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Steric Effects in Hydrogen Evolution Reaction Based on TMX_4 Active Center: Fe–BHT as a Case Study

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Table S1. Lattice constant, cohesive energy (E_{coh}), area of the optimized unit cell (S_0), $\partial^2 E_{total}/\partial\varepsilon^2$ and band gap of TM–BHTs considered in this work.

TM–BHT	Lattice constant (Å)	E_{coh} (eV/atom)	S_0 (Å^2)	$\partial^2 E_{total}/\partial\varepsilon^2$	Band gaps (eV)
Sc–BHT	9.37	5.67	76.03	1168.27	0
Ti–BHT	9.09	5.47	71.56	1106.37	0
V–BHT	8.85	5.39	67.83	1088.45	0
Cr–BHT	8.67	5.35	65.10	945.87	0
Mn–BHT	8.55	5.39	63.31	781.41	0.03
Fe–BHT	8.46	5.41	61.98	862.95	0
Co–BHT	8.44	5.36	61.69	794.372	0
Ni–BHT	8.56	5.36	63.46	838.17	0
Cu–BHT	8.75	5.32	66.31	834.412	0

Table S2. Gibbs free energy change (ΔG_{H^*}) of TM–BHTs for hydrogen adsorption on different active sites (TM and S). "/" means that the adsorbed hydrogen moves to TM sites after structural optimization. The unit is eV.

TM–BHT	ΔG_{H^*}–TM	ΔG_{H^*}–S
Sc–BHT	–0.42	/
Ti–BHT	–0.38	/
V–BHT	1.36	/
Cr–BHT	0.29	/
Mn–BHT	0.75	/
Fe–BHT	0.09	1.22
Co–BHT	–0.45	0.14
Ni–BHT	–1.21	–0.85
Cu–BHT	1.16	0.49

Table S3. ΔG_{H^*}, $\Delta\varepsilon_{d_{z^2}}^{\uparrow\downarrow}$ for different active center $FeS_{4-x}N_x$. The unit is eV.

$FeS_{4-x}N_x$	ΔG_{H^*}	$\varepsilon_{unoccupied}$	$\varepsilon_{occupied}$	$\Delta\varepsilon_{d_{z^2}}^{\uparrow\downarrow}$
FeS_4	0.09	0.70	–2.86	3.56
FeS_3N	0.14	0.75	–2.86	3.61
FeS_2N_2	0.26	0.81	–2.93	3.74
$FeSN_3$	0.39	0.80	–3.02	3.82
FeN_4	0.64	0.94	–3.54	4.48

Table S4. ΔG_{H^*} and $\Delta\varepsilon_{d_{z^2}}^{\uparrow\downarrow}$ for Fe–BHT under strain. The unit is eV.

strain	ΔG_{H^*}	$\varepsilon_{unoccupied}$	$\varepsilon_{occupied}$	$\Delta\varepsilon_{d_{z^2}}^{\uparrow\downarrow}$
4%	0.46	0.85	–3.14	3.99
3%	0.36	0.86	–3.06	3.92
2%	0.22	0.82	–2.93	3.75
1%	0.17	0.74	–2.93	3.67
0%	0.09	0.70	–2.86	3.56
–1%	0.04	0.66	–2.87	3.53
–2%	0.03	0.62	–2.86	3.48

Table S5. ΔG_{H^*} of $TiS_{4-x}N_x$ and strained Ti–BHT. The unit is eV.

$TiS_{4-x}N_x$	ΔG_{H^*}	strain	ΔG_{H^*}
TiS_4	–0.38	0%	–0.38
TiS_3N	–0.31	1%	–0.13
TiS_2N_2	–0.26	2%	0.28
$TiSN_3$	–0.16	3%	0.30
TiN_4	–0.05	4%	0.45

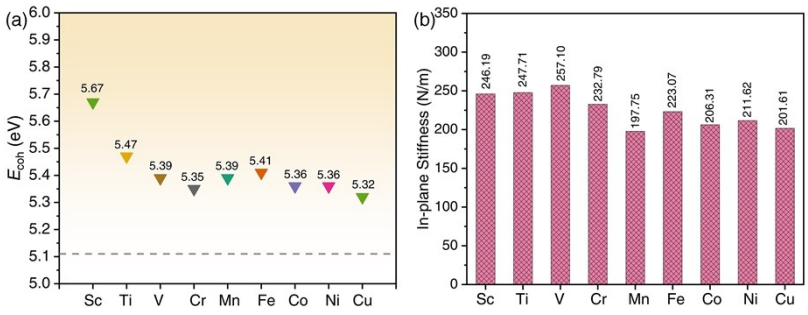

Fig. S1 (a) Cohesive energy (E_{coh}) of TM–BHTs of consideration, the horizontal dashed line represents the previous value of Cu–BHT of 5.11 eV/atom. (b) In-plane stiffness of TM–BHTs of interest in this work.

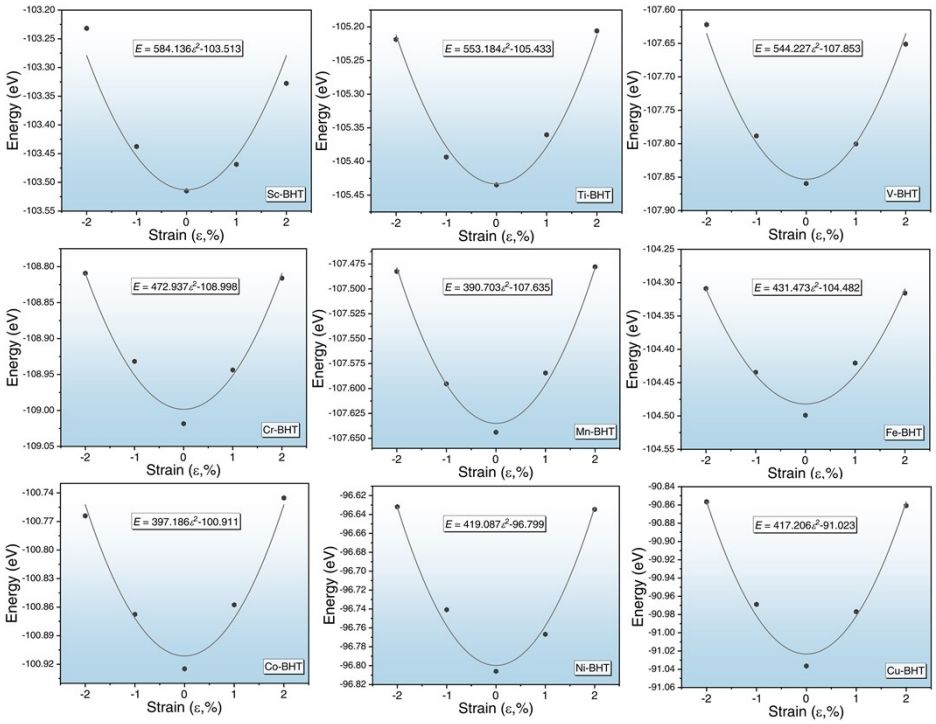

Fig. S2 Relationship between the total energy and strain along *b* axis.

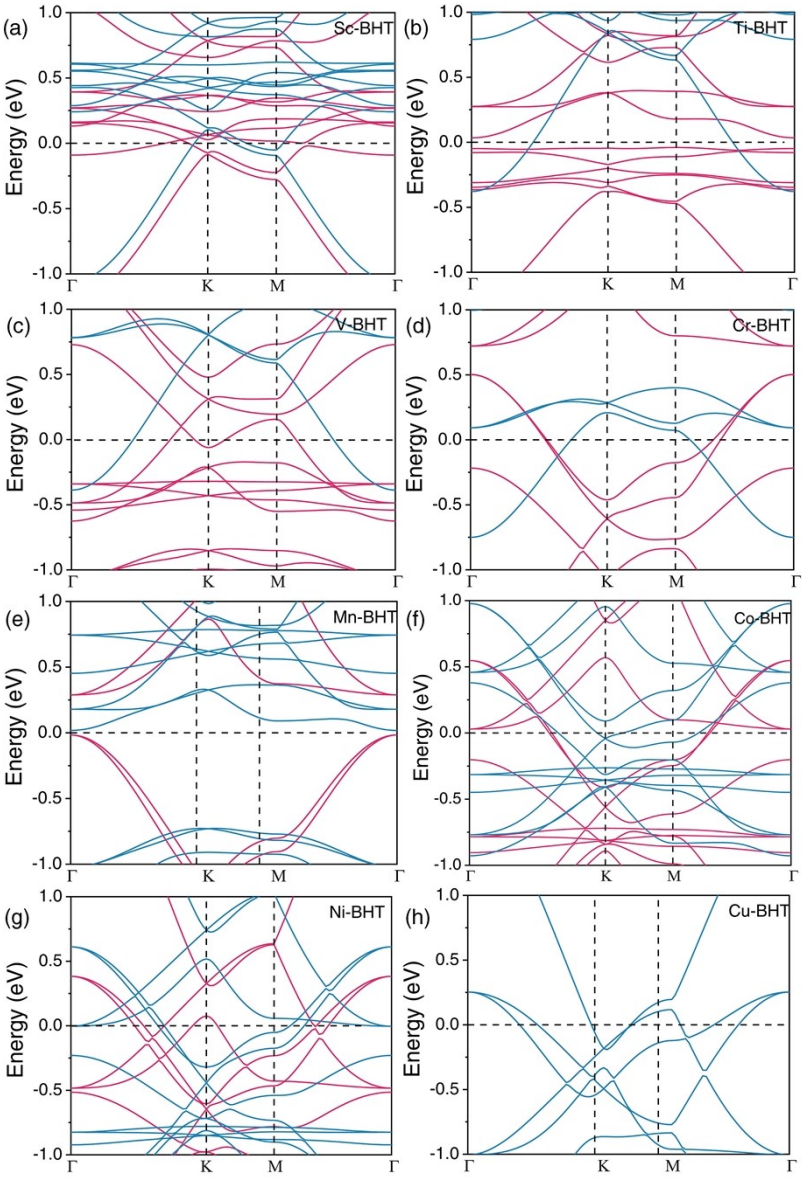

Fig. S3 Band structures of 2D TM–BHTs studied in this work, the Fermi level is set to zero.

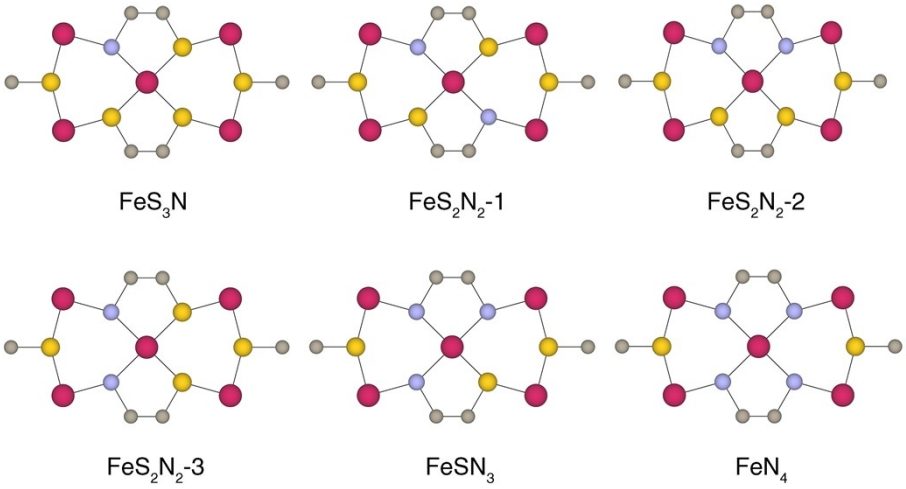

Fig. S4 Local structure of FeS_3N, FeS_2N_2–1, FeS_2N_2–2, FeS_2N_2–3, $FeSN_3$ and FeN_4 active centers in Fe–BHT.

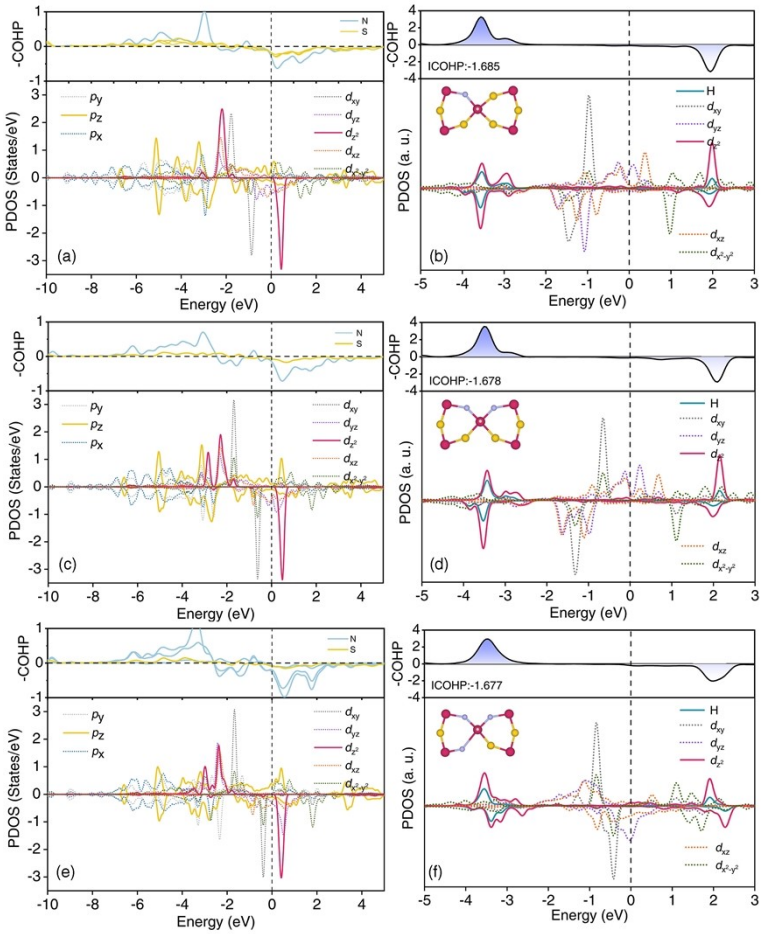

Fig. S5 Projected density of states (PDOS) on S *p* and Fe *d* orbitals for (a) FeS_3N, (c) FeS_2N_2 and (e) $FeSN_3$. Crystal orbital Hamilton population (COHP), integrated COHP (ICOHP), and PDOS for H *s* and Fe *d* orbitals for (b) FeS_3N, (d) FeS_2N_2 and (f) $FeSN_3$. Insets are hydrogen adsorption configurations. The vertical dashed line represents the Fermi level.

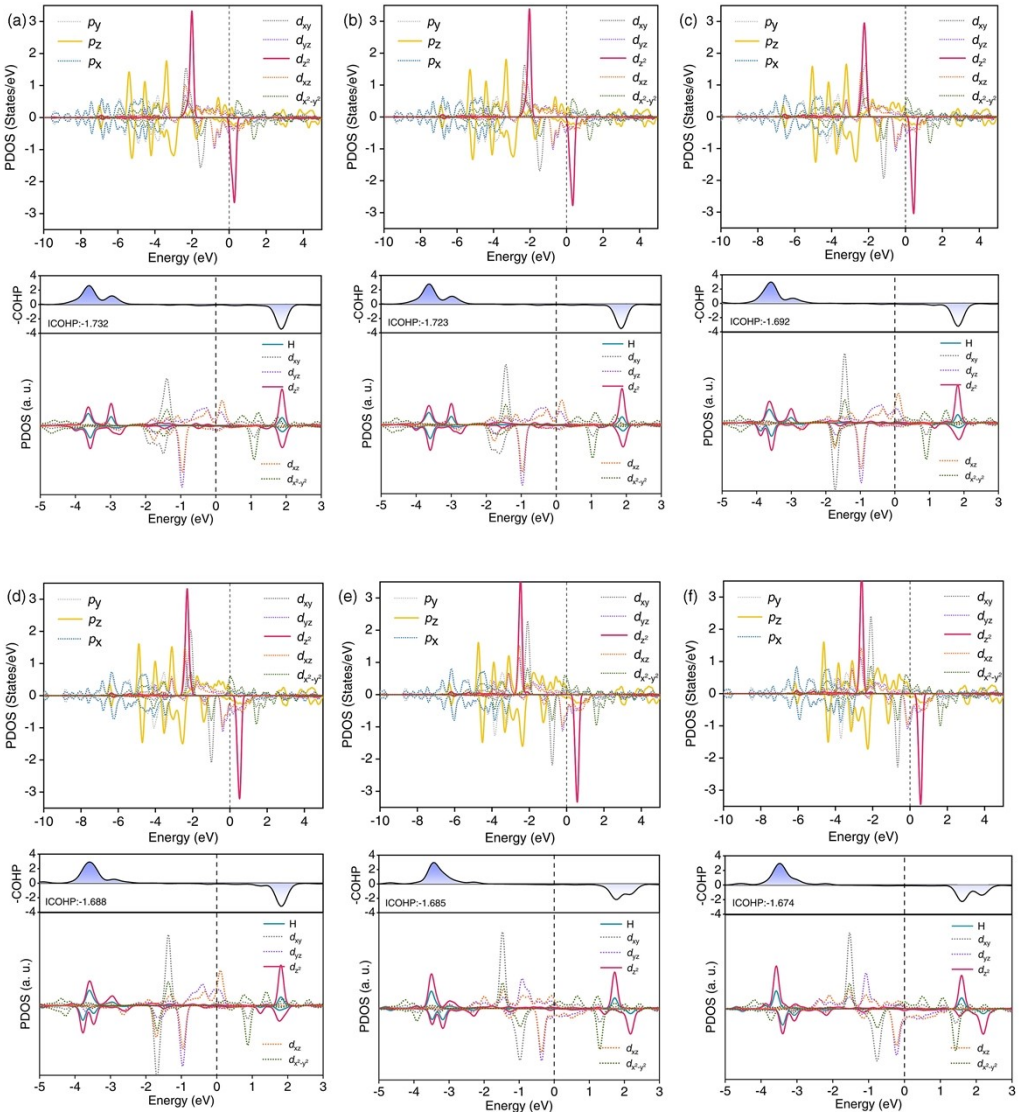

Fig. S6 Projected density of states (PDOS), crystal orbital Hamilton population (COHP) and integrated COHP (ICOHP) of Fe–BHT under strain, (a) –2%, (b) –1%, (c) 1%, (d) 2%, (e) 3% and (f) 4%. Upper: PDOS on S *p* and Fe *d* orbitals. Bottom: COHP, ICOHP and PDOS on H *s* and Fe *d* orbitals. The vertical dashed line represents the Fermi level.

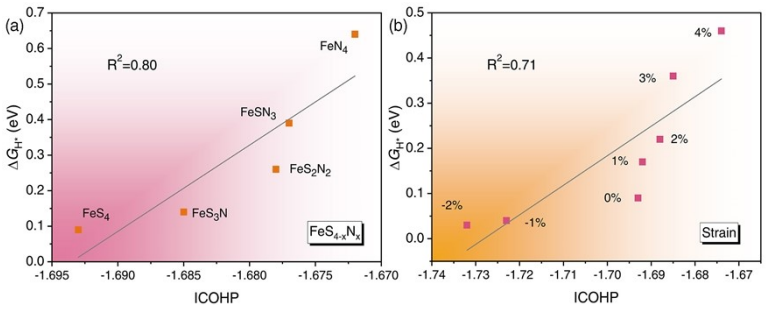

Fig. S7 Relationship between ΔG_{H*} and ICOHP for (a) $FeS_{4-x}N_x$ and (b) strained Fe–BHT.

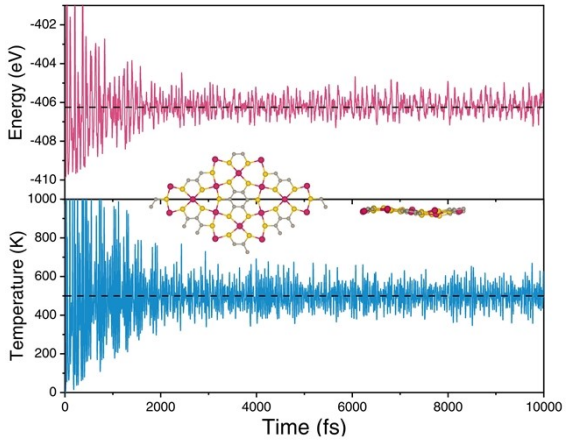

Fig. S8 Variation of energy and temperature versus the AIMD simulation time for Fe–BHT. Insets denote the top and side views of Fe–BHT after AIMD simulation lasting for 10 ps with a time step of 1 fs at T = 500 K.