Electronic Supplementary Information (ESI)

Theoretical Investigation of the Non-metal Site of Two-Dimensional Metal-

Benzenehexathiol for Hydrogen Evolving Activity Enhancement

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1. Computational details

The calculations of all catalysts were performed under the density functional theory (DFT) implemented in the Vienna ab initio simulation package (VASP).¹ The optimized structures and energies were obtained using the Generalized Gradient Approximation-PBE² exchange correlation functional combined with DFT-D2 dispersion correction.³ The ion-electron interactions were represented by the projector augmented wave (PAW) approach.⁴ All calculations related to Co-BHT are spin polarized. Mo-BHT is tested to be non-spin polarized. The models in the present work are periodic along y- and z-directions of the extended surface, and a thickness of 15 Å vacuum in the xdirection was added, which is thick enough to safely ignore interactions between surfaces in adjacent cells. The Brillouin zone integration was calculated in Monkhorst-Pack mesh and a high cutoff energy of 500 eV for the plane-wave basis set was applied. The k-meshes of $2 \times 2 \times 3$ (Co-BHT cell), $2 \times 2 \times 3$ (Mo-BHT cell), 1×2×2 (Co-BHT 001 surface), 1×2×2 (Mo-BHT 001 surface) were used for relaxation, and 1×3×3 (Co-BHT 001 surface) and 1×3×3 (Mo-BHT 001 surface) for density of states calculations. According to previous studies, the eclipsed stacking modes of Co-BHT are adopted here in our theoretical calculations.⁵ To simulate the layer-by-layer stacking structure of M-BHT, the (001) surface with two layers, one fixed and the other one full relaxed, was adopted to take van der Waals interactions between layers into consideration.

The Hubbard corrections, which can also improve the poor description by the GGA of the highlylocalized *d* orbitals of both transition metals Co and Mo, were also applied to search for the equilibrium geometries of Co-BHT and Mo-BHT. The Hubbard U (3.1 eV) of Mo in Mo-BHT is calculated via the linear response approach in VASP. And the U value (3.3 eV) was set for Co as suggested by references^{6, 7}. The 2D structure and the stacking mode obtained from PBE+U results are almost identical to that in PBE-D2. The lattice constants of Co-BHT obtained from PBE+U results are 14.75 Å and 14.75 Å, which are almost the same as that of PBE-D2 results (14.70 Å and 14.70 Å). The lattice constants of Mo-BHT obtained from PBE+U results are 15.51 Å and 15.42 Å, which are also slightly larger than that of PBE-D2 results (15.43 Å and 15.37 Å). This indicates that PBE-D2 can give a good description of M-BHT systems. Therefore, we chose the cost-effective PBE-D2 functional in the present work.

2. The geometric parameters and stability of Co-BHT and Mo-BHT

Their geometric parameters are listed in Table S1, where the lattice constant of Co-BHT is in good agreement with previous report.⁸ Here the formation energy (E_f) is calculated through Equation 1:

$$E_f = (E_{M-BHT} - a\mu(M) - b\mu(S) - c\mu(C))/N$$
(1)

where $E_{\text{M-BHT}}$ is the total energy of M-BHT cell, $\mu(\text{M})$, $\mu(\text{S})$ and $\mu(\text{C})$ are the chemical potential of the metal atom (reference state: their respective the most stable bulk metal structures), S atom (reference state: S8), and C atom (reference state: graphite), respectively. *a*, *b* and *c* are the number of M, S and C atoms in the M-BHT cell, respectively. N is the total number of atoms in M-BHT cell. Taking the E_f of experimentally prepared Co-BHT as a comparison, the negative value of E_f (Mo-BHT) demonstrates its stability and plausibility.

3. Calculation of the Gibbs free energy change

The Gibbs free energy change for H^{*} adsorption on a catalyst surface (${}^{\Delta G}_{H*}$) is an effective descriptor to determine their electrochemical performance.⁹ When the value of $|{}^{\Delta G}_{H*}|$ is closer to zero, the electrocatalytic HER activity is higher according to the "volcano plot".^{9, 10} The value of ${}^{\Delta G}_{H*}$ was calculated from Equation 2:⁹

$$\Delta G_{H*} = \Delta E_{H*} + \Delta E_{ZPE} - T\Delta S \tag{2}$$

where the adsorption energy ΔE_{H*} follows Equation 3:

$$\Delta E_{H*} = E_{(surf + H*)} - E_{(surf)} - \frac{1}{2}E_{H2}$$
(3)

where $E_{(surf + H *)}$ and $E_{(surf)}$ are total energies of the catalyst surface with and without H* atom, respectively. The asterisk represents active site on the catalyst surface. E_{H2} is the energy of an isolated molecular hydrogen. ΔE_{ZPE} and ΔS are the zero-point energy change and the entropy change between the adsorbed H* and half of the gaseous hydrogen, respectively. The zero-point energy and entropy of adsorbed H* and isolated H₂ are obtained by vibrational frequency calculations. The value of TS of H₂ is calculated to be 0.402 eV, which is consistent with the standard value of 0.404 eV in the NIST Standard Reference Database. T is the temperature of 298.15 K.



Fig. S1 (a) Top view and (b) side view of bulk Co-BHT. (c) Top view and (d) side view of bulk Mo-BHT. Blue, sulfur; grey, carbon; orange, cobalt; and red, molybdenum.



Fig. S2 (a) Top view and (b) side view of Co-BHT. (c) Top view and (d) side view of Mo-BHT. In Mo-BHT, the distance between the S3 site and the Mo atom below in the adjacent layer is 2.46 Å, and the distance between the Mo site and the S atom below is 2.34 Å. The average bond length of Mo-S in Mo-BHT is 2.37 Å. Therefore, the Mo-S bonds has formed between two Mo-BHT layers.



Fig. S3 (a) All adsorption sites on Co-BHT: the Co site, the C site, and the S site. (b) All adsorption sites on Mo-BHT: the Mo site, the C site, the S1, S2, and S3 site.



Fig. S4 There are two stable geometries of Ni-BHT: AA stacking mode and AB stacking mode. (a) Top view and (b) side view of Ni-BHT in AA stacking mode. (c) Top view and (d) side view of Ni-BHT in AB stacking mode. (e) Top view and (f) side view of Fe-BHT. Brown, Ni; purple, Fe.

	Electrical conductivities			HER performance		
	Characterization	Conductivities	Ref.	Solution	HER overpotential at	Ref.
	method	(S/cm)			10 mA/cm ² (mV)	
Cu₃BHT	4-Probe	48-280	11	рН 0.0, H ₂ SO ₄	450	11
	4-Probe	1580	12	рН 0.0, Н ₂ SO ₄	760	11
	4-Probe	2500	13		*	
Ni ₃ (BHT) ₂	2-Probe	0.15	14	рН 1.3, Н ₂ SO ₄	331	15
	2-Probe	6.7×10 ⁻³	14		*	
	2-Probe	2.8	16		*	
	2-Probe	160	16		*	
Pd ₃ (BHT) ₂	4-Probe	2.8×10 ⁻²	17		*	
Co ₃ (BHT) ₂		*		рН 1.3, Н ₂ SO ₄	340	18
		*		рН 1.3, Н ₂ SO ₄	185	15
		*		рН 1.3, Н ₂ SO ₄	213	15
		*		рН 1.3, Н ₂ SO ₄	192	15
		*		рН 1.3, Н ₂ SO ₄	225	15
		*		рН 1.3, Н ₂ SO ₄	246	15
FeBHT		*		pH 1.3, H₂SO₄	473	15

Table S1. Summary of the literature reported electrical conductivities and the HER performance of M-BHTs.

*Not reported.

	Lattice constant [Å]	Interlayer distance [Å]	Formation energy [eV/atom]
Co-BHT	a=14.70, b=14.70	3.13	-0.752
Mo-BHT	a=15.43, b=15.37	2.95	-0.650

Table S2. Geometric parameters and formation energies of Co-BHT and Mo-BHT.

Table S3. The 3*p* band center, the adsorption energy (${}^{\Delta E_{H*}}$) and the Gibbs free energy change for H^{*}

Structure	3p band center (eV)	${}^{\Delta E}{}_{H*}$ (eV)	ΔG_{H*} (eV)
Ni-BHT (AA)	-2.81	-0.05	0.19
Ni-BHT (AB)	-2.63	-0.01	0.22
Fe-BHT	-2.37	-0.87	-0.65

(${}^{\Delta G_{H}}$) on the S sites of Ni-BHT (AA and AB stacking modes) and Fe-BHT.

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