Supplementary Information

Synthesis of Fe-doped Octahedral Pt_3Ni Nanocrystals with High Electro-catalytic Activity and Stability in Oxygen Reduction Reaction

Yujing Li,*[†,‡] Fanxin Quan,[‡] Lin Chen,[‡] Wenjing Zhang,[‡] Haobo Yu,[‡] Changfeng Chen[†,‡]

† State Key Laboratory of Heavy Oil, China University of Petroleum, Beijing, 102249, China and
‡ Department of Materials Science and Engineering, College of Science, China University of Petroleum, Beijing, 102249, China

Experimental details

Synthesis of octahedral NCs: $Pt(acac)_2$, $Ni(acac)_2$, and $Fe(acac)_3$ were used as metallic precursors of the synthesis. Appropriate amount of precursors were dissolved in 16mL N, N-Dimethylformamide (DMF) which also serves as reducing agent. Oleylamine (OAm), oleic acid (OAc), and n-octadecylphosphonic acid (ODPA) were also dissolved in DMF and used as capping agent. The starting solution was stirred for 10 minutes and transferred into a Teflon-lined autoclave. The solution was heated up to 210 ^oC at the rate of 3 ^oC/min and kept at this temperature for 2 hours, and then cooled to room temperature in the air. The products were separated from the reaction solution by centrifuge. The NCs were dispersed in 2 mL of chloroform, precipitated by 15 mL of ethanol, sonicated for 10 min, and then centrifuged at 7000 RPM for 10 min. The washing procedure was repeated three times. The NCs were stored in chloroform.

Preparation of carbon-supported catalysts: Carbon black (Vulcan XC-72, CB) is used as the catalyst support. For a typical catalyst preparation, CB was dissolved in chloroform at a concentration of 1 mg/mL, and sonicated for 1 hour. Appropriate amount of octahedral Pt_3Ni-Fe NCs dissolved in chloroform was ultrasonicated and mixed with the CB solution, with the NC/CB mass ratio fixed at 1/4, further sonicated for another 1 hour, and then stirred overnight. The catalysts were then collected by centrifuge at the rate of 8000 rpm, washed with chloroform, and then dried under a N_2 stream. As-prepared catalysts were redispersed in n-butylamine at the concentration of 1 mg/mL, sonicated for 15 min, and stirred again for three days. The solid catalysts were collected by centrifuge, redispersed in methanol or ethanol, sonicated for 15 min, and then centrifuged, which was repeated twice. For the thermal treatment procedure, the catalysts were heated in air for 2 hours, followed with a flow of H_2/N_2 (1/9) mixed gas for another 2 hours at the same temperature. The final products were weighted and stored in ethanol or isopropanol (IPA).

Characterization: Transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), and energy dispersive X-Ray spectroscopy (EDX) were taken on FEI TECNAI F-20 field emission microscope at an accelerating voltage of 200 kV.

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) was used to determine the atomic/mass ratio of Pt/Ni/Fe for the NCs before they are loaded onto CB. After being loaded to the CB support, thermogravimetric analysis (TGA) was used to determine the exact mass ratio of NC/CB. When doing TGA, after balancing of empty alumina boat, a known volume of concentrated catalysts ink (in methanol) was pipetted into the boat and the solvent was dried at 100 ^{o}C for 30 minutes. During the TGA test, the sample was heated at the rate of 15 ^{o}C/min to 600 ^{o}C in air followed by annealing at 600 ^{o}C for 10 minutes in pure hydrogen stream. In this way, the wt% of Pt for the catalyst and weight concentration of the catalyst ink can be calculated combining the ICP-OES and TGA results.

Electrochemical measurement: All electrochemical measurements were carried out in a home-made three-electrode cell. Catalyst inks were prepared by dispersing NC/CB in IPA/H_2O (volume ratio: 3/1) with the concentration between 0.5~2 mg/mL according to the wt% of Pt determined with the mentioned method. Appropriate amounts of inks, usually 8-10 μL depending on the catalyst concentration, were pipetted onto a rotating disk electrode (Pine Instrumentation) made with glassy carbon (GCE) with diameter of 5 mm. The total loading masses of the metal (excluding CB) were controlled at the level of 16 μg/cm^2.

In this work, the electrode was prepared by a two-step approach. The carbon-supported electro-catalysts form the first layer, followed by a Nafion® film formed by drying 10 μL of 100-time-diluted Nafion® solution on top. The catalysts were electrochemically activated by applying cyclic voltammograms (CV) between 0 and 1.2 V (vs. reversible hydrogen electrode, RHE) for 50 cycles in 0.1 M $HClO_4$ electrolyte, at the scan rate of 100 mV/s. Electrochemical surface area (ECSA) were determined from CV curves recorded between 0 and 1.1 V at the rate of 50 mV/s. The charges induced by the adsorption/desorption of hydrogen species were calculated by integrating the area between 0.05 and 0.4 V under the CV curve. ORR was studied by recording linear scan polarization (LSV) curves between 0 and 1.1 V in oxygen-saturated $HClO_4$ electrolyte at the rotating rate of 1600 rpm. The electrolyte was bubbled with oxygen prior to, and during the measurement as well. The durability tests were conducted by applying CV scans up to 4000 cycles each time at the scan rate of 50 mV/s, and recording CV curves as mentioned above, and then studying ORR afterwards. After each set of measurement, another round of ADT was applied, and a total of 16000 cycles was applied to each catalyst for the evaluation of durability. For comparison, commercial Pt/C (20 wt% of Pt supported on CB) catalyst purchased from Johnson Matthey was also tested with the same procedure.

First principal calculation: The calculation was carried out with the same method proposed by Wang et al, briefly described as follows.[1] The (111) surface was constructed with a five-layer surface slab, separated by a five layer-equivalent-layer vacuum, in a periodic super cell geometry. A 2 × 2 unit cell was used, and Pt_3Ni-Fe surface was established by replacing one Pt atom with a Fe atom in one of top three layers in the surface slab. During geometrical optimization, the outermost three layers were allowed to relax while the bottom two layers were fixed to the optimized bulk Pt_3Ni crystal.

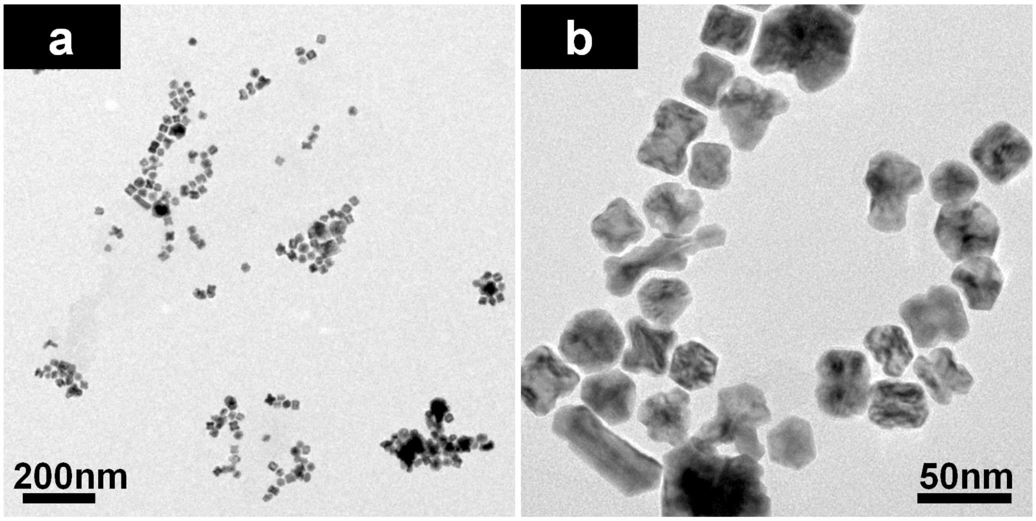

Figure S1. Pt_3Ni-Fe NCs synthesized with $Fe(acac)_2$ as the precursor of iron.

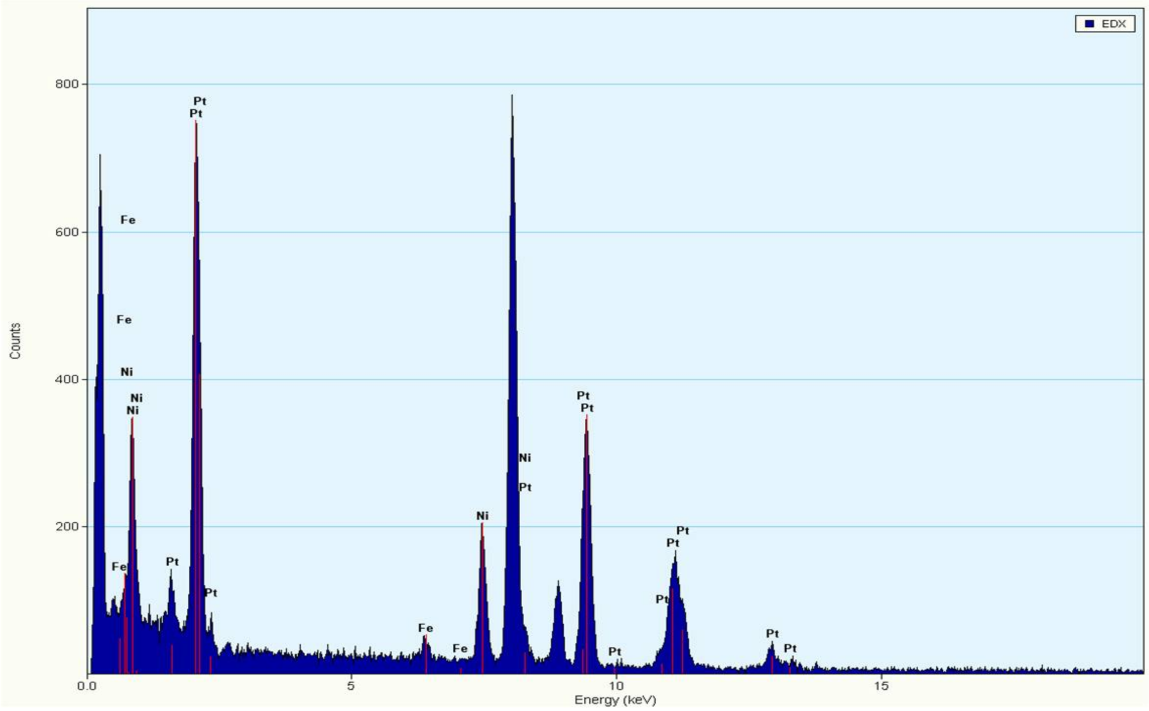

Figure S2. EDX spectrum of a single 7nm NC of Pt_3Ni-Fe.

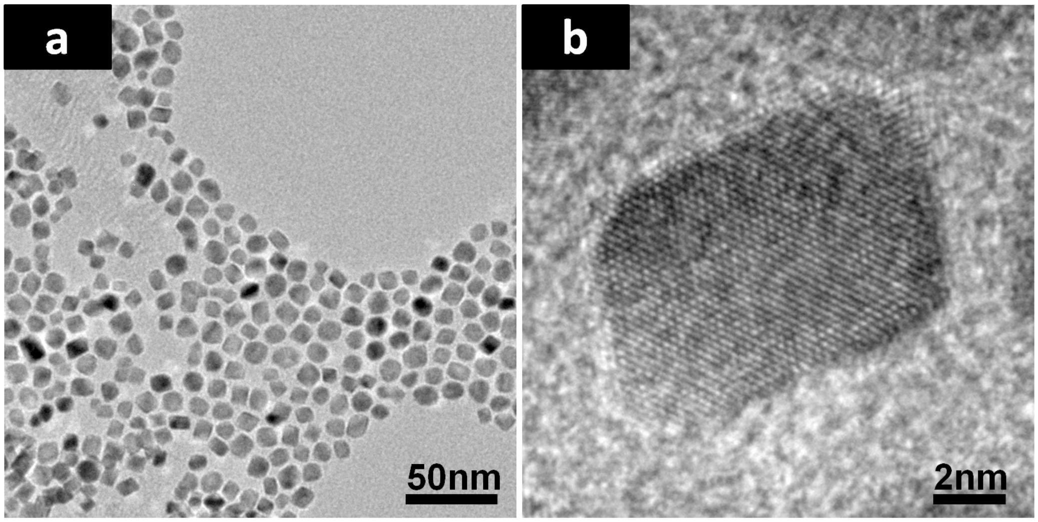

Figure S3. (a). TEM and (b). HRTEM images of 10nm octahedral Pt_3Ni NCs without the Fe doping.

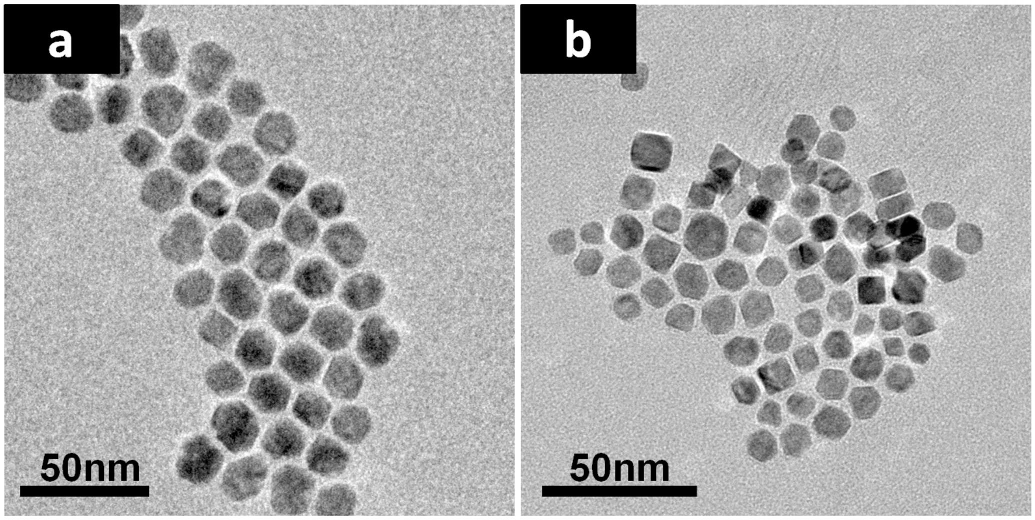

Figure S4. (a) Alloy NCs synthesized with OAm and OAc (without ODPA). (b) Alloy NCs synthesized with only ODPA (without OAm and OAc).

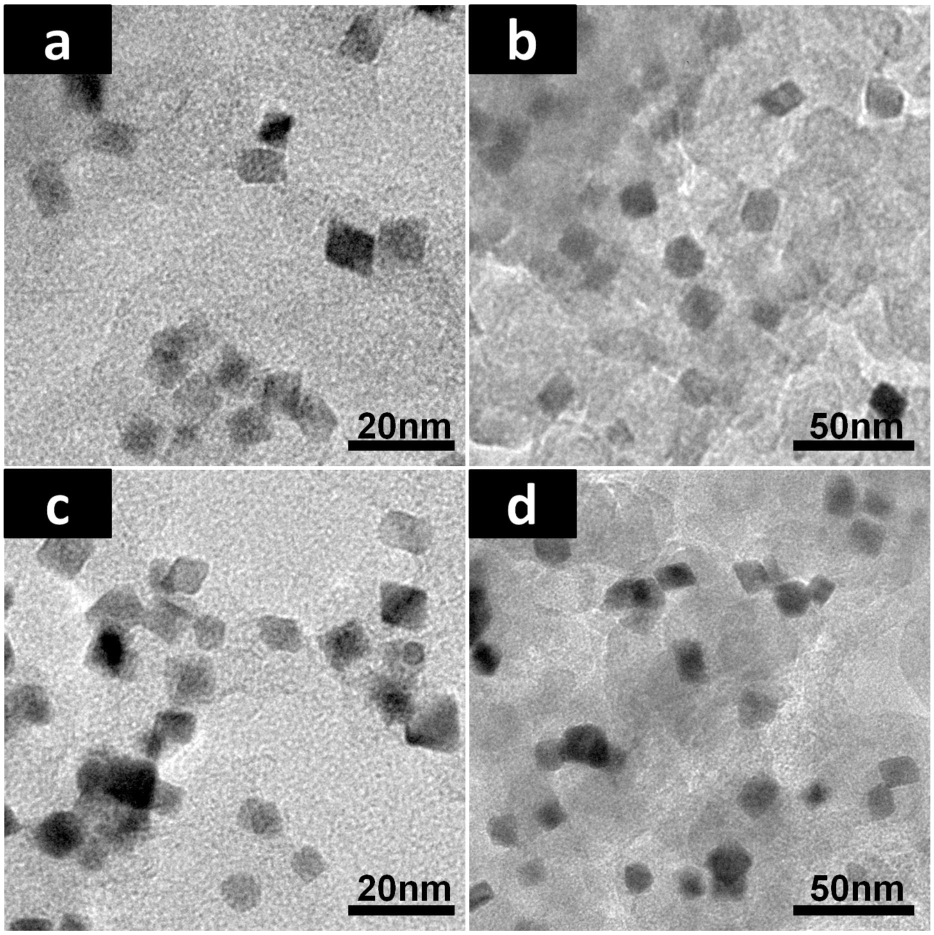

Figure S5. CB-supported octahedral NCs (a, b) before and (c, d) after thermal treatment. (a, c) with 7nm NCs (heated at 260°C); (b, d) with 19nm (heated at 260°C).

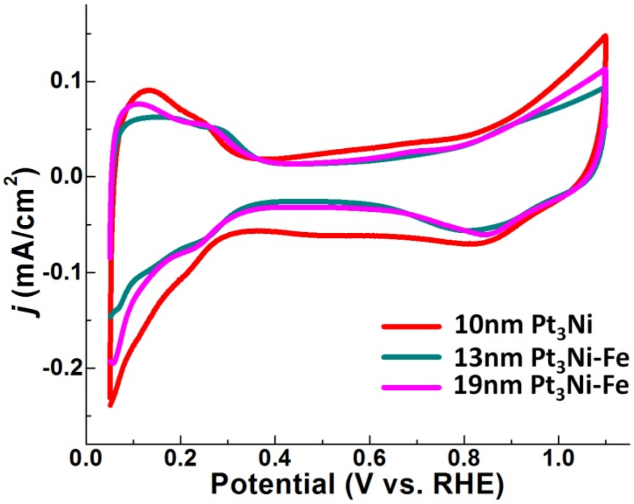

Figure S6. CV curves of 10nm Pt_3Ni, 13nm and 19nm Pt_3Ni-Fe/C electro-catalysts.

Table S1. ECSAs of carbon-supported octahedral (OH) NCs with different sizes, as well as commercial JM Pt/C catalyst.

Sample Sample	Loading Mass of Pt (μg)	ECSA (m^2/g_{Pt})
JM Pt/C	3.0	68.8
10nm PtNi/C	2.7	20.1
7nm PtNi-Fe/C	3.0	22.2
13nm PtNi-Fe/C	3.5	28.9
19nm PtNi-Fe/C	3.5	21.2

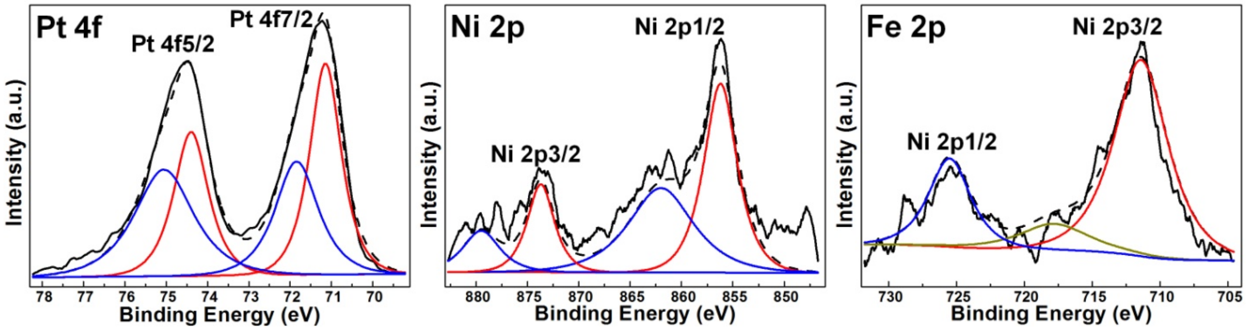

Figure S7. XPS spectra of Pt 4f, Ni 2p and Fe 2p regions for 7nm octahedral Pt_3Ni-Fe NCs.

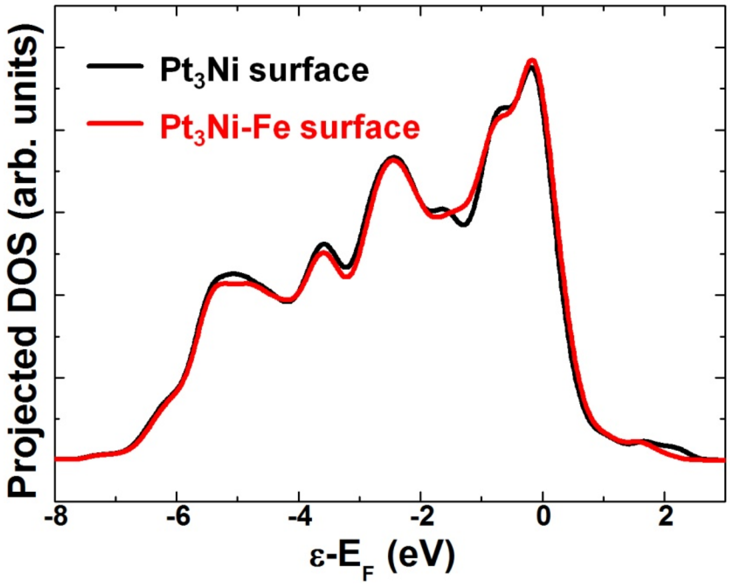

Figure S8. Density of states (DOS) of d-band for Pt_3Ni surface (black) and Pt_3Ni-Fe surface (red).

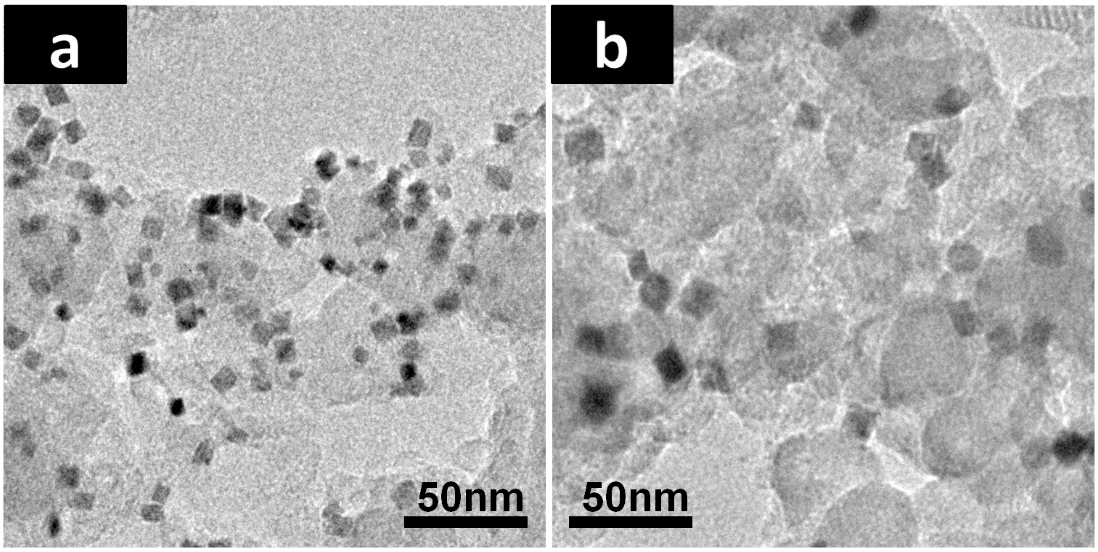

Figure S9. (a) 7nm and (b) 19nm octahedral Pt_3Ni-Fe NCs supported on carbon black.

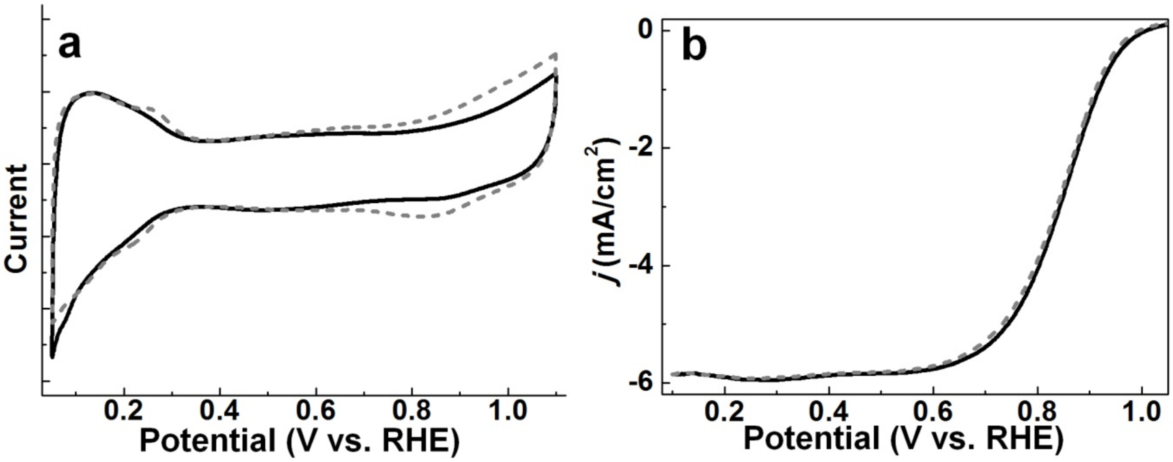

Figure S10. (a) CV and (b) LSV of 10nm octahedral Pt_3Ni/C catalysts before and after the durability test. (Solid black curve: Initial curve. Dashed grey curve: Final curve after durability test.)

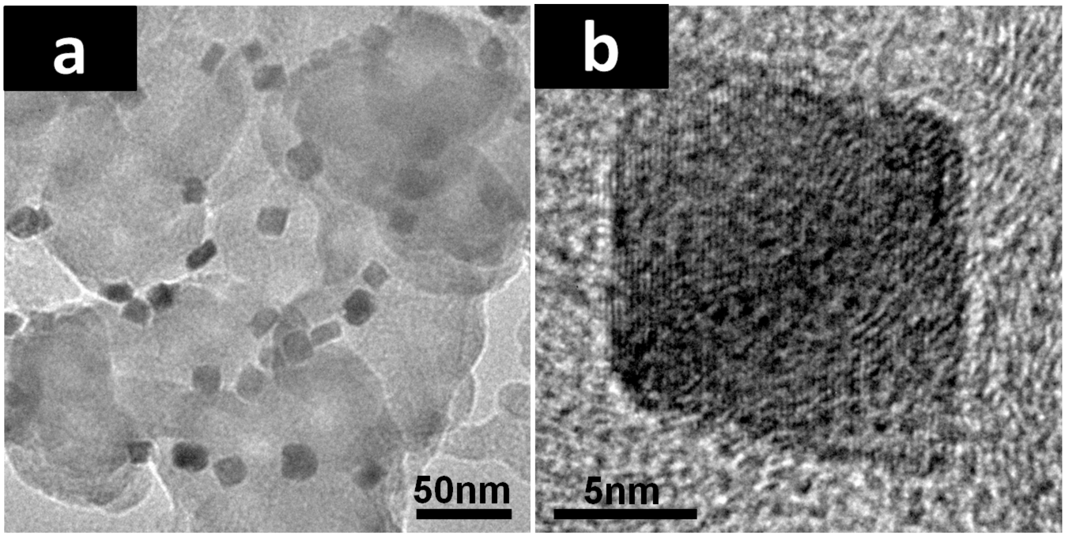

Figure S11. (a, b) 19nm octahedral NCs supported on carbon black after durability test.

References

(1) Zhang, Y.; Duan, Z.; Xiao, C.; Wang, G. *Surf. Sci.* **2011**, *605*, 1577-1582.