Submitted to: Surface Science

Date: 11/16/2105

**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 TiO_2 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 $\text{TiO}_2(110)\text{-}1\times 1$. In contrast with the well-studied bridge-bonded OH species ($\alpha\text{-H}$) originating from H_2O dissociation on the surface oxygen vacancy site on $\text{TiO}_2(110)$, atomic H adsorption on the $\text{TiO}_2(110)$ (denoted as $\beta\text{-H}$) exhibits special high sensitivity to the electronic excitation of the $\text{TiO}_2(110)$ by either electrons or UV photons. The formation of molecular H_2 gas by photoexcitation of $\beta\text{-H}/\text{TiO}_2(110)$ surfaces has been observed, which may shed light on the basic understanding of the processes of photocatalytic H_2 production by splitting water.

Keywords:

Electron stimulated desorption, $\text{TiO}_2(110)$, H_2O , Atomic H

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 CO₂⁷ 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 calculations¹⁵⁻¹⁷ on both the stoichiometric TiO₂(110) and reduced TiO₂(110) surfaces with BBOV sites. As shown in the inset of Figure 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 $\text{TiO}_2(110)$ 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 TiO_2 . Adsorbed atomic H in the TiO_2 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 TiO_2 .^{25,26} Similar results are reported also for ZnO .²⁷ Recently a rather unstable form of bound hydrogen was produced electrochemically on a $\text{TiO}_2(001)$ crystal cathode and was found to migrate into the bulk of the TiO_2 .²⁸ This hydrogenic species can be removed by exposure to air at 300 K. Atomic H produced electrochemically on Nb_2O_5 and on WO_3 was reported to reduce $\text{Cu}^{2+}(\text{aq})$ to Cu metal.²⁸ All of these observations combined lead to the viewpoint that atomic H may be stabilized on TiO_2 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}

Here we show that a new form of atomic H species (denoted as β -H) can be stabilized on $\text{TiO}_2(110)$ surface. The species is chemically distinct from the well-known H_2O -produced surface α -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 β -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 mm $\times$ 7 mm $\times$ 1 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 H₂/D₂ ($P_{\text{H}_2/\text{D}_2} = 1 \times 10^{-7}$ mbar) on a hot W filament producing β -H or β -D/TiO₂ species on TiO₂(110) at 90 K. Water vapor was exposed to the TiO₂(110) surface at 320 K producing α -H/TiO₂(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 TiO₂(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 β -H, and to clearly distinguish it from the well-known surface α -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 a IR filter was transferred to the sample by a fiber optic cable with 1.4×10^{-3} W/cm² 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 ± 0.1 eV energy ($F_{\text{hv}} = 2.5 \times 10^{14}$ photons cm⁻² s⁻¹) for the UV experiments indicated in the text. The UV exposure does not influence the sample temperature notably (less than ~0.1 K).

3. Results and Discussion

Using 210 eV electrons and a pulse-counting ion angular distribution apparatus, it is found that α -H species from adsorbed OH (from sub-monolayer (ML) H₂O adsorption) and from atomic H adsorption (β -H) on TiO₂(110) yield almost identical H⁺ time-of-flight (TOF) distributions, as shown in Figure 1. The 0.5 μ s flight time, corrected for ion acceleration in the apparatus, corresponds to an H⁺ kinetic energy for ion ejection of 9 ± 3 eV for ESD from both α -H and β -H adsorbed species. While the ion energies are very similar, the ion angular distributions for α -H and β -H differ significantly as shown in Figure 2A-B. β -H/TiO₂ yields an almost circularly symmetric, normally-oriented H⁺ angular distribution while α -H/TiO₂ yields a highly elongated H⁺ angular distribution. The elongation of the angular distribution of H⁺

from α -H/TiO₂ 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 Figure 2B. The elongated H⁺ ESDIAD pattern for α -H/TiO₂ 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 β -H and α -H species differ greatly as shown in Figure 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 30s has been chosen during the measurement to diminish the ESD effect of H depletion by incident electrons, as been discussed below in Figure 3.) For β -H/TiO₂ species, depletion by heating in vacuum occurs already below 350 K, as shown in Figure 2C. Following β -H/TiO₂ depletion, a fractional ML remaining coverage of α -H/TiO₂ (due to impurity H₂O adsorption) is found to deplete above ~350 K. The α -H species are inadvertently added to the surface during bombardment by atomic H from small quantities of H₂O present in the ultrahigh vacuum chamber; this was excluded in an alternative atomic D experiment (Figure S1) where only a small amount of α -D species are produced. When only H₂O is adsorbed, to produce only α -H/TiO₂, the behavior of the α -H/TiO₂ upon heating is shown in Figure 2D, showing that α -H/TiO₂ thermal depletion occurs only above ~350 K. The thermal stability of α -H/TiO₂ shown in Figure 2C-D exceeds that of β -H/TiO₂, showing that the energy and structure of two kinds of surface hydrogen differ chemically. The thermal loss of α -H/TiO₂ is accompanied by H₂O desorption.²⁴ The thermal desorption from β -H/TiO₂ has not been well described in this work. From the data in Figure 2C-D, we see that the saturation coverage of β -H/TiO₂ above the background due to α -H/TiO₂ gives about $19 \times 10^3 \text{ H}^+ \text{ ESD counts/30 s}$, whereas the saturation coverage of α -H/TiO₂ gives about $33 \times 10^3 \text{ H}^+ \text{ ESD counts/30 s}$. These count rates are consistent with those measured by integration in Figure 1.

The chemical difference between α - and β - H/TiO₂ is also vividly demonstrated by comparing their sensitivity to electron stimulated desorption. Figure 3 shows the almost complete lack of sensitivity of α -H/TiO₂ to electron stimulated desorption (V_e

= 210 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 Figure 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 (Figure S2). This very large total cross section (which exceeds typical molecular cross sections by a factor of ~ 100 or more) indicates that multiple elementary electronic excitation events occur in TiO_2 during 210 eV electron bombardment of the TiO_2 semiconductor surface; the H atoms from the $\beta\text{-H/TiO}_2$ 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 $\beta\text{-H/TiO}_2$, the total cross section for $\alpha\text{-H/TiO}_2$ 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 $\beta\text{-H/TiO}_2$ further supports the concept of a large chemical difference between the two kinds of bound H on the $\text{TiO}_2(110)$ 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 $\beta\text{-H}$ by incident electrons in the measurements), it is seen that $\beta\text{-H/TiO}_2$ 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. Figure 4 shows the effect of UV irradiation on $\beta\text{-H/TiO}_2$ coverage. It may be seen that an exponential decay is observed, and that by $\sim 5 \times 10^{16} \text{ photons cm}^{-2}$ exposure, all $\beta\text{-H/TiO}_2$ species have been desorbed by UV irradiation. A control experiment in the dark does not lead to depletion of H species and in addition $\alpha\text{-H/TiO}_2$ is found to be insensitive to UV photons (Figure S3), which agrees with previous experiments³⁴⁻³⁶. At the red arrow in Figure 4, about 50 ML of 3.4 eV photons have completely removed the $\beta\text{-H/TiO}_2$ monolayer. The large total

photodesorption cross section ($\sim 10^{-16} \text{ cm}^2$) for $\beta\text{-H/TiO}_2$ is $\sim 10^{-3}$ that of the very high total cross section of the ESD process caused by 210 eV electrons for $\beta\text{-H/TiO}_2$ (Figure S2). It is clear that $\beta\text{-H/TiO}_2$ is very sensitive to electronic excitation either by electrons or by 3.4 eV photons, whereas $\alpha\text{-H/TiO}_2$ is orders of magnitude less able to be desorbed or ionized by electrons or photons.

The depletion product of $\beta\text{-H/TiO}_2$ 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 $\text{TiO}_2(110)$ instead of atomic H. Figure 5 shows the desorption of D_2 from $\beta\text{-D/TiO}_2$ surfaces excited by UV photons. Similar to the previous O_2 photodesorption experiment on O_2 -exposed $\text{TiO}_2(110)$ 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 the depletion of $\beta\text{-D/TiO}_2$ species. The time-of-flight spectra of D^+ (Figure S4) produced by low-electron bombardment from $\beta\text{-D/TiO}_2$ surface before and after UV irradiation have shown that almost all the $\beta\text{-D}$ species have been removed upon UV irradiation, which agrees with Figure 4. The photo yield of D_2 increases with the $\beta\text{-D/TiO}_2$ adsorption by increasing the atomic D exposing time, as shown in Figure 5B. The direct observation of photochemical molecular D_2 formation from $\beta\text{-D/TiO}_2$ surface is very important in understanding the processes of hydrogen production from photo splitting of water on TiO_2 -based materials. This has never been observed on single crystal surface study of TiO_2 until a recent study by Wu *et al.*¹⁶ Further studies are needed to explore the detailed mechanism of D_2 production in the future.

The above experimental results therefore indicate that the $\beta\text{-H/TiO}_2$ 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 $\alpha\text{-H}$ species. However, the exact location of $\beta\text{-H}$ species on $\text{TiO}_2(110)$ cannot be directly determined in this experiment. Table 1 summarized the calculated binding energies of different energy sites of H on $\text{TiO}_2(110)$ (relative to H atoms) from previous publications.¹⁵⁻¹⁷ On the stoichiometric $\text{TiO}_2(110)$ surface, H on BBO site ($\alpha\text{-H}$) 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 Figure 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 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 $\alpha\text{-H}$ 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 $\beta\text{-H}$ species observed in Figure 2 may be due to the deeper diffusion of subsurface H species upon annealing.

The detailed mechanism of electron- and UV-induced depletion of $\beta\text{-H}$ on $\text{TiO}_2(110)$ still has not been well understood. For $\alpha\text{-H}$ species on $\text{TiO}_2(110)$, electrons can excite $\alpha\text{-H}$ 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 Figure 1, the desorbed H^+ ions by electron excitation from both $\alpha\text{-H}$ and $\beta\text{-H}$ species have similar kinetic energies, which may indicate that the ESD H^+ processes from both $\alpha\text{-H}$ and $\beta\text{-H}$ species follow the same mechanism and have similar H^+ ESD cross section. The large depletion rates (total cross section) of $\beta\text{-H}$ species in Figure 3 may be due to the production of atomic H and/or H_2 species by incident electrons. The QMS experiment in Figure 5 indicates the production of H_2 from $\beta\text{-H}$ species. A recent work by Wu *et al.*¹⁶ also confirmed the production of H_2 by UV irradiation of atomic H exposed $\text{TiO}_2(110)$ surface. The authors speculated that the H_2 production by UV irradiation is hole-mediated based upon their calculated H configuration on TiO_2 surfaces. Further experiment and theoretical work are needed to understand the bonding mechanism of the $\beta\text{-H}$ species and the mechanism of the electron and photon-induced H desorption.

4. Conclusions

In conclusion, a new type of surface H species ($\beta\text{-H}/\text{TiO}_2$) have been prepared and identified on $\text{TiO}_2(110)$ surfaces by dosing atomic H. In comparison with the well-studied $\alpha\text{-H}$ species produced by H_2O dissociation on BBOV sites, $\beta\text{-H}$ presents different physical and chemical properties. It is less thermally stable and extremely sensitive to the incident electrons and UV photons compared to H_2O -derived $\alpha\text{-H}/\text{TiO}_2$. $\beta\text{-H}$ on $\text{TiO}_2(110)$ can be excited by UV irradiation producing molecular H_2 gas, which may shed light on the mechanism of photosplitting H_2O producing H_2 .

The direct ESD observation of the less stable β -H species on $\text{TiO}_2(110)$ may also corroborate the previous proposal of highly mobile H species on metal oxide surfaces prepared by electrochemical hydrogenation²⁸ or by spillover from supported metal clusters.^{1,45}

The high electronic excitation sensitivity of β -H/ TiO_2 species by incident electrons or UV photons and less thermal stability may be the reason of the ignorance of β -H/ TiO_2 species in the previous surface science study. More experimental and theoretical studies are needed for a better understanding of this new H species.

Acknowledgements:

We acknowledge with thanks the support of DOE (DE-FG02-O9ER16080) for this work. We thank Prof. Ian Harrison, Prof. Horia Metiu, Dr. Henrik Kritoffersen, Prof. Charles T. Campbell, Prof. Jens Norskov, Dr. Aleksandra Vojvodic for helpful discussions.

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-TiO₂ (Ref. 15)	s-TiO₂ (Ref. 17)	s-TiO₂ (Ref. 16)	r-TiO₂ (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	--	--	--

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

Figure 2. H⁺ ESDIAD patterns on (A). β -H/TiO₂ and (B). α -H/TiO₂ surfaces. In (A), the contribution of α -H/TiO₂ 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/TiO₂(110) and α -H/TiO₂(110) using integration of the TOF spectra of H⁺ yields.

H/TiO₂ – ESD Cross Section Measurement

Figure 3. H species depletion by incident electrons with 210 eV on α -H/TiO₂ and β -H/TiO₂ species on TiO₂(110). ($Q_{(\beta\text{-H})} = \sim 7 \times 10^{-14} \text{ cm}^2$, $Q_{(\alpha\text{-H})} = \sim 10^{-20} \text{ cm}^2$)

Figure 4. H species depletion by incident UV photons (3.4 eV) on β -H/TiO₂ measured by H⁺ ESD yield.

Figure 5. (A) QMS signal of D_2 photo production on β -D/ $TiO_2(110)$ surface upon UV irradiation (Hg lamp with IR filter, 1.1 - 5.4 eV). (B). The evolution of the integration of D_2 photo production yield at first 30 s after UV irradiation with atomic D exposing time.

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