Computational Materials Science 150 (2018) 484–490

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

First-principles calculations of water adsorption on perfect and defect WO_3(0 0 1)

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ARTICLE INFO

Keywords:
Water adsorption
Water dissociation
Excess electrons
Tungsten trioxides

ABSTRACT

The interactions between water and semiconductor metal oxides are critical to photocatalytic reactions. In this work, the water adsorption on stoichiometric, non-stoichiometric and hydrogenated WO_3(0 0 1) were investigated by first-principles calculations. The results show that the adsorption of the intact water molecule is more favorable than the adsorption of the dissociated ones on stoichiometric WO_3(0 0 1) at different coverages. As the coverage of the water molecules on the surface increases, the molecular and dissociated states tend to coexist on the stoichiometric WO_3(0 0 1). In addition, the oxygen vacancy and hydrogen atom affect the electronic properties of WO_3(0 0 1) by introducing the excess electrons, and the water adsorption could change distribution of excess electrons which are introduced by oxygen vacancy and hydrogen atoms. The water molecule can readily dissociate at the surface oxygen vacancy sites, while water molecules prefer remaining intact than being dissociated on the WO_3(0 0 1) with sub-surface oxygen vacancy or hydrogen.

1. Introduction

In the recent years, great progress has been made on the semiconductor photocatalysts for a wide range of applications such as degradation of organic pollutants, dye-sensitized solar cells and photo electrochemical water dissociation [1–8]. Tungsten trioxide, as an n-type Lewis acid semiconductor catalysts material, has been investigated extensively for many years, both experimentally and theoretically, due to its relatively small band gap, good performance in generating photocurrents and good photosensitivity [9,10]. WO_3 is semiconductor material with a direct band gap around 2.70 eV, *i.e.* about 0.30 eV smaller than the band gap of TiO_2 Rutile, which allows the WO_3 to utilize the solar energy in the visible region. The valence band maximum is below the oxidation potential of O_2/H_2O, which implies that WO_3 can be used as photoelectrode in potential photocatalytic water splitting applications [11,12]. However, the semiconducting properties of WO_3 are sensitive to various factors including the polymorphs, tilting of WO_6 octahedral, surface hydrogenation and defects [13–15]. Therefore, it remains great challenges to achieve the high catalytic activity and to determine the catalytically active sites [9,16]. As is known, the phase of bulk structure, adsorbate on surface and surface vacancy are critical to catalytic activities and reaction mechanisms [14,17–21]. WO_3 can form several different polymorphs under different temperature and pressure conditions, including the triclinic, γ-monoclinic, tetragonal, and orthorhombic phases [22,23]. Among these polymorphs, γ-monoclinic is most stable at room temperature and its (0 0 1) surface has the lowest surface energy [24]. As a consequence, monoclinic WO_3(0 0 1) surface has often been used as a porotype model to study the WO_3 surfaces. On such surfaces, the W−O bond lengths along x, y and z axis are different [25]. Recently, the properties of WO_3(0 0 1) surface were widely investigated experimentally and theoretically [26]. For example, the oxygen vacancies [27–29], adsorption of the atomic and molecular hydrogens [30], and catalytic reactions of methanol [31] and water [32] on WO_3(0 0 1) have been extensively explored by first-principles calculations and experimental measurements.

Water adsorption on semiconductor surface is the key step for practical applications and scientific research, especially for hydrogen production and industrial effluent decontamination [33,34]. The adsorption and reaction properties of water on semiconductor oxides were widely investigated, such as water adsorption on BiOX and TiO_2 [35–37]. Similarly, the photo-oxidation mechanisms of water on different faces of tungsten trioxides have been investigated by first-principles calculations [38]. The result indicated that the photo-oxidation reaction are driven by holes. Besides, the adsorption structures of water on WO_3 surface and the influence on the water adsorption of different water coverages have not been extensively studied yet. The according studies are especially lacked for understanding the water adsorption

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https://doi.org/10.1016/j.commatsci.2018.04.056
Received 28 February 2018; Received in revised form 19 April 2018; Accepted 24 April 2018
0927-0256/ © 2018 Published by Elsevier B.V.

behaviors on the defective WO_3, as oxygen vacancy is commonly found in WO_3. In addition, on the defective WO_3 surface, the hydrogen atoms can readily adsorb, which will have additional affects on the water adsorption. To the best of our knowledge, such effects have not been systematically studied yet. Hence, we systematically investigate the water adsorption properties on different type of WO_3 surface.

In this work, we investigate water adsorption on the stoichiometric, oxygen defective and hydrogenated WO_3(0 0 1) by the first-principles calculations, focusing on understanding the water adsorption state. The water adsorption energies on the different coverages were firstly examined, and the results show that water molecules prefer the molecular state than the dissociated one at the low coverage. When the water coverage increases to one monolayer (ML), water molecules could partially dissociate. Water adsorption affects the electronic structure of defective WO_3(0 0 1), but the water adsorption states were slightly affected by the excess electrons introduced by oxygen vacancy or hydrogen atom in the WO_3(0 0 1).

2. Computational details

The density functional theory (DFT) calculations were performed by CP2K/Quickstep package [39], and the PBE exchange correlation functional was used in all calculations. Hubbard U correction was applied to W 5d orbitals with the corresponding U values set to 6.20 eV and a test of U values were performed bellow. A 320 Ry cut off energy was used for basis set of plane waves. The wave function of valence electrons were expanded in terms of Gaussian function with molecularly optimized double-zeta polarized basis sets (m-DZVP) [40]. The norm-conserving Goedecker, Teter, and Hutter (GTH) pseudopotentials were used to describe core electrons [41]. All atoms were relaxed until the largest component in the forces for each atom becomes smaller than 0.01 eV/Å. In this work, the optimization of structures are performed by fixing the lattice parameter at the optimized values, all the atoms are fully relaxed [42].

The unit cell of WO_3 was optimized, and the corresponding lattice constants were used to build the 2×2 WO_3(0 0 1) surface, which is 15.34 Å × 15.44 Å. The slab was fully relaxed and the effects caused by fixing the geometry of the slab will be discussed bellow. The slab used in this work has a thickness of about 16 Å and 10 Å vacuum layer was added to the model slab along z axis. The periodic boundary conditions is considered here. The adsorption energies (abbreviation as E_a) are calculated with the equation: $E_a = (E_{(WO3/water)} - E_{WO3} - nE_{water})/n$, where $E_{(WO3/water)}$, E_{WO3}, E_{water} and n represent total energy of WO_3(0 0 1) with adsorbates, total energy of WO_3(0 0 1) substrate (stoichiometric, defective and hydrogenated), total energy of water and the number of adsorbed water molecules. The more negative adsorption energy for per H_2O molecule indicates more energetically favorable adsorption. The oxygen vacancy formation energy is calculated by the equation: $E_f = E_{defect} + u_o - E_{perfect}$, where the E_f, E_{defect}, u_o and $E_{perfect}$ represent the oxygen vacancy formation energy, total energy of the defective structure, oxygen chemical potential and total energy of the perfect structure, respectively.

3. Results and discussion

3.1. Water adsorption on perfect WO_3(0 0 1)

3.1.1. Water adsorption at 1/8 ML

The top view of (0 0 1) surface and monoclinic WO_6 cage are shown in Fig. 1(a) and (b), respectively. The WO_3 cell is composed by periodic WO_6 cages as shown in Fig. 1(a). Table 1 listed the values of W—O bond lengths. The bond lengths for W—O bonds along the z axis (labeled as z and −z in Fig. 1) and W—O bonds in the xy plane (labeled as x, −x, y, −y in Fig. 1) are found to be different, which indicates that the octahedral crystal field of W atom is distorted, and hence the O atoms along the z axis and in the xy plane are not equal.

In the following, the water adsorption on the stoichiometric WO_3(0 0 1) surface was carefully explored. The WO_3 (0 0 1) surface was firstly relaxed before water adsorption. The super cell for the slab model used in this work contains eight W atoms on the WO_3 (0 0 1) surface. Hence, the full monolayer (ML) adsorption of water can be modeled by adsorption of 8 water molecules on the 8 surface W sites in the super cell, denoted as 1 ML. Similarly 1/8 ML and 1/2 ML coverage can be modeled by adsorption of 1 and 4 water molecules on WO_3(0 0 1) with respect to the supercell. In order to know the coverages effect, several typical coverages, such as 1/8 ML, 1/2 ML and 1 ML, were considered. All possible adsorption geometries were considered at each coverage, and the most stable structures are discussed. Meanwhile, in order to determine the stable water adsorption structure, both the molecular and dissociated sates are calculated, and the relative stability at each coverage was examined.

Fig. 1(c) and (d) show the configurations of one water adsorption on the perfect (2×2) WO_3(0 0 1), corresponding to 1/8 ML. The adsorption energies for the molecular and dissociated water are −0.78 eV and −0.62 eV, respectively. As for the molecular states, the oxygen atom of the water adsorbs over the W atom, and the two hydrogen atoms point to the surface oxygen atoms of the WO_3(0 0 1) surface, forming two hydrogen bonds. We calculated the adsorption energies of dissociated hydrogen atom on O atoms along x, y and z directions, respectively. The adsorption along z direction is the most stable one with the adsorption energy of −0.62 eV. Thus, when the water molecule dissociates, one proton of the water molecule is transferred to the surface oxygen atom along z direction, forming one hydrogen bond with the hydroxyl. The molecular state is about 0.16 eV more stable than the dissociated state, which suggests that molecular state is more favorable at the low coverage of 1/8 ML. The water dissociation barrier was also examined with the nudged elastic band (NEB) technique [43,44]. During the NEB calculation, five images are uniformly distributed along the reaction path connecting the initial and final states. As shown in Fig. 2, the calculated dissociation barrier is about 0.33 eV on the perfect WO_3(0 0 1) surface.

In order to choose a reasonable U, the adsorption energies of 1/8 ML water on perfect surface were examined with several different U values (5 eV, 6.2 eV, and 7 eV). As shown in Table 2, the adsorption energies for the molecular and dissociated states vary within 0.1 eV with different U, whereas the relative stability between molecular and dissociated states are essentially invariant to the choice for the U parameter. In this work, we set the values according to the Ref. [45] and our tested results, and U = 6.2 eV was used in the following.

In this work, we calculated the adsorption energies of water on both the fully and partially relaxed slab models. As for the partially fixed model, the two bottom O—W—O layers were fixed. The 1/8 ML water adsorption was examined. The adsorption energies of molecular and dissociated states on the partially relaxed structures are −0.75 eV and −0.53 eV, respectively, which are about 0.03 eV and 0.09 eV smaller than the correspond results obtained by using the fully relaxed slab. Therefore, the fully and partially relaxed models give comparable predictions that lead to the essentially same conclusion that water prefers to adsorb on perfect WO_3(0 0 1) in its molecular state. Some previous studies have suggested that the partially relaxed WO_3(0 0 1) slab may introduce unphysical gap states, which can affect the surface reactivities [46,47]. Therefore, in the following, we used the fully relaxed model.

To validate the computational model, we calculated the adsorption energy of water on the five-layered WO_3(0 0 1) surface model. The five-layered WO_3(0 0 1) surface is fully relaxed and the calculated adsorption energy is −0.77 eV and −0.60 eV for the molecular and dissociated water adsorption. The adsorption energies of molecular and dissociated water on five-layered WO_3(0 0 1) surface are about 0.01 eV and 0.02 eV smaller than that of on four-layered WO_3(0 0 1) surface, the relative stability of molecular and dissociated states does not change. The lattice constant and band gap of WO_3 bulk were also calculated and

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