Electronic Supplementary Material (ESI) for Energy Advances.
This journal is © The Royal Society of Chemistry 2023

Electronic supplementary information

for

Generation of covalent organic framework-derived porous N-doped carbon nanosheets for highly efficient electrocatalytic hydrogen evolution

Sayan Halder,[a] Anup Kumar Pradhan,[a] Soumen Khan,[a,b] and Chanchal Chakraborty*[,a,b]

[a] Department of Chemistry, Birla Institute of Technology & Science (BITS) Pilani, Hyderabad Campus. Jawaharnagar, Samirpet, Hyderabad, Telangana 500078, India.

[b] Materials Center for Sustainable Energy & Environment (McSEE), Birla Institute of Technology and Science, Hyderabad Campus, Hyderabad 500078, India

*Corresponding Author: Chanchal Chakraborty

E-mail: chanchal@hyderabad.bits-pilani.ac.in

ORCID ID: https://orcid.org/0000-0002-4829-1367

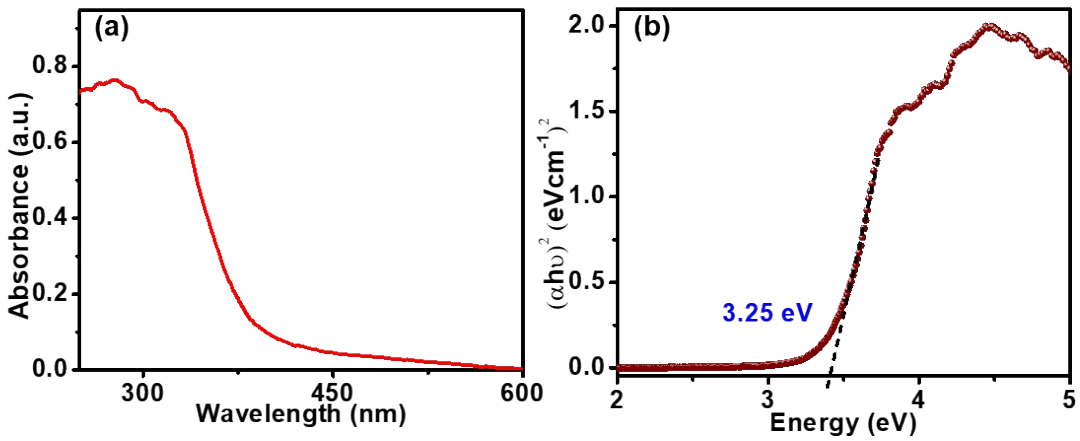

Fig. S1 (a) Solid-state UV-vis spectra and (c) corresponding Kubelka-Munk plot for optical bandgap for TP-COF.

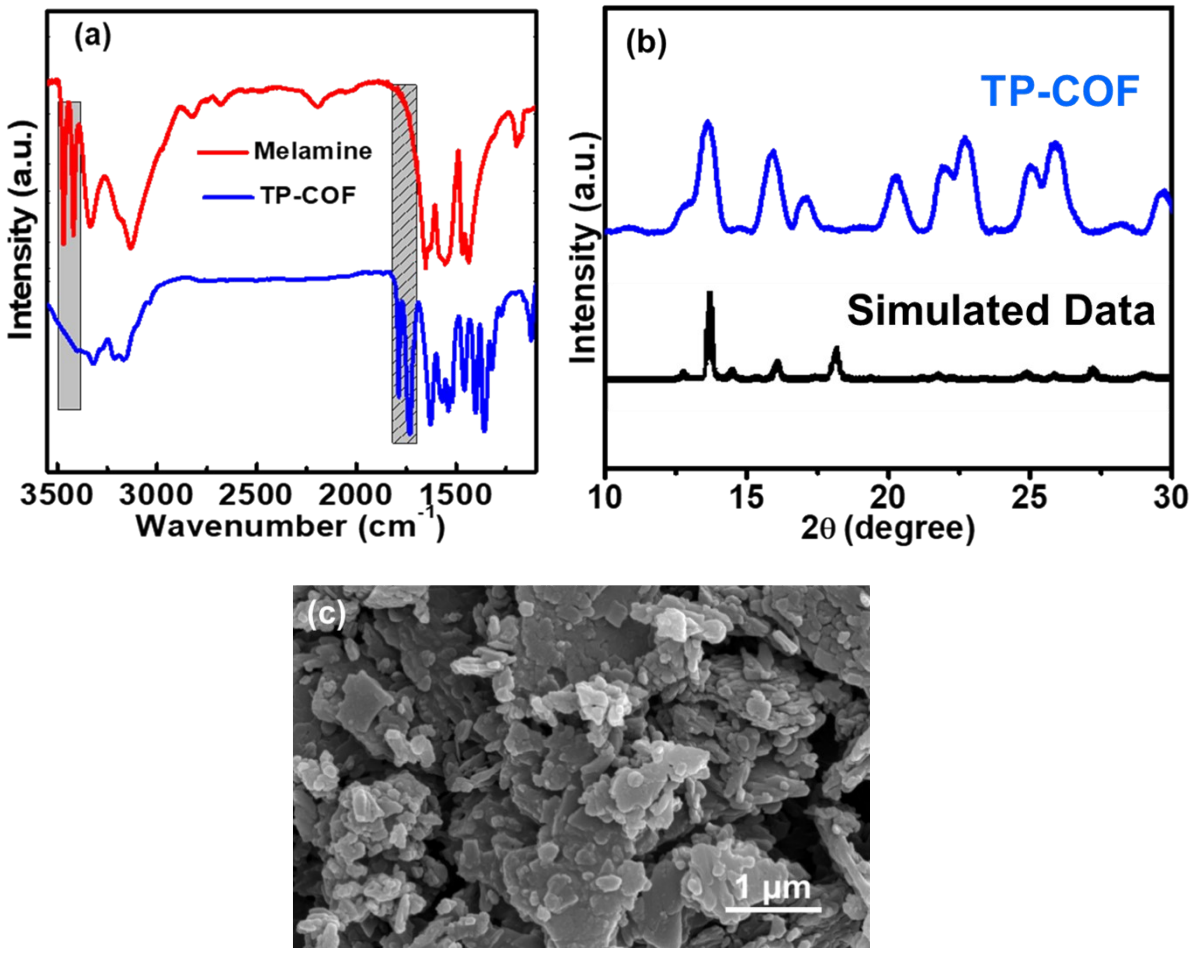

Fig. S2 (a) FT-IR plots of melamine and TP-COF, (b) PXRD plot of TP-COF. The simulated data is referenced from earlier literature[1]. (c) FESEM image of TP-COF.

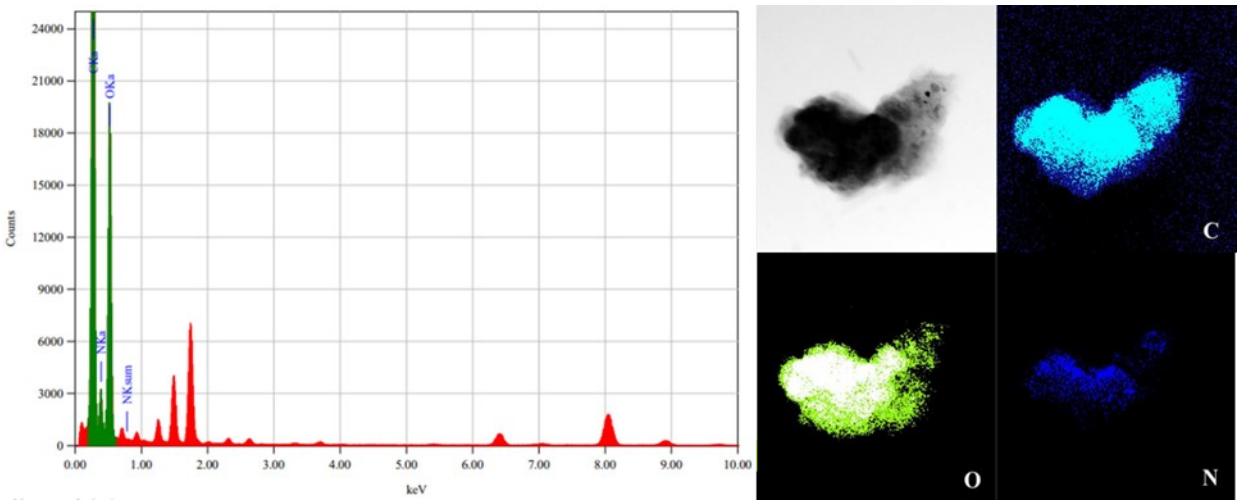

Fig. S3 The overall TEM-EDX and elemental mapping of TP-COF and the individual elemental mapping of C, N, and O on the TP-COF surface.

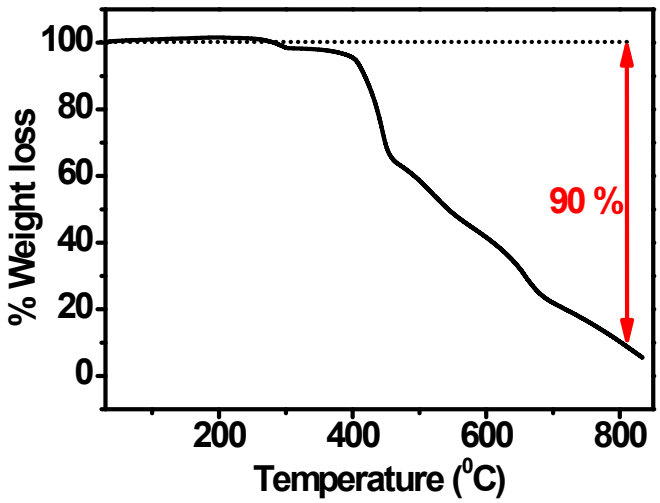

Fig. S4 TGA thermograph of TP-COF under N_2 environment.

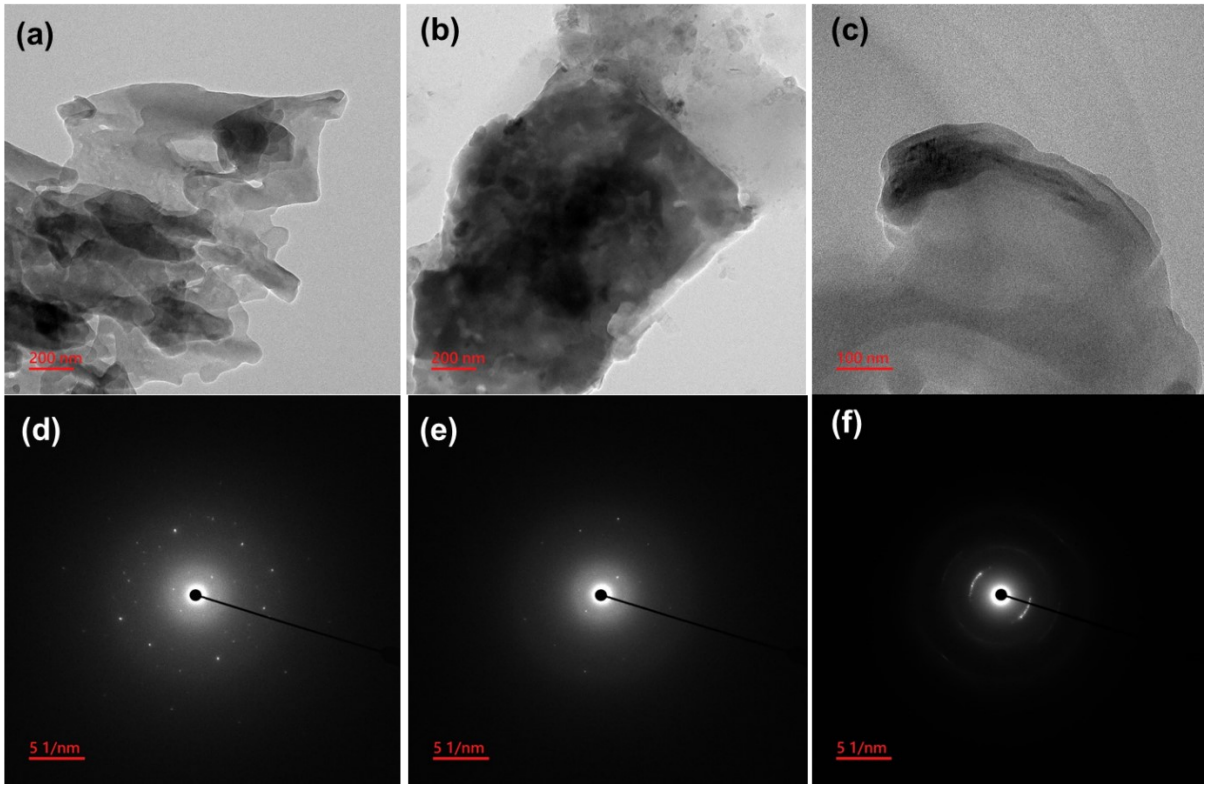

Fig. S5 HRTEM of (a), (b), and (c) for TP-COF pyrolyzed at 400, 500, and 800 °C, respectively. Corresponding SAED images (d), (e), and (f) of TP-COF at 400, 500, and 800 °C, respectively.

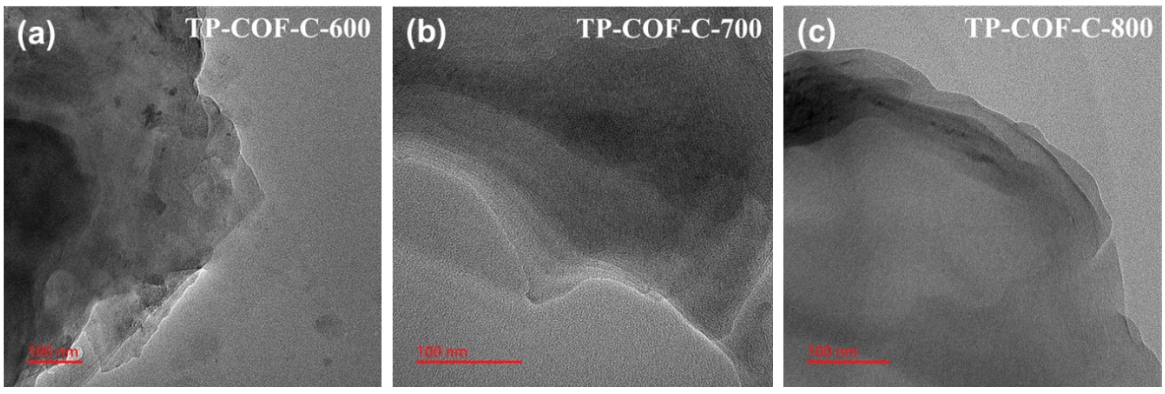

Fig. S6. TEM of (a) TP-COF-C-600, (b) TP-COF-C-700, and (c) TP-COF-C-800.

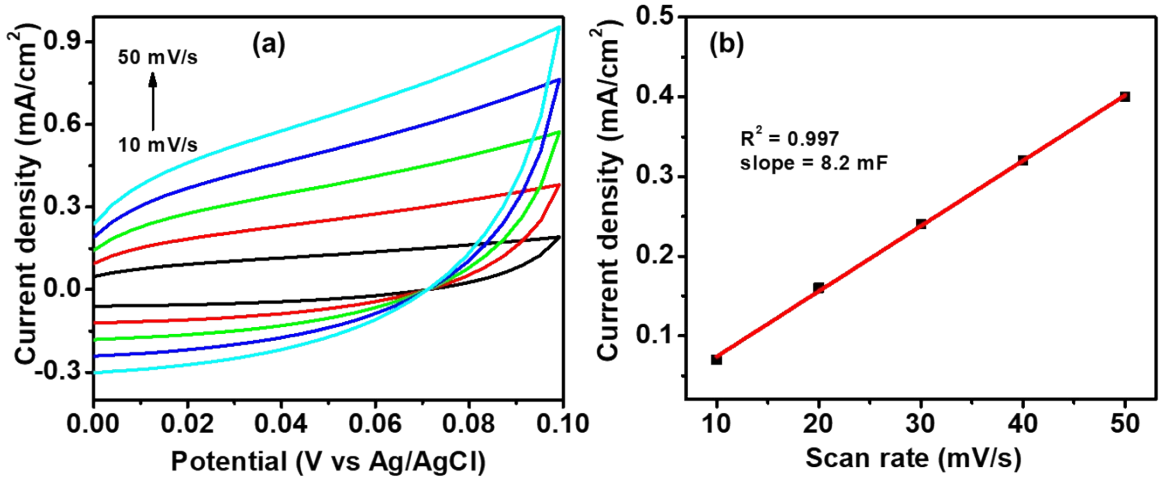

Fig. S7. (a) Scan rate dependant CV study and (b) average current density vs. scan rate plot of TP-COF-C700 in the non-faradic region (0 to 0.1 V vs. Ag/AgCl-sat. KCl) for the calculation of C_{dl}.

Faradic Efficiency (FE) calculation of HER for TP-COF-C700:

We have calculated the faradic efficiency of TP-COF-C700 using the following procedure. The chronoamperometry of TP-COF-C700 was conducted at a current density of -0.3 V (RHE) for 30 min.

So, charge passed (area under the curve of chronoamperometry) = 53.795 Coulomb

Again, 53.795 Coulomb = (53.795/96485) mole electron

Here, one hydrogen molecule was produced by involving 2 electrons transfer, so the theoretical hydrogen produced = (53.795/(96485×2)) mole

= (53.795×22400)/(96485×2) mL (1 mole gas = 22400 mL at STP)

= 6.244 mL

The amount of the hydrogen gas evolve was collected and measured in a centrifuged vial by water displacement. The Faradic Efficiency (FE) or HER reaction was calculated using the following equation.

FE = (amount of H_2 evolved (mL) × 100) / Theoretical yield of H_2 (mL)

FE = (6.1× 100)/6.244

FE = 98 %

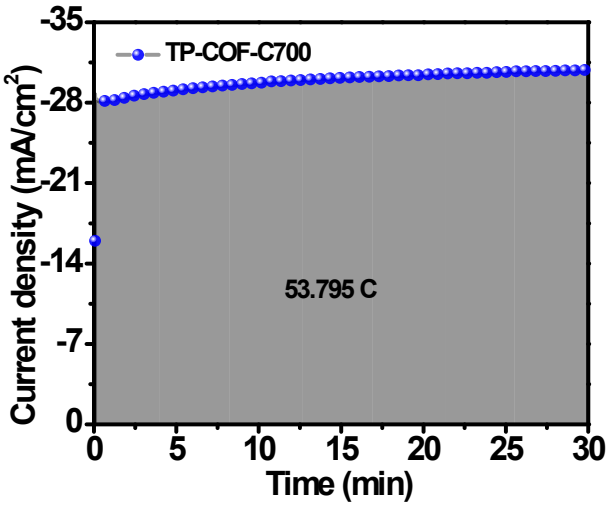

Fig. S8 (a) Chronoamperometry plot of TP-COF-C700 at -0.3 V (vs. RHE) potential for 30 min.

Table S1. Comparison of XPS-based surface elemental composition.

Materials	**% C**	**% N**	**% O**
TP-COF	56.64	18.81	24.55
TP-COF-C-700	80.15	12.01	7.84

Table S2. Comparison of electrocatalytic performance of different electrode materials.

Materials	Overpotential (mV) @ 10 mA/cm^2	Tafel slope (mV/Dec)	References
Pt electrode	60	31	2-4
CoP-2ph-CMP-800	360	121	5
Cu-MOF	209	84	6
N, P-graphene	420	91	7
P-doped graphene	533	133	7
N-doped graphene	490	116	7
F-CTF-1-AA	200	97	8
g-C_3N_4 nanoribbon-G	207	54	9
THTNi 2DSP	333	80.5	10
N,P,O doped porous carbon	233	275	11
TAT-TFBE	222	73	12
TP-COF-C700	**94**	**128**	**This work**

References.

1. H. Duan, P. Lyu, J. Liu, Y. Zhao, and Y. Xu, Semiconducting Crystalline Two-Dimensional Polyimide Nanosheets with Superior Sodium Storage Properties, *ACS Nano* 2019, **13**, 2473–2480.

2. B.E. Conwaya, G. Jerkiewicz, Relation of energies and coverages of underpotential and overpotential deposited H at Pt and other metals to the 'volcano curve' for cathodic H2 evolution kinetics, *Electrochim. Acta,* 2000, **45**, 4075-4083.

3. K. Kunimatsu, T. Senzaki, M. Tsushima, M. A. Osawa, Combined surface-enhanced infrared and electrochemical kinetics study of hydrogen adsorption and evolution on a Pt electrode, *Chem. Phys. Lett.*, 2005, **401**, 451-454.

4. E. S. Lason, G. S. Karlberg, J. Rossmeisl, T. Bligaard, J. Greeley, H. J. Nsson, J. K. Nørskov, Density functional theory calculations for the hydrogen evolution reaction in an electrochemical double layer on the Pt (111) electrode, *Phys. Chem. Chem. Phys*., 2007, **9**, 3241-3250.

5. H. Jia, Y. Yao, Y. Gao, D. Lu, P. Du, Pyrolyzed cobalt porphyrin-based conjugated mesoporous polymers as bifunctional catalysts for hydrogen production and oxygen evolution in water, *Chem. Commun*., 2016, **52**, 13483-13486.

6. M. Jahan, Z. Liu, K. P. A. Loh, Graphene oxide and copper-centered metal organic framework composite as a tri-functional catalyst for HER, OER, and ORR, *Adv. Funct. Mater*., 2013, **23**, 5363-5372.

7. Y. Zheng, Y. Jiao, L. Li, Y. Xing, Y. Chen, M. Jaroniec, S. Z. Qiao, Toward design of synergistically active carbon-based catalysts for electrocatalytic hydrogen evolution, *ACS. Nano*, 2014, **8**, 5290-5296.

8. Y. Zhao, T. Li, J. Gu, B. Zhang, P. Zhai, Z. Xue, H. Gao, Q. Li, Covalent triazine frameworks based on different stacking model as electrocatalyst for hydrogen evolution, *Appl. Surface Sci.,* 2023, **618**, 156697.

9. Y. Zhao, F. Zhao, X. Wang, C. Xu, Z. Zhang, G. Shi, L. Qu, Graphitic carbon nitride nanoribbons: graphene-assisted formation and synergic function for highly efficient hydrogen evolution, *Angew. Chem. Int. Ed.,* 2014, **53**, 13934-13939.

10. R. Dong, M. Pfeffermann, H. Liang, Z. Zheng, X. Zhu, J. Zhang, X. Feng, Large-area, free-standing, two-dimensional supramolecular polymer single-layer sheets for highly efficient electrocatalytic hydrogen evolution, *Angew. Chem. Int. Ed.,* 2015, **54**, 12058-12063.

11. Y. Zhang, L. Chen, L. Hou, X. Liu, N-, P-, and O-doped porous carbon as advanced trifunctional metal-free electrocatalysts, *Catal. Sci. Technol.,* 2023, **13**, 910-916.

12. S. Karak, K. Koner, A. Karmakar, S. Mohata, Y. Nishiyama, N. T. Duong, N. Thomas, T. G. Ajithkumar, M. S. Hossain, S. Bandyopadhyay, S. Kundu, Morphology Tuning via Linker Modulation: Metal-Free Covalent Organic Nanostructures with Exceptional Chemical Stability for Electrocatalytic Water Splitting, *Adv. Mater.,* 2023**,** 2209919.