Supporting Information

Tuning the Nanoarchitectonics of $NaNbO_3$ for Overall Photocatalytic Nitrogen Fixation: Insights into Defect Engineering and Heteroatom Doping

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S1. Materials characterization

Powder X-ray diffraction (PXRD) measurements were done in 2θ ranging from 5^o to 80^o by using Rikagu SmartLab rotating anode X-ray diffractometer (9 kV) with Ni-filtered Cu K_α irradiation having wavelength 0.1542 nm with a scanning rate of 2 ^{o}C min^{-1} with 45 kV and 100 mA. Raman spectroscopic studies were carried out with high-resolution Horiba LabRAM using a 532 nm laser for excitation. FTIR measurements were done on PerkinElmer Spectrum 2 spectrometer in the range 400 to 4000 cm^{-1}. Photoluminescence (PL) studies were done on Agilent Technologies Cary Eclipse fluorescence spectrophotometer. The absorbance of as-prepared samples was recorded by using diffuse reflectance spectroscopy (DRS) employing polytetrafluoroethylene (PTFE) polymer as a standard on Perkin Elmer UV-visible-NIR lambda 750 spectrophotometer. The morphological studies were done by scanning electron microscope (SEM), FEI Nova Nano SEM-450 instrument, and high-resolution images were taken on transmission electron microscope (TEM), FEI Technai G 20 S-twin microscope operating at 200 kV. X-ray photoelectron spectroscopy (XPS) studies were performed on the samples using ThermoFisher Scientific NEXSA photoemission spectrometer working at 12 kV anode voltage and 6.50 mA filament current using Al K_α (1486.6 eV) anode as a source. The obtained data were analyzed using Avantage software. EPR spectra were recorded on Bruker EMX MicroX spectrometer. The TGA analysis was done on the NETZSCH STA 449 F1 Jupiter. About 2 mg of sample was heated under a nitrogen atmosphere from room temperature to 800 °C at a heating rate of 10 ^{o}C min^{-1}. The BEL/CAT2 instrument was used for temperature programmed desorption studies (TPD). The Brunauer-Emmett-Teller (BET) surface area studies were carried out at 77 K on Quantachrome Autosorb-iQ-MP-XR system. Mott-Schottky and photocurrent studies were done on AUTOLAB electrochemical workstation. The photocatalytic experiments were done in a home-built photoreactor setup consisting of three 45 W white LED lamps and UV-vis spectra of collected samples were recorded on Shimadzu UV-2450 spectrophotometer. The nuclear magnetic resonance (NMR) spectra were measured using a JEOL-USA (JNMECX500) spectrometer in DMSO-d_6 using tetramethyl silane (TMS) as an internal standard. The coupling constant "J" was calculated in Hz. ^{1}H-NMR spectra were recorded at 500 MHz frequency. The fluorescence lifetime was measured using Horiba Scientific Delta Flex TSCPC system with pulsed nanoLED sources.

S2. Quantification of NH_3 using Different Methods

(1) Nessler's Reagent

The quantification of NH_3 using Nessler's reagent method was done using UV-vis spectroscopy. For NH_3 detection, standard stock solutions with concentrations of 3.12, 6.25, 12.50, 25, 50, 100 μM were prepared using NH_4Cl. For quantification, 1 mL of ammonia mixture was taken in a vial, to which 50 μL of sodium potassium tartrate ($C_4H_4O_6KNa{\cdot}4H_2O$) and 100 μL of Nessler's reagent was added. The UV-vis measurement was carried out in the range of 200-800 nm to obtain the analogous calibration curve. In this method, iodide and mercury ions react with ammonia under alkaline conditions to produce a reddish brown complex which shows absorbance at 420 nm. The corresponding amount was quantified with respect to the measured absorbance value and was compared with absorbance of standard solutions.[1]

(2) Nuclear Magnetic Resonance (NMR)

The amount of NH_3 produced in the reaction mixture was also determined using NMR.30 mL of reaction mixture was taken out after centrifugation. Afterward, 2M H_2SO_4 was added to the reaction mixture until the pH was equal to 2. Then, the solution was evaporated using rotary evaporator until 1 mL of the mixture remained. 700 μL of the remaining mixture and 300 μL DMSO-d_6 were mixed. Afterward, 800 μL solution was taken out and NMR spectra was recorded. The number of scans to record the NMR spectra were kept at 8000.

S3. Quantification of Hydrazine using Watt & Chrisp method

The presence of hydrazine (N_2H_4) is determined by Watt and Chrisp method.[2] 2g of para (dimethyamino) benzaldehyde with 10 mL of concentrated HCl and 100 mL of ethanol were mixed. The above solution mixture was used as a reagent for hydrazine test. For the detection of hydrazine, 1 mL of ammonia mixture was taken in a vial with 1 mL of reagent mixture. The solution was left to react for 1 h at room temperature and then the absorbance was measured at 455 nm using a UV-VIS spectrophotometer. The concentration of N_2H_4 was determined by comparing the measured absorbance to a calibration curve generated using standard solutions of N_2H_4.

S4. Quantification of nitrate (NO_3^-) and nitrite (NO_2^-)

The quantification of NO_3^- and NO_2^- ions was done using UV-vis spectroscopy. For NO_3^- ion detection, standard stock solutions with varying concentrations (0 to 100 µmol L^{-1}) were prepared using $NaNO_3$. Then, 1 mL of standard solution was taken, and UV-vis measurement was carried out in the range of 200-300 nm to obtain the analogous calibration curve. Similarly, the amount of NO_3^- present in the reaction mixture was determined using UV-vis spectrophotometer, wherein the peak at 220 nm of wavelength corresponds to the absorption of nitrates and the corresponding amount was quantified with respect to the measured absorbance value.

For the detection of NO_2^-, a diazotization reaction was carried out. In diazotization reaction, sulfanilamide reacts with NO_2^- ions under an acidic environment, followed by coupling with N-(1-napthyl) ethylenediamine dihydrochloride, resulting in pink azo dyes. Two reagents were separately prepared for the detection of NO_2^- ions. Firstly, 0.5 g of sulfanilamide was dissolved in 50 mL of 2 M HCl, and the solution was named reagent A. 20 mg of N-(1-napthyl) ethylenediamine dihydrochloride was dissolved in 20 mL of deionized water and named as reagent B. For the calibration curve, 1 mL of standard or sample solutions were taken in glass vials, to which 20 µL of A was added and allowed to stand for 10 min, followed by the addition of 20 µL of B, respectively. After mild shaking, the solution mixture was kept undisturbed for 30 min and the amount of NO_2^- was estimated at the wavelength of 540 nm, from which calibration curves were extracted and plotted.

S5. Preparation of samples for photoluminescence (PL) and photocurrent studies

For PL studies, the 2 mg of photocatalysts (NNO, DNNO1, DNNO2, DNNO3, NVNO0.25, NVNO0.50 and NVNO0.75) was measured and dispersed in 4 mL of deionized water. The resultant solutions were sonicated for 30 min and then subjected to the PL studies. The excitation wavelength used in this study was 320 nm.

For photocurrent studies, the measured quantity (5 mg) of photocatalysts (NNO, DNNO2 and NVNO0.25) was taken. Then, 400 μL of deionized water and 400 μL of IPA were added to each of the catalysts separately. Further, 10 μL of Nafion was added to the resultant mixtures of catalysts and subjected to the sonication for 30 min. Afterward, the 40 μL of resultant solutions were dispersed on indium tin oxide (ITO) substrates. 0.1 M of Na_2SO_4 solution was used as electrolyte solution and photocurrent studies were recorded at 0 V vs Ag/AgCl.

Table S1. Calculated lattice parameters of pristine NNO, oxygen vacancy-rich (DNNO1, DNNO2, DNNO3) and V-doped samples (NVNO0.25, NVNO0.50, NVNO0.75).

Sl. No.	Sample Name	Average Crystallite Size (nm)	Lattice Strain (ε X 10^{-3})	Lattice Parameters (nm)
1.	NNO	20.36	5.11	a = 0.384, b = 0.391, c = 0.419
2.	DNNO1	26.32	3.29	a = 0.384, b = 0.389, c = 0.397
3.	DNNO2	21.09	4.60	a = 0.387, b = 0.387, c = 0.386
4.	DNNO3	28.96	2.99	a = 0.387, b = 0.387, c = 0.386
5.	NVNO.25	20.11	5.84	a = 0.389, b = 0.388, c = 0.396
6.	NVNO0.50	19.30	6.15	a = 0.389, b = 0.388, c = 0.378
7.	NVNO0.75	29.27	3.93	a = 0.389, b = 0.389, c = 0.396

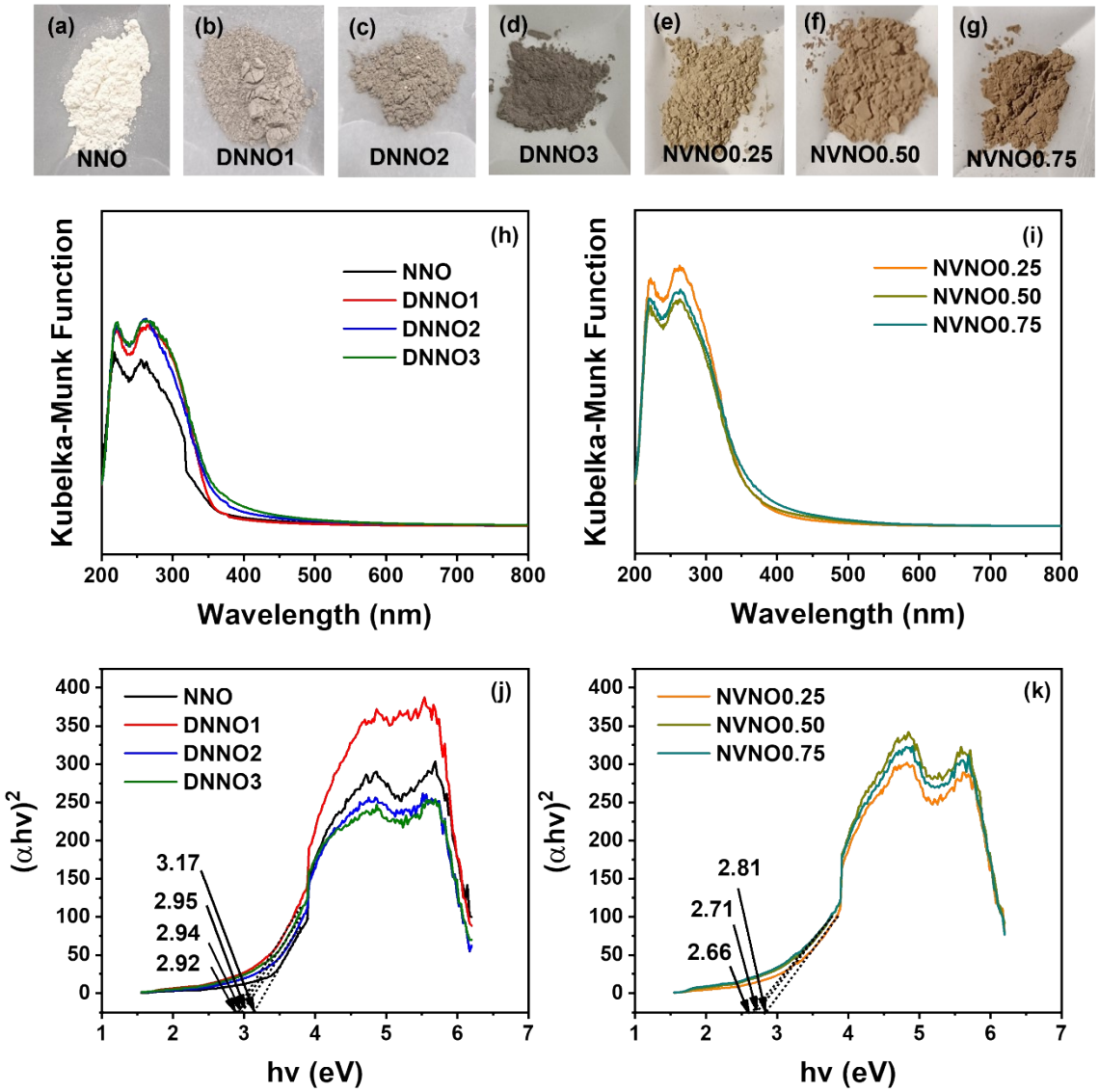

Figure S1. Photographs of (a) pristine NNO; (b-d) oxygen vacancy rich samples (DNNO1, DNNO2 and DNNO3) and (e-g) V-doped samples (NVNO0.25, NVNO0.50 and NVNO0.75), respectively; (h, i) Absorption spectra and (j, k) calculated band gaps of samples (NNO, DNNO1, DNNO2, DNNO3, NVNO0.25, NVNO0.50 and NVNO0.75).

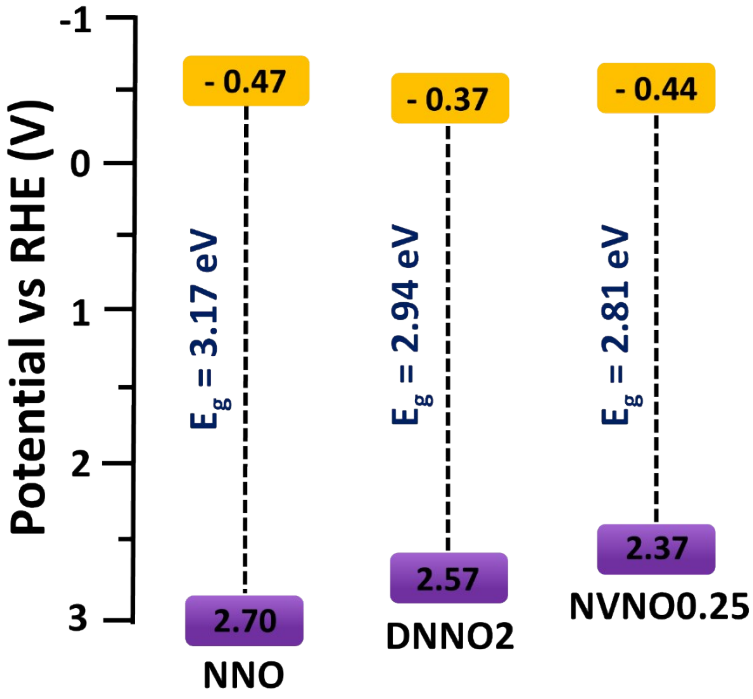

Figure S2. Band diagram of NNO, DNNO2 and NVNO0.25.

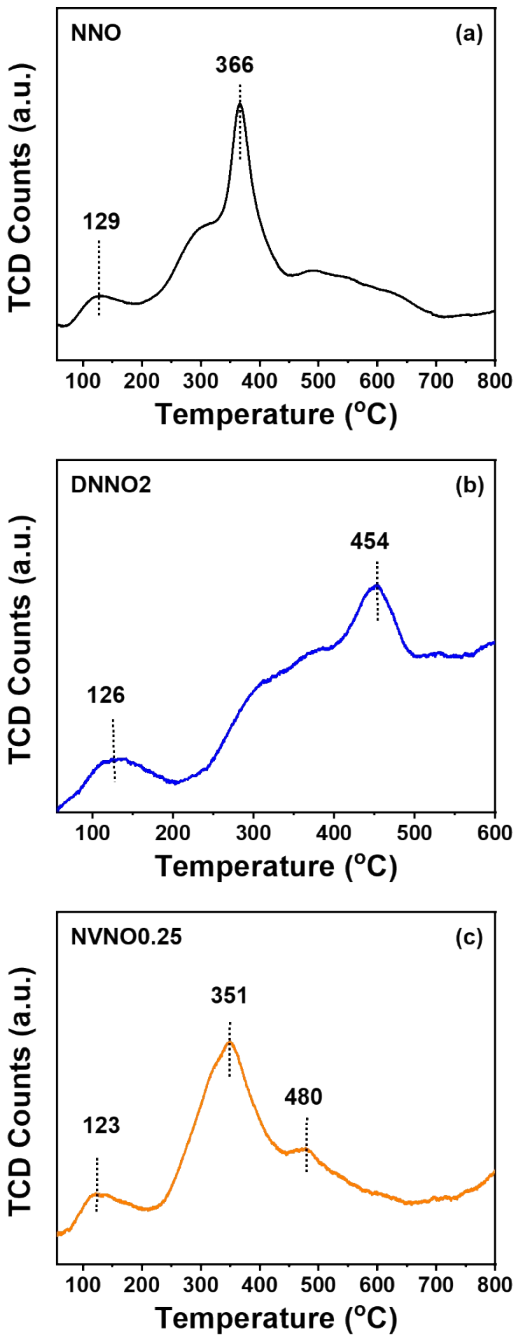

Figure S3. TPD curves of NNO, DNNO2 and NVNO0.25.

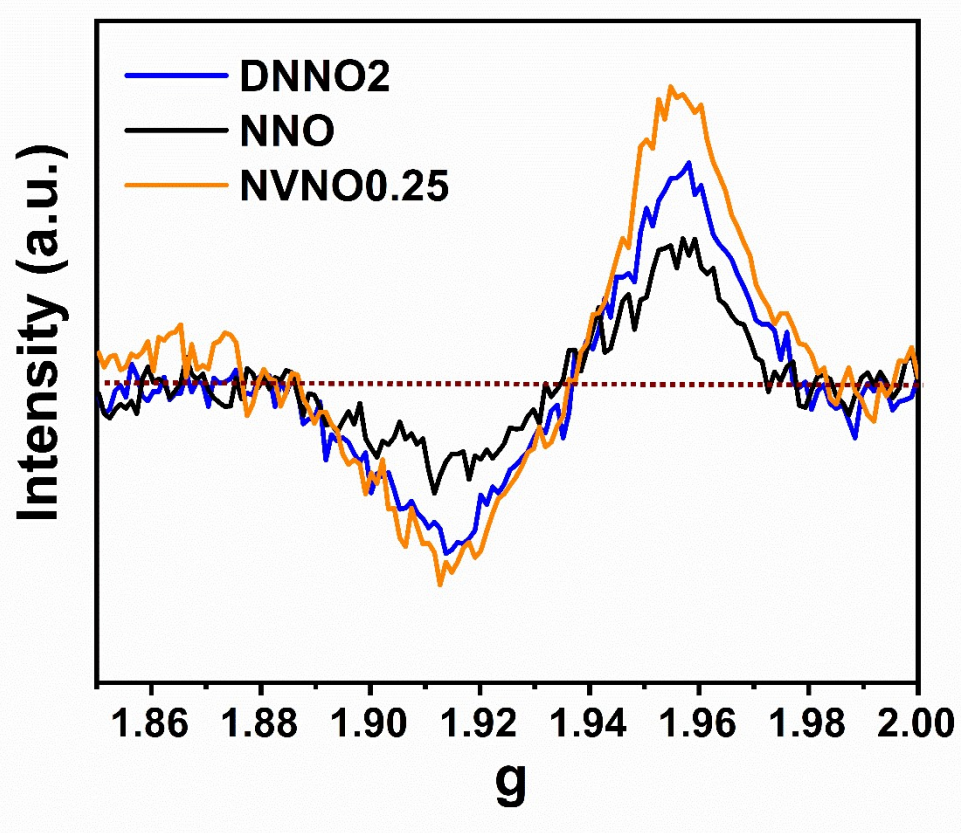

Figure S4. EPR spectra of NNO, DNNO2 and NVNO0.25.

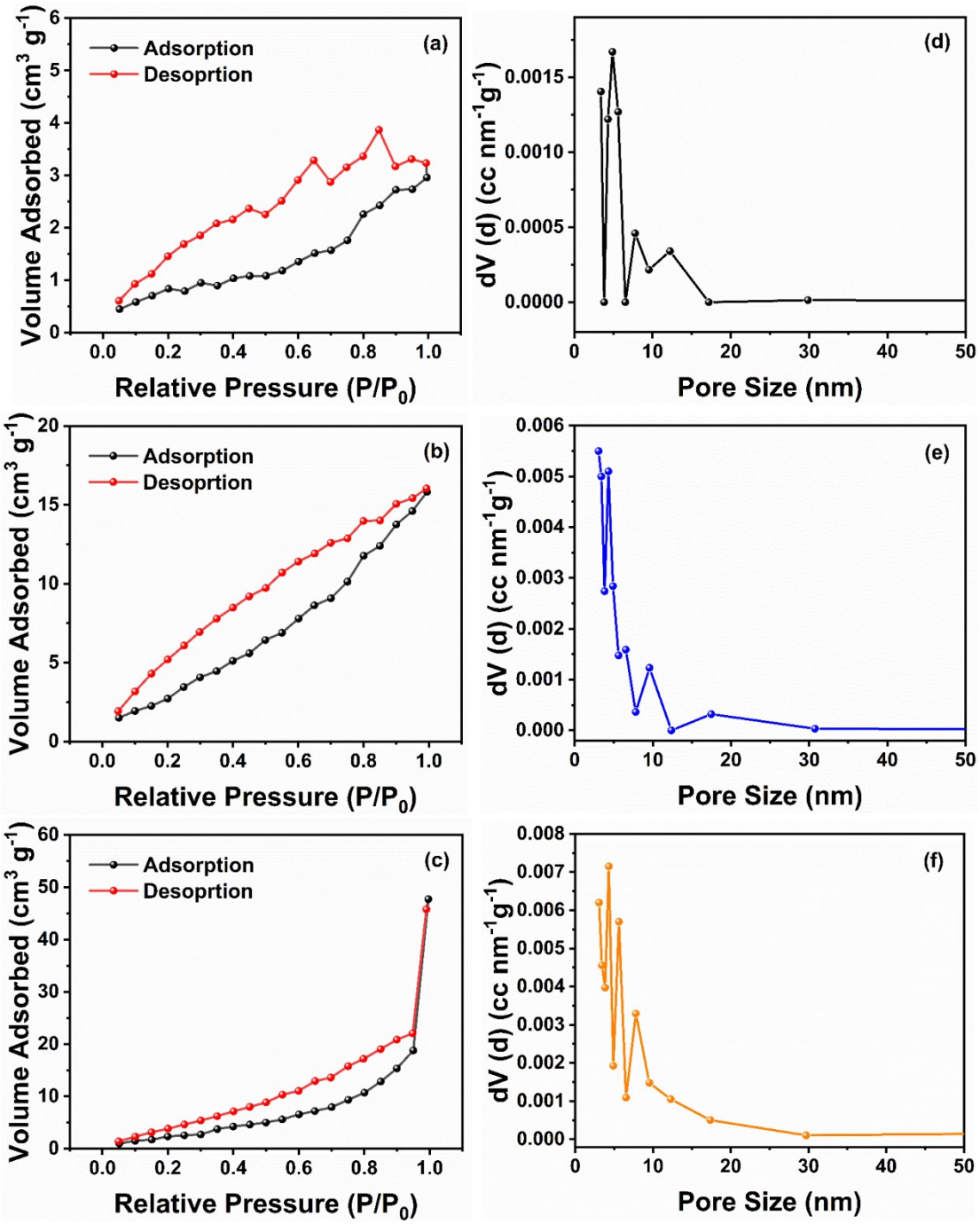

Figure S5. (a-c) N_2 adsorption-desorption isotherms; (d-f) pore size distribution in NNO, DNNO2 and NVNO0.25, respectively.

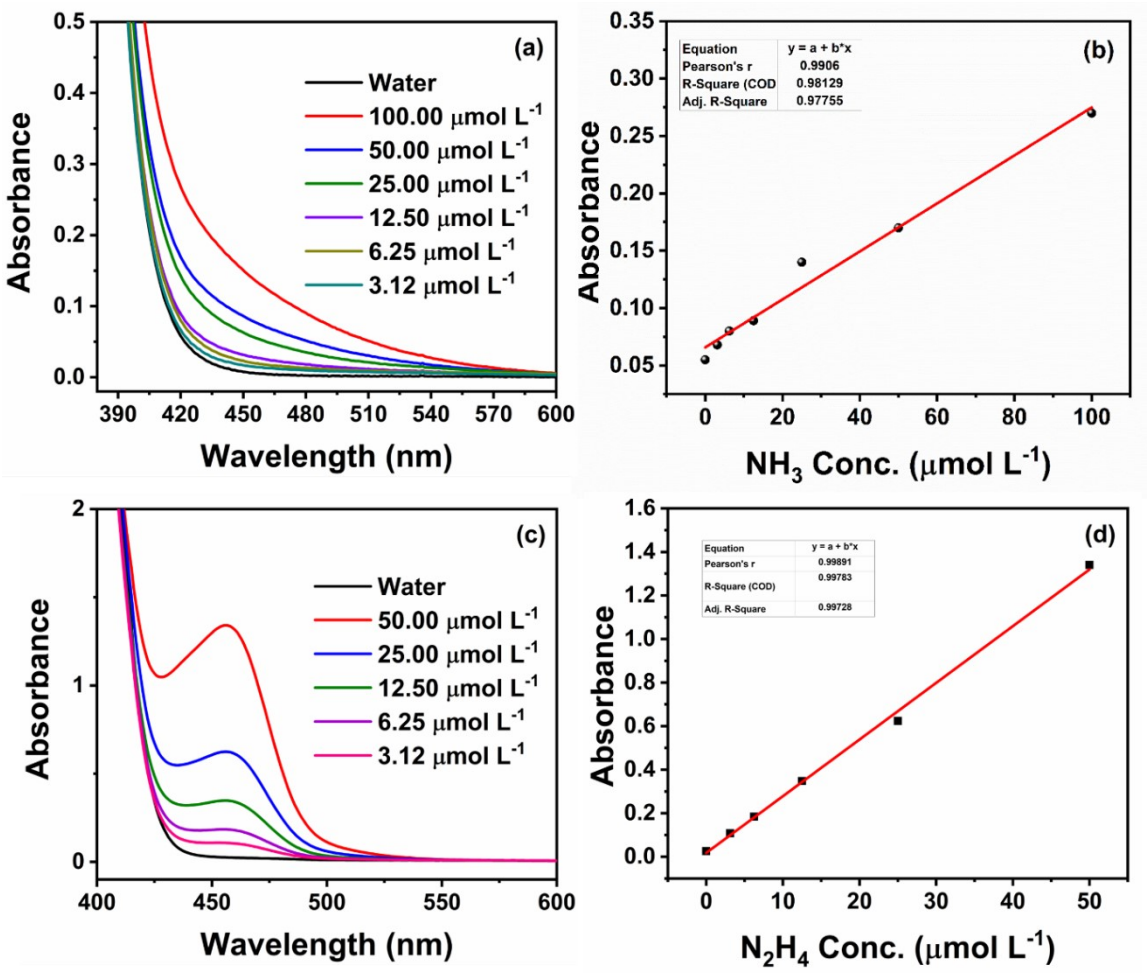

Figure S6. (a, b) Calibration curves for the determination of NH_3 using Nessler's reagent method; (c, d) Calibration curves for the determination of N_2H_4 using Watt-Chrisp method.

S5. Calculation of yield for all photocatalysts:

The yield (μmol g^{-1} h^{-1}) was obtained using the following equation:[3]

$$\text{Yield} = \frac{Ammonia\ yield\ (\mu mol)\ X\ Amount\ of\ water\ (L)}{t\ (h)\ X\ \ weight\ of\ catalyst\ (g)}$$

Here, t corresponds to the time of reaction in hours.

For every reaction, the time for reaction was 120 min (2 h) and weight of catalyst used was 0.025 g and amount of water used was 0.050 L.

For NNO:

Ammonia yield = 3 μmol

So, Yield = 3 μmol g^{-1} h^{-1}

For DNNO1:

Ammonia yield = 23 μmol

So, Yield = 23 μmol g^{-1} h^{-1}

For DNNO2:

Ammonia yield = 26 μmol

So, Yield = 26 μmol g^{-1} h^{-1}

For DNNO3:

Ammonia yield = 18 μmol

So, Yield = 18 μmol g^{-1} h^{-1}

For NVNO0.25:

Ammonia yield = 36 μmol

So, Yield = 36 μmol g^{-1} h^{-1}

For NVNO0.50:

Ammonia yield = 22 μmol

So, Yield = 22 μmol g^{-1} h^{-1}

For NVNO0.75:

Ammonia yield = 15 μmol

So, Yield = 15 μmol g^{-1} h^{-1}

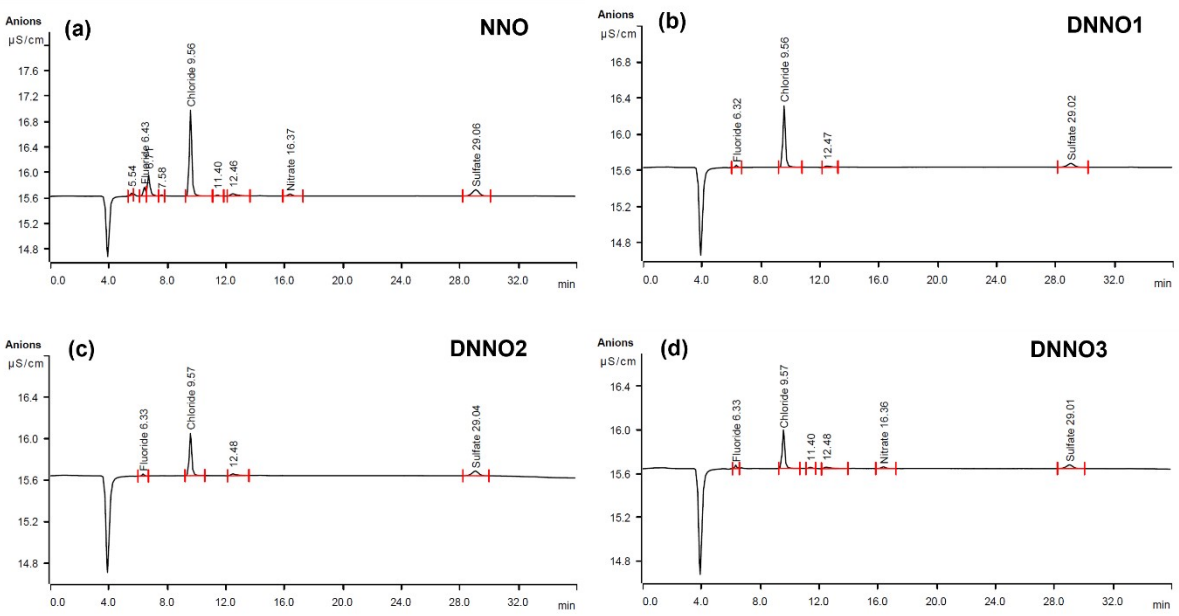

Figure S7. Ion chromatogram for NO_3^- detection of (a) NNO, (b) DNNO1, (c) DNNO2, (d) DNNO3, respectively.

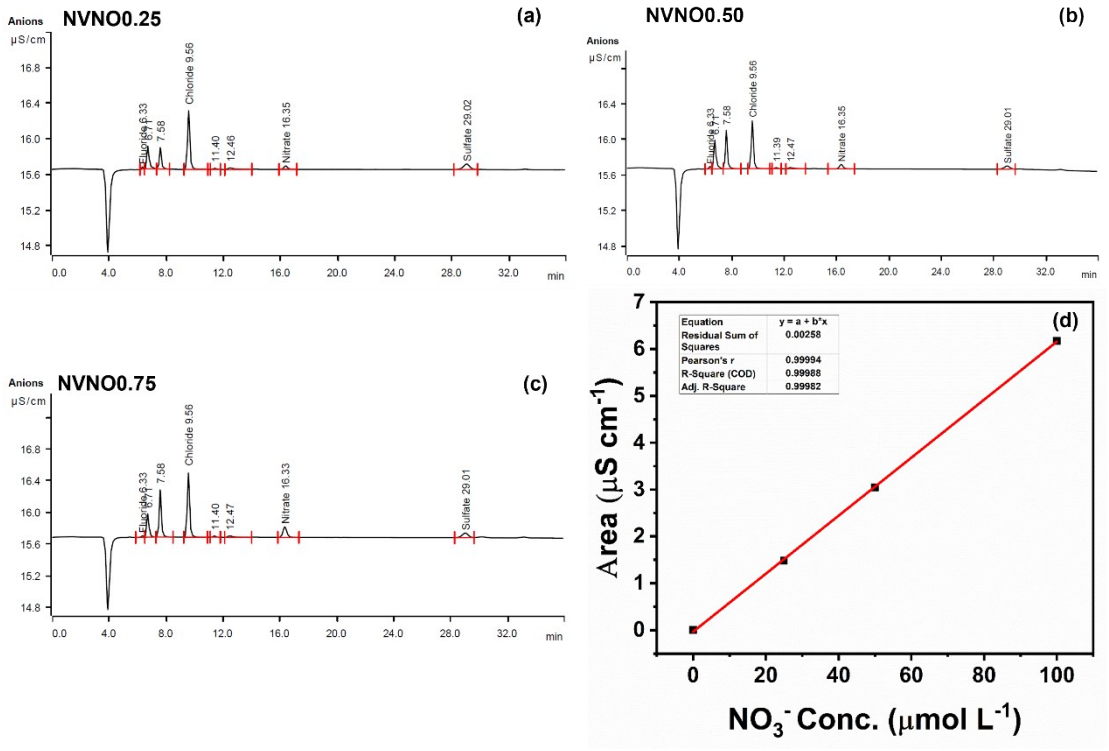

Figure S8. Ion chromatogram for NO_3^- detection of (a) NVNO0.25, (b) NVNO0.50, (c) NVNO0.75, (d) Calibration curve of NO_3^- ions using ion chromatography, respectively.

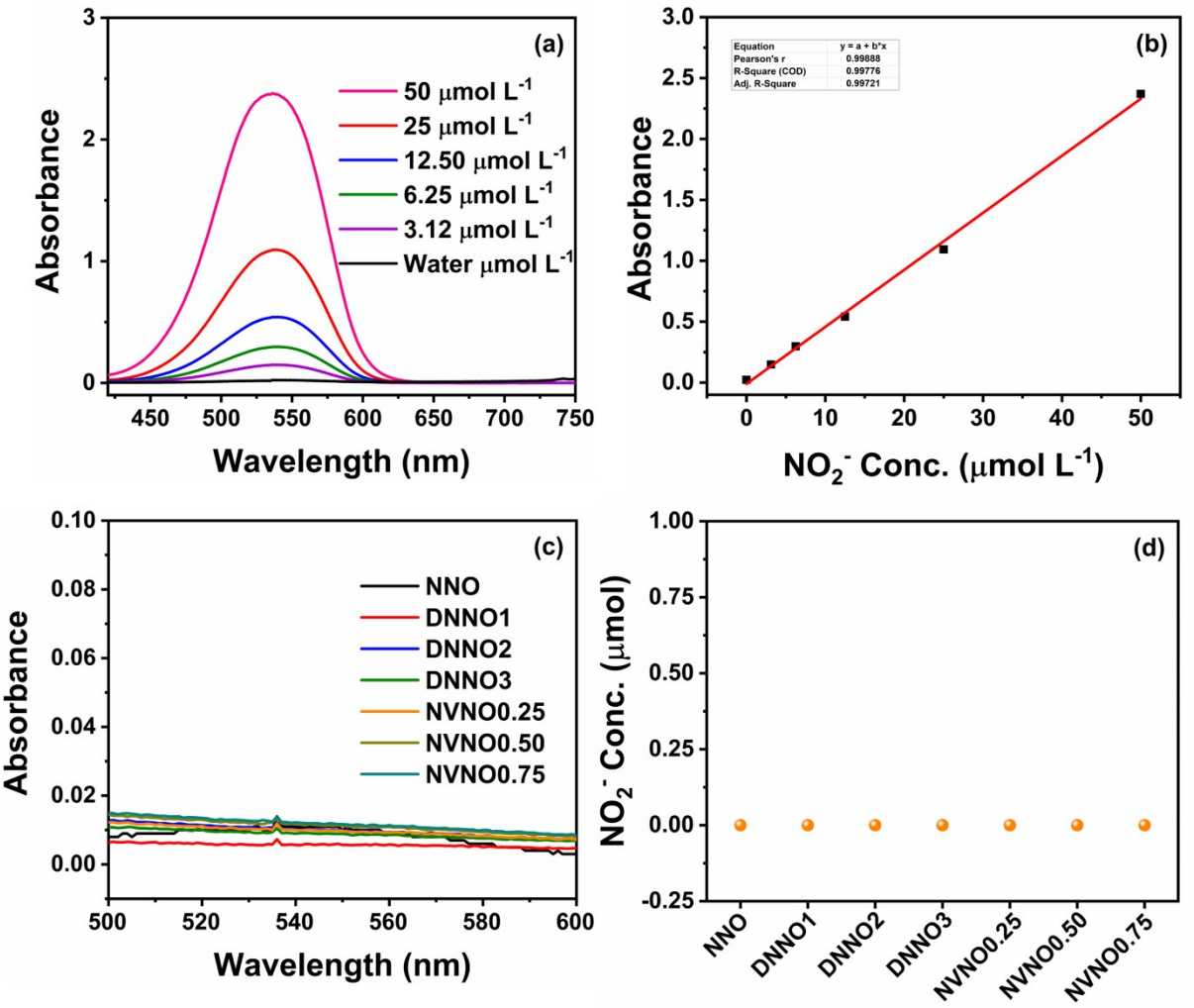

Figure S9. (a, b) Calibration curves for determination of NO_2^- ions, (c) UV-vis absorption for NO_2^-, (d) histogram of NO_2^- concentration produced in NNO, DNNO1, DNNO2, DNNO3, NVNO0.25, NVNO0.50 and NVNO0.75, respectively.

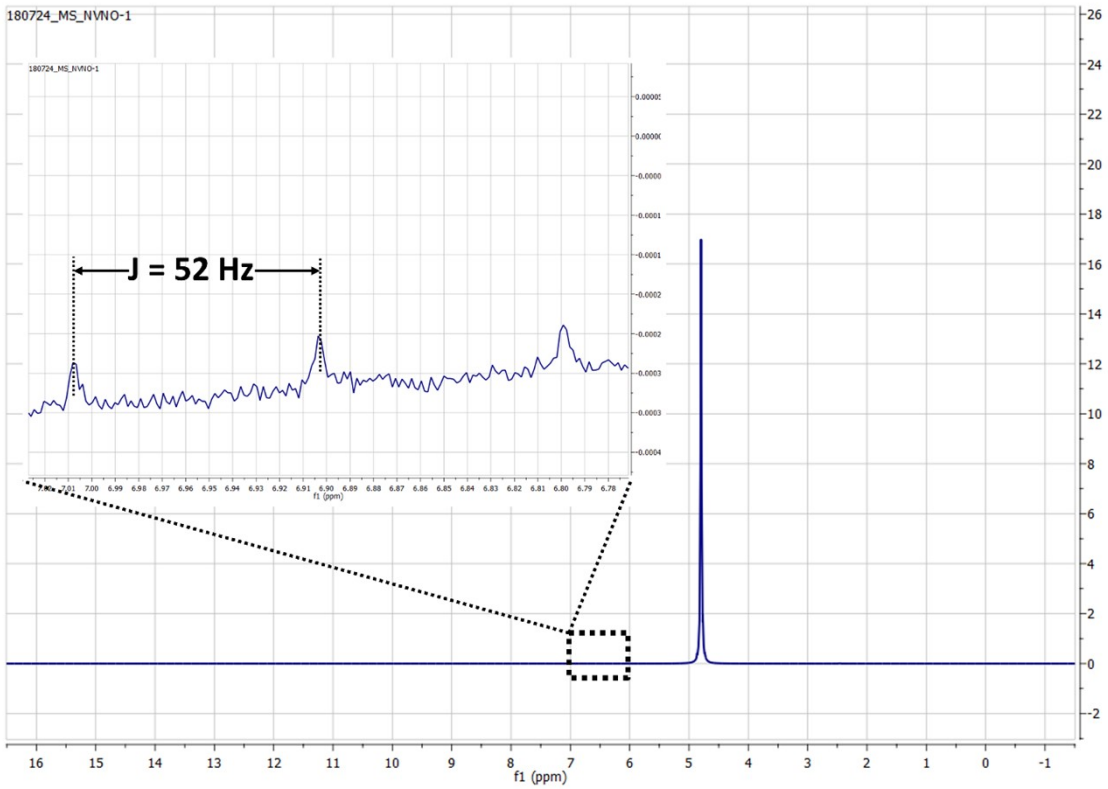

Figure S10. **^{1}H-**NMR of the NH_3 obtained from the reaction mixture.

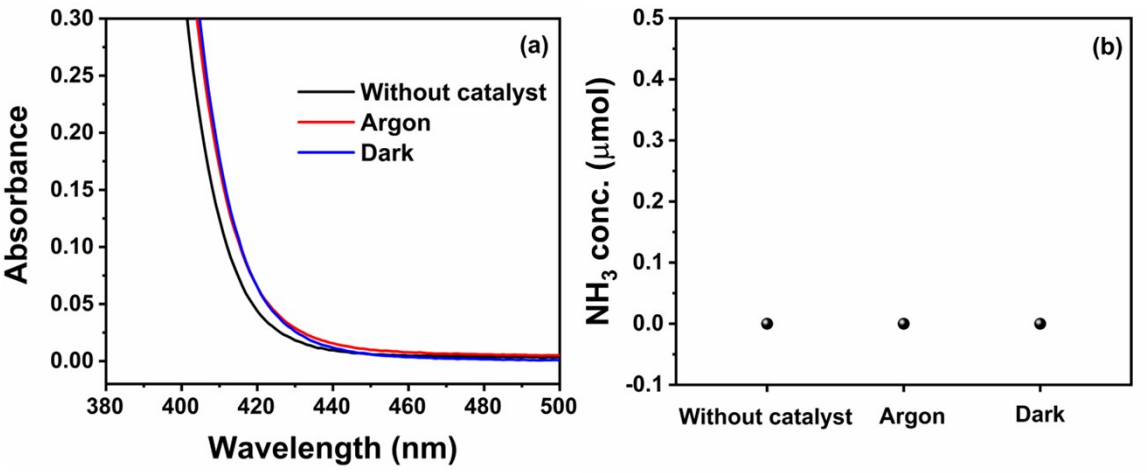

Figure S11. (a) UV-vis absorption spectra; (b) NH_3 concentration produced in control reaction conditions.

S6. Calculation of light to chemical (LCC) efficiency:

The light to chemical conversion efficiency was calculated using the equation:[4]

$$\textbf{LCC} = \frac{\Delta G\ (Jmol^{-1}) \times NH_3(mol)}{Total\ Energy\ Input\ (W) \times Reaction\ time\ (s)} X\ 100$$

For visible light, flux measured = 48900 lux.

In Wm^{-2}, calculated flux = 48900 X 0.0079

= 386.3 W m^{-2}

Irradiated surface area = 84.78 X 10^{-4} m^2

ΔG in NH_3 synthesis = 339 kJ mol^{-1}= 339 X 1000 J mol^{-1}

(a) NNO = 3 µmol

Therefore, calculated LCC = 0.0045%

(b) DNNO2 = 26 µmol

Therefore, calculated LCC = 0.033%

(b) NVNO0.25 = 36 µmol

Therefore, calculated LCC = 0.052%

(a) In sunlight, For NNO, In Wm^{-2}, calculated flux = 63000 X 0.0079

= 497.7 W m^{-2}

Calculted NH_3 yield = 12 µmol

Therefore, calculated LCC = 0.013%

(b) For DNNO2, In Wm^{-2}, calculated flux = 64600 X 0.0079

= 510.3 W m^{-2}

Calculted NH_3 yield = 36 µmol

Therefore, calculated LCC = 0.039%

(b) For NVNO0.25, In Wm^{-2}, calculated flux = 65000 X 0.0079

= 513.5 W m^{-2}

Calculted NH_3 yield = 44 µmol

Therefore, calculated LCC = 0.048%

S7. Calculation of turnover frequency (TOF) for NH_3 generation under visible light

The TOF has been calculated using the following equation:[5]

$$\text{TOF} = \frac{Number\ of\ moles\ of\ NH_3\ generated\ per\ hour}{Number\ of\ active\ sites}$$

(a) For NNO,

Amount of NH_3 generated in 2 h: 3μmol

Number of active sites (From TPD analysis): 0.343 mmol g^{-1}

Amount of catalyst used in the reaction: 25 mg = 0.025 g

Therefore, TOF = 0.009 h^{-1}

(b) For DNNO2,

Amount of NH_3 generated in 2 h: 26 μmol

Number of active sites (From TPD analysis): 0.337 mmol g^{-1}

Amount of catalyst used in the reaction: 25 mg = 0.025 g

Therefore, TOF = 0.077 h^{-1}

(b) For NVNO0.25,

Amount of NH_3 generated in 2 h: 36 μmol

Number of active sites (From TPD analysis): 0.379 mmol g^{-1}

Amount of catalyst used in the reaction: 25 mg = 0.025 g

Therefore, TOF = 0.095 h^{-1}

S8. Calculation of turnover frequency (TOF) for NH_3 generation under sunlight

The TOF has been calculated using the following equation:[5]

$$\text{TOF} = \frac{Number\ of\ moles\ of\ NH_3\ generated\ per\ hour}{Number\ of\ active\ sites}$$

(a) For NNO,

Amount of NH_3 generated in 2 h: 12 µmol

Number of active sites (From TPD analysis): 0.343 mmol g^{-1}

Amount of catalyst used in the reaction: 25 mg = 0.025 g

Therefore, TOF = 0.035 h^{-1}

(b) For DNNO,

Amount of NH_3 generated in 2 h: 36 µmol

Number of active sites (From TPD analysis): 0.337 mmol g^{-1}

Amount of catalyst used in the reaction: 25 mg = 0.025 g

Therefore, TOF = 0.110 h^{-1}

(c) For NVNO0.25,

Amount of NH_3 generated in 2 h: 44 µmol

Number of active sites (From TPD analysis): 0.379 mmol g^{-1}

Amount of catalyst used in the reaction: 25 mg = 0.025 g

Therefore, TOF = 0.120 h^{-1}

Table S2. Comparison of photoactivity of different materials.

Sl.	**Photocatalyst**	**Reaction Medium**	**NH_3 Production ($\mu mol\ g^{-1}\ h^{-1}$)**	**NO_2^-/NO_3^- Production ($\mu mol\ g^{-1}\ h^{-1}$)**	**Year[Ref.]**
1.	Ni-doped TiO_2	Water	46.80	Not detected	2020[6]
2.	Fe-doped TiO_2 nanofibers	Water	64.20	Not detected	2021[7]
3.	WO_{3-x}	1 mM Na_2SO_3 solution	82.41	Not detected	2022[8]
4.	CDS/WO_3	Water	35.80	No NO_2^-/ 14.20	2022[9]
5.	In-doped Bi_2MoO_6	Water	53.40	No NO_2^-/ 54.00	2023[10]
6.	Oxygen Vacancy rich $NaNbO_3$ V-doped $NaNbO_3$	Water	26.00 36.00	Not found No NO_2^-/2.00	This Work

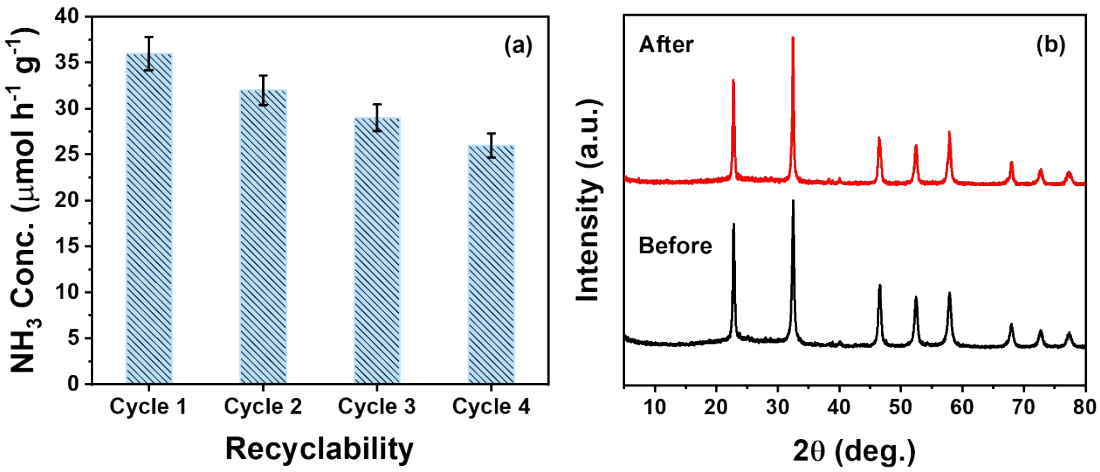

Figure S12. (a, b) NH_3 concentration after 4 cycles; (b) PXRD pattern of NVNO0.25 before and after photocatalysis experiments.

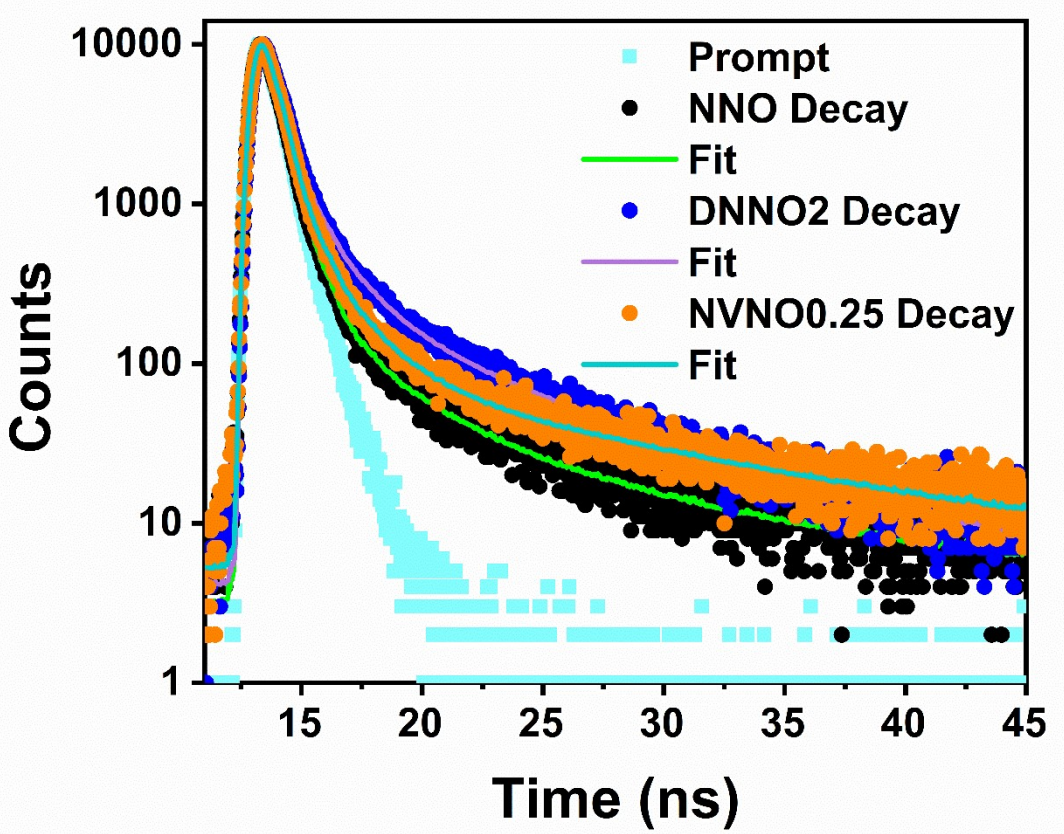

Figure S13. Lifetime decay curves of NNO, DNNO2 and NVNO0.25; reconvolution fitting to the decay curves are indicated.

References

1. M. Sharma, A. Kumar, D. Gill, S. Jaiswal, A. Patra, S. Bhattacharya and V. Krishnan, *ACS Applied Materials & Interfaces*, 2023, **15**, 55765-55778.
2. X. Zhao, X. Lan, D. Yu, H. Fu, Z. Liu and T. Mu, *Chemical Communications*, 2018, **54**, 13010-13013.
3. S. Zhang, Y. Zhao, R. Shi, C. Zhou, G. I. Waterhouse, L. Z. Wu, C. H. Tung and T. Zhang, *Advanced Energy Materials*, 2020, **10**, 1901973.
4. Y. Shiraishi, S. Shiota, Y. Kofuji, M. Hashimoto, K. Chishiro, H. Hirakawa, S. Tanaka, S. Ichikawa and T. Hirai, *ACS Applied Energy Materials*, 2018, **1**, 4169-4177.
5. G. Wang, B. Li, B. Li and L. Wu, *Green Chemistry*, 2023, **25**, 10556-10566.
6. J. Li, D. Wang, R. Guan, Y. Zhang, Z. Zhao, H. Zhai and Z. Sun, *ACS Sustainable Chemistry & Engineering*, 2020, **8**, 18258-18265.
7. Y. Bo, H. Wang, Y. Lin, T. Yang, R. Ye, Y. Li, C. Hu, P. Du, Y. Hu and Z. Liu, *Angewandte Chemie International Edition*, 2021, **60**, 16085-16092.
8. Z. Yang, J. Wang, J. Wang, M. Li, Q. Cheng, Z. Wang, X. Wang, J. Li, Y. Li and G. Zhang, *Langmuir*, 2022, **38**, 1178-1187.
9. P. Xia, X. Pan, S. Jiang, J. Yu, B. He, P. M. Ismail, W. Bai, J. Yang, L. Yang and H. Zhang, *Advanced Materials*, 2022, **34**, 2200563.
10. T. Ma, C. Yang, L. Guo, R. A. Soomro, D. Wang, B. Xu and F. Fu, *Applied Catalysis B: Environmental*, 2023, **330**, 122643.