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Supporting information

Realizing High OER Activity in New SAC Catalysts Formed by Introducing TMN_x (x=3 and 4) Units into Carbon Nanotube under High-Throughput Calculations

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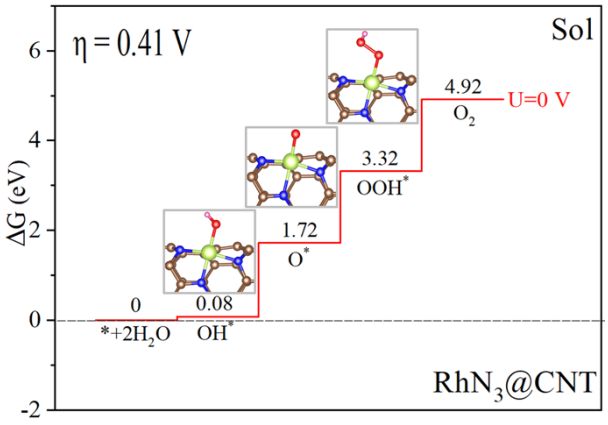

Fig. S1 The free energy diagram of OER in solvation for the sampled RhN_3@CNT.

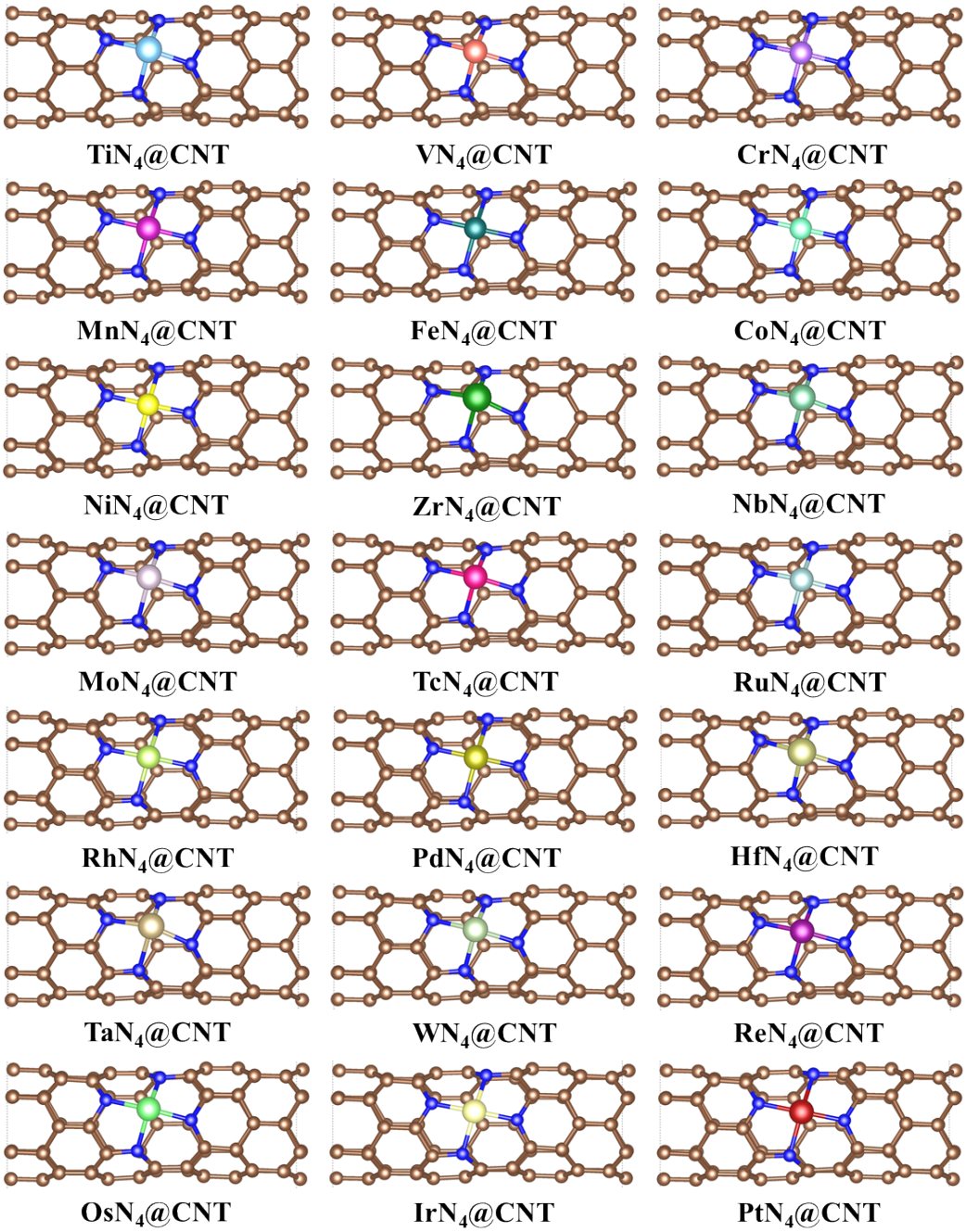

Fig. S2 The optimized structures of TMN_4@CNT (TM = Ti, V, Cr, Mn, Fe, Co, Ni, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Hf, Ta, W, Re, Os, Ir and Pt).

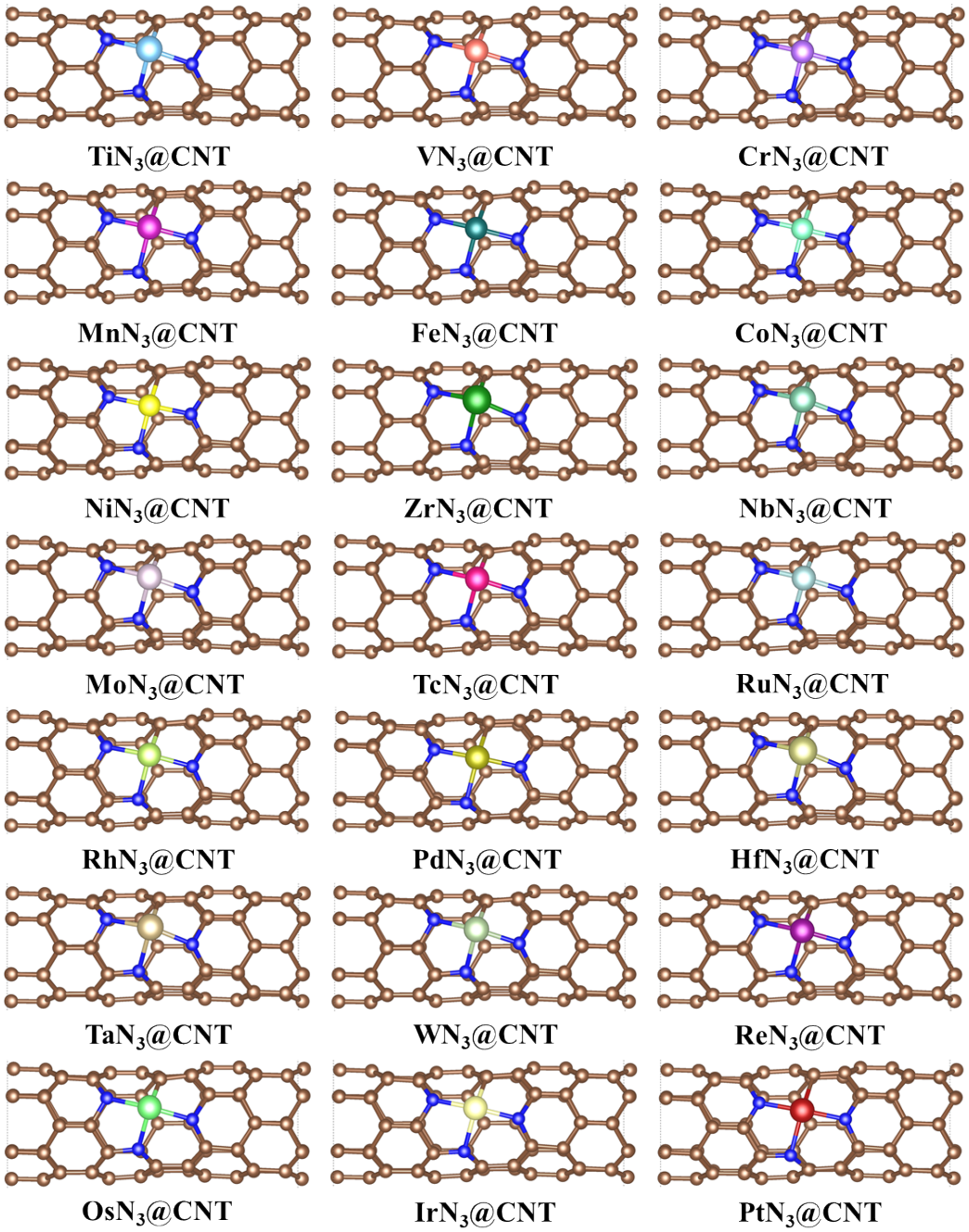

Fig. S3 The optimized structures of TMN_3@CNT (TM = Ti, V, Cr, Mn, Fe, Co, Ni, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Hf, Ta, W, Re, Os, Ir and Pt).

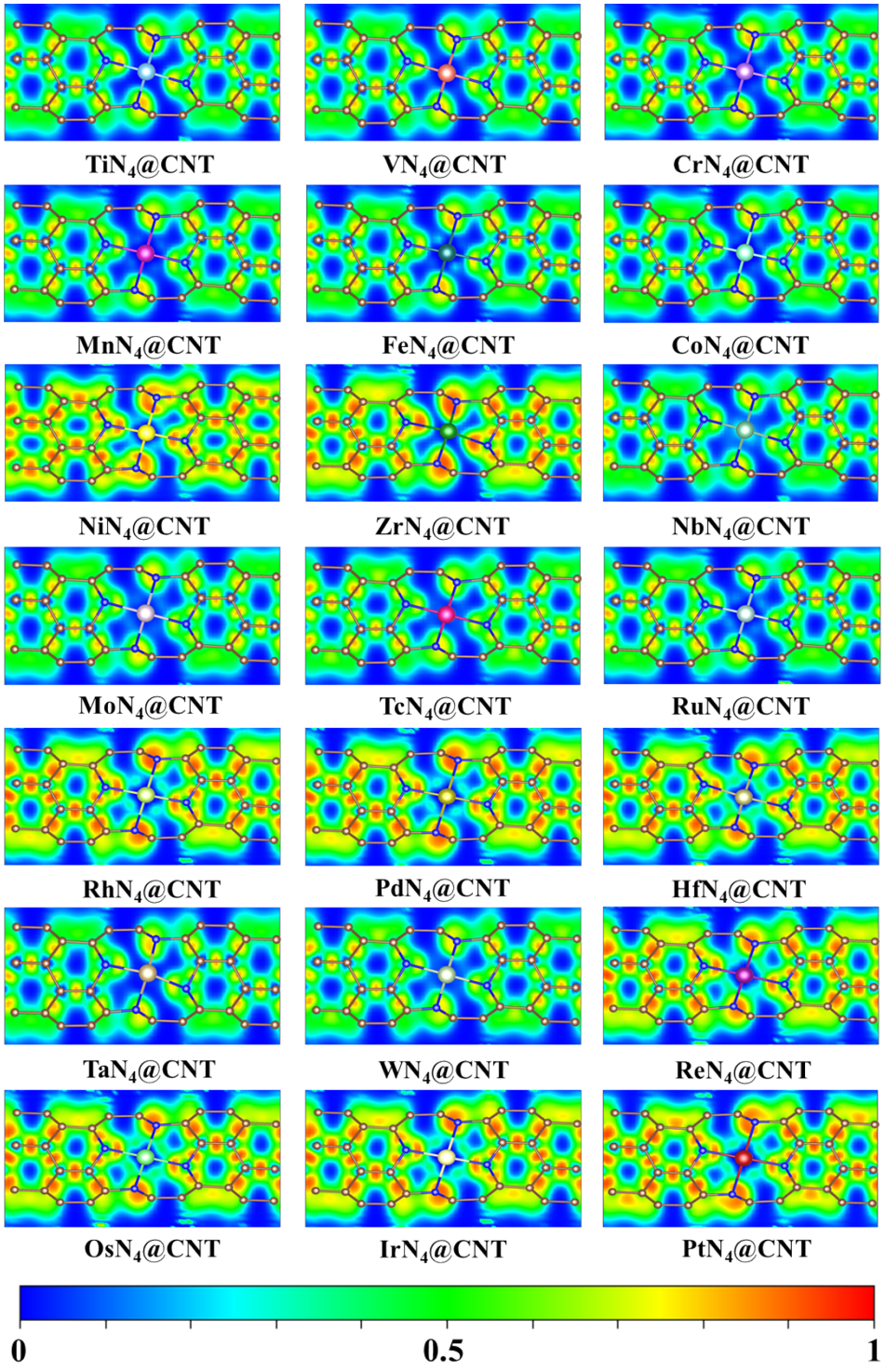

Fig. S4 Plots of electron location function (ELF) for TMN_4@CNT systems. Note that ELF can be characterized in the form of a contour plot within a range of 0-1. The region close to 1 indicates the presence of covalent electrons or lone-pair electrons; the region of 0.5 represents homogenous electron gas; and the region near to 0 suggests a low electron density area.

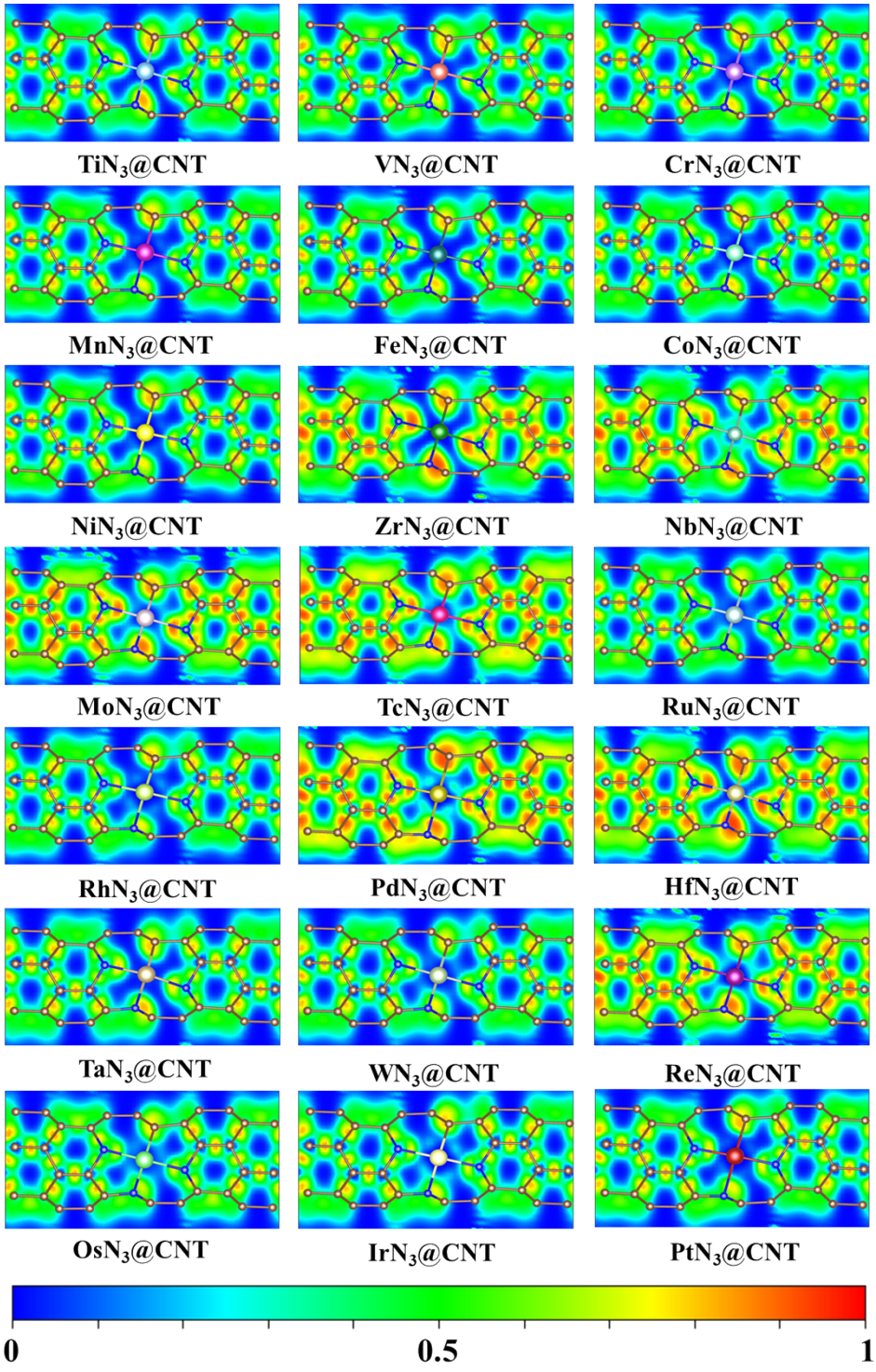

Fig. S5 Plots of electron location function for TMN_3@CNT systems.

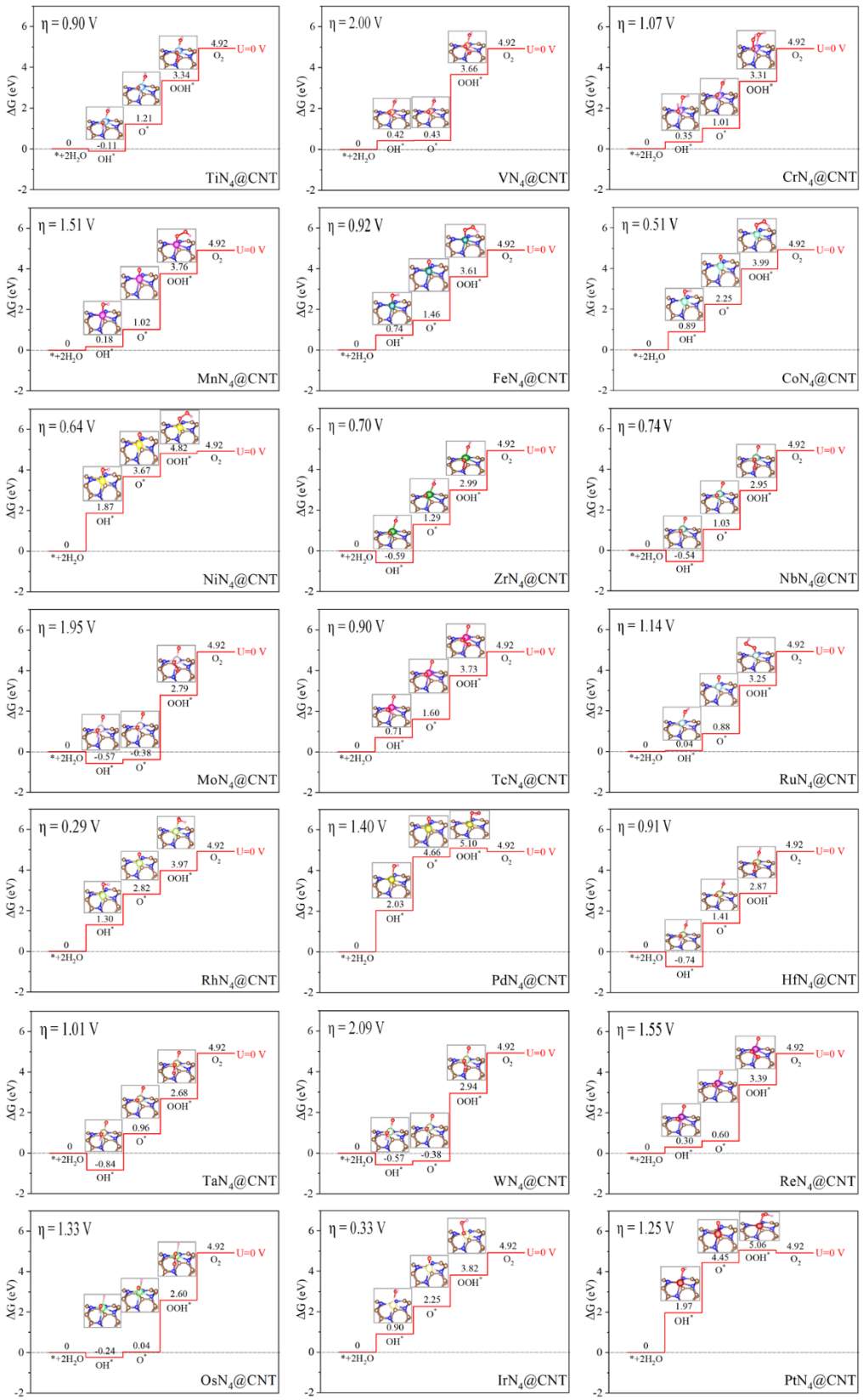

Fig. S6 Gibbs free energy diagram of OER for TMN_4@CNT series.

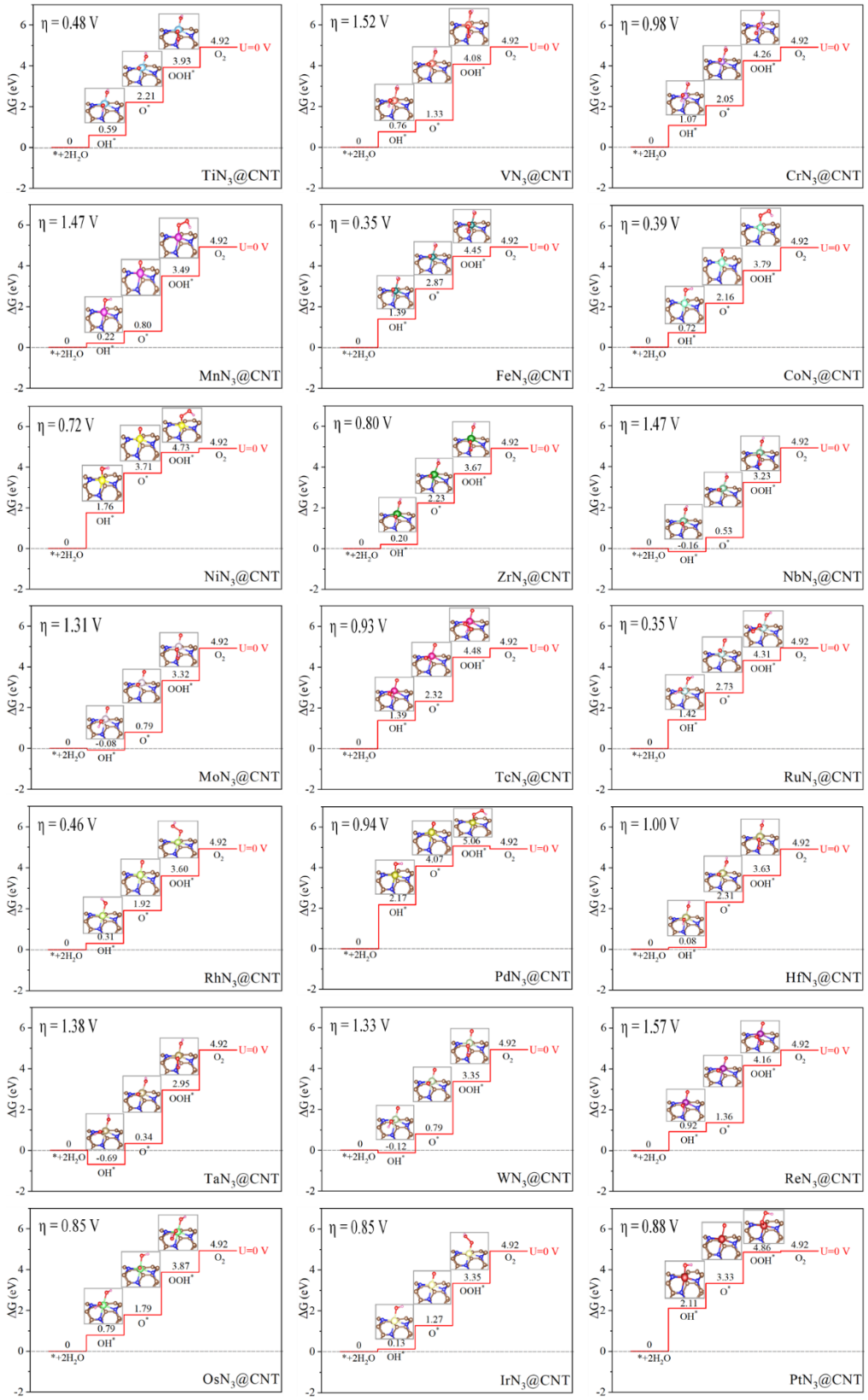

Fig. S7 Gibbs free energy diagram of OER for TMN_3@CNT series.

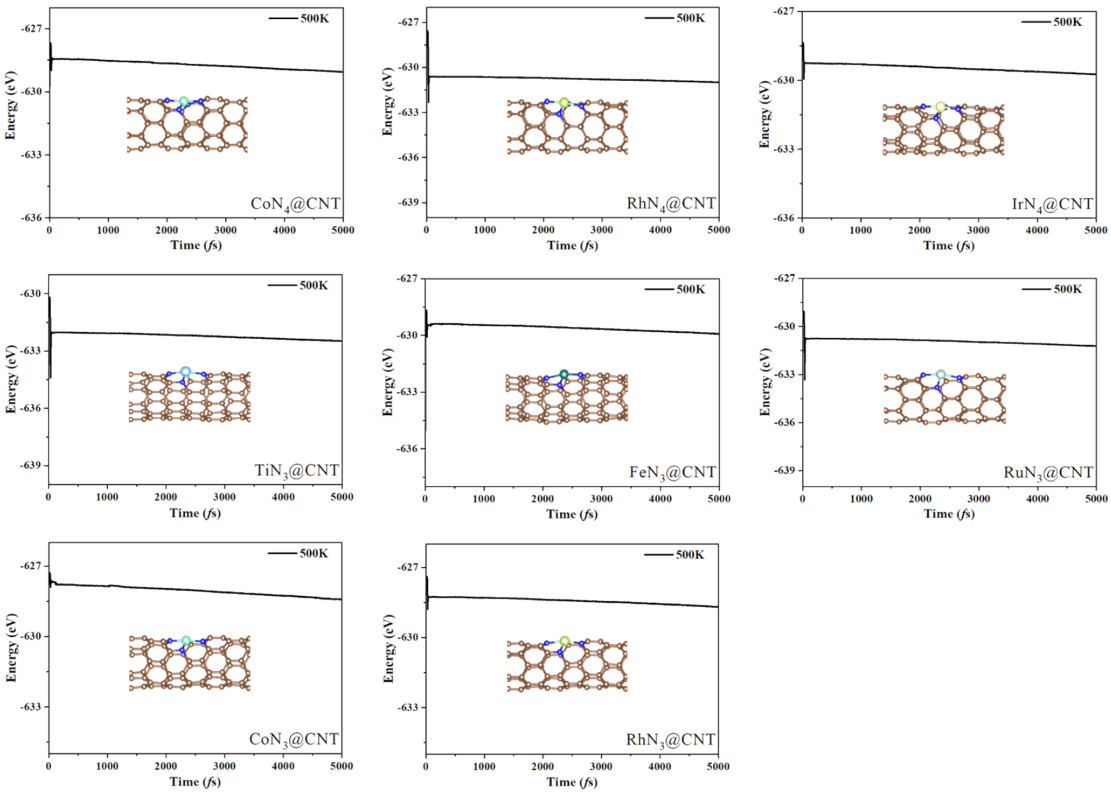

Fig. S8 Ab initio molecular dynamics simulation for the TMN_x@CNT (x = 3 and 4) systems with high OER catalytic activity and their corresponding morphologies after 5000 *f*s at T=500 K.

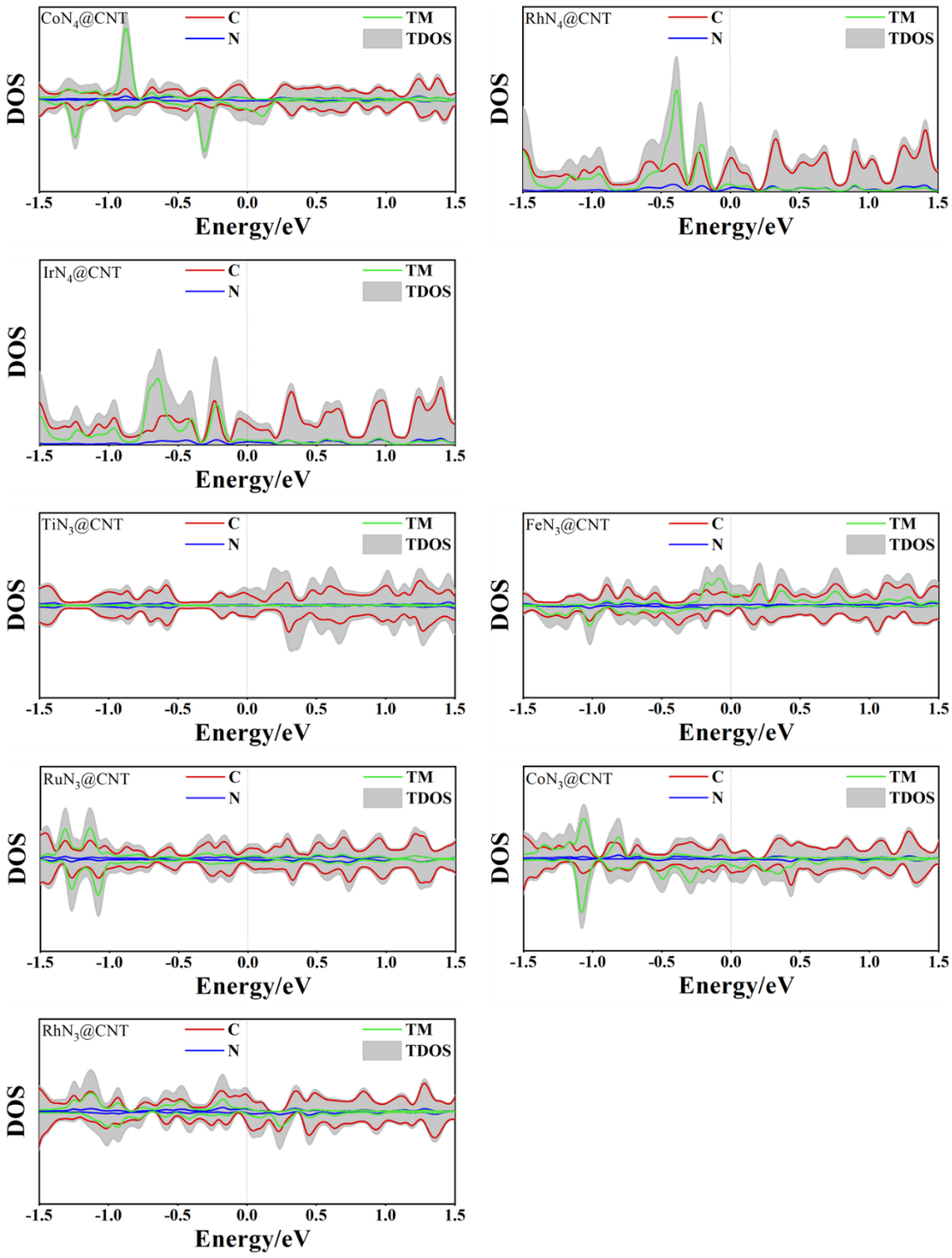

Fig. S9 Density of states for TMN_x@CNT (x = 3 and 4) systems with high OER catalytic activity.

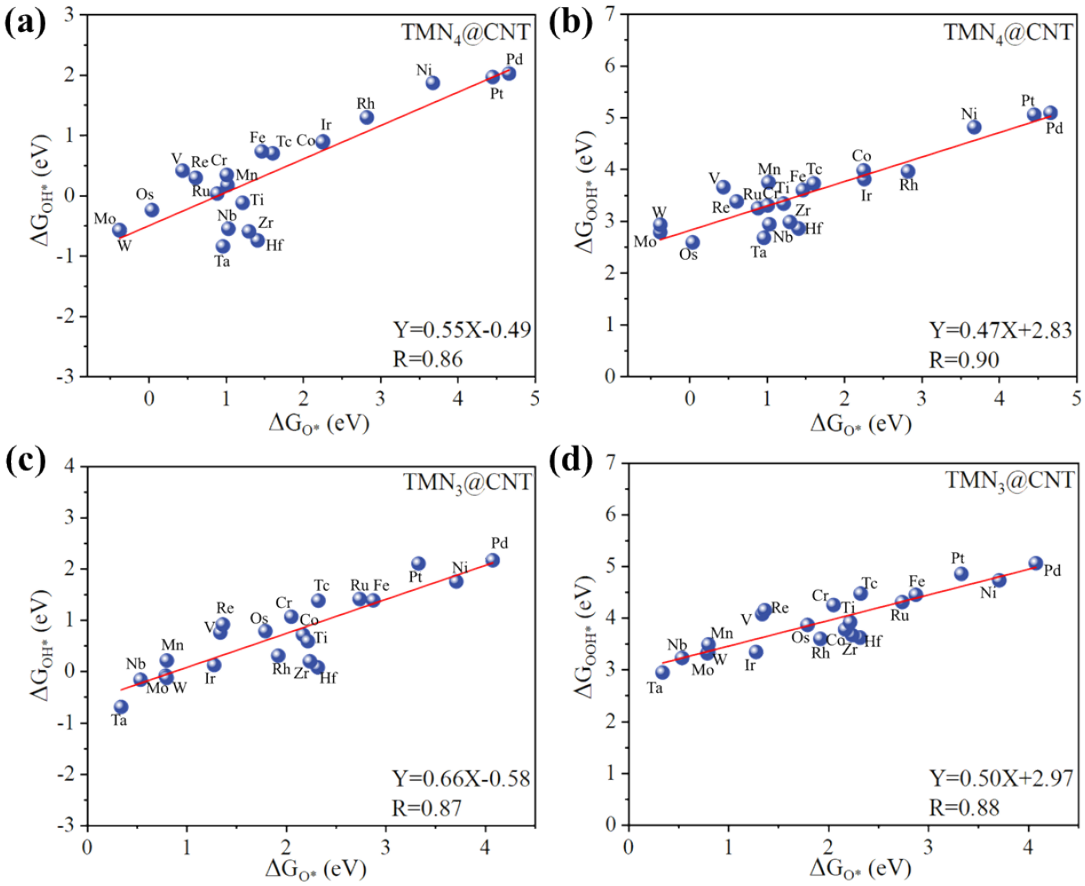

Fig. S10 The scaling relationships of ΔG_{O*} vs. ΔG_{OH*} and ΔG_{O*} vs. ΔG_{OOH*} for TMN_4@CNT (a-b) and TMN_3@CNT (c-d).

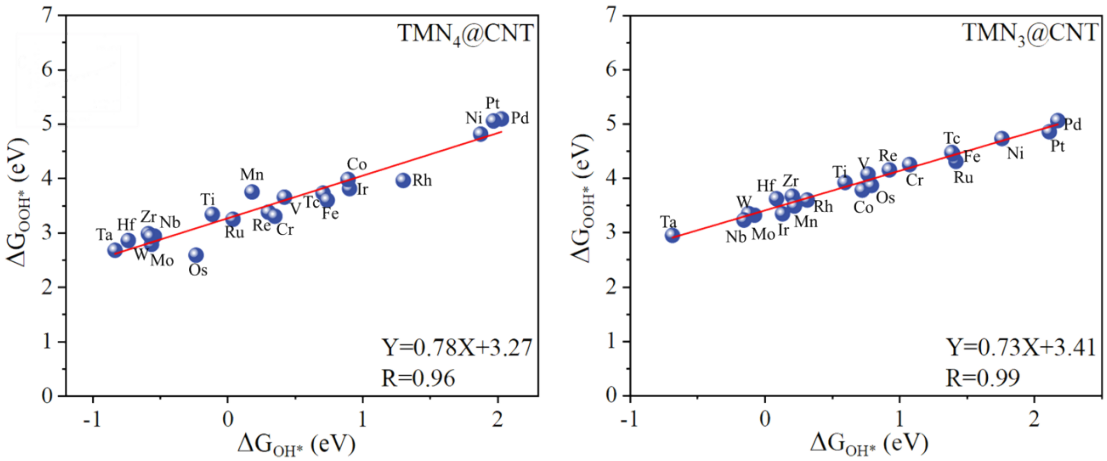

Fig. S11 The scaling relationship between ΔG_{OH^*} and ΔG_{OOH^*} for (a) TMN_4@CNT and (b) TMN_3@CNT systems.

Table S1 Adsorption free energy of the possible species including OH, O, H adsorbed on the TMN_4@CNT and TMN_3@CNT (TM = Ti, V, Cr, Mn, Fe, Co, Ni, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Hf, Ta, W, Re, Os, Ir and Pt) systems ("-" indicates that the species cannot be adsorbed on TM sites)[a].

Systems	OH*	O*	H*
TiN_4@CNT	-1.53	-0.99	-0.42
VN_4@CNT	-1.14	-1.11	0.44
CrN_4@CNT	-0.08	0.07	0.48
MnN_4@CNT	0.18	1.02	0.61
FeN_4@CNT	0.74	1.46	0.42
CoN_4@CNT	0.89	2.25	-
NiN_4@CNT	1.87	3.68	-
ZrN_4@CNT	-2.00	-0.98	-0.51
NbN_4@CNT	-1.75	-1.77	-0.43
MoN_4@CNT	-1.38	-1.59	-0.85
TcN_4@CNT	-0.66	-0.94	-0.01
RuN_4@CNT	0.04	0.88	-
RhN_4@CNT	1.38	2.81	-
PdN_4@CNT	2.03	4.66	-
HfN_4@CNT	-2.42	-1.25	-0.84
TaN_4@CNT	-2.27	-2.35	-0.95
WN_4@CNT	-1.96	-2.48	-0.91
ReN_4@CNT	-1.30	-1.86	-0.56
OsN_4@CNT	-0.21	-0.25	-0.42
IrN_4@CNT	0.90	2.25	-
PtN_4@CNT	1.97	4.45	

TiN_3@CNT	-1.44	-0.49	-0.05
VN_3@CNT	-1.18	-0.94	0.31
CrN_3@CNT	-0.51	-0.31	0.33
MnN_3@CNT	0.22	0.80	-
FeN_3@CNT	-0.18	0.75	-0.09
CoN_3@CNT	0.72	2.16	-
NiN_3@CNT	1.76	3.71	-
ZrN_3@CNT	-1.64	-0.19	-0.17
NbN_3@CNT	-1.59	-1.47	-0.58
MoN_3@CNT	-1.13	-1.22	-0.61
TcN_3@CNT	-0.70	-0.92	-0.03
RuN_3@CNT	-0.21	0.47	-0.10
RhN_3@CNT	0.31	1.92	-
PdN_3@CNT	2.17	4.07	-
HfN_3@CNT	-2.08	-0.46	-0.49
TaN_3@CNT	-2.19	-2.05	-0.89
WN_3@CNT	-1.83	-2.13	-0.75
ReN_3@CNT	-1.27	-1.74	-0.52
OsN_3@CNT	-0.64	-0.48	-0.59
IrN_3@CNT	0.13	1.27	-
PtN_3@CNT	2.11	3.33	-

[a]The specific calculation processes have been provided as follows:

In the OER process, the dissociation of H_2O may result in several surface intermediates, involving OH, O, and H, so we will explore their possible occupation at the TM-site by calculating ΔG_{OH*}, ΔG_{O*} and ΔG_{H*}. To be specific, the dissociation reactions connecting the different states are presented as follows:

$$H_2O + * \leftrightarrow OH* + e^- + H^+ \quad (1)$$

$OH^* + * \leftrightarrow O^* + e^- + H^+$ (2)

$* + e^- + H^+ \leftrightarrow H^*$ (3)

Based on these reactions, the adsorption free energy for OH, O and H can be calculated by the equation $\Delta G = \Delta E + \Delta ZPE - T\Delta S$, where ΔE is the change in the electronic energy before and after adsorption of these species. For the chemical equations (1) and (2), ΔE can be calculated by the formula $\Delta E = E_{ads} + n/2E_{H2} - E_{H2O}$, where n is 1 and 2 for equations (1) and (2), respectively. For equation (3), ΔE can be calculated by the formula $\Delta E = Eads - 1/2E_{H2}$. Note that at standard conditions, the solvated hydrogen ($H^+ + e^-$ in solution) is in equilibrium with H_2 (gas).

Table S2 Gibbs free energy of three intermediates (OH*, O* and OOH*) and the obtained overpotential values of TMN_4@CNT systems.

Systems	$\triangle G_{OH*}$	$\triangle G_{O*}$	$\triangle G_{OOH*}$	η
TiN_4@CNT	-0.11	1.21	3.34	0.90
VN_4@CNT	0.42	0.43	3.66	2.00
CrN_4@CNT	0.35	1.01	3.31	1.07
MnN_4@CNT	0.18	1.02	3.76	1.51
FeN_4@CNT	0.74	1.46	3.61	0.92
CoN_4@CNT	0.89	2.25	3.99	0.51
NiN_4@CNT	1.87	3.67	4.82	0.64
ZrN_4@CNT	-0.59	1.29	2.99	0.70
NbN_4@CNT	-0.54	1.03	2.95	0.74
MoN_4@CNT	-0.57	-0.38	2.79	1.95
TcN_4@CNT	0.71	1.60	3.73	0.90
RuN_4@CNT	0.04	0.88	3.25	1.14
RhN_4@CNT	1.30	2.82	3.97	0.29
PdN_4@CNT	2.03	4.66	5.10	1.40
HfN_4@CNT	-0.74	1.41	2.87	0.91
TaN_4@CNT	-0.84	0.96	2.68	1.01
WN_4@CNT	-0.57	-0.38	2.94	2.09
ReN_4@CNT	0.30	0.60	3.39	1.55
OsN_4@CNT	-0.24	0.04	2.60	1.33
IrN_4@CNT	0.90	2.25	3.82	0.33
PtN_4@CNT	1.97	4.45	5.06	1.25

Table S3 Gibbs free energy of three intermediates (OH*, O* and OOH*) and the obtained overpotential values of TMN_3@CNT systems.

Systems	$\triangle G_{OH*}$	$\triangle G_{O*}$	$\triangle G_{OOH*}$	η
TiN_3@CNT	0.59	2.21	3.93	0.48
VN_3@CNT	0.81	1.38	4.13	1.52
CrN_3@CNT	1.07	2.05	4.26	0.98
MnN_3@CNT	0.22	0.80	3.49	1.47
FeN_3@CNT	1.39	2.87	4.45	0.35
CoN_3@CNT	0.72	2.16	3.79	0.39
NiN_3@CNT	1.76	3.71	4.73	0.72
ZrN_3@CNT	0.20	2.23	3.67	0.80
NbN_3@CNT	-0.16	0.53	3.23	1.47
MoN_3@CNT	-0.08	0.79	3.32	1.31
TcN_3@CNT	1.39	2.32	4.48	0.93
RuN_3@CNT	1.42	2.73	4.31	0.35
RhN_3@CNT	0.31	1.92	3.60	0.46
PdN_3@CNT	2.17	4.07	5.06	0.94
HfN_3@CNT	0.08	2.31	3.63	1.00
TaN_3@CNT	-0.69	0.34	2.95	1.38
WN_3@CNT	-0.12	0.79	3.35	1.33
ReN_3@CNT	0.92	1.36	4.16	1.57
OsN_3@CNT	0.79	1.79	3.87	0.85
IrN_3@CNT	0.13	1.27	3.35	0.85
PtN_3@CNT	2.11	3.33	4.86	0.88