

Supporting Information for:

Control of Architecture in Rhombic Dodecahedral Pt-Ni Nanoframe Electrocatalysts

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Experimental Details:

Chemicals

Nickel (II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\geq 98.5\%$), chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, $\geq 37.5\%$ Pt basis), oleylamine (technical grade, 70%), and hexane ($\geq 98.5\%$) were purchased from Sigma-Aldrich. Toluene ($\geq 99.9\%$) was purchased from Fisher Scientific and acetic acid ($\geq 99.7\%$) was purchased from EMD.

Synthesis of H-SD and E-SD

For H-SD, 20 mg $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and 21.5 mg $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 0.8 mL oleylamine. The solution was injected into 9.2 mL oleylamine which had been kept at 160 °C under Ar for one hour. The reaction was then kept under vacuum for 2.5 minutes. Then, the reaction was heated to 265 °C with a ramping rate of 15 °C/min under Ar atmosphere. The color of the reaction solution changed to black after reaching 265 °C. The reaction was stopped 5 min after the color turned to black. The reaction flask was carefully transferred into a water bath in order to quench the growth process. The produced H-SD was washed twice with ethanol and hexane. For E-SD, the procedures were kept the same except that 20 mg $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and 11.5 mg $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 0.6 mL oleylamine and injected into 9.4 mL oleylamine.

Chemical corrosion to H-NF and E-NF

For H-NF, H-SD was dispersed in 4 mL toluene and mixed with 4 mL acetic acid and 0.2 mL oleylamine, followed by heating at 90 °C in an oil bath for 2 hours with reflux system. The collected sample was washed twice with ethanol and hexane. E-NF could be evolved from E-SD with the same procedure.

Characterization

The prepared samples were analyzed by SEM (Zeiss Gemini Ultra-55 analytical field emission scanning electron microscope), TEM (Hitachi H-7650), HRTEM (FEI Tecnai F20) and STEM-HAADF and EDS mapping (FEI TitanX 60-300). XRD was performed using a Bruker AXS D8 Advance diffractometer with Cu K α source. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was utilized for total composition analysis with PerkinElmer Optima 7000 DV. XPS was carried out with PHI 5600 X-ray photoelectron spectrometer and analyzed using CasaXPS.

Interpretation of XRD, ICP, and XPS Data

Figure S4a compares powder X-ray diffraction (XRD) patterns of NFs and corresponding SD samples. All samples showed face-centered cubic structures with diffraction peak positions dependent on their composition. Therefore, the Pt-rich NFs had (111) peak positions at lower 2θ than the corresponding SDs. The full width at half maximum (FWHM) of E-NF and H-NF measured 1.13° and 1.83°, respectively, at the (111) peak position (Figure S4b). The smaller FWHM in the E-NF pattern is a manifestation of a larger crystal grain size, consistent with the extended sheet structure connected to the edges of the frame of E-

NF.¹ Figure S4c and S4d indicate the degree of asymmetry in the (111) peak of H-SD and E-SD. The (111) peak of H-SD has a sharp component from its large grain of Ni-rich phase and asymmetry toward lower 2θ due to the significant segregation of Pt to the edges of H-SD. E-SD revealed less Pt segregation than H-SD as observed by the smaller degree of asymmetry.

Table 1 presents the compositions of SDs and NFs. The asymmetry of the XRD patterns of both SD samples made it difficult to assign a bulk composition based on XRD. However, bulk composition information was obtained from inductively coupled plasma optical emission spectroscopy (ICP-OES). The near-surface composition was estimated by X-ray photoelectron spectroscopy (XPS) measurements (Figure S5) because the intensity of emitted photoelectrons reaching the electron analyzer decays exponentially with the depth from which the electrons are emitted.² In this case, an Al K α source with 1486.6 eV X-rays was used, providing an inelastic mean free path of ~ 1.1 nm for Ni 2p and ~ 1.7 nm for Pt 4f photoelectrons. The surface composition of H-SD showed an increased Pt concentration compared to the bulk due to Pt segregation to the exterior edges of H-SD. In contrast, E-SD showed a similar Pt composition at the surface versus the bulk. This comparison indicated that the Pt-rich domains are not solely located on the outer regions (edges or facets) of E-SD and rather exist as inner sheet structure that survives chemical corrosion to E-NF. Therefore, the XPS and ICP comparison confirmed the location of the sheet structure in E-NF to be consistent with electron microscopy analysis.

EXAFS Data Collection and Analysis

Extended x-ray absorption fine structure (EXAFS) data were collected at the Advanced Light Source Beamline 10.3.2. The x-ray wavelength was monochromatized by a Si(111) double-crystal, fixed exit monochromator. The intensity of the incident x-ray radiation, I_0 , was monitored with a nitrogen filled ionization chamber. All data were collected in fluorescence mode with a 7-element Ge detector (Canberra). The data at the Ni K-edge and Pt L₃-edge were calibrated to a Ni foil and Pt foil, respectively. All spectra at a given edge were aligned according to a glitch in I_0 near each absorption edge.

EXAFS data reduction and EXAFS fitting was performed using the IFEFFIT based programs Athena and Artemis.³ Edge step normalization for each spectra was performed by subtracting the pre-edge and post-edge backgrounds in Athena. For EXAFS background removal, a cubic spline was fit to the data and the k -space data was Fourier transformed resulting in an R -space spectrum which was fit in Artemis. EXAFS data was fit to the following EXAFS function:

$$\chi(k) = S_0^2 \sum_{i=1}^{shells} \frac{N_i}{kR_i^2} F_i(k) e^{-2k^2\sigma_i^2} e^{-2R_i/\lambda(k)} \sin[2kR_i - \varphi_i(k)]$$

The amplitude of the contribution from each coordination shell in the EXAFS function is summed to generate a fit to the data. S_0^2 represents an amplitude reduction factor which is typically assumed to be chemically transferable and is affected by shake-up effects at the absorbing atom. It was estimated by performing a fit to EXAFS transmission measurements on Ni and Pt metal foils. Values for S_0^2 were determined to be 0.80 for Pt and 0.78 for Ni. N_i and R_i are the coordination number and half-path length between the central absorbing atom and a scattering atom, respectively. The mean-square disorder in the distance from the central absorbing atom to a given shell due to thermal fluctuation and structural disorder is represented by σ_i^2 . These parameters are calculated by fitting the experimental data. The photoelectron

mean free path is represented by λ . Lastly, $F_i(k)$ is the backscattering amplitude and $\varphi_i(k)$ is the phase factor for a given coordination shell. These parameters are calculated through *ab initio* methods using FEFF6 as embedded in Artemis and Atoms.

The Ni *K*-edge and Pt *L₃*-edge were fit together for H-NF and E-NF using first shell paths generated from a FEFF model of a disordered face-centered cubic Pt-Ni alloy with seven Pt and five Ni atoms randomly placed around the central absorbing atom. Outer shell sites were also randomly assigned to hold either a Pt or Ni atom, maintaining the composition to be approximately that identified by ICP for H-NF and E-NF. The following restraints were also applied in co-fitting the two edges:

- $R_{\text{NiPt}} = R_{\text{PtNi}}$
- $\sigma^2_{\text{NiPt}} = \sigma^2_{\text{PtNi}}$

The extent of alloying parameters, J_{Ni} and J_{Pt} were calculated using the method of Hwang et al,⁴ according to the following equations:

$$J_{\text{Pt}} = \frac{\frac{N_{\text{PtNi}}}{N_{\text{Pt}}}}{x_{\text{Ni}}} \times 100\% \quad J_{\text{Ni}} = \frac{\frac{N_{\text{NiPt}}}{N_{\text{Ni}}}}{x_{\text{Pt}}} \times 100\%$$

Where x_{Ni} and x_{Pt} are the mole fractions in each sample as measured by ICP analysis. See Table S1 for the results to the fits.

Electrochemical characterization

After chemical corrosion, H-NF or E-NF were dispersed in chloroform and added to carbon (Cabot, Vulcan XC-72) in a ratio which produced a loading of 15-18 wt% Pt. The mixture was sonicated in chloroform for 30 to 45 minutes to complete the loading process. The catalyst was collected by centrifugation (10,000 rpm), washed once with hexanes, and recollected by centrifugation. The resulting catalyst powder was heated at 200 °C in air for 14 hours in order to remove organic surfactants. The catalyst was then dispersed in water with a concentration of 0.5 mg_{catalyst}/mL. The actual concentration of Pt in the ink was determined by ICP-OES. The catalyst ink was dropcast onto a 5 mm glassy carbon disk (Pine Instruments) in the appropriate volume to achieve 4.6 µg_{Pt}/cm² loading density and allowed to air dry. The commercial Pt/C catalyst (Alfa, ~20wt% Pt) had a loading density of 7.8 µg_{Pt}/cm². The electrochemical measurements were conducted in a three-compartment glass electrochemical cell with a Pine rotating disk electrode (RDE) setup and a Biologic VSP potentiostat. A saturated Ag/AgCl electrode and a Pt wire were used as reference and counter electrodes, respectively, and 0.1 M HClO₄ prepared from 67% HClO₄ (Sigma-Aldrich) was used as the electrolyte. All potentials are presented versus the reversible hydrogen electrode (RHE). Hydrogen underpotential deposition measurements were performed by saturating the electrolyte with argon before collecting the CV at a sweep rate of 50 mV/s. Electrooxidation of adsorbed CO, or CO-stripping measurements, were performed by purging CO through the electrolyte while holding the potential at 0.05 V. Argon was then purged to remove CO from the electrolyte and the CV was collected at a sweep rate of 50 mV/s. The ORR measurements were collected under O₂ purging conditions and at 20 mV/s with an RDE rotation rate of 1600 rpm. The current densities for ORR were corrected for ohmic iR drop.

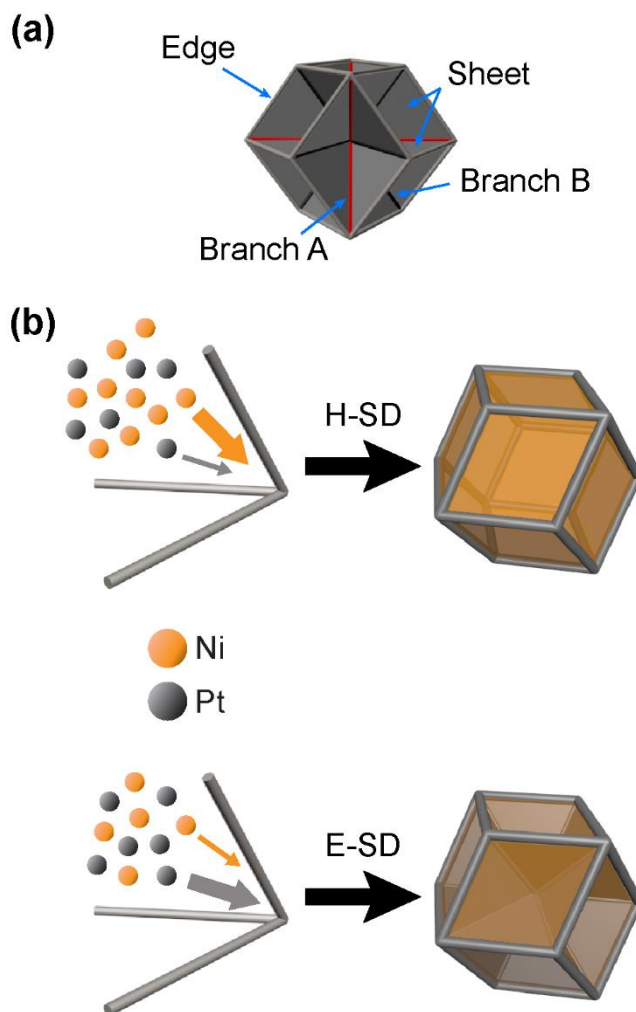


Figure S1. (a) Explanation of terminology used throughout this paper to describe the locations of the atoms. On its exterior, the rhombic dodecahedron has 24 *edges*. On its interior, it also has 6 *branches* of type A (red) and 8 *branches* of type B (black) that extend from the origin to each vertex. Branch A grows in the $\langle 100 \rangle$ direction while branch B grows in the $\langle 111 \rangle$ direction. There are 24 triangular *sheets* whose sides are made up of one branch A, one branch B, and one edge. (b) The previously elucidated synthetic mechanism for the formation of Pt-Ni rhombic dodecahedra suggests that solid dodecahedra (H-SD), which can be etched into hollow nanoframes (H-NF), are formed by Ni deposition that is favored (indicated by thick orange arrow) between branch sites.⁵ Therefore, after lowering the Ni precursor concentration, Pt deposition became more favorable (indicated by thick gray arrow), leading to solid dodecahedra (E-SD) that can be etched into excavated nanoframes (E-NF). Eleven of the fourteen branches have been left out of the scheme for clarity. In the models, orange represents Ni-rich regions and gray represents Pt-rich regions.

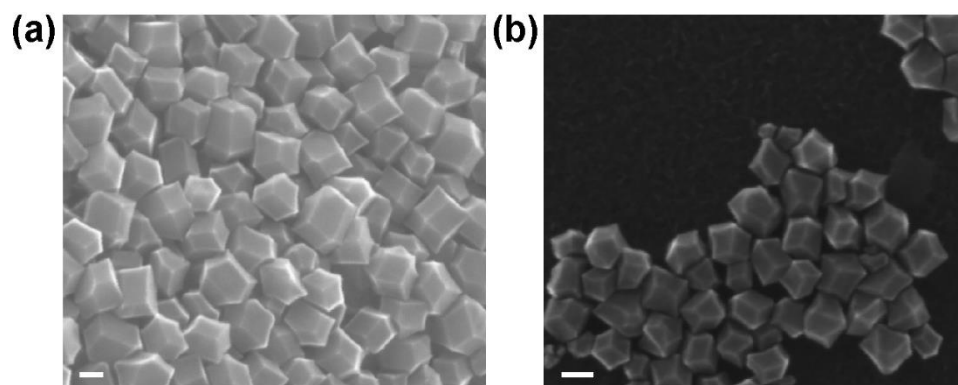


Figure S2. SEM images of solid rhombic dodecahedral precursors to (a) hollow nanoframe and (b) excavated nanoframe. The solid precursors to the nanoframes were named H-SD and E-SD, respectively. Scale bars represent 30 nm.

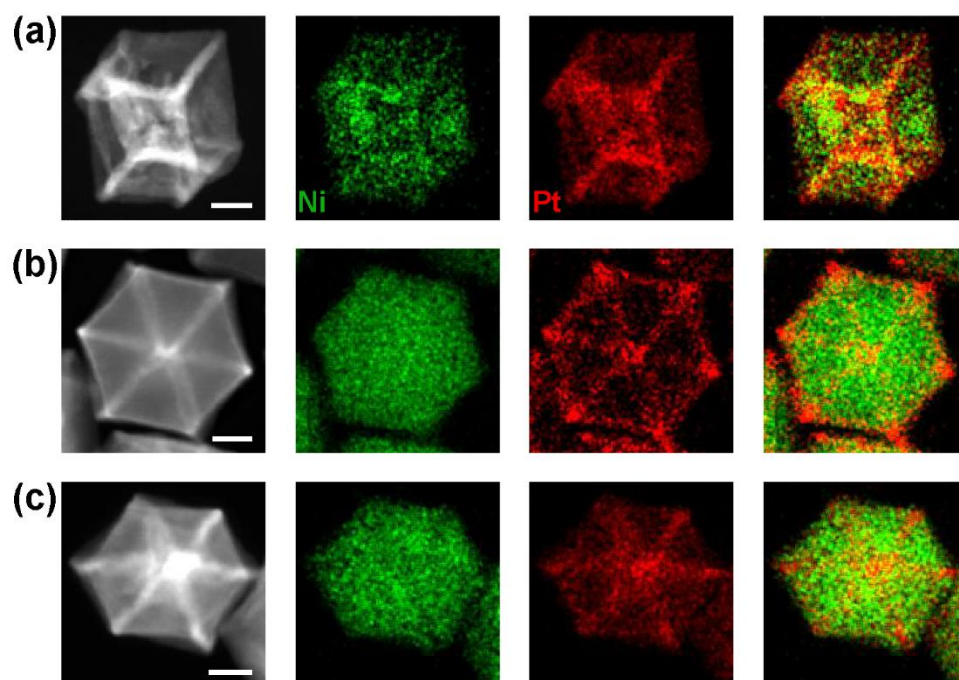


Figure S3. STEM-HAADF and EDS mapping of (a) E-NF, oriented in the $\langle 110 \rangle$ direction, and (b) H-SD and (c) E-SD, both oriented in the $\langle 111 \rangle$ direction. Scale bars represent 10 nm.

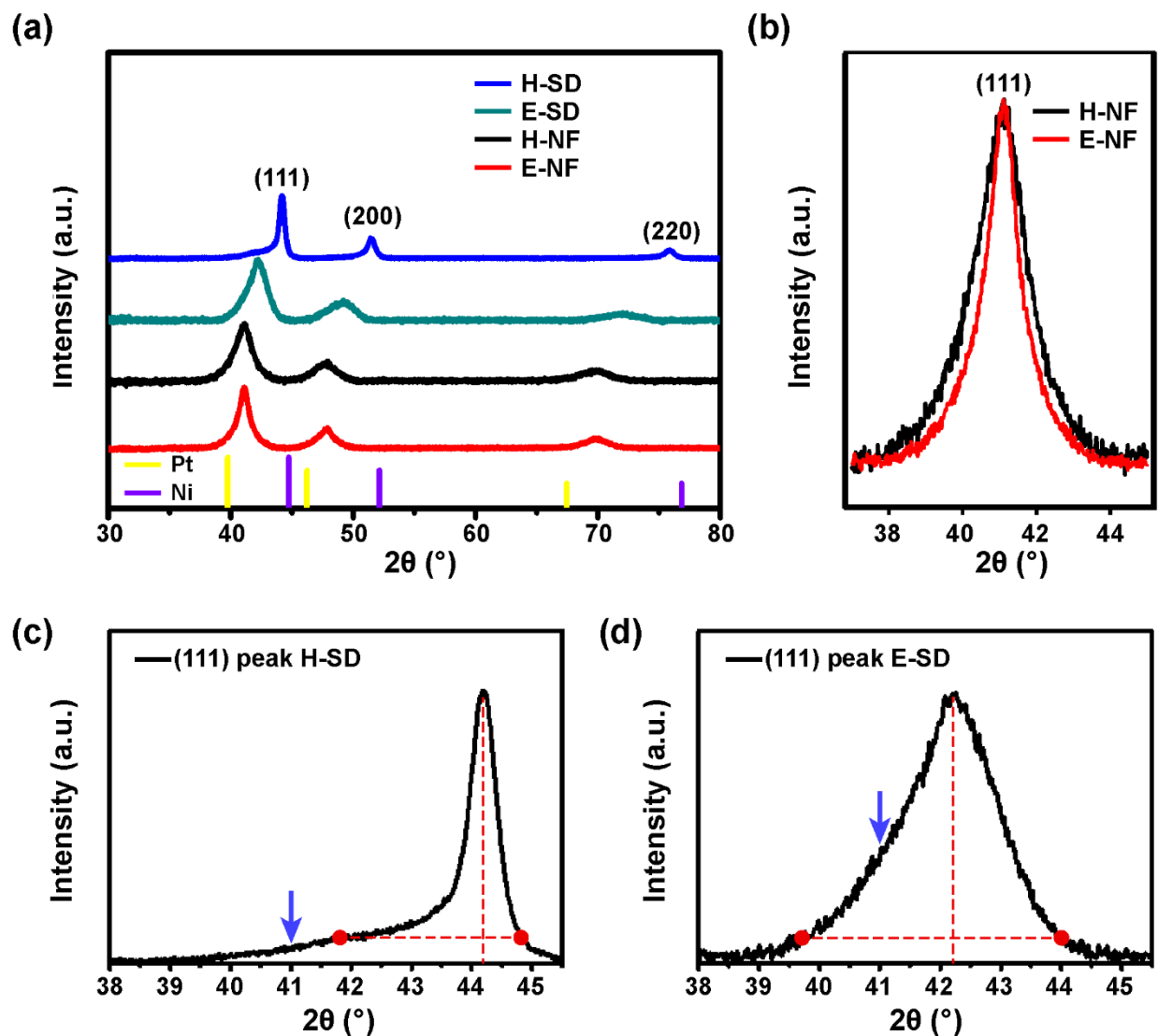


Figure S4. (a) XRD patterns for H-SD, E-SD, H-NF, and E-NF. (b) Magnified and overlapped (111) peak of H-NF and E-NF showing larger FWHM for H-NF. Magnified asymmetry of the (111) peak for (c) H-SD and (d) E-SD. Red dashed lines are a guide to indicate the degree of asymmetry of each peak. The blue arrows in (c) and (d) correspond to the position of the (111) peak of NFs, which is the diffraction contribution from the Pt-rich phase in the SD samples. In addition to the (111) peak position of E-SD being at lower 2θ than that of H-SD, the intensity at the position of the blue arrow is much larger in E-SD, indicating a larger fraction of the Pt-rich phase.

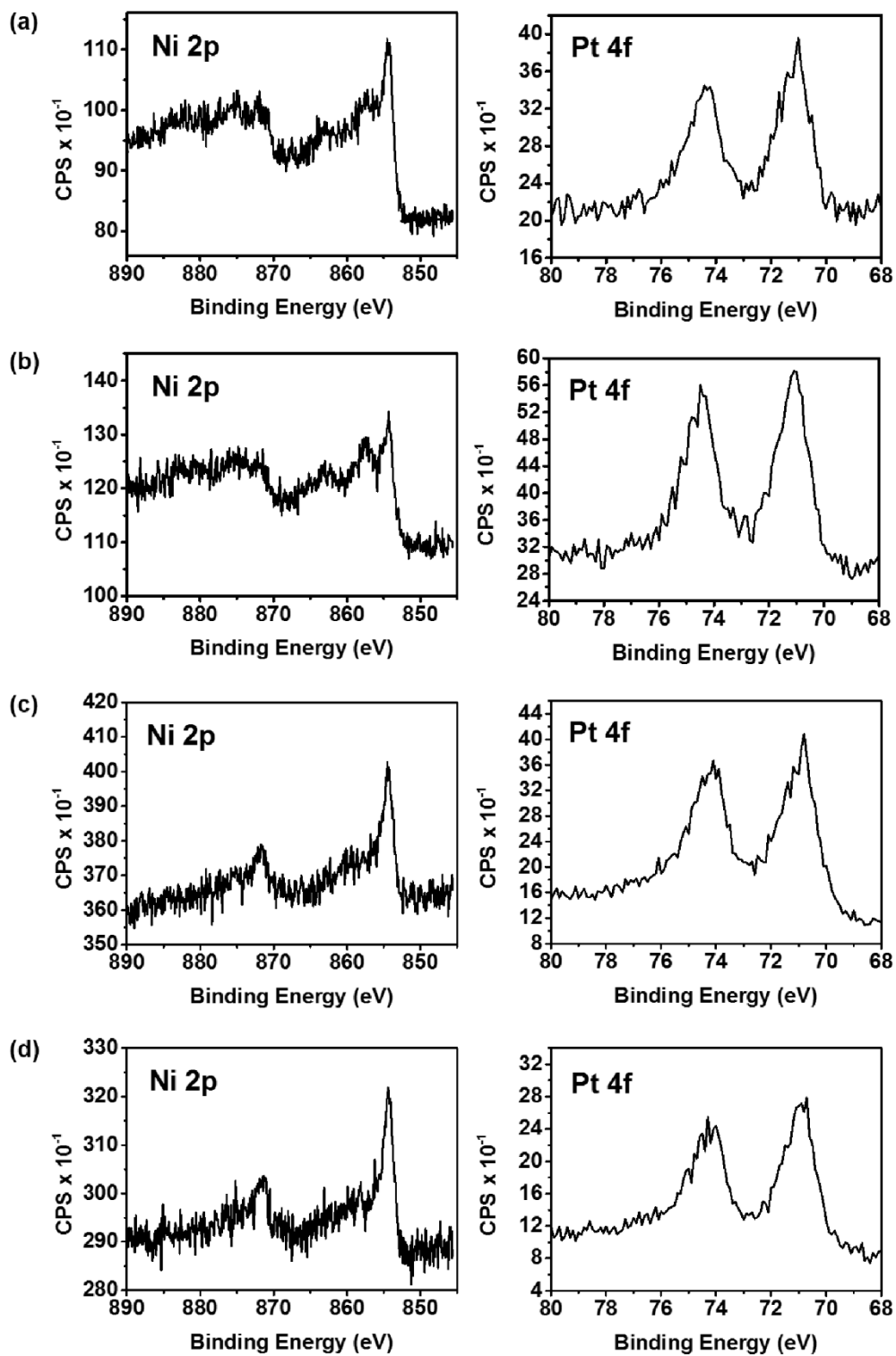


Figure S5. XPS spectra of the Ni 2p and Pt 4f core levels for (a) H-SD, (b) E-SD, (c) H-NF, and (d) E-NF.

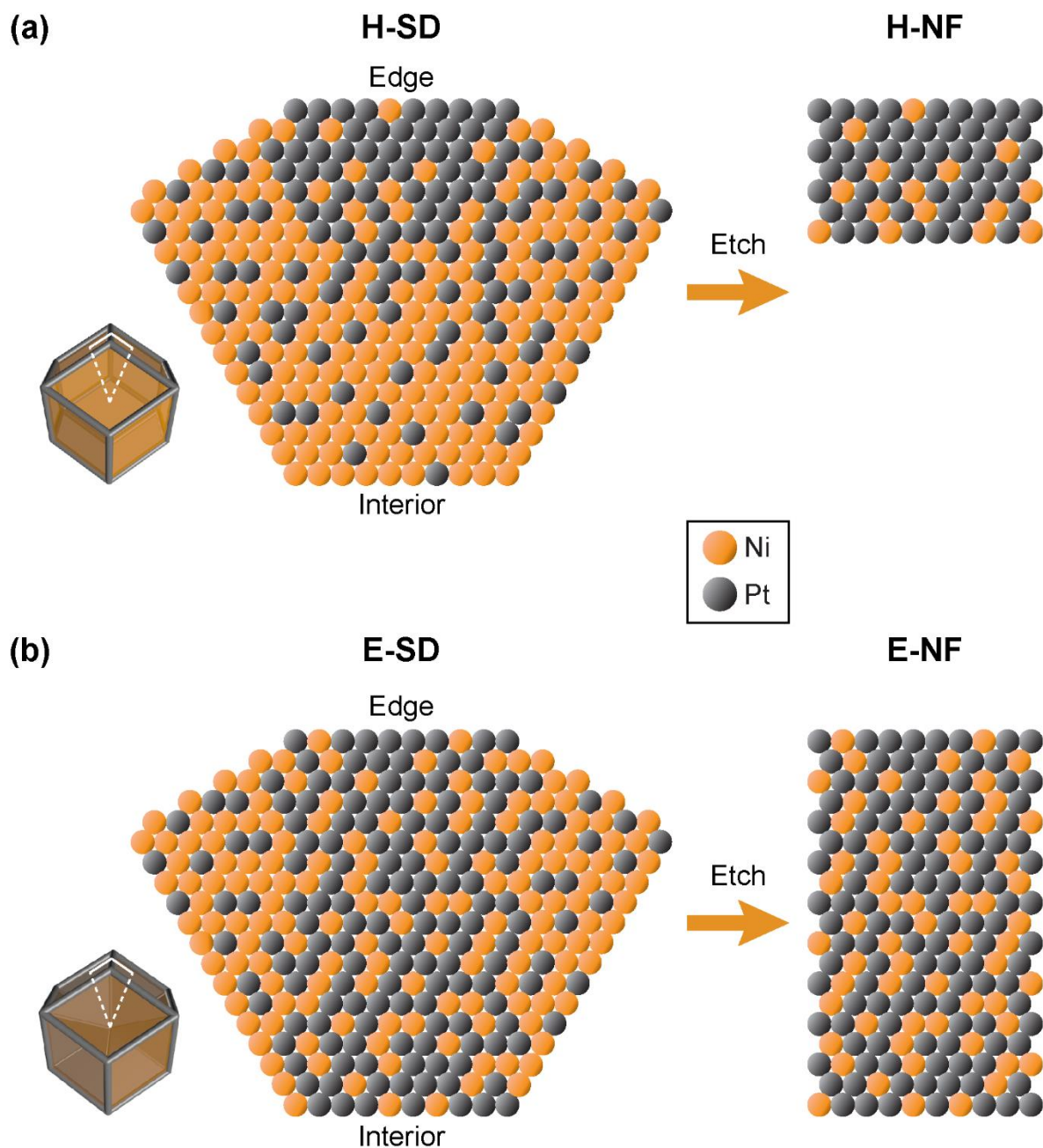


Figure S6. Schematic diagram of atomic compositional gradient for (a) H-SD and (b) E-SD and their chemical etching into NFs. White border in three-dimensional SD models indicates cross-section of SD that is atomically modeled in two dimensions. In the 3-D models, orange represents Ni-rich regions and gray represents Pt-rich regions.

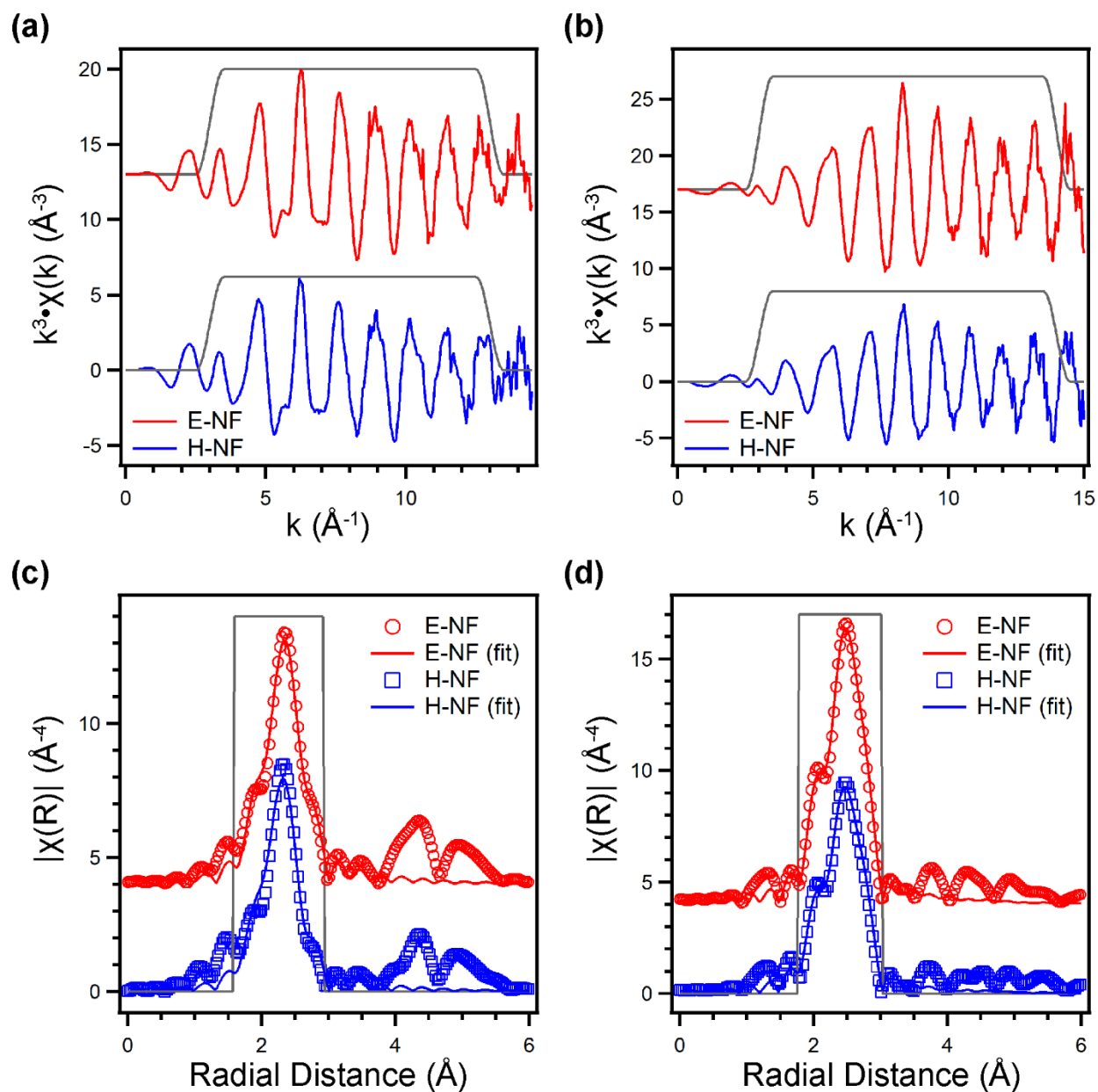


Figure S7. EXAFS $\chi(k)$ data at the (a) Ni K -edge and (b) Pt L_3 -edge for both H-NF and E-NF. Magnitude of Fourier transformed EXAFS spectra for R-space plots at the (c) Ni K -edge and (d) Pt L_3 -edge. All plots show either k -space or R-space fitting windows in gray, which were applied during co-fits of the Ni and Pt edges for each sample.

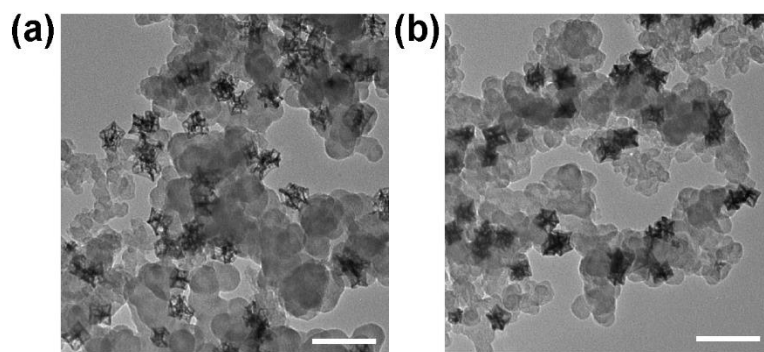


Figure S8. TEM images of (a) H-NF and (b) E-NF after loading on carbon. Scale bars represent 100 nm.

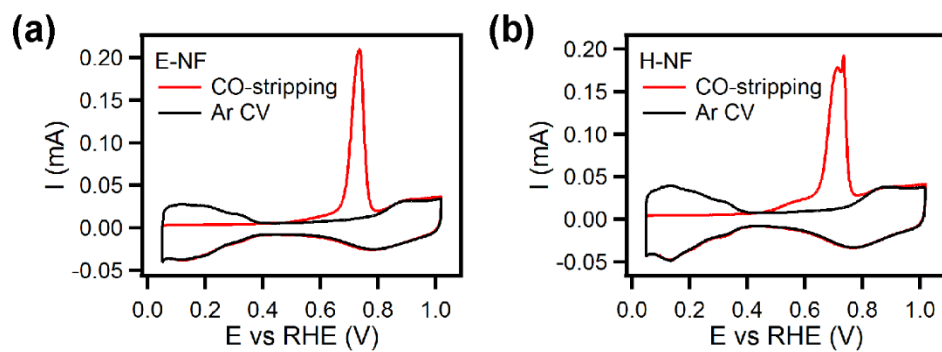


Figure S9. Representative CO-stripping and hydrogen underpotential deposition measurements for (a) E-NF and (b) H-NF recorded at room temperature in Ar-saturated 0.1 M HClO_4 solution with a sweep rate of 50 mV/s. CO-stripping measurement is recorded after catalyst is poisoned with CO, and excess CO is purged by Ar. Both E-NF and H-NF exhibited ratios of $\text{ECSA}_{\text{CO}}/\text{ECSA}_{\text{Hupd}} = 1.03$, indicating no Pt-skin formation.⁶

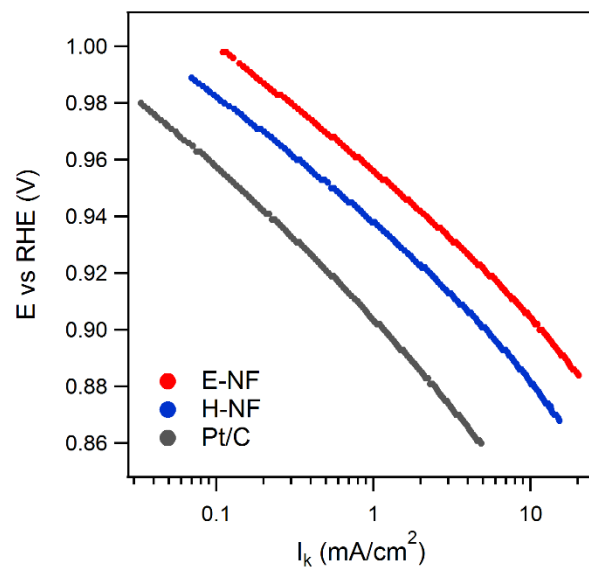


Figure S10. Tafel plot of kinetic current density normalized by ECSA determined by H_{upd} for E-NF (red), H-NF (blue), and Pt/C commercial catalyst (gray).

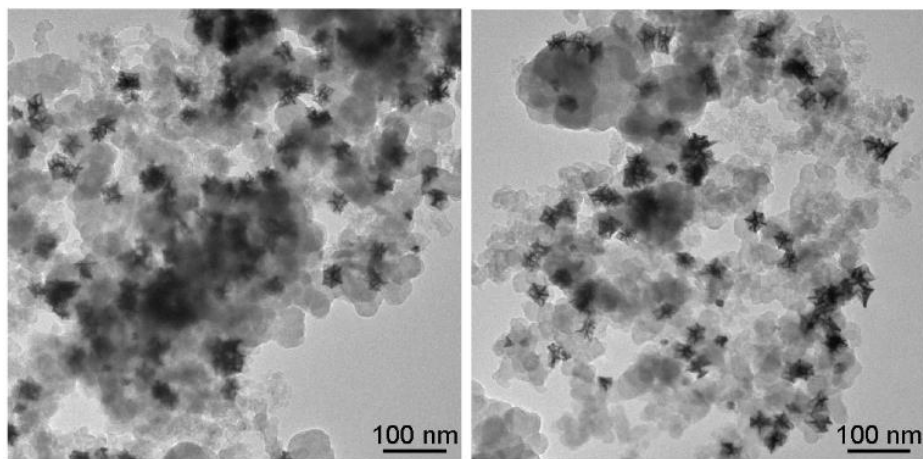


Figure S11. Two examples of E-NF after electrochemical ORR test demonstrating that the morphology of the thin sheet structure is maintained within the nanoframe.

Table S1. EXAFS fitting results for co-fits to the Pt L_3 -edge and Ni K -edge for both H-NF and E-NF samples.

	H-NF	E-NF
R_{PtNi}	2.63 (1)	2.63 (1)
R_{PtPt}	2.70 (1)	2.71 (1)
R_{NiPt}	2.63 (1)	2.63 (1)
R_{NiNi}	2.61 (1)	2.61 (1)
σ_{PtNi}^2	0.0073 (22)	0.0066 (13)
σ_{PtPt}^2	0.0074 (12)	0.0065 (8)
σ_{NiPt}^2	0.0073 (22)	0.0066 (13)
σ_{NiNi}^2	0.0159 (32)	0.0144 (23)
N_{PtNi}	2.0 (8)	2.7 (6)
N_{PtPt}	7.4 (1.8)	7.9 (1.4)
$N_{Pt,total}$	9.4 (2.6)	10.6 (2.0)
N_{NiPt}	3.0 (1.0)	3.6 (7)
N_{NiNi}	6.9 (1.9)	5.9 (1.2)
$N_{Ni,total}$	9.9 (2.9)	9.5 (1.9)
$\Delta E_{0,Pt}$	5.9 (1.2)	6.8 (8)
$\Delta E_{0,Ni}$	3.2 (1.0)	3.9 (7)
R-factor	0.0095	0.0044
Red. χ^2	298	123
J_{Pt}	64%	73%
J_{Ni}	45%	58%

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