Supplementary Information

Curvature-Switched Activity of Carbon Nanotube-Supported Single Atom Catalysts for Hydrogen Evolution Reaction

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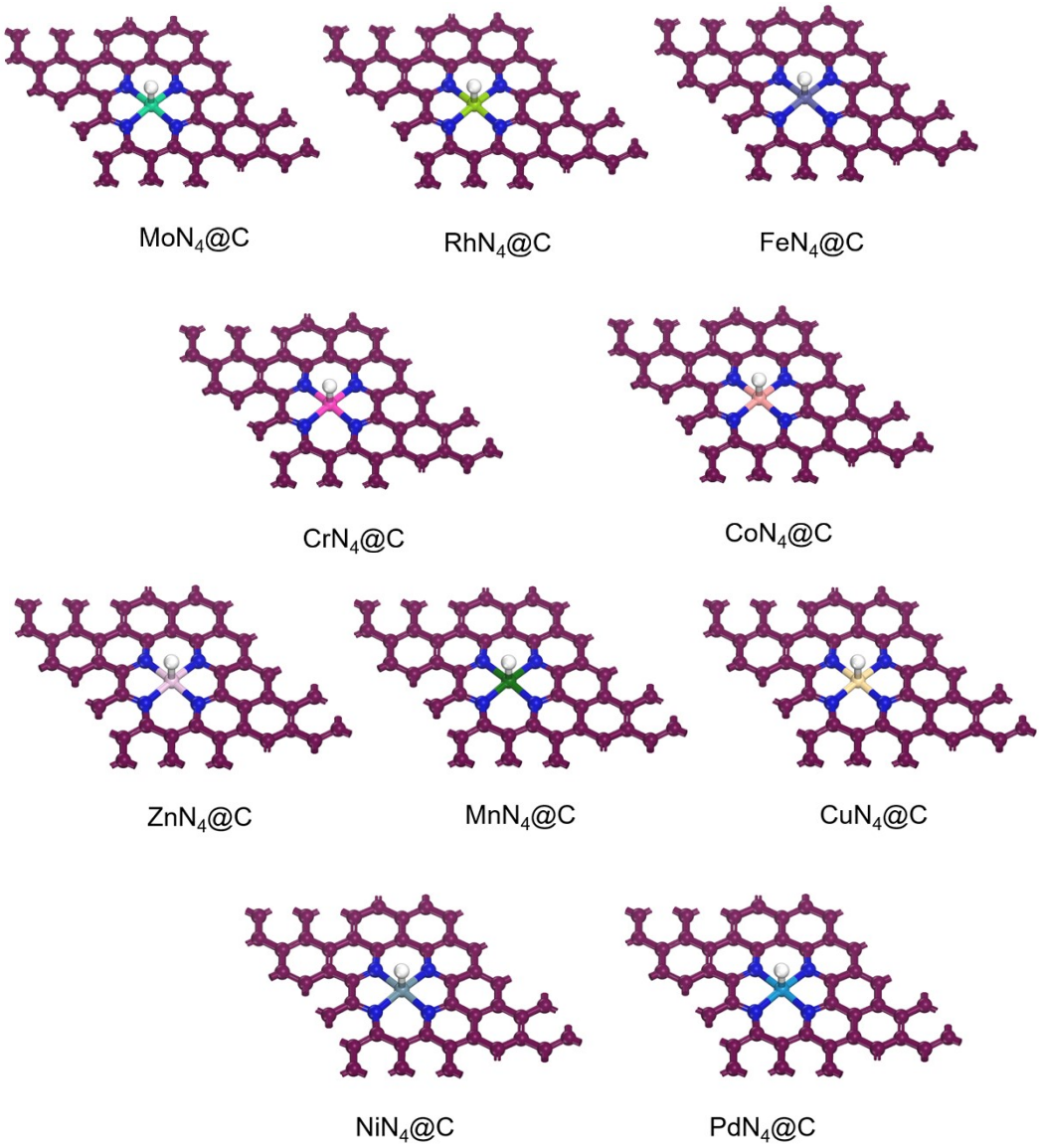

Fig. S1 Optimized geometries of H adsorption on TMN_4@C (TM=Mo, Rh, Fe, Cr, Co, Zn, Mn, Cu, Ni, Pd). The lattice parameters were set to be 12×12×15 $Å^3$.

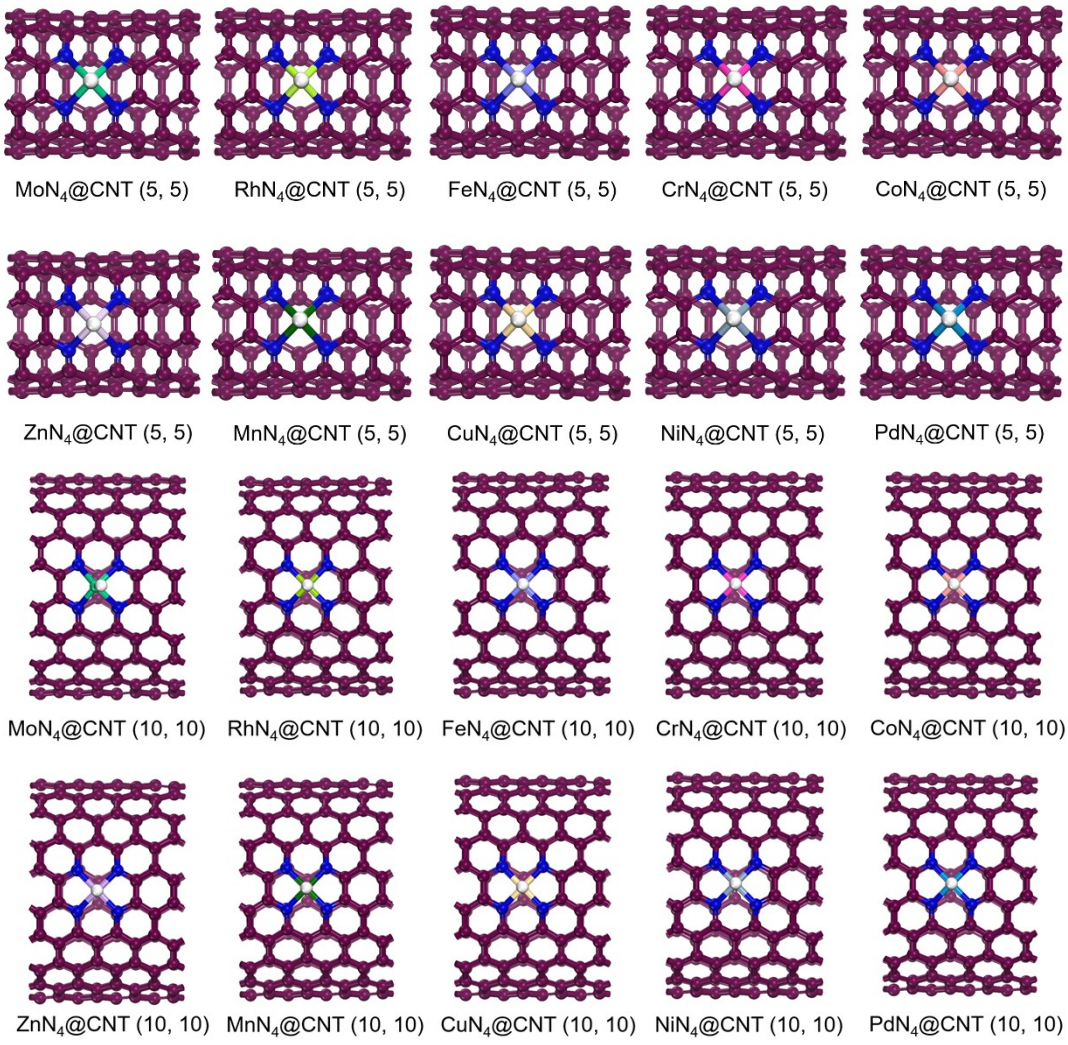

Fig. S2 Optimized geometries of H adsorption on TMN_4@CNTs (n, n) (n=5, 10) (TM=Mo, Rh, Fe, Cr, Co, Zn, Mn, Cu, Ni, Pd). The lattice parameters were set to be 15×15×10 $Å^3$ for CNTs (5, 5) and 23×23×10 $Å^3$ for CNTs (10, 10).

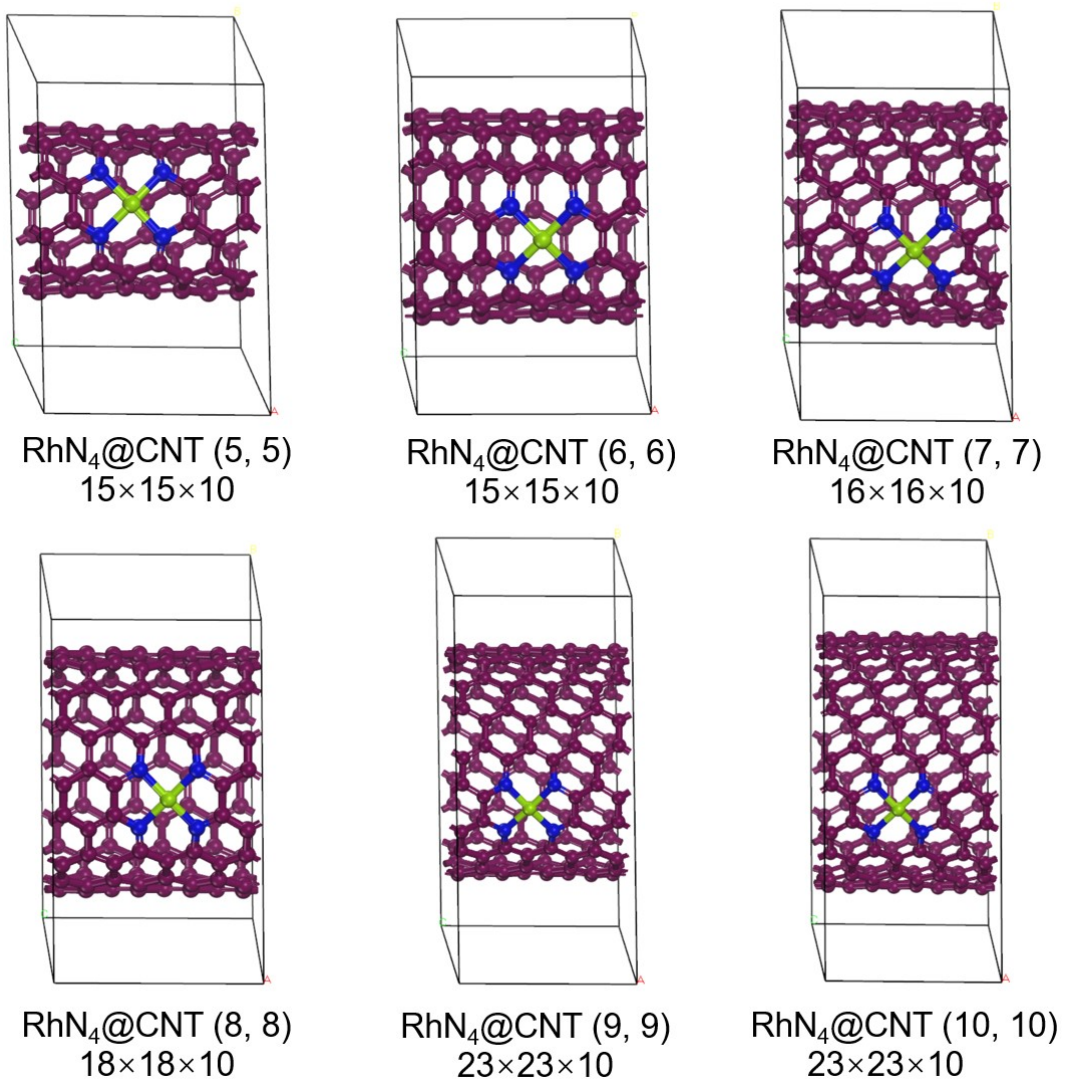

Fig. S3 Optimized configurations of RhN_4@CNTs (n, n) (n=5-10) labeled with the lattice parameters.

Table S1 The binding energies (E_b) of TMs on graphene, the difference between binding energy and cohesion energy (E_{coh}) of TMs, Gibbs free energies for H* adsorption ($\triangle G_{H^*}$) on TMN_4@C , and DFT-calculated entropies (S) for H* adsorption on TMN_4@C.

	E_b (eV)	E_b-E_{coh} (eV)	$\triangle G_{H^*}$ (eV)	S (J/K/mol)
MoN_4@C	-4.981	0.208	-0.614	6.979
RhN_4@C	-6.476	-1.654	-0.041	4.374
FeN_4@C	-5.614	-1.509	0.043	3.760
CrN_4@C	-5.733	-1.293	0.189	7.434
CoN_4@C	-6.422	-3.278	0.260	2.379
ZnN_4@C	-2.448	-1.890	0.462	6.652
MnN_4@C	-5.552	-2.485	0.467	3.739
CuN_4@C	-3.901	-0.636	1.235	6.644
NiN_4@C	-6.744	-2.320	1.620	4.013
PdN_4@C	-4.507	-1.683	1.807	6.714

Table S2 The binding energies (E_b) of TMs on CNTs (n, n) (n=5, 10), the difference between binding energy and cohesion energy (E_{coh}) of TMs, Gibbs free energies for H* adsorption ($\triangle G_{H^*}$) on TMN_4@CNTs (n, n) (n=5, 10), and DFT-calculated entropies (S) for H* adsorption on TMN_4@CNTs (n, n) (n=5-10).

	E_b (eV)	E_b-E_{coh} (eV)	$\triangle G_{H^*}$ (eV)	S (J/K/mol)
MoN_4@CNT (5, 5)	-5.365	-0.176	-0.195	11.123
RhN_4@CNT (5, 5)	-5.690	-0.868	0.254	3.359
FeN_4@C (5, 5)	-5.478	-1.373	0.340	3.256
CrN_4@C (5, 5)	-5.257	-0.817	0.317	9.615
CoN_4@C (5, 5)	-5.946	-2.802	0.436	2.378
ZnN_4@C (5, 5)	-1.802	-1.244	0.742	7.167
MnN_4@C (5, 5)	-5.056	-1.989	0.601	5.208
CuN_4@C (5, 5)	-3.585	-0.320	1.595	7.430
NiN_4@C (5, 5)	-6.378	-1.954	1.757	4.125
PdN_4@C (5, 5)	-3.641	-0.817	1.897	6.967
MoN_4@CNT (10,10)	-5.281	-0.092	-0.358	12.083
RhN_4@CNT (10, 10)	-6.210	-1.388	0.005	2.816
FeN_4@C (10, 10)	-6.151	-2.046	0.253	2.920
CrN_4@C (10, 10)	-4.777	-0.337	0.190	5.907
CoN_4@C (10, 10)	-6.470	-3.326	0.249	2.136
ZnN_4@C (10, 10)	-2.380	-1.821	0.636	6.666
MnN_4@C (10, 10)	-5.542	-2.475	0.513	3.683
CuN_4@C (10, 10)	-3.625	-0.360	1.330	7.267
NiN_4@C (10, 10)	-6.868	-2.444	1.678	3.597
PdN_4@C (10, 10)	-4.281	-1.457	1.849	5.607

Table S3 C-N bonding length (d_{C-N}), Rh-N bonding length (d_{Rh-N}), d-band center of Rh atom, Gibbs free energies for H* adsorption ($\triangle G_{H*}$).

	d_{C-N}	d_{Rh-N}	ε_d	$\triangle G_{H*}$ (eV)
RhN_4@CNT (5,5)	1.357	1.940	-1.60	0.254
RhN_4@CNT (6,6)	1.357	1.934	-1.50	0.168
RhN_4@CNT (7,7)	1.356	1.931	-1.43	0.104
RhN_4@CNT (8,8)	1.356	1.932	-1.38	0.063
RhN_4@CNT (9,9)	1.356	1.933	-1.37	0.031
RhN_4@CNT (10,10)	1.357	1.933	-1.33	0.005
de-RhN_4@CNT (5,5)	1.355	1.943	-1.50	0.134
de-RhN_4@CNT (6,6)	1.355	1.942	-1.51	0.047
de-RhN_4@CNT (7,7)	1.355	1.940	-1.47	-0.002
de-RhN_4@CNT (8,8)	1.355	1.940	-1.47	-0.031
de-RhN_4@CNT (9,9)	1.355	1.936	-1.44	-0.091
de-RhN_4@CNT (10,10)	1.354	1.936	-1.43	-0.102