Supporting Information

Sulfate-Mediated Reactive Oxygen Chemistry for Photocatalytic Nitrogen Fixation

Xin Zhang, Linlin Zhang*, Yaming Hu, Xue Li, Xuesheng Yang, Ping Wang, Hengxin Yu, Shiyou Song, Botao Zhang*, Xin Ding*

College of Chemistry and Chemical Engineering, Qingdao University, Qingdao, China

E-mail: zll@qddu.edu.cn; zhangbotao@qdu.edu.cn; dingxin@qdu.edu.cn

Experimental Procedures

Materials

Chemicals including Titanium tetrachloride ($TiCl_4$, 99.99%), Sodium carbonate ($NaCO_3$, 99.99%), Sodium bicarbonate ($NaHCO_3$, 99.99%), Sodium hydroxide (NaOH), Salicylic acid ($C_7H_6O_3$, 99.99%), Trisodium citrate dihydrate ($C_6H_5Na_3O_7 \cdot 2H_2O$, 99.99%), Sodium hypochlorite aqueous solution (NaClO, 99.9%), Ethylene glycol ($C_2H_6O_2$, 99.99%), Ethyl alcohol (C_2H_5OH, 99.9%), Concentrated hydrochloric acid (HCl, 37.2%) and Concentrated sulfuric acid (H_2SO_4,18%) were purchased from Aladdin Industrial Crop. All ultrapure water in this article is water with resistivity of 18 MΩ*cm (25 ℃).

Synthesis of TiO_2 and S-TiO_2

TiO_2: Titanium tetrachloride (1 ml) was dissolved into 100 ml Ethylene glycol and stir until transparent. Then, the solution was transferred to a 100 ml Teflon autoclave, which was further annealed at 180 ℃ for 10 h hours. After cooling to ambient temperature, TiO_2 was obtained after cleaned by ethanol and water.

S-TiO_2: The obtained TiO_2 was immersed in dilute sulfuric acid solution for 6 hours, then dried by centrifugation and ground. Finally, it was calcined at 450 °C for 3 hours to yield S-TiO_2.

Characterizations

XRD patterns were recorded using Cu Kα radiation (λ=1.5406 Å) over a 2θ range of 10-80°. HRTEM images were obtained on a transmission electron microscope operated at 200 kV. XPS measurements were performed with monochromatic Al Kα radiation (1486.6 eV), and binding energies were calibrated against the C 1s peak at 284.8 eV. In situ FTIR spectroscopy was performed on a Nicolet 6700 spectrometer equipped with a custom-built IR cell featuring two ZnSe windows for infrared transmission and a quartz window for light introduction. The Ir-WO_3 catalyst was placed in the cell, pretreated under Ar flow (10 $mL \cdot min^{-1}$) at 573 K or 673 K for 30 min, and background spectra were collected at 473 K with a resolution

of 1 cm^{-1}.After introducing N_2/O_2 mixture gas (4:1), spectra were recorded in the dark for 5 min, followed by time-resolved measurements under light illumination at 0, 5, 10, 15, 20, 25 and 30 min to monitor the reaction process. Online mass spectrometry was conducted using a quadrupole mass spectrometer, monitoring characteristic ion fragments (m/z = 17, 30, 44, 46) in multiple ion monitoring mode.

Under the optimal reaction conditions, simulated air was prepared with $^{14}N_2$ and $^{15}N_2$ as nitrogen sources respectively (V_{N2}:V_{O2} = 4:1, volume ratio) for photocatalytic reactions. After the reactions, the collected and processed solid products (mainly ammonium salts) were dissolved in dimethyl sulfoxide (DMSO) and adjusted to a concentration suitable for ^{1}H NMR detection, resulting in test solutions containing $^{14}NH_4^+$ and $^{15}NH_4^+$ respectively. The ammonium ions were detected by ^{1}H NMR, and the source of nitrogen in the products was confirmed by comparing the characteristic splitting patterns of $^{14}NH_4^+$ (triplet) and $^{15}NH_4^+$ (doublet).

Gas pretreatment

Prior to entering the photocatalytic reactor, all gases were passed through a potassium permanganate solution and a dilute sulfuric acid solution to remove any possible impurities. Additionally, the reactor was subjected to three cycles of gas purging before the reaction commenced.

Calculations

The generation rate of ammonium salt was calculated using Equation S1, where c(NH_4^+) represents the concentration of ammonium ions, V is the volume of the collected and processed liquid, t is the photocatalytic reaction time, and m_{cat} is the mass of the catalyst.

$$r_{(NH4+)} = \frac{C(NH4+) \times V \times 1000}{18 \times t \times mcat} \quad (S1)$$

Where:

$r_{(NH4+)}$: is ammonia formation rate in μmol h^{-1} $g^{-1}_{cat.}$.

$C_{(NH4+)}$: the concentration of ammonia in the collected solution in μg mL^{-1}.

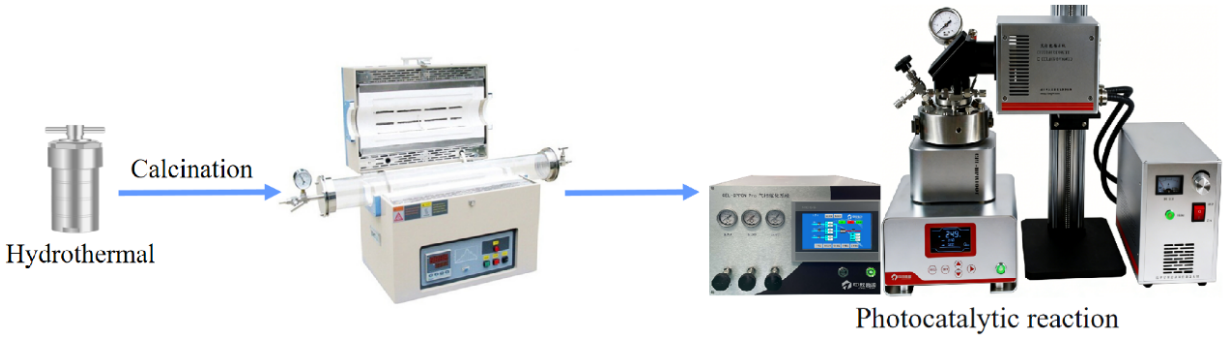
V: is the volume of production in mL.

t: is light irradiation time.

$m_{cat..}$: is mass of catalyst.

Table S1. A comparison of the photocatalytic nitrogen fixation and ammonia synthesis performance of the photocatalysts reported in the literature.

Catalyst	Reaction atmosphere	NH_4^+ yield	Ref.
Fe/TiO_2	Pure N_2 atmosphere	56.87 μmol h^{-1} g^{-1}	1
TiO_2@LSM	Pure N_2 atmosphere	5.41 mg L^{-1} g_{cat}^{-1} h^{-1}	2
TiO_2/ZrO_2 S-type heterojunctions	Pure N_2 atmosphere	516.67 μmol h^{-1} g^{-1}	3
$Pt//TiO_2$	Pure N_2 atmosphere	5114 μg·g^{-1}·h^{-1}	4
TiO_2 (g-C_3N_4/TiO_2-OV)	Pure N_2 atmosphere	31.6 μmol L^{-1}	5
TiO_2-Mo10	Pure N_2 atmosphere	42.05 μmol·g^{-1}·h^{-1}	6
F-Vo-TiO_2	Pure N_2 atmosphere	206 μmol·h^{-1}·g^{-1}	7
NTO-0.5	Pure N_2 atmosphere	80.09 μmol $g^{-1}h^{-1}$	8
Ru-TiO_2	Pure N_2 atmosphere	38.7 μmol g^{-1} h^{-1}	9
Fe-WO_3	Simulated air	477 μg g_{cat}^{-1} h^{-1}	10
Bi-MOF/CN	Simulated air/ sacrificial agent	209.96 μmol h^{-1} g_{cat}^{-1}	11
MXene/TiO_2/Co-0.5%	N_2 and air ambient	110 μmol g^{-1} h^{-1}	12
S-TiO_2	Simulated air	217.24 μmol h^{-1} $g^{-1}_{cat.}$	This work



Scheme S1. Preparation process of S-TiO_2 and schematic diagram of the reaction setup.

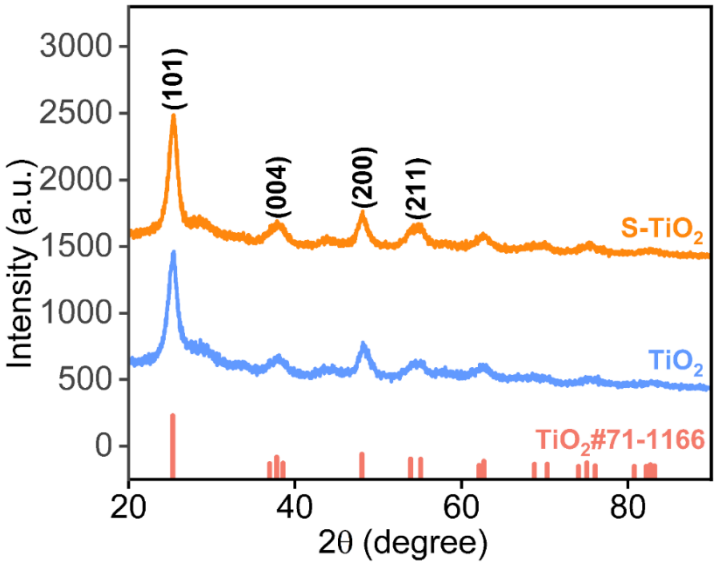


Fig. S1. XRD images of TiO_2 and S-TiO_2.

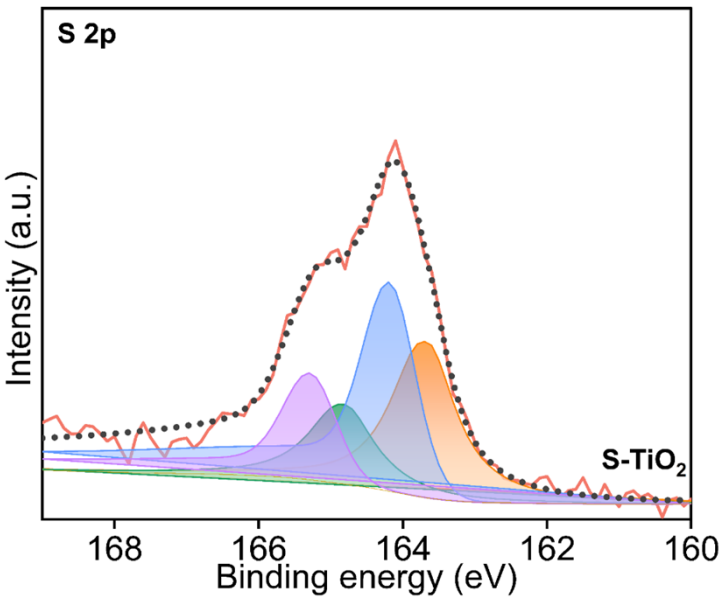


Fig. S2. XPS images of S 2p of S-TiO_2.

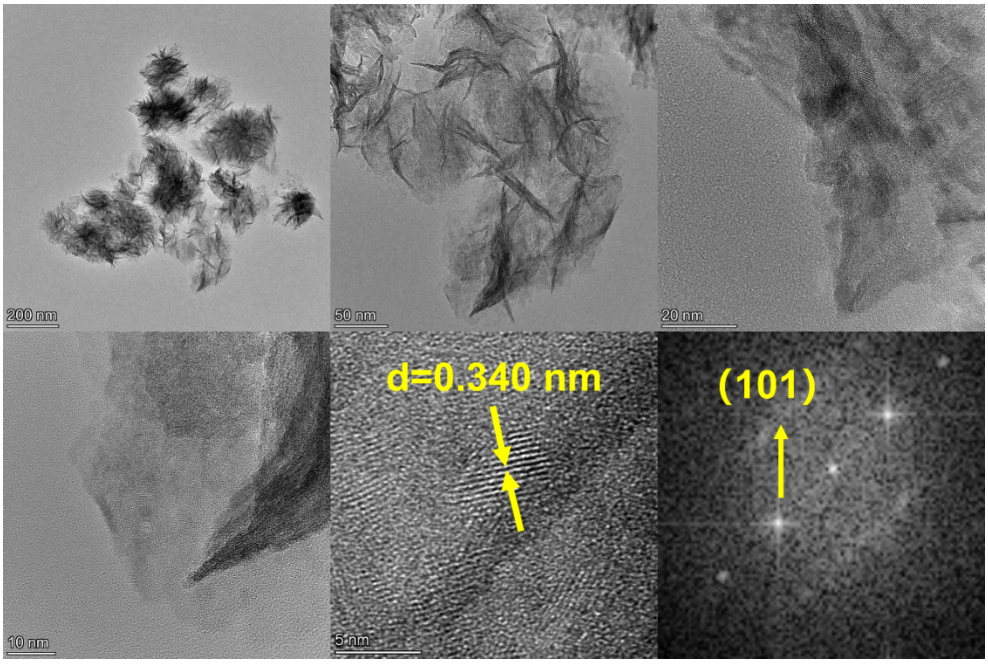


Fig. S3. HR-TEM images of TiO_2.

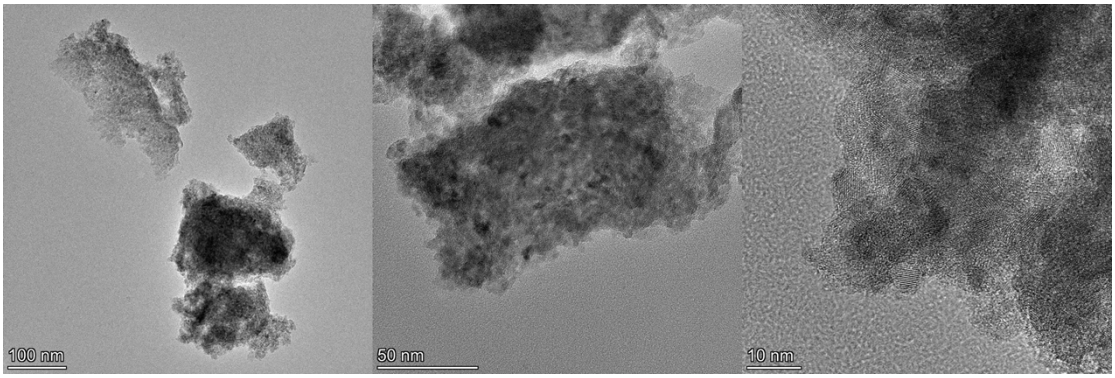


Fig. S4. HR-TEM images of S-TiO_2.

Table 2. ICP-OES Elemental Analysis Results for S-TiO_2 (Mass Fraction).

Sample	Element	Weight percent (wt%)
S-TiO_2	S	1.9908%
	Ti	47.0317%

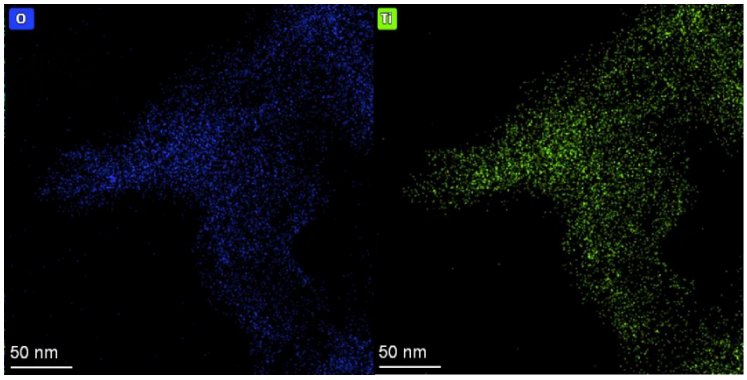


Fig. S5. EDS images of TiO_2.

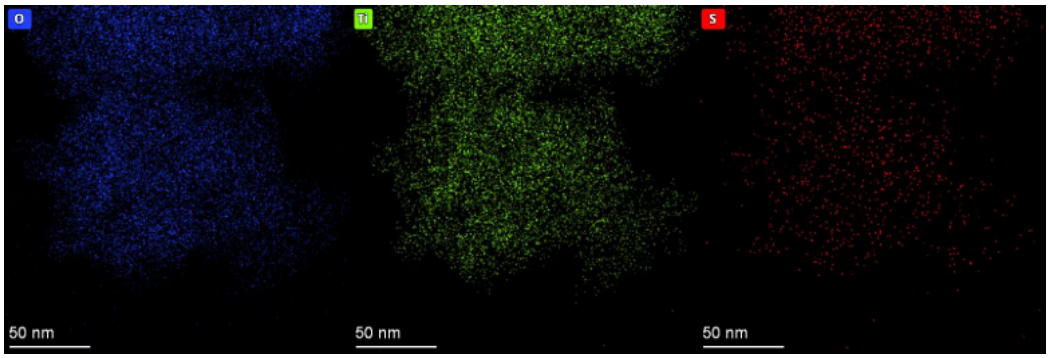


Fig. S6 EDS images of S-TiO_2

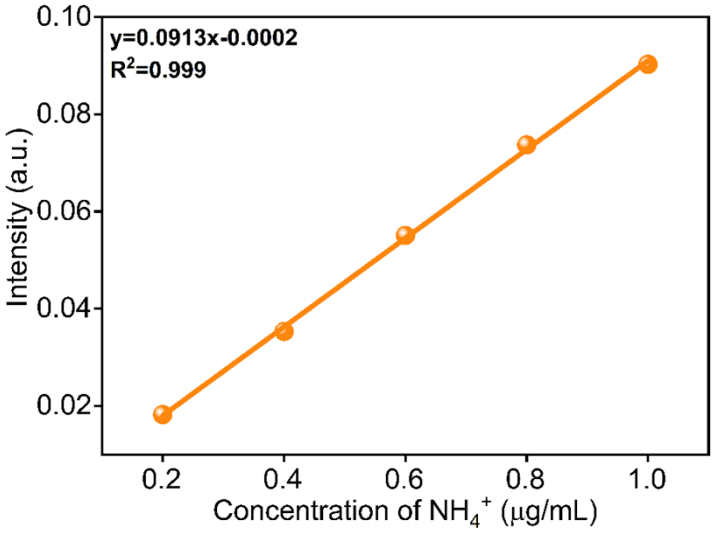


Fig. S7 Plots of the fitting of IC area-concentration curves for different NH_4^+ standard solutions.

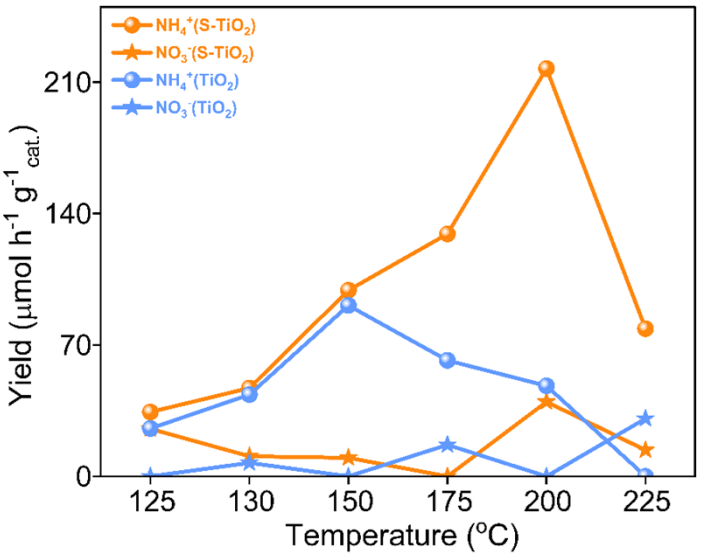


Fig. S8 Temperature-dependent NH_4^+ and NO_3^- production rates over TiO_2 and pristine S-TiO_2 photocatalysts.

Table S3. Control experiments for photocatalytic N_2 fixation.

Conditions	Dark	No-catalyst	Argon-only
Yield (μmol h^{-1} $g^{-1}_{cat.}$)	0	0	0

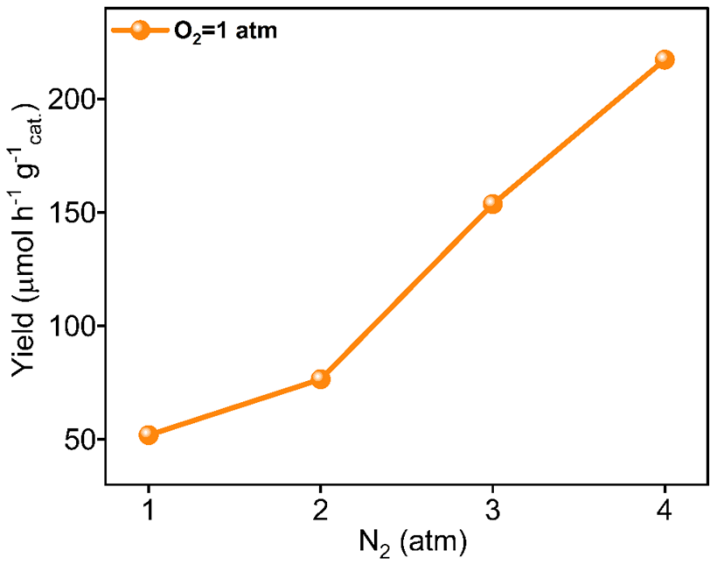


Fig. S9 Ammonia yield at different nitrogen pressures.

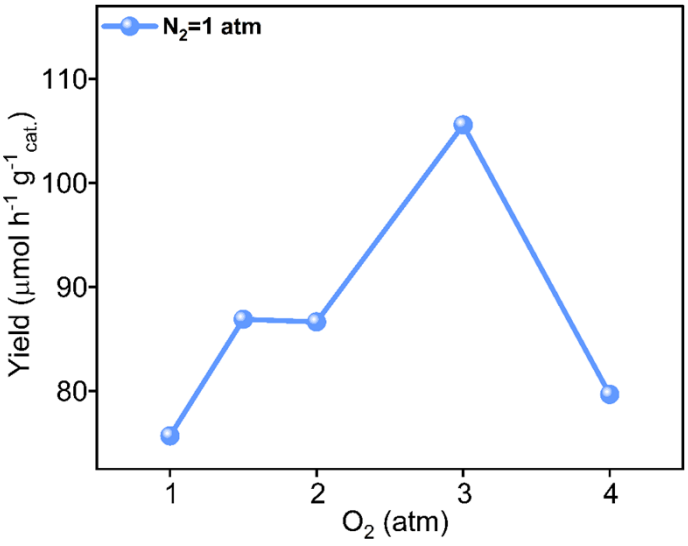


Fig. S10 Ammonia yield at different oxygen pressures.

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