

The distribution of excess carriers and their effects on water dissociation on rutile (110) surface



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ARTICLE INFO

Article history:

Received 14 February 2017

Received in revised form 20 April 2017

Accepted 21 April 2017

Available online 29 May 2017

Keywords:

Excess carrier

Water dissociation

Hybrid functional

Titanium dioxide

ABSTRACT

The excess carrier widely exists in the metal oxides, while its effect on the water splitting is still unclear. Here, the first-principle calculations were carried out to investigate how the effects of excess carriers affect the water dissociation on rutile (110). The result shows that the excess electron and hole play different roles in the reactions because of the distinct behaviors. The excess electron is easily to be trapped in the lattice Ti atom, and the trapped electron slightly changes the reaction barrier of water dissociation. However, the excess hole prefers to stick with the hydroxyl radical, which can obviously lower the energy barrier of water dissociation from 0.39 eV to 0.24 eV. The results further show that the dissimilar behaviors of excess electron and hole mainly come from their abilities of trapping and distinct interaction with proton in rutile TiO₂. Such work helps to understand carrier's distribution and its effect on water splitting, which should help to reveal the role of excess electron and hole in TiO₂.

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1. Introduction

TiO₂ as a cheap, stable, abundant and effective photocatalysis have been widely applied in water splitting and organic pollutant degradation [1–3]. This versatile material has been intensely investigated theoretically and experimentally for several decades. Different techniques have been developed and many mechanisms have been proposed to understand its good performance in catalysis. As a stepping stone, many investigations suggested that defects could greatly affect the electronic structures of TiO₂ and play an important role in its photocatalytic activity. As reported in some previous works [4–9], ubiquitous defects in n-type defective TiO₂, such as oxygen vacancy, interstitial titanium and surface hydroxyls usually introduce excess electrons into the system. And the excess electrons can form the defect states within the band gap around 0.8–1.0 eV below the conduction band minimum (CBM), which obviously improve the fermi energy and the carrier density in TiO₂. These improvements have been proved to have extraordinary effects on its photocatalytic activity. Recently, the p-type TiO₂ related to the Ti vacancy or anions doping such as N, C and S were also reported to have better performance in H₂ generation and photo degradation [10–12]. However, some reports also suggested

that the defects may be considered as the recombination centers for photon-excited electrons and holes and thus suppress rather than improve the catalytic activity of TiO₂. It remains in debate that whether or not the defects play a negative role in TiO₂'s catalysis, but one consensus is agreed that defective TiO₂ (such as hydroxylated or doped TiO₂) have better performance and can be more effective [11,13–16].

Nowadays, different kinds of defective TiO₂ have been synthesized by experiments. These materials exhibit better photon absorption [15,17], harmful pollutant degradation [11] and hydrogen evolution [18–20], as compared to the perfect TiO₂. All properties can be originated from the appearance of the shallow or deep defect states within TiO₂'s large band gap. Specifically, usually it's the excess electrons or holes trapped in defective TiO₂ that leads to the enhanced photo and catalytic properties. For example, very recently, some theoretical reports demonstrated that the excess electrons could trigger water dissociation on the anatase (101) surface [21] and promote CO₂ adsorption and reduction on rutile (110) surface. In addition, it is also possible that the defects provide active sites rather than excess electrons or holes to promote the catalytic activity. For instance, it is reported that oxygen vacancy on anatase (001) surface can activate CO₂ dissociation [22].

Among all the defects appeared in Titania, surface hydroxyl is a common one, which can be easily get by water dissociation on the surface [13]. And this kind of defect is also a very simple proto model to simulate defective TiO₂. It's reported that water will not

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dissociate on perfect TiO₂ surface [23]. But an article reported that water can easily dissociate with the help of excess holes on the surface [24]. What's more, Ji et al. also found that the excess holes can help electron's transfer via water decomposing when the water approaches to the hole [25,26]. However, the GGA + U method applied in their study may lead to a different barrier for water decomposition, because GGA + U always predicates the stability of molecular and dissociative water inversely. Another paper reported that hole's trapping is related to the first layer of water on the surface. This phenomenon indicates a strong connection between holes and the adsorbed water. Then what exactly the effect of excess electron or hole on the surface? As far as we know, there's no reports give the specific answer to this question. In order to know the effect of carriers, not only excess electron but also excess hole, both pure and hybrid functional are used in this work to study water dissociation.

In spite of these studies, up to date, the theoretical description of the defect states introduced by excess electrons or holes remains a large challenge. Pure DFT always fails to describe the distribution of excess electrons and energy level of the defect state. Hybrid functional could reproduce the energy level of the defect state and give a much better description of excess electrons' localization, while it is quite computationally demanding [27–30]. As a result, it's very essential to know if different results will be obtained while studying the defective TiO₂ with different functional.

In this work, systematically investigations have been made to understand the behavior of excess electrons and holes on rutile (110) surface and their effects on the water dissociation on the surface. Unlike easy trapping of the excess electrons, excess holes prefer to stick with the O_tH hydroxyls rather than be trapped at specific sites on the surface. This behavior makes the water dissociation easier on the (110) surface with excess holes than the surface with excess electrons. These results in this work may give more information and insight to understand the nature of carriers in catalysis.

2. Computational details

DFT calculations were performed with the CP2K/Quickstep package, where a hybrid Gaussian and plane-waves was used in this approach [31]. In such method, the valence electrons were expanded in terms of Gaussian functions with molecularly optimized double-zeta polarized basis sets (m-DZVP) [32]. For the auxiliary basis set of plane waves a 280 Ry cut-off was used. The Heyd, Scuseria, Erzerhof (HSE06) hybrid functional were performed for all the calculations [33–35]. The proportion of exact exchange interaction of HSE06 hybrid functional is 25% [33]. The generalized gradient approximation (GGA) of Perdew, Burke and Ernzerhof (PBE) exchange–correlation functional was also chosen for selected calculations [36]. Core electrons were described with norm-conserving Goedecker, Teter, and Hutter (GTH) pseudopotentials [37]. All atoms in the slab were relaxed until the maximum residual force for each atom is smaller than 0.02 eV/Å.

The rutile-TiO₂ (110) surface was modeled using a repeated slab geometry with four TiO₂ tri-layers and a (4 × 2) (11.836 Å × 12.994 Å) surface cell (Fig. 1). The vacuum separation between slabs was around 15 Å. The 1/8 ML water coverage was modeled by adsorbing 1 water molecule on the Ti_{5c} sites on the TiO₂ (110). The excess electrons are introduced by bridge bonded O adsorbed hydroxyls (O_{br}H) and holes are introduced by surface unsaturated Ti adsorbed hydroxyls (O_tH), as indicated in Fig. 1. The O_{br}H hydroxylated system is created by adding a hydrogen atom to bridging oxygen site near the dissociated water and the O_tH hydroxylated surface is modeled by adding an OH radical on the Ti_{5c} atom. To describe the reaction's potential energy, a con-

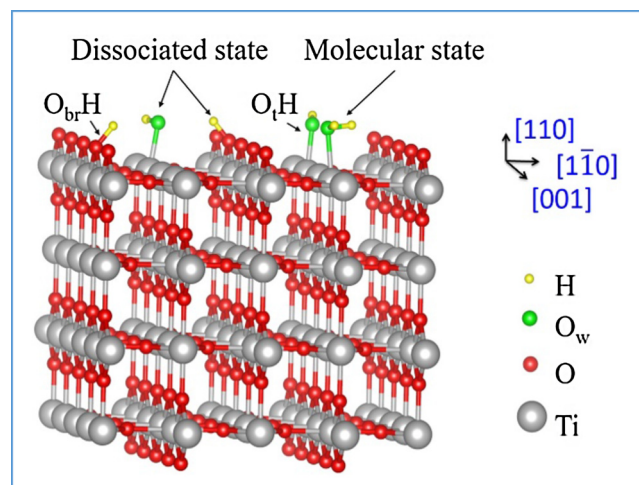


Fig. 1. The different water adsorption states on the TiO₂ (110). Here, the molecular state, dissociated state, and the radical are all considered. The molecular state water and O_tH radical adsorbed on the 5-coordinated Ti atom. The O_{br}H radical is created by adding a H on bridge bonded O atom. The dissociated state water consists of an O_tH and a transferred H (proton). The gray, red, green and yellow spheres represent Ti, O in TiO₂, O in water (O_w) and H atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

strained approach was applied in our calculations as used in Refs. [38,39]. The distance of H atom from the water and bridge O atom from the surface involved in the dissociation is used as the reaction coordinate and varying the distance can obtain the reaction energy profiles. The initial state (IS) and final state (FS) are chosen by using the relaxed structure of rutile surface with molecularly and dissociative adsorbed water, respectively. To determine the transition state, different intermediate structures have been obtained by varying different reaction coordinates. The transition state (TS) is identified by requiring (a) that the ionic forces at the TS vanish and (b) that the TS is a maximum along the reaction coordinate, but a minimum with respect to all remaining degrees of freedom [40]. For each intermediate structure, a spring coefficient is applied to fix the unstable geometry. Then the geometry with the highest energy is chosen as the step-determined structure or the TS.

3. Results and discussion

To determine the water adsorption states (molecular or dissociative state) on TiO₂ (110) surface, the first-principle calculations are carried out by hybrid HSE06 functional. Firstly, we examine the 1/8 ML coverage of water molecule on the perfect TiO₂ (110). The dissociated state is predicted to be about 0.13 eV higher than the molecular state by HSE06 functional (see Table 1). It suggests that water is not energetically favored to dissociate on the perfect surface. This observation agrees well with the previous works [14,41]. However, the energy difference is so small that they can also be degenerated. It is worth mentioning that the molecular and dissociative states of water were demonstrated to coexist on the surface by many theories and experiments [42–44]. Thus, we conclude that the smaller relative energy between the two states get by HSE06 functional is convincing. We further calculate the energy barrier for water dissociation on the perfect surface. As shown in the potential energy profile of Fig. 2A, the water dissociates by crossing an energy barrier of 0.39 eV.

To further investigate the effects of excess electrons or holes on water dissociation process, the above system containing 1/8 ML O_{br}H or O_tH hydroxyl are explored. In order to accurately describe the behaviors of the excess carriers, HSE06 was chosen in the fol-

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