Electronic Supplementary Information

$Ni_3V_2O_8$@g-CN nanocomposite-based p-n heterojunction: Mechanistic insights on photocatalytic activation of inert C(sp^3)-H bond

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1. Characterization

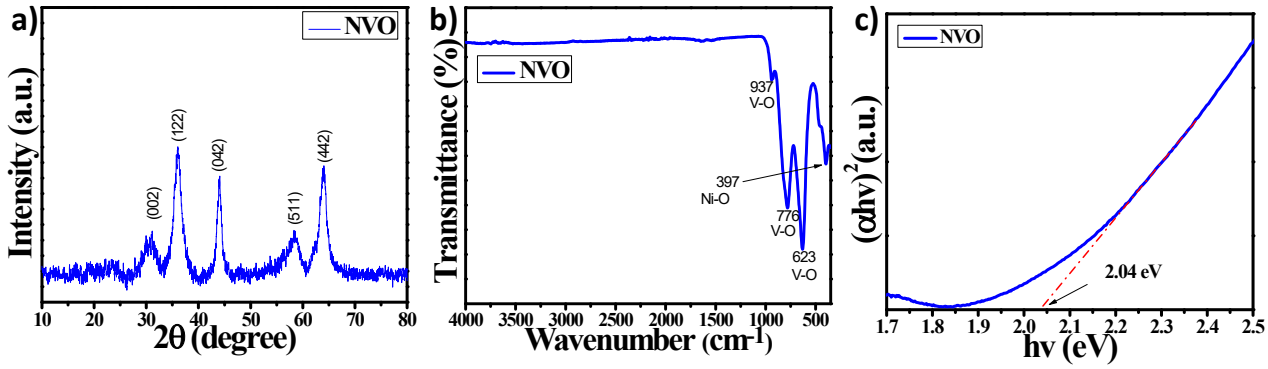

Figure S1 a) XRD pattern, b) FTIR spectra, and c) Tauc plot of NVO.

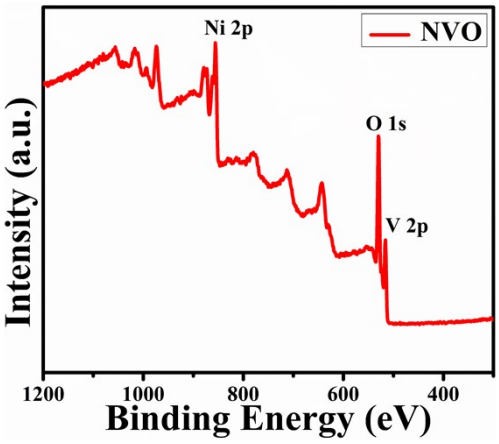

Figure S2 XPS Survey scan of NVO.

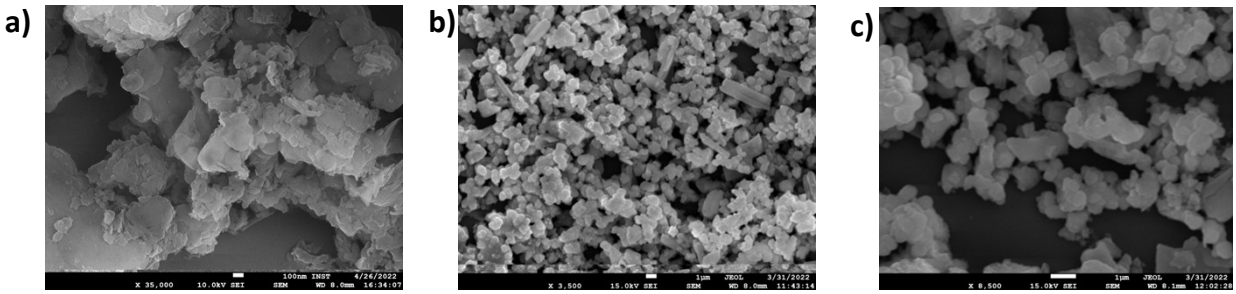

Figure S3 a) FESEM image of g-CN, b) & c) FESEM images of NVO.

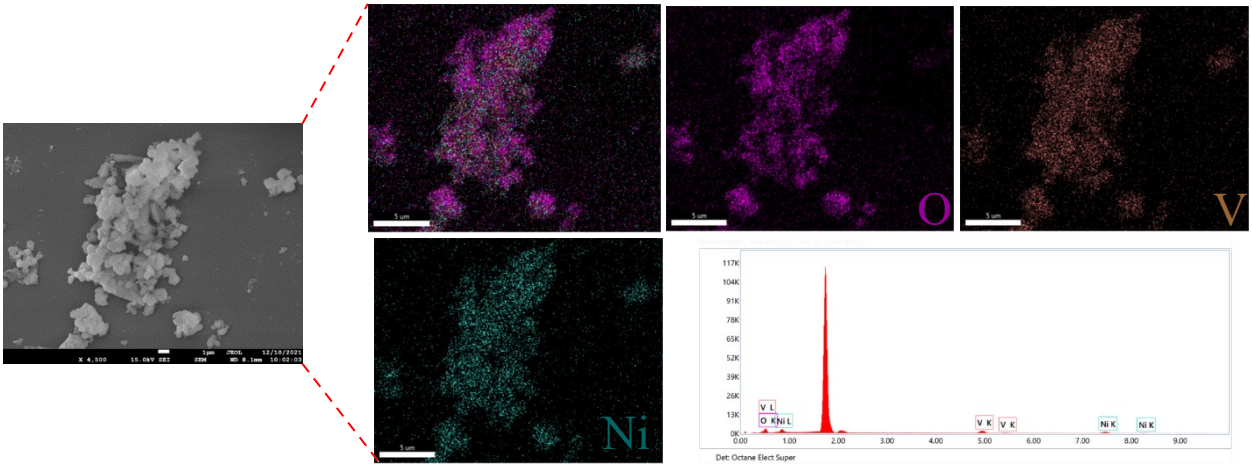

Figure S4 Elemental mapping and EDX of NVO.

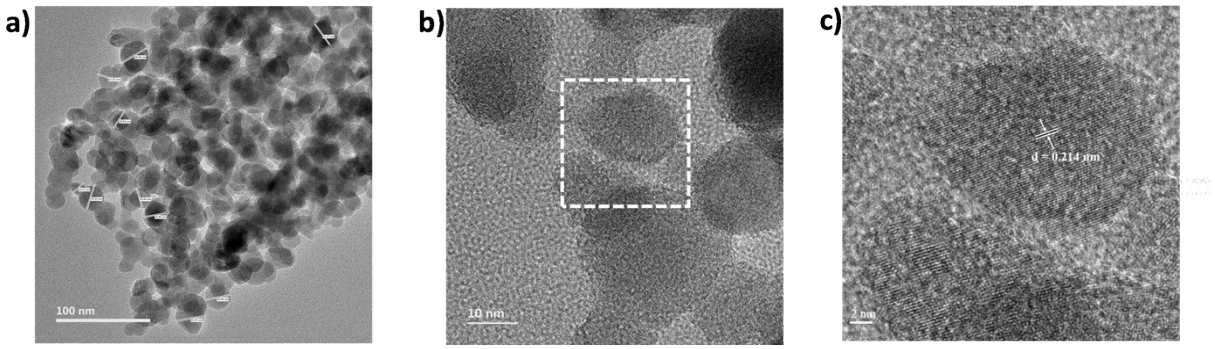

Figure S5 a) TEM and b) & c) HRTEM images of NVO.

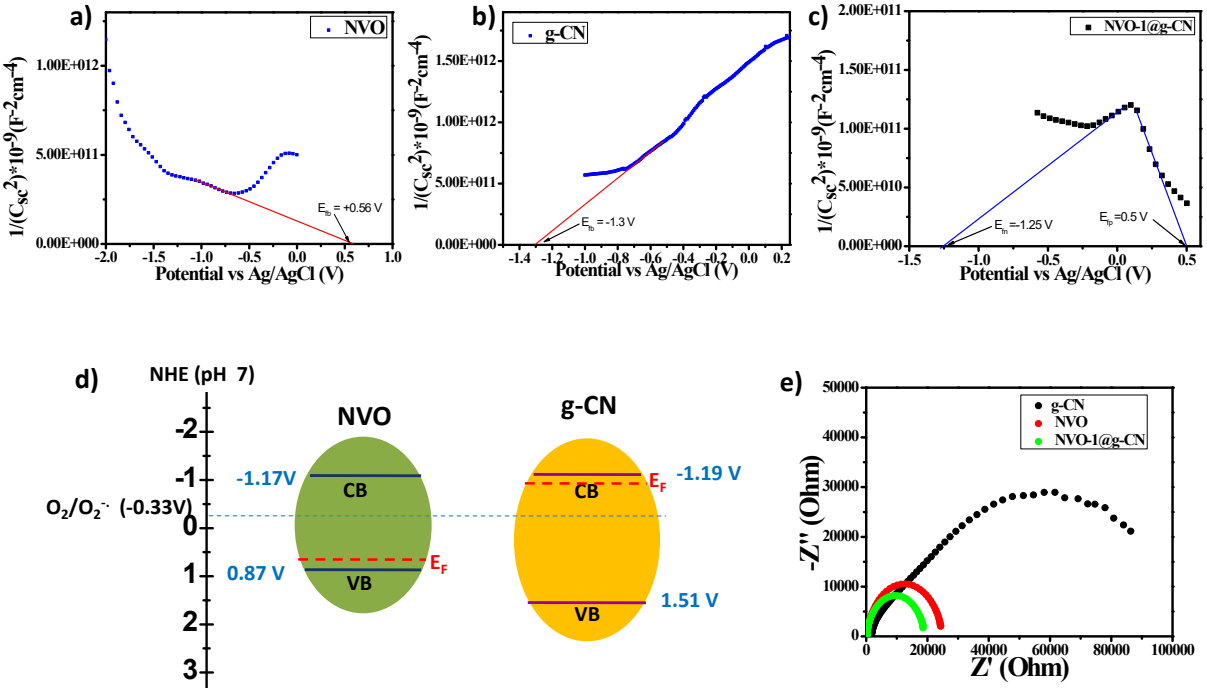

Figure S6 Mott-Schottky plot of a) NVO, b) g-CN and c) NVO-1@g-CN, d) Band structure of NVO and g-CN and e) Nyquist plot of NVO, g-CN and NVO-1@g-CN.

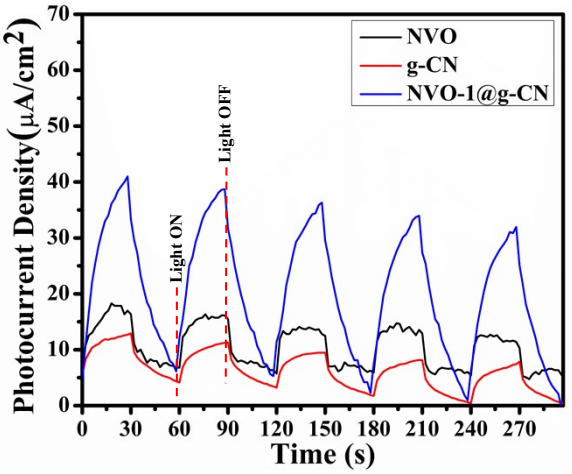

Figure S7 Transient Photocurrent response NVO, g-CN and NVO-1@g-CN.

2. Comparison table for cyclohexane oxidation

Table S1 Photocatalytic oxidation of cyclohexane catalyzed by various catalysts.

S.No.	Catalyst	Reaction conditions	Light source	Yield ($\mu mol.g^{-1}.h^{-1}$)		Cyclohexanone selectivity (%)	Ref
				Cyclohexanone	Cyclohexanol		
1	NVO-1@g-CN	5 mg catalyst, 5 ml cyclohexane	Solar simulator	66.6	4.6	93.4	Present work
2	$BiVO_4$	50 mg catalyst, 5 mmol of cyclohexane, 5 ml ACN, 0.1 ml HCl	W-Br lamp	15.5 % conversion of cyclohexane		71	1
3	Cu/g-CN	5 mg catalyst, 10 mmol of cyclohexane, 5 ml ACN, 20 mmol H_2O_2.	Xe Lamp, Full arc	37 % conversion of cyclohexane		94	2
4	Au/g-CN	500 mg catalyst, 10 ml cyclohexane, 200 ml H_2O, 60°C	Xe Lamp, Full arc	10 % conversion of cyclohexane		100	3
5	Sulphated vanadium doped TS1	50 mg catalyst,5 mmol cyclohexane, 5 ml ACN +0.1 ml HCL	W-Br Lamp (UV filter)	3.4 % conversion of cyclohexane		100	4

Table S2 Photocatalytic oxidation of cyclohexane catalysed under different reaction conditions by NVO-1@g-CN.

S.No.	Reaction conditions	Yield ($\mu mol.g^{-1}.h^{-1}$)		Selectivity (%)	
		Cyclohexanone	Cyclohexanol	Cyclohexanone	Cyclohexanol
1	5 mg catalyst, 5 ml ACN, 5 mmol cyclohexane, 0.1 ml HCL, O_2	134	834	14	86
2	5 mg catalyst, 5 ml ACN, 10 mmol cyclohexane, 20 mmol H_2O_2, 60 °C	167	2500	6.3	93.7

3	5 mg catalyst, 4 ml H_2O, 2 ml cyclohexane, 60 °C	8	103	6.9	93.1
4	5 mg catalyst, 5 ml cyclohexane, 60 °C, O_2	167	367	31.3	68.7

3. Experimental Analysis

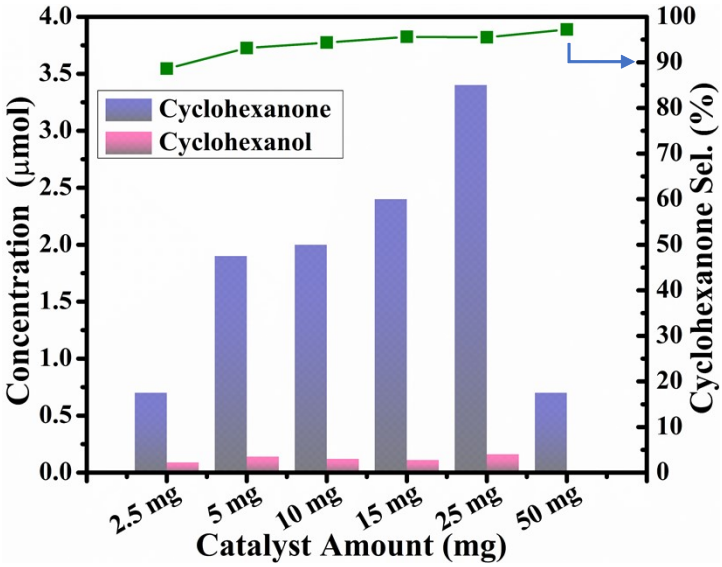

Figure S8 Photocatalyst optimization for photocatalytic oxidation of cyclohexane to cyclohexanone for NVO-1@g-CN. Reaction conditions: cyclohexane - 5 mL; Oxygen atmosphere; Reaction time – 6h; Oriel Solar Simulator, & 100 mW cm^{-2}. Selectivity of cyclohexanone (%) = (cyclohexanone / (cyclohexanone + cyclohexanol)) * 100.

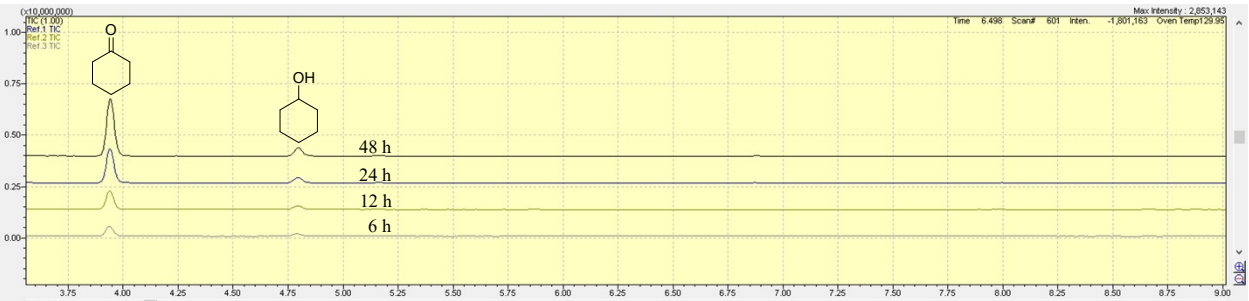

Figure S9 GC-MS graph for cyclohexane photo-oxidation by NVO-1@g-CN for 6h, 12h, 24h and 48h.

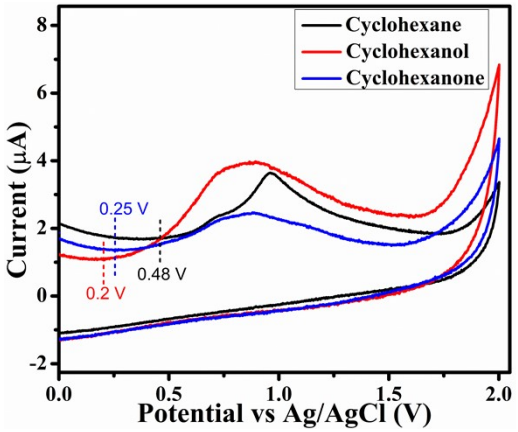

Figure S10 Cyclic voltammetry plot of cyclohexane, cyclohexanol and cyclohexanone.

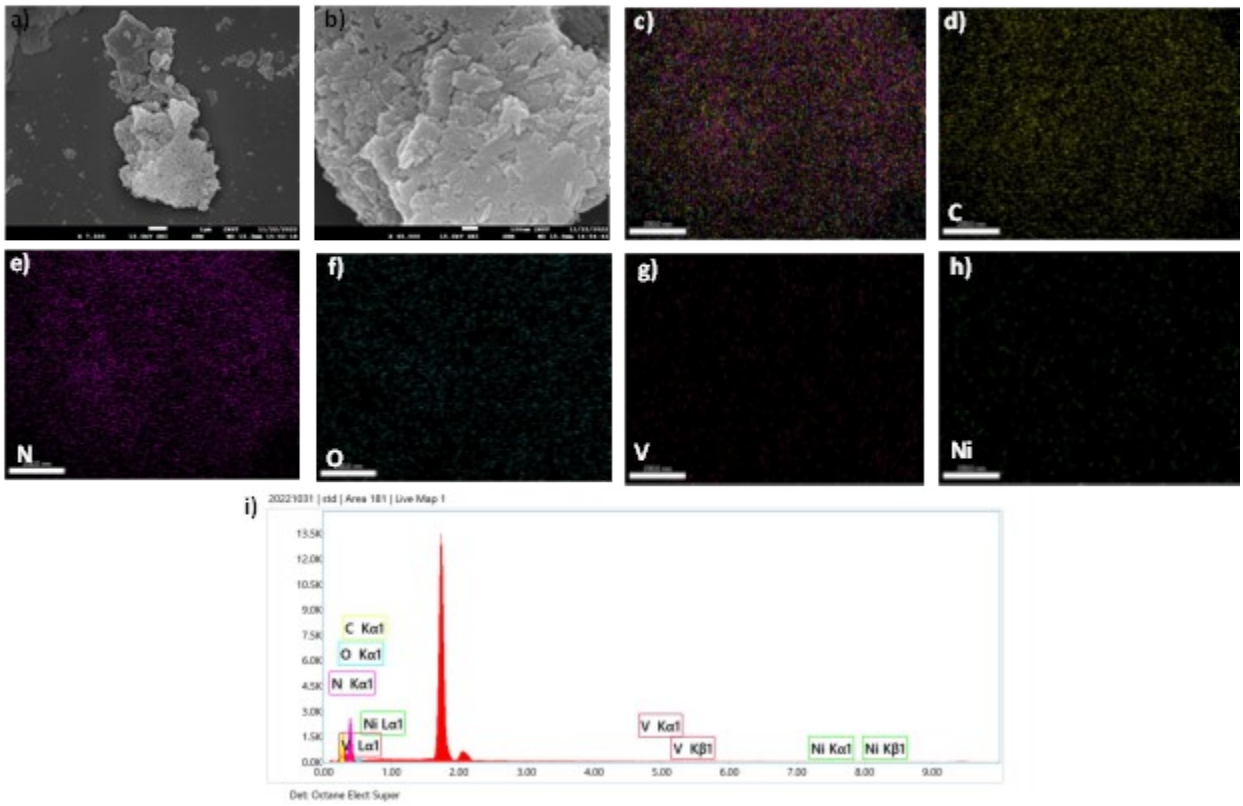

Figure S11 a) and b) FESEM images; c) to h) Elemental mapping and i) EDX of NVO-1@g-CN after 4 cycles.

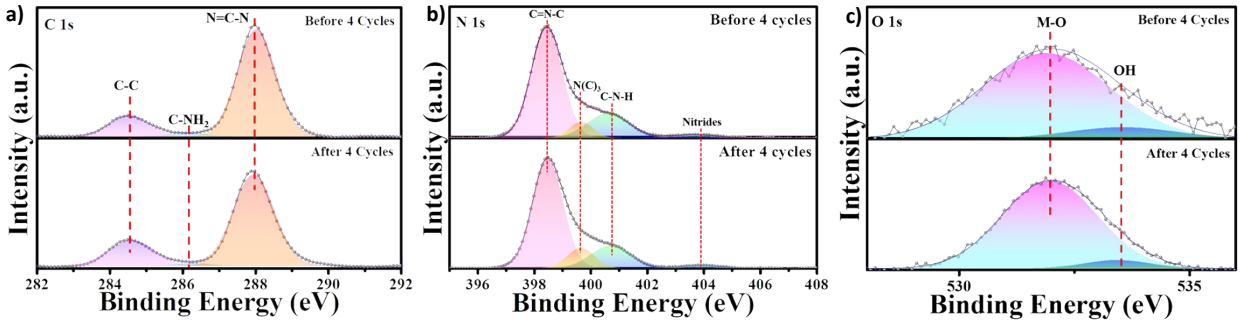

Figure S12 a) C1s spectrum b) N1s spectrum and c) O1s spectrum of NVO-1@g-CN nanocomposite before and after 4 cycles.

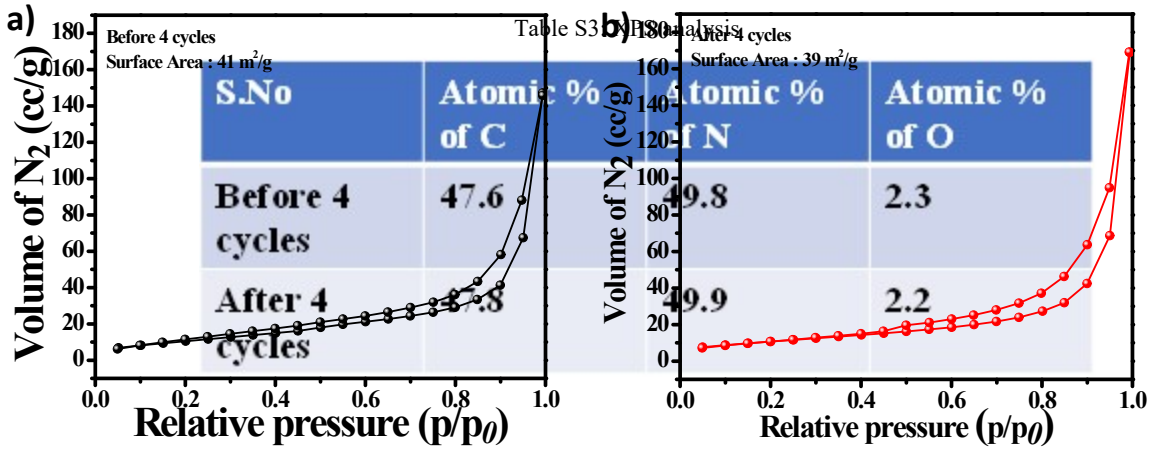

Table S3 XPS analysis

S.No	Atomic % of C	Atomic % of N	Atomic % of O
Before 4 cycles	47.6	49.8	2.3
After 4 cycles	47.8	49.9	2.2

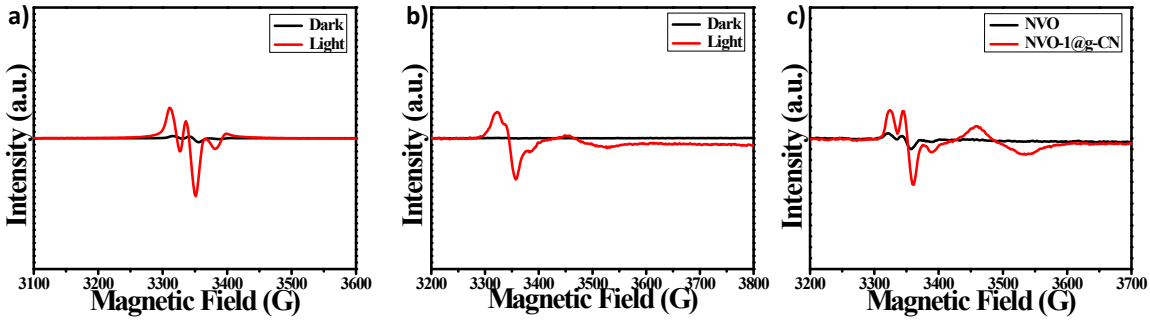

Figure S14 EPR spectra of a) $^1O_2$ using NTPD and b) $O_2^{\bullet-}$ using DMPO for NVO-1@g-CN and c) Cyclohexyl radical using PBN for NVO and NVO-1@g-CN.

Figure S13: N_2 adsorption and desorption isotherm of NVO-1@g-CN a) before 4 cycles and b) after 4 cycles.

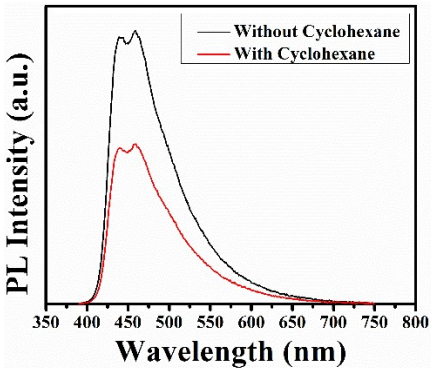

Figure S15 Photoluminescence (PL) spectra of NVO-1@g-CN before and after addition of cyclohexane.

References:

1 L. Xiang, J. Fan, W. Zhong, L. Mao, K. You and D. Yin, *Appl. Catal. A Gen.*, 2019, **575**, 120–131.

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4 W. Zhong, T. Qiao, J. Dai, L. Mao, Q. Xu, G. Zou, X. Liu, D. Yin and F. Zhao, *J. Catal.*, 2015, **330**, 208–221.