Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Enhanced Photocatalytic Activity of Titanium Dioxide in Nitrogen Fixation by Photon Localization Effect of SiO_2 Opal Photonic Crystal

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1. The detailed preparation procedures of SiO_2 microspheres

One mixture containing methanol anhydrous, ammonia and ultra-pure water and another mixture containing methanol anhydrous and Tetraethoxysilane were concurrently dropped into the seed solution including methanol anhydrous, LUDOX AS-40 colloidal silica, ultra-pure water and ammonia under stirring condition at 198 rpm. After all the reagents were added dropwise, the SiO_2 suspension was continuously stirred for 2 hours, and finally monodisperse SiO_2 microspheres with suitable diameter were sorted out by the gravity settling method.

2. Calculation of UV-Vis-to-ammonia efficiency

The catalytic experiment for determining UV-Vis-to-ammonia efficiency(E) was performed in pure water (60 mL) without sacrificial reagent, and the irradiation area was 38 cm^2. TiO_2/SiO_2 opal composite membrane was used as the photocatalyst. The 500 W Xe lamp (Zolix LSH-X500) was employed as the light source. The E was determined by the following equation:

$$E = \frac{\Delta G_A \times n_A}{W \times S \times t} \times 100\%$$

where ΔG_A is the Gibbs free energy for ammonia generation from water and N_2 (339 kJ • mol^{-1}); n_A is the molar number of generated ammonia; W, S and t represent the incident light intensity, irradiation area and time, respectively.

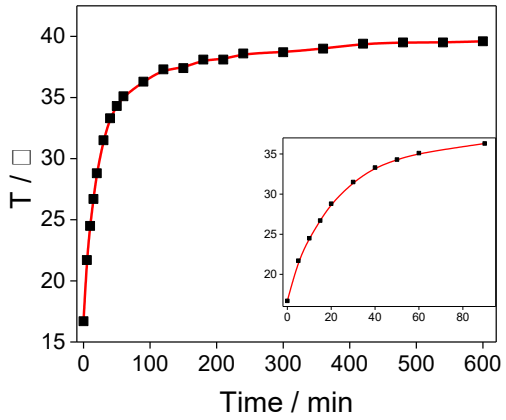

Figure S1. The change of reaction temperature with time.

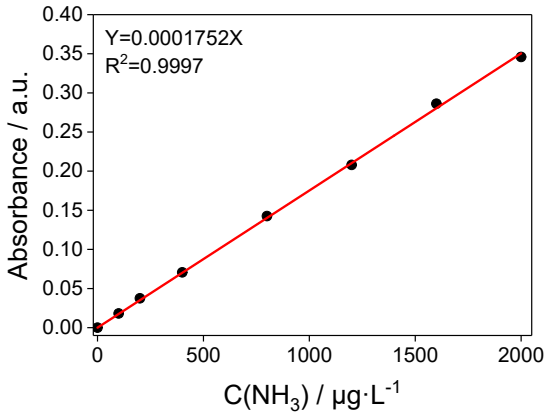

Figure S2. Standard curve of NH_4^+ with Nessler's regent.

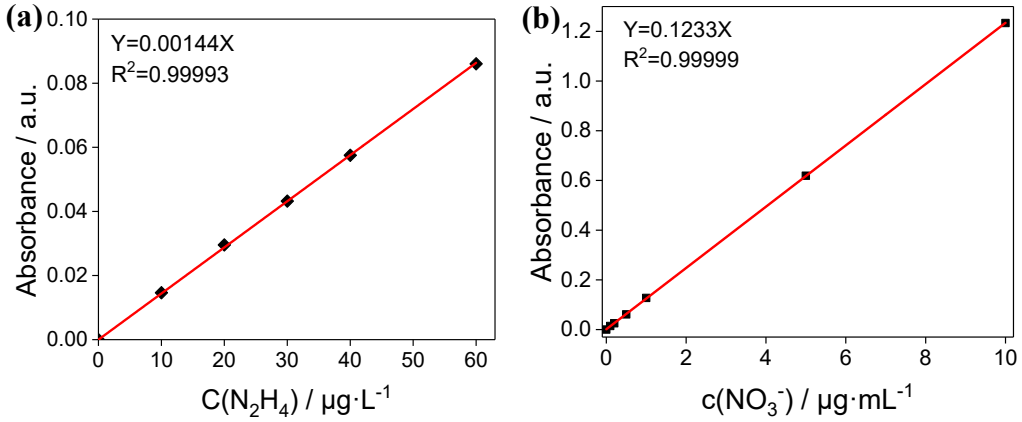

Figure S3. (a) Standard curve of N_2H_4 with para-(dimethylamino) benzaldehyde; (b) standard curve for NO_3^- and ammonium sulfamate.

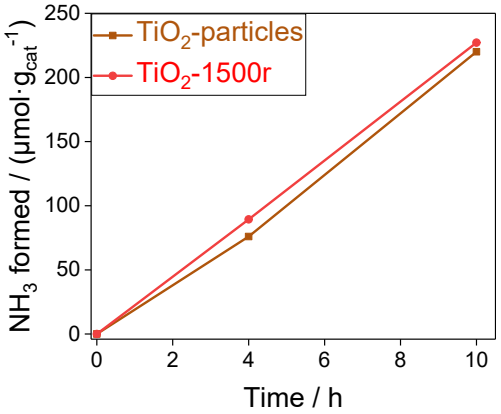

Figure S4. N_2 fixation catalytic performance of TiO_2-1500r and TiO_2-particles photocatalysts. Reaction conditions: pure water (60 mL), catalyst (38 cm^2); light irradiation conditions: full-spectrum, 2.8mW•cm^{-2}.

(b)

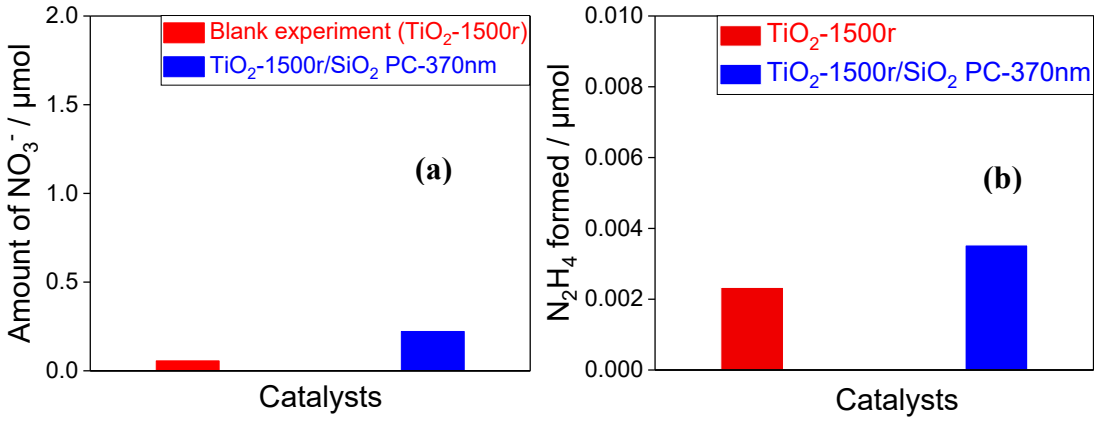

Figure S5. (a) Blank experiment for NO_3^- detection. Reaction conditions: pure water (60 mL), TiO_2-1500r catalyst (38 cm^2), no light. And NO_3^- formed in photocatalytic reactions over TiO_2-1500r/SiO_2 PC-370nm catalysts. (b) Hydrazine formed in photocatalytic reactions over TiO_2-1500r, TiO_2-1500r/SiO_2 PC-370nm catalysts.

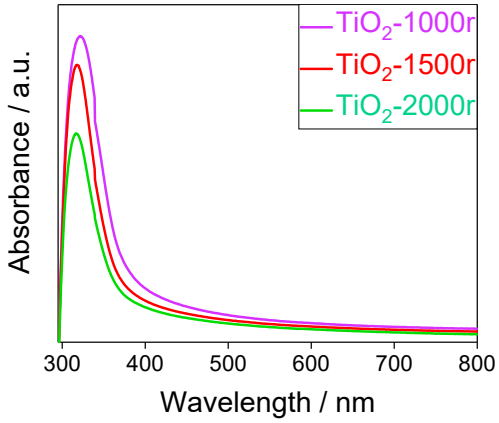

Figure S6. The UV-Vis absorption spectra of TiO_2 films with different thicknesses.

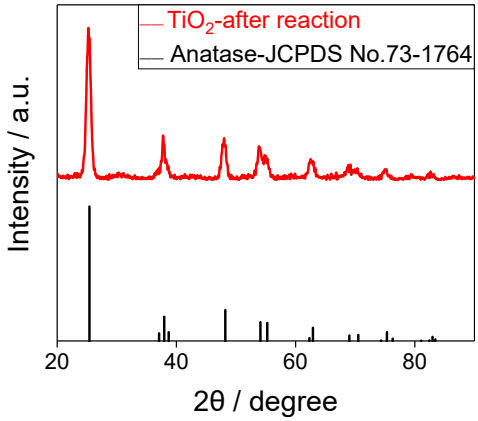

Figure S7. X-ray diffraction patterns of the reacted TiO_2.

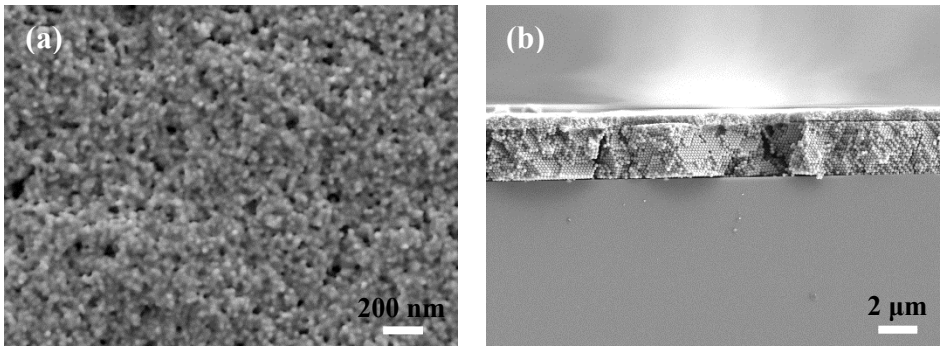

Figure S8. SEM images of top view (a) and cross section (b) of the reacted TiO_2-1500r/SiO_2 PC-370nm composite membranes.

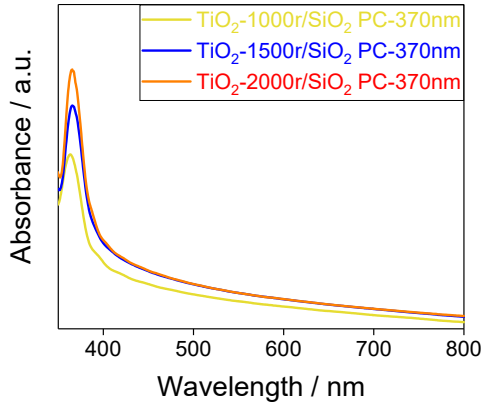

Figure S9. The UV-Vis absorption spectra of SiO_2 PC-370nm in TiO_2-1000r/SiO_2 PC-370nm, TiO_2-1500r/SiO_2 PC-370nm and TiO_2-2000r/SiO_2 PC-370nm photocatalysts, respectively.

Table S1. Nitrogen Fixation Rate of Various Photocatalysts for Photocatalytic N_2 Fixation

Catalyst	Reaction solvent	Light Source	Hole scavenger	Ammonia production rate	Ref.
0.2 wt% Fe-doped TiO_2	Water	360-W Hg-Arc Lamp (UV)	No	10μmol·g_{cat}^{-1}·h^{-1}	11
0.4 wt% Co-doped TiO_2	Water	360-W Hg-Arc Lamp (UV)	No	6.3μmol·g_{cat}^{-1}·h^{-1}	11
0.4 wt% Mo-doped TiO_2	Water	360-W Hg-Arc Lamp (UV)	No	6.7μmol·g_{cat}^{-1}·h^{-1}	11
Defect TiO_2	Pure water	Hg lamp (λ>280nm)	No	0.73μmol·g_{cat}^{-1}·h^{-1}	12
Defective TiO_2 nanobamboo	Pure water	300 W Xe lamp (Full spectrum)	No	48.3 mg·m^{-2}·h^{-1}	13
TiO_2/$SrTiO_3$/g-C_3N_4	Water	300 W Xe lamp (AM 1.5G)	10 vol% methanol	219.2μmol·g_{cat}^{-1}·h^{-1}	14
Fe-TiO_2/Au	Deionized water	300 W Xe lamp (λ>420nm)	No	22.4μmol·g_{cat}^{-1}·h^{-1}	15
Fe-doped TiO_2-SiO_2	Water	300 W Xe lamp (Full spectrum)	No	32μmol·g_{cat}^{-1}·h^{-1}	16

F-Vo-TiO_2	Deionized water	300 W Xe lamp (Full spectrum)	No	206μmol·g_{cat}^{-1}·h^{-1}	18
TiO_2/Au/a-TiO_2	Deionized water	300 W Xe lamp (AM 1.5G)	No	13.4nmol·cm^{-2}·h^{-1}	42
TiO_2-1500r/SiO_2 PC-370nm	Ultra-pure water	500 W Xe lamp (Full spectrum)	No	31μmol·g_{cat}^{-1}·h^{-1}	this work
TiO_2-2000r/SiO_2 PC-370nm	Ultra-pure water	500 W Xe lamp (Full spectrum)	No	42.6μmol·g_{cat}^{-1}·h^{-1}	this work