Supplementary Electronic information

Photo Upscaling of Formic Acid to H_2 and C(sp^2)-N Cross-Coupling via K^+ Intercalated Carbon Nitride: A New Sustainable Horizon Towards Fuel and High-end Pharmaceutics

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1. Experimental Section

1.1. Materials

Melamine and $H_2PtCl_6.6H_2O$ were purchased from Sigma-Aldrich. Potassium chloride (KCl), Formic acid (FA) and 1,2-Phenylenediamine were purchased from TCI. Methanol (MeOH) was purchased from Sigma-Aldrich.

1.2. Synthesis of potassium intercalated polymeric CN (KPCN): 10 g of melamine was mixed with certain amount of Potassium chloride and mechanically grinded using mortar pestle. Then, the mixture was well dispersed in 40 mL DI water under constant stirring. Further, it was heated to dryness to obtain white powder. After that, it was calcined at 550 °C for 3 h at a ramp rate of 5 °C/min. Further, the sample was powdered and again heated at 500 °C for 1 h to exfoliate the bare KPCN samples. The formed yellow coloured product was further washed with DI water and ethanol, centrifuged and dried at 80 °C overnight to obtain K^+ intercalated polymeric CN (KPCN). Different amount of potassium loaded KPCN samples (0.5KPCN, 1KPCN, 2KPCN, 5KPCN and 7KPCN) were synthesized by varying the KCl amount (0.5 g, 1 g, 2 g, 5 g, 7 g), respectively. For comparison, pristine CN was prepared according to the aforementioned procedure, by calcination at 550 °C for 3 h at a ramp rate of 5 °C/min and exfoliating at 500 °C for 1 h.

1.3. Synthesis of Pt/KPCN: Platinum (Pt) co-catalyst was deposited over the surface of KPCN using photo-deposition method. Firstly, certain amount of KPCN was dispersed in 42 mL of DI water in a 100 mL round bottom flask. Afterwards, 18 mL MeOH was added as sacrificial agent in 3:7 ratio with DI water. Pt loading was carried out by the addition of appropriate amount of $H_2PtCl_6.6H_2O$. Then, the reaction mixture was ultra-sonicated for 30 min

for uniform dispersion. Henceforth, the resulting solution was sealed and purged with Argon gas for 30 min under continuous stirring to create inert conditions. The sealed reaction setup was illuminated under 1.5 AM solar simulator with 100 mW cm^{-2} intensity for 3 h. The colour of the reaction mixture changed to grey confirming the deposition of Pt over KPCN. Afterwards, the photodeposited Pt/KPCN were recovered by centrifugation, washed with DI water and ethanol and eventually dried at 80 °C. Likewise, different K^+ loaded Pt/0.5KPCN, Pt/1KPCN, Pt/2KPCN, Pt/5KPCN and Pt/7KPCN were prepared. For comparison, Pt/CN was also prepared according to the aforementioned procedure.

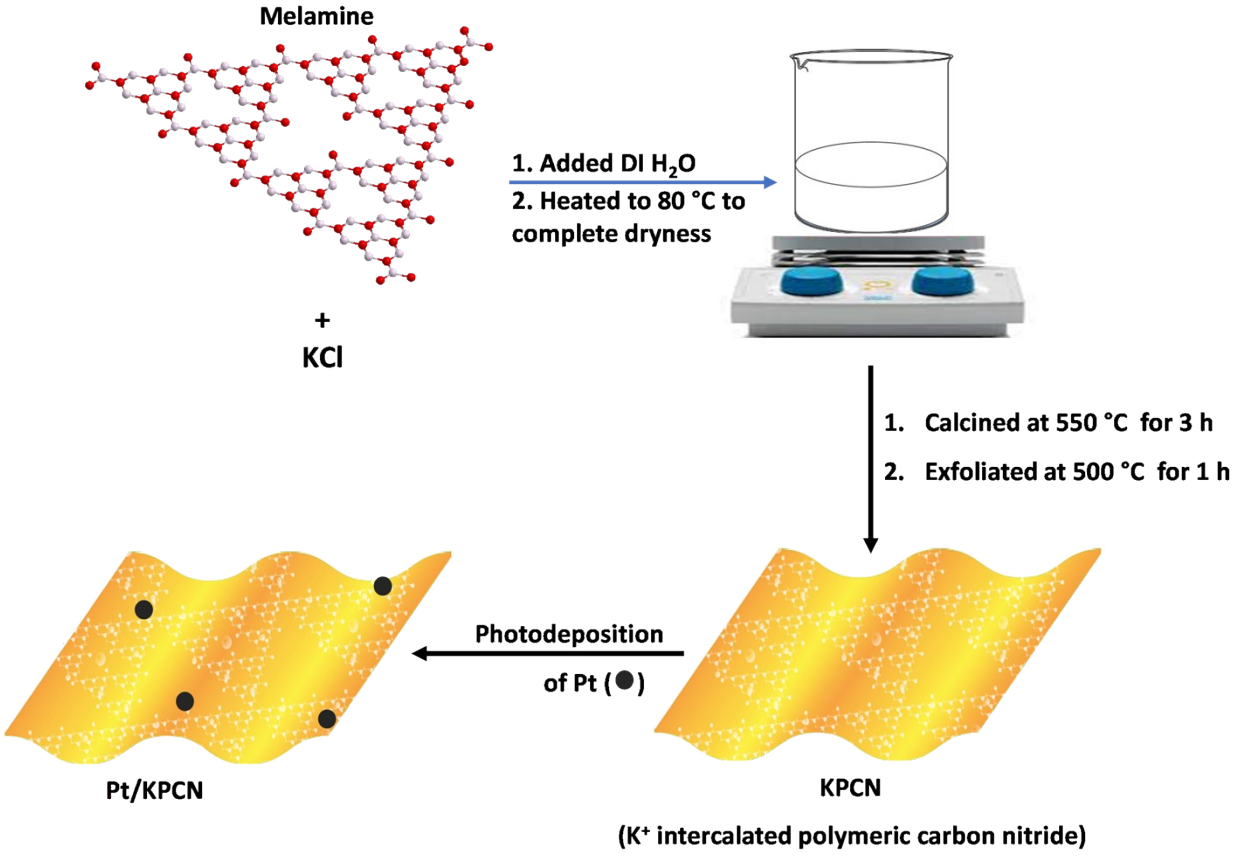


Figure S1 Schematic illustration of the Pt/KPCN synthesis.

1.4. Analytical Techniques

The crystal structures of the samples were analyzed by powder X-Ray diffraction (PXRD) technique using Bruker D8 Advance diffractometer aligned with scintillation counter detector with radiation source of Cu Kα (λ = 0.15418 nm, operating at 40 mV and 40 mA). Diffuse reflectance UV-Vis (DR UV-Vis) spectra of solid powdered samples were recorded on Agilent Cary 100 UV-Vis spectrophotometer. Al Kα Photoelectron Spectrometer (UK) provided

by Thermo Fischer Scientific was employed to carry out X-ray photoelectron spectroscopy (XPS) analysis to determine the elemental composition and oxidation states of constituent elements of the samples. Transmission spectra of solid samples were measured using FTIR Bruker Vertex 70 spectrometer. The morphology of the samples was investigated by Field emission scanning electron microscopy (FESEM) operated on JEOL JSM-7610F Plus and high-resolution TEM (HRTEM) operated on JEOL with 200 kV acceleration voltage. The photoluminescence (PL) spectra and Time resolved PL (TRPL) spectra were measured on Horiba Fluorolog 3-221 Fluorimeter. Electrochemical investigations were carried out on Metrohm Autolab workstation. The standard three electrode cell setup with Ag/AgCl as reference, Pt wire as counter and glassy carbon coated with sample as working electrode was employed with 0.1 M Na_2SO_4 as electrolyte solution for electrochemical experiments. Along with this, photoelectrochemical experiments were carried out under 400 W Xe lamp (Newport). BELCAT II from MicrotracBEL Corp was employed to carry out CO_2-Temperature Programmed Desorption (CO_2-TPD) measurements. Electron paramagnetic resonance (EPR) measurements were recorded on Bruker A300-9.5/12/S/W at room temperature. After the photocatalytic experiments, the gaseous products (H_2 and CO) were quantified by Shimadzu Gas Chromatography (GC) and estimation of liquid products were done by Shimadzu QP2020 Gas Chromatography-Mass Spectrometer (GC-MS).

1.5. Photocatalytic Activity Measurements

Photo-redox activity of Pt/KPCN for cross coupling of FA with PDA was performed in a 10 mL round bottom (RB) flask under solar simulator with Air Mass 1.5G filter (100 mW cm^{-2}). In the reaction setup, certain amount of catalyst was dispersed in 3 mL DI H_2O in the RB. Then, 0.1 mmol PDA and 100 µL FA was added to the reaction mixture. Afterwards the RB flask was sealed and purged with Ar gas for 20 min to maintain the inert atmosphere and to remove the dissolved oxygen gas. The sealed reaction setup was kept under solar simulator with 100 mW cm^{-2} intensity. After different time intervals, at first, possible gaseous product (H_2 and CO) were quantified by Shimadzu GC. Afterwards, the liquid mixture was separated from the catalyst by centrifugation and scrutinized the by GC-MS. Moreover, the catalyst obtained after centrifugation was washed multiple times with DI H_2O, followed by ethanol, dried in oven at 80 °C overnight and further used for recycling experiments.

1.6. Apparent Quantum Yield Calculations:

(i) The number ($N_{photons}$) of absorbed photons:

$$N_{photon} = \frac{t(s) * P\ (W\ cm^{-2}) * \lambda(m) * S(cm^2)}{h(J-s) * c\ (m\ s^{-1})}$$

Where, time (*t,* 43200 *s*), intensity (*P,* 0.00117 $W\ cm^{-2}$), wavelength (λ, 450 * 10^{-9} *m*), irradiation area (*S,* 11.45 cm^2), Planck's constant (*h*, 6.62 * 10^{-34} *J-s*), and light velocity (*c*, 3 * 10^8 ms^{-1})

(ii) The AQY is obtained by following equation:

$$AQY = \frac{2 * nH_2\ (mol) * N_A\ (mol^{-1})}{N_{photon}} * 100$$

Where, yield of H_2 (1.77* 10^{-6} *mol*) and Avogadro number (N_A, 6.02 * 10^{23} mol^{-1})

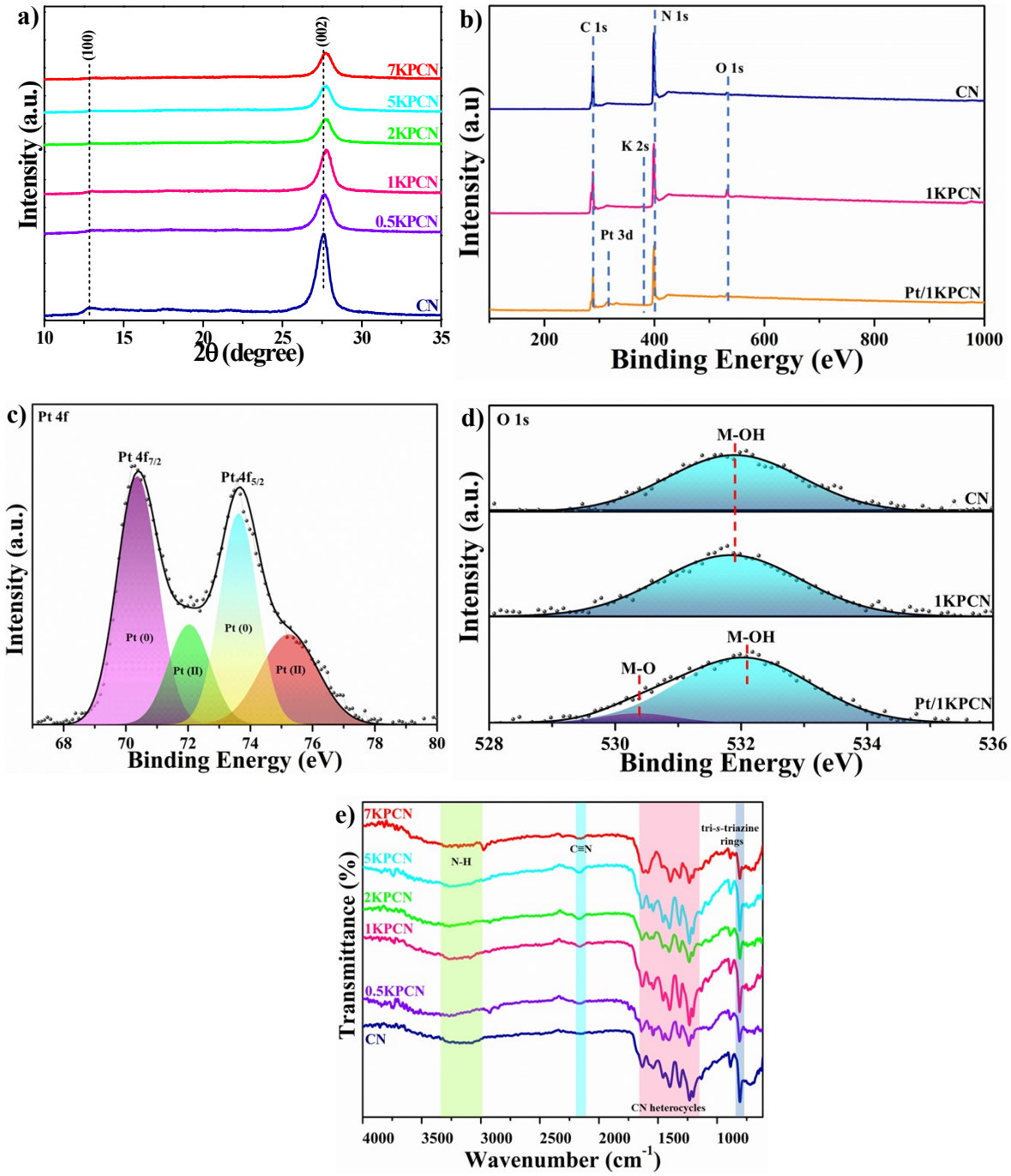


Figure S2 a) PXRD pattern of KPCN samples; b) XPS survey spectrum of CN, 1KPCN, and Pt/1KPCN; XPS spectra of c) Pt 4f, and d) O 1s of Pt/1KPCN; and e) FTIR spectra of all KPCN samples.

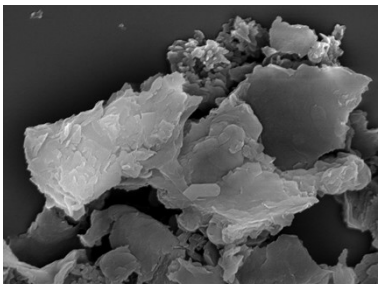
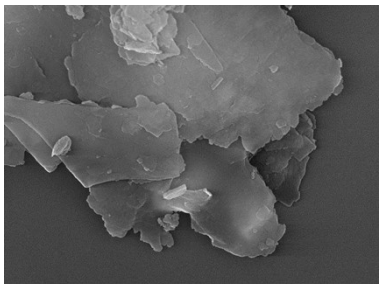
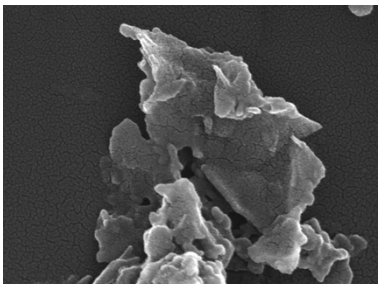
a)  b)  c) 

Figure S3 FESEM images of a) CN, b) 1KPCN, and c) Pt/1KPCN.

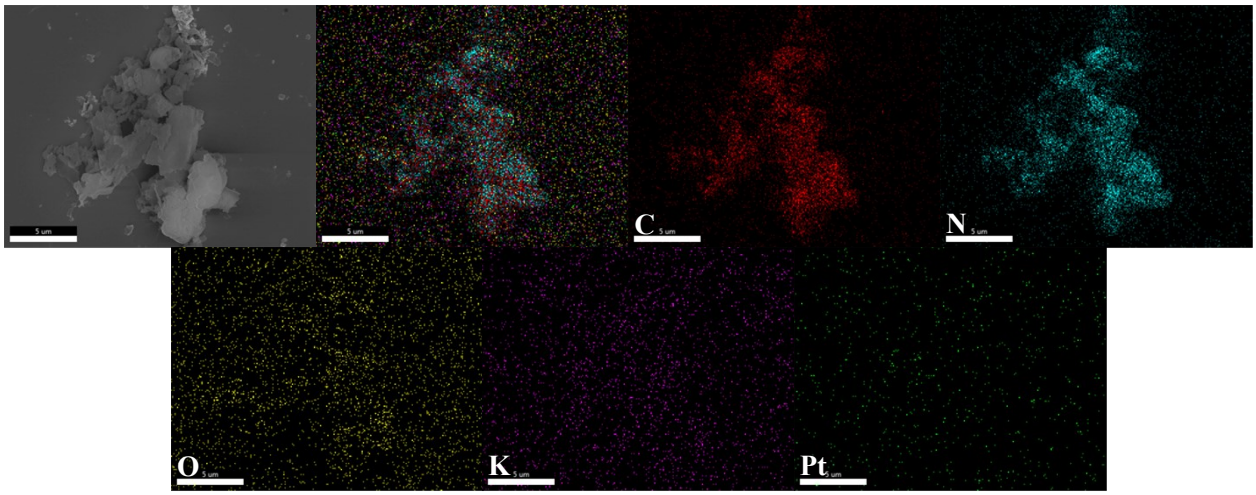


Figure S4 FESEM elemental mapping of Pt/1KPCN.

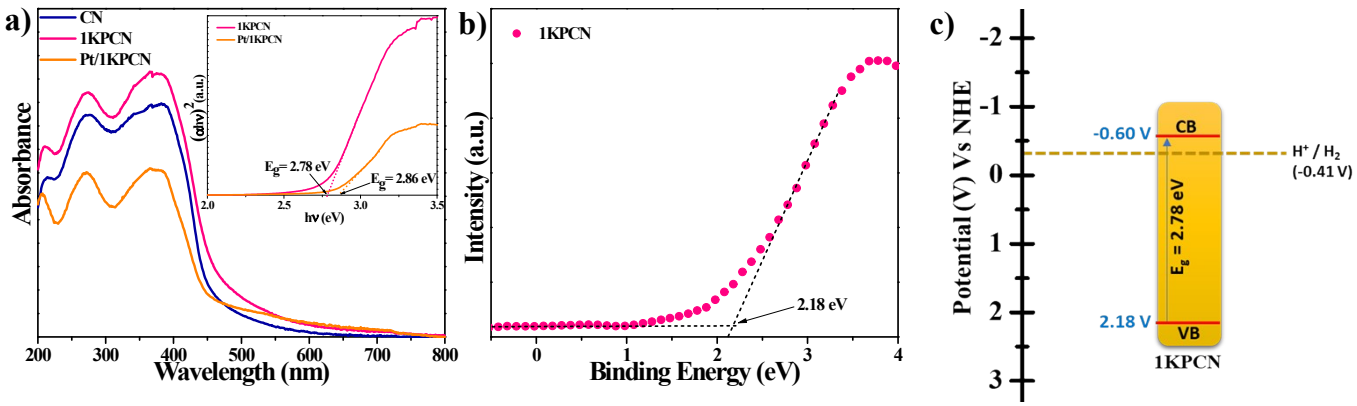


Figure S5 a) UV-Vis DRS spectra of CN, 1KPCN, and Pt/1KPCN, b) Valence band XPS of 1KPCN, and c) Band energy diagram of 1KPCN.

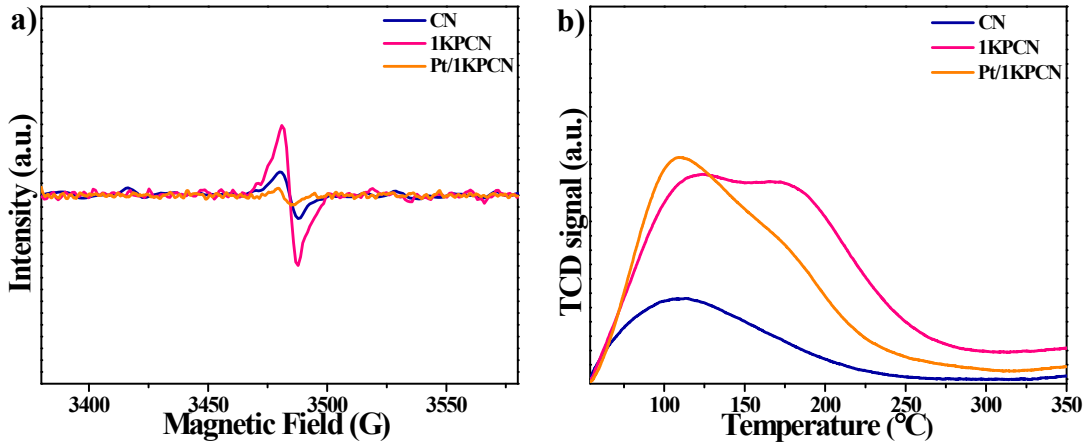


Figure S6 a) EPR spectra, and b) CO_2 TPD profile of CN, 1KPCN and Pt/1KPCN.

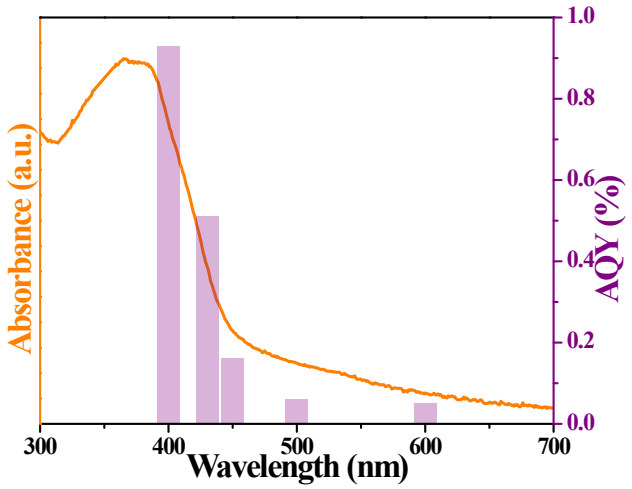


Figure S7 AQY action spectrum of H_2 production for Pt/1KPCN. Reaction conditions: Photocatalyst - 10 mg; H_2O - 3 mL; Ar atmosphere; Reaction time – 12 h; Room temperature; and Oriel Solar Simulator - 100 mW cm^{-2}.

Table S1 Scavenger study.

S. No.	Scavenger	Light	Hydrogen production rate ($\mu mol.h^{-1}.g^{-1}$)	PDA conversion (%)	BA selectivity (%)
1	FA	✓	94	50	>99
2[a]	FA	X	-	-	-
3[b]	FA	✓	-	-	-
4[c]	-	✓	-	-	-
5	$Na_2S_2O_8$	✓	3	98	>99
6	KI	✓	30	26	>99
7	CO_2, H_2	✓	-	-	-
8	CO_2, 0.1 mM HCl solution	✓	-	-	-

Reaction conditions: Photocatalyst - 10 mg; Reaction time - 12 h; H_2O - 3 mL; Ar atmosphere; Room temperature; and Oriel Solar Simulator - 100 mW cm^{-2}. [a]Without light. [b]Without catalyst. [c]Without FA.

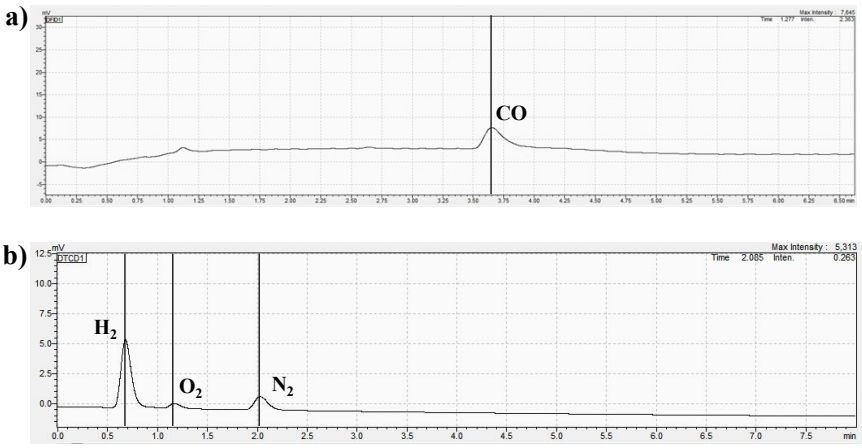


Figure S8 a) Snapshot of GC spectra for CO formation, and b) Snapshot of GC spectra for H_2 for Pt/1KPCN.
Reaction conditions: Photocatalyst - 30 mg; Reaction time - 12 h; H_2O - 3 mL; Ar atmosphere; Room temperature; and Oriel Solar Simulator - 100 mW cm^{-2}.

Note: O_2 and N_2 are observed due to the air from atmosphere during sample collection.

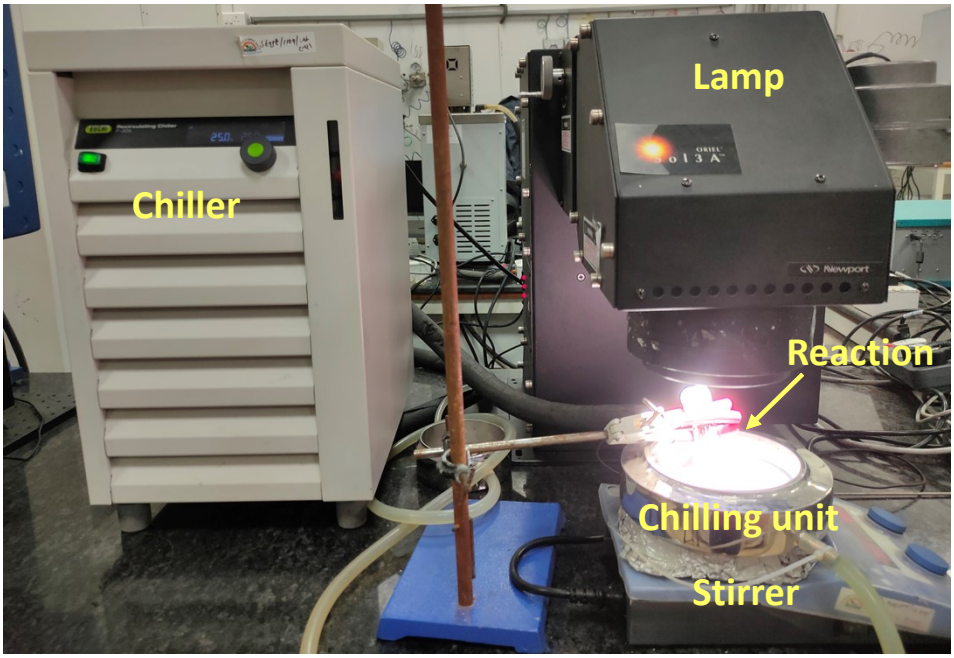


Figure S9 Snapshot of reaction setup for photocatalytic reaction.