Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Transition metal embedded two-dimensional C_3N as highly active electrocatalysts for oxygen evolution and reduction reactions

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1. The Figures in the supporting information (Fig. S1 ~ Fig. S8)

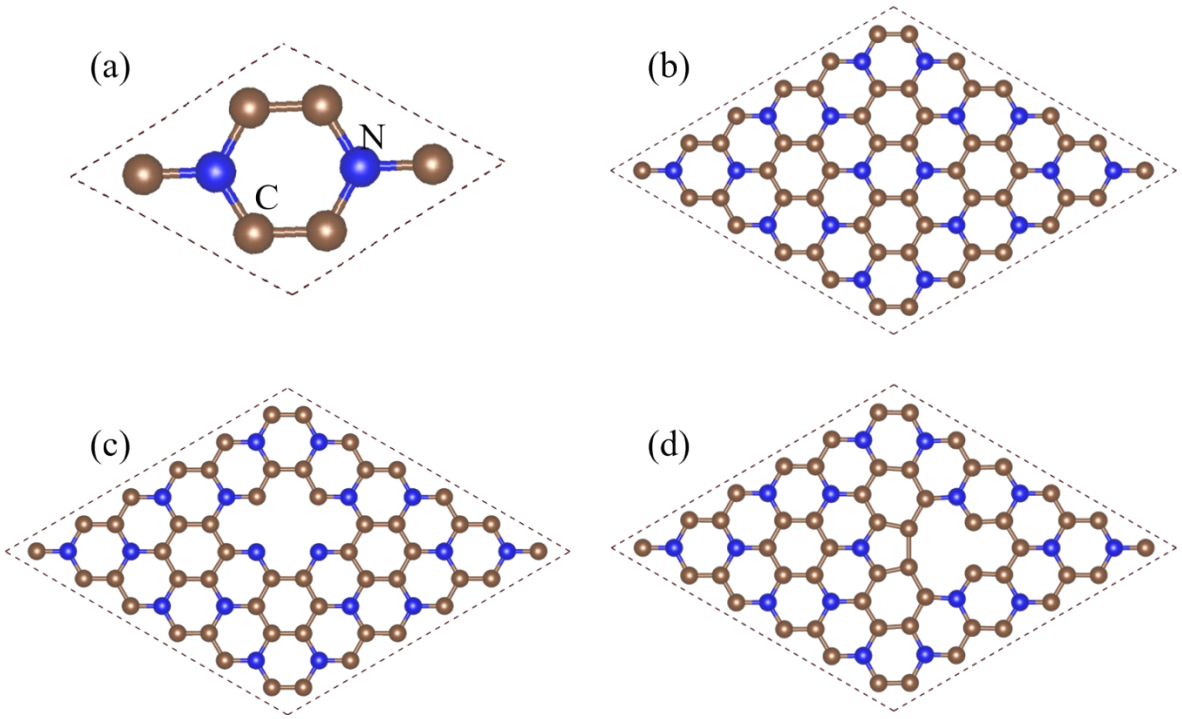

Fig. S1 The optimized configurations of (a) C_3N primitive unit cell, (b) (3 x 3) p-C_3N monolayer, (c) (3 x 3) V_{CC} monolayer, and (c) (3 x 3) V_{CN} monolayer, respectively. The brown and blue balls represent the C and N atoms, respectively.

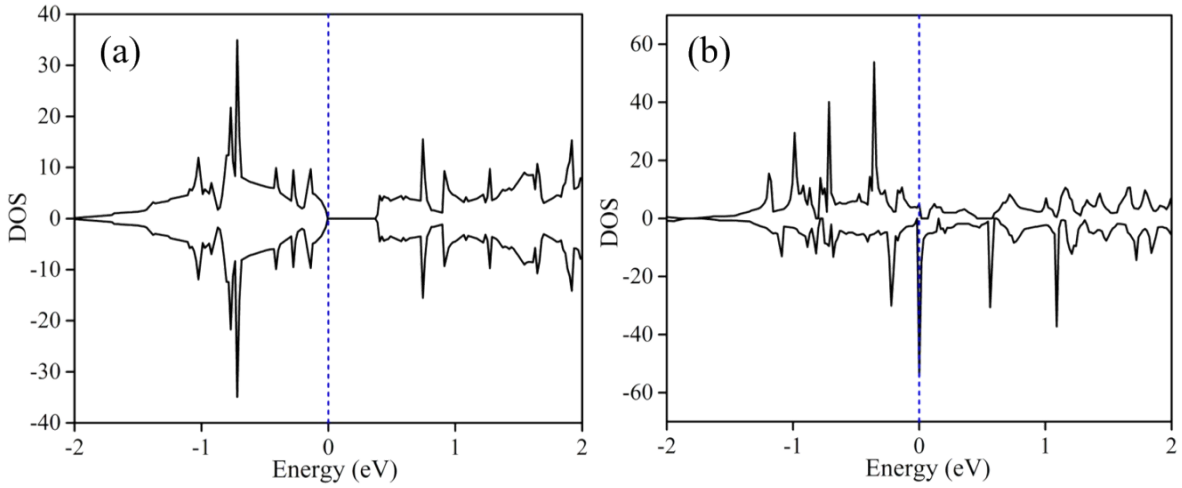

Fig. S2 The DOS of (a) p-C_3N monolayer, and (b) V_{CC} monolayer. The Fermi level is set to zero (blue dash line).

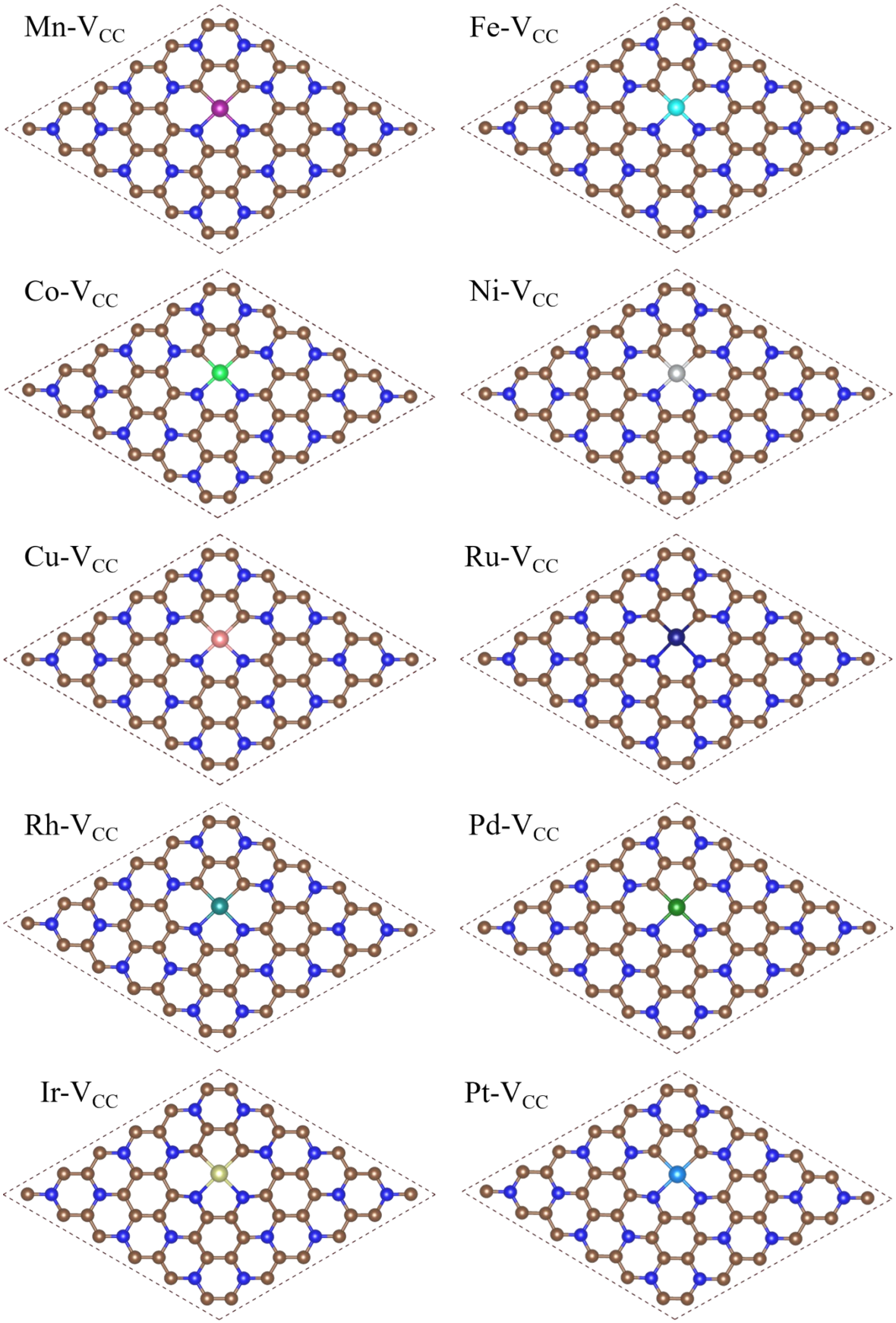

Fig. S3 The optimized configurations of TM-V_{CC} (top view).

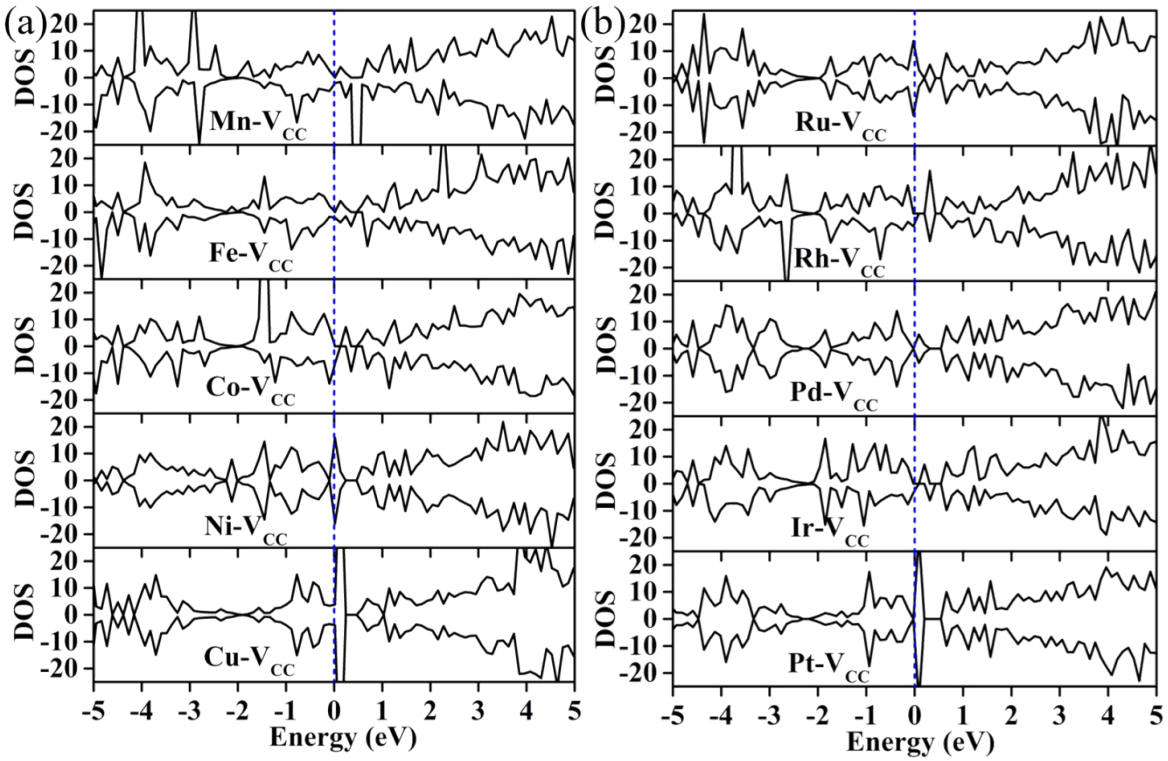

Fig. S4 Calculated DOS of the TM-V_{CC} systems (a) TM refers to Mn, Fe, Co, Ni and Cu; (b) TM refers to Ru, Rh, Pd, Ir and Pt, respectively. The Fermi level is set at the zero of energy (blue dash line).

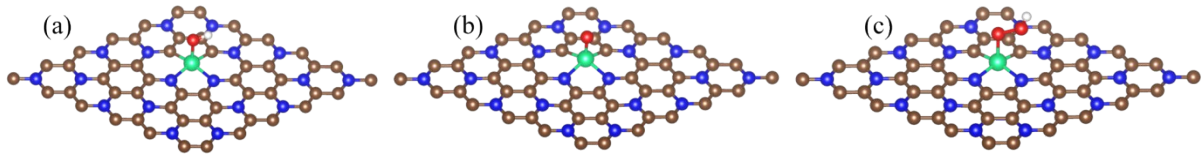

Fig. S5 The optimized configurations of (a) HO* adsorbed on the Co-V_{CC}, (b) O* adsorbed on the Co-V_{CC}, and (c) HOO* adsorbed on the Co-V_{CC}. The white, brown, blue, red, and green balls represent the H, C, N, O, and Co atoms, respectively.

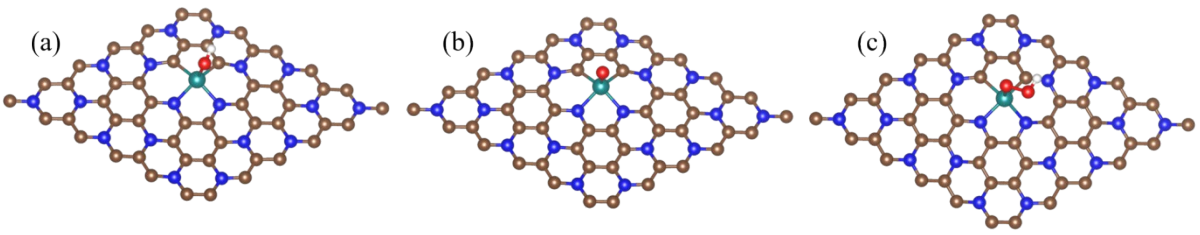

Fig. S6 The optimized configurations of (a) HO* adsorbed on the Rh-V_{CC}, (b) O* adsorbed on the Rh-V_{CC}, and (c) HOO* adsorbed on the Rh-V_{CC}. The white, brown, blue, red, and

cyan balls represent the H, C, N, O, and Rh atoms, respectively.

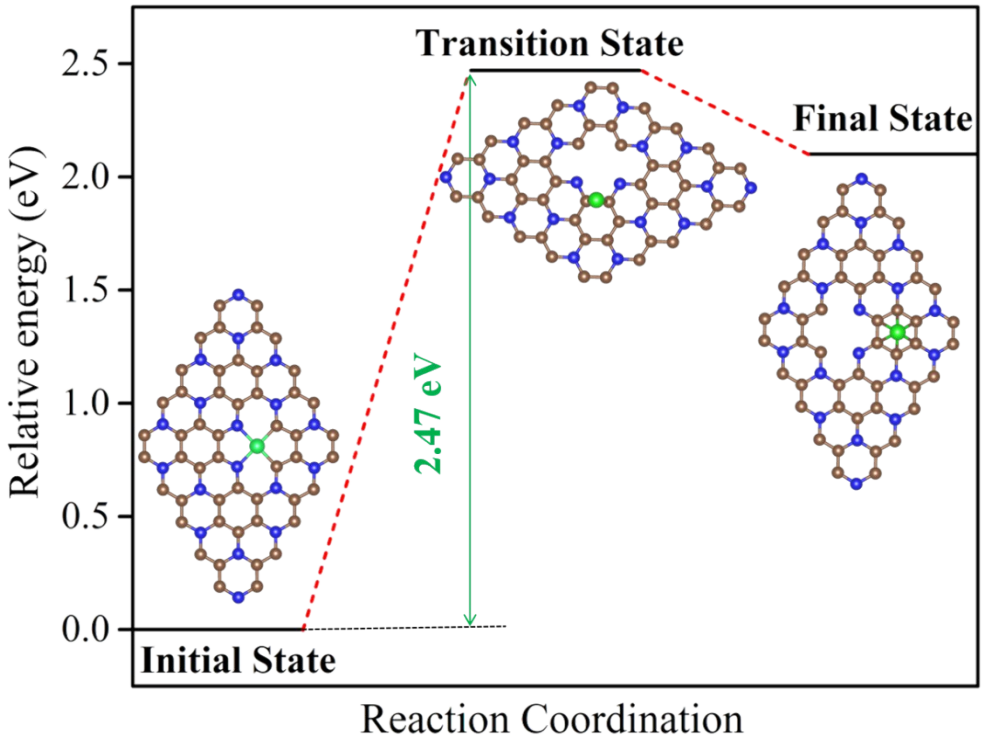

Fig. S7 The minimum energy pathway of the adsorbed Co atom diffused from the defect adsorption site to a neighboring hollow site.

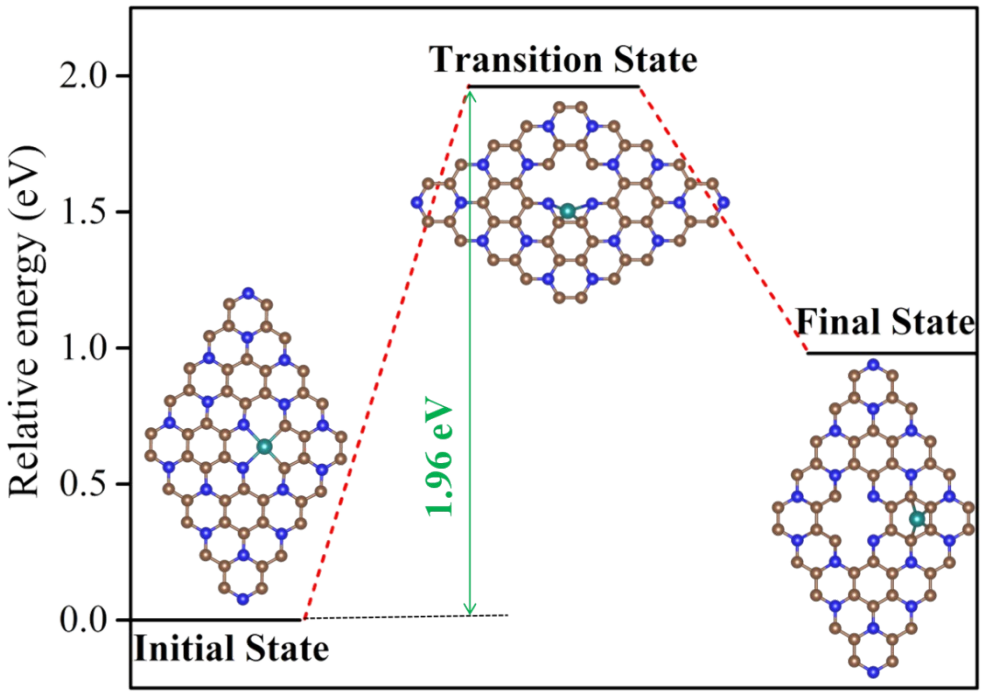

Fig. S8 The minimum energy pathway of the adsorbed Rh atom diffused from the defect

adsorption site to a neighboring hollow site.

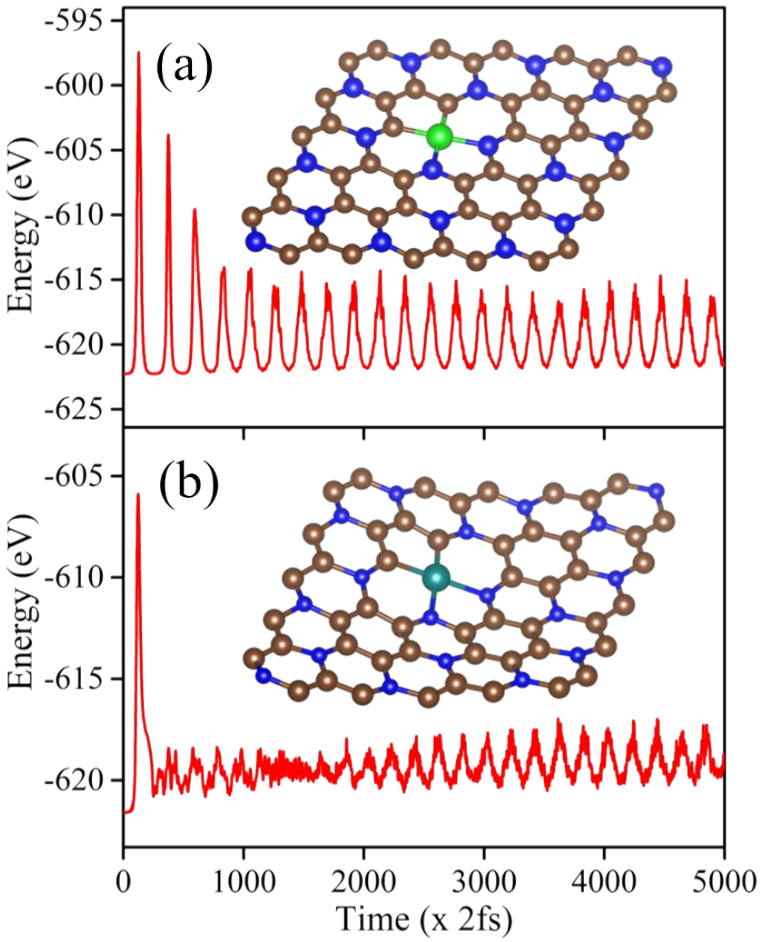

Fig. S9 Total energy variations of Co-V_{CC} and Rh-V_{CC} as the function of time for AIMD simulation, and the snapshot of atomic configuration at the end of the AIMD simulation is inserted.

2. The Tables in the supporting information (Table S1 ~ Table S5)

Table S1 Vibrational frequencies of the intermediates adsorbed on Co-V_{CC} and Rh-V_{CC} catalysts.

System	Vibration Frequencies (cm^{-1})
HO*-Co-V_{CC}	3715, 855, 457, 186,136,122
O*-Co-V_{CC}	659, 146, 128
HOO*-Co-V_{CC}	3623, 1256, 788, 463, 314,256,137,90,36
HO*-Rh-V_{CC}	3714, 867, 456, 150,112,91
O*-Rh-V_{CC}	645, 104, 77
HOO*-Rh-V_{CC}	3601, 1278, 811, 467, 371,212,145,84,55

Table S2 The zero-point energy (ZPE) and entropic corrections (TS) in determining the free energy of reactants, intermediates, and products adsorbed on catalysts at 298K. For the adsorbates, the ZPE value is not sensitive to the metal since they have close value.

Species	ZPE(eV)	TS(eV)
H_2O	0.56	0.67
H_2	0.27	0.41
O*	0.05	0
HO*	0.36	0
HOO*	0.44	0

Table S3 Computed adsorption free energies of HO*, O* and HOO* (ΔG_{HO*}, ΔG_{O*}, ΔG_{HOO*}), overpotentials for OER (η^{OER}) and ORR (η^{ORR}) on TM-V_{CC} systems, as well as the d band center values that related to Fermi level of TM-V_{CC}. The unit for ΔG is eV, while for η is V.

System	ΔG_{HO*}	ΔG_{O*}	ΔG_{HOO*}	η^{OER}	η^{ORR}	ε_d
Mn-V_{CC}	0.26	0.38	3.47	1.86	1.11	-0.56
Fe-V_{CC}	0.49	1.18	3.56	1.16	0.74	-1.12
Co-V_{CC}	1.08	2.45	4.11	0.43	0.42	-1.18
Ni-V_{CC}	1.82	3.79	4.54	0.74	0.85	-1.88
Cu-V_{CC}	1.98	4.03	4.85	0.82	1.16	-2.99
Ru-V_{CC}	0.17	0.33	3.12	1.56	1.07	-2.10
Rh-V_{CC}	0.99	2.34	3.96	0.35	0.27	-2.24
Pd-V_{CC}	2.23	4.34	5.03	1.00	1.34	-3.42
Ir-V_{CC}	1.07	2.06	4.12	0.84	0.43	-2.31
Pt-V_{CC}	2.09	5.02	4.85	1.70	1.24	-3.85

Table S4 For comparison, the calculated overpotentials for OER (η^{OER}) and ORR (η^{ORR}) on the metal doped carbon materials are listed. The unit for for η is V.

Composites	Methods	η^{OER}	η^{ORR}	Reference
Co-HAB	VASP/PBE	0.41	-	1
Rh-HAB		0.32	-	

RhN3-Gra	VASP/PBE	-	0.33	2
RhN4-Gra		-	0.34	
Ni@GDY	VASP/PBE	0.29	0.40	3
Pt@GDY		0.46	0.46	
CoN_3	MS/DMol^3	1.33	0.63	4
CoN_4		0.69	0.47	
Co1/g-C_3N_4	VASP/PBE	0.50	0.59	5
FeN_4/C	VASP/PBE	-	0.65	6
3N-Co	VASP/PBE	1.26	-	7
4N-Co		0.38	-	
Co-V_{CC}	VASP/PBE	0.43	0.42	This work
Rh-V_{CC}		0.35	0.27	