

Supporting Information for:

Atomic Structure of Pt₃Ni Nanoframe Electrocatalysts by *in Situ* X-ray Absorption Spectroscopy

Nigel Becknell¹, Yijin Kang², Chen Chen^{1†}, Joaquin Resasco³, Nikolay Kornienko¹, Jinghua Guo⁴, Nenad M. Markovic², Gabor A. Somorjai^{1,5}, Vojislav R. Stamenkovic², Peidong Yang^{1,5,6,*}

1 Department of Chemistry, University of California, Berkeley, Berkeley, California 94720, United States

2 Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439, United States

3 Department of Chemical Engineering, University of California, Berkeley, Berkeley, California 94720, United States

4 The Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

5 Materials Sciences Division, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, California 94720, United States

6 Kavli Energy Nanoscience Institute, Berkeley, California 94720, United States

† Department of Chemistry, Tsinghua University, Beijing 100084, P. R. China

*Correspondence to: p_yang@berkeley.edu

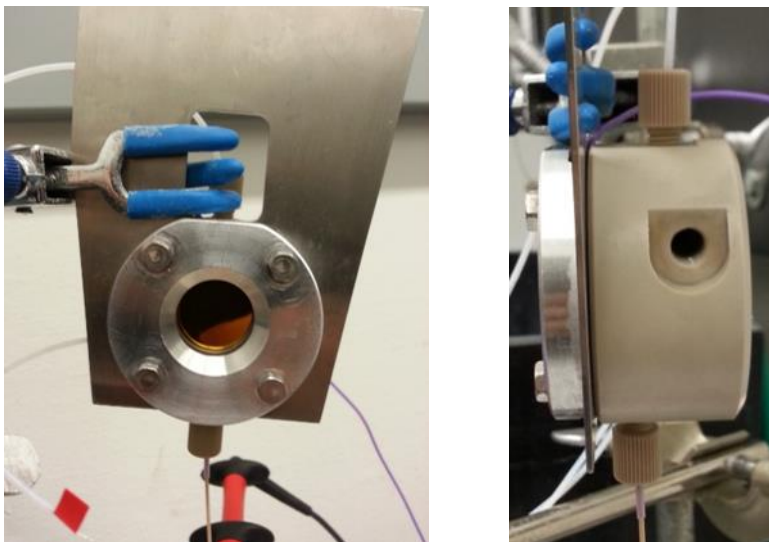


Figure S1. Front and side views of *in situ* electrochemical XAS cell. The bottom has a port for a Ag/AgCl reference electrode and the top has a port for a Pt wire counter electrode. Gas or liquid flow can be carried out through the side ports.

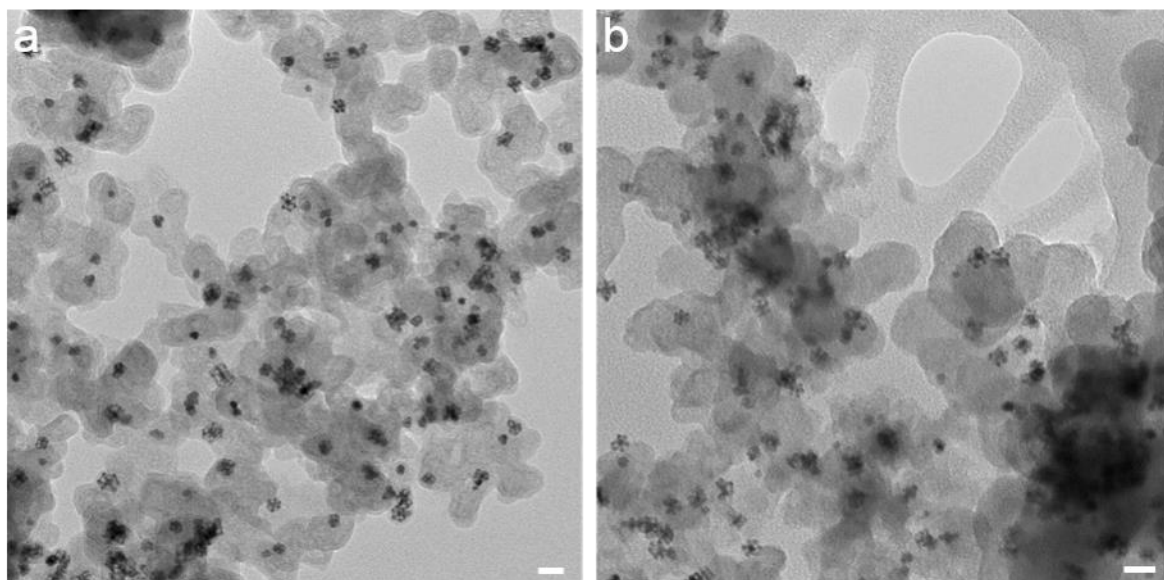


Figure S2. TEM images of (a) $\text{Pt}_3\text{Ni}(1.0)$ and (b) $\text{Pt}_3\text{Ni}(1.5)$. Scale bars = 25 nm.

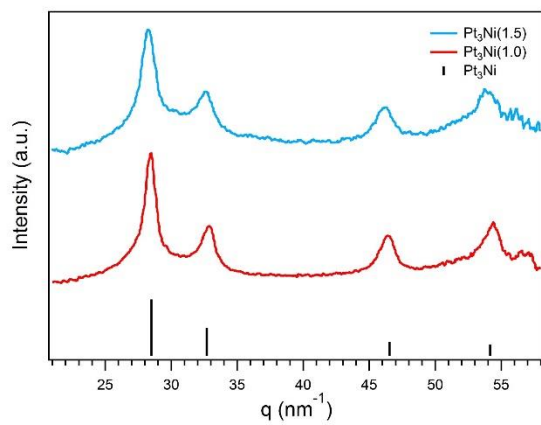


Figure S3. X-ray diffraction patterns of $\text{Pt}_3\text{Ni}(1.0)$ and $\text{Pt}_3\text{Ni}(1.5)$ as-prepared after annealing on carbon support.

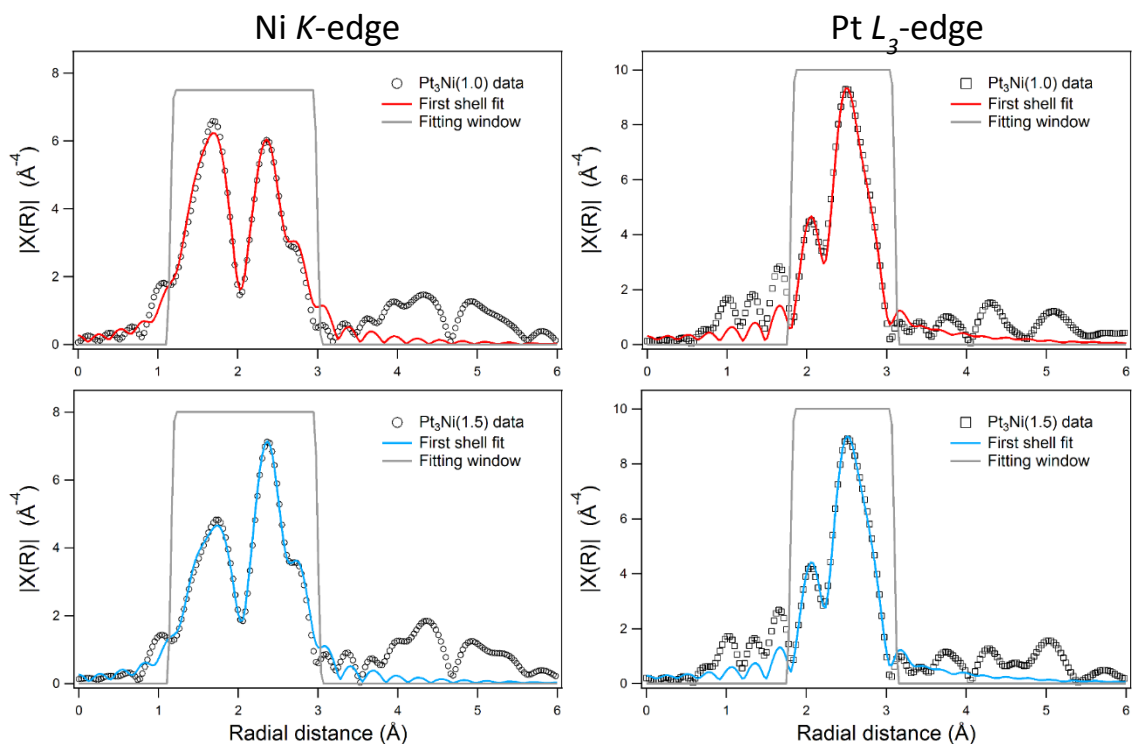


Figure S4. EXAFS fitting of first coordination shell for Ni *K*-edge and Pt *L*₃-edge data of the as-prepared nanoframe catalyst (after annealing and before electrochemistry). For Ni *K*-edge EXAFS, $\Delta k = 2-13 \text{ \AA}^{-1}$ and $\Delta R = 1.2-3 \text{ \AA}$. For Pt *L*₃-edge EXAFS, $\Delta k = 2-14 \text{ \AA}^{-1}$ and $\Delta R = 1.8-3.1 \text{ \AA}$.

Table S1. Fitting parameters from EXAFS fitting of as-prepared nanoframe catalysts

	N_{PtNi}	N_{NiPt}	N_{PtPt}	N_{NiNi}	N_{Pt}	N_{Ni}	R_{PtNi}	R_{PtPt}	R_{NiNi}	N_{NiO}	R_{NiO}
Pt ₃ Ni(1.0)	4.4 (1.7)	7.9 (1.5)	4.7 (1.5)	0.7 (0.4)	9.1 (3.2)	8.6 (1.9)	2.661 (0.023)	2.710 (0.010)	2.637 (0.015)	4.8 (0.5)	2.050 (0.008)
Pt ₃ Ni(1.5)	3.1 (1.3)	7.9 (1.4)	5.0 (1.3)	1.0 (0.6)	8.1 (2.6)	8.9 (2.0)	2.664 (0.019)	2.720 (0.010)	2.646 (0.015)	3.4 (0.5)	2.051 (0.010)

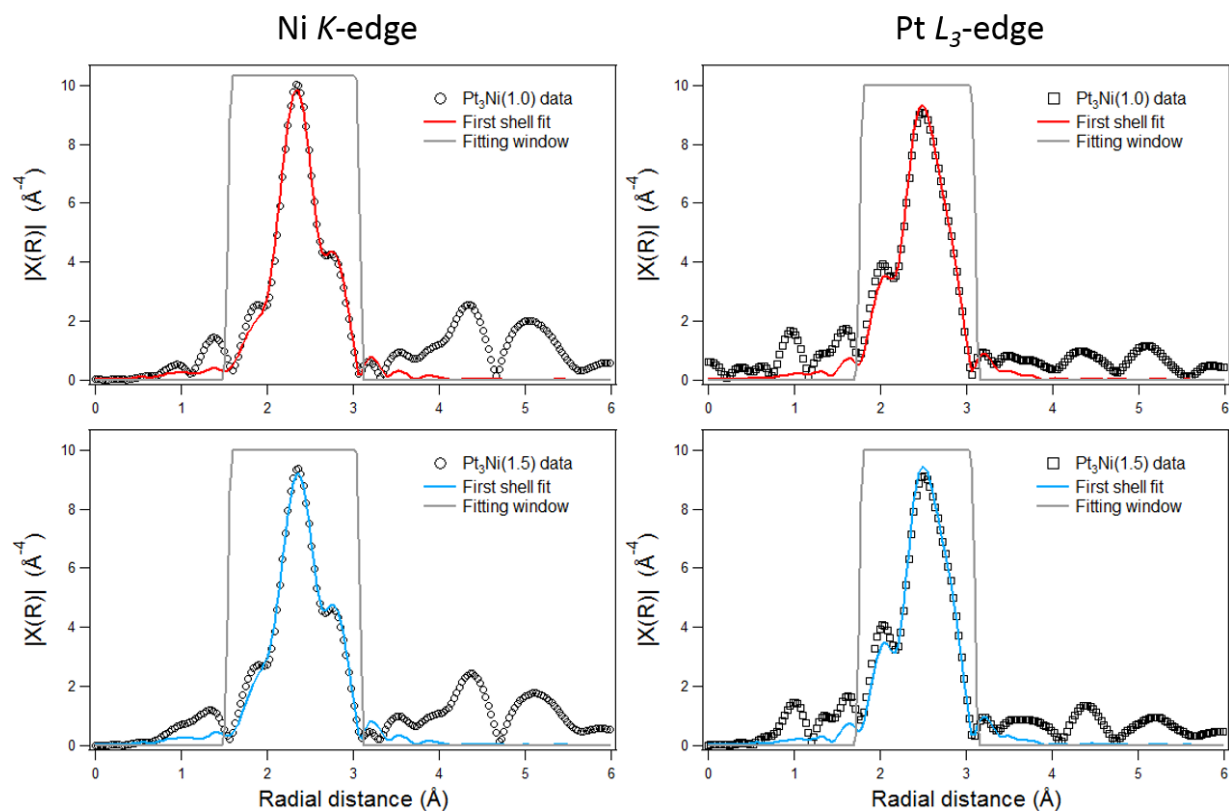


Figure S5. EXAFS fitting of first coordination shell for Ni *K*-edge and Pt *L*₃-edge data of the nanoframe catalyst after electrochemistry (rinsed with DI water and dried under N₂). For Ni *K*-edge EXAFS, $\Delta k = 2$ - 12 \AA^{-1} and $\Delta R = 1.5$ - 3.1 \AA . For Pt *L*₃-edge EXAFS, $\Delta k = 2$ - 13.5 \AA^{-1} and $\Delta R = 1.8$ - 3.1 \AA .

Table S2. Fitting parameters from EXAFS fitting of nanoframe catalyst after electrochemistry

	N_{PtNi}	N_{NiPt}	N_{PtPt}	N_{NiNi}	N_{Pt}	N_{Ni}	R_{PtNi}	R_{PtPt}	R_{NiNi}	$J_{\text{Pt}} (\%)$	$J_{\text{Ni}} (\%)$
Pt ₃ Ni(1.0)	2.1 (0.7)	5.7 (1.0)	5.6 (1.0)	4.1 (1.0)	7.7 (1.7)	9.8 (2.0)	2.660 (0.008)	2.715 (0.008)	2.651 (0.009)	109	77
Pt ₃ Ni(1.5)	1.6 (0.7)	5.5 (1.3)	6.3 (1.2)	4.4 (1.2)	7.9 (1.9)	9.9 (2.5)	2.671 (0.007)	2.725 (0.010)	2.659 (0.010)	79	74

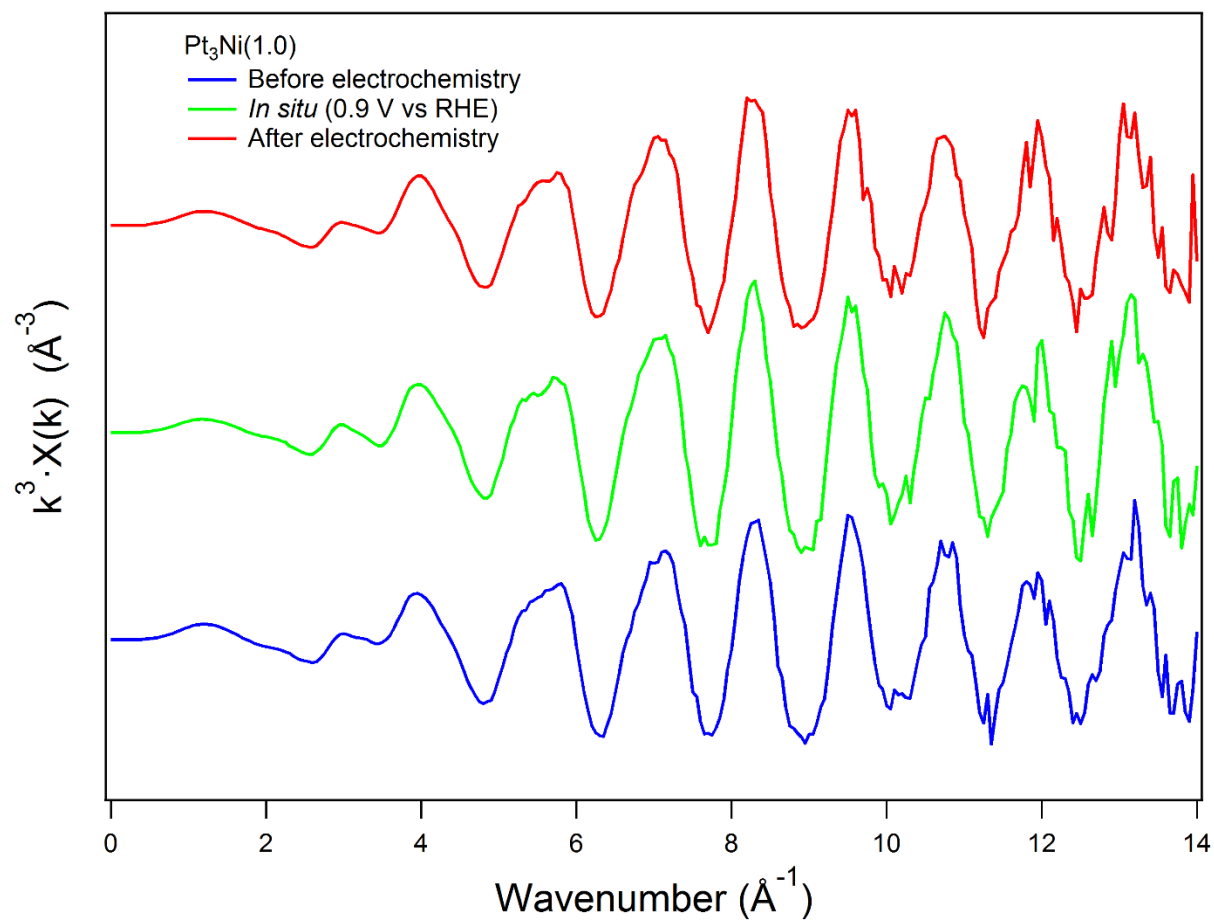


Figure S6. Raw k^3 -weighted $\chi(k)$ EXAFS spectra for Pt L₃-edge of Pt₃Ni(1.0) in three conditions; before, during, and after the oxygen reduction reaction.

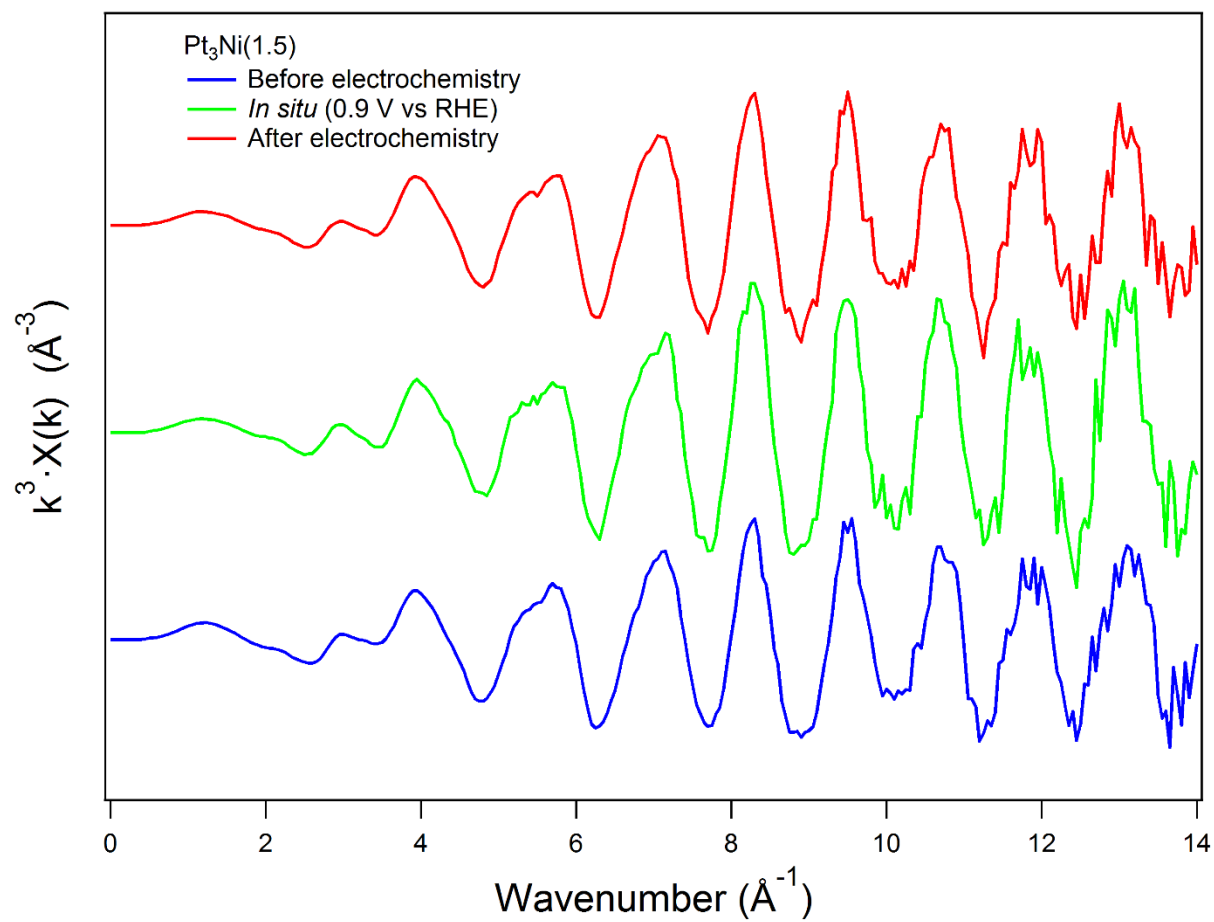


Figure S7. Raw k^3 -weighted $\chi(k)$ EXAFS spectra for Pt L₃-edge of Pt₃Ni(1.5) in three conditions; before, during, and after the oxygen reduction reaction.