

Hydrogen Evolution Reaction at Anion Vacancy of Two-dimensional Transition Metal Dichalcogenides: *Ab Initio* Computational Screening

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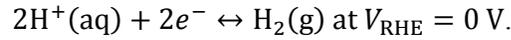
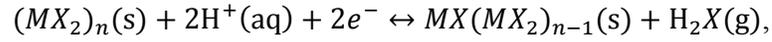
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Section1. Determination of chemical potential of X

For the calculation of the vacancy formation energy, we need to determine the chemical potential X , μ_X . This chemical potential is a variable to reflect the experimental conditions where materials are thermally equilibrated. In the present study, we consider two reactions below to determine μ_X :



In equilibrium, i.e., $\Delta G = 0$ for these reactions, we can express μ_X as a function of other energy terms that can be obtained from DFT calculations and a partial pressure of H_2X gas. An H_2X pressure of 10^{-6} bar was chosen following standard corrosion resistance^{S1,S2}, which gives μ_X as follows:

$$\mu_X = E(H_2X) - E(H_2) + \Delta ZPE - T\Delta S + k_B T \ln(10^{-6}).$$

Section2. Dependence of ΔG_H on exchange-correlational functionals

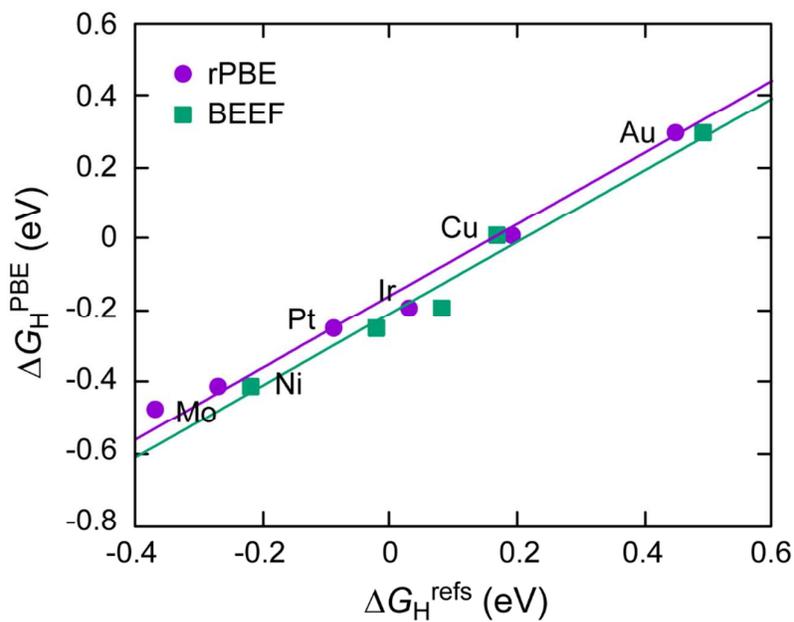


Figure S1 Comparison of ΔG_H of transition metals calculated using PBE and those obtained using BEEF and rPBE in previous literature.^{S3,S4}

We calculate hydrogen binding energies on (111) surfaces of several metals using PBE functional and compare them with BEEF and rPBE results from previous works^{S3,S4} (see Figure S1). The PBE results are ~ 0.2 eV higher than others, but relative values among different materials are well maintained. Therefore, ΔG_H 's relative to that on Pt ($\Delta\Delta G_H$) have little dependence on the type of exchange-correlational functional.

Section 3. V_X levels and structural distortion in group 5 TMDs

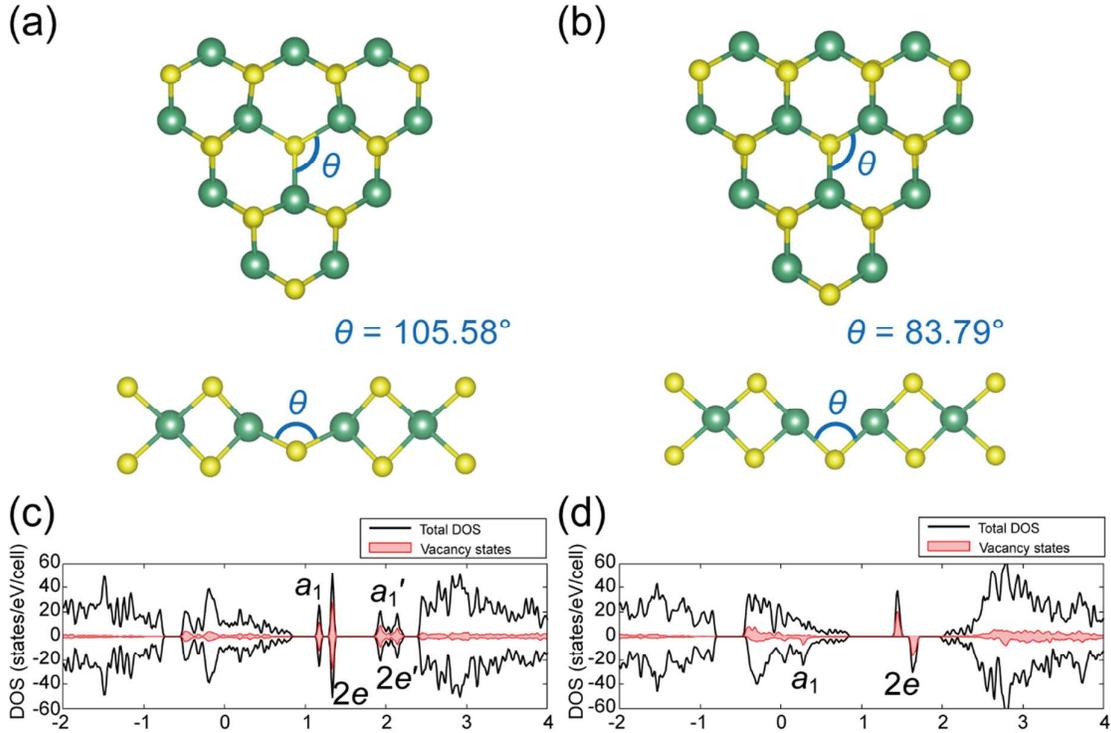


Figure S2 Atomic structures of (a) V_S -NbS₂ and (b) V_S -NbS₂ after hydrogen is adsorbed {we do not mark a hydrogen atom for showing the structural difference between (a) and (b) more clearly}. (c) and (d) show density of states (DOS) corresponding to the atomic structures in (a) and (b), respectively. For clarifying influence of the structural distortion on defect levels, we obtain DOS in (d) without hydrogen.

We present an example showing impacts of the large structural distortion in the group 5 TMD with V_X on electronic structures. In NbS₂ that is one of group 5 TMDs, V_S causes a significant change in the atomic structure; the S-Nb-S angle in the vicinity of V_S is 105.58° {see Figure S2(a)} while 84.81° in clean NbS₂. Electronic structure analysis shows there are six V_S -induced levels (a_1 , a_1' , two e , and two e' states) as shown in Figure S1(c). Among them, a_1' and e' states are not found in group 4 and 6-10 TMDs where only a_1 and two e states are identified. On the other hand, when hydrogen is adsorbed on a vacancy site, the S-Nb-S angle (83.79°) almost recovers that of non-defective system {see Figure S2(b)}, resulting in the disappearance of three additional localized states, namely a_1' and e' states, as can be seen in

Figure S2(d).

Section 4. Backward elimination method in multiple linear regression

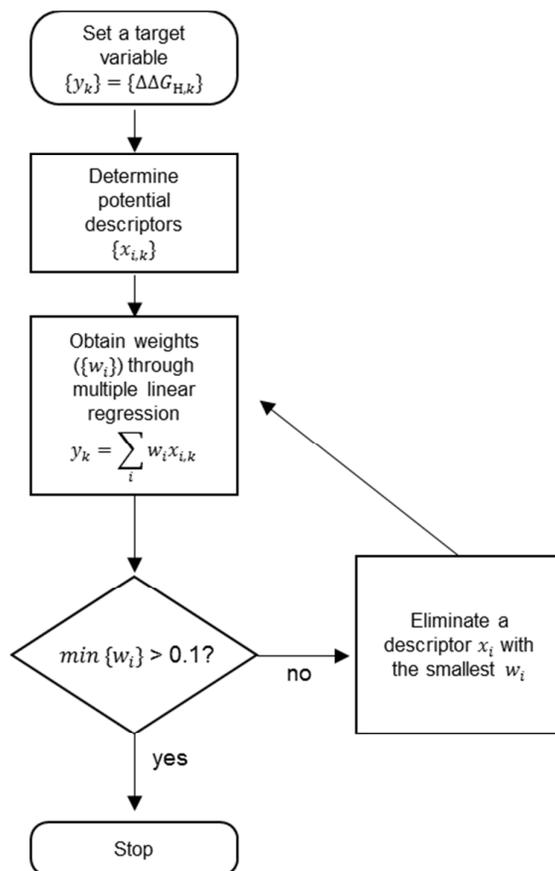


Figure S3 Flowchart of backward elimination method in multiple linear regression.

We carry out backward elimination method in multiple linear regression following a procedure shown in the flowchart in Figure S3 to identify key quantity correlating with the binding strength of hydrogen to anion vacancy of TMDs. We number off TMDs and set $\Delta\Delta G_{H,k}$ as a target variable y_k , where k denotes the number index of a specific TMD. Then we extract 15 potential descriptors for the regression ($\{x_{i,k}\}$ where i runs from 0 to the number of descriptors): formation energy of vacancy, average energy level of cation at the vacancy site, HOMO, LUMO, enthalpy of formation, ionic cohesive energy, valence band width, center of valence band, center of $X-p$ orbitals in valence band, electronegativity of transition metal, and normalized lattice parameter. Once weights are determined through multiple linear regression, we eliminate a descriptor with the smallest weight. We continue this until all weights of remaining descriptors are larger than 0.1.

References

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