Supplementary Information

of

Active hydrogen species on TiO₂ for photocatalytic H₂ production

Zongfang Wu,a† Wenhua Zhang,b† Feng Xiong,a Qing Yuan,a Yuekang Jin,a Jinlong Yanga and Weixin Huangab*

a Hefei National Laboratory for Physical Sciences at Microscale, Suzhou Nano Tech Co-innovation Center and Department of Chemical Physics, University of Science and Technology of China, Hefei 230026, China.

b CAS Key Laboratory of Materials for Energy Conversion and Department of Materials Science and Engineering, University of Science and Technology of China, Hefei 230026, China.

†: These authors contributed equally to the paper.

Corresponding author footnote: *To whom the correspondence should be addressed. E-mail: huangwx@ustc.edu.cn.
Fig. S1 (A) TDS spectra after rutile TiO$_2$(110) surface was exposed to 1000 L D$_2$ at 115 K. Molecular D$_2$ does not chemisorb on rutile TiO$_2$(110) surface under ultra-high vacuum condition and the observed sharp D$_2$ desorption feature at the on-set edge of the spectrum arises from molecularly-chemisorbed D$_2$ on the Ta plate used in the sample assembly. (B) D$_2$ TDS spectra with fitted D$_2$ desorption feature at the on-set edge of the spectrum from the Ta plate of the sample assembly after rutile TiO$_2$(110) surface was exposed to various exposures of atomic D at 115 K. (C) D$_2$ TDS spectra with fitted D$_2$ desorption feature at the on-set edge of the spectrum from the Ta plate of the sample assembly after rutile TiO$_2$(110) surface was exposed to various exposures of atomic D at 115 K and then irradiated with the UV light for 30 s. The fitted D$_2$ desorption feature at the on-set edge of the spectrum from the Ta plate of the sample assembly was acquired by adjusting the D$_2$ desorption feature obtained after an exposure of 1000 L D$_2$ at 115 K (Figure S1A) to make its on-set edge feature coinciding with that of the target D$_2$ desorption spectrum.
Fig. S2 (A) D₂O, (B) HDO and (C) H₂O TDS spectra after rutile TiO₂(110) surface was exposed to 0.01 L D₂O at 115 K with and without subsequent UV light irradiation for 150 s. The peak centering at 315 K and a broad peak at higher temperatures that can be respectively assigned to desorption of molecularly-chemisorbed water on Ti₅C sites and water produced by the reaction between O_BBOH. It can be seen that the UV light irradiation does not affect the D₂O/HDO/H₂O desorption features from rutile TiO₂(110) surface.
Fig. S3 TDS spectra and corresponding integrating peak areas of D$_2$O (A & B), HDO (C & D) and H$_2$O (E & F) after rutile TiO$_2$(110) surface was exposed to various exposures of atomic D at 115 K. It can be seen that the D$_2$O and HDO desorption peaks keep growing with the increase of atomic D exposure.
Fig. S4 (A) O 1s XPS spectra and (B) O 1s XPS difference spectra after rutile TiO$_2$(110) surface was exposed to various exposures of atomic D at 115 K. Inferred from the O 1s XPS difference spectra, surface hydroxyls and molecularly-chemisorbed water on rutile TiO$_2$(110) surface respectively exhibit the O 1s binding energy at 532.5 and 534.3 eV.
Fig. S5 (A) O 1s XPS spectra and (B) O 1s XPS difference spectra after rutile TiO$_2$(110) surface was exposed to 20L atomic D at 115 K followed by annealing at elevated temperatures. Inferred from the O 1s XPS difference spectra, molecularly-chemisorbed water desorbs between 270 and 330 K and surface hydroxyls disappear prior to 700 K.
Fig. S6 (A) D$_2$O, (B) HDO and (C) H$_2$O TDS spectra after rutile TiO$_2$(110) surface was exposed to various exposures of atomic D at 115 K and then irradiated with the UV light for 30 s. The corresponding TDS spectra without UV light irradiation are also included for comparison.
Fig. S7  (A) CO TDS spectra after rutile TiO$_2$(110) surface was exposed to 0.1 L CO at 115 K with and without subsequent UV light irradiation for 150 s. (B) CO$_2$ TDS spectra after rutile TiO$_2$(110) surface was exposed to 0.02 L CO$_2$ at 115 K with and without subsequent UV light irradiation for 150 s. It can be seen that the UV light irradiation does not affect the CO and CO$_2$ desorption features from rutile TiO$_2$(110) surface. On one hand, this demonstrates that the UV light irradiation does not induce the photon-induced desorption of CO and CO$_2$ on rutile TiO$_2$(110) surface; on the other hand, this demonstrates that the slight increase in the temperature of rutile TiO$_2$(110) surface no more than 3 K does not induce detectable thermal desorption of adsorbed CO and CO$_2$. 

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**Note:** The image contains graphs showing TDS spectra for CO and CO$_2$ with and without UV light irradiation. The graphs illustrate the temperature (K) on the x-axis and the partial pressure (m/z 20) (E-8 Torr) on the y-axis. The data show no significant change in desorption features with UV irradiation.
Fig. S8 (A) D$_2$ and (B) HD TDS spectra after rutile TiO$_2$(110) surface was exposed to 5 L atomic D at 115 K and then irradiated with UV light irradiation for different times. (C) D$_2$ and (D) HD PSD spectra after rutile TiO$_2$(110) surface was exposed to 5 L atomic D at 115 K and then irradiated with UV light irradiation for different times.
Fig. S9 Optimized structures and adsorption energies of atomic H adsorption on various sites of stoichiometric rutile TiO$_2$(110) (2x2): (A) H adatom on BBO site; (B) H adatom on oxygen in the basal plane (O$_{3c}$); (C) H adatom on Ti$_{5c}$ in the basal plane. It can be seen that atomic H adsorbs strongly on O sites to form hydroxyl but barely on the Ti$_{5c}$ sites.
Fig. S10 Optimized structures and adsorption energies of atomic H adsorption on various sites of a rutile TiO$_2$(110) (2×2) supercell with one bridging bonding oxygen (BBO) vacancy: (A) H adatom on BBO away from BBO vacancy; (B) H adatom on BBO next to BBO vacancy; (C) H adatom on oxygen in the basal plane (O$_{3c}$); (D) H adatom bridging bonded to two Ti$_{5c}$ sites beneath the BBO vacancy; (E) H adatom on Ti$_{5c}$ in the basal plane.
Fig. S11 Optimized structures and adsorption energies of two atomic H coadsorption on various sites of a rutile TiO$_2$(110) (2×2) supercell with one bridging bonding oxygen (BBO) vacancy: (A) two H adatoms on two BBO sites away from BBO vacancy; (B) one H adatom on BBO next to BBO vacancy and the other H adatom bridging bonded to two Ti$_{5c}$ sites beneath the BBO vacancy; (C) one H adatom on BBO next to BBO vacancy and the other H adatom on oxygen in the basal plane (O$_{3a}$); (D) one H adatom bridging bonded to two Ti$_{5c}$ sites beneath the BBO vacancy and the other H adatom on Ti$_{5c}$ in the basal plane.