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Density functional theory calculations of hydrogen molecule adsorption on monolayer molybdenum and tungsten disulfide

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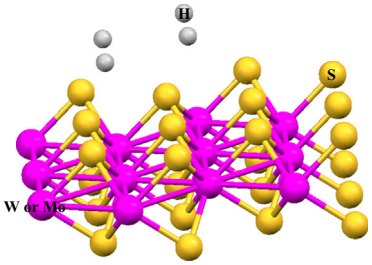
HIGHLIGHTS

- H_2 adsorption on MoS_2 and WS_2 was investigated.
- *First-principles* van der Waals functional (vdW-DF) method was applied for the considered systems.
- The H_2 molecule is physisorbed on the surface of the monolayer MoS_2 and WS_2 with adsorption energies of −131.61 and −169.44 meV.
- Adsorption of two H_2 molecules on one and both sides of the monolayer MoS_2 and WS_2 was examined.
- We calculated the binding energy between the H_2 molecule and the substrate (MoS_2 and WS_2) under axial strain.

GRAPHICAL ABSTRACT

Hydrogen molecule is physisorbed on the surface of the monolayer MoS_2 and WS_2 and the binding energy between the H_2 molecule and the substrate is enhanced by axial strain.



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ABSTRACT

In this work, we report a theoretical study on the adsorption of molecular hydrogen (H_2) on monolayer molybdenum disulfide (MoS_2) and tungsten disulfide (WS_2) using a *first-principles* van der Waals functional (vdW-DF) method. Our calculations show that the most favorable configuration for the adsorption of a H_2 molecule on monolayer MoS_2 is similar to that for the monolayer WS_2 surface. The H_2 molecule is physisorbed on the surface of the monolayers MoS_2 and WS_2 with adsorption energies of −131.61 and −169.44 meV, respectively. Analysis of the electronic structures and charge confirmed that no significant hybridization between the respective orbitals occurs, and quantitative analysis revealed that a small interaction was obtained in terms of binding energies. Furthermore, adsorption of two H_2 molecules on one and both sides of the monolayer MoS_2 and WS_2 was examined. The obtained results indicated that, with the adsorption of the second H_2 molecule on one- and both-side of WS_2, the binding energies were decreased to −155.2 and −153.6 meV, respectively. However, the values for adsorption of the second H_2 on monolayer MoS_2 remained nearly constant compared to the adsorption of the first H_2 molecule. In addition, we calculated the binding energy between the H_2 molecule and the substrate (MoS_2 and WS_2) under axial strain of −10% to 10%, which revealed that the binding energy between the H_2 molecule and the substrate was enhanced by axial strain. Our results also indicated that applying compression to monolayer WS_2 yields higher reactivity with the hydrogen molecule than applying compression to monolayer MoS_2.

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1. Introduction

Hydrogen is a favorable alternative fuel that is widely considered as an economical, nonpolluting, and renewable source of energy that contains much more chemical energy per mass than any petroleum fuel [1]. Hydrogen can be used as a clean fuel for vehicles, personal electronics, and other portable power applications [2]. Some critical challenges for storage materials include the need for chemical stability [3], a large surface area, hydrogen storage at ambient temperature and pressure, reversibility, and fast kinetics [4]. Many different materials have been considered as attractive candidates for safe and economically feasible hydrogen storage media, such as carbon-based materials [5–7], metal or chemical hydrides [8], and microporous polymers [9]. However, no material that can meet all the requirements listed above has been developed.

Two-dimensional (2D) materials have attracted much attention, primarily because of their interesting physical properties, which are strikingly different from those of their three-dimensional (3D) (bulk) counterparts. Graphene is the most famous member of the 2D material family, but nanosheets of transition metal disulfides (TMDs) consisting of a single to a few layers, such as molybdenum disulfide (MoS_2) and tungsten disulfide (WS_2), have recently attracted widespread attention as an alternative to graphitic carbon due to their high energy capacity. For example, the energy capacity of monolayer MoS_2 is approximately 1200 mAh/g [10–13], which is much higher than that of commercial graphite (372 mAh/g) [14] and graphene nanosheets (600–900 mAh/g) [15–17]. Transition metal disulfides have been widely used in numerous applications, such as hydrodesulfurization catalysts, photovoltaic cells, photocatalysts, nanotribology, lithium batteries, and dry lubrication, due to their distinctive electronic, optical, and catalytic properties [18,19]. The structures of MoS_2 and WS_2 are analogous to that of graphite and comprise triple atomic layers: a Mo or W layer in the trigonal prismatic coordination sandwiched between two layers of pyramidal S atoms. The triple layers are stacked and held together by weak van der Waals (vdW) interactions [20]. Monolayer MoS_2 and WS_2 are direct gap semiconductors with a bandgap of 1.8 eV and display good thermal stability [21,22]. MoS_2 and WS_2 nanosheets with one or a few layers were recently synthesized experimentally using scotch-tape or lithium-based intercalation methods shortly after the theoretical predictions [23–25]. The separation between the MoS_2 and WS_2 layers was reported to be in the range of 0.62–0.70 nm [23,26]. Theoretical studies of monolayer MoS_2 and WS_2 as substrates based on density functional theory (DFT) have recently been conducted [20–22,27]. In 2012, Koh et al. [4] investigated hydrogen adsorption on a MoS_2 monolayer based on the DFT method, which revealed that the conductivity of monolayer MoS_2 is greatly enhanced by the adsorption of hydrogen.

In this work, we systematically studied the adsorption properties of hydrogen molecules on monolayer MoS_2 and WS_2 using DFT calculations. We also calculated the adsorption energies of two hydrogen molecules on the MoS_2 and WS_2 substrates. We investigated individually the dispersion of hydrogen molecules that approach either side of a monolayer MoS_2 or WS_2 substrate. This is the first study to use DFT calculations to address the effects of the adsorbed hydrogen molecule on the structural and electronic properties of the WS_2 surface. The investigation of hydrogen molecules on monolayer MoS_2 substrates has seldom been reported. Finally, we introduced two different types of strain in the substrates to improve the binding energy in the systems under consideration.

2. Computational methods

Our calculations of hydrogen adsorption on monolayer MoS_2 and WS_2 substrates were performed within the framework of a *first-principles* DFT method implemented with the Spanish Initiative for Electronic Simulations with Thousands of Atoms (SIESTA) software package [28–31]. We adopted the generalized gradient approximation (GGA) to treat the exchange and correlation potential with the Perdew–Burke–Ernzerhof (PBE) functional [32]. In addition, it is important to consider nonlocal corrections that are responsible for vdW interactions.

Due to the limitation of conventional local DFT calculations in presenting the nonlocal dispersion correlation, we also used a fully nonlocal energy functional (vdW-DF) based on Grimme at the GGA level of theory, in which the PBE exchange functional is favorable for calculating vdW interactions [33,34]. All calculations were performed with a double-ζ basis set of localized numerical atomic orbitals, including polarization functions (DZP), with an energy shift of 50 meV and a split norm of 0.15. The mesh cutoff, an energy that corresponds to the grid spacing, was chosen to equal 150 Ry to represent the charge density. A $4\times4\times1$ Monkhorst-Pack grid for *k*-point sampling of the Brillouin zone was set, and the atomic positions were relaxed until the residual forces on each atom were less than 0.01 eV/Å. The supercell of monolayer MoS_2 or WS_2 consisted of 18 S atoms and 9 Mo/W atoms, and a periodic boundary condition was applied to the supercell. A vacuum width of 18 Å was constructed to eliminate interactions between adjacent images of the supercell. To calculate the interaction between a H_2 molecule and substrate, the basis set superposition error (BSSE) needs to be included in the binding energy calculations for the complexes under consideration. For this propose the counterpoise method using 'ghost' atoms was used according to the following equation:

$$E_b = E_{(TMD-H2)} - E_{(TMD_{ghost}-H2)} - E_{(TMD-H2_{ghost})} \quad (1)$$

where $E_{(TMD-H2)}$is the total energy of the MoS_2 or WS_2 substrate interacting with the H_2 molecule. The 'ghost' TMD/H2 corresponds to additional basis wave functions centered at the position of the H_2 molecule or the substrate, but without any atomic potential.

3. Results and discussion

3.1. Structure optimization and geometry of pristine MoS_2

To investigate the adsorption properties of a hydrogen molecule on monolayer MoS_2, we first optimized the geometric structure of the substrate. The optimized structures and geometric parameters, which comprised the Mo–S bond length (d_{M-S}), Mo–Mo distance (d_{M-M}), and S–S distance (d_{S-S}) of monolayer MoS_2, are illustrated in Fig. 1. The calculated d_{M-M}, d_{M-S}, and d_{S-S} of the substrate were determined to be approximately 3.11, 2.36, and 3.11 Å, respectively. Density of states (DOS) analyses were performed and revealed (Fig. 2) that the pristine MoS_2 may be a semiconductor with a VBM (valence-band maximum)/CBM (conduction-band minimum) energy gap (E_g) of 2.58 eV, which is in agreement with previous reports [1]. The net charge transfer was also calculated by Mulliken population charge analysis and indicated that approximately 1.17 electrons charges are transferred from the molybdenum to the sulfur atom.

3.2. Hydrogen molecule adsorption on pristine MoS_2

To identify the most favorable adsorption configurations, different possible initial configurations were considered, including positioning of the H_2 molecule perpendicular and parallel to the MoS_2 surface on the top, bridge and hollow sites. The top, bridge and hollow sites are directly above the Mo and S atoms, S–S bond, and sulfur trigonal rings of MoS_2, respectively. Fig. 1(b) presents a schematic representation of the different possible adsorption