Prevention of Hydrogen Damage Using MoS$_2$ Coating on Iron Surface

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Received: 20 February 2019; Accepted: 1 March 2019; Published: 6 March 2019

Abstract: The prevention of hydrogen penetration into steels can effectively protect steels from hydrogen damage. In this study, we investigated the effect of a monolayer MoS$_2$ coating on hydrogen prevention using first-principles calculations. We found that monolayer MoS$_2$ can effectively inhibit the dissociative adsorption of hydrogen molecules on an Fe(111) surface by forming a S–H bond. MoS$_2$ coating acts as an energy barrier, interrupting hydrogen penetration. Furthermore, compared with the H-adsorbed Fe(111) film, the work function of the MoS$_2$-coated film significantly increases under both equilibrium and strained conditions, indicating that the strained Fe(111) film with the MoS$_2$ coating also becomes more corrosion resistant. The results reveal that MoS$_2$ film is an effective coating to prevent hydrogen damage in steels.

Keywords: hydrogen adsorption; MoS$_2$; protective barrier; strain; work function

1. Introduction

Hydrogen damage is a severe problem since hydrogen degrades the mechanical properties of steels [1]. For example, hydrogen can induce low yield and fracture stresses in steels. Hydrogen atoms in structural materials usually come from the reduction of hydrogen ions or dissociative adsorptions of some H-containing gases, such as H$_2$, H$_2$O, and H$_2$S. The prevention of hydrogen penetration into steels can effectively protect steels from hydrogen damage, which is typically achieved by applying a thin protective coating of TiN/TiC [2], SiC [3], an aluminum or a chromium rich layer [4–6], some alloy coatings [7], and conductive polymers [8] all of which show resistance to hydrogen or hydrogen isotopic permeability. It has been reported that AlN coatings [9] and Er$_2$O$_3$ coatings on 316L stainless steel [10] and MoS$_2$/Ni$_{60}$Cr$_{20}$ films on pure iron [11] can act as protective barriers of metals against hydrogen or hydrogen isotope permeation. The graphene coating was found to decrease the hydrogen embrittlement susceptibility of the metal substrate, as the hydrogen content in graphene-coated copper was greatly reduced after hydrogen charging [12,13]. It is thought that less hydrogen is introduced to the bulk material by using these surface coatings.

Among various protection coatings, MoS$_2$ possesses excellent physical and chemical properties that are suitable for preventing hydrogen permeation into metals. MoS$_2$ not only has a 1185 °C melting point but is also chemically stable at an ambient atmosphere up to 315 °C. A good mechanical strength has also been reported for monolayer MoS$_2$, which is a flexible and strong material with a high Young’s modulus comparable to steels [14]. Furthermore, monolayer MoS$_2$ is a semiconductor with a direct band gap of ∼1.8 eV [15], and the low electrical conductivity and nearly insulating channel of MoS$_2$ are
also advantageous for hydrogen permeation barriers. For monolayer MoS$_2$, the Mo atoms and S atoms combine with each other by covalent bonds. When coated on metals, the MoS$_2$ layer usually exhibits a good adhesive performance, because S atoms can firmly bind to a metal surface [16]. The stable metal–S interface leads to a high diffusion barrier for hydrogen atoms to overcome in MoS$_2$ coatings than that in metals. It is thought to protect the underlying metal substrate from corrosion and oxidation. Recently, MoS$_2$ coatings of a few micrometers thick on pure iron substrates have been fabricated by magnetron sputtering [11]. However, the current understanding of MoS$_2$ on steels as a protective barrier against hydrogen damage is still limited, which has motivated the present study.

More specifically, steels usually experience a moderate strain in the service environment due to external mechanical loads and residual stresses, which can affect the mechanical and electronic properties of steels [17,18]. Experimental studies have suggested that stress corrosion cracking and hydrogen embrittlement are dominating damages for steels. Thus, strain and hydrogen are two important factors to alter the physical properties of steels. The protective properties of MoS$_2$ coating on iron films have also been investigated with applied stress and hydrogen.

Here we explore monolayer MoS$_2$ as a promising coating for the protection of steels against hydrogen damage using first-principles calculations. To simulate the coating effects of MoS$_2$ on steels, we chose pure iron film as a substrate, instead of steels with various additional elements, to provide a basic understanding. We found that the MoS$_2$ monolayer can stably bind to the Fe(111) surface and effectively inhibit the dissociative adsorption and permeation of hydrogen. MoS$_2$ interrupts hydrogen penetration by the formation of S–H bonds. In addition, compared with the H-adsorbed Fe(111) film, the work function of the MoS$_2$-coated film significantly increases under both equilibrium and strained conditions. The present results suggest the feasibility of MoS$_2$ coating as a protective barrier against hydrogen damage.

2. Calculation Methods

All calculations reported in this work were performed in the framework of the spin-polarized density functional theory (DFT), as implemented in the Vienna ab initio simulation package (VASP, 5.4.1, Universität Wien, Wien, Austria) [19]. The electron–ion interaction was described using the projector augmented wave (PAW) method [20]. The exchange correlation between electrons was treated with generalized gradient approximation (GGA) in the Perdew–Burke–Ernzerhof (PBE) form [21]. Using a $15 \times 15 \times 15$ k-point mesh for the primitive cell, we obtained for body-centered cubic (bcc) Fe a lattice constant of 2.835 Å and a local magnetic moment of 2.20 $\mu_B$ per Fe atom, which agree very well with the experimental values of 2.866 Å [22] and the theoretical results performed with different k-point meshes [23–26].

For the study of H adsorption on the iron surface, we used a $4 \times 4$ surface cell of Fe(111) surface with six layers of Fe atoms, as shown in Figure 1a,b. A plane-wave energy cutoff of 400 eV with a k-point sampling of $3 \times 3 \times 1$ in the Brillouin zone (BZ) was employed for the $4 \times 4$ surface cell. A vacuum region of 15 Å was introduced to eliminate the electronic interactions between the periodic images. The convergence criterion for the energy was set to $10^{-5}$ eV. For structural optimization, the bottom three Fe layers were fixed at their bulk positions and other atoms were fully relaxed until the force on each atom was lower than 0.01 eV/Å. In the case of asymmetric models, owing to the different electronegativity of two neighboring surfaces, a dipolar interaction appears in the z direction and affects the work function. To eliminate such interactions between the periodic replicas, dipole corrections were employed in the z direction for asymmetric slabs by using the method proposed by Neugebauer and Scheffler [27].
where $E$, which is in good agreement with the literature results that report the closest H–Fe distance as 1.66 Å for H on Fe(110) and 1.68 Å for H on Fe(100) [23].

The H atom can form a strong chemical bond with the Fe3 atom with a distance of 1.636 Å, which is in good agreement with the literature results that report the closest H–Fe distance as 1.66 Å for H on Fe(110) and 1.68 Å for H on Fe(100) [23].

The H atom initially locates at the bridge site of the Fe1 and Fe2 atoms, and then binds to the Fe3 atom after significantly affects the density of states (DOS) of the nearby Fe atoms, as shown in Figure 2. The H energy of H is referenced to the H$_2$ molecule and hence reflects a dissociative adsorption. The adsorption energy for H adsorbing at the bridge site was $0.38 \text{ eV}$ [23], respectively. The H atom can form a strong chemical bond with the Fe3 atom with a distance of 1.636 Å, which is in good agreement with the literature results that report the closest H–Fe distance as 1.66 Å for H on Fe(110) and 1.68 Å for H on Fe(100) [23].

Table 1 lists the adsorption energy, $E_{ads}$, which is defined as

$$E_{ads} = E(H/\text{film}) - E(\text{film}) - \frac{1}{2}E(H_2)$$ (1)

where $E(H/\text{film})$ and $E(\text{film})$ are the energy of the Fe(111) film (or MoS$_2$/Fe film) with or without H adsorption. The energy of H is referenced to the H$_2$ molecule and hence reflects a dissociative adsorption energy. The adsorption energy for H adsorbing at the bridge site was $−0.55 \text{ eV}$, suggesting that the H$_2$ molecule can easily dissociate on the Fe(111) surface. Previous theoretical calculations have predicted that H adsorption energy on Fe(110) and Fe(100) surfaces is $−0.71 \text{ eV}$ and $−0.38 \text{ eV}$ [23], respectively. The H atom can form a strong chemical bond with the Fe3 atom with a distance of 1.636 Å, which is in good agreement with the literature results that report the closest H–Fe distance as 1.66 Å for H on Fe(110) and 1.68 Å for H on Fe(100) [23].

3. Results

When the H atom approaches the Fe(111) surface, we found that H chemically adsorbs on Fe atoms. Figure 1a,b displays the geometric structure of the film with one H atom adsorption on the surface. The H atom prefers to adsorb at the bridge site of the two top layer Fe atoms, such as Fe1 and Fe2 presented in Figure 1b. Table 1 lists the adsorption energy, $E_{ads}$, which is defined as

$$E_{ads} = E(H/\text{film}) - E(\text{film}) - \frac{1}{2}E(H_2)$$ (1)

where $E(H/\text{film})$ and $E(\text{film})$ are the energy of the Fe(111) film (or MoS$_2$/Fe film) with or without H adsorption. The energy of H is referenced to the H$_2$ molecule and hence reflects a dissociative adsorption energy. The adsorption energy for H adsorbing at the bridge site was $−0.55 \text{ eV}$, suggesting that the H$_2$ molecule can easily dissociate on the Fe(111) surface. Previous theoretical calculations have predicted that H adsorption energy on Fe(110) and Fe(100) surfaces is $−0.71 \text{ eV}$ and $−0.38 \text{ eV}$ [23], respectively. The H atom can form a strong chemical bond with the Fe3 atom with a distance of 1.636 Å, which is in good agreement with the literature results that report the closest H–Fe distance as 1.66 Å for H on Fe(110) and 1.68 Å for H on Fe(100) [23].

Figure 1. (a) Side and (b) top views of H-adsorbed Fe(111) film with six layers. The brown, green, and silver balls represent Fe atoms in the A, B, and C layer, respectively. The possible adsorption sites of H are marked in (b), on the top site of surface Fe (T), the bridge site of two surface Fe atoms (B), the hcp (hexagonal close packed) hollow site (H), and the fcc (face-centered cubic) hollow site (F). The numbers 1, 2, and 3 in (b) present the Fe1, Fe2, and Fe3 atoms that surround the H atom. (c) Side and (d) top views of H-adsorbed MoS$_2$/Fe(111) film. For the MoS$_2$ and Fe(111) interfaces, one S atom (noted in the red dotted circle in (d)) located at the bridge site of the surface Fe atoms is the most energetically stable configuration.
Table 1. The adsorption energy ($E_{\text{ads}}$), the closest H–Fe distance ($d_{\text{H–Fe}}$), the amount of charge transfer of the adsorbed H atom ($\Delta Q_{\text{H}}$), and the work function ($W_F$) of H adsorptions on the Fe(111), MoS$_2$, and MoS$_2$/Fe(111) films. $E_{\text{ads}}$ is calculated by Equation (1).

|         | $E_{\text{ads}}$ (eV) | $d_{\text{H–Fe}}$ (Å) | $\Delta Q_{\text{H}}$ (e) | $W_F$ (eV) |
|---------|-----------------------|------------------------|---------------------------|------------|
| H on Fe(111) | −0.55                | 1.636                  | 0.355                     | 3.842      |
| H on MoS$_2$  | 1.64                 | 1.417                  | −0.042                    | 4.705      |
| H on MoS$_2$/Fe(111) | 1.26                | 1.425                  | −0.018                    | 4.688      |

The chemisorbed H atom binds to the Fe(111) surface with a strong orbital overlap, which significantly affects the density of states (DOS) of the nearby Fe atoms, as shown in Figure 2. The H atom initially locates at the bridge site of the Fe1 and Fe2 atoms, and then binds to the Fe3 atom after geometric optimization. From Figure 2a, we observe that the projected density of states (PDOS) on Fe1 near the Fermi level slightly decreases after H adsorption, while the closest Fe3 exhibits an evident PDOS reduction as shown in Figure 2b—in particular the down spin. The decrease of Fe PDOS reflects the reduction of the charge density of Fe atoms, as the H atom withdraws 0.355 e from the Fe(111) surface after adsorption, as listed in Table 1. To further illustrate the detailed nature of the charge transfer, we show in Figure 2c the charge difference between the H-adsorbed Fe(111) system and the sum of the isolated Fe(111) and the H atom, which is defined as

$$\Delta \rho = \rho_{\text{H}/\text{Fe}} - (\rho_{\text{Fe}} + \rho_{\text{H}})$$

(2)

where $\rho_{\text{H}/\text{Fe}}$, $\rho_{\text{Fe}}$, and $\rho_{\text{H}}$ are the charge density of the H/Fe(111) film, the Fe(111) film, and the H atom at the same lattice constant with frozen atom positions. The yellow regions represent the charge accumulation and the blue regions represent the depletion of electrons. To have a quantitative picture, we plot in Figure 2d the plane-averaged electron density difference along the perpendicular direction ($z$) to the Fe(111) surface. As seen in Figure 2c,d, the Fe(111) film acts as a donor and the H acts as an acceptor with electrons transferring from the Fe to the H due to the difference in electronegativity.

The above results show that hydrogen molecules can easily dissociate on the clean Fe surface and permeate into the bulk, as reported in literature [23]. The accumulation of H in bulk can generate hydrogen bubbles which are harmful for steels. In order to inhibit hydrogen permeation, a monolayer
MoS$_2$ is coated on the Fe(111) surface. For the model, a $3\sqrt{3} \times 3\sqrt{3}$ MoS$_2$ supercell was constructed in a hexagonal geometry on six layers of $4 \times 4$ Fe(111) film, as shown in Figure 1c,d. We have considered the MoS$_2$/Fe(111) slab as a model, because the hexagonal unit cell on the Fe(111) surface structurally matches the surface cell of MoS$_2$ and a better lattice match is achieved between both materials. The size of the unit cell of the $\sqrt{3} \times \sqrt{3}$ MoS$_2$ slab is 5.473 $\times$ 5.473 Å with an angle of 120$^\circ$, which is a good fit with the Fe(111) surface with the dimensions of 4.009 $\times$ 4.009 Å and an angle of 120$^\circ$. In our setup, the MoS$_2$ was subjected to a small strain ($\approx$2.4%) to make it commensurable with Fe(111), and the effect of the lattice mismatch on the electronic structure of the MoS$_2$ was negligible.

After optimizing the structures from four initial configurations in an interface with the monolayer MoS$_2$, i.e., the top, bridge, fcc hollow, and hcp hollow sites formed by the three Fe atoms in the top layer, we obtained the most stable configurations of the MoS$_2$/Fe(111) interfaces, as shown in Figure 1c,d. The S atom in the dotted red circle was located at the bridge site of two Fe atoms. In terms of the adsorption energy per interfacial sulfur atom, calculated as

$$E_b = \frac{(E_{\text{MoS}_2/\text{Fe}} - E_{\text{Fe}} - E_{\text{MoS}_2})}{N_S}$$  \hspace{1cm} (3)

where $N_S$ is the number of interfacial sulfur atoms and $N_S = 27$ for the calculated model, the Fe(111) surface had a medium adhesion with MoS$_2$ with an $E_b = -0.41$ eV, which is larger than the weak interaction of MoS$_2$–Au but smaller than the strong interaction of MoS$_2$–Sc or MoS$_2$–Ti [28]. The planar plane of the Fe(111) surface was distorted since the top layer Fe atoms were stretched by the MoS$_2$. The average distance between the interfacial sulfur atoms with the top layer Fe atoms was 1.901 Å. The short interfacial distance also suggests that MoS$_2$ forms a stable coating on an iron surface, which is beneficial for preventing hydrogen from transiting to Fe.

It is interesting to study the potential energy of the H atom adsorbing on the MoS$_2$/Fe surface, and then moving through the interface region from the MoS$_2$ part to the Fe substrate. To find the most energetically stable H adsorption site on the MoS$_2$/Fe surface, we examined five possible initial positions for H on the clean monolayer MoS$_2$, i.e., the top and bridge sites of Mo atoms and the top, bridge, and hollow sites of S atoms. In terms of the adsorption energy, we obtained the most energetically stable configuration, that is, H initially locates at the Mo bridge site and then binds to the surface S atom after structural relaxation. In this configuration, the atomic H chemically binds to the top surface of S with an $E_{\text{ads}}$ of 1.64 eV and a S–H distance of 1.417 Å (Table 1), in agreement with previous reports [29]. Figure 1c,d depicts the side and top views of the most stable H adsorption geometries on the MoS$_2$/Fe surface, a similar adsorption configuration is obtained with an $E_{\text{ads}}$ of 1.26 eV. The positive $E_{\text{ads}}$ suggests that the H$_2$ molecule cannot spontaneously dissociate on the MoS$_2$/Fe film, which effectively suppresses the H dissociative adsorption. Experimental measurements have also demonstrated that the planar surface monolayer MoS$_2$ is chemically rather inert while the edge sites of clusters and the defected layers are chemically reactive [30,31], which is consistent with the present results. Furthermore, as an atomic H migrates into the interface, it has been reported that an energy barrier of about 0.57 eV is required to pass through the center of the hexagonal structure in MoS$_2$ [29], because there is a repulsive force induced by a strong electron cloud of MoS$_2$. This energy barrier is up to 6.56 eV for the H$_2$ molecule passing through the hole of the monolayer MoS$_2$ [29], indicating that H is difficult to diffuse into the other side of MoS$_2$. Even if H successfully moves to the interface at a high temperature or under a large tensile strain, the energy for binding to the Fe-contacted S atom is 0.15 eV higher than that of the up-surface S atom. All the results demonstrate that a MoS$_2$ coating acts as an energy barrier which interrupts hydrogen penetration by the formation of S–H bonds.

To gain insight into the H prevention effect of the MoS$_2$ coating, Figure 3a,b depicts the PDOS of the clean MoS$_2$ film and the H-adsorbed MoS$_2$/Fe(111) film. As seen from Figure 3a, a perfect monolayer MoS$_2$ is a semiconductor with a band gap of 1.75 eV, in accordance with literature results [32]. There is no net magnetic moment for S and Mo atoms. When it is fabricated on Fe(111) film, the gap of MoS$_2$ significantly shifts down in energy, as displayed in Figure 3b, i.e., the upward shift of the Fermi
level, indicating that the MoS\(_2\) is n-doped on the Fe(111) surface. Furthermore, the electronic states of S and Mo are broadened within the band gap (−1.6–0.1 eV), due to the strong orbital interfacial hybridization between the Fe and S atoms. The H/MoS\(_2\)/Fe(111) film still presents a ferromagnetic property, with split up and down orbitals for the PDOS in Figure 3b. This magnetic behavior mainly stems from the single \(d\) electron provided by the Fe atom. There is also a weak magnetic moment on the MoS\(_2\) layer induced by the Fe contact, in which Mo reaches 0.05 \(\mu_B\) and the interface S atoms are less than 0.02 \(\mu_B\), in agreement with previous calculations for MoS\(_2\) on a single layer of Fe [33]. Moreover, for the H-adsorbed MoS\(_2\)/Fe(111) film, the total DOS at the Fermi level, \(E_F\), is mainly contributed from the down spin of the Fe 3\(d\) states.

**Figure 3.** (a) Projected density of states on S and Mo atoms in a clean monolayer MoS\(_2\). (b) Total density of states (DOS) and PDOS on Fe, MoS\(_2\), and H in the H/MoS\(_2\)/Fe system. (c) Charge transfer density between the H, the MoS\(_2\), and the Fe(111) film. The yellow and blue colors represent electron accumulation and depletion, respectively. The charge density isosurface was set to 0.003 e Å\(^{-3}\). (d) Interfacial charge transfer between the H, the MoS\(_2\), and the Fe(111) film as a function of the \(z\) coordinate perpendicular to the surface.

Figure 3c,d plots the interfacial charge transfer of the H-adsorbed MoS\(_2\)/Fe(111) film. The differential charge density at the interface is defined as

\[
\Delta \rho = \rho_{H/MoS_2/Fe} - \left( \rho_{MoS_2} + \rho_{Fe} + \rho_H \right)
\]

where \(\rho_{H/MoS_2/Fe}\), \(\rho_{MoS_2}\), \(\rho_{Fe}\), and \(\rho_H\) are the charge densities of the H/MoS\(_2\)/Fe, MoS\(_2\), and Fe(111) films and the H atom. Firstly, at the MoS\(_2\)–Fe interface, there is a large amount of charge transfer from the top two layers of Fe to the interfacial S atoms in MoS\(_2\), a total of 4.91 e (calculated by Bader charge analysis). A strong binding between MoS\(_2\) and Fe with a distance of 1.901 Å allows a strong wave-function overlap between the Fe and the S states. Secondly, the adsorbed H donates 0.018 e to the neighboring S atom by forming a S–H bond, as listed in Table 1.

The above results demonstrate that the MoS\(_2\) coating on the Fe(111) film effectively prevents H adsorption on the iron surface or permeation into the bulk. The influence of the MoS\(_2\) coating on corrosion resistance is also reflected by work function, which is a sensitive parameter for the corrosive behavior of materials. Previous studies have suggested that materials with a lower work function possess a lower corrosion potential and consequently become easily corroded [34,35]. The work function (\(W_F\)) is calculated as the difference between the vacuum level, \(E_{\text{vacuum}}\), and the Fermi energy, \(E_F\):

\[
W_F = E_{\text{vacuum}} - E_F
\]

Here, \(W_F\) reflects the electronic energy level, so it is related to its electrostatic potential. The work function of a clean Fe(111) surface is 3.823 eV, which is lower than the closely packed crystallographic
plane (low-index) Fe(110) surface [36]. After H adsorption, the $W_F$ is slightly enhanced to 3.842 eV, as listed in Table 1, because the H atom withdraws electrons from the Fe and a weak dipole pointing inward (from H to Fe) is formed. Figure 4a plots the $W_F$ of the H-adsorbed Fe(111) with and without the MoS$_2$ coating. The $W_F$ of the H/MoS$_2$/Fe(111) system significantly increases to 4.688 eV, which is lifted by 0.846 eV compared to that without the MoS$_2$ coating, since the H-adsorbed MoS$_2$ exhibits a high $W_F$ of 4.705 eV. It is indispensible to understand why the coating and H adsorption change the work function of these films.

There could be different factors, such as epitaxial strain, structural deformation, hydrogen, and the external environment, affecting the mechanical properties of steels. Experimental studies have suggested that stress corrosion cracking and hydrogen embrittlement are the most dominating damages for steels [17,18]. Next, we discuss the work function changes associated with the H adsorption in the strained system. A biaxial strain by rescaling the in-plane lattice constant was applied to the H/Fe(111) and the H/MoS$_2$/Fe films. Without the MoS$_2$ coating, the $W_F$ of the H/Fe(111) system increases/decreases by $-0.1$ eV under compressive/tensile strain up to 6%, as plotted in Figure 4b. For instance, the $W_F$ is 3.939 eV under 6% compressive strain and 3.756 eV under 6% tensile strain. This property is consistent with the experimental and theoretical results that the $W_F$ of metals decreases with tensile strain [37,38]. In the case of the H/MoS$_2$/Fe(111) system, the $W_F$ shows an opposite response to strain, i.e., it decreases to 4.631 eV under 6% compressive strain while it increases to 4.791 eV under 6% tensile strain. The changes in the $W_F$ of the MoS$_2$-coated film can be attributed to the strained MoS$_2$, which exhibited a $W_F$ decrease under compressive strain and a $W_F$ increase under tensile strain [39,40]. Under both compressive and tensile strains, a much higher work function is observed for the H/MoS$_2$/Fe film than that of the system without the MoS$_2$ coating, indicating that the strained Fe(111) film with the MoS$_2$ coating becomes more corrosion resistant.

The effect of the coating and the strain on the work function depends on how they affect the Fermi energy. To clarify the origin of the $W_F$ changes in the strained systems, Figure 5 plots the orbital-resolved band structures for the H-adsorbed Fe(111) film without or with the MoS$_2$ coating. Figure 5a–c shows the band structures for spin-up orbitals, corresponding with Figure 5d–f for the spin-down orbitals. Only five $d$ orbitals are presented in Figure 5, because the energy bands near the Fermi level are mainly contributed from Fe 3$d$ orbitals, as indicated by the PDOS in Figure 3b. Comparing the H/Fe(111) (Figure 5a,d) with the H/MoS$_2$/Fe system (Figure 5b,e), one prominent property is that the bands near the Fermi level become less dispersive, especially for the down spin in Figure 5e. The flatter bands lead to a low Fermi velocity, indicating a quite low Fermi energy, and then give rise to an enhancement in the work function of H/MoS$_2$/Fe. As a 6% tensile strain is applied to the H/MoS$_2$/Fe(111) film, the flatter feature at the Fermi level is more pronounced in Figure 5f,
suggesting that the $W_F$ of the $\text{H/MoS}_2/\text{Fe}$ system increases with tensile strain. The increased $W_F$ indicates that the MoS$_2$-coated surface becomes more corrosion resistant.

**Figure 5.** Band structures along the M-$\Gamma$-$K$ directions of (a,d) the H-adsorbed Fe(111), (b,e) the H-adsorbed MoS$_2$/Fe, and (c,f) the H-adsorbed MoS$_2$/Fe film with 6% tensile strain for up and down spins. Blue, green, red, purple, and orange lines on the bands illustrate the contribution from $d_{xy}$, $d_{xz}$, $d_{yz}$, $d_{z^2}$, and $d_{x^2-y^2}$ states.

4. Conclusions

In conclusion, we studied the MoS$_2$ coating on an iron surface as a protective barrier against H damage. The monolayer MoS$_2$ can be stably coated on the Fe(111) surface with a binding energy of $-0.41 \text{ eV}$ per surface S atom and an interfacial distance of 1.901 Å. Through the characterization of hydrogen-adsorbed MoS$_2$/Fe(111), it was identified that MoS$_2$ can effectively prevent hydrogen adsorption and penetration by the formation of a S–H bond. The hydrogen adsorption energy on the Fe(111) surface is enhanced from $-0.55 \text{ eV}$ to $1.26 \text{ eV}$ with the MoS$_2$ coating, suggesting that monolayer MoS$_2$ can effectively inhibit the dissociative adsorption of hydrogen molecules. In addition, the work function of MoS$_2$-coated Fe(111) films substantially increases by 0.846 eV, further indicating a more corrosion resistant property of the MoS$_2$-coated Fe(111) films owing to their improved surface properties. The results demonstrate that the MoS$_2$ coating is a proper barrier for H adsorption or permeation and can effectively avoid hydrogen damage. Based on the protective performance of monolayer MoS$_2$, multiple layers of MoS$_2$ or a thin film are expected to possess a better hydrogen prevention effect due to more barriers for hydrogen diffusion. Since it is still a challenge to produce a high quality monolayer MoS$_2$ on a large scale on steels, we suggest that coating with multiple layers of MoS$_2$ film might be more applicable.

**Author Contributions:** X.L. performed the calculation, data analysis, and wrote the manuscript; H.L., C.S., D.W., and Z.M. discussed the results and analyzed the data; and L.C. and L.Q. conceived the models and revised the manuscript.

**Funding:** This research was funded by the National Natural Science Foundation of China (Grant Nos. 51431004, 11634007, U1706221, and 51571030).

**Conflicts of Interest:** The authors declare no conflict of interest.
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