Electronic Supporting Information

Phenyl-grafted carbon nitride semiconductor for photocatalytic CO_2-reduction and rapid degradation of organic dyes

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Characterisation Details

The phase identification of samples was performed in the *2θ* range between 10° and 80° using an X-ray diffractometer (Rigaku: Miniflex-II-DD34863) using Cu Kα radiation (λ = 0.15418 nm) operated at 30 kV and 15 mA at a scan rate of 5° min^{-1}. The TEM images were recorded using a FEI Tecnai T-20 electron microscope operating at 300 kV. Energy dispersive X-ray spectroscopy analysis was carried out using Zeiss FESEM. UV-visible diffuse reflectance spectra (UV-Vis DRS) of all samples were recorded using a Jasco (model V-670) spectrophotometer equipped with an integrating sphere accessory. Barium sulfate was used as reference for the reflectance spectra. Fourier transform infrared (FT-IR) spectra were obtained on Shimadzu IRAffinity-1S spectrophotometer. The chemical composition and oxidation states of the materials were probed using ESCALAB 250-Xi X-ray photoelectron spectrometer microprobe. Surface area analysis was probed by Brunauer–Emmet–Teller (BET) method using a Micromeritics ASAP 2020 V3.04 H surface area analyzer by nitrogen adsorption at 77 K. Photoluminescence (PL) decays and PL lifetime images were recorded on a time–resolved Micro-Time 200 confocal fluorescence lifetime imaging microscopy (FLIM) setup (PicoQuant) equipped with an inverted microscope (Olympus IX 71). All the measurements were performed under ambient conditions, at room temperature, on a powder deposited cover-slip. Samples were excited by a 405 nm ps diode pulse laser with a stable repetition rate of 20 MHz (FWHM: 176 ps). The data acquisition was performed with a SymPhoTime software controlled PicoHarp 300 time-correlated single-photon counting (TCSPC) module in a time tagged time-resolved mode. The overall resolution of the setup was 4 ps.

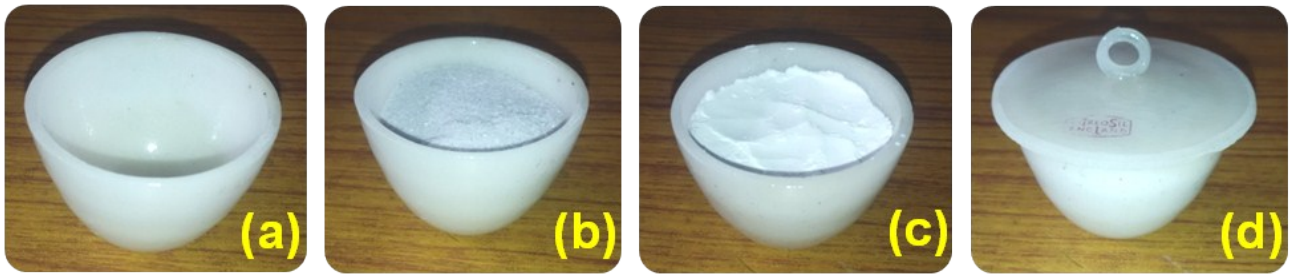

Figure S1. The stepwise procedure of phenyl grafted g-C_3N_4 synthesis: (a) empty silica crucible, (b) mixture containing 10 g of urea, 20 mg of phenyl urea, (c) protective covering using 1.5 g melamine, (d) final closing with silica lid to inhibit the escape of gases.

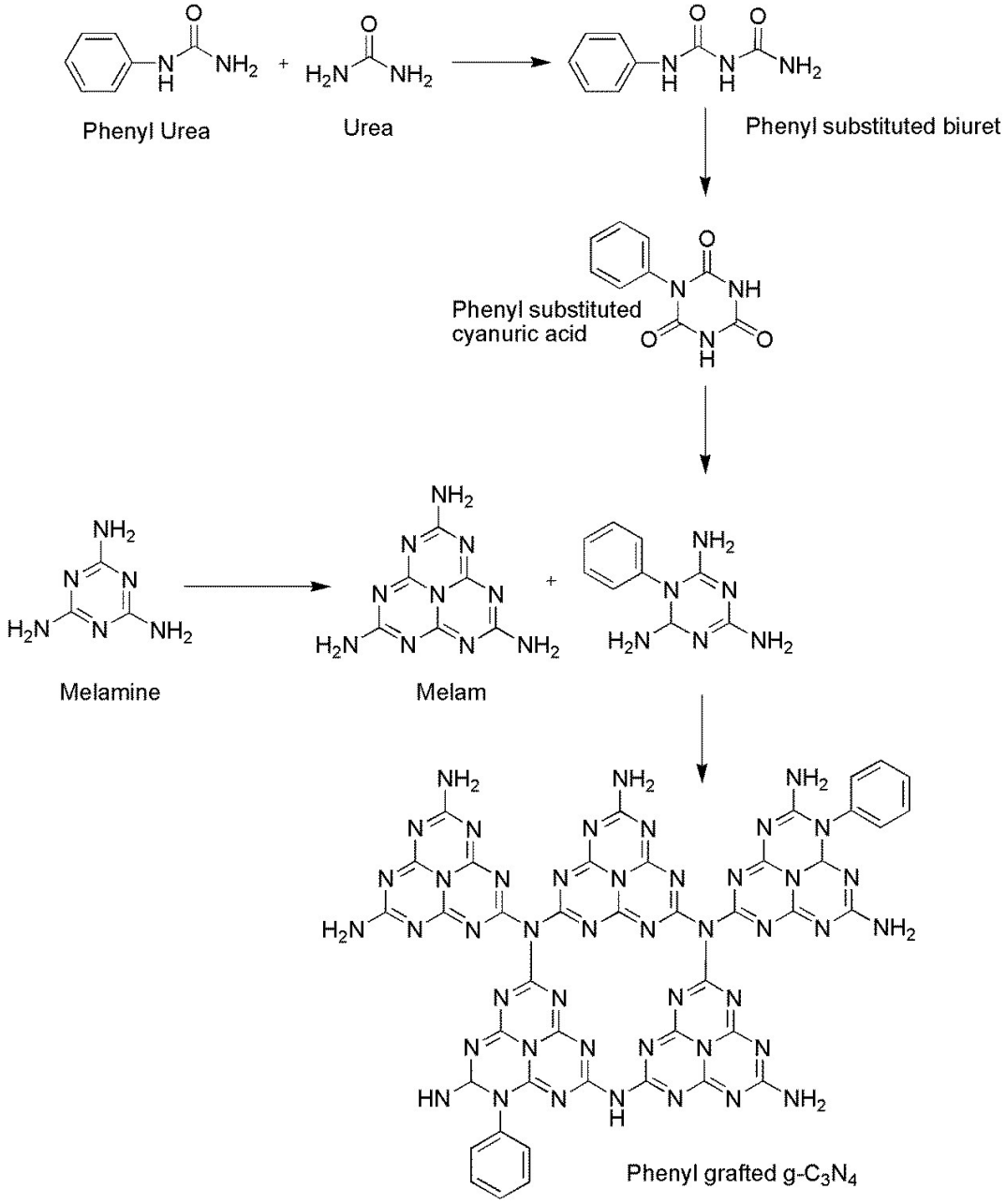

Figure S2. A plausible mechanism for the formation of Ph-g-C_3N_4 network obtained by thermal copolymerisation of phenyl urea, melamine and urea.

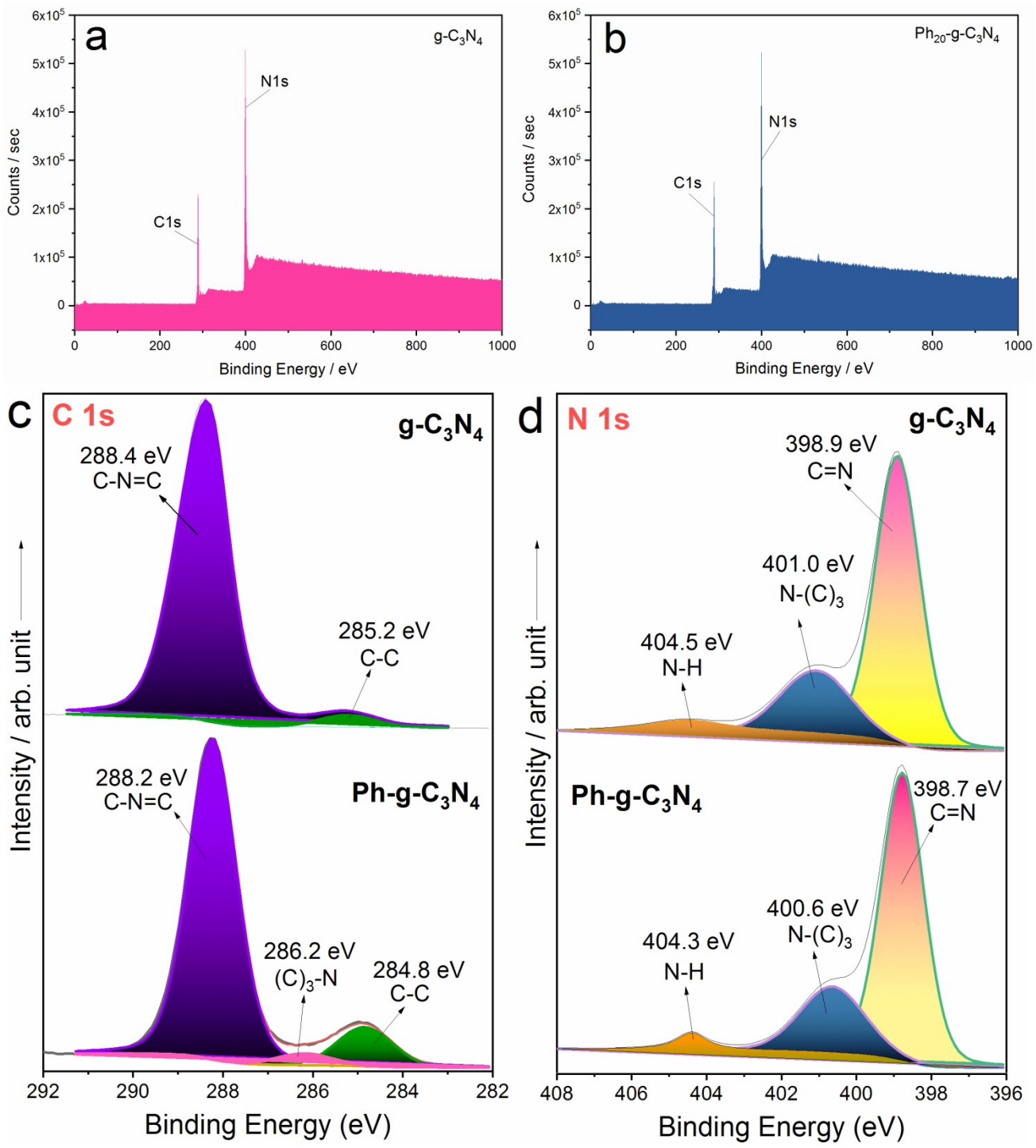

Figure S3. XPS survey spectra of (a) g-C_3N_4 (b) Ph-g-C_3N_4 and high-resolution XPS spectra of (c) C1s and (d) N1s of g-C_3N_4 and Ph_{20}-g-C_3N_4

Table S1. XPS peak parameters table.

Sample	Peak	Binding Energy	FWHM (eV)	Area (P) CPS. eV	Atomic (%)	C/N Ratio
g-C_3N_4	N 1s	399.23	2.62	1126736.26	54.81	**0.77**
	C 1s	288.33	1.44	**563747.81**	42.67	
Ph_{20}-g-C_3N_4	N 1s	399.15	2.62	1123842.10	52.7	**0.84**
	C 1s	288.21	2.32	**612206.66**	44.67	

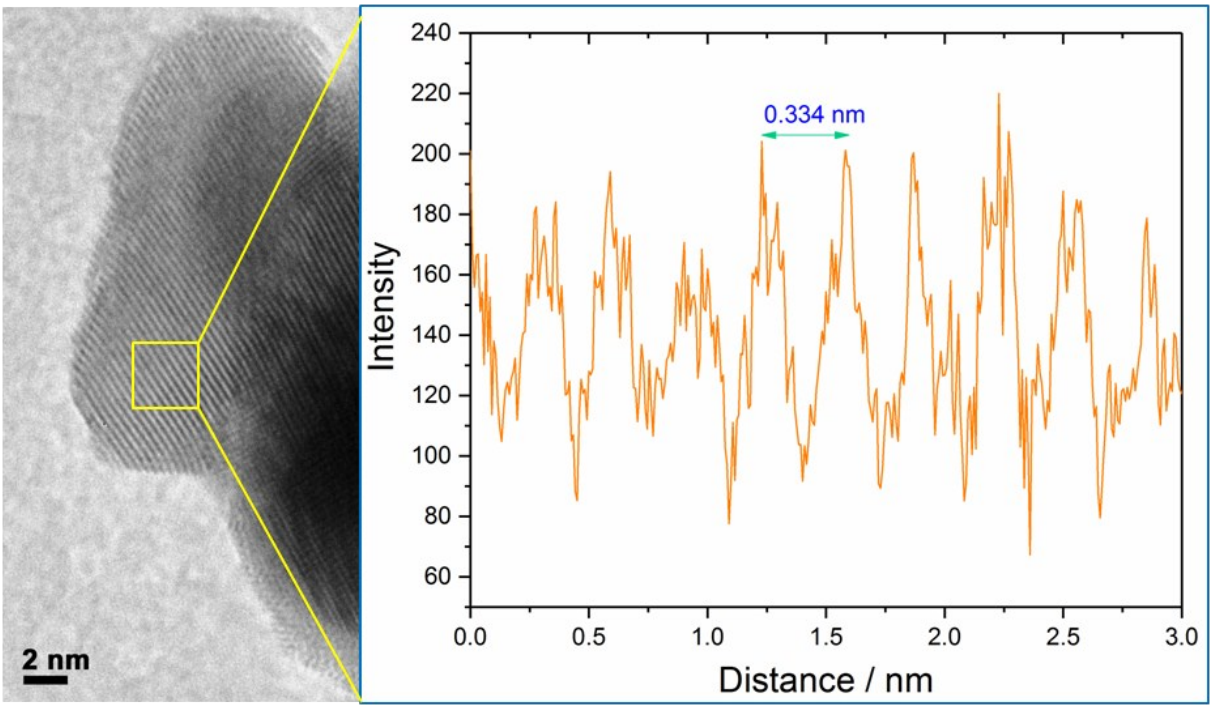

Figure S4. Plot profile graph of Ph_{20}-g-C_3N_4 HRTEM image selected portion obtained by ImageJ 1.50b software.

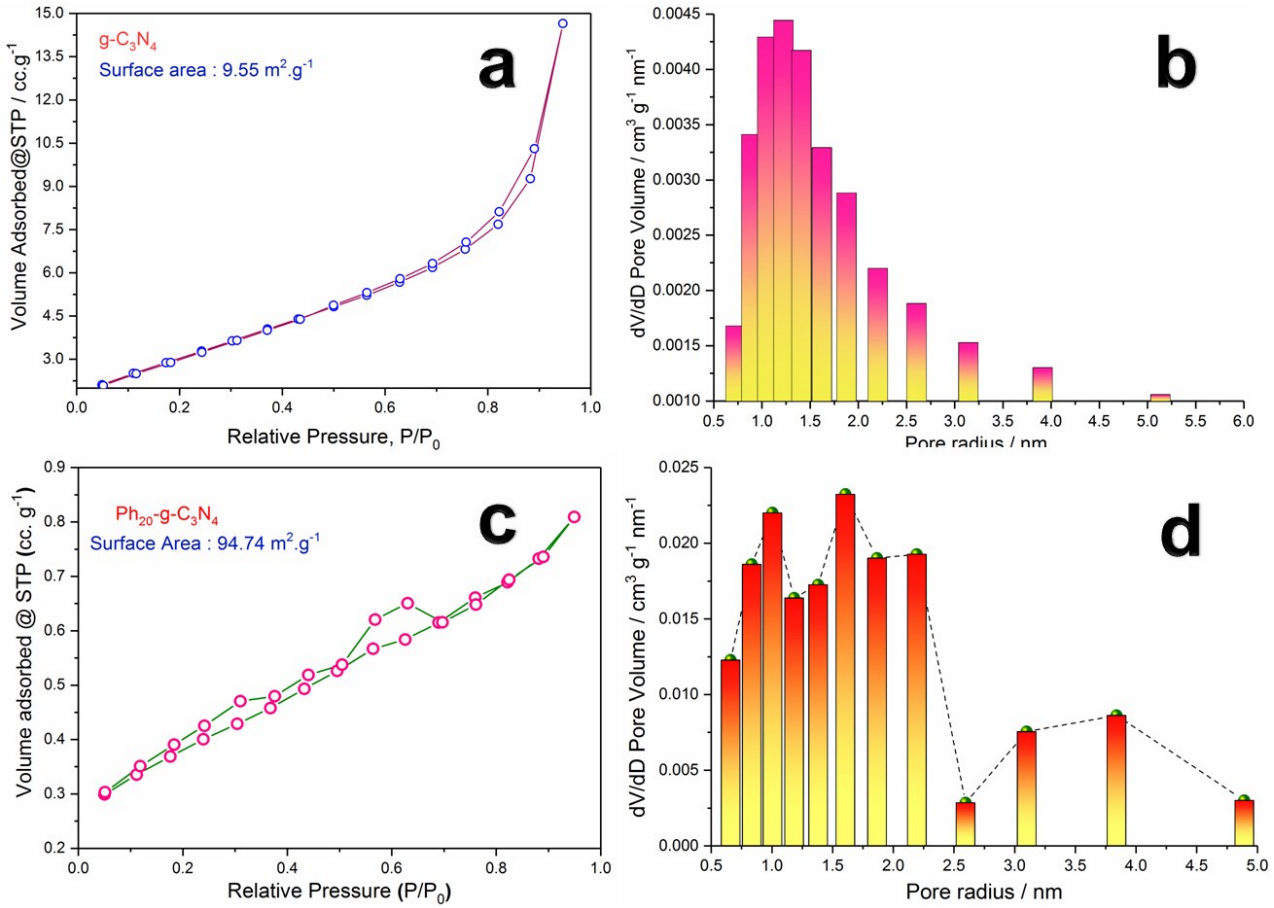

Figure S5. N_2 adsorption-desorption and pore-size distribution plots of (a, b) g-C_3N_4 and (c, d) Ph_{20}-g-C_3N_4, respectively.

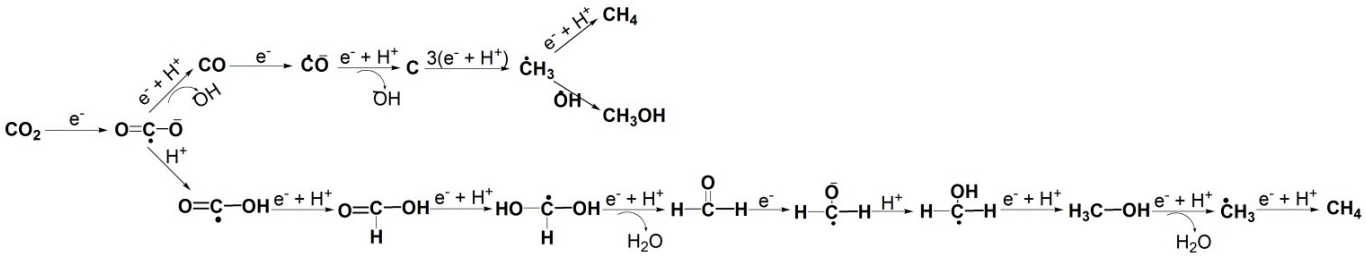

Figure S6. Plausible reactions pathway for CO_2 photoreduction into corresponding hydrocarbon products.

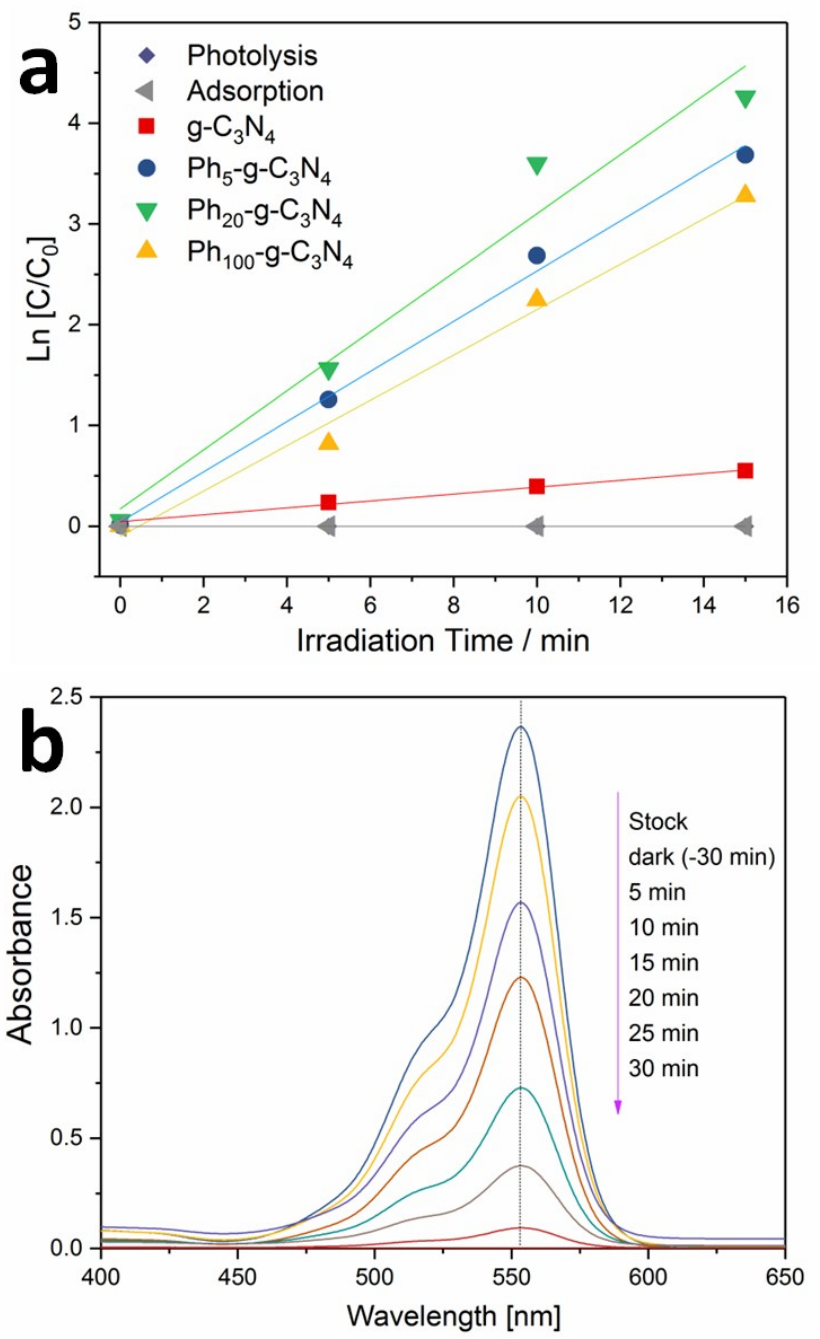

Figure S7. (a) Kinetic data of linear regression using various catalysts and (b) Temporal decay in UV-visible absorbance of RhB dye over Ph-g-C_3N_4 catalyst.

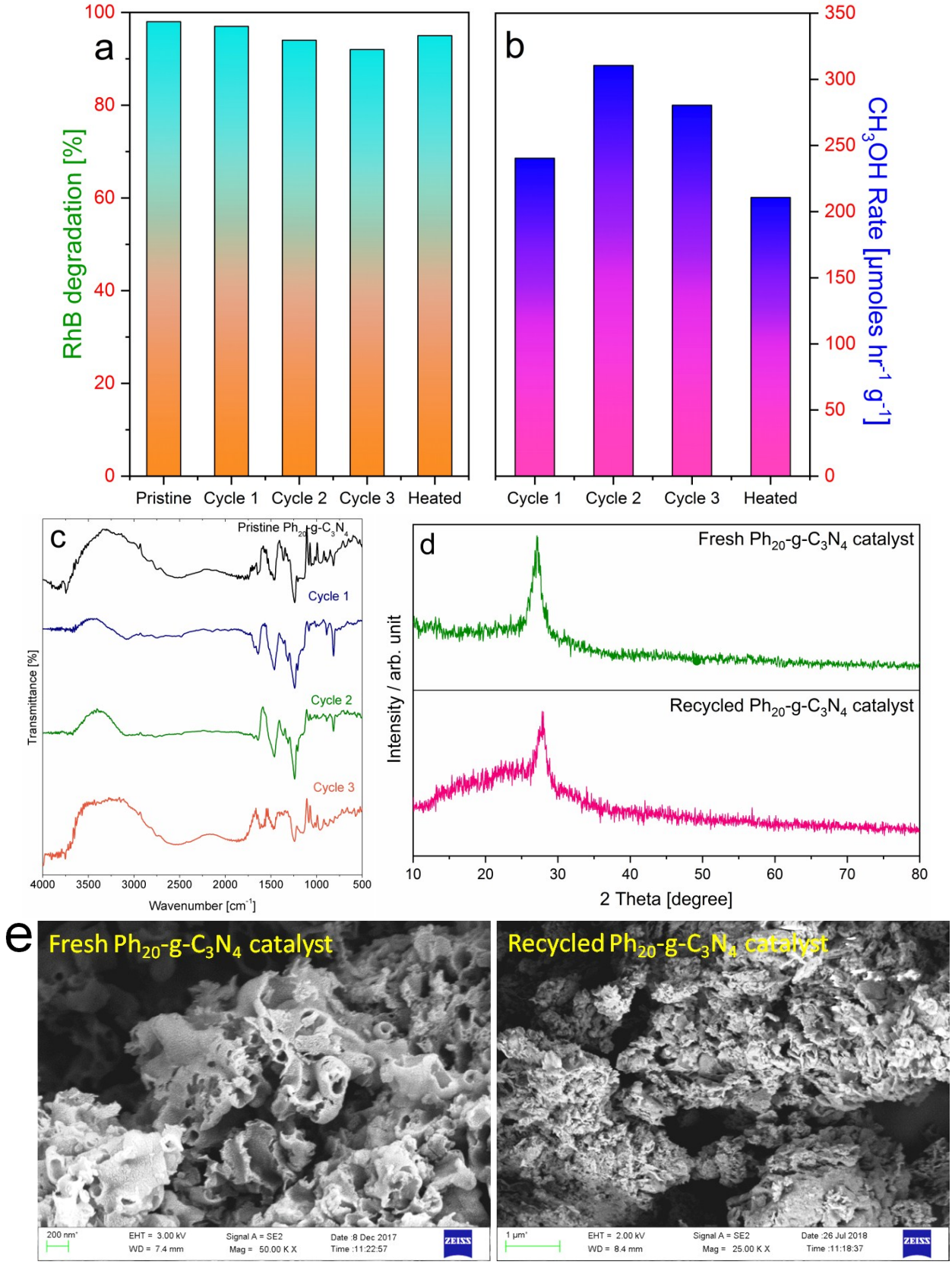

Figure S8. Recyclability test of (a) RhB degradation, (b) CH_3OH production using Ph_{20}-g-C_3N_4 catalyst, (c) FT-IR spectra of the corresponding catalyst after each cycle and (d, e) comparative XRD and SEM images of recycled catalyst after 3 cycles.

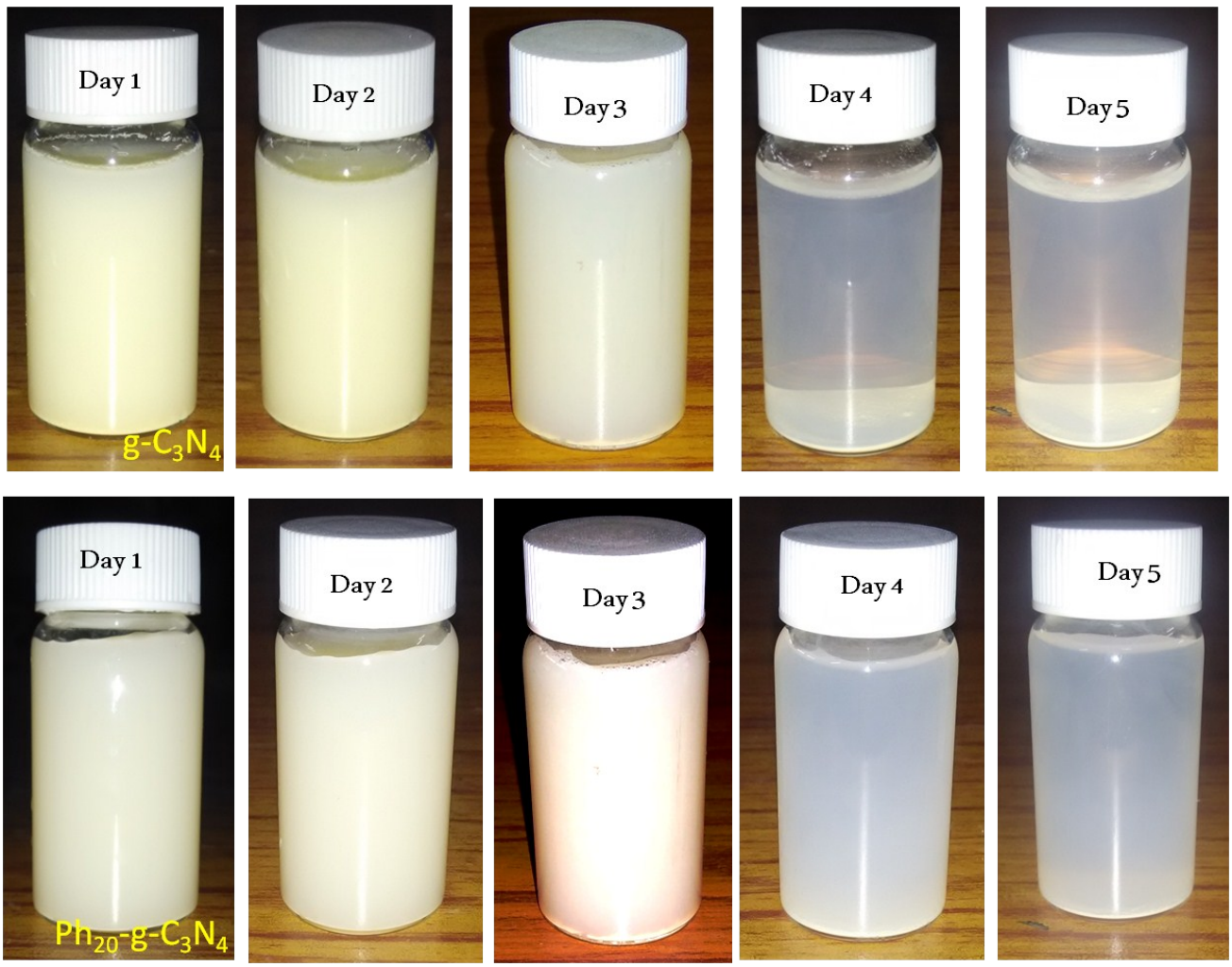

Figure S9. Dispersion properties of g-C_3N_4 (upper row) and Ph_{20}-g-C_3N_4 (second row) in water maintained at room temperature.

Table S2. Comparison of the Ph_x-g-C_3N_4 catalyst CO_2 photoreduction performance with reported photocatalysts.

Catalyst	Main Products	Amount of Products (μmoles g^{-1})	Ref
ZnO/g-C_3N_4	CO, CH_3OH, CH_4, and CH_3CH_2OH	CO : 38.7 μmoles g^{-1} CH_3OH : 19.0 μmoles g^{-1} CH_4 : 5.4 μmoles g^{-1} CH_3CH_2OH : 2.5 μmoles g^{-1}	1
In_2O_3 (10 wt%)–g-C_3N_4	CH_4	76.7 mg L^{-1}	2
30AgBr/pC_3N_4	CH_4	10.92 mol g^{-1}	3
SnO_2/B-P co-doped g-C_3N_4	CH_4	49 μmol g^{-1}	4
Ag_3PO_4/g-C_3N_4	CO, CH_3OH, CH_4, and CH_3CH_2OH	57.5 μmol h^{-1} g^{-1}	5
g-C_3N_4 nanosheets	CH_4 CH_3CHO	0.5 μmol 0.4 μmol	6
g-C_3N_4/$NaNbO_3$ nanowires	CH_4	6.4 μmol h^{-1} g^{-1}	7
Ph_x-g-C_3N_4	**CH_4 CH_3OH HCOOH**	**0.907 μmol 445.5 μmol h^{-1} g^{-1} 5.1 V/V%**	**This work**

Quantum Yield Calculation:

CO_2 photoreduction to methanol quantum efficiency was determined for the following possible reaction:

$$CO_2 + 6H^+ + 6^- \xrightarrow{h\upsilon} CH_3OH + H_2O$$

$$Quantum\ Yield\ (QY) = \frac{N_{MeOH}\ (6\ x\ Number\ of\ mole\ of\ MeOH\ per\ unit\ time)}{N_p(Number\ of\ incident\ photons\ per\ unit\ time)}$$

Here, '6' is the number of electrons required for CO_2 reduction into methanol (MeOH). The number of moles of MeOH per unit time was measured from obtained CH_3OH rate (445.5 μmol h^{-1} g^{-1})

N_{MeOH} = (6*CH_3OH rate in mole h^{-1} / 3600) / N_A

Where N_A is the Avagadro number (6.023 X 10^{23}).

N_{MeOH} = [(6*0.000445)/3600] / 6.023 X 10^{23}

= 4.467E+17

In the present CO_2 photoreduction experimental setup, the 20W LED bulb is located inside the reactor, therefore it is difficult to calculate the absorbed photons. It is further measured by the ratio of total energy reaching the reactor per second to the energy absorbed photons (E_λ).

$$Np = \text{Bulb Wattage} \div E_\lambda\ (hC/\lambda_{max})$$

Where, Bulb wattage= 20W = 20 Joule/ Second; h is the Plank's constant (6.626 X 10^{-34}Js); C is the velocity of light (3 x 10^8 m/s); λ_{max} is the wavelength of absorbed photons, it is obtained from average value of absorption band edge for Ph_{20}-g-C_3N_4.

$$Np = [20 \div (6.626 * 10^{-34} \text{ X } 3 \times 10^8)/ 461]$$

$$= 4.64E+19$$

$$QY\ (\%) = (N_{MeOH} / Np)*100$$

$$= 0.96\ \%$$

References

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