Supporting Information

Improved N_2 Photo- fixation Performance of Nanocrystalline TiO_2 Film by Photon Localization Effect and Fe Doping

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1. Regents

Titanium tetraisopropanolate, ammonium chloride (99.5%), ammonia solution (25%-28%) and hydrazine dihydrochloride were bought from Shanghai Aladdin Biochemical Technology Co., Ltd. (China). Ferric nitrate (99.5%), ethanol (≥99.7%) and nitric acid (65%-68%) were provided by the Beijing Chemical Works (China). Tetraethoxysilane (TEOS) (98%), LUDOX AS-40 colloidal silica, Nessler, 4-dimethylaminobenzaldehyde, polyethylene glycol 2000 (PEG 2000) and acetic acid (≥99.7%) were purchased from Aldrich Chemical Co., Inc. (USA), Sigma-Aldrich Co., Tianjin Aopusheng Chemical Co., Ltd. (China), Ailan (Shanghai) Chemical Technology Co., Ltd. (China), Shanghai Titan Scientific Co., Ltd. (China) and Shanghai Macklin Biochemical Co., Ltd. (China), respectively. All the chemicals were analytical grade and could be used without further purification. All the experiments were performed with distilled water. Glass slides with a size of 38×25×1 mm were used as the catalyst substrates.

2. Structural and optical characterizations

Powder X-ray diffraction (XRD) patterns were acquired with a Panalytical empyrean diffractometer. The X-ray photoelectron spectroscopy (XPS) measurements were performed with an ULTRAAXIS DLD with an Al Kα (1253.6 eV) achromatic X-ray source. The electron paramagnetic resonance (EPR) spectrums were collected with a Bruker EMXplus spectrometer. The morphologies and structures of the materials were characterized by scanning electron microscopy (SEM, Gemini SEM 300 instrument operated at 15-30 kV). The high-resolution transmission electron microscopy (HRTEM) images were obtained on a FEI Tecnai G^2 F20 with an acceleration voltage of 200 kV. Nitrogen adsorption-desorption isotherms were recorded on a TriStar II 3020 nitrogen adsorption apparatus. The absorption spectra and the diffuse reflectance spectra (DRS) were measured using an UV-Vis spectrometer (UV-1800 S, Shanghai Macy Instrument Co. Ltd., China). Photoluminescence (PL) spectroscopy measurements were conducted with a Hitachi F-7000 Fluorescence Spectrophotometer with a xenon lamp (λ = 280 nm). The transient photocurrents were

analyzed by using a CHI-660E electrochemical workstation equipped with a standard three-electrode system in 0.5 $M \cdot L^{-1}$ Na_2SO_4 solution. The sizes of microspheres were measured by dynamic light scattering (DLS) on a Malvern Zetasizer Nano ZS90.

3. The apparent quantum efficiency

According to the N_2 reduction reaction, the apparent quantum efficiency (AQE) is calculated through the following Eq. (S1):

$$AQE = \frac{Number\ of\ reacted\ electrons}{Number\ of\ incident\ photons} \times 100\%$$
$$= \frac{6 \times number\ of\ generated\ NH_3\ molecules}{Number\ of\ incident\ photons} \times 100\%$$
$$= \frac{6N_A Mhc}{ISt\lambda} \times 100\% \quad (S1)$$

where N_A, M, h, c are Avogadro's constant, mole number of generated NH_3, Planck constant and speed of light, respectively; I, S, t and λ are light density, irradiation area, irradiation time and wavelength of monochromatic light, respectively.

4. DFT calculations

All chemical simulation calculations were performed within the framework of density functional theory (DFT) using the DMol^3 module in Materials Studio 2020 software. The Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) method was selected to describe exchange-correlation energy of atom. The DFT semi-core pseudopotential (DSPP) was applied for core treatment and adopting double numerical plus polarization (DNP) basis set. The k-point was chosen as 2×2×1, and the self-consistent field (SCF) was set to 10^{-5} eV. A vacuum layer of 20 Å was applied. Three layers of the subsurface TiO_2 (101) was fixed in all the calculations.

The adsorption energy of N_2 was calculated with Eq. (S2):

$$E_{ads} = E_{N_2-slab} - \left(E_{N_2} + E_{slab}\right) \quad (S2)$$

where E_{N_2-slab} is the energy of N_2 adsorbed on slab (the constructed material model), E_{N_2} is the energy of N_2 molecule (-10.73 eV), E_{slab} is the energy of slab. The more

negative the absorption energy, the stronger the adsorption.

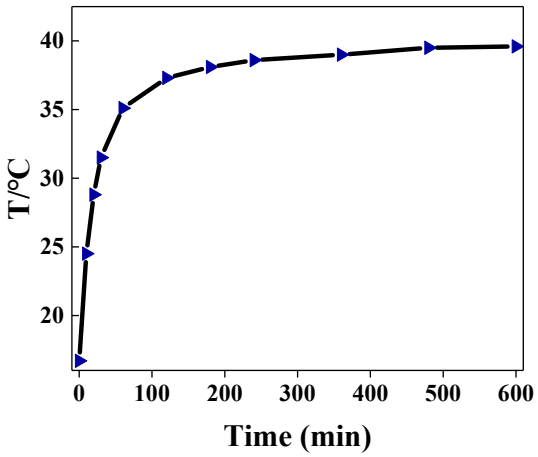


Fig. S1. The change of reaction temperature with time.

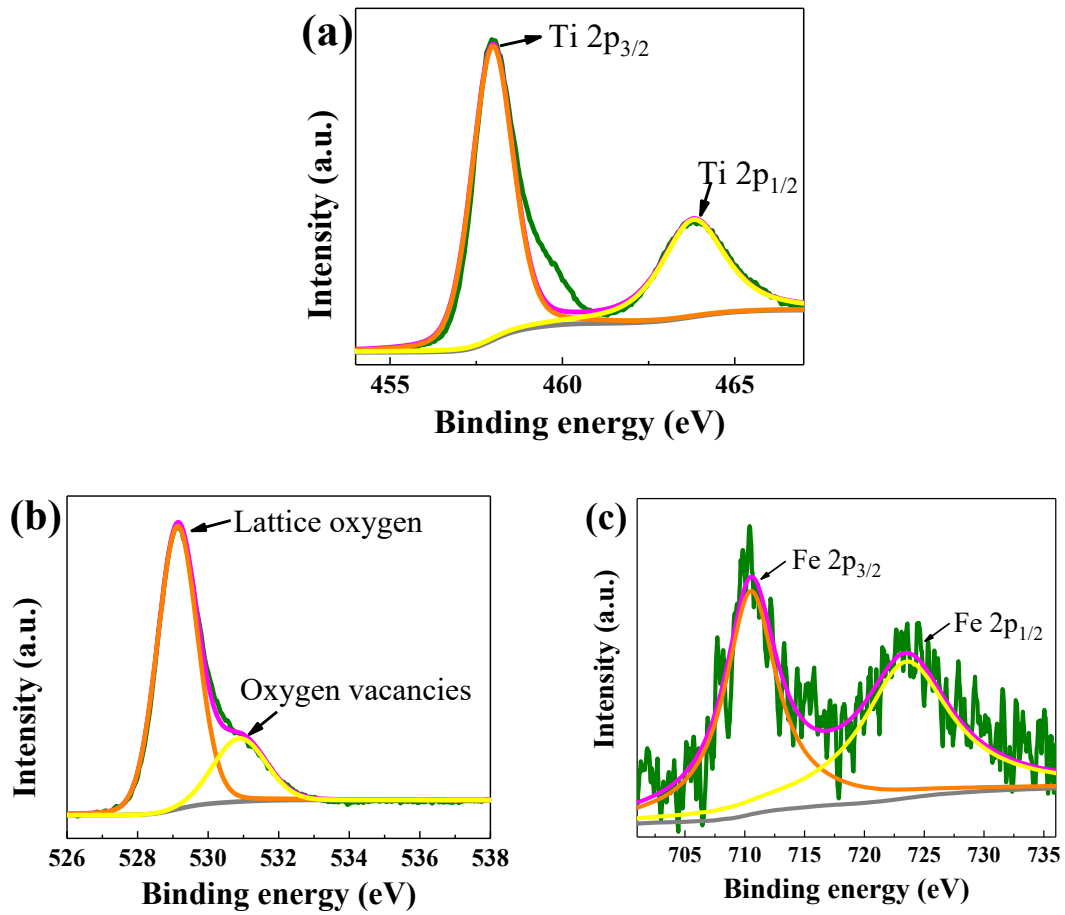


Fig. S2. XPS spectra of Ti 2p (a), O 1s (b) and Fe 2p (c) of 6% FT sample.

Table S1. Nitrogen Fixation Rate of Various Photocatalysts for N_2 Photo-fixation

Catalyst	Light Source	Hole scavenger	Ammonia production rate	Ref.
Single-atom Fe- TiO_2-SiO_2	300 W Xe lamp	No	32μmol·g_{cat}^{-1}·h^{-1}	29
Fe-abtc	300 W Xe lamp	K_2SO_3	49.8μmol·g_{cat}^{-1}·h^{-1}	33
Fe-Based MOFs [MIL-101(Fe)]	300 W Xe lamp	No	50.4μmol·L^{-1}·h^{-1}	34
Fe-TiO_2/Au	300 W Xe lamp (λ>420nm)	No	22.4μmol·g_{cat}^{-1}·h^{-1}	36
Fe-BiOBr	300 W Xe lamp (λ>420nm)	No	382.7μmol·L^{-1}·h^{-1}	37
TiO_2-1500r/SiO_2 PC-370nm	500 W Xe lamp	No	31μmol·g_{cat}^{-1}·h^{-1}	50
6% FT/SOPC-380	500 W Xe lamp	No	55.6μmol·g_{cat}^{-1}·h^{-1}	this work

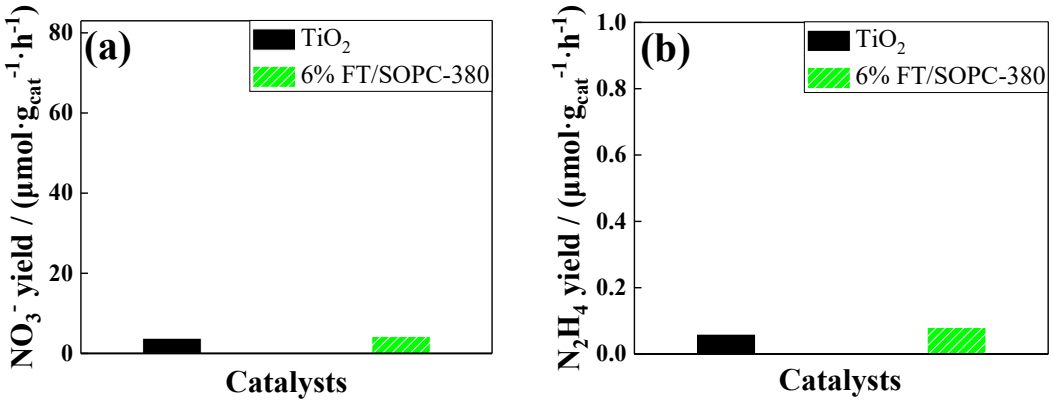


Fig. S3. (a) Nitrate formed in phototatalytic reactions over TiO_2 and 6% FT/SOPC-380 catalysts; (b) hydrazine formed in phototatalytic reactions over TiO_2 and 6% FT/SOPC-380 catalysts. Reaction conditions: pure water (60 mL), catalyst (38 cm^2); light irradiation conditions: full-spectrum, 2.8 mW·cm^2.

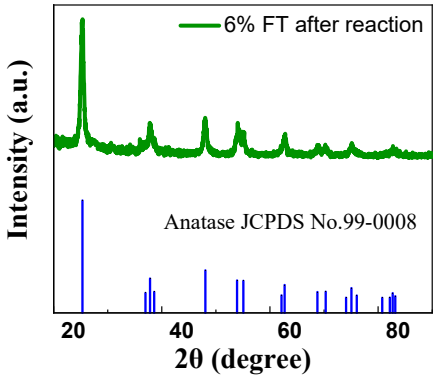


Fig. S4. X-ray diffraction diagrams of 6% FT after reaction.

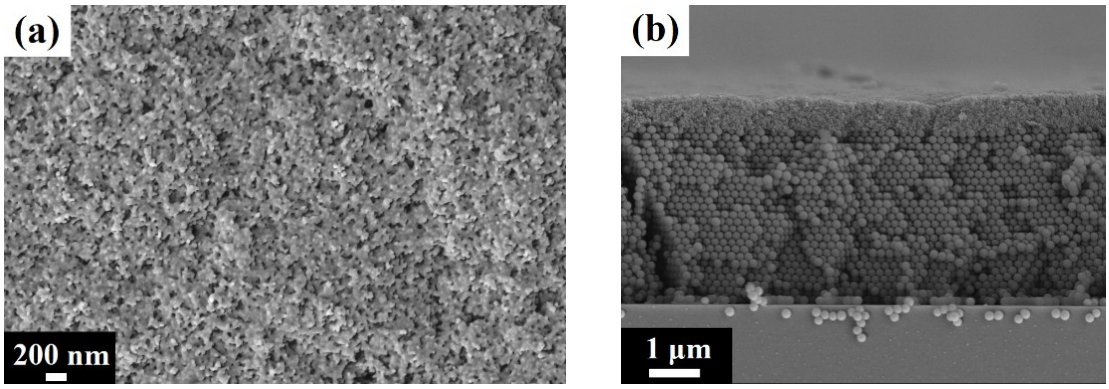
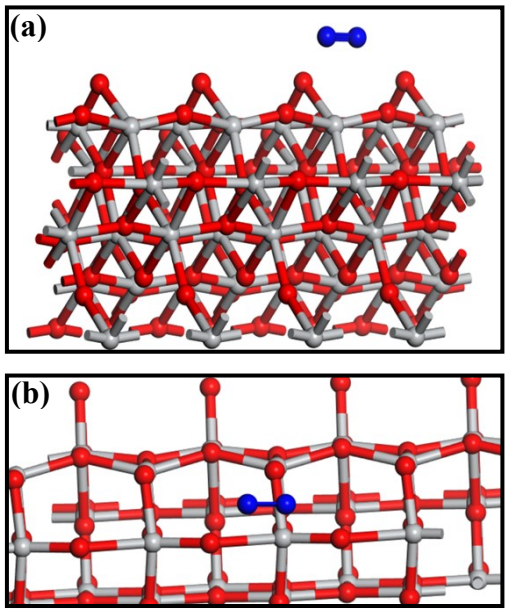


Fig. S5. SEM images of the top view and cross sectional view of 6% FT/SOPC after reaction.

Table S2. DFT Calculation Results of Nitrogen Adsorption.

Slab	**E / eV**	**Slab**	**E / eV**
TiO_2 (101)	-768.52	N_2_TiO_2 (101)	-779.79
Fe_TiO_2 (101)	-761.11	N_2_Fe_TiO_2 (101) OV-1	-772.47

Energy	**E / eV**	**Adsorption type**
$E_{ads\text{-}TiO2\ (101)}$	-0.52	parallel
$E_{ads\text{-}Fe\_TiO2\ (101)}$	-0.63	parallel



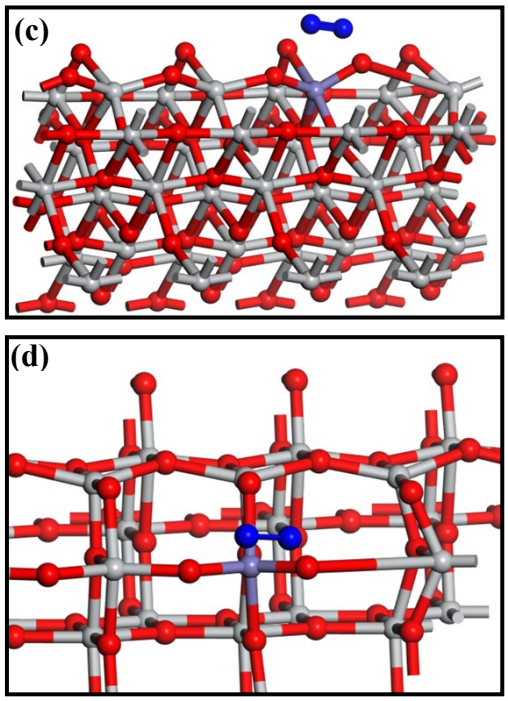


Fig. S6. Front-view (a) and top view (b) images of N_2_TiO_2 (101) models; front view (a) and top view (b) images of N_2_Fe_TiO_2 (101) models. Ti, O, Fe and N atoms are shown in grey, red, purple and blue color, respectively.