

Supporting Information

for

Enhanced Hydrogen Production from Methanol Photolysis on a Formate Modified Rutile-TiO₂(110) Surface

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TPD spectra for formate and acetate products on the 0.3 ML CD₃CDO covered R-TiO₂(110) after irradiating for different times TPD signals were collected at mass-to-charge ratios (m/z) of 28 (CO⁺) and 44 (D₂CCO⁺) after irradiating the 0.3 ML CD₃CDO covered TiO₂(110) surfaces for different irradiation times. The 260 K peak in the TPD spectra of $m/z = 28$ and 44 is due to the desorption of CD₃CDO. Bases on our previous works,¹ the 575 K peak in Figure S1A is assigned to CO desorption produced from the decomposition of formate. And the 600 K peak in Figure S1B is assigned to ketone desorption produced from acetate decomposition. The intensity of CO signal is about 20 times bigger than that of ketone, indicating that photoinduced decomposition of CD₃CDO on R-TiO₂(110) mainly produces DCOO⁻. The different ratios of the formate and acetate formation channels from CH₃CHO and CD₃CDO may be attributed to the isotopic effect. By controlling laser irradiation time, the DCOO⁻ pre-covered R-TiO₂(110) surfaces with different DCOO⁻ coverages could be prepared.

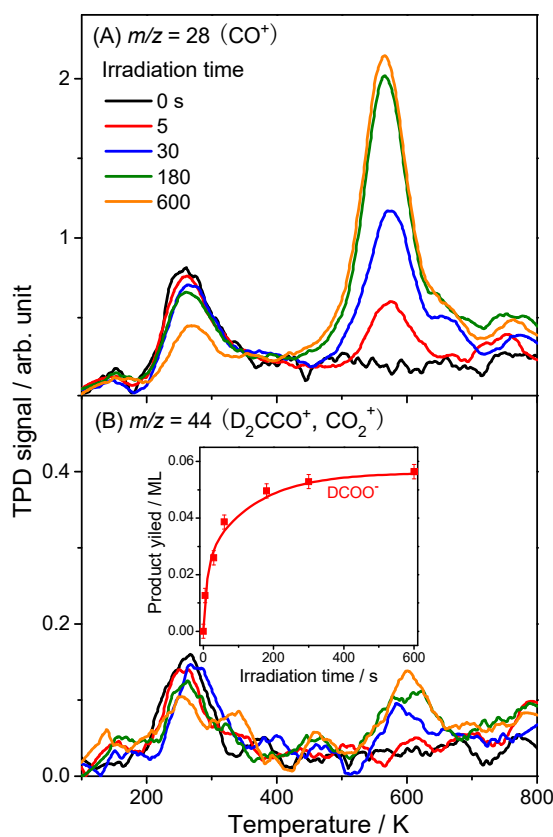


Figure S1. TPD spectra acquired at $m/z = 28$ (CO⁺), 44 (D₂CCO⁺) after adsorbing 0.3 ML CD₃CDO at 120 K on the R-TiO₂(110) surface followed by irradiation for different times. The inset shows the yields of formate (DCOO⁻) product as a function of irradiation time.

TPD spectra collected at $m/z = 20$ and $m/z = 4$ on the 0.3 ML CD_3CDO covered R- $\text{TiO}_2(110)$ after irradiating for different times TPD signals were collected at mass-to-charge ratios (m/z) of 20 (D_2O^+) and 4 (D_2^+) after irradiating the 0.3 ML CD_3CDO covered $\text{TiO}_2(110)$ surfaces for different times. As shown in Figure S2A, three main features are observed in the spectra. The peak (marked with *) centered at 260 K is attributed to the cracking of desorbed CD_3CDO molecules on Ti_{5c} sites in the electron-impact ionizer. A new peak observed at about 450 K comes from the thermal recombination desorption of D_2O by the D atoms on BBO sites produced from CD_3CDO decomposition to acetate.¹ The peak centered at 600 K is attributed to the DCOO^- decomposition to produce CO and D_2O .² Two features are observed in Figure S2B. The peak marked with * is the cracking of parent molecular CD_3CDO , which is depleted during irradiation by CD_3OD photocatalysis. The peak at 500 K is the molecular D_2 formed via thermal recombination desorption of D atoms on BBO sites.³

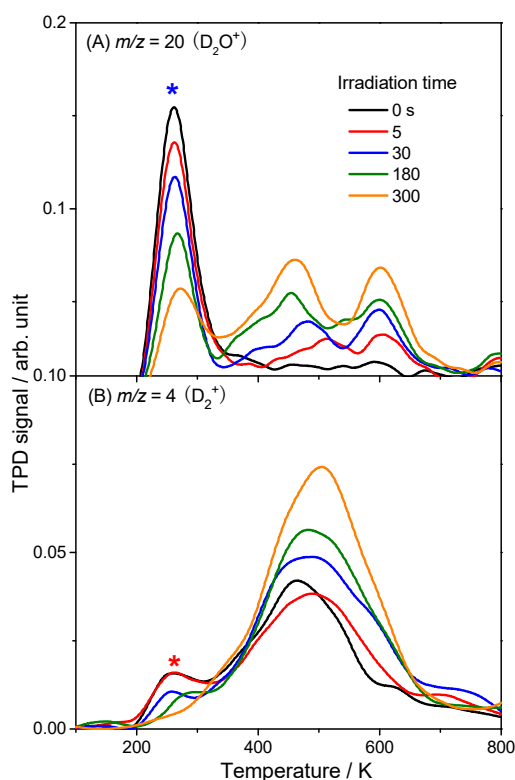


Figure S2. TPD spectra acquired at $m/z = 20$ (D_2O^+) and 4 (D_2^+) after adsorbing 0.3 ML CD_3CDO at 120 K on the R- $\text{TiO}_2(110)$ surfaces follow by irradiation for different times.

TPD spectra collected at $m/z = 28$ on the 0.05 ML DCOO⁻ pre-covered R-TiO₂(110) surfaces with 0.5 ML CD₃OD adsorption as a function of irradiation time. TPD signals were collected at mass-to-charge ratios (m/z) of 28 (CO⁺) on the 0.05 ML DCOO⁻ modified R-TiO₂(110) surfaces with 0.5 ML CD₃OD coadsorption as a function of irradiation time. The 0.05 ML DCOO⁻ modified R-TiO₂(110) surfaces were prepared by irradiating the 0.3 ML CD₃CDO adsorbed R-TiO₂(110) surfaces for 180 s at 120 K followed by flashing to 400 K to remove CD₃CDO molecules. The inlet shows the yield of products CO as a function of irradiation time. With increasing irradiation time, the CO peak at 575 K from DCOO⁻ decomposition gradually shifts to lower temperature and becomes broader, which may be induced by the BBO_v sites formed by recombinative D₂O desorption during the TPD process. However, the area of the CO peak nearly keeps the same for different irradiation times, indicating that the amount of DCOO⁻ species does not depleted upon irradiation.

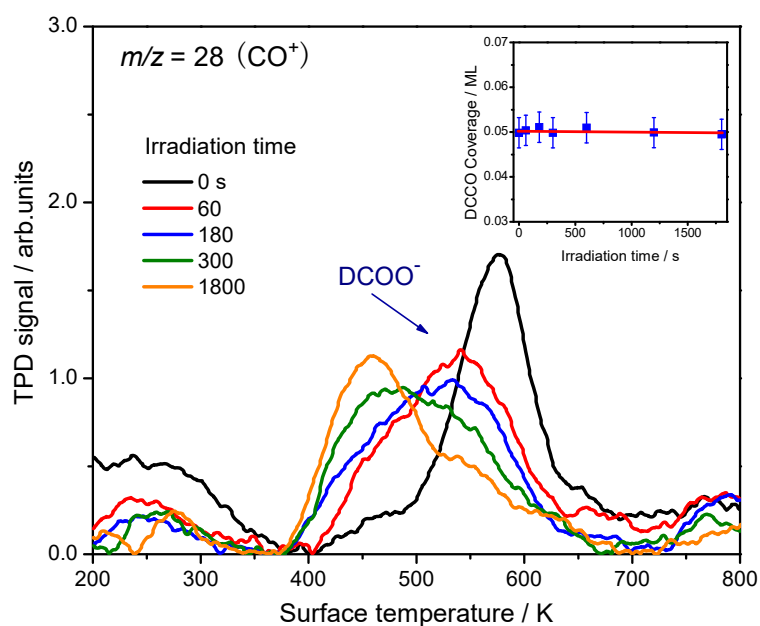


Figure S3. TPD spectra collected at $m/z = 28$ (CO⁺) on the 0.05 ML DCOO⁻ pre-covered R-TiO₂(110) surfaces with 0.5 ML CD₃OD adsorption as a function of irradiation time. The inlet shows the yield of products CO as a function of irradiation time.

H₂ formation pathway For the model with one BBOv and two H_{BBO} atoms adsorbed on the surface, the H atom transferring from the BBO site (S4-1) to the BBOv site (S4-3) is endothermic by 0.48 eV, with a barrier of 1.93 eV (TSS4-2). Then the other H atom transferring from the BBO site (S4-3) to the adjacent BBO site (S4-5) is exothermic by -0.09 eV, with a barrier of 1.03 eV (TSS4-4). The barrier for BBO-H and BBOv-H atoms to produce H₂ (TSS4-6) is 0.77 eV. The H₂ desorption energy is 0.35 eV. The rate-determining step is the transfer of H atom from the BBO site to the BBOv site with an overall barrier of 1.93 eV.

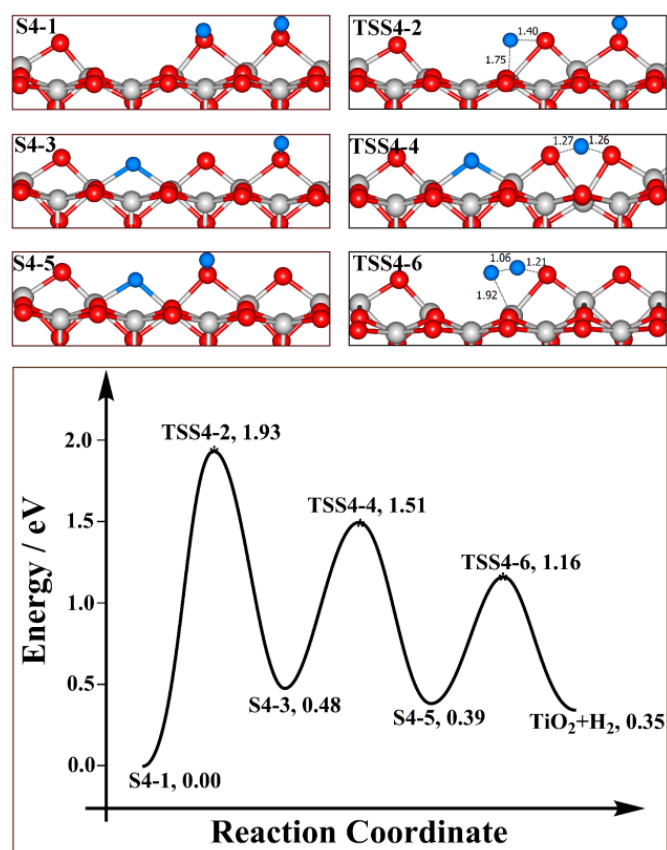


Figure S4. Reaction profiles for H₂ formation on the model where one BBOv and two H_{BBO} atoms adsorb on the surface. The side views of selected intermediates and transition states are shown in the figure with simplified schematic diagrams.

For the model with one BBOv and three H_{BBO} atoms adsorbed on the surface, the H atom transferring from the BBO site (S5-1) to the BBOv site (S5-3) is endothermic by 0.30 eV, with a barrier of 1.82 eV (TSS5-2). The other H atom transferring from the BBO site (S5-3) to adjacent BBO site (S5-5) is exothermic by -0.03 eV, with a barrier of 1.02 eV (TSS5-4). The barrier for BBO-H and BBOv-H atoms to produce H₂ (TSS5-6) is 0.77 eV. The H₂ desorption energy is 0.17 eV. The rate-determining step is the transfer of H atom from the BBO site to the BBOv site with an overall barrier of 1.82 eV.

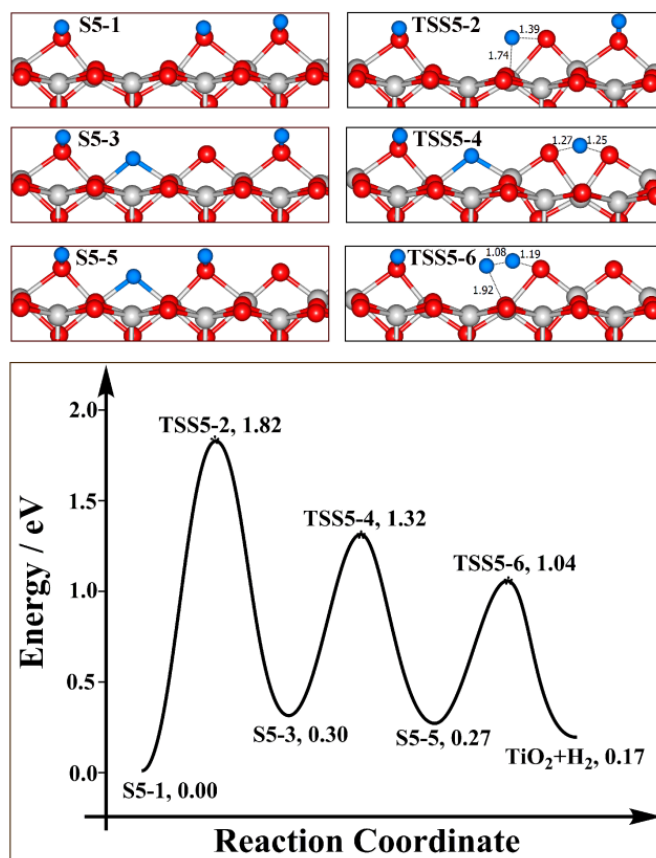


Figure S5. Reaction profiles for H₂ formation on the model with one BBOv where one BBOv and three H_{BBO} atoms adsorb on the surface. The side views of selected intermediates and transition states are shown in the figure with simplified schematic diagrams.

References

- (S1) Xu, C. B.; Yang, W. S.; Guo, Q.; Dai, D. X.; Yang, X. M. Photoinduced Decomposition of Acetaldehyde on a Reduced TiO₂(110) Surface: Involvement of Lattice Oxygen. *Phys. Chem. Chem. Phys.* **2016**, *18*, 30982-30989.
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- (S3) Xu, C. B.; Yang, W. S.; Guo, Q.; Dai, D. X.; Chen, M. D.; Yang, X. M. Molecular Hydrogen Formation from Photocatalysis of Methanol on TiO₂(110). *J. Am. Chem. Soc.* **2013**, *135*, 10206-10209.