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The effect of strain on water dissociation on reduced rutile TiO$_2$(110) surface

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The effect of external uniaxial strain on water dissociation on a reduced rutile TiO$_2$(110) surface has been theoretically studied using first-principles calculations. We find that when the tensile strain along [1$\bar{1}$0] is applied, the energy barrier of water dissociation substantially decreases with the increase of strain. In particular, water almost automatically dissociates when the strain is larger than 3%. Besides, the water dissociation mechanism changes from indirect to direct dissociation when the compressive strain is larger than 1.3% along [1$\bar{1}$0] or 3% along [001]. The results strongly suggest that it is feasible to engineer the water dissociation on the reduced rutile TiO$_2$(110) surface using external strain.

1 Introduction

Titanium dioxide has attracted wide attention due to its promising applications in heterogeneous catalysis, solar cells, gas sensors, photocatalysis, environmental remediation *etc.*[1–7] The aqueous environment is one major application area for TiO$_2$ and the (110) surface is the most stable surface for rutile TiO$_2$. The interaction between water and the TiO$_2$(110) surface has been extensively studied in recent years.[8–10] A bridging oxygen vacancy is one of the most common defects on the surface, and plays a critical role in surface reactions.[6,9–16]

Previous experimental studies showed water splitting at the bridging oxygen vacancy on the reduced TiO$_2$(110) surface, in which hydroxyl was formed.[6,12,13,17–20] Later, theoretical studies showed that water dissociation on a bridging oxygen vacancy chose an indirect pathway. Initially, a hydrogen from water transfers to a neighbor in-plane oxygen (O$_{ip}$) and then hops to the neighbor bridging oxygen (O$_{br}$). The obtained barrier energies of water dissociation range from 0.16 to 0.39 eV, using different theoretical methods.[13,18,20–22]

External strain is an important factor which may influence molecule adsorption and dissociation, since it is unavoidable in the fabrication of nanostructures and thin films.[23–27] For the TiO$_2$ surface, experimental studies have shown that when surface strain is applied through formation of subsurface Ar-filled cavities, surface strain values are up to 4%.[25] The effect of strain on hydrogen adsorption on rutile TiO$_2$(110) has been investigated using scanning tunnelling microscopy (STM), which revealed that the adsorption energy of hydrogen on the

local surface is lower than that on the protrusions.[28] On the other hand, theoretical studies showed that external strain could effectively tune the type of surface oxygen vacancies, diffusion pathways and barriers of the oxygen vacancies, and even surface morphologies.[29–31] The adsorption and dissociation of water on a stoichiometric rutile TiO$_2$(110) surface under external strain has been studied, and the results clearly indicated that external strain can engineer the surface adsorption and dissociation of water.[32] However, the effect of strain on water dissociation on a reduced surface has not been investigated yet.

In this paper, we systematically studied water dissociation on a reduced rutile TiO$_2$(110) surface under external uniaxial strain. We found that when tensile strain along [1$\bar{1}$0] is applied, the energy barrier for water dissociation substantially decreases with increasing strain. In particular, water almost automatically dissociates when the strain is larger than 3%. In contrast, the dissociation path for water changes from an indirect path to a direct path when 1.3% compressive strain along [1$\bar{1}$0] is applied. On the other hand, the energy barrier is steady against tensile strain along [001], and the dissociation mechanism also changes from an indirect path to a direct path when 3% compressive strain along [001] is applied. The results strongly suggest that it is possible to engineer water dissociation on the reduced rutile TiO$_2$(110) surface using external strain.

2 Computational methods

Calculations are based on density functional theory in the PW91 generalized gradient approximation,[33,34] using the Vienna *ab initio* simulation package code with projector augmented wave pseudopotentials.[35,36] An energy cutoff of 500 eV is used for expanding the Kohn–Sham wave functions in order to correctly account for the effects of surface stress. The rutile TiO$_2$(110)

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surface is modeled as a (2×3) supercell slab with x and y along $[1\bar{1}0]$ and $[001]$ directions, respectively. The slab contains five O–Ti–O trilayers ($Ti_{60}O_{120}$) and a vacuum with thickness of 15 Å, with a Γ-centered 1×3 mesh, which has been tested to be well converged. The positions of atoms in the bottom trilayer were fixed to mimic the bulk, and the other atoms were relaxed until the forces were converged to 0.01 eV Å^{-1}. In order to model reduced $TiO_2(110)$ surfaces, a bridge oxygen is removed from one side of the slab, the oxygen vacancy density is 1/6, which is enough to obtain the influence of the oxygen vacancy on the water dissociation.[13,21] The nudged elastic band (NEB) method[37] is used to obtain an accurate dissociation barrier for water. A (1×4) supercell with a 4×2 k-mesh sampling is used to check the [001] direct convergence. The difference is 40 meV at maximum in the dissociation barrier energies of water in an indirect path when the $[1\bar{1}0]$ strain is applied.

In our previous work we demonstrated that spontaneous in-plane polarization does occur on the $TiO_2(110)$ surface when uniaxial tensile strain is applied, furthermore, the polarization and paraelectric surface have the same surface chemistry for water adsorption.[38] Therefore, we use a paraelectric surface when compressive strain or no strain is applied, and use a polarized surface when tensile strain is applied; due to the paraelectric surface being metastable, it will spontaneously relax to the polarized structure.

3 Results and discussion

As shown in Fig. 1, water adsorption on a reduced rutile $TiO_2(110)$ surface preferentially takes place at a bridging oxygen vacancy site, the coverage (θ) of water is 1/6, which is the initial state (IS) for dissociation. Then water dissociates at the oxygen vacancy site and forms a pair of hydroxyl groups, which is the final state (FS). There are two pathways for water dissociation on the surface, which are marked by colored arrows in Fig. 1(b). In the direct path, a hydrogen from water directly jumps onto the neighboring O_{br} in the same row. And in the indirect pathway, the hydrogen atom first jumps onto adjacent O_{ip}, then hops to the neighboring O_{br}.
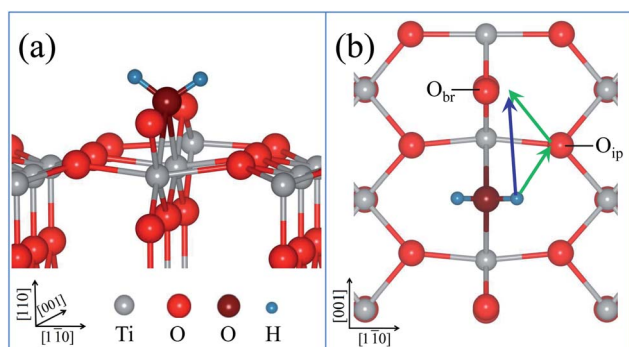

Fig. 1 Configurations of water adsorption on a reduced rutile $TiO_2(110)$ surface. Stereoscopic view (a) and top view (b). Blue and green arrows to (b) represent the direct and indirect dissociation paths for water, respectively.
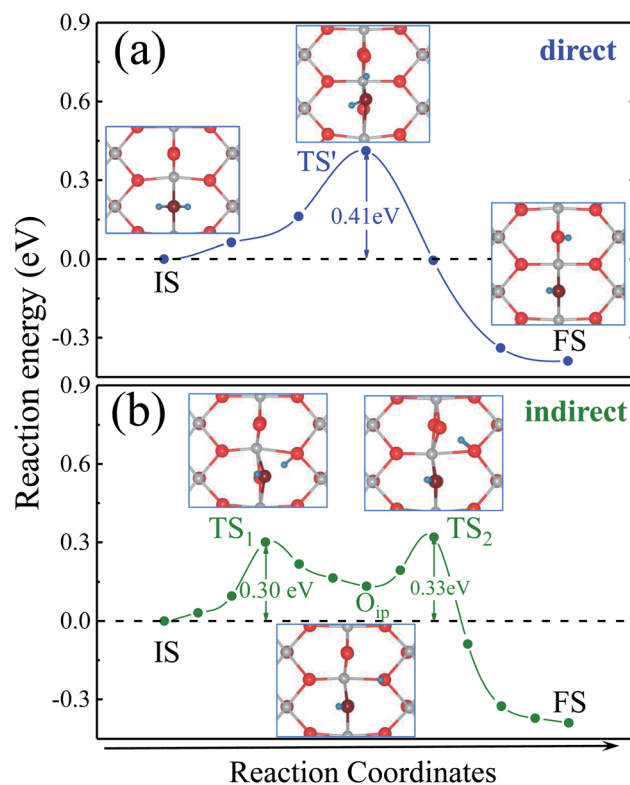

Fig. 2 Energy profiles corresponding to the dissociation pathways in Fig. 1(b). The direct (a) and indirect (b) dissociation pathways. The energies are measured relative to the IS configuration.

The energy profiles of water dissociation and some optimized geometrical structure of transition states are presented in Fig. 2. The transition state of the direct path is denoted as TS′, where the hydrogen is between two neighboring O_{br} atoms. We also locate two transition states along the indirect pathway. The first transition state is denoted as TS_1, and the geometrical structure is a hydrogen atom already removed from the water molecule and close to O_{ip}. The second transition state is denoted as TS_2, the hydrogen atom leaves the O_{ip} and moves closer to the neighbouring O_{br}. The energy barriers of the two paths are shown in Table 1. It is obvious that the energy barrier of the indirect pathway is lower than that of the direct path, which means that water dissociation on the reduced surface proceeds via the indirect pathway. The obtained results are in good agreement with previous results.[13,18,20–22]

The scaling relations limit the catalysis reaction, but this limitation could be broken by strain, as the binding energy is

Table 1 Energy barrier (E_b) and the difference of the surface stress between transition states and the initial state in this work. The units are eV and eV/(1 × 1). The subscripts 11 and 22 denote the $[1\bar{1}0]$ and [001] directions, respectively

Images	E_b	$\Delta\sigma_{11}$	$\Delta\sigma_{22}$
TS′	0.41	0.18	0.36
TS_1	0.30	−0.95	−0.09
TS_2	0.32	−1.10	0.13

determined by the coupling of the adsorbate-induced eigenstress with the external strain.[27] The energy profile of molecule dissociation can be predicted according to the surface stress profile along the dissociation pathway when external strain is applied,[32] and the intrinsic surface stress can be expressed as,[29]

$$\sigma_{\alpha\beta} = \frac{1}{A_L} \frac{\partial(A_L \gamma_L)}{\partial \varepsilon_{\alpha\beta}} = \frac{\partial \gamma_L}{\partial \varepsilon_{\alpha\beta}} \qquad (1)$$

where A_L is the area of the surface in an unstrained state, and γ_L is the Lagrangian surface energy per unit area with an unstrained state. The subscripts α and β denote the directions along the surface. The energy profile of molecule dissociation can be predicted by eqn (2)

$$E_i = E_i^0 + A_L(\Delta\sigma^i \varepsilon) \qquad (2)$$

where E_i is the energy at the ith configuration along the dissociation pathway under externally applied strain. E_i^0 is the energy at the ith configuration in an unstrained state, $\Delta\sigma^i$ is the change of surface stress between the ith and initial state configuration with unstrained surface. A_L is the surface area occupied per water molecule when no strain is applied.

We obtained the difference of surface stress between transition states and initial state, which are shown in Table 1. It is clearly seen that the values of TS_1 and TS_2 along $[1\bar{1}0]$ are -0.95 and -1.10 eV/(1×1), which are much larger than the others, indicating that the energy barriers of TS_1 and TS_2 substantially decrease with increasing tensile strain along $[1\bar{1}0]$. By substituting the data into eqn (2), the decreasing rates of TS_1 and TS_2 can be obtained as 0.057 and 0.066 eV per 1% tensile strain, respectively. When the tensile strain is larger than 5.6%, the dissociation barrier will disappear, which suggests that water will automatically dissociate on the reduced $TiO_2(110)$ surface when sufficient large tensile strain along $[1\bar{1}0]$ is applied. In contrast, the energy barrier of the indirect path increases with compressive strain increase, while that of the direct path changes a little for $\Delta\sigma_{11}^{TS'} = 0.18$eV/$(1 \times 1)$. Therefore, water dissociates through the direct path instead of the indirect pathway when compressive strain is applied along $[1\bar{1}0]$. We also observed that the $\Delta\sigma$ of the transition states changes little under strain along [001], which suggests that the energy barrier of dissociation varies little with strain along [001].

To demonstrate the predicted variation of dissociation paths under external strain, we first calculated the energy profiles under uniaxial strain in the range -4% to 4% using the nudged elastic band (NEB) method, the tensile and compressive strain
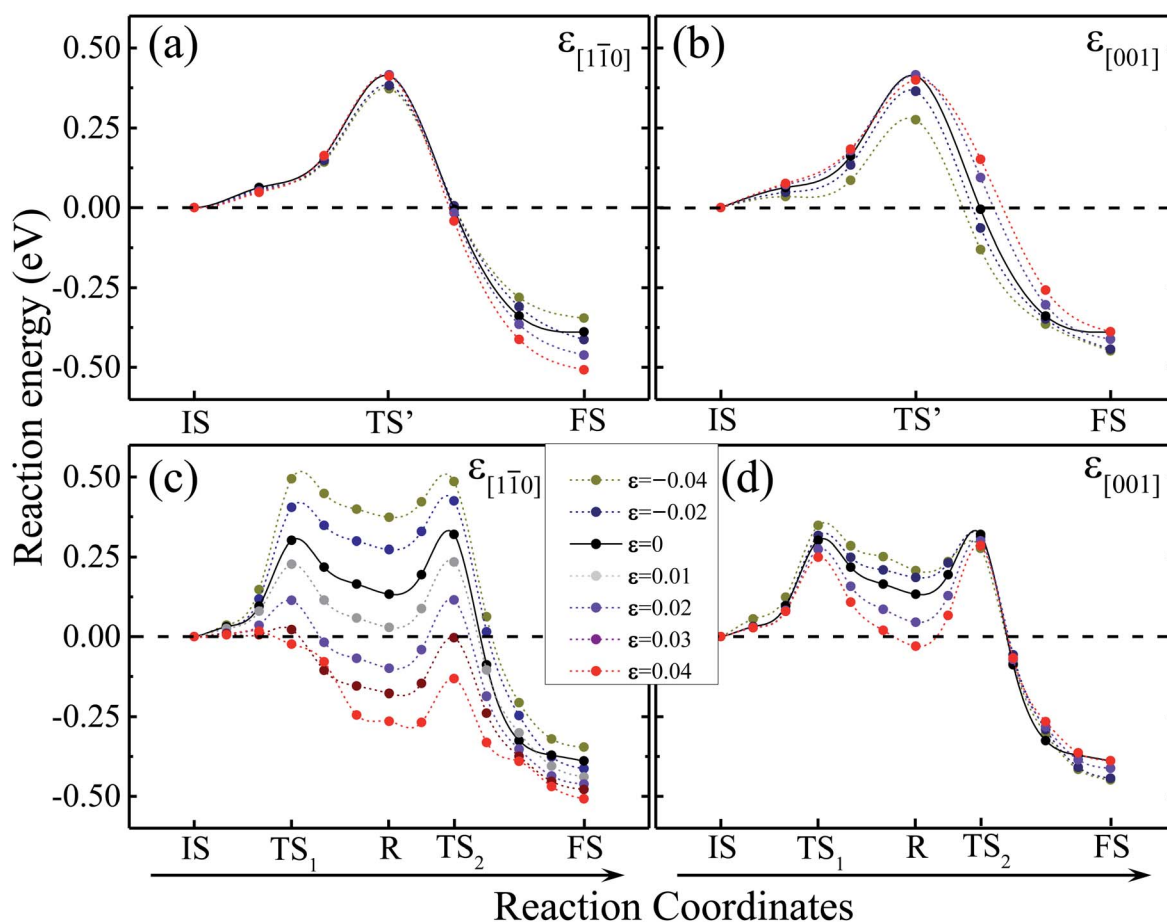

Fig. 3   Variation of the energy profiles for the direct (a and b) and indirect (c and d) dissociation path under external uniaxial strain along $[1\bar{1}0]$ (a and c) and [001] (b and d). The energies are measured relative to the configuration IS. The $\varepsilon = 0.01$, 0.03 are presented only in (c).

are marked by positive and negative signs, respectively, as shown in Fig. 3. Firstly, we investigated the influence of strain on water dissociation on surfaces when strain is applied along $[1\bar{1}0]$. The direct and indirect paths are shown in Fig. 3(a) and (c), respectively. It is worth noting that the energies of TS_1 and TS_2 along the indirect path substantially decrease simultaneously with increasing tensile strain. It is obvious that when the tensile strain is larger than 2%, the energy barrier of TS_1 overtakes that of TS_2 and becomes a new maximum point. As the tensile strain continues to increase to 3%, the energy barrier of the indirect dissociation path decreases to 0.02 eV. The results clearly indicate that water almost automatically dissociates on a reduced $TiO_2(110)$ surface when 3% tensile strain is applied. The energy barrier of the indirect path has a huge increase with compressive strain along the $[1\bar{1}0]$. In contrast, the energy barrier of the direct path changes slightly.

Next we investigate the influence when strain is applied along [001]. The energy profiles of direct and indirect paths are shown in Fig. 3(b) and (d), respectively. When the strain is in the range from −4% to 4%, the energy barrier of the direct path is in the range 0.28 to 0.40 eV and the energy barrier of the indirect path is 0.28 eV to 0.35 eV. Compared with the strain along $[1\bar{1}0]$, the influence of the strain along [001] on water dissociation on a reduced TiO_2 surface is weaker.

In order to get a more intuitive view of the effect of the external uniaxial strain on water dissociation on rutile reduced $TiO_2(110)$ surface, the variation of the energy barrier of each transition state along two dissociation paths are shown in Fig. 4. The solid symbols and lines denote the energy barrier of the most favorable dissociation path under the strain. Firstly, we study the influence of the strain along $[1\bar{1}0]$. It is obvious that the energy barrier of the direct path changes a little under strain along $[1\bar{1}0]$, while that of the indirect pathway varies tremendously. It is worth noting that when the tensile strain is applied, the energy barrier of the indirect pathway is always lower than that of the direct pathway, the energy barrier of the indirect pathway substantially decreases with increasing strain.

Especially, when 3% tensile strain is applied, the energy barrier is obtained as 0.02 eV, which suggests that water almost automatically dissociates on the strained surface *via* the indirect pathway. It is worth mentioning that when the tensile strain is larger than 2%, the TS_1 becomes a new saddle point of the indirect pathway, rather than TS_2. In contrast, when compressive strain is applied, the energy barrier of the indirect pathway substantially increases with increasing strain. Specifically, when the strain is larger than 1.3%, the direct pathway becomes the energetically favorable dissociation pathway due to the lower energy barrier than that of the indirect path.

Next we investigate the influence of strain along [001]. Obviously, the energy barriers of the two pathways change a little under tensile strain, water dissociation *via* the indirect pathway is the as same as the one on the nonstrained surface. In contrast, when compressive strain is applied, the energy barrier of the direct pathway decreases with increasing strain, but that of the indirect pathway increases, in particular, when 3% compressive strain along [001] is applied, the dissociation path for water changes from the indirect path to the direct path, the same as that of 1.3% compressive strain along $[1\bar{1}0]$. By comparing the prediction and calculation results, we found that the predicted results slightly overestimate the energy barrier for the tensile strain along $[1\bar{1}0]$, which is due to the larger space for atoms to relax.

We also compare the geometries before and after the strain is applied, we found that the geometries of adsorbates rarely changed after compressive strain is applied. In contrast, when tensile strain is applied, the adsorbates on the surface get a slight deflection, the deflecting direction is along the surface polarization direction.

4 Conclusion

In summary, the effect of external uniaxial strain on water dissociation on a reduced rutile $TiO_2(110)$ surface has been theoretically studied by using first-principles calculations. We found that tensile strain along $[1\bar{1}0]$ can greatly promote the dissociation of water. In particular, water almost automatically dissociates when the strain is larger than 3%. Moreover, the dissociation path changes from an indirect path to a direct path when the compressive strain is larger than 1.3% along $[1\bar{1}0]$, or 3% along [001]. The results strongly suggest that this is a possible way to engineer water dissociation on a reduced rutile $TiO_2(110)$ surface using external strain, and the external strain also can be used to improve other chemical reactions on a reduced $TiO_2(110)$ surface.

Conflicts of interest

There are no conflicts of interest to declare.
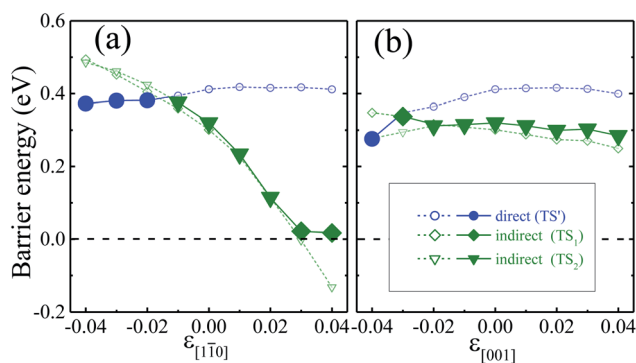
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Fig. 4 The dissociation energy barriers of the different pathways under an external uniaxial strain along $[1\bar{1}0]$ (a) and [001] (b). Blue and green symbols denote the direct and indirect path, respectively. Triangles and diamonds mark the TS_1 and TS_2 along the indirect path. Solid symbols and lines denote the energy barrier of the most favorable dissociation path on the reduced $TiO_2(110)$ under the external uniaxial strain.

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