Supporting Information

Edge sites on TiO_2 as aKey Type of Photocatalytically Active Site

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EXPERIMENTAL SECTION

Experimental section. The experiments were performed in a stainless-steel ultrahigh vacuum (UHV) system equipped with differentially-pumped thermal desorption spectroscopy (TPD), low energy electron diffraction (LEED), X-ray photoelectron spectroscopy (XPS), and ultraviolet photoelectron spectroscopy (UPS). The base pressure for the sample chamber is 1-2×10^{-10} Torr. A rutile $TiO_2(110)$ single crystal (8 mm × 8 mm × 1 mm) purchased from MaTeck was mounted onto a Ta support plate (8 mm × 8 mm × 1 mm) by a mixture of high-temperature alumina-based inorganic adhesive (Aremco 503) and graphite powder (99.9995%, Alfa Aesar China Co., Ltd.). Via two Ta wires spot-welded to its backside, the sample was resistively heated and cooled. The temperature was controlled and measured between 110 and 1273 K by a chromel-alumel thermocouple spot-welded to the backside of the sample plate. The rutile $TiO_2(110)$ surface was first cleaned by repeated cycles of Ar ion sputtering at 1 kV for 10 min, annealing in oxygen at 750 K for 10 min, and vacuum annealing at 1000 K for 10 min until XPS detected no contaminants other than argon. The rutile $TiO_2(110)$ surface was further cleaned before experiments by repeated cycles of annealing in oxygen at 700 K for 30 min and vacuum annealing at 1000 K for 10 min until XPS did not detect the contaminants of argon.CO (>99.99%), CO_2 (>99.999%), and O_2 (>99.999%), purchased from Nanjing ShangYuan Industry Factory, were used as received and were checked their purities by QMS before experiments. All exposures in the experiments were reported in Langmuir ($1\ L = 1.0 \times 10^{-6}$ Torr·s) without corrections for the gauge sensitivity. During TPD measurements, the TiO_2 sample was positioned ~1 mm away from a collecting tube of a differential-pumped QMS and the heating rate is 2 K/s. XPS spectra were recorded by using Mg Kα radiation (hν = 1253.6 eV) with a pass energy of 20 eV. The Ti 2p XPS spectra were peak-fitted with the XPSPEAK software (Version 4.1) using a Shirley-type background.

Hg irradiation was accomplished by using a 100 W high-pressure Hg arc lamp (Oriel 6281), which provides a pressure-broadened emission spectrum in the UV light region from gaseous Hg. The light irradiance of this source is found to be decreased rapidly and is only 0.05 mW/m^2 for the 200 nm light at a distance of 0.5 m when the light wavelength is below 250 nm. Thus the light absorption by methanol/TiO_2 in the UV light region below 200 nm can be neglected under our experimental condition. The IR portion of the emission spectrum was removed by a water filter. The Hg light was focused onto the tip of a single strand, 0.6 mm diameter fused silica fiber-optic cable directed the light through UHV-compatible feedthrough onto the rutile $TiO_2(110)$ surface without exposure to extraneous surfaces. The Hg light resulted in the rising of crystal temperature no more than 0.5 K on $TiO_2(110)$ at 110 K.

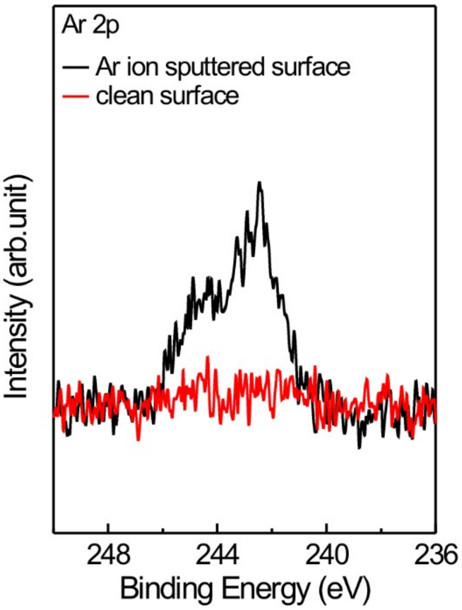

Figure S1. Ar 2p XPS spectra of argon ion sputtered and clean $TiO_2(110)$ surfaces, proving the residual argon was introduced into $TiO_2(110)$ surface after argon-ion bombardment.

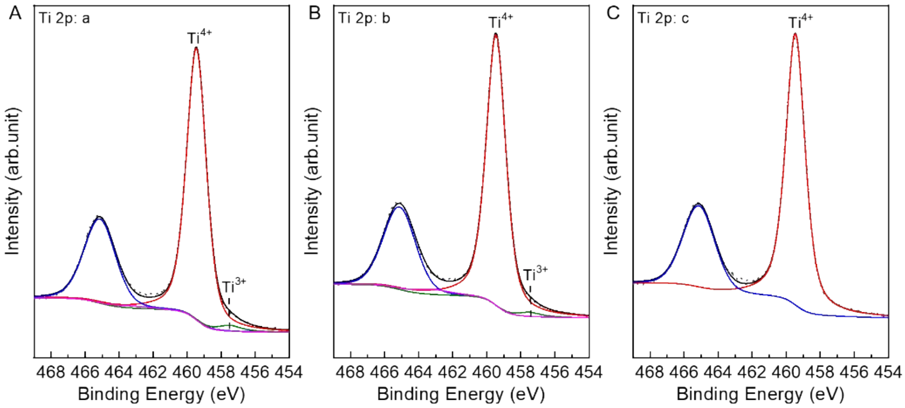

Figure S2. Peak-fitted Ti 2p XPS spectra of r-TiO_2(110)-1000 K, r-TiO_2(110)-800 K, and o-TiO_2(110) surfaces. The Ti^{3+} feature is shown in the Ti 2p XPS spectra of r-TiO_2(110)-1000 K and r-TiO_2(110)-800 K surfaces. Meanwhile, the o-TiO_2(110) surface does not exhibit the Ti^{3+} feature.

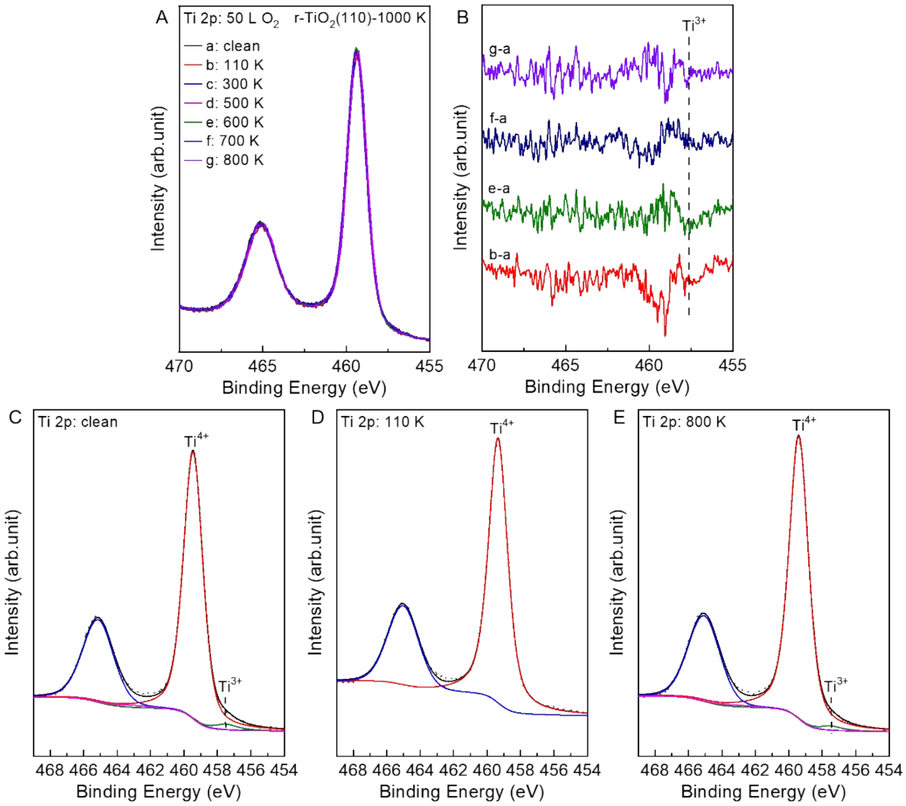

Figure S3. (A) Ti 2p XPS spectra, (B) corresponding difference spectra and (C-E) Peak-fitted Ti 2p XPS spectra after an exposure of 50 L of O_2 on the r-TiO_2(110)-1000 K surface at 110 K followed by annealing at elevated temperatures. In the difference spectra, the negative peak results from the reduction of Ti^{4+} 2p and Ti^{3+} 2p components after an exposure of 50 L of O_2 on the r-TiO_2(110)-1000 K surface at 110 K. The negative Ti^{3+} shoulder feature does not vary upon annealing up to 600 K, and then decreases upon annealing at 700 K and further at 800 K, arising from regeneration of Ti^{3+} by high-temperature annealing. In the peak-fitted spectra, the Ti^{3+} feature disappeared after an exposure of 50 L of O_2 on the r-TiO_2(110)-1000 K surface at 110 K while we observed the Ti^{3+} feature again on the surface followed by annealing at 800 K.

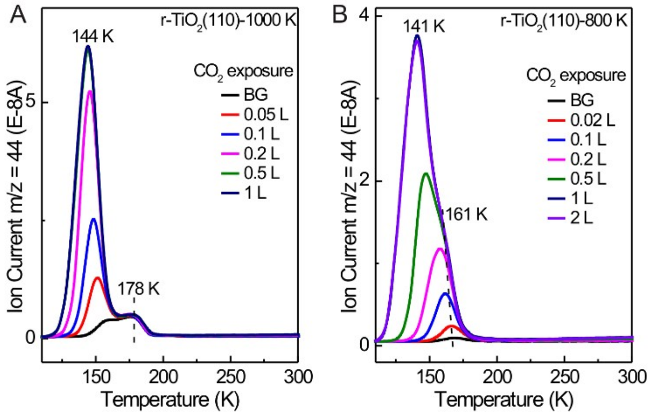

Figure S4. TPD spectra of (A) r-TiO_2(110)-1000 K and (B) r-TiO_2(110)-800 K surfaces with various CO_2 coverages at 110 K.

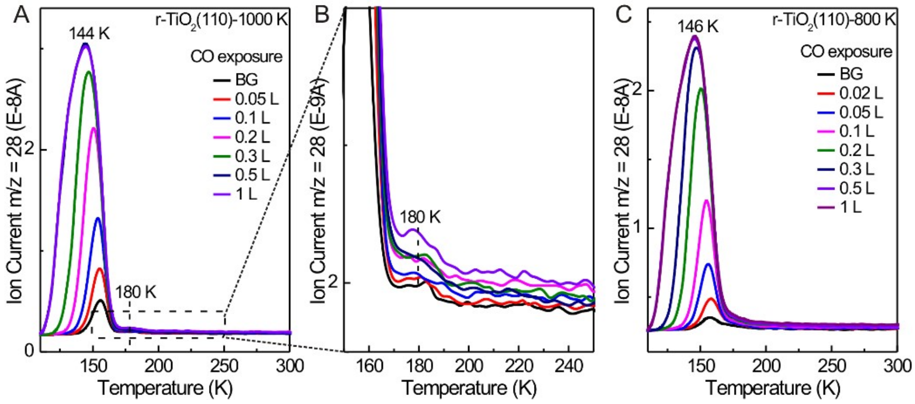

Figure S5. (A) Normal and (B) amplifying TPD spectra of r-TiO$_2$(110)-1000 K surface, and TPD spectra of (C) r-TiO$_2$(110)-800 K surface with various CO coverages at 110 K.

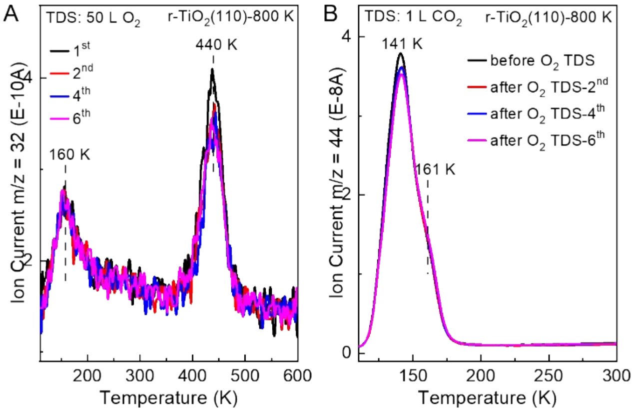

Figure S6. (A) O_2 TPD spectra of r-TiO_2(110)-800 K surface with repeated exposures of 50 L O_2 at 110 K. (B) CO_2 TPD spectra of r-TiO_2(110)-800 K surface exposed to saturated CO_2 before and after O_2 TPD experiments at 110 K.

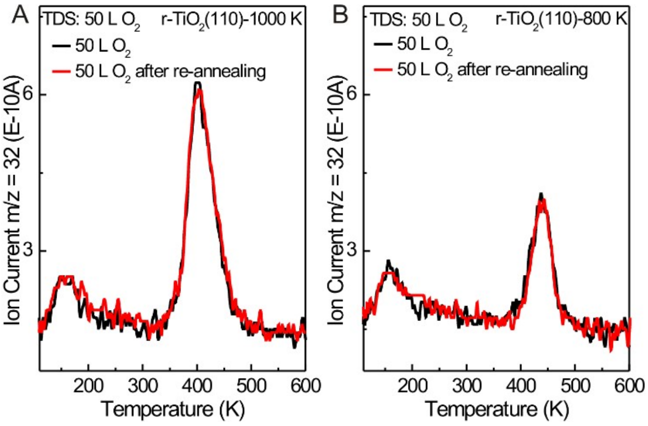

Figure S7. TPD spectra of (A) r-TiO_2(110)-1000 K and (B) r-TiO_2(110)-800 K surfaces exposed to 50 L O_2 at 110 K after a re-annealing of the surface, proving the reproducibility of our method used to prepare both r-TiO_2(110)-1000 K and r-TiO_2(110)-800 K surfaces.

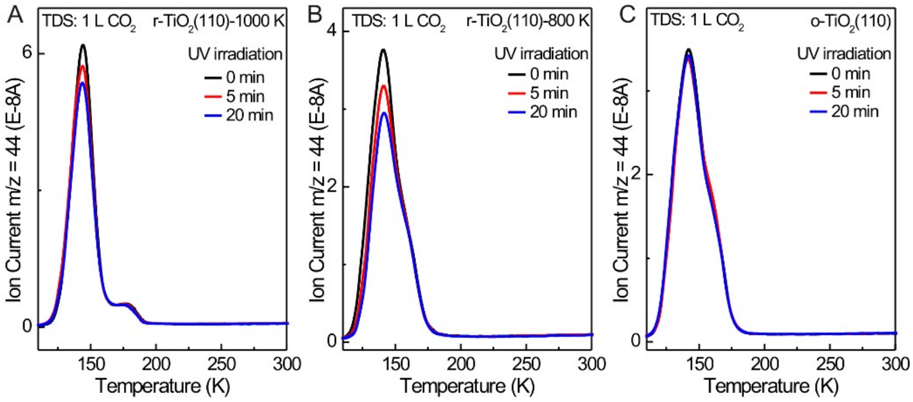

Figure S8. TPD spectra of (A) r-TiO_2(110)-1000 K, (B) r-TiO_2(110)-800 K, and (C) o-TiO_2(110) surfaces exposed to 1 L CO_2 with UV light illumination for various times at 110 K.

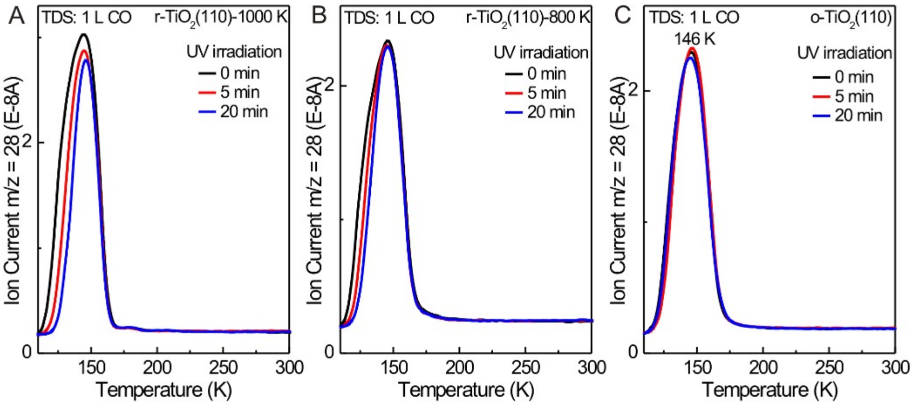

Figure S9. TPD spectra of (A) r-TiO$_2$(110)-1000 K, (B) r-TiO$_2$(110)-800 K, and (C) o-TiO$_2$(110) surfaces exposed to 1 L CO with UV light illumination for various times at 110 K.