Supporting Information for

HF Promoted Increased Nitrogen Doping in TiO_2(B) photocatalyst

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Experimental

Materials

All reagents used are of analytical grade with further purification. Titanium (IV) n-butoxide ($C_{16}H_{36}O_4Ti$, 99%) was purchased from J&K Chemical Co., Ltd (Beijing, China). Acetic acid ($C_2H_4O_2$, ≥99.5%), ethylene glycol ($C_2H_6O_2$, ≥99.0%), ethanol (C_2H_6O, ≥99.7%), sodium hydroxide (NaOH, ≥96.0%), hydrochloric acid (HCl, 36.0~38.0%), and hexachloroplatinic (IV) acid ($H_2PtCl_6 \cdot 6H_2O$, ≥37.0%) were purchased from the Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Rhodamine B (RhB) (≥95%) was obtained from Sigma-Aldrich (USA). Hydrofluoric acid (HF, 50 wt%) was purchase from Macklin Inc. (Shanghai, China). 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) was purchase from Dojindo Molecular Technolgogies, Inc.(Shanghai, China). Deionized water was used in all experiments.

Preparation of catalyst

Preparation of TiO_2(B): TiO_2(B) was prepared according to the previous report.[15] Typically, sodiumtitanate was first prepared via a hydrothermal method. A 6 mL portion titanium(IV) n-butoxide and 3 mL acetic acid were added dropwise to 20 mL ethylene glycol and stirred for 15 min, followed by the addition of 30 mL NaOH solution (15mol/L) and stirring for another 10 min. Afterward, the suspension was transferred into a 100 mL Teflon-lined autoclave and maintained at 180 °C for 24 h. After cooling down to room temperature, the sodium titanate was added to a HCl solution (0.1 mol/L) with constant stirring for 12 h. Then, the resulted mixture was centrifuged and washed with deionized water until the filtrate became neutral. The hydrogen titanate nanowires were obtained after drying at 80 °C for 12 h. Finally, to convert the hydrogen titanate into TiO_2(B), the hydrogen titanate nanowires were annealed in a muffle at 400 °C for 2 h.

Preparation of N-doped TiO_2(B): Typically, 0.5 g as prepared TiO_2(B) was dispersed in a 5 mL aqueous solution containing certain amount of HF and water (5 mL H_2O without HF was used as reference). The resulting slurry sample was centrifuged after stirring for 1 h at room temperature and then dried at 60 °C for 8 h. After that, the samples were annealed in NH_3 at 500 °C for 3 h (purity of NH_3 gas is 99.999%). The obtained products were denoted as x%B-FN (the products annealed in air were named as x%B-F), where x refers to the mass percentage of HF in water. The samples and the corresponded preparation conditions are shown in Table S1. Schematic diagram of the two-step preparation process of TiO_2(B) with different amount of HF is shown in Fig. S2.

Material characterization

XRD patterns were obtained using a Rigaku MiniFlex 600 (Japan) diffractometer with Cu Kα radiation ($V = 40$ kV, $I = 15$mA) over the 10°–70° (2θ) range and with a 0.02° step size. X-ray photoelectron spectroscopy (XPS) measurements were carried out using an Axis Ultra DLD XPS instrument (Kratos Analytical Ltd.) with an Al Kα radiator, and analyzed using casaXPS. Binding energies for the high-resolution spectra were calibrated by setting C 1s to 284.6 eV. UV-Vis diffuse reflection spectra were recorded on a UV-3600 spectrophotometer (Shimadzu, Japan) in the 200–800 nm range. The surface morphologies of the photocatalysts were observed by field emission scanning electron microscopy (FESEM, SU 8020, HitachiHigh-Technologies, Tokyo, Japan) operating at 5 kV. Specific surface areas were obtained by acquiring N_2-adsorption isotherms at a relative pressure of 10^{-6} MPa at 77 K on a Micromeritics ASAP2020 HD88 instrument. All photocatalysts were degassed at 300 °C for 4 h before adsorption experiments. Electron paramagnetic resonance spectra (EPR) were recorded under ambiance at room temperature on a Bruker EPR spectrometer (E500-9.5/12). Superoxide radicals ($O_2\bullet^-$) and hydroxyl radicals (•OH) were detected by trapping with DMPO using methanol and water as solvent, respectively. The sample was detected under dark or under irradiation with a 300 W Xe lamp (CEL-HXF 300, Beijing China Education Au-Light Co., Ltd.). All EPR spectra were recorded under the same experimental conditions: microwave frequency, 9.42 GHz; center field, 3350.4 G; sweep width, 100 G; modulation frequency, 100 kHz; and power, 20.00 mW. Photoluminescence (PL) spectra were recorded on a Hitachi F-4600 fluorescence spectrophotometer with both excitation and emission slits set at 10 nm.

Photocurrent and electrochemical impedance spectroscopy (EIS) were performed on a CorrTest CS310 electrochemical workstation (Wuhan CorrTest Instrument Co. Ltd., China) in a three-electrode cell with Na_2SO_4 electrolyte (1.0 mol/L) at room temperature. The photocatalyst loaded thin film electrode, platinum sheet and saturated Ag/AgCl electrode were used as working electrode, counter electrode, and reference electrode, respectively. The working electrode was prepared by electrophoresis method on the surface of a FTO glass substrate (1 cm × 0.5 cm), followed by drying at 60 °C and annealing at 400 °C for 2 h in a muffle furnace. The photocurrent measurements (i−t curve) were carried out at 0.3 V (vs saturated Ag/AgCl electrode) under chopped illumination with a 300 W Xe lamp as the light source. The EIS data were obtained with a frequency range from 0.01 Hz to 100 kHz at 0.3 V (vs saturated Ag/AgCl electrode).

Photocatalytic Hydrogen Production.

Photocatalytic hydrogen evolution from water was carried out in a CEL-SPH2N photocatalytic activity evaluation system (Beijing China Education Au-Light Co., Ltd.)

at 15 °C, irradiated by a 300 W Xe lamp (PLS-SXE300C, Beijing China Perfectlight Co., Ltd.). Typically, to a 100 mL aqueous solution with 20 vol% of ethanol, 50 mg photocatalyst was dispersed and followed by addition of 0.1 wt % Pt as cocatalyst (in situ photoprecipitation). To ensure the reaction system under inert condition, the suspension was degassed with a mechanical pump for 10 min to completely remove the dissolved oxygen before illumination. A magnetic stirrer was located at the bottom of the reactor to maintain a good dispersion of the photocatalysts throughout the experiment. The evolved hydrogen was analyzed by gas chromatograph (GC) using a thermal conductivity detector (TCD) with argon as carrier gas.

Photocatalytic Degradation of RhB.

In a typical experiment, 50 mg as-prepared photocatalyst was added to a 150 mL RhB aqueous solution (4 mg/L) in the quartz photoreactor. The photocatalytic activity was evaluated under the irradiation of a 300 W Xe lamp (CEL-HXF 300, Beijing China Education Au-Light Co., Ltd.). Before irradiation, the mixture was stirred in the dark for 0.5 h to ensure the adsorption equilibrium and formation of a homogeneous suspension. The temperature of the reaction system was maintained at ~15 °C. During the reaction process, 2 mL reaction solution was taken out every 10 min and diluted to the same volume after the suspended photocatalyst was filtered off with a Millipore filter (pore size 0.22 μm). The solution was then analyzed on a TU-1900 UV−Vis spectrophotometer (Beijing Purkinje General Instrument. Co., Ltd.) within the range of 400−700 nm for monitoring the reaction process. Photocatalytic degradation of RhB can be approximated as the pseudo-first-order reaction when the initial concentration is relatively low. According to the Langmuir−Hinshelwood kinetic model, the reaction rate constant k (min^{-1}) can be obtained by the formula $\ln(C/C_0) = -kt$, where C and C_0 represent the RhB concentrations at time t and initial time. By the linearly fitted slope between $-\ln(C/C_0)$ and t, the value of k can be obtained.

Table S1. The samples and the corresponded preparation conditions

Samples	TiO_2(B) (g)	HF (mL)	H_2O (mL)	Annealed condition
B	0.5	0.00	5.00	AIR, 500 °C, 3 h
0.3%B-F	0.5	0.03	4.97	AIR, 500 °C, 3 h
3.0%B-F	0.5	0.30	4.70	AIR, 500 °C, 3 h
B-N	0.5	0.00	5.00	NH_3, 500 °C, 3 h
0.1%B-FN	0.5	0.01	4.99	NH_3, 500 °C, 3 h
0.3%B-FN	0.5	0.03	4.97	NH_3, 500 °C, 3 h
0.5%B-FN	0.5	0.05	4.95	NH_3, 500 °C, 3 h
1%B-FN	0.5	0.10	4.90	NH_3, 500 °C, 3 h
3%B-FN	0.5	0.30	4.70	NH_3, 500 °C, 3 h
5%B-FN	0.5	0.50	4.50	NH_3, 500 °C, 3 h

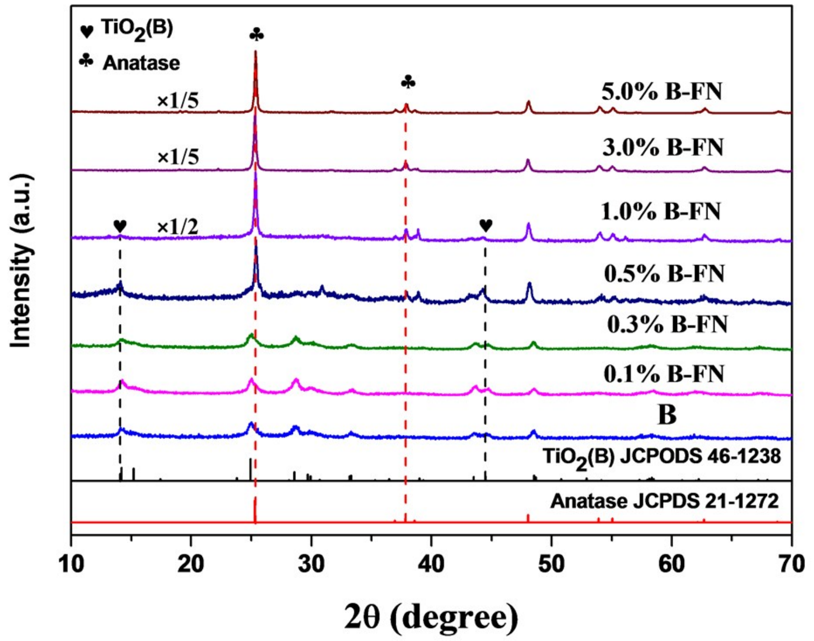

Fig. S1. XRD parttens of x%B-FN with different amount of HF.

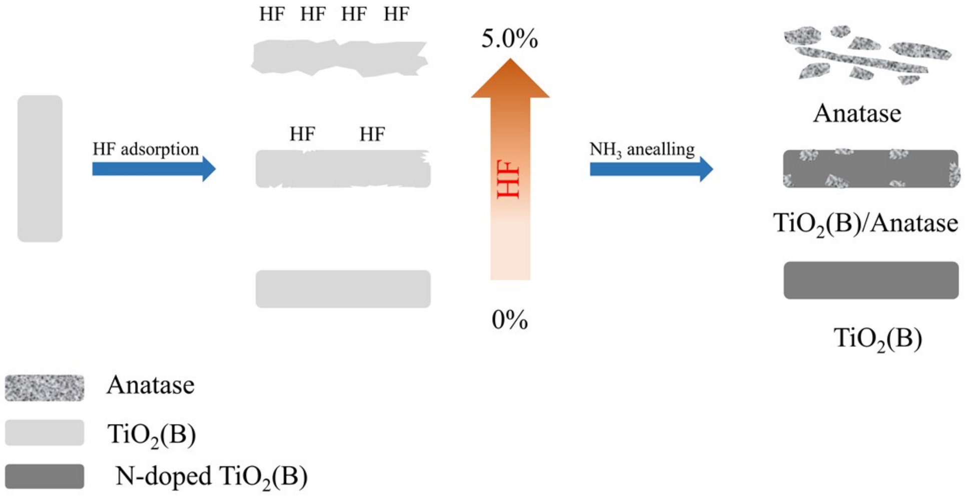

Fig. S2. Schematic diagram of the two-step preparation process of TiO_2(B) with different amount of HF.

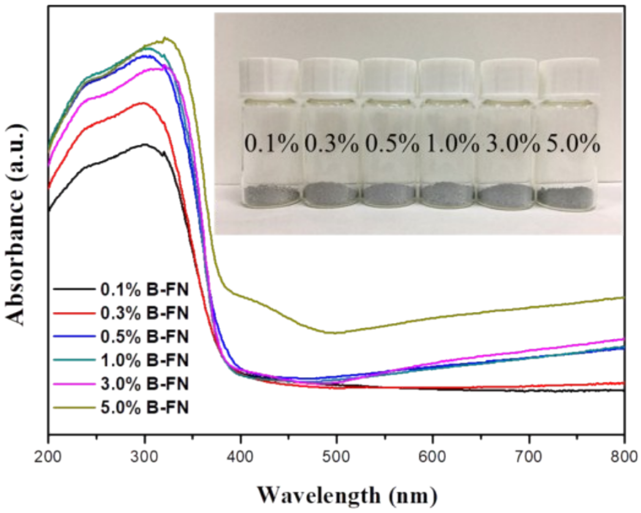

Fig. S3. The UV-Vis diffuse reflectance spectra of the x%B-FN series photocatalysts(inset: digital photograph of the samples).

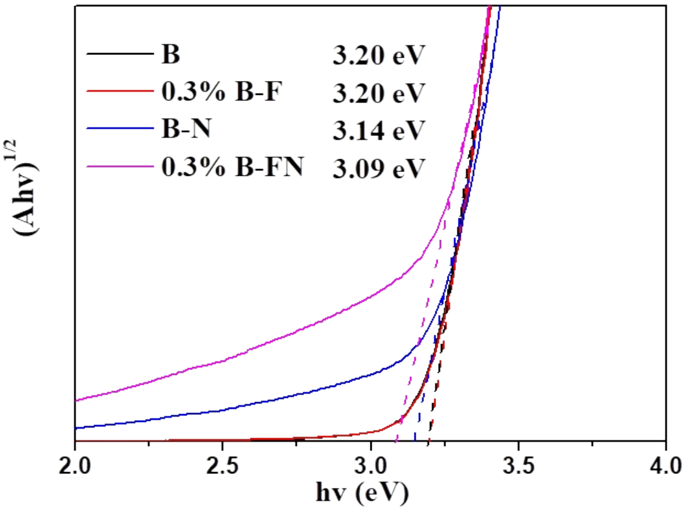

Fig. S4. Kubelka–Munk curves and corresponded bandgaps for B, 0.3%B-F, B-N, and 0.3%B-FN.

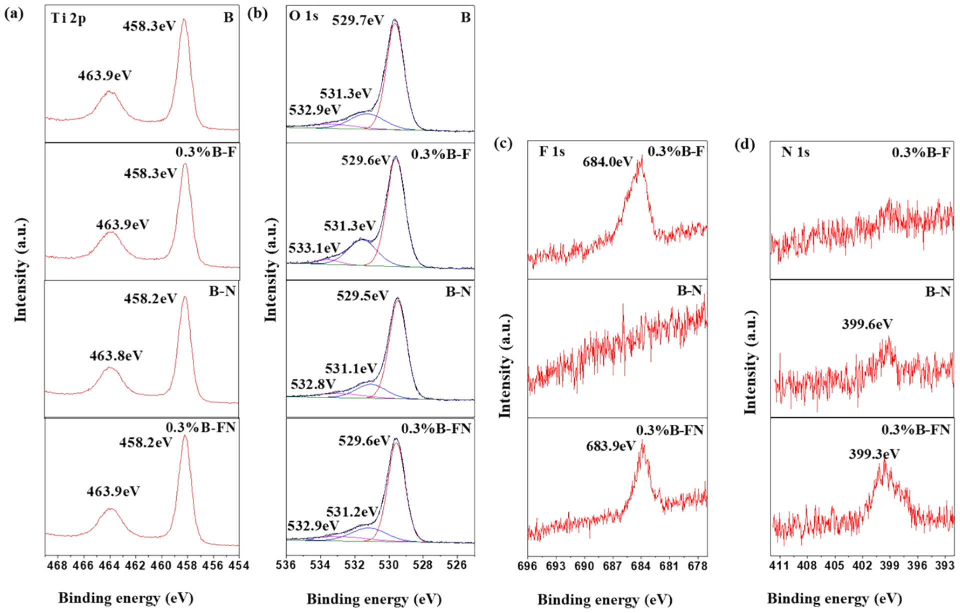

Fig. S5 Ti 2p (a), O 1s (b), F 1s (c) and N1s (d) XPS spectra for B, B-N, 0.3%B-F and 0.3%B-FN

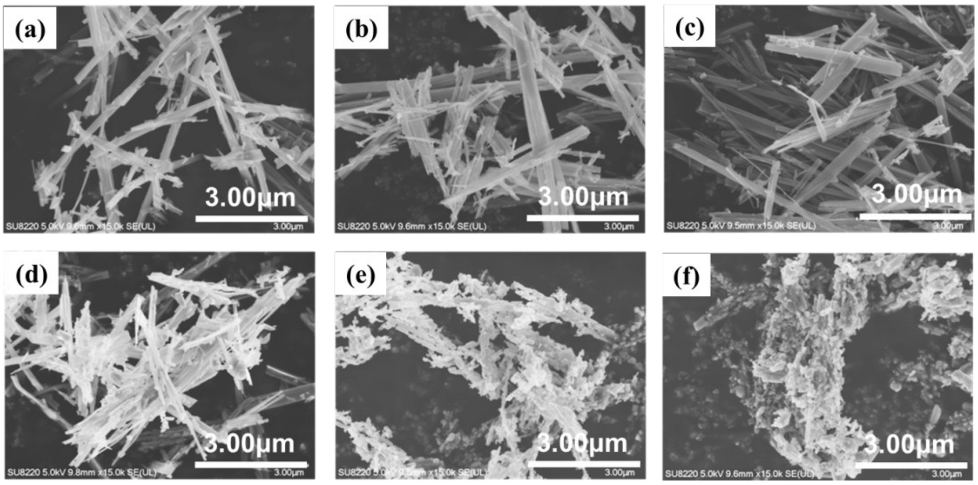

Fig. S6. SEM images of x%B-FN samples: (a) 0.1%B-FN, (b) 0.3%B-FN, (c) 0.5%B-FN, (d)1.0%B-F, (e) 3.0%B-FN, and (f)5.0%B-FN.

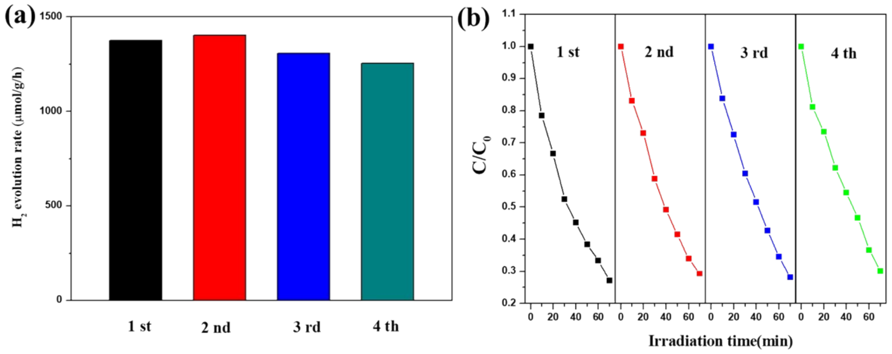

Fig. S7 Recycle reactions of (a) photocatalytic H_2 evolution and (b) RhB degradation over 0.3%B-FN under full light irradiation.

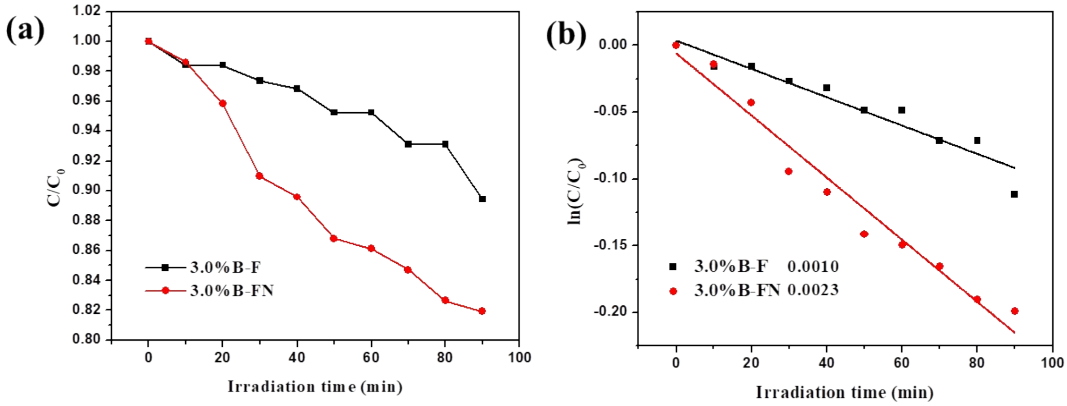

Fig. S8 (a) Normalized concentration (*C*/*C₀*) versus time for photocatalytic degradation of RhB and (b) pseudo first-order kinetic plots over 3.0%B-F and 3.0%B-FN under visible light irradiation (λ ⩾ 420 nm).

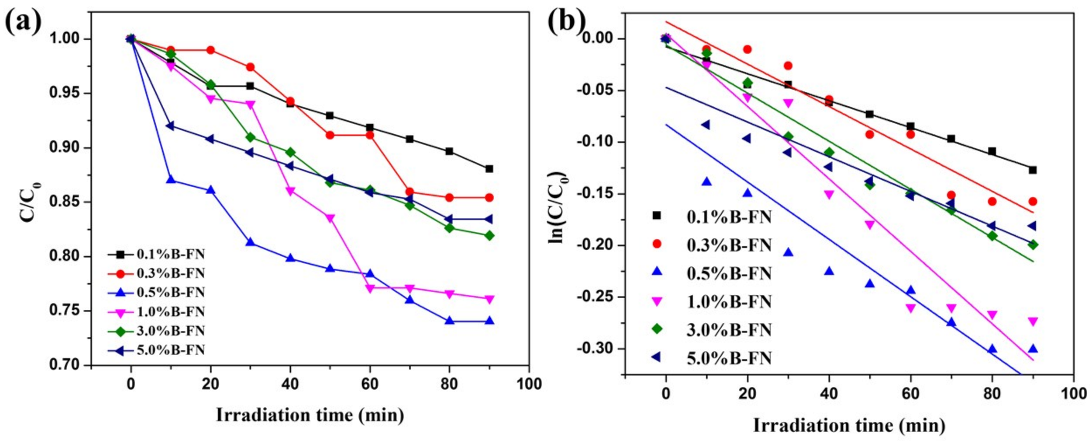

Fig. S9 Photocatalytic degradation of RhB under visible light (λ ⩾ 420 nm) irradiation: (a) Normalized concentration (C/C_0) versus time and (b) pseudo first-order kinetic plots over B-FN series catalysts.