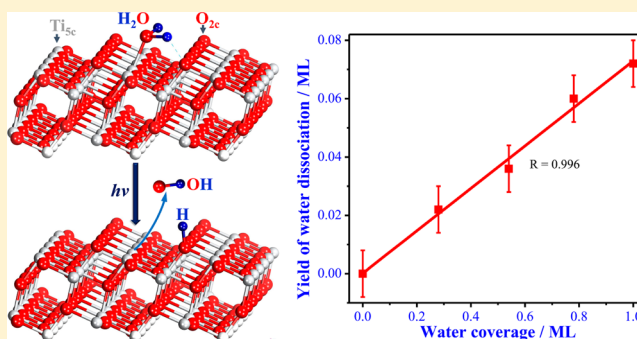


Highly Efficient Water Dissociation on Anatase TiO₂(101)Zhenhua Geng,^{†,‡,§} Xiao Chen,^{†,‡,§} Wenshao Yang,[†] Qing Guo,^{*,†} Chenbiao Xu,[†] Dongxu Dai,[†] and Xueming Yang^{*,†}[†]State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, 457 Zhongshan Road, Dalian 116023, Liaoning, P. R. China[‡]University of Chinese Academy of Sciences, 19 A Yuquan Road, Shijingshan District, Beijing 100049, P. R. China

S Supporting Information

ABSTRACT: Photoinduced water dissociation on anatase-TiO₂(101) has been investigated using a laser surface photolysis technique, in combination with temperature-programmed desorption and time-of-flight methods. Gaseous OH radicals have been clearly detected by the time-of-flight method during laser irradiation. Further result reveals that the water dissociation reaction occurs most likely via transferring a H atom to a two coordinated oxygen site nearby and ejecting an OH radical to the gas phase. As the water coverage increases, the yield of the water dissociation reaction is also enhanced, whereas the dissociation probability of water is nearly the same at different water coverages. In comparison with water dissociation on rutile-TiO₂(110) where the dissociation probability of water is largely inhibited by the strong hydrogen bonds at high water coverage, the reaction on anatase-TiO₂(101) is considerably more efficient at high water coverage, which is most likely due to the much weaker interaction between water molecules on the surface. This provides an important clue that strong hydrogen bond interaction should be avoided on a good photocatalyst for water dissociation.



■ INTRODUCTION

Titanium dioxide (TiO₂) is considered as a good photocatalyst for hydrogen generation because of its excellent resistance to chemical and photochemical corrosion in aggressive aqueous environments and due to its activity toward both light and aqueous solutions, such as water (H₂O) and methanol.¹ Since Fujishima and Honda found that hydrogen production can be achieved from H₂O splitting on a TiO₂ photoelectrode in 1972,² tremendous attentions have been focused on the study of H₂O splitting reaction with TiO₂ photocatalysts^{3–9} with the hope that clean and affordable hydrogen energy from H₂O splitting can be accomplished through solar-to-chemical conversion.

Due to the stability and controllable preparation of rutile(R)-TiO₂(110), the interaction of H₂O with R-TiO₂(110)^{10–26} has been extensively investigated both experimentally and theoretically, whereas fundamental studies of photoinduced H₂O dissociation on R-TiO₂(110) have been rarely carried out.^{27,28} Tan and co-workers²⁷ found that the H₂O dissociation can occur on R-TiO₂(110) with one of the H atoms transferred to a nearby bridging-bonded oxygen (BBO) site under ultraviolet (UV) light irradiation. The OH species left may either desorb from the surface or adsorb as an OH radical at a certain five coordinated Ti⁴⁺ site (Ti_{5c}). Most recently, we have shown²⁸ that the H₂O dissociation is strongly suppressed as the surface H₂O coverage increases on R-TiO₂(110). Further scanning

tunneling microscopy (STM) study indicates that the hydrogen bond between surface H₂O molecules has a dramatic effect on the H₂O dissociation. A single hydrogen bond in H₂O dimers enhances the probability of H₂O dissociation, while one-dimensional strong hydrogen bonds inhibit the reaction. In spite of lots of works focusing on R-TiO₂, the anatase(A)-TiO₂ is the most active polymorph in commercial applications for catalysis actually.²⁹ Even though lots of studies on H₂O splitting have been carried out on A-TiO₂ particles or A-TiO₂ based particles, very little was done on well-defined surfaces. So far, only a few experimental and theoretical studies^{30–42} have been performed on the H₂O/A-TiO₂(101) system. On the basis of the theoretical studies done by Tilocca and Selloni,^{32,34,37} due to the large distance (3.81 Å) between the neighboring Ti_{5c} sites on A-TiO₂(101), no H₂O–H₂O hydrogen bonds are present with submonolayer H₂O adsorption. On defective A-TiO₂(101), dissociative adsorption of water at the Ti_{5c} site close to the Ti interstitial is more favorable. Using X-ray photoelectron spectroscopy (XPS), Walle and co-workers⁴³ found that part of the water dissociatively adsorbs on A-TiO₂(101) with hydroxyl groups on a two coordinated oxygen site (O_{2c}) (OH_{O2c}) and Ti_{5c} site (OH_{Ti}), whereas no evidence

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of H₂O dissociation was observed on A-TiO₂(101) by a series of STM studies.^{35,38} Until now, no fundamental studies of photoinduced dissociation of H₂O on the well-defined surface have been carried out at all. In this study, the H₂O dissociation on A-TiO₂(101) has been investigated using temperature-programmed desorption (TPD) and time-of-flight (TOF) methods. Our results show that the H₂O dissociation reaction takes place via one of the H atoms transferred to an O_{2c} and the OH radical left desorbed from the A-TiO₂(101) surface. In addition, we found that the dissociation probability of H₂O on A-TiO₂(101) remains unchanged ($\sim 7\%$) as the coverage of H₂O increases after 30 min irradiation, which is totally different from that on R-TiO₂(110), indicating that the A-TiO₂(101) surface is more suitable for H₂O dissociation than the R-TiO₂(110) surface at 266 nm irradiation.

EXPERIMENTAL METHODS

The surface photocatalysis-TPD apparatus used in this work has been described previously in detail.²⁸ The experiments were performed in an ultra-high-vacuum (UHV) chamber with better than 5×10^{-11} Torr. An extremely high vacuum of 1.5×10^{-12} Torr in the ionization region was maintained during the experiment for highly sensitive temperature-programmed desorption (TPD) and time-of-flight (TOF) measurements. The third-harmonic (266 nm) with a repetition rate of 1 kHz, which came from a Ti:sapphire femtosecond laser (pulse duration ~ 70 fs), was used for the experiment. The power density is ~ 70 mW/cm² (9.5×10^{16} photons cm⁻² s⁻¹). The A-TiO₂(101) surface with dimensions of $6 \times 6 \times 1$ mm³ was purchased from Princeton Scientific Company. Sample preparation was accomplished by cycles of Ar⁺ sputtering and resistive heating to 800 K in vacuum until all impurities were removed and a sharp LEED pattern was observed (Figure S1). H₂O (Aldrich, >99.5%) was further purified by several freeze-pump-thaw cycles, and then was introduced to the A-TiO₂(101) surface with a calibrated molecular beam doser. As shown in Henderson's work,⁴⁴ the amount of the first layer of H₂O on R-TiO₂(110) is about 5.2×10^{14} molecules/cm². When we turned on the molecular beam doser to dose H₂O on R-TiO₂(110) to make the first layer be saturated at a set time, the absolute flux of H₂O molecules on the surface can be measured; then H₂O coverages can be determined on other surfaces by changing the opening time of the doser. TPD spectra were measured with a ramping rate of 2 K/s, with the surface directly pointing to the mass spectrometer. In addition, TOF measurements for certain photodesorbed products were also carried out during laser irradiation. The distance between sample and ionization region is about 37.1 mm.

RESULTS AND DISCUSSION

Figure 1A–D shows the typical TPD spectra acquired at a mass-to-charge ratio (m/z) of 18 (H₂O⁺) after the A-TiO₂(101) surfaces (at 100 K) adsorbed with different coverages (0.28, 0.54, 0.78, and 1.0 ML) (1 ML $\approx 5.2 \times 10^{14}$ /cm²) of H₂O were irradiated for 0 and 30 min with 266 nm light. Before irradiation, two desorption features are observed in the TPD spectra. The main peak observed at low temperature (<300 K) is assigned to the molecularly adsorbed H₂O at the Ti_{5c} sites (H₂O_{Ti}).³¹ On the basis of the recent study of H₂O/A-TiO₂(101) by He and co-workers,³⁵ on reduced surfaces with subsurface defects, part of the H₂O molecules could exist on the surface even at 400 K, while the

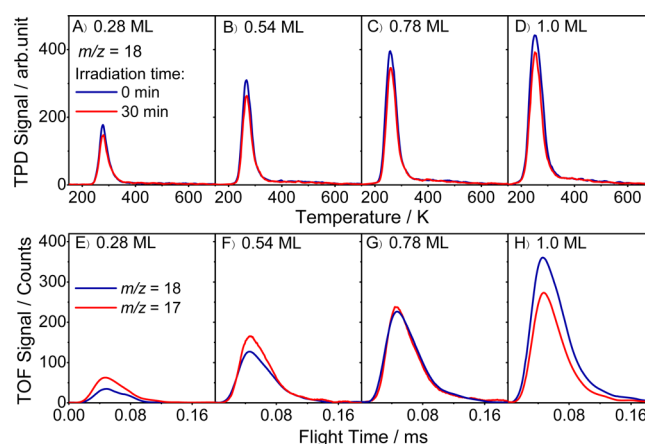


Figure 1. TPD and TOF spectra as a function of the coverage of H₂O. Panels (A)–(D) show TPD spectra acquired at $m/z = 18$ (H₂O⁺) after different coverages of H₂O were adsorbed on A-TiO₂(101) at 100 K and irradiated for 0 min (blue) and 30 min (red) at 100 K by 266 nm, 70 mW/cm². Panels (E)–(H) show TOF spectra collected at $m/z = 18$ (H₂O⁺) and $m/z = 17$ (OH⁺) after different coverages of H₂O were adsorbed on A-TiO₂(101) at 100 K and irradiated for 30 min at 100 K by 266 nm, 70 mW/cm².

subsurface defects (Ti interstitials) could increase the adsorption energy of water molecules. Thus, the broad desorption tail (>350 K) may be due to the molecularly adsorbed H₂O at the Ti_{5c} sites with subsurface defects beneath the site, where the hydrogens of H₂O may form two weak hydrogen bonds with O_{2c} atoms nearby. These authors also found that surface point defects (O_{2c} vacancies) could be rarely formed on the A-TiO₂(101) surface by high temperature annealing.⁴⁵ After irradiating the surfaces with 266 nm for 30 min, the low temperature peak in all of these spectra decreases obviously, but with a considerably different amount of depletion for different H₂O coverages. This suggests that H₂O molecules on the surface are photodesorbed or photodissociated by 266 nm.

To confirm whether the H₂O dissociation reaction occurs under 266 nm irradiation, TOF spectra of the photodesorbed products at $m/z = 18$ (H₂O⁺) and 17 (OH⁺) directly ejected from these surfaces were collected during laser irradiation, as shown in Figure 1E–H. No TOF signal at $m/z = 16$ (O⁺) was observed, implying that nearly no surface point defects were created during UV irradiation and the O_{2c} atoms on A-TiO₂(101) were very stable. The TOF signal at $m/z = 18$ is due to photoinduced H₂O_{Ti} desorption, whereas the TOF signal at $m/z = 17$ may come from two sources. The first is product OH radical from the H₂O_{Ti} dissociation reaction (OH_{Ti}). The second is the ion-fragment signal of the parent H₂O molecule (OH_{crack}). In the TOF spectra collected at 0.28 ML coverage, the $m/z = 17$ TOF signal is considerably larger than the $m/z = 18$ TOF signal. As the H₂O coverage increases, the ratio of the TOF intensity of $m/z = 17$ and 18 changes significantly from 1.55:1 at 0.28 ML coverage to 0.69:1 at 1.0 ML coverage (Figure 1E–H). Because a femtosecond laser with a pulse duration of 70 fs was used for the work, it will induce a localized hot on the surface. As a result, the vibration of photodesorbed H₂O molecules may likely be very hot, and hence may exhibit a larger propensity to crack the OH radical. However, as shown in Figure S2, we have measured the TPD spectra of H₂O on A-TiO₂(110). The H₂O TPD spectra collected from a multilayer H₂O desorption could cover the

temperature from 120 to 600 K. After the TPD profile of $m/z = 17$ is multiplied by 3.3, the new profile is nearly the same with that of $m/z = 18$ in the temperature range of 120–600 K, indicating that a hot H_2O molecule will not exhibit a larger propensity to crack the OH radical. As the H_2O coverage increases, the ratio of the TOF intensity of $m/z = 17$ and 18 changes significantly, whereas the peak positions of TOF spectra collected at $m/z = 17$ and 18 are nearly the same. Correspondingly, the velocity distributions of OH radical and H_2O are nearly the same at different H_2O coverages, indicating that the energy distributions of photodesorbed H_2O molecules are the same at different H_2O coverages, which will not lead to the significant changes in the ratio of TOF signals at $m/z = 17$ and 18. Thus, part of the TOF signal at $m/z = 17$ is from H_2O cracking, and the other part is from the OH radical product formed via the H_2O dissociation reaction.

As calculated from the TPD spectra at $m/z = 17$ and 18, the relative intensities of H_2O at $m/z = 17$ and 18 is 0.30:1. Therefore, the much larger TOF signal at $m/z = 17$ in Figure 1E–H further implies that gas phase OH radicals are produced from the photolysis of H_2O on A-TiO₂(101). The intensity of the $m/z = 17$ TOF signal increases significantly as the H_2O coverage increases, suggesting that the yield of H_2O dissociation on A-TiO₂(101) increases as the H_2O coverage increases. In addition, as shown in the TOF spectra displayed in Figure 1E–H, the $m/z = 18$ and $m/z = 17$ TOF spectra are nearly identical. However, they are not the same actually.

As shown in Figure 2, the translational energy distributions for $m/z = 17$ and 18 resulting from 266 nm photodissociation

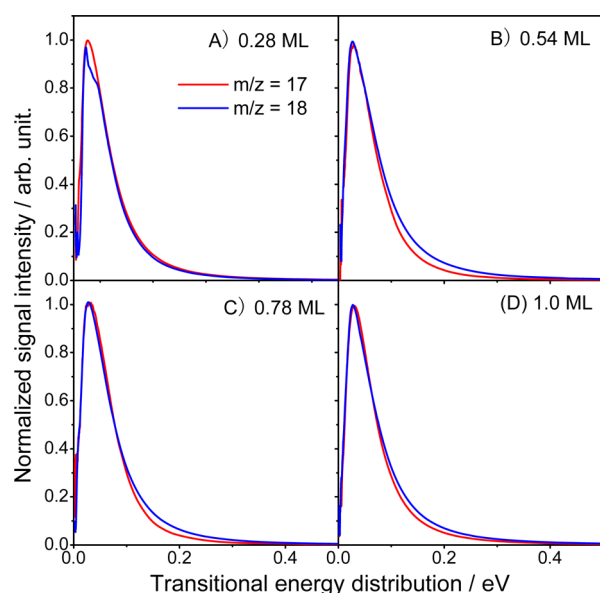


Figure 2. Translational energy distributions for $m/z = 17$ and 18 resulting from 266 nm photodissociation of different coverage of H_2O on A-TiO₂(110) at 100 K, derived from Figure 1E–H.

of different coverage of H_2O on A-TiO₂(110) have been calculated from Figure 1E–H. When we transfer the TOF data to the translational energy distributions, the data have properly been transformed into the flux domain, and then the intensity of the translational energy distributions are normalized to 1. At 0.28 ML coverage, the translational energy distributions for $m/z = 17$ and 18 are very similar. As the H_2O coverage increases, the translational energy distribution for $m/z = 17$ is a little

narrower than that for $m/z = 18$, indicating that the TOF signal at $m/z = 17$ is not totally from the H_2O cracking. The direct photodissociation of H_2O to produce an OH radical is impossible because of the very small adsorption cross section of H_2O at wavelength at 266 nm,⁴⁶ indicating that the direct interaction of H_2O and photons is impossible at 266 nm, and the photodesorption of H_2O and OH radical from the A-TiO₂(101) surface is a substrate mediated process. Meanwhile, the peak of translational energy distributions of the H_2O and OH radical species are at 0.03 eV, and the translational energy distributions for $m/z = 17$ and 18 at different H_2O coverages are nearly the same. At 1.0 ML H_2O coverage, velocity distributions of $m/z = 17$ and 18 fitted with the Maxwell–Boltzmann distribution were carried out (Figure S3). The fitting temperature is 480 K, indicating that, upon a femtosecond pulse excitation, the local temperature of the surface maybe rises to more than 480 K, leading to H_2O desorption.

In the present study, femtosecond laser light has been used to investigate H_2O photochemistry on the well-defined A-TiO₂(101) surface, which has a very high instantaneous power. At such high powers, multiphoton effects may be important for H_2O dissociation. We thus investigated the integrated TOF signals of H_2O and OH radical products as a function of photon flux at 266 nm (Figure 3) with 5 min irradiation. Within

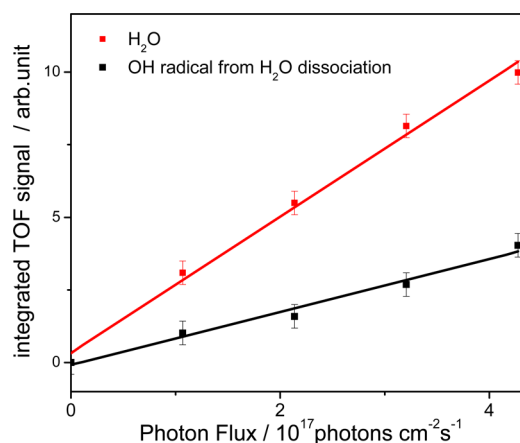


Figure 3. Integrated TOF signals of H_2O and OH radical product from 1 ML H_2O adsorbed A-TiO₂(101) as a function of photon flux with 266 nm irradiation. The irradiation time is 5 min, respectively. The surface temperature (~ 100 K) was nearly unchanged during irradiation.

experimental error, the integrated TOF signals of H_2O and OH radical products are linear with photon flux from 0 to 4.4×10^{17} photons $\text{cm}^{-2} \text{s}^{-1}$, suggesting that there is no obvious evidence for the exponential increase in TOF signals that would be expected for a multiphoton process.

Murakami and co-workers^{47,48} have observed the OH radicals after the exposure of H_2O vapors over TiO₂ powders using the laser-induced-fluorescence (LIF) technique. The authors then proposed that the OH radicals may be formed by the surface reduction of H_2O_2 formed by the complex photocatalytic reactions of two H_2O molecules with A-TiO₂ powders is plausible. Recently, the H_2O dissociation on R-TiO₂(110) under ultra-high-vacuum (UHV) condition has been investigated by Wang's²⁷ and Yang's²⁸ groups; the two groups demonstrate that the reaction occurs with one of the H atoms transferring to a nearby BBO site and the OH species left

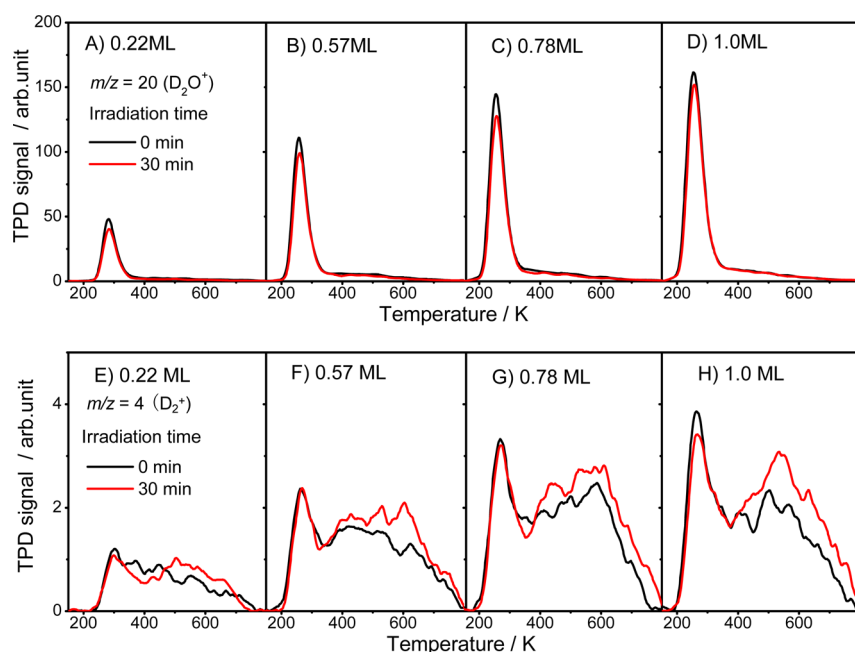


Figure 4. TPD spectra acquired at $m/z = 20$ (D_2O^+) and 4 (D_2^+) after different coverages of D_2O were adsorbed on A- $TiO_2(101)$ at 100 K and irradiated for 0 min (black) and 30 min (red) at 100 K by 266 nm, 70 mW/cm².

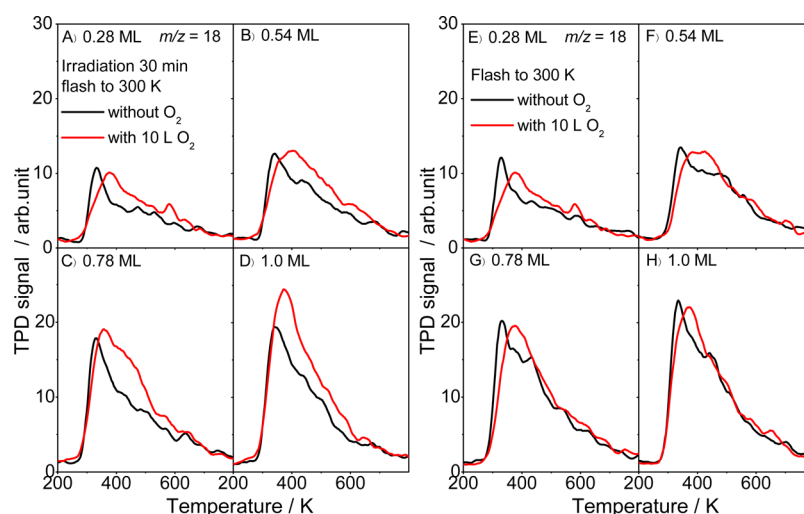


Figure 5. Left: TPD spectra acquired at $m/z = 18$ (H_2O^+) as a function of H_2O coverage on A- $TiO_2(101)$ at 100 K after the surfaces were irradiated for 30 min at 100 K by 266 nm, 70 mW/cm² and then preheated to 300 K, followed by exposing 0 (black line) and 10 L O_2 (red line) to the preheated surfaces at 100 K. Right: TPD spectra acquired at $m/z = 18$ (H_2O^+) as a function of H_2O coverage on A- $TiO_2(101)$ at 100 K and then preheated to 300 K, followed by exposing 0 (black line) and 10 L O_2 (red line) to the preheated surfaces at 100 K before TPD.

either desorbing from the surface or adsorbing as an OH radical at a certain Ti_{5c} site. According to previous theoretical and XPS investigations of water adsorption on A- $TiO_2(101)$ single surfaces,^{32,34,37,43} H_2O dissociation on the Ti_{5c} sites produces an OH_{Ti} radical and $OH_{O_{2c}}$ directly. Under UHV conditions, especially for the low coverage of H_2O (0.28 ML) on A- $TiO_2(101)$, the H_2O_2 formation from complex photocatalytic reactions of two adjacent H_2O molecules is nearly impossible. Thus, combining the TOF result with previous theoretical and XPS investigations of H_2O adsorption on A- $TiO_2(101)$, we proposed that the H_2O dissociation on A- $TiO_2(101)$ is most likely to occur directly via transferring a H atom to an O_{2c} site nearby and then ejecting an OH radical from the surface, similar to that on R- $TiO_2(110)$.

To evaluate the yield of H_2O photolysis on A- $TiO_2(101)$, an isotope labeling study of D_2 formation from D_2O photolysis was carried out on A- $TiO_2(101)$ under the same experimental conditions, as well (Figure 4). Before irradiation, two peaks are observed in the TPD spectra at $m/z = 4$ (D_2^+) (Figure 4E–H). The low temperature peak is assigned to the ion-fragment signals of the molecularly adsorbed D_2O at the Ti_{5c} sites (Figure 4A–D), whereas the broad TPD peak at about 400–800 K may be due to D_2 formation. Considering the detection efficiencies of D_2 in the quadrupole mass detector (the detecting efficiencies of different mass have been calibrated by leaking different kinds of rare gases into the chamber with the same pressure as gauged by the ion gauge.), the coverage of D atoms is less than 0.02 at 1 ML D_2O coverage, which may be formed via spontaneous dissociation of D_2O_{Ti} on surface defect

sites (O_{2c} vacancies). After 30 min irradiation, about 0.09 ML of $\text{D}_2\text{O}_{\text{Ti}}$ is depleted at 1.0 ML coverage; however, the high temperature D_2 peak just increases a little (<0.004 ML for 1 ML D_2O coverage), indicating that the dissociation probability of $\text{D}_2\text{O}_{\text{Ti}}$ is very low or the $\text{D}_{\text{O}_{2c}}$ atoms on A- $\text{TiO}_2(101)$ diffuse into the bulk. No obvious H_2 TPD peak appears at $m/z = 2$ (not shown) after irradiating the 1 ML H_2O covered A- $\text{TiO}_2(101)$ surface. Correspondingly, theoretical investigations^{49,50} indicate that, in comparison with H_2 desorption from recombination of $\text{H}_{\text{O}_{2c}}$ atoms, the diffusion of $\text{H}_{\text{O}_{2c}}$ atoms into the subsurface is found to be at least equally favorable kinetically. Thus, it is not possible to quantify the yield of H_2O dissociation from the TPD of H_2 desorption. An early work done on R- $\text{TiO}_2(110)$ by Henderson and co-workers⁵¹ found that, with increasing O_2 exposure to a 0.28 ML of bridging H atoms (H_{BBO}) covered R- $\text{TiO}_2(110)$ surface, the bridging H atoms will react with O_2 molecules to form terminal OH groups adsorbed at the Ti_{5c} sites ($\text{OH}_{\text{Ti}_{5c}}$) very easily



and then two terminal OH groups will desorb in the form of H_2O during TPD, leaving an O atom on a Ti_{5c} site of the R- $\text{TiO}_2(110)$ surface



This may provide us an indirect method to measure the yield of H_2O dissociation.

As shown in Figure 5 (left), after 30 min irradiation of the H_2O covered A- $\text{TiO}_2(101)$ surfaces, the surfaces were preheated to 300 K to remove most of the $\text{H}_2\text{O}_{\text{Ti}}$ molecules, and then the surfaces were recooled to 100 K to adsorb different amounts of O_2 , followed by TPD spectra measurements. It is obvious that the H_2O TPD peak with O_2 exposure shifts to higher temperature and is bigger than that without O_2 exposure, implying that surface O species reacted with surface H atoms to form $\text{H}_2\text{O}_{\text{Ti}}$ after O_2 exposure. The surface H atoms are most likely from the dissociated H atoms from H_2O dissociation on A- $\text{TiO}_2(101)$ or the H atoms in the bulk. In comparison, TPD spectra were also collected on the H_2O covered surfaces prepared by preheating to 300 K and recooling to 100 K prior to O_2 exposure without irradiation. The area of the H_2O TPD peak with O_2 exposure is a little bigger than that without O_2 exposure at different H_2O coverages (Figure 5, right), demonstrating that little surface $\text{H}_{\text{O}_{2c}}$ atoms are formed after H_2O adsorption, and the H atoms in the bulk do not diffuse to the surface to react with surface O species during the TPD process.

The yield of H_2O dissociation at different coverages could be estimated from Figure 5, as shown in Figure 6. As the coverage of H_2O increases, the yield of H_2O dissociation increases linearly with the coverage of H_2O , with a constant dissociation probability of $\sim 7\%$. However, on R- $\text{TiO}_2(110)$, the dissociation probability of H_2O significantly decreases as the coverage of H_2O increases.²⁸ At 1.0 ML coverage, the dissociation probability nearly decreases to zero, which results from the effect of strong hydrogen bonds between surface H_2O molecules along Ti_{5c} rows ($[001]$), leading to an increase in the OH dissociation energy of H_2O on R- $\text{TiO}_2(110)$. On the basis of previous theoretical studies,^{32,34,37} no H_2O – H_2O hydrogen bonds are present with submonolayer H_2O adsorption. Recent STM investigation of H_2O on A- $\text{TiO}_2(101)$ ³⁵ showed that an O_{2c} atom can accommodate only one hydrogen bond from an adsorbed H_2O molecule; after

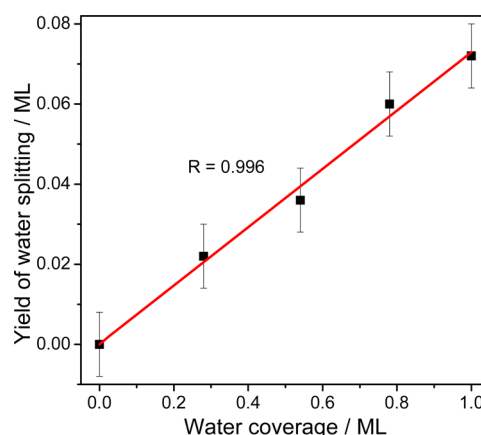


Figure 6. Yield of H_2O splitting versus surface H_2O coverage, obtained from TPD results from Figure 5.

arrival of a second H_2O molecule in its neighborhood (along $[010]$), the competition between the two molecules for the same O_{2c} atom weakens the hydrogen of the first one and effectively lowers its adsorption at high coverage and no H_2O chain forms along the Ti_{5c} row ($[010]$). At high coverage, the occurrence of weak attractive interactions between neighboring H_2O molecules along $[1\bar{1}\bar{1}]/[1\bar{1}\bar{1}]$ could promote H_2O chain formation. The large distance between the neighboring Ti_{5c} sites along $[1\bar{1}\bar{1}]/[1\bar{1}\bar{1}]$ (about 5.4 Å) leads to that the hydrogen bonds between H_2O molecules on the surface are rather weaker than those between H_2O molecules on R- $\text{TiO}_2(110)$ (the distance between the neighboring Ti_{5c} sites along $[001]$ is about 2.96 Å). The feature is not present on R- $\text{TiO}_2(110)$, where STM shows H_2O molecules adsorbed right next to each other along Ti_{5c} rows to form various lengths of one-dimensional H_2O chains through strong hydrogen bonds at high coverage of H_2O ,¹⁷ leading to the enhancement of the H_2O adsorption and OH dissociation energies with increasing the length of the H_2O chain.²⁸ Thus, the constant dissociation probability of H_2O on A- $\text{TiO}_2(101)$ at different H_2O coverages may result from the rather weak interactions between H_2O molecules on A- $\text{TiO}_2(101)$, which has little effect on the OH dissociation energy. Similar to the H_2O dissociation on R- $\text{TiO}_2(110)$,²⁷ part of OH_{Ti} from H_2O dissociation may be left on A- $\text{TiO}_2(101)$; therefore, the measured yield of H_2O dissociation will be a little lower than the actual yield.

SUMMARY

In summary, photoinduced H_2O dissociation on A- $\text{TiO}_2(101)$ has been investigated using TPD and TOF methods. Experimental results show that the H_2O dissociation on A- $\text{TiO}_2(101)$ is most likely to occur via transferring a H atom to an O_{2c} site nearby and ejecting an OH radical from the surface, similar to that on R- $\text{TiO}_2(110)$. More interestingly, the dissociation probability of H_2O on A- $\text{TiO}_2(101)$ is a constant ($\sim 7\%$) at different H_2O coverages, while the H_2O dissociation on R- $\text{TiO}_2(110)$ is much less efficient at high H_2O coverage. This suggests that the H_2O dissociation is more efficient on the A- $\text{TiO}_2(101)$ surface relative to the R- $\text{TiO}_2(110)$ surface with 266 nm irradiation. In comparison with the adsorption structures of H_2O on R- $\text{TiO}_2(110)$ surfaces, the weak interactions between H_2O molecules on A- $\text{TiO}_2(101)$ are most likely the origin of this remarkable behavior. The present investigation of the mechanism of the H_2O dissociation from

H₂O photolysis on A-TiO₂(101) could also help us to understand the nature of H₂O splitting on TiO₂ photocatalysts.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b07774.

LEED pattern and AES for A-TiO₂(101), TPD spectra for H₂O, and Maxwell–Boltzmann distribution fitting (PDF)

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[§]These authors made similar contributions to this work.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Yoong, L. S.; Chong, F. K.; Dutta, B. K. Development of Copper-Doped TiO₂ Photocatalyst for Hydrogen Production under Visible Light. *Energy* **2009**, *34*, 1652–1661.
- (2) Fujishima, A.; Honda, K. Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature* **1972**, *238*, 37–38.
- (3) Fujishima, A.; Zhang, X.; Tryk, D. A. TiO₂ Photocatalysis and Related Surface Phenomena. *Surf. Sci. Rep.* **2008**, *63*, 515–582.
- (4) Lee, J. S. Photocatalytic Water Splitting under Visible Light with Particulate Semiconductor Catalysts. *Catal. Surv. Asia* **2005**, *9*, 217–227.
- (5) Maeda, K.; Domen, K. New Non-oxide Photocatalysts Designed for Overall Water Splitting under Visible Light. *J. Phys. Chem. C* **2007**, *111*, 7851–7861.
- (6) Osterloh, F. E. Inorganic Materials as Catalysts for Photochemical Splitting of Water. *Chem. Mater.* **2008**, *20*, 35–54.
- (7) Kudo, A.; Miseki, Y. Heterogeneous Photocatalyst Materials for Water Splitting. *Chem. Soc. Rev.* **2009**, *38*, 253–278.
- (8) Youngblood, W. J.; Lee, S.-H. A.; Maeda, K.; Mallouk, T. E. Visible Light Water Splitting Using Dye-Sensitized Oxide Semiconductors. *Acc. Chem. Res.* **2009**, *42*, 1966–1973.
- (9) Maeda, K.; Domen, K. Photocatalytic Water Splitting: Recent Progress and Future Challenges. *J. Phys. Chem. Lett.* **2010**, *1*, 2655–2661.
- (10) Henderson, M. A. Structural Sensitivity in the Dissociation of Water on TiO₂ Single-crystal Surfaces. *Langmuir* **1996**, *12*, 5093–5098.
- (11) Brookes, I. M.; Muryn, C. A.; Thornton, G. Imaging Water Dissociation on TiO₂ (110). *Phys. Rev. Lett.* **2001**, *87*, 266103.
- (12) Diebold, U. The Surface Science of TiO₂. *Surf. Sci. Rep.* **2003**, *48*, 53–229.
- (13) Onda, K.; Li, B.; Zhao, J.; Jordan, K. D.; Yang, J.; Petek, H. Wet Electrons at the H₂O/TiO₂(110). *Surf. Sci.* **2005**, *308*, 1154–1158.
- (14) Wendt, S.; Matthiesen, J.; Schaub, R.; Vestergaard, E. K.; Lægsgaard, E.; Besenbacher, F.; Hammer, B. Formation and Splitting of Paired Hydroxyl Groups on Reduced TiO₂(110). *Phys. Rev. Lett.* **2006**, *96*, 066107.
- (15) Hammer, B.; Wendt, S.; Besenbacher, F. Water Adsorption on TiO₂. *Top. Catal.* **2010**, *53*, 423–430.
- (16) Henderson, M. A. A Surface Science Perspective on Photocatalysis. *Surf. Sci. Rep.* **2011**, *66*, 185–297.
- (17) Lee, J.; Sorescu, D. C.; Deng, X.; Jordan, K. D. Water Chain Formation on TiO₂(110). *J. Phys. Chem. Lett.* **2013**, *4*, 53–57.
- (18) Kimmel, G. A.; Baer, M.; Petrik, N. G.; VandeVondele, J.; Rousseau, R.; Mundy, C. J. Polarization- and Azimuth-resolved Infrared Spectroscopy of Water on TiO₂(110): Anisotropy and the Hydrogen-bonding Network. *J. Phys. Chem. Lett.* **2012**, *3*, 778–784.
- (19) Valdés, Á.; Qu, Z.-W.; Kroes, G.-J.; Rossmeisl, J.; Nørskov, J. K. Oxidation and Photo-Oxidation of Water on TiO₂ Surface. *J. Phys. Chem. C* **2008**, *112*, 9872–9879.
- (20) Valdés, Á.; Kroes, G.-J. Cluster Study of the Photo-Oxidation of Water on Rutile Titanium Dioxide (TiO₂). *J. Phys. Chem. C* **2010**, *114*, 1701–1708.
- (21) Salvador, P. Mechanisms of Water Photooxidation at n-TiO₂ Rutile Single Crystal Oriented Electrodes under UV Illumination in Competition with Photocorrosion. *Prog. Surf. Sci.* **2011**, *86*, 41–58.
- (22) Imanishi, A.; Okamura, T.; Ohashi, N.; Nakamura, R.; Nakato, Y. Mechanism of Water Photooxidation Reaction at Atomically Flat TiO₂ (Rutile) (110) and (100) Surfaces: Dependence on Solution pH. *J. Am. Chem. Soc.* **2007**, *129*, 11569–11578.
- (23) Salvador, P. On the Nature of Photogenerated Radical Species Active in The Oxidative Degradation of Dissolved Pollutants with TiO₂ Aqueous Suspensions: A Revision in the Light of the Electronic Structure of Adsorbed Water. *J. Phys. Chem. C* **2007**, *111*, 17038–17043.
- (24) Nakamura, R.; Nakato, Y. Primary Intermediates of Oxygen Photoevolution Reaction on TiO₂ (Rutile) Particles, Revealed by In Situ FTIR Absorption and Photoluminescence Measurements. *J. Am. Chem. Soc.* **2004**, *126*, 1290–1298.
- (25) Tamaki, Y.; Furube, A.; Murai, M.; Hara, K.; Katoh, R.; Tachiya, M. Direct Observation of Reactive Trapped Holes in TiO₂ undergoing Photocatalytic Oxidation of Adsorbed Alcohols: Evaluation of the Reaction Rates and Yields. *J. Am. Chem. Soc.* **2006**, *128*, 416–417.
- (26) Bahnemann, D. W.; Hilgendorff, M.; Memming, R. Charge Carrier Dynamics at TiO₂ Particles: Reactivity of Free and Trapped Holes. *J. Phys. Chem. B* **1997**, *101*, 4265–4275.
- (27) Tan, S.; Feng, H.; Ji, Y.; Wang, Y.; Zhao, J.; Zhao, A.; Wang, B.; Luo, Y.; Yang, J.; Hou, J. G. Observation of Photocatalytic Dissociation of Water on Terminal Ti sites of TiO₂(110)-1 × 1 surface. *J. Am. Chem. Soc.* **2012**, *134*, 9978–9985.
- (28) Yang, W.; Wei, D.; Jin, X.; Xu, C.; Geng, Z.; Guo, Q.; Ma, Z.; Dai, D.; Fan, H.; Yang, X. Effect of the Hydrogen Bond in Photoinduced Water Dissociation: A Double-Edged Sword. *J. Phys. Chem. Lett.* **2016**, *7*, 603–608.
- (29) Henderson, M. A. A Surface Science Perspective on Photocatalysis. *Surf. Sci. Rep.* **2011**, *66*, 185–297.
- (30) Hebenstreit, W.; Ruzyski, N.; Herman, G. S.; Gao, Y.; Diebold, U. Scanning Tunneling Microscopy Investigation of the TiO₂ Anatase (101) Surface. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2000**, *62*, R16334.
- (31) Herman, G. S.; Dohnálek, Z.; Ruzyski, N.; Diebold, U. Experimental Investigation of the Interaction of Water and Methanol with Anatase-TiO₂(101). *J. Phys. Chem. B* **2003**, *107*, 2788–2795.
- (32) Tilocca, A.; Selloni, A. Vertical and Lateral Order in Adsorbed Water Layers on Anatase TiO₂(101). *Langmuir* **2004**, *20*, 8379–8384.
- (33) Sumita, M.; Hu, C.; Tateyama, Y. Interface Water on TiO₂ Anatase (101) and (001) Surfaces: First-Principles Study with TiO₂ Slabs Dipped in Bulk Water. *J. Phys. Chem. C* **2010**, *114*, 18529–18537.
- (34) Tilocca, A.; Selloni, A. Structure and Reactivity of Water Layers on Defect-Free and Defective Anatase TiO₂(101) Surfaces. *J. Phys. Chem. B* **2004**, *108*, 4743–4751.
- (35) He, Y. B.; Tilocca, A.; Dulub, O.; Selloni, A.; Diebold, U. Local Ordering and Electronic Signatures of Submonolayer Water on Anatase TiO₂(101). *Nat. Mater.* **2009**, *8*, 585–589.

- (36) Aschauer, U.; He, Y.; Cheng, H.; Li, S.-C.; Diebold, U.; Selloni, A. Influence of Subsurface Defects on the Surface Reactivity of TiO_2 : Water on Anatase (101). *J. Phys. Chem. C* **2010**, *114*, 1278–1284.
- (37) Tilocca, A.; Selloni, A. DFT-GGA and DFT+ U Simulations of Thin Water Layers on Reduced TiO_2 Anatase. *J. Phys. Chem. C* **2012**, *116*, 9114–9121.
- (38) Setvin, M.; Daniel, B.; Aschauer, U.; Hou, W.; Li, Y.-F.; Schmid, M.; Selloni, A.; Diebold, U. Identification of Adsorbed Molecules via STM Tip Manipulation: CO , H_2O , and O_2 on TiO_2 Anatase (101). *Phys. Chem. Chem. Phys.* **2014**, *16*, 21524–21530.
- (39) Li, Y.; Gao, Y. Interplay Between Water and TiO_2 Anatase (101) Surface with Subsurface Oxygen Vacancy. *Phys. Rev. Lett.* **2014**, *112*, 206101.
- (40) Scheiber, P.; Fidler, M.; Dulub, O.; Schmid, M.; Diebold, U.; Hou, W.; Aschauer, U.; Selloni, A. (Sub)Surface Mobility of Oxygen Vacancies at the TiO_2 Anatase (101) Surface. *Phys. Rev. Lett.* **2012**, *109*, 136103.
- (41) Li, Y.-F.; Selloni, A. Theoretical Study of Interfacial Electron Transfer from Reduced Anatase $\text{TiO}_2(101)$ to Adsorbed O_2 . *J. Am. Chem. Soc.* **2013**, *135*, 9195–9199.
- (42) Setvín, M.; Aschauer, U.; Scheiber, P.; Li, Y.-F.; Hou, W.; Schmid, M.; Selloni, A.; Diebold, U. Reaction of O_2 with Subsurface Oxygen Vacancies on TiO_2 Anatase (101). *Science* **2013**, *341*, 988–991.
- (43) Walle, L. E.; Borg, A.; Johansson, E. M. J.; Plogmaker, S.; Rensmo, H.; Uvdal, P.; Sandell, A. Mixed Dissociative and Molecular Water Adsorption on Anatase $\text{TiO}_2(101)$. *J. Phys. Chem. C* **2011**, *115*, 9545–9550.
- (44) Zehr, R. T.; Henderson, M. A. Influence of O_2 -induced Surface Roughening on the Chemistry of Water on $\text{TiO}_2(110)$. *Surf. Sci.* **2008**, *602*, 1507–1516.
- (45) He, Y.; Dulub, O.; Cheng, H.; Selloni, A.; Diebold, U. Evidence for the Predominance of Subsurface Defects on Reduced Anatase $\text{TiO}_2(101)$. *Phys. Rev. Lett.* **2009**, *102*, 106105.
- (46) Fillion, J. H.; van Harreveld, R.; Ruiz, J.; Castillejo, M.; Zanganeh, A. H.; Lemaire, J. L.; van Hemert, M. C.; Rostas, F. Photodissociation of H_2O and D_2O in B, C, and D States (134–119 nm). Comparison between Experiment and ab Initio Calculations. *J. Phys. Chem. A* **2001**, *105*, 11414–11424.
- (47) Murakami, Y.; Kenji, E.; Nosaka, A. Y.; Nosaka, Y. Direct Detection of OH Radicals Diffused to the Gas Phase from the UV-Irradiated Photocatalytic TiO_2 Surfaces by Means of Laser-Induced Fluorescence Spectroscopy. *J. Phys. Chem. B* **2006**, *110*, 16808–16811.
- (48) Murakami, Y.; Endo, K.; Ohta, I.; Nosaka, A. Y.; Nosaka, Y. Can OH Radicals Diffuse from the UV-Irradiated Photocatalytic TiO_2 Surfaces? Laser-Induced-Fluorescence Study. *J. Phys. Chem. C* **2007**, *111*, 11339–11346.
- (49) Aschauer, U.; Selloni, A. Hydrogen Interaction with the Anatase $\text{TiO}_2(101)$ Surface. *Phys. Chem. Chem. Phys.* **2012**, *14*, 16595–16602.
- (50) Islam, M. M.; Calatayud, M.; Pacchioni, G. Hydrogen Adsorption and Diffusion on the Anatase $\text{TiO}_2(101)$ Surface: A First-Principles Investigation. *J. Phys. Chem. C* **2011**, *115*, 6809–6814.
- (51) Henderson, M. A.; Epling, W. S.; Peden, C. H. F.; Perkins, C. L. Insights into Photoexcited Electron Scavenging Processes on TiO_2 Obtained from Studies of the Reaction of O_2 with OH Groups Adsorbed at Electronic Defects on $\text{TiO}_2(110)$. *J. Phys. Chem. B* **2003**, *107*, 534–545.