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Rhenium Doping Induced Structural Transformation in Mono-layered MoS₂ with Improved Catalytic Activity for Hydrogen Evolution Reaction

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Abstract:

This paper reports a new design methodology to improve catalytic activities of catalysts based on two-dimensional transition metal dichalcogenides through elemental doping which induces structural transformations. Effects of rhenium (Re) doping on structural stability/phase transformation and catalytic activity of mono-layered trigonal prismatic (2H) MoS₂ were investigated using density functional theory as one example. Results show that 2H-Mo_{1-x}Re_xS₂ transforms into 1T'-Mo_{1-x}Re_xS₂MoS₂ as the value of x is larger than 0.4, and the transfer of the electron from Re to Mo is identified as the main reason for this structural transformation. The 1T'-Mo_{1-x}Re_xS₂ shows a good catalytic activity for the hydrogen evolution reaction when $0.75 \leq x \leq 0.94$.

Keywords: Molybdenum disulfides, Structural transformation, Doping, Hydrogen evolution reaction, Density functional theory

1. Introduction

Hydrogen is regarded as one of the most important energy carriers because of its highest energy density per unit mass among all elements and renewable characteristics [1]. However, there is a huge challenge to find an economical way to continuously generate hydrogen in a large scale. Electrochemical hydrogen evolution reaction (HER) has been proposed as a possible way for sustainable production of hydrogen [2]. The first step for HER is that hydrogen atoms are bound to the catalyst's surface, and the corresponding Gibbs free energy of hydrogen adsorption is the critical parameter to describe the rate of reaction, which should be near to zero for an ideal catalyst [3-5]. Platinum (Pt), ruthenium, and iridium are generally regarded as ideal catalysts for the HER [6-8]. However, they are expensive with limited resources, which restrict their large-scale production for hydrogen generation [9, 10]. Therefore, it is urgent to search for new catalysts with cheap and earth-abundant elements for hydrogen production through electrochemical HER.

Layered transition metal dichalcogenides (TMS_2) have attracted extensive research interest due to their excellent electrical, chemical and optical properties [11, 12]. Among these, monolayer molybdenum disulfides (MoS_2) have been applied in rechargeable ion batteries, transistors and catalysts [13-15]. Its good catalytic activity and stability for HER make it one of the promising candidates to replace noble metals including ruthenium, iridium and platinum [16].

In MoS_2 , the molybdenum atoms have a six-fold coordination environment and are hexagonally packed between two atomic layers of trigonal S atoms. There are a variety of

polytypic structures for the MoS₂ depending on the atomic arrangement of the S atoms. MoS₂ typically has a stable 2H-MoS₂ structure at room temperature, in which the Mo atoms are located at the lattice positions of a hexagonal close-packed structure with a trigonal symmetry [17]. However, the basal plane of the 2H-MoS₂ is inert for HER with a large positive Gibbs free energy, and the activity sites are located at the edges of the monolayer or defect sites [18].

MoS₂ can also have a 1T-MoS₂ structure when the Mo atoms are located at the octahedral center composed of six S atoms [17]. However, the structure of the 1T-MoS₂ is metastable. Under an external strain, it will transform into 1T'-MoS₂ phase [19], in which the Mo atoms are located at the disordered octahedrally center composed of six S atoms. The atomic configurations of 2H- and 1T'-MoS₂ are shown in Fig. 1. Sun et al. [13] studied the origin of phase transformation between 2H- and 1T'-MoS₂, and showed that electron doping destabilizes the crystal structure of the 2H-MoS₂, thus causing its structural transformation into the 1T'-MoS₂ phase. The 2H-MoS₂ phase is the most common and stable crystal structure of MoS₂ with a semiconducting character. Whereas transformation from 2H-MoS₂ into 1T'-MoS₂ can be triggered by doping alkali metal atoms (Li, Na and K) [13, 20-22], and the reason is because the alkali metal atoms donate their valence electrons to the MoS₂. Similarly, some other elements such as rhenium (Re) has one more electron than Mo atom, therefore, we believe that by substituting Mo with Re (which acts as electron donors), the phase transformation from 2H phase to 1T' phase can be triggered and the 1T' phase can also be stabilized at room temperature.

MoS₂ and its associated composites have been investigated as catalyst materials for electrochemical HER [19, 23, 24]. The effectiveness of HER is strongly dependent on the

structure of host materials. The basal plane of 2H-MoS₂ is inert for HER [25, 26], whereas the basal plane of 1T'-MoS₂ is catalytically active for HER [25, 26]. Currently, various methods, such as amorphization [27, 28], doping [29-32], and defect generation [33, 34] in the 2H-MoS₂ have been extensively explored to improve the electrochemical HER. For example, Tsai et al. [32] studied the structure and catalytic activity via transition metal doping of S-edge of 2H-MoS₂, and they reported that doing with a reactive metal led to a weaker H binding, and doping with a less reactive metal led to a strong H binding. Chhetri et al. [35] studied the Re-doping of nano-particulate MoS₂ with fullerene-like structures, and obtained a higher current density than that made from the pristine few-layer 2H-MoS₂. Deng et al. [29] demonstrated that Pt-doped layered MoS₂ nanosheets showed a significantly enhanced HER activity compared with that from non-doped MoS₂. Doping the edge sites of MoS₂ with transition-metals (Fe, Co, Ni and Cu) also enhanced its efficiency for HER [31]. However, these metal doping did not modify the 2H structure of MoS₂ monolayer, and the catalytic active sites are still located at the edge of MoS₂ monolayer. It is a more effect way to improve the electrochemical HER through formation and stabilization of the 1T'-MoS₂ to trigger the catalytic active sites in the basal plane of MoS₂ monolayer.

Based on the above discussions, it is critical to use fundamental theories and rational designs to induce the phase transformation from 2H-MoS₂ to 1T'-MoS₂ in order to enhance the electrochemical HER. In this paper, we propose a new design methodology to dope the MoS₂ using the element such as Re in order to induce the phase transformation from 2H- to 1T'-MoS₂ and also stabilize 1T'-MoS₂ at room temperature. The structural transformation and HER

catalytic activity of monolayer MoS₂ upon Re-doping were investigated using a density functional theory (DFT), and we concluded that after Re doping, the 1T'- Mo_{1-x}Re_xS₂ has superior catalytic activities of HER.

2. Computational details

Stability of Re-doped MoS₂ and hydrogen adsorption free energy were investigated using plane-wave simulations performed in the Vienna ab initio simulation package (VASP) [36, 37]. The projector augmented wave [38] method was used to describe electron-ion interaction, and the electron exchange-correlation was described by generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) function [39]. An energy cutoff of 520 eV was used for the plane-wave basis sets. As shown in Fig. 1, super-cells of MoS₂ monolayer (1×2, 2×2 and 4×4) were used to investigate the stability of the 2H- and 1T'-Mo_{1-x}Re_xS₂ with x equals to 0.00, 0.0625, 0.25, 0.50, 0.75, 0.9375 and 1.00, respectively. A larger supercell with 8×8 was used to investigate the adsorption behavior of H atom. Brillouin zone was integrated using the Monkhorst-Pack [40] scheme with 9×5×1 and 2×2×1 k -points for the simulations of structural stability and hydrogen adsorption, respectively. All atom positions and geometric structures were freely relaxed using the conjugate gradient approximation (CG) until the force on each atom is less than 0.02 eV/Å. In order to avoid the periodic image interactions between the adjacent layers, the distance between surface of adjacent layers was kept as 30 Å.

The energy difference (ΔE) between the 2H- and 1T'-MoS₂ as a function of the Re doping concentrations was used to characterize the stability of 2H- and 1T'- phases.

$$\Delta E = E_{2H} - E_{1T} \quad (1)$$

where E_{2H} and E_{1T} are the total energy of 2H- and 1T'- phases per MoS₂ molecule.

The Gibbs free energy of hydrogen adsorption (ΔG_H) is a key parameter to describe the activity of the materials, and is calculated using equation (2).

$$\Delta G_H = \Delta E_H + \Delta E_{ZPE} - T\Delta S_H \quad (2)$$

where ΔE_{ZPE} is the difference in zero-point energy of hydrogen in the adsorbed state and the gas phase; ΔS_H is the entropy difference between the adsorbed state and the gas phase of hydrogen; ΔE_H is the hydrogen chemisorption energy, which is defined using equation (3).

$$\Delta E_H = E(\text{MoS}_2 + \text{H}) - E(\text{MoS}_2) - \frac{1}{2}E(\text{H}_2) \quad (3)$$

where $E(\text{MoS}_2 + \text{H})$ and $E(\text{MoS}_2)$ are the total energy values of MoS₂ with and without adsorption of the H atom, and $E(\text{H}_2)$ is the total energy of a molecule hydrogen under the gas phase.

The calculated frequencies of H₂ gas are 4345 cm⁻¹, 58 cm⁻¹, and 42 cm⁻¹. The contribution from the configurational entropy in the adsorbed state is small thus is neglected in this study. The entropy of hydrogen adsorption can then be written as: $\Delta S_H = \frac{1}{2}S_{\text{H}_2}$ where S_{H_2} is the entropy of hydrogen molecule in the gas phase at standard conditions (300 K, 1 bar) [41]. Using the above values, the Gibbs free energy in equation (2) can then be rewritten as:

$$\Delta G_H = \Delta E_H + 0.24.$$

3. Results and discussion

The lattice parameters of the 2H-MoS₂ were calculated to be $a=b=3.19$ Å, which are in a good agreement with reported theoretical values of 3.18-3.20 Å [42-44] and experimental value of 3.16 Å [45]. The lattice parameters of 1T'-MoS₂ were calculated to be $a=b=3.18$ Å.

As shown in Fig. 1, the phase transformation from 2H to 1T'-MoS₂ involves: (1) metal atoms form metal-dimer; and (2) partial S atoms move from one pyramidal position to one hexagonal center position of pristine 2H-MoS₂. Correspondingly the geometrical structure is transformed from a perfect trigonal prismatic one into a disorder octahedral one. The total energies of pristine 2H- and 1T'-MoS₂ were calculated, and the results showed that the energy of 2H phase is 0.55 eV lower than that of 1T' phase per unit cell (which consists of one Mo atom and two S atoms). These results are well consistent with the previously reported values of 0.54 and 0.55 eV [13, 14] and the reported energy of 1T'-MoS₂ which is 0.26 eV lower than 1T-MoS₂ per unit cell [13]. Our results also indicate that the 2H phase is the more stable one for MoS₂.

By substituting Mo with Re, the pure MoS₂ changes into an alloy of Mo_{1-x}Re_xS₂. The calculated values of energy differences (ΔE) between 2H and 1T'-Mo_{1-x}Re_xS₂ phases as a function of Re-doping concentration are shown in Fig. 2. Clearly the 2H phase is more stable than 1T' phase at lower Re-doping concentrations. The 2H→1T' phase transformation occurs by gradually increasing the Re-doping concentration. The calculated results show that the critical value for the 2H→1T'-phase transformation is $x\approx 0.4$. The stability of the 1T' Mo_{1-x}Re_xS₂ is also enhanced by increasing the Re content.

Occupancy of d -orbitals by electrons in $\text{Mo}_{1-x}\text{Re}_x\text{S}_2$ plays an important role on the stability of 2H- and 1T'-phase [13, 46]. The energy of the $4d$ orbitals of Mo ions will be affected by the changes of their surrounding ions. The d -orbitals of 2H-MoS₂ can be split into three parts: (1) electron-filled dz^2 state, (2) empty dx^2-y^2 and dxy states, (3) empty dxz and dyz states [12, 47]. Since Re has one more valence electron than Mo, the electron will occupy the empty d -orbitals after Re-doping. The 2H-MoS₂ shows a semiconducting character with the Fermi energy level located above the valence band maximum. The electron states near the Fermi level are mainly composed of dz^2 , dx^2-y^2 and dxy , which are in good agreements with the previous reports [48-50].

Fig. 3 shows the partial density of states for $\text{Mo}_{1-x}\text{Re}_x\text{S}_2$ with $x = 0.0, 0.25, 0.50$ and 1.0 , respectively. With the Re-doping, the Fermi energy shifts to the conduction band for $\text{Mo}_{0.75}\text{Re}_{0.25}\text{S}_2$. The electronic states of Re and Mo atoms in the conduction bands are partially overlapped, and the electrons occupy the dz^2 , dx^2-y^2 and dxy orbitals of 2H-MoS₂ and 2H- $\text{Mo}_{0.75}\text{Re}_{0.25}\text{S}_2$. With the increase of Re content, the electrons will occupy the dxy , dyz and dzx orbitals of Mo atom as shown in Fig. 3(c). Correspondingly the $\text{Mo}_{0.5}\text{Re}_{0.5}\text{S}_2$ transforms from 2H-phase to 1T'-phase. In addition, the electrons will accumulate at the neighboring S atoms, which results in loss of charges from the Mo-S bonds and also weakens the Mo-S bonds. These will facilitate that the S atom migrates from the apex of the triangular prism to the apex of the octahedron, thus causing the transformation from the 2H-phase to 1T'-phase. With the increasing of the Re content, more electrons will occupy the dxy , dyz and dzx orbitals, and result in a much more stable 1T'-ReS₂. Result also show that the 1T'-ReS₂ has a metallic characteristic.

The HER process using the MoS₂ involves two principal steps: (1) Volmer step in which the hydrogen atoms are bound onto the catalyst (*); (2) Heyrovsky or Tafel step, in which molecular hydrogen is released to the active site of catalyst (*) [10, 51]. The Volmer step is the rate-determining step of HER on MoS₂, which has been proven experimentally [52]. The previous studies using DFT analysis showed that the activity sites of MoS₂ are mainly located at the Mo-edge, whereas the basal plane of 2H-MoS₂ is inert for HER [18]. We have calculated the ΔG_{H} values of the H atom adsorption on the Mo_{1-x}Re_xS₂, and the data are related to the HER activity of the catalyst. Results of the stable sites of H atom adsorption on Mo_{1-x}Re_xS₂ are shown in Fig. 4. Clearly the H atoms prefer to be adsorbed at the top of S atom. The ΔG_{H} value is 2.11 eV for the H atoms adsorbed on the 2H-MoS₂, which is consistent with the previous reported values [53, 54].

The values of free energies for H atoms adsorbed on the Mo_{1-x}Re_xS₂ as a function of Re-doping concentration are shown in Fig. 5. The values of ΔG_{H} decrease with the increase of Re content. Results also indicate that the binding of H atom on Mo_{0.9375}Re_{0.0625}S₂, Mo_{0.75}Re_{0.25}S₂ and Mo_{0.5}Re_{0.5}S₂ is weak with highly positive free energies of 2.13, 1.58 and 1.35 eV, respectively. However, the binding of H atom on the 1T'-ReS₂ is very strong with a free energy of -3.34 eV, which could prevent the release of hydrogen. The free energies are 0.08 eV and 0.13 eV for Mo_{0.25}Re_{0.75}S₂ and Mo_{0.0625}Re_{0.9375}S₂, respectively, which are quite low values, indicating that Mo_{1-x}Re_xS₂ with $0.75 \leq x \leq 0.94$ is good to be used as catalysts.

The local electron densities of states of Mo_{1-x}Re_xS₂ with and without H atom adsorption are summarized in Fig. 6, in which S-p and S-p' represent the *p* states of S before and after hydrogen

adsorption, and H-s represents the *s* state of H. Here the Fermi energy is set to be zero. For 2H-MoS₂ and 2H-Mo_{0.9375}Re_{0.0625}S₂, the *s* states of H atom locate below the Fermi energy level, which indicates that the H atom does not donate its electron to the S atom. A weak bonding of H atom on the Mo_{1-x}Re_xS₂ (with *x*=0 and 0.25) can be found with the adsorption free energies of 2.13 and 1.58 eV, respectively. With the increase of Re content, the adsorption free energy of H on Mo_{1-x}Re_xS₂ decreases as shown in Fig. 5. The *s* state of H atom locates above the Fermi energy for Mo_{0.0625}Re_{0.9375}S₂, indicating that H can donate its electron to S 3*p* state. The hybridization of S 3*p* and H 1*s* states results in splitting of H 1*s* state into bonding and anti-bonding states, which has enhanced the interactions between S and H atoms. These cause the anti-bonding states shifted to an energy value much higher above the Fermi level. The peak of H anti-bonding appears at an energy which is 0.27 eV above the Fermi level of the 1T'-ReS₂, therefore, there is a strong adsorption of H atom on the 1T'-ReS₂ with a free energy of -3.37 eV.

Although the Mo-edge of the 2H-MoS₂ shows a good catalytic activity, the poor charge transfer of 2H-MoS₂ significantly limits the kinetics of HER due to its inherent semiconductor nature, which was verified experimentally [55]. Re-doping induces transformation from 2H-Mo_{1-x}Re_xS₂ into 1T'-Mo_{1-x}Re_xS₂, and Mo_{1-x}Re_xS₂ shows a good catalytic activity for the HER when $0.75 \leq x \leq 0.94$. Therefore, our study provides a fundamental understanding of the Re-doping induced high catalytic activity of MoS₂, and thus verify a new design methodology to improve the catalytic activity of two-dimensional transition metal dichalcogenides based catalysts.

Apart from Re-doping, doping with other elements such as alkali metals intercalation and a high dose electron beam irradiation [56] can all induce the 2H \rightarrow 1T' structural transformation, which could be used to improve the catalytic activity of two-dimensional transition metal dichalcogenides. Therefore, we believe our results provide a general design methodology to improve the catalytic activity of two-dimensional transition metal dichalcogenides based catalysts through elemental doping which induces phase transformation.

4. Conclusion

In conclusion, we investigated the phase transformation from 2H to 1T'-phase and stability of MoS₂ upon Re-doping using spin-polarized DFT calculations. Mo_{1-x}Re_xS₂ transforms from 2H- to 1T'-phase when x is larger than 0.4. The calculated Gibbs free energy of H adsorption on Mo_{1-x}Re_xS₂ decreases with increasing Re content in the Mo_{1-x}Re_xS₂. Mo_{1-x}Re_xS₂ shows a good catalytic activity for the HER as $0.75 \leq x \leq 0.94$ with Gibbs free energy values of 0.08 and 0.13 eV. This study provides a fundamental design methodology to improve the catalytic activity of two-dimensional transition metal dichalcogenides based catalysts.

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Lists of figures captions:

Figure 1 Top view atomistic configuration of (a) 2H- and (b) 1T'-MoS₂ doping with Re. Red, green dash line and black solid line represents the 1×2, 2×2 and 4×4 super cells, respectively.

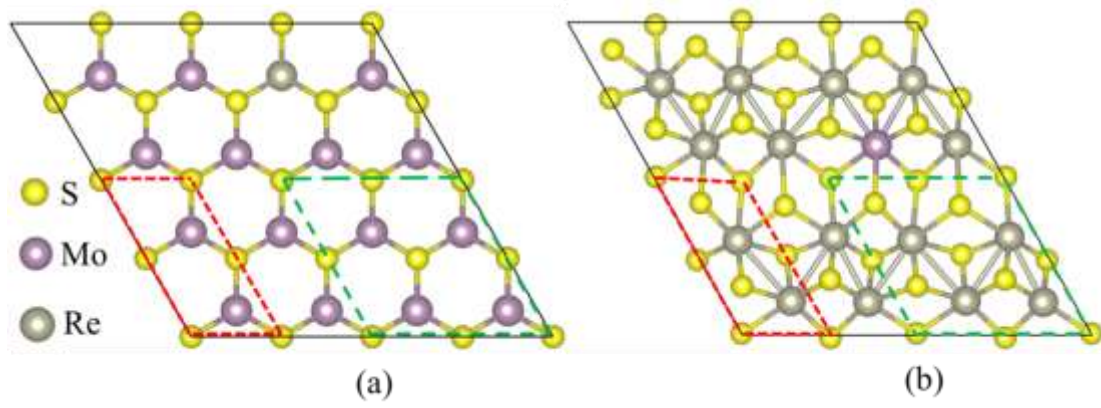
Figure 2 Energy difference per Mo_{1-x}Re_xS₂ molecular between the 2H- and 1T'-phase as a function of Re-doping content.

Figure 3 Density of states of (a) 2H-MoS₂, (b) 2H-Mo_{0.75}Re_{0.25}S₂, (c) 1T'-Mo_{0.50}Re_{0.50}S₂ and (d) 1T'-ReS₂. The Fermi energy level was set to zero.

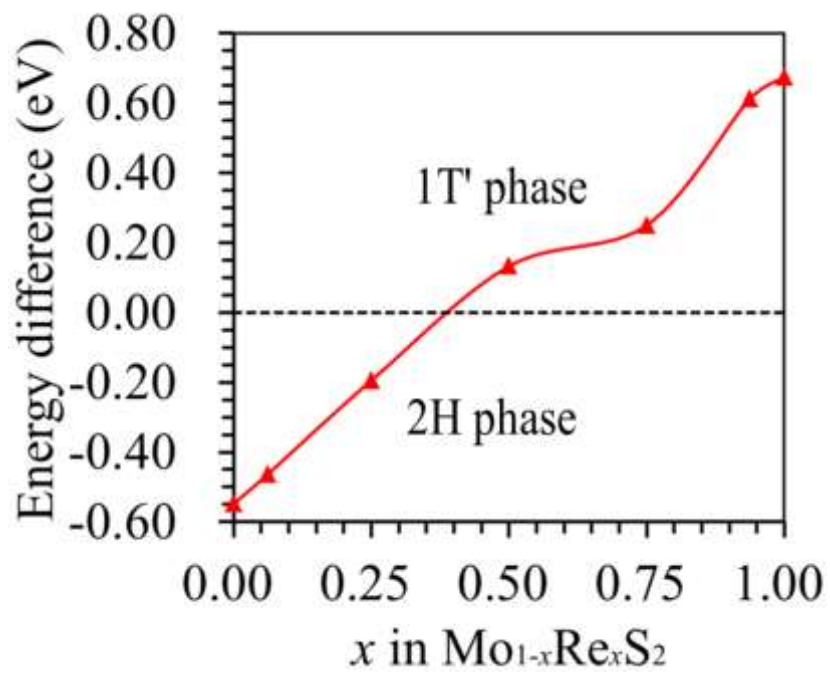
Figure 4 The catalytic activity site of hydrogen adsorption on the (a) 2H- and (b) 1T'-Mo_{1-x}Re_xS₂, the S, Mo, Re and H atom are represented by yellow, purple, silver and green balls, respectively.

Figure 5 The Gibbs free energy with hydrogen adsorption on the stable structure of the Mo_{1-x}Re_xS₂ as a function of Re doping content.

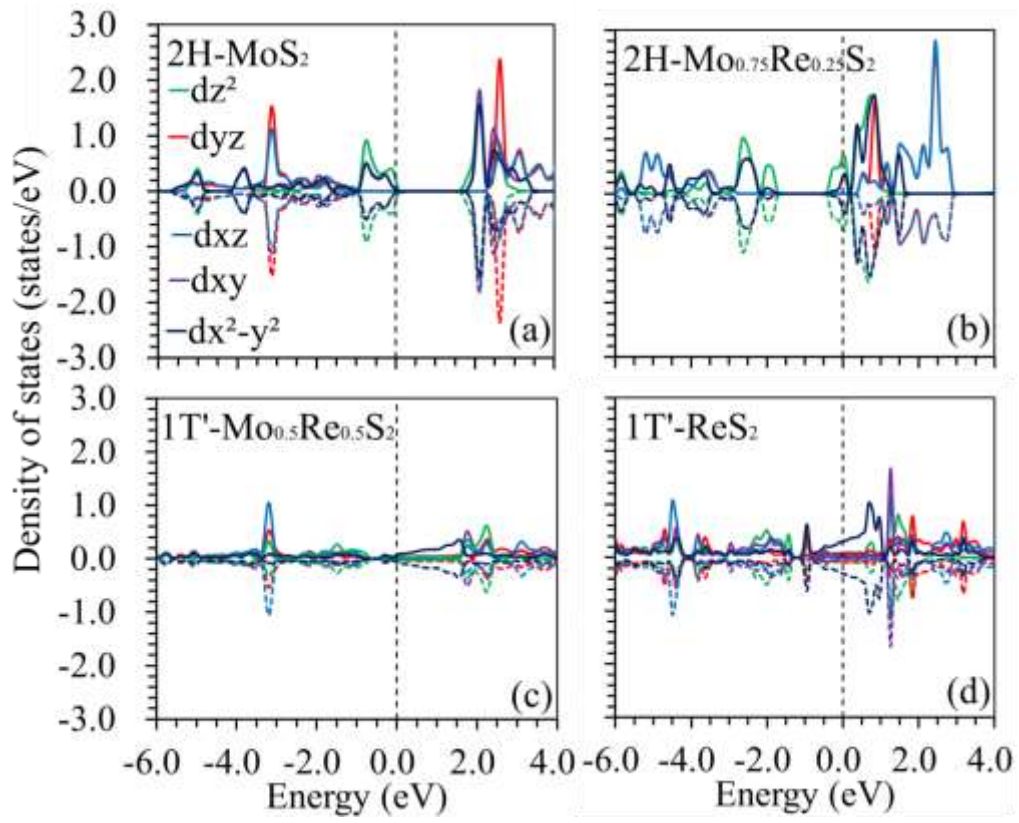
Figure 6 Density of states of hydrogen adsorbed on the (a) 2H-MoS₂, (b) 2H-Mo_{0.50}Re_{0.50}S₂, (c) 1T'-Mo_{0.0625}Re_{0.9375}S₂ and (d) 1T'- ReS₂. S-p and S-p' represent the *p* state of S before and after hydrogen adsorption, H-s represents the *s* state of H. The Fermi energy was set to zero.



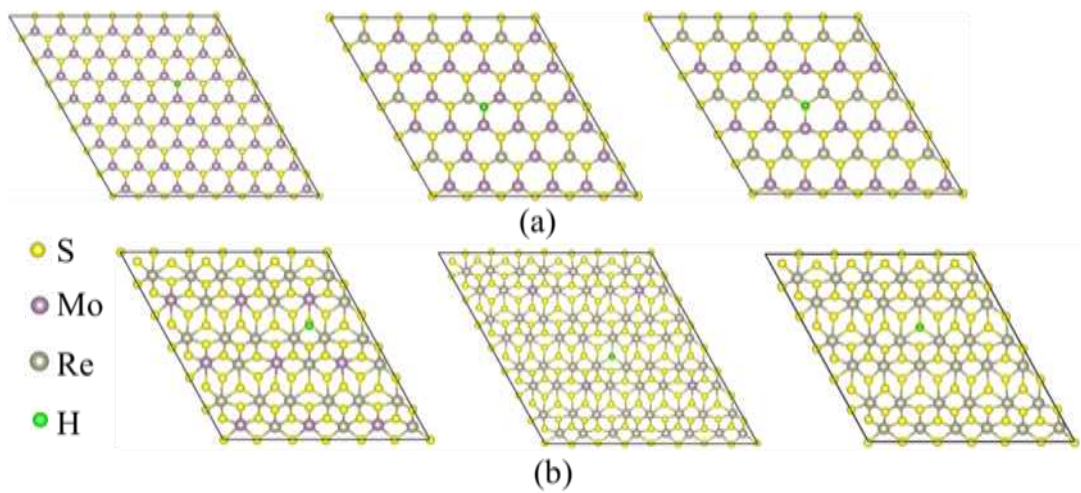
W.W. Shi et al. Figure 1



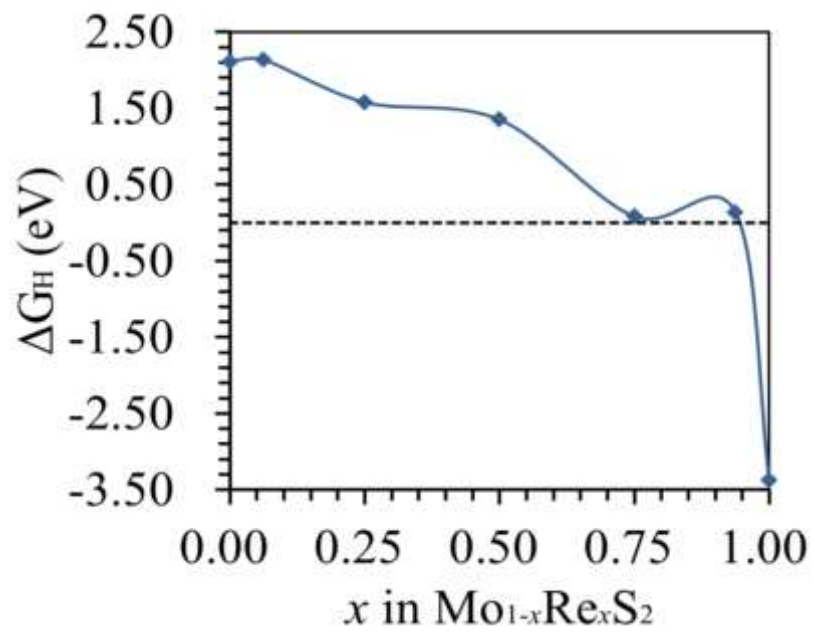
W.W. Shi et al. Figure 2



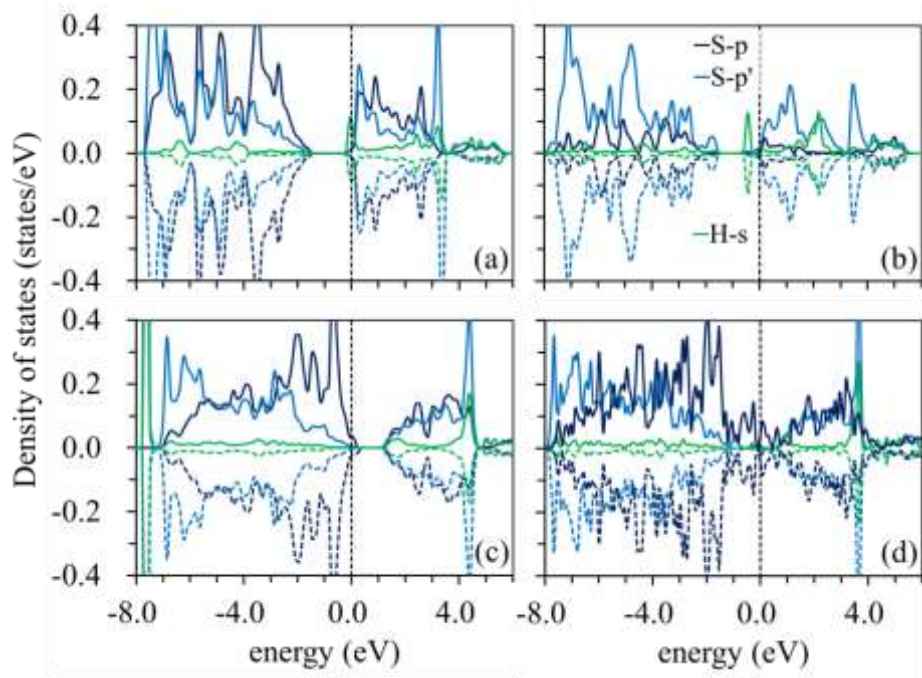
W.W. Shi et al. Figure 3



W.W. Shi et al. Figure 4



W.W. Shi et al. Figure 5



W.W. Shi et al. Figure 6