Supporting Information

Phase Stability of Large-Size Nanoparticle Alloy Catalysts at Ab Initio Quality Using a Nearsighted Force-Training Approach

Cheng Zeng[†], Sushree Jagriti Sahoo[‡], Andrew J. Medford[‡], and Andrew A. Peterson[†,*]

†School of Engineering, Brown University, Providence, Rhode Island, 02912, United States.
‡ School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, Georgia 30318, United States.
**Corresponding author: Email: andrew_peterson@brown.edu, Tel: +1 401-863-2153*

This Supporting Information (SI) includes the representative cubocahedron and icosahedron structures used to generate the training data (atomic chunks) and the corresponding average atomic uncertainties for the relaxed structures of those full-size nanoparticles, statistics for the atomic chunks, validation of force consistency between GPAW and SPARC, energies and configurations for a 147-atom icosahedron and cuboctahedron, energies and configurations for two $Pt_{80}Co_{67}$ icosahedra (one is of corner occupancy and the other is of terrace center occupancy on the surface), fitted size dependency of pure Pt nanoparticle energies including the edge terms, and shell-by-shell compositions and configurations of a $Pt_{96}Co_{105}$ regular truncated octahedron.

S-1 Nanoparticles used to generate training data

Figure. S1 shows average atomic uncertainties of forces for the relaxed structures of representative nanoparticles. The corresponding configurations are shown at the top of each bar.

S-2 Statistics of generated atomic chunks

Figure. S2 shows statistics of the atomic chunks, including DFT-calculated atomic forces on the central atoms (a), number of atoms (b), force prediction residuals (c), and per-atom energy prediction residuals (d). The average force magnitude is calculated to be 0.59 eV/Å. The average number of atoms is around 104 atoms. The mean absolute deviation (MAE) of atomic forces between DFT forces and ML-predicted forces is 0.15 eV/Å. The MAE of per-atom energy between DFT energies and ML-predicted energies is 2.5 meV/atom.

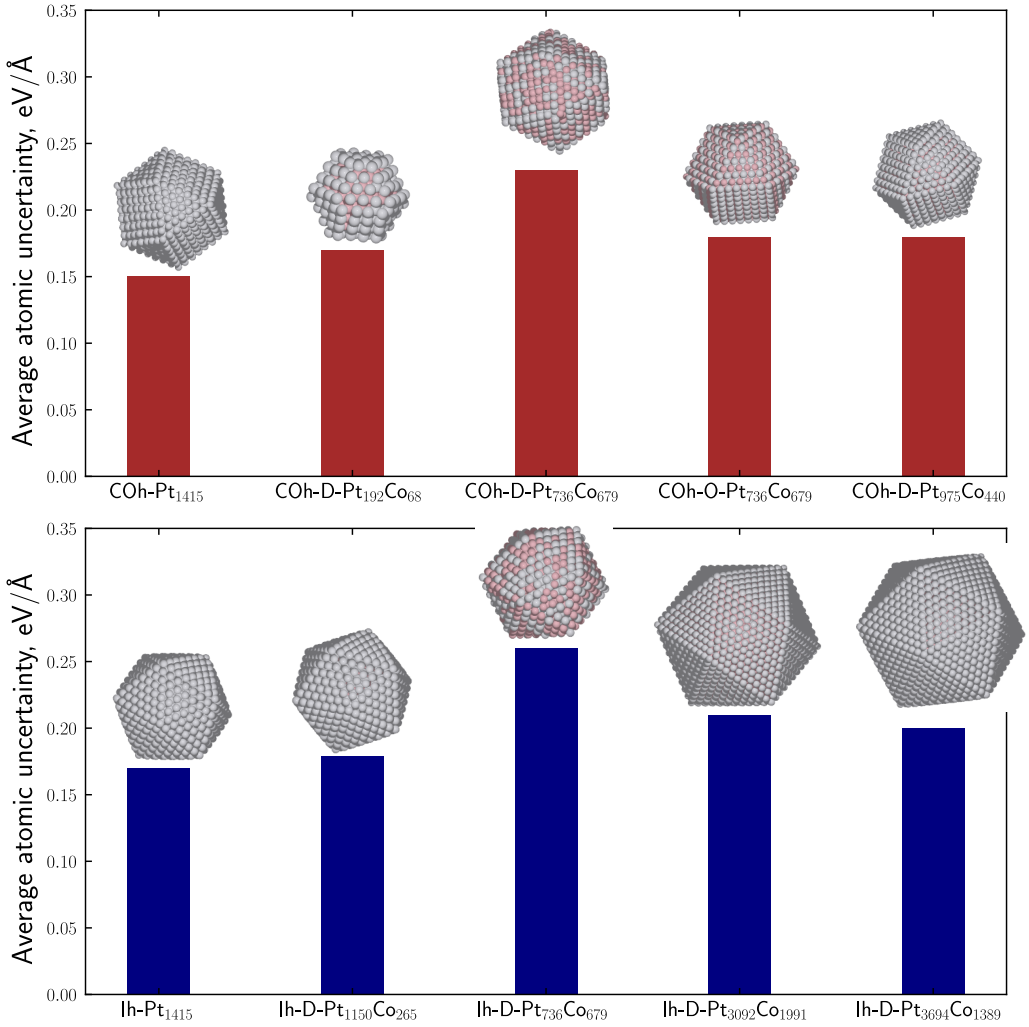

Figure S1: Nanoparticles used to generate atomic chunks and the corresponding average atomic uncertainty of forces of their relaxed structures. COh and Ih represent cuboctahedron and icosahedron, respectively. 'D' and 'O' indicate respective disordered and ordered structures.

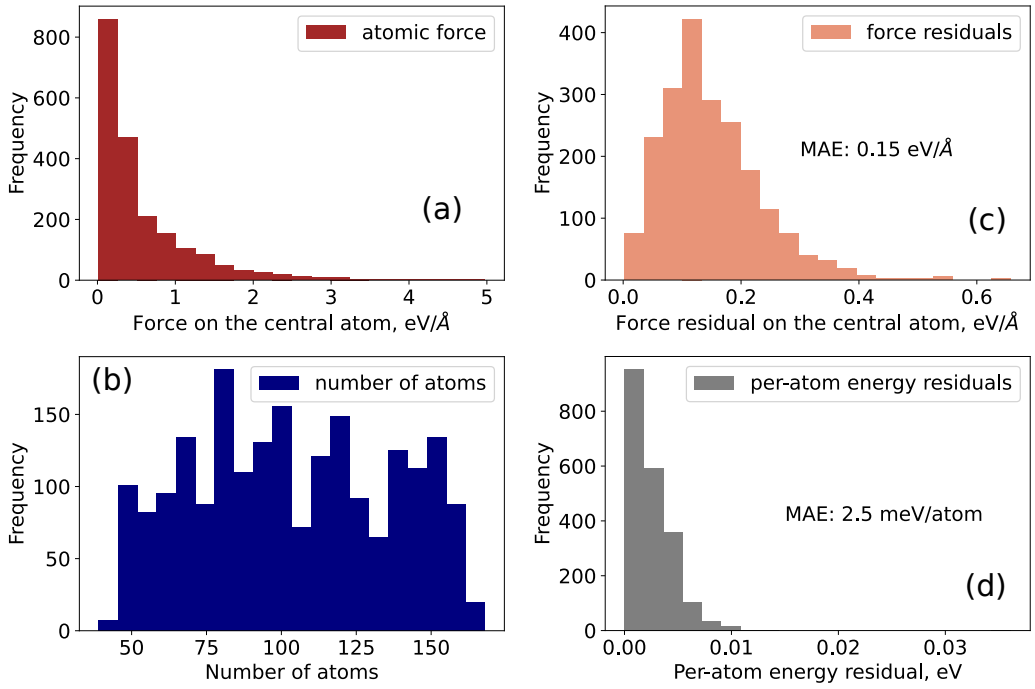

Figure S2: Statistics of generated atomic chunks. (a) Forces on the central atom, (b) Number of atoms in the atomic chunk, (c) Force prediction residuals using the force ensemble model, (d) Per-atom energy prediction residuals using the energy ensemble model.

S-3 Validation of force consistency between GPAW and SPARC

This work is mainly concerned with atomic forces and relative energy differences between different nanoparticles/clusters. We used two DFT codes with different computational settings, namely GPAW and SPARC. To make sure that both codes lead to consistent force predictions, we compare the atomic forces from GPAW and SPARC on various systems, as shown in the Figure. S3. It is clear that small MAEs are observed across all systems, leading to an overall MAE of around 0.023 eV/Å. It confirms the consistency of force predictions between GPAW and SPARC.

S-4 Energies and configurations for a 147-atom icosahedron and cubocahedron

Figure. S4 displays the ML-predicted and DFT-calculated engergies for a 147-atom icosahedron and cubocahedron relaxed by ML models. Both ML models and DFT calculations show that the icosahedron structure is more stable than the cubocahedron structure by around 1 eV.

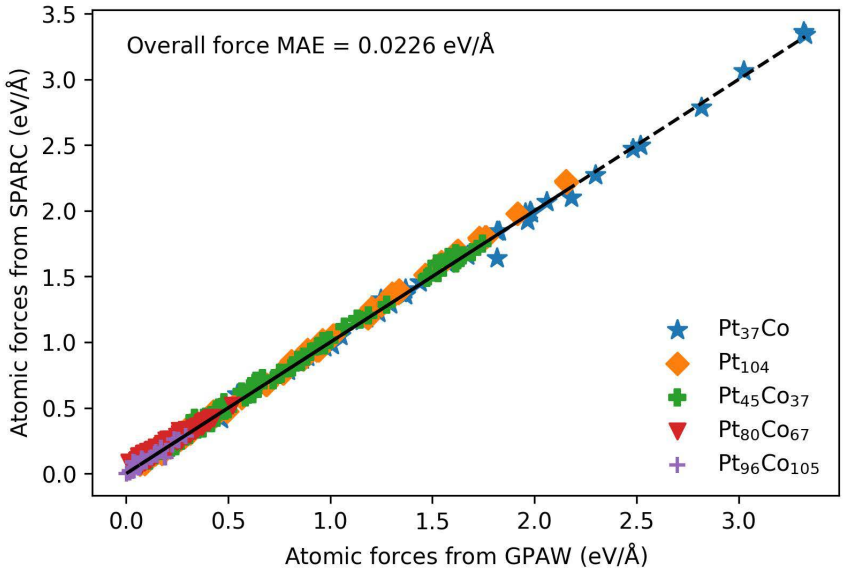

Figure S3: Comparison of forces from GPAW and SPARC on five test clusters, including $Pt_{37}Co$, Pt_{104}, $Pt_{45}Co_{37}$, $Pt_{80}Co_{67}$ and $Pt_{96}Co_{105}$.

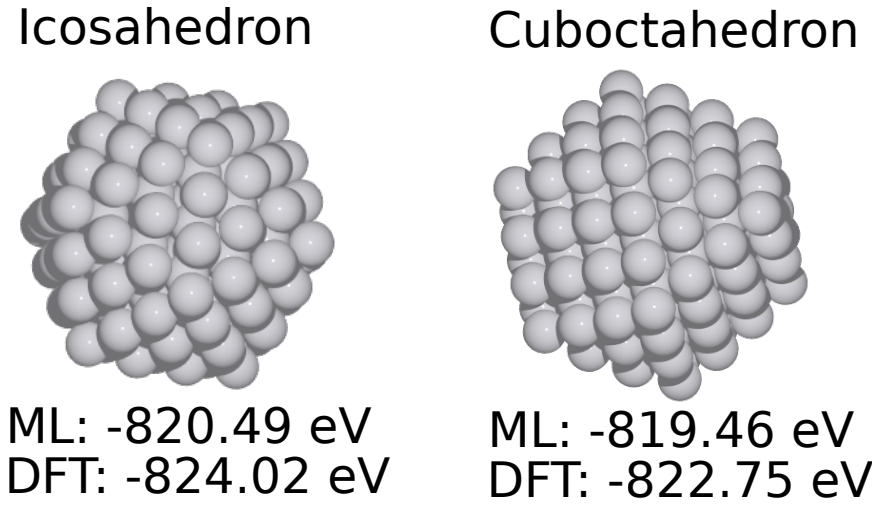

Figure S4: Configurations and energies of a 147-atom icosahedron and cubocahedron.

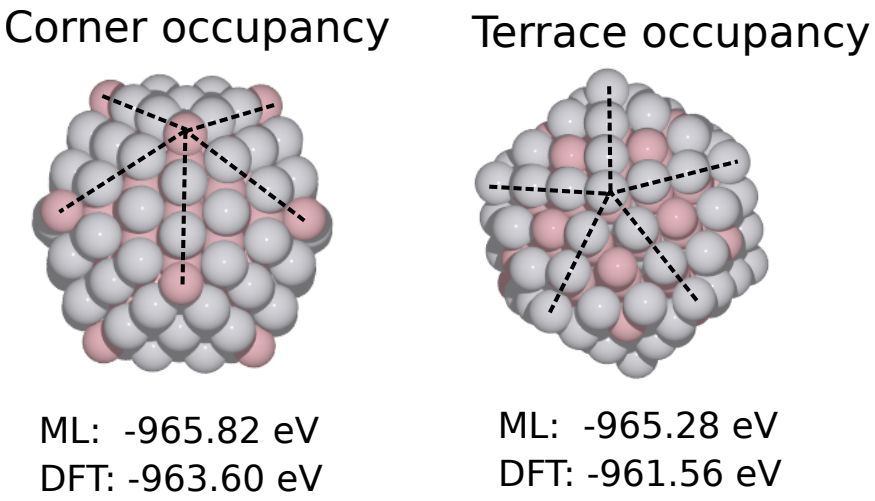

Figure S5: Configurations of two types of $Pt_{80}Co_{67}$, with Co atoms on the surface occupying the corner (Left) and occupying the terrace center (Right).

S-5 Energies and configurations for two types of $Pt_{80}Co_{67}$ icosahedra

Figure. S5 shows two low-energy configurations of $Pt_{80}Co_{67}$. The one with corner occupancy is identified by brute-force DFT calculations [1]. The one with terrace center occupancy is found by the GA study using ML models. Both ML models and DFT calculations suggest that corner occupancy is more energetically favorable than terrace center occupancy by $\sim$4 meV/atom and $\sim$14 meV/atom, respectively. However, the small DFT energy difference between two structures implies that the low-energy configuration of terrace center occupancy is missing in the brute-force approach [1].

S-6 Fitted size dependency of pure Pt nanoparticle energies including the edge terms

Figure S6 shows the raw ML predicted energetics and the fitted results using the Eq. 2. At a first glimpse, the coefficient for edge contributions are comparable to that for surface contributions, but if we take into account the value of $N^{-1/3}$, the edge term becomes much less significant.

S-7 Shell-by-shell compositions and configurations of two $Pt_{96}Co_{105}$ truncated octahedron

For a $Pt_{96}Co_{105}$ truncated octahedron, MC simulations at 300 K were performed to find the putative global minima. A structure after 9200 MC steps was regarded as the MC minima. It was compared to the fully $L1_0$ ordered structure. Both structures were relaxed by the force model and the energetics were obtained by the energy model, and a comparison for the energy difference was made with the DFT result. Both ML models and DFT calculations find the MC structure to be more stable than

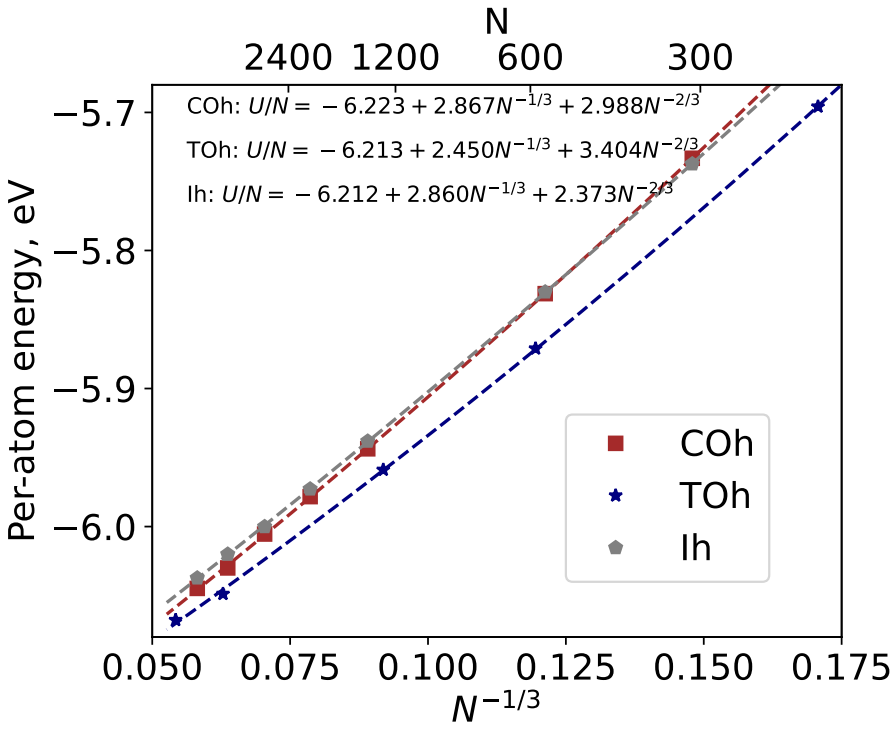

Figure S6: Energies of relaxed structure motifs of Pt nanoparticles, plotted as per-atom energy (U/N) versus $N^{-1/3}$. COh, TOh and Ih represent cuboctahedron, truncated octahedron and icosahedron, respectively. The fitted results were based on Eq. 2 where edge terms were considered.

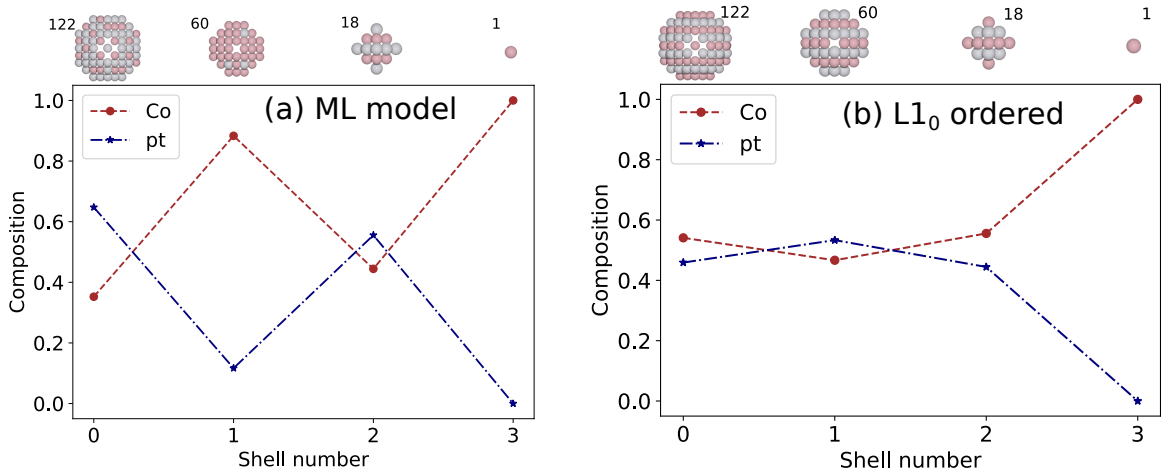

Figure S7: Composition depth profile of a truncated octahedron $Pt_{96}Co_{105}$: the putative global minima found by ML models (a), and the fully $L1_0$ ordered Co–Pt nanoparticle alloy (b). Atomic arrangement at each shell and the total number of atoms are provided at the top.

the $L1_0$ structure, by energy differences of 17.4 eV (0.086 eV/atom) and 22.3 eV (0.111 eV/atom), respectively. The DFT calculated maximum atomic forces for the MC and $L1_0$ structures are 0.41 and 0.29 eV/Å, respectively, both of which are within the maximum atomic uncertainties by ML models, *i.e.* 0.5 and 0.45 eV/Å. It suggests that the most stable atomic arrangement of a Co–Pt truncated octahedron with nearly equal compositions is not fully $L1_0$ ordered.

References

[1] Noh, S.H.; Seo, M.H.; Seo, J.K.; Fischer, P.; Han, B. First principles computational study on the electrochemical stability of Pt–Co nanocatalysts. *Nanoscale* **2013**; 5, 8625–8633. Publisher: The Royal Society of Chemistry.