

Supporting Information

Photon Localization Effect and Surface Oxygen Vacancy Enhanced Photocatalytic Nitrogen Fixation Performance for Nanocrystalline Titanium Dioxide Film

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1. Materials

LUDOX AS-40 colloidal silica, Nessler, 4-dimethylaminobenzaldehyde, polyethylene glycol 2000 (PEG 2000) and acetic acid ($\geq 99.7\%$) were obtained from 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. Titanium isopropoxide and tetraethoxysilane (TEOS) (98%) were bought from Aldrich Chemical Co. Inc. (USA). Ammonium chloride (99.5%), ammonia solution (25%-28%) and hydrazine dihydrochloride were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. (China). Glucose (GOD-PAP method) was acquired from AO Vector-Best Company. Hydrogen peroxide ($>30\%$), methanol ($\geq 99.5\%$), ethanol ($\geq 99.7\%$), sulfuric acid (98%), nitric acid (65%-68%) and hydrochloric acid (36%-38%) were all purchased from the Beijing Chemical Works (China). All the chemicals were analytical grade and could be used without further purification. Distilled water was used in all the experiments. Glass slides with a size of $38 \times 25 \times 1$ mm were used as the catalyst substrates.

2. Structural and optical characterizations

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 G² F20 with an acceleration voltage of 200 kV. Powder X-ray diffraction (XRD) patterns were acquired with a Panalytical empyrean diffractometer. The X-ray photoelectron spectroscopy (XPS) measurements were performed with a Thermo Fisher ESCALAB 250Xi with an Al K α (1486.6 eV) achromatic X-ray source by referencing to the C 1s peak at 284.6 eV. Raman spectra were recorded on a LabRAM HR Evolution Raman spectrometer with a 532 nm laser as the excitation source. The absorption spectra 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 ($\lambda = 280 \text{ nm}$). Nitrogen adsorption-desorption isotherms were recorded on a TriStar II 3020 nitrogen adsorption apparatus. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) equation, and the pore size distributions were obtained by the Barrett-Joyner-Halenda (BJH) method. The electron paramagnetic resonance (EPR) spectrums were collected with a Bruker EMXplus spectrometer. The transient photocurrents were analyzed by using a CHI-660E electrochemical workstation equipped with a standard three-electrode system in $0.5 \text{ M}\cdot\text{L}^{-1} \text{ Na}_2\text{SO}_4$ solution. The sizes of microspheres were measured by dynamic light scattering (DLS) on a Malvern Zetasizer Nano ZS90.

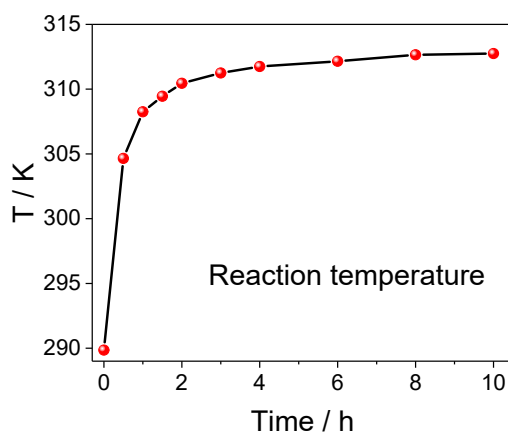
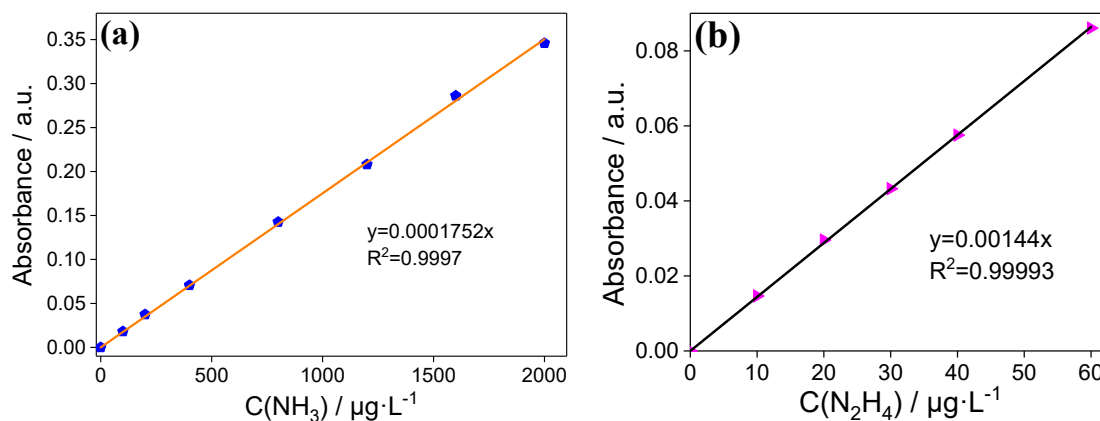


Fig. S1. The change of reaction temperature with time.



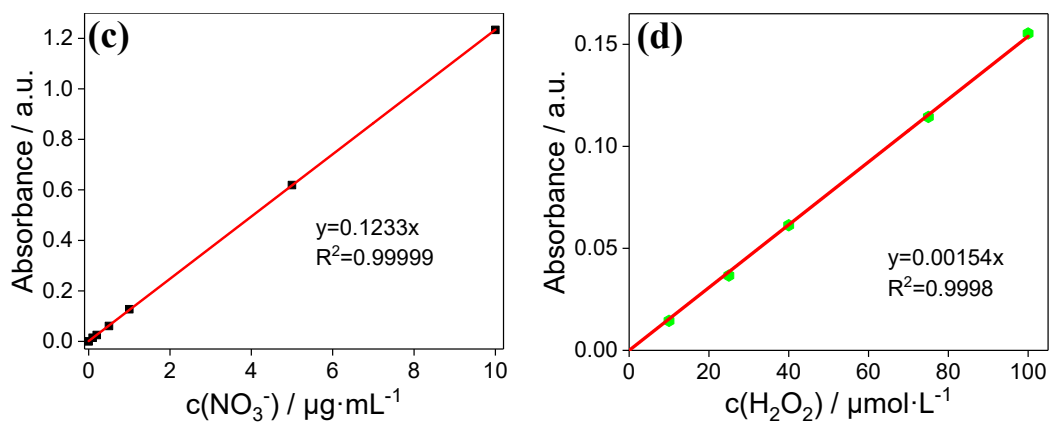


Fig. S2. Standard curves for the concentration of NH_3 (a), N_2H_4 (b), NO_3^- (c), and H_2O_2 (d).

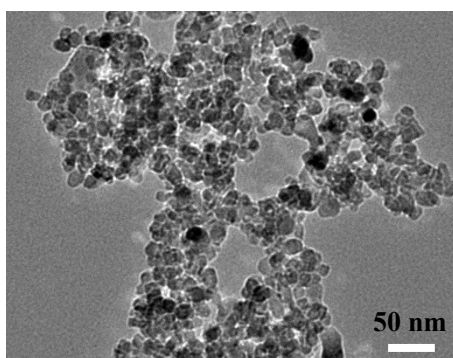


Fig. S3. HRTEM images of TiO_2 nanoparticles.

Table S1. Summary of the results of N_2 adsorption-desorption measurements of TA and TOVs Catalysts

Catalyst	Surface area / $\text{m}^2 \cdot \text{g}^{-1}$	Pore volume / $\text{cm}^3 \cdot \text{g}^{-1}$	Average pore size / nm
TA	103.2	0.37	13
TOVs-2	108.4	0.31	10
TOVs-3	107.6	0.31	10

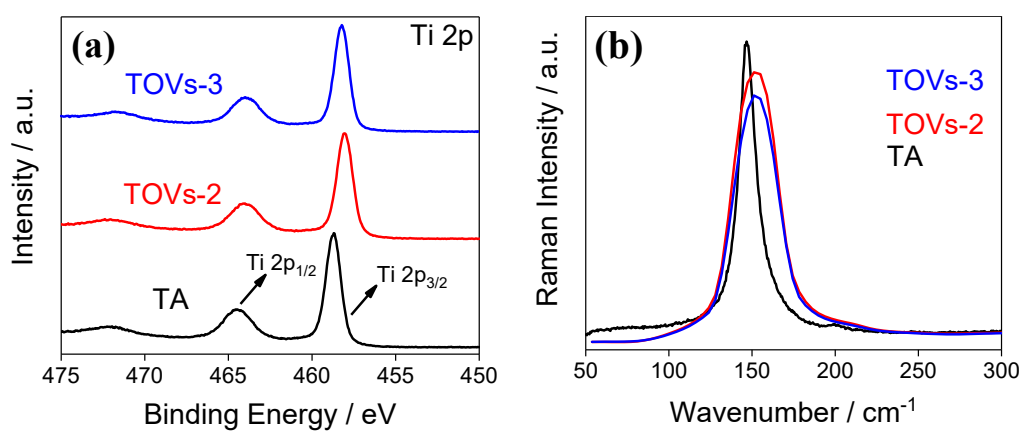


Fig. S4. (a) XPS spectra for Ti 2p of TA, TOVs-2, and TOVs-3 catalysts. (b) Raman main peak spectra of TA, TOVs-2, and TOVs-3 catalysts.

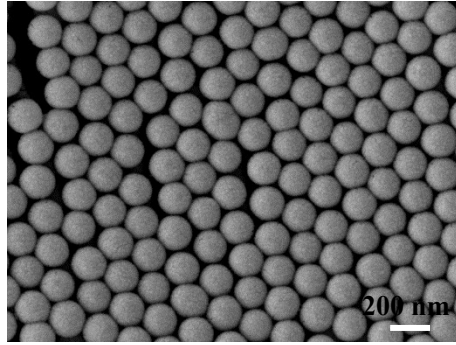


Fig. S5. SEM images of the top view of SPCs-380.

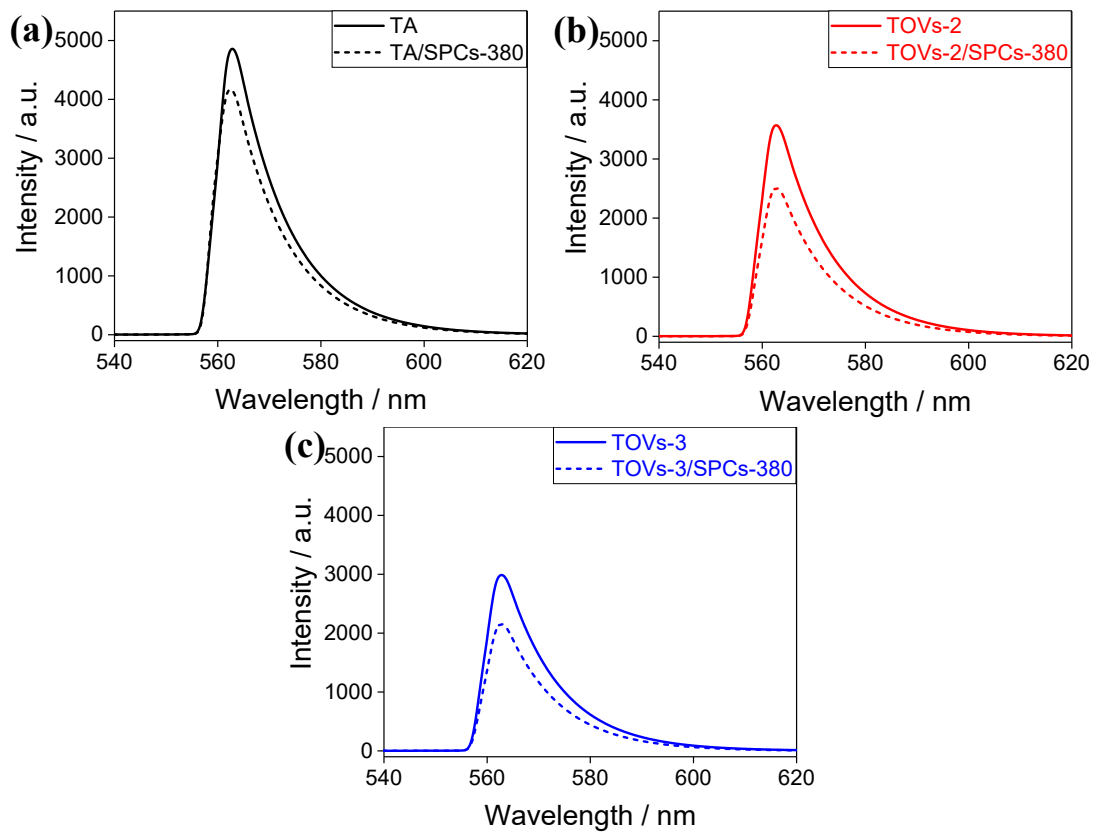


Fig. S6. PL spectra of TA, TOVs, TA/SPCs-380 and TOVs/SPCs-380 composite membranes.

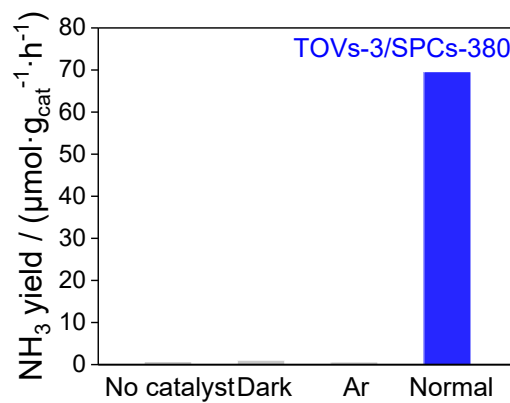


Fig. S7. Contrast experiments. Reaction conditions of normal experiments: pure water (60 mL),

N₂, catalyst (38 cm²); light irradiation: full-spectrum, 6 mW·cm⁻², 10 h. Control experiments were carried out without catalyst, without light irradiation and argon atmosphere, respectively.

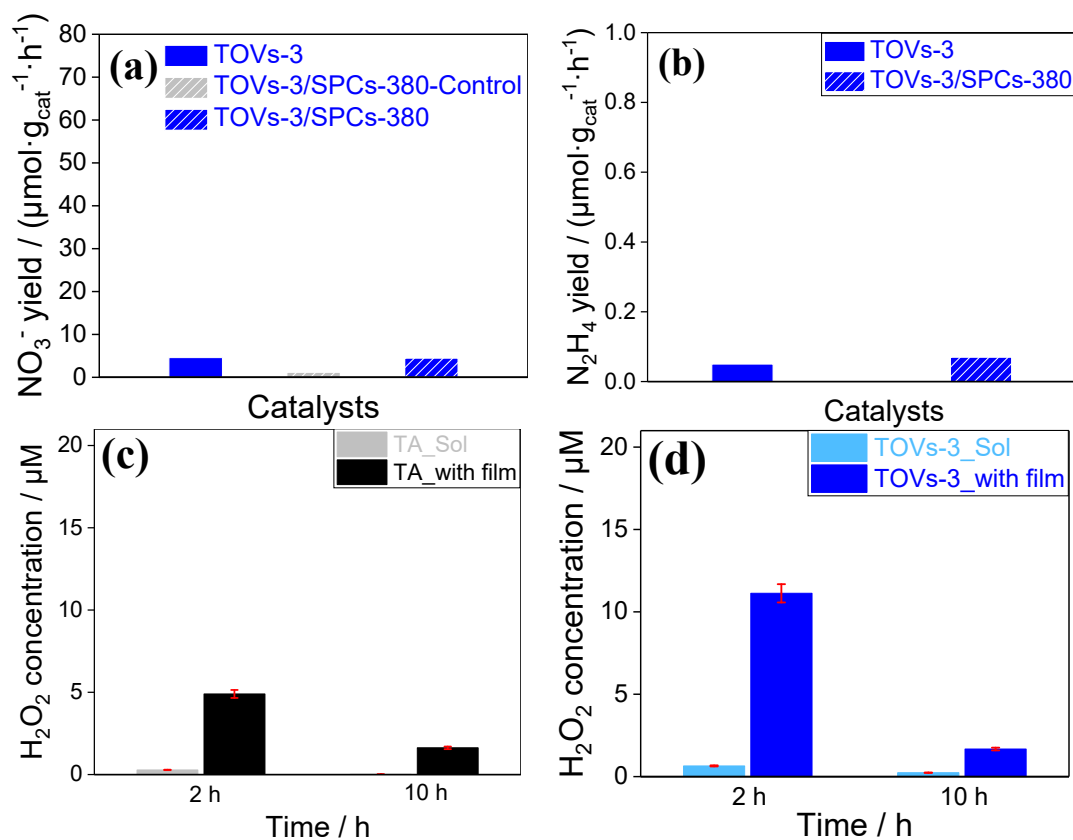


Fig. S8. (a) Nitrate formed in phototatalytic reactions over TOVs-3 and TOVs-3/SPCs-380 catalysts, control experiment on TOVs-3/SPCs-380 catalyst; (b) hydrazine formed in photocatalytic reactions over TOVs-3 and TOVs-3/SPCs-380 catalysts; H₂O₂ concentration in photocatalytic reactions over TA (c) and TOVs-3 (d) catalysts. Reaction conditions: pure water (60 mL), N₂, catalyst (38 cm²); light irradiation: full-spectrum, 6 mW·cm⁻², 10 h; control experiments were carried out without light irradiation.

Table S2. Summary of photocatalytic performance results for all catalysts

Catalyst	Ammonia production rate / $\mu\text{mol}\cdot\text{g}_{\text{cat}}^{-1}\cdot\text{h}^{-1}$	Enhancement Factor / β	AQE
TA	25.3	—	0.29%
TOVs-2	43.7	0.73	0.50%
TOVs-3	49.6	0.96	0.57%
TA/SPCs-380	42.6	0.68	0.49%
TOVs-2/SPCs-380	57.3	1.26	0.66%
TOVs-3/SPCs-380	69.6	1.75	0.80%

$$\beta = \frac{\text{the } \text{NH}_3 \text{ yield of TOVs or TOVs/SPCs} - \text{the } \text{NH}_3 \text{ yield of TA}}{\text{the } \text{NH}_3 \text{ yield of TA}} \quad (\text{S1})$$

Table S3. Nitrogen fixation rate of various photocatalysts for photocatalytic N₂ fixation

Catalyst	Light Source	Hole scavenger	Ammonia production rate	Ref.
Defective Bi ₂ O ₂ CO ₃	Simulated sunlight	Methano	398.8 μmol · g _{cat} ⁻¹ · h ⁻¹	5
F-Vo-TiO ₂	300 W Xe lamp	No	206 μmol · g _{cat} ⁻¹ · h ⁻¹	8
0.5%Cu-ZnAl-LDH	300 W Xe lamp (200-800 nm)	No	110 μmol · g _{cat} ⁻¹ · h ⁻¹	21
6%Cu-TiO ₂	300 W Xe lamp (200-800 nm)	No	78.9 μmol · g _{cat} ⁻¹ · h ⁻¹	22
Single-atom Fe-TiO ₂ -SiO ₂	300 W Xe lamp	No	32 μmol · g _{cat} ⁻¹ · h ⁻¹	25
Fe-TiO ₂ /Au	300 W Xe lamp (λ>420nm)	No	22.4 μmol · g _{cat} ⁻¹ · h ⁻¹	26
Defect TiO ₂	Hg lamp (λ>280nm)	No	0.73 μmol · g _{cat} ⁻¹ · h ⁻¹	29
TiO ₂ -1500r/SiO ₂ PC-370nm	500 W Xe lamp	No	31 μmol · g _{cat} ⁻¹ · h ⁻¹	34
TOVs-3/SPCs-380	500 W Xe lamp	No	69.6 μmol · g _{cat} ⁻¹ · h ⁻¹	this work

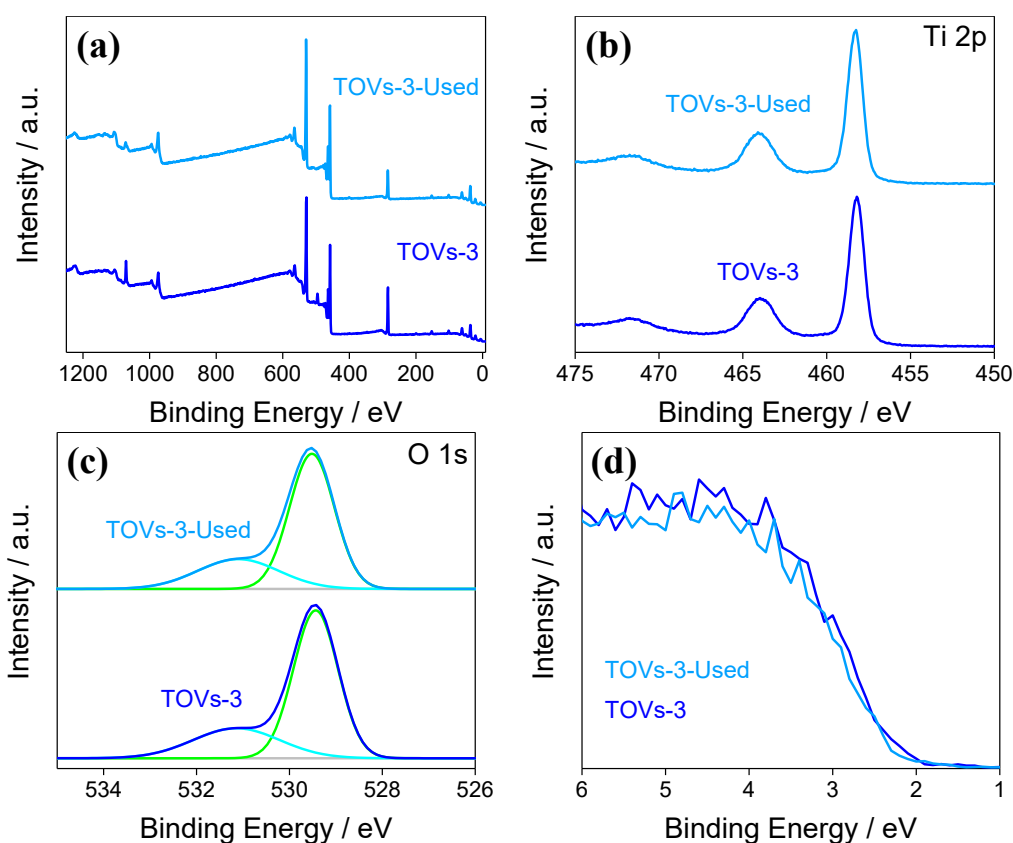


Fig. S9. XPS spectra for survey spectra (a), Ti 2p (b), O 1s (c) and valence band (d) of TOVs-3, TOVs-3-Used catalysts.

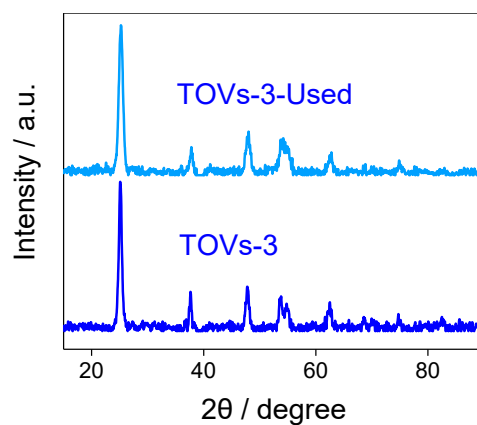


Fig. S10. X-ray diffraction patterns of TOVs-3 and TOVs-3-Used catalysts.

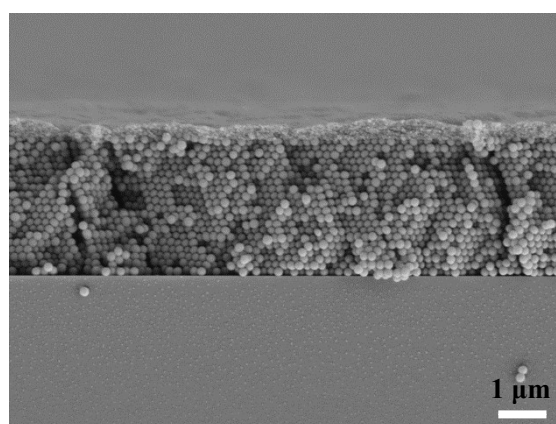


Fig. S11. SEM image of the cross section of TOVs-3/SPCs-380-Used.

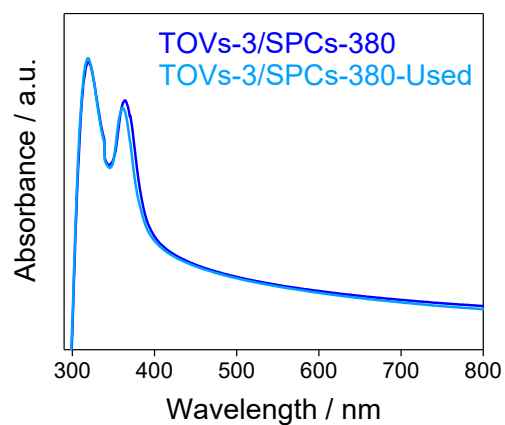
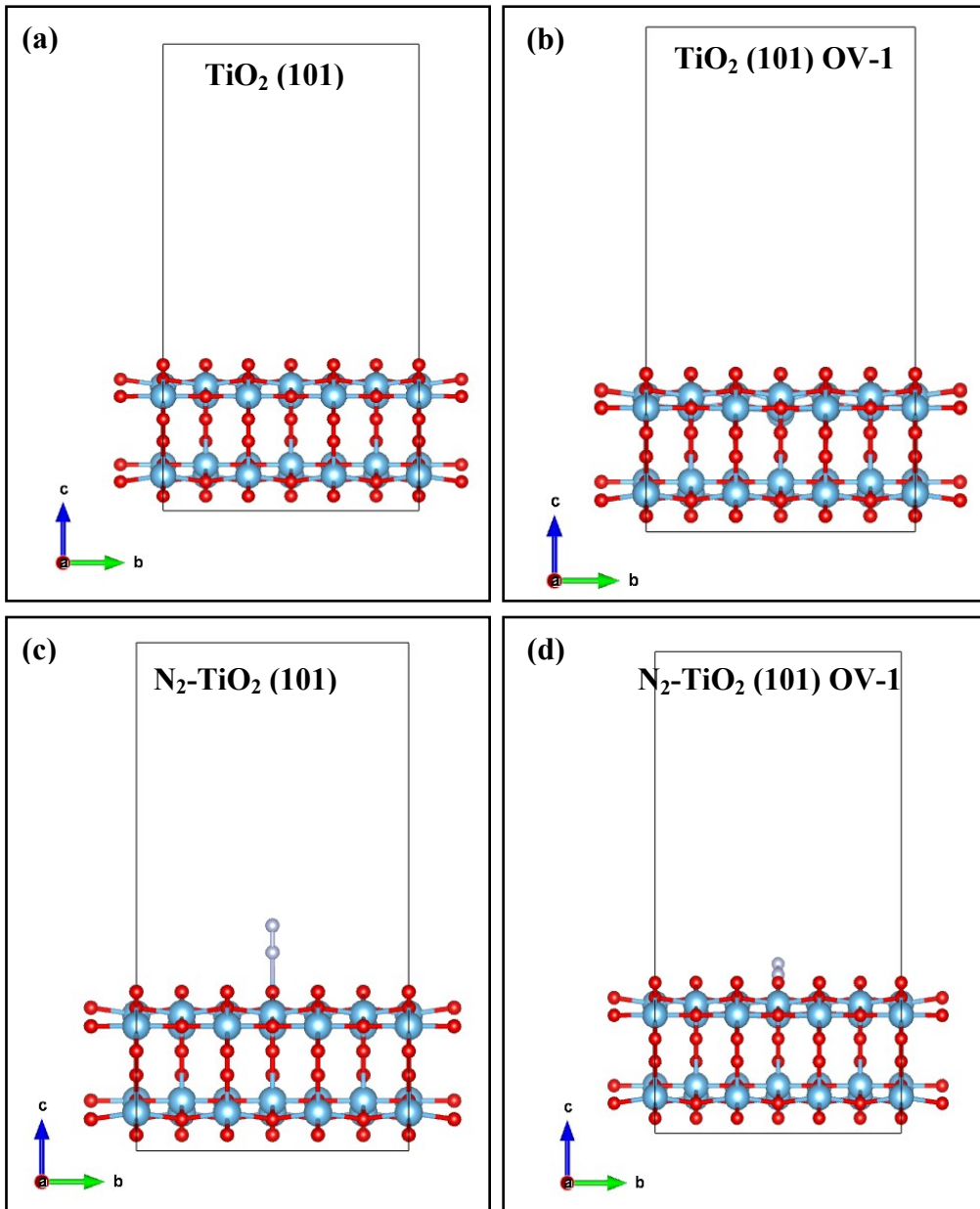


Fig. S12. The UV-Vis absorption spectra of TOVs-3/SPCs-380 and TOVs-3/SPCs-380-Used composite membrane.



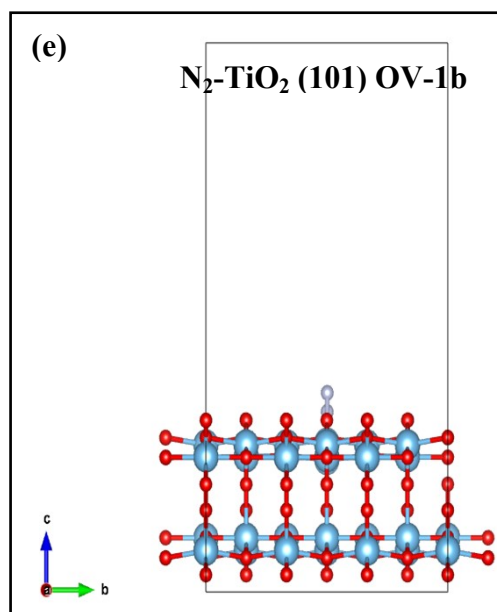


Fig. S13. Front-view images of calculation models. Ti, O, H and N atoms are shown in blue, red, orange and white color, respectively.

Table S4. DFT calculation results of nitrogen adsorption.

Slab	E / eV	Slab	E / eV
TiO_2 (101)	-1296.13	$\text{N}_2\text{-TiO}_2$ (101)	-1313.01
TiO_2 (101) OV-1	-1285.89	$\text{N}_2\text{-TiO}_2$ (101) OV-1	-1303.81
TiO_2 (101) OV-1b	-1285.89	$\text{N}_2\text{-TiO}_2$ (101) OV-1b	-1304.06
TiO_2 (101) OV-2	-1285.68	$\text{N}_2\text{-TiO}_2$ (101) OV-2	-1302.67

Energy	E / eV	Adsorption type
$E_{\text{OV-1}}$	5.28	---
$E_{\text{OV-2}}$	5.49	---
$E_{\text{ads-TiO}_2}$ (101)	0.204	top-on
$E_{\text{ads-TiO}_2}$ (101) OV-1	-0.835	top-on
$E_{\text{ads-TiO}_2}$ (101) OV-1b	-1.085	bridge-on
$E_{\text{ads-TiO}_2}$ (101) OV-2	0.095	top-on

Table S5. DFT calculation results of nitrogen reduction reaction.

Molecular	E / eV
H_2	-6.98
N_2	-17.08
NH_3	-19.39

Species	Adsorption Slab	E / eV	E(ZPE+TS) / eV	$\text{N}\equiv\text{N}$ Bond length / Å
* N_2	TiO_2 (101)	-1313.01	---	1.112
* N_2	TiO_2 (101) OV-1b	-1304.06	0.12	1.185

*NNH	-1307.41	0.42	1.261
*NNH₂	-1311.97	0.72	1.372
*NHNH	-1310.98	0.72	1.347
*NHNH₂	-1315.57	1.10	1.422
*NH₂NH₂	-1318.65	1.40	1.438
*NHNH₃	-1320.87	1.40	—
*NH	-1300.31	0.37	—
*NH₂	-1304.46	0.65	—
*NH₃	-1307.10	0.94	—