Electronic Supplementary Information for Coordination engineering of atomically dispersed zirconium on graphene for oxygen reduction reaction

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Detailed computational methods

Searching of most favorable adsorption sites

Due to chemically stable π conjugation in sp^2-hybridized carbons[1], we suggested that the adsorption sites will be located near the O-Zr-N_4 site. We have search all possible adsorption site near the O-Zr-N_4 site with the help of Pymatgen package[2]. It is found that the oxygen-containing intermediates preferred to be adsorbed in the Zr atom due to high electronegativity difference between O and Zr.

Detailed calculation of Gibbs free energy

Due to the difficulties in calculating the exact energy of *OH, and *OOH, the Gibbs free energy of $^{\Delta G}{}_{*O}$, $^{\Delta G}{}_{*OH}$, and $^{\Delta G}{}_{*OOH}$ were calculated relatively to the Gibbs free energy of a number of H_2O (g) and H_2 (g):

$$\Delta G_{*O} = \Delta G\left(H_2O(g) + * \rightarrow O^* + H_2(g)\right)$$
$$= G_{*O} + G_{H_2} - G_{H_2O} - G_*$$
$$= \left(E_{*O} + E_{H_2} - E_{H_2O} - E_*\right) + \left(E_{ZPE(*O)} + E_{ZPE(H_2)} - E_{ZPE(H_2O)} - E_{ZPE(*)}\right) - T\left(S_{*O} + S_{H_2} - S_{H_2O} - S_*\right)$$

$$\Delta G_{*OH} = \Delta G\left(H_2O(g) + * \rightarrow OH^* + \frac{1}{2}H_2(g)\right)$$
$$= G_{*OH} + \frac{1}{2}G_{H_2} - G_{H_2O} - G_*$$
$$= \left(E_{*OH} + \frac{1}{2}E_{H_2} - E_{H_2O} - E_*\right) + \left(E_{ZPE(*OH)} + \frac{1}{2}E_{ZPE(H_2)} - E_{ZPE(H_2O)} - E_{ZPE(*)}\right)$$

$$\Delta G_{*OOH} = \Delta G\left(2H_2O(g) + * \rightarrow OOH^* + \frac{3}{2}H_2(\right.$$
$$= G_{*OOH} + \frac{3}{2}G_{H_2} - 2G_{H_2O} - G_*$$
$$= \left(E_{*OOH} + \frac{3}{2}E_{H_2} - 2E_{H_2O} - E_*\right) + \left(E_{ZPE(*OOH)} + \frac{3}{2}E_{ZPE(H_2)} - 2E_{ZPE(H_2O)} - E_{ZPE}\right.$$

The temperature were taken as 298.15 K. The entropy and ZPE of gas molecules of H_2, H_2O, and H_2O_2 were obtained from standard values. The entropy of adsorbates and adsorption sites were neglected. The ZPE of adsoption sites were neglected. ZPE of adsorbates were calculated from vibrational frequencies calculation (ph.x).

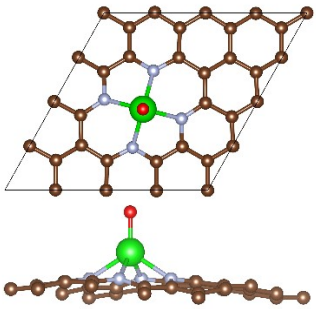
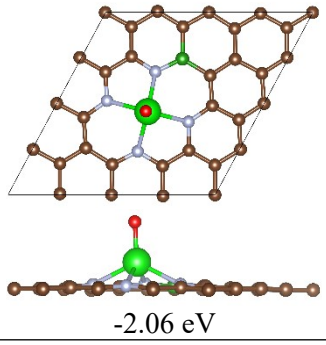
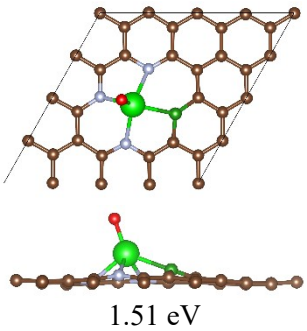
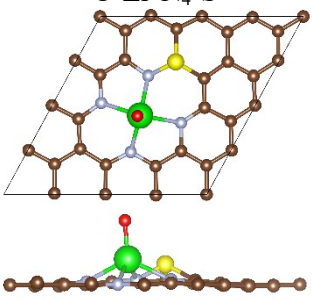
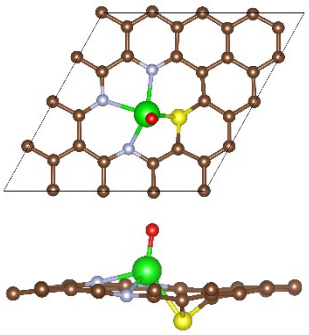
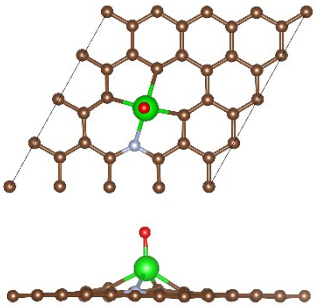
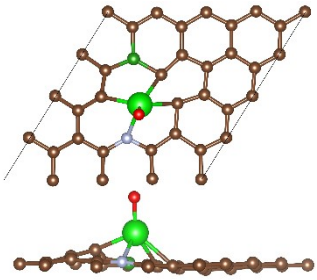
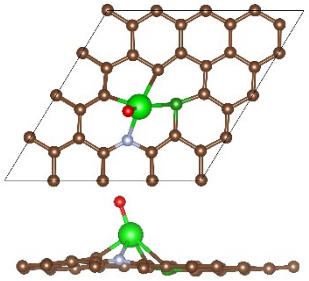
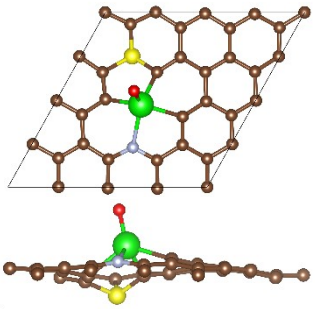
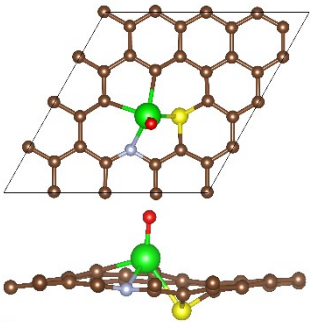
To calculate the $2e^-$ mechanism, the following reaction were considered

$OOH^* + H^+ + e^- \rightarrow H_2O_2 + *$

The Gibbs free energy change of the process is:

$$\Delta G = \Delta G\left(OOH^* + H^+ + e^- \rightarrow H_2O_2 + *\right)$$
$$= G_{H_2O_2} + G_* - \left(G_{*OOH} + G_{H^+} + \mu_{e^-}\right)$$
$$= G_{H_2O_2} + G_* - \left(G_{*OOH} + \frac{1}{2}G_{H_2}\right)$$

Table S1. Relaxed structures of all active sites and their corresponding formation energy calculated with respect to their pristine structures

O-Zr-N_4  0.00 eV	O-Zr-N_4-B  -2.06 eV	O-Zr-N_3-B  1.51 eV
	O-Zr-N_4-S  1.72 eV	O-Zr-N_3-S  0.39 eV
O-Zr-N_1-C_3  0.00 eV	O-Zr-N_1-C_3-B  -0.40 eV	O-Zr-N_1-C_2-B  -0.81 eV
	O-Zr-N_1-C_3-S  2.25 eV	O-Zr-N_1-C_2-S  -0.77 eV

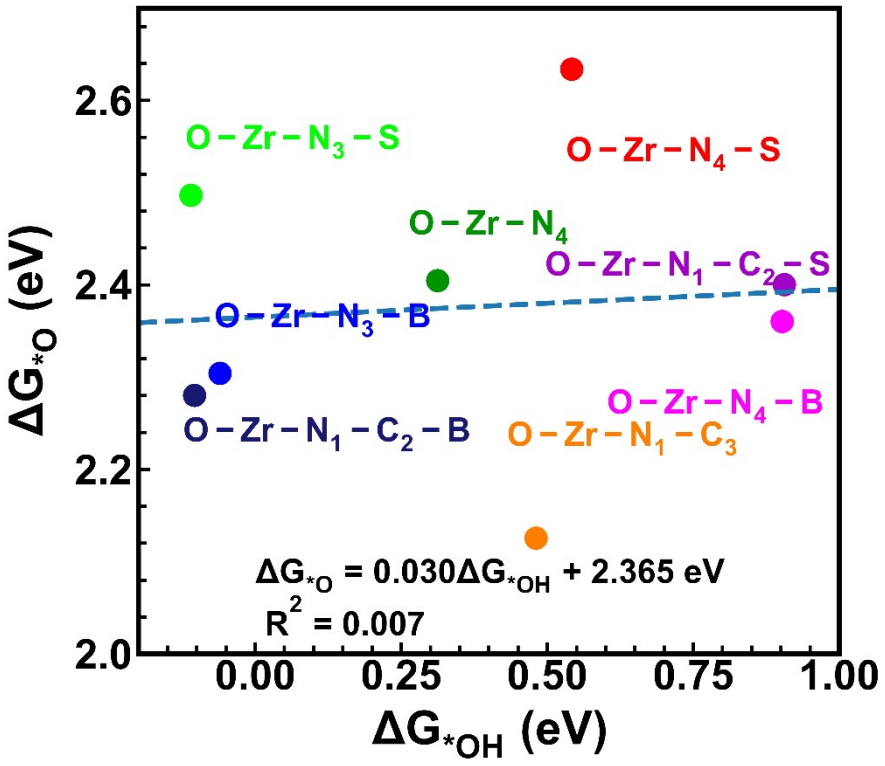


Figure S1. Relationship between $^{\Delta G_{*OH}}$ and $^{\Delta G_{*O}}$

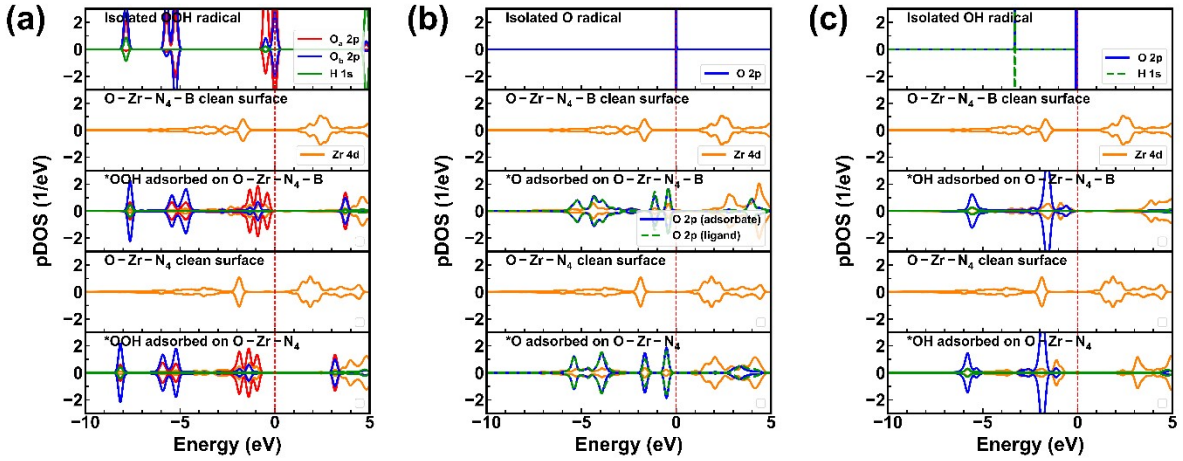


Figure S2. Comparation of projected density of states of isolated radical, clean surface of O-Zr-N_4-B and O-Zr-N_4, and surface after adsorption of (a) OOH, (b) O, (c) OH intermediate

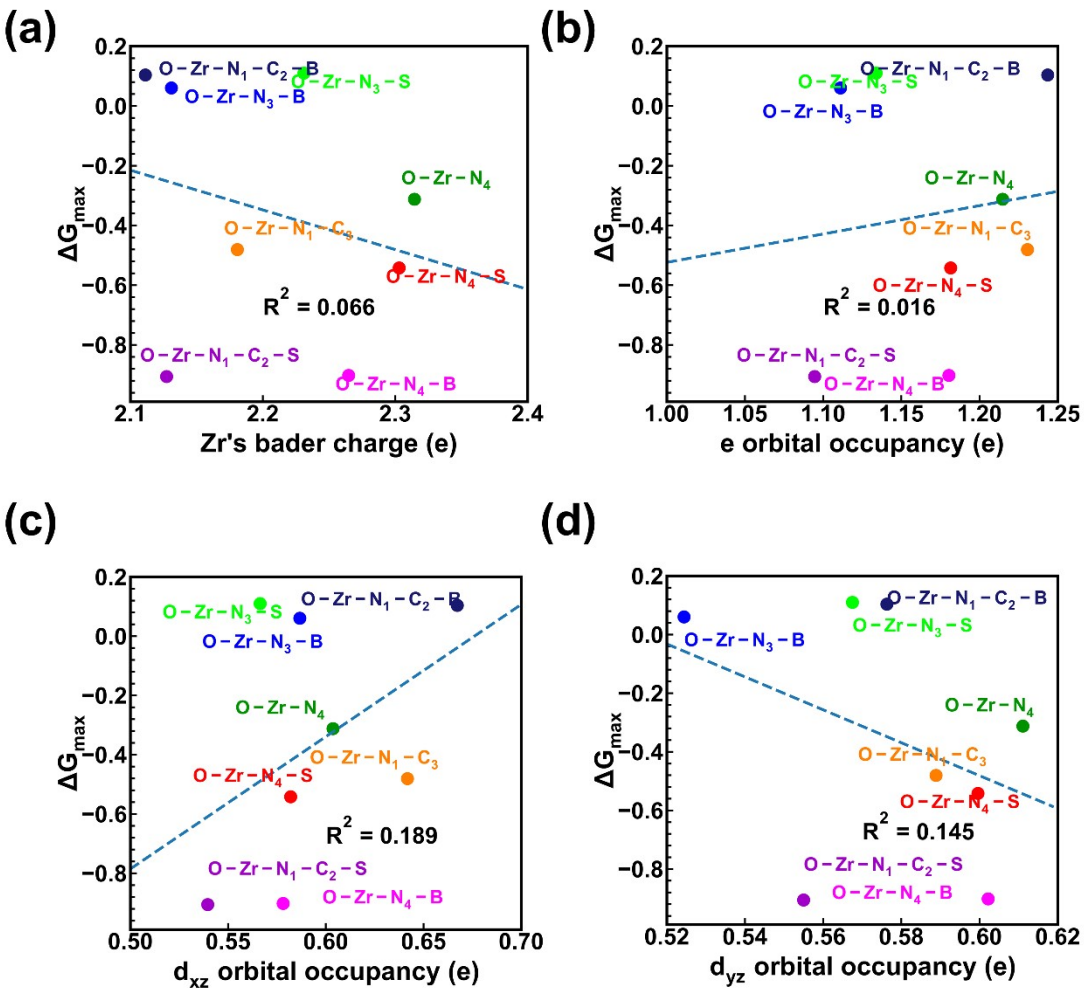


Figure S3. Relationship of Zr's Bader charge with $^{\Delta G_{max}}$

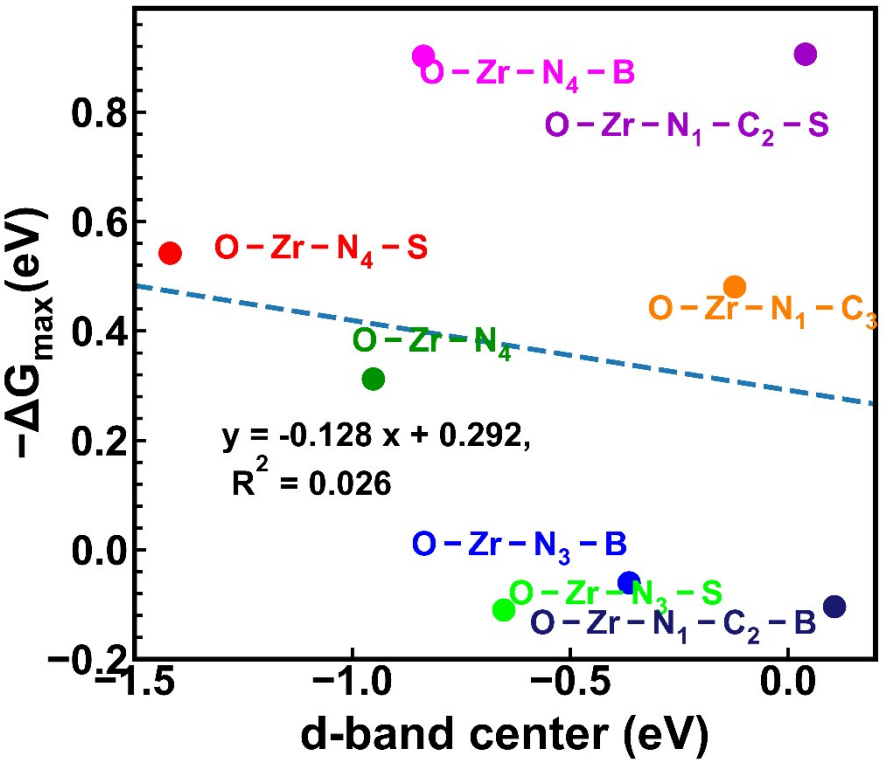


Figure S4. Relationship between d-band center and $^{-\Delta G_{max}}$

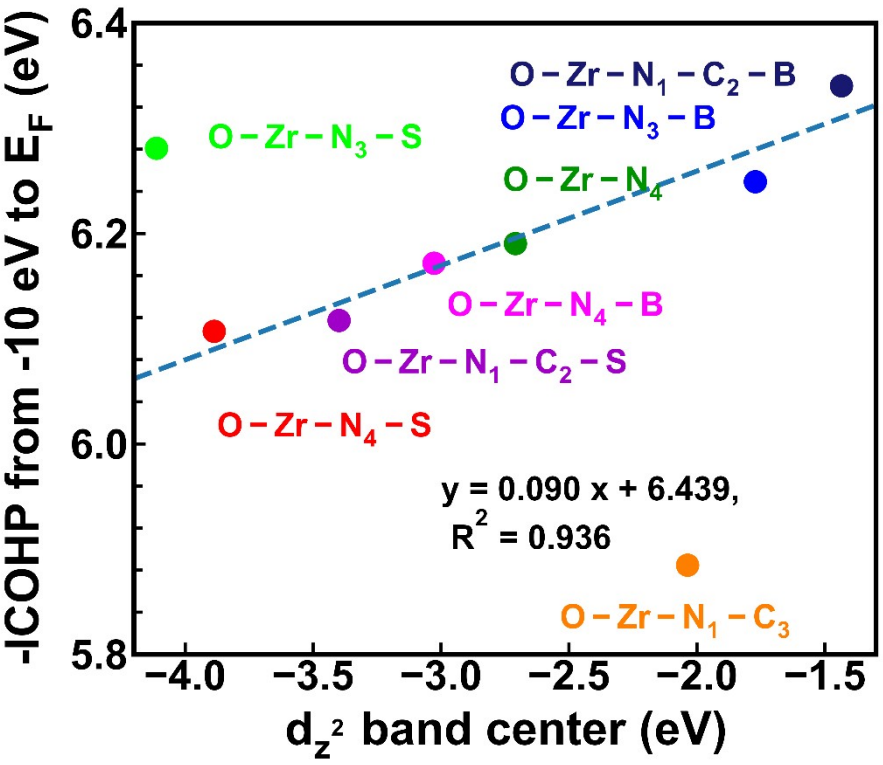


Figure S5. Relationship between $^{d_{z^2}}$ band center and -ICOHP of Zr-O bond from $^{-10\ eV}$ to ^{E_F}

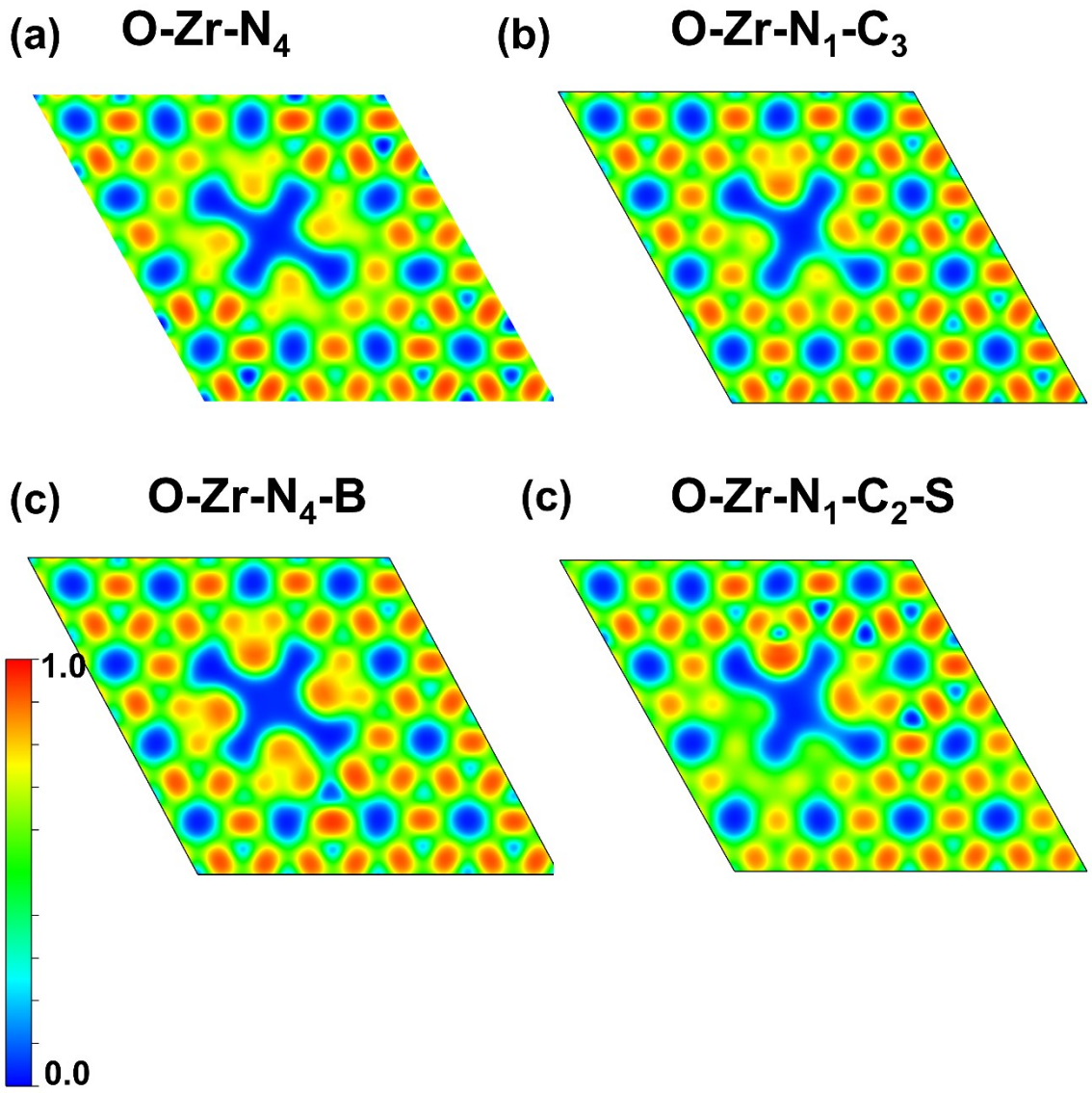


Figure S6. Electron localization function of (a) O-Zr-N4, (b) O-Zr-N1-C3, (c) O-Zr-N4-B, and (d) O-Zr-N1-C2-S site

Table S2. Valence charge of adsorbed OOH and Zr atom on O-Zr-N_4-B obtained using Bader charge analysis

	Number of valence charge (e)			
	Zr	O_a	O_b	H
Before adsorption	9.74	6.55	6.09	0.368
After adsorption	9.66	6.56	6.71	0.365
Δe	-0.08	0.01	0.62	-0.002

Table S3. Valence charge of adsorbed OOH and Zr atom on O-Zr-N_4 obtained using Bader charge analysis

	Number of valence charge (e)			
	Zr	O_a	O_b	H
Before adsorption	9.68	6.55	6.09	0.368
After adsorption	9.69	6.57	6.72	0.360
Δe	0.01	0.02	0.63	-0.007

Table S4. Valence charge of adsorbed O and Zr atom on O-Zr-N_4-B obtained using Bader charge analysis

	Number of valence charge (e)	
	Zr	O
Before adsorption	9.74	6.00
After adsorption	9.64	6.58
Δe	-0.10	0.58

Table S5. Valence charge of adsorbed O and Zr atom on O-Zr-N_4 obtained using Bader charge analysis

	Number of valence charge (e)	
	Zr	O
Before adsorption	9.68	6.00
After adsorption	9.63	6.60
Δe	-0.05	0.60

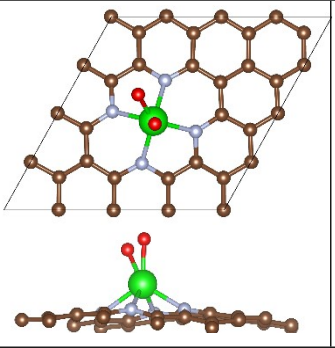
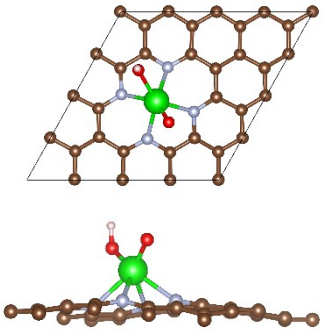
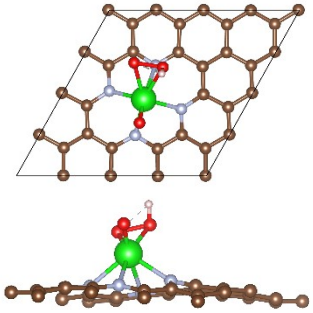
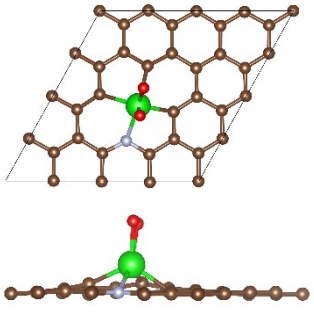
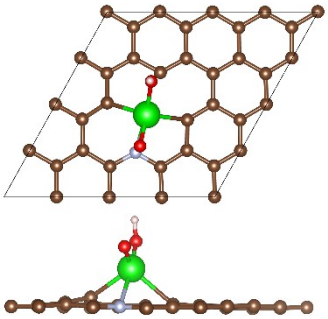
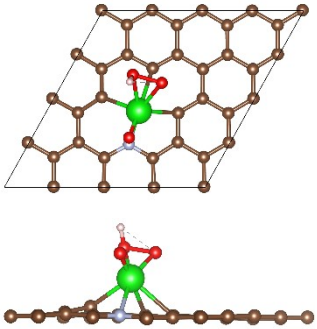
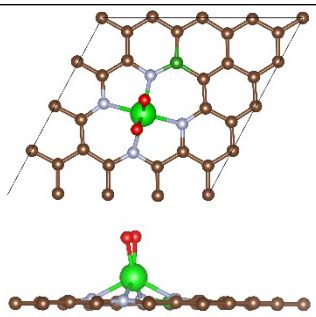
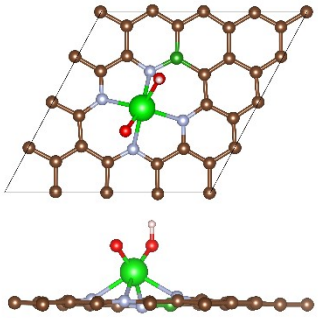
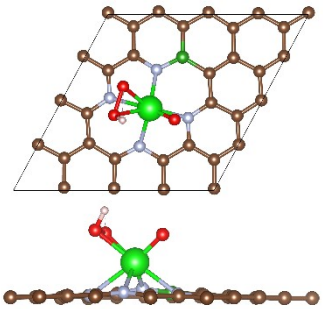
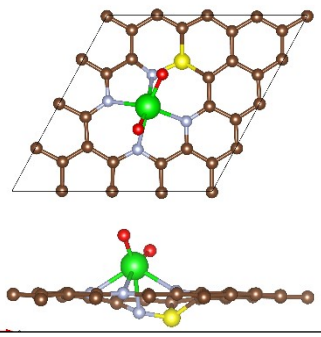
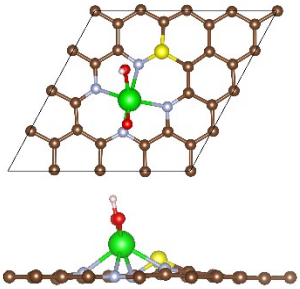
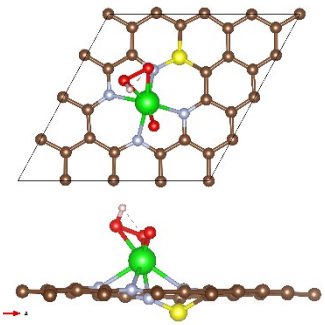
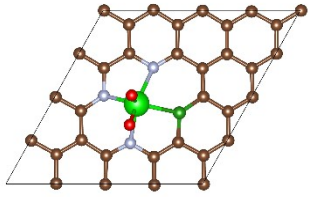
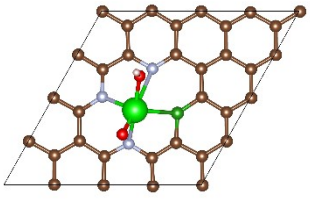
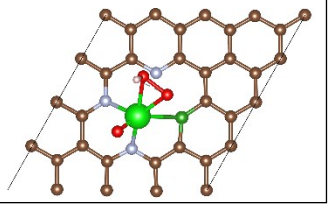
Table S6. Valence charge of adsorbed OH and Zr atom on O-Zr-N_4-B obtained using Bader charge analysis

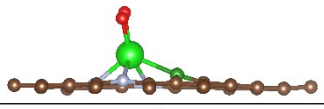
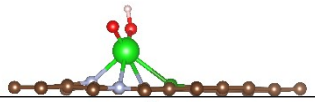
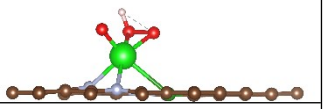
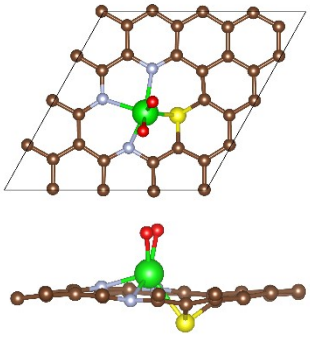
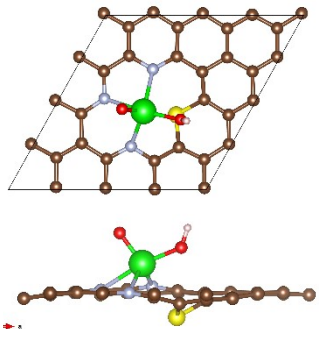
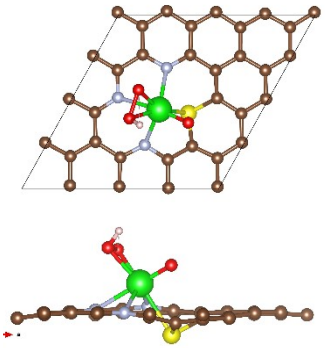
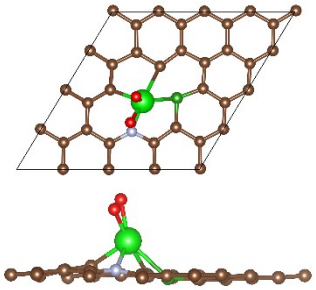
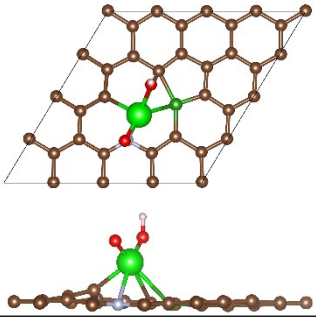
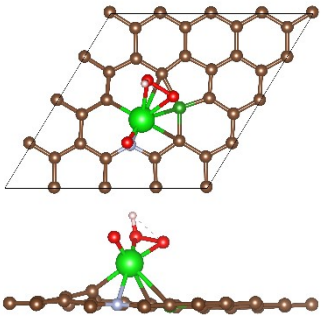
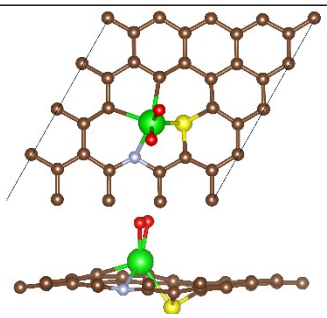
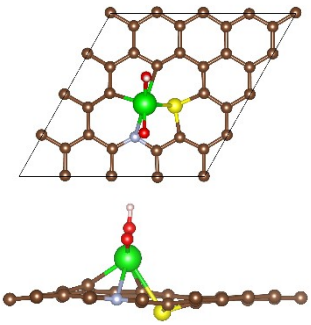
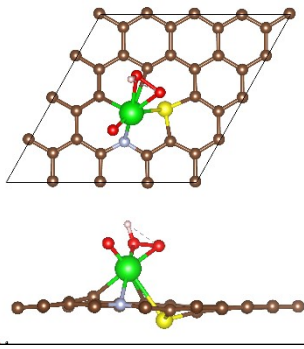
	Number of valence charge (e)		
	Zr	O	H
Before adsorption	9.74	6.59	0.407
After adsorption	9.64	7.24	0.412
Δe	-0.10	0.65	0.005

Table S7. Valence charge of adsorbed OH and Zr atom on O-Zr-N_4 obtained using Bader charge analysis

	Number of valence charge (e)		
	Zr	O	H
Before adsorption	9.68	6.59	0.407
After adsorption	9.64	7.27	0.401
Δe	-0.04	0.68	-0.006

Table S8. Optimized structures of each intermediate adsorption.

Active site	*O	*OH	*OOH
O-Zr-N_4			
O-Zr-N_1-C_3			
O-Zr-N_4-B			
O-Zr-N_4-S			
O-Zr-N_3-B			

			
O-Zr-N_3-S			
O-Zr-N_1-C_2-B			
O-Zr-N_1-C_2-S			

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