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A new form of chemisorbed photo- and electro-active atomic H species on the TiO₂(110) surface

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ABSTRACT

Hydrogen adsorption on TiO₂ is of importance in chemical and photochemical reduction processes. Using several surface science methods, we clearly distinguish two kinds of H species on the surface of rutile TiO₂(110)-1 × 1. In contrast with the well-studied bridge-bonded OH species (α-H) originating from H₂O dissociation on the surface oxygen vacancy site on TiO₂(110), atomic H adsorption on the TiO₂(110) (denoted as β-H) exhibits special high sensitivity to the electronic excitation of the TiO₂(110) by either electrons or UV photons. The formation of molecular H₂ gas by photoexcitation of β-H/TiO₂(110) surfaces has been observed, which may shed light on the basic understanding of the processes of photocatalytic H₂ production by splitting water.

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1. Introduction

Chemisorbed H species play important roles in the wide applications of metal oxides in the fields of catalysis [1,2], photocatalysis [3,4] and electronics [5,6]. Surface-bound atomic hydrogen, H/TiO₂, should be centrally important in solar-driven chemical reduction processes of the future such as for the production of useful hydrogenated organic products from CO₂ [7] as well as H₂ from H₂O [3,8]. Such photochemical reduction processes involving H/TiO₂ species will become important in the future capture, storage and transport of solar energy as fuels. Also in heterogeneous catalysis, atomic H spilled over from H₂ dissociation from supported metals and stabilized on metal oxides, such as TiO₂, is important in surface reduction processes even in the absence of light activation [1]. Additionally, the absorption of H in TiO₂ crystals significantly changes the TiO₂ geometric and electronic structure, increasing the solar light absorption efficiency and photocatalytic activity [3,4,9].

The rutile-TiO₂(110) surface is the prototype oxide surface, widely studied as a model photocatalytic material (band gap = 3.1 eV) as well as a model support for metallic catalyst particles [10–13]. It is a reducible oxide which may be partially reduced by heating in vacuum to ~900 K, exhibiting up to ~10% bridge-bonded oxygen vacancy (BBOV) defects at the surface [14]. Several possible H adsorption configurations have been studied by DFT calculations [15–17] on both the stoichiometric TiO₂(110) and reduced TiO₂(110) surfaces with BBOV sites. As shown in the inset of Fig. 1, five energetically favorable H adsorption sites relative to gas phase atomic H on the top of TiO₂(110) surfaces

have been suggested: (1). H on the BBO sites (α-H species); (2). H on the in-plane O sites; (3). H on the BBOV sites; (4). H on the Ti5c sites; (5) H near the subsurface O sites.

So far, the most experimentally studied H species on TiO₂(110) is α-H, which can be made from water adsorption at BBOV defects producing 2 OH species per adsorbed H₂O molecule on the bridge-bonded oxygen (BBO) sites [18–20]. It has been detected by surface science methods, such as the vibrational spectroscopies [21], scanning tunneling microscopy (STM) [19,20,22,23], photoelectron spectroscopy (PES) [22], electron stimulated desorption (ESD) and temperature programmed desorption (TPD) [21,24]. The influence of α-H groups on the surface electronic structures and chemical behaviors on TiO₂(110) surfaces has also been studied [2,24].

Besides the well-studied α-H groups, there are other adsorbed H species proposed which have also been involved in photochemical/chemical processes on TiO₂. Adsorbed atomic H in the TiO₂ lattice has previously been shown to result in the production of electronic states near the bottom of the conduction band which can be excited by IR radiation into continuum states in the conduction band of TiO₂ [25,26]. Similar results are reported also for ZnO [27]. Recently a rather unstable form of bound hydrogen was produced electrochemically on a TiO₂(001) crystal cathode and was found to migrate into the bulk of the TiO₂ [28]. This hydrogenic species can be removed by exposure to air at 300 K. Atomic H produced electrochemically on Nb₂O₅ and on WO₃ was reported to reduce Cu²⁺(aq) to Cu metal [28]. All of these observations combined lead to the viewpoint that atomic H may be stabilized on TiO₂ and other oxide surfaces in a manner involving a new type of adsorbed H and that it can act as a powerful reducing agent. Compared with the well-known α-H species, these H species have not been well studied by surface science methods and still remain elusive [15,29,30].

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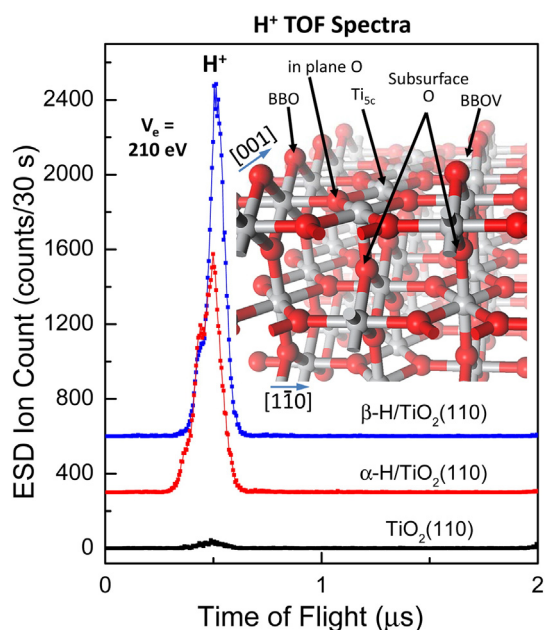


Fig. 1. Time-of-flight spectra of H^+ produced by 210 eV electron bombardment on $\text{TiO}_2(110)$, $\alpha\text{-H/TiO}_2(110)$ and $\beta\text{-H/TiO}_2(110)$ surfaces. $F_e = 6.25 \times 10^{10}$ electrons $\text{cm}^{-2} \text{s}^{-1}$. Inset shows the atomic structure of $\text{TiO}_2(110)$ with bridge-bonded (BBOV) oxygen vacancy site.

Here we show that a new form of atomic H species (denoted as $\beta\text{-H}$) can be stabilized on $\text{TiO}_2(110)$ surface. The species is chemically distinct from the well-known H_2O -produced surface $\alpha\text{-H}$ groups on the bridge-bonded oxygen (BBO) rows, and one of its distinguishing properties is that it can be efficiently activated both by electrons and UV photons. In photocatalytic and catalytic processes on TiO_2 , this $\beta\text{-H/TiO}_2$ species may act as strong reducing agent, which can affect the surface chemistry of TiO_2 .

2. Experimental

All the experiments were carried out in a stainless-steel ultrahigh vacuum chamber (base pressure below 3×10^{-11} mbar). A clean $\text{TiO}_2(110)$ surface (Princeton Scientific, $7 \text{ mm} \times 7 \text{ mm} \times 1 \text{ mm}$) with $\sim 8\%$ BBOV (in dark-blue color) was prepared by cycles of Ar^+ sputtering and annealing at 950 K. The cleanliness and 1×1 structure of the crystal have been tested by Auger electron spectroscopy and low-energy electron diffraction apparatus. Atomic H/D were generated by dissociation of H_2/D_2 ($P_{\text{H}_2/\text{D}_2} = 1 \times 10^{-7}$ mbar) on a hot W filament producing $\beta\text{-H}$ or $\beta\text{-D/TiO}_2$ species on $\text{TiO}_2(110)$ at 90 K. Water vapor was exposed to the $\text{TiO}_2(110)$ surface at 320 K producing $\alpha\text{-H/TiO}_2(110)$ surface by water dissociation on BBOV sites. 210 eV electron bombardment of single crystal surfaces at 83 K to cause electron stimulated desorption (ESD) has been used here to characterize the chemisorbed H species on $\text{TiO}_2(110)$ by the observation of the H^+ fragment product. We have used time-of-flight H^+ electron stimulated desorption, the H^+ ion angular distributions by TOF-ESDIAD (time-of-flight electron stimulated desorption ion angular distribution) and the measurement of total cross section for ESD to characterize the new form of surface $\beta\text{-H}$, and to clearly distinguish it from the well-known surface $\alpha\text{-H}$ species. The H^+ angular distribution often relates simply to the chemical bond directions when ESD-induced bond dissociation and ionization result in a Coulomb explosion. Deflection of H^+ ions by final state effects can also influence ESDIAD ion angular distributions [31,32]. The UV light from a broad-band Hg lamp with an IR filter was transferred to the sample by a fiber optic cable with $1.4 \times 10^{-3} \text{ W/cm}^2$ in the photon energy range 1.1–5.4 eV during the full spectrum UV exposure experiment. Sometimes, a 395 nm bandpass filter was used to get UV photons with

$3.4 \pm 0.1 \text{ eV}$ energy ($F_{\text{h\nu}} = 2.5 \times 10^{14}$ photons $\text{cm}^{-2} \text{s}^{-1}$) for the UV experiments indicated in the text. The UV exposure does not influence the sample temperature notably (less than $\sim 0.1 \text{ K}$).

3. Results and discussion

Using 210 eV electrons and a pulse-counting ion angular distribution apparatus, it is found that $\alpha\text{-H}$ species from adsorbed OH (from submonolayer (ML) H_2O adsorption) and from atomic H adsorption ($\beta\text{-H}$) on $\text{TiO}_2(110)$ yield almost identical H^+ time-of-flight (TOF) distributions, as shown in Fig. 1. The $0.5 \mu\text{s}$ flight time, corrected for ion acceleration in the apparatus, corresponds to an H^+ kinetic energy for ion ejection of $9 \pm 3 \text{ eV}$ for ESD from both $\alpha\text{-H}$ and $\beta\text{-H}$ adsorbed species. While the ion energies are very similar, the ion angular distributions for $\alpha\text{-H}$ and $\beta\text{-H}$ differ significantly as shown in Fig. 2A–B. $\beta\text{-H/TiO}_2$ yields an almost circularly symmetric, normally-oriented H^+ angular distribution while $\alpha\text{-H/TiO}_2$ yields a highly elongated H^+ angular distribution. The elongation of the angular distribution of H^+ from $\alpha\text{-H/TiO}_2$ is in the $[1\bar{1}0]$ direction perpendicular to the rows of bridge-bonded O atoms on the outer surface, as shown in the insert to Fig. 2B. The elongated H^+ ESDIAD pattern for $\alpha\text{-H/TiO}_2$ indicates that the O–H bonds are inclined to the left or right in the $[1\bar{1}0]$ direction as has been suggested by DFT calculations [17], or alternatively that high amplitude OH bending modes are present [33].

The thermal properties of the $\beta\text{-H}$ and $\alpha\text{-H}$ species differ greatly as shown in Fig. 2C–D. Here we use the time- and angle-integrated yield of H^+ by ESD as a probe for study of the coverage of the two surface hydrogenic species as temperature is increased in vacuum. (Low electron flux of $0.31 \times 10^{10} \text{ e cm}^{-2} \text{s}^{-1}$ and short exposing time of 30 s has been chosen during the measurement to diminish the ESD effect of H depletion by incident electrons, as been discussed below in Fig. 3.) For $\beta\text{-H/TiO}_2$ species, depletion by heating in vacuum occurs already below 350 K, as shown in Fig. 2C. Following $\beta\text{-H/TiO}_2$ depletion, a fractional ML remaining coverage of $\alpha\text{-H/TiO}_2$ (due to impurity H_2O adsorption) is found to deplete above $\sim 350 \text{ K}$. The $\alpha\text{-H}$ species are inadvertently added to the surface during bombardment by atomic H from small quantities of H_2O present in the ultrahigh vacuum chamber; this was excluded in an alternative atomic D experiment (Fig. S1) where only a small amount of $\alpha\text{-D}$ species is produced. When only H_2O is adsorbed, to produce only $\alpha\text{-H/TiO}_2$, the behavior of the $\alpha\text{-H/TiO}_2$ upon heating is shown in Fig. 2D, showing that $\alpha\text{-H/TiO}_2$ thermal depletion occurs only above $\sim 350 \text{ K}$. The thermal stability of $\alpha\text{-H/TiO}_2$ shown in Fig. 2C–D exceeds that of $\beta\text{-H/TiO}_2$, showing that the energy and structure of two kinds of surface hydrogen differ chemically. The thermal loss of $\alpha\text{-H/TiO}_2$ is accompanied by H_2O desorption [24]. The thermal desorption from $\beta\text{-H/TiO}_2$ has not been well described in this work. From the data in Fig. 2C–D, we see that the saturation coverage of $\beta\text{-H/TiO}_2$ above the background due to $\alpha\text{-H/TiO}_2$ gives about $19 \times 10^3 \text{ H}^+$ ESD counts/30 s, whereas the saturation coverage of $\alpha\text{-H/TiO}_2$ gives about $33 \times 10^3 \text{ H}^+$ ESD counts/30 s. These count rates are consistent with those measured by integration in Fig. 1.

The chemical difference between $\alpha\text{-}$ and $\beta\text{-H/TiO}_2$ is also vividly demonstrated by comparing their sensitivity to electron stimulated desorption. Fig. 3 shows the almost complete lack of sensitivity of $\alpha\text{-H/TiO}_2$ to electron stimulated desorption ($V_e = 210 \text{ eV}$) at an electron flux $F_e = 6.25 \times 10^{10} \text{ e cm}^{-2} \text{s}^{-1}$ at 83 K. In contrast, for $\beta\text{-H/TiO}_2$, for F_e in the range $0.31\text{--}3.13 \times 10^{10} \text{ e cm}^{-2} \text{s}^{-1}$, a monotonically increasing and large rate of H depletion by ESD is observed. $\beta\text{-H/TiO}_2$ is very sensitive to electrons and responds both by ionization to produce H^+ and by the breaking of the X–H (X may be Ti or O) bond by incident electrons (presumably to yield desorbing H). The data shown in Fig. 3 are combined to determine the $\beta\text{-H/TiO}_2$ total desorption cross section during ESD. A total cross section of $Q = \sim 7 \times 10^{-14} \text{ cm}^2$ is found (Fig. S2). This very large total cross section (which exceeds typical molecular cross sections by a factor of ~ 100 or more) indicates that multiple

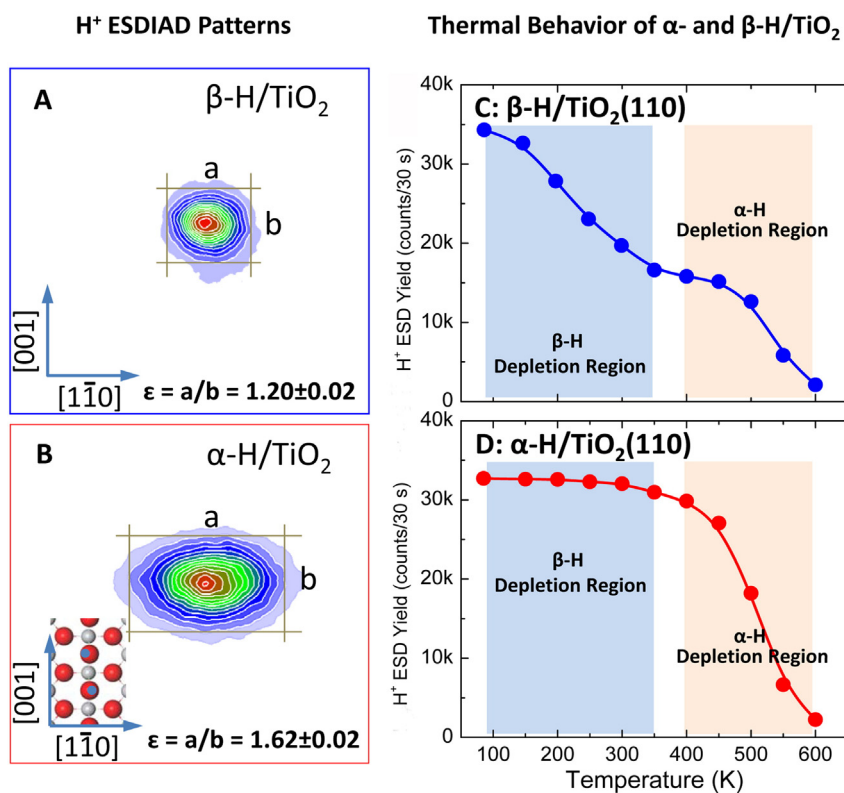


Fig. 2. H^+ ESDIAD patterns on (A), β -H/ TiO_2 and (B), α -H/ TiO_2 surfaces. In (A), the contribution of α -H/ TiO_2 is removed by thermal treatment of the surface based on the behavior shown in (C). (C) and (D) show the thermal depletion behavior of β -H/ TiO_2 (110) and α -H/ TiO_2 (110) using integration of the TOF spectra of H^+ yields.

elementary electronic excitation events occur in TiO_2 during 210 eV electron bombardment of the TiO_2 semiconductor surface; the H atoms from the β -H/ TiO_2 species probably desorb by excitation processes involving the production of multiple charge carriers per incident 210 eV electron in the TiO_2 . In contrast to the very high cross section for β -H/ TiO_2 , the total cross section for α -H/ TiO_2 destruction by ESD is

estimated to be only $\sim 10^{-20} \text{ cm}^2$, a more-normal total ESD-cross section [31]. This large ~ 5 order of magnitude difference in total cross section for ESD of H from α - and β -H/ TiO_2 further supports the concept of a large chemical difference between the two kinds of bound H on the TiO_2 (110) surface.

The influence of UV irradiation on the H/ TiO_2 species has also been investigated by monitoring the H^+ -ESD yield at low electron bombardment rate during UV irradiation. Using (for H coverage measurement) the ESD production of H^+ from H/ TiO_2 (at $F_e = 0.31 \times 10^{10} \text{ e cm}^{-2} \text{ s}^{-1}$, which is too low to cause significant depletion of β -H by incident electrons in the measurements), it is seen that β -H/ TiO_2 species are also able to be desorbed by UV photons of $3.4 \pm 0.1 \text{ eV}$ energy, just above the TiO_2 bandgap. Fig. 4 shows the effect of UV irradiation on β -H/ TiO_2 coverage. It may be seen that an exponential decay is observed, and that by $\sim 5 \times 10^{16}$ photons cm^{-2} exposure, all β -H/ TiO_2 species have been desorbed by UV irradiation. A control experiment in the dark does not lead to depletion of H species and in addition α -H/ TiO_2 is found to be insensitive to UV photons (Fig. S3), which agrees with previous experiments [34–36]. At the red arrow in Fig. 4, about 50 ML of 3.4 eV photons have completely removed the β -H/ TiO_2 monolayer. The large total photodesorption cross section ($\sim 10^{-16} \text{ cm}^2$) for β -H/ TiO_2 is $\sim 10^{-3}$ that of the very high total cross section of the ESD process caused by 210 eV electrons for β -H/ TiO_2 (Fig. S2). It is clear that β -H/ TiO_2 is very sensitive to electronic excitation either by electrons or by 3.4 eV photons, whereas α -H/ TiO_2 is orders of magnitude less able to be desorbed or ionized by electrons or photons.

The depletion product of β -H/ TiO_2 irradiated by UV light has also been detected by QMS. To exclude the influence of high background of H_2 during QMS measurements, alternative atomic D has been exposed to TiO_2 (110) instead of atomic H. Fig. 5 shows the desorption of D_2 from β -D/ TiO_2 surfaces excited by UV photons. Similar to the previous O_2 photodesorption experiment on O_2 -exposed TiO_2 (110) surfaces [37], D_2 signal quickly reached the maximum within the first 0.2–0.4 s after the UV light is on and monotonically decreased over time due to

H/ TiO_2 – ESD Cross Section Measurement

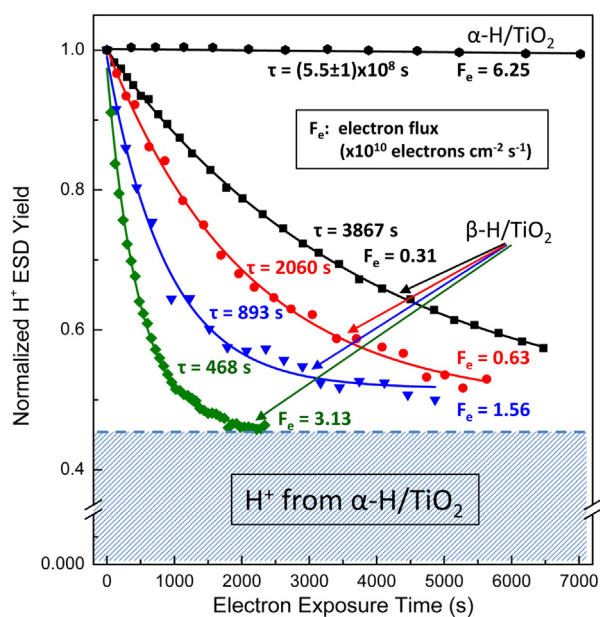


Fig. 3. H species depletion by incident electrons with 210 eV on α -H/ TiO_2 and β -H/ TiO_2 species on TiO_2 (110). ($Q_{(\beta-H)} = \sim 7 \times 10^{-14} \text{ cm}^2$, $Q_{(\alpha-H)} = \sim 10^{-20} \text{ cm}^2$).

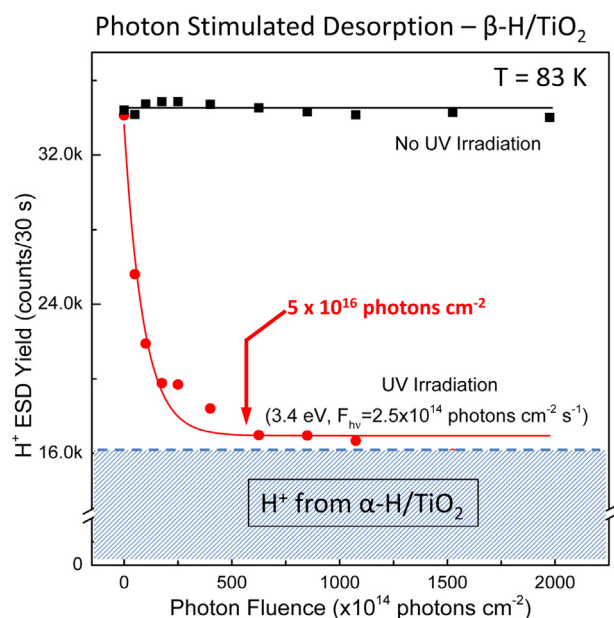


Fig. 4. H species depletion by incident UV photons (3.4 eV) on β -H/TiO₂ measured by H⁺ ESD yield. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the depletion of β -D/TiO₂ species. The time-of-flight spectra of D⁺ (Fig. S4) produced by low-electron bombardment from β -D/TiO₂ surface before and after UV irradiation have shown that almost all the β -D species have been removed upon UV irradiation, which agrees with Fig. 4. The photo yield of D₂ increases with the β -D/TiO₂ adsorption by increasing the atomic D exposing time, as shown in Fig. 5B. The direct observation of photochemical molecular D₂ formation from β -D/TiO₂ surface is very important in understanding the processes of hydrogen production from photo splitting of water on TiO₂-based materials. This has never been observed on single crystal surface study of TiO₂ until a recent study by Wu et al. [16]. Further studies are needed to explore the detailed mechanism of D₂ production in the future.

The above experimental results therefore indicate that the β -H/TiO₂ species have low thermal stability and extremely high sensitivity to incident electronic excitation by electrons and photons, which is

completely opposite to the behavior of the α -H species. However, the exact location of β -H species on TiO₂(110) cannot be directly determined in this experiment. Table 1 summarized the calculated binding energies of different energy sites of H on TiO₂(110) (relative to H atoms) from previous publications [15–17]. On the stoichiometric TiO₂(110) surface, H on BBO site (α -H) is more stable than H on the in-plane O site while H on the Ti5c site is not energetically stable. Meanwhile, H can also diffuse into the bulk forming subsurface hydroxyl species [15]. However, on the highly defective surface (BBOV% = 0.25 ML), Wu et al. [16] found that H on the BBOV site has almost the same binding energy as α -H species. Our experimental results generally agree with the previous DFT calculation results indicating that the α -H species is more energetically favorable than other H species.

Based on our experimental results and the previous theoretical work [15–17], we speculate the possible β -H configuration is H near subsurface O (subsurface hydroxyl) sites: (1). The control experiments of α -H/TiO₂ species shows significantly different activity of thermal and photo- and electron-stimulated losses compared to β -H/TiO₂. That means atomic H does not adsorb on the BBO site. (2). H on BBOV sites has been excluded. The binding energy of H on BBOV site is similar to the α -H/TiO₂ species, which contradicts the thermal experiment in Fig. 2 [16]. The new H/TiO₂ species is reduced by only 50% in its saturation coverage by filling the oxygen vacancies with preadsorbed α -H/TiO₂ groups (data not shown), which excludes BBOV sites as being directly responsible for the new H/TiO₂ species. (Full occupancy of BBOV sites by BBOH (α -H) species would result in a 100% reduction of H/TiO₂ capacity if these sites were specifically involved in H/TiO₂ bonding.) (3). While DFT calculations indicate that H on the in-plane O atom is energetically possible [15–17], the calculated diffusion energy barrier for H migration from in-plane O to BBO sites is very low (below ~0.3 eV) [38,39], which makes the stabilized H adsorption configuration on in-plane O less possible. (4). It is less likely that β -H/TiO₂ is the H on Ti5c sites. DFT calculations indicated that the H adsorption on Ti5c sites is not stable on stoichiometric TiO₂(110) surface and can only occur at highly defective surface with 25% BBOV concentration [16]. Such a highly-reduced TiO₂(110) surface would not have (1 × 1) structure and is not irrelevant to current study. The presence of H on Ti5c sites had been observed using low-energy ion scattering spectroscopy by Pan et al. [30] at room temperature (RT). However, the recent HREELS and TPD experiments by Yin et al. [15] denied the presence of Ti5c-H species by exposing atomic H to TiO₂(110) at RT. (5). β -H/TiO₂ may be the subsurface hydroxyl species formed by the diffusion of

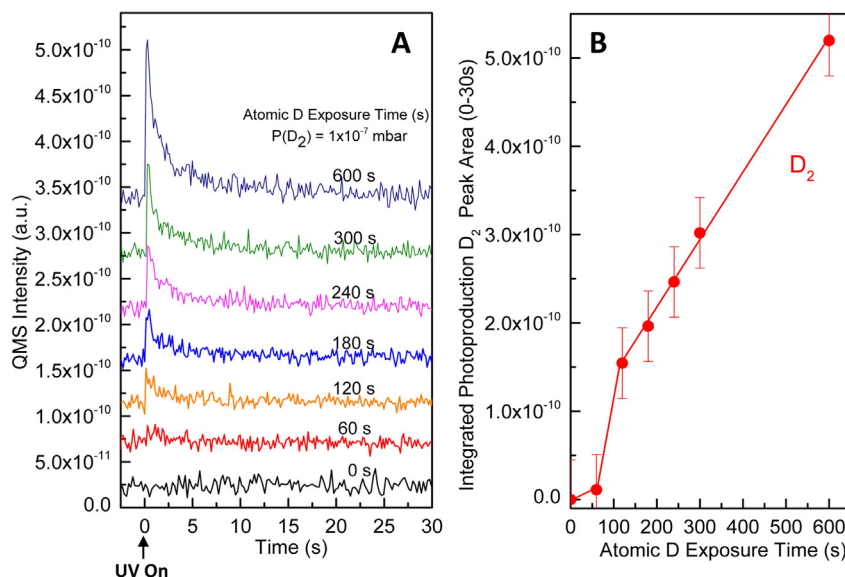


Fig. 5. (A) QMS signal of D₂ photo production on β -D/TiO₂(110) surface upon UV irradiation (Hg lamp with IR filter: 1.1–5.4 eV). (B). The evolution of the integration of D₂ photo production yield at first 30 s after UV irradiation with atomic D exposing time.

Table 1

Summary of binding energies (eV) of H on TiO₂(110) surfaces (relative to H atoms) calculated by DFT calculations. (s-TiO₂: stoichiometric TiO₂; r-TiO₂: reduced TiO₂).

H adsorption sites	s-TiO ₂ (Ref. 15)	s-TiO ₂ (Ref. 17)	s-TiO ₂ (Ref. 16)	r-TiO ₂ (Ref. 16)
BBO	−2.52	−2.84	−2.64	−2.47
in-plane O	−1.76	−2.22	−2.19	−1.90
BBOV	–	–	–	−2.47 (−2.44)
Ti5C	0.01	0.06	−0.07	−1.17
subsurface O	−2.34	–	–	–

atomic H from the surface to the bulk [15,38,40,41]. H from the subsurface hydroxyl species can be excited in the form of H⁺ by electrons and transports through surface layer and desorbs [42,43]. Even though the binding energy of subsurface hydroxyl species is similar to α -H species, the migration energy barrier (~1 eV) of subsurface hydroxyl species further into the bulk is notably lower [15,17]. The less thermal stability of new β -H species observed in Fig. 2 may be due to the deeper diffusion of subsurface H species upon annealing.

The detailed mechanism of electron- and UV-induced depletion of β -H on TiO₂(110) still has not been well understood. For α -H species on TiO₂(110), electrons can excite α -H species producing H⁺ with a threshold energy of 22 eV, which is near to the O 2s level. The desorption mechanism, which involves the creation of O 2s holes and subsequent Auger decay processes, has been proposed by Knotek and Feibelman [44]. In Fig. 1, the desorbed H⁺ ions by electron excitation from both α -H and β -H species have similar kinetic energies, which may indicate that the ESD H⁺ processes from both α -H and β -H species follow the same mechanism and have similar H⁺ ESD cross section. The large depletion rates (total cross section) of β -H species in Fig. 3 may be due to the production of atomic H and/or H₂ species by incident electrons. The QMS experiment in Fig. 5 indicates the production of H₂ from β -H species. A recent work by Wu et al. [16] also confirmed the production of H₂ by UV irradiation of atomic H exposed TiO₂(110) surface. The authors speculated that the H₂ production by UV irradiation is hole-mediated based upon their calculated H configuration on TiO₂ surfaces. Further experiment and theoretical work are needed to understand the bonding mechanism of the β -H species and the mechanism of the electron and photon-induced H desorption.

4. Conclusions

In conclusion, a new type of surface H species (β -H/TiO₂) has been prepared and identified on TiO₂(110) surfaces by dosing atomic H. In comparison with the well-studied α -H species produced by H₂O dissociation on BBOV sites, β -H presents different physical and chemical properties. It is less thermally stable and extremely sensitive to the incident electrons and UV photons compared to H₂O-derived α -H/TiO₂. β -H on TiO₂(110) can be excited by UV irradiation producing molecular H₂ gas, which may shed light on the mechanism of photosplitting H₂O producing H₂. The direct ESD observation of the less stable β -H species on TiO₂(110) may also corroborate the previous proposal of highly mobile H species on metal oxide surfaces prepared by electrochemical hydrogenation [28] or by spillover from supported metal clusters [1,45].

The high electronic excitation sensitivity of β -H/TiO₂ species by incident electrons or UV photons and less thermal stability may be the reason of the ignorance of β -H/TiO₂ species in the previous surface science study. More experimental and theoretical studies are needed for a better understanding of this new H species.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.susc.2016.04.015>.

References

- [1] R. Prins, Chem. Rev. 112 (2012) 2714.
- [2] S.C. Li, L.N. Chu, X.Q. Gong, U. Diebold, Science 328 (2010) 882.
- [3] X.B. Chen, L. Liu, P.Y. Yu, S.S. Mao, Science 331 (2011) 746.
- [4] L. Liu, P.Y. Yu, X.B. Chen, S.S. Mao, D.Z. Shen, Phys. Rev. Lett. 111 (2013) 065505.
- [5] M.D. McCluskey, M.C. Tarun, S.T. Teklemichael, J. Mater. Res. 27 (2012) 2190.
- [6] Y. Kobayashi, O.J. Hernandez, T. Sakaguchi, T. Yajima, T. Roisnel, Y. Tsujimoto, M. Morita, Y. Noda, Y. Mogami, A. Kitada, M. Ohkura, S. Hosokawa, Z.F. Li, K. Hayashi, Y. Kusano, J.E. Kim, N. Tsuji, A. Fujiwara, Y. Matsushita, K. Yoshimura, K. Takegoshi, M. Inoue, M. Takano, H. Kageyama, Nat. Mater. 11 (2012) 507.
- [7] S.N. Habisreutinger, L. Schmidt-Mende, J.K. Stolarczyk, Angew. Chem. Int. Ed. 52 (2013) 7372.
- [8] A. Fujishima, K. Honda, Nature 238 (1972) 37.
- [9] X.B. Chen, L. Liu, F.Q. Huang, Chem. Soc. Rev. (2015), <http://dx.doi.org/10.1039/C4CS00330F>.
- [10] A.L. Linsebigler, G.Q. Lu, J.T. Yates Jr., Chem. Rev. 95 (1995) 735.
- [11] T.L. Thompson, J.T. Yates Jr., Chem. Rev. 106 (2006) 4428.
- [12] U. Diebold, Surf. Sci. Rep. 48 (2003) 53.
- [13] M.A. Henderson, Surf. Sci. Rep. 66 (2011) 185.
- [14] M.A. Henderson, W.S. Epling, C.L. Perkins, C.H.F. Peden, U. Diebold, J. Phys. Chem. B 103 (1999) 5328.
- [15] X.-L. Yin, M. Calatayud, H. Qiu, Y. Wang, A. Birkner, C. Minot, C. Wöll, ChemPhysChem 9 (2008) 253.
- [16] Z.F. Wu, W.H. Zhang, F. Xiong, Q. Yuan, Y.K. Jin, J.L. Yang, W.X. Huang, Phys. Chem. 16 (2014) 7051.
- [17] P.M. Kowalski, B. Meyer, D. Marx, Phys. Rev. B 79 (2009) 115410.
- [18] S. Wendt, J. Matthiesen, R. Schaub, E.K. Vestergaard, E. Lægsgaard, F. Besenbacher, B. Hammer, Phys. Rev. Lett. 96 (2006) 066107.
- [19] Z.R. Zhang, O. Bondarchuk, B.D. Kay, J.M. White, Z. Dohnalek, J. Phys. Chem. B 110 (2006) 21840.
- [20] O. Bikondoa, C.L. Pang, R. Ithnin, C.A. Muryn, H. Onishi, G. Thornton, Nat. Mater. 5 (2006) 189.
- [21] M.A. Henderson, Surf. Sci. 355 (1996) 151.
- [22] S. Wendt, P.T. Sprunger, E. Lira, G.K.H. Madsen, Z.S. Li, J.Ø. Hansen, J. Matthiesen, A. Blekinge-Rasmussen, E. Lægsgaard, B. Hammer, F. Besenbacher, Science 320 (2008) 1755.
- [23] R. Schaub, P. Thostrup, N. Lopez, E. Lægsgaard, I. Stensgaard, J.K. Nørskov, F. Besenbacher, Phys. Rev. Lett. 87 (2001) 266104.
- [24] Z. Zhang, K. Cao, J.T. Yates Jr., J. Phys. Chem. Lett. 4 (2013) 674.
- [25] D.A. Panayotov, J.T. Yates Jr., Chem. Phys. Lett. 436 (2007) 204.
- [26] H. Sezen, M. Buchholz, A. Nefedov, C. Natzeck, S. Heissler, C. Di Valentin, C. Wöll, Sci. Rep. 4 (2014) 3808.
- [27] H. Noei, H.S. Qiu, Y.M. Wang, M. Muhler, C. Wöll, ChemPhysChem 11 (2010) 3604.
- [28] W.P. Chen, K.F. He, Y. Wang, H.L.W. Chan, Z.J. Yan, Sci. Rep. 3 (2013) 3149.
- [29] S. Suzuki, K.-I. Fukui, H. Onishi, Y. Iwasawa, Phys. Rev. Lett. 84 (2000) 2156.
- [30] J.-M. Pan, B.L. Maschhoff, U. Diebold, T.E. Madey, J. Vac. Sci. Technol. A 10 (1992) 2470.
- [31] R.D. Ramsier, J.T. Yates Jr., Surf. Sci. Rep. 12 (1991) 246.
- [32] Z. Mišković, J. Vukanić, T.E. Madey, Surf. Sci. 169 (1986) 405.
- [33] J.T. Yates Jr., J. Ahner, D. Mocuta, Proc. Natl. Acad. Sci. U. S. A. 95 (1998) 443.
- [34] Y. Du, N.G. Petrik, N.A. Deskins, Z. Wang, M.A. Henderson, G.A. Kimmel, I. Lyubinsky, Phys. Chem. Chem. Phys. 14 (2012) 3066.
- [35] C.B. Xu, W.S. Yang, Q. Guo, D.X. Dai, M.D. Chen, X.M. Yang, J. Am. Chem. Soc. 135 (2013) 10206.
- [36] S.J. Tan, H. Feng, Y.F. Ji, Y. Wang, J. Zhao, A.D. Zhao, B. Wang, Y. Luo, J.L. Yang, J.G. Hou, J. Am. Chem. Soc. 134 (2012) 9978.
- [37] Z. Zhang, J.T. Yates Jr., J. Phys. Chem. C 114 (2010) 3098.
- [38] G.H. Enevoldsen, H.P. Pinto, A.S. Foster, M.C.R. Jensen, W.A. Hofer, B. Hammer, J.V. Lauritsen, F. Besenbacher, Phys. Rev. Lett. 104 (2010) 119604.
- [39] S.C. Li, Z.R. Zhang, D. Sheppard, B.D. Kay, J.M. White, Y. Du, I. Lyubinsky, G. Henkelman, Z. Dohnalek, J. Am. Chem. Soc. 130 (2008) 9080.
- [40] G.H. Enevoldsen, H.P. Pinto, A.S. Foster, M.C.R. Jensen, W.A. Hofer, B. Hammer, J.V. Lauritsen, F. Besenbacher, Phys. Rev. Lett. 102 (2009) 136103.
- [41] M. Calatayud, X.-L. Yin, H. Qiu, Y. Wang, A. Birkner, C. Minot, C. Wöll, Phys. Rev. Lett. 104 (2010) 119603.
- [42] M. Akbulut, N.J. Sack, T.E. Madey, Surf. Sci. Rep. 28 (1997) 177.
- [43] M.L. Knotek, Surf. Sci. 101 (1980) 334.
- [44] M.L. Knotek, P.J. Feibelman, Phys. Rev. Lett. 40 (1978) 964.
- [45] D.A. Panayotov, J.T. Yates Jr., J. Phys. Chem. C 111 (2007) 2959.