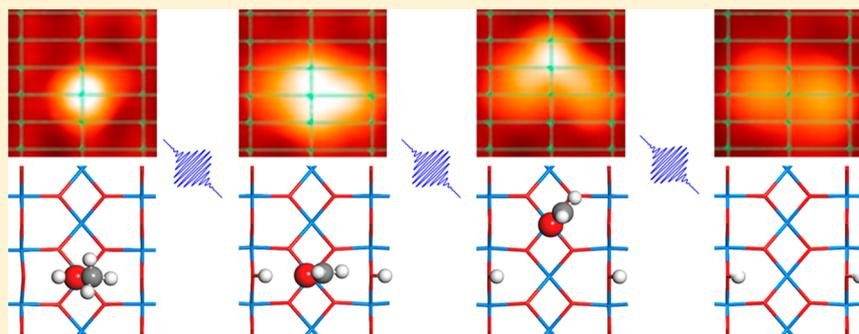


Direct Imaging Single Methanol Molecule Photocatalysis on Titania

Dong Wei,^{†,§} Xianchi Jin,^{†,§} Chuanqi Huang,^{‡,§} Dongxu Dai,[†] Zhibo Ma,^{*,†} Wei-Xue Li,^{*,‡}
and Xueming Yang^{*,†}[†]State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics and [‡]State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Science, Dalian, Liaoning 116023, China

Supporting Information



ABSTRACT: Photocatalysis of a single methanol molecule on the $\text{TiO}_2(110)$ surface was investigated using a high-resolution scanning tunneling microscopy (STM) technique. Three different types of elementary methanol photocatalytic processes, methanol photodissociation, photoinduced migration of formaldehyde, and formaldehyde photodesorption, were clearly observed. Detailed chemical structures of the intermediates were obtained through careful comparisons between experimental STM images and theoretical simulations based on density functional theory (DFT) calculations. This work demonstrates that elementary photocatalytic processes of a single methanol molecule on the surface can be followed step by step using advanced STM imaging techniques. Such a study can provide unprecedented insights into the surface photocatalytic processes and will greatly help us to understand photocatalysis at the most fundamental level.

INTRODUCTION

Since water splitting was first demonstrated in a photoelectrochemical cell in the early 1970s,¹ photocatalysis on TiO_2 has received extensive and increasing attention because of its potential applications in clean hydrogen production.^{2–6} Despite enormous progress made in this area, a fundamental understanding of heterogeneous photocatalysis is still lacking. It is known that TiO_2 alone was found not very active for water splitting to produce hydrogen, whereas adding methanol would dramatically enhance hydrogen production.⁷ In order to apprehend the role of methanol in the photocatalysis of water on TiO_2 , it is essential to investigate methanol photocatalysis on TiO_2 at the atomic and molecular level. This will help us to understand the underlying mechanism of why TiO_2 is inactive for water splitting and why methanol can enhance hydrogen production.

Methanol photocatalysis has been studied on TiO_2 single crystalline surfaces as well as on supported nanoparticles using various spectroscopic techniques.^{8–15} It was generally believed that under the UV-light irradiation methanol dehydrogenates sequentially to formaldehyde, which could desorb or go through further cross coupling with another methoxy radical to form methyl formate. Even though these studies have provided valuable insights into the methanol photocatalysis mechanism, the detailed picture of how a single methanol

molecule on TiO_2 evolves into the final products under light irradiation remains unclear.

Scanning tunneling microscope (STM) studies with submolecular resolution can provide detailed structural information on reaction intermediates on surfaces.^{16–20} The STM technique with submolecular resolution coupled with light irradiation is also expected to be a good approach to directly image molecular photocatalysis. The $\text{TiO}_2(110)$ surface has been studied in great detail using the STM technique.^{21–30} The clear STM image of the surface structure provides a solid foundation for us to investigate single methanol molecule photocatalysis on the $\text{TiO}_2(110)$ surface. However, to directly image the molecular photocatalysis step by step is still a big challenge. This requires us to follow a single molecule on the surface going through different elementary chemical and physical processes in the photocatalytic process using the sophisticated STM technique. Such a study is greatly needed for understanding the surface photocatalysis process at the most fundamental level.

In this work, we present for the first time a real-space imaging of a complete photocatalytic process for a single methanol molecule on the rutile $\text{TiO}_2(110)$ surface, under the

Received: May 28, 2015

Published: July 10, 2015



UV-light radiation by direct high-resolution STM imaging. Density functional theory (DFT) simulation was carried out to understand these STM images and to obtain structural information on the intermediates. Elementary reaction steps from methanol adsorption, photocatalytic dissociation, diffusion, and desorption of the key intermediate and the final product left on the surface are mapped out in great details. The structures of key intermediates and product were also resolved with a submolecular resolution using molecular orbital STM imaging. Direct visualization of the entire process of methanol photocatalysis on TiO_2 provides us a detailed picture of molecular photocatalysis that has never been achieved before.

RESULTS AND DISCUSSION

First, we prepared a clean and ordered $\text{TiO}_2(110)$ surface sample using many cycles of argon ion bombardment and annealing. The STM image was taken using a low-temperature STM machine for the bare clean $\text{TiO}_2(110)$ surface at 80 K with a positive bias voltage (Figure 1a). The bright rows in the

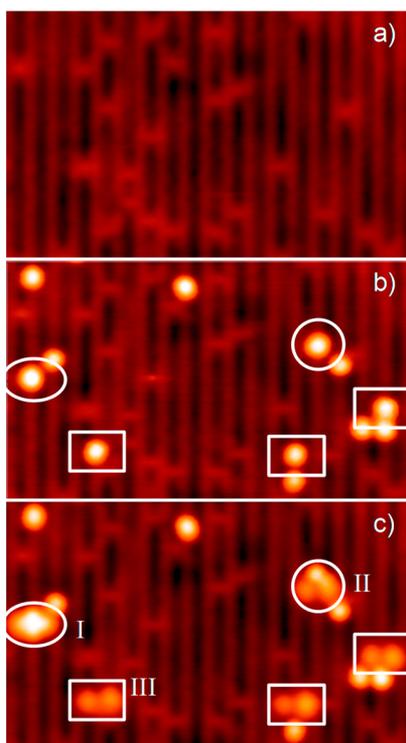


Figure 1. STM images of the photochemical process of methanol on $\text{TiO}_2(110)$ at 80 K. (a) Imaging of bare $\text{TiO}_2(110)$ - 1×1 surface (size of $11.5 \times 6.8 \text{ nm}^2$, acquired at bias of +1.25 V and set point current of 100 pA). (b) Surface with low exposure of methanol appeared as a small round spot image. (c) Surface with the adsorbed methanol molecules after 355 nm laser irradiation and then three different types of images observed: I, II, and III, marked by ellipse, circle, and rectangle, respectively.

STM image are due to the in-plane 5-fold coordinated Ti (5f-Ti) atom rows, and the dark rows are from the bridge-bonded oxygen (BBO) ridges. The spots connecting the 5f-Ti rows are the oxygen vacancies on the BBO ridges. The surface studied here has a BBO vacancy concentration of 4%, as one can measure directly from the STM image. In the photocatalysis study here, the clean $\text{TiO}_2(110)$ surface was dosed with 0.03 ML of methanol. The STM image (Figure S1 in Supporting

Information) of the methanol-dosed $\text{TiO}_2(110)$ surface shows many bright round spots on the surface located exclusively at the 5f-Ti sites (Figure 1b). These bright spots can be clearly assigned to single methanol molecules adsorbed molecularly at the 5f-Ti sites.

The methanol-dosed $\text{TiO}_2(110)$ surface was then irradiated for 10 min with 20 mW of 355 nm light. Considerable changes of STM images of the adsorbed methanol molecules have been detected over the entire irradiated surface area (Figure S1). By examining a large surface area and following more than 600 individual methanol molecules, we found that the round spots (methanol molecules on TiO_2) in the STM image were changed to three different image structures after the surface was irradiated. The changed images are shown in Figure 1c (see more details in SI part 3). The three typical types of images are labeled by I, II, and III in marked ellipse, circle, and rectangle areas, respectively. For the type I image, the original small round spot image of the adsorbed methanol is expanded in both $[1-10]$ and $[001]$ directions and became a larger and rhombohedral spot, while for the type II image, three clear features in the image could be well resolved: one brighter spot appearing at the neighboring 5f-Ti site from the site of the originally adsorbed methanol molecule and the two bright spots on the two adjacent BBO rows. The third type of image is a pair of bright spots at the two adjacent BBO rows centering at the initial methanol adsorbed 5f-Ti site. Compared with the BBO vacancies, the two spots are brighter and larger. We attributed these two spots in the image III to two bridging hydroxyls (OH_{BBO}) on $\text{TiO}_2(110)$. This assignment was confirmed using the STM technique developed previously,^{24,26,31} in which the H atom on the BBO site can be removed selectively if one applies a high bias voltage ($>2 \text{ V}$) on the STM tip.^{26,32} The three different types of images observed are actually different states in the methanol photocatalysis on $\text{TiO}_2(110)$.

To understand how a single methanol molecule on $\text{TiO}_2(110)$ evolves into different chemical states under UV light irradiation, we have performed a series of photocatalysis experiments to try to follow the evolution of the STM image of a single methanol molecule on $\text{TiO}_2(110)$ with three consecutive light irradiation periods. After each irradiation period, a STM scan was taken to trace the image change of the methanol molecule adsorbed on $\text{TiO}_2(110)$. Before irradiation, the methanol molecule is molecularly adsorbed at the 5f-Ti site (for reference, the surface lattice grid is indicated in Figure 2), exhibiting a small round spot in the STM image (similar to Figure 1b). After the first 10 min of UV light irradiation (20 mW), the STM image of the same methanol molecule becomes considerably expanded, and the resulting rhombohedra image is

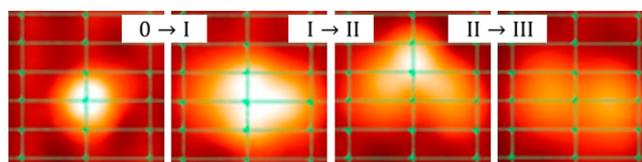


Figure 2. Evolution of the photochemical single-molecule process of the adsorbed methanol on $\text{TiO}_2(110)$ under multiple irradiation periods at the surface temperature 80 K. The photochemical process from adsorbed methanol (labeled as 0) toward the structural motif I, II, and III sequentially (size of $1.4 \times 1.4 \text{ nm}^2$, acquired at bias of +1.25 V and set point current of 100 pA).

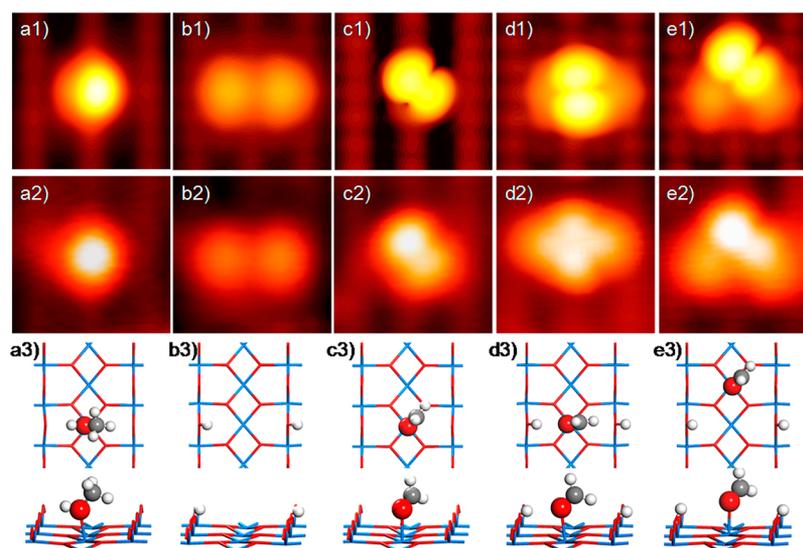


Figure 3. Theoretical (top panel) and experimental (middle panel) STM images for the reactant and important intermediates involved in the photochemical process of methanol on $\text{TiO}_2(110)$: the adsorbed methanol at 5f-Ti site (a), the OH pair on the neighboring BBO rows (b), isolated formaldehyde (c), formaldehyde at the 5f-Ti site with two OH_{br} at two opposite sides (d), and formaldehyde displacing to the next 5f-Ti site (e) (size of $1.5 \times 1.5 \text{ nm}^2$, acquired at a bias of +1.25 V and set point current of 100 pA). The bottom panel shows the schematic structure models for different chemical adsorption states. For simplification, only the $\text{TiO}_2(110)$ surface frame is indicated; the white, gray, and red balls represent hydrogen, carbon, and oxygen atoms, respectively.

nearly identical with the image I shown in Figure 1c. The expanded STM image of the methanol molecule after light irradiation indicates that the photocatalytic reaction for the adsorbed methanol occurred. This process is the initial photocatalytic methanol dissociation ($0 \rightarrow \text{I}$). We then expose this dissociated methanol molecule (image I) to another 10 min of UV irradiation using higher photon flux (50 mW). The STM image was changed again, with the middle brighter spot seemingly moved to the adjacent 5f-Ti site from the originally methanol-adsorbed site and two bright spots left on the adjacent BBO rows. The resulting image resembles very much image II shown in Figure 1c. We assign this process to the photoinduced chemical state change from I to II. The structure with the image II was then irradiated with 200 mW 355 nm light for 30 min. The brighter spot in the image II at the 5f-Ti site then disappeared, while the two spots at the adjacent BBO rows remained, similar to the image III observed in Figure 1c. We assign this process to the photochemical process $\text{II} \rightarrow \text{III}$. The STM experiment also shows that the structure III (two hydrogen atoms on BBO sites) cannot be changed under further UV light irradiation, suggesting that this is the final of the methanol photocatalysis on $\text{TiO}_2(110)$ under UV light irradiation. From these serial multiple irradiation experiments for a single methanol molecule on $\text{TiO}_2(110)$, we can now be sure that the methanol molecule experienced three consecutive photochemical processes on TiO_2 : $0 \rightarrow \text{I}$, $\text{I} \rightarrow \text{II}$, and $\text{II} \rightarrow \text{III}$, as shown clearly in Figure 2. This experiment demonstrates that a complete photocatalytic process for a single methanol molecule on the $\text{TiO}_2(110)$ surface can be directly visualized using the STM technique that couples with laser light irradiation.

In these multi-irradiation experiments, in addition to the serial photochemical processes ($0 \rightarrow \text{I} \rightarrow \text{II} \rightarrow \text{III}$) described above (Figure 2), we have also observed direct image change from 0 to II ($0 \rightarrow \text{II}$), from 0 to III ($0 \rightarrow \text{III}$), and from I to III ($\text{I} \rightarrow \text{III}$) in one period of light irradiation. These direct image changes are most likely because the adsorbed methanol

molecule experienced two or three elementary steps of photochemical processes in one period of UV light irradiation. This is obviously possible due to the surface heterogeneity. The reversed individual photochemical processes, such as $\text{III} \rightarrow \text{II}$, $\text{III} \rightarrow \text{I}$, $\text{III} \rightarrow 0$, $\text{II} \rightarrow \text{I}$, $\text{II} \rightarrow 0$, and $\text{I} \rightarrow 0$, were not observed in the present experiment. The surface photocatalytic processes for the low coverage methanol on $\text{TiO}_2(110)$ at low temperature are therefore irreversible.

To reveal the exact chemical states of the different images observed, it is worthy to mention that previous studies have shown that methanol on $\text{TiO}_2(110)$ can be photocatalytically dissociated in two hydrogen atoms on the BBO rows and a formaldehyde molecule on 5f-Ti based on temperature-programmed desorption (TPD), two-photon photoemission studies, and DFT calculations.^{11,12} The formaldehyde molecule can be desorbed by surface heating or photon, with two H atoms left on the BBO sites eventually. These results provide valuable information on the chemical identities of the STM images observed in the above single methanol molecule photocatalysis on $\text{TiO}_2(110)$.

We now use DFT calculations and STM simulations (see more detailed descriptions in part 2 of SI) to uncover the chemical identities and the exact structures of the methanol photocatalysis intermediates observed above. We start with the simulation of the STM image (image 0) of the molecularly adsorbed methanol via the O-end at the 5f-Ti top. The simulated STM image (Figure 3a1) for the optimized structure in the DFT calculation appears to be a bright round spot, which agrees very well with the experimental images of the adsorbed methanol in Figure 3a2 (also in Figures 1 and 2) before light irradiation. The bright image comes mainly from the geometrically high-lying CH_3 group in methanol (Figure 3a3).

Figure 3b1 is the simulated STM image for the OH pair located at the adjacent BBO rows (Figure 3b3), whereas the experimental image for the observed structure of the image III is given in Figure 3b2. The agreement between the measured and simulated STM images is excellent (more in Figure S2 for

single OH). This confirms the experimental assignment of the image III to the OH pair on the neighboring BBO sites. It is interesting to point out that the two dissociated H atoms dissociated from methanol were always found on the two neighboring BBO rows of the initially methanol adsorption site (Figures S3 and S4). This clearly indicates that the two hydrogen atoms dissociated from methanol always go separate ways to the neighboring BBO rows and never go to the same BBO row. This means that if the hydroxyl hydrogen in methanol dissociates to one BBO row the methyl hydrogen in methanol would always dissociate to the other neighboring BBO row.

Since image III is the final product state left on the surface after 355 nm light irradiation, the assignment to the OH pair implies that HCHO is the only final dehydrogenated product from methanol photocatalysis. Further dehydrogenation, for instance to HCO, can then be excluded. Formation of the OH pairs located exclusively at the two adjacent BBO rows with mass center at the centered 5f-Ti site also implies that the photoinduced dehydrogenation of CH₃OH toward HCHO takes place at the same 5f-Ti site with two hydrogen atoms dissociating to the two neighboring BBO sites. The dehydrogenated product, formaldehyde, therefore must be on the originally methanol adsorption 5f-Ti site.

Now we look at image I, which is the first intermediate photocatalysis product on the surface after UV light irradiation. One can see that the originally small round STM image (Figure 3a2) of the methanol molecule adsorbed on the 5f-Ti site is stretched considerably after UV light irradiation, forming a larger and rhombohedral spot (Figure 3d2). A cross cut of the STM image I shows the STM height on the two neighboring BBO sites is similar, implying that two hydrogen atoms in methanol are likely dissociated to the neighboring BBO sites (see Figure S5 in SI). This means that the image might be composed of a formaldehyde molecule adsorbed on the 5f-Ti site and two hydrogen atoms on the adjacent O_{br} sites. In order to make the simulation for the STM image more reliable, we have carried out DFT calculations on the adsorption of an isolated HCHO on the 5f-Ti site of TiO₂(110). The calculated result shows that the formaldehyde molecule prefers to sit at the 5f-Ti site with the oxygen end adsorbed to the 5f-Ti site. Its planar structure remains intact and is perpendicular to the surface. The molecular plane is, however, rotated away from the [100] direction (Figure 3c3). The corresponding STM simulation (Figure 3c1) shows an elongated and asymmetrical dumbbell shape. Interestingly, the elongation axis is perpendicular to the molecular plane of HCHO, and the two end spots of the dumbbell shape image are separated at the two sides of the HCHO plane. We then measured the STM image of the formaldehyde molecule on the clean TiO₂(110) at 80 K, and the STM image is given in Figure 3c2 (see more in Figure S6). The experimental and simulated STM images of formaldehyde are in very good agreement, suggesting that the calculated structure of the formaldehyde adsorption on TiO₂(110) is correct.

After successful simulation of the STM image of the single formaldehyde on TiO₂(110), we now move to simulate the STM image I. First, we carried out DFT calculations on the dehydrogenated state of methanol on TiO₂(110), with a formaldehyde molecule on 5f-Ti and two hydrogen atoms on the two adjacent BBO sites, and the optimized structure is shown in Figure 3d3. In comparison with the simulated small round spot STM image for the adsorbed methanol molecule

(Figure 3a1), the simulated STM image I (Figure 3d1) becomes significantly larger. The simulated STM image I agrees quite well with the observed STM image I, suggesting that the observed dissociated state of methanol is that two hydrogen atoms dissociated from methanol to the BBO sites with a formaldehyde molecule left on the original 5f-Ti site. It is interesting to point out that the molecular plane of dissociated formaldehyde is along the [100] direction, which is different from the structure of the single formaldehyde molecule adsorbed on TiO₂(110) that is tilted away from the [100] direction.

In the STM image II, the middle bright spot in the image I moved away from the original methanol adsorption site to the adjacent 5f-Ti site after UV light irradiation. According to the above simulation, one can see that this is due to photoinduced migration of the formaldehyde product to the next 5f-Ti site. DFT calculations were then performed on this formaldehyde migrated state, and the calculated structure is shown in Figure 3e3. Interestingly, the formaldehyde adsorption structure away from the original adsorption site is similar to the free formaldehyde adsorption structure, with its molecular plane rotated away from the [001] direction. The calculated STM image (Figure 3e1) agrees very well with the experimental image II (Figure 3e2), with the rotated dumbbell shape due to the adsorbed formaldehyde molecule.

The distinct dumbbell STM feature observed for the HCHO/TiO₂(110) originated from HCHO's LUMO 2π* antibonding states. Figure 4a is the corresponding projected density of states. In the wide energy window of the conduction band responsible for STM measurement and simulation, there is a considerable HCHO 2π* orbital, though Ti 3d orbitals are dominant. To see their contribution to the tunneling current,

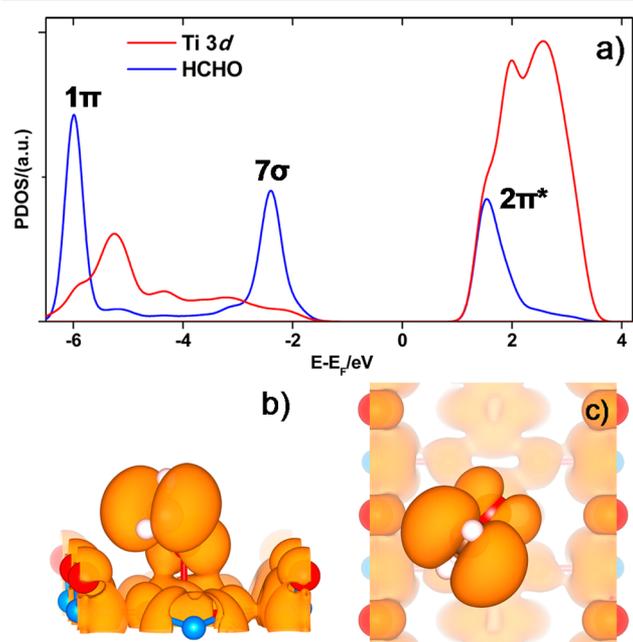


Figure 4. Electronic properties of HCHO on TiO₂(110). (a) Projected density of states for HCHO* and coordinated 5f-Ti. The frontier states of HCHO* are labeled as HCHO in the gas phase, and 2π* is centered at 1.50 eV above the Fermi level. (b) and (c) Side and top views of the electronic density integrated at the energy window of 1.50 ± 0.1 eV above the Fermi level, and the surface atoms are also indicated.

the electron density in the energy window of 1.25 ± 0.1 eV above the Fermi level was integrated and plotted in Figure 4b and c (perspective and top views). Four prominent ellipsoids separated by two characteristic perpendicular node planes from HCHO's LUMO $2\pi^*$ orbitals (Figure S7) could be clearly seen. Importantly, the $2\pi^*$ orbitals considerably higher than that of the 5f-Ti atoms since HCHO's position is well above the surface. As a result, the dumbbell shape image is mapped out when the STM tip approaches from the top. This type of molecular orbital imaging allows us to conclusively determine the structures of the different states of methanol photocatalysis on TiO_2 .

After all the species and structures of products are clarified, some new features should be mentioned. As an important photoreaction, the dissociation of methanol always was considered as a stepwise process. The O–H bond is easier to break than the C–H bond on the methyl.¹² However, in the real-space STM results, the first step of the whole process which is the dissociation of methanol is a simultaneous bond cleavage, where two hydrogen atoms moved to the adjacent BBO sites. We have never observed any methanol just cracking only the O–H bond. Even the power of the laser was decreased to about 2 mW to reduce the reactivity, and most of the reacted methanol rested on step I as shown in Figure 5c. There is almost no step II and III of the products. Even so, all the

products are still symmetrical, and the feature was exactly the same as we mentioned before. This distinct difference between macroscopic and microscopic experimental results belonged to the different coverages. There are many factors on the high-coverage surface that could complicate the photochemical reaction, such as surface hydroxyl, steric hindrance, intermolecular hydrogen bonding, etc. We suggest that the photoreaction of the high coverage methanol/ $\text{TiO}_2(110)$ system should be further investigated by multitechniques. Another meaning of low power irradiation is reducing the heating effect of the laser irradiation on the surface which cannot be avoidable in photoreaction. In addition to reducing the power of the laser, we have also tried to determine the thermal effects on this surface system by heating directly. The thermally driven effects could not induce reaction of methanol which suggested the dissociation is photosensitive relative to thermo-driven dissociation (see Figure S8 in SI).

CONCLUSIONS

From the above experimental and simulated STM images, we can now conclude that photocatalysis of methanol on $\text{TiO}_2(110)$ occurs with three elementary steps: (1) methanol dehydrogenation to form formaldehyde on 5f-Ti and two hydrogen atoms on BBO; (2) photon-induced migration of the formaldehyde molecule formed to the adjacent 5f-Ti site with two hydrogen atoms unmoved; (3) photodesorption of the formaldehyde molecule from the $\text{TiO}_2(110)$ surface, with the two hydrogen atoms dissociated from methanol left on the surface. The structures of the intermediate photocatalysis products are also determined through the STM orbital imaging of the $2\pi^*$ orbitals of formaldehyde. The detailed STM studies of methanol photocatalysis on $\text{TiO}_2(110)$ in this work allow us for the first time to follow the elementary photocatalytic processes of a single methanol molecule on TiO_2 one step at a time. Such investigations with the support of DFT calculations and STM image simulations can provide unprecedented insights into surface photocatalytic processes and will help us to understand photocatalysis at the most fundamental level.

METHODOLOGY

The experiments were performed in a UHV chamber equipped with a low-temperature scanning tunneling microscope (LT-STM) (Matrix, Omicron). The vacuum in the STM chamber was maintained at about 4×10^{-11} Torr. The methanol was dosed on $\text{TiO}_2(110)$ at 80 K, and the real space STM images were recorded at the same temperature. In the photocatalysis experiment, we always make a STM scan on the clean and the methanol-dosed surface before each light irradiation period, and the STM tip is then pulled back by about $20 \mu\text{m}$ from the surface during light irradiation. After a light irradiation period is completed, we then engage the STM tip to the surface again and find the same surface area to trace the change of each individual molecule.

DFT calculations were performed using the PAW-based Vienna ab initio simulation package (VASP).^{33–36} The PBE+U scheme with an U_{eff} of 5.5 eV on Ti was applied for electron exchange correlation, as suggested by a previous study.^{37–39} Tersoff and Hamann's formula implemented in the bSKAN code was employed to simulate STM images.^{40,41} See the Supporting Information for further details about the in situ experiments and theoretical simulations.

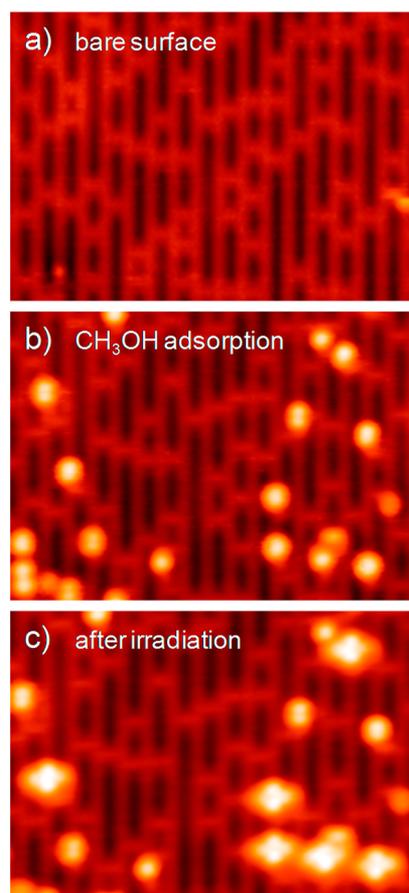


Figure 5. Photodissociation under low power laser. (a) Bare surface. (b) Methanol-adsorbed surface. The power was decreased to 2 mW, and the duration time is 10 min. All the reacted CH_3OH was controlled at the first step (c). All the protrusions which are reacted were symmetrical, and H atoms on the BBO row are resolved clearly.

■ ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.5b05074.

Experimental details, computational details, statistics for three structures of photoproducts, STM images and simulations of BBO_v and OH_{br} , STM images for structure III, cutting profiles and possible products of structure I, STM images of HCHO on $\text{TiO}_2(110)$, electronic structure of isolated HCHO, and the influence effect for the dissociation (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: zhbma@dicp.ac.cn.

*E-mail: wxli@dicp.ac.cn.

*E-mail: xmyang@dicp.ac.cn.

Author Contributions

§Authors who contributed equally to this work.

Author Contributions

D. W., X. J., and Z. M. performed STM experiments. Z. M. and D. D. oversee the STM experiments, and X. Y. directed the STM project.

C. H. performed DFT calculations and STM image simulations, and W.X. L. directed the DFT project.

Z. M., W.X. L., and X. Y. wrote the paper.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Chinese Academy of Sciences, National Science Foundation of China (21225315, 21173210), and the Ministry of Science and Technology (2013CB834605, 2013CB834603). We appreciated Prof. Bing Wang and Dr. Shijing Tan for the insightful suggestion about the equipment's design and installation.

■ REFERENCES

- (1) Fujishima, A.; Honda, K. Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature* **1972**, *238* (5358), 37.
- (2) Fujishima, A.; Zhang, X. T.; Tryk, D. A. TiO_2 photocatalysis and related surface phenomena. *Surf. Sci. Rep.* **2008**, *63* (12), 515–582.
- (3) Osterloh, F. E. Inorganic materials as catalysts for photochemical splitting of water. *Chem. Mater.* **2008**, *20* (1), 35–54.
- (4) Kudo, A.; Miseki, Y. Heterogeneous photocatalyst materials for water splitting. *Chem. Soc. Rev.* **2009**, *38* (1), 253–278.
- (5) 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* (12), 1966–1973.
- (6) Maeda, K.; Domen, K. Photocatalytic Water Splitting: Recent Progress and Future Challenges. *J. Phys. Chem. Lett.* **2010**, *1* (18), 2655–2661.
- (7) Sato, S.; White, J. M. Photo-Decomposition of Water over P- TiO_2 Catalysts. *Chem. Phys. Lett.* **1980**, *72* (1), 83–86.
- (8) Tamaki, Y.; Furube, A.; Murai, M.; Hara, K.; Katoh, R.; Tachiya, M. Direct observation of reactive trapped holes in TiO_2 undergoing photocatalytic oxidation of adsorbed alcohols: Evaluation of the reaction rates and yields. *J. Am. Chem. Soc.* **2006**, *128* (2), 416–417.
- (9) Chen, T.; Feng, Z. H.; Wu, G. P.; Shi, J. Y.; Ma, G. J.; Ying, P. L.; Li, C. Mechanistic studies of photocatalytic reaction of methanol for hydrogen production on Pt/ TiO_2 by in situ Fourier transform IR and time-resolved IR spectroscopy. *J. Phys. Chem. C* **2007**, *111* (22), 8005–8014.

(10) Wu, N. L.; Lee, M. S.; Pon, Z. J.; Hsu, J. Z. Effect of calcination atmosphere on TiO_2 photocatalysis in hydrogen production from methanol/water solution. *J. Photochem. Photobiol., A* **2004**, *163* (1–2), 277–280.

(11) Zhou, C. Y.; Ren, Z. F.; Tan, S. J.; Ma, Z. B.; Mao, X. C.; Dai, D. X.; Fan, H. J.; Yang, X. M.; LaRue, J.; Cooper, R.; Wodtke, A. M.; Wang, Z.; Li, Z. Y.; Wang, B.; Yang, J. L.; Hou, J. G. Site-specific photocatalytic splitting of methanol on $\text{TiO}_2(110)$. *Chem. Sci.* **2010**, *1* (5), 575–580.

(12) Guo, Q.; Xu, C. B.; Ren, Z. F.; Yang, W. S.; Ma, Z. B.; Dai, D. X.; Fan, H. J.; Minton, T. K.; Yang, X. M. Stepwise Photocatalytic Dissociation of Methanol and Water on $\text{TiO}_2(110)$. *J. Am. Chem. Soc.* **2012**, *134* (32), 13366–13373.

(13) Guo, Q.; Xu, C. B.; Yang, W. S.; Ren, Z. F.; Ma, Z. B.; Dai, D. X.; Minton, T. K.; Yang, X. M. Methyl Formate Production on $\text{TiO}_2(110)$, Initiated by Methanol Photocatalysis at 400 nm. *J. Phys. Chem. C* **2013**, *117* (10), 5293–5300.

(14) Xu, C. B.; Yang, W. S.; Guo, Q.; Dai, D. X.; Chen, M. D.; Yang, X. M. Molecular Hydrogen Formation from Photocatalysis of Methanol on $\text{TiO}_2(110)$. *J. Am. Chem. Soc.* **2013**, *135* (28), 10206–10209.

(15) Phillips, K. R.; Jensen, S. C.; Baron, M.; Li, S. C.; Friend, C. M. Sequential Photo-oxidation of Methanol to Methyl Formate on $\text{TiO}_2(110)$. *J. Am. Chem. Soc.* **2013**, *135* (2), 574–577.

(16) Jiang, Y.; Huan, Q.; Fabris, L.; Bazan, G. C.; Ho, W. Submolecular control, spectroscopy and imaging of bond-selective chemistry in single functionalized molecules. *Nat. Chem.* **2013**, *5* (1), 36–41.

(17) Guo, J.; Meng, X. Z.; Chen, J.; Peng, J. B.; Sheng, J. M.; Li, X. Z.; Xu, L. M.; Shi, J. R.; Wang, E. G.; Jiang, Y. Real-space imaging of interfacial water with submolecular resolution. *Nat. Mater.* **2014**, *13* (2), 184–189.

(18) Gross, L.; Moll, N.; Mohn, F.; Curioni, A.; Meyer, G.; Hanke, F.; Persson, M. High-Resolution Molecular Orbital Imaging Using a p-Wave STM Tip. *Phys. Rev. Lett.* **2011**, *107* (8), 086101 DOI: 10.1103/PhysRevLett.107.086101.

(19) Liljeroth, P.; Repp, J.; Meyer, G. Current-induced hydrogen tautomerization and conductance switching of naphthalocyanine molecules. *Science* **2007**, *317* (5842), 1203–1206.

(20) Lee, H. J.; Ho, W. Single-bond formation and characterization with a scanning tunneling microscope. *Science* **1999**, *286* (5445), 1719–1722.

(21) Stipe, B. C.; Rezaei, M. A.; Ho, W. Single-Molecule Vibrational Spectroscopy and Microscopy. *Science* **1998**, *280* (5370), 1732–1735.

(22) Stipe, B. C.; Rezaei, M. A.; Ho, W. Coupling of vibrational excitation to the rotational motion of a single adsorbed molecule. *Phys. Rev. Lett.* **1998**, *81* (6), 1263–1266.

(23) Minato, T.; Sainoo, Y.; Kim, Y.; Kato, H. S.; Aika, K.; Kawai, M.; Zhao, J.; Petek, H.; Huang, T.; He, W.; Wang, B.; Wang, Z.; Zhao, Y.; Yang, J. L.; Hou, J. G. The electronic structure of oxygen atom vacancy and hydroxyl impurity defects on titanium dioxide (110) surface. *J. Chem. Phys.* **2009**, *130* (12), 124502.

(24) Tan, S. J.; Feng, H.; Ji, Y. F.; Wang, Y.; Zhao, J.; Zhao, A. D.; Wang, B.; Luo, Y.; Yang, J. L.; Hou, J. G. Observation of Photocatalytic Dissociation of Water on Terminal Ti Sites of $\text{TiO}_2(110)-1 \times 1$ Surface. *J. Am. Chem. Soc.* **2012**, *134* (24), 9978–9985.

(25) Hansen, J. O.; Huo, P.; Martinez, U.; Lira, E.; Wei, Y. Y.; Streiber, R.; Laegsgaard, E.; Hammer, B.; Wendt, S.; Besenbacher, F. Direct Evidence for Ethanol Dissociation on Rutile $\text{TiO}_2(110)$. *Phys. Rev. Lett.* **2011**, *107* (13), 136102 DOI: 10.1103/PhysRevLett.107.136102.

(26) Zhang, Z.; Bondarchuk, O.; Kay, B. D.; White, J. M.; Dohnalek, Z. Imaging water dissociation on $\text{TiO}_2(110)$: Evidence for inequivalent geminate OH groups. *J. Phys. Chem. B* **2006**, *110* (43), 21840–21845.

(27) Zhang, Z. R.; Bondarchuk, O.; White, J. M.; Kay, B. D.; Dohnalek, Z. Imaging adsorbate O-H bond cleavage: Methanol on $\text{TiO}_2(110)$. *J. Am. Chem. Soc.* **2006**, *128* (13), 4198–4199.

(28) Wendt, S.; Sprunger, P. T.; Lira, E.; Madsen, G. K. H.; Li, Z. S.; Hansen, J. O.; Matthiesen, J.; Blekinge-Rasmussen, A.; Laegsgaard, E.;

Hammer, B.; Besenbacher, F. The role of interstitial sites in the Ti_{3d} defect state in the band gap of Titania. *Science* **2008**, *320* (5884), 1755–1759.

(29) Diebold, U.; Lehman, J.; Mahmoud, T.; Kuhn, M.; Leonardelli, G.; Hebenstreit, W.; Schmid, M.; Varga, P. Intrinsic defects on a $\text{TiO}_2(110)(1 \times 1)$ surface and their reaction with oxygen: a scanning tunneling microscopy study. *Surf. Sci.* **1998**, *411* (1–2), 137–153.

(30) Diebold, U.; Anderson, J. F.; Ng, K. O.; Vanderbilt, D. Evidence for the tunneling site on transition-metal oxides: $\text{TiO}_2(110)$. *Phys. Rev. Lett.* **1996**, *77* (7), 1322–1325.

(31) Cui, X. F.; Wang, Z.; Tan, S. J.; Wang, B.; Yang, J. L.; Hou, J. G. Identifying Hydroxyls on the $\text{TiO}_2(110)-1 \times 1$ Surface with Scanning Tunneling Microscopy. *J. Phys. Chem. C* **2009**, *113* (30), 13204–13208.

(32) Bikondoa, O.; Pang, C. L.; Ithnin, R.; Muryn, C. A.; Onishi, H.; Thornton, G. Direct visualization of defect-mediated dissociation of water on $\text{TiO}_2(110)$. *Nat. Mater.* **2006**, *5* (3), 189–192.

(33) Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1996**, *54*, 11169–11186.

(34) Kresse, G.; Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci.* **1996**, *6*, 15–50.

(35) Blochl, P. E. Projector Augmented-Wave Method. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1994**, *50*, 17953–17979.

(36) Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1999**, *59*, 1758–1775.

(37) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.

(38) Dudarev, S. L.; Botton, G. A.; Savrasov, S. Y.; Humphreys, C. J.; Sutton, A. P. Electron-energy-loss spectra and the structural stability of nickel oxide: An LSDA+U study. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1998**, *57*, 1505–1509.

(39) Papageorgiou, A. C.; Beglitis, N. S.; Pang, C. L.; Teobaldi, G.; Cabailh, G.; Chen, Q.; et al. Electron traps and their effect on the surface chemistry of $\text{TiO}_2(110)$. *Proc. Natl. Acad. Sci. U. S. A.* **2010**, *107*, 2391–2396.

(40) Tersoff, J.; Hamann, D. R. Theory of the Scanning Tunneling Microscope. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1985**, *31*, 805–813.

(41) Hofer, W. A. Challenges and errors: interpreting high resolution images in scanning tunneling microscopy. *Prog. Surf. Sci.* **2003**, *71*, 147–183.