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

Supporting information

Theoretically revealing the activity origin of hydrogen evolution reaction on carbon-based single-atom catalysts and finding the ideal catalysts for water splitting

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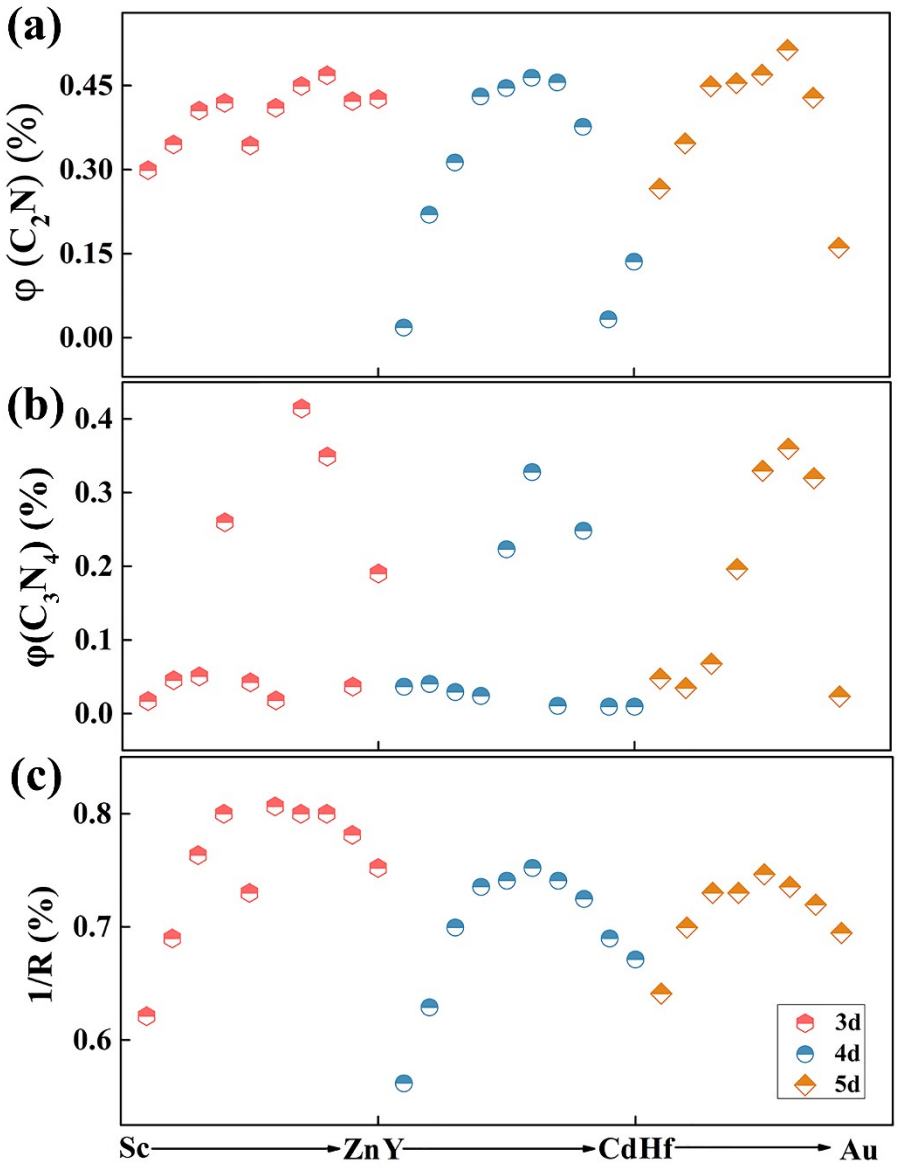

Fig. S1 Deviation degree (φ) between the TM atoms and the defect center in (a) C_2N (b) C_3N_4. (c) 1/R of the 3*d*, 4*d* and 5*d* TM atoms.

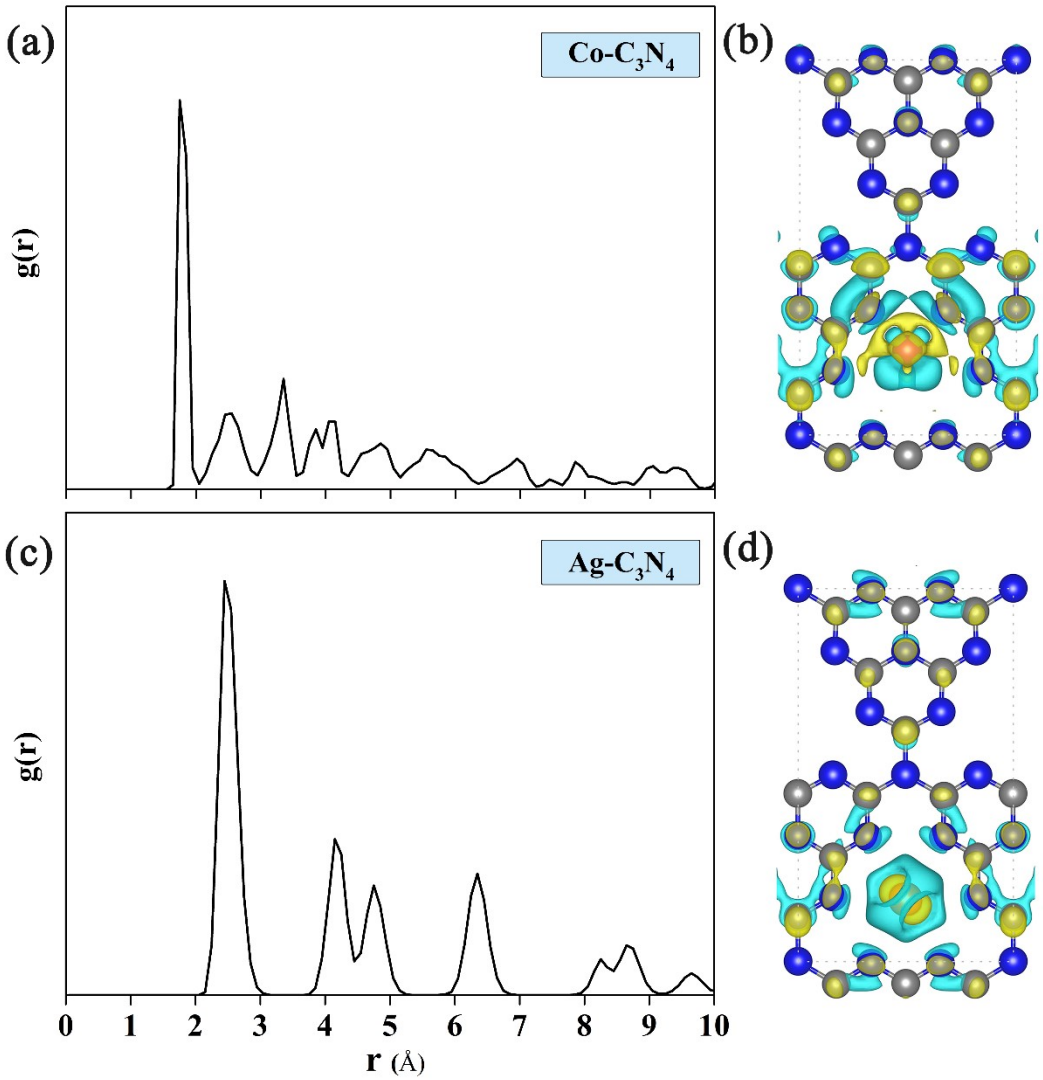

Fig. S2 (a) Radial distribution function (RDF) between Co and N on C_3N_4. (b) The charge density difference (CDD) of Co-C_3N_4. (c) RDF between Ag and N on C_3N_4. (d) The CDD of Ag-C_3N_4. Yellow and cyan regions represent the charge accumulation and depletion, respectively. The value of iso-surface is 0.003 e $Å^{-3}$.

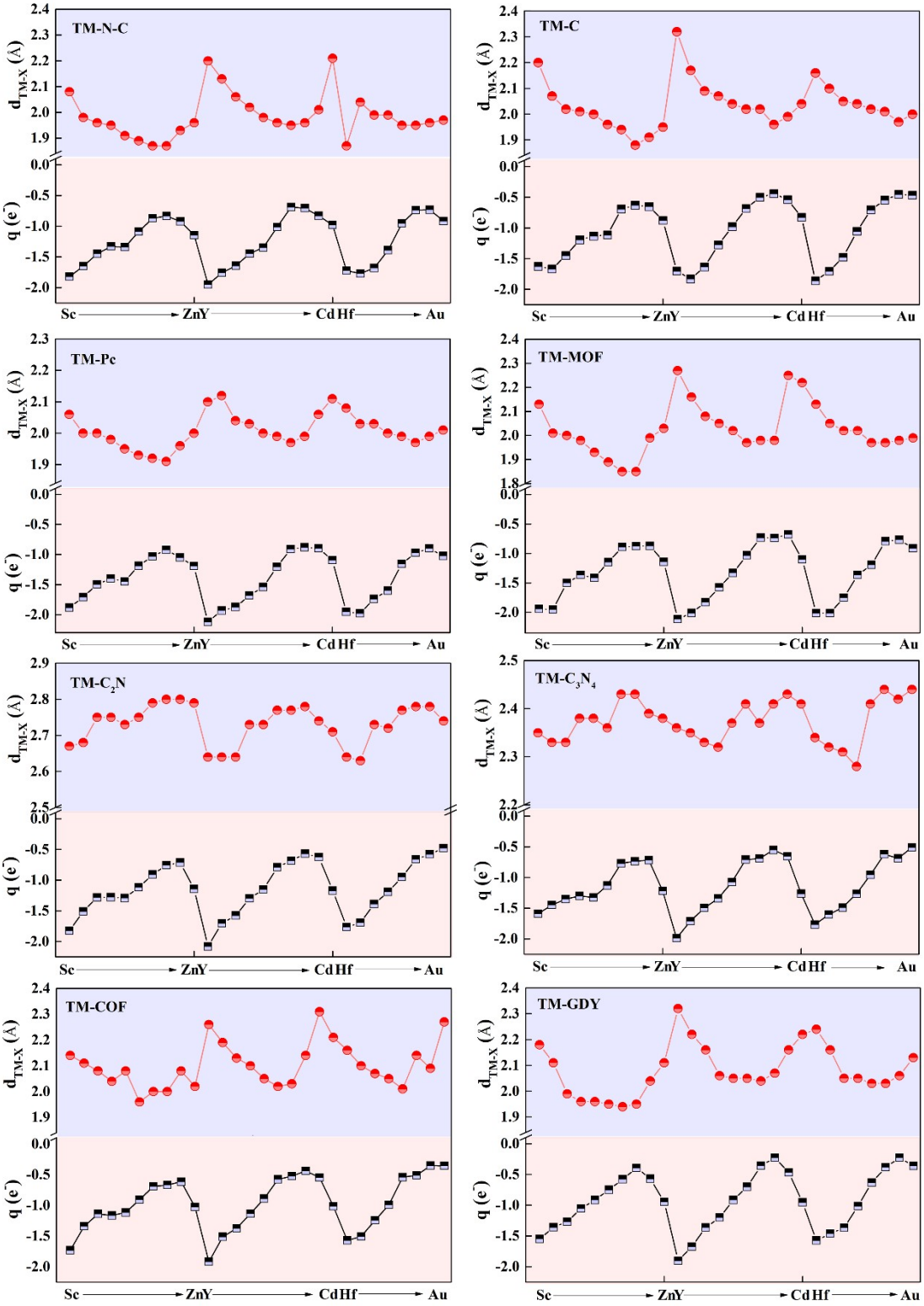

Fig. S3 The red dots represent the average bond lengths (d_{TM-X}) between the TM atom and the coordination atoms, the black squares are the charge transfer from the TM atoms to carbon-based supports.

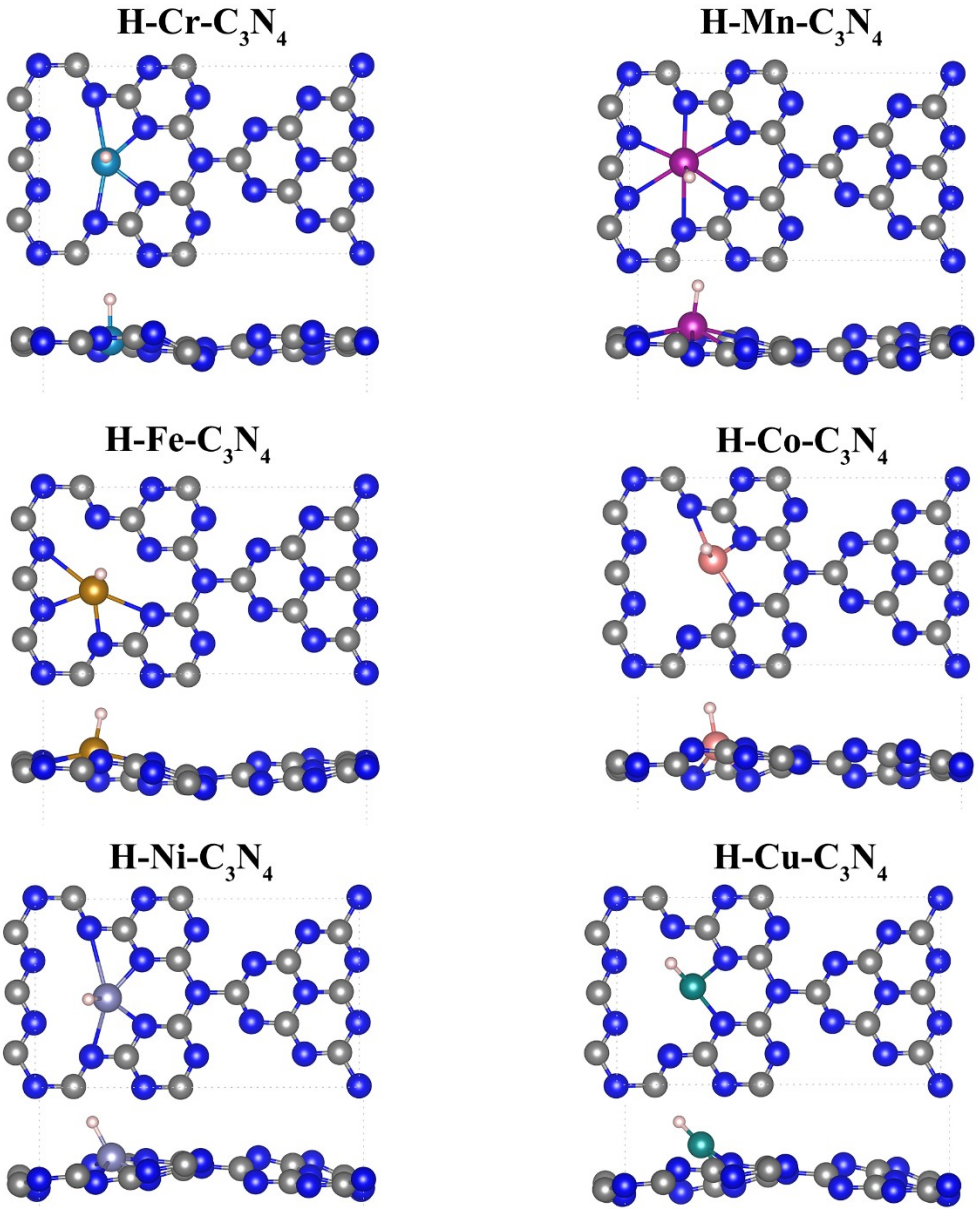

Fig. S4 The top and side views of H adsorbed on Cr/Mn/Fe/Co/Ni/Cu-C_3N_4 (denoted as H-TM-C_3N_4). The blue, grey, cyan, purple, golden, pink, white, light-blue, dark-green and spheres represent the N, C, Cr, Mn, Fe, Co, H, Ni and Cu atoms, respectively.

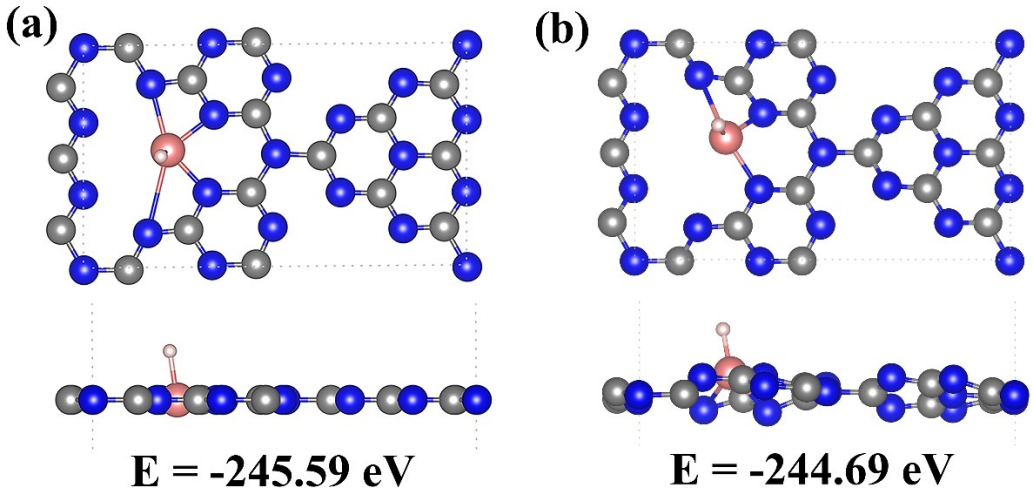

Fig. S5 Top and side views of (a) planar and (b) buckle H-Co-C_3N_4, respectively. The blue, grey, pink and white spheres represent the N, C, Co and H atoms, respectively.

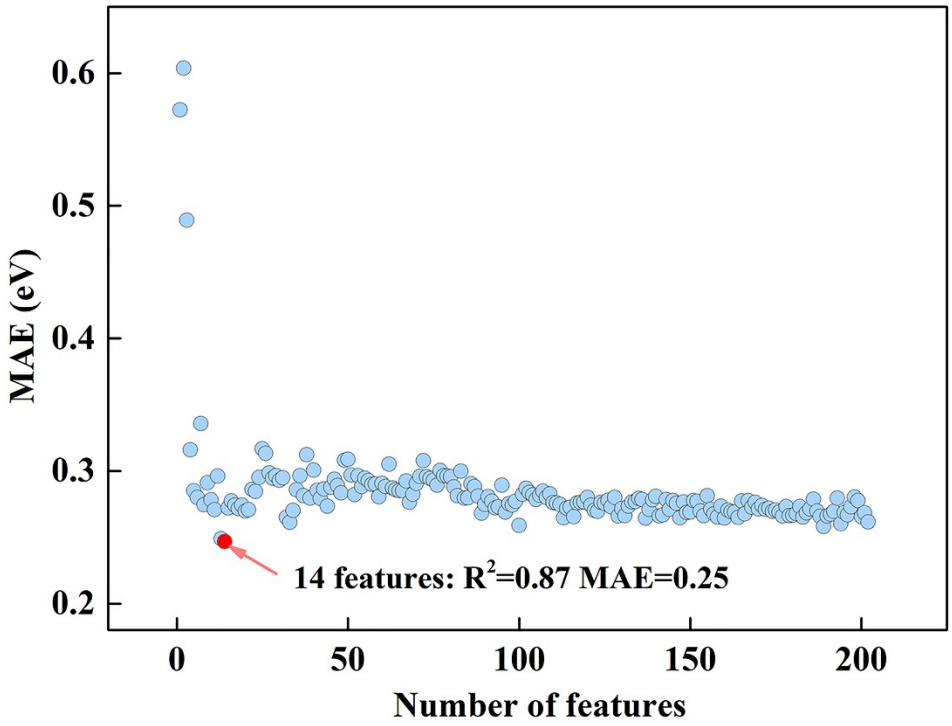

Fig. S6 GB model prediction accuracy by the stepwise feature selection method. Each dot indicates a combination of features. The red dot represents the combination with the minimum MAE and maximum R^2.

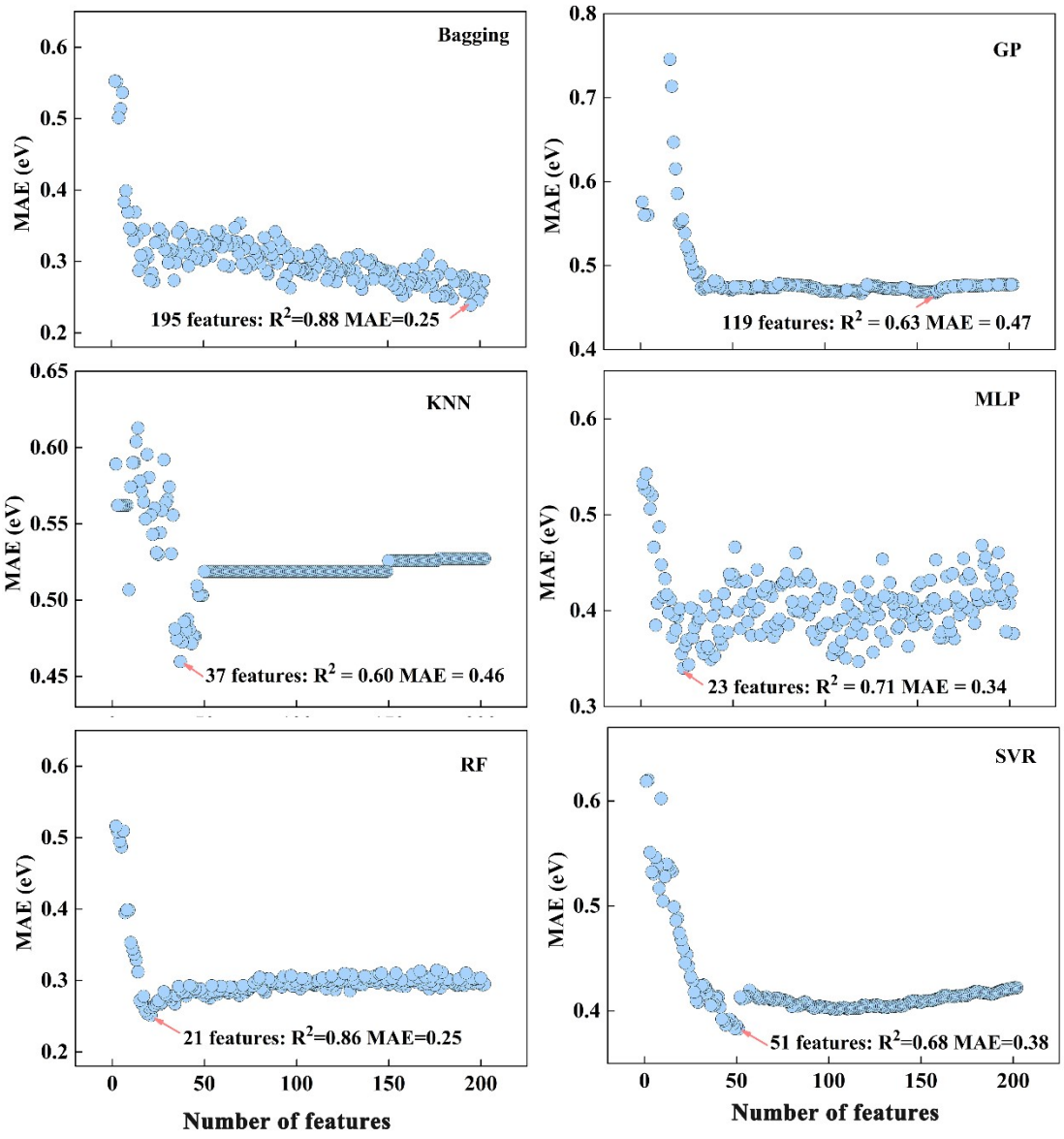

Fig. S7 Different model prediction accuracy by the stepwise feature selection method. Each dot indicates a combination of features. The combination with the minimum MAE and maximum R^2 has been listed.

In order to clarify whether the accuracy of other ML models will be higher than that of GB model after dimensionality reduction, we also performed RFE (combining features importance ranking) for other ML models in Fig. S7. The results indicated that the GB model remains to exhibit the highest accuracy. For KNN, GP, MLP and SVR models, we adopted the analysis framework of SHAP (Shapley Additive exPlanation) to interpret the importance of each feature and performed feature importance ranking.

Table S1 Average bond distance (Å) between TM atom and coordination atoms on TM-N-C, TM-C, TM-MOF and TM-COF catalysts.

TM	TM-N-C	TM-C	TM-MOF	TM-COF
Sc	2.08	2.20	2.13	2.14
Ti	1.98	2.07	2.01	2.11
V	1.96	2.02	2.00	2.08
Cr	1.95	2.01	1.98	2.04
Mn	1.91	2.00	1.93	2.08
Fe	1.89	1.96	1.89	1.96
Co	1.87	1.94	1.85	2.00
Ni	1.87	1.88	1.85	2.00
Cu	1.93	1.91	1.99	2.08
Zn	1.96	1.95	2.03	2.02
Y	2.20	2.32	2.27	2.26
Zr	2.13	2.17	2.16	2.19
Nb	2.06	2.09	2.08	2.13
Mo	2.02	2.07	2.05	2.10
Tc	1.98	2.04	2.02	2.05
Ru	1.96	2.02	1.97	2.02
Rh	1.95	2.02	1.98	2.03
Pd	1.96	1.96	1.98	2.14
Ag	2.01	1.99	2.25	2.31
Cd	2.21	2.04	2.22	2.21
Hf	1.87	2.16	2.13	2.16
Ta	2.04	2.10	2.05	2.10
W	1.99	2.05	2.02	2.07
Re	1.99	2.04	2.02	2.05
Os	1.95	2.02	1.97	2.01
Ir	1.95	2.01	1.97	2.14
Pt	1.96	1.97	1.98	2.09
Au	1.97	2.00	1.99	2.27

Table S2 Average bond distance (Å) between TM atom and coordination atoms on TM-Pc, TM-GDY, TM-C_2N and TM-C_3N_4 catalysts.

System	TM-Pc	TM-GDY	TM-C_2N	TM-C_3N_4
Sc	2.06	2.18	2.67	2.35
Ti	2.00	2.11	2.68	2.33
V	2.00	1.99	2.75	2.33
Cr	1.98	1.96	2.75	2.38
Mn	1.95	1.96	2.73	2.38
Fe	1.93	1.95	2.75	2.36
Co	1.92	1.94	2.79	2.43
Ni	1.91	1.95	2.80	2.43
Cu	1.96	2.04	2.80	2.39
Zn	2.00	2.11	2.79	2.38
Y	2.10	2.32	2.64	2.36
Zr	2.12	2.22	2.64	2.35
Nb	2.04	2.16	2.64	2.33
Mo	2.03	2.06	2.73	2.32
Tc	2.00	2.05	2.73	2.37
Ru	1.99	2.05	2.77	2.41
Rh	1.97	2.04	2.77	2.37
Pd	1.99	2.07	2.78	2.41
Ag	2.06	2.16	2.74	2.43
Cd	2.11	2.22	2.71	2.41
Hf	2.08	2.24	2.64	2.34
Ta	2.03	2.16	2.63	2.32
W	2.03	2.05	2.73	2.31
Re	2.00	2.05	2.72	2.28
Os	1.99	2.03	2.77	2.41
Ir	1.97	2.03	2.78	2.44
Pt	1.99	2.06	2.78	2.42
Au	2.01	2.13	2.74	2.44

Table S3 The calculated E_f (eV) and U_{diss} for 3*d*, 4*d* and 5*d* TM embedding in N-C, C, C_3N_4 and MOF.

	TM-N-C		TM-C		TM-C_3N_4		TM-MOF	
TM	**E_f**	**U_{diss}**	**E_f**	**U_{diss}**	**E_f**	**U_{diss}**	**E_f**	**U_{diss}**
Sc	-4.15	-0.70	-3.13	-1.04	-2.57	-1.22	-5.73	-0.17
Ti	-2.69	-0.28	-3.86	0.30	-1.14	-1.06	-4.75	0.75
V	-2.18	-0.09	-2.76	0.20	0.11	-1.23	-3.97	0.80
Cr	-2.84	0.51	-2.85	0.52	0.75	-1.29	-3.86	1.02
Mn	-2.87	0.25	-3.08	0.35	0.55	-1.46	-3.87	0.75
Fe	-2.42	0.76	-2.70	0.90	1.48	-1.19	-3.24	1.17
Co	-2.75	1.09	-2.80	1.12	1.69	-1.13	-3.45	1.44
Ni	-2.85	1.17	-3.13	1.31	1.58	-1.05	-3.14	1.31
Cu	-1.63	1.16	-3.17	1.92	1.51	-0.41	-2.20	1.44
Zn	-2.51	0.50	-3.38	0.93	1.09	-1.30	-3.35	0.92
Y	-4.04	-1.02	-2.94	-1.39	-3.05	-1.35	-5.50	-0.54
Zr	-2.67	-0.78	-4.03	-0.44	-1.71	-1.02	-5.09	-0.18
Nb	-1.17	-0.71	-0.05	-1.08	0.05	-1.12	-3.20	-0.03
Mo	-0.02	-0.19	-2.45	0.62	1.97	-0.86	-2.54	0.65
Tc	-0.46	0.63	-2.83	1.82	2.95	-1.07	-2.25	1.53
Ru	-0.76	0.84	-2.99	1.96	3.03	-1.06	-2.32	1.62
Rh	-1.93	1.57	-2.93	2.07	2.56	-0.68	-3.12	2.16
Pd	-2.51	2.20	-2.67	2.29	1.81	0.05	-3.06	2.48
Ag	0.24	0.56	-2.17	2.97	1.12	-0.32	-1.37	2.17
Cd	-0.73	-0.03	-2.04	0.62	0.88	-0.84	-2.38	0.79
Hf	-2.67	-0.88	-3.74	-0.62	-1.39	-1.20	-4.55	-0.41
Ta	-0.80	-0.33	-3.02	0.41	0.86	-0.89	-3.22	0.47
W	0.80	-0.17	-2.06	0.79	3.05	-0.92	-1.88	0.73
Re	0.55	0.12	-2.30	1.07	4.06	-1.05	-1.59	0.83
Os	-0.09	0.85	-2.67	1.17	4.42	0.29	-2.17	1.11
Ir	-1.63	1.70	-3.07	2.18	3.27	0.07	-3.06	2.18
Pt	-2.85	2.61	-4.16	3.26	2.91	-0.28	-3.60	2.98
Au	0.18	1.44	-3.31	2.60	3.09	0.47	-0.84	1.78

Table S4 The calculated E_f (eV) and U_{diss} for 3*d*, 4*d* and 5*d* TM embedding in C_2N, COF, Pc and GDY.

	TM-C_2N		TM-COF		TM-Pc		TM-GDY	
TM	E_f	U_{diss}	E_f	U_{diss}	E_f	U_{diss}	E_f	U_{diss}
Sc	-3.59	-0.88	-0.50	-1.91	-6.74	0.17	1.62	-2.62
Ti	-1.82	-0.72	0.53	-1.89	-6.02	1.38	1.89	-2.58
V	-0.65	-0.86	0.98	-1.67	-5.98	1.81	2.69	-2.53
Cr	-0.35	-0.73	1.17	-1.49	-5.89	2.03	2.16	-1.99
Mn	-0.45	-0.97	1.20	-1.79	-5.62	1.62	0.87	-1.62
Fe	0.51	-0.70	2.03	-1.47	-4.99	2.05	0.86	-0.88
Co	0.74	-0.65	1.61	-1.09	-5.09	2.26	-0.03	-0.27
Ni	0.56	-0.54	1.38	-0.95	-5.26	2.37	2.55	-1.53
Cu	0.51	0.08	1.44	-0.38	-4.15	2.41	0.65	0.02
Zn	-0.19	-0.67	1.13	-1.32	-5.17	1.83	1.91	-1.72
Y	-4.91	-0.73	-0.58	-2.18	-7.85	0.25	2.77	-3.29
Zr	-2.72	-0.77	0.69	-1.62	-5.48	-0.08	3.20	-2.25
Nb	-0.72	-0.86	2.02	-1.77	-4.14	0.28	3.62	-2.31
Mo	0.74	-0.45	2.61	-1.07	-3.79	1.06	2.31	-0.97
Tc	1.32	-0.26	2.80	-1.00	-3.78	2.29	3.72	-1.46
Ru	1.53	-0.30	2.35	-0.71	-3.74	2.33	3.17	-1.13
Rh	0.77	0.21	1.54	-0.17	-4.62	2.91	1.96	-0.38
Pd	0.38	0.76	1.35	0.28	-5.42	3.66	0.73	0.59
Ag	-0.31	1.11	1.30	-0.50	-2.86	3.66	1.86	-1.06
Cd	-0.78	-0.01	1.61	-1.20	-3.43	1.31	3.15	-1.97
Hf	-2.27	-0.98	0.93	-1.78	-5.17	-0.26	3.28	-2.37
Ta	-0.05	-0.58	2.68	-1.49	-4.06	0.75	4.12	-1.97
W	2.03	-0.58	3.86	-1.19	-3.05	1.12	5.16	-1.62
Re	2.65	-0.58	4.16	-1.09	-2.97	1.29	4.56	-1.22
Os	2.61	0.51	3.34	0.42	-3.15	1.23	3.75	0.37
Ir	1.52	0.65	2.31	0.39	-4.51	2.66	2.30	0.39
Pt	1.27	0.55	1.83	0.27	-5.88	4.12	0.84	0.76
Au	1.47	1.01	2.70	0.60	-2.71	2.40	2.55	0.65

Table S5 Bond distance ($d_{H\text{-}TM}$ in Å) between adsorbed hydrogen and TM atom, magnetic moment (M in μ_B) for H-adsorbed systems, and the hydrogen adsorption Gibbs free energies (ΔG_{H^*} in eV) for the TM-N-C and TM-C catalysts.

	TM-N-C			TM-C		
System	$\mathbf{d_{H\text{-}TM}}$	**M**	$\mathbf{\Delta G_{H^*}}$	$\mathbf{d_{H\text{-}TM}}$	**M**	$\mathbf{\Delta G_{H^*}}$
Sc	2.38	0.00	0.28	2.65	0.00	0.92
Ti	1.74	0.39	-0.75	2.40	0.00	0.49
V	1.66	0.57	0.09	1.66	0.00	-0.09
Cr	1.6	2.71	0.24	1.58	2.14	0.26
Mn	1.55	2.21	0.35	1.57	2.19	0.32
Fe	1.49	0.94	0.17	1.47	2.72	0.32
Co	1.44	0.00	0.11	1.44	0.98	0.23
Ni	1.52	0.04	1.60	1.69	0.20	-0.47
Cu	1.56	0.45	1.70	1.89	0.00	-0.35
Zn	1.56	0.00	0.98	1.64	0.00	1.85
Y	2.04	0.00	-0.10	2.80	0.14	1.09
Zr	2.35	0.00	-0.90	1.91	0.00	0.68
Nb	1.81	0.00	-0.76	1.79	0.00	-0.30
Mo	1.7	1.06	-0.50	1.73	0.88	-0.23
Tc	1.62	1.70	-0.32	1.71	0.82	0.13
Ru	1.58	0.51	-0.51	1.66	0.00	0.26
Rh	1.53	0.00	-0.23	1.60	0.00	0.03
Pd	1.62	0.00	1.88	1.51	0.00	0.24
Ag	1.62	0.00	0.92	2.07	0.00	-0.29
Cd	1.69	0.00	0.04	1.80	0.00	2.10
Hf	1.87	0.00	-1.15	2.36	0.00	0.22
Ta	1.79	0.00	-1.07	1.79	0.00	-0.78
W	1.72	0.91	-1.17	1.75	0.00	-0.60
Re	1.64	1.69	-0.70	1.72	0.91	-0.34
Os	1.60	1.00	-0.63	1.70	0.00	-0.07
Ir	1.56	0.00	-0.35	1.63	0.00	-0.33
Pt	1.60	0.00	1.54	1.53	0.10	0.27
Au	1.92	0.10	2.20	1.58	0.00	1.57

Table S6 Bond distance ($d_{H\text{-}TM}$ in Å) between adsorbed hydrogen and TM atom, magnetization values (M in μ_B) for H-adsorbed systems, and the hydrogen adsorption Gibbs free energies (ΔG_{H^*} in eV) for the TM-MOF and TM-COF catalysts.

	TM-MOF			TM-COF		
System	$d_{H\text{-}TM}$	**M**	ΔG_{H^*}	$d_{H\text{-}TM}$	**M**	ΔG_{H^*}
Sc	2.43	0.00	2.13	2.37	0.00	-0.38
Ti	1.70	0.11	-0.49	1.74	3.09	-0.49
V	1.65	1.33	0.08	1.66	2.11	-0.02
Cr	1.59	2.32	0.28	1.66	3.22	-0.12
Mn	1.52	2.38	0.21	1.64	4.04	-0.14
Fe	1.49	0.96	-0.06	1.56	1.78	-0.47
Co	1.45	0.00	-0.03	1.51	1.26	-0.10
Ni	1.49	0.00	0.91	1.48	0.16	-0.09
Cu	1.55	0.20	1.54	1.50	0.00	-0.02
Zn	2.40	0.00	2.53	1.53	0.01	0.71
Y	2.63	0.00	2.25	2.54	0.20	-0.74
Zr	1.67	0.22	-0.61	1.84	0.34	-0.85
Nb	1.76	0.05	-0.86	1.75	0.00	-0.89
Mo	1.69	1.12	-0.41	1.68	1.46	-0.49
Tc	1.63	1.24	-0.42	1.62	0.04	-0.80
Ru	1.58	0.29	-0.43	1.57	0.12	-0.54
Rh	1.53	0.00	0.03	1.61	0.00	-0.20
Pd	1.60	0.00	1.40	1.56	0.04	-0.25
Ag	1.61	0.00	1.12	1.62	0.00	0.11
Cd	1.73	0.00	1.64	3.47	0.00	1.32
Hf	2.25	1.52	-0.45	2.31	0.59	-1.05
Ta	1.76	0.01	-1.21	1.74	0.00	-1.11
W	1.71	0.86	-1.30	1.69	1.26	-0.72
Re	1.65	1.06	-0.73	1.65	1.27	-1.05
Os	1.60	0.34	-0.23	1.60	0.17	-0.69
Ir	1.56	0.00	-0.11	1.63	0.00	-0.87
Pt	1.57	0.00	1.10	1.58	0.00	-0.64
Au	1.65	0.00	1.50	1.57	0.00	-0.21

Table S7 Bond distance ($d_{H\text{-}TM}$ in Å) between adsorbed hydrogen to TM atom, magnetization values (M in μ_B) for H-adsorbed systems, and the hydrogen adsorption Gibbs free energies (ΔG_{H^*} in eV) for the TM-Pc and TM-GDY catalysts.

	TM-Pc			**TM-GDY**		
System	$\mathbf{d_{H\text{-}TM}}$	**M**	$\mathbf{\Delta G_{H^*}}$	$\mathbf{d_{H\text{-}TM}}$	**M**	$\mathbf{\Delta G_{H^*}}$
Sc	2.71	0.00	2.10	3.74	0.00	1.04
Ti	2.60	0.00	0.59	3.60	0.00	1.10
V	1.64	1.50	0.44	1.68	0.00	-1.98
Cr	1.58	2.62	0.45	1.61	0.00	-0.75
Mn	1.51	2.32	0.53	1.54	1.69	0.06
Fe	1.47	1.02	0.43	1.48	1.06	0.10
Co	1.43	0.00	0.07	1.43	0.00	0.06
Ni	1.65	0.33	1.94	1.44	0.00	1.46
Cu	1.68	0.72	2.08	1.56	0.17	1.93
Zn	1.70	0.11	2.13	1.53	0.00	-0.73
Y	2.82	0.01	0.98	3.98	0.00	-0.26
Zr	1.87	0.02	-0.99	1.92	1.00	0.22
Nb	1.77	0.75	-0.69	1.83	0.00	-2.97
Mo	1.69	1.88	-0.41	1.74	0.00	-2.12
Tc	1.61	1.58	-0.47	1.66	0.57	-1.75
Ru	1.57	0.51	-0.60	1.59	0.58	-1.11
Rh	1.51	0.00	-0.68	1.53	0.00	-0.73
Pd	1.82	0.25	1.99	1.52	0.00	1.19
Ag	1.82	0.59	2.10	1.42	0.00	0.29
Cd	1.7	0.00	2.39	1.41	0.00	-1.70
Hf	1.84	0.00	-1.60	1.89	0.00	-0.56
Ta	1.75	0.36	-0.96	1.82	0.00	-2.33
W	1.70	1.49	-0.76	1.75	0.00	-2.54
Re	1.63	1.49	-0.82	1.68	0.42	-2.25
Os	1.59	0.59	-0.83	1.61	0.52	-1.32
Ir	1.55	0.00	-0.79	1.56	0.00	-0.77
Pt	1.62	0.18	1.77	1.54	0.00	0.89
Au	1.97	0.10	2.21	1.51	0.00	-0.53

Table S8 Bond distance ($d_{H\text{-}TM}$ in Å) between adsorbed hydrogen and TM atom, magnetization values (M in μ_B) for H-adsorbed systems, and the hydrogen adsorption Gibbs free energies (ΔG_{H^*} in eV) for the TM-C_2N and TM-C_3N_4 catalysts.

	TM-C_2N			**TM-C_3N_4**		
System	**$d_{H\text{-}TM}$**	**M**	**ΔG_{H^*}**	**$d_{H\text{-}TM}$**	**M**	**ΔG_{H^*}**
Sc	2.38	0.33	-0.45	2.13	0.00	-0.25
Ti	1.82	2.32	0.05	1.7	0.83	-0.52
V	1.64	2.08	0.06	1.63	1.91	-0.33
Cr	1.6	2.93	0.45	1.59	2.91	-0.10
Mn	1.64	4.21	0.32	1.66	4.36	-0.22
Fe	1.58	3.27	0.28	1.61	3.52	-0.12
Co	1.51	1.81	0.35	1.53	1.79	0.34
Ni	1.51	1.07	0.50	1.52	1.08	0.02
Cu	1.50	0.00	0.58	1.50	0.00	-0.32
Zn	1.53	0.00	-0.22	1.52	0.00	-1.00
Y	2.59	0.06	0.32	1.95	0.00	-0.64
Zr	1.81	0.21	-0.58	1.83	0.00	-0.97
Nb	1.72	0.00	-0.57	1.74	1.15	-0.73
Mo	1.67	1.71	-0.37	1.66	0.26	-0.53
Tc	1.60	1.41	-0.51	1.61	0.99	-0.54
Ru	1.56	0.00	-0.65	1.56	0.10	-0.80
Rh	1.54	0.00	0.14	1.52	0.00	-0.61
Pd	1.53	0.00	0.83	1.54	0.00	0.05
Ag	1.64	0.00	1.24	1.62	0.00	-0.11
Cd	1.72	0.00	0.21	1.71	0.00	1.05
Hf	1.79	0.13	-0.80	1.8	0.00	-1.18
Ta	1.72	0.00	-0.86	1.73	0.80	-0.99
W	1.68	1.15	-0.76	1.67	0.00	-0.82
Re	1.63	1.51	-0.92	1.61	0.00	-1.32
Os	1.59	0.00	-0.79	1.58	0.02	-0.97
Ir	1.58	0.00	-0.35	1.61	0.00	-0.64
Pt	1.56	0.00	-0.47	1.57	0.00	-1.44
Au	1.57	0.00	0.01	1.57	0.00	-1.90

Table S9 The comparison in the values of ΔG_H^* on TM-N-C between our DFT-calculation results and previous DFT-calculation results.

	ΔG_H^* (eV)			
TM	**This work**	**Ref. 1**	**Ref. 2**	**Ref. 3**
Sc	0.28	-0.34	-0.28	-0.19
Ti	-0.75	-0.53	-0.53	-0.50
V	0.09	-0.13	-0.15	-0.27
Cr	0.24	0.32	0.28	0.31
Mn	0.35	0.53	0.39	0.43
Fe	0.17	0.44	0.28	0.25
Co	0.11	0.32	0.16	0.15
Ni	1.60	1.61	1.61	1.59
Cu	1.70	1.31	1.72	1.68
Zn	0.98	1.15	0.85	0.76
Y	-0.10	-0.22	-0.12	Not given
Zr	-0.9	-0.90	-0.90	-0.90
Nb	-0.76	-0.74	-0.89	-0.76
Mo	-0.50	-0.37	-0.44	-0.91
Tc	-0.32	-0.36	-0.46	-0.46
Ru	-0.51	-0.43	-0.56	-0.56
Rh	-0.23	-0.07	-0.26	-0.17
Pd	1.88	1.57	1.85	1.84
Ag	0.92	0.36	0.82	0.73
Cd	0.04	-0.06	0.02	-0.06
Hf	-1.15	-1.09	-1.13	-1.04
Ta	-1.07	-1.00	-1.08	-1.08
W	-1.17	-0.82	-0.93	-1.45
Re	-0.7	-0.83	-0.8	-0.91
Os	-0.63	-0.66	-0.7	-0.73
Ir	-0.35	-0.21	-0.37	-0.30
Pt	1.54	1.68	1.51	1.49
Au	2.20	1.71	2.16	2.24

Table S10 The selected input features obtained from the Mendeleev's periodic table and simple DFT calculation.

Feature	Description
M	Atomic mass
R_{COV}	Covalent radius
Z	Atomic number
N_P	Period number
N_G	Group number
R	Atomic radius of the TM atom
χ	Pauling electronegativity
I_1	First ionization potential
I_2	Second ionization potential
V_{en}	Valance electrons
e_d	Electrons number of d orbital
ε_d(TM)	The d-band center of the corresponding pure metal surface of TM atom
H_{xf}	Enthalpy of hydride formation
χ	Average distance between TM atom and the coordination atoms The product of Pauling electronegativity of TM atom and bond length between TM and coordination atoms
N_c	The number of coordination atoms. (N_c = 4 for N-C, C, Pc, MOF, N_c = 3 for COF, N_c = 4/6 for C_3N_4, C_2N, and N_c = 6 for GDY supports. Though for C_3N_4 and C_2N supports, the results of RDF indicated that the coordination atoms may be 2.02 or 6, Weighing the computational cost (it is difficult to perform *ab initio* molecular dynamics for all systems) and considering the results of CDD, the charge transferring of TM to 4N/6N were observed, finally we adopted the N_c = 4/6 for C_2N and C_3N_4 systems.)
Z_c	Atomic number of coordination atoms
I_c	First ionization potential of coordination atoms
I_1-I_c	The difference in first ionization potential between TM and coordination atoms
χ_c	The Pauling electronegativity of coordination atoms
χ_{TM}-χ_X	The difference in Pauling electronegativity of metal atoms and coordination atoms
ε_d	The d-band center of the metal in system
θ_d	Electrons number of unfilled d orbital
cm_1 to cm_{231}	Coulomb matrix elements based on DFT optimized geometries

Table S11 The reaction free energies (eV) of elementary step for OER on TM-C_3N_4, TM-C_2N, TM-COF, TM-MOF, TM-Pc, TM-N-C and TM-C (TM = Cr, Mn, Fe, Co, Ni, Cu). The value highlighted in red indicates the PDS.

System		ΔG_1	ΔG_2	ΔG_3	ΔG_4
C_3N_4	Cr	-0.91	0.51	2.66	2.66
	Mn	-0.89	1.4	1.95	2.46
	Fe	-0.64	1.05	1.94	2.57
	Co	-0.56	1.07	2.00	2.41
	Ni	-0.41	1.49	1.65	2.19
	Cu	-0.69	2.24	1.10	2.27
C_2N	Cr	-0.34	0.58	2.40	2.28
	Mn	-0.18	1.23	2.08	1.79
	Fe	-0.15	1.19	2.04	1.84
	Co	0.00	1.12	1.85	1.95
	Ni	0.44	1.57	1.43	1.48
	Cu	0.75	1.94	1.10	1.13
COF	Cr	-1.00	0.95	2.29	2.68
	Mn	-0.78	0.90	2.45	2.35
	Fe	-0.98	0.74	2.65	2.51
	Co	-0.35	1.25	1.52	2.50
	Ni	-0.21	1.52	1.65	1.96
	Cu	-0.02	1.92	1.25	1.77
MOF	Cr	0.08	0.05	2.92	1.87
	Mn	0.33	0.67	2.47	1.45
	Fe	0.29	1.08	1.97	1.58
	Co	0.88	1.52	1.39	1.13
	Ni	1.46	1.94	1.05	0.47
	Cu	1.73	2.11	0.78	0.30
Pc	Cr	0.27	0.32	2.83	1.50
	Mn	0.75	0.72	2.56	0.89
	Fe	0.90	0.71	2.16	1.15
	Co	1.39	1.42	1.44	0.67
	Ni	2.29	2.17	0.52	-0.06
	Cu	2.54	2.23	0.26	-0.11
N-C	Cr	-0.11	-0.01	3.15	1.89
	Mn	0.48	0.45	2.69	1.30
	Fe	0.49	0.81	2.11	1.51
	Co	0.96	1.69	1.23	1.04
	Ni	2.03	2.17	0.62	0.10
	Cu	1.88	2.23	0.71	0.10
C	Cr	-0.98	0.25	3.05	2.60
	Mn	-0.49	0.20	3.04	2.17

	Fe	0.10	0.14	2.75	1.93
	Co	0.16	0.92	2.05	1.79
	Ni	1.43	1.48	1.56	0.45
	Cu	2.35	2.02	0.61	-0.06
GDY	Cr	-1.88	-0.56	4.07	3.29
	Mn	-0.12	-0.11	3.26	1.89
	Fe	0.32	0.71	2.38	1.51
	Co	1.11	1.08	1.87	0.86
	Ni	-0.69	1.90	0.92	2.79
	Cu	1.97	1.81	1.06	0.08

Table S12 Calculated overpotentials for OER (η^{OER}) and the corresponding PDS on TM-C_3N_4, TM-C_2N, TM-COF, TM-MOF, TM-Pc, TM-N-C and TM-C (TM = Cr, Mn, Fe, Co, Ni, Cu).

System		PDS	η^{OER} (V)
C_3N_4	Cr	③O* → OOH*	1.43
	Mn	④OOH* → O_2	1.23
	Fe	④OOH* → O_2	1.34
	Co	④OOH* → O_2	1.18
	Ni	④OOH* → O_2	0.96
	Cu	④OOH* → O_2	1.04
C_2N	Cr	③O* → OOH*	1.17
	Mn	③O* → OOH*	0.85
	Fe	③O* → OOH*	0.81
	Co	④OOH* → O_2	0.72
	Ni	②OH* → O*	0.34
	Cu	②OH* → O*	0.71
COF	Cr	④OOH* → O_2	1.45
	Mn	③O* → OOH*	1.22
	Fe	③O* → OOH*	1.42
	Co	④OOH* → O_2	1.27
	Ni	④OOH* → O_2	0.73
	Cu	④OOH* → O_2	0.69
MOF	Cr	③O* → OOH*	1.69
	Mn	③O* → OOH*	1.24
	Fe	③O* → OOH*	0.74
	Co	②OH* → O*	0.29
	Ni	②OH* → O*	0.71
	Cu	②OH* → O*	0.88
Pc	Cr	③O* → OOH*	1.6
	Mn	③O* → OOH*	1.33
	Fe	③O* → OOH*	0.93
	Co	③O* → OOH*	0.21
	Ni	①H_2O → OH*	1.06
	Cu	①H_2O → OH*	1.31
N-C	Cr	③O* → OOH*	1.92
	Mn	③O* → OOH*	1.46
	Fe	③O* → OOH*	0.88
	Co	②OH* → O*	0.46
	Ni	②OH* → O*	0.94
	Cu	②OH* → O*	1.00
C	Cr	③O* → OOH*	1.82
	Mn	③O* → OOH*	1.81

	Fe	③O* → OOH*	1.52
	Co	③O* → OOH*	0.82
	Ni	③O* → OOH*	0.33
	Cu	①H_2O → OH*	1.12
GDY	Cr	③O* → OOH*	2.84
	Mn	③O* → OOH*	2.03
	Fe	③O* → OOH*	1.15
	Co	③O* → OOH*	0.64
	Ni	④OOH* → O_2	1.56
	Cu	①H_2O → OH*	0.74

Table S13 Calculated adsorption free energies of intermediate (ΔG_O* and ΔG_{OOH}*), and the reaction free energies (ΔG_1, ΔG_2, ΔG_3 and ΔG_4 in eV) of elementary step for OER (η^{OER}) on the SAC with 0.44 eV ≤ ΔG_{OH}* ≤ 1.46 eV.

System		ΔG_{OH*}(Ref. [4])	ΔG_{O*}	ΔG_{OOH*}	ΔG_1	ΔG_2	ΔG_3	ΔG_4
C_2N	Ni	0.44	2.01	3.44	0.44	1.57	1.43	1.48
	Cu	0.75	2.69	3.79	0.75	1.94	1.10	1.13
	Rh	0.60	1.81	3.39	0.60	1.21	1.58	1.53
	Pd	1.04	2.81	3.51	1.04	1.77	0.70	1.41
	Cd	0.55	-1.59	3.83	0.55	2.56	0.72	1.09
	Au	0.91	2.85	3.99	0.91	1.95	1.14	0.93
COF	Ag	0.45	2.78	3.68	0.45	2.33	0.90	1.24
MOF	Co	0.88	2.40	3.79	0.88	1.52	1.39	1.13
	Ni	1.46	3.40	4.45	1.46	1.94	1.05	0.47
	Zn	0.83	3.30	4.06	0.83	2.47	0.50	1.12
	Rh	1.25	2.81	4.20	1.25	1.56	1.34	0.77
	Cd	1.44	2.30	4.39	1.44	0.86	2.09	0.53
	Os	0.49	0.27	3.52	0.49	-0.23	3.25	1.40
	Ir	1.28	2.43	4.20	1.28	1.15	1.77	0.72
Pc	Mn	0.75	1.47	4.03	0.75	0.72	2.56	0.89
	Fe	0.90	1.61	3.77	0.9	0.71	2.16	1.15
	Co	1.39	2.81	4.25	1.39	1.42	1.44	0.67
	Rh	0.91	2.62	3.84	0.91	1.71	1.22	1.08
	Ir	0.96	2.42	3.94	0.96	1.46	1.52	0.98
GDY	Co	1.11	2.19	4.06	1.11	1.08	1.87	0.86
	Rh	0.79	1.91	3.57	0.79	1.11	1.67	1.35
	Ir	0.62	1.77	3.59	0.62	1.15	1.82	1.33
N-C	Mn	0.48	0.93	3.62	0.48	0.45	2.69	1.3
	Fe	0.49	1.30	3.41	0.49	0.81	2.11	1.51
	Co	0.96	2.65	3.88	0.96	1.69	1.23	1.04
	Rh	0.96	2.57	3.89	0.96	1.62	1.32	1.03
	Zn	0.91	3.44	4.13	0.91	2.53	0.69	0.79
	Ir	1.01	2.31	3.97	1.01	1.30	1.66	0.95
C	Ni	1.43	2.91	4.47	1.43	1.48	1.56	0.45
	Pd	1.22	2.89	4.27	1.22	1.67	1.38	0.65
	Pt	1.09	2.19	4.23	1.09	1.10	2.04	0.69

Table S14 Calculated PDS and the corresponding overpotentials for OER (η^{OER}) on the SAC with 0.44 eV ≤ ΔG_{OH}* ≤ 1.46 eV.

System		PDS	η^{OER}
C_2N	Ni	②OH* → O*	0.34
	Cu	②OH* → O*	0.71
	Rh	③O* → OOH*	0.35
	Pd	②OH* → O*	0.54
	Cd	②OH* → O*	1.33
	Au	②OH* → O*	0.72
COF	Ag	②OH* → O*	1.10
MOF	Co	②OH* → O*	0.29
	Ni	②OH* → O*	0.71
	Zn	②OH* → O*	1.24
	Rh	②OH* → O*	0.33
	Cd	③O* → OOH*	0.86
	Os	③O* → OOH*	2.02
	Ir	③O* → OOH*	0.54
Pc	Mn	③O* → OOH*	1.33
	Fe	③O* → OOH*	0.93
	Co	③O* → OOH*	0.21
	Rh	②OH* → O*	0.48
	Ir	③O* → OOH*	0.29
GDY	Co	③O* → OOH*	0.64
	Rh	③O* → OOH*	0.44
	Ir	③O* → OOH*	0.59
N-C	Mn	③O* → OOH*	1.46
	Fe	③O* → OOH*	0.88
	Co	②OH* → O*	0.46
	Rh	②OH* → O*	0.39
	Zn	②OH* → O*	1.30
	Ir	③O* → OOH*	0.43
C	Ni	③O* → OOH*	0.33
	Pd	②OH* → O*	0.44
	Pt	③O* → OOH*	0.81

Table S15 The comparison in the values of ΔG_{OH}*, ΔG_{O}* and ΔG_{OOH}* on Mn/Fe/Co/Rh/Zn/Ir-N-C and Ni/Pd/Pt-C between our DFT-calculation results and the previous DFT-calculation results.

Systems		ΔG_{OH}* (eV)		ΔG_{O}* (eV)		ΔG_{OOH}* (eV)	
		This work	**Ref. [1]**	**This work**	**Ref. [1]**	**This work**	**Ref. [1]**
N-C	**Mn**	0.48	0.37	0.93	0.82	3.62	3.53
	Fe	0.49	0.56	1.3	1.17	3.41	3.44
	Co	0.96	0.98	2.65	2.31	3.88	4.08
	Rh	0.96	0.96	2.57	2.37	3.89	3.90
	Zn	0.91	0.56	3.44	3.03	4.13	3.78
	Ir	1.01	1.04	2.31	2.07	3.97	3.97
C	**Ni**	1.43	0.88	2.91	2.23	4.47	3.79
	Pd	1.22	1.06	2.89	2.4	4.27	4.02
	Pt	1.09	1.01	2.19	1.99	4.23	4.23

Solvent effect

The effect of solvent on η^{OER}, η^{HER}, ΔG_H*, ΔG_O*, ΔG_{OH}* and ΔG_{OOH}* for the screened systems have been calculated by VASPsol,[5] a dielectric constant of 80 is set to simulate the water environment. The calculated results of ΔG_H* and η^{HER} with and without considering solvation correction have shown in Table S16. For the HER overpotentials, the solvent effect is found to be insignificant, and the η^{HER} for the screened SACs also can satisfy the activity criteria of $|\eta HER| \leq 0.15$ V after considering the solvent effect. In Table S17, we listed the η^{OER}, ΔG_O*, ΔG_{OH}* and ΔG_{OOH}* with and without considering solvation correction. Our results indicated that most of the ΔG_O*, ΔG_{OH}* and ΔG_{OOH}* decrease by ~0.20 eV after considering solvation correction, however, the values of η^{OER} is not changed significantly by solvation effects, the corrected values are at the range of -0.07 ~ 0.06 V.

Table S16 The calculated ΔG_H* for Co-N-C, Co-Pc, V/Fe/Co/Rh/Ir-MOF, and V/Tc/Rh/Os-C with (VASPsol) and without (VASP) considering solvation correction.

System	ΔG_H* (eV)		η^{HER} (V)	
	VASP	VASPsol	VASP	VASPsol
Co-N-C	0.11	0.15	-0.11	-0.15
Co-Pc	0.07	0.10	-0.07	-0.10
V-MOF	0.08	-0.05	-0.08	-0.05
Fe-MOF	-0.06	0.02	-0.06	-0.15
Co-MOF	-0.03	0.08	-0.03	-0.08
Rh-MOF	0.03	0.10	-0.03	-0.10
Ir-MOF	-0.11	-0.01	-0.11	-0.01
V-C	-0.09	0.02	-0.09	-0.02
Tc-C	0.13	0.12	-0.13	-0.12
Rh-C	0.03	0.04	-0.03	-0.04
Os-C	-0.07	0.01	-0.07	-0.01

Table S17 The calculated η^{OER}, ΔG_O*, ΔG_{OH}* and ΔG_{OOH}*for Co/Rh/Ir-MOF, Co/Rh/Ir-Pc, Co/Rh-N-C and Ni/Pd-C with (VASPsol) and without (VASP) considering solvation correction.

System	ΔG_{OH}* (eV)		ΔG_{O}* (eV)		ΔG_{OOH}* (eV)		η^{OER} (V)	
	VASP	VASPsol	VASP	VASPsol	VASP	VASPsol	VASP	VASPsol
Co-MOF	0.88	0.70	2.40	2.23	3.79	3.62	0.29	0.29
Rh-MOF	1.25	1.07	2.81	2.57	4.20	3.99	0.33	0.27
Ir-MOF	1.28	1.14	2.43	2.22	4.20	4.04	0.54	0.59
Co-Pc	1.39	1.27	2.81	2.73	4.25	4.13	0.21	0.23
Rh-Pc	0.91	0.66	2.62	2.44	3.84	3.55	0.48	0.55
Ir-Pc	0.96	0.71	2.42	2.20	3.94	3.66	0.29	0.23
Co-N-C	0.96	0.75	2.65	2.38	3.88	3.64	0.46	0.40
Rh-N-C	0.96	0.79	2.57	2.34	3.89	3.68	0.39	0.33
Ni-C	1.43	1.27	2.91	2.78	4.47	4.32	0.33	0.31
Pd-C	1.22	1.06	2.89	2.72	4.27	4.04	0.44	0.43

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