

Supplementary Information

Fine-tuning of ultrathin carbon shell coated on metal nanoparticles: carbon etching and defect healing effects

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1. Experimental Section

1.1. Chemicals and materials

Carbon blacks (Vulcan XC72, Cabot) were purchased from Cabot Inc. (Alpharetta, GA, USA). 1-Octadecene (90%), platinum acetylacetonate ($\text{Pt}(\text{acac})_2$, 97%), oleylamine (70%), Nafion ionomer (5 wt%), and 2-propanol (99.5%) were procured from Sigma-Aldrich Inc. (St. Louis, MO, USA). n-Hexane (95 %) and ethanol (95 %) were acquired from Samchun Pure Chemicals (Daejeon, Korea). A rotating disk electrode (RDE) with glassy carbon (0.196 cm^2) was purchased from Metrohm-Autolab (Netherlands).

1.2. Catalyst preparation

In a vial, 0.0509 g of $\text{Pt}(\text{acac})_2$, 5 mL of oleylamine, and 13 mL of 1-octadecene were mixed *via* ultrasonication for 20 min. Using a three-necked flask, 0.1 g of carbon black and 5 mL of oleylamine were also dispersed in 147 mL of 1-octadecene through ultrasonication for 20 min. After the metal precursor solution in the vial was transferred to a three-necked flask, it was sonicated for 5 min. The solution temperature was then raised to 300 °C in a flask and maintained for 2 h for pyrolysis of the metal precursors. After the solvothermal reaction was complete, the solution was cooled to 80 °C and filtered using n-hexane and ethanol for washing. The as-prepared catalysts were dried in a vacuum oven at 60 °C. Thereafter, a carbon shell layer was formed by annealing at 900 °C for 2 h in Ar or H_2 5%/N₂ balance or CO gas atmosphere. Samples annealed in Ar, H_2 5%/N₂ balance, and CO gas atmospheres were named Pt@C/C Ar, Pt@C/C H₂, and Pt@C/C CO, respectively. Finally, the Pt@C/C H₂ catalyst additionally heat-treated in the CO gas atmosphere was designated as Pt@C/C H₂_re CO.

1.3 Physical characterization

A transmission electron microscope (TEM) (Tecnai G2 F30 S-Twin, FEI) was used to confirm the particle size and distribution of the prepared catalysts, and high-resolution TEM (HR-TEM) (JEOL 2010 FasTEM microscope) analysis was performed to clearly identify the carbon shells coated on Pt nanoparticles. Furthermore, the crystal structures of the Pt@C/C catalysts were investigated by X-ray diffraction (XRD) (D/MAX-2200 Ultima, Rigaku International Co.).

1.4 Electrochemical measurements

All electrochemical measurements were performed in a standard three-compartment electrochemical cell with a RDE, Pt wire, and Ag/AgCl electrode as the working, counter, and reference electrodes, respectively. Herein, all potential values are represented by a reversible hydrogen electrode (RHE). The catalyst inks were prepared by mixing 5 mg of the catalyst with 68.7 μL of Nafion solution and 500 μL of 2-propanol. The catalyst loading on the glassy carbon of RDE was 35.9 $\mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$ for all catalysts. In Ar-saturated 0.1 M HClO_4 , cyclic voltammograms (CVs) were scanned in the potential range of 0.05–1.05 V at 20 mV s^{-1} . In addition, CO stripping tests were performed to determine the EMSA values of the catalysts by integrating the CO oxidation current. While the working electrode potential was kept at 0.05 V, 99.999 % CO gas first bubbled for 15 min in 0.1 M HClO_4 for CO adsorption on the Pt surface, and then was replaced by Ar to remove the CO residue from the electrolyte. After Ar bubbling for 15 min, CO stripping was conducted at a scan rate of 20 mV s^{-1} in the potential range of 0.05–1.05 V. The hydrogen oxidation reaction (HOR) performance was evaluated in H_2 -saturated 0.1 M HClO_4 at a scan rate of 1 mV s^{-1} and a rotation speed of 1600 rpm in the potential range of 0.0–0.1 V. For oxygen reduction reaction (ORR), the polarization curves were obtained in O_2 -saturated 0.1 M HClO_4 at a scan rate of 5 mV s^{-1} and a rotation speed of 1600 rpm in the potential range of 0.05–1.05 V.

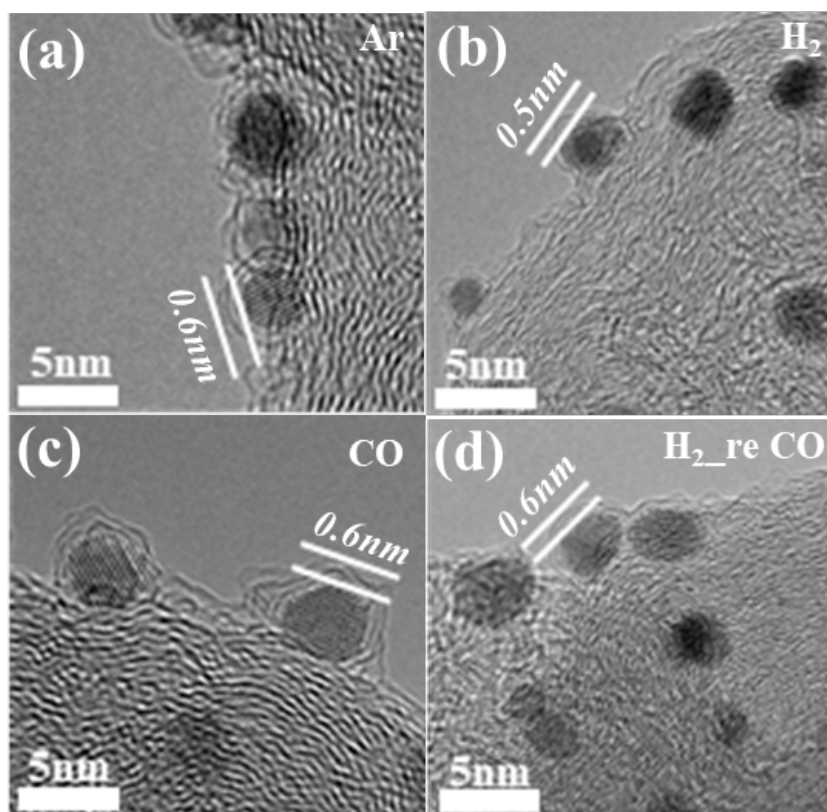


Fig. S1 High-resolution TEM images of (a) Pt@C/C Ar, (b) Pt@C/C H₂, (c) Pt@C/C CO, and (d) Pt@C/C H₂_re CO.

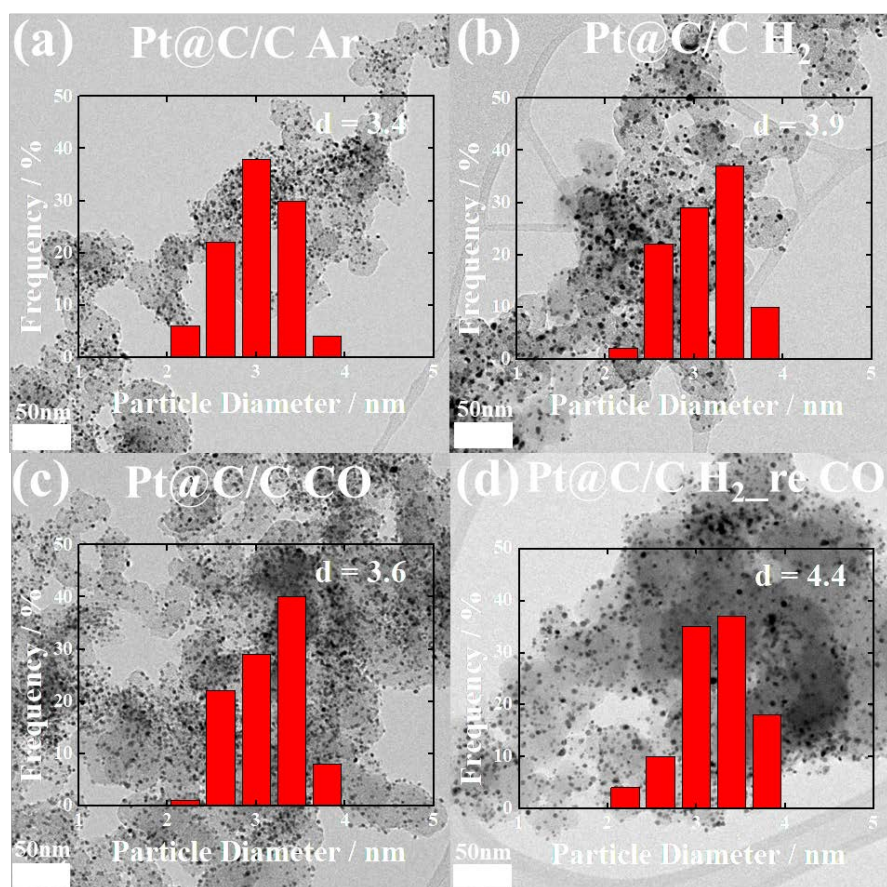


Fig. S2 TEM images and particle size distribution of Pt@C/C catalysts. (a) Pt@C/C Ar, (b) Pt@C/C H₂, (c) Pt@C/C CO, and (d) Pt@C/C H₂_re CO.

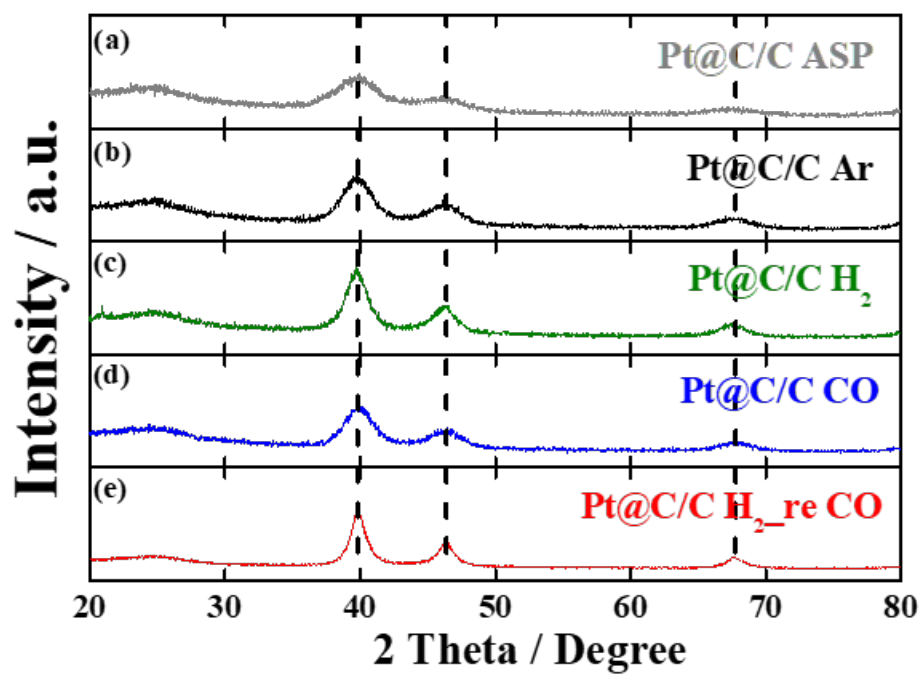


Fig. S3 XRD patterns of Pt@C/C ASP, Pt@C/C Ar, (b) Pt@C/C H₂, (c) Pt@C/C CO, and (d) Pt@C/C H₂_re CO.

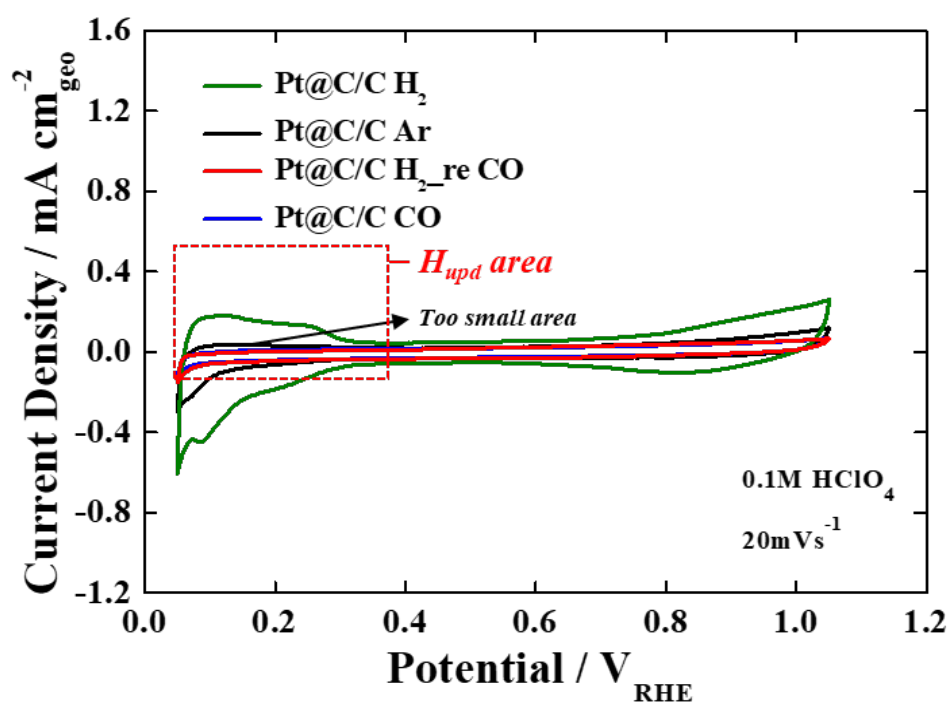


Fig. S4 Cyclic voltammograms (CVs) of Pt@C/C catalysts.

Table S1 Crystallite size (from XRD patterns) and particle size (from TEM analysis) of Pt@C/C catalysts annealed under different gas atmospheres.

	Pt@C/C Ar	Pt@C/C H₂	Pt@C/C CO	Pt@C/C H₂_re CO
Crystallite size	2.4 nm	3.2 nm	2.8 nm	4.2 nm
Particle size	3.4 nm	3.9 nm	3.6 nm	4.4 nm