Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

# Supplementary Information

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# Active hydrogen species on $TiO_2$ for photocatalytic $H_2$ production

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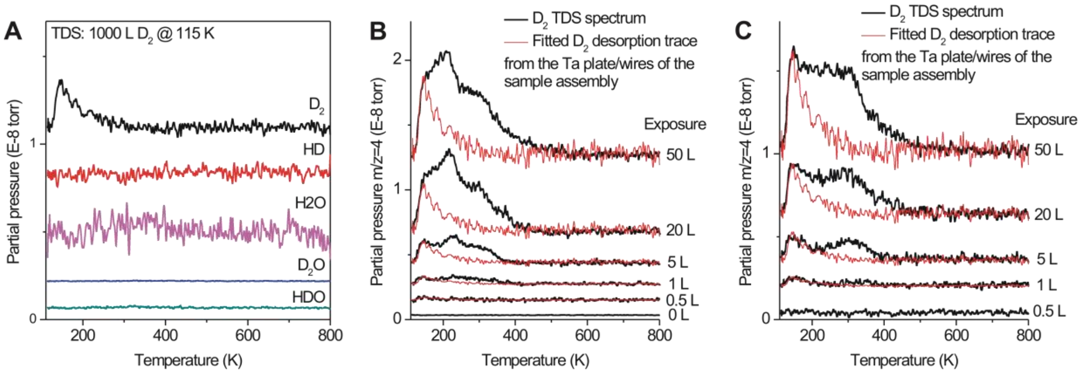

**Fig. S1** (**A)** TDS spectra after rutile $TiO_2(110)$ surface was exposed to 1000 L $D_2$ at 115 K. Molecular $D_2$ does not chemisorb on rutile $TiO_2(110)$ surface under ultra-high vacuum condition and the observed sharp $D_2$ desorption feature at the on-set edge of the spectrum arises from molecularly-chemisorbed $D_2$ 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.

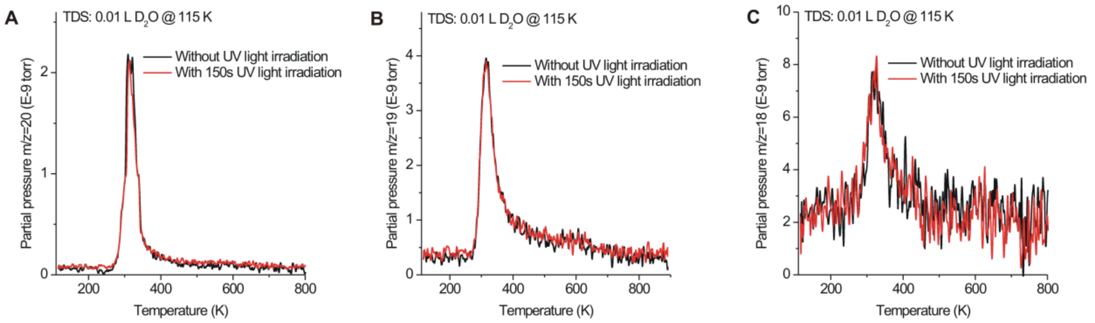

**Fig. S2 (A)** $D_2O$, **(B)** HDO and (**C**) $H_2O$ TDS spectra after rutile $TiO_2(110)$ surface was exposed to 0.01 L $D_2O$ at 115 K with and without subsequent UV light irradiation for 150 s. The peak centering at 315 K and a broad peak at higher temperatures that can be respectively assigned to desorption of molecularly-chemisorbed water on $Ti_{5C}$ sites and water produced by the reaction between $O_{BBO}H$. It can be seen that the UV light irradiation does not affect the $D_2O$/HDO/$H_2O$ desorption features from rutile $TiO_2(110)$ surface.

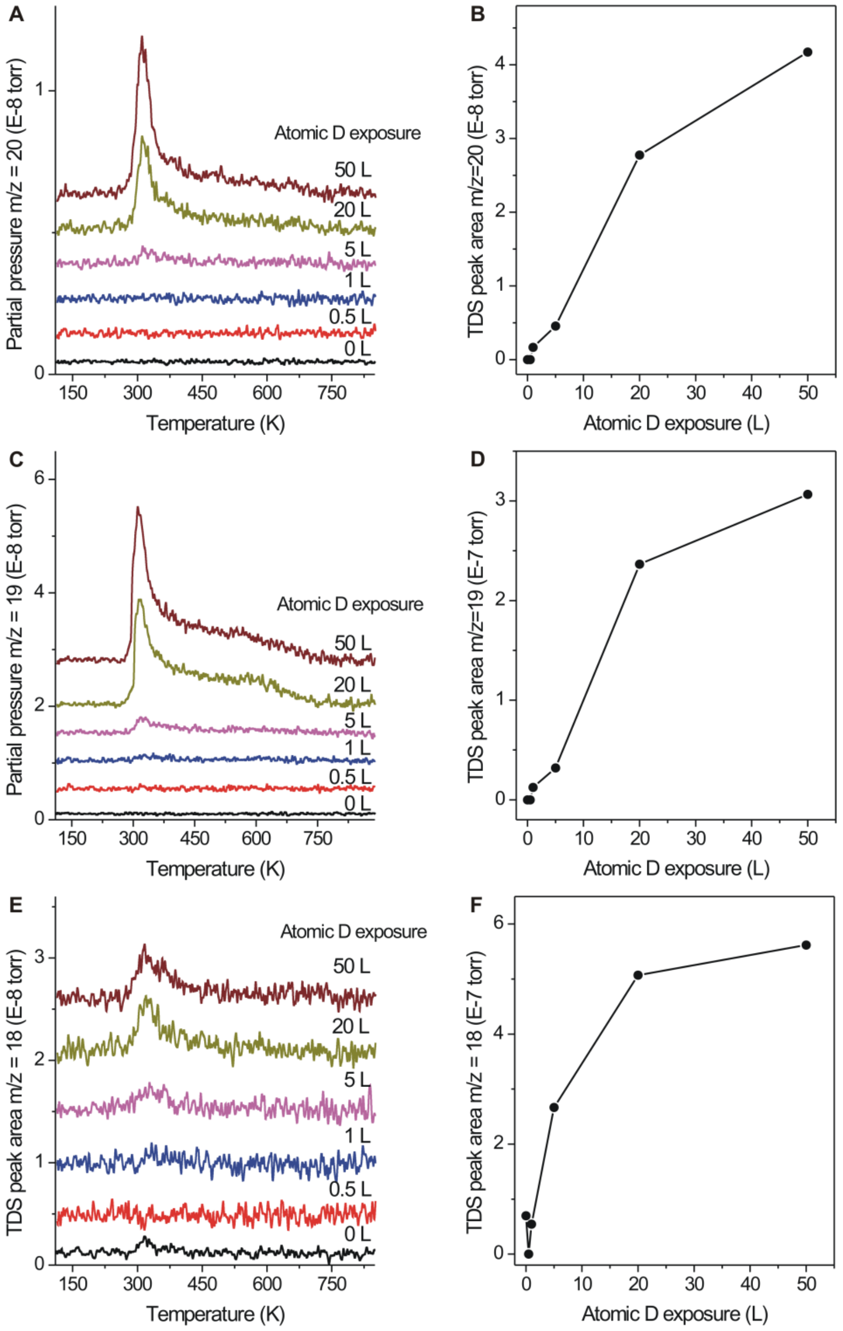

**Fig. S3** TDS spectra and corresponding integrating peak areas of $D_2O$ (**A** & **B**), HDO (**C** & **D**) and $H_2O$ (**E** & **F**) after rutile $TiO_2(110)$ surface was exposed to various exposures of atomic D at 115 K. It can be seen that the $D_2O$ and HDO desorption peaks keep growing with the increase of atomic D exposure.

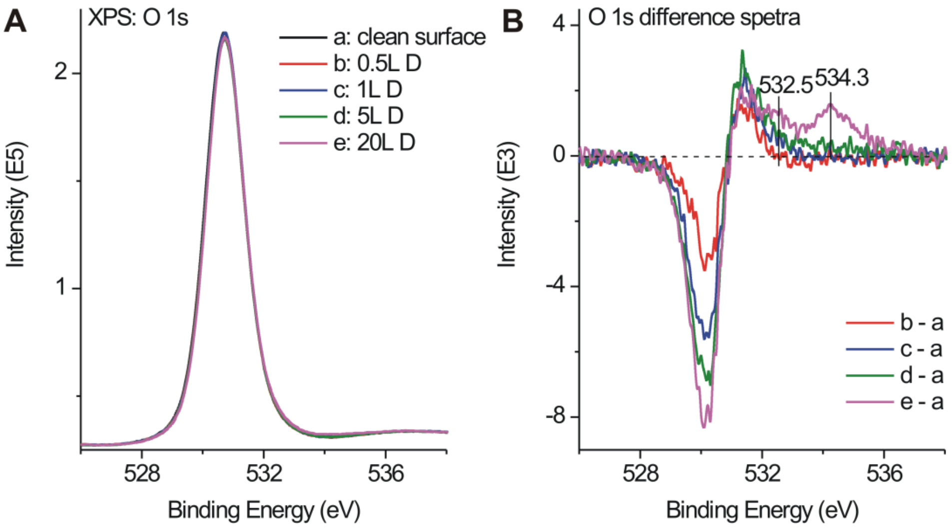

**Fig. S4 (A)** O 1s XPS spectra and **(B)** O 1s XPS difference spectra after rutile $TiO_2$(110) surface was exposed to various exposures of atomic D at 115 K. Inferred from the O 1s XPS difference spectra, surface hydroxyls and molecularly-chemisorbed water on rutile $TiO_2$(110) surface respectively exhibit the O 1s binding energy at 532.5 and 534.3 eV.

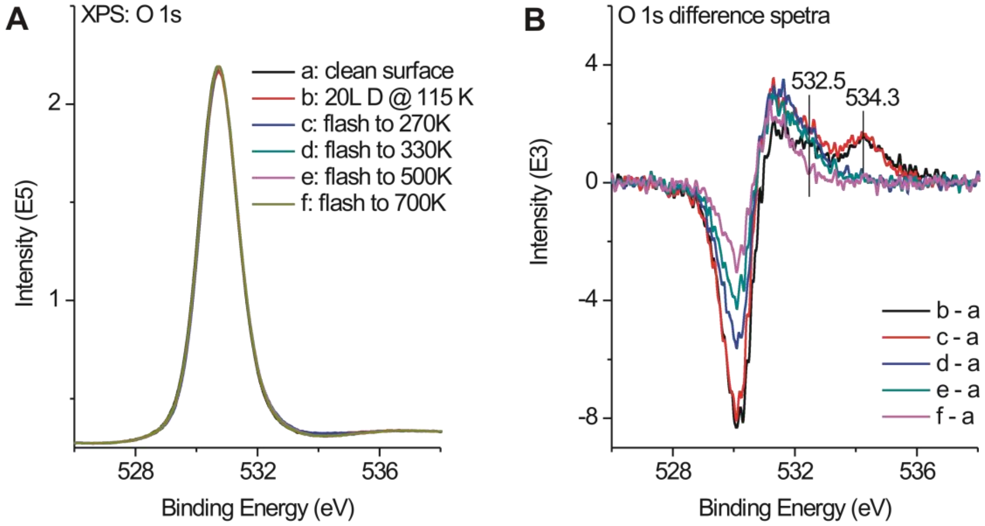

**Fig. S5 (A)** O 1s XPS spectra and **(B)** O 1s XPS difference spectra after rutile $TiO_2$(110) surface was exposed to 20L atomic D at 115 K followed by annealing at elevated temperatures. Inferred from the O 1s XPS difference spectra, molecularly-chemisorbed water desorbs between 270 and 330 K and surface hydroxyls disappear prior to 700 K.

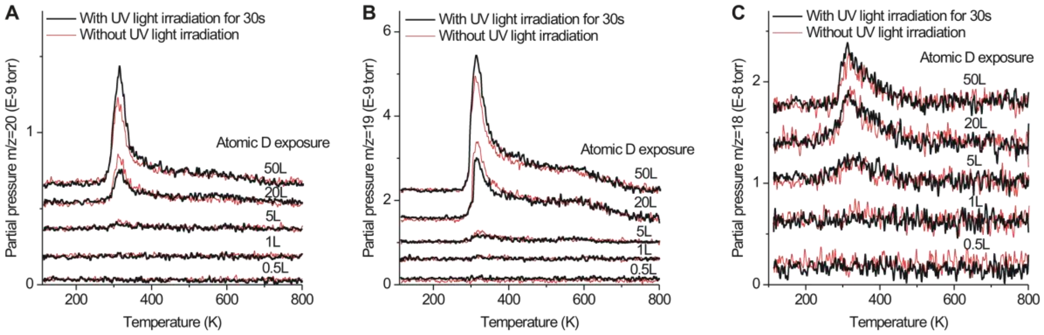

**Fig. S6 (A)** $D_2O$, **(B)** HDO and **(C)** $H_2O$ TDS spectra after rutile $TiO_2(110)$ surface was exposed to various exposures of atomic D at 115 K and then irradiated with the UV light for 30 s. The corresponding TDS spectra without UV light irradiation are also included for comparison.

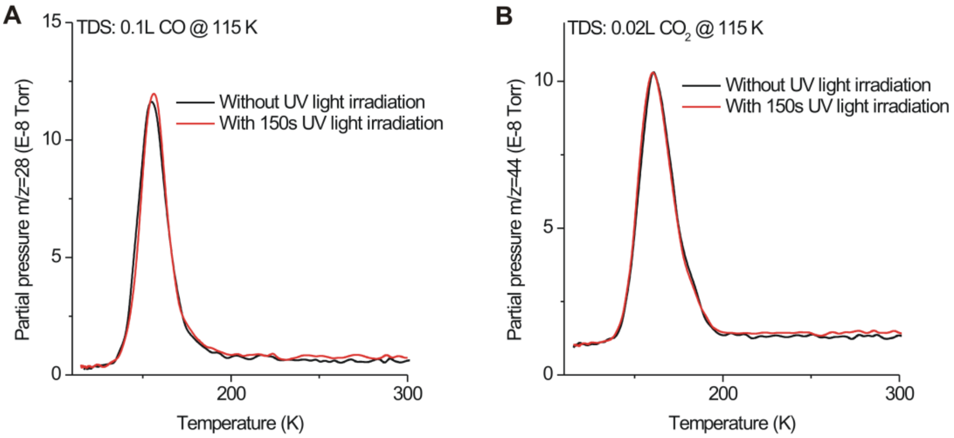

**Fig. S7 (A)** CO TDS spectra after rutile $TiO_2$(110) surface was exposed to 0.1 L CO at 115 K with and without subsequent UV light irradiation for 150 s. **(B)** $CO_2$ TDS spectra after rutile $TiO_2$(110) surface was exposed to 0.02 L $CO_2$ at 115 K with and without subsequent UV light irradiation 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 induced 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 $CO_2$.

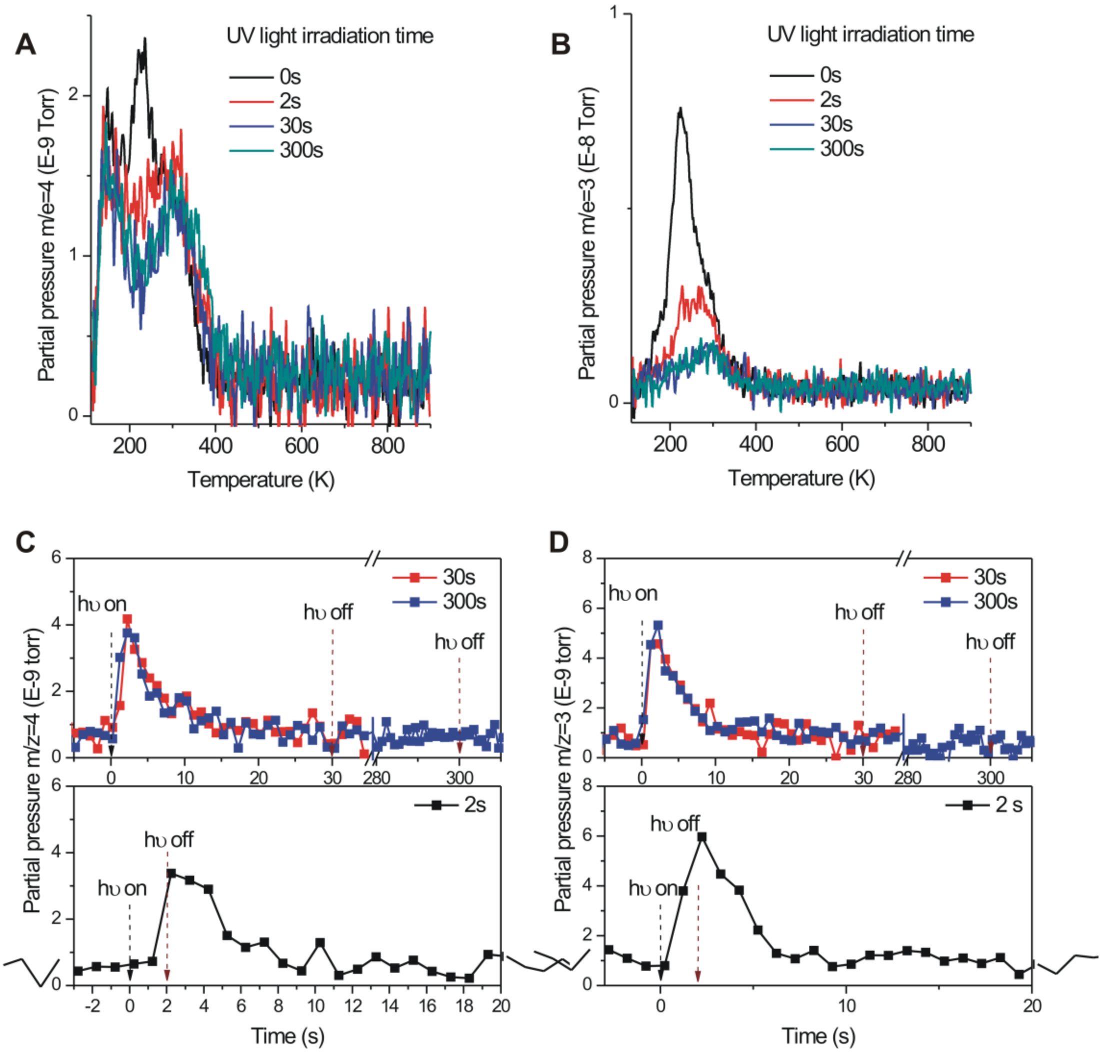

**Fig. S8 (A)** $D_2$ and **(B)** HD TDS spectra after rutile $TiO_2(110)$ surface was exposed to 5 L atomic D at 115 K and then irradiated with UV light irradiation for different times. **(C)** $D_2$ and **(D)** HD PSD spectra after rutile $TiO_2(110)$ surface was exposed to 5 L atomic D at 115 K and then irradiated with UV light irradiation for different times.

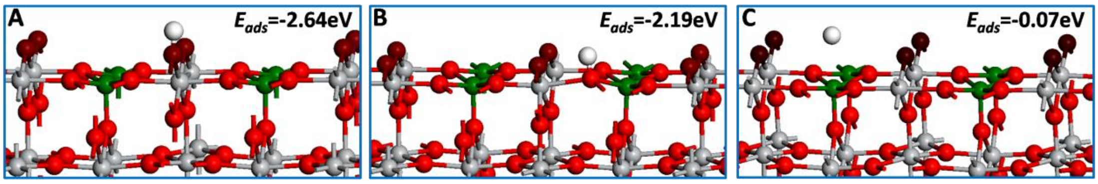

**Fig. S9** Optimized structures and adsorption energies of atomic H adsorption on various sites of stoichiometric rutile $TiO_2(110)$ (2×2): **(A)** H adatom on BBO site; **(B)** H adatom on oxygen in the basal plane ($O_{3c}$); **(C)** H adatom on $Ti_{5c}$ in the basal plane. It can be seen that atomic H adsorbs strongly on O sites to form hydroxyl but barely on the $Ti_{5c}$ sites.

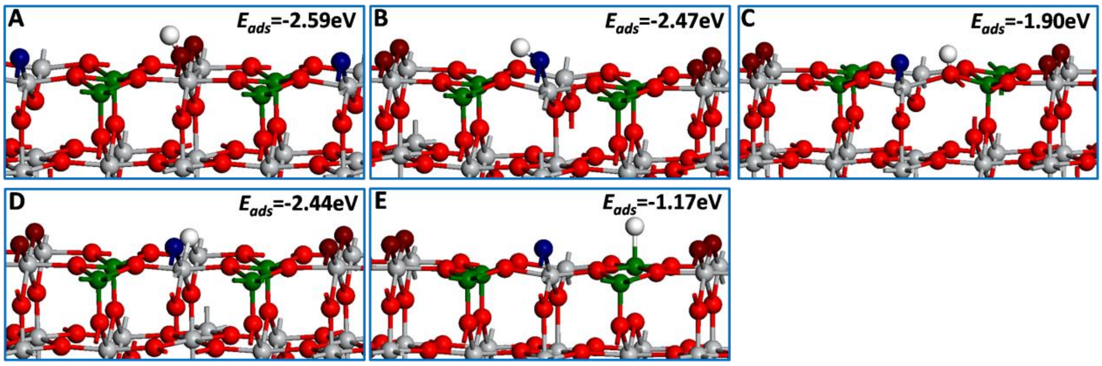

**Fig. S10** Optimized structures and adsorption energies of atomic H adsorption on various sites of a rutile $TiO_2$(110) (2×2) supercell with one bridging bonding oxygen (BBO) vacancy: **(A)** H adatom on BBO away from BBO vacancy; **(B)** H adatom on BBO next to BBO vacancy; **(C)** H adatom on oxygen 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.

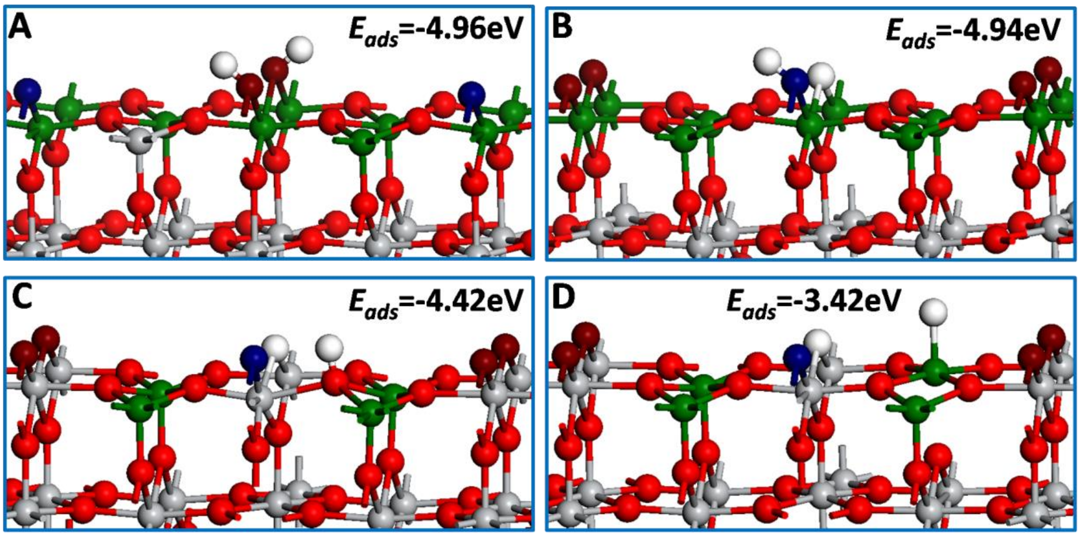

**Fig. S11** Optimized structures and adsorption energies of two atomic H coadsorption on various sites of a rutile $TiO_2$(110) (2×2) supercell with one bridging bonding oxygen (BBO) vacancy: **(A)** two H adatoms on two BBO sites away from BBO vacancy; **(B)** one H adatom on BBO next to BBO vacancy 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 ($O_{3c}$); **(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.