Supporting Information

Constructing a tunable defect structure in TiO_2 for photocatalytic nitrogen fixation

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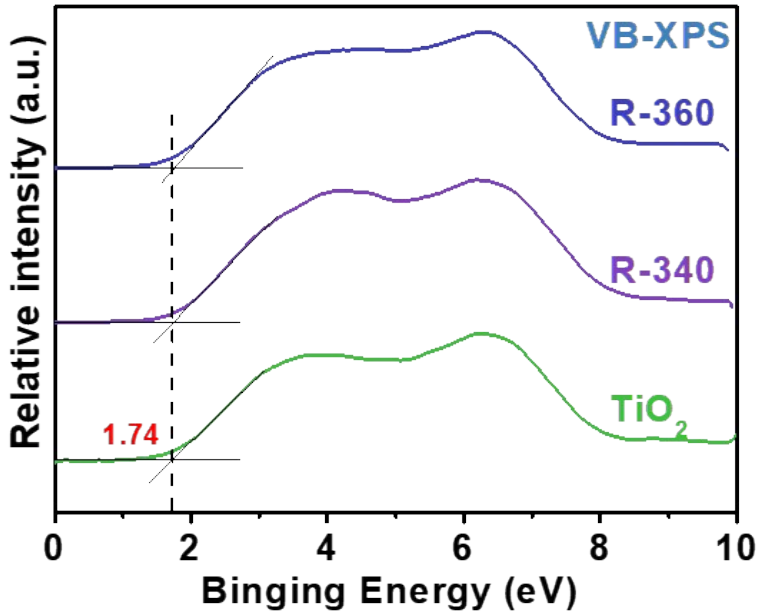

Figure S1. VB-XPS of anatase, R-340 and R-360.

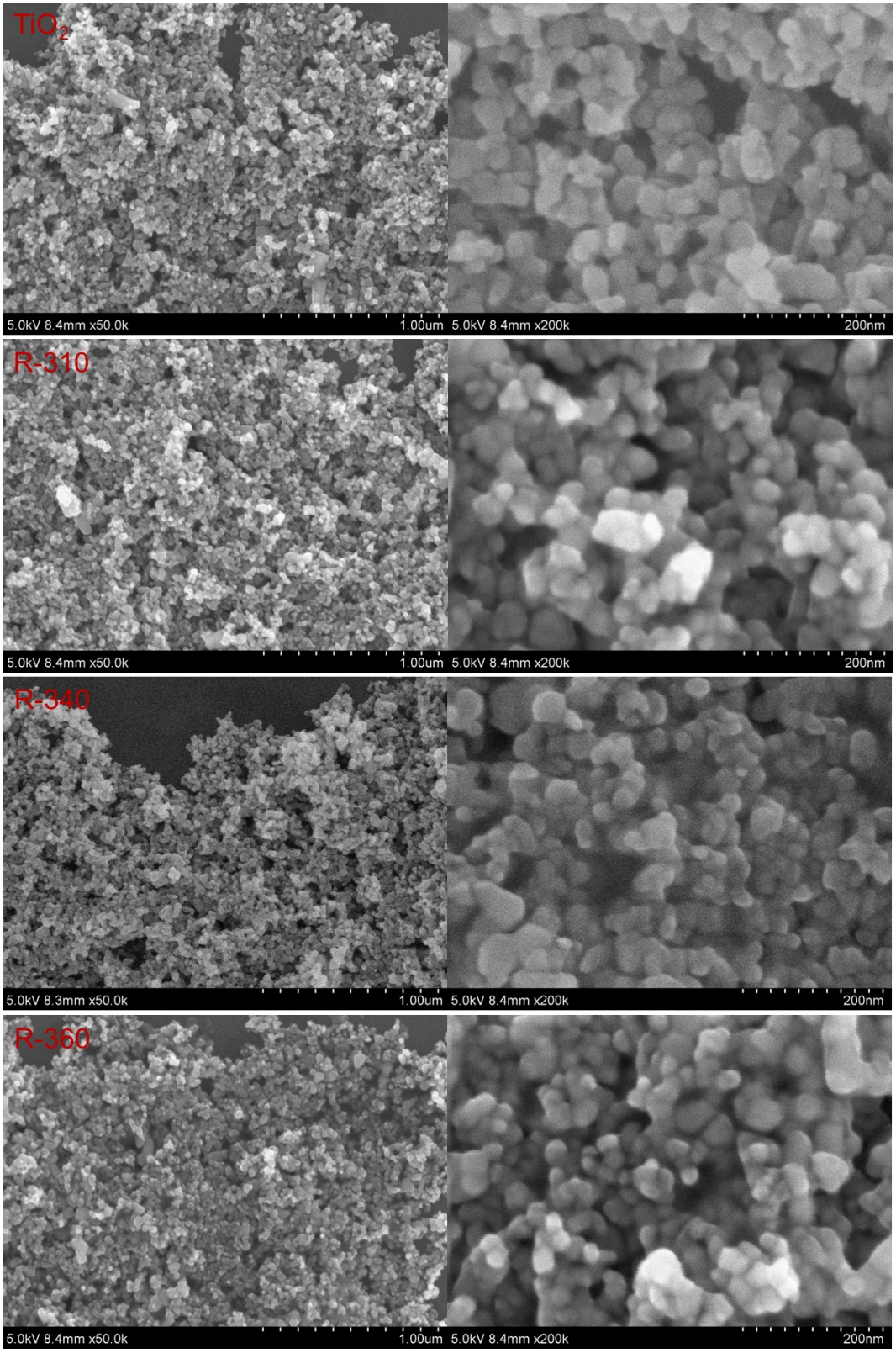

Figure S2. The SEM images of anatase and reduced TiO_2 (R-310, R-340, R-360).

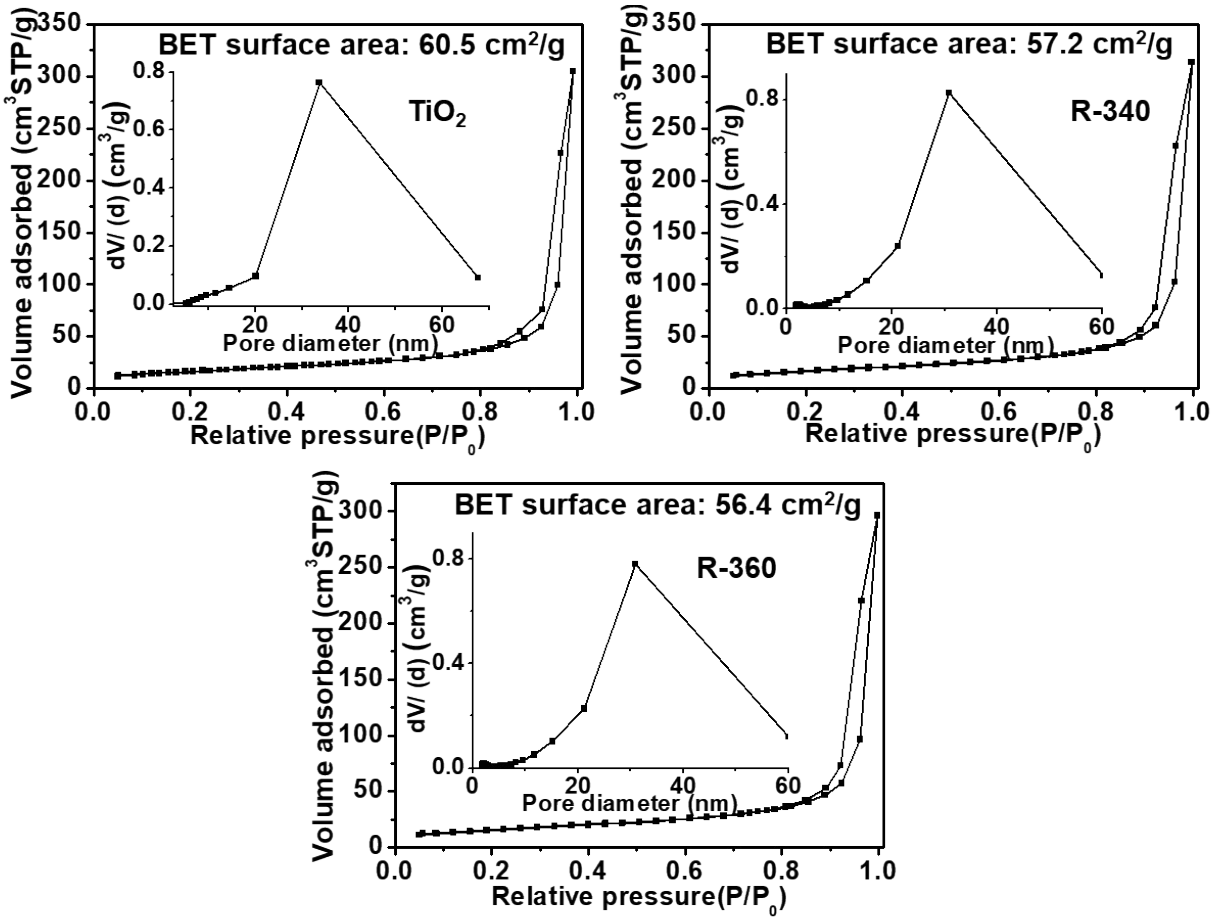

Figure S3. The N_2 adsorption-desorption isotherms of anatase and reduced TiO_2 (R-340, R-360), insets are pore size distributions.

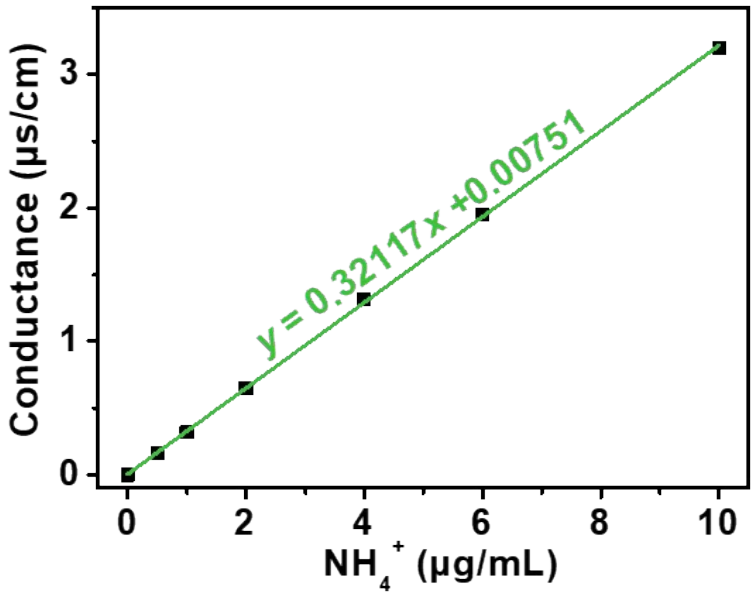

Figure S4. The standard curve of NH_4^+ amount detected by cation exchange

chromatography.

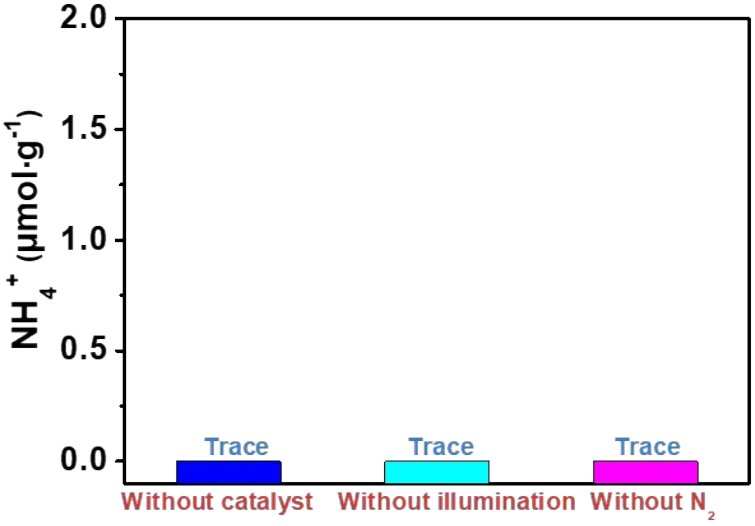

Figure S5. Control experiments for N_2 fixation reaction conducted in the absence of any one of the following: light irradiation, N_2 or the catalyst.

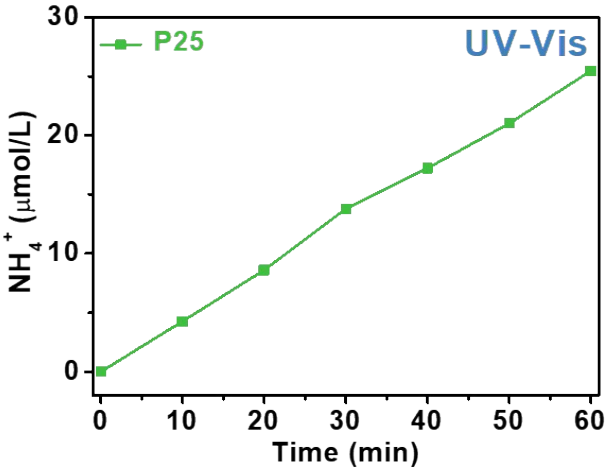

Figure S6. The full spectrum N_2 fixation of P25. The 50 mg of P25 samples were dispersed into 100 mL of 10 vol% methanol solution under full spectrum irradiations for N_2 fixation.

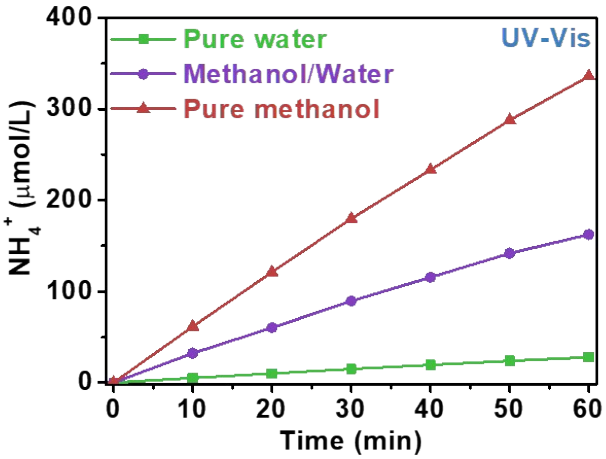

Figure S7. The full spectrum nitrogen fixation of R-340 in pure water, methanol/water and methanol.

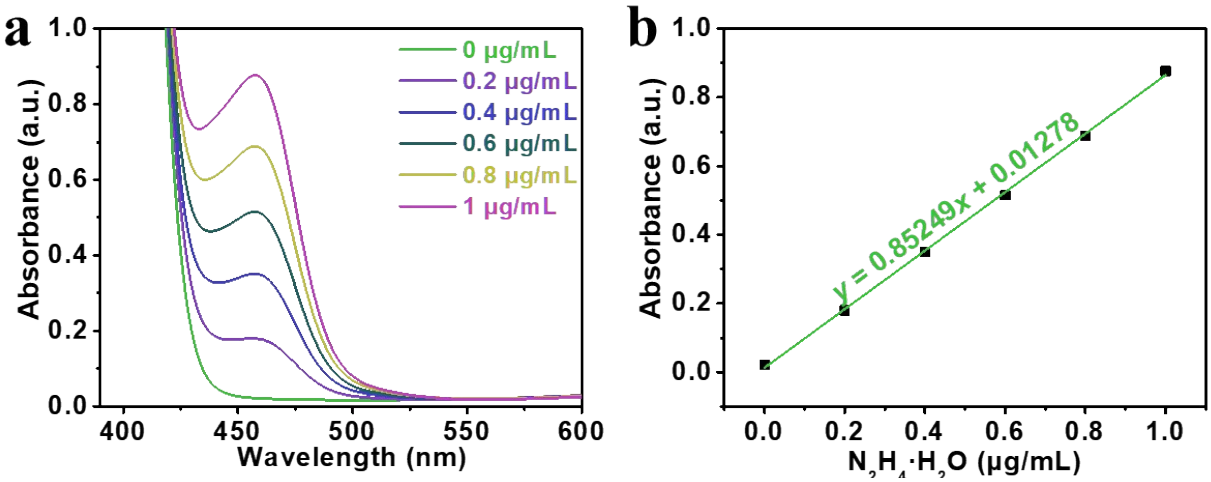

Figure S8. The detection of hydrazine, UV-Vis spectra curves (a) and the standard curve of hydrazine content (b).

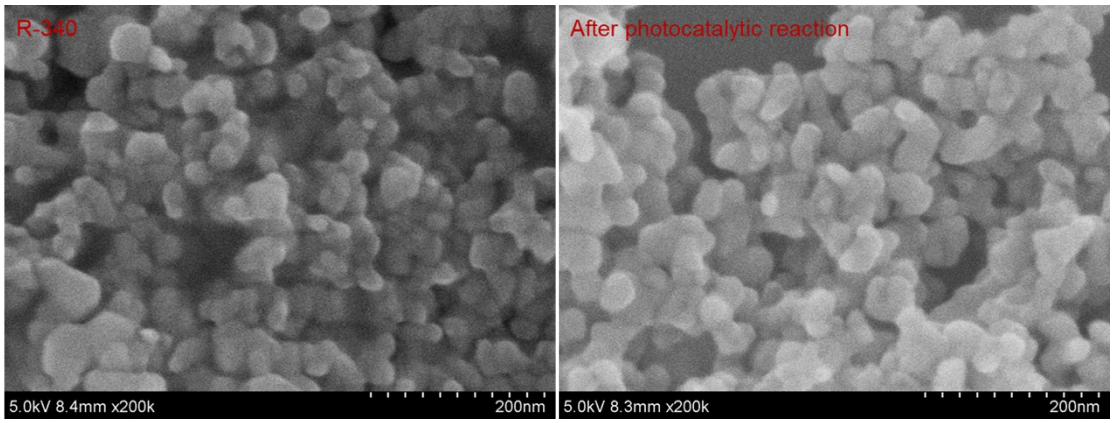

Figure S9. The SEM images of R-340 samples before and after photocatalytic reaction.

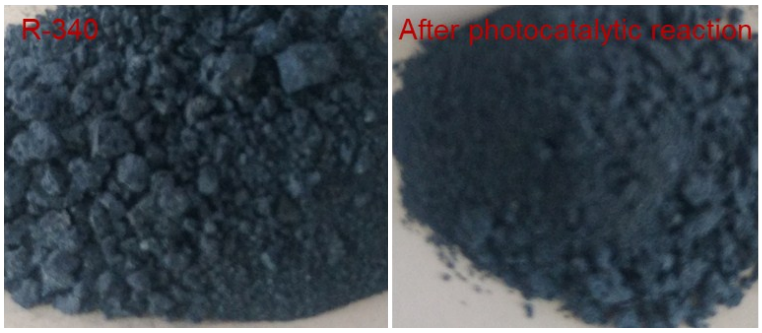

Figure S10. The optical images of R-340 samples before and after photocatalytic reaction.

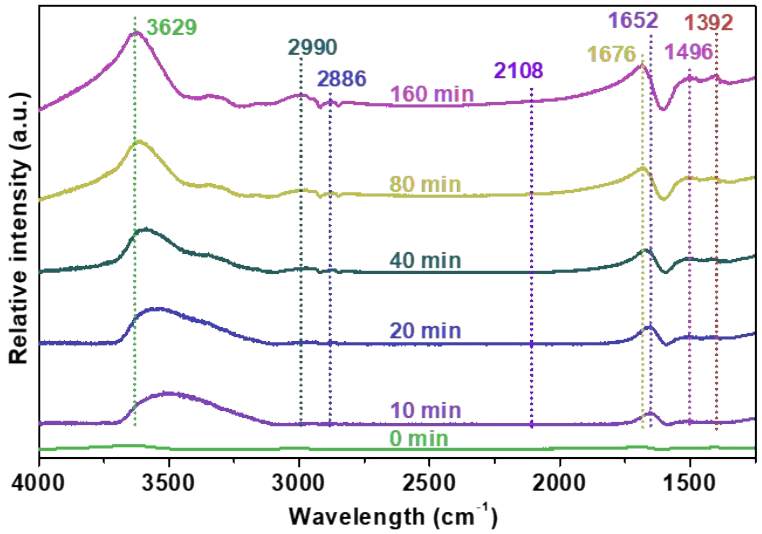

Figure S11. *In situ* DRIFTS detected as a function of time in the N_2 fixation reaction. on the anatase TiO_2.

Table S1. Comparison of reduced TiO_2 with other reported photocatalysts towards N_2 fixation under full spectrum.

catalyst	light source	conditions	NH_3 production rate μmol/h/g	AQE	**Ref.**
TiO_2-OV	300 W Hg lamp	water	0.73	0.7% at λ < 350 nm	1
CuCr	300 W Xe lamp	water	92.4	0.44% at 380 nm	2
Diamond	450 W high pressure Hg/Xe lamp	35 mL water, 11.6 mg KI	7.43	0.6% at 211.5 nm, 0.15% at 223.5 nm	3
BiOBr-OV	300 W Xe lamp	water	223.3	1.3% at 380 nm	4
FeS-SnS chalcogel	150 W Xe lamp	10 mL water, 150 mg wet chalcogel	1.2	/	5
Fe@3D graphene	500 W high pressure Hg lamp	Gas reactor of 944 mL in capacity	24	/	6
C-WO_3	500 mW/cm^2 Xe lamp	water	205	/	7
Sb/TiO_2	300 W Xe lamp	Methanol (20 vol%) solution	32.2	/	8
Ru-TiO_2	300 W Xenon lamp	Ethanol (20 vol%) solution	3.31	/	9
Reduced TiO_2	300 W Xe lamp	Methanol (10 vol%) solution	324.9	1.1% at 365 nm	This work

	Bond length (Å)
N2	1.11337
N2H4	1.43802
TiO2-OV-N2	1.13821
TiO2-OV-N2H	1.25419
TiO2-OV-N2H2	1.37064
TiO2-OV-N2H3	1.42996

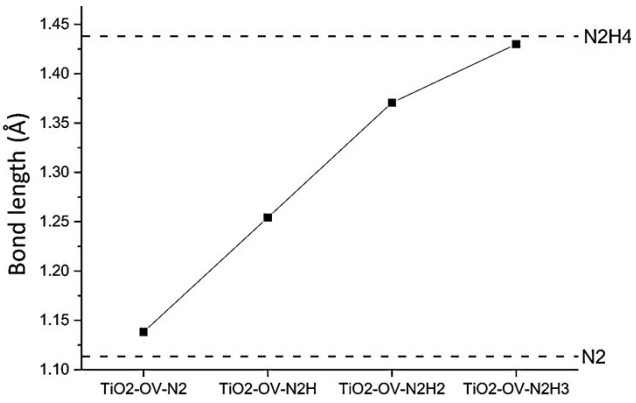

Figure S12. Theoretical calculation of each step of photocatalytic nitrogen fixation and the change of bond length of nitrogen molecule.

	Energy/eV	Adsorption energy eV
TiO2	-986.443168	
TiO2-OV	-976.428616	
N2	-16.633372	
NH3	-19.093341	
H	-1.117086	
N2H4	-30.325537	
TiO2-OV-N2	-994.153488	-1.0915
TiO2-OV-N2H	-1000.43333	-5.16275
TiO2-OV-N2H2	-1005.09892	-3.54851
TiO2-OV-N2H3	-1008.40921	-2.19321
TiO2-OV-N2H4	-1014.66064	-5.13434
TiO2-OV-NH2+NH3	-1018.66491	-2.88719
TiO2-OV-NH3	-1021.21519	-1.43319

Figure S13. Theoretical calculation of energy changes at each step in the photocatalytic nitrogen fixation process.

Reference

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