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Atomistic Explanation of the Dramatically Improved Oxygen Reduction Reaction of Jagged Platinum Nanowires, 50 times better than Pt

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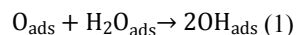
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ABSTRACT: Pt is the best catalyst for the oxygen reduction reactions (ORR) but it is far too slow. Huang and coworkers showed that dealloying 5 nm Ni₇Pt₃ Nanowires (NW) led to 2 nm pure Pt Jagged NW (J-PtNW) with ORR 50 times faster than Pt/C. They suggested that the under-coordinated surface Pt atoms, mechanical strain, and high electrochemically active surface area (ECSA) are the main contributors. We report here multiscale atomic simulations that further explain this remarkably accelerated ORR activity from the atomistic perspective. We used the ReaxFF reactive force field to convert the 5 nm Ni₇Pt₃ NW to the jagged 2 nm NW. We applied Quantum Mechanics to find that 14.4% of the surface sites are barrier-less for O_{ads} + H₂O_{ads} → 2OH_{ads}, the rate determining step (RDS). The reason is that concave nature of many surface sites pushes the OH bond of the H₂O_{ads} close to the O_{ads}, leading to a dramatically reduced barrier. We used this observation to predict the performance improvement of the J-PtNW relative to Pt (111). Assuming every surface site reacts independently with this predicted rate leads to a 212-fold enhancement at 298.15K, compared to 50 times experimental. The atomic structures of the active sites provide insights for designing high-performance electrocatalysts for ORR.

1. INTRODUCTION

Proton Exchange Membrane Fuel Cells (PEMFCs) provide the most promising means for addressing the global renewable energy supply and clean environment¹⁻³. Currently the main impediment for large-scale PEMFCs commercialization is the sluggish oxygen reduction reactions (ORR), which dramatically increases catalyst costs. Extensive efforts are underway to develop electrocatalysts for ORR with much higher performance and lower cost⁴⁻⁶. Pt-alloy nanomaterials show enhanced performance⁷⁻¹², especially PtNi alloys¹³⁻¹⁷. In particular, very dramatically improved performance has been observed in dealloyed Pt nanomaterials¹⁸⁻²². Thus Debe and coworkers showed that Ni₇Pt₃ nanoparticles (NP) led to significantly improved ORR activity, 4 times higher than pure Pt and 60% higher than for the NSTF standard Pt₆₈Co₂₉Mn₃ alloy²³⁻²⁶. However, no Ni was observed in the XPS, suggesting the NP was a dealloyed Pt NP. Fortunelli and Goddard (FG) used the ReaxFF reactive force field²⁷ to predict the structure of the dealloyed Debe NP and found that starting with 70% Ni, led to a porous Pt with significant interior area exposed to the surface. FG found that the O_{ads} hydration reaction,



which is the rate determining step (RDS) on Pt (111), is dramatically accelerated on this porous NP compared to Pt (111)²⁸.

Later, Huang, Duan, Goddard, and co-workers²⁹ showed that dealloying 5 nm Ni₇Pt₃ Nanowires (NW) led to 2 nm Pt Jagged NW (J-PtNW) with 50 times faster ORR than current state-of-

the-art Pt/C, but they found that all Ni was extracted! Building this dramatically improved performance into commercial fuel cells would be a game-changer, dramatically decreasing the costs of hydrogen fuel cells needed to extract the power from fuel generated and stored at solar power plants to provide practical transportation without CO₂ emissions.

Although several factors, such as under-coordinated surface Pt atoms, mechanical strain, and high electrochemically active surface area (ECSA), have been suggested to contribute to this remarkably accelerated ORR activity²⁹, there was no atomistic explanation about which sites on this very complex surface are responsible, leaving no roadmap to build this activity into practical electrodes.

To address this conundrum, we report here multiscale simulations to explain the dramatically improved performance and to characterize the atomic features of active sites responsible. Starting with the J-PtNW synthesized computationally using ReaxFF reactive force field, we selected randomly 500 of the more than 10,000 surface sites and carried out Quantum Mechanics (QM) Calculations on clusters within 8 Å of the surface site. Here we considered reaction (1), the RDS on Pt (111). We observed a strong correlation between OO Distance (the distance between O_{ads} and the O of H₂O_{ads}) and the free energy barrier for reaction (1). Indeed 14.4% of the 500 surface sites sampled are barrier-less of reaction (1) at room temperature, compared to 0.29 eV for Pt (111) and hence increased reaction rate. We then modeled the reaction rates of all surface sites based on their OO Distances and estimated the performance of the whole J-PtNW.

We found two distinct geometric patterns,

- Triangles where the H₂O binds to one vertex and O to the other two;
- Concave-Up Rhombi where O binds to one edge and the H₂O to one of the remaining two vertices.

The atomic structure of these active sites provides insights on designing high-performance electrocatalysts for ORR.

2. RESULTS AND DISCUSSION

2.1 Structure Analysis and Surface Extraction of J-PtNW

Starting with the J-PtNW synthesized using ReaxFF reactive molecular dynamics (RMD) as in the previous work²⁹, we identified all surface atoms using the surface vector based methodology. The detailed description of structure synthesis and surface vector based methodology are listed in **S1 and S2 of Supporting Information**. The nanowire has 6926 Pt atoms, with 3881 on the surface (surface ratio: 56.0%). We partitioned these surface sites into coordination groups based on the number of first-neighbor atoms, using a first-neighbor cut-off at 3.50 Å based on the radial distribution functions in **Figure S2(a) of Supporting Information**. The J-PtNW showed broader peaks with the first peak located close to the first peak of Pt single crystal, as expected. We observed many under-coordinated and over-coordinated sites both on the surface and in the bulk. The surface site distribution versus coordination is shown in **Figure S2(b) of Supporting Information**. For better visualization, we plotted the surface in **Figure S3 of Supporting Information**, with all surface sites colored by their coordination (ranging from 3 to 12). This structural analysis showed that the J-PtNW have an extremely disordered and irregular surface, making it challenging to characterize experimentally and computationally.

2.2 Bridge Nanocluster Model

To study the relationship between the structure and catalytic activity, we need to define a physical descriptor that might correlate with the performance (reaction rate). Based on the reaction mechanism revealed by earlier work^{30–32}, we focused on the O_{ads} hydration, reaction (1).

Our full solvent QM Metadynamics showed that this step is the rate determining step (RDS) for applied potentials of $U \leq 0.9$ V reversible hydrogen electrode (RHE)^{30,33,34}. Since this reaction requires two sites for water adsorption and oxygen adsorption, instead of the single site nanocluster model used in our previous machine learning studies for Copper^{35,36} and Gold^{37,38}, we developed a new bridge nanocluster model in this work. As shown in **Figure 1**, we generated the bridge nanocluster by cutting two spheres of size R around the Pt atom for water adsorption (Pt-1) and the Pt atom for oxygen adsorption (Pt-2). Then, we merged these two spheres to a single nanocluster. The choice of R was based on the benchmark calculations in **S3 of Supporting Information**. We found that 8.0 Å is already sufficient to provide 0.02 eV accuracy in the adsorption energy for both reactants and products. Therefore, we consider that 8.0 Å provides the best balance between accuracy and efficiency and used this cut-off throughout this work.

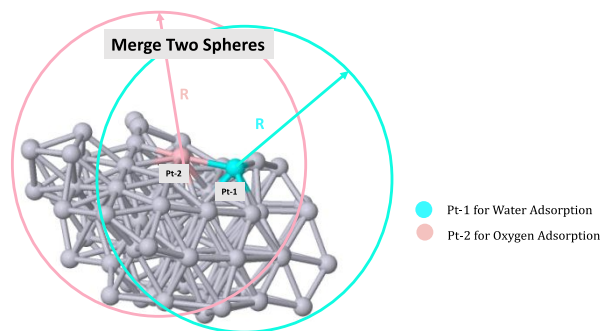


Figure 1. Bridge Nanocluster Model. We first cut two spheres of size R around Pt-1 (cyan atom) and Pt-2 (pink atom), where Pt-1 is specifically for water adsorption and Pt-2 is for oxygen adsorption. These two spheres are then merged to a single nanocluster. R here is optimized to 8 Å. This bridge nanocluster will later be used for DFT calculations.

2.3 OO Distance as Physical Descriptor

We carried out DFT calculations³⁹ for the O_{ads} hydration, reaction (1), using the bridge nanocluster model defined in **Section 2.2**. We chose the free energy barrier (G_a) of reaction (1) as the physical descriptor to evaluate the performance of each bridge nanocluster. We expect that sites with lower G_a should have better ORR performance. With such a disordered and irregular surface, we might have to sample all bridging surface sites to be sure to properly represent the activity of the full NW. DFT calculations on the transition state reaction barrier for the whole J-PtNW, would require far too much computational resources⁴⁰. Instead we defined a physical descriptor, OO Distance (d-OO), the distance between the O of H₂O_{ads} and the O_{ads}. Then we showed that d-OO is highly correlated with the free energy barrier (G_a), $G_a = G_{TS} - G_{Reactants}$, but much faster to calculate.

To obtain d-OO, we need only to optimize the structure of the reactants, H₂O and O. We show in **Figure S7 of Supporting Information** three examples illustrating the correlation between d-OO and G_a at room temperature. By comparing to our reference case Pt (111), which has $G_a = 0.29$ eV and d-OO = 3.36 Å, we observed that shorter d-OO leads to much lower G_a (d-OO at 2.60 Å leads to $G_a = 0.00$ eV) and larger d-OO leads to higher G_a (d-OO at 3.98 Å leads to $G_a = 0.35$ eV). In addition, thermodynamic reaction energy ($\Delta G = G_{Products} - G_{Reactants}$), doesn't correlate with G_a , as expected. Therefore, we used d-OO as the physical descriptor to evaluate performance of each bridge nanocluster. All our calculations include solvation effect using the VASPsol implicit solvation model⁴¹. As shown in **Figure S5 and S6 in Supporting Information**, solvation affects d-OO in a non-negligible manner. The free energy barriers (G_a) at room temperature (298.15 K) are obtained by adding to the DFT electronic energy (E), the zero-point energy (ZPE), enthalpy and entropy contribution from vibrational modes of surface species. More computational details of d-OO and G_a are listed in **S4 and S5 of Supporting Information**.

2.4 Data Sampling for DFT calculations (d-OO)

To generate all possible bridge pairs from 3881 surface Pt atoms of the J-PtNW, we first examined Pt-1 for water adsorption of all surface Pt atoms. Then, for each Pt-1, we examined its first-

neighbors on the surface to select Pt-2 for binding an O atom. This defines a bridge pair. The definition of Pt-1 and Pt-2 are the same as in **Figure 1**. Then, we cut the corresponding bridge nanoclusters from the NW. This generates the same nanocluster twice with Pt-1 and Pt-2 swapping the labels, but we consider them as different structures since Pt-1 is specifically for water adsorption and Pt-2 is specifically for oxygen adsorption. The two Pts are not identical when binding adsorbates. An example of two nanoclusters of same coordinates but defined as different structures is shown in **Figure S8 of Supporting Information**.

In this way, we generated 21,057 bridge pairs. Since H₂O binds weakly to high-coordination sites, we expect that they would be inactive for ORR. To test this, we selected randomly 50 sites for which Pt-1 has a coordination larger than 9 and calculated water adsorption. We found water desorbed from all 50 sites. Therefore, we discarded the high-coordination bridge pairs (coordination of Pt-1 > 9), which leaves 12,400 bridge nanoclusters for further sampling. This procedure is illustrated schematically in **Figure 2**.

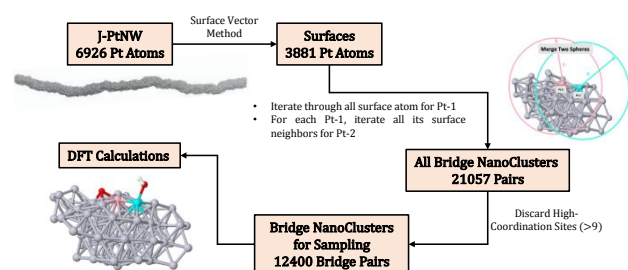


Figure 2. Generating All Bridge Pairs for Data Sampling. Starting from the J-PtNW with 6926 Pt atoms, we identified 3881 surface atoms using surface vector methodology. Then, we iterated first over the whole surface for Pt-1 and for each Pt-1 we iterated over its surface neighbors for Pt-2. In this way, we generated a total number of 21,057 bridge pairs. We showed that sites with coordination larger than 9, cannot adsorb water. Discarding these bridge pairs with coordination of Pt-1 larger than 9 leaves 12,400 bridge pairs for data sampling.

We then randomly sampled 500 bridge nanoclusters from these 12,400 pairs for DFT calculations. For each nanocluster, we put water on Pt-1 and oxygen on Pt-2, and then optimized the structure to find the best conformation for the adsorbates. Solvation effect are included here using the VASPsol implicit solvation model. Additional DFT calculation details, including all benchmark calculations are listed in **Section S4, Table S1–S3 and Figure S5–S6 of Supporting Information**. The sampled bridge centers are plotted back on the NW in **Figure S9 of Supporting Information**. The bridge centers are distributed throughout the whole nanowire, indicating our sample is a good representation of the whole J-PtNW.

The distribution of d-OO among 500 nanoclusters is shown in **Figure 3**. We see that d-OO ranges from 2.50 Å to 6.01 Å. However, 35.2% of the sites have d-OO distance shorter than the d-OO (3.36 Å) for Pt (111). We expect these sites to have much lower free energy barrier for O_{ads} hydration and hence to contribute significantly to the dramatically improved performance of J-PtNW at ORR. To help provide a better understanding of how the geometry of different sites affects d-OO and free energy barrier, several representative structures with different d-OO are also shown at the bottom of **Figure 3**.

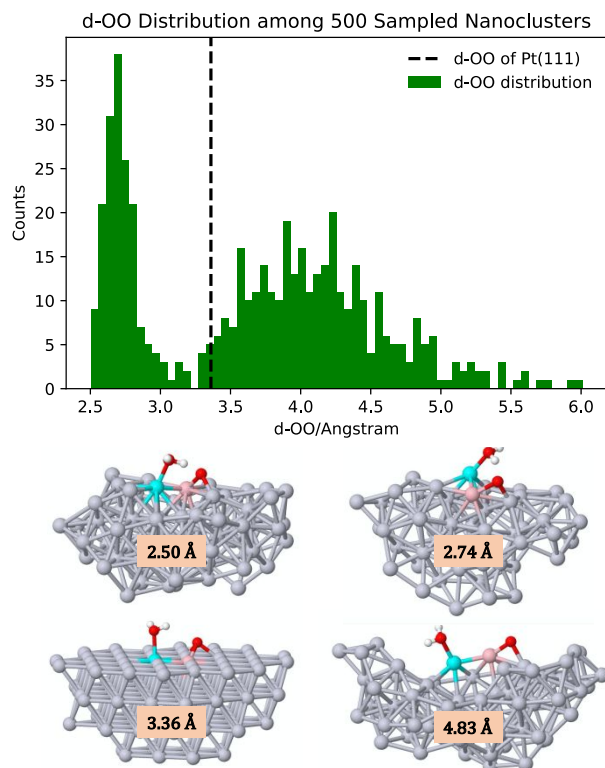


Figure 3. d-OO Distribution among 500 Sampled Bridge Nanoclusters. Our sample showed a broad range of d-OO, from 2.50 Å to 6.01 Å. The d-OO of Pt (111) is marked in the plot as the dashed line. We observed 35.2% of the sites lying to the left to Pt (111), showing much shorter d-OO. We expect these sites to have much lower energy barrier for O_{ads} hydration, thus leading to higher ORR performance. Four representative structures with different d-OO are attached here for understanding the correlation between structure and catalytic activities.

2.5 Correlation of d-OO with Catalytic Activity

To further understand the correlation between d-OO and the catalytic activity of each bridge site, we selected 18 structures with various d-OO and calculated the transition state and free energy barriers. The structures were selected randomly and independently but in such a way to ensure that we covered a broad range of d-OO. For each structure, we carried out the transition state search using the climbing image nudged elastic band (NEB) method with implicit solvation using VASPsol tool. The free energy barriers (G_a) for the O_{ads} hydration at room temperature (298.15 K) are then obtained by adding to the DFT electronic energy (E), the zero-point energy (ZPE), enthalpy and entropy contribution from vibrational modes of surface species. The data for the 18 structures, including d-OO and free energy barriers (G_a) at room temperature are listed in **Table 1**. More computation details toward the transition state search are included in **S5 of Supporting Information**.

Table 1. Correlation Between d-OO and Free Energy Barrier (G_a) at Room temperature 298.15K

d-OO/ Å	$G_a(298.15K, eV)$	d-OO/ Å	$G_a(298.15K, eV)$	d-OO/ Å	$G_a(298.15K, eV)$
2.50	0.00	2.76	0.01	3.50	0.20
2.56	0.00	2.80	0.06	3.57	0.19
2.60	0.00	2.93	0.12	3.70	0.14
2.64	0.00	2.99	0.10	3.75	0.40
2.68	0.00	3.12	0.16	3.98	0.35
2.74	0.01	<u>3.36</u>	<u>0.29</u>	4.22	0.28

We observed a strong correlation between d-OO and G_a , as shown in **Table 1**. The sites with small d-OO shows low free energy barriers, especially with d-OO \leq 2.68 Å, O_{ads} hydration step becomes barrier-less. And with larger d-OO, G_a generally becomes higher, but in a non-linear manner. Pt (111) shows d-OO at 3.36 Å and G_a at 0.29 eV, underlined in Table 1. To better correlate d-OO with catalytic activity, we used transition state theory (TST) to estimate the reaction rate as $k = (k_B T/h) \exp(-G_a/k_B T)$. The reaction rates are plotted versus d-OO of 18 structures in **Figure 4**. Here, we used the sigmoid function to fit the $k(d-OO)$ curve at room temperature. The fitted curve is also shown in **Figure 4** with R^2 at 0.9894.

Therefore, we found that a large portion of sites on the J-PtNW surface exhibit dramatically improved performance toward O_{ads} hydration, the RDS. We claim that this is the main contributor to the dramatically improved ORR performance. In addition, we showed that d-OO is a good descriptor for evaluating catalytic activity of any specific bridge pair. **Appendix of the Supporting Information** provides coordinates of the pathway for three representative structures from **Table 1**.

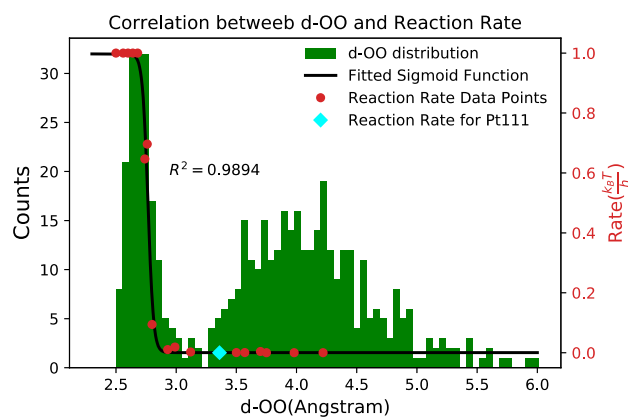


Figure 4. Correlation Between d-OO and Reaction Rate. we used transition state theory (TST) to estimate the reaction rate as $k = (k_B T/h) \exp(-G_a/k_B T)$ of 18 selected structures listed in Table 1. The reaction rates are plotted in the unit of $(k_B T/h)$ versus d-OO. We then used the sigmoid function to fit the $k(d-OO)$ curve at room temperature, $k = L / (1 + \exp(A \times (d-OO - x_0))) + b$. The parameters at ($A = 47.1056$, $x_0 = 2.7659$, $b = 0.0003$, $L = 0.9968$) gives the $R^2=0.9894$.

2.6 Performance Prediction of the Whole J-PtNW

Since our dataset is sampled randomly and independently, we consider it to be representative of the whole J-PtNW surface. Thus, we estimated the performance of the whole nanowire by mapping the statistics of our sample back to the full NW. The

J-PtNW has 6926 Pt atoms with 3881 surface atoms, which leads to 21,057 bridge pairs. Among these 21,057 pairs, 8657 are high-coordination involved pairs, which we assume are inactive. The remaining 12,400 pairs should have the similar d-OO distribution as the 500 samples.

To estimate the performance improvement at different temperatures, we first calculated the free energy barriers at different temperature, and refit the sigmoid functions. In other words, $k(d-OO)$ is dependent of T. Three examples of fitting $k(d-OO)$ at different temperatures are shown in **Figure S10 of Supporting Information**.

$$k(d-OO|T) = L / (1 + \exp(A \times (d-OO - x_0))) + b \quad (2)$$

Then, the total performance of J-PtNW is calculated by mapping the sample statistic to total 12400 pairs:

$$p_{NW}(T) = \left(\sum_{i=0}^{N_s} k(d-OO_i|T) \right) \times \left(\frac{N_t - N_h}{N_s} \right) \quad (3)$$

Where

1) the N_t is the total number of bridge pairs, N_h is the high coordination bridge pairs and N_s is the sampled bridge pairs. Here, $N_t = 21057$, $N_h = 8657$, $N_s = 500$;

2) $k(d-OO|T)$ is the fitted sigmoid function at temperature T;

The experiments showed that the J-PtNW performance is 50 times better than Pt/C at room temperature at mass activity. We considered that Pt/C is Pt (111) with 6926 surface Pt atoms, since the J-PtNW has 6926 Pt atoms in total with 3881 on the surface. In this way, we ensure the performance we are comparing is mass activity. This leads to 41,574 pairs. Therefore, the performance of Pt (111) can be estimated as following:

$$p_{pt(111)}(T) = k(d-OO_0|T) \times N_0 \quad (4)$$

where $N_0 = 41,574$ is the total number of bridge pairs, and $k(d-OO_0|T)$ is the reaction rate for Pt (111) at temperature.

We then define the improvement of the performance as $PI(T)$, which is dependent of temperature and calculated by formula (5):

$$PI(T) = p_{NW}(T) / p_{pt(111)}(T) \quad (5)$$

Figure 5 shows the temperature dependence of the estimated performance improvement. At room temperature, our model leads to $PI = 212.21$ for the J-PtNW. This is a factor of 4 higher than the experimental $PI=50$ ²⁹. We consider that this agreement validates our explanation. This model, allows us to predict the performance improvement of J-PtNW at increased temperatures. For example, low-temperature PEMFCs use a water-based acidic polymer membrane as the electrolyte, with platinum-based electrodes. Thus the upper temperature limit is around 80 °C. Our model, estimates $PI = 19.70$ at 353.15 K (marked as red diamond in **Figure 5**). Correcting by the same

factor 4, we predict the performance of J-PtNW should be around 5 time better than Pt (111) at 80 °C. This may provide guidance in choosing optimal conditions for the real J-PtNW.

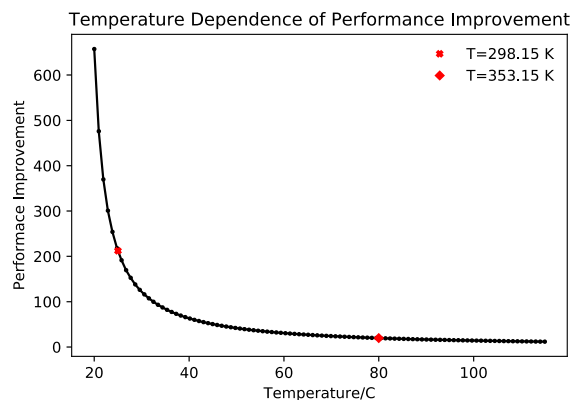


Figure 5. Temperature Dependence of Performance Improvement, which is calculated by formula (4). With increasing temperature, the performance improvement decreases. The PI at 298.15 K is marked in red, is PI=212.21 is 4 times larger than experimental = 50. The temperature limit of low-temperature PEMFCs is also marked as red diamond, PI=19.70 at 353.15 K.

2.7 Active Sites Identification

To reveal the important features of the active sites and to provide insights for designing high-performance electrocatalysts, we characterized the structures of barrier-less sites ($d\text{-OO} \leq 2.68 \text{ \AA}$). They account for 72 out of the 500 bridge nanoclusters sampled. Among these 72 structures, many share similar geometric features. Thus, we further partitioned them into three subgroups:

- I1) Concave-up Rhombus (30.8%);
- I2) Triangle (43.6%);
- I3) Others (25.6%).

Figure 6, shows one representative structure from each group. We consider that the Triangle group and Concave-Up Rhombus group play an important role in the dramatically improved performance. We summarized their geometry features and analyzed their statistics among the 500 structures in the following session.

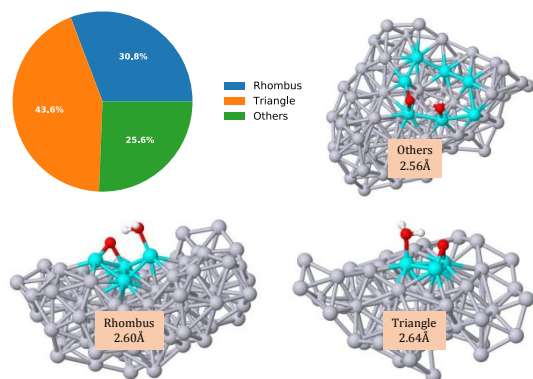


Figure 6. Identification Results of Barrier-Less Sites ($d\text{-OO} \leq 2.68 \text{ \AA}$). Among the 72 barrier-less sites, 30.8% of them are in the Concave-up Rhombus group and 43.6% of them are in the Triangle group. One representative structure of each group is attached with their $d\text{-OO}$ marked as well.

2.7.1 Triangle Group Statistics

As shown in **Figure 6**, Triangle group I2 is an important part of barrier-less sites (43.6%). We define a structure as a triangle structure if its three Pts, the one binding water, and the other two binding O, form a closed ring, marked as cyan in **Figure 6**. Based on this definition, we picked out all triangle structures from the 500 sampled bridge nanoclusters and plotted their distribution toward $d\text{-OO}$ in **Figure 7**. There are 143 triangles in sample with the main peak located at $\sim 2.75 \text{ \AA}$. Although several triangles showed large $d\text{-OO}$ (one representative structure of a bad triangle is shown in **Figure 7**), we see that major percentage the triangles lead to dramatically improved performance of the J-PtNW. Thus, a synthetic strategy might focus on generating triangle structures. Additional Triangle structures with various $d\text{-OO}$ are shown in **Figure S11** in **Supporting Information**.

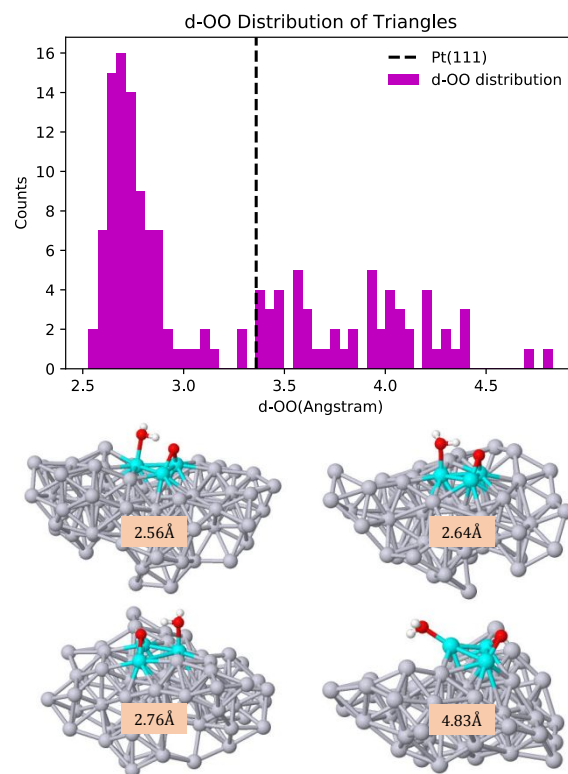


Figure 7. Statistics of Triangle Group among 143 out of 500 Sampled Bridge Nanoclusters. (a) There are 143 Triangles in total, and 87 of them show shorter $d\text{-OO}$ than Pt (111). A small fraction of the triangles showed large $d\text{-OO}$, but the main peak is located way left from Pt (111), (dashed line in the plot). (b) Four representative structures of different $d\text{-OO}$. More structures are included in **Figure S11** in **Supporting Information**.

2.7.2 Concave-Up Rhombus Group Statistics

We then examined all Concave-up Rhombus structures among the 500 sampled bridge nanoclusters. The Concave-Up Rhombus is defined as following: the three Pts, One Pt binding H_2O , and the other two Pts binding O, cannot form a closed ring. Instead another surface Pt is required to close the ring, forming a concave-up rhombus. As shown in **Figure 8**, we then define the dihedral angle of a rhombus as the dihedral angle between two surfaces defined by (Pt1, Pt2, Pt4) and (Pt2, Pt3, Pt4). The larger dihedral angle is, the more concave-up the rhombus is. There are a total number of 234 rhombi out of 500

with different dihedral angles We plotted the correlation between the dihedral angle and d-OO in **Figure 8(a)**, and we

found the Concave-Up Rhombus with dihedral angle larger than 30° mostly show short d-OO.

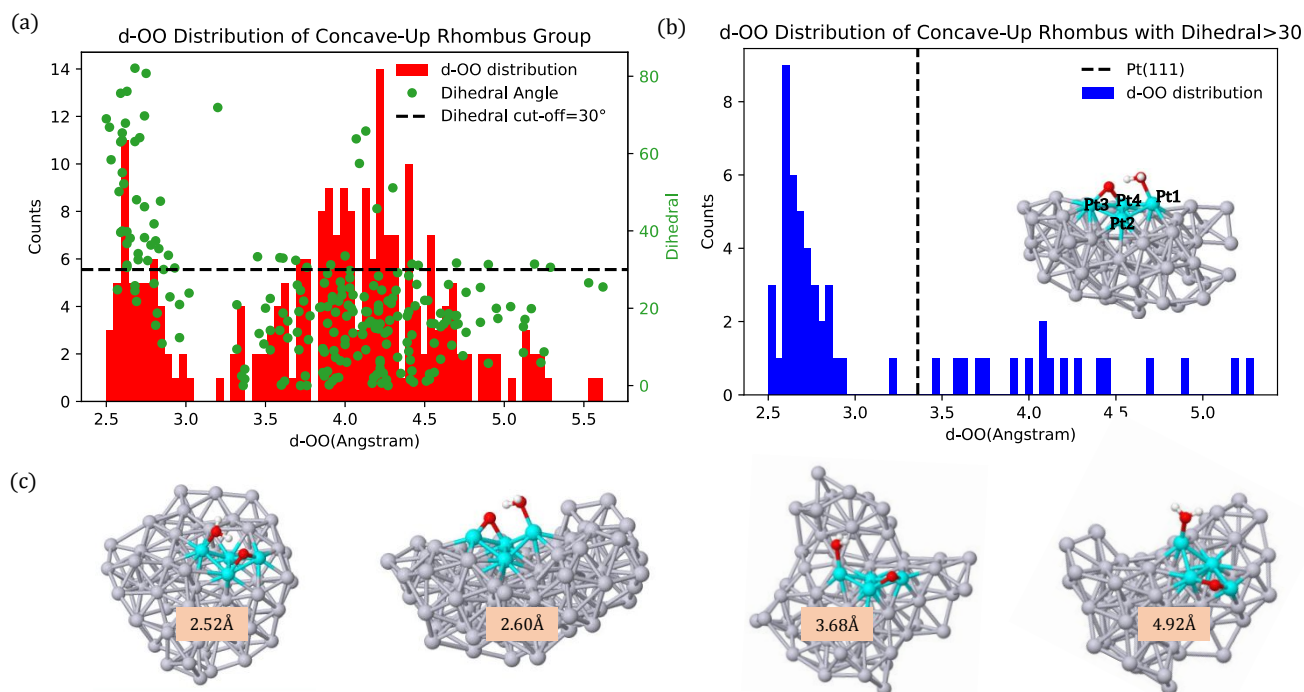


Figure 8. Statistics of Concave-Up Rhombus among 234 out of 500 Sampled Bridge Nanoclusters. (a) The correlation between dihedral angle and d-OO is shown in plot. Here dihedral angle is defined as the angle between two surfaces defined by (Pt1, Pt2, Pt4) and (Pt2, Pt3, Pt4). As we could see, the rhombus with dihedral angle larger than 30° mostly show short d-OO; (b) Statistics of Concave-up Rhombus with Dihedral Angle $>30^\circ$. Most of structures in this groups shows the small d-OO with the main peak located at 2.6 Å; (c) Four representative structures with different d-OO are attached here and more structures are available in **Figure S12 in Supporting Information**.

Thus, if we cut off the dihedral angle to 30° , the population of active Concave-Up Rhombic becomes 57 out of 500. Therefore, we define our active Concave-Up Rhombic as those with dihedral angle $>30^\circ$. These 57 active Concave-Up Rhombic are plotted in the **Figure 8(b)**, along with several representative structures shown in **Figure 8(c)**. More structures with different d-OO distances are available in **Figure S12 in Supporting Information**

2.8 Comparison with Previous Literature

The above discussion, shows the atomistic explanation of the dramatically improved performance. Thus, the jagged NW has many sites with a concave nature that pushes the OH bond of the $\text{H}_2\text{O}_{\text{ads}}$ toward the O_{ads} , leading to a dramatically reduced energy barrier for O_{ads} hydration. Earlier, Huang and coworkers suggested that mechanical strain, high ECSA, and under-coordinated surface Pt atoms may affect this remarkably accelerated ORR activity²⁹. Consistent with these previous literature results, our analysis also finds numerous under-coordinated Pt surface atoms and a high 56.0% surface atom ratio (Section 2.1), which will affect the ECSA.

To correlate the mechanical strain with catalytic activity, we plotted the E_a versus the strain of the selected 18 structures from **Section 2.5**. Here we used the average Pt-Pt bond length around the adsorption sites to represent the local strain. As shown in **Figure S13 of Supporting Information**, there is a linear correlation between the catalytic activity and strain. In general, the sites with compressive strains show lower energy barriers and sites with tensile strains show higher energy barriers. The correlation is weak with small R^2 at 0.46, but we agree that

mechanical strain plays a role in reduced energy barrier of O_{ads} hydration. Our work, with overall agreement with experiment in NW structure characterization and performance prediction, explains the dramatically improved ORR of J-PtNW from a very different atomistic perspective.

3. CONCLUSION

Starting from the J-PtNW synthesized using the ReaxFF reactive force field, we developed the bridge nanocluster model for DFT calculations. Using sites randomly selected from the surface, we observed a strong correlation between d-OO and the free energy barrier G_a of the RDS, O_{ads} hydration. This dramatically reduced the computational cost but accurately described the performance of each bridge pair. We found 14.4% of the sampled surface sites are barrier-less for the RDS. Identification of these active sites led to two groups sharing similar geometrical patterns, the Triangle group and Concave-up Rhombus. Using the model developed above, we could predict the performance improvement of the whole J-PtNW. We report the atomistic structure of the active sites, which provide some insights in designing high-performance electrocatalysts for ORR.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Description of DFT calculations, transition state search used in this work, benchmark calculations for bridge nanocluster model, more

structures of Triangle and Concave-Up Rhombic Groups and additional calculations. (PDF)

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Notes

The authors declare no competing financial interest.

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