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Supplementary Information

Surface-Composition-Driven Patchy Carbon Shells Unlock High Activity and Durability in PtCu Oxygen Reduction Catalysts

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1. Experimental Section

Synthesis of catalyst

For the synthesis of 20 wt% carbon incorporated PtCu alloy (PtCu_ASP) catalyst, $Pt(acac)_2$ (97%, Sigma-Aldrich, USA) and $Cu(acac)_2$ (99.9%, Sigma-Aldrich, USA), which contain organic ligands acetylacetonate (acac) acting as carbon sources, were used as metal precursors. The precursors with a molar ratio of Pt to Cu of 1:1 were prepared, and then dispersed along with 0.1 g of carbon black (Vulcan XC-72, Cabot, USA) in a mixed solution of 160 mL of 1-octadecene (90%, Sigma-Aldrich, USA) and 15 mL of oleylamine (70%, Sigma-Aldrich, USA). To remove impurities such as moisture and oxygen, the mixture was stirred at 120°C for 30 min under an Ar atmosphere. Subsequently, the temperature was raised to 300 °C and maintained for 2 h for thermal decomposition. After the reaction, the solution was cooled to 80 °C and washed with excess n-hexane (95%, Samchun Pure Chemical) and ethanol (95%, Samchun Pure Chemical). The resulting powder was filtered and dried in a vacuum oven at 60 °C to obtain the catalyst sample before heat treatment (PtCu_ASP). To induce surface Pt segregation and patchy carbon shell formation in the PtCu_ASP sample, a continuous heat treatment was performed by flowing 20% CO gas at 200 °C for 1 h and then at 800 °C for 1 h to produce the PtCu@PCS sample. For conformal carbon shell formation in the PtCu_ASP sample, a continuous heat treatment was performed by flowing Ar gas at 800 °C for 1 h to produce the PtCu@CCS sample.

Physical and electrochemical characterization

To examine the structure and the particle size of the commercial Pt/C (20 wt%, Premetek, USA), PtCu_ASP, PtCu@PCS and PtCu@CCS samples, TEM (JEM-ARM200F, JEOL, Japan) analysis was conducted. The crystal structures of Pt/C, PtCu@PCS and PtCu@CCS samples were analyzed using XRD (SmartLab, Rigaku, Japan). To analyze the surface elemental composition, XPS (K-alpha+, Thermo Scientific, USA) was performed, and to examine the carbon shell structure, HADDF-STEM imaging and EDS (Titan cubed G2 60-300, FEI, Netherlands) was conducted. Electrochemical properties of the catalysts were evaluated at room temperature using a three-electrode electrochemical cell with a potentiostat (Metrohm, Autolab, Netherlands) connected to a rotating disk electrode (RDE). The cell employed an Ag/AgCl reference electrode, a Pt electrode as the counter electrode, and a glassy carbon electrode with a geometric area of 0.196 cm^2 as the working electrode. All measured potentials

were converted to the reversible hydrogen electrode (RHE) scale, and currents were normalized to the geometric area of the electrode. To prepare uniform catalyst ink, 5 mg of catalyst was dispersed in a mixture of 32.3 μL Nafion solution (5 wt%, Chemours, USA) and 2-propanol (99.5%, Sigma-Aldrich, USA). The volume of 2-propanol was 500 μL for Pt/C and 369 μL for PtCu samples. The mixture was ultrasonicated to obtain homogeneous ink. Then, 5 μL of the catalyst ink was dropped onto the carbon electrode surface of the RDE, dried at room temperature, and electrochemical measurements were performed. Commercial Pt/C, PtCu@PCS and PtCu@CCS samples had a Pt loading of 47.9 μg cm^{-2}. Cyclic voltammetry (CV) was conducted at room temperature in 0.1 M $HClO_4$ and 0.1 M KOH under Ar atmosphere at a scan rate of 20 mV s^{-1}. To measure EMSA, CO stripping was performed by applying 0.05 V to the working electrode while exposing the catalyst surface to CO in 0.1 M $HClO_4$ for 15 min, followed by removing residual CO by Ar bubbling and conducting CV measurement in the same manner. To evaluate dealloying behavior in a KOH electrolyte, surface Cu was first removed by electrochemical dealloying in 0.1 M $HClO_4$ by conducting CV measurements in the same manner. After this dealloying step, CV measurements were then conducted in the KOH electrolyte in the same manner. ORR performance was evaluated in O_2-saturated 0.1 M $HClO_4$ solution at a rotation speed of 1600 rpm and scan rate of 5 mV s^{-1} using RDE after CV measurement. ADTs were carried out in 0.1 M $HClO_4$ by cycling potential between 0.6 and 1.1 V_{RHE} at a scan rate of 20 mV s^{-1} for 10,000 cycles.

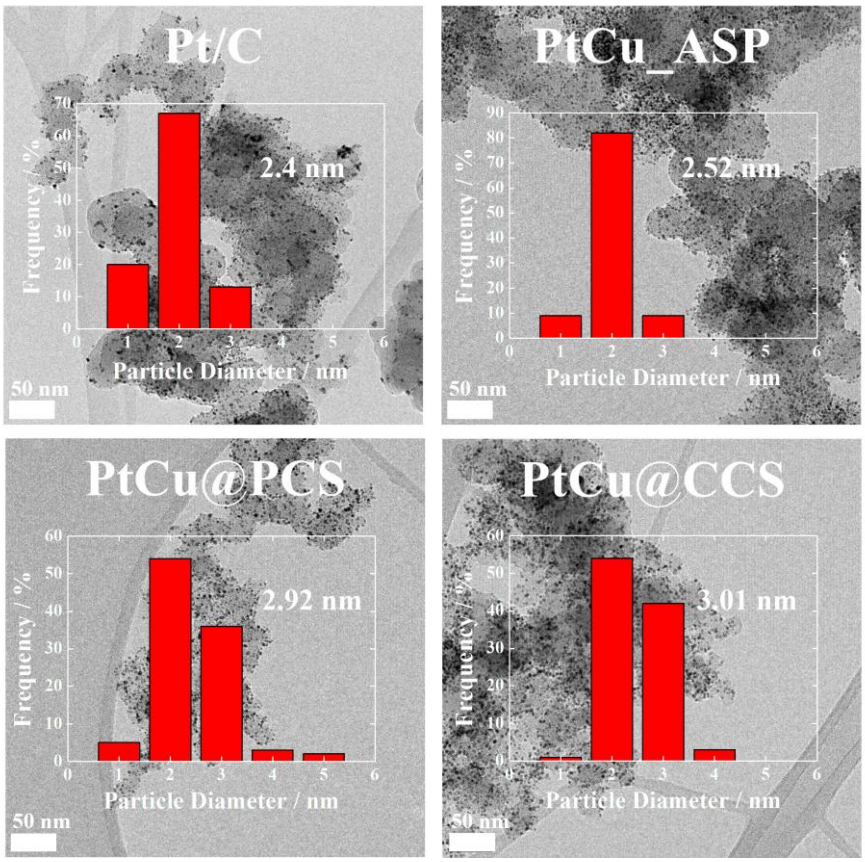

Fig. S1 TEM images of Pt/C, as-prepared PtCu_ASP, PtCu@PCS and PtCu@CCS showing nanoparticle dispersion on the carbon support and particle size distribution.

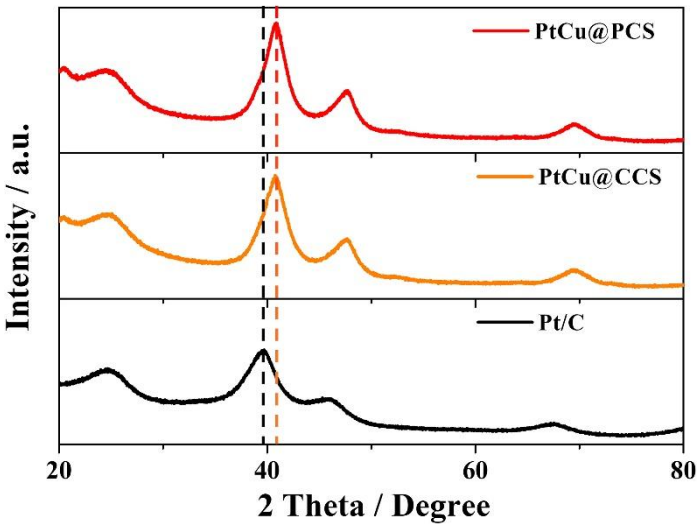

Fig. S2 XRD patterns of PtCu@CCS and PtCu@PCS compared with commercial Pt/C, confirming Pt–Cu alloy formation.

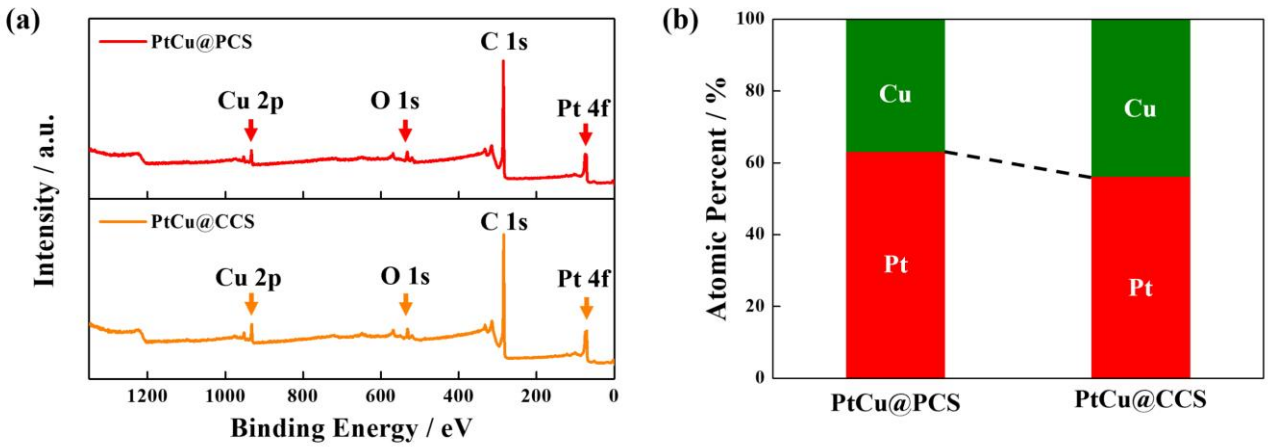

Fig. S3 (a) XPS survey spectra and (b) near-surface atomic composition of PtCu@PCS and PtCu@CCS.

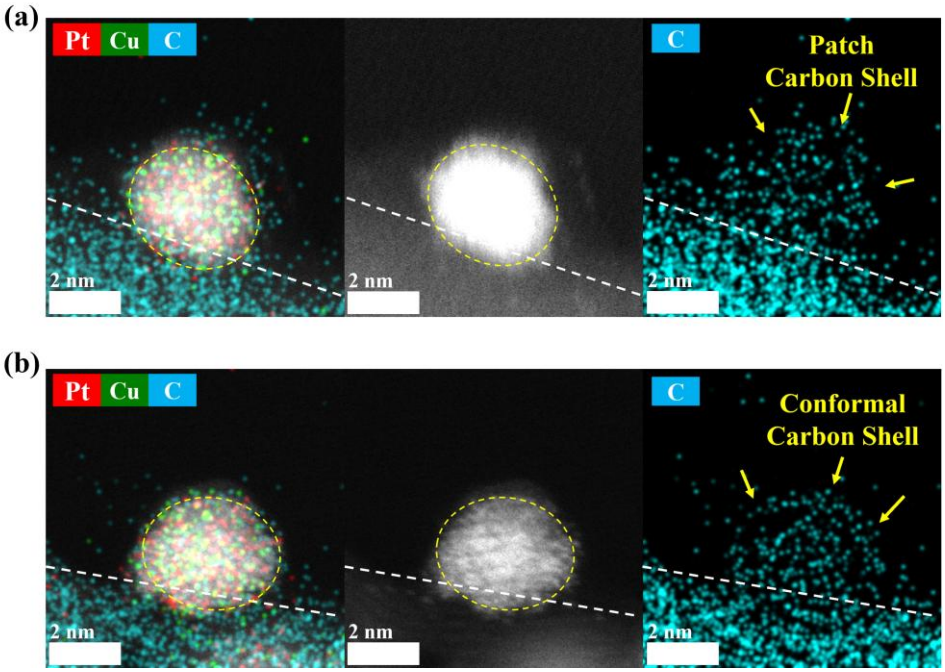

Fig. S4 EDS mapping and STEM images of (a) PtCu@PCS and (b) PtCu@CCS showing different carbon shell structure.

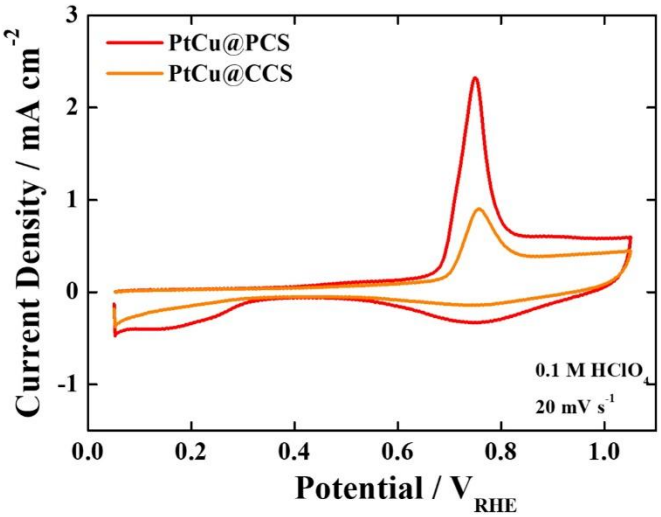

Fig. S5 CO stripping voltammograms of PtCu@PCS and PtCu@CCS measured in an acidic electrolyte.

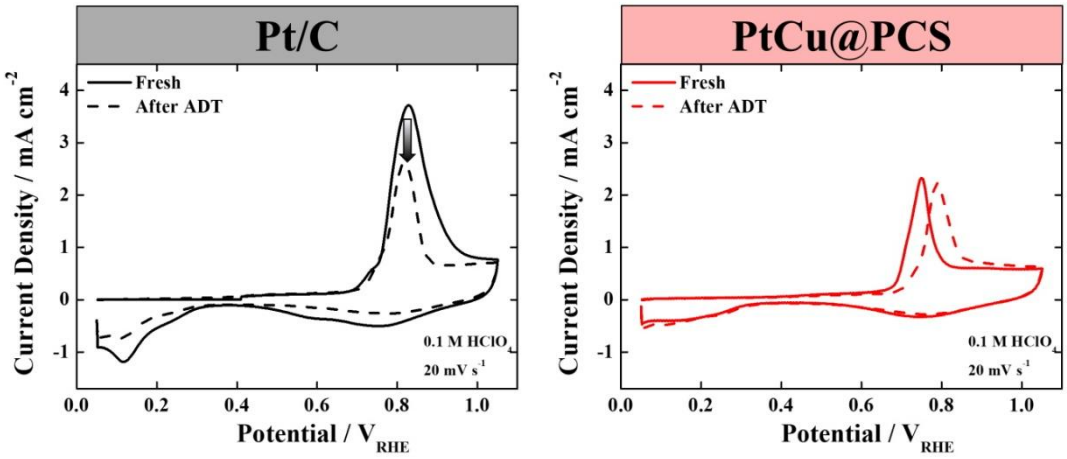

Fig. S6 CO stripping voltammograms before and after ADT for Pt/C and PtCu@PCS.

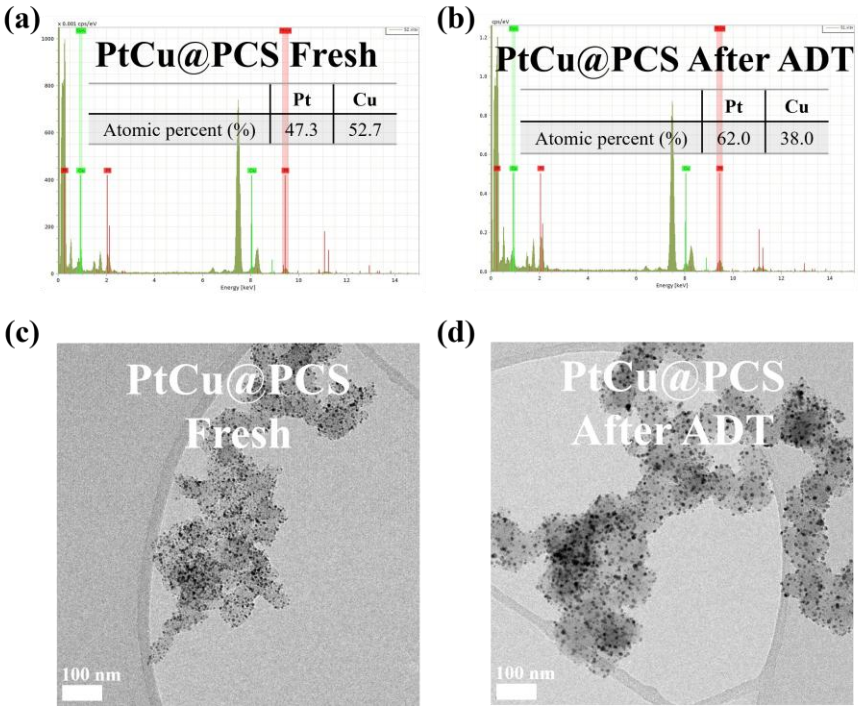

Fig. S7 EDS spectra of PtCu@PCS (a) before and (b) after ADT. TEM images for PtCu@PCS (c) before and (d) after ADT.

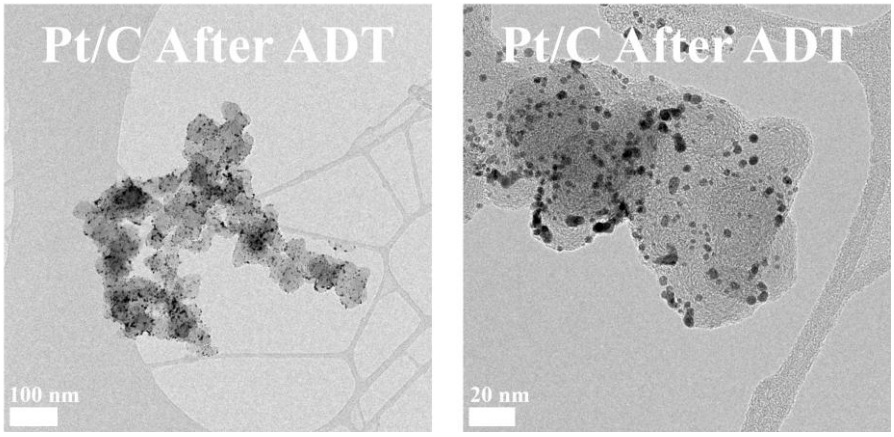

Fig. S8 TEM images for Pt/C after ADT.