

## Supplementary Material for

# High-performance transition metal-doped Pt<sub>3</sub>Ni octahedra for oxygen reduction reaction

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#### **Materials and Methods**

#### 1. Chemicals

Platinum(II) acetylacetonate (Pt(acac)<sub>2</sub>, 97%), nickel(II) acetylacetonate (Ni(acac)<sub>2</sub>, 95%), cyclopentadienylvanadium(0) carbonyl (C<sub>5</sub>H<sub>5</sub>V(CO)<sub>4</sub>, 98%), chromium(0) hexacarbonyl (Cr(CO)<sub>6</sub>, 98%), dimanganese(0) decacarbonyl (Mn<sub>2</sub>(CO)<sub>10</sub>, 98%), iron(0) pentacarbonyl (Fe(CO)<sub>5</sub>, >99.99%), dicobalt(0) octacarbonyl (Co<sub>2</sub>(CO)<sub>8</sub>, >99.99%), molybdenum(0) hexacarbonyl (Mo(CO)<sub>6</sub>, 98%), tungsten(0) hexacarbonyl (W(CO)<sub>6</sub>, 97%), dirhenium(0) decacarbonyl (Re<sub>2</sub>(CO)<sub>10</sub>, 98%), benzoic acid (C<sub>6</sub>H<sub>5</sub>COOH,  $\geq$ 99.5%), and N, N-dimethylformamide (DMF,  $\geq$ 99.9%) were all purchased from Sigma-Aldrich. All the chemicals were used as received without further purification. The water (18 MΩ/cm) used in all experiments was prepared by passing through an ultra-pure purification system (Aqua Solutions).

#### 2. Preparation of octahedral Pt<sub>3</sub>Ni/C catalyst

In a typical preparation of octahedral  $Pt_3Ni/C$  catalyst, platinum(II) acetylacetonate ( $Pt(acac)_2$ , 8.0 mg), nickel(II) acetylacetonate ( $Ni(acac)_2$ , 4.0 mg), benzoic acid ( $C_6H_5COOH$ , 61 mg) and 10 mL commercial carbon black dispersed in DMF (2 mg/mL, Vulcan XC72R carbon) were added into a vial (volume: 30 mL). After the vial had been capped, the mixture was ultrasonicated for around 5 minutes. The resulting homogeneous mixture was then heated at 160 ° C for 12 h in an oil bath, before it was cooled to room temperature. The resulting colloidal products were collected by centrifugation and washed three times with an ethanol/acetone mixture.

#### 3. Preparation of transition-metal doped Pt<sub>3</sub>Ni/C catalyst (M-Pt<sub>3</sub>Ni/C catalyst)

The Mo-Pt<sub>3</sub>Ni/C catalyst was obtained by the further growth of Mo on the preformed octahedral Pt<sub>3</sub>Ni/C catalyst. In a typical preparation of octahedral Mo-Pt<sub>3</sub>Ni/C catalyst, platinum(II) acetylacetonate (Pt(acac)<sub>2</sub>, 2.0 mg), nickel(II) acetylacetonate  $(Ni(acac)_2, 1.0 \text{ mg})$  and molybdenum hexacarbonyl (Mo(CO)<sub>6</sub>, 0.4 mg) were added to the suspension of unpurified Pt<sub>3</sub>Ni/C catalyst prepared above. After the vial had been capped, the mixture was ultrasonicated for around 30 minutes. The resulting mixture was then heated at 170 °C for 48 h in an oil bath, before it was cooled to room temperature. The resulting colloidal products were collected by centrifugation and washed three times with an ethanol/acetone mixture. The surface doping approach was robust and readily extended to other metals [V, Cr, Mn, Fe, Co, W, or Re] by replacing Mo(CO)<sub>6</sub> with other transition-metal carbonyl compounds in the above described process. In all of these other transition-metal doped Pt<sub>3</sub>Ni/C catalysts, highly dispersive NCs with octahedral morphology anchored on carbon black were obtained (Fig. S7). The structures and compositions of all the transition-metal doped Pt<sub>3</sub>Ni/C catalysts were confirmed by XPS and ICP-AES, confirming similar structure and surface compositions, as shown in Fig. S8 and Table S1. The successful fabrication of various transition-metal doped Pt<sub>3</sub>Ni/C catalysts with well-defined size, morphology and surface composition readily enables us to compare the doping effects for Pt<sub>3</sub>Ni/C made by various transition metals (Fig. 2).

#### 4. Characterizations

Transmission electron microscopy (TEM) images were carried out on an FEI CM120 transmission electron microscope operated at 120 kV. High resolution TEM images (HRTEM) and the high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM)-energy-dispersive X-ray spectroscopy (EDS) were taken on a FEI TITAN transmission electron microscope operated at 300 kV. The STEM electron energy loss spectroscopy (EELS) were performed on an aberration corrected TEM. The samples were prepared by dropping ethanol dispersion of catalysts onto carbon-coated copper TEM grids (Ted Pella, Redding, CA) using pipettes and dried under ambient condition. Powder X-ray diffraction (PXRD) patterns were collected on a Panalytical X'Pert Pro X-ray Powder Diffractometer with Cu-Kα radiation. X-ray photoelectron spectroscopy (XPS) tests were done with Kratos AXIS Ultra DLD spectrometer. The concentration of catalysts was determined by the inductively coupled plasma atomic emission spectroscopy (TJA RADIAL IRIS 1000 ICP-AES).

#### 5. Electrochemical Measurements

A three-electrode cell was used to do the electrochemical measurements. The working electrode was a glassy-carbon Rotating Disk Electrode (RDE) (diameter: 5 mm, area: 0.196 cm<sup>2</sup>) from Pine Instruments. Ag/AgCl (3 M Cl<sup>-</sup>) was used as reference electrode. Pt wire was used as counter electrode. The Pt loading of octahedral M-Pt<sub>3</sub>Ni/C and octahedral Pt<sub>3</sub>Ni/C were all 0.8  $\mu$ g (i. e., 4.08  $\mu$ g<sub>Pt</sub>/cm<sup>2</sup> based on the geometric electrode area of 0.196 cm<sup>2</sup>). During the preparation of working electrode, we could hardly get a uniform catalyst layer over the whole disk once we further reduced the mass loading of the catalyst, indicating that the lowest mass loading of the catalyst is around 0.80 µg. The electrochemical active surface area (ECSA) measurements were determined by integrating the hydrogen adsorption charge on the cyclic voltammetry (CV) at room temperature in nitrogen saturated 0.1 M HClO<sub>4</sub> solution. The potential scan rate was 100 mV/s for the CV measurement. Oxygen reduction reaction (ORR) measurements were conducted in oxygen saturated  $0.1 \text{ M HClO}_4$  solution which was purged with oxygen during the measurement. The scan rate for ORR measurement was 10 mV/s. The ORR polarization curves were collected at 1600 rpm. The accelerated durability tests (ADTs) were performed at room temperature in oxygen saturated 0.1 M HClO<sub>4</sub> solutions by applying cyclic potential sweeps between 0.6 and 1.1 V versus reversible hydrogen electrode (RHE) at a sweep rate of 50 mV/s for 8000 cycles. For comparison, Commercial Pt/C catalyst (Alfa Aesar, 20 wt. % Pt, Pt particle size: 2-5 nm) was used as the baseline catalysts, and the same procedure as described above was used to conduct the electrochemical measurement, and the Pt loadings was 4.08  $\mu g_{Pt}/cm^2$  for the commercial Pt/C catalyst.

#### 6. DFT Calculations

Density functional theory (DFT) calculations (36) were done using the Vienna Abinitio Software Package (VASP) (39) with the revised Perdew-Burke-Eznerhof (RPBE) exchange-correlation functional (40). All DFT calculations were run with spinpolarization enabled. The Mo\_pv, Ni, Pt\_pv\_GW, O\_GW, and H\_GW PBE projectoraugmented wave (PAW) (41) potentials provided with VASP were used, and VASP was run with high precision. A single *k*-point at the center of the Brillouin zone was used for each nanoparticles. For bulk materials, a  $16 \times 16 \times 16$  k-point grid was used for a fcc unit cell, and the k-point grid was scaled appropriately for larger cells. Second-order Methfessel-Paxton smearing (42) with a width of 0.2 eV was used to set partial occupancies. Real-space projectors were used to evaluate the non-local part of the PAW potential. Calculations were stopped when the difference for the total energy in successive ionic relaxation steps was less than 1 meV. The surface d-band centers were calculated using the site-projected densities of states for surface atoms.

#### 7. Cluster expansion

Cluster expansions are parameterized models that are capable of very rapidly and accurately predicting the energies of different arrangements of atoms and vacancies on a lattice of sites. Although cluster expansions have been used previously to model the shapes (43,44) or internal atomic arrangements (45-48) in nanoparticles separately, to our knowledge this is the first use of a single cluster expansion to predict the energies of nanoparticles as a function of shape, size, and internal atomic order. A quaternary cluster expansion was generated on an fcc lattice in which each site could be occupied by molybdenum, nickel, platinum, or a vacancy. Site variable values of 0, 1, 2, and 3 respectively were assigned to these species. A discrete cosine basis was used to generate the cluster functions, where the  $b^{th}$  basis function of the site variable s is given by

$$\Theta_b = \begin{cases} 0 & \text{for } b = 0\\ \sqrt{2}\cos(\pi b(2s+1)/8) & \text{for } b > 0 \end{cases}$$

for  $b \in \{0, 1, 2, 3\}$ .

To create the initial 136 structures used for the training data, a "dummy" cluster expansion was generated, consisting only of nearest-neighbor pair clusters, with effective cluster interactions (ECI) chosen in a way that assigned a value of -1 eV to atom-atom interactions (regardless of the species involved) and no energy to other interactions. These cluster expansions were used in Monte Carlo simulations at 2000 – 4500 K to generate random snapshots of nanoparticles. Two different sets of random nanoparticles were created. The first set of nanoparticles contained only Ni and Pt, where the numbers of Pt and Ni atoms were independently and randomly selected from a uniform distribution over all integers from 0 to 100. The second set of nanoparticles contained Mo, Ni, and Pt, where the numbers of Mo, Ni, and Pt atoms were independently and randomly selected from uniform distributions over integers from 0 to 10, 0 to 50, and 0 to 150 respectively. All nanoparticles were generated under the constraint that there had to be more than 85 total atoms in the nanoparticle, as the inclusion of smaller particles was found to lead to cluster expansions with poor predictive accuracy for multi-nanometer nanoparticles (potentially due to quantum size effects). Nanoparticles that experienced significant reconstruction upon relaxation, defined as an atom traveling more than 75% the nearest-neighbor distance from its initial site, were excluded. These particles accounted for about 20% of the random structures generated. All nanoparticles were contained in a cubic cell with a lattice parameter of 28.8 Å. The resulting set of random nanoparticles included 74 Ni-Pt nanoparticles and 62 Mo-Ni-Pt nanoparticles. In addition to these structures, the training data consisted of the pure elements Mo, Ni, and Pt in a

bulk fcc crystal, vacuum (a lattice containing only vacant sites), and various low-energy structures predicted over the course of this research, for a total of 195 unique structures. To reduce the prediction error of the cluster expansion, the pure elements and vacuum were included twice in the training set (49), and the ECI were fit to the DFT-calculated formation energies of fully relaxed nanoparticles relative to these reference states (34).

The cluster expansion included the empty cluster, the one-body (point) cluster, all 2body clusters up to the 10<sup>th</sup>-nearest neighbor, all 3-body clusters up to the third-nearest neighbor, and all 4-, 5-, and 6-body clusters up to the second-nearest neighbor, for a total of 374 symmetrically distinct cluster functions. The ECI for these cluster functions were fit to the training data using the Bayesian approach (35) with a multivariate Gaussian prior distribution. The inverse of the covariance matrix for the prior,  $\Lambda$ , was diagonal, with elements given by

$$\lambda_{\alpha\alpha} = \begin{cases} 0 & \text{for } n_{\alpha} = 0 \\ \lambda_{1} & \text{for } n_{\alpha} = 1 \\ \lambda_{2}(1 + r_{\alpha})^{\lambda_{3}} e^{\lambda_{4} n_{\alpha}} & \text{for } n_{\alpha} > 1 \end{cases}$$

where  $n_{\alpha}$  is the number of sites in cluster function  $\alpha$ ,  $r_{\alpha}$  is the maximum distance between sites, and the parameters  $\lambda_1$ ,  $\lambda_2$ ,  $\lambda_3$ , and  $\lambda_4$  were determined by using a conjugate gradient algorithm to minimize the leave-one-out cross validation score, an estimate of prediction error (50). The final values for these parameters were  $10^{-8}$ ,  $1.102 \times 10^{-12}$ , 6.103, and 4.312 respectively. The resulting cluster expansion had a root mean square leave-one-out cross validation error of 0.742 meV per site, equivalent to 3.87 meV per atom.

#### 8. Sample structures

The cluster expansions were used in Monte Carlo simulations to calculate thermodynamic averages, identify ground state structures, and identify sample structures. The structures referenced in the text include a nanoparticle with composition Mo<sub>6</sub>Ni<sub>41</sub>Pt<sub>178</sub>, a 9-layer (111) slab with composition Mo<sub>2</sub>Ni<sub>7</sub>Pt<sub>27</sub>, and 4573-atom nanoparticles with compositions Ni<sub>1175</sub>Pt<sub>3398</sub> and Mo<sub>73</sub>Ni<sub>1143</sub>Pt<sub>3357</sub>.

The nanoparticle with composition  $Mo_6Ni_{41}Pt_{178}$  (Fig. S15) was identified by the cluster expansion as the ground state structure at this composition using a simulated annealing algorithm that simultaneously optimized the particle shape and internal atomic order. Although this nanoparticle is smaller than the experimentally-observed nanoparticles, it retains key structural features and is small enough to be modeled using density functional theory. To evaluate the chemical effects of Mo doping independent of shape/size effects, the particle was compared with an undoped particle with composition  $Ni_{47}Pt_{178}$  generated by replacing the Mo atoms on sub-surface edge sites with Ni atoms.

The 9-layer (111) slab with composition  $Mo_2Ni_7Pt_{27}$  (Fig. S16) was identified by the cluster expansion as the ground-state structure at this composition. To prevent interaction between neighboring surfaces (and adsorbed molecules) in the periodic unit cell, a distance of 2.25 nm was provided between opposing surfaces. All calculations on slabs were done in a way to preserve the symmetry between the two slab surfaces.

In Fig. 4, the oxygen binding energy on the Pt<sub>3</sub>Ni(111) surface was calculated using the ground-state 9-layer slab predicted by the cluster expansion. This structure is the same as the structure shown in Fig. S16, with Mo atoms replaced by Ni atoms. Binding energies were evaluated at all symmetrically distinct fcc and hcp sites at <sup>1</sup>/<sub>4</sub> monolayer coverage, and the largest binding energy was used in Fig. 4. For the Pt(111) surface, the oxygen binding energy was calculated at the fcc site of a 9-layer slab at <sup>1</sup>/<sub>4</sub> monolayer coverage.

The 4573-atom nanoparticles were created by generating octahedra with the six vertex atoms removed. The length of the remaining edges is estimated to be about 4.1 nm, consistent with nanoparticles observed experimentally. The shapes of these nanoparticles were held fixed, and only the internal atomic order was allowed to vary. The compositions of the nanoparticles were set to match the Ni<sub>0.257</sub>Pt<sub>0.743</sub> and Mo<sub>0.016</sub>Ni<sub>0.25</sub>Pt<sub>0.734</sub> compositions observed experimentally. The average site occupancies of these particles at 170°C are shown in Fig. 4, and a snapshot of a representative Ni<sub>1175</sub>Pt<sub>3398</sub> particle at 170°C is shown in Fig. S13.

The most favorable site for Mo surface segregation in the presence of an adsorbed oxygen atom for the  $Mo_6Ni_{41}Pt_{178}$  particle was determined by evaluating Mo segregation to each of the nearest face, vertex, and edge sites for each of the symmetrically distinct Mo atoms. In each case, the adsorbed oxygen atom was placed atop the surface Mo atom, as our calculations indicate that this is the most favorable site for oxygen adsorption.

#### 9. Surface segregation

To assess the energetics surface segregation, DFT calculations were performed on both the extended (111) slab and the  $Mo_6Ni_{41}Pt_{178}$  particle. For the clean slab in vacuum, Mo is more stable at a subsurface site than the lowest-energy surface site by 0.881 eV per Mo atom. For the nanoparticle in vacuum, the subsurface site is favored over the lowestenergy neighboring surface site by 1.110 eV. The situation reverses in the presence of oxygen. In the presence of adsorbed oxygen on the (111) surface (with  $\frac{1}{4}$  monolayer coverage), there is a driving force of 1.559 eV per Mo atom for Mo to segregate to the surface, and the oxygen preferentially adsorbs atop the surface Mo atom. For the Mo<sub>6</sub>Ni<sub>41</sub>Pt<sub>178</sub> nanoparticle, similar results were found: in the presence of an adsorbed oxygen atom Mo preferentially segregates to a vertex site, and the driving force for this segregation is 1.533 eV. The  $Mo_6Ni_{41}Pt_{178}$  nanoparticle with a single Mo atom segregated to the energetically-preferred vertex site was used to assess the stability of surface Mo-oxide species against reduction to H<sub>2</sub>O. The structures used in these calculations, consisting of one, two, and three oxygen atoms adsorbed on the vertex Mo atom, are shown in Fig. S17. The computational hydrogen electrode model (51) was used to calculate stability, where the energies of  $H_2O$ ,  $H_2$ , and the nanoparticle were calculated using DFT. Zero-point energies were calculated in the harmonic approximation using DFT and the finite differences method. The slab with Mo segregated to the surface was used to estimate the zero point energy for O adsorbed atop a Mo atom, where the positions of the atoms in the slab were held fixed. Gas-phase free energies for  $H_2$  and  $H_2O$  were taken from reference (52). The adsorbed O was calculated to be stable against reduction to H<sub>2</sub>O down to potentials of 0.6 V (for the first atom removed), 0.3 (for the second atom), and -1.0 V (for the third atom) vs. the reversible hydrogen electrode.

Due to the relatively strong Mo-Pt and Ni-Pt nearest-neighbor bonds, both Mo and Ni prefer to occupy similar sites with many Pt nearest neighbors. However in oxidizing conditions the energetic driving force for Mo segregation to the surface is much stronger than the driving force for Ni segregation. For the Mo<sub>2</sub>Ni<sub>7</sub>Pt<sub>27</sub> slab with <sup>1</sup>/<sub>4</sub> monolayer oxygen coverage, the calculated driving force for 2<sup>nd</sup>-layer Mo to migrate to the surface is 1.559 eV per atom, as opposed to 0.284 eV per atom for Ni. This suggests that in oxidizing conditions Mo atoms may "crowd out" Ni atoms on the particle surface, reducing the number of surface Ni atoms available for dissolution.

#### 10. Stability enhancements

The cluster expansion was used to evaluate the effects of substituting a single Mo atom into all the sites in the representative Ni<sub>1175</sub>Pt<sub>3398</sub> particle (Fig. S13). The presence of a Mo atom increases the energy required to remove a Pt atom from a neighboring surface site by an average of 377 meV, with values ranging from 180 to 491 meV depending on the local atomic structure. The energy required to remove a Ni atom from a neighboring surface site increases by an average of 240 meV, with values ranging from 81 to 338 meV. The smallest increase in the energy required to remove surface Pt (180 meV) was observed to occur for a Pt atom at a face site, with a Mo atom in the second layer beneath it. The greatest increase in the energy required to remove surface Pt (491 meV) was also observed to occur for a Pt atom at a face site, with a Mo atom in the second layer beneath it. The smallest increase in the energy required to remove surface Pt (491 meV) was observed to occur for a Pt atom at a face site, with a Mo atom in the second layer beneath it. The smallest increase in the energy required to remove surface Ni (81 meV) was observed to occur for a Ni atom at a face site, with a Mo atom in the layer beneath it. The greatest increase in the energy required to remove surface Ni (338 meV) was observed to occur for a Ni atom at a non-vertex edge site, with a Mo atom in the layer beneath it.

If the Mo atom is on an edge or vertex site, the energy required to remove a Pt (Ni) atom from a neighboring edge or vertex site increases by an average of 362 (201) meV, with values ranging from 346 (160) to 444 (214) meV. These values are supported by DFT calculations on the Mo<sub>6</sub>Ni<sub>41</sub>Pt<sub>178</sub> nanoparticle which predict that the presence of a Mo atom on a vertex site stabilizes the Pt atom on the neighboring vertex site by 458 (444) meV with (without) an oxygen atom adsorbed atop the Mo atom. The smallest increase in the energy required to remove Pt from an edge or vertex site (346 meV) was observed to occur with the Mo atom at a non-vertex edge site, with the Pt atom on a neighboring non-vertex edge site. The greatest increase in the energy required to remove Pt from an edge or vertex site (444 meV) was observed to occur with the Mo atom at a vertex site and the Pt atom on a neighboring vertex site. The smallest increase in the energy required to remove Ni from an edge or vertex site (160 meV) was observed to occur with the Mo atom at a vertex site, with the Ni atom on a neighboring non-vertex edge site. The greatest increase in the energy required to remove Ni from an edge or vertex site (214 meV) was observed to occur with the Mo atom at a non-vertex edge site and the Ni atom on a neighboring non-vertex edge site.

The effects of second- and third-nearest-neighbor interactions were also investigated. If the Mo atom is on an edge or vertex site, the energy required to remove a Pt (Ni) atom from a second-nearest-neighbor site on an edge or vertex increases by an average of 3 (-15) meV, with values ranging from 0 (-21) to 21 (-6) meV. If the Mo atom is on an edge or vertex site, the energy required to remove a Pt (Ni) atom from a thirdnearest-neighbor site on an edge or vertex increases by an average of -16 (-3) meV, with values ranging from -42 (-26) to 17 (39) meV.

**Supplementary Figures and Tables:** 



**Fig. S1** Schematic illustration of (A) the one-pot fabrication of highly dispersive octahedral  $Pt_3Ni/C$  catalyst and (B) the fabrication of various well-defined octahedral transition-metal doped  $Pt_3Ni/C$  catalysts.



**Fig. S2** Representative (A,B) TEM and (C) HAADF-STEM images of the octahedral Pt<sub>3</sub>Ni/C catalyst. (D) Representative TEM image of the octahedral Mo-Pt<sub>3</sub>Ni/C catalyst.



Fig. S3 Typical powder X-ray diffraction (PXRD) patterns for various transition-metal doped octahedral  $Pt_3Ni/C$  catalysts.



**Fig. S4** Representative TEM images of (A, B) octahedral  $Pt_3Ni/C$  and (D, E) octahedral Mo-Pt\_3Ni/C catalysts before (left panels) and after (middle panels) 8,000 potential sweep cycles between 0.6 and 1.1 V versus RHE in an O<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub> solution at 50 mV s<sup>-1</sup>. TEM-EDS spectra of (C) octahedral Pt\_3Ni/C catalyst and (F) octahedral M-Pt\_3Ni/C catalyst before and after 8,000 potential sweep cycles.



**Fig. S5** Representative TEM images for the commercial Pt/C catalyst (Alfa Aesar, 20 wt. % Pt, Pt particle size: 2-5 nm).



**Fig. S6** (A) The CO stripping curves of octahedral Mo-Pt<sub>3</sub>Ni/C, octahedral Pt<sub>3</sub>Ni/C and commercial Pt/C catalysts recorded at room temperature in CO-saturated 0.1 M HClO<sub>4</sub> solution. Scanning rate =  $50 \text{ mVs}^{-1}$ . (B) The electrochemically active surface area (ECSA, up panel) and specific activity (bottom panel) at 0.9 V versus RHE for these transition-metal doped Pt<sub>3</sub>Ni/C catalysts, which are given as kinetic current densities normalized to the ECSA calculating from the charge in CO stripping curves. The middle panel in (B) is the ratio between ECSA values determined by integrated charge from CO stripping (ECSA<sub>CO</sub>) and deposited hydrogen (ECSA<sub>H</sub>). In (A), the current densities were normalized in reference to the geometric area of the RDE (0.196 cm<sup>2</sup>).



**Fig. S7** Representative TEM images for various transition-metal doped **octahedral** Pt<sub>3</sub>Ni/C catalysts: (A) octahedral V-Pt<sub>3</sub>Ni/C catalyst, (B) octahedral Cr-Pt<sub>3</sub>Ni/C catalyst, (C) octahedral Mn-Pt<sub>3</sub>Ni/C catalyst, (D) octahedral Fe-Pt<sub>3</sub>Ni/C catalyst, (E) octahedral Co-Pt<sub>3</sub>Ni/C catalyst, (F) octahedral Mo-Pt<sub>3</sub>Ni/C catalyst, (G) octahedral W-Pt<sub>3</sub>Ni/C catalyst and (H) octahedral Re-Pt<sub>3</sub>Ni/C catalysts: (I) octahedral V-Pt<sub>3</sub>Ni/C catalyst, (J) octahedral Cr-Pt<sub>3</sub>Ni/C catalyst and (K) octahedral Co-Pt<sub>3</sub>Ni/C catalyst. (L) Line-scanning profile across an octahedral Co-Pt<sub>3</sub>Ni/C nanocrystal, which is indicated in the inset of (L).



**Fig. S8** XPS spectra of various transition-metal doped octahedral Pt<sub>3</sub>Ni/C catalysts : (A) V-Pt<sub>3</sub>Ni/C catalyst, (B) Cr-Pt<sub>3</sub>Ni/C catalyst, (C) Mn-Pt<sub>3</sub>Ni/C catalyst, (D) Fe-Pt<sub>3</sub>Ni/C catalyst, (E) Co-Pt<sub>3</sub>Ni/C catalyst, (F) Mo-Pt<sub>3</sub>Ni/C catalyst, (G) W-Pt<sub>3</sub>Ni/C catalyst and (H) Re-Pt<sub>3</sub>Ni/C catalyst.



**Fig. S9** Representative oxygen reduction reaction (ORR) polarization curves for various transition-metal doped octahedral  $Pt_3Ni/C$  catalysts recorded at room temperature in an  $O_2$ -saturated 0.1 M HClO<sub>4</sub> aqueous solution with a sweep rate of 10 mV/s and a rotation rate of 1600 rpm : (A)  $Pt_3Ni/C$  catalyst, (B) V- $Pt_3Ni/C$  catalyst, (C) Cr- $Pt_3Ni/C$  catalyst, (D) Mn- $Pt_3Ni/C$  catalyst, (E) Fe- $Pt_3Ni/C$  catalyst, (F) Co- $Pt_3Ni/C$  catalyst, (G) Mo- $Pt_3Ni/C$  catalyst, (H) W- $Pt_3Ni/C$  catalyst and (I) Re- $Pt_3Ni/C$  catalyst. Insets show their corresponding cyclic voltammogram (CV) curves recorded at room temperature in  $N_2$ -purged 0.1 M HClO<sub>4</sub> solution with a sweep rate of 100 mV/s.



**Fig. S10** Pt and Ni spectra for the octahedral  $Pt_3Ni/C$  catalyst before (A) and after (B) 8,000 potential sweep cycles. Pt, Ni and Mo XPS spectra for the octahedral Mo-Pt\_3Ni/C catalyst before (C) and after (D) 8,000 potential sweep cycles. The Ni 2p and Pt 4f XPS spectra of Mo doped  $Pt_3Ni/C$  catalyst show that the majority of the surface Ni was in the oxidized state and the surface Pt was mainly in the metallic state. Mo exhibits mainly Mo(6+) and Mo(4+) state, which showed Mo largely present in the form of  $MoO_x$  on surface in Mo-Pt\_3Ni/C alloy nanoparticles.



**Fig. S11** The average site occupancies of the (A) first, (B) second, and (C) third layers in the  $Ni_{1175}Pt_{3398}$  nanoparticle and the (D) first, (E) second, and (F) third layers in the  $Mo_{73}Ni_{1143}Pt_{3357}$  nanoparticle at 170°C as determined by a Monte Carlo simulation. Blue spheres represent pure Pt, green represent pure Ni, and red represent pure Mo. Other colors represent fractional occupancies, as indicated by the color triangle on the right. Small spheres represent the positions of atoms in the outer layers.



**Fig. S12** STEM-EELS analysis of as-synthesized Fe-Pt<sub>3</sub>Ni/C octahedra. A and D, STEM images of two different oriented Pt<sub>3</sub>Ni nanoparticles. B and E, schematics of particle orientations corresponding to the respective STEM images. The arrows in A, B, D, E represent the EELS line scan directions. C and F, EELS line scans indicate that the preferential locations of Fe atoms are at the edges/tips of octahedra for both particles (Fe-Pt<sub>3</sub>Ni/C was chosen for EELS for its higher signal to noise ratio at this low concentration.).



**Fig. S13** The (A) first, (B) second, (C) third, and (D) fourth layers of a representative  $Ni_{1175}Pt_{3398}$  nanoparticle taken from a Monte Carlo simulation at 170°C. Grey spheres represent Pt and blue represent Ni. Small spheres represent the positions of atoms in the outer layers.



**Fig. S14** (A) The changes of normalized mass activity of Mo-Pt<sub>3</sub>Ni/C and Pt<sub>3</sub>Ni/C catalysts and (B) the changes of normalized specific activity of Mo-Pt<sub>3</sub>Ni/C and Pt<sub>3</sub>Ni/C catalysts during the potential cycles between 0.6-1.26 V versus RHE. The composition changes of (C) Pt<sub>3</sub>Ni/C and (D) Mo-Pt<sub>3</sub>Ni/C catalysts after 2000 cycles between 0.6-1.26 V versus RHE. Significant activity loss and elemental loss were observed for Mo-Pt<sub>3</sub>Ni/C catalyst in this new ADT condition, which is similar to what happened to Pt<sub>3</sub>Ni/C catalyst. This result is consistent with the calculation results that Mo increases the energy to remove Ni atoms from particle's surface and thus contributes to the stability enhancement.



**Fig. S15** The (A) first, (B) second, and (C) third layers of the predicted ground state  $Mo_6Ni_{41}Pt_{178}$  nanoparticle. Grey spheres represent Pt, blue represent Ni, and green represent Mo. Small spheres represent the positions of atoms in the outer layers.



**Fig. S16** The top five layers of the nine-layer  $Mo_2Ni_7Pt_{27}$  slab. Grey spheres represent Pt, blue represent Ni, and green represent Mo. The third and fourth layers are aligned so that the Ni atom is in the hollow site formed by three Pt atoms in the layer below it. The second layer is aligned so that the Mo atom falls in the hollow site formed by three Pt atoms in the third layer. The four bottom layers (not shown) are symmetrically equivalent to the four top layers.



**Fig. S17** The relaxed structures used to calculate the stability of (A) one, (B) two, (C) and three oxygen atoms adsorbed on a Mo atom on the vertex of  $Mo_6Ni_{41}Pt_{178}$ . Grey spheres represent Pt, green represent Mo, and red represent oxygen.

	Catalwat	Composition /molar%					
	Catalyst	Pt	Ni	М			
1	Pt <sub>3</sub> Ni/C	74.2±0.8	25.8±0.7	0			
2	V-Pt <sub>3</sub> Ni/C	73.9±0.6	24.7±0.8	1.4±0.2			
3	Cr-Pt <sub>3</sub> NiC	74.2±0.5	24.1±0.4	1.7±0.4			
4	Mn-Pt <sub>3</sub> Ni/C	74.4±0.7	24.1±0.6	1.5±0.3			
5	Fe-Pt <sub>3</sub> Ni/C	73.7±0.4	24.4±0.5	1.9±0.5			
6	Co-Pt <sub>3</sub> Ni/C	73.5±0.9	24.7±0.8	1.8±0.5			
7	Mo-Pt <sub>3</sub> Ni/C	73.9±0.5	24.5±0.5	1.6±0.4			
8	W-Pt <sub>3</sub> Ni/C	74.3±0.6	24.2±0.3	1.5±0.5			
9	Re-Pt <sub>3</sub> Ni/C	74.5±0.4	23.9±0.7	1.6±0.3			

 Table S1 Composition distribution for various transition-metal doped Pt<sub>3</sub>Ni/C catalysts.

Catalysts		Based on H <sub>upd</sub>				Based on CO stripping					
		ECSA	Specific activity		Mass activity		ECSA	Specific activity		Mass activity	
		$(m^2/g_{Pt})$	$(mA/cm^2)$		(A/mg <sub>Pt</sub> )		$(m^2/g_{Pt})$	(mA/cm <sup>2</sup> )		( A/mg <sub>Pt</sub> )	
			@ 0.9 V	@ 0.95 V	@ 0.9 V	@ 0.95 V		@ 0.9 V	@ 0.95 V	@ 0.9 V	@ 0.95 V
1	Pt <sub>3</sub> Ni/C	66.6	2.7	0.55	1.80	0.37	81.9	2.2	0.45	1.80	0.37
2	V-Pt <sub>3</sub> Ni/C	65.1	2.6	0.51	1.69	0.33	82.0	2.1	0.41	1.69	0.33
3	Cr-Pt <sub>3</sub> NiC	67.7	6.6	1.43	4.47	0.97	86.0	5.2	1.13	4.47	0.97
4	Mn-Pt <sub>3</sub> Ni/C	65.3	3.2	0.70	2.09	0.46	84.9	2.5	0.54	2.09	0.46
5	Fe-Pt <sub>3</sub> Ni/C	66.4	3.8	0.81	2.52	0.54	83.0	3.0	0.65	2.52	0.54
6	Co-Pt <sub>3</sub> Ni/C	67.5	5.1	0.99	3.46	0.67	86.1	4.0	0.78	3.46	0.67
7	Mo-Pt <sub>3</sub> Ni/C	67.7	10.3	2.08	6.98	1.41	83.9	8.2	1.74	6.98	1.41
8	W-Pt <sub>3</sub> Ni/C	66.4	5.5	1.10	3.54	0.73	82.4	4.4	0.89	3.54	0.73
9	Re-Pt <sub>3</sub> Ni/C	68.7	6.1	1.21	4.20	0.83	86.1	4.9	0.96	4.20	0.83
Ref. 53	PtNi/C	50	3.14	NA	1.45	NA	NA	NA	NA	NA	NA
Ref. 24	PtNi/C	48	3.8	NA	1.65	NA	NA	NA	NA	NA	NA
Ref. 21	PtNi <sub>2.5</sub> /C	21	NA	NA	3.3	NA	31	NA	NA	3.3	NA
Ref. 28	Pt <sub>3</sub> Ni/C nanoframes	NA	NA	NA	5.7	0.97	NA	NA	1.48	5.7	0.97

**Table S2** Performance of various transition metal doped Pt<sub>3</sub>Ni/C catalysts in this work and several representative results with high performance from recent published works.

### **References and Notes**

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