

Electronic Supporting Information

Enhancing photocatalytic activity of defective titania for carbon dioxide photoreduction *via* surface-functionalization

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Experimental Section

CO₂ adsorption tests: Before the CO₂ adsorption tests, all samples were degassed at 120 °C for 12 h. The adsorption volume of CO₂ is set as 0.1% CO₂ versus 1 mL of standard gas, which corresponds to approximately 0.3 MPa in the digital pressure gauge. The competitive adsorption tests of CO₂ and H₂O were carried out in a homemade reactor. First, the to-be-tested sample was degassed at room temperature under vacuum for 30 min. At the end of degassing, 1 mL of the CO₂ standard gas was injected into the homemade reactor. Then 5 mL of H₂O was injected into the reactor to achieve solubility equilibrium for 1 h. Finally, the gas mixture of CO₂ and H₂O was monitored in the container. After 1 h of adsorption equilibrium, the gas mixture was extracted and quantified by gas chromatography.

Characterization: The photocatalytic decomposition of water to yield hydrogen was analyzed by gas phase chromatograph (GC-2018C; SHIMADZU, China) equipped with a thermal conductivity detector (TCD).

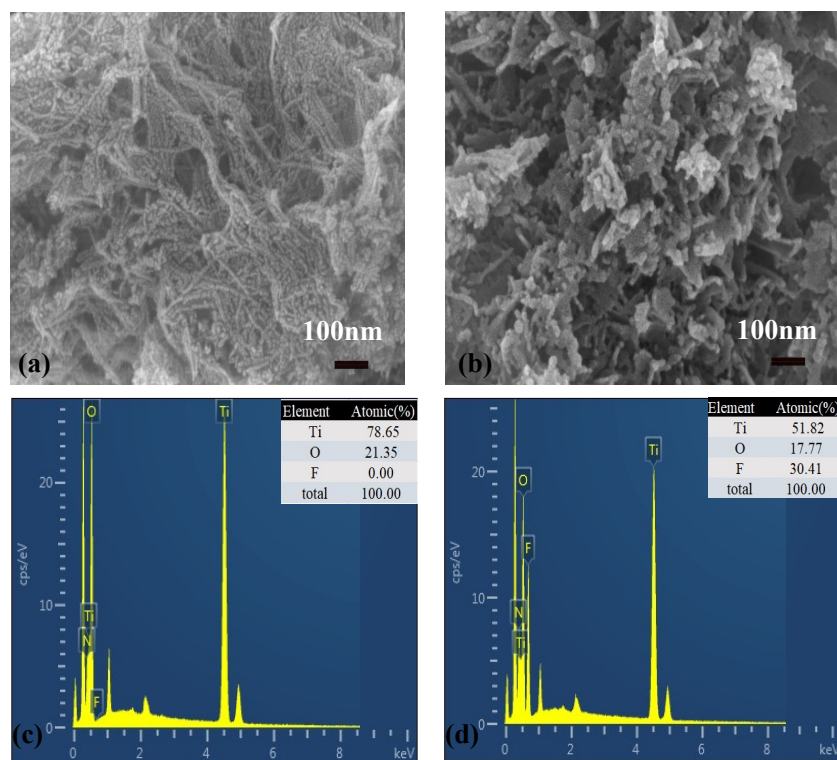


Fig. S1 SEM and EDS images of (a, c) TiO₂-SBO, (b, d) F-TiO₂-SBO-3.

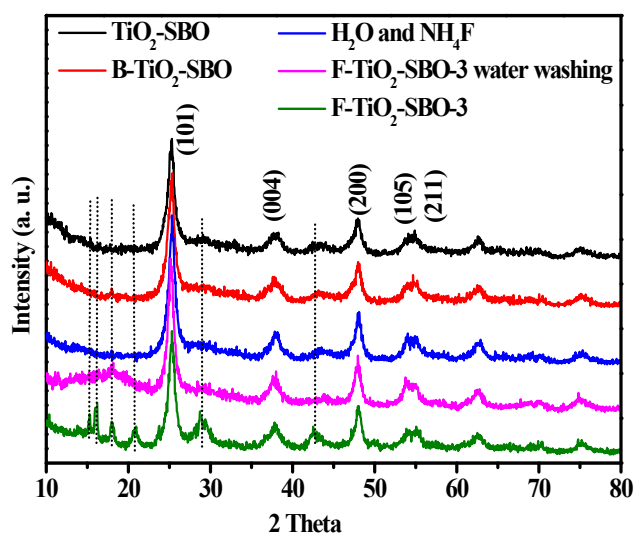


Fig. S2 XRD patterns of the prepared samples.

In order to prove that TiO₂-SBO has new XRD impurity peaks after fluorination, we conducted the comparative experiments. The B-TiO₂-SBO sample was prepared in the same way as F-TiO₂-SBO-3, except that only IPA was added and without NH₄F

during the preparation process; The preparation process of the water and NH_4F sample was the same as that of F-TiO₂-SBO-3, but the H₂O replaces IPA solvent; The F-TiO₂-SBO-3 water washing catalyst was washed with distilled water for several times; In Fig. S2, two new XRD diffraction peaks of 17.98° and 42.57° were appeared on the sample of B-TiO₂-SBO, and this indicated that the adsorption of IPA solvent on the surface of the catalyst, which was difficult to completely remove, would affect the XRD diffraction peaks on TiO₂-SBO. No new diffraction peaks appeared when the water aqueous was the solvent. However, the co-existence of IPA and NH_4F would appeared XRD peak signals at 15.19°, 16.06°, 17.98°, 21.05°, 28.65°, 42.57° and the as-washed sample showed no changes in the crystal structure of the defective TiO₂. In other words, the new XRD peaks should be derived from the residual NH_4F and IPA that can hardly be completely removed by washing with water, and the dispersion of non-metal elements was not incompletely uniform, which contributed to small changes in the crystal of defective TiO₂.

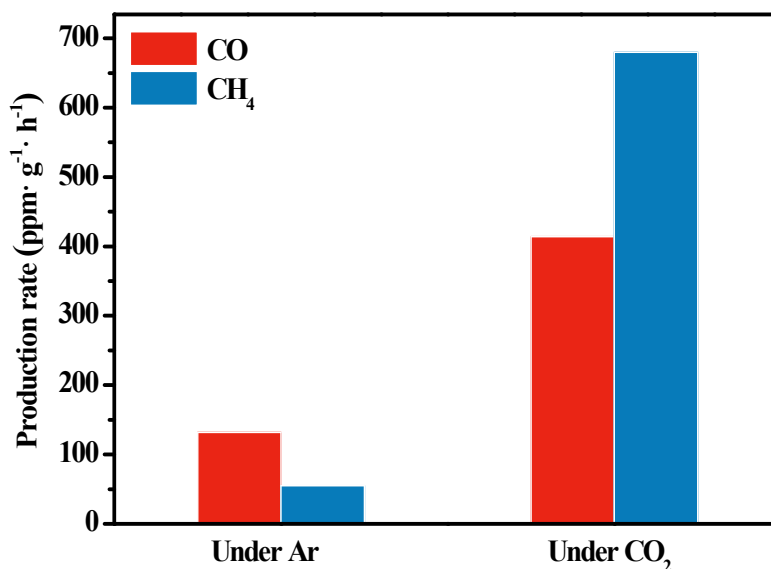


Fig. S3 Photocatalytic reduction of CO₂ under Ar and CO₂.



Fig. S4 The optical diagram of $\text{TiO}_2\text{-SBO}$ and $\text{F-TiO}_2\text{-SBO-3}$ samples dispersed in water.

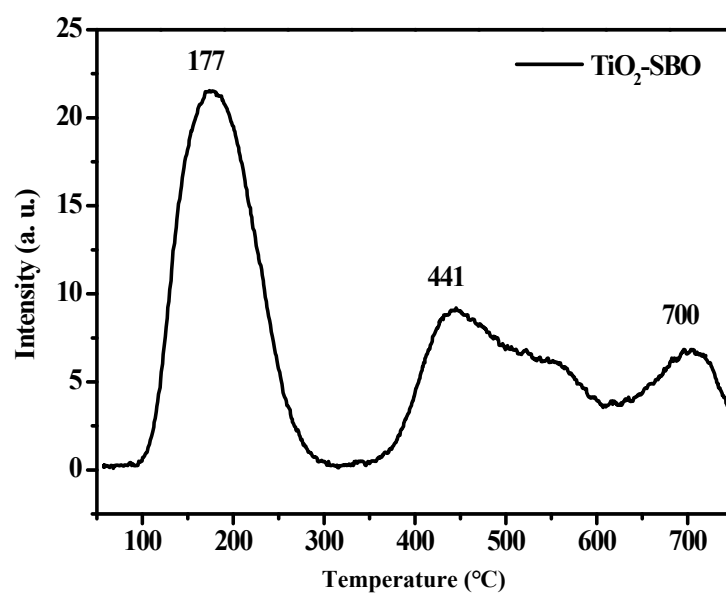


Fig. S5 CO_2 -TPD diagram of $\text{TiO}_2\text{-SBO}$.

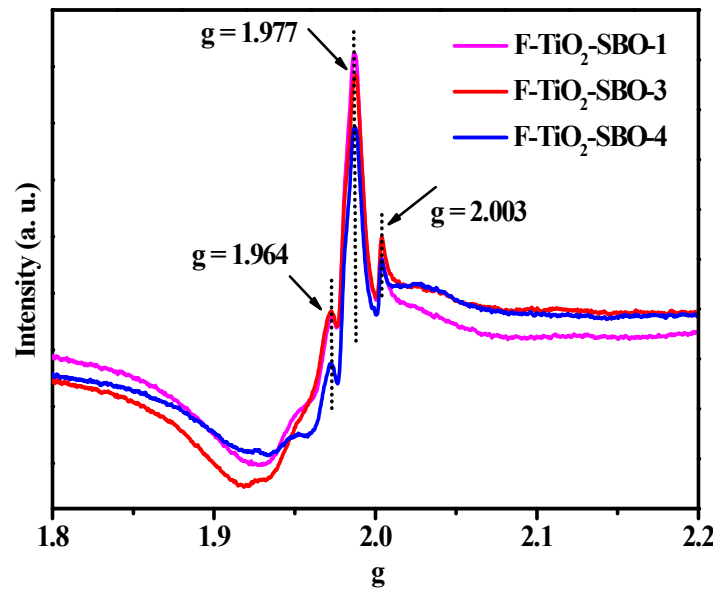


Fig. S6 ESR spectra of the TiO₂-SBO-1, F-TiO₂-SBO-3 and F-TiO₂-SBO-4.

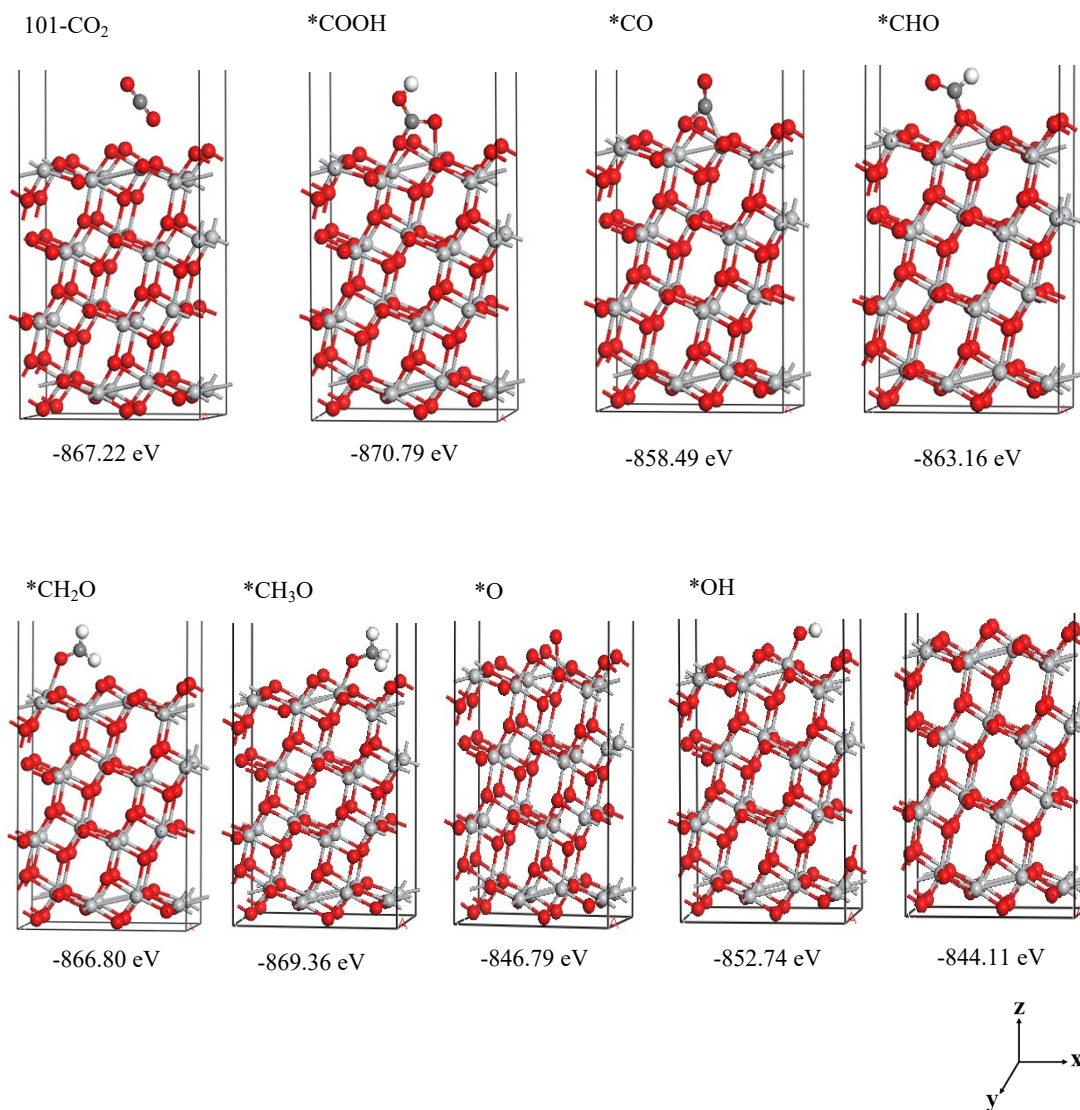


Fig. S7 Geometries of intermediates of CO₂ reduction on clean anatase (101). Red, gray, dark gray, white are O atoms, Ti atoms, C atoms and H atoms. (*) represents surface.

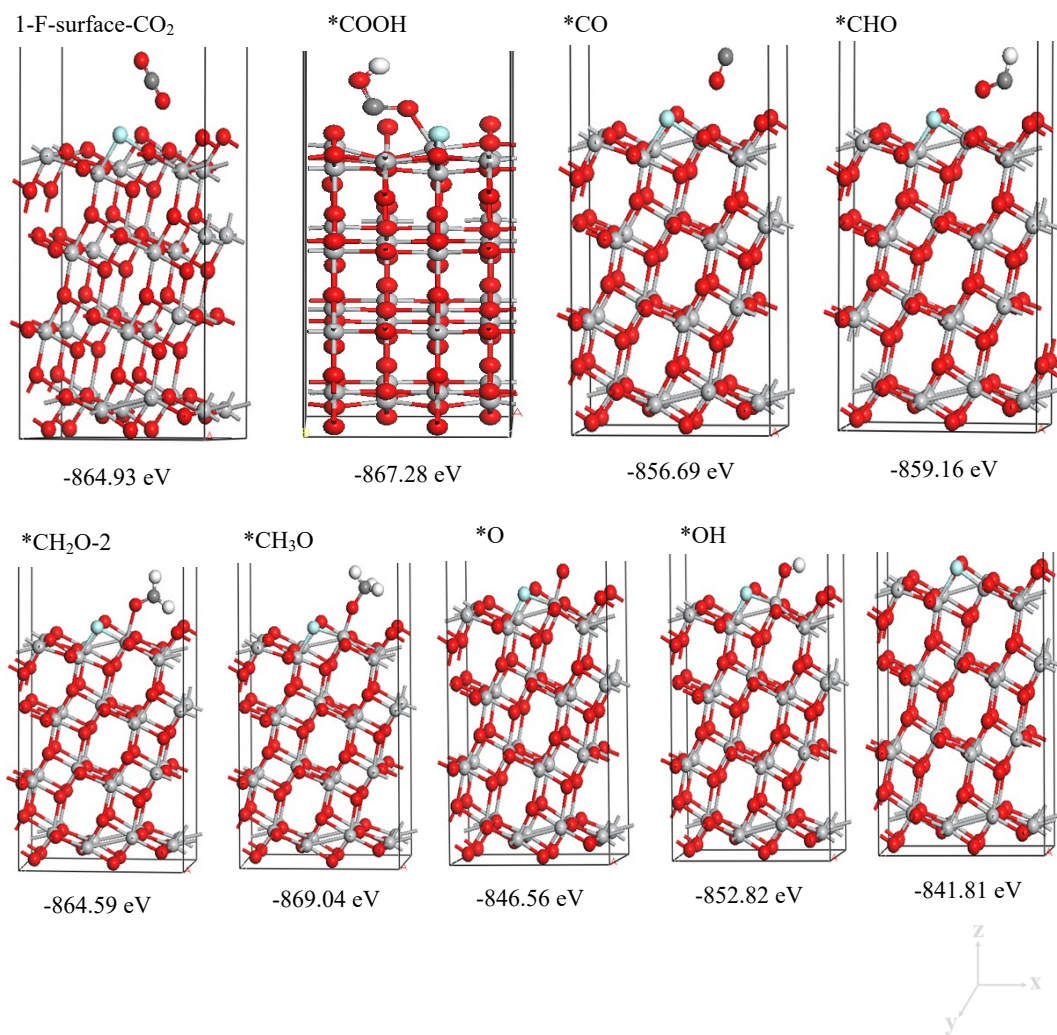


Fig. S8 Geometries of intermediates of CO₂ reduction on F doped anatase (101). Red, gray, dark gray, white, wathet are O atoms, Ti atoms, C atoms, H atoms and F atoms. (*) represents surface.

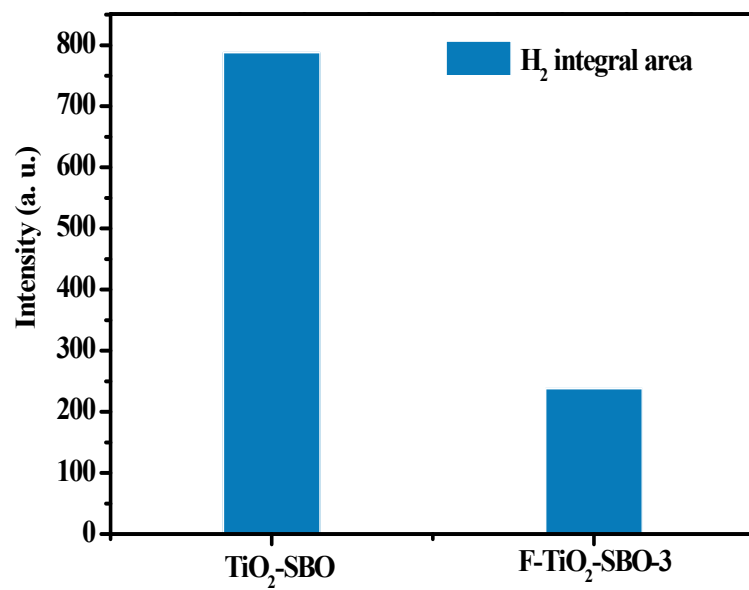


Fig. S9 H₂ integral area of TiO₂-SBO and F-TiO₂-SBO-3.