Electronic Supporting Information

Computational Screening of Single Atom Catalysts Supported by VS_2 Monolayer for Electrocatalytic Oxygen Reduction/Evolution Reactions

Zengming Qin,[a] Zhongxu Wang,[a] Jingxiang Zhao[a,*]

[a] *Key Laboratory for Photonic and Electronic Bandgap Materials, Ministry of Education, School of Physics and Electronic Engineering, Harbin Normal University, Harbin, 150025, P. R. China*

[*] *To whom correspondence should be addressed. Email: xjz_hmily@163.com (JZ)*

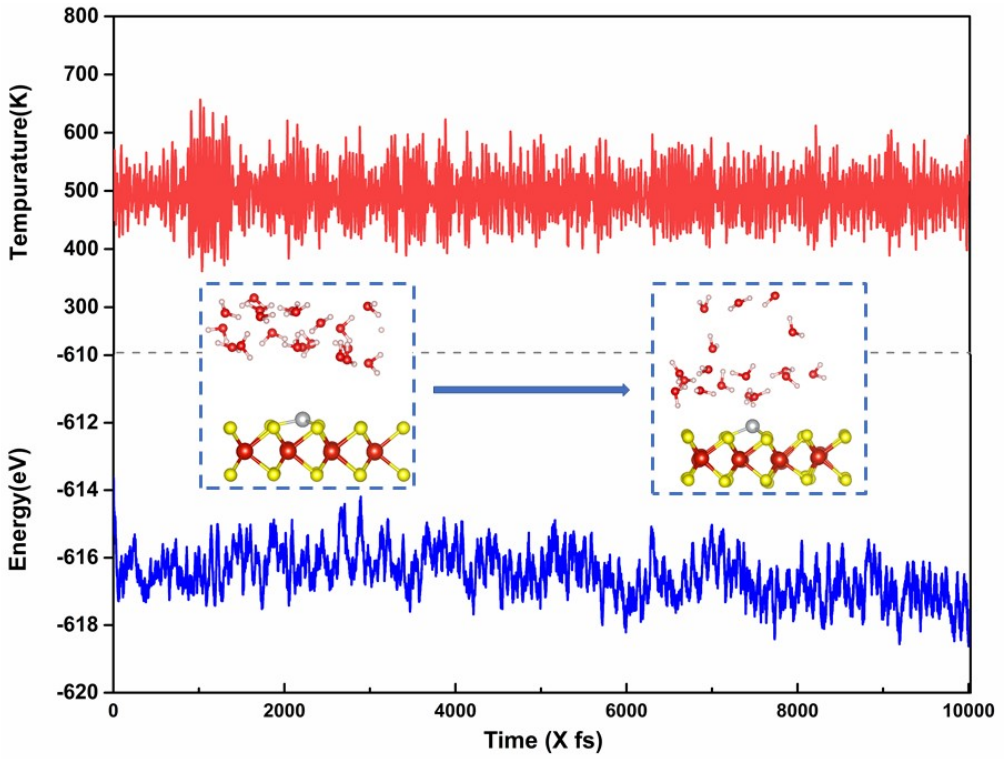
Table S1. The computed ΔG values of each elemenatry step in ORR on Ni@VS_2 catalyst with and without DFT+U approach.

Elemental Step	**without DFT+U**	**with DFT+U**
$O_2 \rightarrow OOH^*$	-0.78	-0.71
$OOH^* \rightarrow O^*$	-1.54	-1.57
$O^* \rightarrow OH^*$	-1.45	-1.52
$OH^* \rightarrow H_2O$	-1.16	-1.12

Table S2. The computed free adsorption energies (ΔG, eV) of oxygenated intermediates on various TM@VS_2 materials.

TM	ΔG_{OH*}	ΔG_{O*}	ΔG_{OOH*}
Ti	–1.50	–0.65	2.15
V	–1.50	–1.28	1.90
Cr	–0.86	–0.59	2.61
Mn	–0.30	0.73	3.10
Fe	0.11	1.44	3.51
Co	0.44	1.65	3.67
Ni	1.16	2.60	4.14
Cu	0.87	3.11	3.99
Zr	–1.94	–1.02	1.84
Nb	–1.68	–1.40	1.82
Mo	–1.00	–1.16	2.07
Ru	–0.54	–0.26	2.96
Rh	0.22	1.10	3.27
Pd	1.04	2.85	4.05
Ag	1.43	3.77	4.44
Hf	–2.31	–1.09	1.54
Ta	–2.21	–1.87	1.33
W	–1.62	–1.88	1.42
Re	–0.85	–1.15	2.44

Os	–0.11	0.00	2.98
Ir	–0.29	0.45	3.05
Pt	0.44	1.65	3.50



(a)

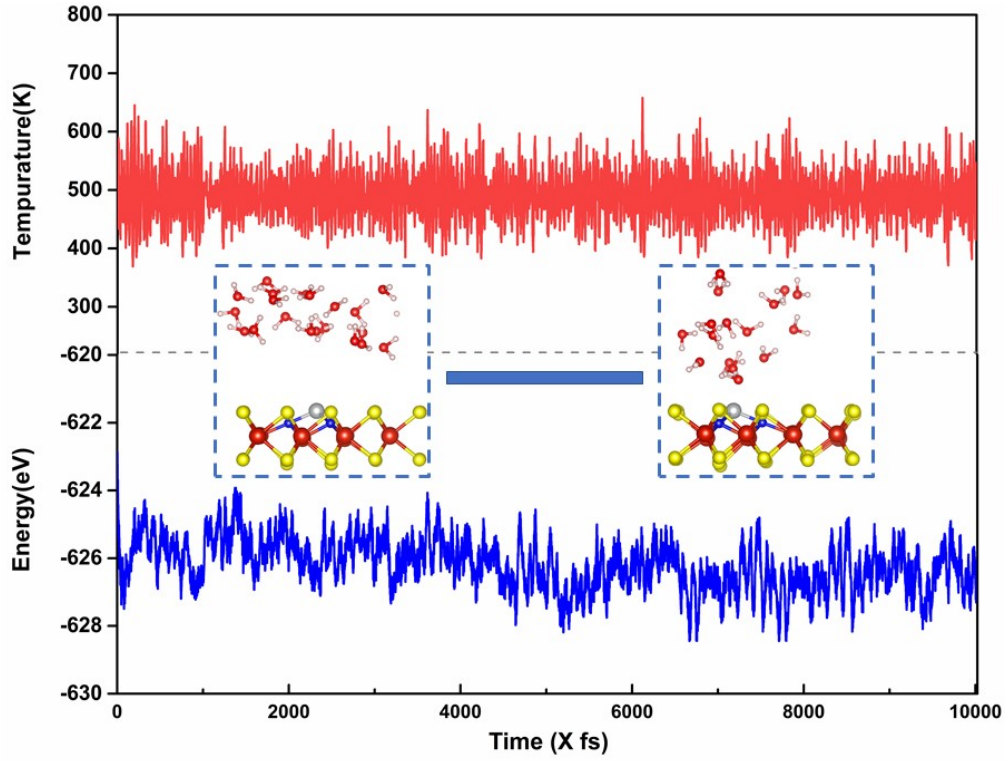
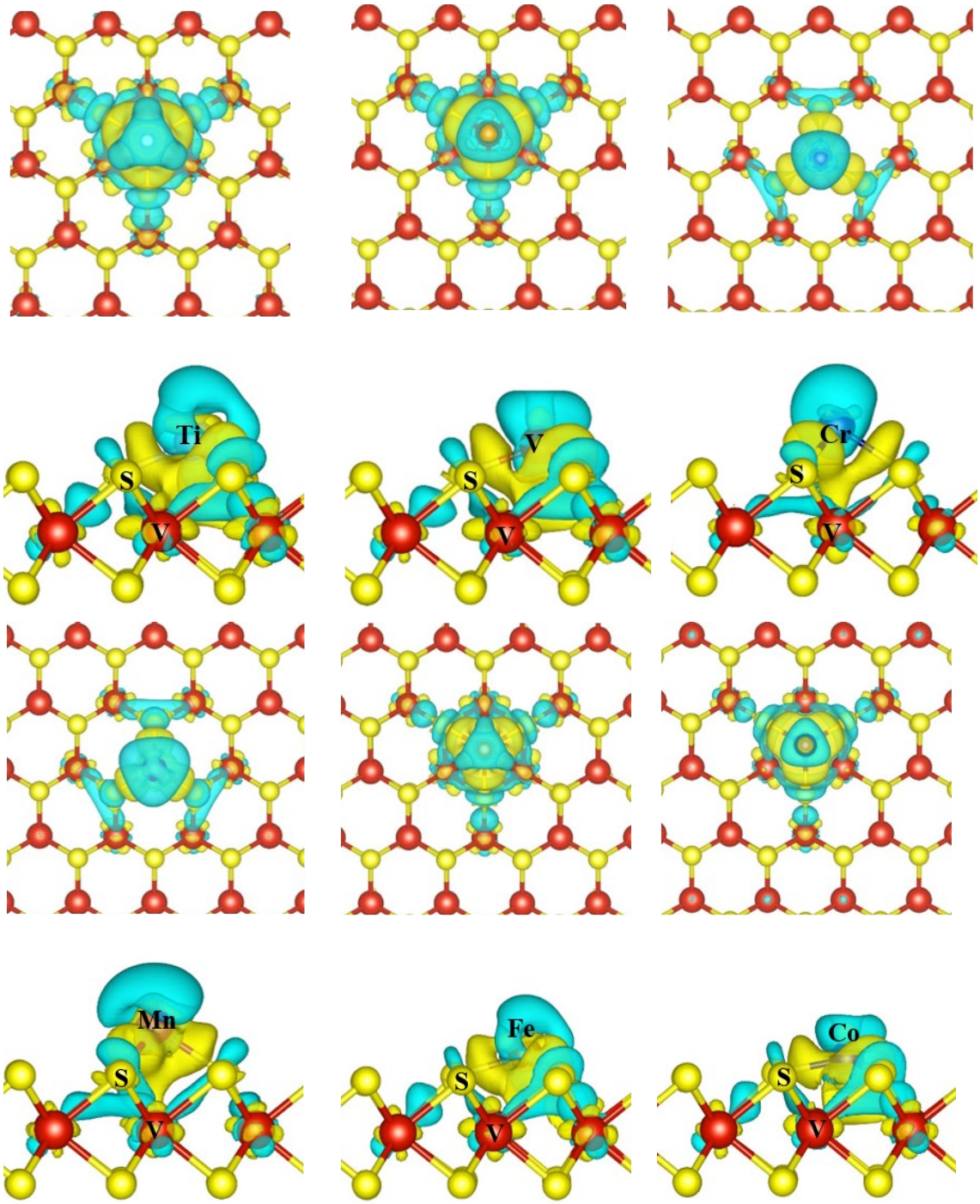
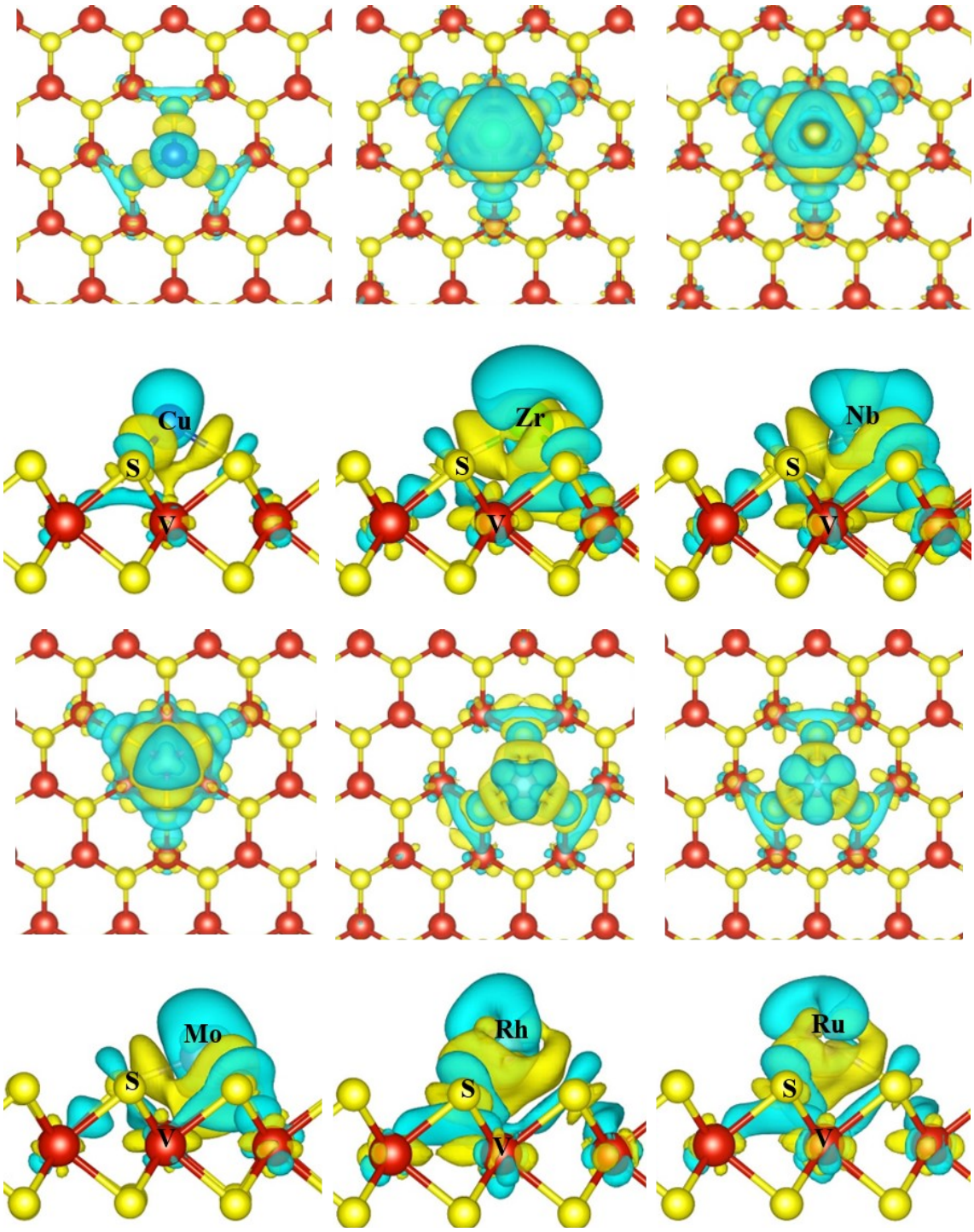
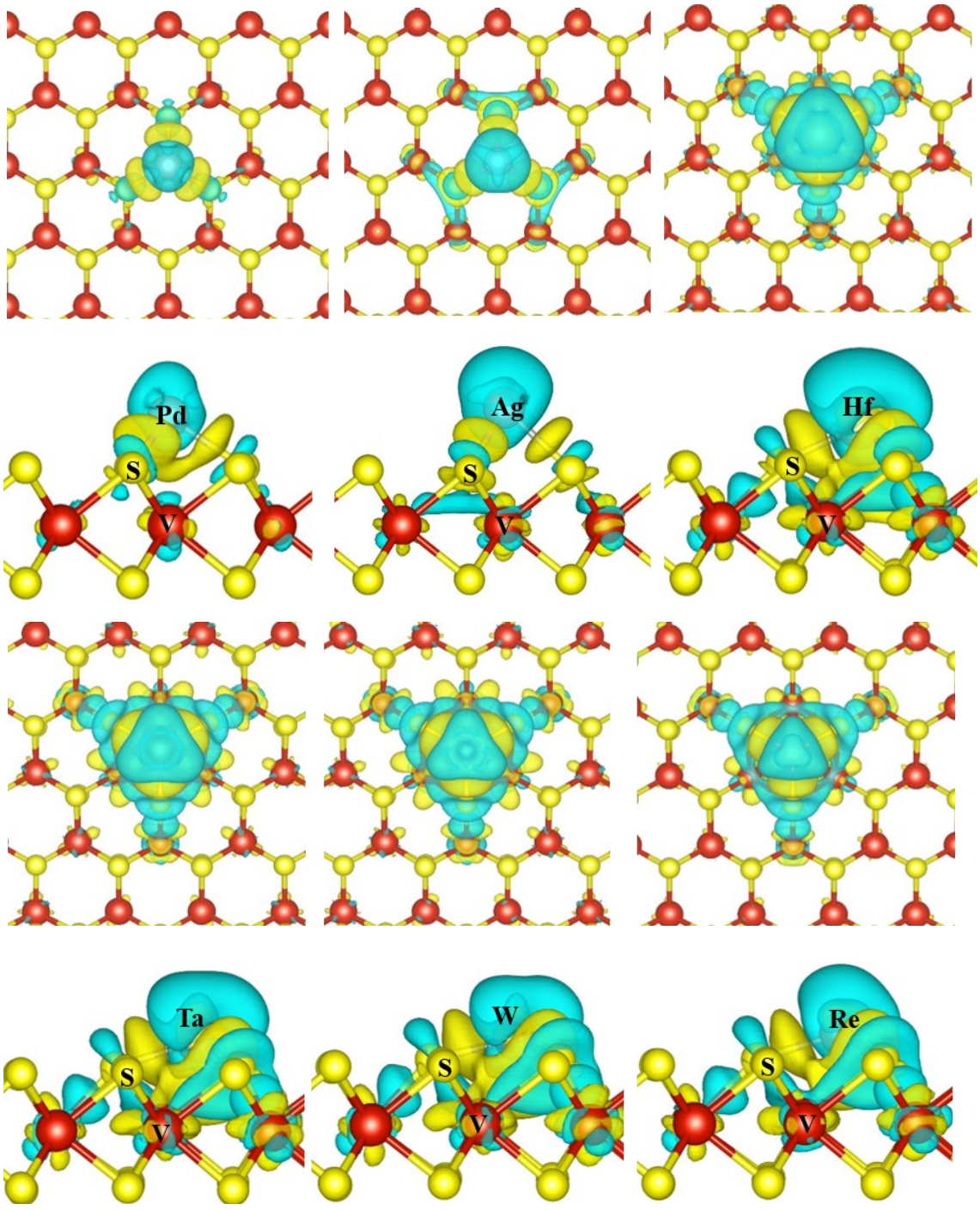


Fig. S1. The computed ab initio molecular dynamics (AIMD) simulations at 500 K under the water environments with an overall time scale of 10 ps using the Nosé−Hoover method for (a) Ni@VS_2 and (b) NiN_3@VS_2material.


Ti
S
V
V
S
V
Cr
S
V
Mn
S
V
Fe
S
V
Co
S
V


Cu
S
V
Zr
S
V
Nb
S
V
Mo
S
V
Rh
S
V
Ru
S
V


Pd
S
V
Ag
S
V
Hf
S
V
Ta
S
V
W
S
V
Re
S
V

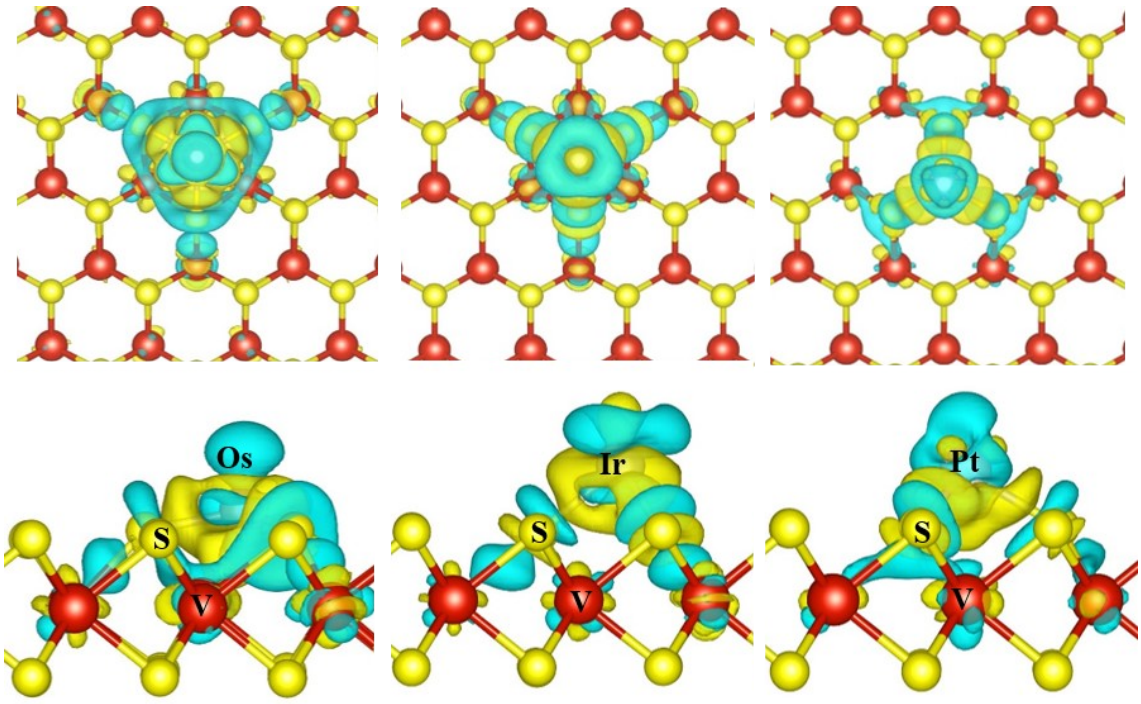
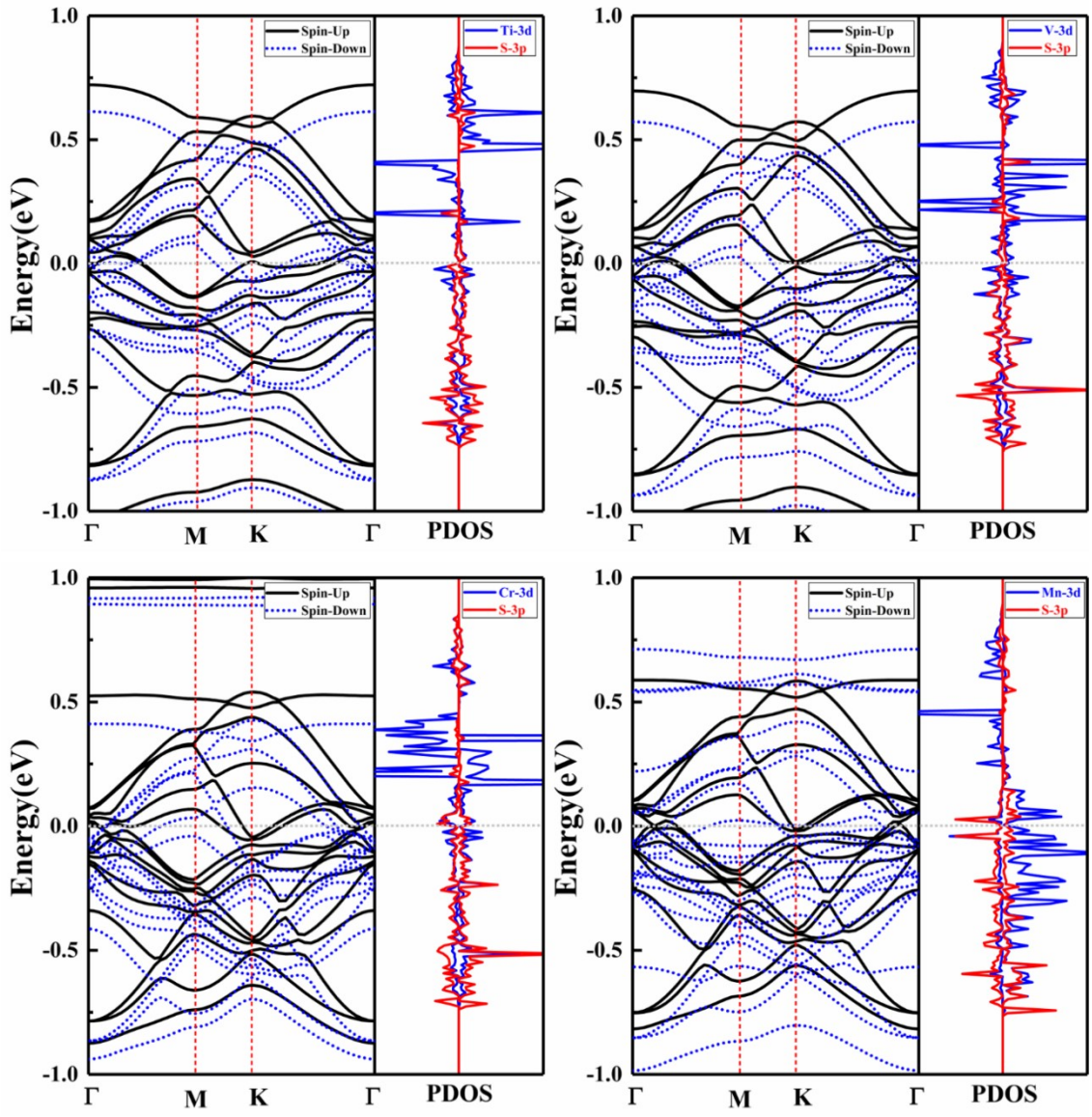
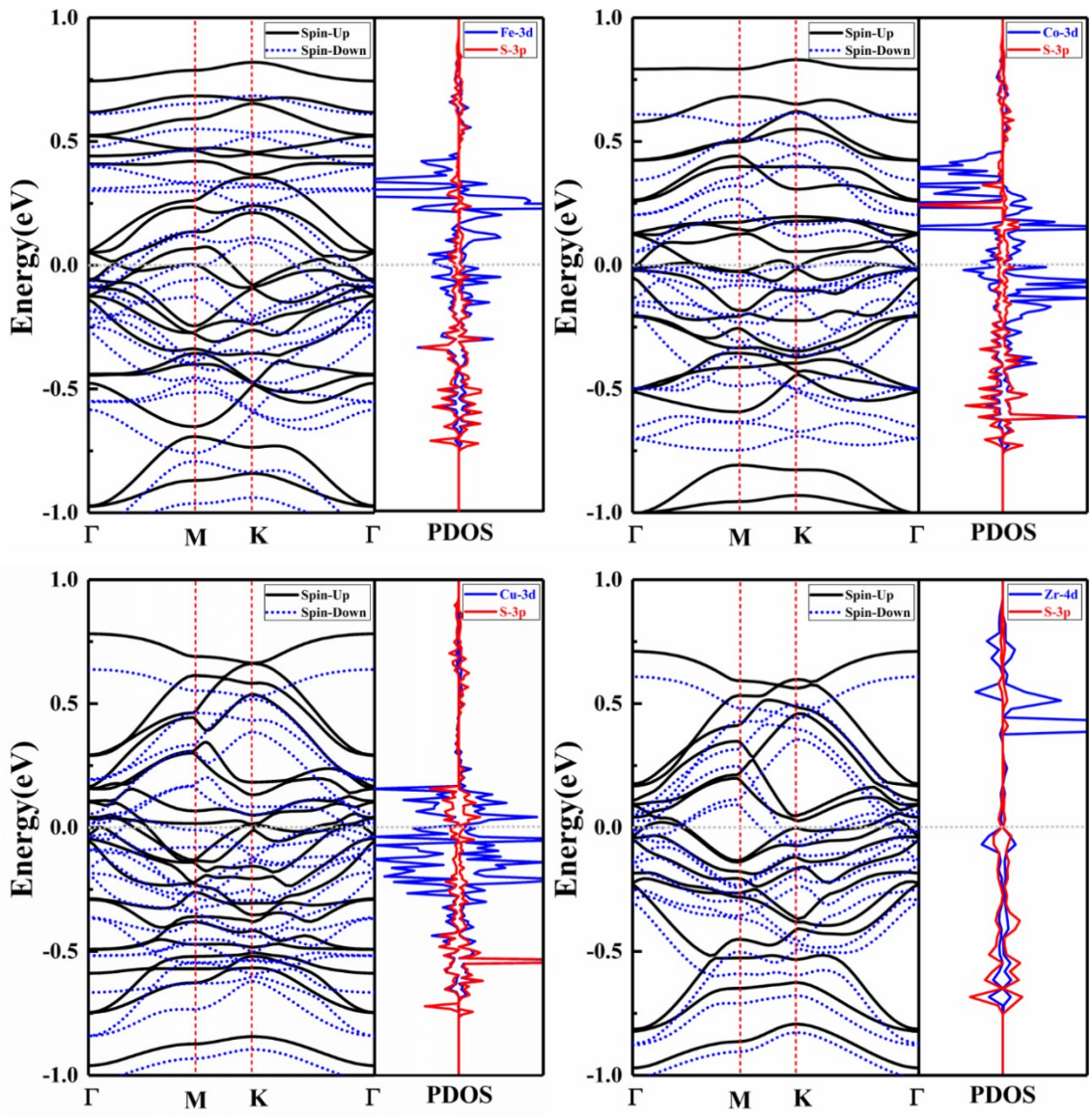
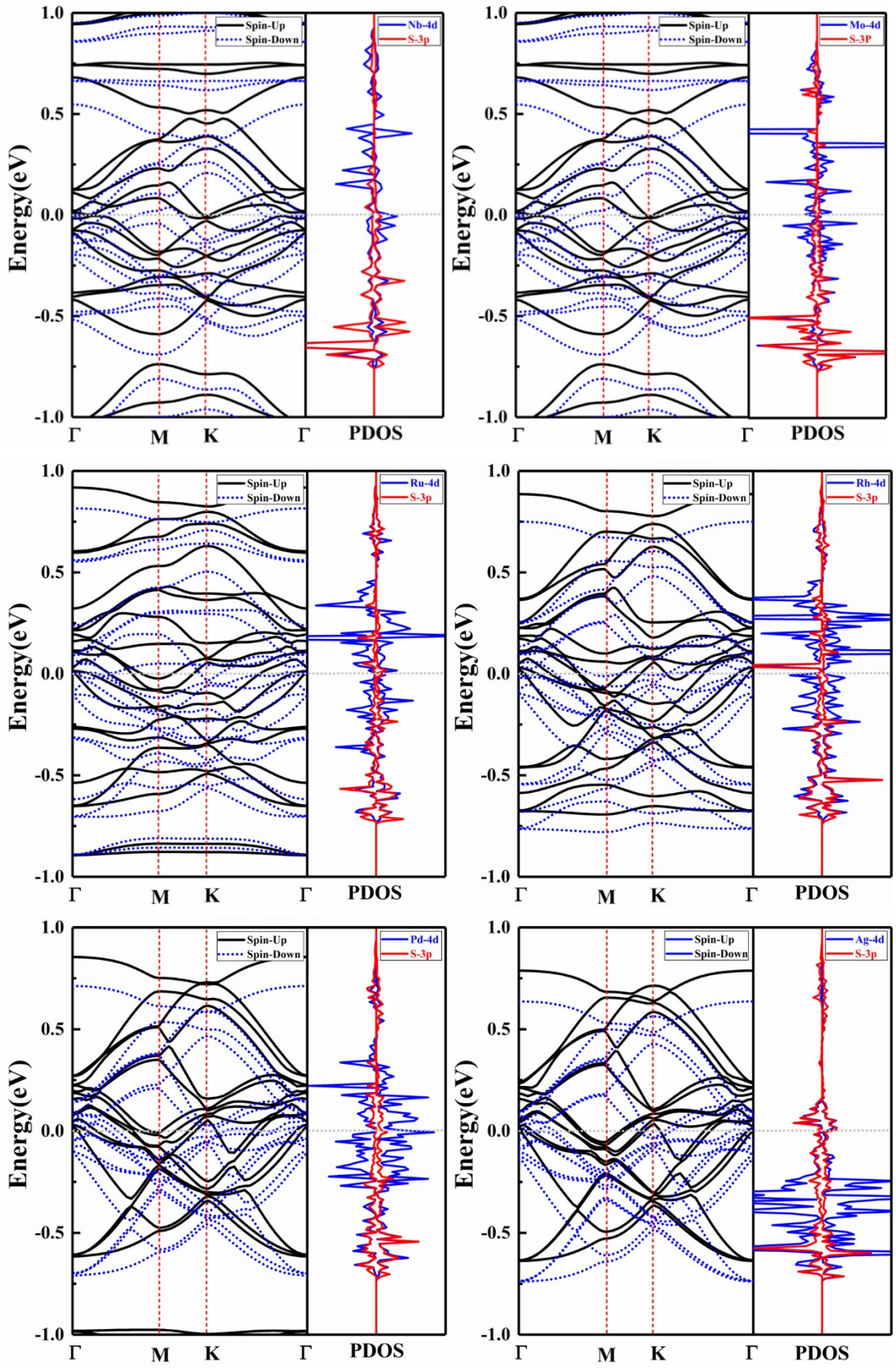
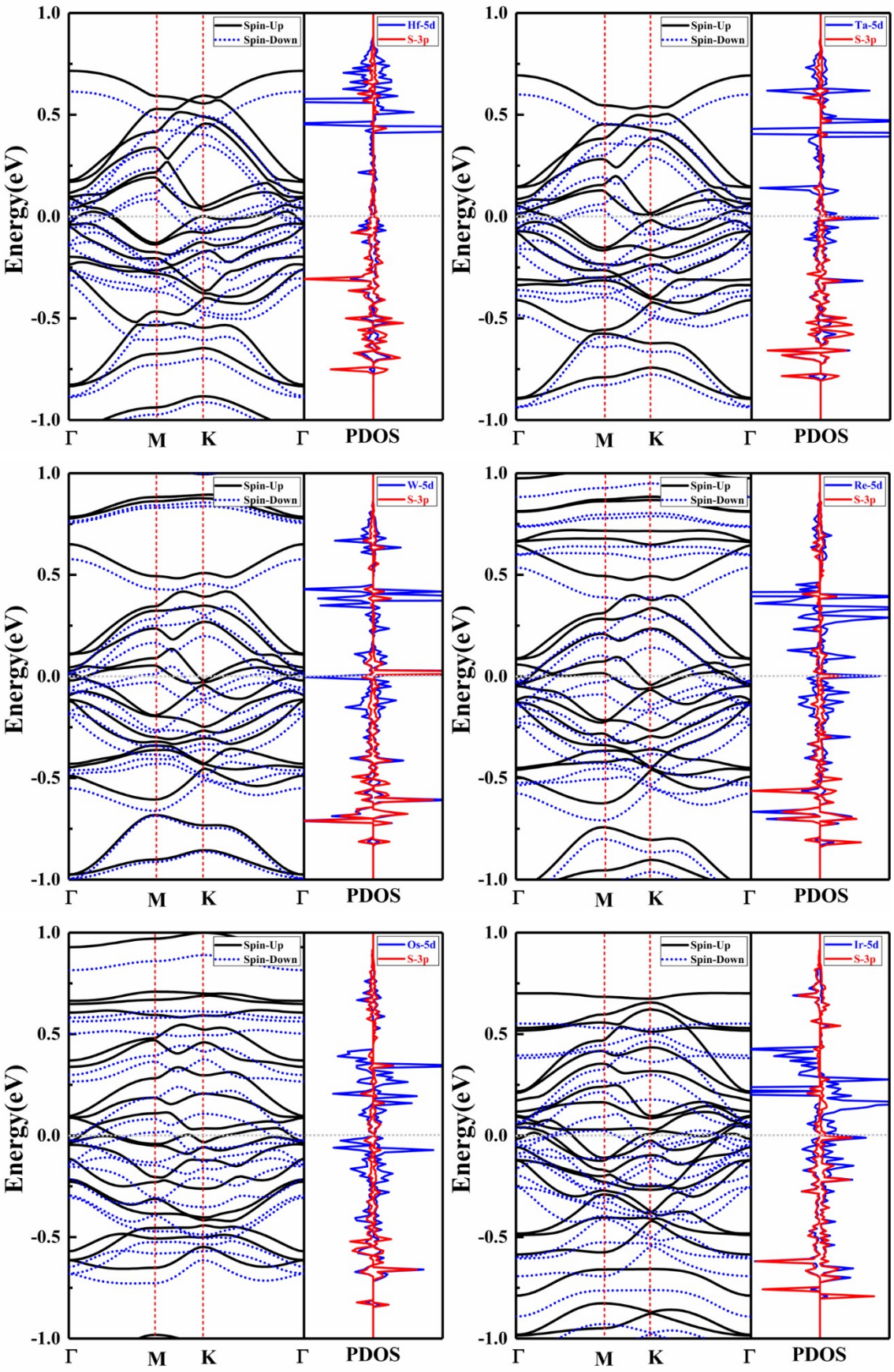


Fig. S2. The computed charge density difference of various TM@VS_2 materials. The cyan and yellow areas represent charge depletion and charge accumulation, respectively.


Energy(eV)
1.0
0.5
0.0
-0.5
-1.0
Γ
M
K
Γ
PDOS
Spin-Up
Spin-Down
Ti-3d
S-3p
V-3d
Cr-3d
Mn-3d


Energy(eV)
1.0
0.5
0.0
-0.5
-1.0
Γ
M
K
Γ
PDOS
Spin-Up
Spin-Down
Fe-3d
S-3p
Co-3d
Cu-3d
Zr-4d


Energy(eV)
1.0
0.5
0.0
-0.5
-1.0
Γ
M
K
Γ
PDOS
Spin-Up
Spin-Down
Nb-4d
S-3p
Mo-4d
S-3P
Ru-4d
S-3p
Rh-4d
S-3p
Pd-4d
S-3p
Ag-4d
S-3p


Energy(eV)
1.0
0.5
0.0
-0.5
-1.0
Γ
M
K
Γ
PDOS
Spin-Up
Spin-Down
Hf-5d
S-3p
Ta-5d
W-5d
Re-5d
Os-5d
Ir-5d

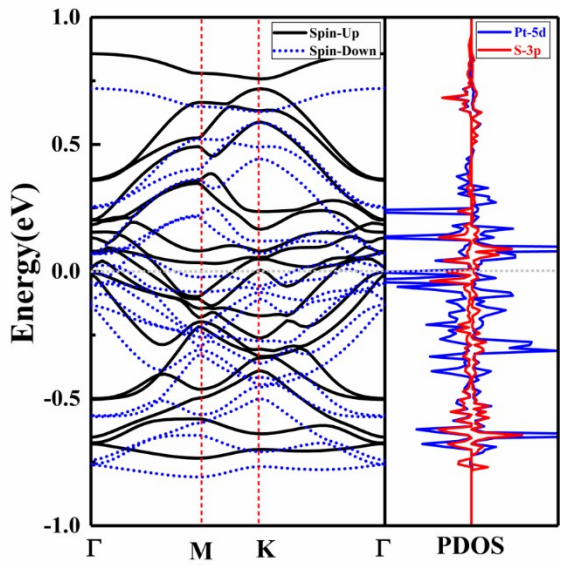
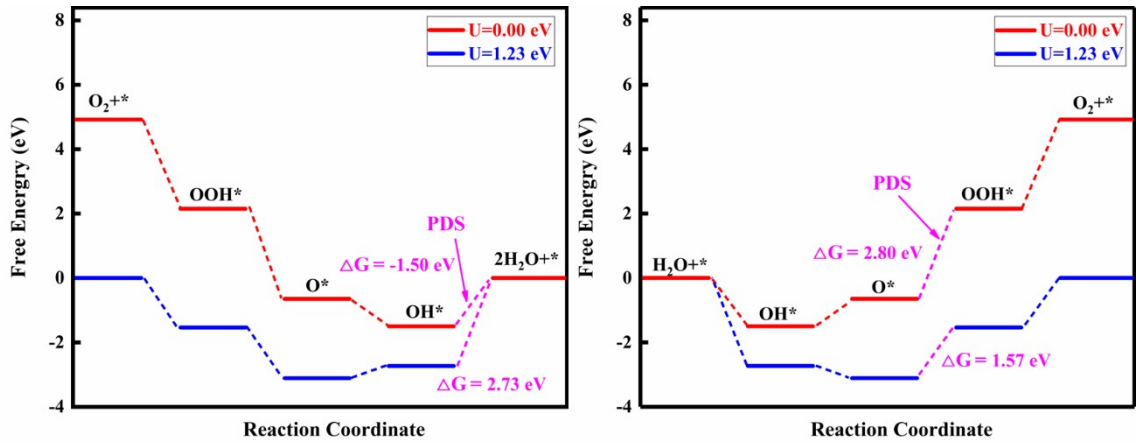
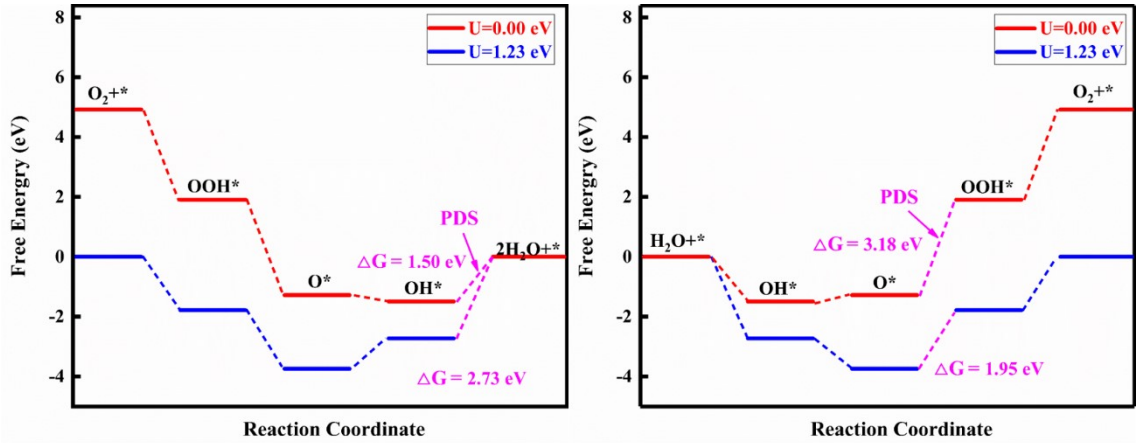


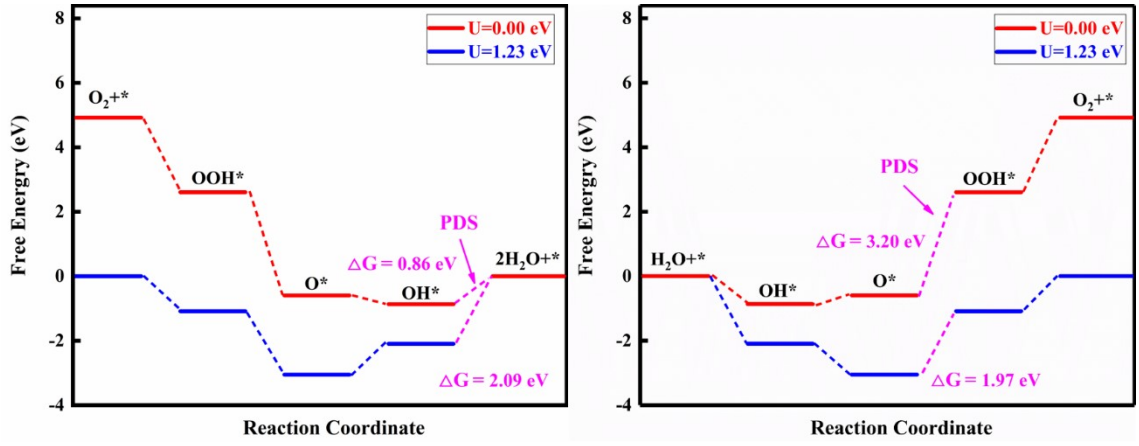
Fig. S3. The computed band structures and projected density of states (PDOSs) of various TM/VS_2 materials. The Fermi level was set to zero.


U=0.00 eV
U=1.23 eV
Free Energy (eV)
Reaction Coordinate
O2+*
OOH*
O*
OH*
2H2O+*
PDS
ΔG = -1.50 eV
ΔG = 2.73 eV
H2O+*
ΔG = 2.80 eV
ΔG = 1.57 eV

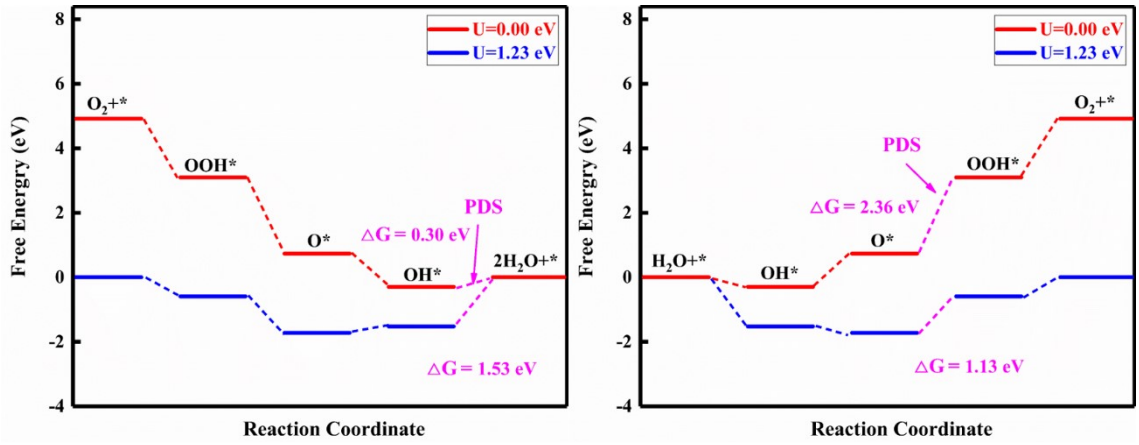
(a)


U=0.00 eV
U=1.23 eV
Free Energy (eV)
Reaction Coordinate
O2+*
OOH*
O*
OH*
2H2O+*
PDS
ΔG = 1.50 eV
ΔG = 2.73 eV
H2O+*
ΔG = 3.18 eV
ΔG = 1.95 eV

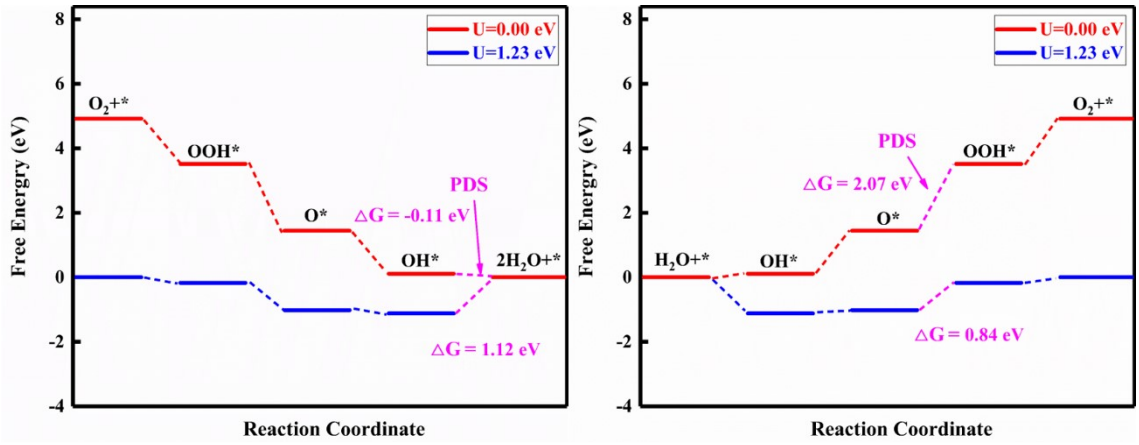
(b)


U=0.00 eV
U=1.23 eV
Free Energy (eV)
Reaction Coordinate
O2+*
OOH*
O*
OH*
2H2O+*
PDS
ΔG = 0.86 eV
ΔG = 2.09 eV
H2O+*
ΔG = 3.20 eV
ΔG = 1.97 eV

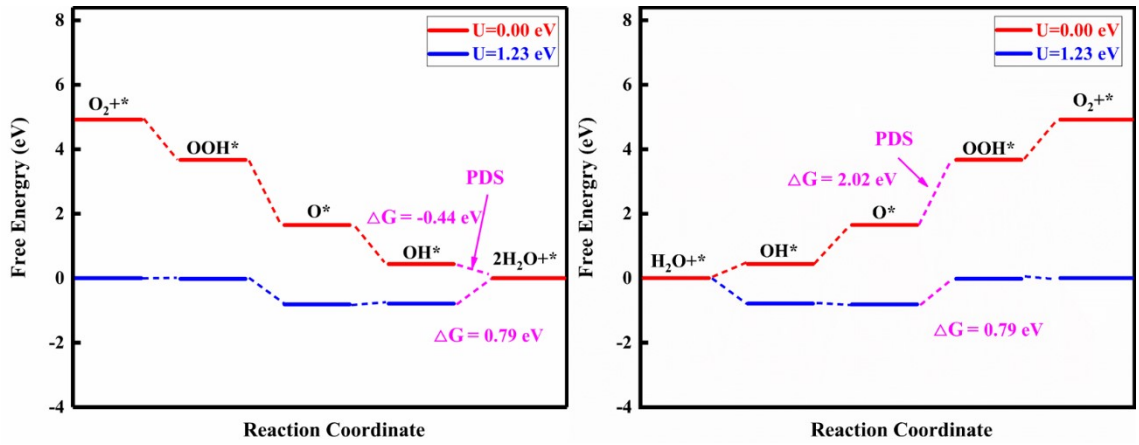
(c)


U=0.00 eV
U=1.23 eV
Free Energy (eV)
Reaction Coordinate
O2+*
OOH*
O*
OH*
2H2O+*
PDS
△G = 0.30 eV
△G = 1.53 eV
H2O+*
△G = 2.36 eV
△G = 1.13 eV

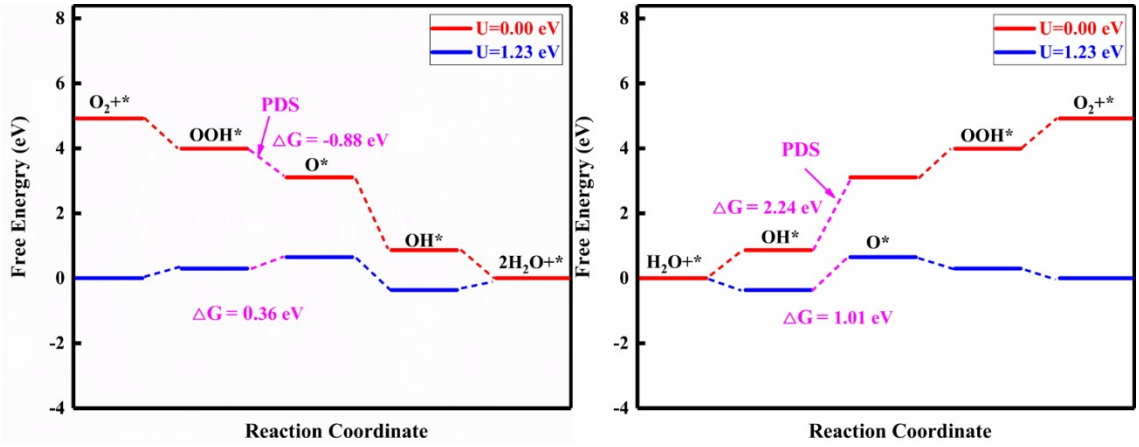
(d)


U=0.00 eV
U=1.23 eV
Free Energy (eV)
Reaction Coordinate
O2+*
OOH*
O*
OH*
2H2O+*
PDS
△G = -0.11 eV
△G = 1.12 eV
H2O+*
△G = 2.07 eV
△G = 0.84 eV

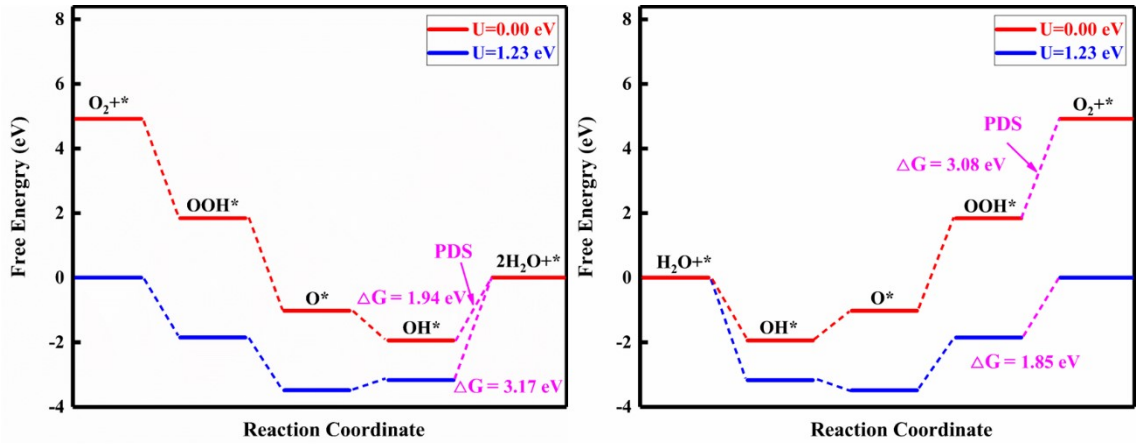
(e)


U=0.00 eV
U=1.23 eV
Free Energy (eV)
Reaction Coordinate
O2+*
OOH*
O*
OH*
2H2O+*
PDS
△G = -0.44 eV
△G = 0.79 eV
H2O+*
△G = 2.02 eV
△G = 0.79 eV

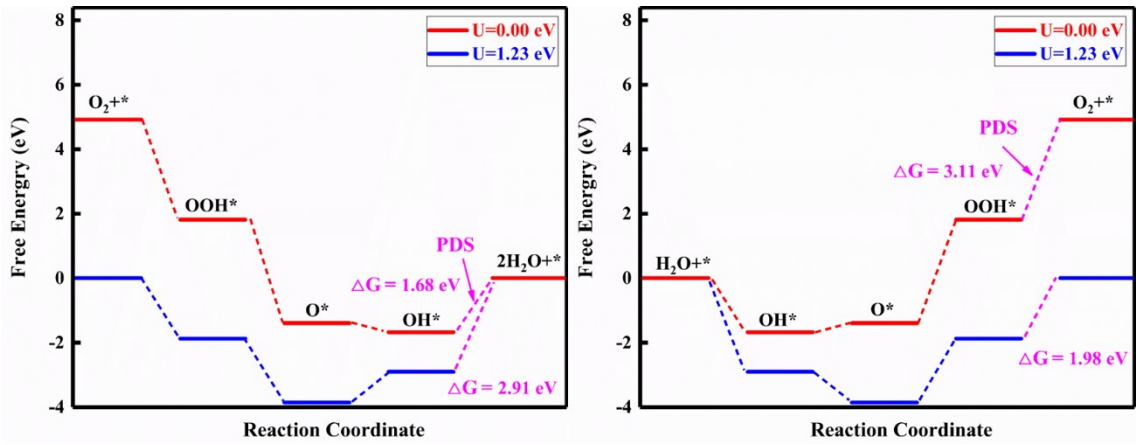
(f)


U=0.00 eV
U=1.23 eV
Free Energy (eV)
Reaction Coordinate
O2+*
OOH*
PDS
ΔG = -0.88 eV
O*
OH*
2H2O+*
ΔG = 0.36 eV
H2O+*
ΔG = 2.24 eV
ΔG = 1.01 eV

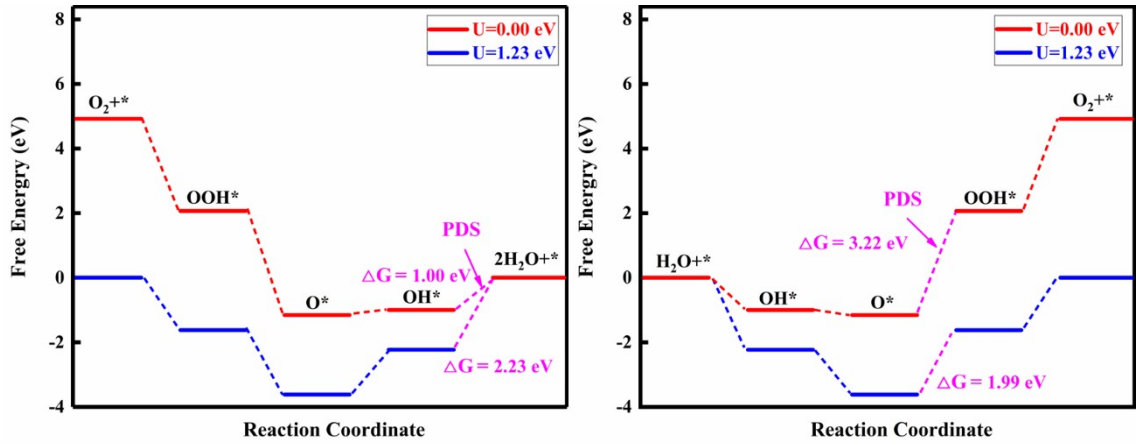
(g)


U=0.00 eV
U=1.23 eV
Free Energy (eV)
Reaction Coordinate
O2+*
OOH*
PDS
2H2O+*
O*
ΔG = 1.94 eV
OH*
ΔG = 3.17 eV
H2O+*
ΔG = 3.08 eV
ΔG = 1.85 eV

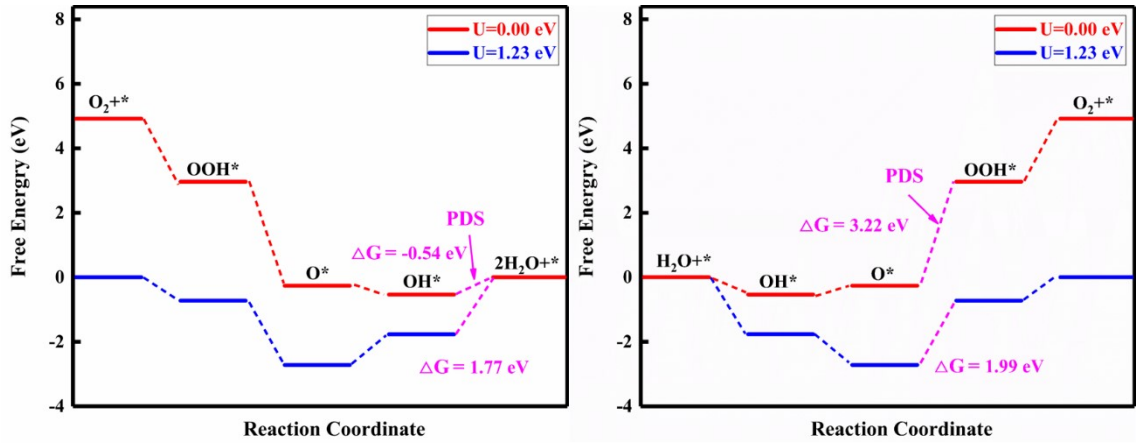
(h)


U=0.00 eV
U=1.23 eV
Free Energy (eV)
Reaction Coordinate
O2+*
OOH*
PDS
2H2O+*
ΔG = 1.68 eV
O*
OH*
ΔG = 2.91 eV
H2O+*
ΔG = 3.11 eV
ΔG = 1.98 eV

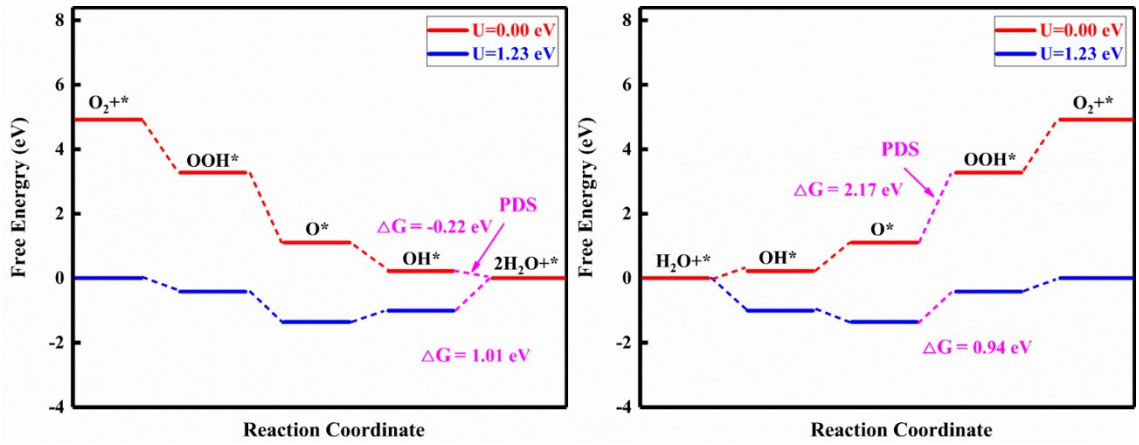
(i)


U=0.00 eV
U=1.23 eV
Free Energy (eV)
Reaction Coordinate
O2+*
OOH*
O*
OH*
2H2O+*
PDS
ΔG = 1.00 eV
ΔG = 2.23 eV
H2O+*
ΔG = 3.22 eV
ΔG = 1.99 eV

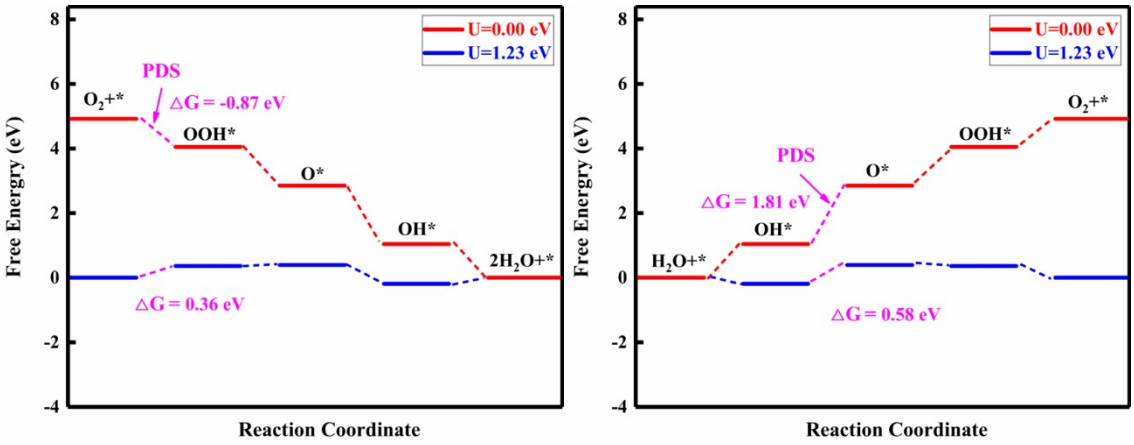
(j)


U=0.00 eV
U=1.23 eV
Free Energy (eV)
Reaction Coordinate
O2+*
OOH*
O*
OH*
2H2O+*
PDS
ΔG = -0.54 eV
ΔG = 1.77 eV
H2O+*
ΔG = 3.22 eV
ΔG = 1.99 eV

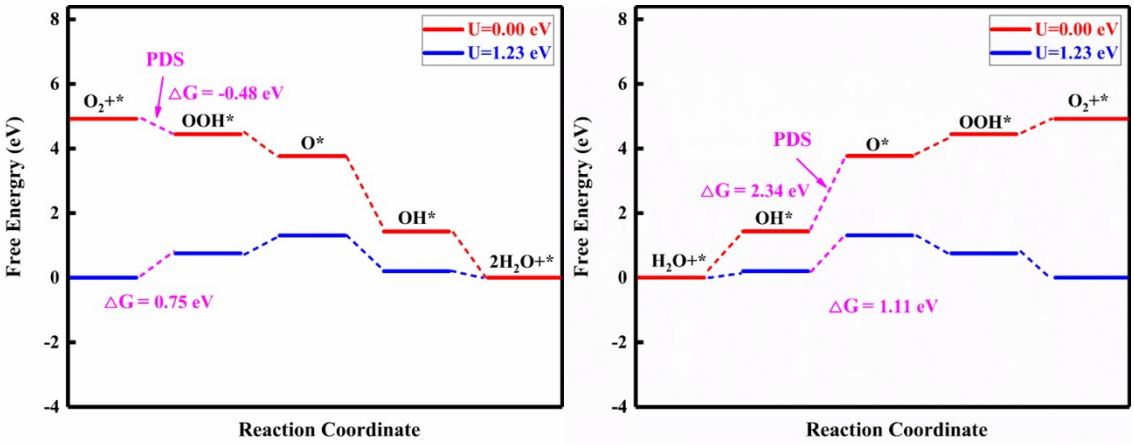
(k)


U=0.00 eV
U=1.23 eV
Free Energy (eV)
Reaction Coordinate
O2+*
OOH*
O*
OH*
2H2O+*
PDS
ΔG = -0.22 eV
ΔG = 1.01 eV
H2O+*
ΔG = 2.17 eV
ΔG = 0.94 eV

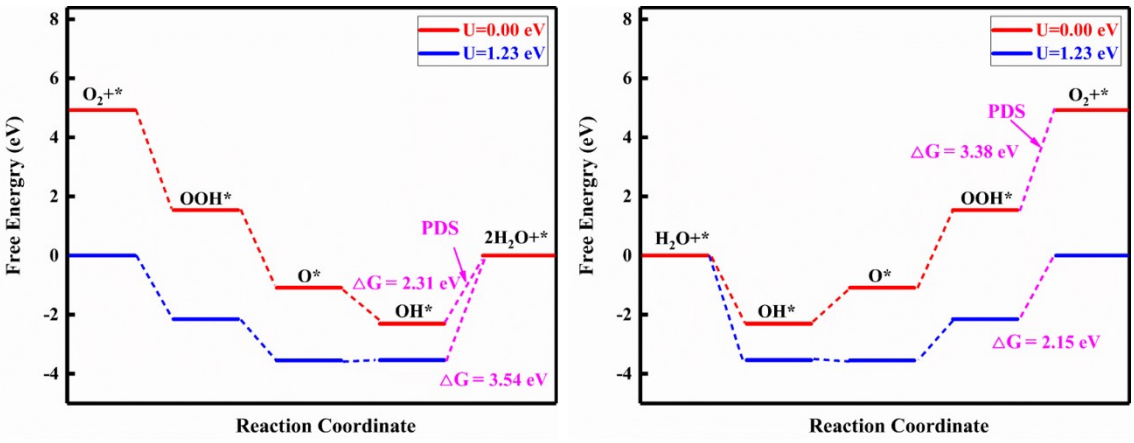
(l)


U=0.00 eV
U=1.23 eV
PDS
O_2+*
△G = -0.87 eV
OOH*
O*
OH*
2H_2O+*
△G = 0.36 eV
Free Energy (eV)
Reaction Coordinate
H_2O+*
△G = 1.81 eV
△G = 0.58 eV

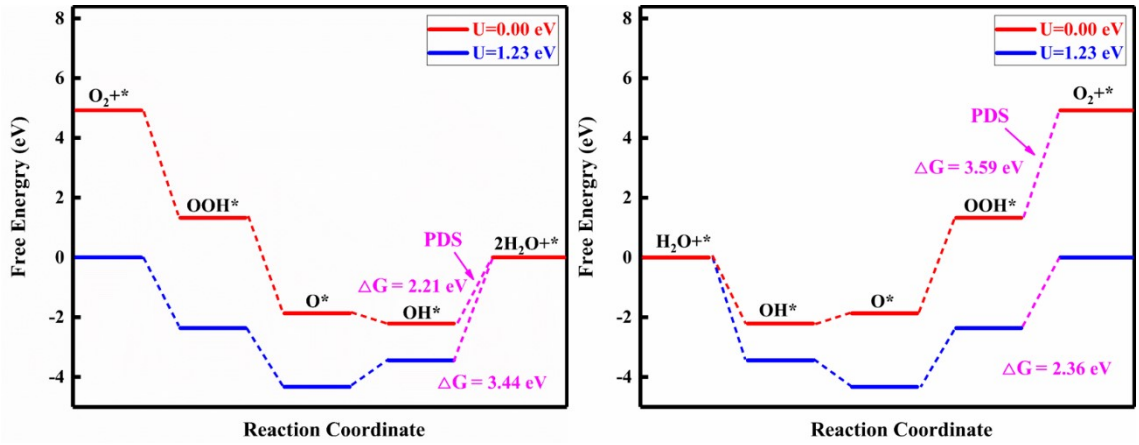
(m)


U=0.00 eV
U=1.23 eV
PDS
O_2+*
△G = -0.48 eV
OOH*
O*
OH*
2H_2O+*
△G = 0.75 eV
Free Energy (eV)
Reaction Coordinate
H_2O+*
△G = 2.34 eV
△G = 1.11 eV

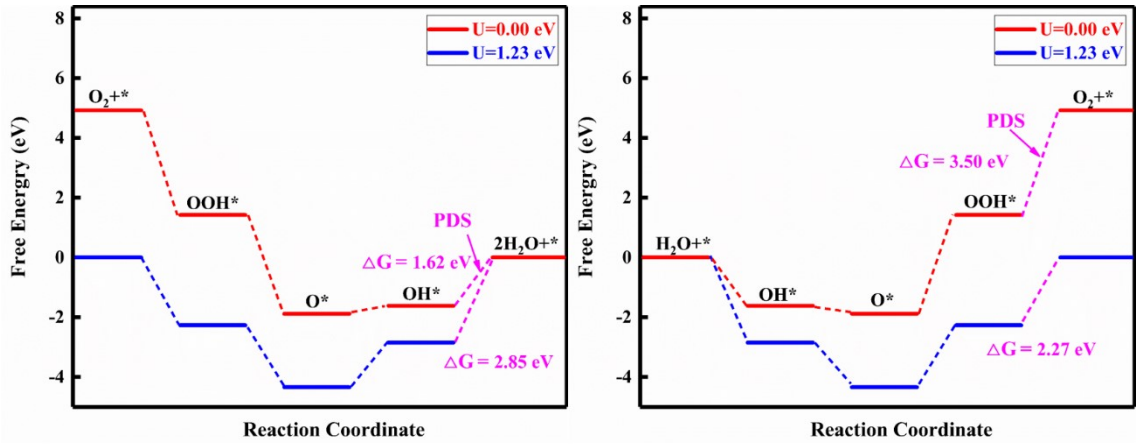
(n)


U=0.00 eV
U=1.23 eV
O_2+*
OOH*
PDS
2H_2O+*
O*
△G = 2.31 eV
OH*
△G = 3.54 eV
Free Energy (eV)
Reaction Coordinate
H_2O+*
△G = 3.38 eV
△G = 2.15 eV

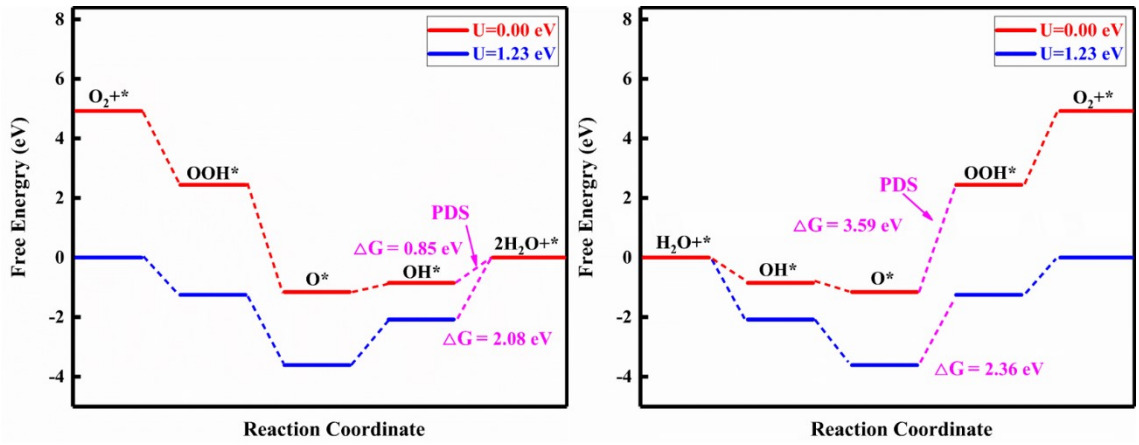
(o)


U=0.00 eV
U=1.23 eV
Free Energy (eV)
Reaction Coordinate
O2+*
OOH*
O*
OH*
2H2O+*
PDS
ΔG = 2.21 eV
ΔG = 3.44 eV
H2O+*
ΔG = 3.59 eV
ΔG = 2.36 eV

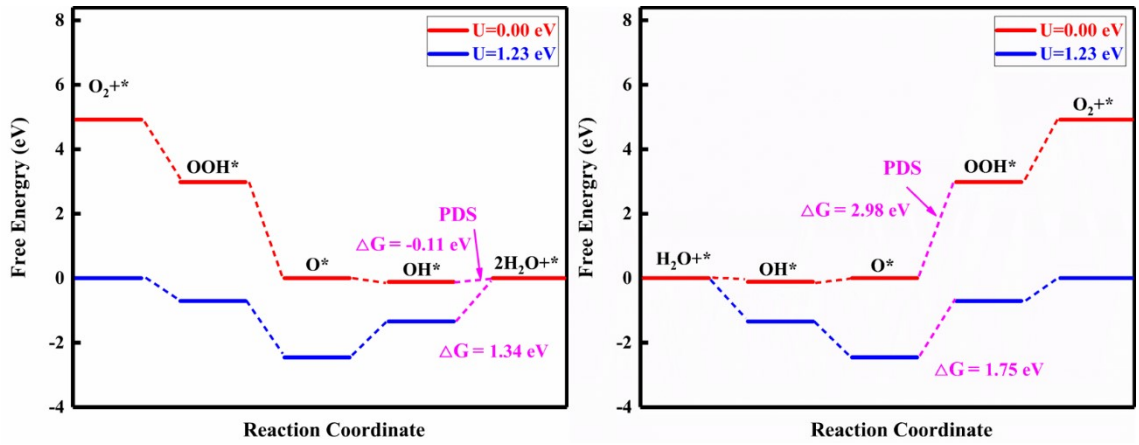
(p)


U=0.00 eV
U=1.23 eV
Free Energy (eV)
Reaction Coordinate
O2+*
OOH*
O*
OH*
2H2O+*
PDS
ΔG = 1.62 eV
ΔG = 2.85 eV
H2O+*
ΔG = 3.50 eV
ΔG = 2.27 eV

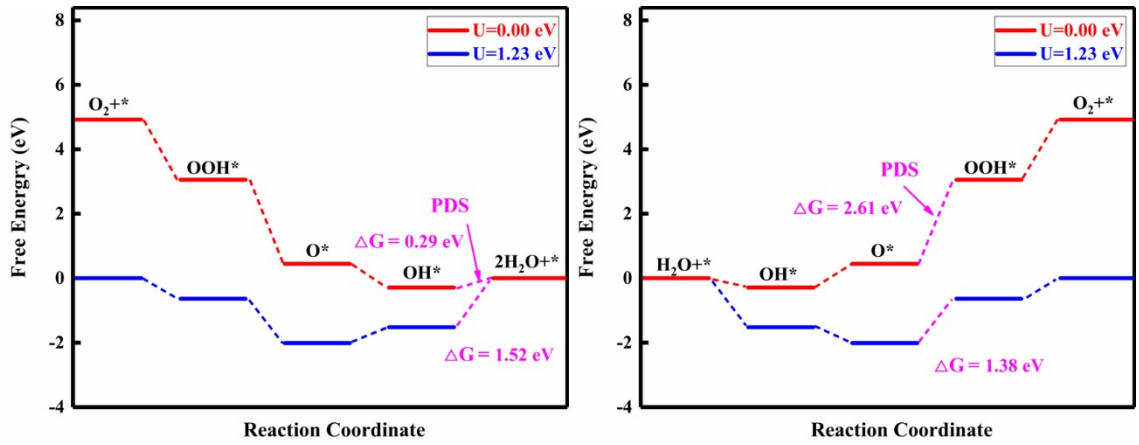
(q)


U=0.00 eV
U=1.23 eV
Free Energy (eV)
Reaction Coordinate
O2+*
OOH*
O*
OH*
2H2O+*
PDS
ΔG = 0.85 eV
ΔG = 2.08 eV
H2O+*
ΔG = 3.59 eV
ΔG = 2.36 eV

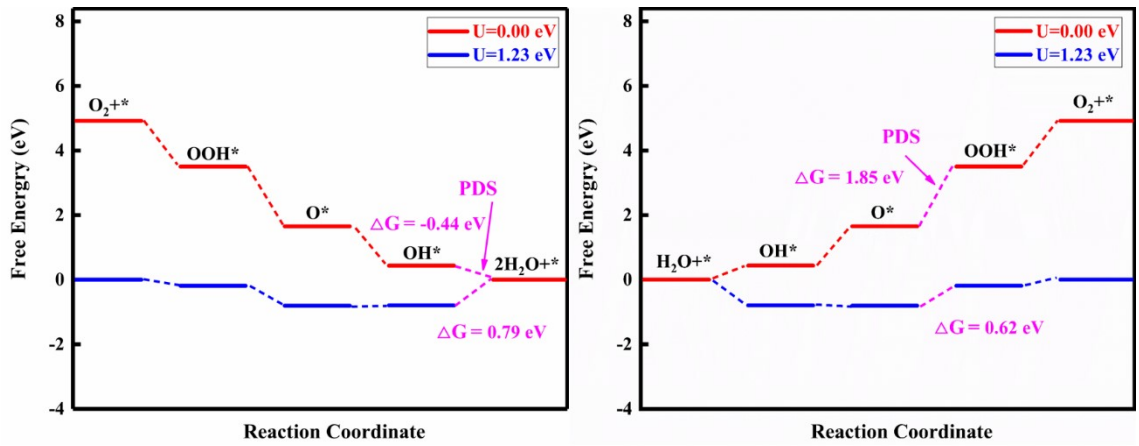
(r)



(s)



(t)



(u)

Fig. S4. The computed free energy profiles of ORR (left) and OER (right) on (a) Ti, (b) V, (c) Cr, (d) Mn, (e) Fe, (f) Co, (g) Cu, (h) Zr, (i) Nb, (j) Mo, (k) Ru, (l) Rh, (m)

Pd, (n) Ag, (o) Hf, (p) Ta, (q) W, (r) Re, (s) Os, (t) Ir, and (u) Pt atoms anchored on VS_2 monolayer.

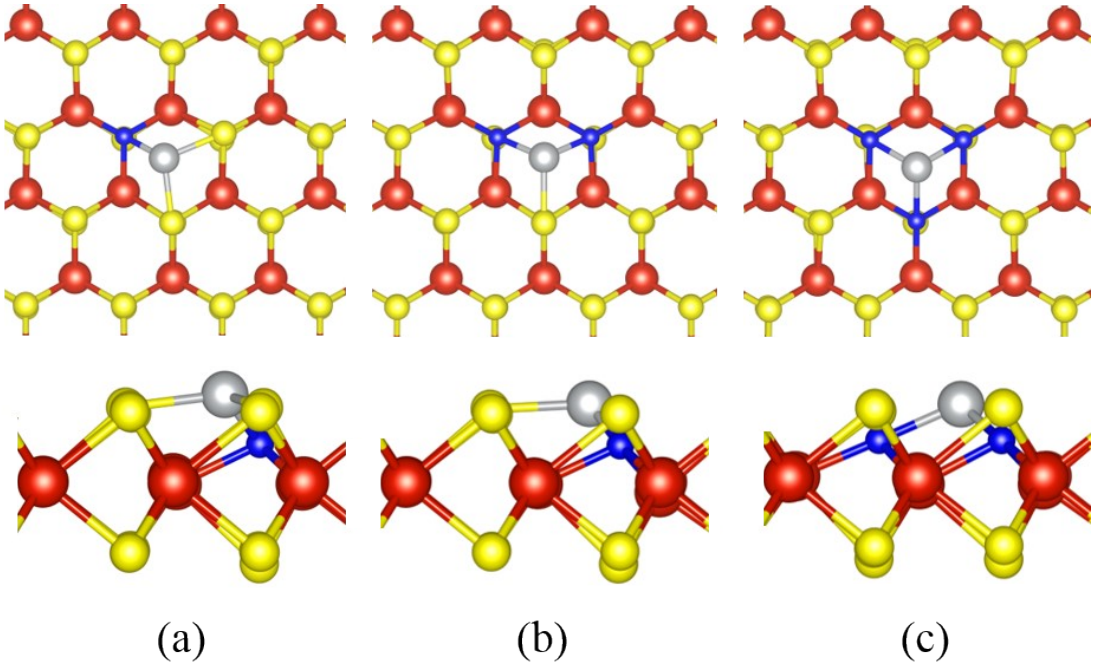


Fig. S5. The optimized structures of (a) NiN_1, (b) NiN_2, and (c) NiN_3.

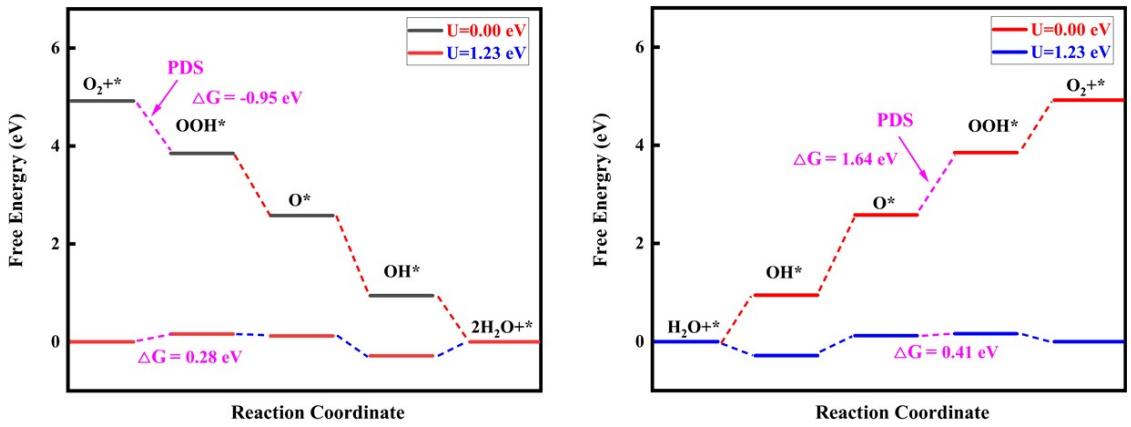


Fig. S6. The computed free energy profiles for ORR and OER on NiN_3@VS_2 monolayer with solvent effects.