Electronic Supplementary Information for

Transition metal-N_4 embedded black phosphorus carbide as high-performance bifunctional electrocatalyst for ORR/OER

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Calculation methods

Based on the reversible hydrogen electrode (RHE) developed by Nørskov et al[1], the chemical potential of one proton electron pair is equal to the potential of half of one hydrogen molecule, that is:

$$\mu_{H^+} + \mu_{e^-} = \frac{1}{2}\mu_{H_2} \tag{1}$$

The calculation is under the circumstances of U=0 V and P_{H2}=1 bar. The free energies of isolated molecules are calculated as follow:

$$G_{\text{molecule}} = E_{\text{ele}_{\text{molecule}}} + ZPE_{\text{molecule}} - T \times S_{\text{molecule}} \tag{2}$$

where G_{molecule} is the free energy of the isolated molecule (H_2, H_2O), and the $\text{ZPE}_{\text{molecule}}$ is the zero-point energy while the S_{molecule} is the entropy. All the temperature is set as 298 K. The free energy of H_2O(l) is equal to that of H_2O(g) in the condition of 0.035 bar. The free energy of O_2(g) is calculated on the equations of:

$$G_{O_2(g)} = 2G_{H_2O(l)} - 2G_{H_2(g)} + 4.92 \text{ eV} \tag{3}$$

where the value of 4.92 is four times of the set of U_0(1.23 V) in 4-electron process of ORR.

The adsorption free energies of three related ORR/OER intermediates (OH^*, O^*, OOH^*) are calculated as follow:

$$\begin{aligned}\Delta G_{OH^*} &= \Delta G\left(* + H_2O(l) \rightarrow OH^* + \left(H^+ + e^-\right)\right) \\ &= \left(E_{OH^*} + \frac{1}{2} \times E_{H_2} - E_{H_2O} - E_*\right) \\ &\quad + \left(ZPE_{OH^*} + \frac{1}{2} \times ZPE_{H_2} - ZPE_{H_2O} - ZPE_*\right) \\ &\quad - T \times \left(S_{OH^*} + \frac{1}{2} \times S_{H_2} - S_{H_2O} - S_*\right)\end{aligned} \tag{4}$$

$$\begin{aligned}\Delta G_{O^*} &= \Delta G\left(* + H_2O(l) \rightarrow O^* + H_2\right) \\ &= \left(E_{O^*} + E_{H_2} - E_{H_2O} - E_*\right) \\ &\quad + \left(ZPE_{O^*} + ZPE_{H_2} - ZPE_{H_2O} - ZPE_*\right) \\ &\quad - T \times \left(S_{O^*} + S_{H_2} - S_{H_2O} - S_*\right)\end{aligned} \tag{5}$$

$$\Delta G_{OOH^*} = \Delta G\left(* + 2H_2O(l) \rightarrow OOH^* + \frac{3}{2}H_2\right)$$
$$= \left(E_{OOH^*} + \frac{3}{2} \times E_{H_2} - 2 \times E_{H_2O} - E_*\right)$$
$$+ \left(ZPE_{OOH^*} + \frac{3}{2} \times ZPE_{H_2} - 2 \times ZPE_{H_2O} - ZPE_*\right)$$
$$- T \times \left(S_{OOH^*} + \frac{3}{2} \times S_{H_2} - 2 \times S_{H_2O} - S_*\right) \quad (6)$$

where $\Delta G(OH^*)$, $\Delta G(O^*)$ and $\Delta G(OOH^*)$ are the adsorption free energy of OH^*, O^*, and OOH^*, respectively. The entropy of the adsorbent (substrate) and the adsorbate (OH^*, O^*, or OOH^*) can be neglected and the ZPE of each adsorbate can be seen as a constant value [2]. All the applied values of ZPE and S are listed in **Table S1**. The value is very similar with the previous study[2, 3].

The Gibbs reaction free energy of each reaction can be calculated as:

$$\Delta G = \Delta E_{ele} + \Delta ZPE - T \times \Delta S + \Delta G_U + \Delta G_{pH} \quad (7)$$

where ΔE_{ele}, ΔZPE and ΔS is the calculated difference of total electronic energy obtained by DFT, zero-point energy and entropy. The effect by the external applied potential is defined as: $\Delta G_U = -neU$, where U is the external potential versus RHE, e is the electron transfer and n is the number of proton electron pairs. The effect by pH is defined as: $\Delta G_{pH} = -k_B T \times \ln[H^+] = pH \times k_B T \times \ln 10$. k_B is the Boltzmann constant while T is the reaction temperature. In this study, pH=0.

For ORR reaction, the Gibbs reaction free energy (ΔG_1, ΔG_2, ΔG_3, ΔG_4) is calculated as:

$$\Delta G_1 = \Delta G_{OOH^*} - 4.92 \quad (8)$$

$$\Delta G_2 = \Delta G_{O^*} - \Delta G_{OOH^*} \quad (9)$$

$$\Delta G_3 = \Delta G_{OH^*} - \Delta G_{O^*} \quad (10)$$

$$\Delta G_4 = -\Delta G_{OH^*} \quad (11)$$

For OER reaction, the free energy (ΔG_5, ΔG_6, ΔG_7, ΔG_8) is defined as:

$$\Delta G_5 = \Delta G_{OH^*} \quad (12)$$

$$\Delta G_6 = \Delta G_{O^*} - \Delta G_{OH^*} \tag{13}$$

$$\Delta G_7 = \Delta G_{OOH^*} - \Delta G_{O^*} \tag{14}$$

$$\Delta G_8 = 4.92 - \Delta G_{OOH^*} \tag{15}$$

For ORR, the overpotential is given by:

$$\eta_{ORR(4e^-)} = \frac{\max\{\Delta G_1,\ \Delta G_2,\ \Delta G_3,\ \Delta G_4\}}{e} + 1.23 \tag{16}$$

The overpotential of OER is defined as follow:

$$\eta_{OER} = \frac{\max\{\Delta G_5,\ \Delta G_6,\ \Delta G_7,\ \Delta G_8\}}{e} - 1.23 \tag{17}$$

The solvent model was managed by using a constant value of –0.20 eV for OH^* and –0.10 eV for OOH^*[4]. Although some study used a larger value of about –0.50 eV for OH^* and –0.25 eV for OOH^* on metal surface[5], or –0.30 eV for both OH^* and OOH^* on SACs[2, 6], Vallejo et al pointed out that the solvent effect is obviously affected by the different TM atoms on SACs[7]. If the interactions between the TM (such as Cr, Mn, Fe, Co) and the adsorbate are strong enough to form ionic characterized bond, the solvent effect is very small. If only covalence bond is likely to form between TM (such as Ni, Cu) and adsorbate, the solvent effect may be more obvious. In view of this, the solvent effect on most SACs may be smaller than some metal surface, and Siahrostami et al evaluated the solvent effect on Rh based SAC, which is about –0.20 eV for OH^* and –0.10 eV for OOH^*[4]. Although these values may somewhat underestimate the solvent effect on Ni, Cu, Pd, Ag, Pt, Au based SACs, they are suitable for most of other SACs.

To search the relationship of the different TM-N_4 structures and the adsorption free energy of the intermediate, several composition descriptors have been taken into consideration. The first is the number of electrons of d orbitals (φ_d), the second is the number of valence electrons ($\varphi_{valence}$), the third is the produce of φ_d and electronegativity of metal atom ζ: $\varphi_d \times \zeta$. The fourth is the produce of $\varphi_{valence}$ and electronegativity of metal atom ζ: $\varphi_{valence} \times \zeta$. The fifth is ψ_1. The sixth is ψ_2. The calculation of ψ_1^2 and ψ_2^3 is as follow. The seventh is the value of d band center (ε_d) and the eighth is the d_{z2} band center (ε_{dz2}). All the composition descriptors are listed:

1) φ_d
2) $\varphi_{valence}$
3) $\varphi_d \times \zeta$
4) $\varphi_{valence} \times \zeta$
5)

$$\psi_1 = \varphi_{\mathrm{d}} \times \left(\zeta_{\mathrm{TM}} + \zeta_{\mathrm{N}} \times 4\right) \tag{18}$$

where ζ_{TM} is the electronegativity of introduced TM atom and ζ_{N} is the electronegativity of N atom. And 4 is the number of N atoms.

6)

$$\psi_2 = \frac{\varphi_{\mathrm{valence}}}{\zeta_{\mathrm{TM}} + \left(\zeta_{\mathrm{N}} \times 4 + \zeta_{\mathrm{P}} \times 44 + \zeta_{\mathrm{C}} \times 46\right) \div 94} \tag{19}$$

where ζ_{P} is the electronegativity of P atom and ζ_{C} is the electronegativity of C atom. And 44 is the number of P atoms while 46 is the number of C atoms. 94 is the sum of N, P, and C atoms.

7)

$$\varepsilon_d = \frac{\int_{-\infty}^{+\infty} E \times D_{PDOS-d}(E)dE}{\int_{-\infty}^{+\infty} D_{PDOS-d}(E)dE} \tag{20}$$

where D is one of the states of d orbitals of TM atom and E is the energy of D.

8)

$$\varepsilon_{d_{z^2}} = \frac{\int_{-\infty}^{+\infty} E \times D_{PDOS-d_{z^2}}(E)dE}{\int_{-\infty}^{+\infty} D_{PDOS-d_{z^2}}(E)dE} \tag{21}$$

where D is one of the states of d_{z2} orbitals of TM atom and E is the energy of D.

To discuss the stability of the structure, the formation energy as well as the cohesive energy between TM and the substrate is defined as follow:

$$E_{\mathrm{Form}} = E_{\mathrm{TM\text{-}N_4\text{-}bPC}} - E_{\mathrm{pure\ bPC}} - \sum n_{\mathrm{TM}}\mu_{\mathrm{TM}} - \sum n_{\mathrm{N}}\mu_{\mathrm{N}} + \sum n_{\mathrm{P}}\mu_{\mathrm{P}} + \sum n_{\mathrm{C}}\mu_{\mathrm{C}} \tag{22}$$

where $E_{\mathrm{TM\text{-}N4\text{-}bPC}}$, $E_{\mathrm{pure\ bPC}}$ is the calculated total energy of TM-N_4 embedded b-PC and pure b-PC by DFT, and n_{TM}, n_{N} is the number of introduced TM atom and N atom. In this study, n_{TM}=1 and n_{N}=4. n_{P}, n_{C} is the number of removed P atom and C atom. In this study, n_{P}=4 and n_{C}=2. μ_{TM}, μ_{N}, μ_{P} and μ_{C} are the calculated chemical potential of single atom from the most stable simple substance by DFT. The calculated energy is from the bulk metal, N_2, bulk black phosphorus and graphite.

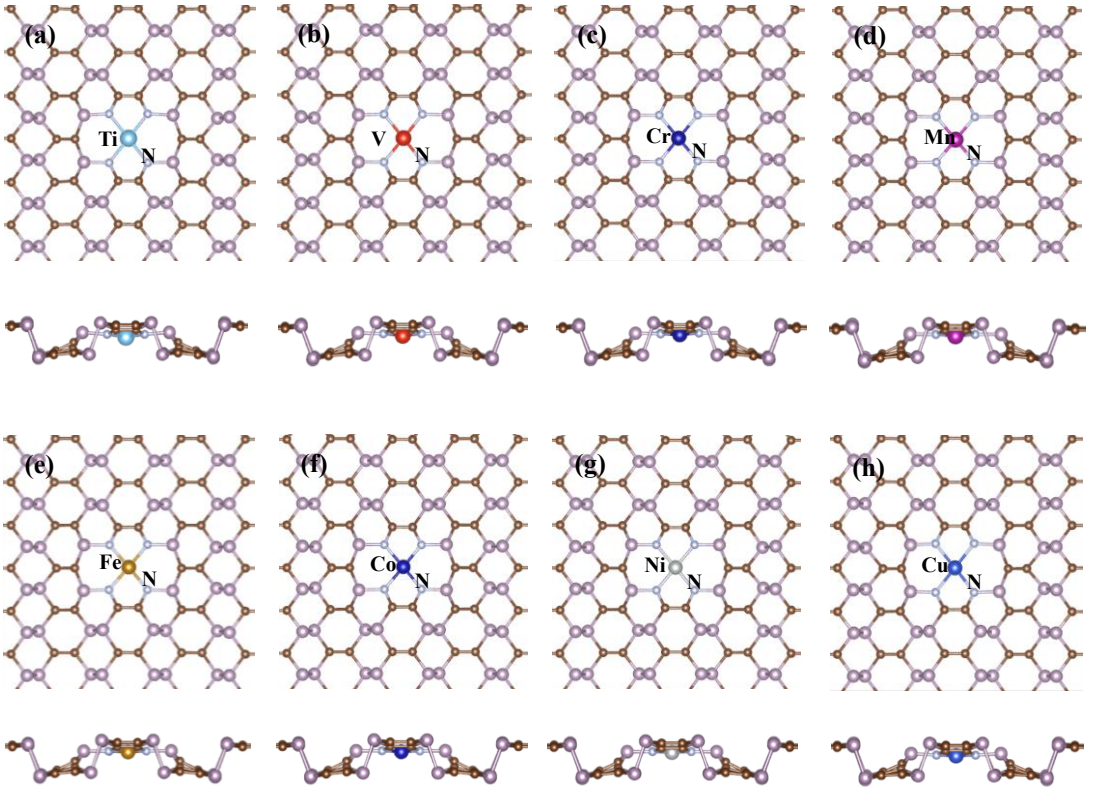
To evaluate the bonding strength between the TM and the substrate, the binding energy is calculated as:

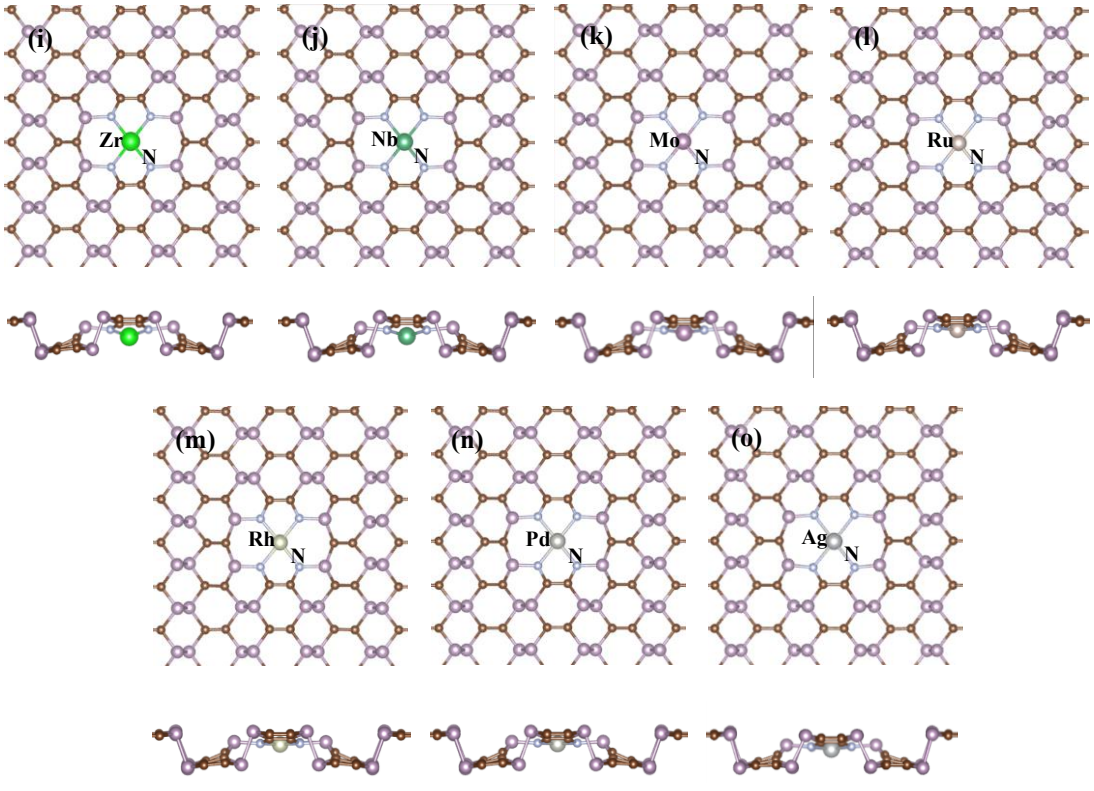
$$E_{\mathrm{Bind}} = E_{\mathrm{TM\text{-}N_4\text{-}bPC}} - E_{\mathrm{N_4\text{-}bPC}} - E_{\mathrm{metal\ atom}} \tag{23}$$

where $E_{\mathrm{N4\text{-}bPC}}$, $E_{\mathrm{metal\ atom}}$ is the calculated total energy of N_4-bPC and isolated one TM atom by DFT. Also, to compare the bonding strength in TM-N_4-bPC and in bulk metal, the cohesive energies in bulk metal are also calculated:

$$E_{\mathrm{Coh(bulk)}} = \mu_{\mathrm{TM}} - E_{\mathrm{metal\ atom}} \tag{24}$$

Figures


(a)
Ti
N
(b)
V
N
(c)
Cr
N
(d)
Mn
N
(e)
Fe
N
(f)
Co
N
(g)
Ni
N
(h)
Cu
N


(i)
Zr
N
(j)
Nb
N
(k)
Mo
N
(l)
Ru
N
(m)
Rh
N
(n)
Pd
N
(o)
Ag
N

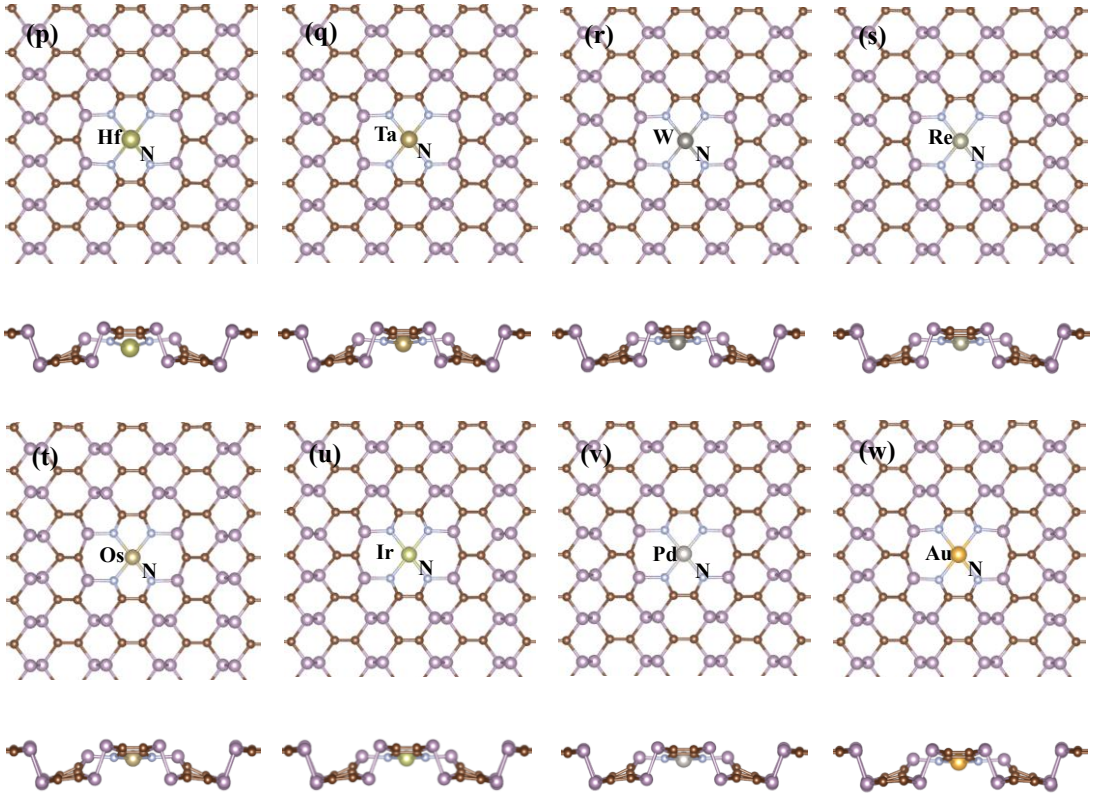


Figure S1 Optimized 23 geometric structures of transition metal-N_4 embedded b-PC monolayer. The structures contain top view and front view.

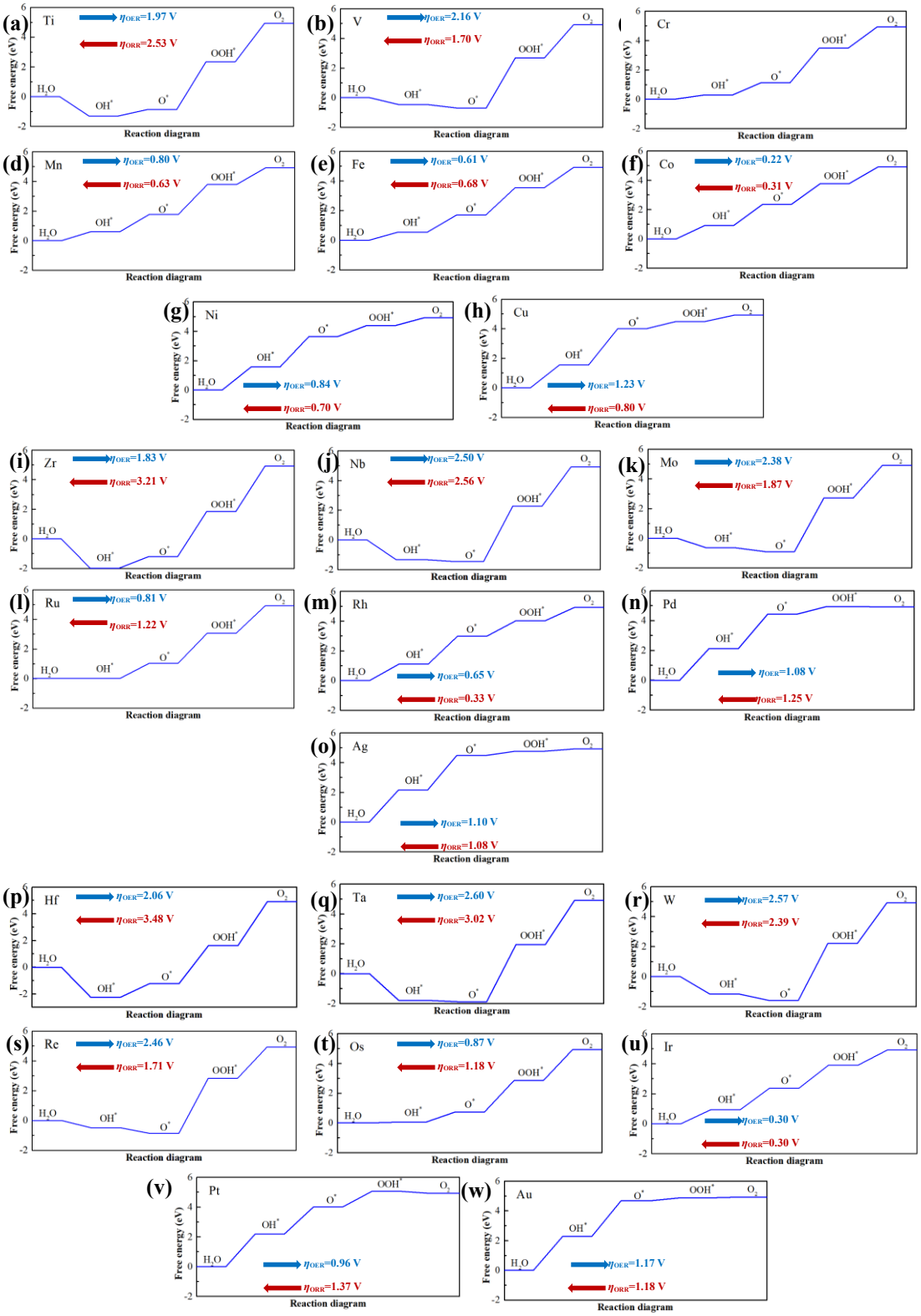


Figure S2 Reaction diagram of ORR/OER on transition metal-N_4 embedded b-PC monolayer (side 1). The calculated overpotentials are marked in the diagrams.

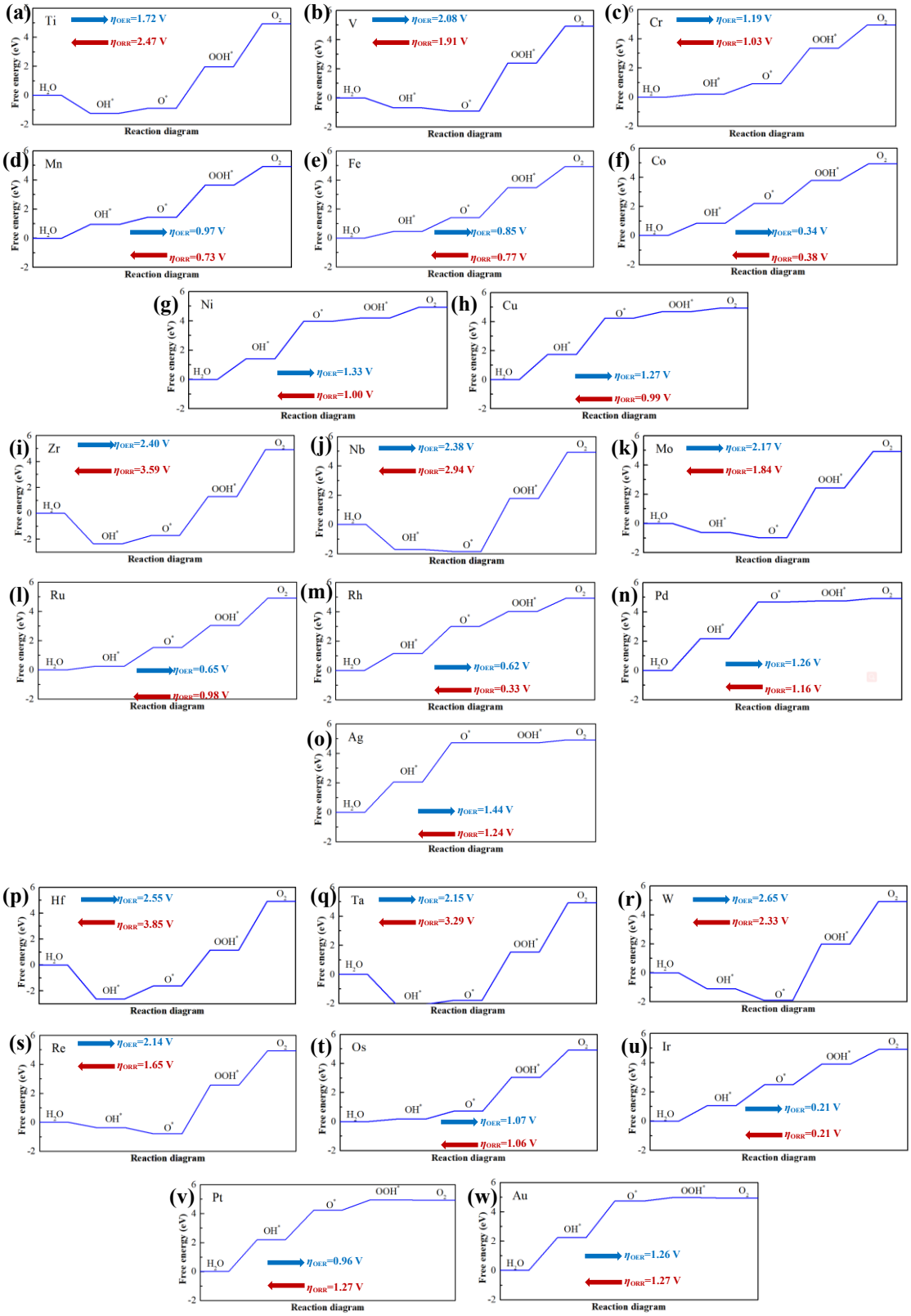
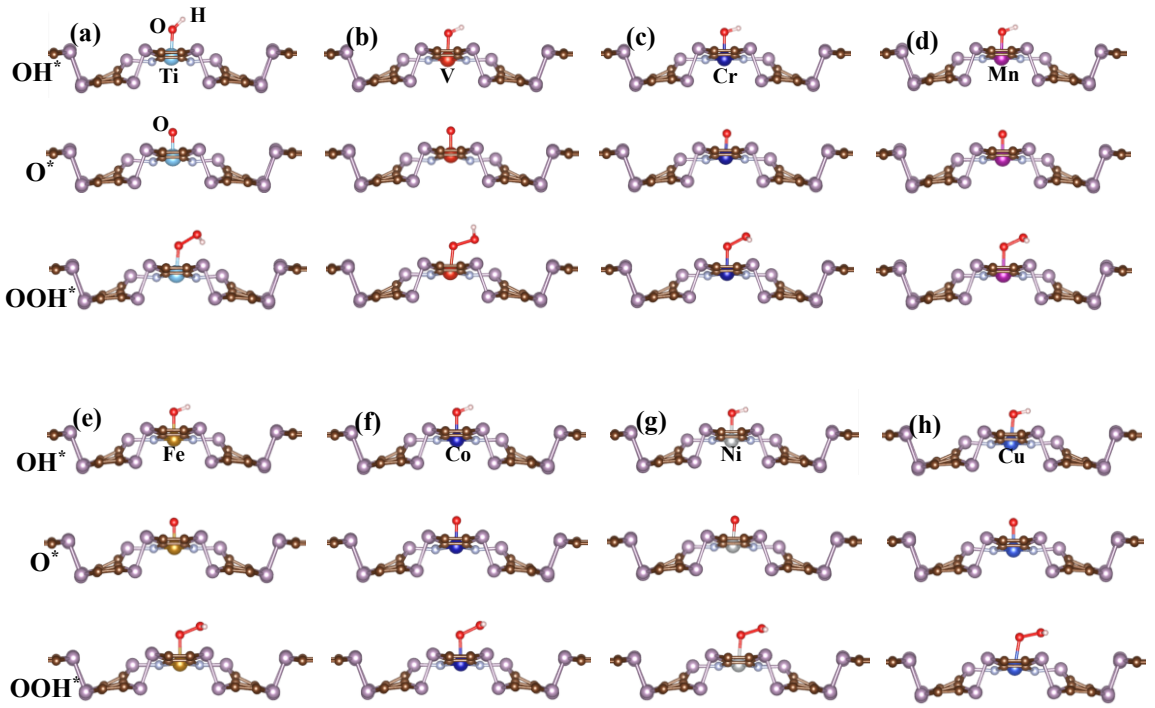


Figure S3 Reaction diagram of ORR/OER on transition metal-N_4 embedded b-PC monolayer (side 2). The calculated overpotentials are marked in the diagrams.


(a)
O
H
Ti
OH*
O*
OOH*
(b)
V
(c)
Cr
(d)
Mn
(e)
Fe
(f)
Co
(g)
Ni
(h)
Cu
(i)
Zr
(j)
Nb
(k)
Mo
(l)
Ru
(m)
Rh
(n)
Pd
(o)
Ag

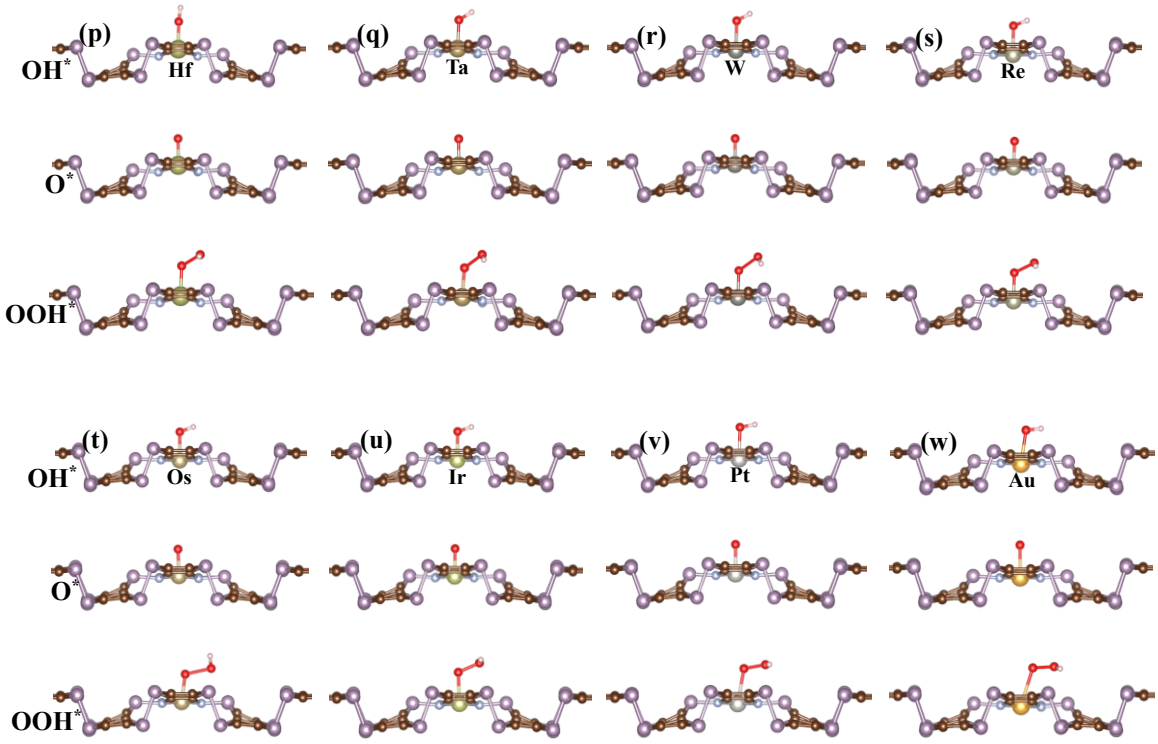
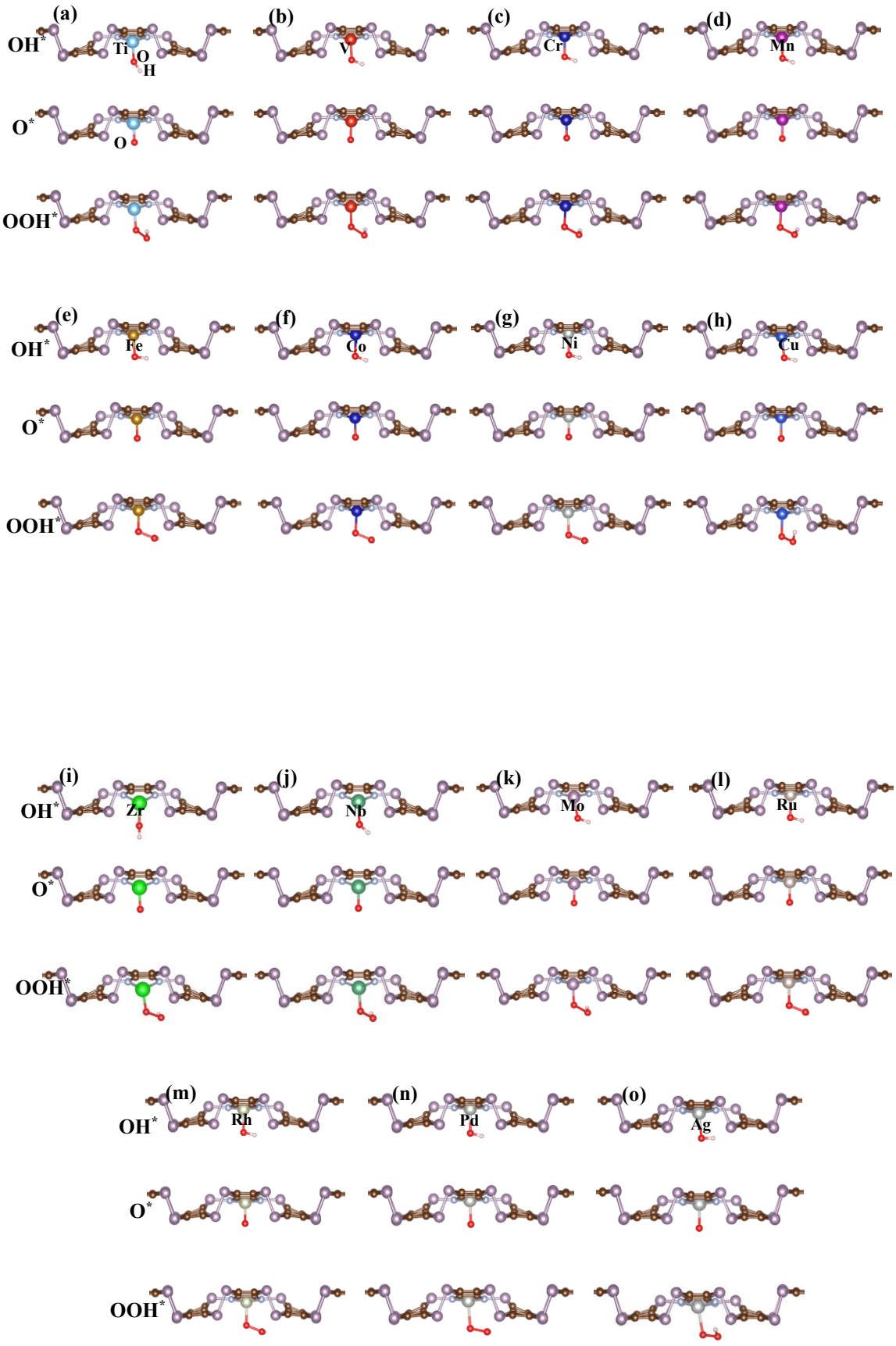


Figure S4 Geometric structure of ORR/OER species (OH^*, O^* and OOH^*) adsorbed on transition metal-N_4 embedded b-PC monolayer (side 1).


(a)
(b)
(c)
(d)
OH*
Ti
O
H
V
Cr
Mn
O*
O
OOH*
(e)
(f)
(g)
(h)
OH*
Fe
Co
Ni
Cu
O*
OOH*
(i)
(j)
(k)
(l)
OH*
Zr
Nb
Mo
Ru
O*
OOH*
(m)
(n)
(o)
OH*
Rh
Pd
Ag
O*
OOH*

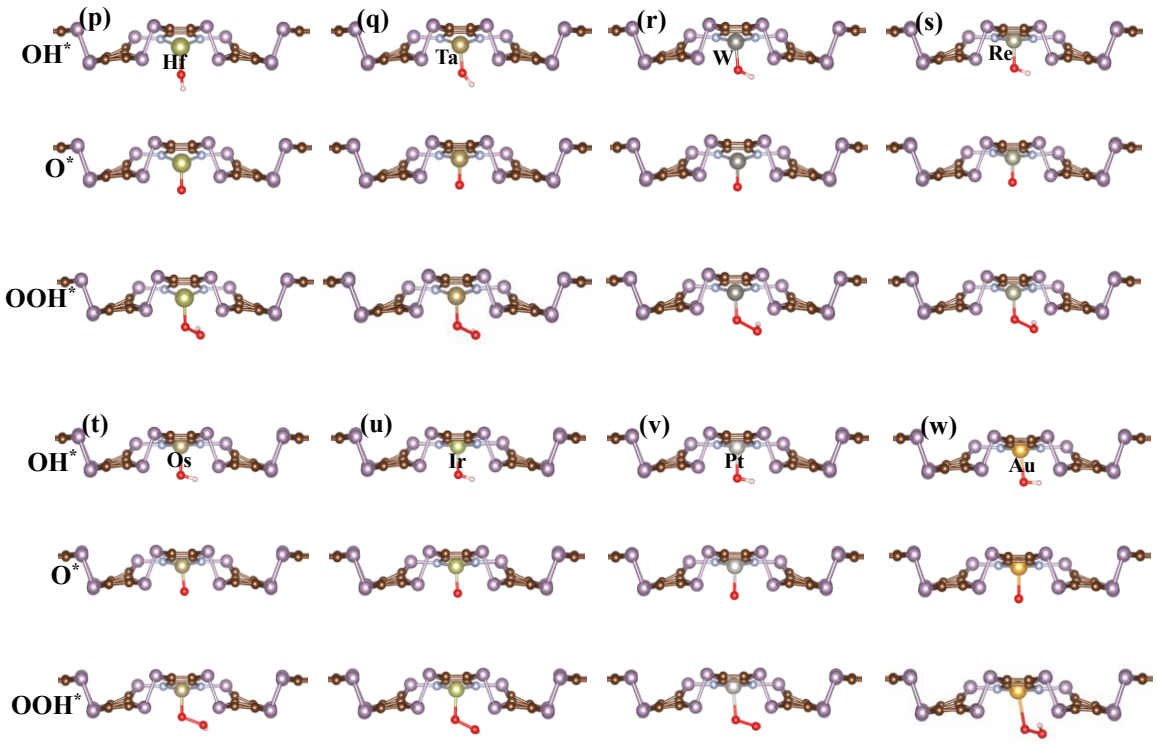


Figure S5 Geometric structure of ORR/OER species (OH^*, O^* and OOH^*) adsorbed on transition metal-N_4 embedded b-PC monolayer (side 2).

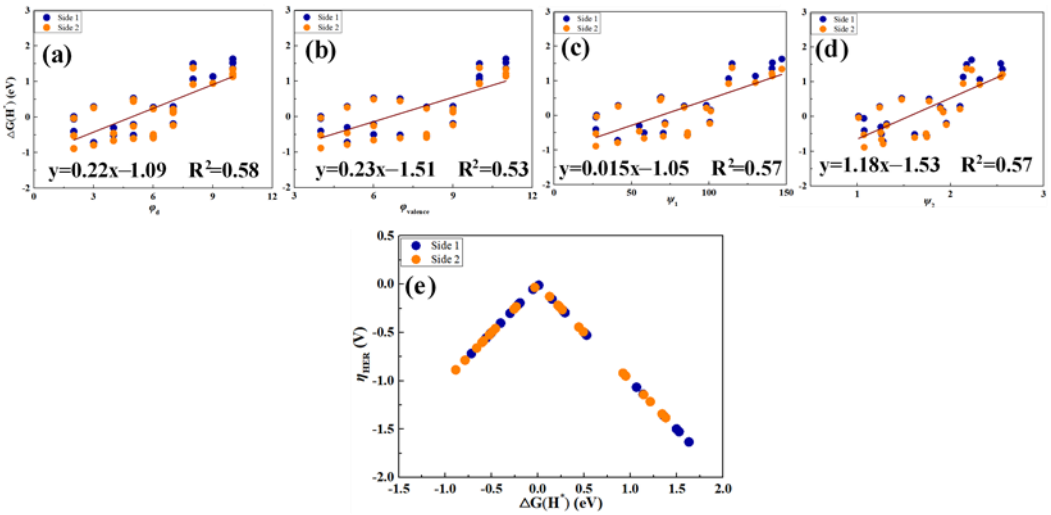


Figure S6 Adsorption free energy of $\Delta G(H^*)$ on TM-N_4 embedded b-PC monolayer; (a) relationship between the number of electrons of d orbital (φ_d) with $\Delta G(H^*)$; (b) relationship between the number of valence electrons ($\varphi_{valence}$) with $\Delta G(H^*)$; (c) relationship between ψ_1 with $\Delta G(H^*)$; (d) relationship between ψ_2 with $\Delta G(H^*)$; (e) volcanic relationship between $\Delta G(H^*)$ and calculated overpotential of HER (η_{HER}).

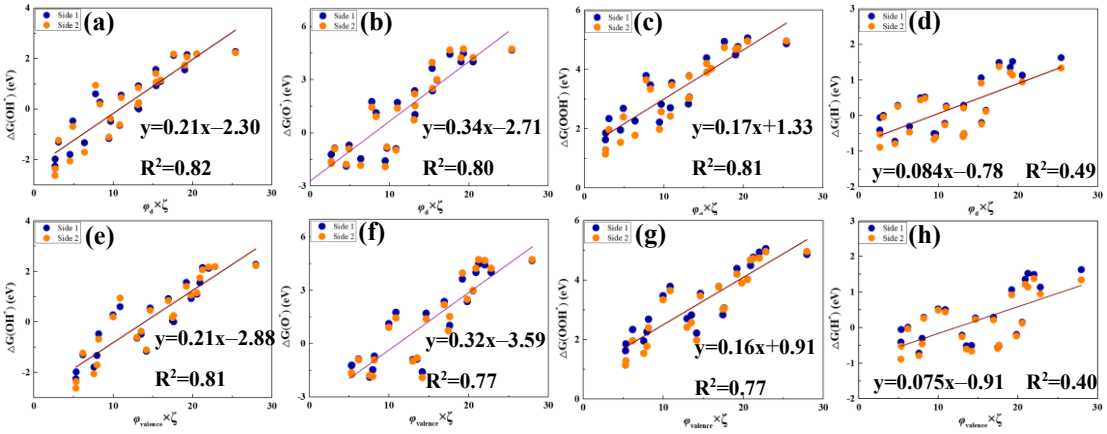


Figure S7 Adsorption free energy of ORR and OER related species on transition metal-N_4 embedded b-PC monolayer; (a) to (d) relationship between $\varphi_d \times \zeta$ with $\Delta G(OH^*)$, $\Delta G(O^*)$, $\Delta G(OOH^*)$, and $\Delta G(H^*)$; (e) to (h) relationship between $\varphi_{valence} \times \zeta$ with $\Delta G(OH^*)$, $\Delta G(O^*)$, $\Delta G(OOH^*)$, and $\Delta G(H^*)$.

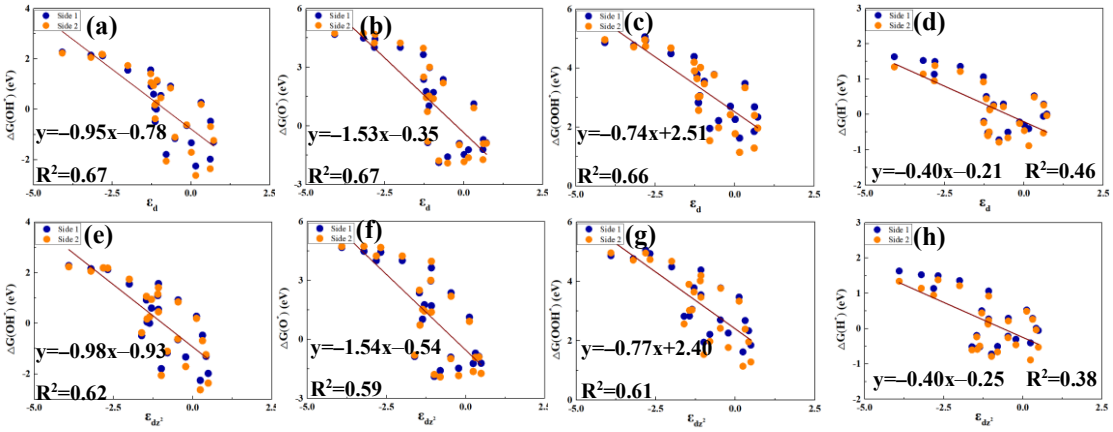


Figure S8 Adsorption free energy of ORR and OER related species on transition metal-N_4 embedded b-PC monolayer; (a) to (d) relationship between the d band center (ε_d) with $\Delta G(OH^*)$, $\Delta G(O^*)$, $\Delta G(OOH^*)$, and $\Delta G(H^*)$; (d) to (f) relationship between the d_{z2} band center (ε_{dz2}) with $\Delta G(OH^*)$, $\Delta G(O^*)$, $\Delta G(OOH^*)$, and $\Delta G(H^*)$.

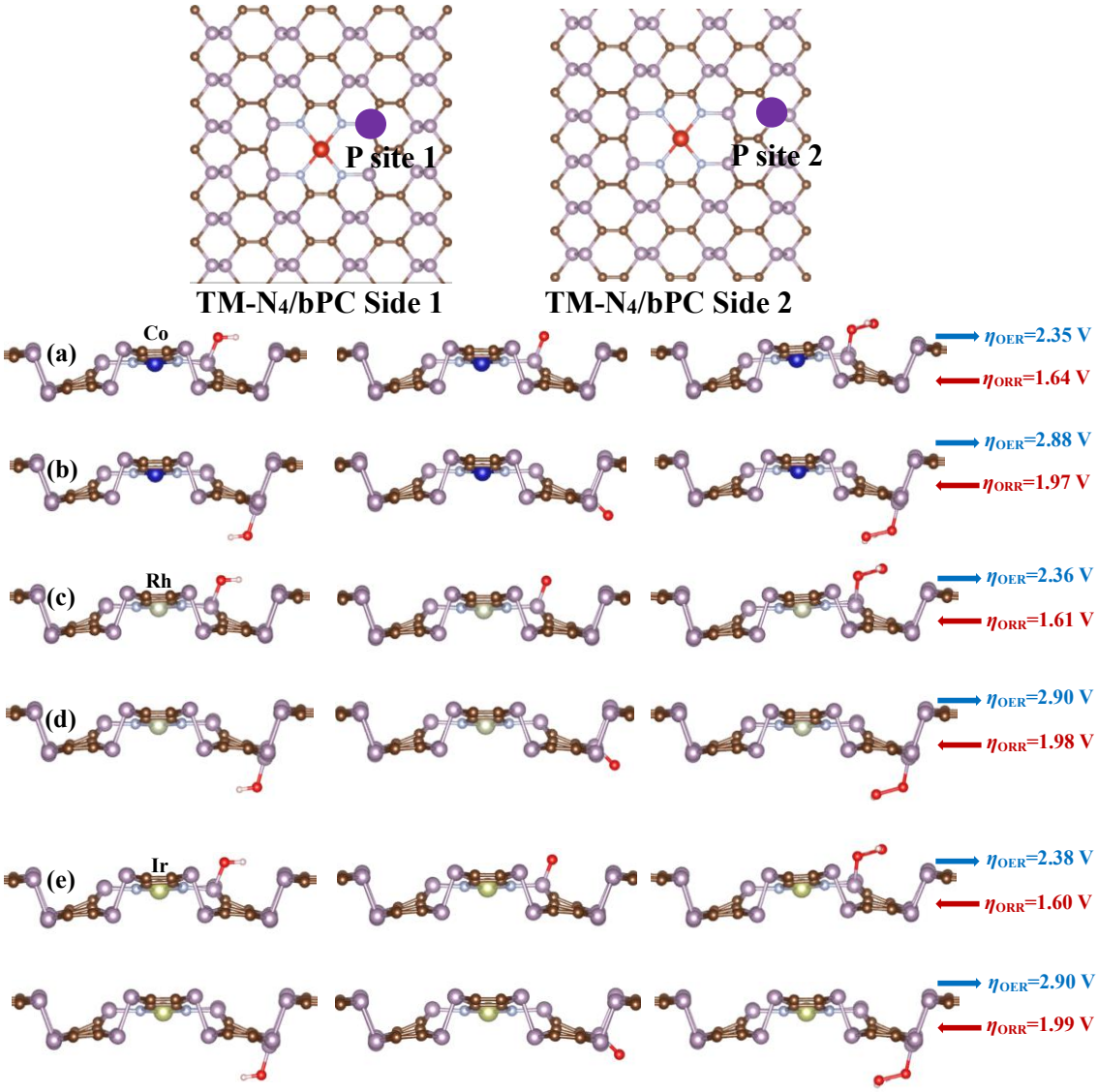


Figure S9 Geometric structure of ORR/OER species (OH^*, O^* and OOH^*) adsorbed on (a) P side of Co-N_4/bPC (side 1), (b) P side of Co-N_4/bPC (side 2), (c) P side of Rh-N_4/bPC (side 1), (d) P side of Rh-N_4/bPC (side 2), (e) P side of Ir-N_4/bPC (side 1), (f) P side of Ir-N_4/bPC (side 2).

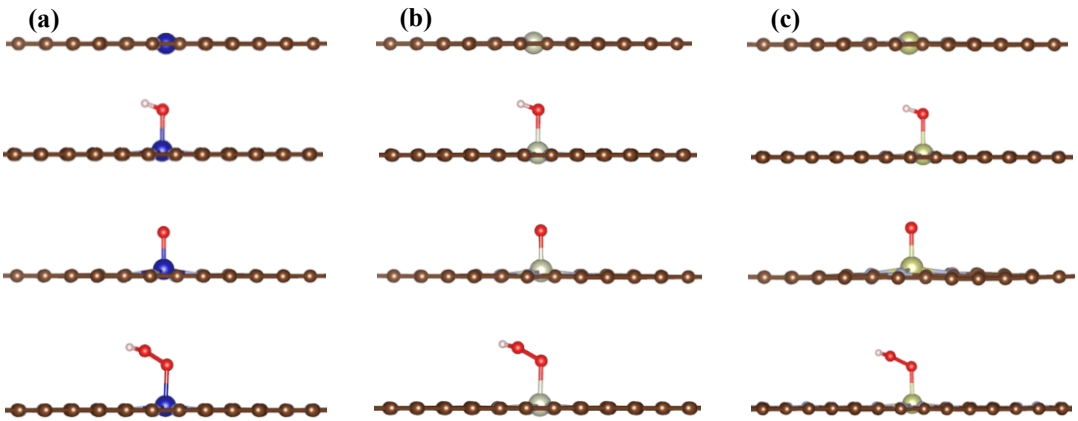


Figure S10 Geometric structure of ORR/OER species (OH^*, O^* and OOH^*) adsorbed on (a) Co-N_4/graphene, (b) Rh-N_4/graphene, and (c) Ir-N_4/graphene.

Tables

Table S1. Number of valence electrons in d orbital of metal atom (φ_d), number of valence electrons of metal atom ($\varphi_{valence}$), electronegativity of atoms (ζ) of atom

Atom type	φ_d	$\varphi_{valence}$	ζ
Ti	2	4	1.54
V	3	5	1.63
Cr	5	6	1.66
Mn	5	7	1.55
Fe	6	8	1.83
Co	7	9	1.88
Ni	8	10	1.92
Cu	10	11	1.90
Zr	2	4	1.33
Nb	4	5	1.59
Mo	5	6	2.16
Ru	6	8	2.20
Rh	7	9	2.28
Pd	8	10	2.20
Ag	10	11	1.93
Hf	2	4	1.32
Ta	3	5	1.51
W	4	6	2.36
Re	5	7	1.93
Os	6	8	2.18
Ir	7	9	2.20
Pt	9	10	2.28
Au	10	11	2.54
N	/	/	3.04

Table S2. Bond length of TM-N, bond angle of N-TM-N of TM-N_4 embedded b-PC

TM atom	TM-N (Å)	N-TM-N (°)
Ti	2.11	76.4
V	2.07	77.4
Cr	2.04	79.2
Mn	2.01	80.6
Fe	2.00	80.5
Co	1.98	80.0
Ni	2.03	80.0
Cu	2.10	76.7
Zr	2.18	73.6
Nb	2.15	74.7
Mo	2.11	76.3
Ru	2.07	76.8
Rh	2.07	77.7
Pd	2.10	76.7
Ag	2.22	75.5
Hf	2.17	74.0
Ta	2.11	76.5
W	2.11	76.4
Re	2.07	76.0
Os	2.03	76.5
Ir	2.05	76.2
Pt	2.06	77.5
Au	2.15	75.1

Table S3. The values of the calculated total energy using PBE method, the zero-point energy, the entropy and the free energy corrections of the relevant molecules, the adsorbed species. The temperature is set as 298K and the entropies of the adsorbed species and the substrates can be neglected. The free energy of O_2 is calculated by the four-electron chemical equation of ORR/OER

Species	Total energy by PBE (eV)	Zero-point energy (eV)	Entropy at 298K (eV)	Solvent correction (eV)	Gibbs free energy (eV)
OH^*	/	0.36	0	–0.20	/
O^*	/	0.07	0	0	/
OOH^*	/	0.43	0	–0.10	/
$H_2O(l)$	–14.23	0.57	0.67	/	–14.33
$H_2(g)$	–6.77	0.27	0.40	/	–6.90
$O_2(g)$	/	/	/	/	–9.94

Table S4. Values of ΔG_{OH*}, ΔG_{O*} and ΔG_{OOH*} on TM-N_4 embedded b-PC (side 1)

TM atom	ΔG_{OH*} (eV)	Bond length of OH* structures (TM-O) (Å)	ΔG_{O*} (eV)	Bond length of O* structures (TM-O) (Å)	ΔG_{OOH*} (eV)	Bond length of OOH* structures (TM-O) (Å)
Ti	-1.30	1.80	-0.86	1.67	2.34	1.84
V	-0.47	1.75	-0.70	1.61	2.69	1.76
Cr	0.28	1.79	1.13	1.56	3.48	1.80
Mn	0.60	1.76	1.76	1.57	3.79	1.81
Fe	0.55	1.77	1.71	1.60	3.55	1.83
Co	0.92	1.77	2.37	1.65	3.78	1.85
Ni	1.57	1.84	3.64	1.69	4.39	1.92
Cu	1.55	1.89	4.01	1.76	4.49	1.97
Zr	-1.98	1.97	-1.21	1.78	1.86	1.97
Nb	-1.33	1.92	-1.46	1.74	2.26	1.89
Mo	-0.64	1.93	-0.90	1.69	2.71	1.86
Ru	0.01	1.91	1.03	1.72	3.06	1.87
Rh	1.10	1.92	2.98	1.78	4.02	2.01
Pd	2.12	2.09	4.43	1.88	4.94	2.27
Ag	2.15	2.06	4.48	2.07	4.77	2.36
Hf	-2.25	1.86	-1.22	1.77	1.63	1.93
Ta	-1.79	1.89	-1.88	1.71	1.95	1.87
W	-1.16	1.91	-1.58	1.69	2.22	1.81
Re	-0.48	1.91	-0.86	1.70	2.83	1.87
Os	0.05	1.93	0.73	1.77	2.84	1.81
Ir	0.93	1.91	2.37	1.83	3.90	2.01
Pt	2.19	2.10	4.01	1.91	5.06	2.28
Au	2.28	2.17	4.67	2.08	4.87	2.55

Table S5. Values of ΔG_{OH*}, ΔG_{O*} and ΔG_{OOH*} on TM-N_4 embedded b-PC (side 2)

TM atom	ΔG_{OH*} (eV)	Bond length of OH* structures (TM-O) (Å)	ΔG_{O*} (eV)	Bond length of O* structures (TM-O) (Å)	ΔG_{OOH*} (eV)	Bond length of OOH* structures (TM-O) (Å)
Ti	-1.24	1.77	-0.90	1.65	1.97	1.83
V	-0.68	1.76	-0.91	1.59	2.40	1.76
Cr	0.20	1.78	0.92	1.54	3.34	1.79
Mn	0.95	1.81	1.44	1.63	3.65	1.81
Fe	0.46	1.81	1.39	1.62	3.47	1.77
Co	0.85	1.81	2.20	1.62	3.77	1.88
Ni	1.41	1.86	3.97	1.71	4.20	1.87
Cu	1.74	1.82	4.24	1.77	4.68	1.93
Zr	-2.36	1.87	-1.72	1.78	1.29	1.89
Nb	-1.71	1.86	-1.84	1.71	1.78	1.89
Mo	-0.61	1.86	-0.97	1.67	2.42	1.84
Ru	0.25	1.90	1.53	1.70	3.04	1.91
Rh	1.15	1.95	3.00	1.78	4.02	2.00
Pd	2.18	2.02	4.67	1.93	4.74	2.24
Ag	2.06	2.09	4.73	1.98	4.72	2.30
Hf	-2.62	1.83	-1.63	1.73	1.14	1.93
Ta	-2.06	1.83	-1.78	1.69	1.54	1.88
W	-1.10	1.83	-1.90	1.69	1.98	1.79
Re	-0.37	1.85	-0.80	1.66	2.57	1.82
Os	0.17	1.93	0.73	1.74	3.03	1.86
Ir	1.06	1.91	2.50	1.80	3.90	1.97
Pt	2.19	2.04	4.24	1.96	4.96	2.26
Au	2.24	2.14	4.73	2.05	4.96	2.51

Table S6. Values of ΔG_{H^*} on TM-N_4 embedded b-PC

TM atom	ΔG_{H^*} (eV) (side 1)	Bond length of H* structures (TM-H) (Å)	ΔG_{H^*} (eV) (side 2)	Bond length of H* structures (TM-H) (Å)
Ti	0.01	1.68	-0.03	1.66
V	0.29	1.58	0.26	1.61
Cr	0.53	1.57	0.49	1.56
Mn	0.51	1.49	0.44	1.53
Fe	0.27	1.47	0.23	1.47
Co	0.29	1.44	0.22	1.44
Ni	1.07	1.44	0.92	1.46
Cu	1.36	1.51	1.21	1.52
Zr	-0.05	1.80	-0.52	1.89
Nb	-0.30	1.75	-0.46	1.77
Mo	-0.21	1.66	-0.26	1.67
Ru	-0.51	1.56	-0.49	1.55
Rh	0.15	1.50	0.13	1.51
Pd	1.50	1.55	1.38	1.56
Ag	1.53	1.60	1.14	1.61
Hf	-0.40	1.79	-0.89	1.80
Ta	-0.72	1.73	-0.79	1.71
W	-0.50	1.65	-0.66	1.68
Re	-0.51	1.61	-0.60	1.61
Os	-0.56	1.57	-0.59	1.56
Ir	-0.19	1.53	-0.23	1.53
Pt	1.14	1.52	0.95	1.57
Au	1.63	1.59	1.34	1.60

Table S7. d band center of TM atom in TM-N_4 embedded b-PC

TM atom	d band center (d sum) (eV)	d band center (d_{z2})(eV)
Ti	0.72	0.42
V	0.62	0.31
Cr	0.32	0.12
Mn	-1.19	-1.30
Fe	-0.96	-1.08
Co	-0.65	-0.46
Ni	-1.28	-1.08
Cu	-2.01	-2.00
Zr	0.61	0.49
Nb	0.01	-0.22
Mo	-0.14	-0.47
Ru	-1.10	-1.36
Rh	-1.08	-1.10
Pd	-2.81	-2.68
Ag	-3.18	-3.21
Hf	0.15	0.24
Ta	-0.79	-0.99
W	-0.51	-0.80
Re	-1.14	-1.61
Os	-1.15	-1.44
Ir	-1.27	-1.46
Pt	-2.83	-2.82
Au	-4.09	-3.91

Table S8. Reaction free energy of every step of ORR and OER on TM-N_4 embedded b-PC (side 1)

TM atom	ORR				OER			
	ΔG_1 (eV)	ΔG_2 (eV)	ΔG_3 (eV)	ΔG_4 (eV)	ΔG_5 (eV)	ΔG_6 (eV)	ΔG_7 (eV)	ΔG_8 (eV)
Ti	-2.58	-3.20	-0.44	1.30	-1.30	0.44	3.20	2.58
V	-2.23	-3.39	0.23	0.47	-0.47	-0.23	3.39	2.23
Cr	-1.44	-2.35	-0.85	-0.28	0.28	0.85	2.35	1.44
Mn	-1.13	-2.03	-1.16	-0.60	0.60	1.16	2.03	1.13
Fe	-1.37	-1.84	-1.16	-0.55	0.55	1.16	1.84	1.37
Co	-1.14	-1.41	-1.45	-0.92	0.92	1.45	1.41	1.14
Ni	-0.53	-0.75	-2.07	-1.57	1.57	2.07	0.75	0.53
Cu	-0.43	-0.48	-2.46	-1.55	1.55	2.46	0.48	0.43
Zr	-3.06	-3.06	-0.77	1.98	-1.98	0.77	3.06	3.06
Nb	-2.66	-3.73	0.13	1.33	-1.33	-0.13	3.73	2.66
Mo	-2.21	-3.61	0.26	0.64	-0.64	-0.26	3.61	2.21
Ru	-1.86	-2.04	-1.02	-0.01	0.01	1.02	2.04	1.86
Rh	-0.90	-1.05	-1.88	-1.10	1.10	1.88	1.05	0.90
Pd	0.02	-0.50	-2.31	-2.12	2.12	2.31	0.50	-0.02
Ag	-0.15	-0.29	-2.33	-2.15	2.15	2.33	0.29	0.15
Hf	-3.29	-2.85	-1.03	2.25	-2.25	1.03	2.85	3.29
Ta	-2.97	-3.83	0.09	1.79	-1.79	-0.09	3.83	2.97
W	-2.70	-3.80	0.42	1.16	-1.16	-0.42	3.80	2.70
Re	-2.09	-3.69	0.38	0.48	-0.48	-0.38	3.69	2.09
Os	-2.08	-2.10	-0.68	-0.05	0.05	0.68	2.10	2.08
Ir	-1.02	-1.53	-1.45	-0.93	0.93	1.45	1.53	1.02
Pt	0.14	-1.05	-1.82	-2.19	2.19	1.82	1.05	-0.14
Au	-0.05	-0.19	-2.40	-2.28	2.28	2.40	0.19	0.05

Table S9. Reaction free energy of every step of ORR and OER on TM-N_4 embedded b-PC (side 2)

TM atom	ORR				OER			
	ΔG_1 (eV)	ΔG_2 (eV)	ΔG_3 (eV)	ΔG_4 (eV)	ΔG_5 (eV)	ΔG_6 (eV)	ΔG_7 (eV)	ΔG_8 (eV)
Ti	-2.95	-2.86	-0.34	1.24	-1.24	0.34	2.86	2.95
V	-2.52	-3.31	0.23	0.68	-0.68	-0.23	3.31	2.52
Cr	-1.58	-2.42	-0.72	-0.20	0.20	0.72	2.42	1.58
Mn	-1.27	-2.20	-0.50	-0.95	0.95	0.50	2.20	1.27
Fe	-1.45	-2.08	-0.94	-0.46	0.46	0.94	2.08	1.45
Co	-1.15	-1.57	-1.35	-0.85	0.85	1.35	1.57	1.15
Ni	-0.72	-0.23	-2.56	-1.41	1.41	2.56	0.23	0.72
Cu	-0.24	-0.44	-2.50	-1.74	1.74	2.50	0.44	0.24
Zr	-3.63	-3.01	-0.64	2.36	-2.36	0.64	3.01	3.63
Nb	-3.14	-3.61	0.13	1.71	-1.71	-0.13	3.61	3.14
Mo	-2.50	-3.40	0.36	0.61	-0.61	-0.36	3.40	2.50
Ru	-1.88	-1.51	-1.28	-0.25	0.25	1.28	1.51	1.88
Rh	-0.90	-1.02	-1.85	-1.15	1.15	1.85	1.02	0.90
Pd	-0.18	-0.07	-2.49	-2.18	2.18	2.49	0.07	0.18
Ag	-0.20	0.01	-2.67	-2.06	2.06	2.67	-0.01	0.20
Hf	-3.78	-2.77	-1.00	2.62	-2.62	1.00	2.77	3.78
Ta	-3.38	-3.32	-0.27	2.06	-2.06	0.27	3.32	3.38
W	-2.94	-3.88	0.80	1.10	-1.10	-0.80	3.88	2.94
Re	-2.35	-3.37	0.42	0.37	-0.37	-0.42	3.37	2.35
Os	-1.89	-2.30	-0.56	-0.17	0.17	0.56	2.30	1.89
Ir	-1.02	-1.40	-1.44	-1.06	1.06	1.44	1.40	1.02
Pt	0.04	-0.72	-2.05	-2.19	2.19	2.05	0.72	-0.04
Au	0.04	-0.23	-2.49	-2.24	2.24	2.49	0.23	-0.04

Table S10. The values of theoretical onset potential (U_{ORR} and U_{OER}) and overpotential (η_{ORR} and η_{OER}) for ORR and OER on TM-N_4 embedded b-PC (side 1)

TM atom	U_{ORR} (V)	η_{ORR} (V)	U_{OER} (V)	η_{OER} (V)
Ti	-1.30	2.53	3.20	1.97
V	-0.47	1.70	3.39	2.16
Cr	0.28	0.95	2.35	1.12
Mn	0.60	0.63	2.03	0.80
Fe	0.55	0.68	1.84	0.61
Co	0.92	0.31	1.45	0.22
Ni	0.53	0.70	2.07	0.84
Cu	0.43	0.80	2.46	1.23
Zr	-1.98	3.21	3.06	1.83
Nb	-1.33	2.56	3.73	2.50
Mo	-0.64	1.87	3.61	2.38
Ru	0.01	1.22	2.04	0.81
Rh	0.90	0.33	1.88	0.65
Pd	-0.02	1.25	2.31	1.08
Ag	0.15	1.08	2.33	1.10
Hf	-2.25	3.48	3.29	2.06
Ta	-1.79	3.02	3.83	2.60
W	-1.16	2.39	3.80	2.57
Re	-0.48	1.71	3.69	2.46
Os	0.05	1.18	2.10	0.87
Ir	0.93	0.30	1.53	0.30
Pt	-0.14	1.37	2.19	0.96
Au	0.05	1.18	2.40	1.17

Table S11. The values of theoretical onset potential (U_{ORR} and U_{OER}) and overpotential (η_{ORR} and η_{OER}) for ORR and OER on TM-N_4 embedded b-PC (side 2)

TM atom	U_{ORR} (V)	η_{ORR} (V)	U_{OER} (V)	η_{OER} (V)
Ti	-1.24	2.47	2.95	1.72
V	-0.68	1.91	3.31	2.08
Cr	0.20	1.03	2.42	1.19
Mn	0.50	0.73	2.20	0.97
Fe	0.46	0.77	2.08	0.85
Co	0.85	0.38	1.57	0.34
Ni	0.23	1.00	2.56	1.33
Cu	0.24	0.99	2.50	1.27
Zr	-2.36	3.59	3.63	2.40
Nb	-1.71	2.94	3.61	2.38
Mo	-0.61	1.84	3.40	2.17
Ru	0.25	0.98	1.88	0.65
Rh	0.90	0.33	1.85	0.62
Pd	0.07	1.16	2.49	1.26
Ag	-0.01	1.24	2.67	1.44
Hf	-2.62	3.85	3.78	2.55
Ta	-2.06	3.29	3.38	2.15
W	-1.10	2.33	3.88	2.65
Re	-0.42	1.65	3.37	2.14
Os	0.17	1.06	2.30	1.07
Ir	1.02	0.21	1.44	0.21
Pt	-0.04	1.27	2.19	0.96
Au	-0.04	1.27	2.49	1.26

Table S12. Formation energy and binding energy of TM-N_4 embedded b-PC (comparing wit cohesive energy of bulk metal obtained by PBE)

TM atom	Formation energy (eV)	Binding energy (eV)	Cohesive energy of bulk metal (eV)
Ti	-2.77	-8.07	-5.70
V	-2.11	-7.14	-5.43
Cr	-2.31	-5.95	-4.04
Mn	-2.31	-5.65	-3.73
Fe	-1.37	-6.31	-5.34
Co	-1.29	-6.55	-5.65
Ni	-0.94	-5.47	-4.93
Cu	-0.67	-3.74	-3.47
Zr	-2.97	-9.13	-6.56
Nb	-1.20	-7.80	-6.99
Mo	-0.67	-6.62	-6.35
Ru	-0.48	-7.36	-7.29
Rh	-1.26	-6.98	-6.12
Pd	-0.85	-4.20	-3.74
Ag	0.45	-1.65	-2.50
Hf	-2.71	-9.16	-6.85
Ta	-1.29	-9.42	-8.53
W	0.02	-8.05	-8.47
Re	0.39	-7.02	-7.81
Os	0.14	-8.01	-8.55
Ir	-1.02	-8.34	-7.73
Pt	-1.40	-6.60	-5.61
Au	0.18	-2.44	-3.03

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