

**Matter, Volume 3**

**Supplemental Information**

**Neural Network-Assisted Development  
of High-Entropy Alloy Catalysts: Decoupling  
Ligand and Coordination Effects**

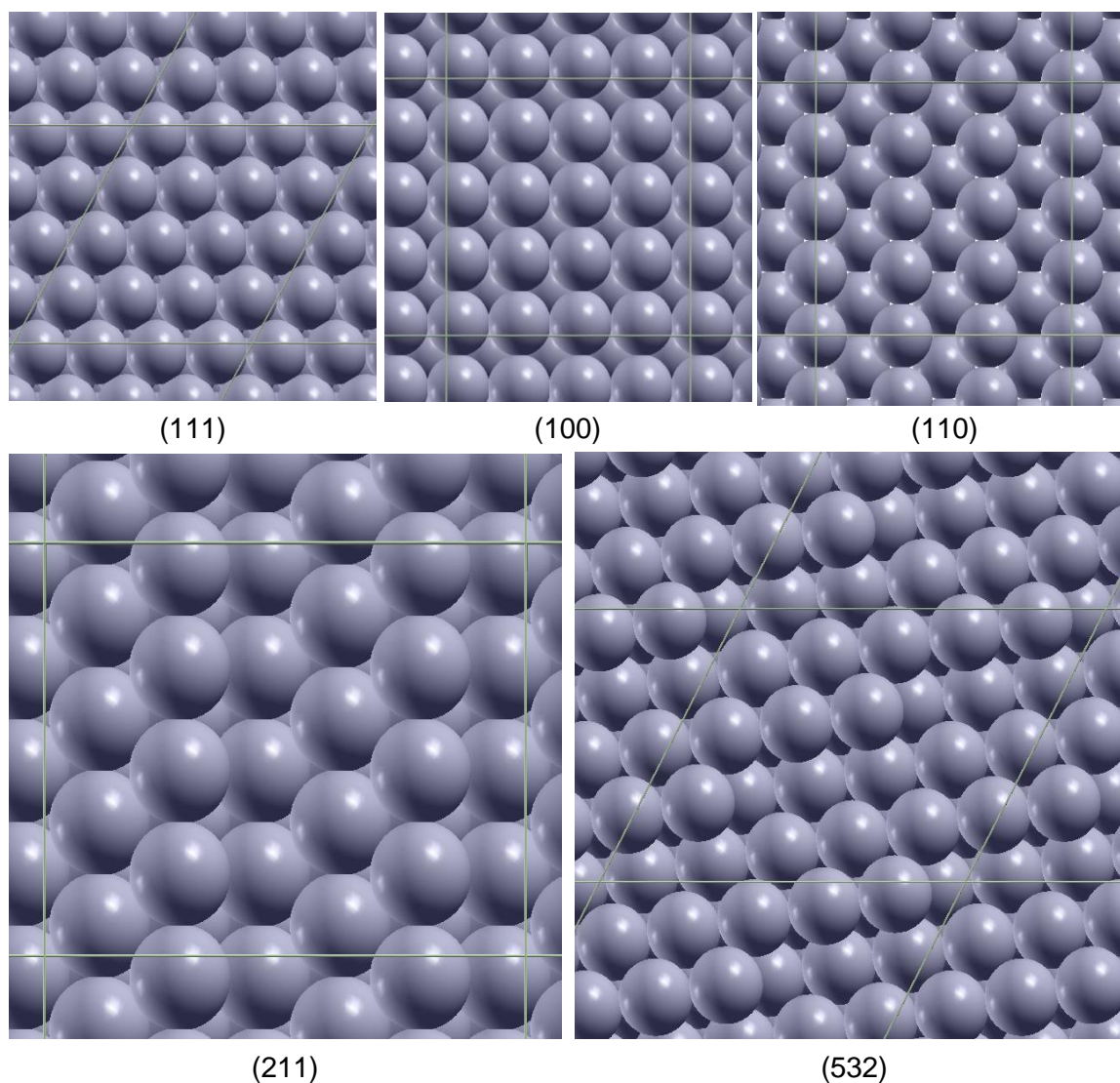
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## Supplemental Data Items

### 1. Surface models

Top views of the surface models used in this work, corresponding to Figure 1 in main text, are shown in Figure S1.

Figure S1. Top views of surface models used in this study, corresponding to the side views in Figure 1 in main text.



### 2. Trained weights of NN

Sample trained NN weights are given below. Note that before NN training, the group number, period number and atomic radii were first normalized by subtracting these values from those of Ru. So in order to use these weights directly, one needs to first reference the group number, period number and atomic radii (in pm) with respect to Ru. In other words, use Ru: 0,0,0, Rh: 0,1,0, Pd: 0,2,3, Ir: 1,1,1.5, Pt: 1,2,4.5.

Note there are 30 parameters in first NN layer and 6 in second, giving 36 in total.

First NN layer:

[[-0.192935, -2.128473, -0.5890434, -0.23783036, -1.0142646, -0.01790326],  
 [ 0.486281, -0.2363347, 1.713717, -0.66623807, -0.8341955, 0.14510955],  
 [ 0.3745039, -0.8992171, 0.26786217, 0.20112726, 0.7327471, 0.50042224],  
 [-0.392292, 0.6304792, 0.15683521, 0.21771273, 0.3118519, -0.35696217],  
 [-0.2945569, -3.8742847, -2.6877038, -1.4017274, -0.6213934, -0.60586584]],

Second NN layer:

[[ 0.74206084],  
 [-0.04996059],  
 [ 0.42490107],  
 [ 0.7585831 ],  
 [-0.7749046 ],  
 [-0.5185522 ]]

### 3. Coordination numbers of surface models used in this work

Table S1. Coordination numbers of surface models used in this work, as depicted in Figure 1.

	Active site atoms		Nearest neighbours													
9-9 (111)	9	9	9	9	9	9	9	9	9	9	12	12	12	12	12	
8-8 (100)	8	8	8	8	8	8	12	12	12	12	12	12				
7-7 (110)	7	7	7	7	11	11	11	11	11	11	12	12				
7-7 (211)	7	7	7	7	9	9	9	12	12	12	13	13				
7-10 (211)	7	10	7	7	9	9	9	9	10	10	12	12	12	12	12	
9-10 (211)	9	10	7	7	7	9	9	10	10	12	12	12	12	12	12	12
6-7 (532)	6	7	12	12	9	9	8	11	10	10	8					
6-8 (532)	6	8	12	10	7	9	11	12	12	10	9	7				
7-8 (532)	7	8	9	9	6	12	12	10	11	6	9	10	12			
7-10 (532)	7	10	8	9	9	6	12	12	11	9	9	10	12	12	12	
6-10 (532)	6	10	7	9	8	12	11	10	9	8	9	12	12	12		
8-10 (532)	8	10	6	12	10	11	9	9	6	7	12	12	12	12	11	

### 4. Training curve

We show how NN is iterative trained to approach its maximal accuracy using the training curve shown in Figure S2. The majority of training is done within the first 1000 epochs, and limited improvement is observed beyond 2000 epochs.

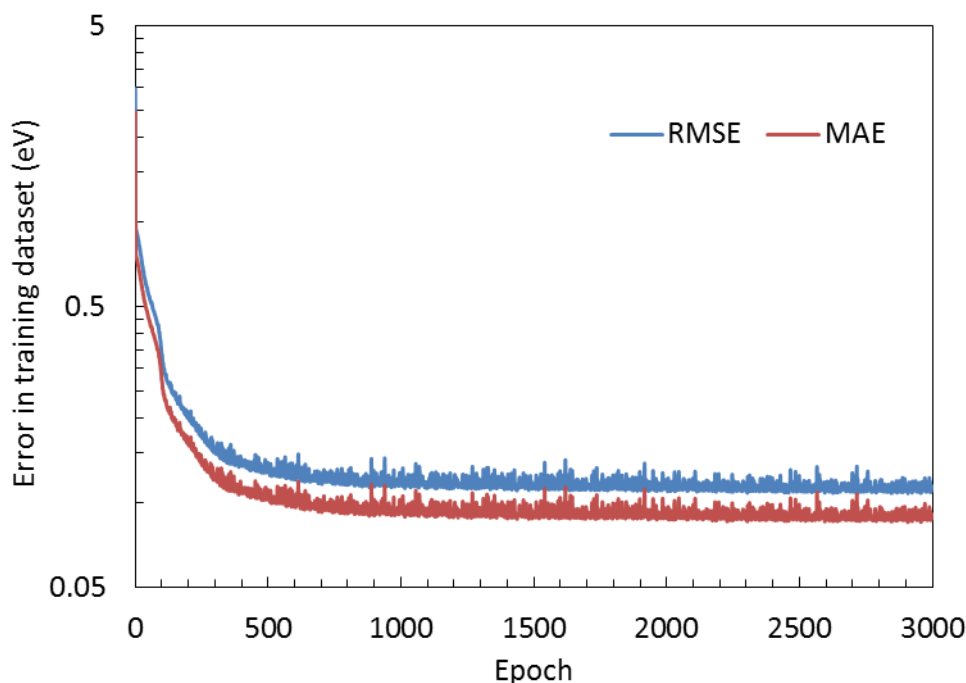


Figure S2. Training curve of NN model referenced in neural network description in main text.

### 5. Conversion between calculated electronic energy ( $E$ ) and free energy ( $G$ )

This work assumes the associative mechanism of ORR where the elementary steps follow

- (1)  $O_2 + (H^+ + e^-) \rightarrow *OOH$
- (2)  $*OOH + (H^+ + e^-) \rightarrow *O + H_2O$
- (3)  $*O + (H^+ + e^-) \rightarrow *OH$
- (4)  $*OH + (H^+ + e^-) \rightarrow H_2O$

and the potential limiting is either the initial or final steps.<sup>1</sup>

The theoretical overpotential is, therefore,

$$U_L = \max(\Delta G_{OOH}, -\Delta G_{OH})$$

where  $\Delta G$  is the free energy of each elementary step.  $\Delta G$  is related to the calculated electronic energy,  $\Delta E$ , as  $\Delta G = \Delta E + \text{ZPE} + T\Delta S$ , where ZPE is the zero-point energy correction,  $T$  is the temperature, and  $\Delta S$  is the change in entropy corresponding to the elementary step.

To convert from  $\Delta E$ , which is the quantity predicted by the NN model in this work, to  $\Delta G$ , we use the approximation  $\Delta G_{OH} = \Delta E_{OH} + 0.35$  eV which was established by previous work.<sup>2</sup> This approximation hinges on the fact that the ZPE and entropy correction do not vary much across different metallic surfaces, even when the surface coordination varies.<sup>3</sup> To obtain  $\Delta G_{OOH}$ , we used  $\Delta G_{OOH} = \Delta G_{OH} + 3.2$  eV as established by linear scaling relationship.<sup>1</sup>

### 6. Data for experimental validation

In Experimental Validation section of the main text, the activity measurements of all studies were conducted at mostly identical conditions, including temperature, electrolyte, and scan rate, and therefore values can be compared fairly. Additionally, all referenced studies were ensured that either the studied catalyst is well-mixed solid solution or at least top two atomic layers are well-mixed solid solution (as opposed to, for example, core-shell structures where the surface has one element only), as the NN model assumes random distribution of all elements. Lastly, measurements where one component's molar ratio is lower than 20% are excluded, since such samples are significantly inconsistent the near-equimolar requirement of HEAs.

For making predictions of the adsorption energy values of the data points in Figure 7, all predictions are made on a fully-trained NN model using all data points available, as also for the case of Figures 3-5. For cubes, the average value of the full adsorption energy distribution on 8-8 (100) sites is taken. For octahedra, the average value of the full adsorption energy distribution on 9-9 (111) and 9-10 (211) sites is taken, because, as pointed out in the referenced papers, the synthesized octahedra possess concave structures, so 9-10 (211) (which is a concave site) is added on top of 9-9 (111) to reflect the presence of these concave sites. The only mixed (cubo-octahedron) site is the Pt point, serving as a reference material. Its adsorption energy is taken as the average value of the full adsorption energy distribution on 9-9 (111) and 8-8 (100) sites.

## 7. Van der Waals correction

We test the effect of van der Waals (vdW) correction on DFT data by randomly selecting 25 data points from the dataset and compare DFT-calculated OH\* adsorption energy values with and without vdW correction. To account for vdW interactions, Grimme's DFT-D3 method was used.<sup>4</sup> The results are shown in Figure S3. Note that this comparison was directly made on the final model output, i.e. the OH\* adsorption energy referenced to Pt(111),  $\Delta E_{\text{OH}} - \Delta E_{\text{OH,Pt(111)}}$ . Linear regression shows a slope near 1 and an intercept near 0, indicating that vdW correction yields negligible change to the dataset output variable. Furthermore, the residual values,  $[\Delta E_{\text{OH}} - \Delta E_{\text{OH,Pt(111)}}]_{\text{without VdW}} - [\Delta E_{\text{OH}} - \Delta E_{\text{OH,Pt(111)}}]_{\text{with VdW}}$ , have an average value of 0.03 eV and a standard deviation of 0.07 eV, which are consistent the ~0.12 eV RMSE of the NN model. This is possibly due to the cancellation of vdW effects when all calculations were made in reference to Pt(111). Therefore, vdW correction was not used for generating the dataset.

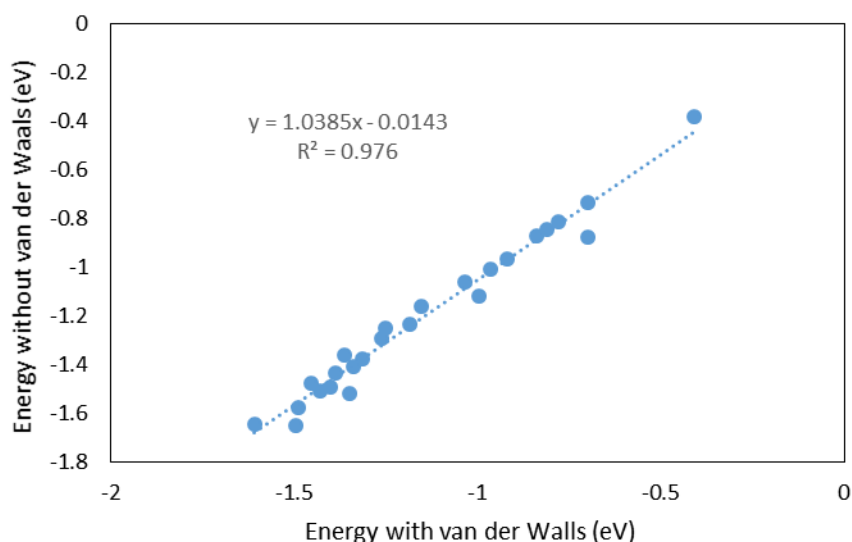


Figure S3. Comparison between DFT-calculated adsorption energy ( $\Delta E_{\text{OH}} - \Delta E_{\text{OH,Pt(111)}}$ ) with and without van der Waals corrections.

## 8. Data and code availability

The data and code necessary for examining the NN architecture and for reproducing figures in this work are publically available at online repository: <https://github.com/jol-jol/neural-network-design-of-HEA>. The data is also presented in the attached csv file "HEA\_data.csv", in more compact form. In "HEA\_data.csv" file, each line contains a new HEA structure, and the format of each line is as follows: name\_of\_surface\_type, name\_of\_active\_site\_type, element\_of\_atom\_1, CN\_of\_atom\_1, element\_of\_atom\_2, CN\_of\_atom\_2, element\_of\_atom\_3, CN\_of\_atom\_3, ..., element\_of\_atom\_N, CN\_of\_atom\_N, adsorption\_energy\_OH\_relative\_to\_Pt(111)

## Supplemental References

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2. Nørskov, J.K., Rossmeisl, J., Logadottir, A., Lindqvist, L., Kitchin, J.R., Bligaard, T., and Jónsson, H. (2004). Origin of the overpotential for oxygen reduction at a fuel-cell cathode. *J. Phys. Chem. B* 108, 17886–17892.
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