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Supporting information

First-principles investigation of the hydrogen evolution reaction on different surfaces of MnS_2, FeS_2, CoS_2, NiS_2

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Density of states of different surfaces

We calculated the total density of states of four surface models of MnS_2, FeS_2, CoS_2, NiS_2 (see Fig. 1). It is shown that the gaps of electronic states of these four surfaces are zero. From the density of states of spin up and down, there are nonzero magnetizaton for MnS_2, FeS_2, and CoS_2 surfaces.

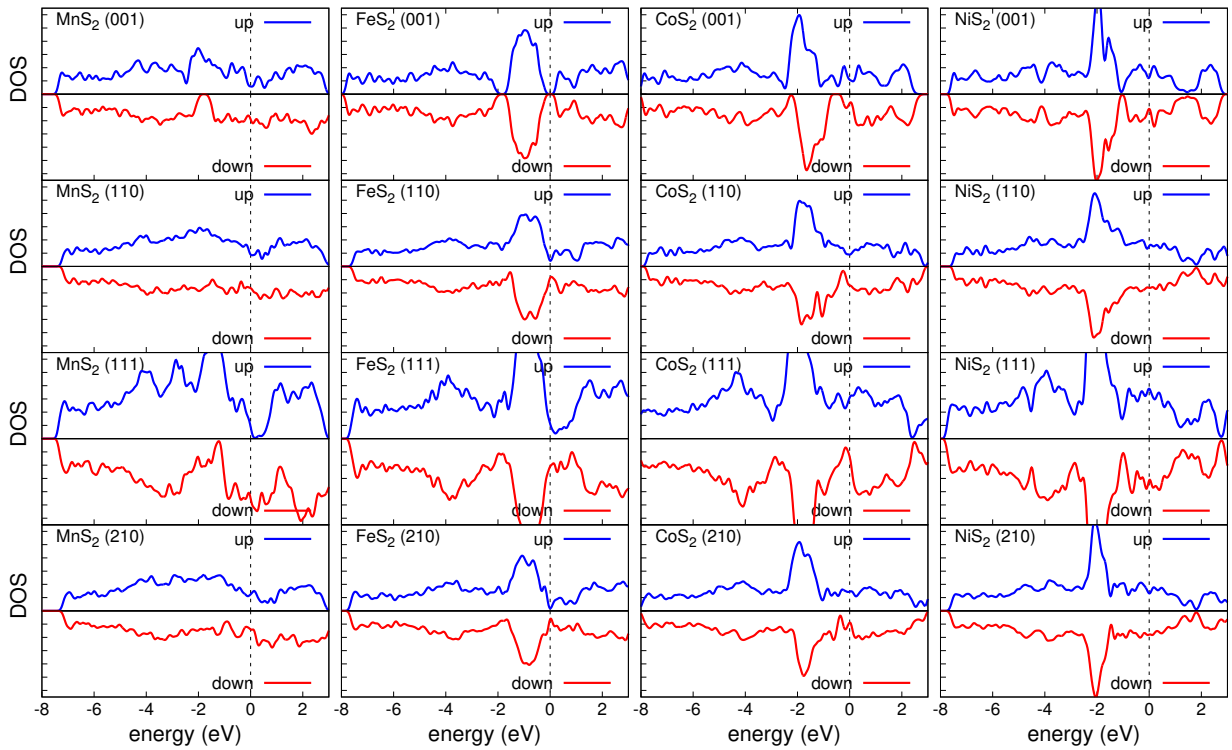

Figure 1: Total density of state of four surface models of MnS_2, FeS_2, CoS_2, NiS_2

Trend of H adsorptions on the (110) surfaces of FeS_2, CoS_2, and NiS_2

As discussed in the manuscript, H adsorptions on the (110) and (210) surfaces are gradually weakened from FeS_2, to CoS_2, and to NiS_2 (the ΔG_{H^*} = -1.55, -0.19, 0.00 eV for the (110) surfaces of FeS_2, CoS_2, and NiS_2, and the ΔG_{H^*} = -1.06, -0.19, -0.14 eV for the (210) surfaces of FeS_2, CoS_2, and NiS_2 respectively.). While the adsorption sites on (210) surfaces of FeS_2, CoS_2, and NiS_2 are different (transition metal sites for FeS_2 and CoS_2, and S top site for NiS_2), the adsorption sites on the (110) are all transition metal sites and their adsorption shows the wakened trend from iron to cobalt, and then nickle disulfides.

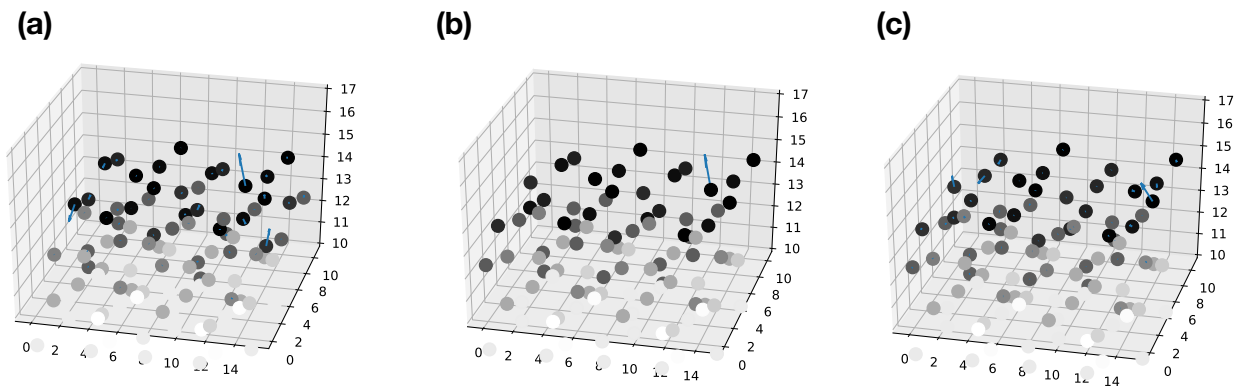

Figure 2: The displacements of atoms of (110) surface slab of (a) FeS_2, (b) CoS_2, and (c) NiS_2. The displacement vectors are represented by the blue arrows, and the atoms by the solid balls.

From the density of states, Fe, Co, and Ni sulfides do not show very different hybridization strength with hydrogen. Besides the hybridization with the hydrogen, the surface reconstruction/relaxation also contributes to the free energy difference. We have analyzed the displacements of all atoms of the (110) surface slab model as the hydrogen is adsorbed (see Fig. 2). We used the norm of the all displacements ($\left(\sum_i^N |\vec{d_i}|^2\right)^{1/2}$, where $\vec{d_i}$ is the displacement of the i-th atom)as a measure of the surface structure modification, and it is 2.80 Å for FeS_2, 2.35 Å for CoS_2, and 1.67 Å for NiS_2. Therefore, FeS_2 has the largest structure modification upon the hydrogen adsorption, followed by CoS_2, then NiS_2, which is consistent

with the order of free energy difference.The lattice constants of the considered pyrites are in the order: $FeS_2 < CoS_2 < NiS_2$, thus the hydrogen adsorption impact greater on the FeS_2, as the atoms has less space to relax.

The convergence test (the energy vs. the energy cutoff)

We performed density functional theory calculations implemented in the Vienna ab-initio simulation package (VASP)[1,2] with generalized gradient approximation (GGA) in Perdew-Burke-Ernzerhof (PBE)[3] parameterization as the exchange correlation functional. The structures of models and the first Brillouin Zone are described in the manuscript. Plane wave cutoff energies 300 eV, 400 eV, 500 eV, 600 eV, and 700 eV were used to determine the cutoff adopted for our calculations thereafter. According to the result (see Fig. 3), We chose 300 eV as the reasonable cutoff energy for later calculations. The accuracy is within 0.35 meV/atom for bulk, 1.5 meV/atom for (001) surface slab, 1 meV/atom for (110) surface slab, 1 meV/atom for (111) surface slab, 1.1 meV/atom for (210) surface slab. This energy cutoff is consistent with the previous first-principles calculations of the hydrogen evolution reaction for the same pyrite structure CoS_2.[4]

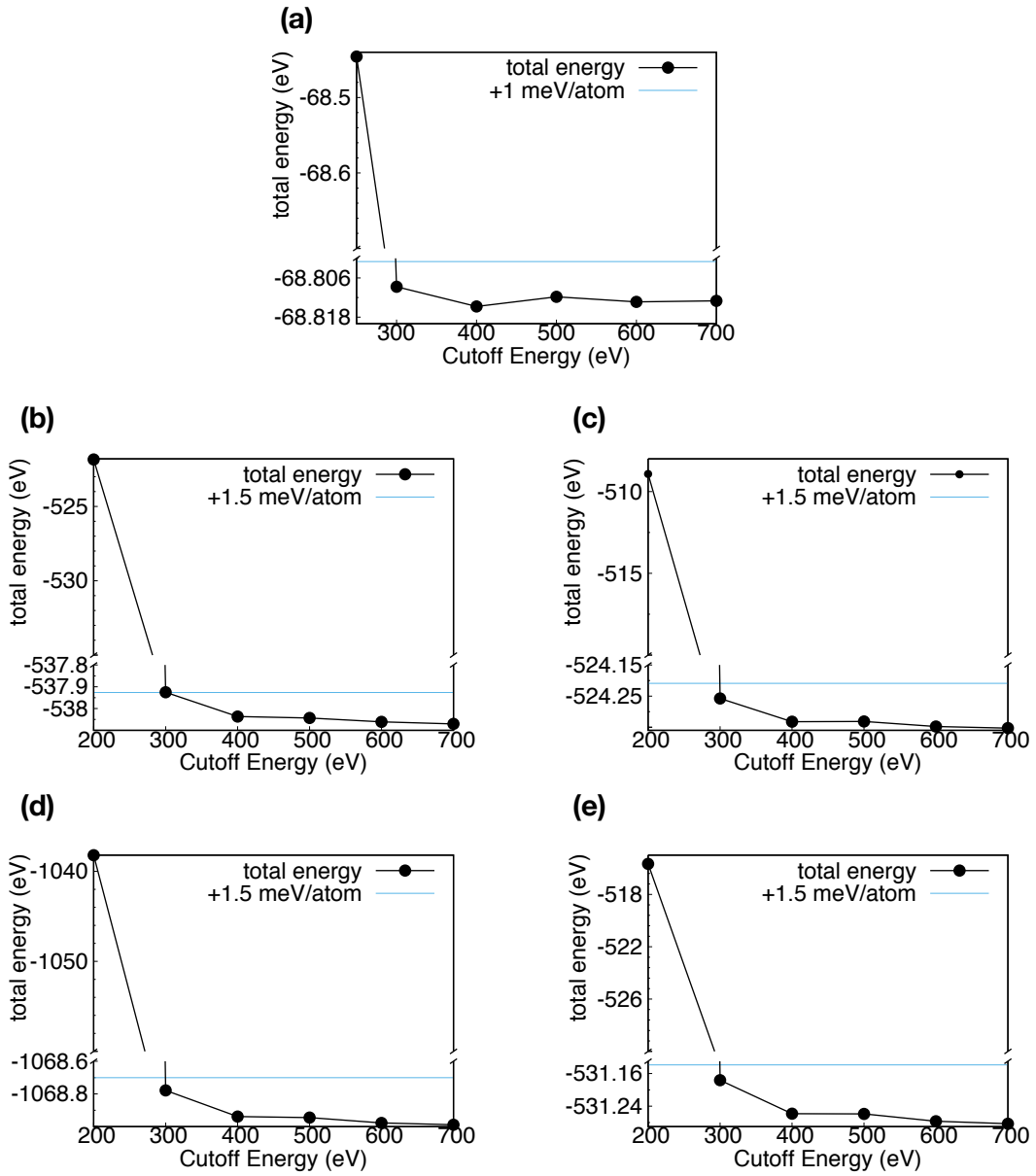

Figure 3: Bulk and four surface models of CoS_2 energy cutoff convergence test (a) bulk (b) (001), (c) (110), (d) (111), and (e) (210).

References

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(4) Cabán-Acevedo, M.; Stone, M. L.; Schmidt, J. R.; Thomas, J. G.; Ding, Q.; Chang, H. C.; Tsai, M. L.; He, H.; Jin, S. Efficient hydrogen evolution catalysis using ternary pyrite-type cobalt phosphosulphide. *Nat. Mater.* **2015**, *14*, 1245–1251.