Supporting Information

Activating Transition Metal Dichalcogenides Monolayers as Efficient Electrocatalysts for Oxygen Reduction Reaction via Single Atom Doping

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The detain mechanism of $4e^-$ pathway in ORR was employed in this study as the following four steps:

$$*O_2 + H^+ + e^- \leftrightarrow *OOH \quad \text{(R1)}$$

$$*OOH + H^+ + e^- \leftrightarrow *O + H_2O \quad \text{(R2)}$$

$$*O + H^+ + e^- \leftrightarrow *OH \quad \text{(R3)}$$

$$*OH + H^+ + e^- \leftrightarrow * + H_2O \quad \text{(R4)}$$

Accordingly, the effect of electrode potential was considered, and the reaction free energy of process R1-R4 can be expressed by:

$$\Delta G_1 = G_{*OOH} - G_{*O_2} - 0.5G_{H_2} + eU \quad \text{(1a)}$$

$$\Delta G_2 = G_{*O} + G_{H_2O} - G_{*OOH} - 0.5G_{H_2} + eU \quad \text{(1b)}$$

$$\Delta G_3 = G_{*OH} - G_{*O} - 0.5G_{H_2} + eU \quad \text{(1c)}$$

$$\Delta G_4 = G_{H_2O} + G_* - G_{*OH} - 0.5G_{H_2} + eU \quad (1d)$$

All free energies of elementary steps were calculated by using the energy of H_2 (g) and H_2O (l) as benchmark due to the high-spin ground state of O_2 molecule feebly described in DFT simulations. Therefore, the reaction free energies of process of 2a-2d were calculated by:

$$* + 2H_2O \leftrightarrow *O_2 + 2H_2 \quad (2a)$$

$$* + 2H_2O \leftrightarrow *OOH + 3/2H_2 \quad (2b)$$

$$* + H_2O \leftrightarrow *O + H_2 \quad (2c)$$

$$* + H_2O \leftrightarrow *OH + 1/2H_2 \quad (2d)$$

The reaction free energy of process of 2a-2d can be denoted as:

$$\Delta G_{*OOH} = G_{*OOH} - G_* - 2G_{H_2O} + 3/2G_{H_2} \quad (3a)$$

$$\Delta G_{*O} = G_{*O} - G_* - G_{H_2O} + G_{H_2} \quad (3b)$$

$$\Delta G_{*OH} = G_{*OH} - G_* - G_{H_2O} + 1/2G_{H_2} \quad (3c)$$

Under the equilibrium potential (U = 1.23 V), the value of the reaction free energy of $O_2 + 4H^+ + 4e^- \leftrightarrow 2H_2O$ is 4.92 eV. ΔG_1 can be defined as $\Delta G_1 = 4.92 - (\Delta G_2 + \Delta G_3 + \Delta G_4)$. Therefore, the reaction free energy of process of R1-R4 can be calculated by:

$$\Delta G_1 = \Delta G_{*OOH} - 4.92 + eU \quad (4a)$$

$$\Delta G_2 = \Delta G_{*O} - \Delta G_{*OOH} + eU \quad (4b)$$

$$\Delta G_3 = \Delta G_{*OH} - \Delta G_{*O} + eU \quad (4c)$$

$$\Delta G_4 = -\Delta G_{*OH} + eU \quad (4d)$$

Table S1. Changes in the reaction free energy (ΔG) of various pristine TMDs. (The unit is eV)

Catalysts	ΔG_1	ΔG_2	ΔG_3	ΔG_4
1T-TiS_2	1.55	-1.75	0.37	-0.18
2H-TiS_2	1.45	-2.45	0.22	0.77
1T-VS_2	1.59	-2.52	0.51	0.40
2H-VS_2	1.94	-2.41	0.16	0.30
1T-NbS_2	1.47	-1.95	0.74	-0.25
2H-NbS_2	1.22	-1.83	0.40	0.21
1T-TaS_2	1.43	-1.91	0.82	-0.34
2H-TaS_2	1.59	-2.15	0.47	0.07
1T′-WS_2	1.50	-2.09	0.60	-0.01
2H-WS_2	1.42	-1.77	1.63	-1.28
1T-HfS_2	1.54	-1.19	0.19	-0.54
1T-ZrS_2	1.66	-1.43	0.37	-0.60
1T-PtS_2	1.35	-2.22	1.54	-0.67
1T′-ReS_2	1.98	-2.46	0.85	-0.37

Table S2. The number of electrons (n_e) involved in the dissolution for pure metals, standard dissolution potentials ($U^{o}_{diss(metal)}$, pH = 0, refer to Guo et al.[1]), and computed dissolution potentials (U_{diss}) for M@TMDs.

Catalysts	$\mathbf{n_e}$	U^{0}_{diss}	$\boldsymbol{U_{diss}}$	**Catalysts**	$\mathbf{n_e}$	U^{0}_{diss}	$\boldsymbol{U_{diss}}$
Fe@1T-NbS_2	2	-0.45	-0.48	**Fe@2H-NbS_2**	2	-0.45	-0.38
Co@1T-NbS_2	2	-0.28	-0.09	**Co@2H-NbS_2**	2	-0.28	-0.23
Ni@1T-NbS_2	2	-0.26	-0.27	**Fe@2H-TiS_2**	2	-0.45	-0.41
Co@1T-TiS_2	2	-0.28	-0.15	**Co@2H-TiS_2**	2	-0.28	-0.02
Ni@1T-TiS_2	2	-0.26	-0.18	**Ni@2H-TiS_2**	2	-0.26	-0.08
Fe@1T-VS_2	2	-0.45	0.17	**Co@2H-VS_2**	2	-0.28	-0.33
Co@1T-VS_2	2	-0.28	0.53	**Co@2H-TaS_2**	2	-0.28	-0.34
Ni@1T-VS_2	2	-0.26	0.05	**Fe@1T′-MoS_2**	2	-0.45	-1.81
Co@1T-TaS_2	2	-0.28	-0.24	**Co@1T′-MoS_2**	2	-0.28	-1.18
Fe@1T-ZrS_2	2	-0.45	-0.48	**Ni@1T′-MoS_2**	2	-0.26	-1.07
Co@1T-ZrS_2	2	-0.28	-0.27				

Ni@1T-ZrS_2	2	-0.26	-0.20
Co@1T′-ReS_2	2	-0.28	-0.22

Table S3. The Gibbs adsorption free energy of ORR intermediates on M@TMDs surface.

Catalysts	ΔG_{*OOH}	ΔG_{*O}	ΔG_{*OH}	Catalysts	ΔG_{*OOH}	ΔG_{*O}	ΔG_{*OH}
Fe@1T-NbS_2	3.13	1.22	0.17	**Fe@2H-NbS_2**	3.23	1.50	0.10
Co@1T-NbS_2	3.62	2.09	0.68	**Co@2H-NbS_2**	3.44	1.79	0.41
Ni@1T-NbS_2	3.92	3.46	1.06	**Fe@2H-TiS_2**	3.33	1.19	0.24
Co@1T-TiS_2	3.59	2.23	0.74	**Co@2H-TiS_2**	3.62	2.21	0.79
Ni@1T-TiS_2	4.01	2.81	1.15	**Ni@2H-TiS_2**	4.02	2.85	1.24
Fe@1T-VS_2	2.50	0.88	-0.36	**Co@2H-VS_2**	3.20	0.06	-0.68
Co@1T-VS_2	4.49	4.00	1.55	**Co@2H-TaS_2**	3.52	1.90	0.67
Ni@1T-VS_2	4.43	3.39	1.50				
Co@1T-TaS_2	3.64	2.33	0.77				
Fe@1T-ZrS_2	3.38	1.89	0.20				
Co@1T-ZrS_2	3.59	1.85	0.37				
Ni@1T-ZrS_2	4.07	2.86	1.24				
Co@1T′-ReS_2	4.53	2.73	1.05				

Table S4. The number of electron transferred that different catalysts.

Catalysts	N_e	Catalysts	N_e
Fe/1T-NbS_2	0.37	**Fe/2H-NbS_2**	0.38
Co/1T-NbS_2	0.17	**Co/2H-NbS_2**	0.30
Ni/1T-NbS_2	0.21	**Fe/2H-TiS_2**	0.63
Co/1T-TiS_2	0.33	**Co/2H-TiS_2**	0.31
Ni/1T-TiS_2	0.30	**Ni/2H-TiS_2**	0.23
Fe/1T-VS_2	0.49	**Co/2H-VS_2**	0.39

Co/1T-VS_2	0.34	**Co/2H-TaS_2**	0.12
Ni/1T-VS_2	0.29		
Co/1T-TaS_2	0.10		
Fe/1T-ZrS_2	0.51		
Co/1T-ZrS_2	0.30		
Ni/1T-ZrS_2	0.22		
Co/1T′-ReS_2	0.37		

Table S5. The E_f of various N/P-doped TMDs.

Catalysts	E_f **(eV)**	**Catalysts**	E_f **(eV)**
N/2H-TaS_2	1.37	P/2H-TaS_2	1.82
N/2H-NbS_2	1.61	P/2H-NbS_2	1.78
N/2H-TiS_2	0.76	P/2H-TiS_2	0.91
N/2H-VS_2	0.74	P/2H-VS_2	0.72
N/2H-WS_2	1.73	P/2H-WS_2	1.55
N/1T-TaS_2	0.53	P/1T-TaS_2	1.20
N/1T-NbS_2	0.94	P/1T-NbS_2	1.23
N/1T-TiS_2	1.23	P/1T-TiS_2	1.88
N/1T-VS_2	1.15	P/1T-VS_2	1.20
N/1T-PtS_2	3.32	P/1T-PtS_2	0.68
N/1T-HfS_2	1.53	P/1T-HfS_2	2.46
N/1T-ZrS_2	1.66	P/1T-ZrS_2	2.34
N/1T′-WS_2	1.84	P/1T′-WS_2	1.40
N/1T′-ReS_2	2.28	P/1T′-ReS_2	0.87
N/2H-MoS_2	1.98	P/2H-MoS_2	1.51

Table S6. Gibbs adsorption free energy of ORR intermediates on P/N-doped TMDs surface.

Catalysts	ΔG_{*OOH}	ΔG_{*O}	ΔG_{*OH}	**Catalysts**	ΔG_{*OOH}	ΔG_{*O}	ΔG_{*OH}

N/2H-TaS_2	4.24	1.81	1.11	P/2H-TaS_2	2.53	0.06	-0.96
N/2H-NbS_2	5.20	1.56	0.89	P/2H-NbS_2	2.52	-0.01	-1.01
N/2H-TiS_2	4.12	1.37	0.65	P/2H-TiS_2	3.36	0.90	-0.10
N/2H-VS_2	5.77	2.27	1.75	P/2H-VS_2	2.89	0.25	-0.96
N/2H-WS_2	4.04	2.02	0.93	P/2H-WS_2	2.85	0.15	-0.66
N/1T-TaS_2	5.05	2.26	2.26	P/1T-TaS_2	3.23	0.29	-0.20
N/1T-NbS_2	4.94	2.21	1.89	P/1T-NbS_2	3.14	0.24	-0.28
N/1T-TiS_2	5.18	2.24	1.56	P/1T-TiS_2	2.87	0.06	-0.55
N/1T-VS_2	5.71	2.63	2.22	P/1T-VS_2	2.94	-0.13	-0.63
N/1T-PtS_2	3.07	0.54	0.08	P/1T-PtS_2	2.66	-0.23	-0.83
N/1T-HfS_2	5.18	1.66	1.27	P/1T-HfS_2	2.96	0.53	-0.39
N/1T-ZrS_2	5.18	1.53	1.21	P/1T-ZrS_2	3.02	0.40	-0.43
N/1T′-WS_2	4.44	2.27	1.42	P/1T′-WS_2	2.96	0.12	-0.51
N/1T′-ReS_2	4.84	1.07	1.09	P/1T′-ReS_2	3.00	0.14	-0.49

Table S7. Changes in the reaction free energy (ΔG) of N/P-doped TMDs surface (under 1.23 eV).

Catalysts	**ΔG_1**	**ΔG_2**	**ΔG_3**	**ΔG_4**	**Catalysts**	**ΔG_1**	**ΔG_2**	**ΔG_3**	**ΔG_4**
N/2H-TaS_2	0.55	-1.21	0.54	0.11	P/2H-TaS_2	-1.16	-1.24	0.20	2.19
N/2H-NbS_2	1.51	-2.40	0.55	0.34	P/2H-NbS_2	-1.16	-1.31	0.24	2.23
N/2H-TiS_2	0.43	-1.51	0.50	0.57	P/2H-TiS_2	-0.32	-1.22	0.22	1.32
N/2H-VS_2	2.08	-2.27	0.71	-0.52	P/2H-VS_2	-0.79	-1.41	0.02	2.19
N/2H-WS_2	0.35	-0.78	0.13	0.29	P/2H-WS_2	-0.83	-1.47	0.41	1.88
N/1T-TaS_2	1.36	-1.56	1.22	-1.03	P/1T-TaS_2	-0.45	-1.70	0.72	1.43
N/1T-NbS_2	1.25	-1.49	0.89	-0.65	P/1T-NbS_2	-0.54	-1.66	0.70	1.50
N/1T-TiS_2	1.49	-1.70	0.54	-0.34	P/1T-TiS_2	-0.81	-1.58	0.61	1.77
N/1T-VS_2	2.02	-1.84	0.82	-0.99	P/1T-VS_2	-0.74	-1.84	0.72	1.85
N/1T-PtS_2	-0.61	-1.30	0.77	1.14	P/1T-PtS_2	-1.02	-1.65	0.63	2.05
N/1T-HfS_2	1.49	-2.29	0.84	-0.05	P/1T-HfS_2	-0.72	-1.20	0.31	1.62
N/1T-ZrS_2	1.48	-2.41	0.91	0.02	P/1T-ZrS_2	-0.66	-1.38	0.39	1.66

N/1T′-WS_2	0.75	-0.94	0.38	-0.19	P/1T′-WS_2	-0.72	-1.61	0.59	1.74
N/1T′-ReS_2	1.15	-2.53	1.25	0.13	P/1T′-ReS_2	-0.68	-1.63	0.59	1.72

Table S8. The number of electron transferred and the value of E_p of various N/P-doped TMDs.

Catalysts	N_e(|e|)	E_p *(eV)*	**Catalysts**	N_e(|e|)	E_p *(eV)*
N/2H-TaS_2	1.17	-3.84	P/2H-TaS_2	0.62	-0.76
N/2H-NbS_2	1.21	-4.86	P/2H-NbS_2	0.63	-0.77
N/2H-TiS_2	1.09	-5.71	P/2H-TiS_2	0.24	-4.81
N/2H-VS_2	0.98	-3.82	P/2H-VS_2	0.42	-0.34
N/2H-WS_2	1.03	-3.89	P/2H-WS_2	0.37	-0.68
N/1T-TaS_2	1.24	-4.97	P/1T-TaS_2	0.71	-1.43
N/1T-NbS_2	1.27	-4.87	P/1T-NbS_2	0.68	-1.34
N/1T-TiS_2	1.09	-3.92	P/1T-TiS_2	0.63	-0.62
N/1T-VS_2	1.00	-4.54	P/1T-VS_2	0.44	-0.95
N/1T-PtS_2	0.59	-0..93	P/1T-PtS_2	-0.41	-0.02
N/1T-HfS_2	1.32	-2.93	P/1T-HfS_2	0.89	-0.13
N/1T-ZrS_2	1.45	-2.88	P/1T-ZrS_2	0.93	-0.29
N/1T′-WS_2	1.07	-6.10	P/1T′-WS_2	0.34	-1.68
N/1T′-ReS_2	0.89	-6.47	P/1T′-ReS_2	0.11	-2.17

Table S9. The zero-point energy (ZPE) and the entropy change (T*S) of free molecules and the ORR intermediates.

	Gas molecules					
T=298.15K	**H_2O**	**ZPE**	**0.56**	**H_2**	**ZPE**	**0.27**
		TS	**0.67**		**TS**	**0.41**
	***OOH**		***O**		***OH**	
catalysts	**ZPE**	**TS**	**ZPE**	**TS**	**ZPE**	**TS**
1T-TiS_2	0.397	0.141	0.070	0.066	0.345	0.082
2H-TiS_2	0.438	0.129	0.075	0.056	0.345	0.067
1T-VS_2	0.391	0.197	0.074	0.064	0.354	0.109
2H-VS_2	0.397	0.237	0.079	0.058	0.344	0.078

1T-NbS_2	0.391	0.200	0.074	0.059	0.337	0.079
2H-NbS_2	0.381	0.109	0.075	0.057	0.347	0.072
1T-TaS_2	0.389	0.188	0.073	0.061	0.337	0.076
2H-TaS_2	0.375	0.116	0.074	0.057	0.348	0.069
1T'-WS_2	0.391	0.203	0.078	0.052	0.350	0.066
2H-WS_2	0.394	0.253	0.078	0.053	0.315	0.095
1T-HfS_2	0.379	0.172	0.064	0.076	0.340	0.082
1T-ZrS_2	0.375	0.050	0.065	0.076	0.341	0.085
1T-PtS_2	0.420	0.174	0.079	0.052	0.331	0.088
1T'-ReS_2	0.383	0.167	0.067	0.078	0.349	0.072
Fe@2H-NbS_2	0.434	0.218	0.060	0.094	0.316	0.099
Co@2H-NbS_2	0.429	0.219	0.062	0.076	0.329	0.131
Fe@2H-TiS_2	0.411	0.081	0.011	0.031	0.341	0.118
Co@2H-TiS_2	0.424	0.174	0.057	0.109	0.334	0.128
Ni@2H-TiS_2	0.430	0.153	0.055	0.087	0.328	0.075
Co@2H-VS_2	0.426	0.221	0.052	0.048	0.321	0.138
Co@2H-TaS_2	0.427	0.225	0.059	0.076	0.332	0.136
Fe@1T-NbS_2	0.434	0.218	0.059	0.094	0.316	0.099
Co@1T-NbS_2	0.429	0.219	0.062	0.076	0.329	0.132
Ni@1T-NbS_2	0.430	0.219	0.055	0.087	0.325	0.085
Co@1T-TiS_2	0.413	0.200	0.059	0.078	0.346	0.085
Ni@1T-TiS_2	0.420	0.179	0.054	0.084	0.320	0.098
Fe@1T-VS_2	0.447	0.165	0.066	0.068	0.343	0.102
Co@1T-VS_2	0.443	0.178	0.060	0.077	0.339	0.116
Ni@1T-VS_2	0.445	0.175	0.052	0.085	0.341	0.109
Co@1T-TaS_2	0.426	0.221	0.059	0.083	0.328	0.075
Fe@1T-ZrS_2	0.429	0.153	0.052	0.002	0.316	0.100
Co@1T-ZrS_2	0.431	0.214	0.061	0.075	0.334	0.117
Ni@1T-ZrS_2	0.426	0.167	0.052	0.093	0.320	0.092
Co@1T'-ReS_2	0.435	0.136	0.056	0.041	0.339	0.138
N/2H-TaS_2	0.443	0.114	0.076	0.068	0.365	0.055
P/2H-TaS_2	0.439	0.183	0.064	0.035	0.349	0.121
N/2H-NbS_2	0.374	0.125	0.077	0.073	0.365	0.121
P/2H-NbS_2	0.431	0.146	0.076	0.064	0.350	0.119
N/2H-TiS_2	0.440	0.202	0.086	0.034	0.376	0.057
P/2H-TiS_2	0.433	0.201	0.075	0.069	0.353	0.106
N/2H-VS_2	0.423	0.167	0.056	0.047	0.316	0.156
P/2H-VS_2	0.426	0.221	0.052	0.047	0.321	0.138
N/2H-WS_2	0.454	0.153	0.086	0.047	0.376	0.109
P/2H-WS_2	0.439	0.182	0.078	0.059	0.358	0.105
N/1T-TaS_2	0.391	0.256	0.076	0.052	0.359	0.064
P/1T-TaS_2	0.434	0.180	0.076	0.065	0.340	0.082
N/1T-NbS_2	0.380	0.105	0.073	0.051	0.375	0.091

P/1T-NbS_2	0.429	0.198	0.078	0.063	0.344	0.074
N/1T-TiS_2	0.387	0.147	0.093	0.067	0.392	0.067
P/1T-TiS_2	0.424	0.213	0.078	0.064	0.351	0.119
N/1T-VS_2	0.447	0.165	0.065	0.068	0.343	0.102
P/1T-VS_2	0.443	0.178	0.060	0.076	0.339	0.116
N/1T-PtS_2	0.431	0.126	0.091	0.059	0.381	0.082
P/1T-PtS_2	0.423	0.104	0.078	0.064	0.349	0.064
N/1T-HfS_2	0.377	0.121	0.083	0.039	0.396	0.063
P/1T-HfS_2	0.428	0.213	0.069	0.078	0.345	0.083
N/1T-ZrS_2	0.374	0.125	0.085	0.038	0.396	0.065
P/1T-ZrS_2	0.411	0.135	0.069	0.082	0.343	0.086
N/1T'-WS_2	0.449	0.156	0.092	0.049	0.366	0.058
P/1T'-WS_2	0.427	0.218	0.078	0.061	0.356	0.104
N/1T'-ReS_2	0.435	0.091	0.052	0.057	0.315	0.040
P/1T'-ReS_2	0.434	0.135	0.056	0.041	0.339	0.138

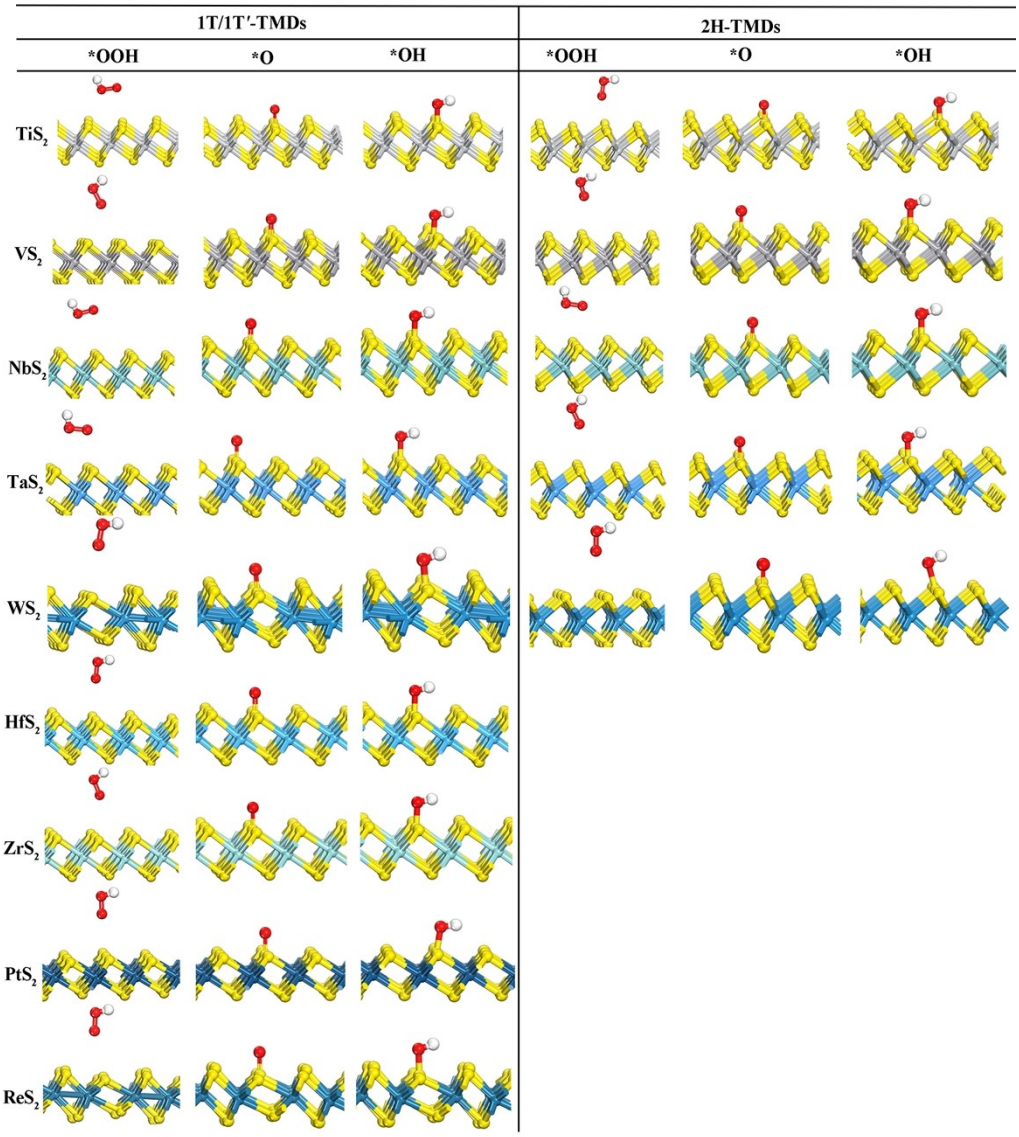

Figure S1. The adsorption configuration of oxygen intermediates (*OOH, *O,*OH) on the pristine TMDs.

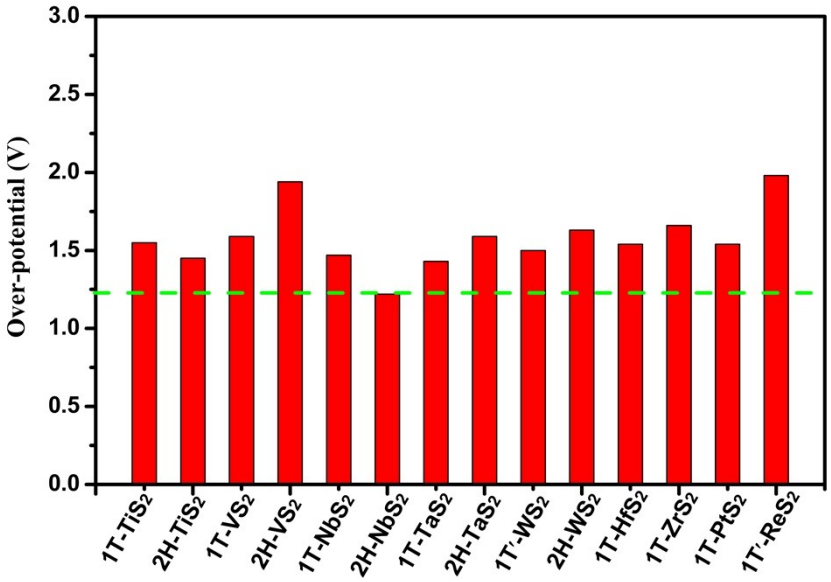

Figure S2. The over-potential of the pristine TMDs. The green dotted line represents the equilibrium electrode potential.

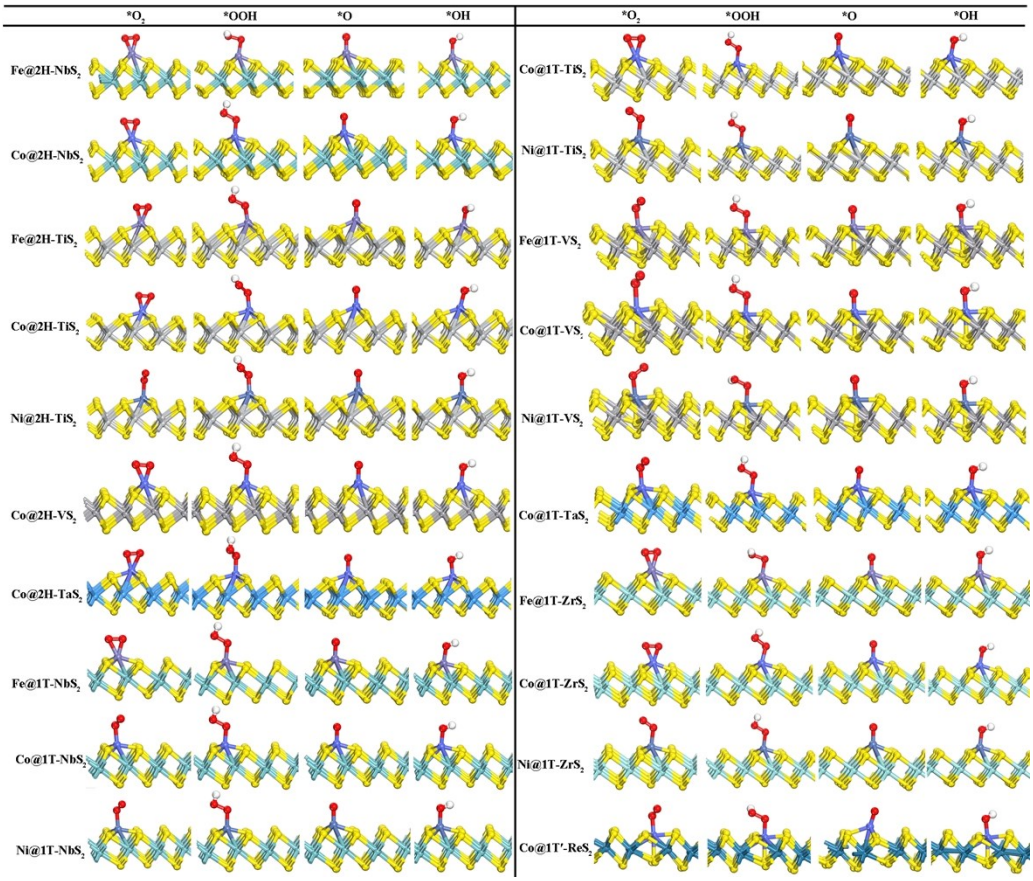

Figure S3. The adsorption configuration of oxygen molecule and oxygen intermediates (*OOH,

*O,*OH) on the M@ TMDs.

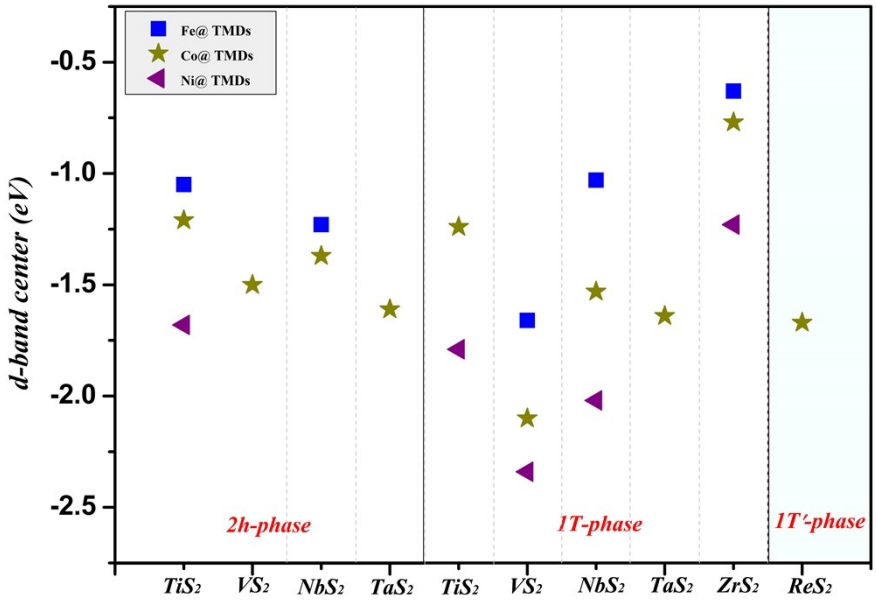

Figure S4. The d-band center of the transition metal doped on various TMDs.

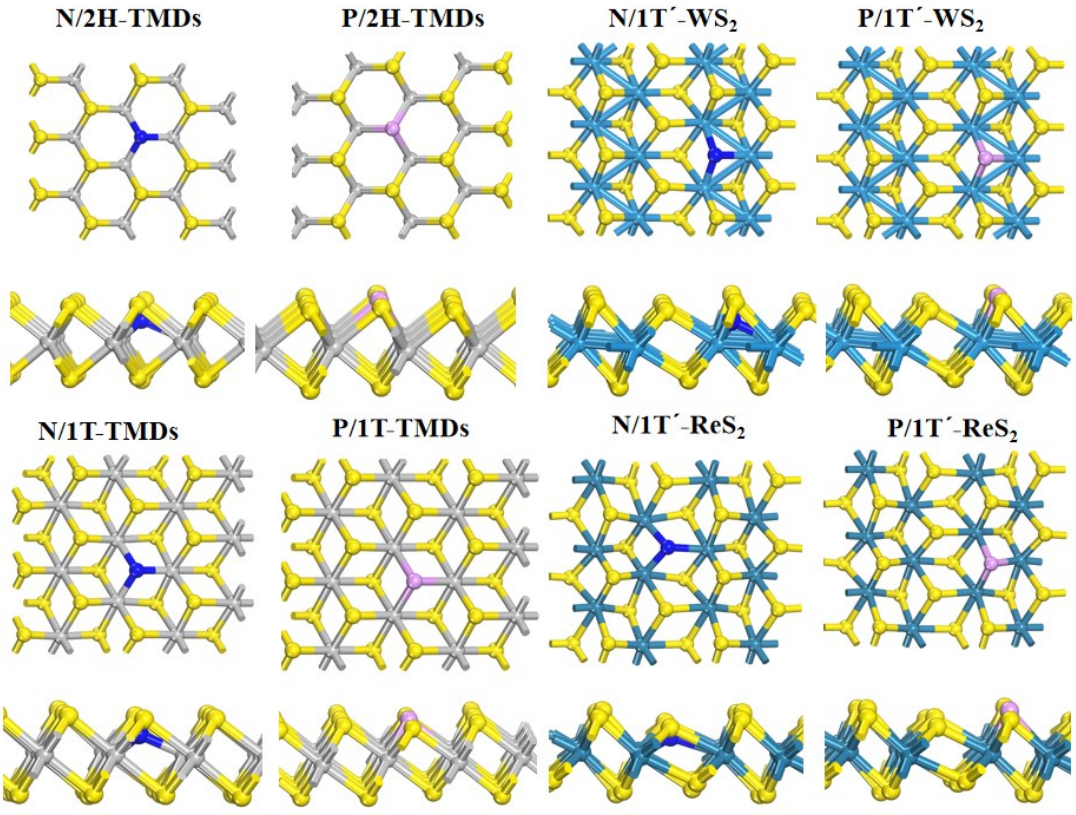

Figure S5. The stable structure of N/P substitutional doping on various types of TMDs.

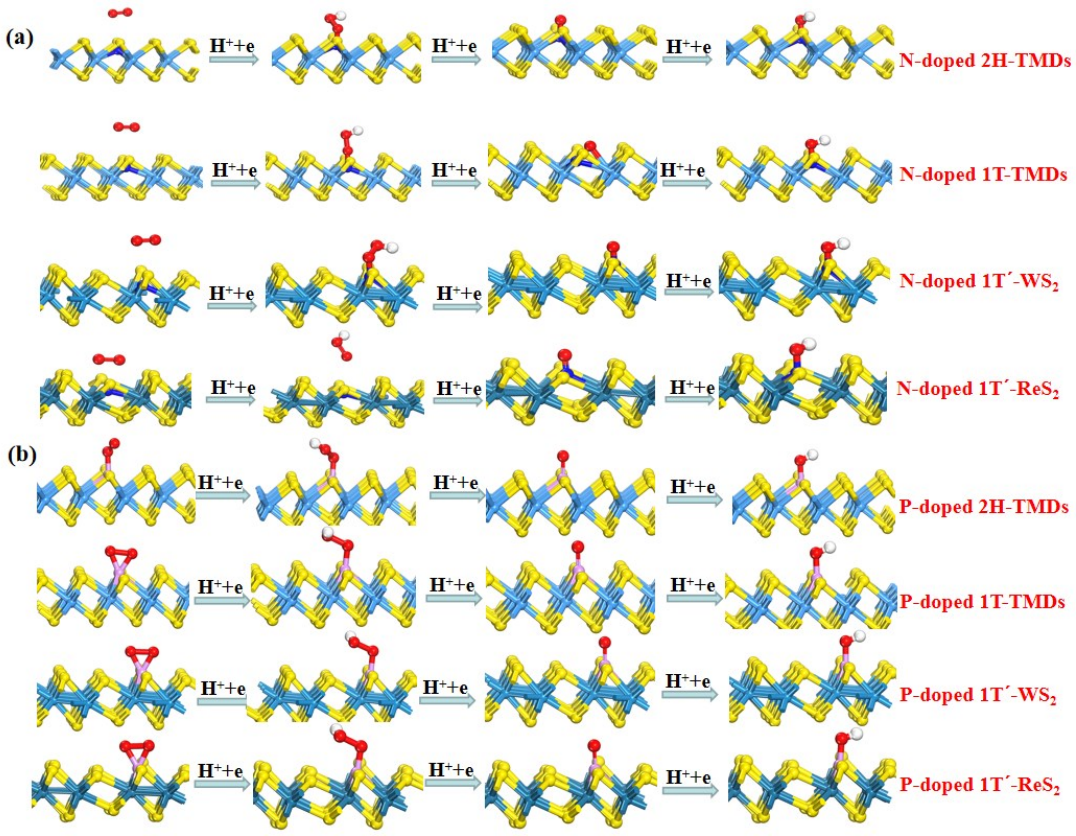

Figure S6. The ORR process of oxygen species at each elementary step on N doped- TMDs (a), P doped-TMDs (b).

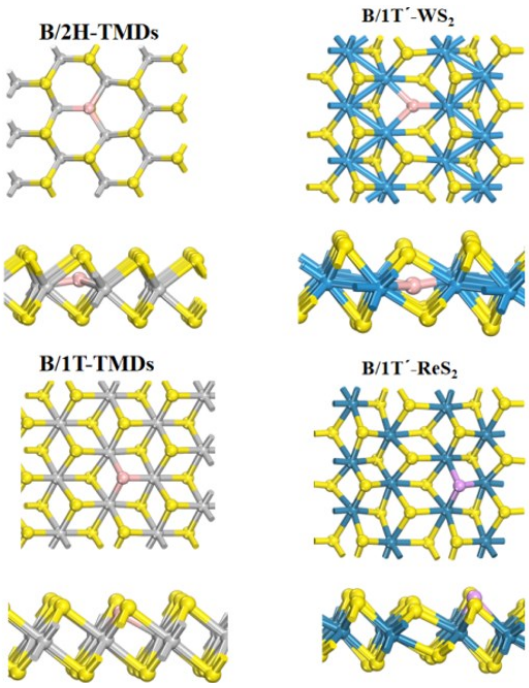

Figure S7. The optimized structure of B substitutional doping on various types of TMDs.

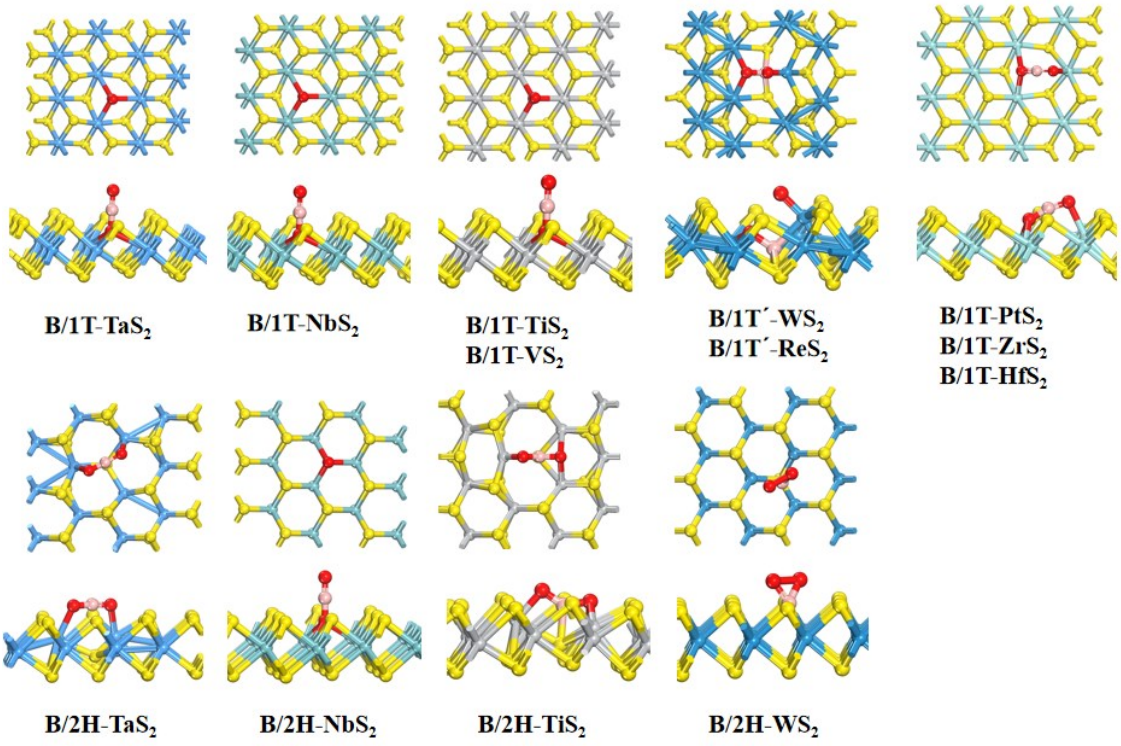

Figure S8. The adsorption configurations of oxygen molecules on B/TMDs.

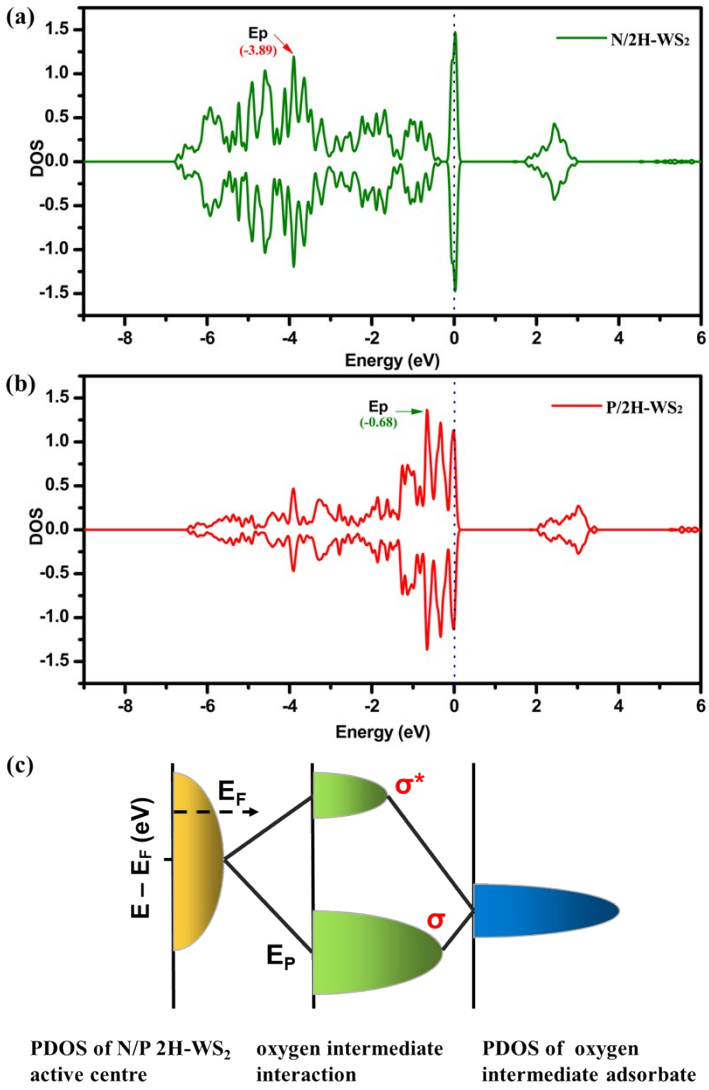

Figure S9. The DOS for N and P element in N- and P-doped 2H-WS_2 model (a), (b). Energy level diagram showing orbital hybridization of active sites and oxygen intermediate adsorbate. E_F is the Fermi level of the substrate; σ and σ* indicate bonding and anti-bonding states, respectively (c).

Reference

1. X. Y. Guo, J. X. Gu, S. R. Lin, S. L. Zhang, Z. F. Chen and S. P. Huang, *J. Am. Chem. Soc.*, 2020, **142**, 5709-5721.