Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Remarkably improved photocatalytic selective oxidation of toluene to benzaldehyde with O_2 over metal-free delaminated g-C_3N_4 nanosheets: Synergistic effect of enhanced textural properties and charge carriers separation

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Fig. S15	(a) Recyclability data using E-g-C_3N_4(3) for toluene oxidation reaction ((Reaction conditions- E-g-C_3N_4 (3) (25 mg), light source (250W Hg lamp), toluene (0.05 mmol), solvent acetonitrile (3 ml), time 6 h and oxygen atmosphere), (b) SEM images of fresh and spent E-g-C_3N_4(3), (c) XRD of fresh and spent E-g-C_3N_4(3), (d) DRUV-vis spectra of fresh and spent E-g-C_3N_4(3), and (e) FT-IR spectra of fresh and spent E-g-C_3N_4(3).	S28

Experimental section

Materials

All chemicals used in this study were of AR grade and used as received without any further treatment. Urea, toluene, and acetonitrile were obtained from Merck India Pvt. Ltd., whereas NaOH, KI, and ammonium molybdate were procured from Loba Chemie, Pvt. Ltd., India. Nitro blue tetrazolium (NBT), and 2-hydroxyl terephthalic acid (THA) were purchased from Sigma Aldrich.

Catalyst preparation

Synthesis of g-C_3N_4

Graphitic carbon nitride (g-C_3N_4) was synthesized by thermal pyrolysis of urea. 15 g of urea was crushed in a mortar pestle and then transferred into the capped crucible. The crucible was kept in a muffle furnace. The material was calcined at 550 ˚C for 3 h with a ramp of 2.5 ˚C per minute. The resulting yellow material was removed from the crucible and crushed well to make it into powder.

Thermal exfoliation of g-C_3N_4

The yellow powder of g-C_3N_4 was transferred into a crucible. About 300 mg of material was taken into a 25 ml crucible. The crucible was transferred to a muffle furnace, and the material was heated at 500 ˚C with a ramp rate of 5 ˚C per minute for various intervals of time (1.5 h, 2 h, 2.5 h, 3 h, 3.5 h, and 4 h). After the calcination, the material lost its weight, and the colour progressively became white.

Photocatalytic reactions

The photochemical toluene oxidation was conducted in a 10 mL round bottom flask in which 3 ml of acetonitrile was mixed with 0.05 mmol of toluene. 25 mg of catalyst was added to the reaction mixture, and the flask was purged with oxygen for 5 min. The oxygen balloon was attached to the round bottom flask using a glass adapter and rubber pipe. Then the mixture was magnetically stirred for an hour to establish adsorption-desorption equilibrium. Finally, the solution was exposed to a 250 W Hg lamp (or sunlight) equipped with a magnetic stirrer. On completion of the reaction, the catalyst was removed from the reaction mixture using a centrifuge. The distance between the round bottom flask and the light source was 1 cm, and the light intensity at 1 cm was 1010 W/m^2. The reactions were also conducted at a variable distance from the light source. The light intensity at 15 cm was 220 W/m^2.

Photocatalytic reaction setup

The photocatalytic reaction was performed inside the box using a 250 W Hg lamp (Fig. 1a). The cooling to the system was provided by water circulation through the chiller, where the temperature was maintained at 25 °C (298 K). The magnetic stirrer was used for the continuous string of the reaction solution. The light intensity was measured by using a power meter. For the reaction's kinetics, light intensity variation was provided by performing the reaction at different distances from the lamp at a constant temperature of 25 °C maintained by the water circulation (Fig. 1b). The reaction was performed at variable temperatures. The desirable temperature was maintained using the magnetic stirrer with a hot plate (Fig. 1c).

Analysis of the reaction mixture

The reaction mixture was analyzed with gas chromatography (GC) (Yonglin; 6100; GC column: BP-5; 30 m×0.25 mm×0.25 μm) fitted with an FID detector. High-purity N_2 gas (99.99%, GC grade) was used as the carrier gas with a flow rate of 10 ml/min, whereas H_2 (99.99%, GC grade) and Air (99.99%, GC grade) were used as ignition gases. The injector and detector temperature were set at 280 ˚C. GC column oven temperature was programmed as follows: Initial temperature = 60 ˚C, hold time = 2 min followed by temperature ramping to a final temperature of 280 ˚C with a ramp rate of 5 ˚C /min. 0.2 μL of the sample was injected for the analysis. The calibration curves were constructed for pure toluene and benzaldehyde (diluted in 2-propanol) for the determination of conversion and selectivity. Products were also confirmed using GC-MS (Shimadzu GCMS-QP 2010 Ultra; Rtx-5 Sil Ms; 30 m × 0.25 mm × 0.25 μm).

GC Calibration details

Herein, the calibration curves were plotted using different concentrations of reactants and products. The five standards (different concentrations) were prepared for reactants and products in isopropanol with an internal standard (benzene). The prepared standards were injected in GC (triplicate injection), and the area was recorded. After the completion of the GC analysis, the calibration curves were plotted with concentration (mmol) vs peak area (Fig. S2), and the conversion of reactant and product selectivity were determined using the following expression.

$$\text{Conversion} = \frac{C_0 - C_t}{C_0} \text{ x } 100\%$$

$$\text{Selectivity} = \frac{C_p}{C_0 - C_t} \text{x } 100\%$$

Where initial reactant concentration (C_0), reactant concentration after time t (C_t), and product concentration at time t (C_p).

Apparent Quantum Yield Calculation

The quantum yield of the reaction was calculated using eq (4), which gives the ratio between the electron involved in the reaction and the molar flow of photons introduced into the reactor (eqn (1)). The apparent wavelength (λ) of photons was estimated from the band gap of the catalyst, determined from Tauc plots. The quantum yield calculated in this manner was not the exact value but served as a reference to compare the photo efficiency of photocatalytic system.

$$Apparent\ Quantum\ Yeald\ (\phi)\ = \frac{Number\ of\ reacted\ electron\ \times 100}{Number\ of\ incident\ photon} \tag{1}$$

$$Number\ of\ reacted\ electron = Reactant\ conversion\ \left(mol^{-1}\right)\ \times\ N_A\ (mol) \tag{2}$$

$$Number\ of\ incident\ photon = \frac{Light\ intansity\ \left(Wm^{-2}\right)\ \times\ Area\ \left(m^2\right) \times\ Time\ (s)}{\frac{h\ (Js)\ c\ (ms^{-1})}{\lambda\ (m)}} \tag{3}$$

$$\phi = \frac{Reactant\ conversion\ \left(mol^{-1}\right)\ \times\ N_A\ (mol)\ \times\ h\ (Js)c\ (ms^{-1}) \times 100}{Light\ intansity\ \left(Js^{-1}m^{-2}\right)\ \times\ Area\ \left(m^2\right)\ \times\ Time\ (s)\ \times\ \lambda\ (m)} \tag{4}$$

Photoelectrochemical measurement

The photoelectrochemical studies were conducted using a PGSTAT302N Autolab electrochemical workstation with a standard three-electrode arrangement in Pyrex cell with a 0.1 M aqueous electrolyte solution of sodium sulphate. The sample acts as a photoanode (working electrode), Pt wire electrode as a counter electrode, and Ag/AgCl as a reference electrode. Photoanode was prepared by coating photocatalyst on glass slides containing fluorine-doped tin oxide (FTO), cleaned with acetone, rinsed with DI water, and oven-dried before use. The catalyst was coated over the FTO surface using the drop-casting method. The electrochemical impedance spectroscopy was calculated in the frequency range of 1 MHz to 1 Hz using a sinusoidal A.C. perturbation signal of 5 mV. Mott-Schottky experiment was conducted at 1000 Hz constant frequency in dark conditions. LSV and transient photocurrent measurements were carried out under dark and illumination conditions using a 300 W Xenon arc lamp (Newport-R22) with a cut-off filter ($\lambda > 420$ nm and intensity of 100 $mW.cm^{-2}$).

Nitro blue tetrazolium (NBT) test

10 mL of 2.5×10^{-5} M aqueous solution of NBT was mixed with the 5 mg of the catalyst. This mixture was illuminated with light for 3 h under continuous stirring. After 10 min, the catalyst was separated from the solution using a centrifuge. The solution was monitored using a UV-visible spectrophotometer, and its absorbance for NBT was compared with the neat stock solution. A decreased absorbance peak of NBT after light illumination confirms the capability of the photocatalyst for the generation of $^{\bullet}O_2^{-}$.

Terephthalic acid (THA) test

The 5×10^{-3} M aqueous solution of THA was prepared in the presence of a small amount of NaOH to make THA soluble in an aqueous medium. 20 mg of catalyst was mixed with the 20 ml of THA solution and exposed to light for 1 h. Then catalyst was separated from the solution using a centrifuge. The clear solution was monitored using a fluorescence spectrophotometer with an excitation wavelength of 330 nm. The emission peak at 425 nm confirms the presence of 2-hydroxyl terephthalic acid in the reaction mixture. The OH radicals react with THA (non-fluorescent) and convert it into THA (fluorescent). The emission peak of the reaction mixture was compared with the stock solution.

Iodometric test for H_2O_2 detection

The 0.1 M solution of potassium iodide (KI) and the 0.1 M solution of ammonium molybdate were prepared. The photocatalytic toluene oxidation reaction was performed for a different interval of time. The 3 ml of the reaction mixture was mixed with 0.5 ml of KI and 0.5 ml of ammonium molybdate solution. The obtained mixture was analysed using UV spectrophotometer. H_2O_2 in the solution oxidizes iodide to form iodine which gives a peak at 360 nm in UV visible spectrometer. The intensity of the 360 nm peak gives the amount of H_2O_2 present in the reaction mixture.

Catalysts characterization

X-ray diffraction (XRD) patterns were recorded from the RIGAKU Mini-flex diffractometer using Cu Kα radiation on the 2θ scale 5° to 80°. The surface area and porosity were examined using N_2 adsorption-desorption measurements with the BELSORP instrument. All the materials were outgassed in the degassing port at 200 ˚C for 4 h before performing the N_2 adsorption. The relative pressure from 0.05 to 0.3 was chosen to analyze the specific surface area by applying Brunauer-Emmett-Teller (BET) equation. For the IR spectra of all the photocatalyst was obtained using Bruker Tensor 27 FT-IR spectrometer. JEOL instrument was used for the SEM analysis of the materials' morphology using an accelerating voltage of 10 kV. UV-DRS study of all catalysts was performed on a UV-visible spectrophotometer of Shimadzu (UV-2600) using $BaSO_4$ as standard reference material. The liquid UV analysis was also conducted using a UV-visible spectrophotometer of Shimadzu (UV-2600). Furthermore, the nanostructure level analysis was performed using a high-resolution transmission electron microscope (JEOL, Model: JEM 2100F) at an accelerating voltage of 200 kV (IIT Bombay). The X-Ray Photoelectron Spectroscopy (XPS) was carried out on a Thermofisher scientific 'Nexsa Base' instrument (IIT Mandi). Valance band X-Ray Photoelectron Spectroscopy (VB-XPS) and Ultraviolet Photoelectron Spectroscopy UPS experiment were performed using a Thermofisher scientific escalab Xi^+ instrument. Bulk elemental analysis was conducted with Thermofisher scientific analyzer. Fluorescence analysis was done by using Perkin Elmer LS55. The fluorescence decay time was evaluated using TCSPC instrument of Fluorolog 3-221 fluorimeter equipped with LED laser (INST Mohali). The total basicity present in the materials was analyzed using the temperature-programmed desorption (CO_2-TPD) technique on a Quantachrome Autosorb-iQ2-TPX, CHEMBETTM TPR/TPD instrument. Before the analysis, samples were outgassed at 200 °C with a heating ramp of 10 °C min^{-1} under continuous He gas flow for 30 min. After cooling to room temperature, the probe gas (CO_2) was adsorbed for 30 min, and the physically adsorbed gas was removed by flowing He gas for 30 min. Finally, the desorbed gases were analyzed on thermal conductivity (TCD) detector against temperature with a ramp rate of 10 °C min^{-1} in the temperature range from 50 °C – 300 °C. Electron paramagnetic resonance (EPR) spectroscopy was performed at room temperature by using a spectrometer (Bruker ER073, USA) equipped with an EPR magnet system (at IIT Roorkee).

Table S1 Surface elemental composition determined from XPS data.

Entry	Catalyst	Carbon Atomic %	Nitrogen Atomic %	Oxygen Atomic %	N/C Ratio	C/N Ratio
1	g-C_3N_4	45.2 (34.7)[a]	52.7 (62.9)[a]	1.8	1.17 (1.81)[a]	0.85 (0.55)[a]
2	E-g-C_3N_4(3)	44.2 (31.8)[a]	53.7 (64.6)[a]	2.1	1.22 (2.03)[a]	0.82 (0.49)[a]

All atomic percentage values in the peak table are corrected for sensitivity factors. [a]Value in the parenthesis was determined from bulk elemental analysis.

Entry	Catalyst	Pre-exponential functions				Decay lifetimes (ns)					Fractional contribution			
		α_1	α_2	α_3	α_4	τ_1	τ_2	τ_3	τ_4	$\langle\tau\rangle$	f_1	f_2	f_3	f_4
1	g-C_3N_4	0.40	0.17	0.32	0.1	4.6	19.3	1.1	122.1	87.9	0.10	0.19	0.02	0.68
2	E-g-C_3N_4(3)	0.36	0.13	0.08	0.42	8.5	37.9	198.6	2.5	135	0.12	0.20	0.63	0.04

Table S2 Best fitted parameters of multiexponential components for decay curve.

Table S3 The band edge potentials and bandgap of all the photocatalysts.

Entry	**Catalyst**	**Slope value**	**Band Gap**	**Flat Band Potential vs. Ag/AgCl**	**Conduction Band edge Potential vs. Ag/AgCl**	**Conduction Band Edge Potential vs. NHE**	**Valance Band Edge Potential vs. NHE**
1	g-C_3N_4	1.10×10^{10}	2.72	-1.11	-1.21	-1.01	1.71
2	E-g-C_3N_4(1.5)	6.99×10^{9}	2.73	-1.32	-1.42	-1.22	1.51
3	E-g-C_3N_4(2)	8.04×10^{9}	2.75	-1.42	-1.52	-1.32	1.24
4	E-g-C_3N_4(2.5)	6.87×10^{9}	2.76	-1.23	-1.33	-1.13	1.63
5	E-g-C_3N_4(3)	5.05×10^{9}	2.77	-1.57	-1.67	-1.47	1.30
6	E-g-C_3N_4(3.5)	4.50×10^{9}	2.78	-1.53	-1.63	-1.43	1.36
7	E-g-C_3N_4(4)	4.29×10^{9}	2.81	-1.48	-1.58	-1.38	1.43

Table S4 Concentration of basicity amount present in catalyst

Entry	Catalyst	Catalyst amount	Area under sample peck	Total basicity (mol/g)
1	g-C_3N_4	10 mg	260	0.83×10^{-6}
2	E-g-C_3N_4(3)	10 mg	627	2.02×10^{-6}

Table S5 Comparative catalytic activity for photocatalytic selective toluene oxidation to benzaldehyde.

Entry	Catalyst	Reaction conditions	Light source	Toluene Conversion	Benzaldehyde yield	AQY	Reference
1	TiO_2-pillared clays	Catalyst (50 mg), toluene (0.5 mg/ml), H_2O (20 ml), and reaction time 1h.	125W Hg lamp	35.5	10	-	[26]
2	CdS−ZnS (CZ-2)	10 mmol of toluene and 50 mg of photocatalyst	300 W Xe lamp	-	1078 $\mu mol \cdot g^{-1} \cdot h^{-1}$	-	[25]
3	Nb_2O_5-N	Catalyst (5 mg), toluene (0.1 mmol), acetonitrile (1 mL), O_2 (1 atm), and reaction time 12 h	6 W LED	1.56	>99	-	[22]
4	Fe-UiO-66	Catalyst (10 mg), toluene (5 µL), acetonitrile (1 mL), H_2O (20 µL), O_2 (1 atm), and reaction time 1h.	300 W Xe Lamp	70.1	19.3	-	[84]
5	$CdIn_2S_4$-CdS-140	Catalyst (10 mg), toluene (47.2 µmol), acetonitrile (1 mL) and reaction	300 W Xe lamp	80.3	98.8	7×10^{-3}	[17]

		time 8h					
6	E-g-C_3N_4(3)	Catalyst (25 mg), 0.05 mmol toluene, 3 mL acetonitrile, O_2 (1 atm), and reaction time 8h	250W Hg lamp	84.4	>99	77×10^{-3}	This Study

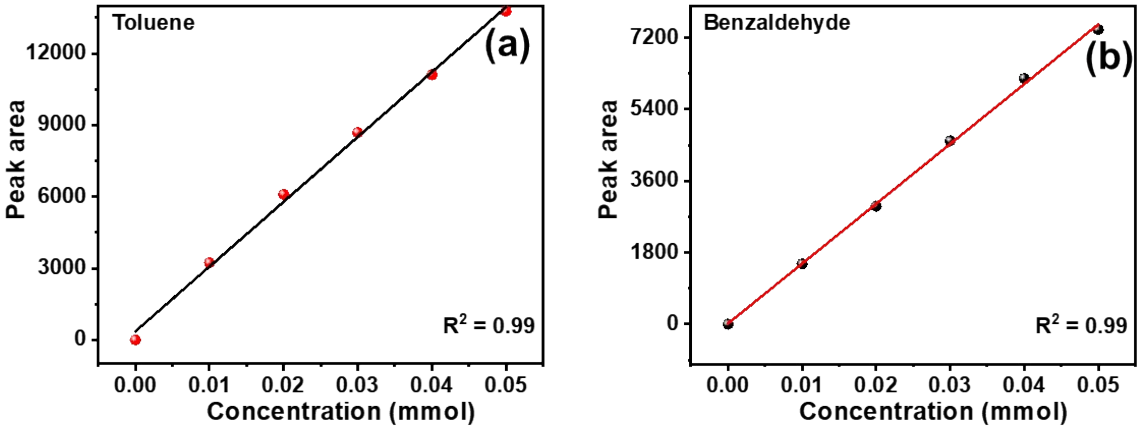

Fig. S1 GC Calibration curve of (a) Toluene, and (b) Benzaldehyde.

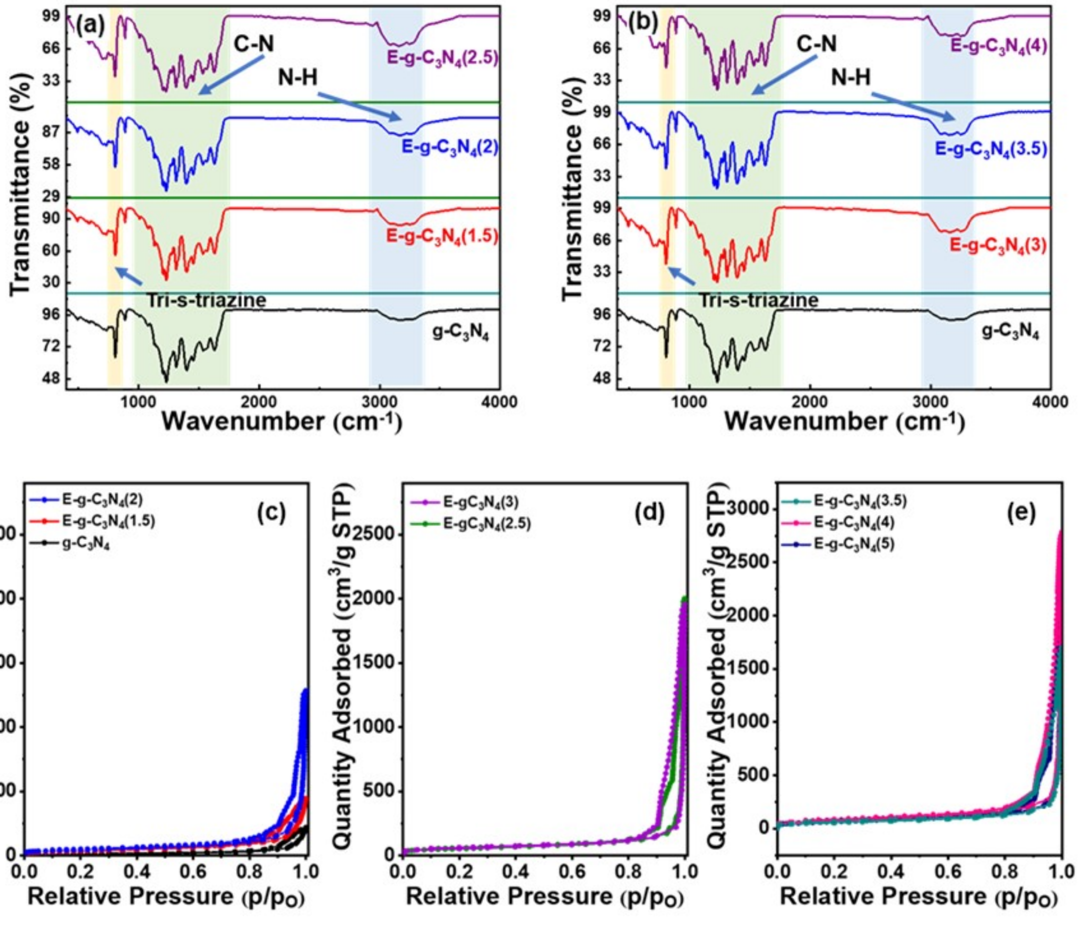

Fig. S2 (a, b) FT-IR spectra of pristine g-C_3N_4 and exfoliated g-C_3N_4 samples. N_2-adsorption-isotherms of (c) g-C_3N_4, E-g-C_3N_4(1.5), and E-g-C_3N_4(2), (d) E-g-C_3N_4(2.5), and E-g-C_3N_4(3), and (e) E-g-C_3N_4(3.5), E-g-C_3N_4(4), and E-g-C_3N_4(5).

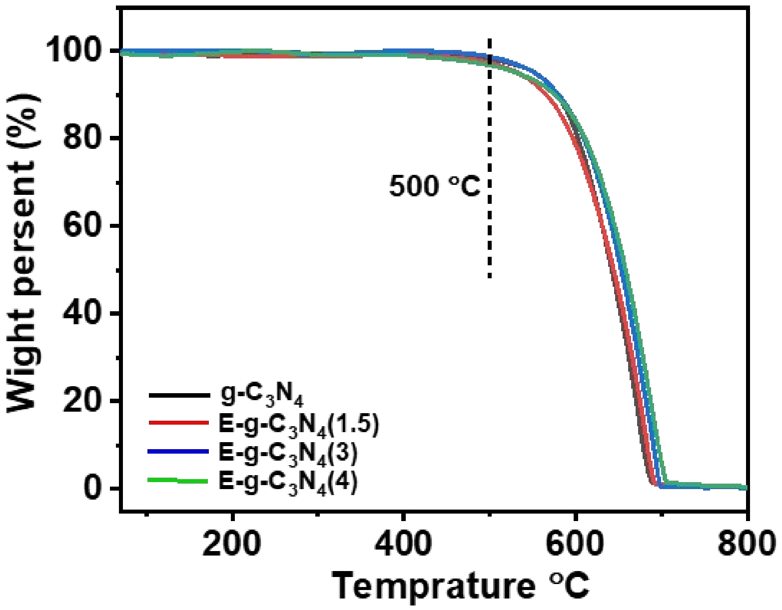

Fig. S3 Thermograms of g-C_3N_4, E-g-C_3N_4(1.5), E-g-C_3N_4(3), and E-g-C_3N_4(4).

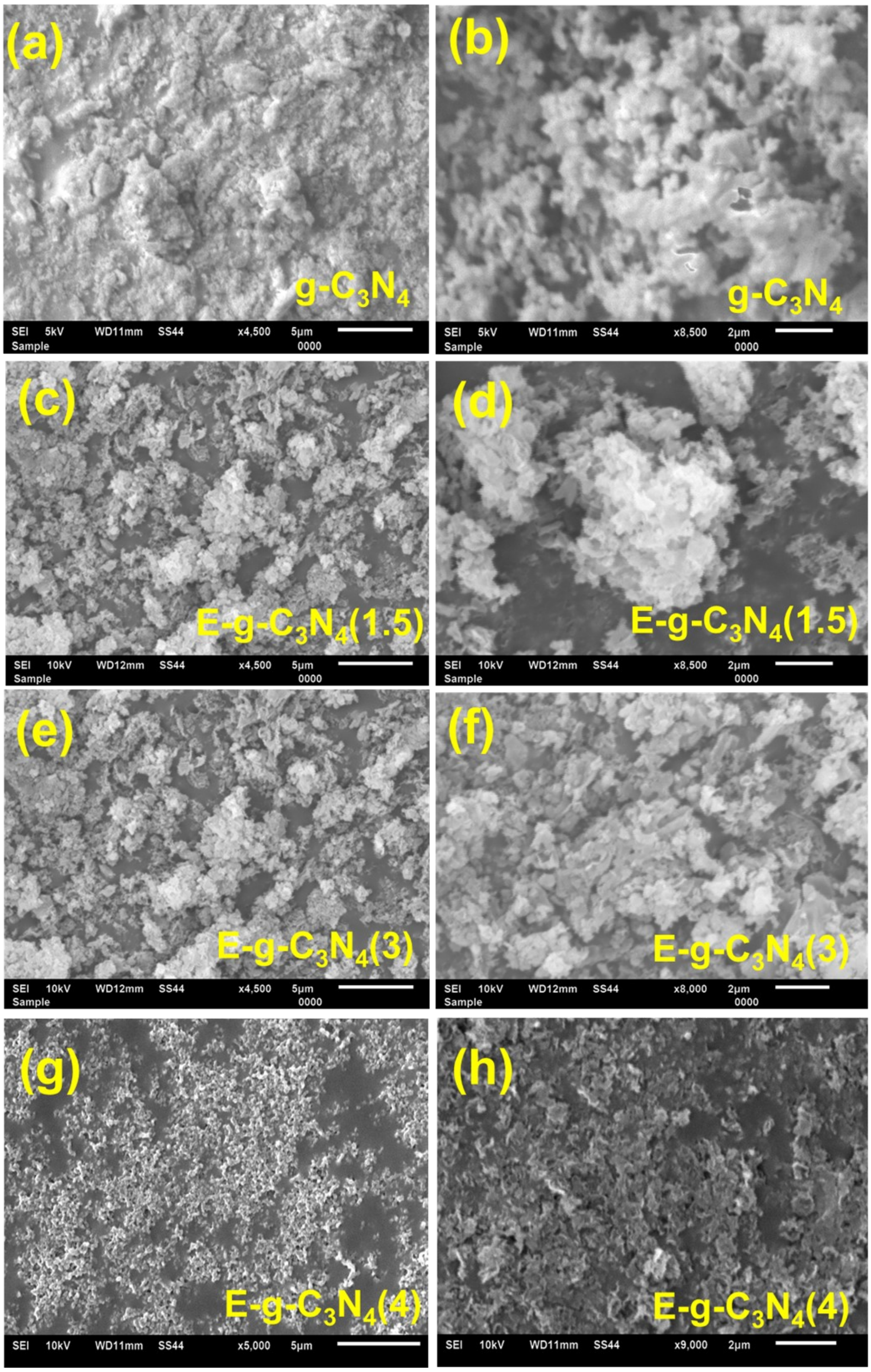

Fig. S4 SEM images of (a, b) g-C_3N_4, (c, d) E-g-C_3N_4(1.5), and (e, f) E-g-C_3N_4(3), and (g, h) E-g-C_3N_4(4).

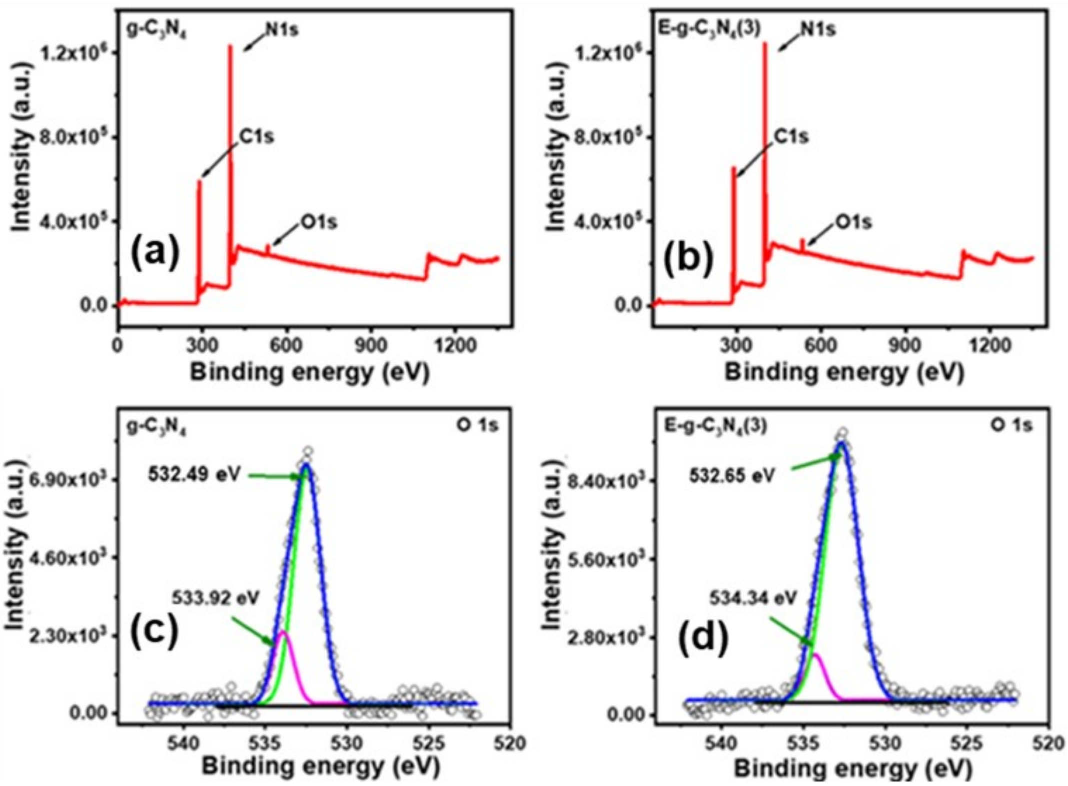

Fig. S5 (a), (b) XPS survey spectra of pristine g-C_3N_4 and E-g-C_3N_4(3), and (c), (d) high-resolution O 1s XPS spectra of pristine g-C_3N_4 and E-g-C_3N_4(3)

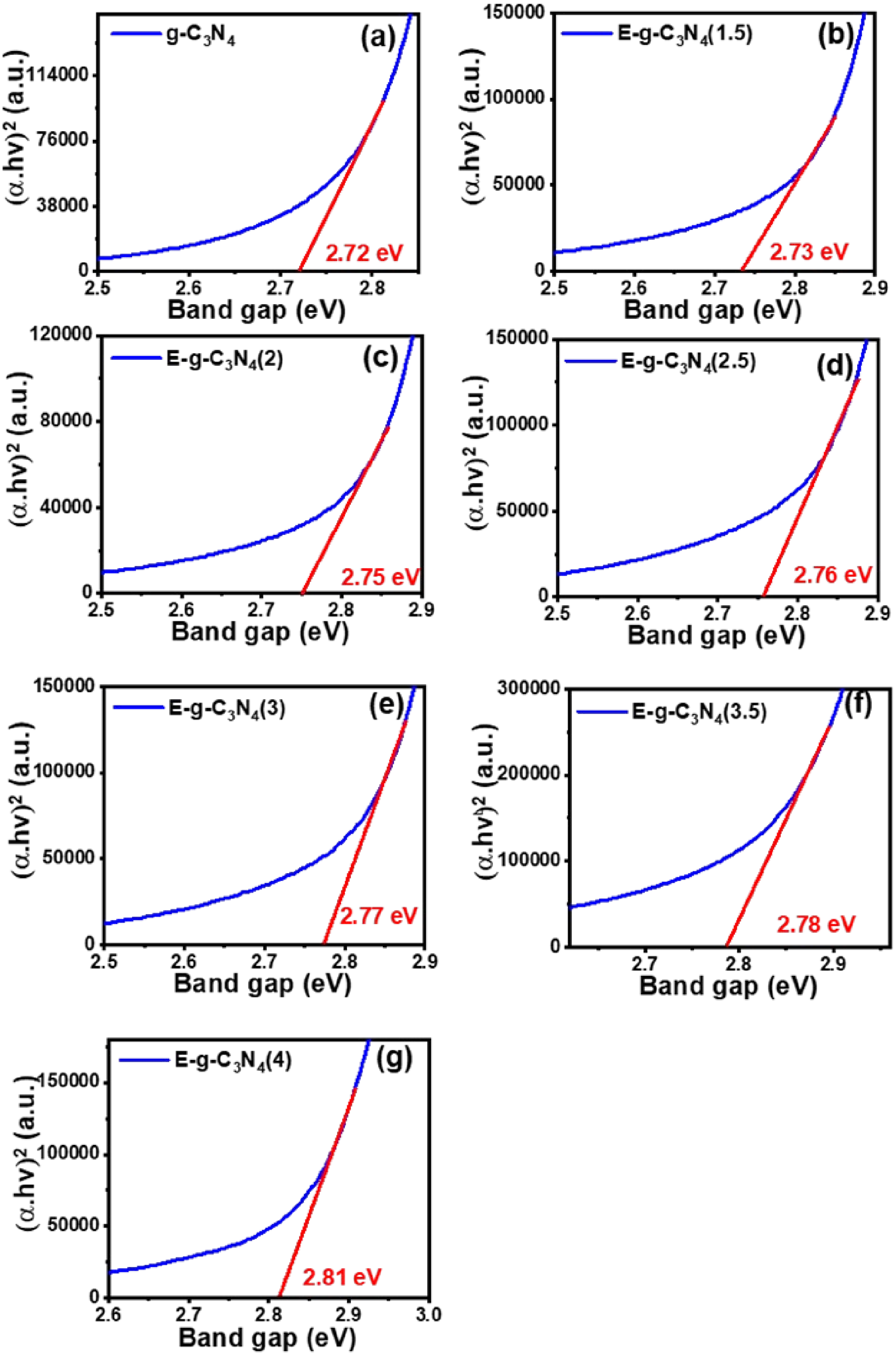

Fig. S6 Tauc plots of (a) g-C_3N_4, (b) E-g-C_3N_4(1.5), (c) E-g-C_3N_4(2), (d) E-g-C_3N_4(2.5), (e) E-g-C_3N_4(3), (f) E-g-C_3N_4(3.5), and (g) E-gC_3N_4(4).

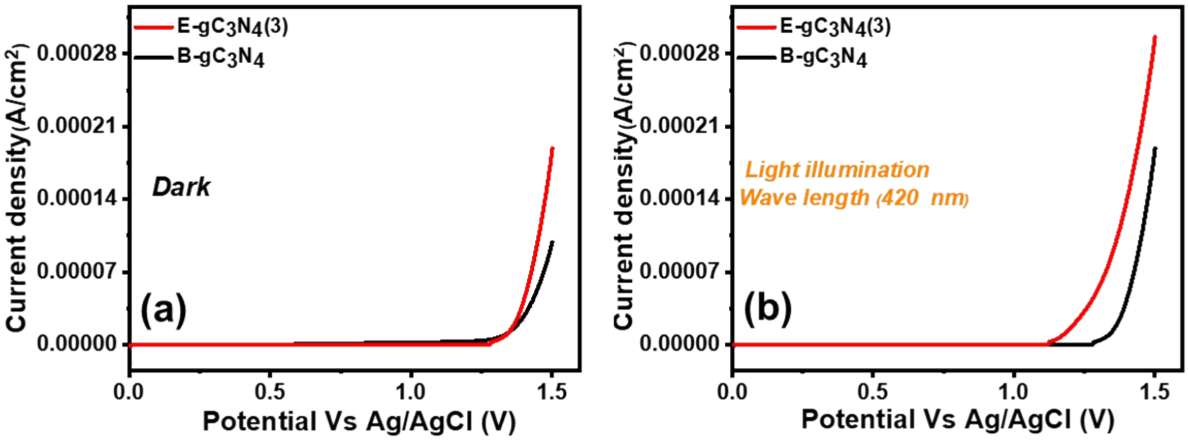

Fig. S7 LSV spectra of pristine g-C_3N_4 and exfoliated E-g-C_3N_4(3) in (a) dark and (b) in light.

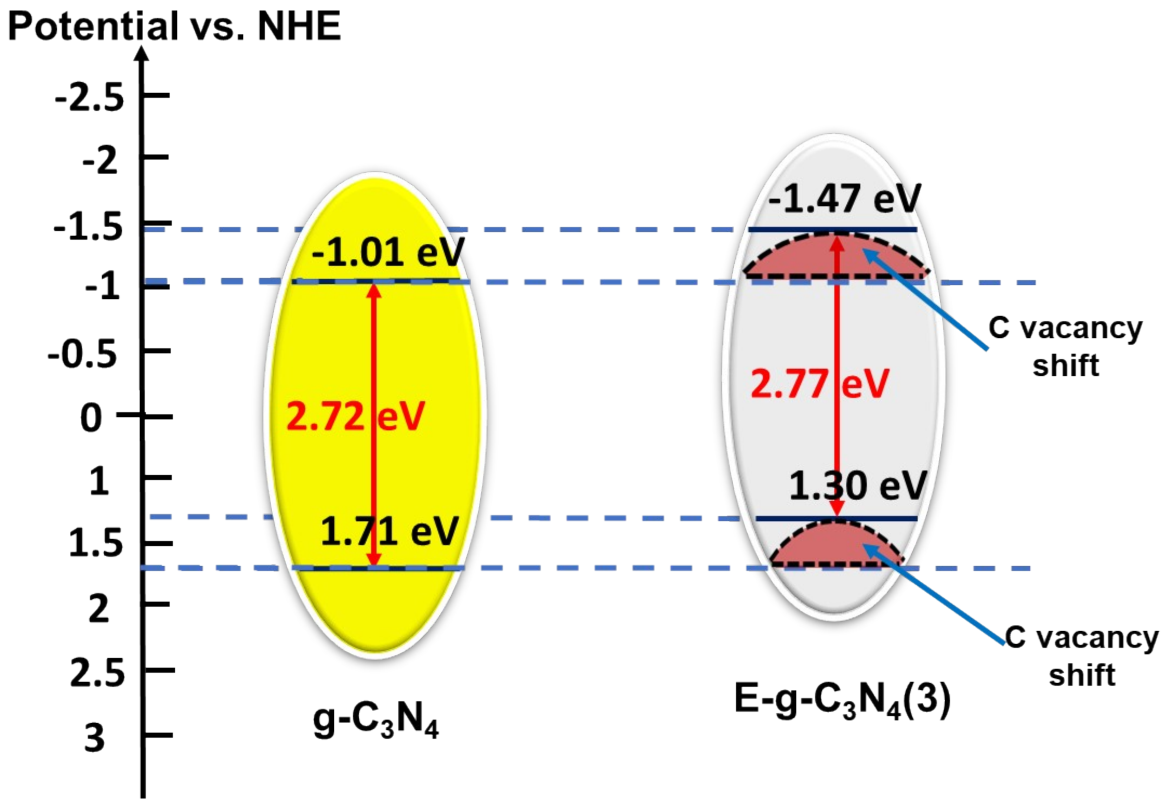

Fig. S8 Comparing the change in band structures of g-C_3N_4 before and after the exfoliation (band edges estimated through combining Mott–Schottky analysis and DRUV-vis spectra)

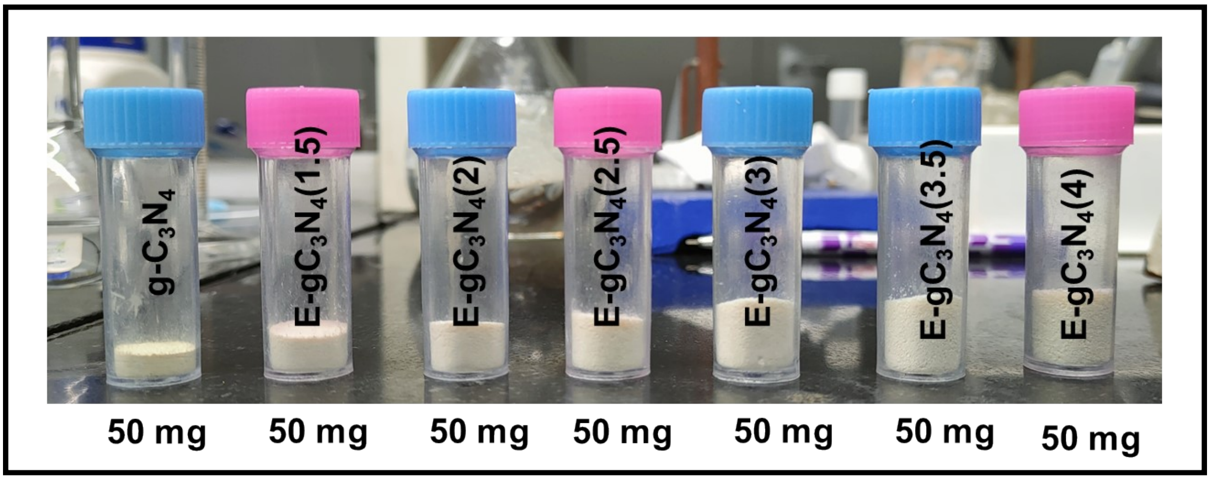

Fig. S9 The digital image showing the volume to weight ratio comparison of pristine and exfoliated catalysts where 50 mg of all catalyst were taken in different vials.

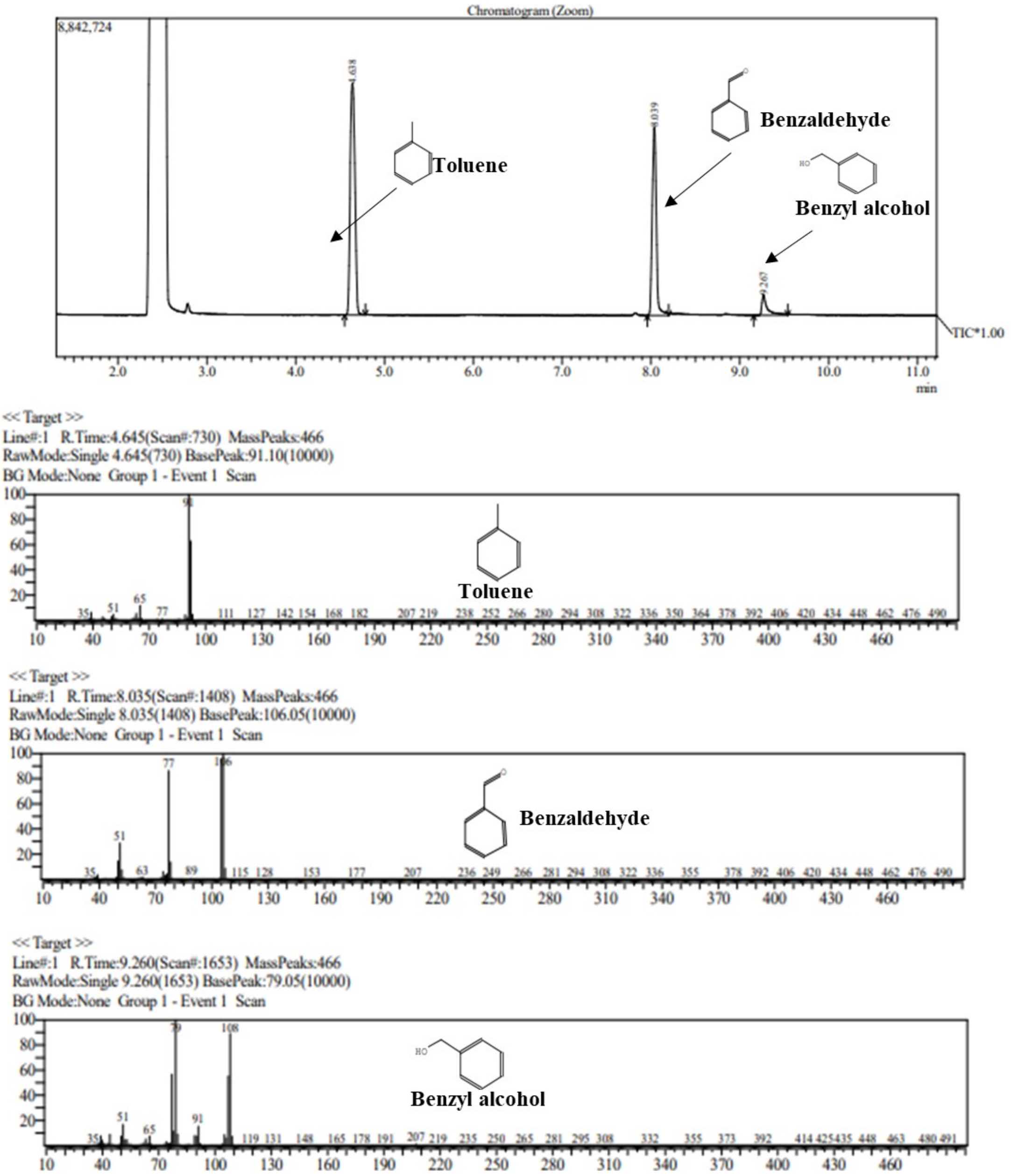

Fig. S10 GC-MS chromatograph of reaction mixture after 2 h (Reaction conditions- E-g-C_3N_4 (3) (25 mg), light source (250W Hg lamp), toluene (0.05 mmol), solvent acetonitrile (3 ml), time 2 h, and oxygen atmosphere).

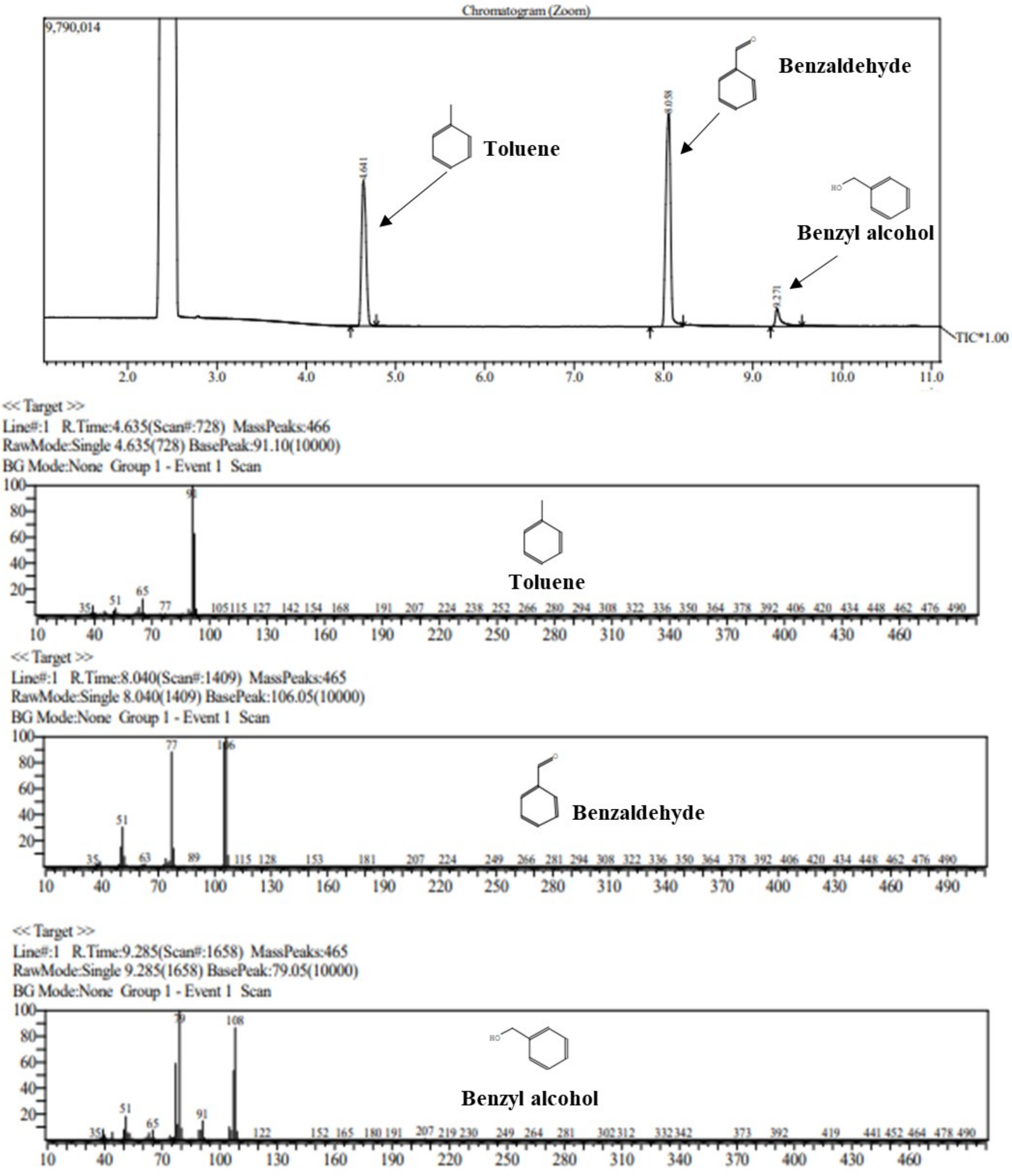

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Fig. S11 GC-MS chromatograph of reaction mixture recovered after 4 h (Reaction conditions- E-g-C_3N_4 (3) (25 mg), light source (250 W Hg lamp), toluene (0.05 mmol), solvent acetonitrile (3 ml), time 4 h, and oxygen atmosphere).

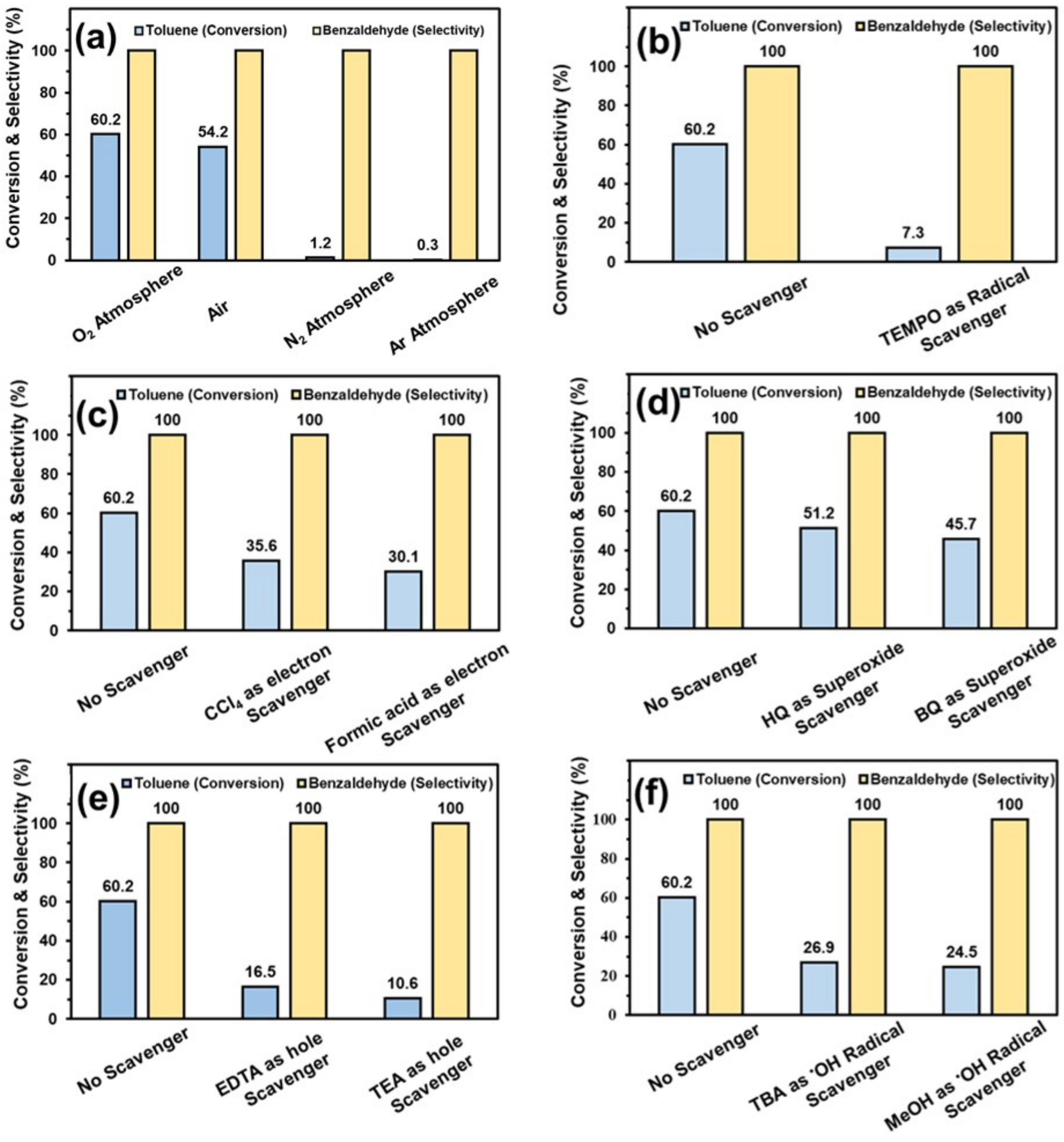

Fig. S12 Control experiments (Reaction conditions- E-g-C_3N_4 (3) (25 mg), light source (250W Hg lamp), toluene (0.05 mmol), solvent acetonitrile (3 ml), time 6 h, and oxygen atmosphere) with (a) variation of atmosphere, (b) using 1.5 mmol of TEMPO as radical scavenger, (c) using 1.5 mmol of electron scavenger, (d) using 1.5 mmol of superoxide scavenger, (e) 1.5 mmol of hole scavenger, and (f) using 1.5 mmol of $OH^•$ radical scavenger.

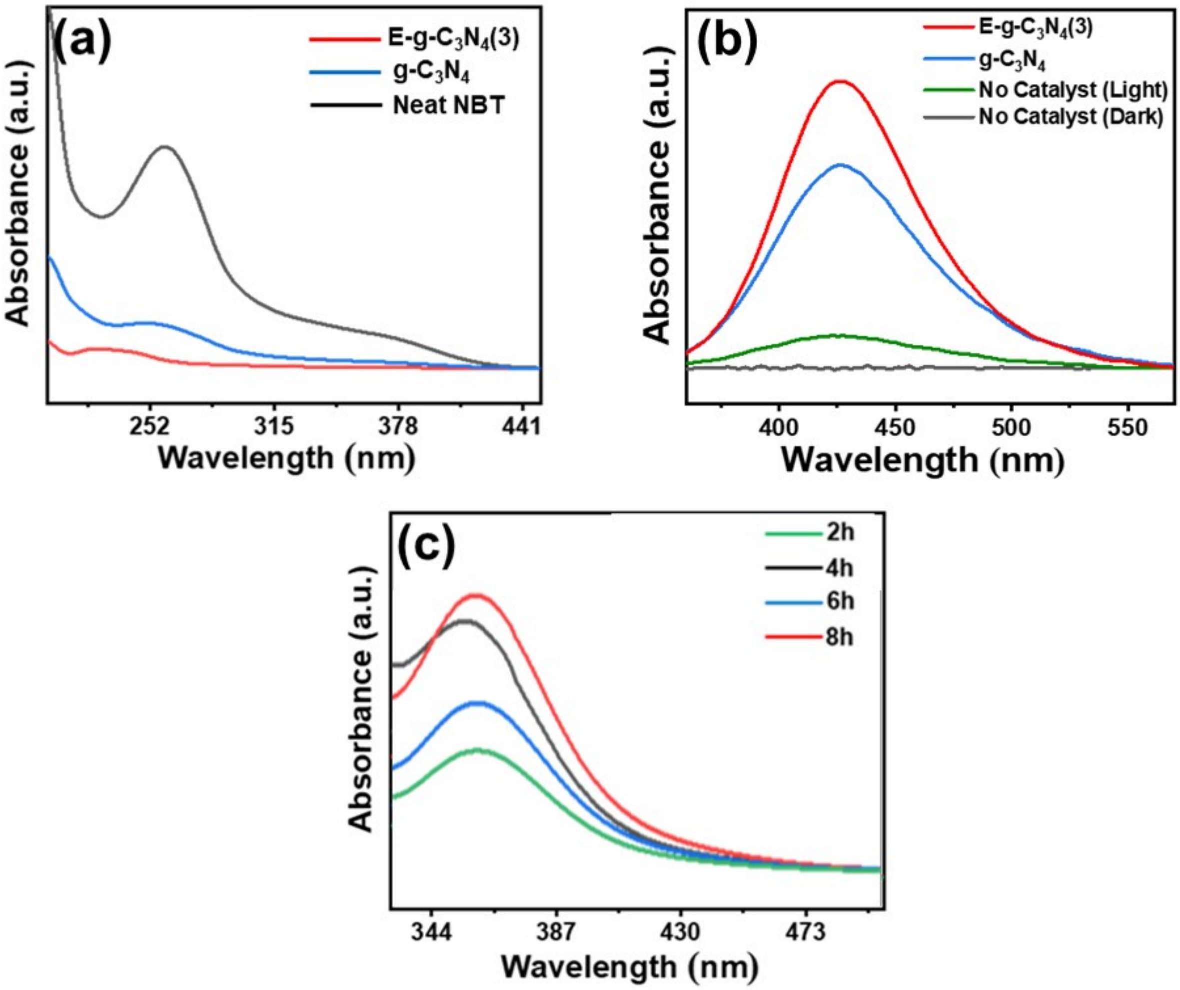

Fig. S13 (a) Comparative absorption spectra of NBT solution before and after light illumination for 10 minutes over pristine and exfoliated g-C_3N_4, (b) Comparative fluorescence spectra of THA solution before and after light illumination for 60 minutes over pristine and exfoliated g-C_3N_4, and in the absence of catalyst, (c) UV spectra recorded during iodometric test for the analysis of photogenerated H_2O_2 during the reaction.

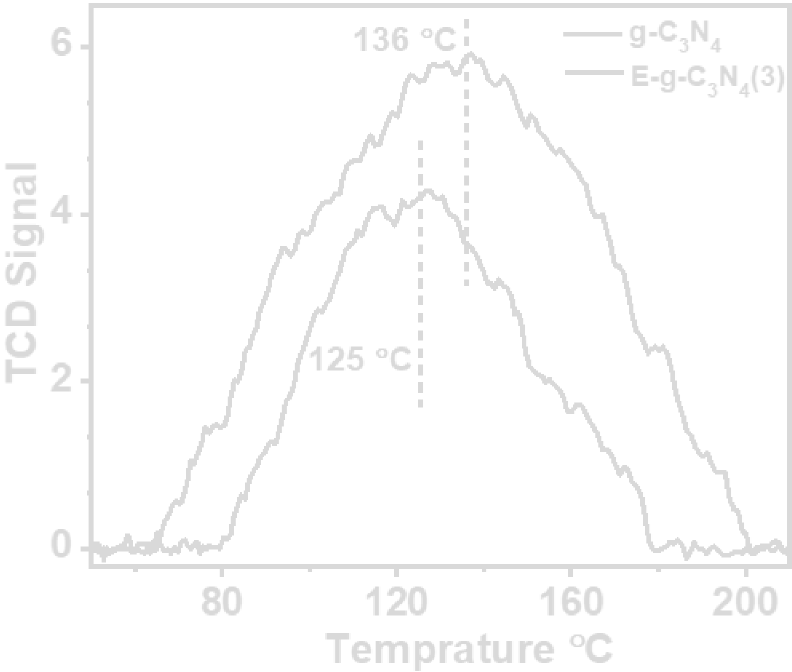

Fig. S14 CO_2-TPD profiles of g-C_3N_4 and E-g-C_3N_4 (3).

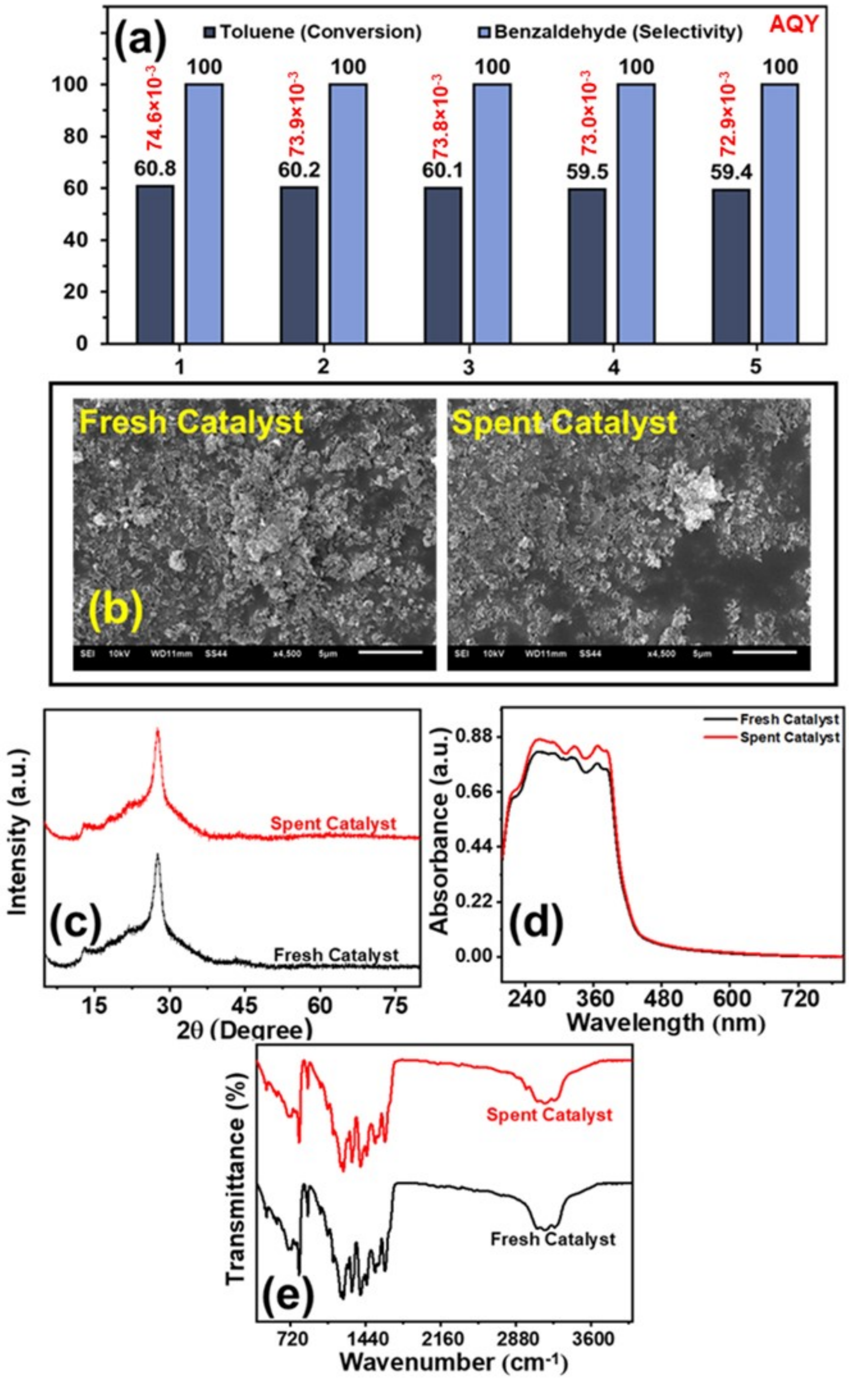

Fig. S15 (a) Recyclability data using E-g-C_3N_4(3) for toluene oxidation reaction ((Reaction conditions- E-g-C_3N_4(3) (25 mg), light source (250W Hg lamp), toluene (0.05 mmol), solvent acetonitrile (3 ml), time 6 h and oxygen atmosphere), (b) SEM images of fresh and spent E-g-C_3N_4(3), (c) XRD of fresh and spent E-g-C_3N_4(3), (d) DRUV-vis spectra of fresh and spent E-g-C_3N_4(3), and (e) FT-IR spectra of fresh and spent E-g-C_3N_4(3). The calculation method for apparent quantum yield (AQY) is provided above.