Prediction of hydrogen plasma induced modified anatase TiO$_2$ (001) surface with desirable water splitting performance

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We show that exposing TiO$_2$ anatase (001) surface to hydrogen plasma causes a slight structural modification of the surface. On the modified surface the topmost TiO$_2$ layer is intact, but out of registry with the bottom layers. Nevertheless, the modified surface has significantly improved ability to split water under exposure to sunlight. First, we show by explicit calculation of the water splitting reaction that the energy barrier that exists on a pristine surface isn’t present on the modified surface. Second, we show that the valence band maximum of the surface is raised relative to the pristine surface, which is a favorable way of adjusting the band gap in TiO$_2$ to the solar spectrum.

I. INTRODUCTION

Anatase TiO$_2$ is a promising and well studied material for photocatalytic water splitting. TiO$_2$ is cheap, environment-friendly, and stable. As is well known, due to its large band gap, TiO$_2$ can’t utilize the sunlight efficiently. Furthermore, to provide enough driving force for the photo oxidation of water, the valence band maximum (VBM) of TiO$_2$ should be increased and positioned closer to, but lower than, the potential of H$_2$O/O$_2$ pair. Up to now, plenty of research has been conducted to narrow its band gap and to elevate the VBM.

Doping is one common strategy to reduce the band gap of TiO$_2$. Doping can be done with either a metal ion (La, V, Co, Nb, Ag) or a nonmetal ion (S, B, C, N). However, some dopants, especially the metal ions, can lead to severe carrier recombination which reduces the overall quantum efficiency. Moreover, the metal ion dopants are often polluting.

An alternative approach for narrowing the band gap, and raising the VBM, is to modify the surface structure of anatase TiO$_2$ by hydrogenation. This treatment changes the color of anatase TiO$_2$ from white to black, and produces highly rough and amorphous surface of TiO$_2$, both in the case of nanoparticles and nanotubes. Furthermore, according to the X-ray photoelectron spectroscopy (XPS) measurement, the band gap narrowing of black TiO$_2$ is achieved by raising the VBM without changing the CBM (conduction band minimum) which is a favorable band alignment for photocatalytic water splitting. While it remains unknown exactly which structural modification leads to the favorable band alignment of black TiO$_2$, there is evidence that likely the increase in VBM is due to the surface modification of TiO$_2$. On the other hand, XPS study on a similar system (nanowires instead of nanoparticles) by Wang et al. found no shift in the valence band. They assigned the dark color of nanowires to the formation of defect states or impurities. Furthermore, Alberto and co-workers synthesized black TiO$_2$ nanoparticles with crystalline core and disordered shell morphology, and found that in addition to the surface modification, the presence of oxygen vacancies could also contribute to the visible light absorption of TiO$_2$.

In this work we explore possible structural changes to the surface of TiO$_2$ induced by absorption of hydrogen atoms to the TiO$_2$ surface. Our calculations show that the structure of pristine (001) surface of TiO$_2$ anatase is modified when exposed to a hydrogen atom pressure of 0.3–30 Pa, which can be achieved in the laboratory. Furthermore, by doing an explicit calculation of the water splitting process, we find that the structural modification induced by hydrogen atom removes the rate-limiting step for the water splitting process. More specifically, while the pristine anatase TiO$_2$ (001) surface has a barrier of 0.55 eV in the Gibbs free energy profile of the oxygen evolution reaction, there is no such barrier on the modified surface. Therefore, our calculations show that the hydrogen-plasma treated anatase TiO$_2$ (001) surface is a suitable candidate for water splitting applications.

This paper is organized as follows: in Sec. II we describe the calculation details. In Sec. III and Sec. IV we present and discuss our results. We give an outlook and conclude in Sec. V.

II. CALCULATION DETAILS

For our calculations we use density functional theory as implemented in the Quantum Espresso package. We use the Generalized Gradient Approximation (GGA) of Perdew, Burke and Ernzerhof (PBE) along with the ultra-soft pseudopotentials from the GBRV database. These pseudopotentials describe the valence electrons 3s3p3d4s in Ti, 2s2p in O and 1s in H. In order to obtain sufficient precision, we cutoff the plane wave basis for the wavefunction at 40 Ry and 400 Ry for the density. We use 15 Å of vacuum to avoid the interaction between neighboring slabs. In cases when the surfaces of the slab are different, for example when molecules are absorbed on one of the sides of the slab, we use the dipole correction in the direction perpendicular to the surface. All
surface energies in the paper are reported per one side of the slab. We sample the electron’s Brillouin zone on a $6 \times 6 \times 1$ Monkhorst-Pack grid.

To model a slab of TiO$_2$ we set the in-plane lattice constant of the slab equals to the in-plane bulk lattice constant. Each time we fully relax the slab with an only constraint that the in-plane lattice constant remains unchanged. We use slab with a thickness of 8 layers of TiO$_2$. For most calculations we use minimal in-plane unit cell, but for the water adsorption and oxygen evolution reaction processes, we use an in-plane supercell that is doubled along one of the in-plane lattice vectors.

We calculate the surface energy density $\Delta \gamma$ as

$$\Delta \gamma = \frac{1}{A} [E_{\text{slab}} - E_{\text{clean}} - N_H \mu_H(T,p)]$$  \hspace{1cm} (1)

Here $E_{\text{slab}}$ is the energy of the slab with $N_H$ hydrogen atoms adsorbed on the surface. $E_{\text{clean}}$ is the energy of the slab without adsorbed hydrogen atoms. The surface area is $A$. $\mu_H(T,p)$ is the chemical potential of H atom as a function of temperature ($T$) and pressure ($p$),

$$\mu_H(T,p) = \Delta \mu_H(T,p) + \frac{1}{2} E_{H_2},$$  \hspace{1cm} (2)

$$\Delta \mu_H(T,p) = \frac{1}{2} [\bar{\mu}_{H_2}(T,p^0) + k_B T \ln(p_{H_2}/p^0)].$$  \hspace{1cm} (3)

Here, $p^0$ is the pressure of a reference state, and the temperature dependence of the chemical potential $\bar{\mu}_{H_2}(T,p^0)$ is tabulated in the thermochemical reference tables.$^{26}$

III. HYDROGEN INDUCED SURFACE MODIFICATION

Now we present our results on the hydrogen-atom induced structural modification of the TiO$_2$ anatase (001) surface. In the next section we will study its water splitting performance.

The conventional unit cell of bulk anatase TiO$_2$ is shown in Fig. 1a. Anatase TiO$_2$ crystallizes in space group $I4_1/amd$ (space group 141). Titanium atoms are at Wyckoff orbit $b$ while oxygen atoms are at Wyckoff orbit $c$. Therefore, all titanium atoms in the crystal structure are equivalent to each other, and all oxygen atoms are equivalent to each other. Our calculated relaxed lattice parameters of bulk anatase TiO$_2$ are $a = b = 3.804$ Å and $c = 9.695$ Å, which is close to the experimental result $a = b = 3.804$ Å and $c = 9.614$ Å (0.84% deviation).$^{27}$ The structural unit of TiO$_2$ anatase is a TiO$_6$ octahedron with Ti atom in the center of the octahedron, and O atoms in the corners of the octahedron. These octahedra are connected to each other and are forming an edge sharing network. Each O atom is bonded to three Ti atoms.

Based on our calculation of bulk anatase TiO$_2$ we constructed a model of pristine (001) surface. This surface is shown in Fig. 1b. While in the bulk TiO$_2$ all Ti atoms are six-fold coordinated, this is clearly not the case on the (001) surface. Here, the breaking of the Ti–O bond perpendicular to the surface reduces the coordination of the topmost Ti atom from six to five. Furthermore, there are now two symmetry inequivalent oxygen atoms at the surface: only one of which is nominally saturated, as it is surrounded by three Ti atoms. Another oxygen atom is unsaturated, as it is surrounded by only two Ti atoms. Therefore, all Ti and half of the O atoms at the topmost layer of TiO$_2$ (001) surface are nominally unsaturated.

A. Hydrogen adsorbed on a pristine surface

We now discuss the hydrogen passivization of the (001) surface. We consider all the Ti and O atoms on both the first and second layer of the surface as potential hydrogen atom adsorption sites. Relative energies of sites with strongest (optimal) absorption are shown in Fig. 2 as a function of number of adsorbed H atoms.

When only one H atom is adsorbed per surface unit cell we find that the H atom prefers to absorb horizontally on the surface two-coordinated O atom. The adsorption energy is $-2.23$ eV. The negative sign for the adsorption energy means that it is energetically favorable for H atom to absorb on the surface. This binding energy is specified relative to a single isolated H atom. With two adsorbed H atoms, one prefers to adsorb again to the topmost two-coordinated O atom, while the second adsorbs on the surface Ti atom. The total adsorption energy for these two
H atoms taken together is $-4.06$ eV. Therefore, adsorption energy per atom is now decreased from $-2.23$ eV to $-4.06/2 = -2.03$ eV. With three adsorbed H atoms we find that first two adsorb as before, while the third one prefers to adsorb on the O atom in the second layer. In this case the total adsorption energy for all three atoms is $-5.33$ eV. Finally, we find that with four adsorbed H atoms, two are adsorbed in the first layer, and another two on the second layer. The total adsorption energy for these four H atoms is $-6.85$ eV. The adsorption energy per hydrogen atom in this case is therefore reduced to $-6.85/4 = -1.71$ eV.

We find that the pristine (001) surface can't absorb more than four H atoms per cell. If we try adding the fifth H atom to the surface, we find that the added H atom combines with another H atom on the surface to generate a H$_2$ molecule and moves away from the surface. Therefore, we conclude that the unsaturated pristine surface of (001) TiO$_2$ anatase can be saturated by adsorption of at most four H atoms per surface unit cell.

In all of these cases we fully relaxed the TiO$_2$ surface in the presence of hydrogen atoms. The surface relaxation is significant, with the maximal atomic displacements on the order of 0.4 Å. As one would expect, surface relaxation is smallest with one adsorbed hydrogen atom and largest with four adsorbed hydrogen atoms.

**B. Hydrogen adsorbed on a modified surface**

Now we consider the possibility that presence of adsorbed hydrogen atoms will lead (001) surface to reconstruct in a distinct basin of energy, with structure that is significantly different from the pristine (001) surface.

Indeed, our calculations show that when four hydrogen atoms are adsorbed per a single surface unit cell that the surface of TiO$_2$ (001) anatase is reconstructed. This reconstruction is similar to the bulk structure discussed in Ref. 28. The structure can be approximately described as translation of Ti atoms on the surface by $(a/2, a/2)$ relative to the pristine surface. This translation vector is shown in Fig. 1. Note that if the topmost layer was isolated from the other layers, that the pristine and reconstructed surface would be indistinguishable from each other. This can easily be seen from Fig. 1, or by realizing that in a surface primitive unit cell oxygen atoms are at coordinates $(0, a/2)$ and $(a/2, 0)$ while titanium atom is at the origin, $(0, 0)$. Therefore, if we translate titanium atom by $(a/2, a/2)$ we get a crystal structure equivalent to the one where we translate both all atoms by $(a/2, a/2)$, as oxygen atoms get mapped into periodic images of each other. Therefore, this modified structure is in some sense minimally perturbed relative to the pristine surface, as the only difference of the modified surface is that the topmost layer is out of registry with the rest.

We studied adsorption of hydrogen atoms to the modified surface following steps analogous to those used for the pristine surface. The calculated relative energy of modified surface adsorbed with different number of H atoms is indicated in Fig. 2 with red color. We took the energy of the pristine surface without H atom adsorption as a reference state with zero energy.

We find that without H atom adsorption, the energy of the modified surface is 1.4 eV higher than that of pristine surface. However, once H atoms are adsorbed the energy difference between modified and pristine surface diminishes. Eventually, with four adsorbed H atoms the modified surface becomes energetically favorable compared to the pristine surface.

More specifically, we find that the absorption energy of the first hydrogen atom is $-2.32$ eV. While this surface absorbs hydrogen atom slightly more strongly than the pristine surface ($-2.32$ eV compared to $-2.23$ eV on a pristine surface), the difference is not large enough to compensate for the increased surface energy of the modified surface relative to the pristine surface (1.4 eV). However, if we increase the number of hydrogen atoms to two per surface unit cell, the total adsorption energy increases to $-4.58$ eV (compared to $-4.06$ eV in the pristine case). With three hydrogen atoms, it is $-6.52$ eV, and finally, it is $-8.34$ eV with four H atoms. Therefore, when four H atoms are adsorbed, the modified surface becomes favorable relative to the pristine surface, as the stronger preference of H-adsorption on the modified surface ($-8.34$ eV versus $-6.85$ eV on the pristine surface, the difference is $-6.85 + 8.34 = 1.49$ eV) is large enough to compensate for the difference in the surface energy between modified and pristine surface (1.4 eV). However the energy difference between pristine and modified surfaces with four adsorbed H atoms is very small, only 0.09 eV, and it is likely comparable to the error of the GGA approximation used in our calculation. Nevertheless, our calculation clearly shows that the modified surface has tendency to absorb more hydrogen atoms and will thus be energetically more and more favorable at high enough
pressure of hydrogen atoms.

C. Required hydrogen pressure

Based on the surface adsorption energies of H atoms we will now determine the required pressure of hydrogen atoms needed to modify the pristine TiO$_2$ surface. Figure 3 shows the surface energy $\Delta \gamma$ of the pristine and modified surfaces as a function of the hydrogen chemical potential $\mu_H$. As can be seen from the figure, surface without hydrogen atom adsorption $N_H = 0$ is favorable at hydrogen chemical potential below $-2.25$ eV. As hydrogen chemical potential is increased, preferred surface becomes the pristine surface with $N_H = 1$ hydrogen atom adsorption. At $\mu_H = -1.83$ eV the preferred surface becomes the pristine surface with $N_H = 2$. Finally, when the hydrogen chemical potential is larger than $-1.44$ eV, the modified surface with $N_H = 4$ becomes the most favorable surface. Since a small difference in the chemical potential can cause a large change of the pressure, based on equations (2) and (3), we report the needed pressure of hydrogen atoms as a range 0.3–30 Pa. This range assumes a 10% error in the calculated hydrogen chemical potential.

D. Energy barrier between pristine and modified surface

Now we turn to calculating the barrier between the pristine and modified surface. We calculated the barrier using the nudged elastic band (NEB) approach. As shown in Fig. 4 the barrier is very high when there are no hydrogen atoms adsorbed on the surfaces (it is 2.3 eV, per primitive surface unit cell). However, once four hydrogen atoms are adsorbed on the surface, the barrier is reduced to only 0.5 eV per primitive surface unit cell. The reduced energy pathway between pristine and modified surface is indicated with a dash line in Fig. 4.

As discussed earlier, hydrogen atoms do not absorb at the equivalent locations in the case of pristine and modified surface. In particular, on the pristine surface one of the hydrogen atoms is optimally bonded below the O atom in the second layer, while it is bonded above on the modified surface. However, both configurations, on either of the surfaces, are nearly degenerate in energy (they differ by 0.18 eV). Therefore, for the sake of comparison, we performed the NEB calculation only between the structures in which hydrogen atoms are adsorbed at equivalent locations. This path is indicated with points 1 through 6 in Fig. 4. Point 7 indicates energy of a modified structure with the optimal configuration of adsorbed hydrogen atoms.

E. Other potential structural modifications

So far we only discussed one reconstruction of TiO$_2$ anatase (001) surface in the presence of hydrogen atoms. In what follows we consider some other possible reconstructions compatible with the minimal 1×1 surface unit cell, and show that they are all energetically less stable. We leave to future studies the possibility of other reconstructions, especially those that might increase the size of the primitive surface unit cell, as that would make the calculation more computationally demanding.

Modified structure of TiO$_2$ we discussed earlier can be constructed by translating the top most Ti atom by $(a/2, a/2)$. This translation breaks one of the Ti-O bonds, the one that is perpendicular to the surface, which is why the energy of the surface increases by 1.4 eV.

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**Fig. 3.** The surface energy density $\Delta \gamma$ of the pristine (solid) and modified (dashed) surfaces with $N_H = 0$ through 4. Above $\mu_H = 1.44$ eV modified surface (dashed green) becomes the most favorable surface.

**Fig. 4.** Calculated energy profiles for the structure transformation from the pristine to the modified structure, both without (solid line) and with (dash line) adsorbed hydrogen.
However, as discussed earlier, this energy difference is compensated by the fact that the surface with broken Ti-O bond can absorb more hydrogen atoms. Motivated by this finding, we will now consider different ways to break Ti-O bonds on the surface and check whether they can also be compensated energetically by absorbing additional hydrogen atoms.

The first alternative way to break Ti-O bond we considered was to simply increase the vertical distance between Ti and O atoms. If we try inserting additional H atom between the bond-breaking Ti and O, we find that instead of formation of Ti-H or O-H bond, hydrogen atoms bind together and form a H$_2$ molecule inside the slab. The energy of this structure is 0.45 eV higher than the total energy of the pristine surface adsorbed with four H atoms (plus one isolated H atom, to keep total number of H atoms the same). Therefore, we conclude that hydrogen atoms can’t stabilize breaking of the vertical Ti-O bond, unless one translates Ti atom by ($a/2$, $a/2$), as in the modified structure.

The second structure we tried has a broken Ti-O bond that is parallel to the surface. As in the previous case, we broke the bond simply by increasing the distance between the Ti and O atoms in the bond. If we try adding two additional H atoms between Ti and O, we find that two H$_2$ molecules are generated during the structural relaxation. The energy of this configuration is 0.52 eV higher than the total energy of the pristine surface adsorbed with four H atoms (plus energy of two isolated H atoms). Therefore, we conclude that in this scenario hydrogen atoms can’t break the in-plane Ti-O bond.

The third structure we tried contains oxygen vacancy at the surface. To form a vacancy we removed one surface two-coordinated O atom. Next we tried to stabilize this surface by putting one additional H atom at the vacancy site. We again find that during the relaxation process one H$_2$ molecule is generated. The formation energy of this oxygen vacancy is very high (it is 3.74 eV), so this structure can’t be stabilized by addition of hydrogen atoms. We quantified the formation energy of the vacancy by taking a difference between the total energy of the slab with a vacancy (plus one isolated O atom) and the total energy of the pristine surface adsorbed with four H atoms (plus one isolated H atom).

IV. WATER SPLITTING PERFORMANCE OF THE MODIFIED SURFACE

After showing that the modified surface becomes favorable at high hydrogen plasma pressure, now we turn to the study of the water splitting performance of the modified surface.

![Density of states](image)

**FIG. 5.** Density of states of (a) pristine (001) surface and (b) modified (001) surface with one water molecule on the surface. The conduction band shown is scissor shifted by 1.39 eV following Ref. 28. Blue line shows oxygen 2p-like states projected onto two topmost layers of TiO$_2$.

### A. Water adsorption

When anatase TiO$_2$ is used to catalyze water splitting, the catalyst is immersed in the aqueous environment. Therefore, we will first compare the adsorption of water molecule on pristine and modified surfaces. We find that after full structural relaxation the water molecule binds to the pristine surface by forming a bond between the Ti atom on the surface and O atom of the water molecule (bond length is 2.339 Å). One of the H atom in the water molecule interacts with the surface O atom and generates a bond with length of 1.620 Å. We expect that a very similar binding geometry will occur on the modified surface, as the top layer is nearly the same as in the pristine case. This is precisely what we find, as the Ti-O bond length on the modified surface is 2.343 Å while the H-O bond length is 1.636 Å.

Despite similarities in the structure, the energy level alignments are not the same on two surfaces. Figure 5 shows calculated density of states (DOS) of the pristine and modified surfaces with adsorbed water molecule. The energy in that figure is aligned relative to the vacuum level above the surfaces. While we find that the conduction band minimum (CBM) is nearly the same in the pristine and the modified surface, the valence band maximum (VBM) is higher by 1 eV on the modified surface. Furthermore, as indicated in the figure, this increase in the VBM originates from the oxygen 2p states in the first and second layer (blue line) on the TiO$_2$ surface and not from the oxygen 2p states in the water (yellow line).
B. Reaction path

Since the modified surface has a higher VBM than the pristine surface, the reduced band gap of the modified surface should contribute to better water splitting performance. To test this hypothesis, we studied the explicit chemical reaction on the surfaces. Several groups have already studied theoretically the mechanism of photocatalytic water splitting on the pristine anatase TiO$_2$ surface.\textsuperscript{29,30} Since pristine and modified surface differ only in the registry between the two top-most layers of TiO$_2$, we suspect that the reaction pathways might be similar. After all, the topmost layer of TiO$_2$ that is exposed to the water molecules is structurally nearly the same in two cases. However, the magnitude of energy barriers needs not be the same, as electronic structures are different.

As a reference path for the pristine TiO$_2$ surface we took the reaction path proposed by Liu et al. in Ref.\textsuperscript{29}. We didn’t implement the solvation effects in our calculations as solvation effects have a small effect on the relative energy of each state. For example, we find that the rate-limiting barrier without solvation effects is 0.55 eV while Ref.\textsuperscript{29} reports that the same barrier is 0.61 eV with solvation effects.

Figure 6 shows calculated Gibbs free energy profiles of oxygen evolution reaction on the pristine (black line) and modified surface (red line). State 1 on the figure represents the surface adsorbed with one dissociated water molecule where one H$^+$ ion is adsorbed on the surface O atom and one OH$^-$ ion adsorbed on the surface Ti atom. This state 1 is the initial state of the water splitting reaction. From state 1 to state 2, one H$^+$ ion is extracted away from the surface,

$$\text{H}_2\text{O/TiO}_2 + h^+ \rightarrow \text{OH/TiO}_2 + \text{H}^+$$

(Adsorption of H$_2$O or OH on the surface we denoted with H$_2$O/TiO$_2$ and OH/TiO$_2$. The hole is denoted by h$^+$.) In step 2 $\rightarrow$ 3 the second H$^+$ ion is extracted. Next, another water molecule absorbs on the surface (state 4), and the third H$^+$ ion is extracted away from the surface (state 5). From state 5 $\rightarrow$ 8 the fourth H$^+$ ion is extracted away from the surface and one O$_2$ molecule is generated during the process. State 9 is the final state of water splitting reaction without any adsorption. State 9 will go back to state 1 after chemical adsorption of one water molecule. States 1 through 9 shown in Fig. 6 are equivalent to states 9 through 17 in Ref.\textsuperscript{29}. The Gibbs energy difference between the beginning state 1 and state 9 is the reaction energy ($\Delta G$) for process

$$2\text{H}_2\text{O} + 4h^+ \rightarrow 4\text{H}^+ + \text{O}_2.$$  

The Gibbs energy difference between state 9 and the last state 1 is the chemisorption energy of one H$_2$O molecule on the surface.

As already found in Ref.\textsuperscript{29} the rate-controlling step on the pristine surface is the first proton removal step $1 \rightarrow 2$. However, this barrier does not exist on the modified surface, as $1 \rightarrow 2$ on the modified surface is exothermic by $-0.49$ eV. The rate-controlling step on the modified surface is the fourth proton removal step $7 \rightarrow 8$, with a relatively small barrier of only 0.13 eV. Therefore, we find that the modified (001) surface has much better water splitting performance than the pristine surface.

C. Origin of the reduced energy barrier

Now we will discuss possible origin of the reduced energy barriers on the modified TiO$_2$ surface. Fig. 7 shows the optimized structures of states 1 and 2 in the reaction path. Comparing Fig. 7 (b) and (d), we find that the Ti-O bond lengths in state 2 are shortened on the modified state 2 compared to the pristine surface. We can rationalize this by noting that the surface Ti atom is less saturated on the modified than on the pristine surface. Therefore, the Ti atoms binds more firmly to O atom and OH$^-$. As a result, this relatively lower energy of the modified state 2 shown in Fig. 6 contributes to the reduced energy barrier on the modified TiO$_2$ surface.

Furthermore, as shown in Fig. 5, the VBM of modified TiO$_2$ surface after adsorbing one H$_2$O is higher than that of pristine TiO$_2$ surface. Which is well known to contribute to the improved chemical activity on the surface.\textsuperscript{31}

V. OUTLOOK AND CONCLUSION

Our calculations show that the modified (001) surface of TiO$_2$ anatase has electronic structure that is favorable for water photocatalysis. There are several ways to synthesize TiO$_2$ (001) films in experiment. One is by adding hydrofluoric acid into the TiO$_2$ precursor, since the hydrofluoric acid can act as a shape controlling agent and
Another is to grow the (001)-oriented anatase TiO$_2$ (001) film on a seed layer substrate, such as RbLaNb$_2$O$_7$, and amine functionalized glasses.

According to our calculations, the (001) surface of TiO$_2$ anatase can be modified when exposed to partial pressure of hydrogen atoms about 0.3–30 Pa. Such pressures can be obtained in the experiments. For example, Nakamura$^{22}$ synthesized the plasma-treated TiO$_2$ photocatalyst. In his experiment, the chamber pressure was about 270 Pa. Dobele$^{39}$ measured the H$_2$ dissociation degree in processing plasma, and found the dissociation ratio is about 4.85%. According to this H$_2$ dissociation ratio, the H atom partial pressure is roughly 13 Pa in Nakamura’s experiment. Therefore, the hydrogen atom pressure range of 0.3–30 Pa is within the experimental range of achievable hydrogen plasma conditions.

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