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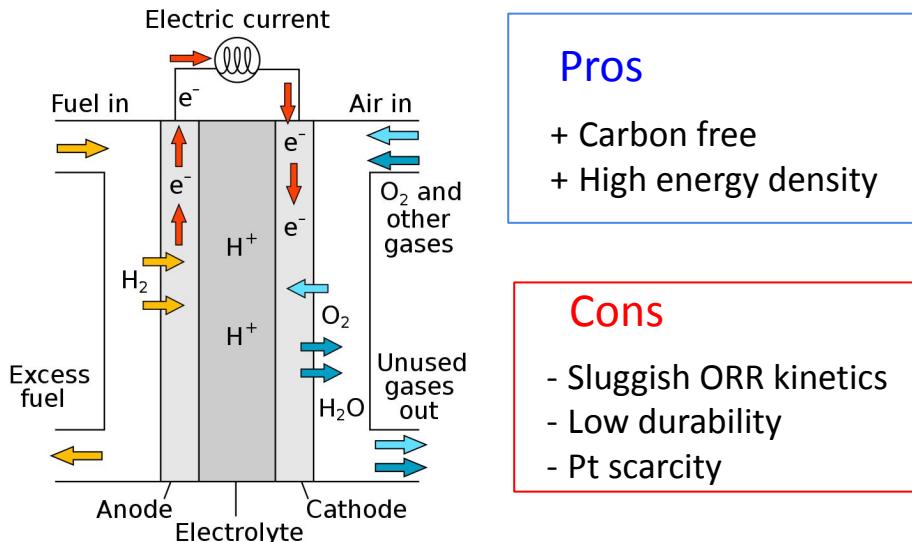
Catalyst
Design Lab

Computational Design of Co-Pt Nanoparticles for Enhanced Oxygen Reduction

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School of Engineering, Brown University

Fuel cell – oxygen reduction reaction (ORR)

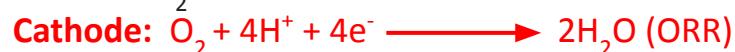


Pros

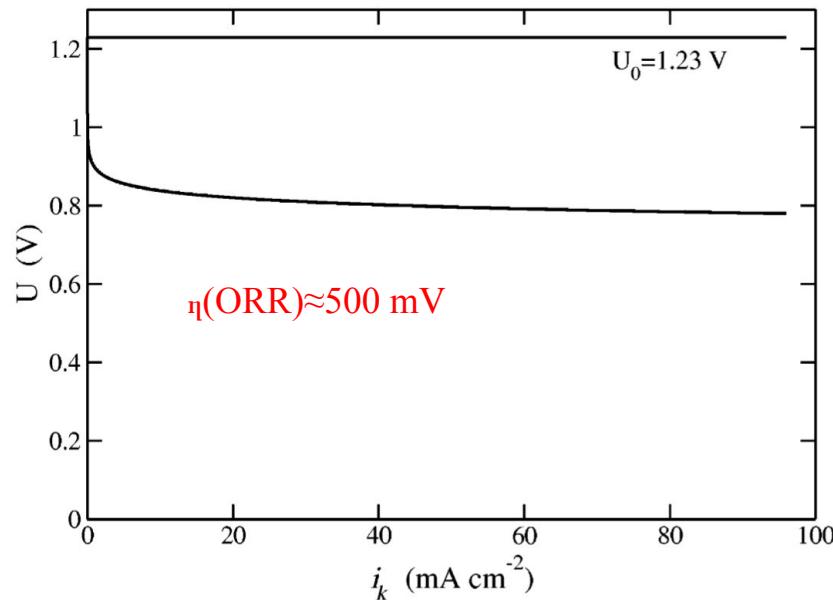
- + Carbon free
- + High energy density

Cons

- Sluggish ORR kinetics
- Low durability
- Pt scarcity

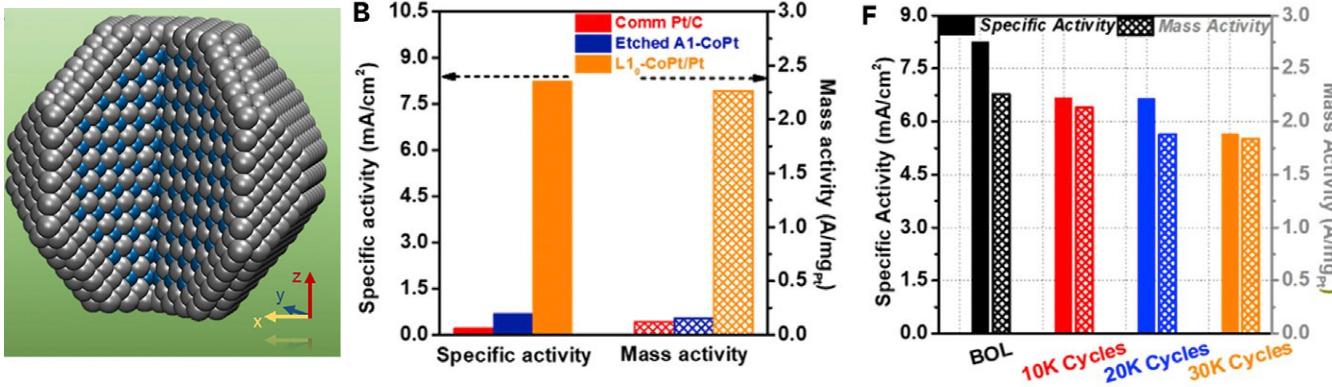


The best elemental catalyst (Platinum)



CoPt/Pt core-shell nanoparticles for enhanced ORR

Surpassing DOE 2020 targets for both ORR activity and durability

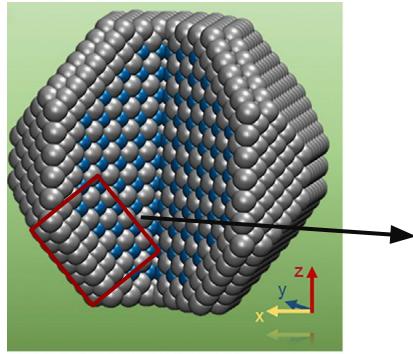


J. Li et al., Joule, 3: 124-135 (2019)

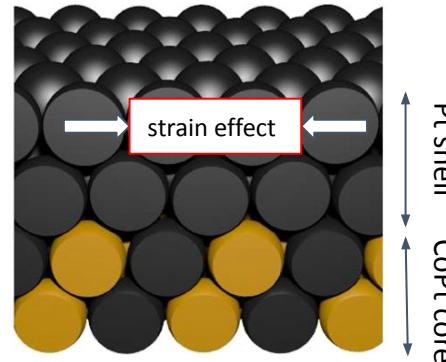
- 8.9 nm L1₀-CoPt/Pt core-shell nanoparticles with a Co composition of 44%.
- Mass activity 19 times that of commercial Pt/C.
- 18% loss of mass activity after 30,000 durability test cycles.

Motivation

Realistic scale: ~20000 atoms



Slab system: 48 atoms



J. Li et al., *Joule*, **3**: 124-135 (2019)

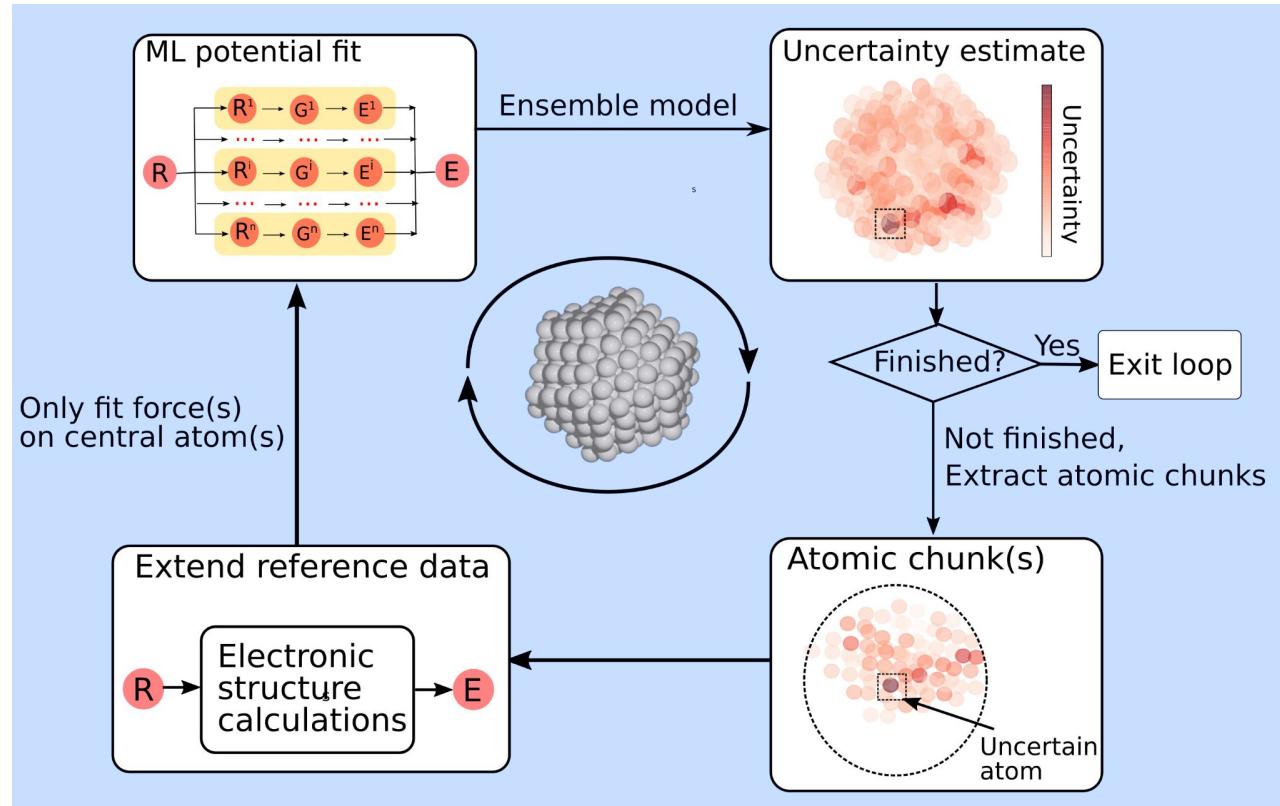
S. Sharma, C. Zeng and A. A. Peterson,
J. Chem. Phys., **15** (2019)

- Stable structure of full-scale nanoparticles
- Strain effect on adsorption energies

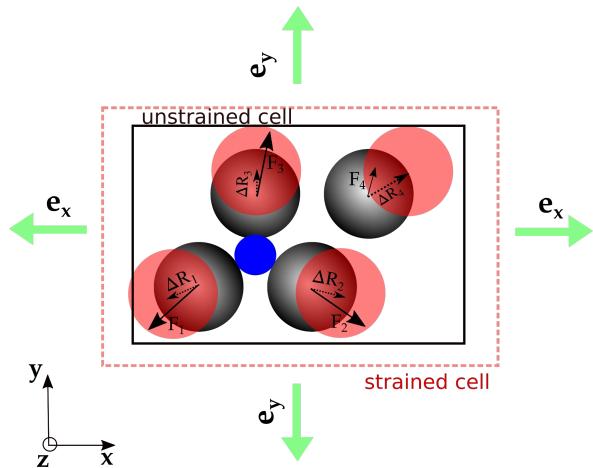
A nearsighted force-training (NFT) approach

Atomic uncertainty

$$\delta_i = 2.58\sigma_f = 2.58 \sqrt{\frac{\sum_{j=1}^M \left\| \mathbf{f}_i^{(j)} - \bar{\mathbf{f}}_i \right\|^2}{M - 1}}$$



Atomistic models for strain effect



$$\Delta E_b(\epsilon_0) = E_b(\epsilon_0) - E_b(\mathbf{0})$$

$$E_b[A] = E[A*] - E[*] - E_{\text{ref}}[A]$$

$$\Delta E_b(\varepsilon_0) \approx - \sum_{i \in S} [F_i^\dagger] \cdot [\Delta R_i]$$

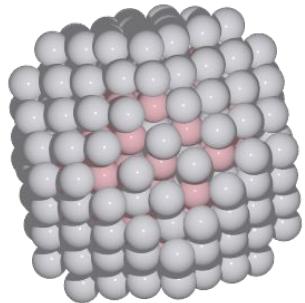
Adsorbate-induced
forces (eigenforces)

Displacement due to an
external strain

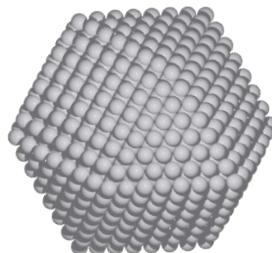
- C. Zeng & A. A. Peterson. Atomistic models for strain effect on metal surface reactivity, including the role of surface relaxation (In preparation)
- J. Li*, S. Sharma*, K. Wei, Z. Chen, D., H. Lin, C. Zeng, M. Chi, Z. Yin, M. Muzzio, M. Shen, P. Zhang, A. A. Peterson, S. Sun. Anisotropic strain tuning of L1₀ ternary nanoparticles for oxygen reduction. *JACS*, 142(45), 19209-19216, 2020. (*Equal contributions)
- S. Sharma, C. Zeng & A. A. Peterson. Face-centered tetragonal (FCT) Fe and Co alloys of Pt as catalysts for the oxygen reduction reaction (ORR): A DFT study. *The J. of Chem. Phys.*, 15(4), 041704, 2019.

Learning Co-Pt nanoparticles with NFT

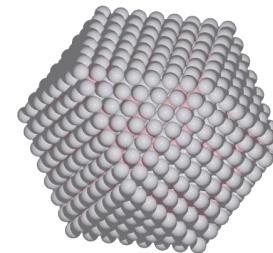
$\text{Pt}_{192}\text{Co}_{68}$, Pt shell, disordered PtCo core



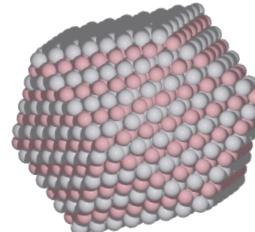
Pt_{1415} , octahedron



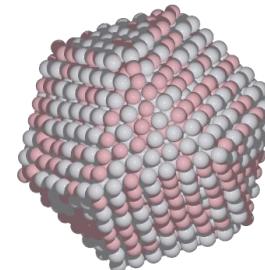
$\text{Pt}_{975}\text{Co}_{440}$, core-shell
disordered core



$\text{Pt}_{736}\text{Co}_{679}$, PtCo L₁₀
ordered alloy



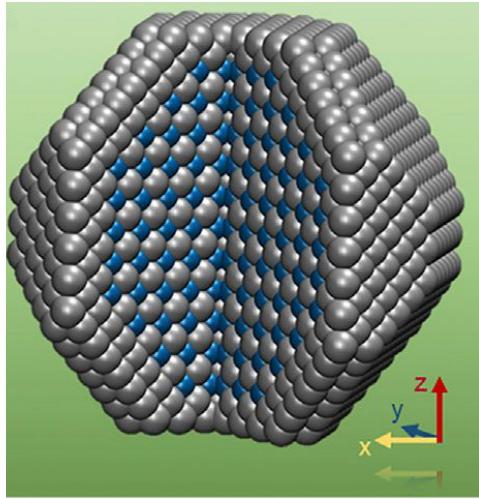
$\text{Pt}_{736}\text{Co}_{679}$, PtCo
disordered alloy



Training data: 18 CoPt bulk cells and
1777 atomic chunks

A full-scale core-shell CoPt/2Pt truncated octahedron (TOh)

17561-atom Pt₉₈₃₅Co₇₇₂₆,
8.5 nm, 44% Co



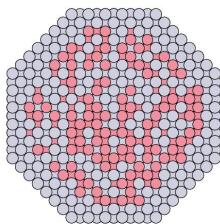
Most probable radius

Bond	Predicted R [Å]	Exp. R [Å]
Pt-Pt	2.68	2.69
Co-Co	2.62	2.65

*Exp. size and Co composition: 8.9 nm and 44% Co

J. Li et al., Joule, 3: 124-135 (2019)

A microkinetic model for ORR mass activity

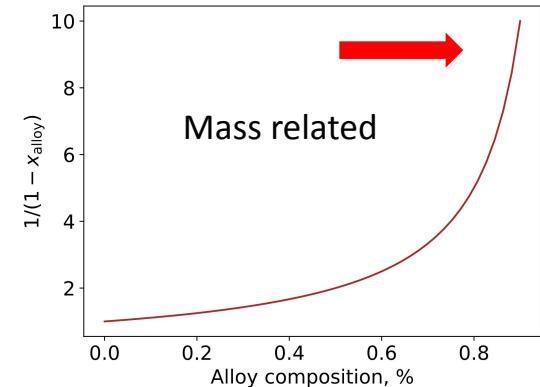
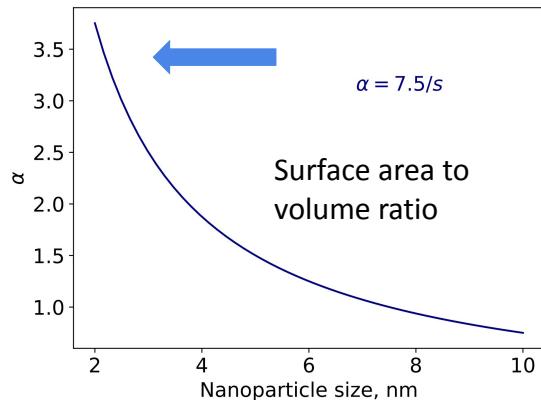
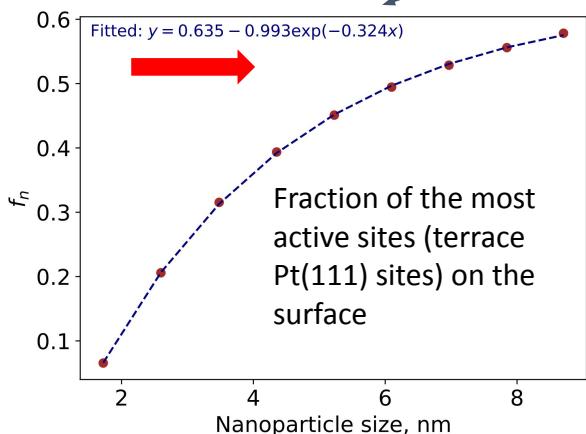


Mass activity of Pt or Core-shell CoPt/2Pt truncated octahedrons

$$j(U) = \frac{n}{M_{\text{Pt}}} (j_0 \cdot e^{-\Delta G(U)/k_B T}) = \frac{n}{n_{\text{sites}}} \cdot \frac{n_{\text{sites}}}{A} \cdot \frac{A}{V} \cdot \frac{V}{M_{\text{Pt}}} \cdot (j_0 \cdot e^{-\Delta G(U)/k_B T})$$

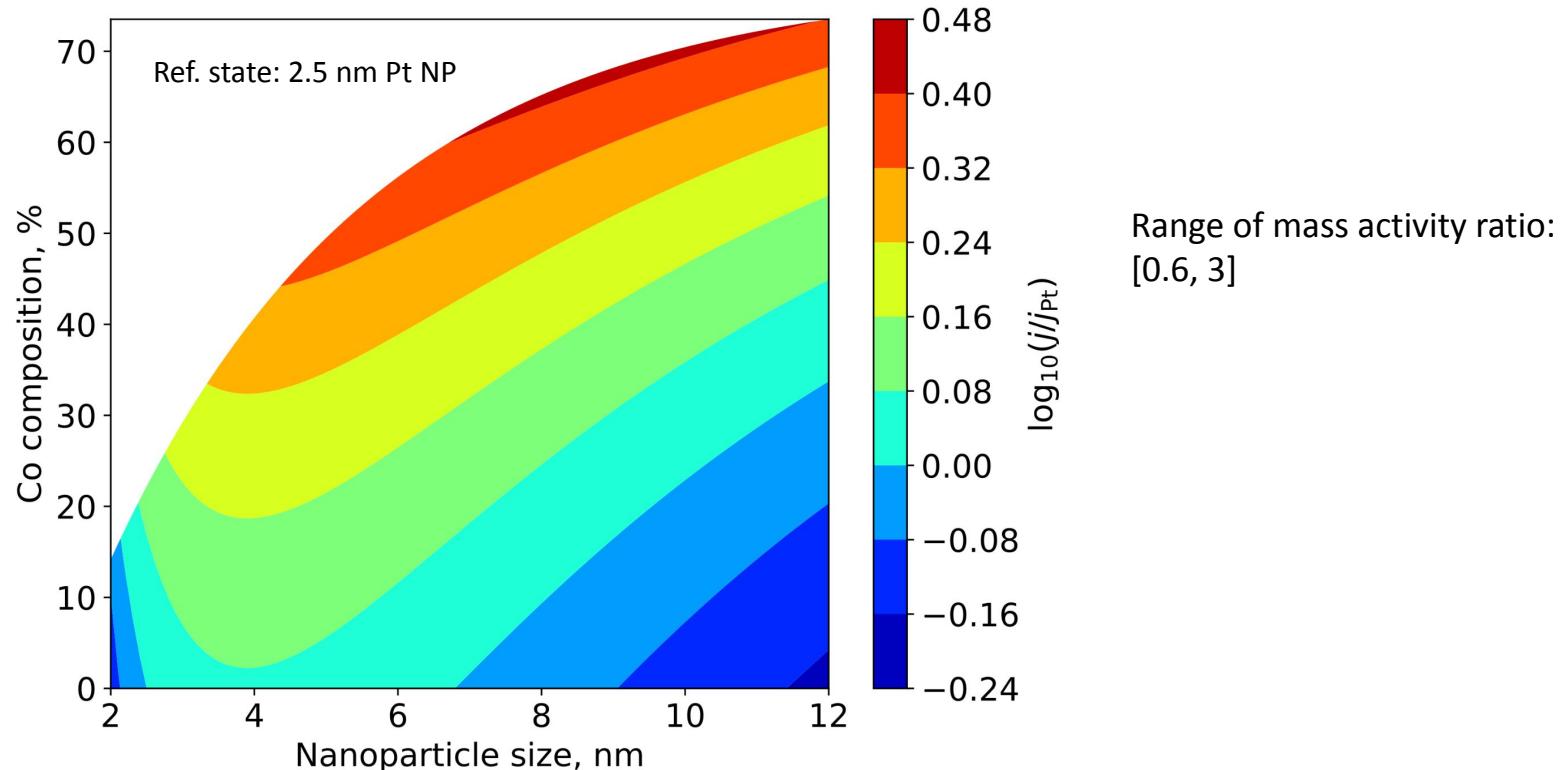
Number of sites per surface area, constant

Reaction barrier



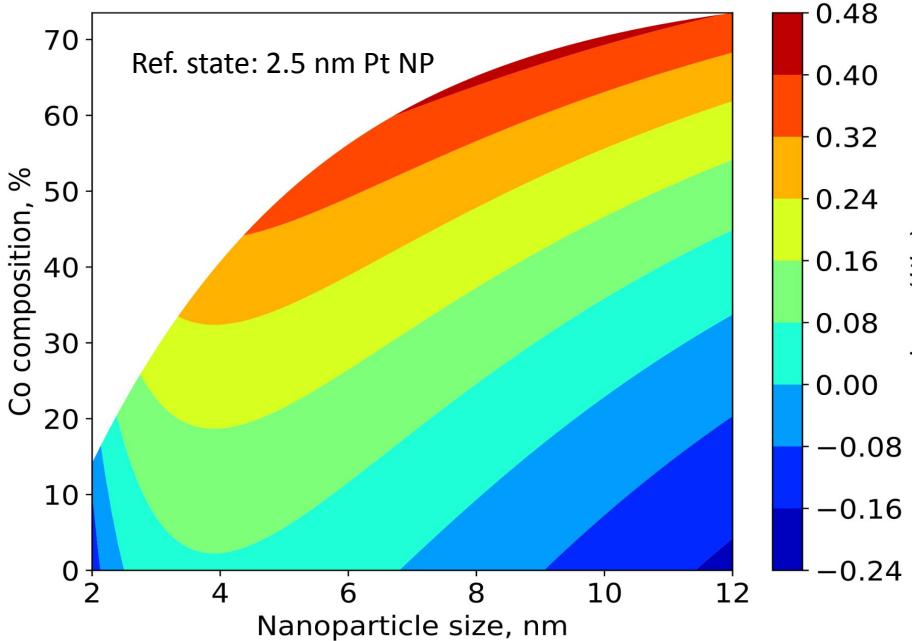
*Specifically, we consider U=1.23 V vs RHE, and mass activity ratio of $j(U)/j_{\text{Pt}}(U)$.

Trends in ORR activity without reaction barriers



Trends in ORR activity for core-shell CoPt/2Pt TOh

$$j(U) = \frac{n}{M_{\text{Pt}}} (j_0 \cdot e^{-\Delta G(U)/k_B T}) = \frac{n}{n_{\text{sites}}} \cdot \frac{n_{\text{sites}}}{A} \cdot \frac{A}{V} \cdot \frac{V}{M_{\text{Pt}}} \cdot (j_0 \cdot e^{\boxed{-\Delta G(U)/k_B T}})$$



ORR free energy diagram
 $\Delta G_0(U = 1.23V) = 0.52 \text{ eV}$



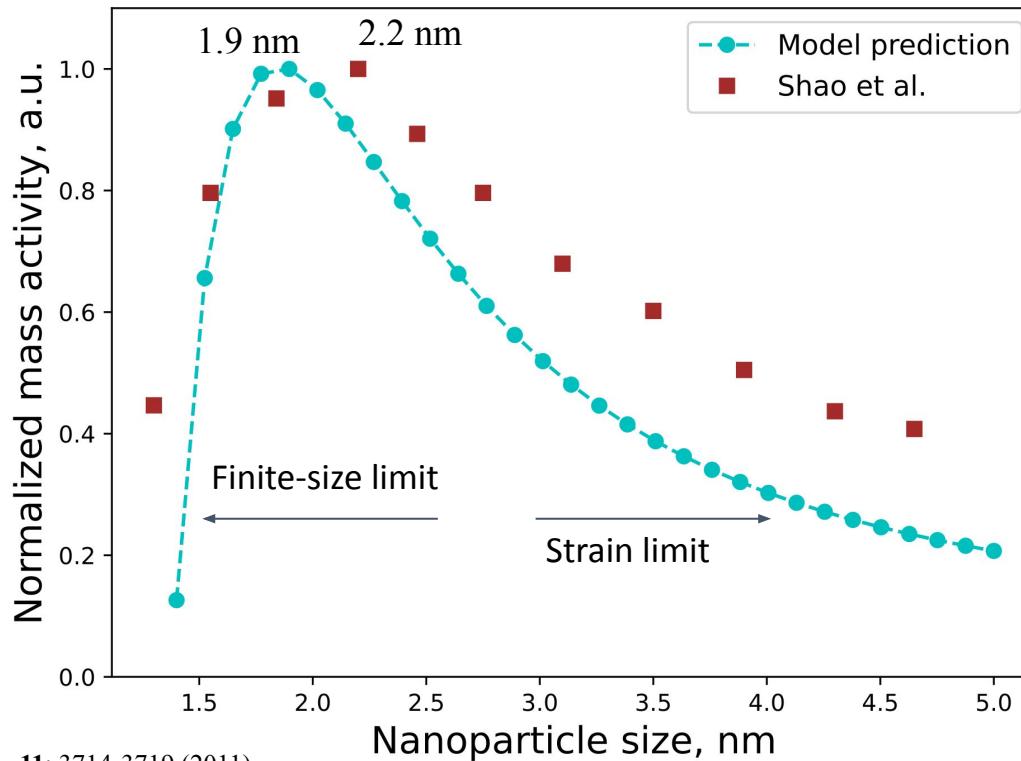
ML models
 $\varepsilon_{\text{T111}}(\text{size}, x_{\text{Co}})$

Eigenforce model + DFT

$$\Delta G[*\text{OH}] = \frac{0.165}{-4.16} \varepsilon_{\text{T111}}(\text{size}, x_{\text{Co}}) + 0.12 * x_{\text{Co,core}}$$

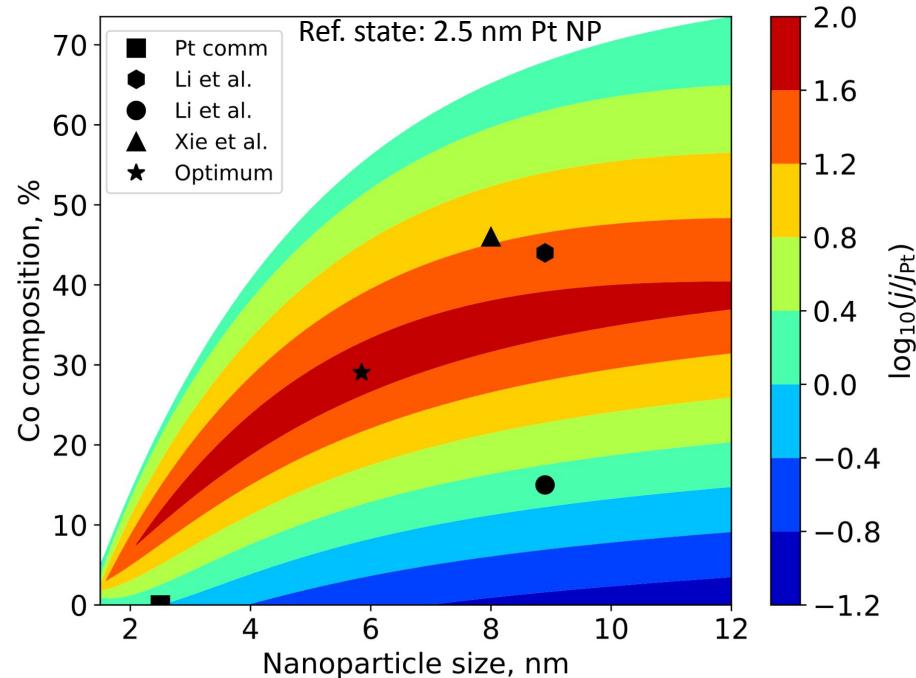
Reaction barrier
 $\Delta G(\text{size}, x_{\text{Co}})$

Trends in ORR activity for pure Pt TOh



M. Shao et al., *Nano. Lett.*, **11**: 3714-3719 (2011)

Trends in ORR activity for core-shell CoPt/2Pt TOh



Predicted mass activity versus Experimental data

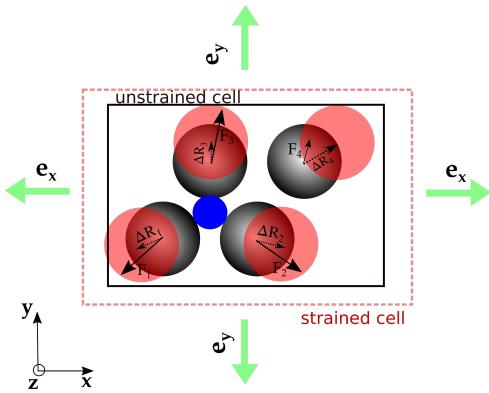
(size [nm], x_{Co} [%])	Model [j/j_{pt}]	Experiments [j/j_{pt}]
(8.9, 15)	1.6	1.3
(8.9, 44)	22	19
(8.0, 46)	14.1	13.4
(5.8, 29)	72	?

J. Li et al., Joule, 3: 124-135 (2019)

M. Xie et al., JACS 143: 8509-8518 (2021)

Take home messages

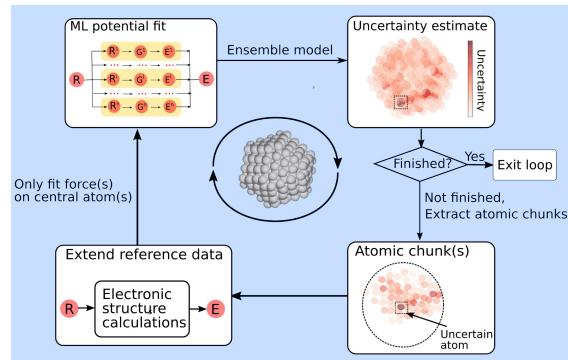
Atomistic models



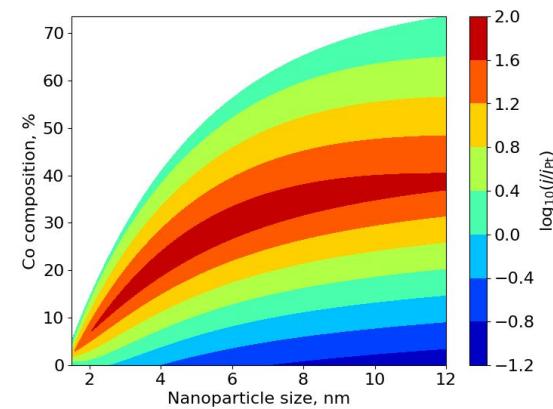
- Atomic forces and displacements used to quantify strain effect.

A novel ML framework

- Nearsighted force training to systematically explore building chunks for potential energy surfaces.



Design principle of catalysts



- A combined approach to computationally design realistic scale catalysts for desirable activity and stability.

Acknowledgements



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Andrew Peterson

Collaborators

- Pradeep Guduru (Brown University)
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- Junrui Li (Brown University)
- Shouheng Sun (Brown University)
- Sushree Jagriti Sahoo (Georgia Tech)
- Andrew Medford (Georgia Tech)

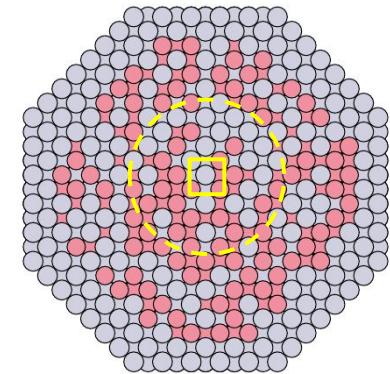
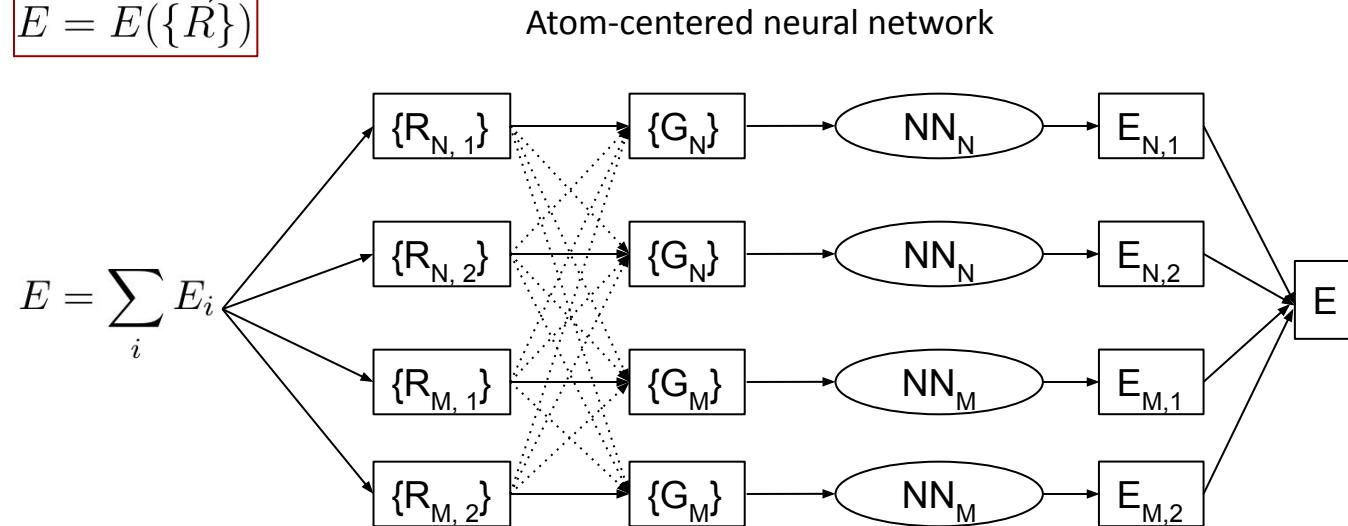


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Atom-centered Neural Network Potential

Neural network (NN) regression has gained its momentum in the last two decades because it can fit any arbitrary function, which makes it ideal for fitting the PES whose function form is unknown.

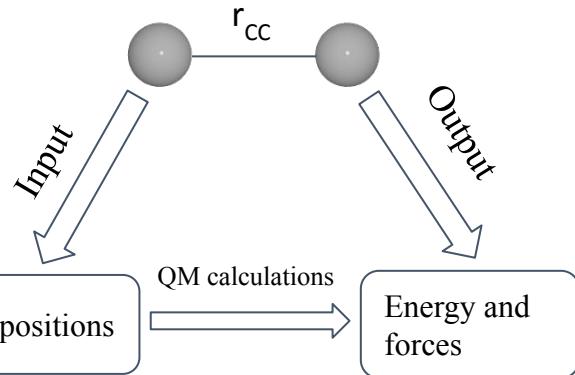
$$E = E(\{\vec{R}\})$$



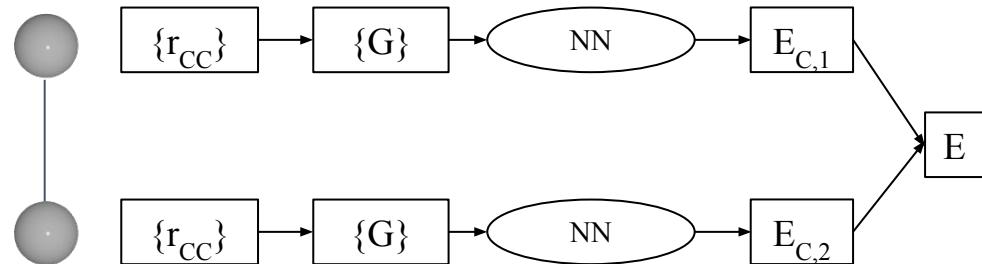
- Each atomic energy comes from the atom interacting with its neighbors (local chemical environment).

How Atom-centered NN Potential Works?

An example structure



Journey of a structure in atom-centered NN

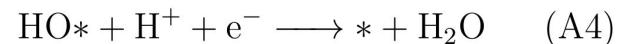
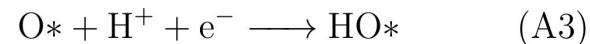
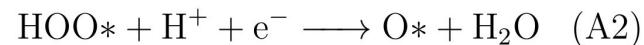
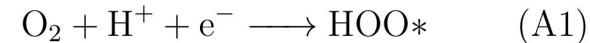
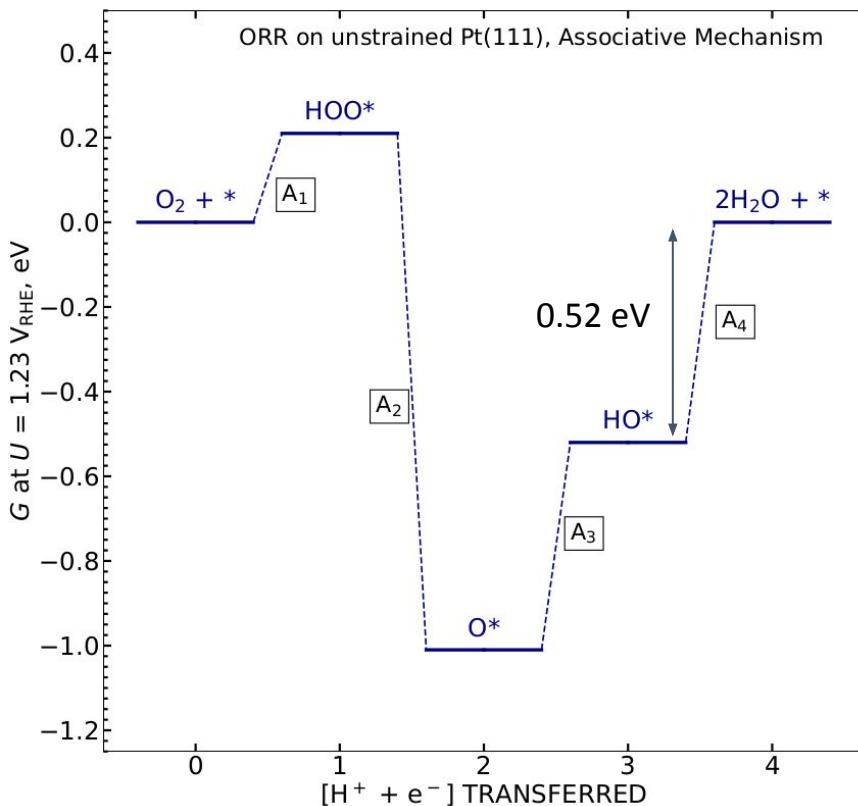


$$\text{Forces: } \mathbf{F}_i = - \left(\frac{\partial E}{\partial \mathbf{R}_i} \right)_{j \neq i}$$

Loss function

$$Loss = \frac{1}{2} \sum_{j=1}^M \left\{ \left(E_j/N_j - \hat{E}_j/N_j \right)^2 + \frac{\alpha}{3N_j} \sum_{k=1}^3 \sum_{i=1}^{N_j} \left(F_{ik} - \hat{F}_{ik} \right)^2 \right\}$$

ORR free energy diagram



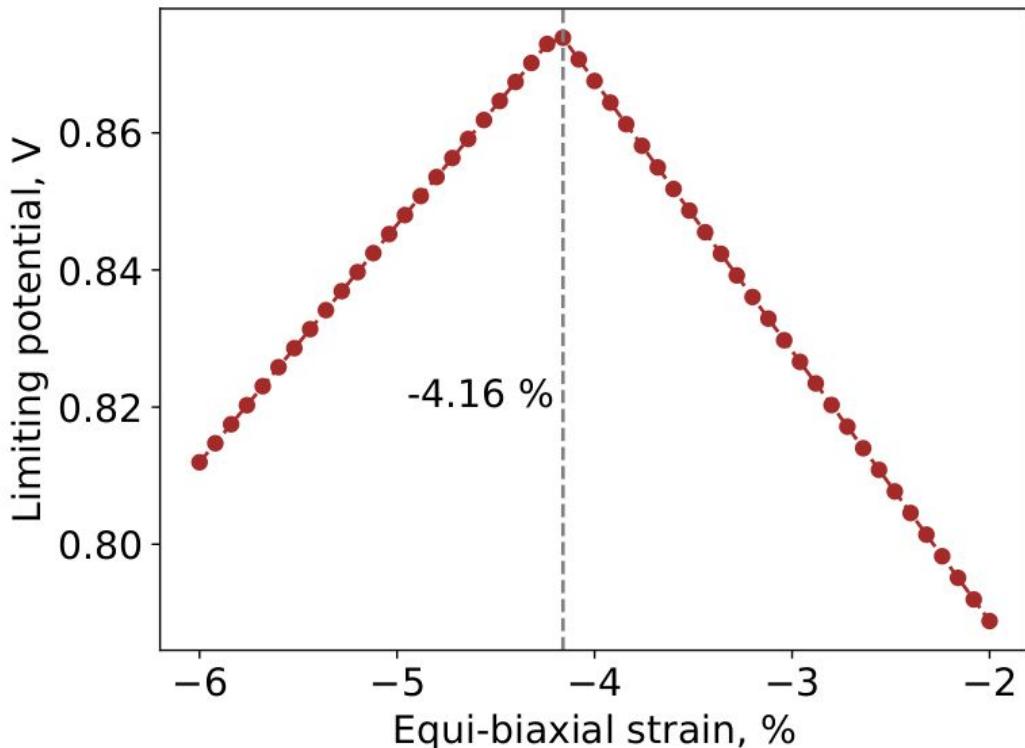
- On unstrained Pt(111) surface, the limiting potential is 0.71 V.

$$\Delta E_b[O^*] = 2\Delta E_b[HO^*]$$

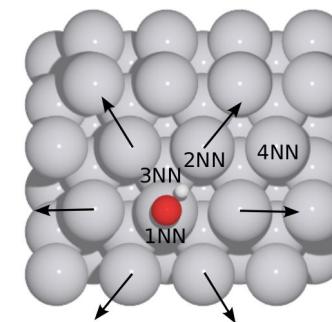
$$\Delta E_b[HOO^*] = 0.88\Delta E_b[HO^*]$$

- HO^* binding energy as the descriptor.
- Optimal HO^* binding energy: ~ 0.165 eV weaker than that on unstrained Pt(111).

Finding optimal strain by an eigenforce model



Positive eigenforces, compressive strains weaken binding energies.



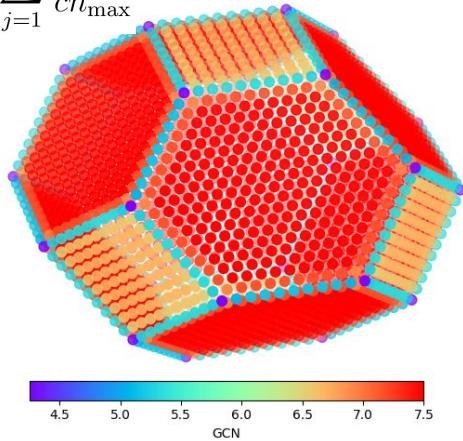
$$\Delta E_b^I[*\text{OH}] = - \sum_{i \text{ in } S} F_i^\dagger \Delta R_i$$

$$\Delta G[*\text{OH}] = \frac{0.165}{-4.16} \varepsilon$$

Relating structure to limiting potential

Generalized coordination number

$$\overline{CN}_i = \sum_{j=1}^{M_i} \frac{cn(j)}{cn_{\max}}$$

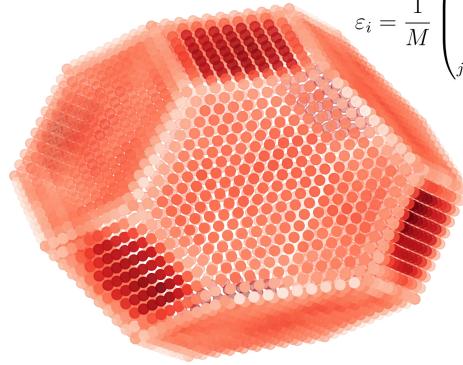


HO* binding energy at different unstrained sites

$$E_b^{(0)}[*OH] = -1.00 + 0.23\overline{CN}$$

Atom-level local surface strain

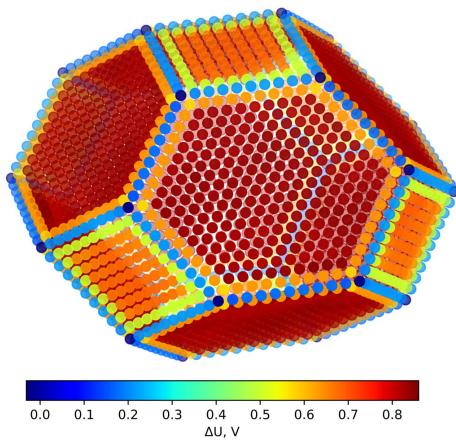
$$\varepsilon_i = \frac{1}{M} \left(\sum_{\substack{j=1 \\ j \in \{\text{NN}_i\}}}^M \frac{d_{ij} - d_{Pt}}{d_{Pt}} \right)$$



HO* binding energy at the same site, with various strains

$$\Delta E_b[*OH] = \frac{0.165}{-4.16} \varepsilon \quad (\text{T111 sites})$$

Atom-level limiting potential

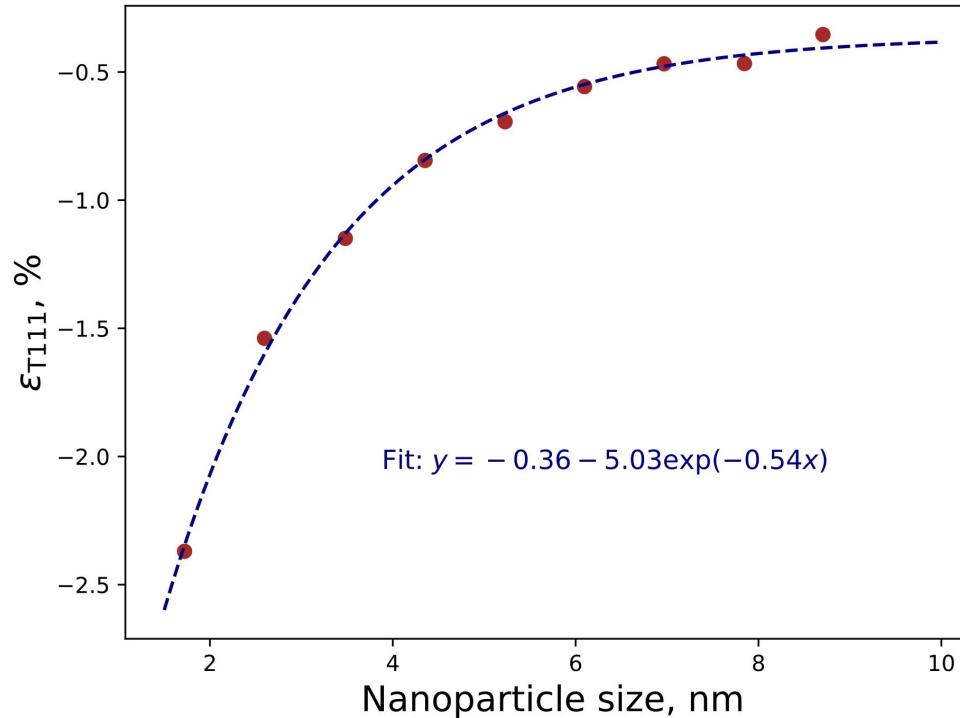


Limiting potential as a function of HO* binding energy

Size dependence

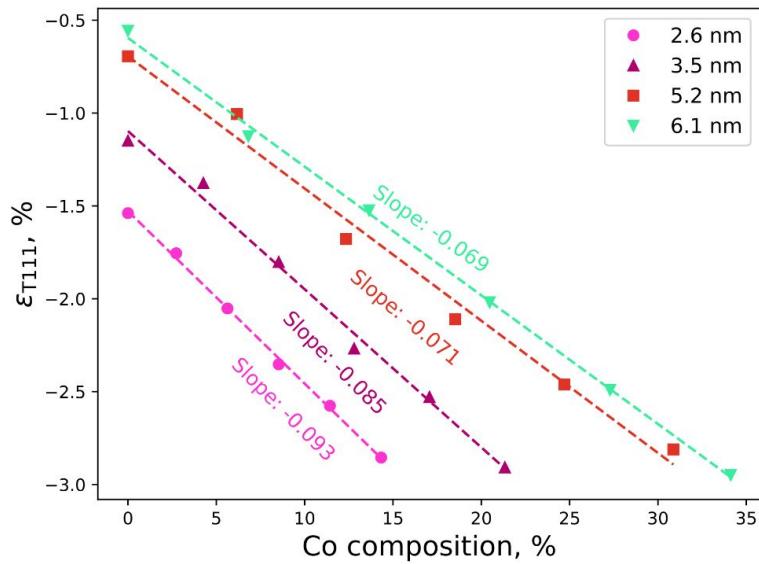
Average surface strain on fcc(111) terrace sites

Average strain on terrace (111) sites (ε_{T111}) as the single descriptor for the strain effect on reaction barrier of a Co-Pt nanoparticle.



Co composition dependence

Vegard's law in core-shell CoPt/2Pt TOh



Size-coupled composition dependence

