Cationic vacancy engineering of p-TiO_2 for enhanced photocatalytic nitrogen fixation

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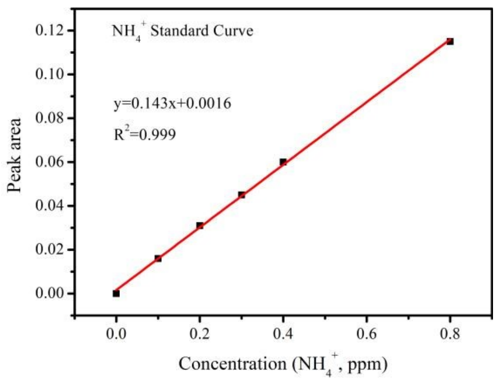


Fig. S1. Standard curve for NH_4^+ concentration.

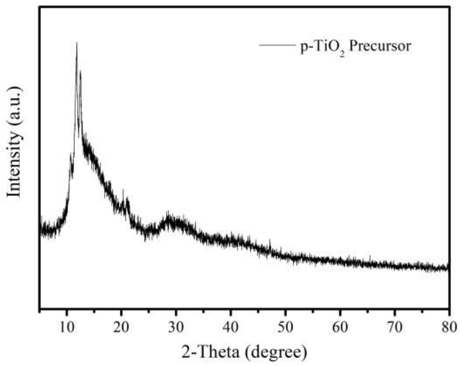


Fig. S2. XRD patterns of p-TiO_2 precursor.

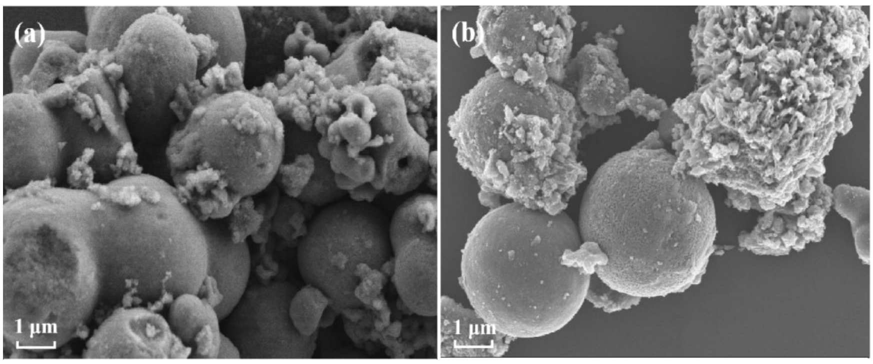


Fig. S3. SEM images of (a) n-TiO_2 and (b) p-TiO_2 (II).

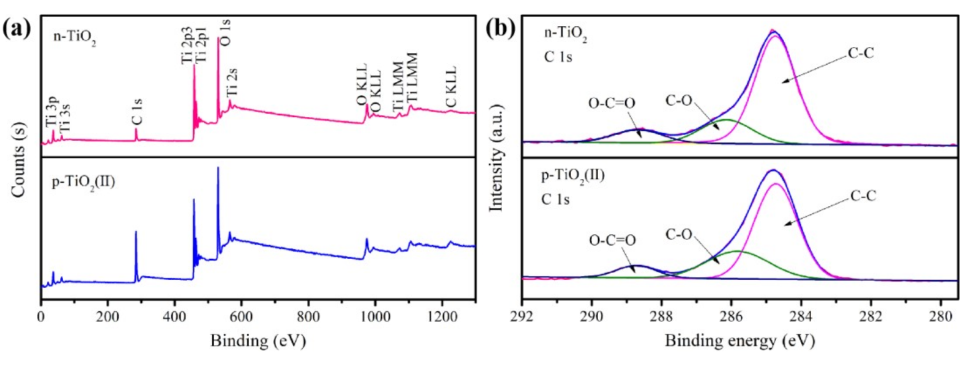


Fig. S4. (a) total XPS spectrum, (b) XPS spectra for C 1s of n-TiO_2 and p-TiO_2 (II).

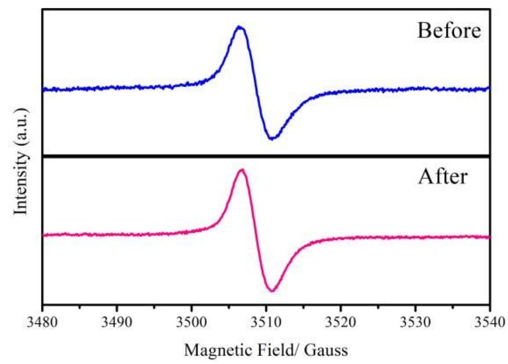


Fig. S5. The EPR of p-TiO_2 (II) before and after cycle reaction.

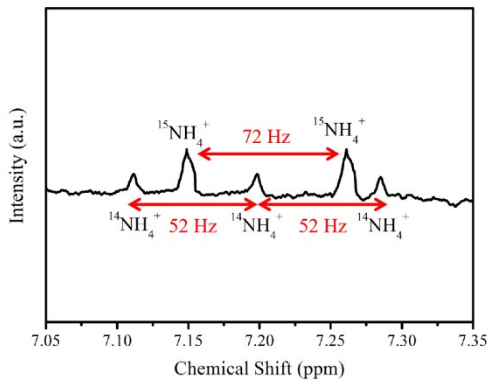
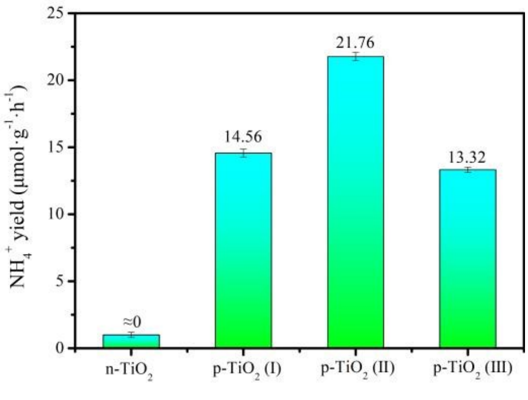


Fig. S6. 1H NMR spectrum of the solution obtained after NRR on TiO_2 (II) using $^{15}N_2$ as the reaction gas



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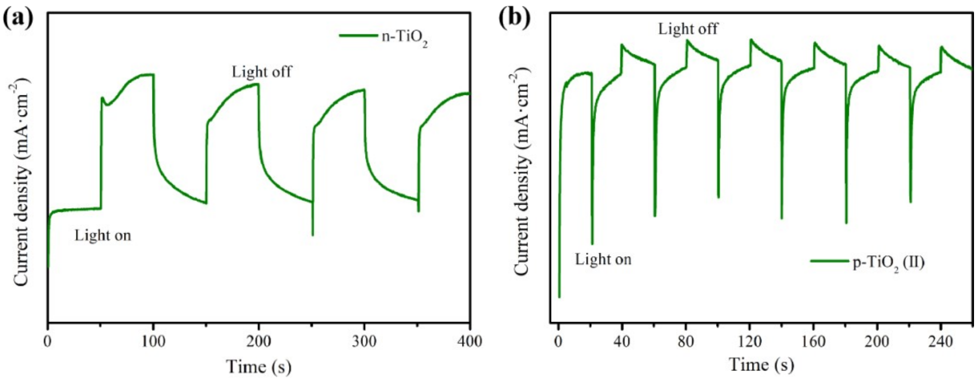

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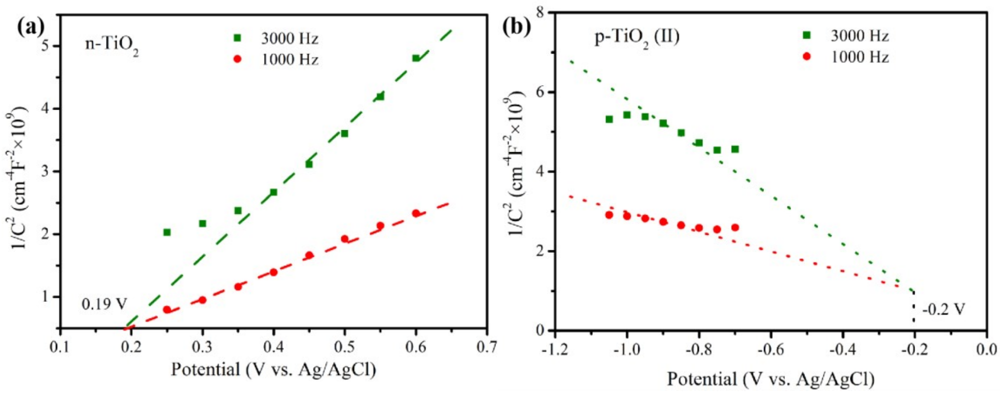

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Table S1. The result for photocatalytic N_2 fixation in previous literature about other photocatalysts and our work.

Catalyst	Reaction medium	Scavenger	Light Source	Ammonia generation rate	Reference
V_{Ti}-p-TiO_2	H_2O (l)	No	300 W Xenon lamp, Full Spectrum	64.8 μmol·g^{-1}·h^{-1}	This work
Fe-doped TiO_2	H_2O (g) 40 °C	No	360 W Hg-Arc Lamp, Full Spectrum	11.5 μmol·g^{-1}·h^{-1}	S1
Ru/TiO_2	H_2O (l)	No	150 W Xe arc lamp, Full Spectrum	29.4 μmol·g^{-1}·h^{-1}	S2
Ru/TiO_2	H_2O (l), alkaline	Ascorbic acid	250 W Xenon lamp, Full Spectrum	13.6 μmol·g^{-1}·h^{-1}	S3
Cu-doped TiO_2	H_2O (l)	No	300 W Xenon lamp,	78.9 μmol·g^{-1}·h^{-1}	S4

			Full spectrum		
CN-OvTiO$_2$	H_2O (l)	No	300 W Xenon lamp, Full spectrum	48.7 μmol·g^{-1}·h^{-1}	S5
TiO_2 nanotube	H_2O (l) Methanol	Methanol	300 W Xenon lamp, Full spectrum	318 μmol·g^{-1}·h^{-1}	S6
N-doping TiO_2	H_2O (l)	No	300 W Xenon lamp, λ> 400 nm	80.09 μmol·g^{-1}·h^{-1}	S7
Ov-TiO_2	H_2O (l) Methanol	Methanol	300 W Xenon lamp, Full spectrum	324.8 μmol·g^{-1}·h^{-1}	S8

[S1] Schrauzer G N, Guth T D. Photolysis of water and photoreduction of nitrogen on titanium dioxide. Journal of the American Chemical Society, 2002, 99(22): 7189-7193.

[S2] Ranjit K T, Varadarajan T K, Viswanathan B. Photocatalytic reduction of dinitrogen to ammonia over noble-metal-loaded TiO_2. Journal of Photochemistry and Photobiology A: Chemistry, 1996, 96(1-3): 181-185.

[S3] Rao N N, Dube S. Manjubala; Natarajan, P. Photocatalytic Reduction of Nitrogen over (Fe, Ru or Os)/TiO_2 Catalysts. Applied Catalysis B: Environmental, 1994, 5: 33-42.

[S4] Zhao Y, Zhao Y, Shi R, et al. Tuning oxygen vacancies in ultrathin TiO_2 nanosheets to boost photocatalytic nitrogen fixation up to 700 nm. Advanced Materials, 2019, 31(16): 1806482.

[S5] Wu S, He C, Wang L, et al. High-efficiency electron tandem flow mode on carbon nitride/titanium dioxide heterojunction for visible light nitrogen photofixation. Chemical Engineering Journal, 2022, 443: 136425.

[S6] Comer, Benjamin M., and Andrew J. Medford. Analysis of photocatalytic nitrogen fixation on rutile TiO_2 (110). ACS Sustainable Chemistry & Engineering, 2018, 6(4): 4648-4660.

[S7] LI, Chang, et al. N-doping TiO_2 hollow microspheres with abundant oxygen vacancies for highly photocatalytic nitrogen fixation. Journal of Colloid and Interface Science, 2022, 609: 341-352.

[S8] Zhang, Guoqiang, et al. Constructing a tunable defect structure in TiO_2 for photocatalytic nitrogen fixation. Journal of Materials Chemistry A, 2020, 8(1): 334-341.