Anisotropic phase segregation and migration of Pt in nanocrystals en route to nanoframe catalysts

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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 L_3 -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 Artemis¹. 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 using multiple *k*-weight fitting (k^1 , k^2 , k^3). 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 atom². 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 the phase factor for a given coordination shell. These parameters are calculated through *ab initio* methods using FEFF6 as embedded in Artemis and Atoms.

As mentioned in the main text, the Ni *K*-edge and Pt L_3 -edge were fit together for RD-3 and RD-10, using first shell paths generated from a FEFF6 model of a disordered Pt₁₀Ni₉₀ face-centered cubic solid solution. The Pt₁₀Ni₉₀ disordered face-centered cubic model was generated by creating a Ni face-centered cubic lattice and randomly substituting Pt atoms at 10% of the lattice positions. The Pt atoms were distributed evenly throughout the various coordination shells and the lattice constant was the same as determined

from XRD. No multiple shell fitting was performed, so all paths mentioned in the following discussion are first shell, single scattering paths. The Pt-Pt path was omitted due to the dilution of Pt in the $Pt_{10}Ni_{90}$ phase which lowered the frequency of Pt-Pt bonding. If the Pt-Pt path was included, the fit could not converge on physically reasonable values for the variables. However, it is obvious from the ~2% misfit to both RD-3 and RD-10 EXAFS data (Table S1) and the slight asymmetry of the first shell peak towards larger R in Supplementary Fig. 8b, d that the model could be improved by using a linear combination of the Pt₁₀Ni₉₀ phase and a Pt-rich phase. This is not possible because the number of independent data points limits the number of variables which can be used to model the EXAFS data. The following restraints were also applied for the co-fit of RD-3 and RD-10³:

$$R_{NiPt} = R_{PtNi}$$
 $\sigma^2_{NiPt} = \sigma^2_{PtNi}$ $N_{PtNi} = (x_{Ni}/x_{Pt}) \times N_{NiPt}$

Again, as mentioned in the main text, RD-30 was co-fit using paths generated from a Pt₂₅Ni₇₅ FEFF file created in a similar manner to the Pt₁₀Ni₉₀ model. RD-30 was fit with similar constraints as listed above for RD-3 and RD-10. However, the Pt-Pt scattering path was able to be included in a successful fit to RD-30, unlike in the fits to RD-3 and RD-10, due to the increased frequency of Pt-Pt bonding in RD-30. The method of Hwang et al was then used to calculate extent of alloying parameters, J_{Ni} and J_{Pt}^4 . See Table S1 for the results of the co-fits to the Ni *K*-edges and Pt L_3 -edges of RD-3, RD-10, and RD-30 and the extent of alloying parameters.



Supplementary Figure 1.

HRTEM images of interim ill-defined branch products collected when the growth solution is yellow. The growth directions of the short arms in these branch structures are identified as <111> and <200>, regardless of the particle sizes. Insets in **a** and **c**, as well as the right panel of **b** show the corresponding FFTs. Most branch particles are single crystals, while some have grain boundaries as shown in **b**. Step sites are observed at the bottom of the short arms as indicated by black arrows in **b** and **c**.



Supplementary Figure 2.

Size distributions of solid Pt-Ni rhombic dodecahedra and chemically-corroded products. (a) Histograms of size distributions of RD-3, RD-10, and RD-30. (b) Histograms of axis or edge thickness distributions of RD-3-cor, RD-10-cor, and RD-30-cor.



Supplementary Figure 3.

TEM images of corroded products of RD-3 with different magnifications. Low-magnification image illustrates that the uniformity of the product is maintained after chemical-corrosion. High-magnification image illustrates the many projections possible for a tetradecapod.



Supplementary Figure 4.

Geometric model of rhombic dodecahedron. The differences between the identifiers used in the main text are indicated: *axis*, *edge*, two types of *vertex* and *origin* are labeled.



Supplementary Figure 5.

In-depth examination of tetradecapod geometry. (**a**–**c**) TEM images of the RD-3-cor tetradecapod with typical projections that are similar to the geometrical models to their right. (**d**) HRTEM image of a typical tetradecapod viewed along [111] zone axis. The growth directions of the marked two arms are along <1-11> and <200> as indicated by corresponding FFTs (**e**, **f**). The structure is in perfect agreement with the geometrical model (**b**, right). Scale bars in a–c are 5 nm.



Supplementary Figure 6.

Change in surface composition proven by X-ray photoelectron spectroscopy. Raw XPS spectra of Ni 2p (**left column**) and Pt 4f (**right column**) core levels for RD-3, RD-10, and RD-30.



Supplementary Figure 7.

Progression of phase segregation over time in Pt-Ni rhombic dodecahedra. Time-resolved powder XRD patterns of samples stopped at finer time resolution, clearly showing the progression of the diffraction patterns from asymmetric peaks to split peaks and the change in peak intensity ratios.



Supplementary Figure 8.

EXAFS results for Pt-Ni rhombic dodecahedra. Ni *K*-edge (left column) and Pt L_3 -edge (right column) EXAFS spectra and fits to the first coordination shell (**a**–**f**). Numerical results of each fit are displayed in Table S1. Raw k³-weighted χ (k) EXAFS spectra for Ni *K*-edge (**g**) and Pt L_3 -edge (**h**) for Pt-Ni rhombic dodecahedra. The ΔR fitting windows are indicated on the plots and the Δk fitting windows were 2-14 Å⁻¹ for the Ni *K*-edge and 2-12 Å⁻¹ for the Pt L_3 -edge.



Supplementary Figure 9.

Intermediate three-dimensional structures between tetradecapod and nanoframe. (a) Schematic illustration of phase migration from RD-3 to RD-10 via an intermediate structure with Pt-rich phase segregated on both axes and edges. TEM images of products (b) stopped between RD-3 and RD-10 and the corresponding products after chemical corrosion (c). The corroded structures show Pt-rich phase co-exists on both axes and edges.



Supplementary Figure 10.

Ex situ annealing converts RD-3 into "RD-10-like" dodecahedron. TEM images of RD-3 (a) and corresponding RD-3-cor (b), as well as RD-3 after *ex situ* annealing (c) and corresponding corroded product (d). The two distinct pathways are 1) $\mathbf{a} \rightarrow \mathbf{b}$ or 2) $\mathbf{a} \rightarrow \mathbf{c} \rightarrow \mathbf{d}$.



Supplementary Figure 11.

Oxygen reduction activity of tetradecapods and nanoframes. Hydrogen underpotential deposition cyclic voltammograms (**a**) performed in Ar-saturated 0.1 M HClO₄ at 50 mV/s. Rotating disk electrode oxygen reduction curves (**b**) collected in O₂-saturated 0.1 M HClO₄ at 20 mV/s with a rotation rate of 1600 rpm. Specific activity (**c**) and mass activity (**d**) of tetradecapods and nanoframes compared to commercial Pt/C. All Pt-Ni catalysts had a CO_{ad} :H_{upd} = 1.0, where CO_{ad} and H_{upd} represent the electrochemical surface area calculated from the CO-stripping and hydrogen underpotential deposition techniques, repsectively.⁵ Specific surface area measurements were determined to be 54.4 m²/g_{Pt} (RD-3), 53.0 m²/g_{Pt} (RD-10), and 50.4 m²/g_{Pt} (RD-30).

	RD-3 (co-fit)	RD-10 (co-fit)	RD-30 (co-fit)
$\Delta E_{0,Ni}$	6.0 (0.9)	6.1 (0.8)	5.8 (0.6)
$\Delta E_{0,Pt}$	7.5 (2.0)	7.3 (1.8)	8.5 (1.2)
N _{NiNi}	7.8 (1.0)	7.2 (0.8)	7.1 (0.6)
N _{NiPt}	1.1 (0.2)	1.1 (0.2)	1.6 (0.3)
N _{PtNi}	9.7 (1.8)	10.0 (1.8)	4.7 (0.9)
N _{PtPt}	-	-	5.9 (1.5)
R _{NiNi}	2.50 (1)	2.50(1)	2.50(1)
R _{NiPt}	2.57 (1)	2.57 (1)	2.59 (1)
R _{PtNi}	2.57 (1)	2.57 (1)	2.59 (1)
R _{PtPt}	-	-	2.72 (1)
σ² _{NiNi}	0.0070 (11)	0.0065 (10)	0.0070 (10)
σ^2_{NiPt}	0.0082 (15)	0.0081 (13)	0.0073 (16)
σ^2_{PtNi}	0.0082 (15)	0.0081 (13)	0.0073 (16)
σ^{2}_{PtPt}	-	-	0.0065 (17)
R-factor	2.5%	2.0%	0.7%
$\mathbf{J}_{\mathbf{N}\mathbf{i}}$	124%	133%	74%
\mathbf{J}_{Pt}	111%	111%	59%

Supplementary Table 1. EXAFS fitting parameters for RD-3, RD-10, and RD-30.

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