Supporting Information

Metal-Free Photocatalytic Transformation of Waste Polystyrene into Valuable

Chemicals: Advancing Sustainability through Circular Economy

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	source (250W Hg lamp), PS (104 mg), solvent (4 ml), time 8 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. S15	(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, (c) UV spectra recorded during iodometric test for the analysis of photogenerated H_2O_2 during the reaction.	S36
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Experimental section

Materials

All chemicals used in this study were of AR grade and used as received without any further treatment. Urea, acetone, H_2SO_4 (98%), ethanol, benzene, acetonitrile, and ethylacetate were purchased from Merck India Pvt. Ltd., whereas NaOH, KI, and ammonium molybdate were obtained from Loba Chemie, Pvt. Ltd., India. Waste polystyrene (PS) was obtained from the waste packing material. Nitro blue tetrazolium (NBT), and 2-hydroxyl terephthalic acid (THA) were purchased from Sigma Aldrich.

Catalyst preparation

Synthesis of g-C$_3$N$_4$

The graphitic carbon nitride (g-C$_3$N$_4$) was synthesised using a previously reported method. In this method, 15 g of urea was first crushed into a fine powder using a mortar and pestle. The powder was then placed in a capped crucible. The muffle furnace was programmed to heat the material at 550 °C for 3 h, with a ramp rate of 2.5 °C per minute. Upon completion of the program, the material was removed from the furnace and ground in a mortar and pestle.

Synthesis of S-g-C$_3$N$_4$

A batch of 500 mg of graphitic carbon nitride (g-C$_3$N$_4$) was homogenised with 150 ml of ethanol through mechanical stirring for 30 minutes. The resulting suspension was subjected to ultrasonic treatment for 4 h to facilitate dispersion and exfoliation of the g-C$_3$N$_4$. The solvent, ethanol, was evaporation at 80 °C. The dried g-C$_3$N$_4$ was further processed by mechanical grinding in a mortar and pestle to obtain a fine powder.

Synthesis of C-g-C$_3$N$_4$

The 500 mg of g-C$_3$N$_4$ powder was suspended in 20 ml of 98% sulfuric acid and stirred for 8 h at ambient temperature to ensure homogeneity. Subsequently, the suspension was diluted with 200 ml of deionised water and subjected to ultrasonication for 4 h to facilitate exfoliation. The resulting solution underwent a colour change to pale yellow, indicating successful exfoliation of the g-C$_3$N$_4$. The exfoliated g-C$_3$N$_4$ was recovered from the solution via centrifugation at 6000 RPM. The resulting solid material was washed with deionised water until the supernatant reached a neutral pH, followed by two washing cycles with ethanol to

remove any residual acid. The final product was dried overnight under a vacuum to remove any residual moisture.

Synthesis of T-g-C$_3$N$_4$

The 500 mg of g-C$_3$N$_4$ was placed in a boat-shaped crucible inside the tube furnace. The inert atmosphere inside the tube was provided by argon gas. The material was treated at 500 ˚C for 3 h in a static Ar atmosphere. The obtained pale yellow colour material was uniformly crushed in mortar pastel.

Synthesis of F-g-C$_3$N$_4$

The 500 mg of g-C$_3$N$_4$ was loaded into a boat-shaped crucible within a 90-meter-long quartz tube with an outer diameter of 53 mm (as shown in Fig. 1b). One side of the tube was sealed with high-temperature glass wool, while the other side remained open. The material was placed at the centre of the tube, and the temperature was set at 600 ˚C for 3 h under an argon flow of 20 ml/min, as depicted in Fig. 1a. To create a temperature gradient within the tube, one side was cooled to room temperature via water circulation (Fig. 1d). The material was then transported from the hot area to the colder area of the tube (Fig. 1a), where it condensed over the colder side of the quartz tube (Fig. 1c). After recovery, the condensed material was washed with ethanol and water to remove impurities and dried overnight in a vacuum oven.

Photocatalytic experiment

Photocatalytic PS reforming

The 100 mg of used polystyrene (PS) was taken in a glass beaker, and 4 ml of a binary organic solvent system consisting of ethyl acetate and acetonitrile was added to the beaker (Fig. S1a). The mixture was stirred until complete miscibility of the PS was achieved with the solvents (Fig. S1b). Thereafter, 30 mg of the photocatalyst was introduced into a round-bottom flask (RB) and the mixture of solvent, and PS was transferred to the RB. An oxygen-rich atmosphere was established within the flask via the addition of oxygen via a balloon. The photocatalyst was allowed to equilibrate in the dark for 30 minutes (Fig. S1b). The system was then subjected to a light source for the desired duration of time (Fig. S1c). Upon completion of the reaction,

the catalyst was recovered from the reaction mixture through centrifugation, yielding a clear and concentrated reaction mixture (Fig. S1d)

Analysis of the reaction mixture

To evaluate the composition of the reaction mixture, the unreacted plastic was precipitated by adding a specific amount of ethanol (Fig. S1e). The precipitated material was then separated from the mixture through simple filtration (Fig. S1f), and its mass was measured to determine the conversion of PS. The remaining filtrate was analysed for the formation of acetophenone and benzoic acid. The selectivity of the products was obtained by analysing the filtrate using gas chromatography (GC).

The GC analysis was performed using a Youngling 6100 GC system equipped with a BP-5 column (30 m x 0.25 mm x 0.25 μm). The carrier gas was high-purity nitrogen (99.99% GC grade) with a flow rate of 10 ml/min, and hydrogen (99.99% GC grade) and air (99.99% GC grade) were used as the ignition gases. The injector and detector temperatures were set at 280 °C. The GC column oven temperature was programmed as follows: initial temperature of 80 °C with a hold time of 2 minutes, followed by a ramp to a final temperature of 280 °C with a ramp rate of 5 °C/min. A 0.2 μL sample was injected for analysis. The resulting chromatogram showed the presence of only two products, acetophenone and benzoic acid (Fig S2). The presence of the products was further confirmed using GC-MS analysis with a Shimadzu GCMS-QP 2010 Ultra instrument equipped with an Rtx-5 Sil MS column (30 m x 0.25 mm x 0.25 μm) (Fig S2).

GC calibrations for relative selectivity of products

Here, the calibration curves for acetophenone and benzoic acid were constructed by employing various concentrations of the analytes. The five standards of distinct concentrations were prepared for each analyte using ethanol as the solvent and toluene as an internal standard. The prepared standards were subjected to GC analysis with triplicate injections, and the resulting peak areas were recorded. The calibration curves were then generated by plotting the peak area against the corresponding concentration (in mmol) of the analytes, as illustrated in Fig. S5 and Table S1. Furthermore, the relative product selectivity was calculated using the equation provided in Table S1.

Apparent Quantum Yield Calculation

The quantum yield of the reaction was calculated using eq (S4), which gives the ratio between the electron involved in the reaction and the molar flow of photons introduced into the reactor. 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 the photocatalytic system.

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

(S1)

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

(2)

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

(3)

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

(4)

Tauc plot for band gap calculations

The equation $((\alpha h\nu)^{1/r} = \beta(h\nu - E_g))$ was utilised to determine the exact band gap.[57] The value of r is contingent on the transition nature, where r = ½ is appropriate for direct and r = 2 signify indirect transitions. The $(\alpha h\nu)^{1/r}$ vs. (hν) plots with r = ½, enabling estimation of the band-gap for direct allowed transitions by straight line extrapolation in the case of g-C$_3$N$_4$.[58]

Time-Correlated Single Photon Counting

The data analysis employed double-exponential fitting to determine the average lifetimes and

their percentage contributions, employing the equation (
$$y = y_\circ + \sum_{i=1}^{n} \alpha_i\, e^{-\left(\frac{t}{\tau_i}\right)}$$
).[38,39] To

calculate the average decay time, $\langle\tau\rangle$, the
$$\langle\tau\rangle = \frac{\sum_{i=1}^{n} \alpha_i \tau_i^2}{\sum_{i=1}^{n} \alpha_i \tau_i}$$
) was utilised, and $\sum \alpha_i$ was

normalised to 1.

Mott-Schottky analysis

This method involved the relation $1/C^2 = 2\ [V-V_{fb}-(k_bT/e)]/(\varepsilon\varepsilon_0 eA2N_d)$.[72] Plots of $1/C^2$ vs. applied potential were constructed. All the materials possess a positive slope, indicating their n-type semiconducting behaviour.[73] The MS plots' x-intercepts yielded the flat-band position (E_{fb}), which was -1.11 V vs. Ag/AgCl for g-C_3N_4 (Fig. 5f). In n-type semiconductors, the E_{fb} lies below to conduction band (CB) edge.[74] The E_{fb} values were used to determine the position of the CB edge (E_{CB}) through the relation $E_{CB} = E_{fb}$ -0.1 V.[72] Potential values were standardised using the equation ($E_{NHE} = E_{Ag/AgCl} + 0.196$),[72] and Table S5 presents the calculated E_{CB} vs. NHE values for all the material. Finally, the valence band positions (E_{VB}) were obtained by applying the relation $E_{VB} = E_{CB} + E_g$, where E_{CB} represents the conduction band potential and E_g is the band gap.[75,76]

Photoelectrochemical measurement

The photoelectrochemical analyses were performed with PGSTAT302N Autolab electrochemical workstation using standard three-electrode grouping in Pyrex cell with a 0.1 M aqueous sodium sulfate solution as electrolyte. The coated photocatalyst 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. To make a binder solution, 1.5 ml of ethanol was mixed with 1 ml of water and 40 µl of nefion. 20 ml of the photocatalyst was added in the binder solution and sonicated for 10 minutes. The binder solution was cast dropwise over the glass surface using a dropper and hotplate with a temperature of 45 °C. The electrochemical impedance spectroscopy was calculated in the frequency range of 1 MHz to 1 Hz using a sinusoidal AC perturbation signal of 5 mV. The 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 under continuous stirring. After 15 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 with 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 2-hydroxyl terephthalic acid (THA) 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 reaction was performed for different intervals. The 3 ml of

the obtained filtrate, after removing unreacted polystyrene, 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 oxidises 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.

Materials characterisation

Physicochemical characterisation

X-ray diffraction (XRD) patterns were collected using a RIGAKU Mini-flex diffractometer with Cu Kα radiation over the 2θ range of 5° to 80° at IIT Ropar. Surface area and porosity were determined via N_2 adsorption-desorption measurements using the BELSORP instrument. Prior to N_2 adsorption, all materials were degassed at 200 ˚C for 4 h in the degassing port. The specific surface area was calculated by applying the Brunauer-Emmett-Teller (BET) equation to the relative pressure range of 0.05 to 0.3 (IIT Ropar). The FESEM analysis of the material's morphology was carried out using a Joel instrument at an accelerating voltage of 10 kV (IIT Ropar). UV-DRS study of all catalysts was performed on a Shimadzu UV-visible spectrophotometer (UV-2600) using $BaSO_4$ as standard reference material. Liquid UV analysis was also conducted using a Shimadzu UV-visible spectrophotometer (UV-2600) at IIT Ropar. A bulk elemental study (CHNSO) was performed using a Thermofisher scientific analyser. X-Ray photoelectron spectroscopy (XPS) was carried out using a Thermofisher scientific 'Nexsa Base' instrument at IIT Ropar. UPS and VBXPS analysis was performed using the same instrument. Fluorescence analysis was conducted using a Perkin Elmer LS55 at IIT Ropar. TGA analysis was performed using a Mettler Toledo TGA/DSC 1 STARe SYSTEM instrument at a temperature increment of 10 °C min -1 under a nitrogen atmosphere from 27 °C to 600 °C (IIT Ropar). Finally, fluorescence decay time was evaluated using the TCSPC instrument of DeltaFlex TCSPC Lifetime Fluorimeter at IRCC IIT Bombay.

Table S1 GC calibrations for the relative selectivity of products.

Entry	Concentration Acetophenone mmol	Peak area Benzoic acid	R_f for Acetophenone	Concentration Benzoic acid m mol	Peak area Benzoic acid	R_f for Benzoic acid
1	0.1	2742600	27426000	0.1	1820810	18208100
2	0.2	6826890	34134400	0.2	4365750	21820800
3	0.3	9754640	22515500	0.3	6419470	21398200
4	0.4	13771200	3442800	0.4	9501090	23752700
5	0.5	17942700	3588500	0.5	11598100	23196300

Average response factor for acetophenone ($R_f(AP)$) = 30877866

Average response factor for Benzoic acid ($R_f(BA)$) = 21676808

Let the relative sensitivity factor for acetophenone ($S_f(AP)$) = 1.00

The relative sensitivity factor for Benzoic acid ($S_f(BA)$) = ($R_f(AP)$) / ($R_f(BA)$) = 1.42

Relative Selectivity % of Acetophenone =

$$\left(\frac{Peak\ area\ of\ acetophenone\ \times\ Sf\ (AP)}{Peak\ area\ of\ acetophenone\ \times\ Sf\ (AP) + Peak\ area\ of\ Benzoic\ acid\ \times\ Sf\ (BA)} \times 100 \right)\%$$

$$= \left(\frac{Peak\ area\ of\ acetophenone\ \times\ 1}{Peak\ area\ of\ acetophenone\ \times\ 1 + Peak\ area\ of\ Benzoic\ acid\ \times\ 1.42} \times 100 \right)\%$$

Relative Selectivity % of Benzoic acid =

$$\left(\frac{Peak\ area\ of\ Benzoic\ acid\ \times\ Sf\ (BA)}{Peak\ area\ of\ acetophenone\ \times\ Sf\ (AP) + Peak\ area\ of\ Benzoic\ acid\ \times\ Sf\ (BA)} \times 100\right)\%$$

$$= \left(\frac{Peak\ area\ of\ Benzoic\ acid\ \times\ 1.42}{Peak\ area\ of\ acetophenone\ \times\ 1 + Peak\ area\ of\ Benzoic\ acid\ \times\ 1.42} \times 100\right)\%$$

Table S2. The textural properties of catalysts prepared in this study.

Entry	Catalyst	BET surface area (m^2g^{-1})	Total pore volume ($cm^3\ g^{-1}$)
1	g-C_3N_4	38	0.260
2	S-g-C_3N_4	61	0.310
3	C-g-C_3N_4	126	0.325
4	T-g-C_3N_4	227	0.339
5	F-g-C_3N_4	177	0.332

Table S3 Elemental composition of the catalysts.

Surface elemental composition determined from XPS					
Entry	**Catalyst**	**Carbon Atomic %**	**Nitrogen Atomic %**	**Oxygen Atomic %**	**Nitrogen/Carbon Ratio**
1	g-C$_3$N$_4$	44.8	53.1	2.1	1.18
2	F-g-C$_3$N$_4$	45.5	46.3	8.2	1.02
3	V-g-C$_3$N$_4$	45.1	54.2	0.7	1.20
Bulk elemental composition determined from CHNS(O)					
Entry	**Catalyst**	**Carbon %**	**Nitrogen %**	**Oxygen %**	**Nitrogen/Carbon Ratio**
1	g-C$_3$N$_4$	35.7	55.3	7.1	1.54
2	F-g-C$_3$N$_4$	34.0	48.7	15.3	1.43
3	V-g-C$_3$N$_4$	36.8	61.2	2.0	1.66

Table S4. Best fitted parameters of multiexponential components for decay curve.

Entry	Catalyst	Pre-exponential functions		Decay lifetimes (ns)			Fractional contribution	
		α_1	α_2	τ_1	τ_2	$\langle\tau\rangle$	f_1	f_2
1	g-C$_3$N$_4$	70	30	0.8	4.0	3.0	31	69
2	S-g-C$_3$N$_4$	72	28	1.7	4.6	3.2	49	51
3	C-g-C$_3$N$_4$	75	25	1.2	5.9	4.1	38	62
4	T-g-C$_3$N$_4$	71	29	1.5	6.8	4.9	35	65
5	F-g-C$_3$N$_4$	65	35	0.5	3.0	2.4	22	78

Table S5. The band edge potentials and bandgap of all the photocatalysts according to Mott Schottky analysis.
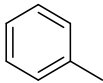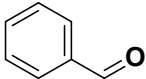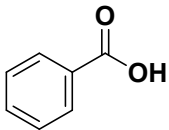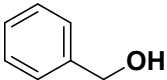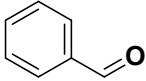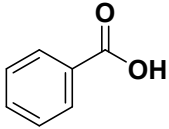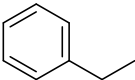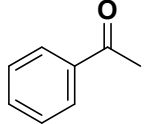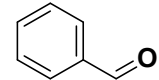
Entry	Catalyst	Band Gap	Flat Band Potential vs. Ag/AgCl	Conduction Band edge Potential vs. Ag/AgCl	Conduction Band Edge Potential vs. NHE	Valance Band Edge Potential vs. NHE
1	g-C$_3$N$_4$	2.75	-1.11	-1.21	-1.01	1.74
2	S-g-C$_3$N$_4$	2.77	-1.15	-1.25	-1.05	1.72
3	T-g-C$_3$N$_4$	2.79	-1.19	-1.29	-1.09	1.70
4	C-g-C$_3$N$_4$	2.80	-1.21	-1.31	-1.11	1.69
5	F-g-C$_3$N$_4$	2.59	-0.98	-1.08	-0.88	1.71
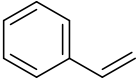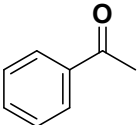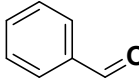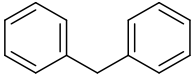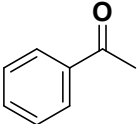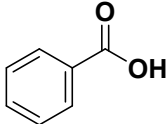
Table S6. AQY for the photocatalytic PS oxidation with different photocatalyst

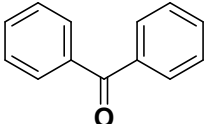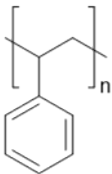| Entry	Catalyst	PS Conversion	AP Selectivity	BA Selectivity	AQY
1	g-C$_3$N$_4$	27.6	90.8	9.2	25×10^{-2}
2	Meso-g-C$_3$N$_4$	40.2	85.4	14.6	37×10^{-2}
2	S-g-C$_3$N$_4$	35.6	89.2	10.8	33×10^{-2}
3	C-g-C$_3$N$_4$	54.6	86.6	13.4	39×10^{-2}
4	T-g-C$_3$N$_4$	54.6	85.2	14.8	50×10^{-2}
5	F-g-C$_3$N$_4$	68.8	82.1	17.9	59×10^{-2}

(Reaction conditions- Photocatalyst (30 mg), light source (250W Hg lamp), PS (104 mg), solvent (benzene: acetonitrile (1:1) (4 ml)), and O_2 1 bar)

Table S7 The photocatalytic oxidation for the various aromatic substrates.

Substrate	Conv. (%)	Product Selectivity	Product Selectivity
Toluene	25.5	Benzaldehyde (92 %)	Benzoic acid (8 %)
Benzyl alcohol	75.5	Benzaldehyde (72 %)	Benzoic acid (28%)
Ethyl benzene	68.6	Acetophenone (90 %)	Benzaldehyde (10 %)
Styrene	71.2	Acetophenone (88%)	Benzaldehyde (12%)

Diphenylmethane	67.4	Benzophenone (100 %)	-
Polystyrene	63.2	Acetophenone (86 %)	Benzoic acid (14 %)

Reaction conditions: Photocatalyst (30 mg), light source (250 W Hg lamp), Reactant (1mmol), solvent (4 ml)), time (8 h), and O_2. The calculation method for apparent quantum yield (AQY) is provided above.

Table S8. Comparative photocatalytic activity of F-g-C_3N_4 in polystyrene (PS) reforming with reported literatures.

Entry	Catalyst	Reaction conditions	Light source & Time	PS Conversion	Acetophenone Selectivity	Benzoic acid Selectivity	Reference
1	Fluorenone (20 mol %)	10 mmol (1.04 g) PS, 0.2 equiv of fluorenone, 1 equiv of H_2SO_4, 20 mL of EtOAc, and O_2 balloon.	blue LED for 48 h	-	-	38 % (yield)	[26]
2	$FeCl_2$	PS (0.5 mmol), catalyst (2 mol %), and DCM/MeCN (3 : 2 v/v, 2 mL), O2 (1 atm) at	20 W 400 nm LED for 66 h	100 %	-	65 %	[83]

#	Catalyst	Conditions	Light				Ref
		ambient temperature					
3	FeCl$_3$	Using 20 mg of commercial PS and 10 wt % FeCl$_3$ dissolved in acetone (0.25 mL), with air cooling and O$_2$ balloon	White LED for 20 h	-	-	13.8 mol persent	[84]
4	pTsOH (5 % mol)	104 mg of PS in the presence of an acid catalyst in 2 mL of a solvent (benzene/CH$_3$CN) under O$_2$ (1 bar).	Violet-blue light (405 nm, 9 W) for 15 h	-	2 % (yield)	43 % (yield)	[20]
5	N-Bromosuccinimide	N-Bromosuccinimide (15 mol %), CF$_3$SO$_2$Na (50 mol %) Solvent EtOAC 1 bar O2	390 nm 52 W LED for 16 h	-	-	73 % (yield)	[85]
6	Anthraquinone	100 mg PS, Anthraquinone (10 mg, 0.048 mmol, 5 mol), solvent 2 ml (MeCN) O$_2$ (1 atm).	390 nm LED for 48 h	-	-	28.2 % (yield)	[86]
7	g-C$_3$N$_4$	500 mg PS, 200 mg g-C$_3$N$_4$, solvent 40 ml (MeCN) O$_2$ (10	300 W Xenon lamp at **150 °C** for 8 h	90 %	15 %	74 %	[87]

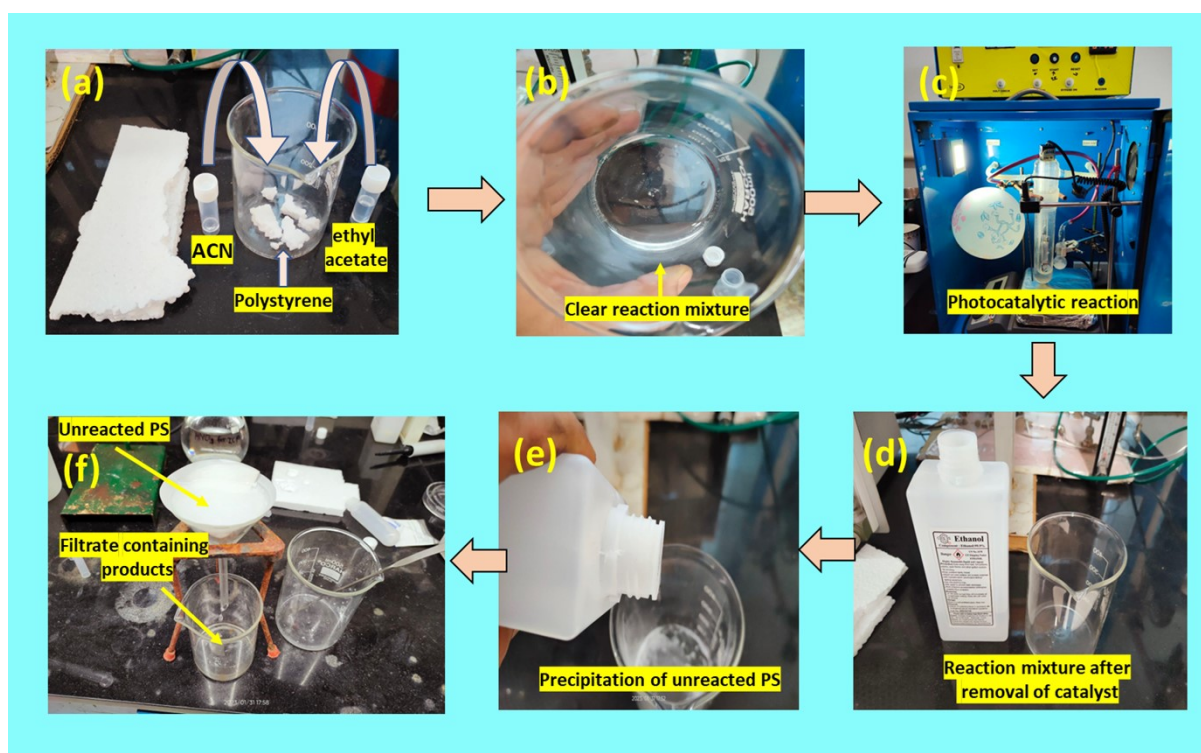| 8	F-g-C$_3$N$_4$	104 mg PS, 30 mg F-g-C$_3$N$_4$, solvent 4 ml (MeCN/EtOH) O$_2$ (1 atm).	250 W Hg lamp for 8 h	63.2 %	86 %	14 %	This work
		bar).					

Fig. S1 The digital photographs show the various steps involved in the photocatalytic upscaling of PS, including: (a) mixing PS in a binary solvent system, (b) the clear solution obtained after mixing, (c) the 250 W Hg lamp-based photocatalytic reaction setup, (d) the reaction mixture

after recovery of photocatalyst, (e) the precipitation of unreacted PS using ethanol, and (f) the separation of unreacted PS from the reaction solution.
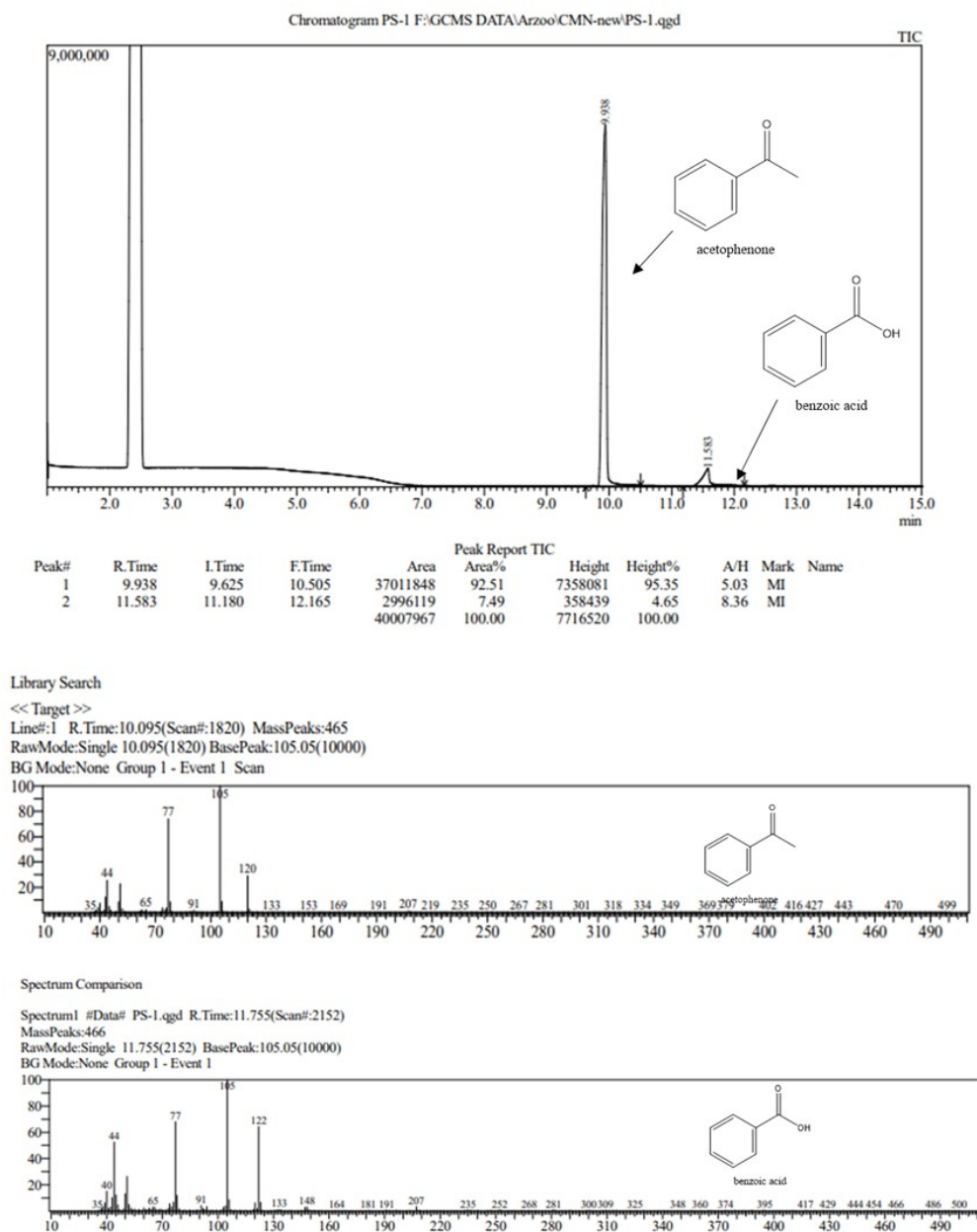
Chromatogram PS-1 F:\GCMS DATA\Arzoo\CMN-new\PS-1.qgd

TIC

9,000,000

9.938

acetophenone

11.583

benzoic acid

2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0 11.0 12.0 13.0 14.0 15.0
min

Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
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2	11.583	11.180	12.165	2996119	7.49	358439	4.65	8.36	MI	
				40007967	100.00	7716520	100.00			

Library Search

<< Target >>
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40
20

105
77
44
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acetophenone

Spectrum Comparison

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122
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40
35   65   91   133   148   164   181 191   207   235   252   268 281   300 309   325   348 360 374   395   417 429   444 454 466   486 500

benzoic acid

Fig. S2 GC-MS chromatograph of obtained filtrate after 6 h of reaction (((Reaction conditions-F-g-C$_3$N$_4$ (30 mg), light source (250W Hg lamp), PS (104 mg), solvent [Ethyl acetate: Acetonitrile (1:0.142)] (4 ml), and oxygen atmosphere))
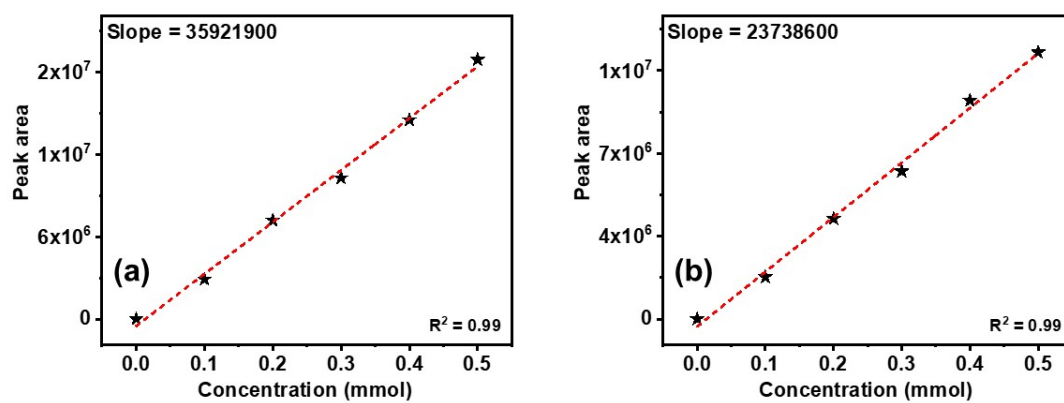
Fig. S3 GC Calibration curve of (a) Acetophenone and (b) Benzoic acid.
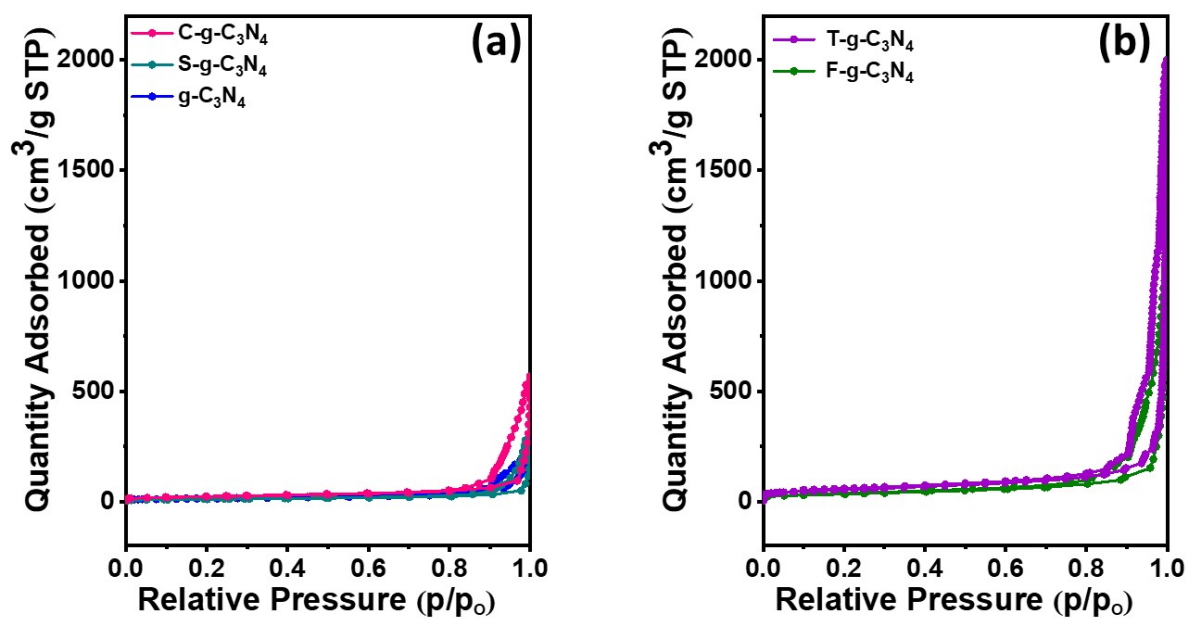
Fig. S4 N_2-adsorption-isotherms of (a) g-C_3N_4, S-g-C_3N_4, and C-g-C_3N_4, (b) T-g-C_3N_4, and F-g-C_3N_4.
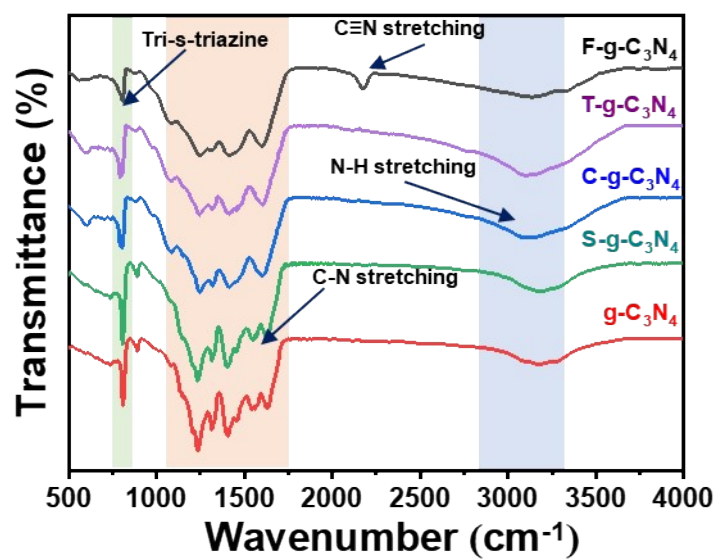
Fig. S5 FT-IR spectra of pristine g-C_3N_4 and exfoliated g-C_3N_4 samples.
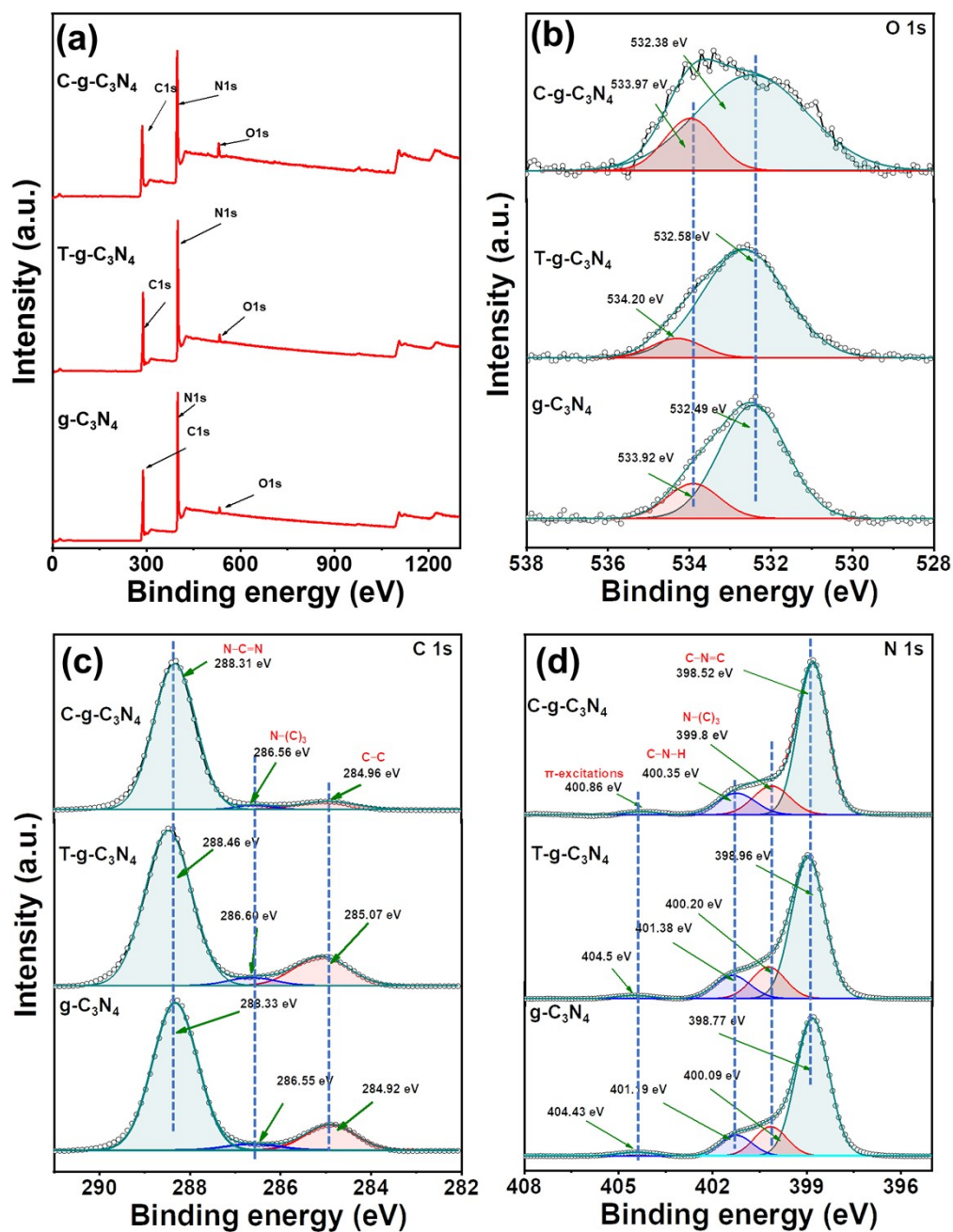
Fig. S6 (a) XPS survey of pristine g-C_3N_4, T-g-C_3N_4 and C-g-C_3N_4, (b) high-resolution O 1s XPS spectra of g-C_3N_4, T-g-C_3N_4 and C-g-C_3N_4, (c) high-resolution C 1s XPS spectra of g-C_3N_4, T-g-C_3N_4 and C-g-C_3N_4, and (d) (c) high-resolution N 1s XPS spectra of g-C_3N_4, T-g-C_3N_4 and C-g-C_3N_4.
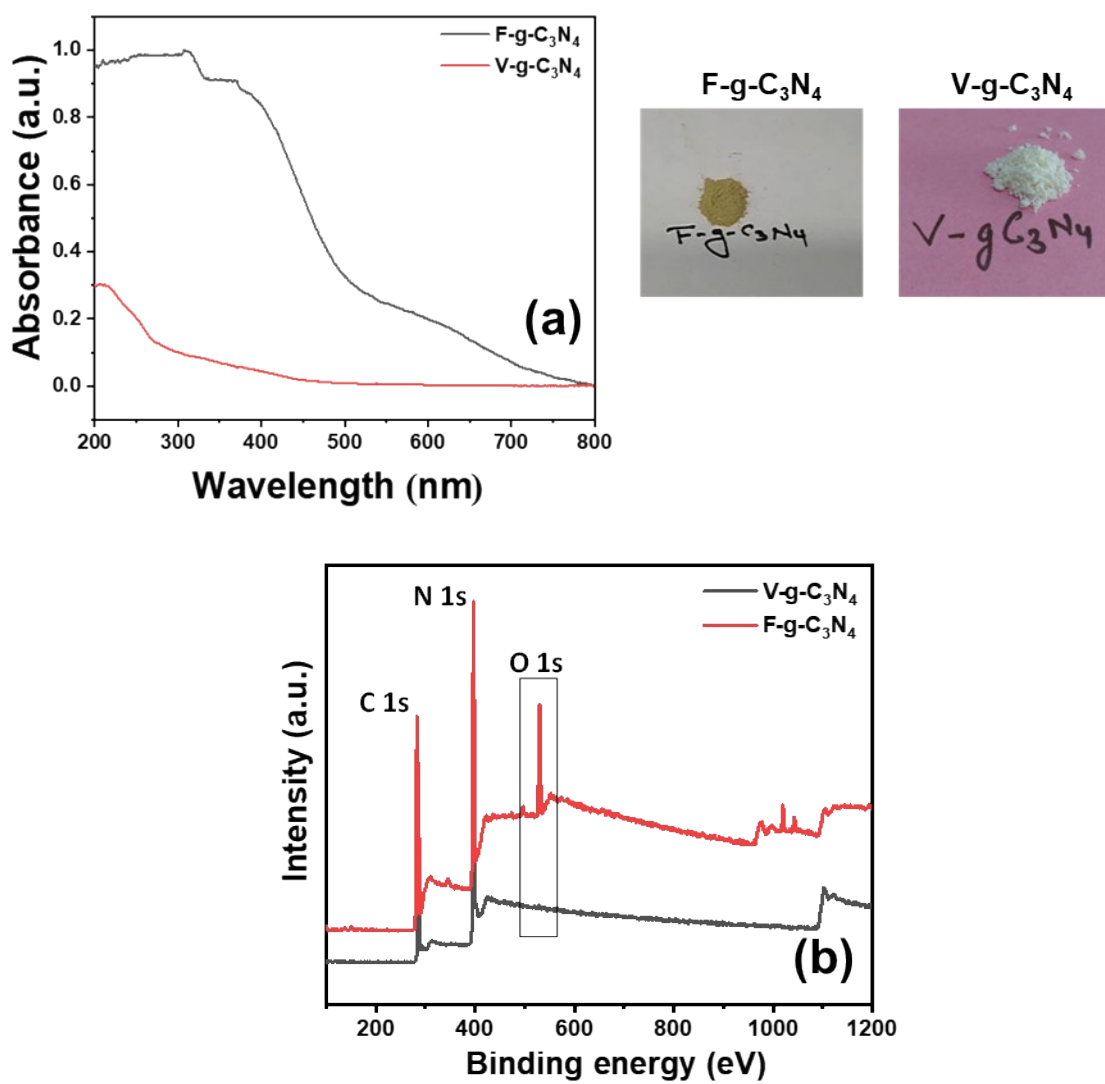
Fig. S7 (a) Ultraviolet-visible absorption spectra, and (b) XPS survey spectra of F-g-C$_3$N$_4$ and V-g-C$_3$N$_4$.
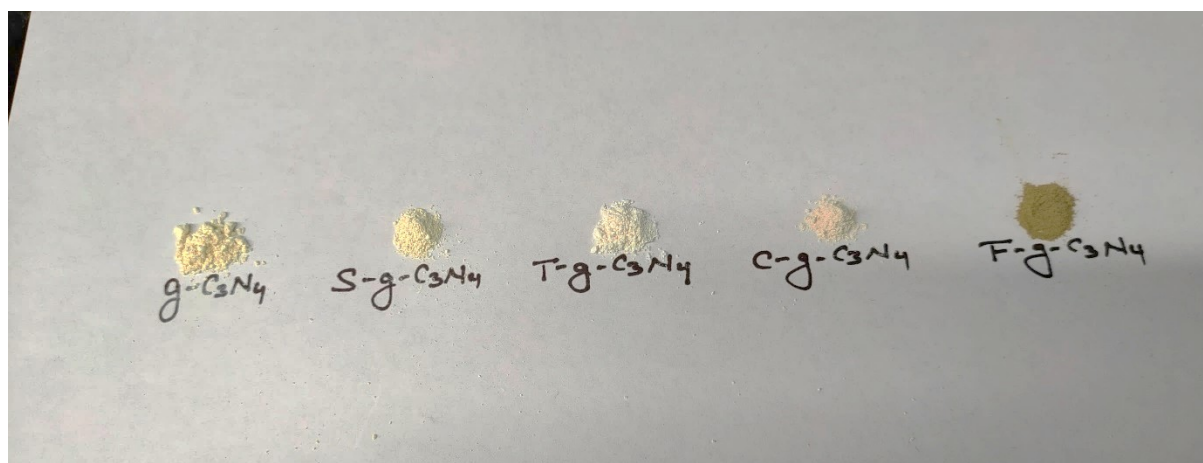
Fig. S8 Digital images of all synthesised photocatalysts.
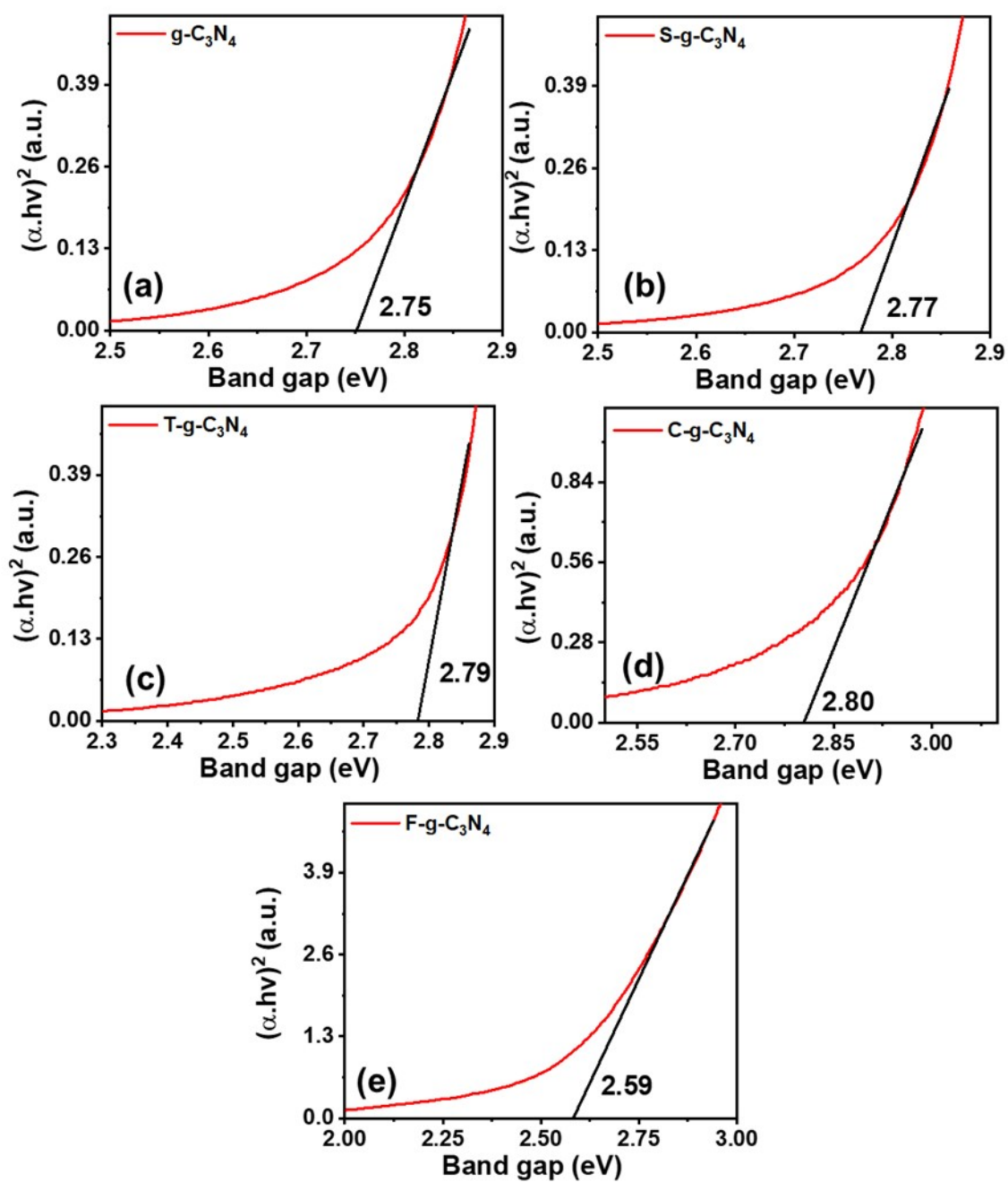
Fig. S9 Tauc plots of (a) g-C$_3$N$_4$, (b) S-g-C$_3$N$_4$, (c) T-g-C$_3$N$_4$, (d) C-g-C$_3$N$_4$, and (e) F-g-C$_3$N$_4$.
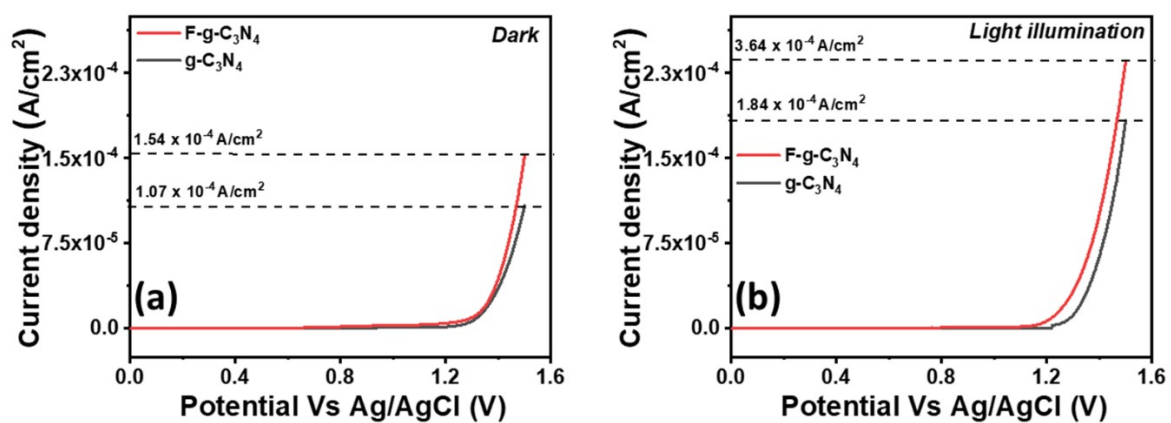
Fig. S10 LSV spectra of pristine g-C$_3$N$_4$ and exfoliated F-g-C$_3$N$_4$ in (a) dark and (b) in light.
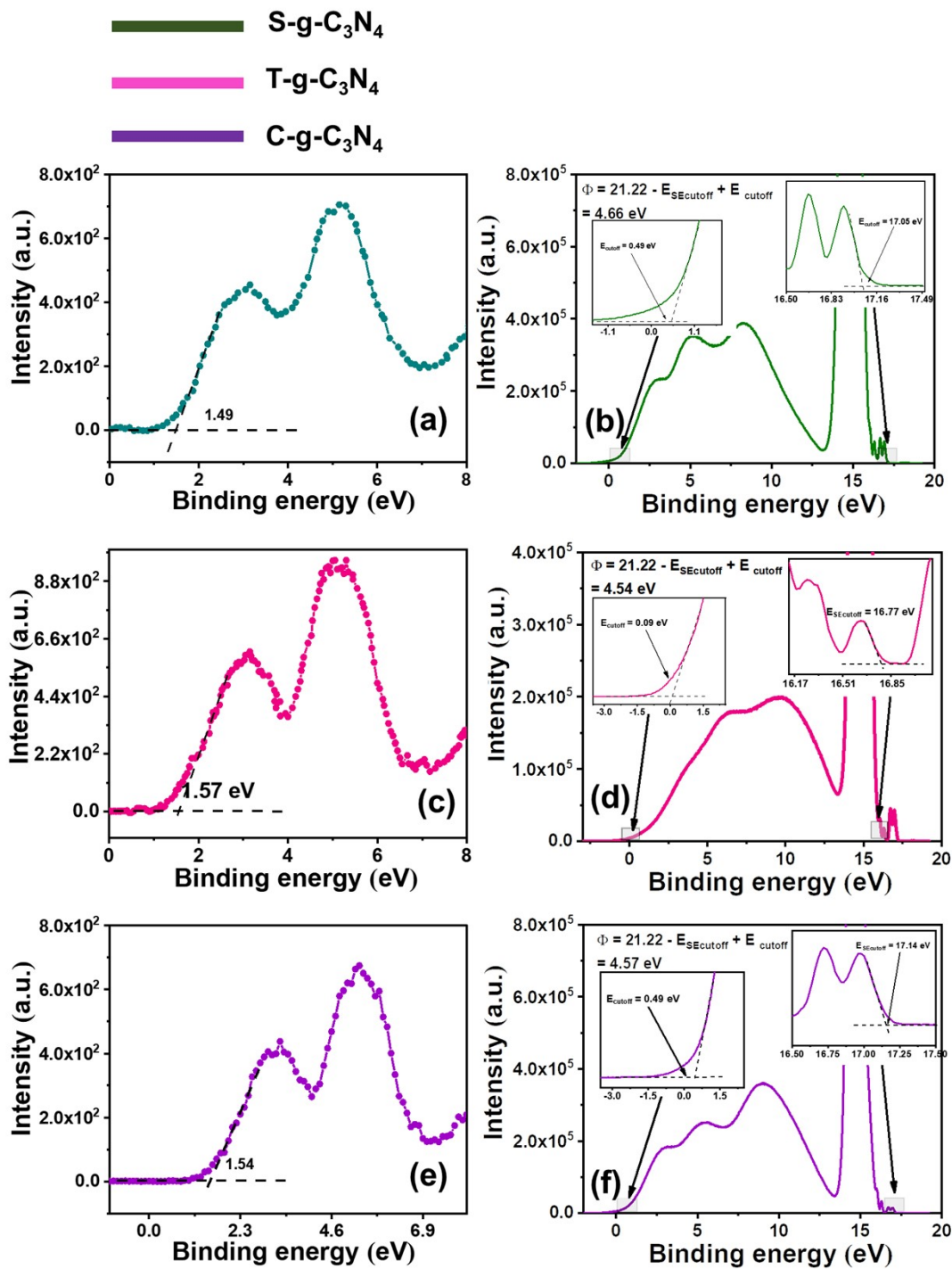
Fig. S11 (a) VB-XPS spectrum of S-g-C$_3$N$_4$, (b) UPS spectrum of S-g-C$_3$N$_4$, (c) VB-XPS spectrum of T-g-C$_3$N$_4$ (d) UPS spectrum of T-g-C$_3$N$_4$, (e) VB-XPS spectrum of C-g-C$_3$N$_4$, and (f) UPS spectrum of C-g-C$_3$N$_4$.
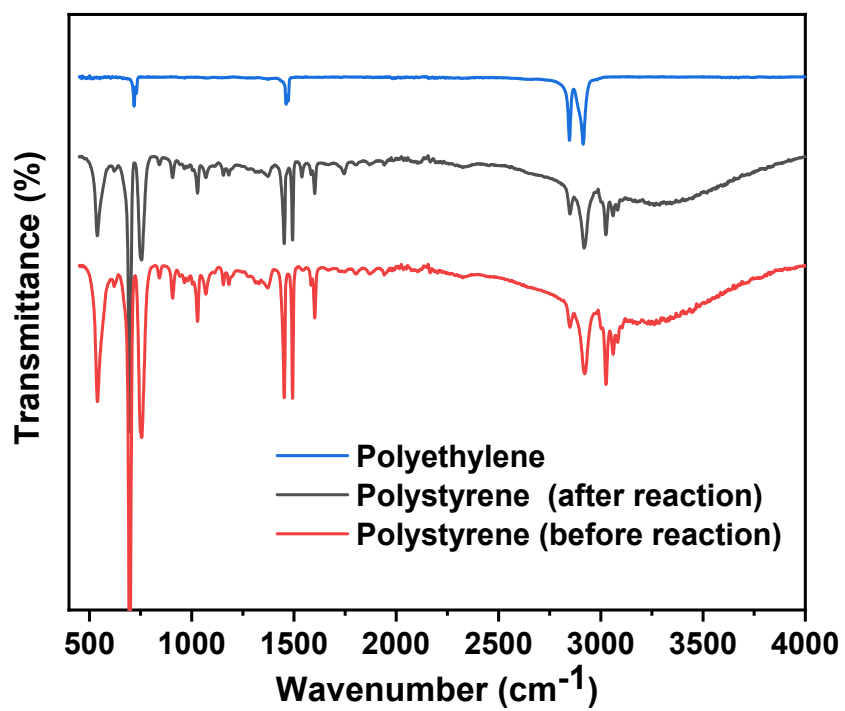
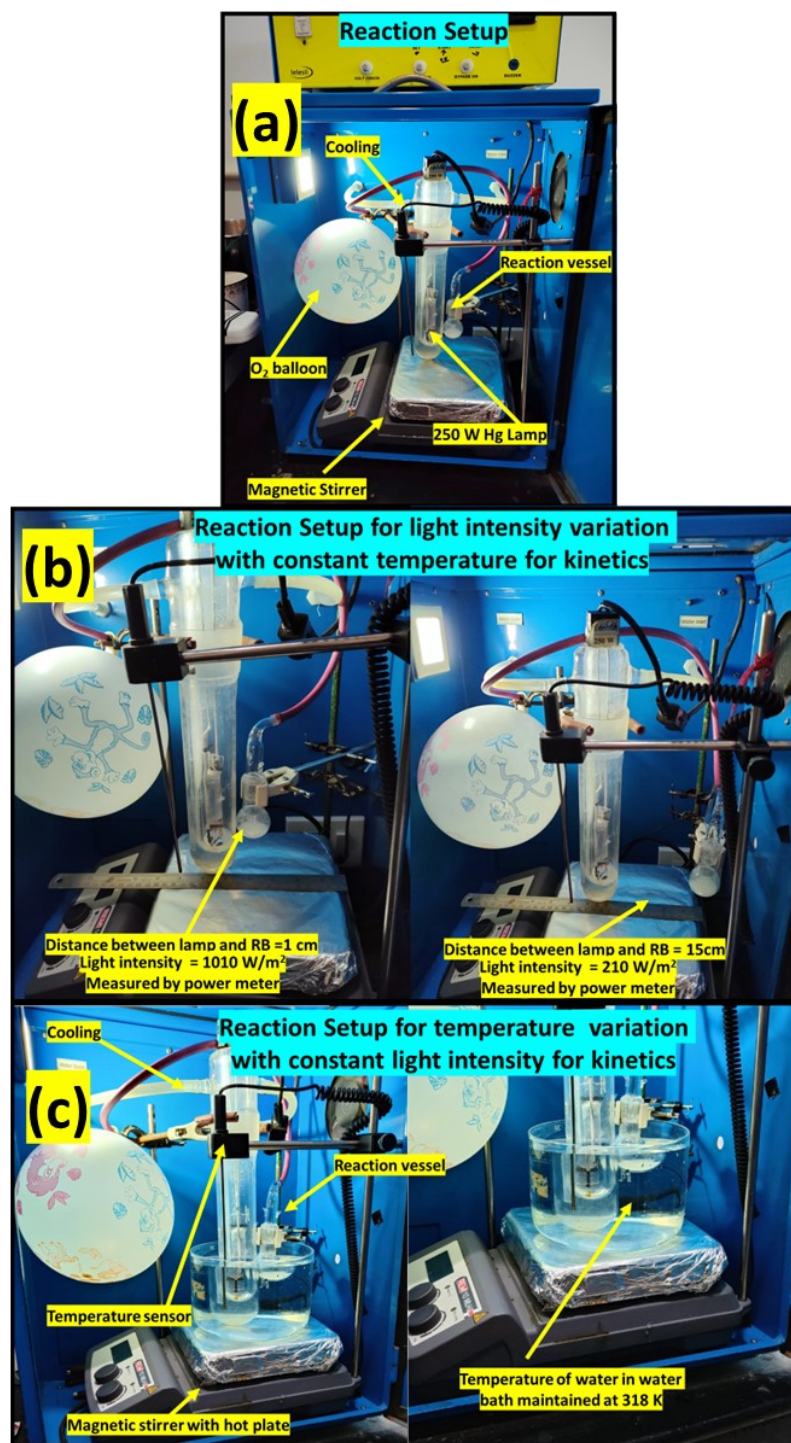**Fig. S12** FT-IR spectra of PE, PS before reaction, and PS after reaction.

Fig. S13 The digital image of the photocatalytic reactor and reaction setup for the photocatalytic toluene oxidation (a) with constant temperature and light intensity, (b) with a variation of light intensity at a constant temperature, and (c) with a variation of temperature with constant light intensity.
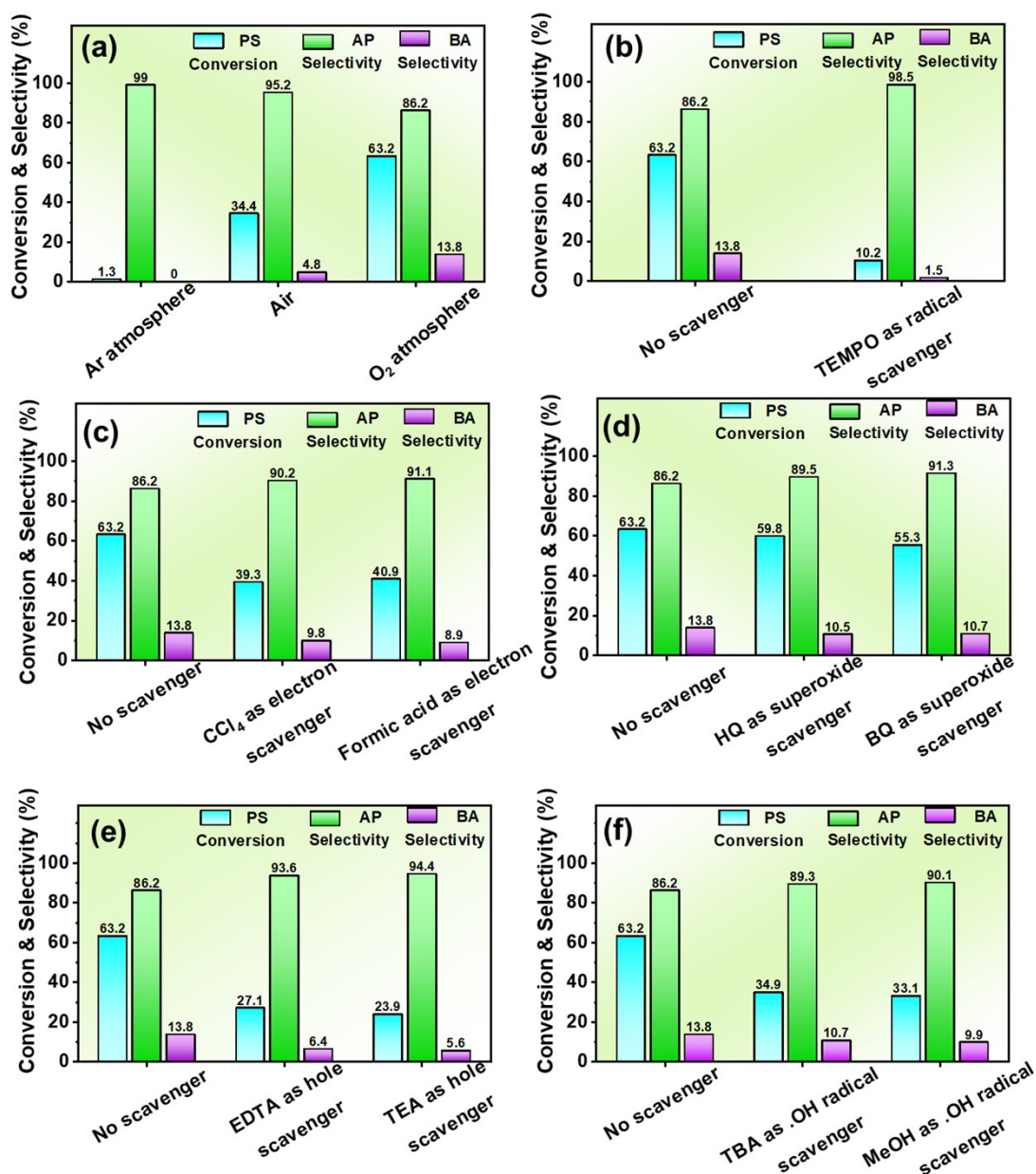
Fig. S14 Control experiments (Reaction conditions- F-g-C$_3$N$_4$ (30 mg), light source (250W Hg lamp), PS (104 mg), solvent [Ethyl acetate:Acetonitrile (1:0.142)] (4 ml), time 8 h, and oxygen atmosphere) with (a) variation of atmosphere, (b) using 1.5 mmol of TEMPO as radical scavenger, (c) using 1.5 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.
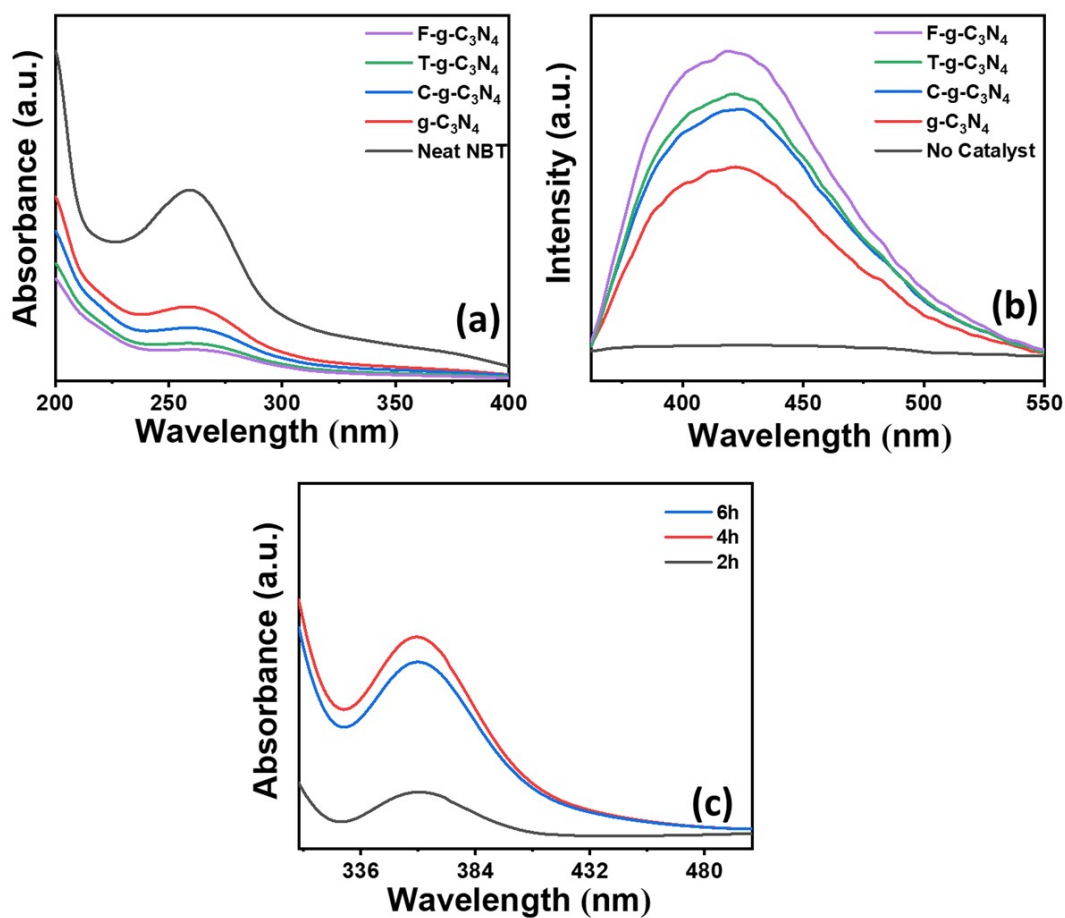
Fig. S15 (a) Comparative absorption spectra of NBT solution before and after light illumination for 10 minutes over pristine and exfoliated g-C_3N_4, (b) Comparative fluorescence spectra of THA solution before and after light illumination for 60 minutes over pristine and exfoliated g-C_3N_4, (c) UV spectra recorded during iodometric test for the analysis of photogenerated H_2O_2 during the reaction.
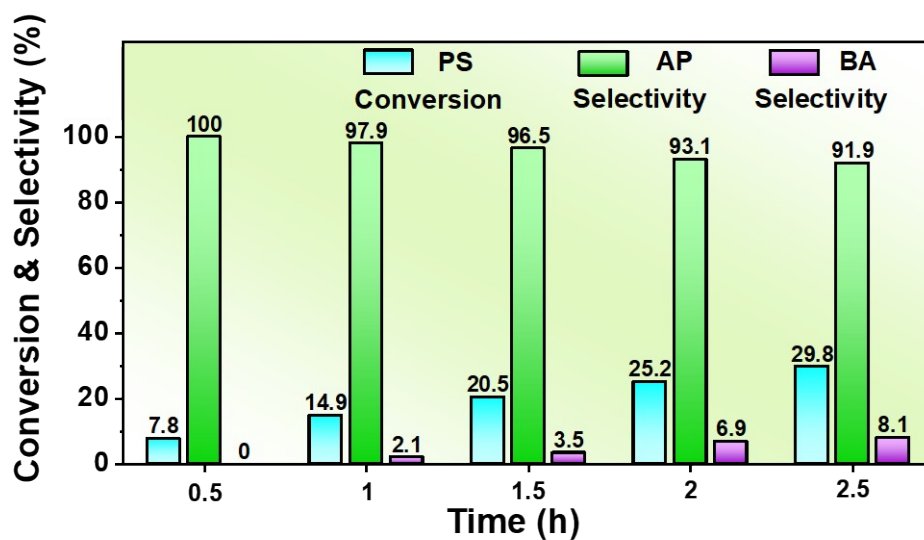
Fig. S16 PS Oxidation at different intervals of time. (Reaction conditions- F-g-C$_3$N$_4$ (30 mg), light source (250W Hg lamp), PS (104 mg), solvent [Ethyl acetate: Acetonitrile (1:0.142)] (4 ml), and oxygen atmosphere).
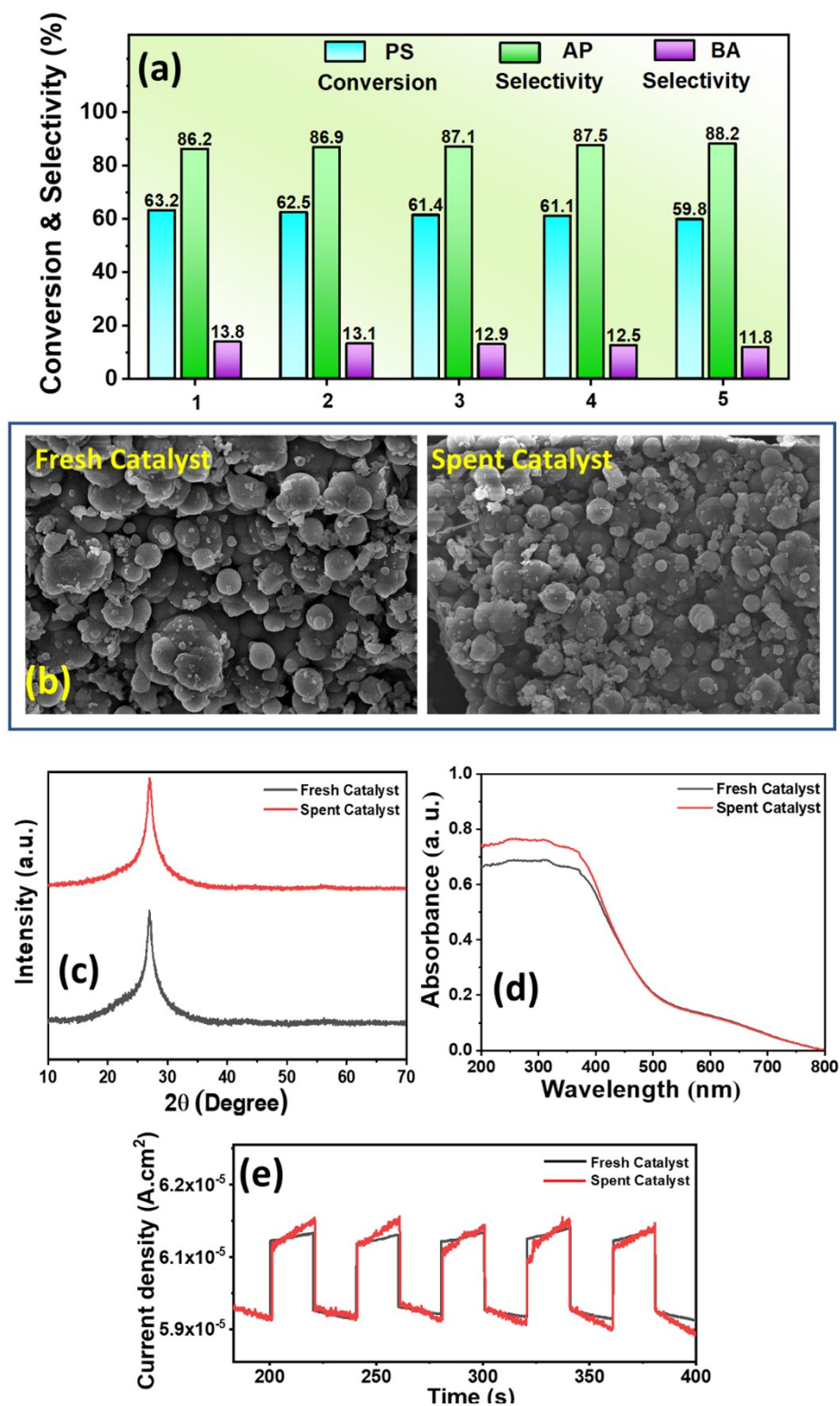
Fig. S17 (a) Recyclability data using F-g-C$_3$N$_4$ for PS reforming reaction ((Reaction conditions- F-g-C$_3$N$_4$ (30 mg), light source (250W Hg lamp), PS (104 mg), solvent [Ethyl acetate: Acetonitrile (1:0.142)] (4 ml), time 6 h and oxygen atmosphere), (b) SEM images of fresh and spent F-g-C$_3$N$_4$, (c) XRD of fresh and spent F-g-C$_3$N$_4$, (d) DRUV-vis spectra of fresh and spent F-g-C$_3$N$_4$, (e) response of transient photocurrent for fresh and spent F-g-C$_3$N$_4$.