

Band-Gap States of $\text{TiO}_2(110)$: Major Contribution from Surface Defects

Xinchun Mao,^{†,||} Xiufeng Lang,^{‡,||} Zhiqiang Wang,[†] Qunqing Hao,[†] Bo Wen,^{‡,§} Zefeng Ren,[§] Dongxu Dai,[†] Chuanyao Zhou,^{*,†} Li-Min Liu,^{*,‡} and Xueming Yang^{*,†}

[†]State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Chinese Academy of Science, 457 Zhongshan Road, Dalian, 116023, Liaoning, People's Republic of China

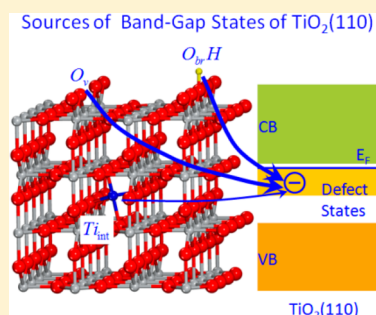
[‡]Beijing Computational Science Research Center, 3 Heqing Street, Haidian District, Beijing, 100084, People's Republic of China

[§]International Center for Quantum Materials, Peking University, Beijing, 100871, People's Republic of China

Supporting Information

ABSTRACT: Many physical and chemical processes on TiO_2 surface are linked to the excess electrons originated from band gap states. However, the sources (surface and/or subsurface defects) of these states are controversial. We present quantitative ultraviolet photoelectron spectroscopy (UPS) measurements on the band gap states of $\text{TiO}_2(110)$ with constant subsurface defect density and varied surface bridging hydroxyls ($\text{O}_{\text{br}}\text{H}$) prepared through photocatalyzed splitting of methanol, in combination with density functional theory (DFT) calculations. Our results clearly suggest both surface and subsurface defects contribute to the band gap states, whereas the contribution of subsurface defects corresponds to that of only 1.9% monolayer $\text{O}_{\text{br}}\text{H}$ at the current bulk reduction level. As the surface defect concentration is usually much larger than 1.9% monolayer in real studies and applications, our work demonstrates the importance of surface defects in changing the electronic structure of TiO_2 , which dictates the surface chemistry.

SECTION: Surfaces, Interfaces, Porous Materials, and Catalysis



Titanium dioxide (TiO_2) has attracted much attention because of its wide range of applications in physics, chemistry and materials.^{1–3} Rutile (110), partly due to its stability, has become a prototypical system of metal oxide.³ On this surface, the protruding two-coordinated bridging oxygen (O_{br}) row is located between two five-coordinated titanium (Ti_{5c}) rows run in the [001] direction. Upon charged particle bombardment and ultrahigh vacuum (UHV) annealing, two kinds of major point defects, i.e., surface O_{br} vacancies and subsurface Ti interstitials (Ti_{int}) can be introduced. After reduction, the Fermi level (E_{F}) is pinned to the bottom of conduction band (CBM), and defect states appear at about 0.8 eV below the E_{F} .⁴ The excess electrons originate from the defect states greatly affect the surface chemistry on TiO_2 .^{5–7} Hence, the origin of the defect states is an important issue, which could provide new insights into the application of TiO_2 .

Experimental and theoretical studies have been performed to explore the origin of the band gap states. Henrich et al. suggested O_{br} vacancies were responsible for the band gap states on TiO_2 .⁴ A linear dependence of the band gap states on the O_{br} vacancy/bridging hydroxyls ($\text{O}_{\text{br}}\text{H}$) concentration has been reported, and these surface defects are suggested to be the major origin of the band gap states.⁸ Though the method used in this work for O_{br} vacancy creation, i.e., low energy electron (75 eV) bombardment, has been argued to cause subsurface damage,⁹ two-photon photoemission (2PPE) results have

revealed that it had no effect on the subsurface structure.^{10,11} Whereas the study of hydroxylated surface involved the exposure of oxygen which leads to complicated species on $\text{TiO}_2(110)$.^{8,9} A recent resonant photoelectron diffraction (RPED) study shows that O_{br} vacancy is the sole origin of the band gap states on $\text{TiO}_2(110)$.¹² In addition, two adjacent $\text{O}_{\text{br}}\text{H}$ and an O_{br} vacancy have been reported to contribute equivalently to the band gap states.^{13–15} An alternative picture on the origin of these defect states has been proposed by Wendt and co-workers.¹⁶ Their experimental results indicated that the intensity of band gap states maintains 70% of its original value when the $\text{O}_{\text{br}}\text{H}$ groups are fully consumed on a hydroxylated $\text{TiO}_2(110)$ surface. Based on these findings and accompanying DFT calculations, they proposed that subsurface Ti_{int} is the main origin of the band gap states. Recently, Mitsuhashi et al. showed experimental evidence that both O_{br} vacancies and Ti_{int} contribute to the band gap states.¹⁷ Nevertheless, the density of both defects changed during the preparation, which brought uncertainty to the conclusion. Theoretical calculations have also shown that both O_{br} vacancies and Ti_{int} can generate band gap states, although the specific position is very sensitive to the methods used.^{15,16,18,19}

Received: September 24, 2013

Accepted: October 30, 2013

Technologically, the creation of O_{br} vacancies involves the usage of energetic charged particle bombardment and UHV annealing. These processes might introduce subsurface defects which are difficult to quantitatively assessed, thus it becomes complicated to disentangle various contributions to the band gap states of $TiO_2(110)$. In contrast, reduction of $TiO_2(110)$ surface by hydroxylation is a much milder manner. In addition, $O_{br}H$ groups play an important role in TiO_2 surface chemistry. For example, $O_{br}H$ can assist the diffusion of adsorbates across the $TiO_2(110)$ surface^{20,21} and affect the nucleation of metal clusters²² and CO photooxidation.^{23–25} Specially, $Ti(III)-OH^-$ is the electron trap center in TiO_2 photocatalysis.²⁶ These physical and chemical processes are strongly related to the surface excess electrons which have been reported to contribute to the band gap states of $TiO_2(110)$.^{13–15}

In order to gain insight into the origin of the band gap states, we have conducted a combined experimental and theoretical study. To avoid ambiguity of the defect density, we use photocatalytic dissociation of methanol to prepare hydroxylated $TiO_2(110)$ surfaces in a controlled way.²⁷ This is a gentle method to vary the $O_{br}H$ density, while the subsurface defect density maintains constant as confirmed by 2PPE and ultraviolet photoelectron spectroscopy (UPS) (Supporting Information (SI), Section 3, Figures S1–S2). Therefore, we can clearly separate the contribution of surface defects to the band gap states of $TiO_2(110)$ from that of subsurface defects by monitoring the UPS spectra as a function of $O_{br}H$ concentration which was precisely characterized by temperature programmed desorption (TPD). Linear dependence of the intensity of band gap states on $O_{br}H$ density has been established in both experiments and DFT calculations. Our results also show that the contribution of subsurface defects in the current TiO_2 substrate to the band gap states is equal to that of only 1.9% monolayer (ML, where ML is defined by the density of the Ti ions on the surface of $TiO_2(110)$, i.e., $5.2 \times 10^{14} \text{ cm}^{-2}$) $O_{br}H$. Because the surface defect density is usually much larger than 1.9% ML in real studies and applications, our work indicates surface defects play a dominant role in determining the electronic structure in the band gap of TiO_2 , which will significantly affect the surface chemistry.

Precise measurement of the $O_{br}H$ coverage is critical to establish the quantitative correlation between band gap states and surface defects. In a TPD process, $O_{br}H$ is involved in the recombinative desorption as water with $O_{br}H$ and as methanol with $O_{br}CH_3$, and also the production of formaldehyde. The desorption of a methanol abstracts the H from an $O_{br}H$, while the formation of a formaldehyde increases an $O_{br}H$. In addition, the measured amount of methanol and that of formaldehyde are equivalent (SI, Section 4, Figure S3). Therefore the recombinative desorption of water reflects the real amount of $O_{br}H$ which contributes in the UPS experiments. Figure 1A shows the TPD spectra at mass 18 as a function of the laser fluence. $O_{br}H$ coverage accumulates from 5.3% ML to 16.8% ML as the fluence of the laser increases from 0.7×10^{20} photons/cm² to 40.3×10^{20} photons/cm².

To study the quantitative correlation between the intensity of band gap states and the density of $O_{br}H$, UPS has been utilized to measure the electronic structure of $O_{br}H$ covered $TiO_2(110)$. Figure 1B shows the UPS spectra of $TiO_2(110)$ with the corresponding $O_{br}H$ coverage in Figure 1A. The valence band is located between 3 and 10 eV, while the OH 3σ feature has a binding energy around 11 eV. The inset graph in Figure 1B displays the band gap state region of the UPS spectra

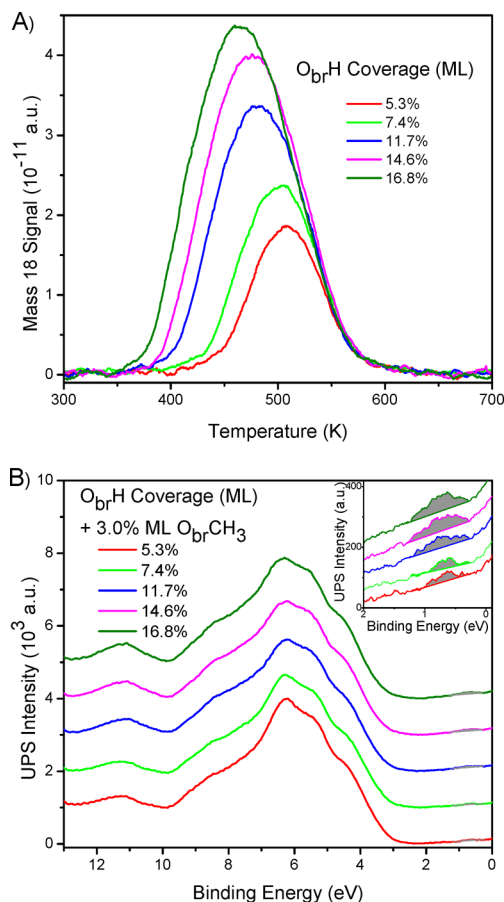


Figure 1. (A) Water TPD ($m/z = 18$) acquired after saturated first layer methanol covered $TiO_2(110)$ surface had been exposed to laser light (400 nm, flux: 2.24×10^{18} photons/cm²/s) for various period of time followed by heating to 390 K. (B) UPS ($h\nu = 40.8$ eV) spectra for hydroxylated $TiO_2(110)$ with corresponding $O_{br}H$ coverage specified in Figure 1A. The spectra were collected at 110 K.

in more detail. The peak position is at about 0.80 eV, and the intensity is clearly enhanced by the increase of the $O_{br}H$ coverage.

The occupation of all the O_{br} vacancies is guaranteed by the diffusion of methanol at elevated temperature and spontaneous dissociation at O_{br} vacancies, producing $O_{br}CH_3$ and $O_{br}H$ pair.²⁸ The O_{br} vacancy concentration of the current $TiO_2(110)$ surface is 3.0% ML as measured by water TPD method.²⁹ Therefore, the above UPS spectra were acquired on $TiO_2(110)$ surface with various $O_{br}H$ densities and also 3.0% ML $O_{br}CH_3$. The contribution of 3.0% ML $O_{br}CH_3$ to band gap states is equal to that of 3.0% ML $O_{br}H$, which was demonstrated by UPS measurement (SI, Section 5, Figure S4). Thus the total $O_{br}H$ coverage could be regarded as the sum of the amount of $O_{br}H$ measured by the TPD method and the density of $O_{br}CH_3$. The subsurface defect density is invariant (SI, Section 3, Figure S1–S2), therefore, the evolution of the band gap states should arise purely from the change of the $O_{br}H$ density. In an effort to map out the correlation between the band gap state density and the $O_{br}H$ coverage, the UPS spectra in Figure 1B were subtracted by the secondary electron background and fitted by a Gaussian function. The integrated band gap state signal was displayed in Figure 2 as a function of the $O_{br}H$ coverage. The data can be well fitted to a straight line,

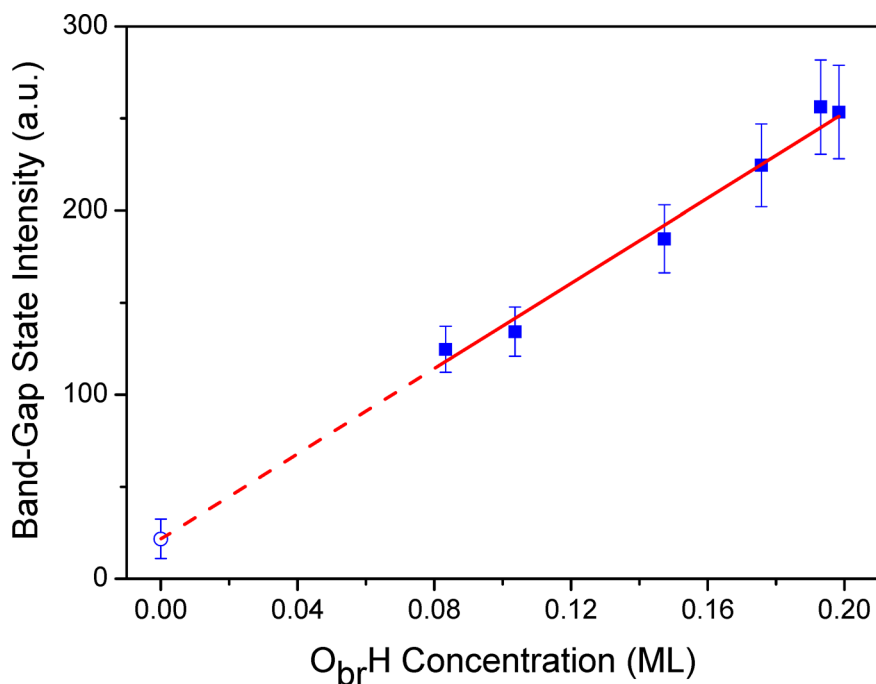


Figure 2. O_{br}H coverage dependence of the normalized band gap states on TiO₂(110) and the linear fitting. The dashed line means the extrapolation of the linear fitting, while the blue circle (21.7 ± 10.7) is the extrapolation result at zero O_{br}H coverage.

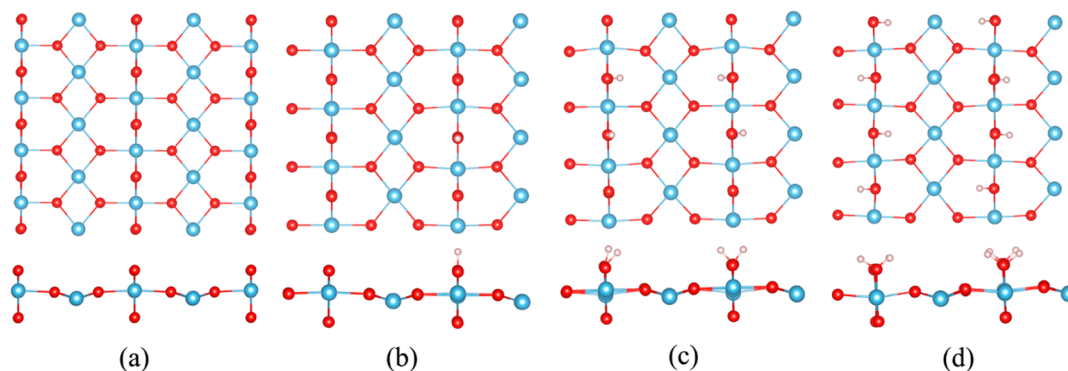


Figure 3. Top and side views of optimized adsorption structures for (a) clean, (b) 1/8 ML O_{br}H, (c) 1/2 ML O_{br}H and (d) 1 ML O_{br}H on the TiO₂(110)-(4 × 2) surface unit cell. The red, light blue, and white balls represent the O, Ti, and H atoms, respectively.

suggesting the increase of O_{br}H coverage is responsible for the rise of the band gap state intensity.

To further confirm our experimental results, DFT calculations have been performed to study the variation of band gap state in the hydroxylated TiO₂(110) surfaces as a function of the O_{br}H density (0, 1/8, 1/4, 1/2, 3/4 and 1 ML). Figure 3 shows the top and side view of the structure of TiO₂ with 0, 1/8, 1/2 and 1 ML O_{br}H respectively. In these structures, all H atoms are occupied by the O_{br} sites. According to previous studies,¹⁵ the addition of H to O_{br} of TiO₂(110) can induce band gap states. To demonstrate the existence of these states, the density-of-states (DOS) curves obtained from our PBE+U calculations are depicted in Figure 4. All the energies are measured relative to CBM. Figure 4a shows the electronic structure of a clean TiO₂(110). The DOS of conduction band is located between 0 and 4.2 eV, while that of valence band ranges from −8 to −1.4 eV. There is no localized state in the band gap. However, when an H (1/8 ML) is added to this surface, a localized state in the band gap does appear (Figure 4b). This result unambiguously suggests the introduction of a band gap

state by adding one H to an O_{br}. As O_{br}H coverage increases, the number of localized states in the band gap increases to two. One is close to the Fermi level, and the other is near the valence band. The localized state near the Fermi energy does not change much, while that near the valence band is obviously heightened and broadened. These results are in consistent with the results obtained with the PBE0 method where one localized state and two localized states are clearly found in the DOS curves of the TiO₂(110) surfaces with 1/8 and 1/2 ML O_{br}H, respectively (SI, Figure S5).

To further clarify the band gap states, we describe the excess charge distribution, which can be obtained by analyzing the localized state in DOS curves. There are one, two, four, six and eight kinds of the charge distributions around the Ti sites in the hydroxylated TiO₂(110) surface with 1/8, 1/4, 1/2, 3/4 and 1 ML O_{br}H, respectively (SI, Figure S6–S10), further indicating the density of localized states in the band gap of these TiO₂(110) surfaces. This is also demonstrated by the PBE0 method (SI, Figure S11–S12). To check the effect of the slab size on the electronic properties of the hydroxylated TiO₂(110)

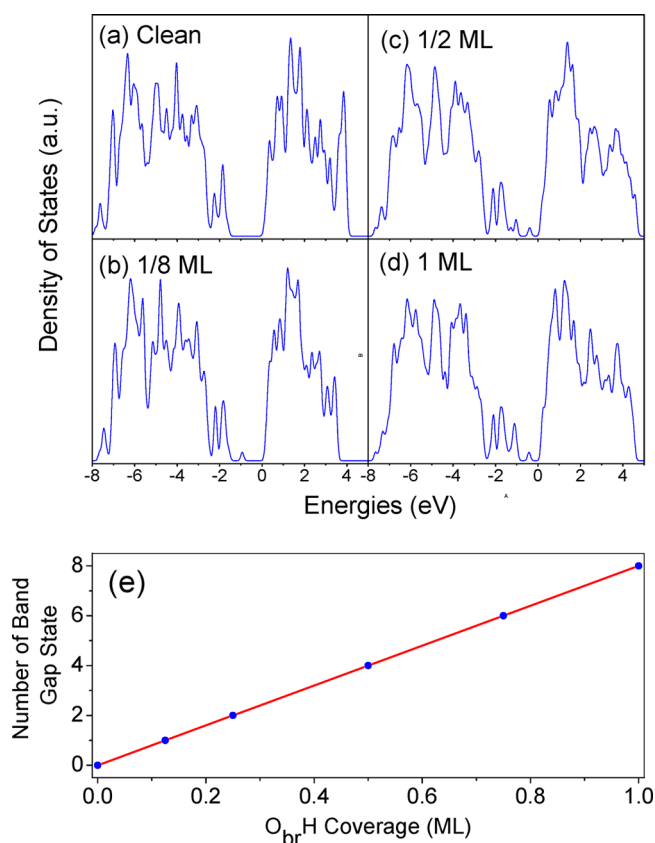


Figure 4. The density of states for the (a) clean and hydroxylated $TiO_2(110)$ surface with (b) 1/8 ML, (c) 1/2 ML and (d) 1 ML $O_{br}H$, respectively. All the energies are aligned by the conduction band minimum. Only the spin-up component is reported, since the spin-down component does not include the localized state in the band gap. (e) Density of band gap states as a function of $O_{br}H$ concentration on the $TiO_2(110)$ surface.

surface, we also used the periodic slabs of 6 TiO_2 trilayers with a 4×2 surface unit cell and 15 Å of vacuum space to calculate the DOS and excess charge distribution of $TiO_2(110)$ surfaces with 1/4 ML $O_{br}H$. Two excess electrons located at two different Ti sites have been found, characterizing the two localized states in the band gap of the hydroxylated $TiO_2(110)$ surface (SI, Figure S13). In addition, we also examined the effect of the different $O_{br}H$ distribution on the density of gap states. The hydroxylated $TiO_2(110)$ surface with 1/2 ML $O_{br}H$, where the $O_{br}H$ species are not distributed next to each other, are considered, and four kinds of charge distributions are observed (SI, Figure S14), thus the distribution of the $O_{br}H$ does not affect the density of the localized states. These results demonstrate that the localized states in the band gap are contributed by the excess electrons in the hydroxylated $TiO_2(110)$ surface. Based on the charge distributions, we plot density of band gap states versus the $O_{br}H$ concentration in Figure 4e. The graph shows in a very clear way that density of band gap states is directly proportional to the excess electrons originated from the addition of H, which agrees well with the experimental observations.

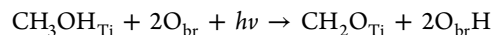
Similar to a previous study,⁸ the fitted line in Figure 2 does not go through the origin, suggesting other sources, e.g., subsurface defects, of the band gap states. Subsurface Ti_{int} can induce band gap states, which has been shown by previous studies^{16,17} and by our own DFT calculations (SI, Section 6,

Figure S15–S17). However, the intercept (21.7 ± 10.7) amounts only 8.6% of the band gap state intensity at the largest $O_{br}H$ coverage. This portion becomes 23.8% on our clean $TiO_2(110)$ surface, which is still a minor fraction. In other words, at current bulk reduction level, the contribution from subsurface defects is equal to that from 1.9% ML $O_{br}H$, which corresponds to only about 1.0% ML O_{br} vacancies. In practical applications, TiO_2 photocatalysts are always placed in atmosphere or solution, thus hydroxylation at defects, kinks, steps, etc. are inevitable. Even in the UHV environment, residual water will adsorb dissociatively on the O_{br} vacancies (usually ranges from 3.0% to 11.0% ML), producing $O_{br}H$ pairs.^{30–34} Therefore, the $O_{br}H$ density in real studies and applications are much larger than 1.9% ML, suggesting the contribution of surface defects to band gap states of $TiO_2(110)$ is of major importance.

In summary, UPS measurements and DFT calculations have been utilized to investigate the origin of the band gap states on $TiO_2(110)$. Linear dependence of the band gap states on the $O_{br}H$ concentration has been established using UPS, which is in good agreement with the DFT calculations. Contribution of subsurface defects to the band gap states has also been determined. Experimental results reveals that the contribution of subsurface defects to the band gap states of $TiO_2(110)$ at the current bulk reduction level is equal to that of 1.9% ML $O_{br}H$. This work demonstrates the importance of surface defects in changing the electronic structure of TiO_2 , which will have a great effect on the surface chemistry.

EXPERIMENTAL AND THEORETICAL METHODS

The experiments were carried out in a UHV chamber equipped with a hemispherical electron energy analyzer (PHOIBOS 100, SPECS), a mass spectrometer (SRS, RGA 200) and standard sample preparation and characterization devices.^{35–38} Slightly reduced $TiO_2(110)$ sample was prepared by cycles of Ar^+ sputtering and UHV annealing at 850 K. The O_{br} vacancy density (3.0% ML) is identified by the water TPD method.²⁹ Methanol was further purified by freeze–pump–thaw cycles and dosed onto the $TiO_2(110)$ surface through a microcapillary array doser. A saturated first layer (binds to Ti_{5c}) methanol was prepared at 110 K. Photocatalytic splitting of methanol was realized by exposing the methanol covered $TiO_2(110)$ surface to 400 nm laser light,



where the subscripts “Ti” and “br” represent species adsorb on Ti_{5c} and O_{br} respectively. The surface was then heated to 390 K to remove species on Ti_{5c} sites, and recooled to 110 K. Surfaces with different concentration of $O_{br}H$ are prepared using varied irradiation times. Normal He II ($h\nu = 40.8$ eV, UVS 10/35, SPECS) UPS data were acquired by a hemispherical analyzer with an incident angle of about 60° . E_F was determined from the tantalum sample plate that is electrically connected to the semiconductor sample. After a UPS measurement, the $O_{br}H$ density was characterized by TPD method (Figure S3).

Electronic structure calculations were performed within the framework of DFT, as implemented in the Vienna ab initio simulation program (VASP), a plane-wave pseudopotential package.³⁹ The Perdew–Burke–Ernzerhof (PBE)⁴⁰ exchange–correlation functional within the generalized gradient approximation was supplemented by the rotationally invariant “+U” description.⁴¹ A $U(Ti_d)$ value of 4.2 eV was applied to the Ti d states. Rutile $TiO_2(110)$ surface was modeled using periodic

slabs of 4 TiO₂ trilayers with a 4 × 2 surface unit cell and 15 Å of vacuum space.

■ ASSOCIATED CONTENT

● Supporting Information

Experimental and theoretical details. Characterization of subsurface defects of TiO₂(110). Preparation and characterization of O_{br}H on TiO₂(110). Comparison of the contribution of O_{br}H and O_{br}CH₃ to the band gap states. Distribution of the excess charge of the hydroxylated TiO₂(110) surface. Theoretical evidence for the contribution of Ti interstitials to band gap states of TiO₂(110). This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail address: chuanyaozhou@dicp.ac.cn.

*E-mail address: limin.liu@csr.ac.cn.

*E-mail address: xmyang@dicp.ac.cn; Tel: +86-411-84695174;

Fax: +86-411-84675584.

Author Contributions

These authors made similar contribution to this work.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We acknowledge financial support from the Chinese Academy of Science, the Ministry of Science and Technology (Grant No. 2013CB834605), the National Natural Science Foundation of China (Grant No. 20923002, Grant No. 10979004, Grant No. 21203189 and Grant No. 51222212), and the CAEP foundation (Grant No. 2012B0302052).

■ REFERENCES

- (1) Mills, A.; Davies, R. H.; Worsley, D. Water Purification by Semiconductor Photocatalysis. *Chem. Soc. Rev.* **1993**, *22* (6), 417–425.
- (2) Hoffmann, M. R.; Martin, S. T.; Choi, W.; Bahnemann, D. W. Environmental Applications of Semiconductor Photocatalysis. *Chem. Rev.* **1995**, *95* (1), 69–96.
- (3) Diebold, U. The Surface Science of Titanium Dioxide. *Surf. Sci. Rep.* **2003**, *48* (5–8), 53–229.
- (4) Henrich, V. E.; Dresselhaus, G.; Zeiger, H. J. Observation of Two-Dimensional Phases Associated with Defect States on the Surface of TiO₂. *Phys. Rev. Lett.* **1976**, *36* (22), 1335–1339.
- (5) Petrik, N. G.; Zhang, Z. R.; Du, Y. G.; Dohnalek, Z.; Lyubnitsky, I.; Kimmel, G. A. Chemical Reactivity of Reduced TiO₂(110): The Dominant Role of Surface Defects in Oxygen Chemisorption. *J. Phys. Chem. C* **2009**, *113* (28), 12407–12411.
- (6) Haubrich, J.; Kaxiras, E.; Friend, C. M. The Role of Surface and Subsurface Point Defects for Chemical Model Studies on TiO₂: A First-Principles Theoretical Study of Formaldehyde Bonding on Rutile TiO₂(110). *Chem.—Eur. J.* **2011**, *17* (16), 4496–4506.
- (7) Deskins, N. A.; Rousseau, R.; Dupuis, M. Defining the Role of Excess Electrons in the Surface Chemistry of TiO₂. *J. Phys. Chem. C* **2010**, *114* (13), 5891–5897.
- (8) Yim, C. M.; Pang, C. L.; Thornton, G. Oxygen Vacancy Origin of the Surface Band-Gap State of TiO₂(110). *Phys. Rev. Lett.* **2010**, *104* (3), 036806(1)–036806(4).
- (9) Wendt, S.; Bechstein, R.; Porsgaard, S.; Lira, E.; Hansen, J. O.; Huo, P.; Li, Z.; Hammer, B.; Besenbacher, F. Comment on “Oxygen Vacancy Origin of the Surface Band-Gap State of TiO₂(110)”. *Phys. Rev. Lett.* **2010**, *104* (25), 259703–259703.
- (10) Yim, C. M.; Pang, C. L.; Thornton, G. Comment on “Oxygen Vacancy Origin of the Surface Band-Gap State of TiO₂(110)” Reply. *Phys. Rev. Lett.* **2010**, *104* (25), 259704–259704.
- (11) Onda, K.; Li, B.; Petek, H. Two-Photon Photoemission Spectroscopy of TiO₂(110) Surfaces Modified by Defects and O₂ or H₂O Adsorbates. *Phys. Rev. B* **2004**, *70* (4), 045415–045426.
- (12) Kruger, P.; Jupille, J.; Bourgeois, S.; Domenichini, B.; Verdini, A.; Floreano, L.; Morgante, A. Intrinsic Nature of the Excess Electron Distribution at the TiO₂(110) Surface. *Phys. Rev. Lett.* **2012**, *108* (12), 126803(1)–126803(4).
- (13) Kurtz, R. L.; Stockbauer, R.; Madey, T. E.; Roman, E.; Desegovia, J. L. Synchrotron Radiation Studies of H₂O Adsorption on TiO₂(110). *Surf. Sci.* **1989**, *218* (1), 178–200.
- (14) Henderson, M. A.; Epling, W. S.; Peden, C. H. F.; Perkins, C. L. Insights Into Photoexcited Electron Scavenging Processes on TiO₂ Obtained From Studies of the Reaction of O₂ With OH Groups Adsorbed at Electronic Defects on TiO₂(110). *J. Phys. Chem. B* **2003**, *107* (2), 534–545.
- (15) Di Valentin, C.; Pacchioni, G.; Selloni, A. Electronic Structure of Defect States in Hydroxylated and Reduced Rutile TiO₂(110) Surfaces. *Phys. Rev. Lett.* **2006**, *97* (16), 166803–166806.
- (16) 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 Ti3d Defect State in the Band Gap of Titania. *Science* **2008**, *320* (5884), 1755–1759.
- (17) Mitsuhashi, K.; Okumura, H.; Visikovskiy, A.; Takizawa, M.; Kido, Y. The Source of the Ti 3d Defect State in the Band Gap of Rutile Titania (110) Surfaces. *J. Chem. Phys.* **2012**, *136* (12), 124707(1)–124707(8).
- (18) Morgan, B. J.; Watson, G. W. A DFT+U Description of Oxygen Vacancies at the TiO₂ rutile (110) Surface. *Surf. Sci.* **2007**, *601* (21), 5034–5041.
- (19) Calzado, C. J.; Hernández, N. C.; Sanz, J. F. Effect of On-Site Coulomb Repulsion Term U on the Band-Gap States of the Reduced Rutile (110) TiO₂ Surface. *Phys. Rev. B* **2008**, *77* (4), 045118(1)–045118(10).
- (20) Huo, P.; Hansen, J. O.; Martinez, U.; Lira, E.; Streber, R.; Wei, Y. Y.; Laegsgaard, E.; Hammer, B.; Wendt, S.; Besenbacher, F. Ethanol Diffusion on Rutile TiO₂(110) Mediated by H Adatoms. *J. Phys. Chem. Lett.* **2012**, *3* (3), 283–288.
- (21) Li, S.-C.; Chu, L.-N.; Gong, X.-Q.; Diebold, U. Hydrogen Bonding Controls the Dynamics of Catechol Adsorbed on a TiO₂(110). *Science* **2010**, *328* (5980), 882–884.
- (22) Matthey, D.; Wang, J. G.; Wendt, S.; Matthiesen, J.; Schaub, R.; Laegsgaard, E.; Hammer, B.; Besenbacher, F. Enhanced Bonding of Gold Nanoparticles on Oxidized TiO₂(110). *Science* **2007**, *315* (5819), 1692–1696.
- (23) Liu, L. M.; McAllister, B.; Ye, H. Q.; Hu, P. Identifying an O₂ Supply Pathway in CO Oxidation on Au/TiO₂(110): A Density Functional Theory Study on the Intrinsic Role of Water. *J. Am. Chem. Soc.* **2006**, *128* (12), 4017–4022.
- (24) Petrik, N. G.; Kimmel, G. A. Off-Normal CO₂ Desorption from the Photooxidation of CO on Reduced TiO₂(110). *J. Phys. Chem. Lett.* **2010**, *1* (17), 2508–2513.
- (25) Haruta, M.; Kobayashi, T.; Sano, H.; Yamada, N. Novel Gold Catalysts for the Oxidation of Carbon-Monoxide at a Temperature Far Below 0-Degrees-C. *Chem. Lett.* **1987**, *2*, 405–408.
- (26) Szczepankiewicz, S. H.; Colussi, A. J.; Hoffmann, M. R. Infrared Spectra of Photoinduced Species on Hydroxylated Titania Surfaces. *J. Phys. Chem. B* **2000**, *104* (42), 9842–9850.
- (27) Guo, Q.; Xu, C.; Ren, Z.; Yang, W.; Ma, Z.; Dai, D.; Fan, H.; Minton, T. K.; Yang, X. Stepwise Photocatalytic Dissociation of Methanol and Water on TiO₂(110). *J. Am. Chem. Soc.* **2012**, *134* (32), 13366–13373.
- (28) Zhang, Z. R.; Bondarchuk, O.; White, J. M.; Kay, B. D.; Dohnalek, Z. Imaging Adsorbate O-H Bond Cleavage: Methanol on TiO₂(110). *J. Am. Chem. Soc.* **2006**, *128* (13), 4198–4199.
- (29) Henderson, M. A. The Interaction of Water with Solid Surfaces: Fundamental Aspects Revisited. *Surf. Sci. Rep.* **2002**, *46* (1–8), 1–308.

- (30) Brookes, I. M.; Murn, C. A.; Thornton, G. Imaging Water Dissociation on $\text{TiO}_2(110)$. *Phys. Rev. Lett.* **2001**, 87 (26), 266103–266106.
- (31) Schaub, R.; Thosttrup, P.; Lopez, N.; Laegsgaard, E.; Stensgaard, I.; Norskov, J. K.; Besenbacher, F. Oxygen Vacancies as Active Sites for Water Dissociation on Rutile $\text{TiO}_2(110)$. *Phys. Rev. Lett.* **2001**, 87 (26), 266104–266107.
- (32) Wendt, S.; Schaub, R.; Matthiesen, J.; Vestergaard, E. K.; Wahlstrom, E.; Rasmussen, M. D.; Thosttrup, P.; Molina, L. M.; Laegsgaard, E.; Stensgaard, I.; Hammer, B.; Besenbacher, F. Oxygen Vacancies on $\text{TiO}_2(110)$ and Their Interaction with H_2O and O_2 : A Combined High-Resolution STM and DFT Study. *Surf. Sci.* **2005**, 598 (1–3), 226–245.
- (33) Bikondoa, O.; Pang, C. L.; Ithnin, R.; Murn, 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.
- (34) 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.
- (35) Ren, Z. F.; Zhou, C. Y.; Ma, Z. B.; Xiao, C. L.; Mao, X. C.; Dai, D. X.; LaRue, J.; Cooper, R.; Wodtke, A. M.; Yang, X. M. A Surface Femtosecond Two-Photon Photoemission Spectrometer for Excited Electron Dynamics and Time-Dependent Photochemical Kinetics. *Chin. J. Chem. Phys.* **2010**, 23 (3), 255–261.
- (36) 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.
- (37) Zhou, C.; Ma, Z.; Ren, Z.; Mao, X.; Dai, D.; Yang, X. Effect of Defects on Photocatalytic Dissociation of Methanol on $\text{TiO}_2(110)$. *Chem. Sci.* **2011**, 2, 1980–1983.
- (38) Zhou, C.; Ma, Z.; Ren, Z.; Wodtke, A. M.; Yang, X. Surface Photochemistry Probed by Two-Photon Photoemission Spectroscopy. *Energy Environ. Sci.* **2012**, 5, 6833–6844.
- (39) Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for ab Initio Total-Energy Calculations Using A Plane-Wave Basis Set. *Phys. Rev. B* **1996**, 54 (16), 11169–11186.
- (40) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, 77 (18), 3865–3868.
- (41) 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* **1998**, 57 (3), 1505–1509.