

Supplementary Information

For

Understanding the Activity and Selectivity of Single Atom Catalysts for Hydrogen and Oxygen Evolution via Ab Initio Study

Guoping Gao^{1*}, Steven Bottle¹ and Aijun Du^{1,*}

¹School of Chemistry, Physics and Mechanical Engineering, Queensland University of Technology, Garden Point
Campus, QLD 4001, Brisbane, Australia

1. Supplementary Methods

The formation energy

The formation energies of different coordinated Ni sites are calculated by following Equation 1.

$$E_f = E_{Ni@graphene} - E_{Ni} - E_{graphene} \quad (1)$$

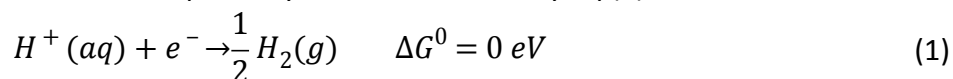
Where $E_{Ni@graphene}$, and $E_{graphene}$ is the total energies of single metal atom decorated graphene and graphene, respectively. E_{Ni} is the average energy of Ni in Ni metal. The results are listed in Table 1.

TableS1 The formation energies of different coordinated Ni sites

0	1-zigzag	1-armchair	2-zigzag	2-armchair	3	4
1.01	-0.90	-0.82	-2.39	-3.69	-3.99	-3.76

The Gibbs free energy of hydrogen adsorption

Under standard conditions, the overall HER pathway can be described by Eq (1),



comprising an initial state $H^+(aq) + e^-$, an intermediate adsorbed H^* and the final product $\frac{1}{2} H_2(g)$.

The total energies of $H^+(aq) + e^-$ and $\frac{1}{2} H_2(g)$ are equal. Therefore, the Gibbs free energy of the

adsorption of intermediate hydrogen on the catalyst ($\Delta G_{H^*}^0$) is a key descriptor for the HER activity of the catalyst, and is obtained by Eq (2)

$$\Delta G_{H^*}^0 = \Delta E_H + \Delta E_{ZPE} - T\Delta S_H \quad (2)$$

where ΔE_{ZPE} , and ΔS_H are the difference in zero-point energy, and the entropy between atomic hydrogen adsorption and hydrogen in the gas phase respectively. The contributions from the catalysts to both ΔE_{ZPE} and ΔS_H are small and neglected. Therefore, ΔE_{ZPE} is obtained by Eq (3)¹

$$\Delta E_{ZPE} = E_{ZPE}^H - \frac{1}{2}E_{ZPE}^{H_2} \quad (3)$$

where, E_{ZPE}^H is the zero point energy of atomic hydrogens on the catalyst without the contribution of catalyst. The vibration frequencies of H^* adsorption on single-coordinated Ni on zigzag edge are 2073.3 cm^{-1} and 435.0 cm^{-1} , which is not sensitive to the metal and coordination. $E_{ZPE}^{H_2}$ is the zero point energy of H_2 in gas phase. The calculated frequency of H_2 gas is 4289.4 cm^{-1} . ΔE_{ZPE} is 0.03 eV, The ΔS_H is obtained by Eq (4)

$$\Delta S_H \cong -\frac{1}{2}S_{H_2}^0 \quad (4)$$

And $S_{H_2}^0$ is the entropy of H_2 gas at the standard condition ($T\Delta S_H$ is 0.20 eV)². Therefore, Eq (2) can be rewritten as Eq (5):

$$\Delta G_{H^*}^0 = \Delta E_H + 0.23 \text{ eV} \quad (5)$$

ΔE_H is the differential hydrogen adsorption energy, which is defined by Eq (6):

$$\Delta E_H = E_{H^*} - E_{catal} - \frac{1}{2}E_{H_2} \quad (6)$$

where * denotes the catalyst. E_{H^*} , E_{catal} , and E_{H_2} represents total energies of the catalyst plus adsorbed hydrogen atom, total energies of the catalyst, and H_2 gas, respectively.

The HER volcano curve

In the volcano curve, the average Gibbs free energy of hydrogen adsorption ($\Delta G_{H^*}^0$) on catalyst are used to calculate the theoretical exchange current i_0 based on the Norskov's assumption³(please see the reference for details). If the $\Delta G_{H^*}^a \leq 0$, the following expression for the exchange current at pH=0 are used:

$$i_0 = -ek_0 \frac{1}{1 + \exp\left(\frac{-\Delta G_{H^*}^a}{k_b T}\right)} \quad (7)$$

For other case ($\Delta G_{H^*}^a > 0$), the exchange current is calculated by:

$$i_0 = -ek_0 \frac{1}{1 + \exp\left(\frac{\Delta G_{H^*}^a}{k_b T}\right)} \quad (8)$$

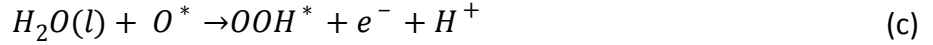
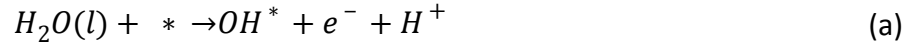
Where k_0 is the rate constant. As there are no experimental data available, the k_0 is set to 1.

OER

The overall OER in an acid environment can be written



In our model, we assume that the ORR processes in the four electrons pathway,



Where the * denotes an active site on the catalyst. (l) and (g) refer to liquid and gas phases.

For each step the reaction free energy ΔG is defined by following equation:

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S + \Delta G_U + \Delta G_{pH} \quad (10)$$

The ΔE , ΔZPE , and ΔS is the different energy, zero-point energy and entropy of the reaction, respectively. The ΔE is obtained from DFT calculation, while the ΔZPE is calculated by vibrational frequencies (listed in table S2, Supporting information). The ΔS are calculated using the values of ref.⁴. To calculate the free energy of O_2 , we assume that the free energy change of the total reaction $H_2O \rightarrow \frac{1}{2}O_2 + H_2$ is fixed at the experimentally found value of 2.46 eV per water molecule. Therefore, $1/2G_{O_2} = 2.46 - G_{H_2O} + G_{H_2}$. $\Delta G_U = -eU$, in which U is the potential related to the standard hydrogen electrode. ΔG_{pH} is the correction free energy of H^+ ions depending on the concentration. $\Delta G_{pH} = -kT \ln 10 \cdot pH$. The minimum overpotential (η) for OER is obtained by:

$$\eta = \frac{\max\{\Delta G_{1a}, \Delta G_{1b}, \Delta G_{1c}, \Delta G_{1d}\}}{e} - 1.23 \quad (11)$$

in which, ΔG_{1a} , ΔG_{1b} , ΔG_{1c} , and ΔG_{1d} are the reaction free energy of reactions (a-d), when $U=0V$, $pH=0$.

Table S2 Frequency analysis of the intermediates on Ni@4

	Vibration Frequencies (cm ⁻¹)
OH*	3697.42, 856.10, 521.19, 469.18, 161.69, 143.98
O*	681.28, 112.81, 50.56
OOH*	3644.94, 1300.08, 814.02, 463.78, 388.53, 258.63, 168.61, 139.21, 103.66

The theoretical OER overpotential volcano

Based on previous studies, the Gibbs free bond energy of adsorbed OOH* (ΔG_{OOH^*}) varies linearly with the Gibbs free bond energy of adsorbed OH* (ΔG_{OH^*} , or ΔG_{1a}) from one metal site to the next. As

shown in S1 supporting information the relationship between ΔG_{OOH^*} and ΔG_{OH^*} can be expressed by $\Delta G_{OOH^*} = 0.82 \Delta G_{OH^*} + 3.21 \text{ eV}$. Since $\Delta G_{OOH^*} = \Delta G_{1a} + \Delta G_{1b} + \Delta G_{1c}$, $\Delta G_{1b} = \Delta G_{O^*} - \Delta G_{OH^*}$, and $\Delta G_{1d} = 4.92 - \Delta G_{OOH^*}$, the ΔG_{1a} , ΔG_{1b} , ΔG_{1c} and ΔG_{1d} can be expressed by only two variables: ΔG_{OH^*} , and $\Delta G_{O^*} - \Delta G_{OH^*}$. Therefore, eq(11) can be expressed by ΔG_{OH^*} , and $\Delta G_{O^*} - \Delta G_{OH^*}$:

$$\eta = \frac{\max\{\Delta G_{OH^*}, \Delta G_{O^*} - \Delta G_{OH^*}, 3.21 - (\Delta G_{O^*} - \Delta G_{OH^*}) - 0.18\Delta G_{OH^*}, 1.71 - 0.82\Delta G_{OH^*}\}}{e} \quad (12)$$

Then we can get η at any position expressed by ΔG_{OH^*} , and $\Delta G_{O^*} - \Delta G_{OH^*}$ in The theoretical OER overpotential volcano. Under the optimum condition: $\Delta G_a = \Delta G_b = \Delta G_c$, the $\max\{\Delta G_a, \Delta G_b, \Delta G_c, \Delta G_d\}$ is ΔG_a , only 1.47 eV, with the overpotential reaches a minimum value of 0.24 V, which is the limitation of metal/graphene composite catalyst.

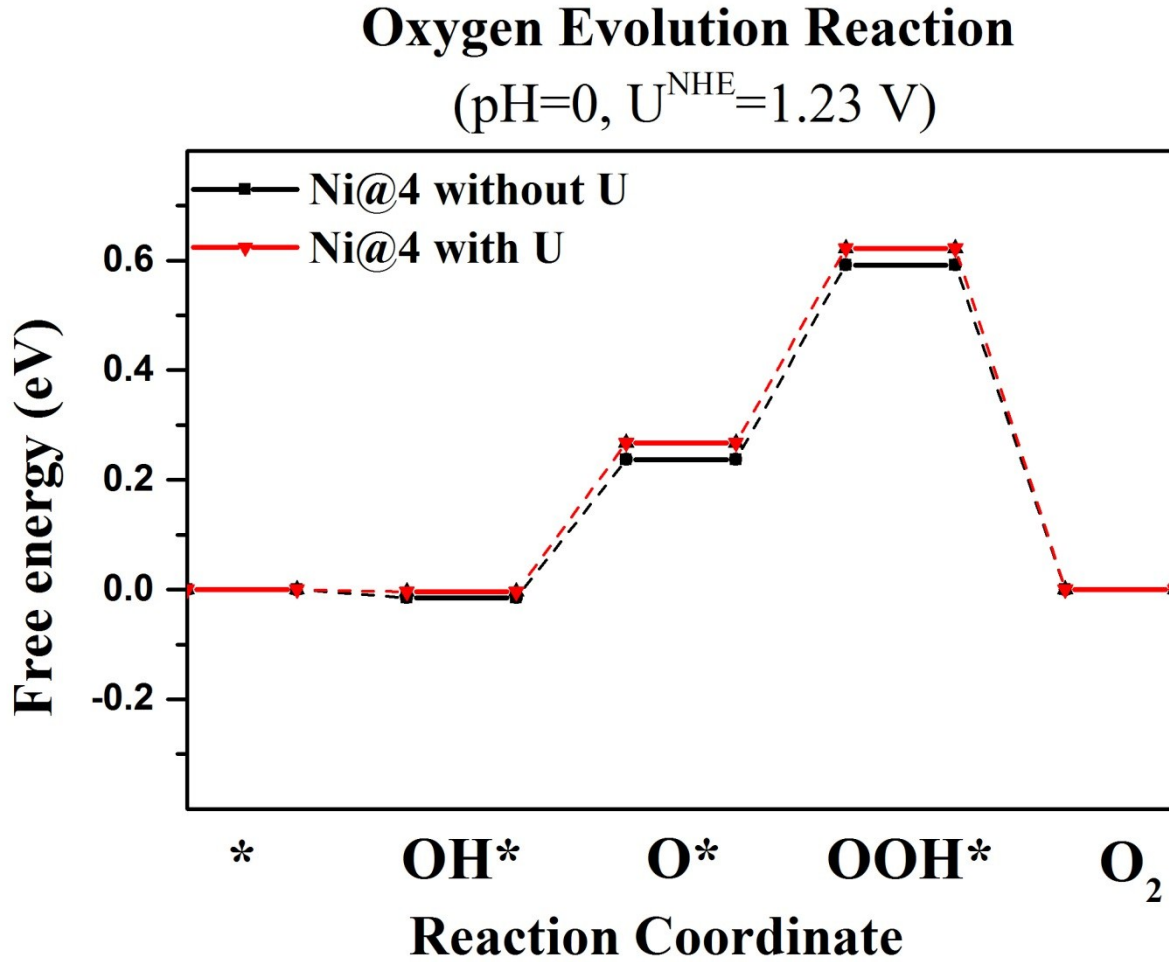


Figure S1 OER performed on Ni@4 at the equilibrium potential based on standard DFT and DFT+U calculations.

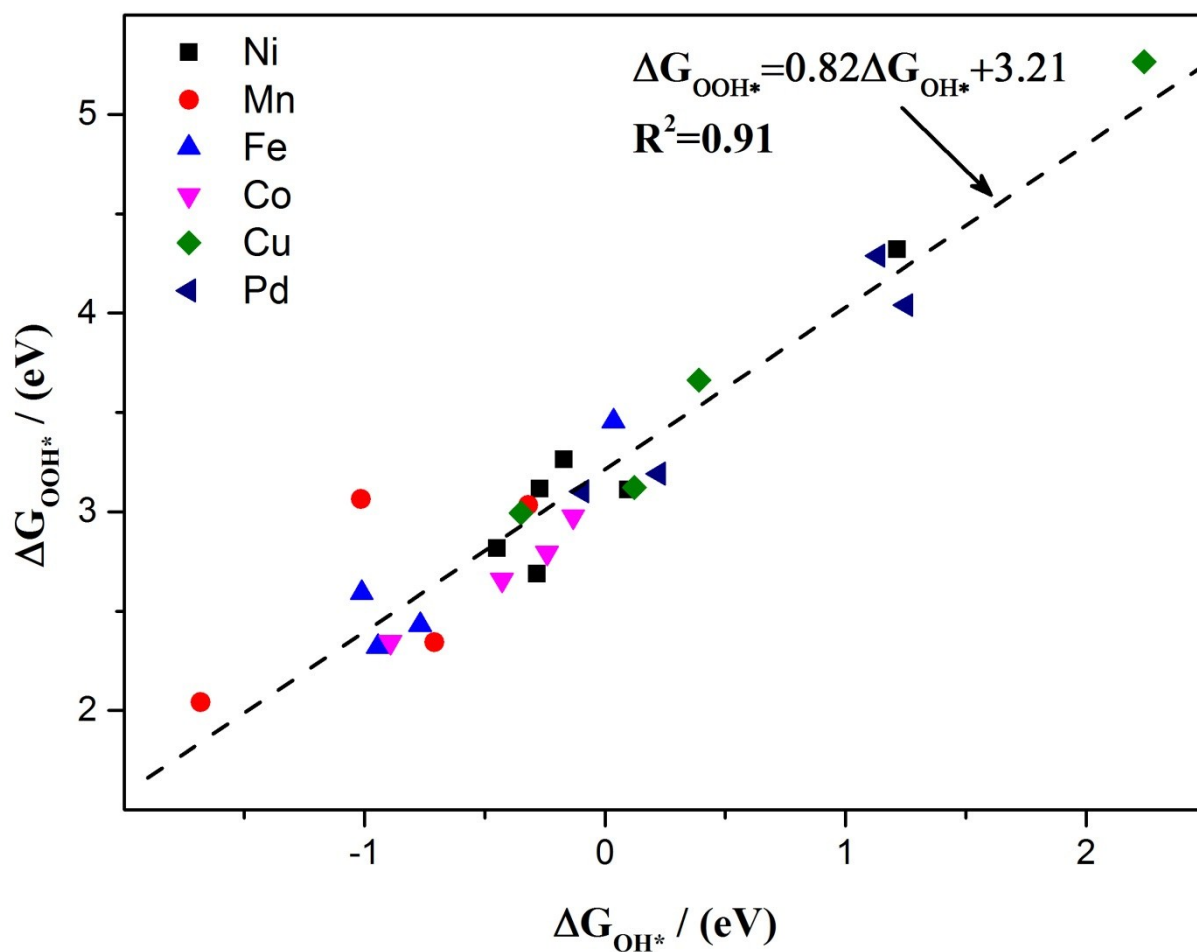


Figure S2 The scale relation between ΔG_{OOH^*} and ΔG_{OH^*} .

2. DOS of zero coordinated Ni/graphene composite catalyst

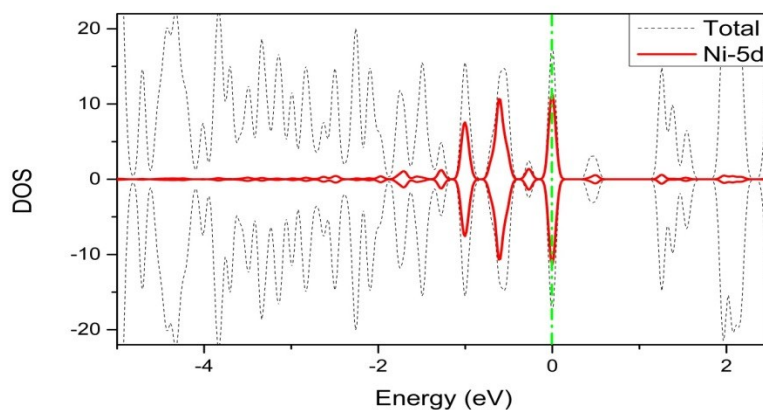


Figure S3 The projected density of states (PDOS) of zero coordinated Ni. The vertical dash-dotted lines correspond to the Fermi level.

The *d*-orbitals of zero-coordinated Ni are isolated from the orbitals of C, and thus no obvious hybridization occurs (see supplementary information Fig. S3), indicating that zero-coordinated Ni can be easily aggregated into clusters⁵.

3. HER performance of metal/graphene composite catalysts

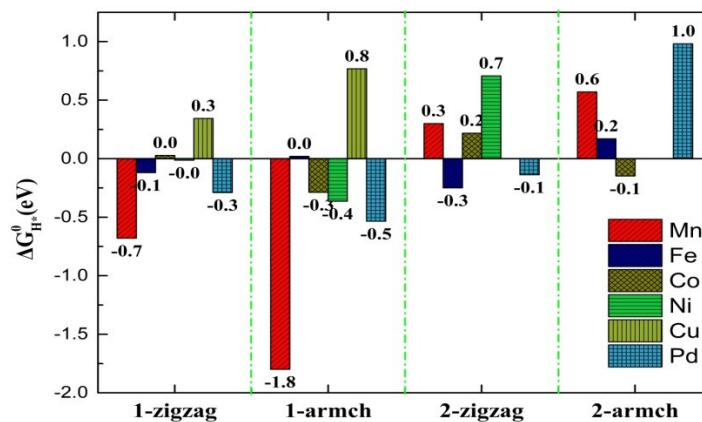


Figure S4 The calculated ΔG_{H^*} on lower coordination (1-2) metals (Mn, Fe, Co, Ni, Cu, and Pd) in metal/graphene composite catalysts.

4. OER performance of metal/graphene composite catalysts

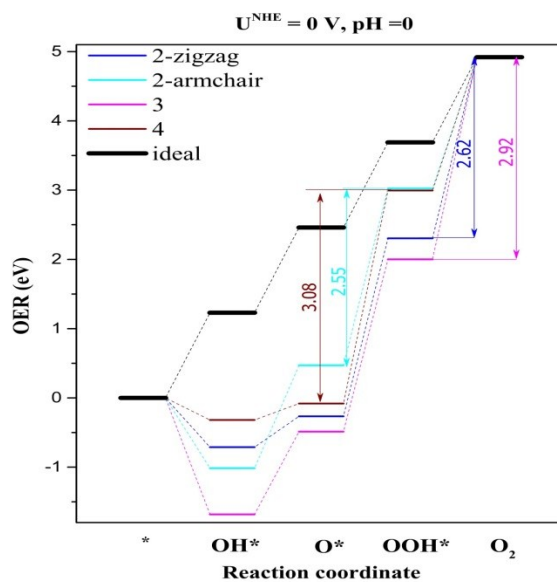


Figure S5 The free energy diagram for oxygen evolution on different coordinated Mn sites.

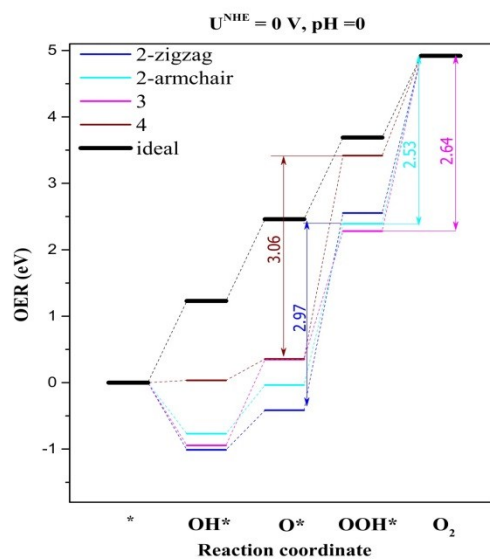


Figure S6 The free energy diagram for oxygen evolution on different coordinated Fe sites.

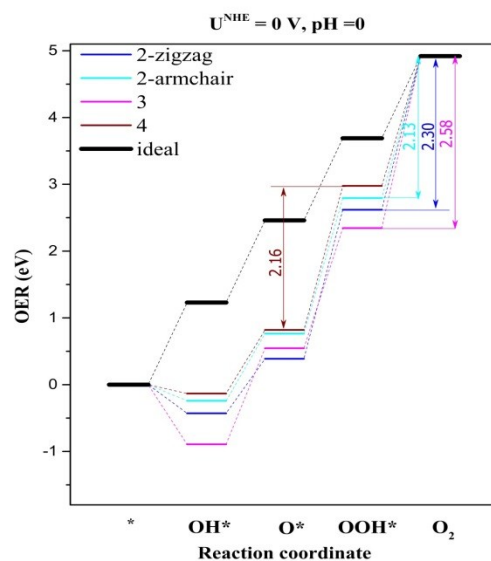


Figure S7 The free energy diagram for oxygen evolution on different coordinated Co sites.

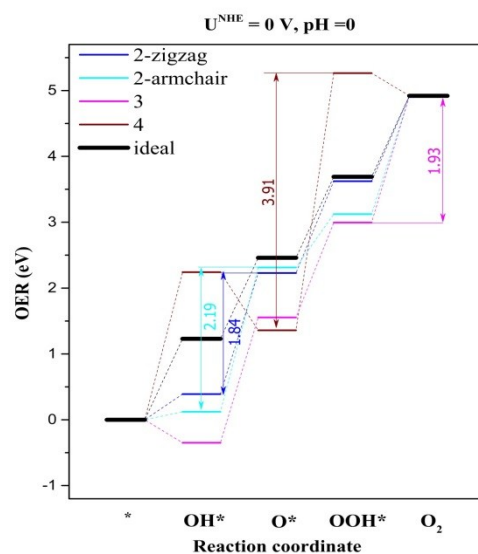


Figure S8 The free energy diagram for oxygen evolution on different coordinated Cu sites.

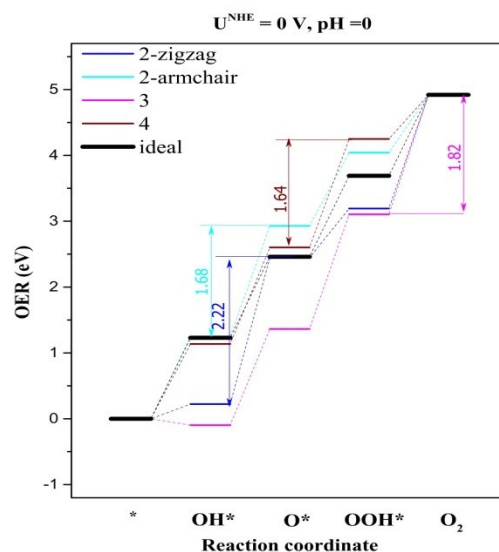


Figure S9 The free energy diagram for oxygen evolution on different coordinated Pd sites.

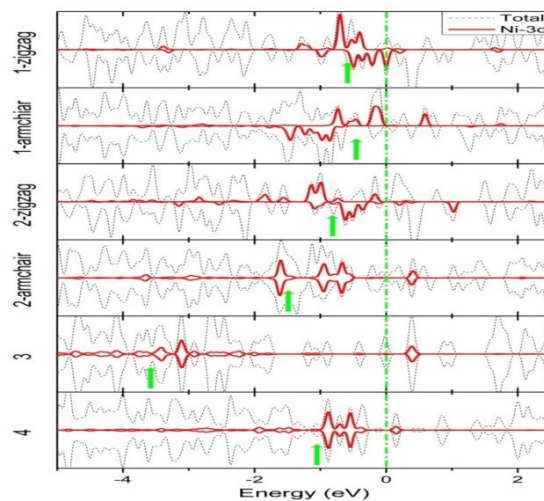


Figure S10 The projected density of states (PDOS) for the Ni-3d. The vertical dash-dotted lines correspond to the Fermi level which is shifted to zero. The *d*-band centres of spin up and spin down are calculated separately and the higher one is pointed by green arrows and listed in table 1. The calculated details of *d*-band centres can be found in our pervious work⁶.

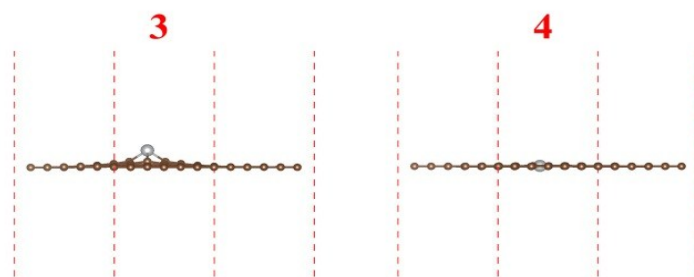


Figure 11 The side view of triple-coordinated Ni and quadruple-coordinated Ni. Color code: Carbon: brown; and Nickel; grey.

References

1. C. Tsai, F. Abild-Pedersen and J. K. Nørskov, *Nano Lett.*, 2014, 14, 1381-1387.
2. P. Atkins, *Physical Chemistry. 10th*, Oxford University Press, 2014.
3. J. K. Nørskov, T. Bligaard, A. Logadottir, J. Kitchin, J. G. Chen, S. Pandalov and U. Stimming, *J. Electrochem. Soc.*, 2005, 152, J23-J26.
4. P. Atkins and J. d. Paula, *Atkins' Physical Chemistry*, Oxford University Press, 2014.
5. C. Zhou, J. A. Szpunar and X. Cui, *ACS Appl. Mater. Interfaces*, 2016, 8, 15232-15241.
6. G.-P. Gao, S.-H. Wei, X. Gu and X.-M. Duan, *Phys. Chem. Chem. Phys.*, 2013, 15, 12846-12851.