 700 ˚C.

0.5 wt% Pt/TiC	Path	Coordination number	Debye-Waller Factor [$\sigma^2/Å^2$]	R [Å]	R-factor [%]
100 ˚C	Pt-Cl	3.001	0.002	2.288	0.039
	Pt-Pt	0.518	0.003	2.779	
	Pt-Ti	0.737	0.003	2.848	
300 ˚C	Pt-Cl	1.596	0.001	2.316	0.097
	Pt-Pt	1.540	0.004	2.738	
	Pt-Ti	1.503	0.002	2.634	
500 ˚C	Pt-Cl	0.784	0.003	2.287	0.022
	Pt-Pt	2.436	0.007	2.737	
	Pt-Ti	1.774	0.006	2.694	
700 ˚C	Pt-Cl	0.047	-0.001	2.338	0.012
	Pt-Pt	5.139	0.005	2.734	
	Pt-Ti	0.373	0.002	2.635	
Pt foil	Pt-Pt	12	0.005	2.765	0.003
	Pt-Pt	6	0.006	3.910	

References

[S1] M. D. Hall, G. J. Foran, M. Zhang, P. J. Beale and T. W. Hambley, *J. Am. Chem. Soc.*, 2003, **125**, 7524-7525.