

Supporting Information for:

## Atomic Structure of Pt<sub>3</sub>Ni Nanoframe Electrocatalysts by *in Situ* X-ray Absorption Spectroscopy

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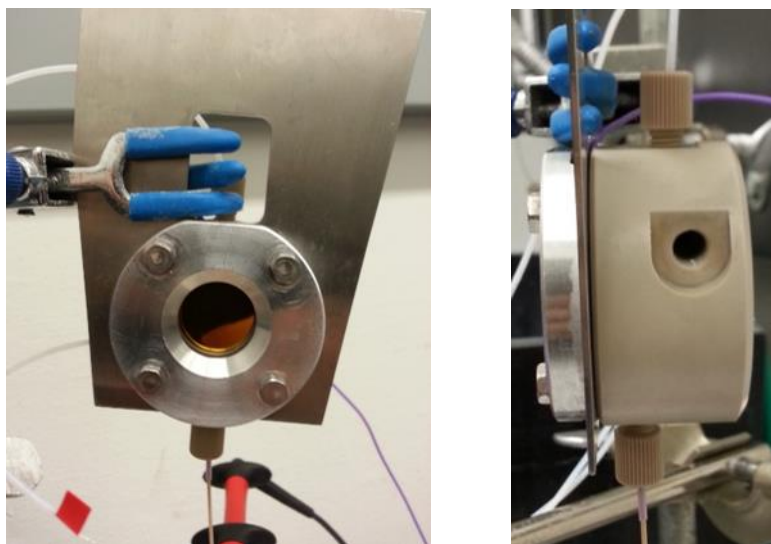


Figure S1. Front and side views of *in situ* electrochemical XAS cell. The bottom has a port for a Ag/AgCl reference electrode and the top has a port for a Pt wire counter electrode. Gas or liquid flow can be carried out through the side ports.

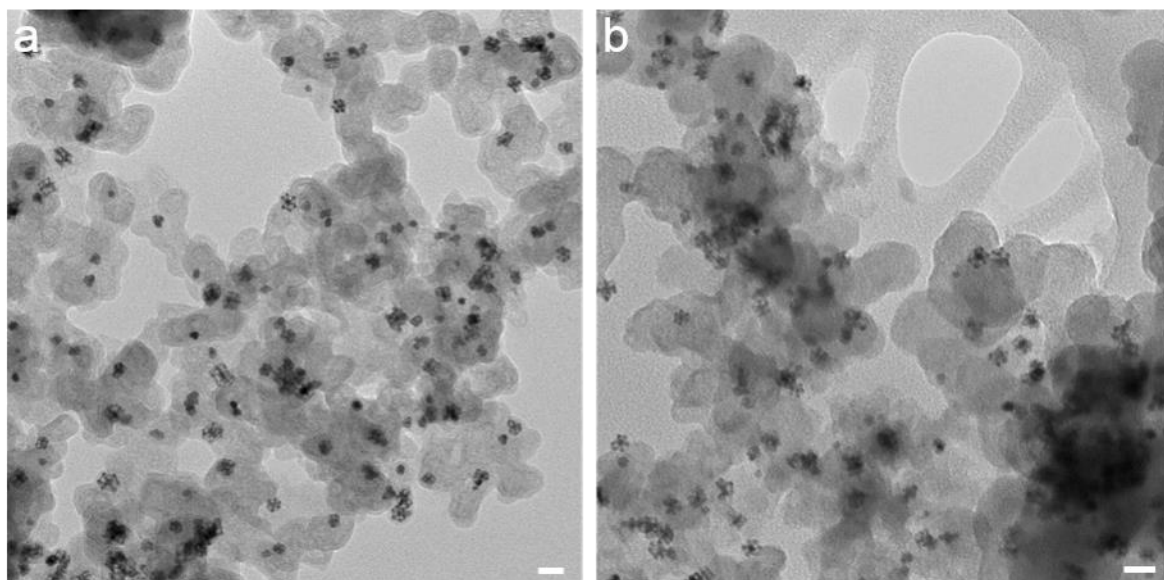


Figure S2. TEM images of (a)  $\text{Pt}_3\text{Ni}(1.0)$  and (b)  $\text{Pt}_3\text{Ni}(1.5)$ . Scale bars = 25 nm.

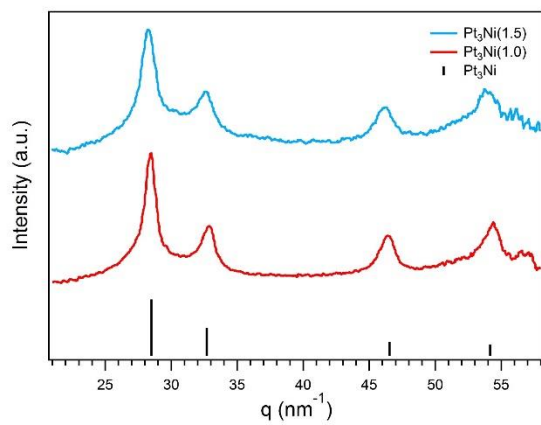


Figure S3. X-ray diffraction patterns of  $\text{Pt}_3\text{Ni}(1.0)$  and  $\text{Pt}_3\text{Ni}(1.5)$  as-prepared after annealing on carbon support.

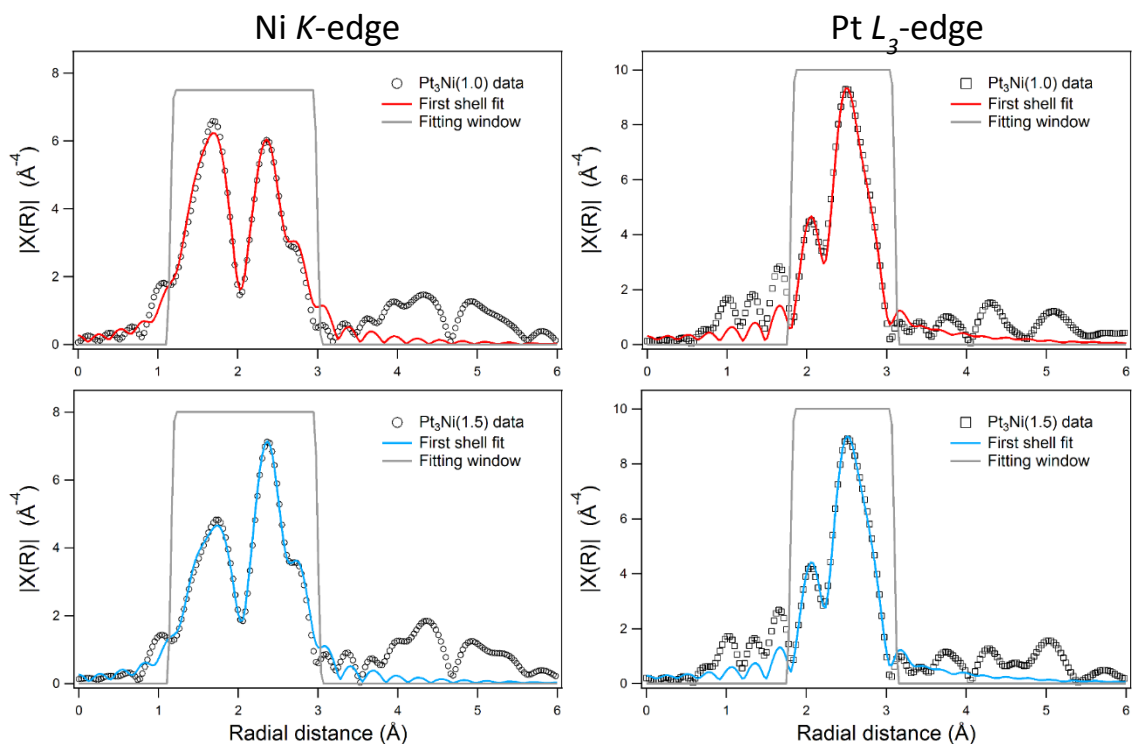


Figure S4. EXAFS fitting of first coordination shell for Ni *K*-edge and Pt *L*<sub>3</sub>-edge data of the as-prepared nanoframe catalyst (after annealing and before electrochemistry). For Ni *K*-edge EXAFS,  $\Delta k = 2-13 \text{ \AA}^{-1}$  and  $\Delta R = 1.2-3 \text{ \AA}$ . For Pt *L*<sub>3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

	$N_{\text{PtNi}}$	$N_{\text{NiPt}}$	$N_{\text{PtPt}}$	$N_{\text{NiNi}}$	$N_{\text{Pt}}$	$N_{\text{Ni}}$	$R_{\text{PtNi}}$	$R_{\text{PtPt}}$	$R_{\text{NiNi}}$	$N_{\text{NiO}}$	$R_{\text{NiO}}$
Pt <sub>3</sub> 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 <sub>3</sub> 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)

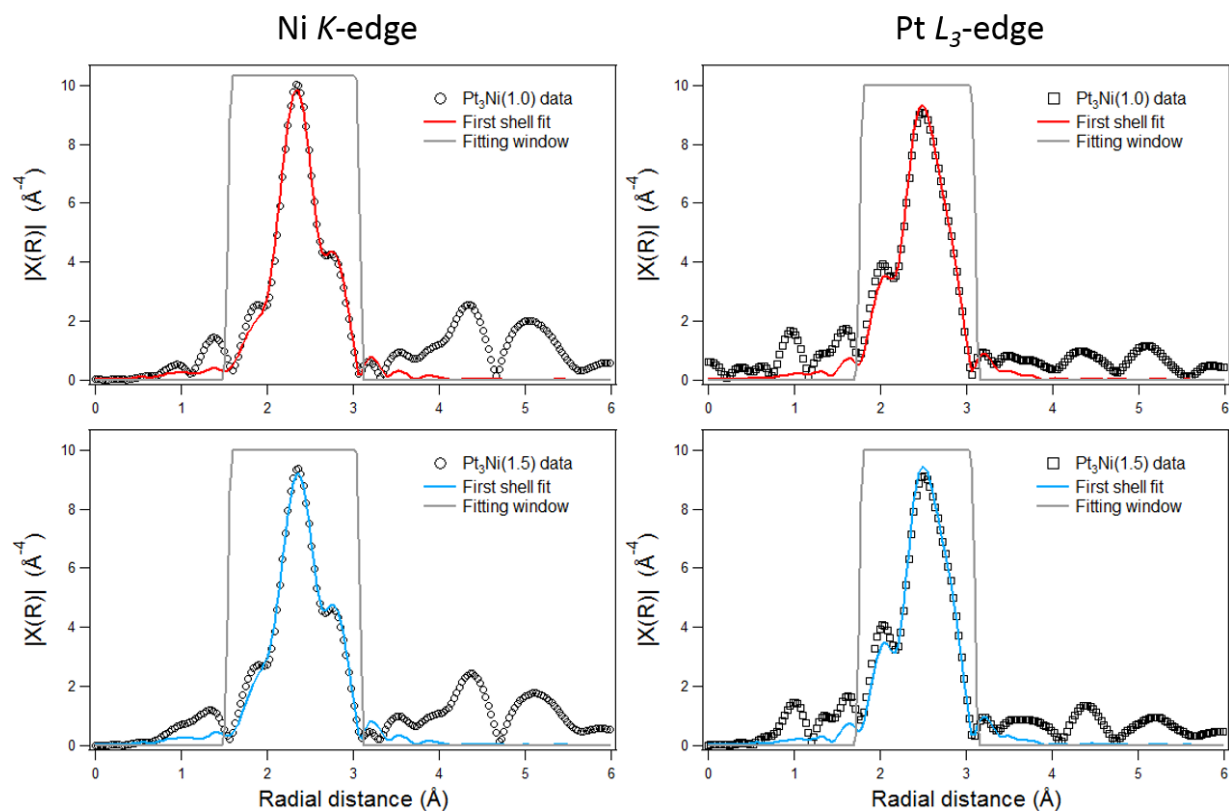


Figure S5. EXAFS fitting of first coordination shell for Ni *K*-edge and Pt *L*<sub>3</sub>-edge data of the nanoframe catalyst after electrochemistry (rinsed with DI water and dried under N<sub>2</sub>). For Ni *K*-edge EXAFS,  $\Delta k = 2$ - $12 \text{ \AA}^{-1}$  and  $\Delta R = 1.5$ - $3.1 \text{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

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

	$N_{\text{PtNi}}$	$N_{\text{NiPt}}$	$N_{\text{PtPt}}$	$N_{\text{NiNi}}$	$N_{\text{Pt}}$	$N_{\text{Ni}}$	$R_{\text{PtNi}}$	$R_{\text{PtPt}}$	$R_{\text{NiNi}}$	$J_{\text{Pt}} (\%)$	$J_{\text{Ni}} (\%)$
Pt <sub>3</sub> 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 <sub>3</sub> 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

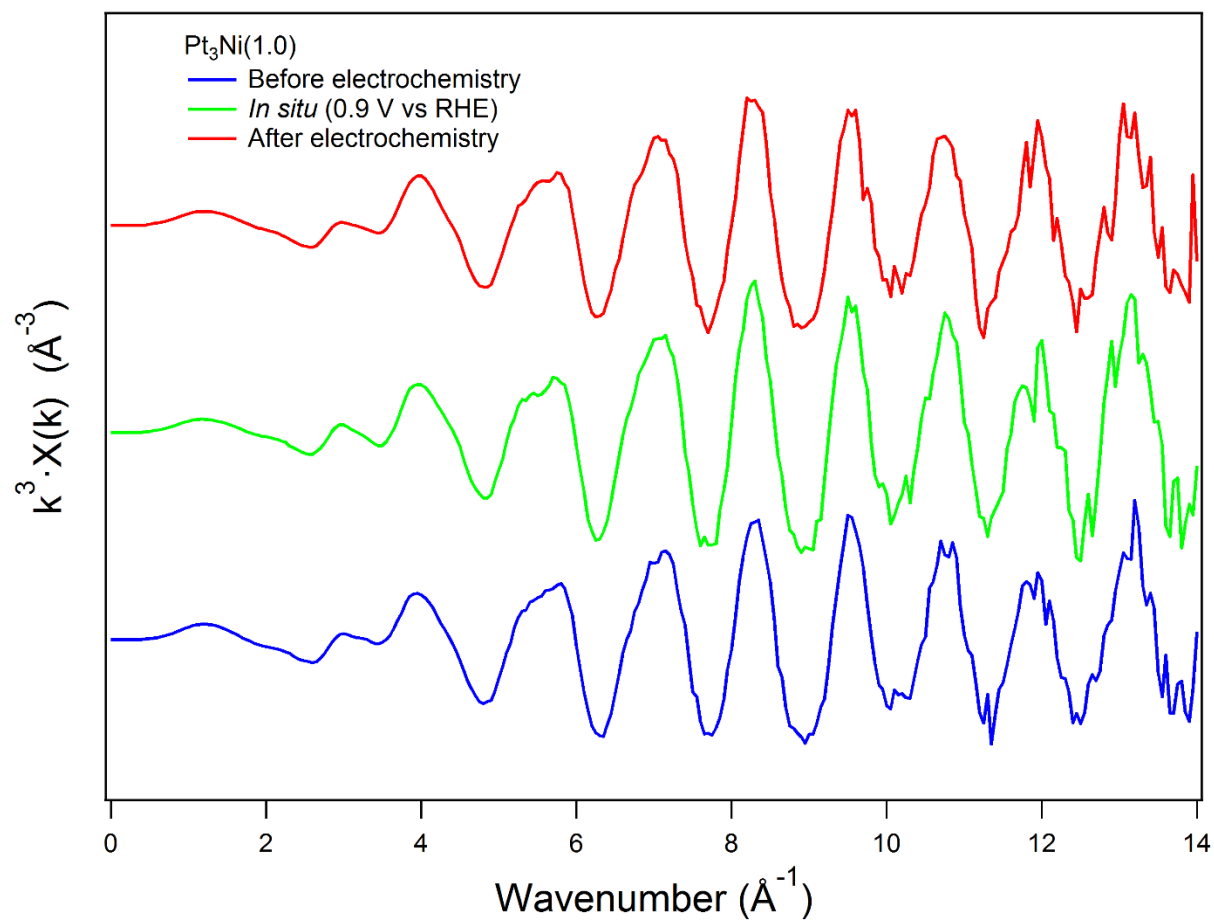


Figure S6. Raw  $k^3$ -weighted  $\chi(k)$  EXAFS spectra for Pt L<sub>3</sub>-edge of Pt<sub>3</sub>Ni(1.0) in three conditions; before, during, and after the oxygen reduction reaction.

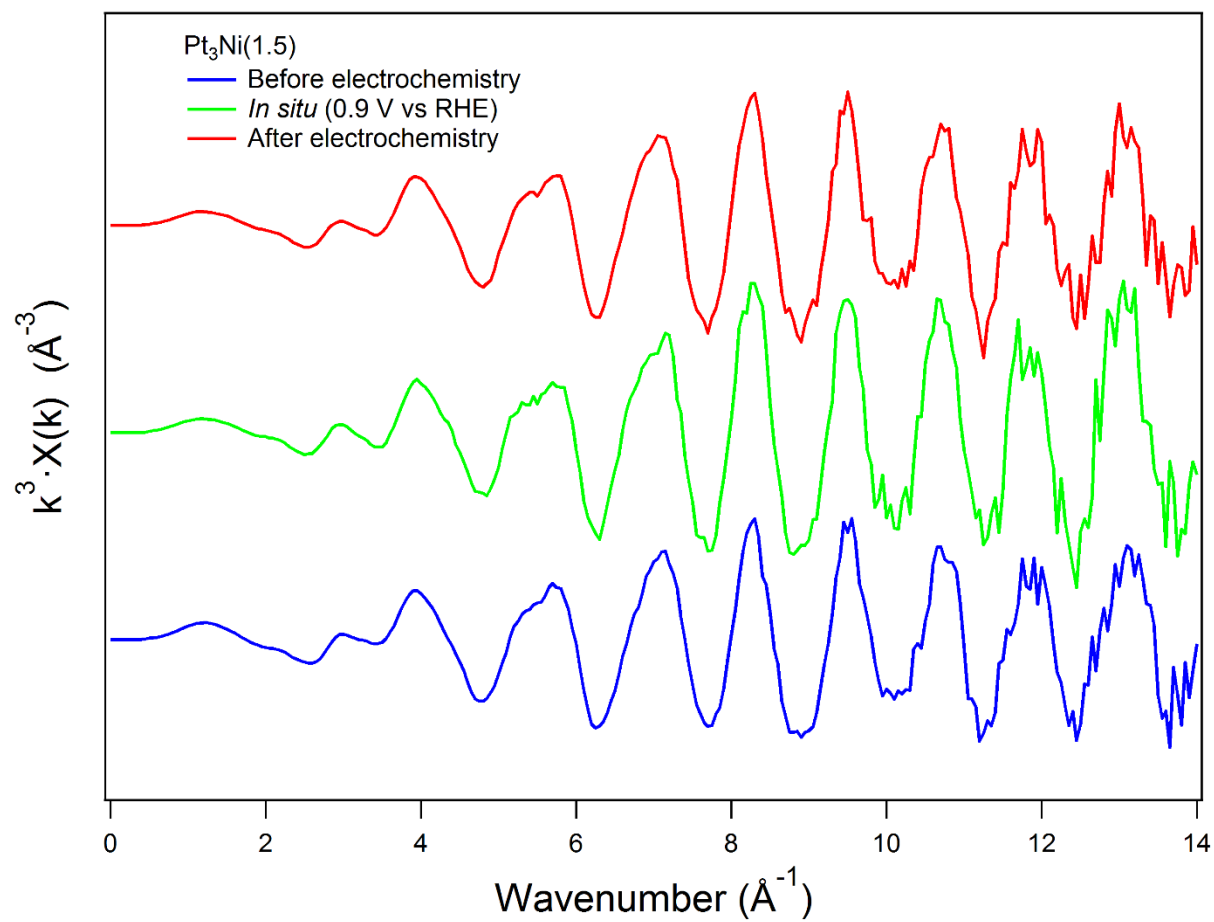


Figure S7. Raw  $k^3$ -weighted  $\chi(k)$  EXAFS spectra for Pt L<sub>3</sub>-edge of Pt<sub>3</sub>Ni(1.5) in three conditions; before, during, and after the oxygen reduction reaction.