Titanium-doped MoS$_2$ monolayer as highly efficient catalyst for hydrogen evolution reaction

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Abstract. The effects of Ti dopants on the catalytic activities of the hydrogen evolution reaction (HER) in monolayer MoS$_2$ basal plane were investigated using density functional theory. Our study shows that Ti dopants that substituted Mo atoms in MoS$_2$ have small formation energy, and the complex dopant structures involving multiple Ti sites are energetically more stable than the isolated ones. Doping Ti atoms greatly improves the catalytic performances of MoS$_2$ with a near-ideal hydrogen-adsorption Gibbs free energy. Projected density of states analysis revealed that the mechanism for the improvement of catalytic activity is due to formation of the density of states near the Fermi energy level upon increasing dopant concentrations. It can be expected from the current results that excellent catalytic performance can be obtained by atomic composition modifications, such as Ti doping in the HER reaction.

1. Introduction

Platinum (Pt) group metals possess the highest catalytic efficiency for the hydrogen evolution reaction (HER). However, the commercialization of Pt-based catalysts is limited due to their scarcity and high cost [1]. Two-dimensional layered molybdenum disulfide (MoS$_2$) could be a potential alternative catalyst to Pt group materials for HER based on both theoretical calculations and experiments [2, 3]. To date, the catalytic efficiency of MoS$_2$ for HER is still inferior to Pt, possibly due to its limited density of active sites [4, 5]. In spite of extensive research into increasing the density of active sites [6, 7], new strategies to increase catalytic activity of MoS$_2$ monolayer is still greatly needed in the HER field.

Recently, strain applying and atomic doping in MoS$_2$ have been widely studied both in theories and experiments [8, 9]. For example, Rhenium (Re) doping in MoS$_2$ results in efficient catalytic performance for HER accompanied by phase transformation from the stable 2H phase to the less stable 1T’ phase [10, 11]. Nobel-metals like Pt have also been studied as dopants to increase the density of active sites for HER, but the high cost hindered their large-scale application. Among all dopants, most of them have more valence electrons than Mo atom. Very few papers have studied the effects of electrons-poor metal doping to MoS$_2$. In this work, titanium (Ti) as dopants substituting Mo atom in MoS$_2$ monolayer was investigated using DFT calculations, since Ti atom has similar atomic radius and less valence electrons compared with Mo atom. The similar atomic radius of Ti (147 pm) and Mo (139 pm) eliminates the effects of strain introduced in the doping process. The calculation results demonstrate that Ti doping has a small defect formation energy and possesses an ideal hydrogen-adsorption Gibbs free energy ($\Delta G_{H}$),
indicating that the Ti-doped MoS$_2$ can be a very promising method to improve the density catalytic activity for HER.

2. Simulation and calculations
All calculations were performed using the spin-polarized density function theory (DFT) within Vienna ab initio Simulation Package (VASP). The electron-ion interactions were described by using projector augmented wave (PAW) potential [12, 13]. The generalized gradient approximation (GGA) in the scheme of Perdew–Burke–Ernzerhof (PBE) was used to describe the exchange and correlation interactions. The plane-wave cut-off energy was set to 520 eV, and the Γ-centered k-point meshes with k-spacing of 0.02 Å$^{-1}$ were employed for sampling the Brillouin zone. The lattice parameters and atomic positions were fully relaxed until the force on each atom was smaller than 0.02 eV/Å, the convergence threshold of energy for the self-consistent was $10^{-5}$ eV. A 15 Å vacuum region was added to avoid the interactions between the neighboring layers.

3. Results and discussion
The optimized lattice parameters of 2H-MoS$_2$ are $a = b = 3.18$ Å, which is consistent with previous experimental values of $a = b = 3.16$ Å [14]. A 5×5×1 supercell was established to simulate the various concentrations of Ti atom doping (the supercell lattice is shown in Fig. 1a). In the smaller Ti doping concentration case (1/49), a larger supercell 7×7×1 was built. The atomic configuration with one Mo atom replaced by one Ti atom is shown in Fig. 1b. The different stable atomic configurations of Ti-doped MoS$_2$ with doping concentration increasing from 1/25 to 3/25 are shown in Fig. 1c-e. The positions of Ti dopants were determined by formation energy ($E_f$) calculations. The detailed equation is shown below:

$$E_f = E_{Ti-MoS_2} - E_{MoS_2} - \mu_{Ti} + \mu_{Mo}$$

It can be interpreted that the Ti doping is exothermic (endothermic) when $E_f$ is negative (positive). Several possible configurations for the complex structures with two or three Ti atoms were considered. The complex dopants structures are energetically more stable than the two or three isolated ones according to our calculations. Interestingly, the $E_f$ shows an increasing trend with the increased doping concentrations until reaching the largest value 0.53 eV when the concentration is 2/25. Then, the $E_f$ decreases to 0.14 eV when concentration is 3/25 (Fig. 1f). The results show that Ti doping in MoS$_2$ will be gradually more feasible upon highly doping concentrations. This trend is vastly different from other dopants like Re and Au in MoS$_2$ monolayer, which needs much higher energy to obtain [15].

The catalytic performance was described and investigated by the $\Delta G_{H}$ calculations. The more negative $\Delta G_{H}$ is, the stronger the bonds between hydrogen and catalyst is during the hydrogen-capture process. A close-to-zero $\Delta G_{H}$ indicates high catalytic activity because it benefits the H atom adsorption.
and the molecule release. The calculated $\Delta G_{H}$ of Ti-doped MoS$_2$ and the most stable adsorption configurations of H are presented in Fig. 2a-e. For the pristine MoS$_2$ monolayer, the H atom prefers to locate on top of S atoms with a bond length of 1.416 Å (as presented in Fig. 2a top and bottom). In the cases of Ti-doped MoS$_2$, the H atom still prefers to locate on top of S atoms near the Ti dopants. Surprisingly, the bond lengths between H and S atoms are consistently around 1.36 Å despite various doping concentrations (as presented in Fig. 2b-e). The corresponding $\Delta G_{H}$ of various Ti dopants substituted are shown in Fig. 2f. For pristine MoS$_2$ monolayer, the $\Delta G_{H}$ is 2.13 eV, which is consistent with previously reported values of 2.11 and 2.18 eV [10]. In the cases of Ti-doped MoS$_2$, the $\Delta G_{H}$ are 0.38, 0.37 0.01 and -0.13 eV at doping concentrations of 1/49, 1/25, 2/25 and 3/25, respectively. The smaller $\Delta G_{H}$ in doped MoS$_2$ catalysts is confirmed by their shorter bond lengths between H and S atoms, compared with pristine MoS$_2$ monolayer. The results indicate that Ti substituted MoS$_2$ are more suitable for the HER, since their calculated $\Delta G_{H}$ are very close to the ideal threshold values (0.0 eV).

Fig. 2 Atomic configurations of H adsorption on various MoS$_2$ with doping concentrations, (a) pristine MoS$_2$, (b-e) H adsorbed on surface of Ti-doped MoS$_2$ with doping concentrations of 1/49, 1/25, 2/25 and 3/25, respectively, (f) Gibbs free energy ($\Delta G_{H}$) of H adsorption on the various catalyst surfaces.

Projected densities of states (PDOS) were also calculated for the MoS$_2$ with or without Ti dopants, as shown in Fig. 3. Pristine MoS$_2$ shows direct band gap with 1.69 eV [16]. The valence band maximum (VBM) mainly originates from the d-orbitals of Mo atom and the conduction band minimum (CBM) are also dominantly from the Mo-d orbitals (as shown in Fig. 3a). When H is adsorbed on the surface of MoS$_2$, there is an obvious decrease in the energy levels of both Mo and S orbitals. As a result, a large number of antibonding states of S and Mo atoms were filled, which is typically associated with a weaker binding between H and catalysts (as shown in Fig. 3b) [17]. This feature can also be seen in the s orbitals of H atoms due to the Fermi energy across the s states, which will lead to the occupied H antibonding (as shown in Fig. 3c). In general, the bonding states are fully filled because they are far below the Fermi energy, while the extent to which the antibonding states are filled depending their relative energy to the Fermi energy. The degree of antibonding state filling can significantly weaken the hydrogen adsorption strength on the catalyst surfaces, resulting in a large positive $\Delta G_{H}$ of 2.13 eV.
Figure 3. Projected density of states (PDOS), (a) pristine MoS$_2$, (b) pristine MoS$_2$ after H adsorption, (c) s states of H atom that adsorbed on the surface MoS$_2$, (d) Ti-doped MoS$_2$ with concentration of 2/25, (e) Ti-doped MoS$_2$ with concentration of 2/25 after H adsorption, (f) s states of H atom that adsorption on the surface of Ti doped MoS$_2$ with doping concentration of 2/25.

In the doped cases, Ti-doping gives rise to gap states both within band gap and near Fermi energy. In addition, it moves the Fermi energy closer to valence band which subsequently leads to p-type doping (as shown in Fig. 3d). The features of PDOS after H adsorption (shown in Fig. 3e) are distinctly different from pristine ones. Both the p and d states of S and Mo atoms are only slightly shifted after H adsorbed. Especially, both the spin-up and spin-down states of H atom are above the Fermi energy, suggesting that less antibonding states are occupied and stronger the sulfur-hydrogen bonds will be formed (Fig. 3f). The $\Delta G_H$ of 0.01 eV can give a strong evidence for the PDOS features. According to above discussion, the Ti-doped MoS$_2$ shows a great doping feasibility with small formation energy and great potential application in HER due to the ideal $\Delta G_H$ of 0.01 eV.

4. Conclusion
In conclusion, DFT calculations were carried out to investigate the potential of Ti-doped MoS$_2$ monolayer as an efficient catalyst material for HER. Our study shows that Ti-doped MoS$_2$ has small formation energy, and the complex dopants structures are energetically more stable than the isolated ones. Doping of Ti atoms greatly improves the catalytic performances of MoS$_2$ with a near-ideal hydrogen-adsorption Gibbs free energy. Our results show that electronic modification, such as Ti-doping in MoS$_2$ monolayers, is a highly promising method to obtain high efficient HER catalysts.

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