Supporting Information

Synthesis and Characterization of Ultra-Small Octahedral PtNiCo Skeletons with High Activity for Oxygen Reduction Reaction

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Materials and Methods

Chemicals.

Fumed silica (S5130), platinum(II) acetylacetonate (Pt(acac)$_2$, 97%), cobalt(II) acetylacetonate (Co(acac)$_2$, 97%), nickel acetylacetonate (Ni(acac)$_2$, 97%), acetic acid (CH_3COOH, 99.99%) were purchased from Sigma-Aldrich. Vulcan carbon (Vulcan XC-72R) was purchased from Fuel Cell. Hydrofluoric acid (HF, 48.0 ~ 51.0%) was purchased from J.T.Baker. Ethanol (EtOH, 99.9%) and toluene ($C_6H_5CH_3$, 99.5%) were purchased from Daejung Chemicals Co. All chemicals were used as received without purification.

Preparation of Octahedral PtNiCo Nanoparticles on Fumed Silica (PtNiCo@fumed).

1.0 g of fumed silica was sonicated with 0.342 mmol of Ni(acac)$_2$, 0.342 mmol of Co(acac)$_2$, and 0.036 mmol Pt(acac)$_2$ in toluene for 1.0 h. After removing toluene by evaporation and drying at 80 °C for 30 min, the silica loaded with metal precursors was ground into a fine powder and transferred to a tube furnace. The powder was then heated under a H_2/CO flow (5/120 sccm) to 200 °C and maintained at that temperature for 1.0 h. The resulting PtNiCo@fumed silica was collected as a black powder. For the PtNi@fumed silica sample, 0.684 mmol of Ni(acac)$_2$ and 0.036 mmol of Pt(acac)$_2$ were used, following the same procedure. Additionally, a PtCo@fumed silica sample was synthesized using 0.684 mmol of Co(acac)$_2$ and 0.036 mmol of Pt(acac)$_2$ under identical conditions.

Preparation of Octahedral PtNiCo Skeletons on Carbon Support.

A mixture of PtNiCo@fumed silica and Vulcan XC-72R was dispersed in a 2.0 wt% HF solution and sonicated for 1.0 h. The precipitate obtained by centrifugation was then re-dispersed in a fresh 2.0 wt% HF solution and shaken for additional 1.0 h. To minimize organic contamination, the carbon-supported nanoparticles were subsequently dispersed in 20 mL of acetic acid and heated at 70 °C for 3.0 h under magnetic stirring. After thorough washing and centrifugation, carbon-supported PtNiCo skeletons were obtained. Similarly, PtNi@fumed silica and PtCo@fumed silica samples were transferred onto the carbon support following the same procedure to obtain PtNi/C and PtCo/C samples, respectively.

Material Characterization.

The PtNiCo skeletons were characterized by X-ray diffraction (XRD, Rigaku Miniflex II (4.5 kW) diffractometer using Cu-Kα radiation at 30 kV and 15 mA), transmission electron microscopy (TEM, JEOL JEM-2100F operated at 200 kV) with selected area electron diffraction (SAED) patterns, and high-angle annular dark field scanning TEM (HAADF-STEM, JEOL ARM-200CF operated at 20 kV) equipped with an electron prove corrector and energy dispersive X-ray spectroscope (EDS). Samples for TEM and STEM investigation were prepared by dropping the diluted samples in ethanol on a 300-mesh carbon support copper grid (Ted Pella, Inc.) The Ni/Co/Pt/carbon ratios in the catalysts were determined using inductively coupled plasma-optical emission spectrometry (ICP-OES, Perkin-Elmer, Avio500). X-ray photoelectron spectroscopy (XPS) measurements were conducted using a K-ALPHA+ system (Thermo Fisher Scientific, U.K.) with a monochromated Al Kα source.

Electrochemical characterization.

Electrochemical experiments were conducted using a multichannel potentiostat (Biologic, England), a compact pine rotator (CPR, Pine Instrument, USA), and a three-compartment electrochemical setup. The setup included a rotating disk electrode (RDE, Pine Research Instrumentation) equipped with a 5 mm diameter glassy carbon disk (GC) as the working electrode (E3TPK). A Pt mesh (1 cm^2) attached with Pt wire and an Ag/AgCl electrode served as the counter and reference electrodes, respectively. All experiments were performed at room temperature, and potentials applied to the working electrode were referenced to the reversible hydrogen electrode (RHE).

Before conducting experiments, the RDE was polished with 0.05 μm Al_2O_3 and rinsed with deionized (DI) water. The commercial Pt/C (20 wt%) was bought from Premetek. Catalyst ink was prepared by mixing approximately 2.5 mg of catalyst powder with 2.0 mL of deionized water, 0.50 mL of isopropyl alcohol (>99.99%, Aldrich), and 10 μL of 5 wt% Nafion solution (Aldrich). This mixture was ultrasonicated for 30 minutes, after which 10.0 μL of the ink was deposited onto the GC and dried in an oven. The Pt loading on the GC electrode was standardized to 10.2 μg cm^{-2}. Cyclic voltammetry (CV) was carried out between 0.05 to 1.00 V_{RHE} in an Ar-saturated 0.1 M $HClO_4$ solution for 50 cycles at 100 mV s^{-1}, with the final CV recorded at 50 mV s^{-1}. The CV curves for the catalysts were normalized by the area of the RDE.

The electrochemical surface area (ECSA) was determined from the CV curves using the hydrogen underpotential deposition (H_{upd}) method, where adsorption/desorption peaks in the range of 0.05 to 0.40 V_{RHE} were analyzed. The charges associated with these peaks were calculated by dividing the integrated charge by a standard value of 210 μC cm^{-2} and the total mass of Pt loading.[1,2]

Oxygen reduction reaction (ORR) measurements were performed in an O_2-saturated 0.1 M $HClO_4$ solution, with the RDE rotating at 1,600 rpm and a scan rate of 10 mV s^{-1}. The ORR polarization curves for the catalysts were taken in the range of 0.1 to 1.10 V_{RHE} and normalized by the area of the RDE. ORR polarization curves were corrected for ohmic resistance (iR compensated). The Koutecky-Levich equation was used to derive the kinetic current density (j), using the formula:

$$\frac{1}{j_o} = \frac{1}{j} + \frac{1}{j_d}$$

$$j = \frac{(j_o \times j_d)}{j_d - j_o}$$

where, j_o and j_d are the obtained current density and the diffusion limiting current, respectively.

Accelerated durability tests (ADT) were conducted in an O_2-saturated 0.1 M $HClO_4$ solution by cycling the potential between 0.6 and 1.0 V_{RHE} at 100 mV s^{-1} for 10,000 and 20,000 cycles. Following these cycles, both CV and ORR polarization curves were re-measured in a fresh 0.1 M $HClO_4$ solution.

MEA Measurements.

The membrane electrode assembly (MEA), with an active area of 5 cm^2, was prepared using the catalyst-coated membrane (CCM) method. Catalyst ink, consisting of Pt/C catalyst, Nafion D-521 dispersion, and isopropyl alcohol, was sprayed onto a Nafion 211 membrane (DuPont®). For anode, 10% Pt on Vulcan XC72(Sigma-Aldrich) was used with a Pt loading of 0.1 mg_{Pt} cm^{-2} and Pt loading of cathode was adjusted to 0.05 mg_{Pt} cm^{-2} for both catalysts. The prepared CCM was sandwiched between two gas diffusion layers (GDLs; Sigracet® 39BB, SGL Carbon Inc.), with the microporous layers placed toward the catalyst surfaces. A seven-layer MEA was fabricated by placing gaskets on both sides of the CCM-GDL structure. This MEA was then assembled in a single-cell hardware comprising graphite plates with serpentine flow fields, covering a geometric area of 5 cm^2.

The single-cell performance tests were carried out using a SMART2 PEM fuel cell test station (WonA-Tech). The cell was operated at 80 °C with 100% relative humidity. Hydrogen and air were supplied at flow rates of 500 ccm (anode) and 1500 ccm (cathode), respectively. In H_2/O_2 atmosphere, H_2 and O_2 were supplied at flow rate of 300 ccm (anode) and 500 ccm (cathode). During the activation step, a constant voltage of 0.4 V was applied at least for two hours. Subsequently, polarization curves (j–V) were measured under a backpressure of 0.5 bar in voltage range of OCV to 0.25V.

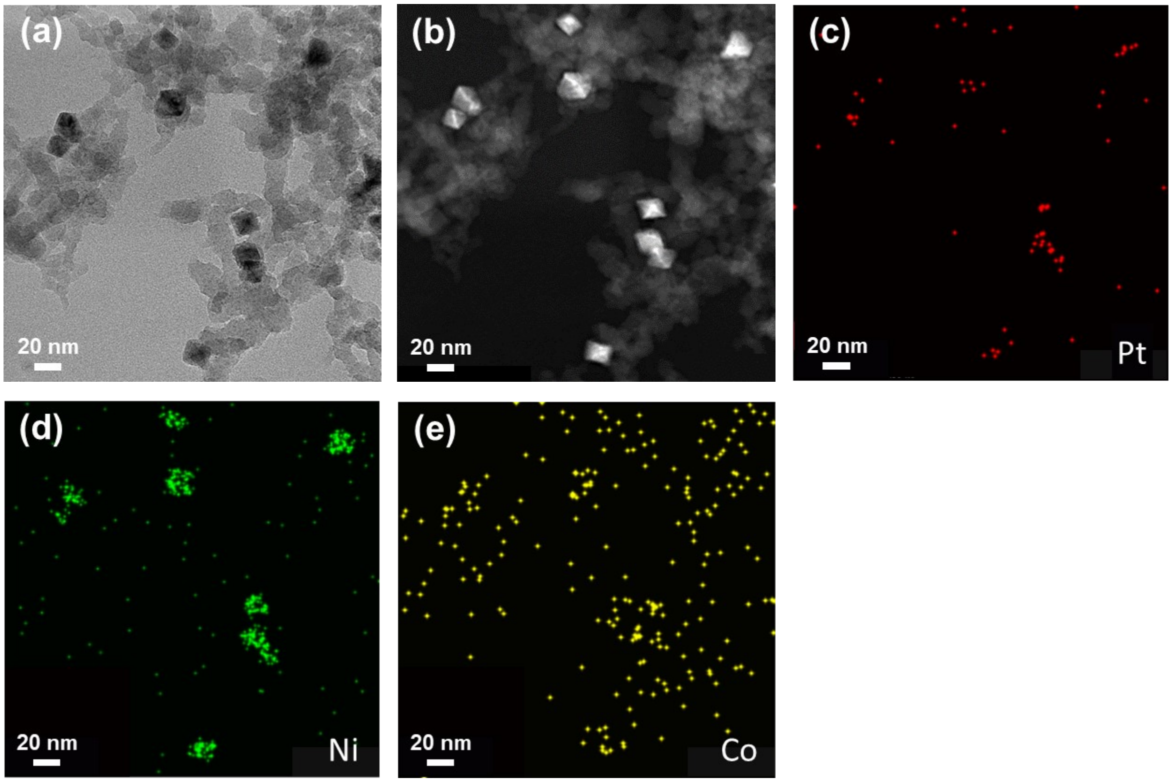

Fig. S1 Characterization of PtNiCo@fumed. (a) TEM, (b) STEM, and (c, d, e) EDS elemental mapping images.

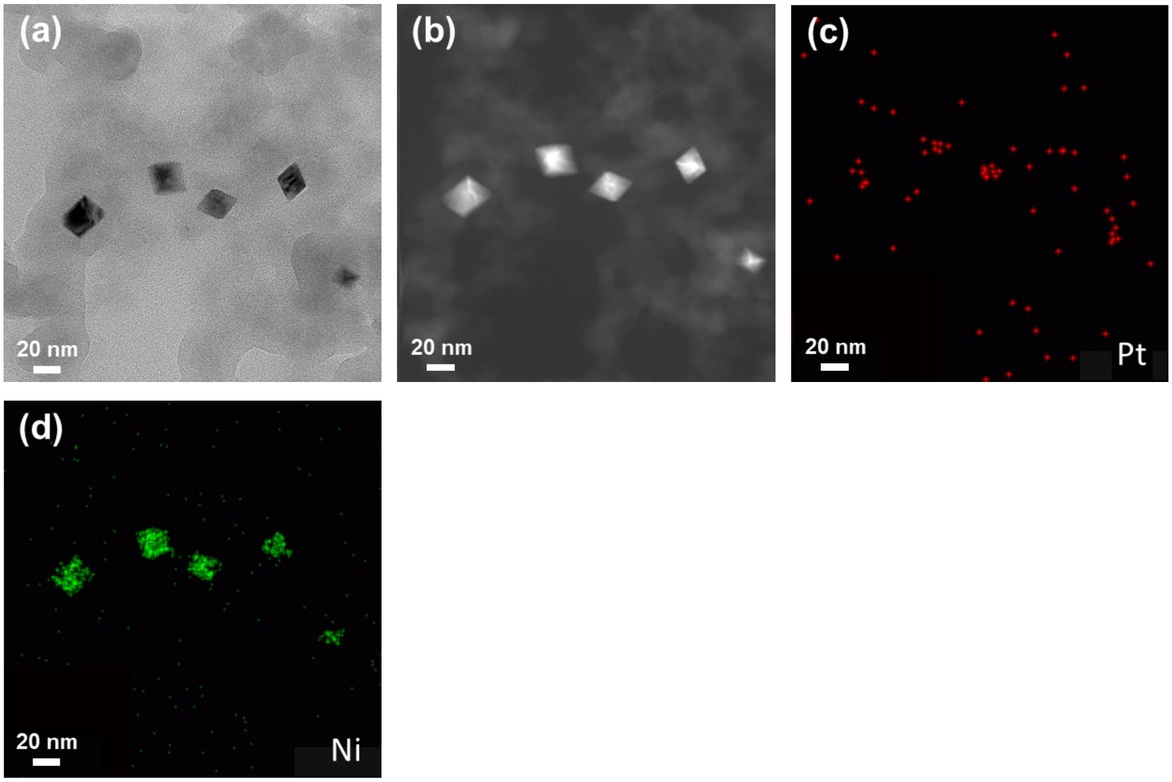

Fig. S2 Characterization of PtNi@fumed. (a) TEM, (b) STEM, and (c, d) EDS elemental mapping images.

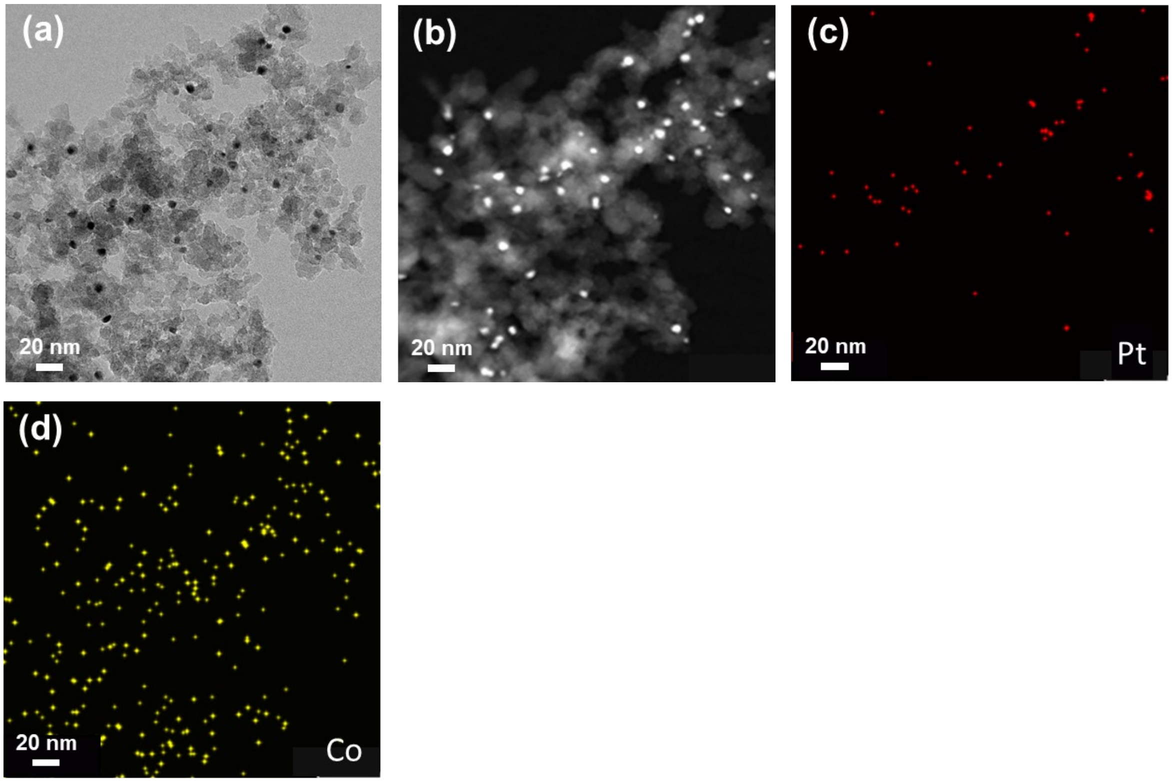

Fig. S3 Characterization of PtCo@fumed. (a) TEM, (b) STEM, and (c, d) EDS elemental mapping images.

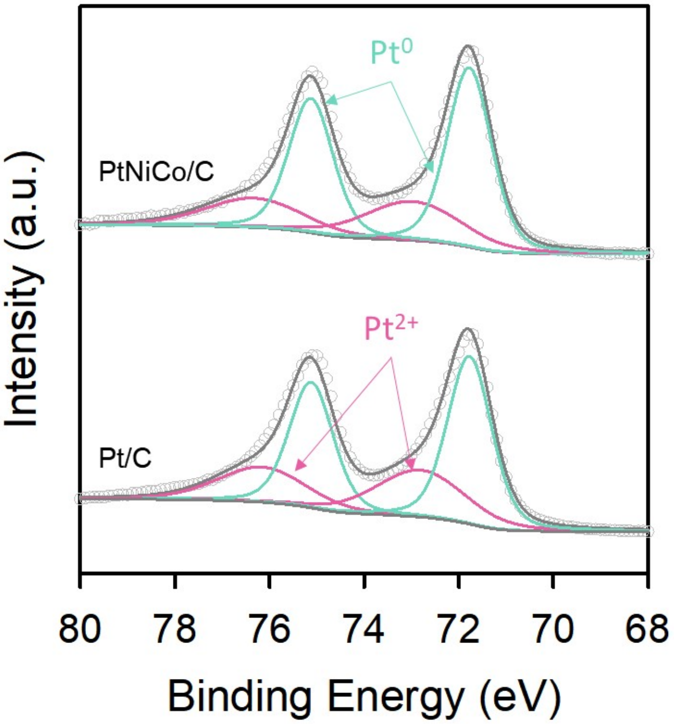

Figure S4. Core-level Pt 4f XPS spectra of PtNiCo/C and commercial Pt/C.

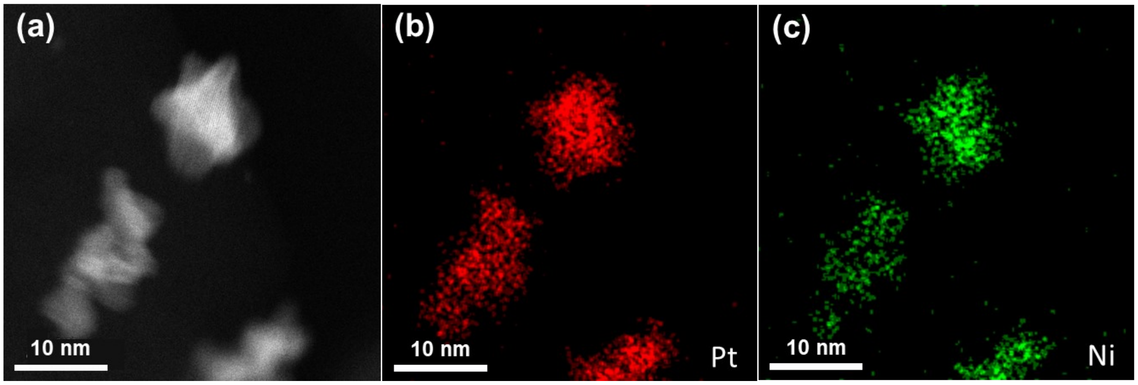

Fig. S5 Characterization of PtNi/C. (a) STEM, and (b, c) EDS elemental mapping images.

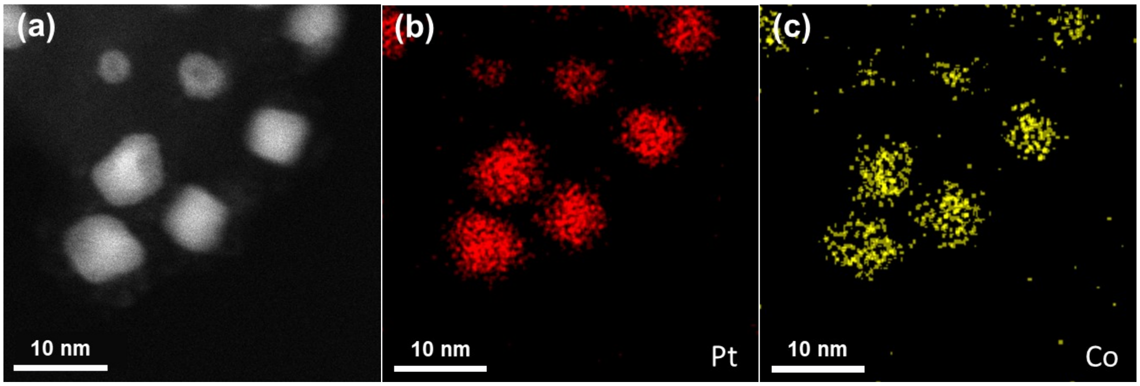

Fig. S6 Characterization of PtCo/C. (a) TEM, (b) STEM, and (c, d) EDS elemental mapping images.

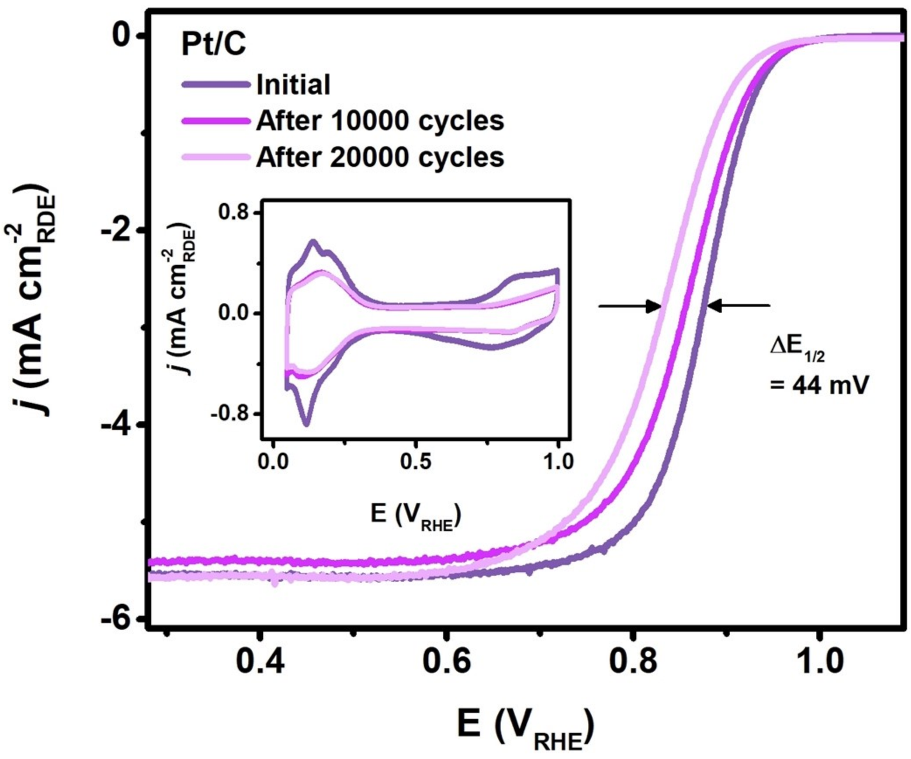

Fig. S7 ORR polarization curves for Pt/C before and after 10,000 and 20,000 cycles in an O_2-saturated 0.1 M $HClO_4$ solution. The insets displaying the CVs before and after the stability test.

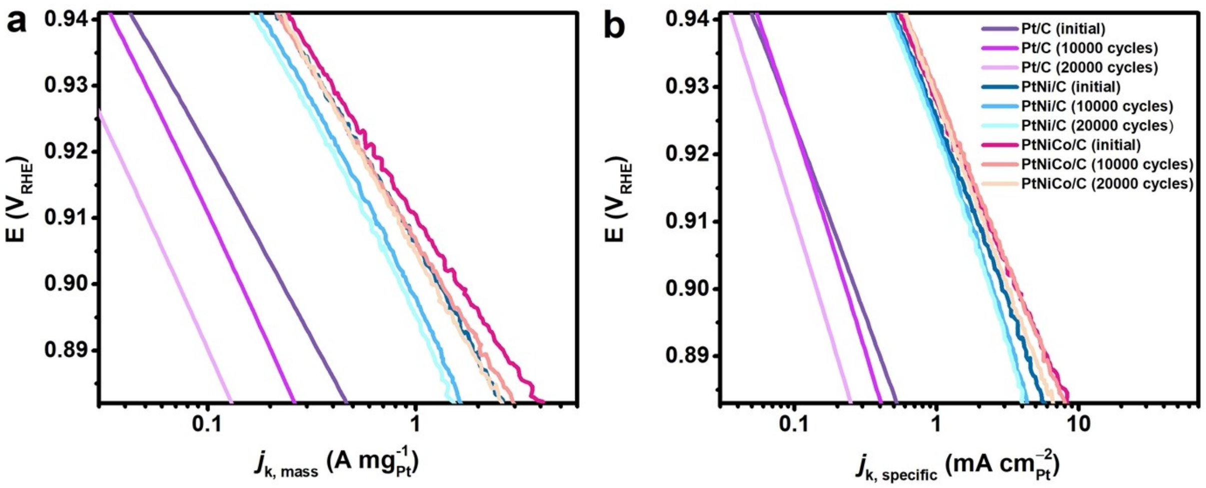

Fig. S8 Tafel plots of (a) mass activities and (b) specific activities presented as kinetic current densities normalized to mass of Pt loading and ECSA.

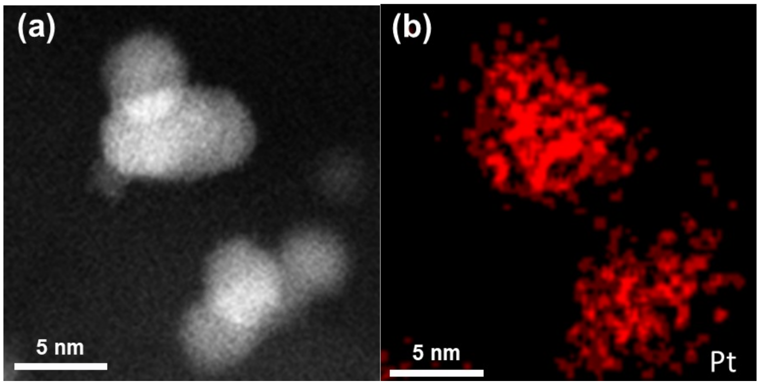

Fig. S9 Characterization of commercial Pt/C after 20,000 cycles of stability test. (a) STEM, and (b) EDS elemental mapping images.

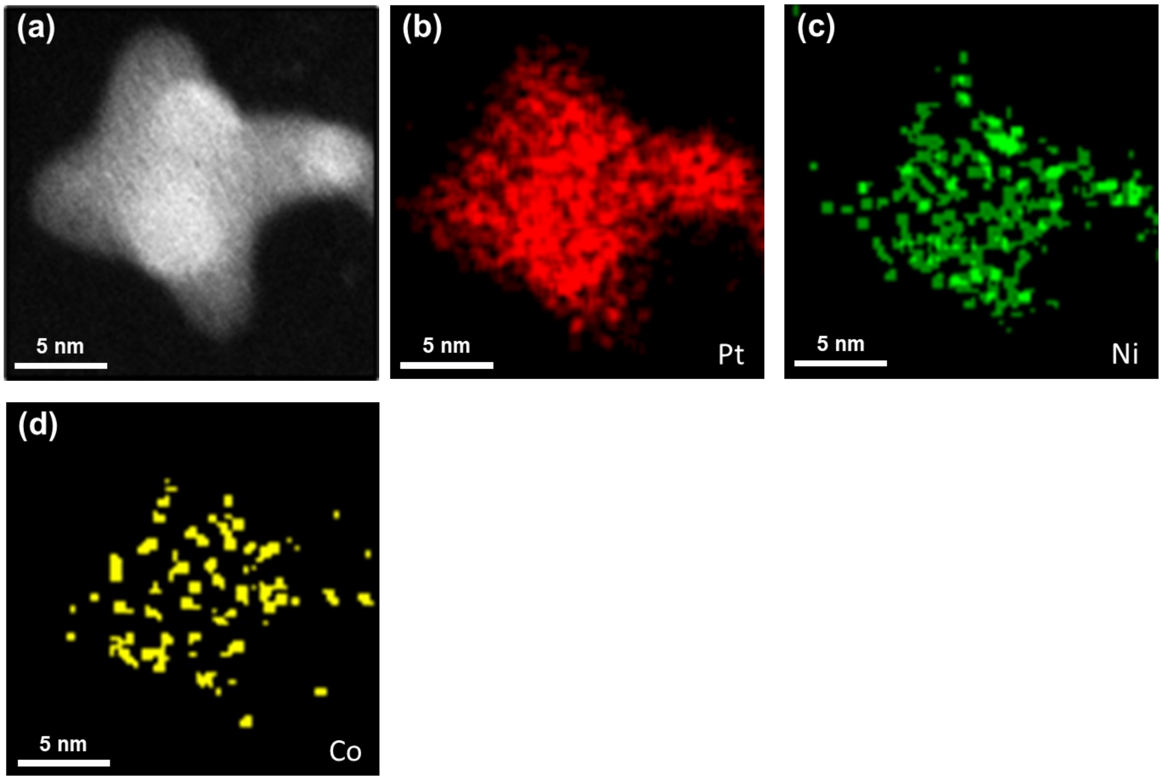

Fig. S10 Characterization of PtNiCo/C after 20,000 cycles of stability test. (a) STEM, and (b, c, d) EDS elemental mapping images.

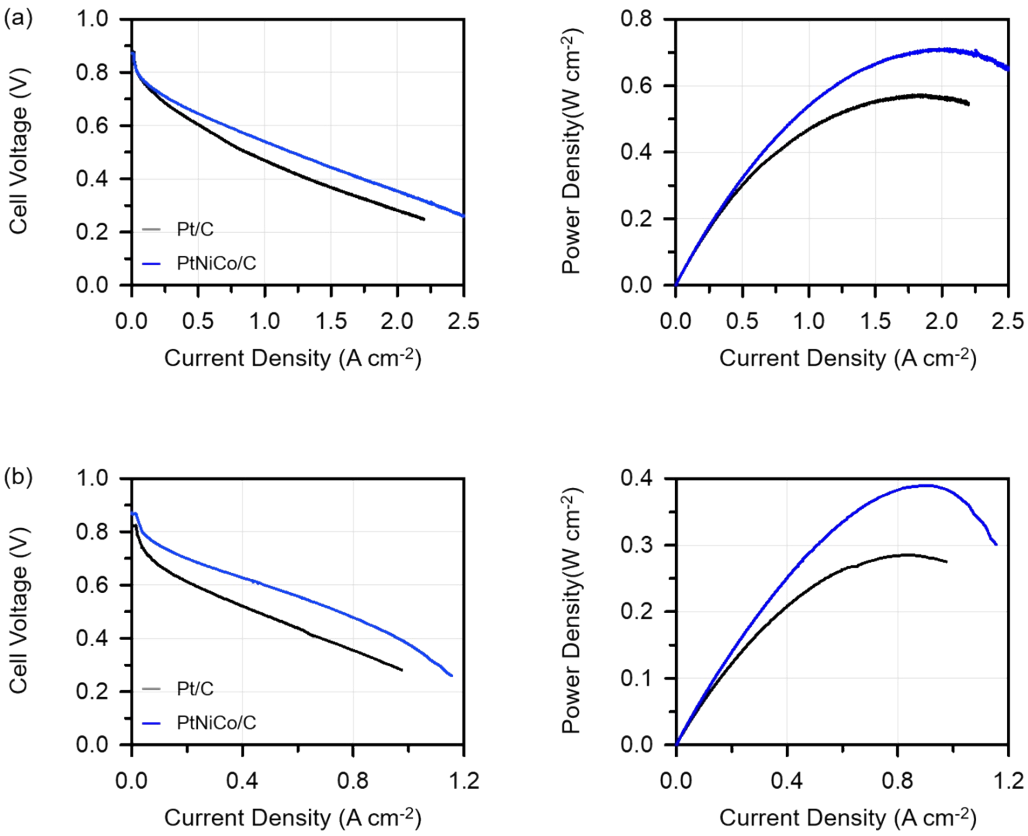

Figure S11. *j*–V polarization and power density curves of Pt/C and PtNiCo/C MEA under (a) H_2/O_2, (b) H_2/Air conditions.

Table S1. ICP-OES results of PtNiCo/C, PtNi/C, and PtCo/C.

Catalyst	Pt(wt%)	Ni(wt%)	Co(wt%)	Pt:Ni:Co atomic ratio
PtNiCo/C	6.62	0.65	0.08	73:24:3
PtNi/C	4.59	0.57	-	71:29:0
PtCo/C	7.42	-	0.47	83:0:17

Table S2. Comparison of ECSAs and specific activities (SAs) of the Pt/C, PtNi /C, and PtNiCo /C catalysts before and after the stability test.

Catalyst	**ECSA$_{HUPD}$ (m^2 g^{-1}$_{Pt}$)**	**SA$_{HUPD}$ (mA cm^{-2}$_{Pt}$)**	**MA (A mg^{-1}$_{Pt}$)**
Pt/C: Initial	85.10	0.26	0.22
After 10,000 cycles	62.51	0.24	0.15
After 20,000 cycles	48.42	0.15	0.07
PtNi /C: Initial	43.82	2.87	1.26
After 10,000 cycles	36.95	2.52	0.93
After 20,000 cycles	35.55	2.33	0.83
PtNiCo /C: Initial	43.91	3.73	1.64
After 10,000 cycles	36.10	3.71	1.34
After 20,000 cycles	34.62	3.47	1.21