1 *Supporting Information for*

2 The bifunctional Lewis acid site improved
3 reactive oxygen species production: a detailed
4 study of surface acid site modulation of TiO$_2$ by
5 ethanol and Br$^-$

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10 Yi Zheng and Junqing Shi are co-first authors of the article.

11 **EXPERIMENTAL SECTION**

12 Photocatalyst Preparation

13 1.2 mL HF (40%) was dropwise added to 10 mL tetrabutyl titanate, stirred for 30 mins, ang then the

14 mixture was transferred to PTFE liner and heat at 180°C for 24 h. After washing with deionized water

15 and ethanol three times and drying at 60°C for 12 h, the specimen was gotten, noted as F-TiO$_2$.

16 0.017 g NH$_4$X (X is Cl, Br, I) and 0.05 g F-TiO$_2$ were added into 50 mL ethanol, stirred 24 h. After

17 washing with deionized water and ethanol, and drying at 60°C for 6 h, SAS regulated TiO$_2$ was obtained,

18 marked as F-TiO$_2$ (EC), F-TiO$_2$ (EB) and F-TiO$_2$ (EI). The amount of NH$_4$Br, ethanol and water were

1 also adjusted respectively, the short name of corresponding specimens and experimental condition were

2 listed at Table S1.

3 Photocatalytic experiments

4 Select RhB, ENR and DIF as target degradation products for degradation. A 300W Xenon lamp was

5 used to simulate sunlight to evaluate the photocatalytic performance of the catalyst. Take 50 mL of RhB

6 solution with a concentration of 10 mg/L (both ENR and DIF concentrations are 25 mg/L), add 50 mg

7 of the prepared catalyst, and mix well with ultrasonic stirring. Stir in a dark environment for 30 minutes,

8 and after reaching the dark adsorption equilibrium, collect 2 mL of suspension for the same time under

9 light conditions, and test the absorbance with a UV-visible spectrophotometer after centrifugation to

10 detect the degradation degree of RhB (ENR, DIF). In the cycle experiment, the used photocatalyst was

11 separated by centrifugation, washed with deionized water, and continued to be used in subsequent

12 degradation experiments.

13 Characterization

14 The samples were characterised by X-ray diffraction (XRD) using monochromatic Cu Kα radiation

15 (Bruker D8 Venture). The microstructure and morphology of the photocatalysts were studied by high

16 resolution scanning electron microscopy (SEM, JSM-6700 F). High resolution transmission electron

17 microscopy (HRTEM) was examined by a JSM-6700 F electron microscope. Optical properties were

18 measured by UV-visible spectrophotometer (UV-2550, Shimadzu, Japan) with UV-visible diffuse

19 reflectance spectroscopy (DRS).PL spectra were recorded on a HITACHI F-4600. Room temperature

20 EPR spectra were recorded on a Bruker EMXplus. The separation properties of the photogenerated

21 charge carriers were tested by surface photovoltage spectroscopy (SPV), which consists of a

1 monochromatic light source with an optical chopper and a lock-in amplifier. FTIR was tested by Thermo

2 Scientific Nicolet iS5. Pyridine FTIR was recorded on a Tensor 27. O_2-TPD was performed on a

3 Micromeritics Autochem II 2920 instrument with TCD detector. The transient photovoltage (TPV) were

4 determined on a home-made system. Excited by a laser radiation pulse (355, with the pulse width of

5 5 ns) from a third harmonic Nd:YAG laser (Polaris II, New Wave Research, Inc.), the TPV signal of

6 sample was picked up by the electrode and passed through a preamplifier, and then was recorded with

7 a 500 MHz digital phosphor oscilloscope (TDS 5054, Tektronix).

8   For quantification, the acid content is calculated by using the peak area at different temperatures. The

9 formula is as follows:

10 Formula 1

11 $$Content_B = \frac{1.88 \times S_B \times 1.3 \times 1.3 \times 1000}{m \times 4}$$

12 Formula 2

13

14 $$Content_L = \frac{1.42 \times S_B \times 1.3 \times 1.3 \times 1000}{m \times 4}$$

sample &	condition		
short name	NH_4X (X=Cl, Br, I)	H_2O	CH_3CH_2OH
F-TiO$_2$ (H)	0.017 g	50 mL	0 mL
F-TiO$_2$ (1E 49H)	0.017 g	49 mL	1 mL
F-TiO$_2$ (E)	0.017 g	0 mL	50 mL
F-TiO$_2$ (E0.008B)	0.008 g	0 mL	50 mL

F-TiO$_2$ (EB)	0.017 g	0 mL	50 mL
F-TiO$_2$ (E0.034B)	0.034 g	0 mL	50 mL
F-TiO$_2$ (E0.3B)	0.3 g	0 mL	50 mL
F-TiO$_2$ (EC)	0.017 g	0 mL	50 mL
F-TiO$_2$ (EI)	0.017 g	0 mL	50 mL

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2 Table S1. The short name of corresponding specimens and experimental condition.
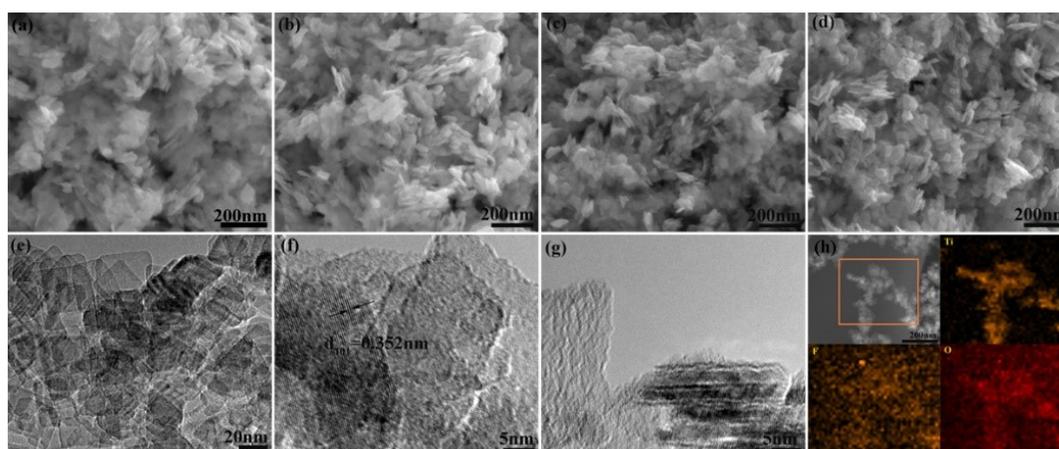
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4 Figure S1. F-TiO$_2$, F-TiO$_2$ (EC), F-TiO$_2$ (EB), and F-TiO$_2$ (EI) SEM images (a, b, c, d); F-TiO$_2$ (EB)

5 TEM image (e, f, g) and mapping diagram (h).

sample	absorption edge (nm)	$E_{(fb)}$ (V) (vs. NHE)	$E_{(CB)}$ (V) (vs. NHE)	$E_{(VB)}$ (V) (vs. NHE)	band gap (eV)
F-TiO$_2$	399	-0.388	-0.488	3.10	2.712
F-TiO$_2$ (EC)	397	-0.408	-0.508	3.12	2.712
F-TiO$_2$ (EB)	396	-0.428	-0.528	3.13	2.702

F-TiO$_2$ (EI)	393	-0.448	-0.548	3.15	2.702

1   Table S2. The band gap and structure data.

sample	S$_{BET}$ (m^2/g)
F-TiO$_2$	97.1752
F-TiO$_2$ (EC)	105.5049
F-TiO$_2$ (EB)	98.0903
F-TiO$_2$ (EI)	96.7741

2   Table S3. BET data of samples
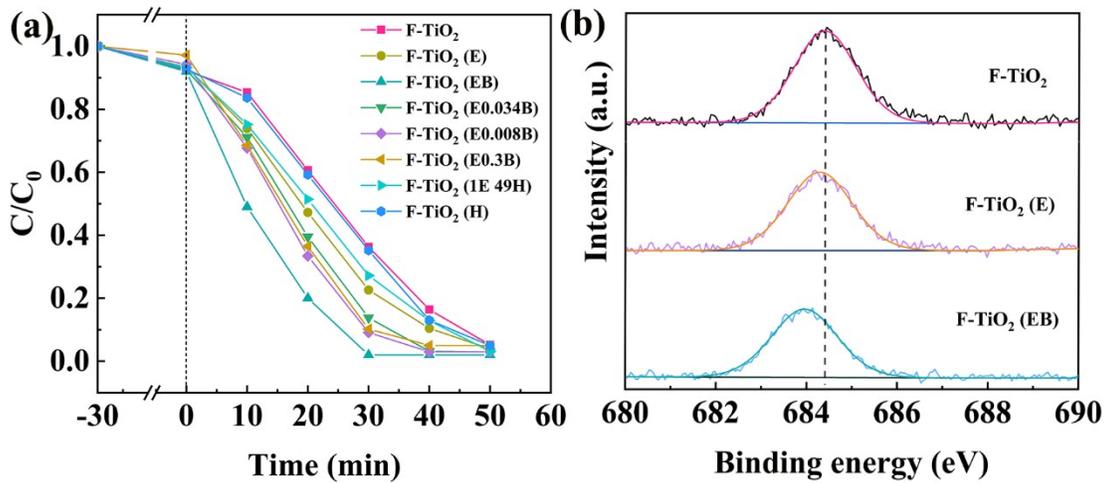
4   Figure S2. Diagram of the photocatalytic degradation of RhB by the sample (a), F1s xps high-

5   resolution maps of F-TiO$_2$, F-TiO$_2$ (E), F-TiO$_2$ (EB).

sample	Ti 2p(eV)	O 1s(eV)	F 1s(eV)	F/Ti (%)	Ti-OH/Ti-O
F-TiO$_2$	458.86	530.05	684.43	25.29	0.15
	464.57	531.80			
F-TiO$_2$ (EC)	458.83	530.01	684.38	22.59	0.17

	Ti 2p	O 1s	F 1s	F/Ti	Ti-OH/Ti-O
	464.51	531.74			
F-TiO$_2$ (EB)	458.81	529.95	684.27	19.90	0.19
	464.48	531.76			
F-TiO$_2$ (EI)	458.82	529.96	684.29	21.29	0.18
	464.55	531.74			

1 Table S4. Ti 2p peak position, O 1s peak position, F 1s peak position, F/Ti and Ti-OH/Ti-O data of F-

2 TiO$_2$, F-TiO$_2$ (EC), F-TiO$_2$ (EB), F-TiO$_2$ (EI).

3
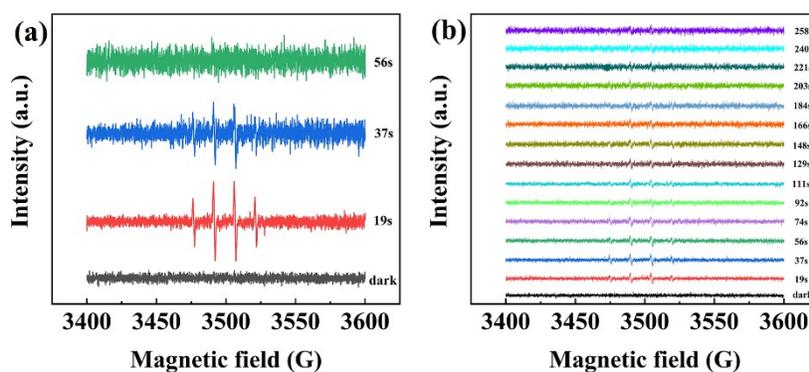
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5 Figure S3. Time-resolved EPR spectra of DMPO-·OH spin trapping of F-TiO$_2$ (a) and F-TiO$_2$ (EB) (b).
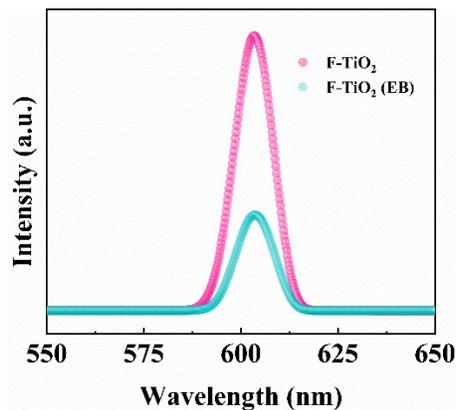
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7 Figure S4. PL diagram of F-TiO$_2$, F-TiO$_2$ (EB).
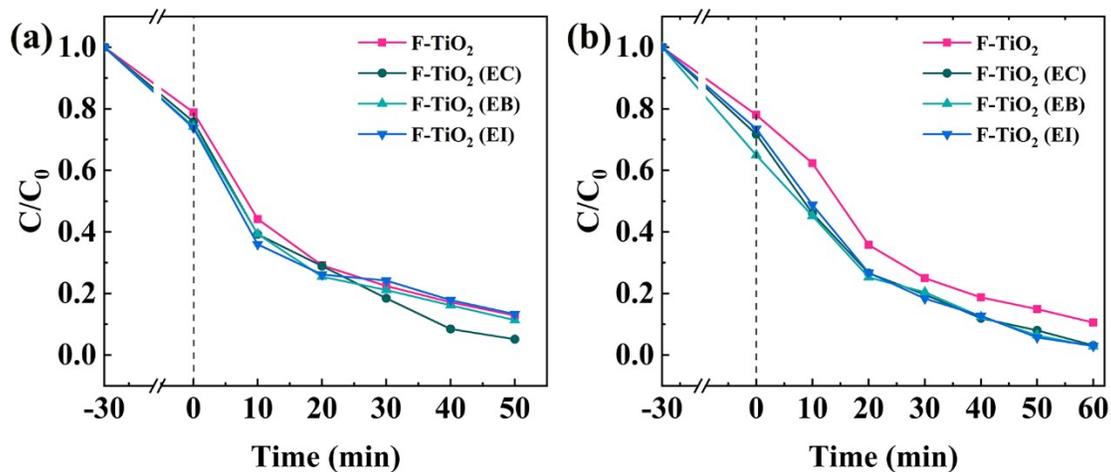
Figure S5. Photocatalytic degradation of DIF (a) and ENR (b) with F-TiO$_2$, F-TiO$_2$ (EC), F-TiO$_2$ (EB),

and F-TiO$_2$ (EI).
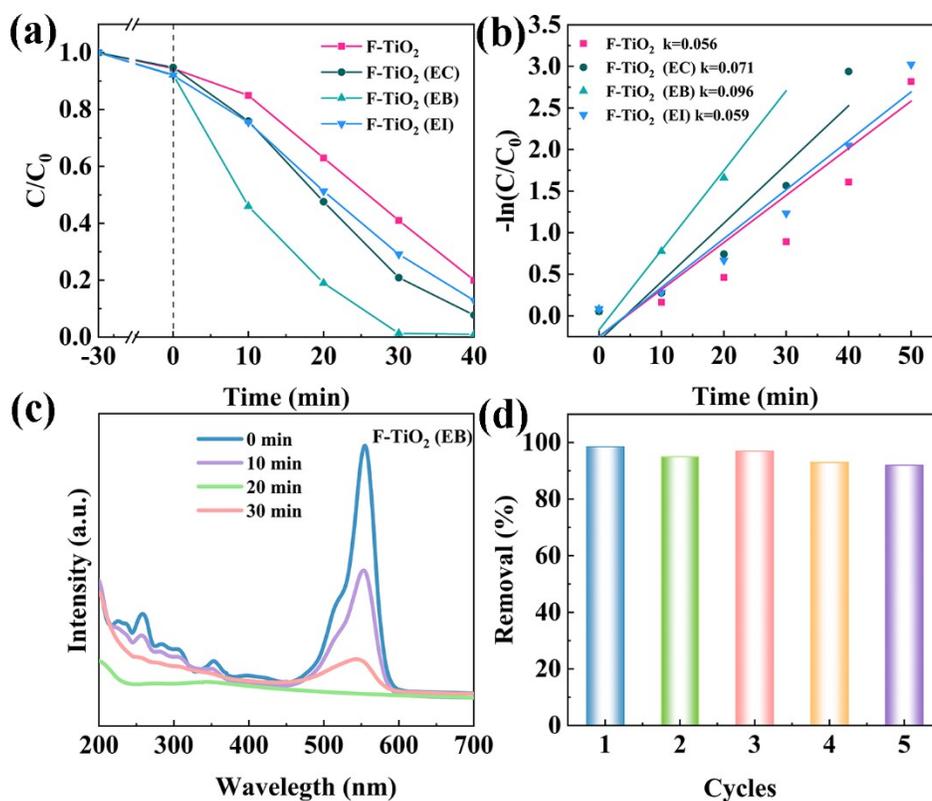
Figure S6. Photocatalytic degradation of RhB with prepared samples (a) and corresponding pseudo-

first-order kinetic curves of the prepared samples (b); RhB Photocatalytic degradation curve of F-TiO$_2$

(EB) (c); cycle experiment of F-TiO$_2$ (EB) for RhB photocatalytic degradation reaction.
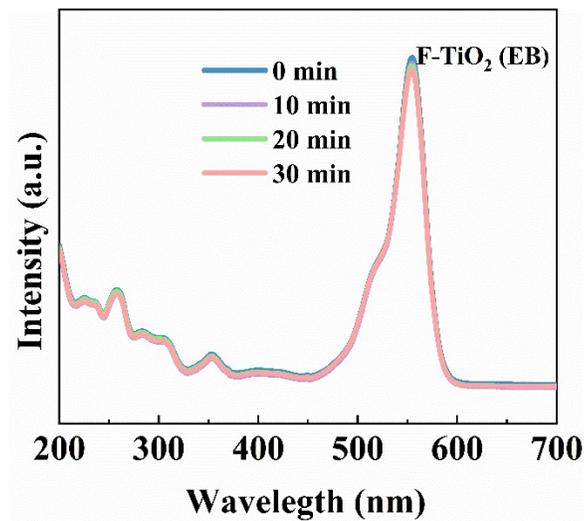
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2   Figure S7. Absorbance spectra of F-TiO$_2$ (EB) after degradation of RhB under 420 nm cut-off filter.
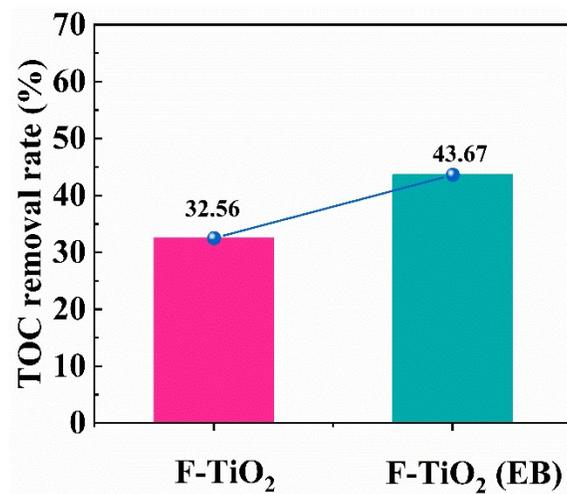
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4   Figure S8. TOC removal of RhB over the samples.

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