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# **Supporting Information**

# Selective Photocatalytic CO<sub>2</sub> Reduction to CH<sub>4</sub> over Metal Free Porous Polyimide in Solid-Gas Mode

Subhash Chandra Shit,<sup>abc</sup> Niket S. Powar,<sup>a</sup> Priyanka Kalita,<sup>b</sup>Ratul Paul,<sup>bc</sup> Shaojun Xu,<sup>d</sup> Jin-Woo Jung,<sup>e</sup> Chang-Hee Cho,<sup>e</sup> Su-II In<sup>\*a</sup> and John Mondal<sup>\*bc</sup>

<sup>a</sup> Department of Energy Science and Engineering, Daegu Gyeongbuk Institute of Science and Technology (DGIST), 333 Techno Jungang-daero, Hyeonpung-eup, Dalseong-gun, Daegu 42988, Republic of Korea. E-mail: insuil@dgist.ac.kr; faraday.in@gmail.com

<sup>b</sup> Catalysis & Fine Chemicals Division, CSIR-Indian Institute of Chemical Technology, Uppal Road, Hyderabad 500 007, India. E-mail: johnmondal@iict.res.in; johncuchem@gmail.com

<sup>c</sup>Academy of Scientific and Innovative Research (AcSIR), Ghaziabad-201002, India

<sup>d</sup> UK Catalysis Hub, Research Complex at Harwell, Didcot, OX11 0FA, UK

<sup>e</sup>Department of Physics and Chemistry, DGIST, 333 Techno Jungang daero, Hyeonpung-eup, Dalseong-gun, Daegu 42988, Republic of Korea

#### 1. Synthesis of Catalysts:

# 1.1. Materials:

Perylene dianhydride, 4,4',4"-(1,3,5-Triazine-2,4,6-triyl) trianiline, melamine and imidazole were obtained from Sigma-Aldrich. Dimethylacetamide, Dimethylformamide (DMF) solvents were purchased from Merck, India. Methanol was received from Spectrochem, India. All the chemicals were used as received without any further purification. Double distilled deionized water was used throughout the experiment.

#### **1.2. Synthesis of Porous Polyimide (PeTt-POP):**

For the synthesis of **PeTt-POP**, perylene dianhydride (**Pe**) (0.362 mmol, 142 mg) was taken in 40 g imidazole and heated at 150 °C under N<sub>2</sub> atmosphere until it dissolves and after that 4,4',4"- (1,3,5-Triazine-2,4,6-triyl) trianiline (**Tt**) (0.241 mmol, 85 mg) in 5 mL dimethylacetamide was mixed with the previous solution. The resultant mixture was stirred at 180 °C for 24 h under an inert atmosphere to which methanol was added after cooling the reaction mixture to 100 °C. The as-obtained purple precipitate was filtered, washed with methanol and DMF and finally collected after drying the sample at 100 °C under a vacuum for overnight.

# **1.3.** Synthesis of g-C<sub>3</sub>N<sub>4</sub>:

g-C<sub>3</sub>N<sub>4</sub> was synthesized by heating melamine in a muffle furnace at 520  $^{\circ}$ C for 4h with a heating rate of 10  $^{\circ}$ C/min.

#### 2. Characterization Techniques:

Powder X-ray diffraction (XRD) patterns of the catalysts were performed on a Rigaku Miniflex (Rigaku Corporation, Japan) X-ray diffractometer using Ni filtered Cu K $\alpha$  radiation ( $\lambda = 1.5406$  Å) with a scan speed of 2° min<sup>-1</sup> and a scan range of 10-80° at 30 kV and 15 mA.

The morphology of the catalysts was obtained by scanning electron microscopy (SEM). The SEM equipment was a FEI Verios 460L field-emission SEM (FESEM) which is an ultrahigh resolution Schottky emitter SEM equipped with an electron diffraction spectroscopy (EDS) detector. Thus, the elemental mapping EDS analysis were also performed in the same SEM instrument. Transmission electron microscopy (TEM) images of the catalysts were captured at 100 kV on a JEOL 1010 TEM.

The surface area was determined through the Brunauer-Emmett-Teller (BET) method. The average pore volume and pore size were measured by the nonlinear density functional theory (NLDFT) method. The BET surface area, pore volume, and pore sizes were determined by using the  $N_2$  adsorption-desorption method using BEL Sorb II Instruments, Japan, at liquid nitrogen temperature. Before the measurement, the samples were degassed at 200 °C for 2 h.

X-ray photoelectron spectroscopy (XPS) was investigated on a Thermo Scientific K $\alpha$  instrument (monochromatic Al K $\alpha$  radiation,  $E_{photon} = 1486.6 \text{ eV}$ ). The binding energy (B.E) in each case (i.e., core levels and valence band maxima) were corrected using an internal reference peak of C 1 s peak centered at 284.8 eV.

FTIR spectrums of catalysts were investigated on a DIGILAB (USA) IR spectrometer using the KBr disc method.

Solid-state <sup>13</sup>C CP MAS NMR studies were performed using a Bruker Avance III HD 400 MHz NMR spectrometer.

Electrochemical analysis was measured using a BioLogic science instrument potentiostat (EC lab software).

CO<sub>2</sub>-TPD analysis was carried out using AutoChem 2950 HP chemisorption analyzer (micromeritics).

BET analysis for CO<sub>2</sub> uptake isotherm was analyzed using a BELSORP analyzer (MicrotracBel Corp.).

Photoluminescence (PL) for TPA-DPA was recorded using the FluroMaX-4 series, Horiba ( $\lambda_{\text{excitation}}$  = 350 nm). TRPL was measured using a PicoQuant, LDH-PFA- 355 at room temperature.

### 3. Photocatalytic CO<sub>2</sub> Reduction Experiment:

In a stainless-steel batch reactor with volume of 15.4 cm<sup>3</sup> and quartz window, photocatalytic gas phase CO<sub>2</sub> reduction was carried out to which 30 mg catalyst was taken and 1000 ppm of CO<sub>2</sub> in He was purged into the reactor via a water bubbler to form a combination of CO<sub>2</sub> and water vapor. The reactor was first charged with CO<sub>2</sub>/H<sub>2</sub>O followed by the elimination of gaseous contaminants using a vacuum. This process was repeated five times before the reactor was once again filled with CO<sub>2</sub> and H<sub>2</sub>O. A solar simulator with a xenon lamp of 100 W and an AM 1.5G filter was used to illuminate the reactor and 500  $\mu$ L gas phase product was injected into the GC instrument fitted with a flame ionization detector. To evaluate the carbon-contaminated products, we used He gas with H<sub>2</sub>O vapor rather than using CO<sub>2</sub>.

#### 4. Operando DRIFTS Measurement:

The operando DRIFTS experiment was carried out using an Agilent Carey 680 FTIR Spectrometer equipped with a Harrick DRIFTS cell. The spectra were recorded at 4 cm<sup>-1</sup> resolution and each spectrum was averaged 64 times. Each sample was pre-treated at 100 °C using 99.999% argon (Ar, BOC gas Ltd.) at a gas flow rate of 50 ml min<sup>-1</sup> for 1h in order to remove adsorbed water and other gas molecules. Then the temperature of the sample was reduced to 30 °C and gas switched to  $CO_2/H_2O$  gas mixture. The water was introduced into a  $CO_2$  using a water bubbler at 30 °C and 50 ml min<sup>-1</sup> of  $CO_2$  flow. After  $CO_2/H_2O$  adsorption has fully saturated over the sample. The sample was purged using a 50 ml min<sup>-1</sup> of Ar to remove the gas phase  $CO_2$  and  $H_2O$  in the DRIFTS cell. Then a complete Xe arc lamp (LOT-Oriel GmbH & Co. KG, LSE140/160.2C model, 25 kV) was used for the photoreaction. Figures:



Fig. S1: FT-IR spectrum of PeTt-POP, triazine and perylene dianhydride monomers.



Fig. S2: Wide energy XP Survey spectrum of PeTt-POP sample



**Fig. S3:** FE-SEM image (a) and corresponding elemental mapping of all elements, C (green), O (yellow), N (red) (b, c, d & e), respectively

FE-SEM image exhibits microtubular bundle shape morphology with length of 1-4  $\mu$ m and the cotton type of morphology over the bundles (Fig. S3a, ESI†). TEM images confirmed the porous carbonaceous framework (Fig. S4d, e and f, ESI†), whereas the darker region might be appeared due to the presence of heteroatoms (N, O) on porous skeleton.



**Fig. S4:** (a)  $N_2$  adsorption/desorption isotherms at 77K with pore size distribution (inset); (b)  $CO_2$  adsorption isotherms analysis 298 K; (c) Wide angle Powder X-ray diffraction study; (d) & (e) TEM images; (f) HR-TEM image with SAED pattern (inset) analysis of **PeTt-POP** 



**Fig. S5:** Equivalent circuit for Nyquist plot to Electrochemical Impedance Spectroscopy (EIS) for **PeTt-POP** sample.

 $R_s$  is bulk resistance which primarily occurs in electrolytes and electrodes.  $R_{carbon}$  is the resistance and capacitance present at the interfacial layer in which the catalyst was deposited on the carbon paper.  $R_{PeTt-POP}$  is the charge transfer resistance which is measured between the working electrodes (catalyst) and counter electrode, which must be low. W accounts for diffusion effects, which are not relevant to our study.



**Fig. S6:** Cyclic voltammetry analysis at different scan rates from 10 to 100 mV/s using a 0.5 M Na<sub>2</sub>SO<sub>4</sub> electrolyte of the **PeTt-POP** sample.



Fig. S7: Current density and scan rate slope calculated the electrical double layer (Cdl) of PeTt-POP



Fig. S8: CO<sub>2</sub>-TPD analysis for PeTt-POP sample.

The CO<sub>2</sub>-TPD profile (Fig. S8) showed significant peaks in three different temperature regions (80  $^{\circ}$ C to 140  $^{\circ}$ C; 150  $^{\circ}$ C to 340  $^{\circ}$ C and 340  $^{\circ}$ C to 420  $^{\circ}$ C) implying three types of basic sites which might be related to the desorption resulting from the chemical adsorption of CO<sub>2</sub> and various type of carbonate species



Fig. S9: Reusability study upto  $5^{th}$  cycle where each cycle was done over 6h under photo illumination.

To examine the stability of **PeTt-POP**, we performed five catalytic cycles where each cycle duration was 6h (**Fig. S9, ESI**). After each cycle, the light irradiation was stopped, the reactor was

evacuated and refilled with CO<sub>2</sub>, and the catalyst was activated at 100 °C for 4 h under vacuum. But the involvements of surface adsorbed reactants, intermediates and its transformation to products could be identified as well as differentiated from catalysts by *in situ* operando vibrational spectroscopy. We have clearly identified the surface adsorbed species reactants CO<sub>2</sub>, H<sub>2</sub>O and hydrocarbon intermediates under various reaction conditions including different time intervals. Also, we have performed PXRD measurements of The **PeTt-POP** before and after experiments (**Fig. S10, SI**) where the peak intensity was increased after photocatalysis. This could be due to the accumulation of surface intermediates and undefined carbon congregation on the **PeTt-POP** surface.



Fig. S10: PXRD pattern of fresh and reused (after 30 h) catalysts PeTt-POP.

We have carried out C, H & N elemental analysis of the fresh and reused catalyst (after 5<sup>th</sup> catalytic cycle). The fresh **PeTt-POP** revealed the existence of 83.55 % C, 4.1 % H & 12.35 % of N in the polymer framework. In contrast, the reused photocatalyst demonstrated a higher amount of C (86.21 %) and consequently lower H (3.8 %) & N (9.99 %) content in the polymeric framework. The enhanced C content in the reused catalyst main because of the deposition of various reaction intermediated in the porous channels formed during the photocatalysis. The adsorption of  $CO_2$  gases and reaction intermediated led to the blockage of pores and resulted in lowering the photoactivity of the **PeTt-POP** compared to the fresh catalyst. This has been clearly demonstrated in the reusability experiment showed in **Fig S9, ESI**.



Fig. S11: (a & b) Plausible mechanistic pathway involved for the photoreduction of  $CO_2$  to  $CH_4$ .



g. S12: Actual photographs of reactor with solar simulator.



#### Fig. S13: EPR spectra of PeTt-POP.

we have performed Electron Paramagnetic Resonance (EPR) characterization of the **PeTt-POP** to study the catalytic mechanism which is shown in **Fig. S13**. As per EPR spectra, the **PeTt-POP** has only one strong single Lorentzian signal (g = 2.003), which is originated from the unpaired electrons on the carbon atoms of the conjugated aromatic rings. The strong signal suggests about better exciton dissociation that might be ascribed to the donor-acceptor moiety in the **PeTt-POP** promoting  $\pi$ -electron delocalization in the conjugated structure.<sup>1</sup> Also, from time-resolved photoluminescence (TRPL) spectroscopy study (**Fig. 2d**) we have found approximately 0.253 ns average lifetime for charge recombination. Both EPR and TRPL study clearly indicates that upon light irradiation on the **PeTt-POP** efficient number of free charge carriers (electron-hole pairs) can be created. With the help of the holes, H<sup>+</sup> is produced using water. In the meantime, the photo-generated electrons are taking part in a number of multi-electron process to produce methane.

On the other hand, in operando DRIFT spectra (Fig. 4a) a broadband was observed at  $3440 \text{ cm}^{-1}$ , which is attributed to the OH stretching of adsorbed H<sub>2</sub>O on the **PeTt-POP** surface. Also, another broadband in the range of  $3750-3550 \text{ cm}^{-1}$  was observed which indicate the presence of gas and adsorbed CO<sub>2</sub> molecules.<sup>2,3</sup> After light irradiation for a time duration of 40 minutes (Fig. 4b) these peaks intensities were decreased. Therefore, it can be said that the photogenerated holes react with the adsorbed water molecules and generate H<sup>+</sup> ions. These H<sup>+</sup> ions and photogenerated electrons initiates reduction with the adsorbed CO<sub>2</sub> on **PeTt-POP** surface, leading to consecutive catalytic reactions. Also, the above-mentioned observations were in good agreement with the other reports.<sup>2, 4</sup>

# Tables:

**Table S1**: BET surface area, t-plot micro- and mesopore area, micro- and mesopore volume, total pore volume.

Sample name	BET Surface area (m <sup>2</sup> g <sup>-1</sup> )	Micropore Surface area (m <sup>2</sup> g <sup>-1</sup> )	Micropo re volume (cc g <sup>-1</sup> )	Mesopore + macropore Surface area (m <sup>2</sup> g <sup>-1</sup> )	Mesopore + macropore volume (cc g <sup>-1</sup> )	Pore volume (cc g <sup>-1</sup> )
PeTt- POP	259.2	0.0	0.0	259.2	0.44	0.44

From the pore size distribution analysis, we have seen the existence of mesopores of  $\sim$ 5nm, rather than the micropores, which was further established from the textural parameters. The overall surface area was found to be 259.2 m<sup>2</sup>g<sup>-1</sup>, which was completely contributed by the mesopores and no contribution from the micropores as evidenced from t-plot analysis. Similarly, the pore volume of 0.44 ccg<sup>-1</sup>, was completely contributed by the mesopores and not by the micropores.

 Table S2: Elemental analysis of PeTt-POP sample

Element	Line	Apparent	k Ratio	Wt%	Wt%	Atomic
	Туре	Concentration			Sigma	%
С	K series	0.46	0.00462	85.76	1.38	88.47
N	K series	0.02	0.00003	4.55	1.44	4.02
0	K series	0.04	0.00014	9.69	0.53	7.51
Total:				100.00		100.00

Table S3: Comparison with other metal free porous organic polymer-based materials for photocatalytic  $CO_2$  reduction

Metal free	Light	Sacrificial	Products	Reference
porous	source	donor and		
organic		other reaction		
polymer		medium		
CPs-BT	300 W Xe	TEOA and	CO (18.2 µmol h <sup>-1</sup> )	Chem. Eur. J.
	lamp (>420	Acetonitrile/H <sub>2</sub> O		2018,
	nm)	(4/1)		24,17454-
				17458
N <sub>3</sub> -COF	500 W Xe	$H_2O: 5 mL,$	CH <sub>3</sub> OH (13.7 $\mu$ mol/g in	Appl. Catal. B
	lamp	pressure:	24 h)	2018,
	(800 nm ≥	0.4 MPa,		239,46-51

		4		
	$\lambda \ge 420 \text{ nm}$ )	80 °C		
PEosinY-1	300 W Xe	H <sub>2</sub> O: 10 mL,	CO (33 µmol g <sup>-1</sup> h <sup>-1</sup> )	Angew. Chem.
	lamp (>420	pressure: 1 atm.	and $H_2$ (5 umol g <sup>-1</sup> h <sup>-1</sup> )	Int.
	nm	temperature:		Ed. 2019, 58.
	)	25 °C		632-636
OXD-TPA	300 W Xe	H <sub>2</sub> O vapor	CO $(37.15 \ \mu mol \ g^{-1} \ h^{-1})$	Green Chem.
	lamp (>420	-		2019, 21, 6606-
	nm)			6610
CT-COF	300 W Xe	$H_2O: 5 mL$ ,	CO (102.7 µmol g <sup>-1</sup> h <sup>-1</sup> )	ChemSusChem
	lamp (>420	pressure: 1 atm.	with little amount of	2020, 13, 1725-
	nm	temperature:	$CH_4$ and $H_2$	1729
		25 °C		
TAPBB-COF	300 W Xe	H <sub>2</sub> O: 1 mL,	CO (295.2 µmol g <sup>-1</sup> h <sup>-1</sup> )	ChemSusChem
	lamp	pressure: 1 atm,	and $H_2$ (13.6 µmol g <sup>-1</sup> h <sup>-</sup>	<b>2020</b> , <i>13</i> , 2973-
	(200≤λ≤10	temperature:		2980
	00 nm)	80 °C		
TPA-PQ	300 W Xe	2 mL of Mili-Q	$CH_4$ (2.15 mmol g <sup>-1</sup> h <sup>-1</sup> )	J. Am. Chem.
	lamp (>420	water, 4 mL		Soc. 2021, 143,
	nm)	acetonitrile, 10		16284-16292
	,	uM BNAH as		
		sacrificial		
		reagent		
TPA-DPA PPK	100 W Xe	$H_2O$ vapor	CH <sub>4</sub> (152.65 ppm g <sup>-1</sup> ) in	ACS Appl.
	lamp with	-	6h	Mater.
	an ÂM			Interfaces 2022,
	1.5G filter			14, 771-783
PeTt-POP	100 W Xe	H <sub>2</sub> O vapor	CH <sub>4</sub> (125.63 ppm g <sup>-1</sup> ) in	Our work
	lamp with	-	6h	
	an ÂM			
	1.5G filter			

Table S4: Comparison of catalytic activity over gas phase photocatalytic CO<sub>2</sub> Reduction

Photocatalysts	Light source	Reaction	Products	Reference
		parameter		
Gold/titania nano composites, GNP/TiO <sub>2</sub>	A 200W Hg/Xe (200- 750 nm) lamp	H <sub>2</sub> O vapor	CH <sub>4</sub> (60 ppm) in 6h (50 mg catalyst)	<i>Chem. Mater.</i> <b>2015</b> , <i>27</i> , 7248-7257
Oxygen-rich TiO <sub>2</sub> (O <sub>2</sub> -TiO <sub>2</sub> )	15-W energy- saving daylight bulbs	H <sub>2</sub> O vapor	CH <sub>4</sub> (1.03 µmol g <sup>-1</sup> ) in 6h	<i>Chem. Eng. J.</i> <b>2015</b> , <i>283</i> , 1254-1263

CZTS-TiO <sub>2</sub> hybrid mesoporous Cu <sub>x</sub> O-TiO <sub>2</sub> mesoporous p-type/n-type heterojunction material	100W Xe solar simulator with an AM 1.5 filter; 100 mW cm <sup>-2</sup> 100W Xe solar simulator with an AM 1.5 filter; 100 mW cm <sup>-2</sup>	H <sub>2</sub> O vapor H <sub>2</sub> O vapor	CH <sub>4</sub> (118.75 ppm g <sup>-1</sup> h <sup>-1</sup> ) CH <sub>4</sub> (221.63 ppm g <sup>-1</sup> h <sup>-1</sup> )	<i>RSC Adv.</i> 2016, 6, 38964- 38971 <i>ACS Omega</i> 2016, <i>1</i> , 868- 875
MnO <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub>	300W Xe lamp	H <sub>2</sub> O vapor	CO (9.6 µmol g <sup>-1</sup> ) in 6h	<i>Carbon</i> <b>2017</b> , <i>120</i> , 23-31
CQDs/g-C <sub>3</sub> N <sub>4</sub>	300W Xenon- arc lamp (> 400 nm)	H <sub>2</sub> O vapor	СО 23.38 µmol g <sup>-1</sup> h <sup>-1</sup> , СН <sub>4</sub> 20.78 µmol g <sup>-1</sup> h <sup>-1</sup>	<i>ChemSusChem</i> <b>2018</b> , <i>11</i> , 4256-4261
OXD-TPA	300 W Xe lamp (>420 nm)	H <sub>2</sub> O vapor	CO (37.15 µmol g <sup>-1</sup> h <sup>-1</sup> )	<i>Green Chem.</i> <b>2019</b> , <i>21</i> , 6606-6610
PCN-601	300W Xenon- arc lamp (≥410 nm)	H <sub>2</sub> O vapor	CH <sub>4</sub> (10.1 µmol g <sup>-1</sup> h <sup>-1</sup> )	J. Am. Chem. Soc. <b>2020</b> , 142 12515-12523
PCN-250-Fe <sub>3</sub>	300W Xenon- arc lamp (≥420 nm)	H <sub>2</sub> O vapor	CO 16.32 μmol g <sup>-1</sup> , CH <sub>4</sub> 4.73 μmol g <sup>-1</sup> (after 4h)	<i>ACS Appl.</i> <i>Energy Mater.</i> <b>2022</b> , <i>5</i> , 2384- 2390
TPA-DPA PPK	100W Xe solar simulator with an AM 1.5 filter; 100 mW cm <sup>-2</sup>	H <sub>2</sub> O vapor	CH <sub>4</sub> (152.65 ppm g <sup>-1</sup> ) in 6h	ACS Appl. Mater. Interfaces <b>2022</b> , 14, 771- 783
PeTt-POP	100W Xe solar simulator with an AM 1.5 filter; 100 mW cm <sup>-2</sup>	H <sub>2</sub> O vapor	CH <sub>4</sub> (125.63 ppm g <sup>-1</sup> ) in 6h	Our work

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