Computational Materials Science 95 (2014) 451–455

Contents lists available at ScienceDirect

Computational Materials Science

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

Mechanism of hydrogen production via water splitting on 3C-SiC's different surfaces: A first-principles study

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ARTICLE INFO

Article history:
Received 13 May 2014
Received in revised form 7 August 2014
Accepted 10 August 2014
Available online 6 September 2014

Keywords:
Water splitting
Photocatalyst 3C-SiC
Reaction mechanism
First-principles calculation

ABSTRACT

The reaction mechanism of producing hydrogen via water splitting on the different surfaces of cubic silicon carbide (3C-SiC), the adsorption energy and the activation energy have been studied here by using density functional theory. The results indicated that the adsorption behavior of water molecule could take place on 3C-SiC's different surfaces and it leads to the surface reconstruction. Besides, the water splitting reaction is found to be a thermally activated process, and the first hydrogen atom is easier decomposing from the adsorbed water molecule than the second one for most of the 3C-SiC surfaces. Furthermore, the water molecule that splitting on 3C-SiC (111) surface requires relatively small activation energy by contrast with other surfaces. Photon excitation is considered to be essential for the overall water splitting reaction to proceed further.

1. Introduction

An attractive way to use solar energy, as a clean, renewable and affluent energy source, is by water splitting process [1,2]. Considering visible light accounts for 43% of the incident sunlight [3–5], to apply solar energy efficiently, one of the available methods is to develop new-type photocatalysts that are able to split water under visible light [6–8]. It is believed that the photocatalytic water splitting reaction is an excellent method to generate energy for hydrogen is demonstrated to be an ideal energy carrier [9,10].

Since 1972, when Fujishima and Honda found the photocatalytic phenomenon in semiconductor TiO_2, many efforts have been devoted to explore effective photocatalysts acting under visible light [11–13]. Nevertheless, there still exist many open problems in this field to date. For instance, taking into account that the suitable band gap of the photocatalysts under visible light is about 2.0 eV, various modified methods have been extensively studied [14–16]. Cubic silicon carbide (3C-SiC) is a promising candidate for photocatalytic water splitting given that its band gap is about 2.4 eV, which could absorb sunlight wavelength greater than 300 nm corresponding to the visible light zone of the incident solar spectrum [17–19]. In addition, the energy band structure of 3C-SiC satisfies the prerequisites of water splitting reaction very well [20–22]. Most importantly, 3C-SiC is remarkable for its good stability, low-cost and it can be easily fabricated [23–27]. Therefore, it does not come as a surprise that many theoretical and experimental studies have explored the catalytic water splitting performance of silicon carbide. For example, in 2003, Amy et al. studied the interaction of H, O_2 and H_2O with 3C-SiC surfaces and found that the water molecule is dissociated at room temperature leading to perfect passivation of the SiC (100) surface with the H and OH group tying up the surface dimmers dangling bonds [17]. In 2004, Cicero et al. explored the interaction of water molecules with SiC (001) surfaces and found that water molecule dissociates on the Si-terminated surface, enhancing the surface hydrophilic character; while the C-terminated surface is hydrophobic [18]. In 2005, Catellani et al. performed first principle simulations of SiC-based interfaces and found that water molecules could dissociate on the Si-terminated surface while water dissociation is an activated process on the C-terminated surface [19]. All these theoretical researches reveal that the water splitting reaction occurs at the SiC surface, so the structure and property of the surface are expected to affect the hydrogen evolution reaction mechanism strongly. In 2008, Gao et al. concluded that through pretreating and loading of NiO on SiC, the photocatalytic performance of SiC may be enhanced greatly [20]. In 2011, He et al. found that ultrathin 3C-SiC nanocrystals possess the surface autocatalytic effect leading to high-efficiency hydrogen evolution from water decomposing [23]. In 2012, Guo et al. proposed the graphene covered silicon carbide powder (GCSP) to be an advanced photocatalytic

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http://dx.doi.org/10.1016/j.commatsci.2014.08.018
0927-0256/

material and verified it via experiment [24]. These experimental studies indicate clearly that SiC is expected to become a promising candidate for hydrogen evolution by means of photocatalytic water splitting process.

As mentioned above, we can see that significant progress has been made about the water splitting process on silicon carbide. However, the interaction between water molecule and silicon carbide is still not well understood. In addition, we note that the different exposed surface for silicon carbide is a key factor related to the reaction mechanism of solar water splitting [22,23]. To investigate these issues, the adsorption behaviors as well as a possible splitting reaction pathway have been studied in this work by performing the first-principle calculations. The results indicate that the adsorption behavior induces the surface reconstruction of 3C-SiC, and the water molecule splitting on the 3C-SiC (111) surface need relatively small activation energy by contrast with other surfaces. The results of our investigations should help people to further understand the photocatalytic water splitting reaction mechanism at the microscopic atomic level.

2. Computational methods

In this work, the first-principles calculations have been performed with the CASTEP (Cambridge Sequence Total Energy Package) program package, in which density functional theory (DFT) and the plane-wave pseudo-potential technique are implemented [28,29]. The generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) exchange–correlation function is used in the calculation process [30,31]. The k-point separation in the Brillouin zone of the reciprocal space is $2 \times 2 \times 1$. The cutoff energy for plane waves has been set as 500 eV in the calculation process. The 3C-SiC surface is modeled by a (3×3) super cell with six layers of the slab and at least a 10 Å vacuum region. The bottom two layers of the system are fixed while the top four layers as well as the adsorbates on it are fully relaxed. The transition state-search (TS-search) tools in the CASTEP model have been used to explore activation energy of the splitting reaction pathway [32]. Complete linear/quadratic synchronous transit (LST/QST) is used as the search protocol [33,29]. Meanwhile, the geometry optimization convergence threshold for the root mean square (RMS) forces on the atoms is set as 0.25 eV/Å. In addition, the LDA+U method in the electronic ground state has been used to correct the band gap, and the parameter U = 5 eV on the C p states is justified and adopted in this study [34,35].

First, we optimized the lattice parameters of cubic silicon carbide. The lattice parameter *a*, obtained for bulk 3C-SiC is 4.368 Å, which agrees well with the experimental and other theoretically predicted value [36]. This confirmed that the computational scheme used in this work is reliable.

3. Results and discussion

The simulation starts with the water molecule at an initial average distance of 1.45 Å from the 3C-SiC substrate, taking the atom of O and Si valence state radii as 1.21 Å and 0.24 Å respectively. All the researching surfaces of 3C-SiC are Si-terminated based on the previous studies [18,19]. To obtain the stable configurations with global minimum energy, each geometric structure involved in the processes, including water molecule, 3C-SiC (111), (110), (101) and (010) surface as well as the system composed of them have been optimized. The following related processes are analyzed on the basis of the optimized stable structures. Although in realistic situations, the 3C-SiC surfaces may have already been passivated more or less and thus the reactivity is being affected. It is noteworthy that here in this study, we simply consider an ideal condition, where the bare surface of 3C-SiC is much more active than in experimental environment due to the unsaturated bonds, with the aim at investigating the processes of water splitting reaction on the different surfaces of 3C-SiC.

3.1. Adsorption behaviors of each reaction system and reconstruction of 3C-SiC surface

In order to carry out proper comparisons, different orientations defined by the water molecule, that is the H_2O vertical or parallel to the 3C-SiC surface, are selected in this work. The adsorption energy [37] of water molecule on 3C-SiC surface is defined as the disparity between the total energy of the bound host H_2O and the sum energies of the separated surface as well as the absorbed water molecule(s). It can be formalized by the following formula:

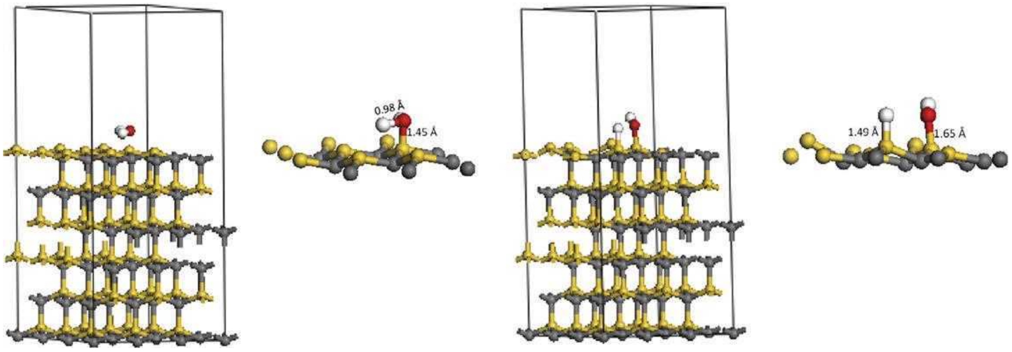
$$E_{adsorb} = E_{system} - (nE_{H_2O} + E_{surface}) \tag{1}$$

In formula (1): E_{system} is the total energy of the system composed of water molecule(s) and 3C-SiC surface, $E_{surface}$ is the energy of 3C-SiC surface, E_{H_2O} is the energy of a single water molecule and n is the number of adsorbed water molecule. Based on the above formula, the adsorption energy of water molecule(s) on the different surfaces of 3C-SiC is being calculated and the results are presented in Table 1. It manifests that the adsorption energy of one single water molecule (H_2O) on 3C-SiC (111), (010), (110) and (101) surfaces are −20.4, −13.6, −13.3 and −9.91 eV, respectively. Given that in realistic situations, there are many water molecules adsorbed on 3C-SiC surfaces, thus we have also calculated the adsorption energy for reaction systems composed of two water molecules ($2H_2O$) with 3C-SiC's different surfaces. The calculated results suggest that the adsorption energy of two water molecules ($2H_2O$) on 3C-SiC (111), (010), (110) and (101) surfaces are −22.3, −18.8, −16.7 and −11.7 eV, respectively. These negative values of adsorption energy correspond to an exothermic process, which means that the adsorption behavior is feasible and can take place from the energetic viewpoint. Besides, the absolute value of adsorption energy for two water molecules is larger than that of one water molecule adsorbed on 3C-SiC's different surfaces, implying that systems with more water molecules on 3C-SiC's surface should make the adsorption behavior easier. All of these outcomes indicate that the water molecule can be adsorbed on the different surfaces of 3C-SiC.

In the adsorptive behavior, the water molecule experiences a moving and rotating process on the 3C-SiC surface until a favorable adsorption site is found. Then the water molecule splits into H and OH groups, and bonds to two adjacent Si atoms of 3C-SiC surfaces spontaneously. The surface reconstruction occurs upon the adsorption of water molecule. In the following, we take the reaction system composed of one single water molecule and 3C-SiC (111) surface as an example to analyze the surface reconstruction induced by the adsorption behavior of H_2O. The configurations of the reaction system consisting of H_2O and 3C-SiC (111) surface before and after optimization are shown in Fig. 1. It suggests that the water molecule undergoes apparent changes after being optimized, from which one of the O–H bond is elongated from the initial 0.98 Å to 3.35 Å, this large distance indicates clearly that the O–H bond in the adsorbed water molecule has been destroyed com-

Table 1
The adsorption energy (eV) of one single water molecule (H_2O) and two water molecule ($2H_2O$) on 3C-SiC (111), (010), (110) and (101) surfaces.

3C-SiC surface	(111)	(010)	(110)	(101)
E_{ads} (H_2O)	−20.4	−13.6	−13.3	−9.91
E_{ads} ($2H_2O$)	−22.3	−18.8	−16.7	−11.7



(a) Before being optimized (b) After being optimized

Fig. 1. The configurations of the reaction system composed of H_2O and 3C-SiC (1 1 1) surface. (a) Before and (b) after being optimized, the lateral graphs are the partial magnified structures. In this and all subsequent figures, yellow (gray) spheres in the substrate represent silicon (carbon) atoms, while red (white) spheres in the adsorbate represent oxygen (hydrogen) atoms. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

pletely. Meanwhile, the decomposition products H and OH group induces obvious distortions of 3C-SiC surface and hence its reconstruction. In addition, the water molecule parallel to the 3C-SiC surface is found to be easier decomposed than the vertical one. The final configurations show the local geometry of the decomposing products presenting common characteristics with the bond length of Si–O and Si–H being about 1.65 Å and 1.49 Å, respectively. The corresponding information for these changes in structure is presented in Table 2. Our observations may be explained by the fact that it is the interactions between hydrogen and silicide atoms weaken the interactions between oxygen and hydrogen atoms [38]. Therefore, we concluded that the adsorption behavior of water molecule induce 3C-SiC's surface reconstruction.

3.2. The possible reaction pathway of water splitting on different 3C-SiC surfaces

To explore the mechanism of hydrogen production via water splitting reaction on 3C-SiC's different surfaces, a possible reaction pathway is being investigated. Based on the above water molecule decomposing processes, we propose in this work that the H atom of hydroxyl (OH) can approach and bond to Si–H species on the 3C-SiC surface, H_2 can then form with the above hydrogen atoms; i.e. the hydrogen atoms on the 3C-SiC surface are reduced to generate hydrogen molecule when the electrons are transferred from the 3C-SiC surface to hydrogen atoms.

The initial and final states involved in the TS processes are all global minimum configurations. In investigating the whole process of hydrogen production via water splitting reaction on 3C-SiC's different surfaces, the initial state is regarded as the start point and the energy reference state. According to the mechanisms being proposed, the water splitting reaction pathways as well as the corresponding energy barriers of the reaction systems (i.e. activation energies of the forward reactions) composed of H_2O and 3C-SiC (1 1 1), (1 1 0), (1 0 1), (0 1 0) surfaces are presented in Fig. 2. The results indicate that the energy barriers of 0.326, 1.609, 2.921 and 2.346 eV should be overcome for the H atom involved in the first step splitting; while 2.081, 1.323, 5.113 and 6.942 eV are needed to provide for the H atom involved in the second step decomposing from H_2O on 3C-SiC (1 1 1), (1 1 0), (1 0 1) and (0 1 0) surfaces, respectively. These results further imply that the hydrogen generation via water splitting reaction on 3C-SiC's different surfaces is a thermally activated process. The 3C-SiC surface might possibly be distributed with Si–H species after the first step of the water splitting reaction finished. Except for 3C-SiC (1 1 0) surface, the first H atom splitting from the adsorbed H_2O needs relatively small activation energy; while the H atom involved in second step splitting from the adsorbed H_2O needs to overcome a larger energy barrier. Therefore, photon excitation of electrons to higher electronic states is considered as a feasible method to overcome this energy barrier. From the above discussions, we may draw a conclusion that in the process of hydrogen generation via water splitting reaction, the hydrogen atom involved in the first step is easier to split from the adsorbed water molecule than the second one for most of the 3C-SiC surfaces studied here. Besides, the water molecule splitting on the 3C-SiC (1 1 1) surface needs relatively small activation energy by contrast with 3C-SiC (1 1 0), (1 0 1) and (0 1 0) surfaces. Therefore, the water molecule is favored to be decomposed on the 3C-SiC (1 1 1) surface. In addition, the water splitting reaction energy barriers on 3C-SiC (1 0 1) and (0 1 0) surfaces are as large as 5.113 eV and 6.942 eV, even higher than the energy barrier of direct thermal splitting of water without a catalyst [39,40]. Given that our investigations of the energy barriers for hydrogen production via water splitting reaction are performed at 0 K, while the barrier of direct thermal splitting of water are measured under the ambient temperatures or even higher, thus the water splitting reaction barriers on 3C-SiC (1 0 1) and (0 1 0) surfaces are larger than that of direct thermal splitting of water without a catalyst can be attributed to the influences of temperature; Since temperature is considered as an important parameter closely related to the water splitting reaction (as is reflected by the Arrhenius equation), it plays a vital role in the process of water splitting reaction [16,40]. Moreover, the processes of hydrogen production via water splitting reaction on 3C-SiC (1 0 1) and (0 1 0) surfaces are proved to be difficult to occur.

Table 2
The changes in the bond length and bond angle of the structure in the reaction system composed of H_2O and the 3C-SiC (1 1 1) surface.

Bond length and angle	$d_{O–H}$ (Å)	$d_{Si–O}$ (Å)	$d_{Si–H}$ (Å)	∠H–O–H (°)
Before being optimized	0.98	1.45	1.89	104.6
After being optimized	3.35	1.65	1.49	45.5

3.3. Possible electrons transfer on the interface of water molecule and 3C-SiC surface

To understand the water splitting reaction mechanism further, the density of state (DOS) of the reaction system and the corresponding partial density of state (PDOS) of hydrogen atom have been calculated by LDA+U method [34,35], given that to perform calculations of photoinduced water splitting on such extended

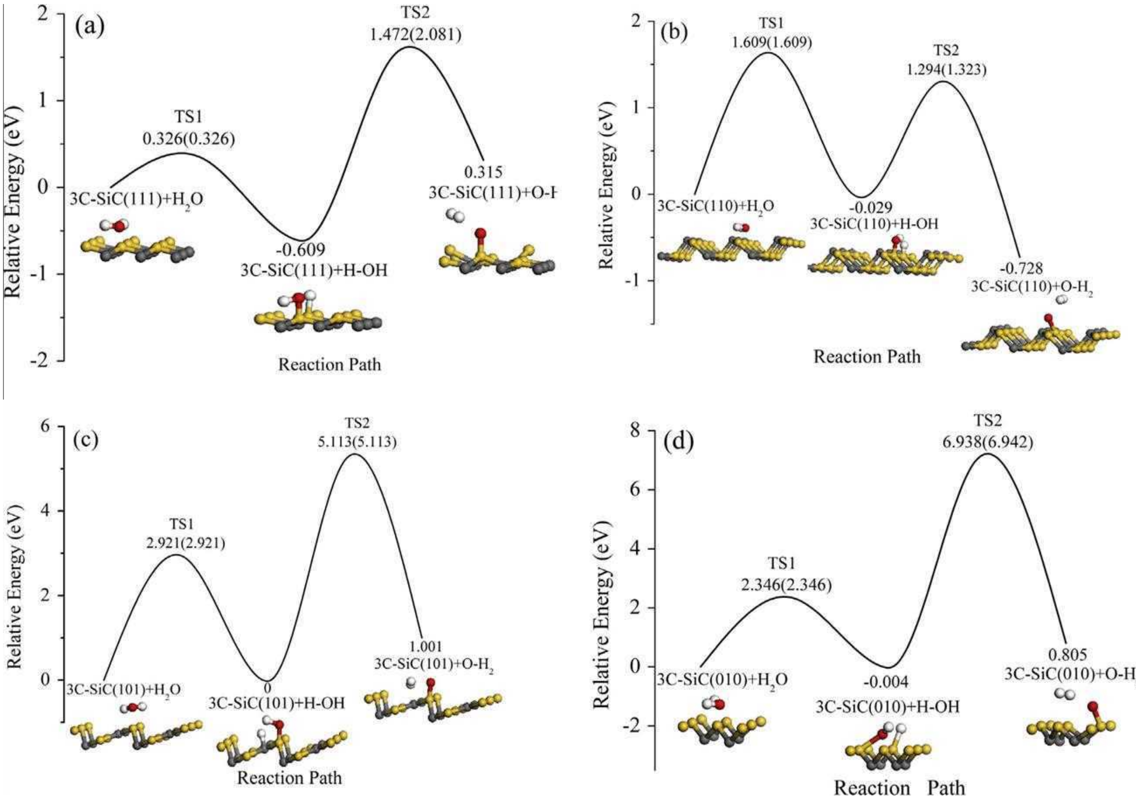


Fig. 2. The possible reaction pathways and the corresponding energy barriers (activation energies of the forward reactions) of the reaction systems, (a–d) are the reaction pathways of water splitting on the 3C-SiC (1 1 1), (1 1 0), (1 0 1) and (0 1 0) surface, respectively. The numbers are the relative energies and inside the parentheses are the energy barriers of each step.

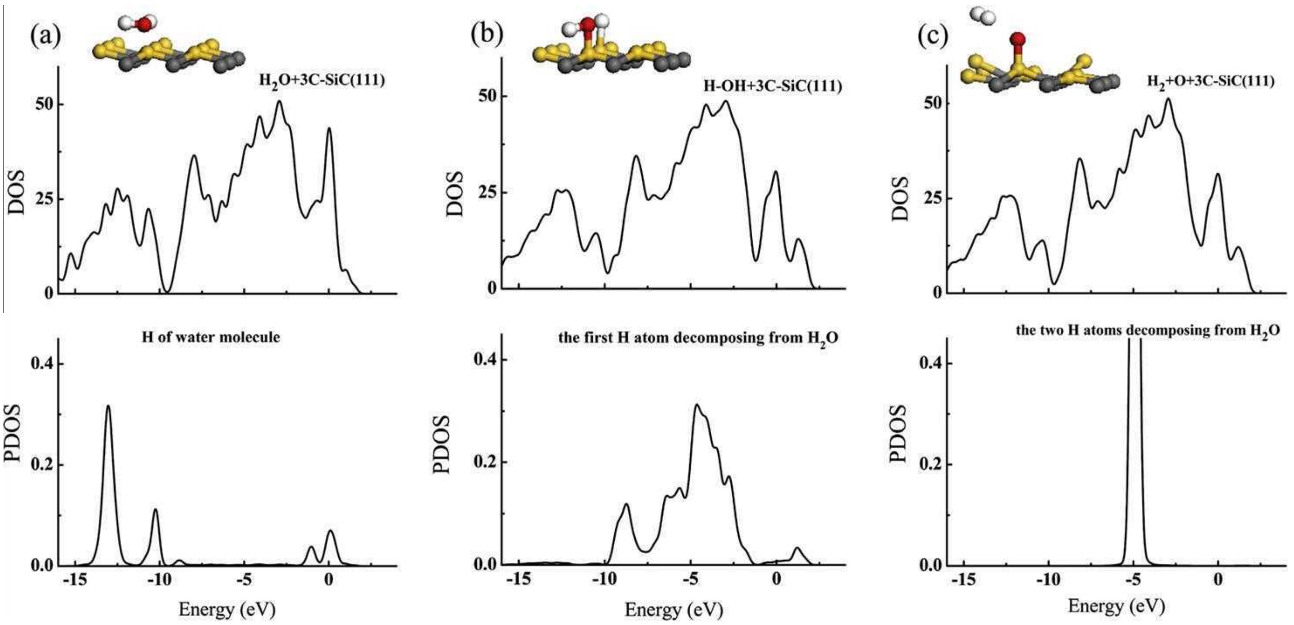


Fig. 3. DOS (density of state) and PDOS (partial density of state) correspond to water molecule decomposing on the 3C-SiC (1 1 1) surface. (a) is H_2O on the 3C-SiC (1 1 1) surface; (b) is the first hydrogen atom decomposing from water molecule; (c) is the two hydrogen atoms decomposing from the adsorbed water molecule.

system via using more accurate methods such as the time-dependent DFT and dynamical mean-field theory [41–43] is still difficult. The large computational effort will be involved in our future researches. Usually, the calculated band gap (~2.385 eV) of 3C-SiC is smaller than the experimental value (~2.417 eV) of the bulk materials [44]. After all, our purpose is to provide theoretical explanations of the electrons transfer during the splitting process instead of pursuing highly accurate values. Here, we also take the reaction system consisted of H_2O and 3C-SiC (1 1 1) surface as an example to analyze the probable electrons transferring between the adsorbed water molecule and the surface of cubic silicon carbide substrate.

In reality, the electrons transferring across the interface between molecule and semiconductor have been established by experimental methods [45]. The obtained DOS and PDOS for the configurations composed of H_2O and 3C-SiC (1 1 1) surface included in whole reaction process are shown in Fig. 3. The result indicates that the reaction system of water molecule adsorbed on 3C-SiC (1 1 1) surface presents an apparent metallic state, implying that there are significant charge transfer between the adsorbate H_2O and the 3C-SiC substrate, as is reflected in Fig. 3a. This can be understood from the fact that although the dangling bonds on 3C-SiC (1 1 1) surface have been partially passivated by the decomposition products (H and OH) of water molecule, the remained dangling bond is still responsible for the metallic state [17]. When a solar photon is being absorbed, an electron on the 3C-SiC's surface can be excited into the unoccupied states and a photogenerated hole is produced correspondingly; then the photogenerated carriers transfer between the 3C-SiC surface and water molecule. All the related processes can facilitate the solar water splitting reaction including the O oxidization as well as the H reduction. Combine the above discussions with the analysis of the DOS in Fig. 3, we conclude that the process of the H atom involved in the first step splitting from the water molecule on the 3C-SiC (1 1 1) surface is relatively easier; however, the H atom involved in the second step decomposing from the adsorbed H_2O needs to overcome a larger energy barrier. Therefore, photoassistance is considered to be essential for the overall water splitting reaction. The DOS in Fig. 3b indicates that photoassistance can possibly occur after the first H atom splitting; the density of states for this H atom is delocalized and broad. It turned out that the photon excited state is higher than the barrier of the second H decomposing, H_2 may then be generated via the effect of internal electronic conversion. The results also imply that the electrons should adsorb photons with higher energy and may be excited to higher electronic states. As is reflected in Fig. 3c, although H_2 is generated on 3C-SiC (1 1 1) surface, the PDOS of H_2 are localized. The main band of H_2 on the 3C-SiC (1 1 1) surface is about -5 eV, which reveals that the electrons transfer across the 3C-SiC-H_2 interface is not easy to occur. Therefore, we propose that extra energy such as the affluent solar energy is necessary to aid H_2 desorbing from the 3C-SiC surfaces.

Through the above discussions, it can be inferred that the formation of electronic interactions between O atom and Si atom weaken the O–H bond in water molecule, facilitating H_2O splitting. The overall process of hydrogen generation via water splitting reaction is sufficiently significant at energy conversion for this to be considered as a promising candidate for a new source of renewable energy.

4. Conclusions

In conclusion, the adsorption behavior and a possible reaction pathway of water splitting on the different surfaces of 3C-SiC have been investigated. The results indicate that the adsorption behaviors could take place on the different surfaces of 3C-SiC. Meanwhile, the water molecule may be decomposed on 3C-SiC's different surface, and the hydrogen atom involved in the first step is easier to split from the adsorbed water molecule than the one involved in the second step for most of the 3C-SiC surfaces studied here. Besides, the reaction of hydrogen generation via water splitting on 3C-SiC's different surfaces is found to be a thermally activated process. Therefore, extra energy such as affluent solar energy is proposed to be essential for the overall splitting reaction proceed further. In addition, the water molecule is favored to split on 3C-SiC (1 1 1) surface. Finally, the microscopic description of the interaction between H_2O and 3C-SiC surface has allowed us to investigate the important photocatalytic properties of 3C-SiC and to provide a vital clue towards 3C-SiC surface reconstruction. Even though the current work shows an ideal case and the realistic situation involves more complex reaction processes, our investigations should still help people to further understand the photocatalytic water splitting reaction mechanism at the microscopic atomic level.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grant No.'s. 51121061, 51131002, 51372215), the Key Basic Research Program of Hebei Province of China (Grant No. 12965135D) and the Natural Science Foundation for Distinguished Young Scholars of Hebei Province of China (Grant No. E2013203265). R.M. acknowledges the support from the NSERC and CRC programs, Canada.

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