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Supplementary Information

Visible light-driven simultaneous H_2 production by water splitting coupled with selective oxidation of HMF to DFF catalyzed by porous carbon nitride

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1. Experimental

1.1 Materials

Cyanamide (CA), tetraethoxy orthosilicate (TEOS), ammonium hydrogen difluoride (NH_4HF_2), HCl (35%, Fisher Scientific) and 5-(Hydroxymethyl)furfural (HMF) were purchased from Sigma Aldrich, India. Furfurylalcohol and 2,5-Diformylfuran (DFF) were purchased from TCI chemicals, India. All the chemicals were used without further purification.

1.2 Catalyst preparation

The mesoporous carbon nitride (SGCN) was synthesized according to the reported literature.[1] Briefly, Cyanamide (CA) was used as carbon nitride precursor and tetraethylorthosilicate (TEOS) was used for template synthesis to get high surface area carbon nitride. Firstly, CA and TEOS were taken in 6:1 molar ratio. The mixture was dissolved in 0.01 M aqueous HCl (4 g) and ethanol (4 g). The pH of the resultant mixture was adjusted to 2 by addition of HCl drop wise. After stirring of the mixture for 30 min, the solvent was evaporated by rotary evaporation and subsequently dried at 80 °C for 24 h. Later, the obtained solid was further calcined at 550 °C under inert atmosphere with a ramping rate of 5 °C/min for 4 h to get the mesoporous carbon nitride-silica composite. The composite was washed with 4 M ammonium bifluoride (NH_4HF_2) solution for 48 h to remove the silica followed by washing with water and ethanol several times to obtain pure mesoporous carbon nitride (SGCN). The obtained SGCN was dried in normal oven for overnight at 120 °C followed by drying in the vacuum oven at 150 °C overnight. The CHNS analysis of SGCN is measured as 33 % of C, 58 % of N, 1.9 % of H, and 7.1 % of residue.

The platinum was used as co-catalyst during the reaction and was deposited by photodeposition method.[2] Briefly, certain amount of as synthesized SGCN was taken in a 200 mL of distilled water (v/v 10 % methanol) containing required amount of H_2PtCl_6. The solution was degassed with Argon for 30 min. Initially, the reaction mixture was stirred in dark prior to photo irradiation for 1 h. Then, the visible light was irradiated by using LED solar simulator for 1 h. After the reaction, the solid was collected by centrifugation and washed several times with water and ethanol. The Pt deposited SGCN was dried at 80 ^{o}C for overnight. The Pt content has been estimated by EDS analysis.

1.3 Characterization techniques

Powder XRD patterns were recorded on a Bruker D8 Advance diffractometer equipped with a scintillation counter detector, with Cu-K_α radiation (λ = 0.15418 nm, 2θ = 5–80^o) source operating at 40 kV and 40 mA. The N_2 physisorption studies were performed at -196 ^{o}C on Autosorb iQ2 instrument (Quantachrome). The surface area was calculated by using 5 point BET method. The pore size and total pore volume was obtained by the amount of N_2 adsorbed at p/p_0 ~ 0.95. The morphology of the samples was analyzed by transmission electron microscope (TEM, JEOL) at an acceleration voltage of 200 kV. The bulk chemical composition of the samples was estimated by energy dispersive X-ray spectroscopy (EDS). The Diffuse reflectance UV-Visible (DRUV-Vis) spectra were recorded on a Shimadzu UV-2550 spectrophotometer. The amount of H_2 generated was measured by GC-2014 by using TCD detector. The liquid samples were analyzed by the HPLC equipped with PDA and Mass detectors (Waters) by using C-18 column. The light-to-fuel efficiency has been calculated as equation (1)[3]:

$$\mathrm{LFE} = \frac{F_{\mathrm{H_2}} \Delta H^{o}_{\mathrm{H_2}}}{S A_{\mathrm{irr}}} \qquad (1)$$

Here, the $F_{\mathrm{H_2}}$ is the hydrogen produced in mols^{-1}, $\Delta H^{o}_{\mathrm{H_2}}$ is the enthalpy corresponds to H_2 combustion, *S* is the total average light irradiance, measured by Newport energy meter in direct sunlight (Wcm^{-2}), and A_{irr} is the area of light irradiation (cm^{-2}).

1.4 Reaction procedure

The photocatalytic H_2 evolution coupled with biomass valorization (HMF oxidation) was performed in a home-made photocatalytic reactor under visible light irradiation (400-800 nm). In a typical reaction, certain amount of catalyst was taken in a 10 mL distilled water contains 0.1 mmol of substrate (HMF). Further, the solution was purged with N_2 gas to remove any dissolved O_2 and inert atmosphere was maintained during the reaction. The reaction was carried out under visible light irradiation by a LED solar simulator (AM 1.5), 100 mW.cm^{-2}. After the reaction, the gas sample was collected by 1 mL gas tight syringe and injected in GC to calculate the amount of H_2 evolved by using calibration curves. The catalyst was separated from the reaction mixture by centrifugation for further characterization. The analysis of the liquid products was carried out by HPLC (Waters) equipped with PDA and Mass detectors using a C-18 column.

2. Characterization of the catalyst

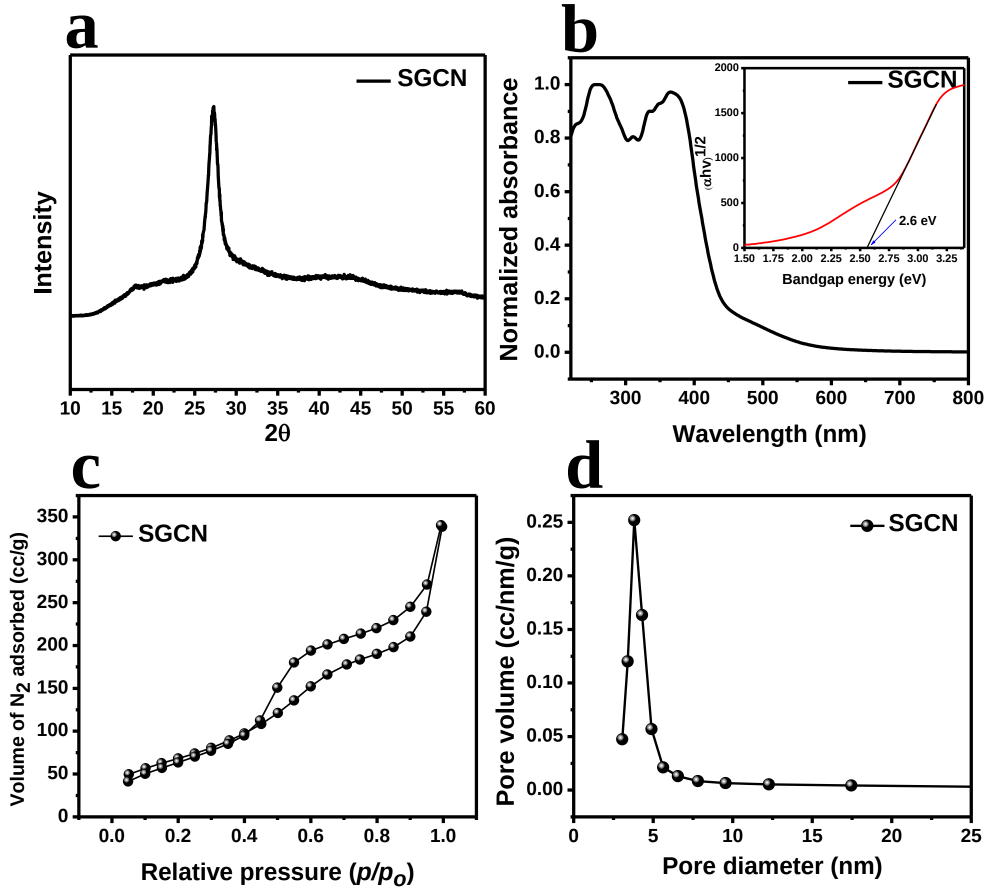

Fig. S1 (a) PXRD pattern, (b) DRUV-vis spectra (Inset shows Tauc plot of SGCN), (c) N_2 physisorption isotherm, and (d) BJH pore size distribution of SGCN.

Solid PL spectra:

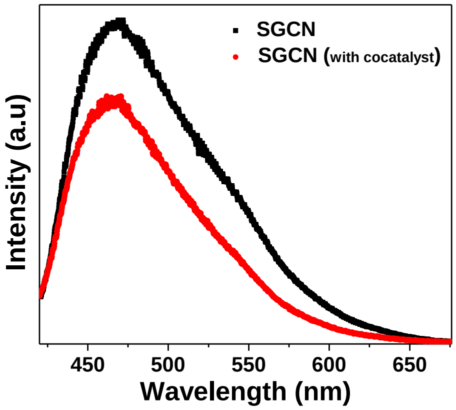

Fig. S2 Solid fluorescence spectra of SGCN and SGCN with co-catalyst.

TEM images:

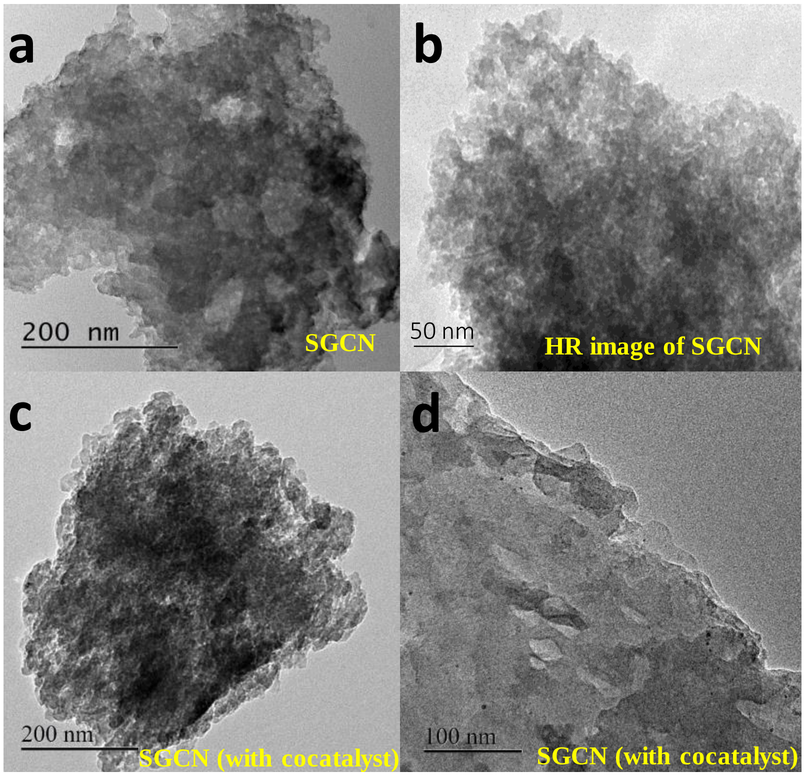

Fig. S3 TEM images of SGCN (a,b) and SGCN with co-catalyst (c,d).

XPS image:

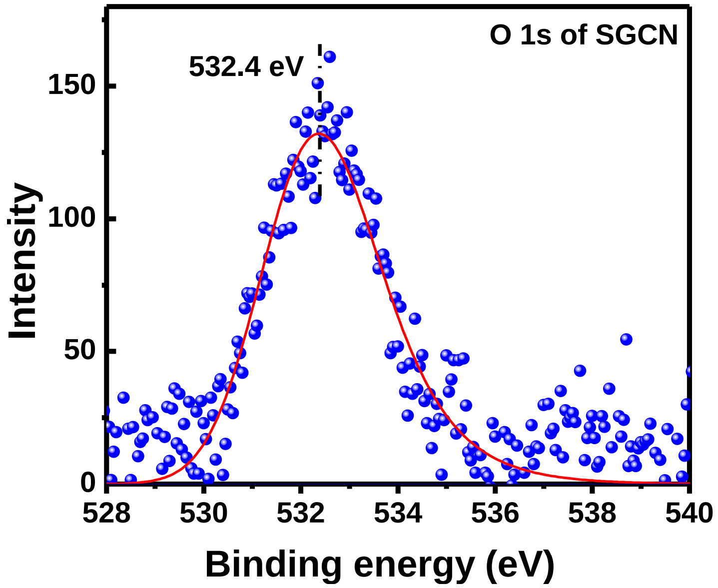

Fig. S4 O 1s spectra of SGCN.

Table S1. Textual properties of SGCN samples.

Entry	Catalyst	Surface area (m^2/g)
1	SGCN	250
2	SGCN (with cocatalyst)	170
3	SGCN with cocatalyst (after 4 cycles)	162

3. Photocatalytic activity

HPLC profiles:

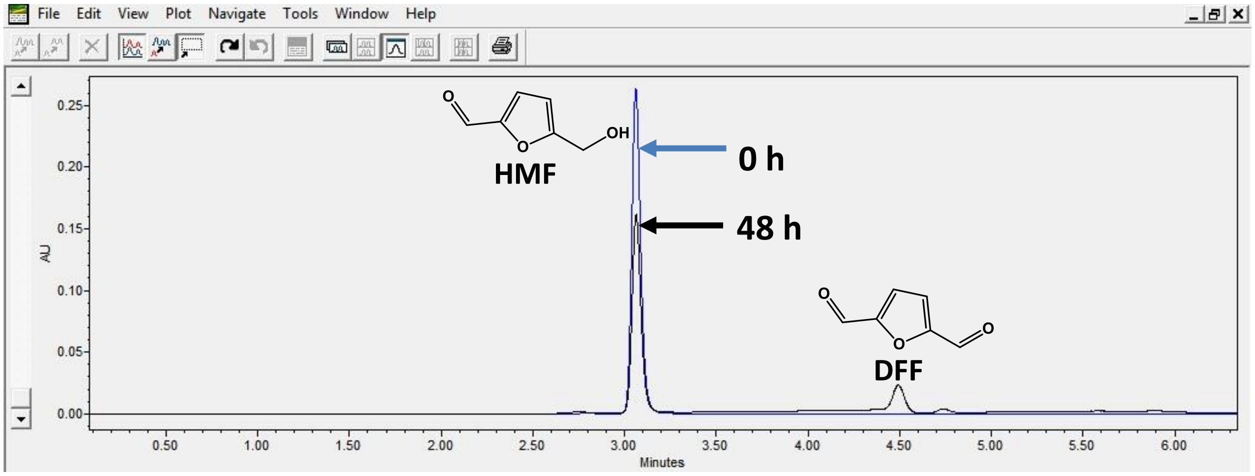

Fig. S5 HPLC profile of the reaction mixture at 0 h and 48 h.

Recyclability tests:

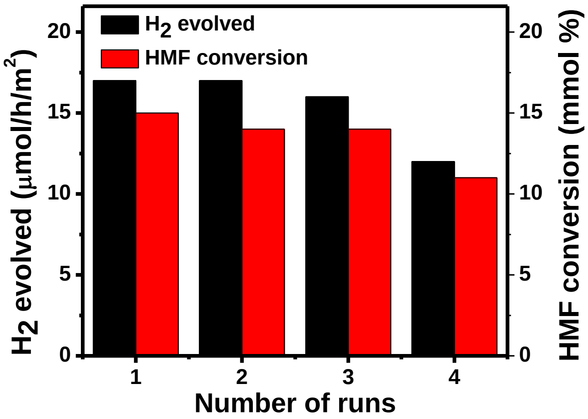

Fig. S6 Recyclability of SGCN towards simultaneous H_2 evolution and HMF oxidation. Reaction conditions: 50 mg catalyst, 0.1 mmol of HMF, and reaction time = 6 h.

4. Characterization of catalyst after 4 cycles

DRUV-vis:

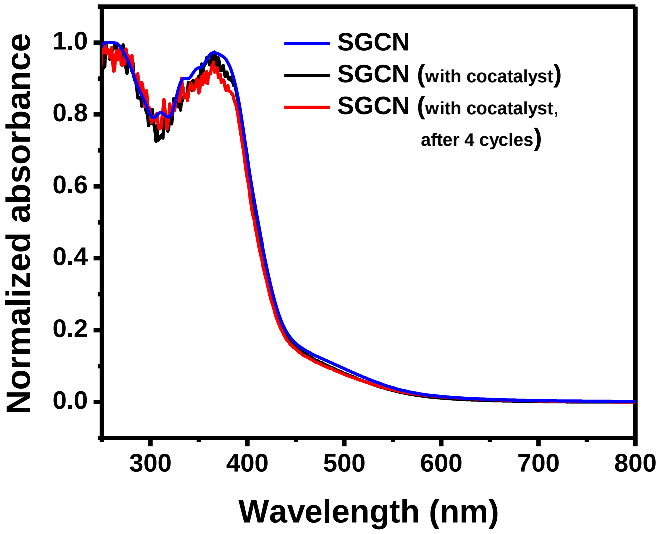

Fig. S7 DRUV-vis of SGCN, SGCN with co-catalyst, and SGCN with co-catalyst (after 4 cycles).

N_2 physisorption isotherms:

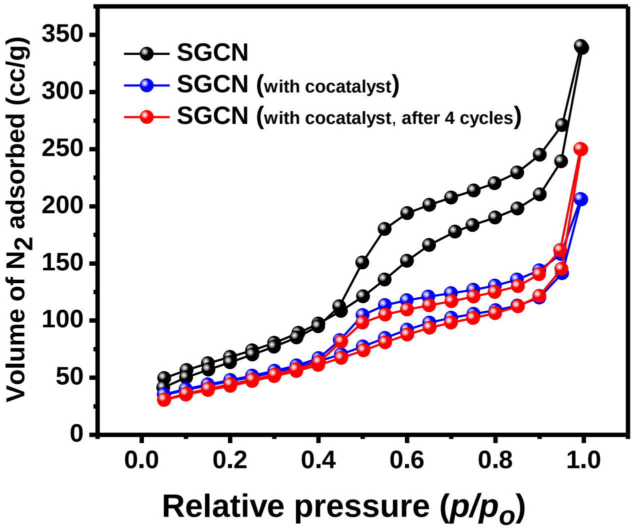

Fig. S8 N_2 physisorption isotherms of SGCN, SGCN with co-catalyst, and SGCN with co-catalyst (after 4 cycles).

PXRD patterns:

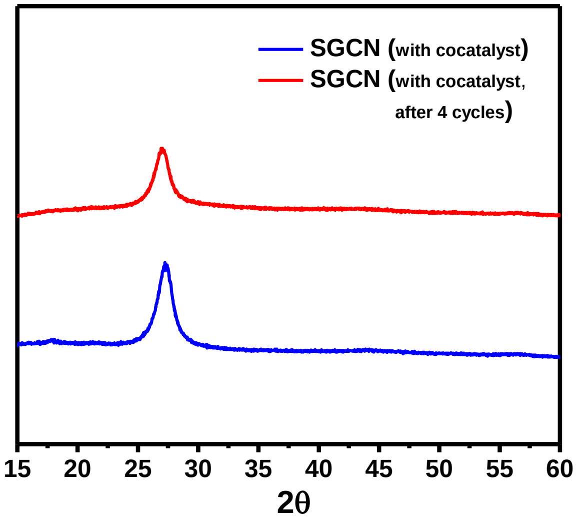

Fig. S9 PXRD patterns of SGCN with co-catalyst, and SGCN with co-catalyst (after 4 cycles).

TEM images:

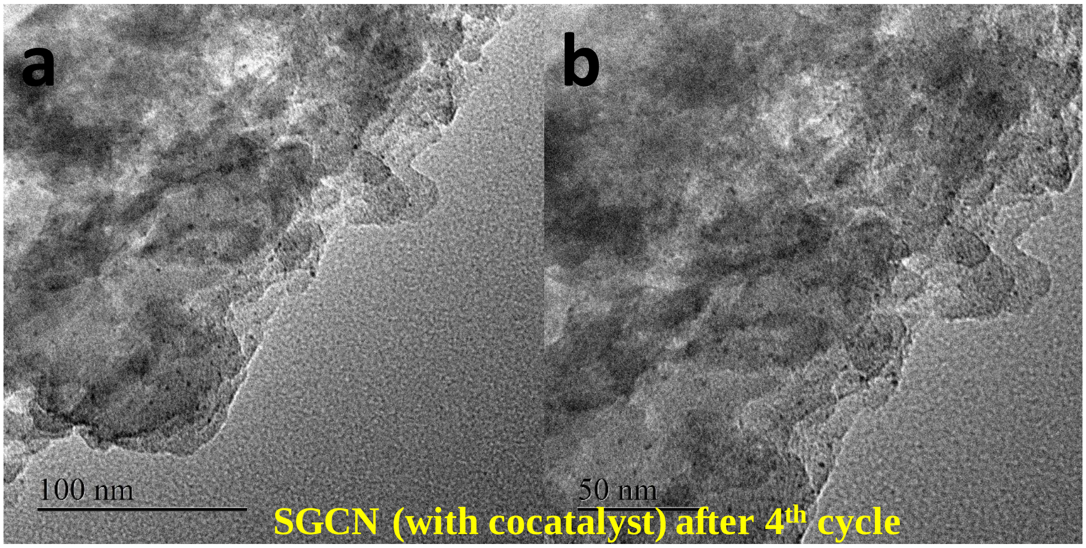

Fig. S10 TEM images of SGCN with co-catalyst (after 4 cycles).

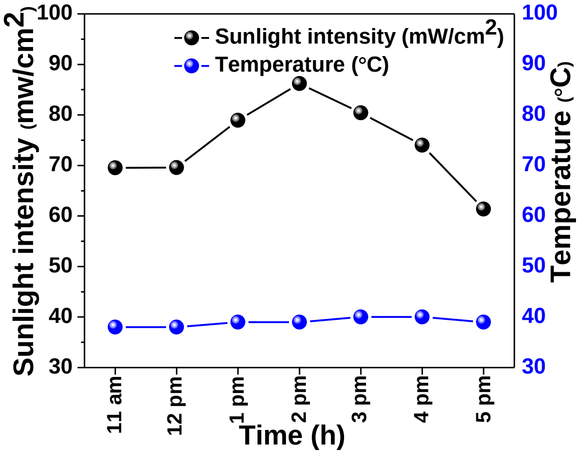

Fig. S11 Sunlight intensity and Temperature profiles on 25/06/2018, Phase 10. Mohali. Punjab.

References:

1. K. Kailasam, J. D. Epping, A. Thomas, S. Losse and H. Junge, *Energy Environ. Sci.,* 2011, **4**, 4668-4674.

2. R. Abe, H. Takami, N. Murakami and B. Ohtani, *J. Am. Chem. Soc.,* 2008, **130**, 7780-7781.

3. A. Dessì, M. Monai, M. Bessi, T. Montini, M. Calamante, A. Mordini, G. Reginato, C. Trono, P. Fornasiero and L. Zani, *ChemSusChem*, 2018, **11**, 793-805.