

Electronic supplementary information (ESI)

Polarons and bipolarons induced charge carrier transportation for enhanced photocatalytic H₂ production.

T.R. Naveen Kumar[#], P. Karthik[#] and B. Neppolian*

SRM Research Institute, SRM Institute of Science and Technology, Chennai- 603203,

Tamil Nadu, India

neppolianb@gmail.com; neppolib@srmist.edu.in

Equal contribution

Contents

1. **Synthesis of PPy-C₃N₄ composite**
2. **Figure S1: a-c) TEM images of PPy-6 with different magnification**
3. **Figure S2: TGA spectra of PPy-5, 6 and 7.**
4. **Figure S3: XPS wide angle spectra of Polypyrrole**
5. **Figure S4: a) Transient photocurrent measurement b) Nyquist plot for different concentrations of oxidizing agent in polypyrrole.**
6. **Figure S5: a) XRD b) FT-IR spectra of g-C₃N₄**
7. **Table S1: Comparison table.**
8. **Equations for conductivity calculations**

Synthesis of PPy-C₃N₄ composite.

g-C₃N₄/ PPy composite was synthesized by wet impregnation method. In detail, 15 mg of PPy was added to 500 mg of g-C₃N₄ in 1:1 ratio of water and methanol and stirred for 5 h at RT. The obtained PPy/g-C₃N₄ was washed with DI water and dried at oven at 60 °C for 10 h.

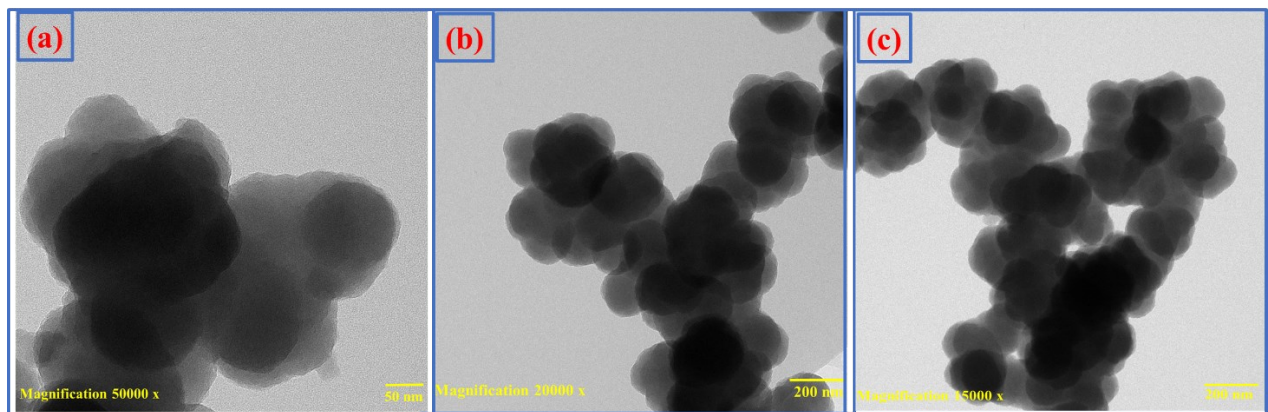


Figure S1: a-c) TEM images of PPy-6 with different magnification.

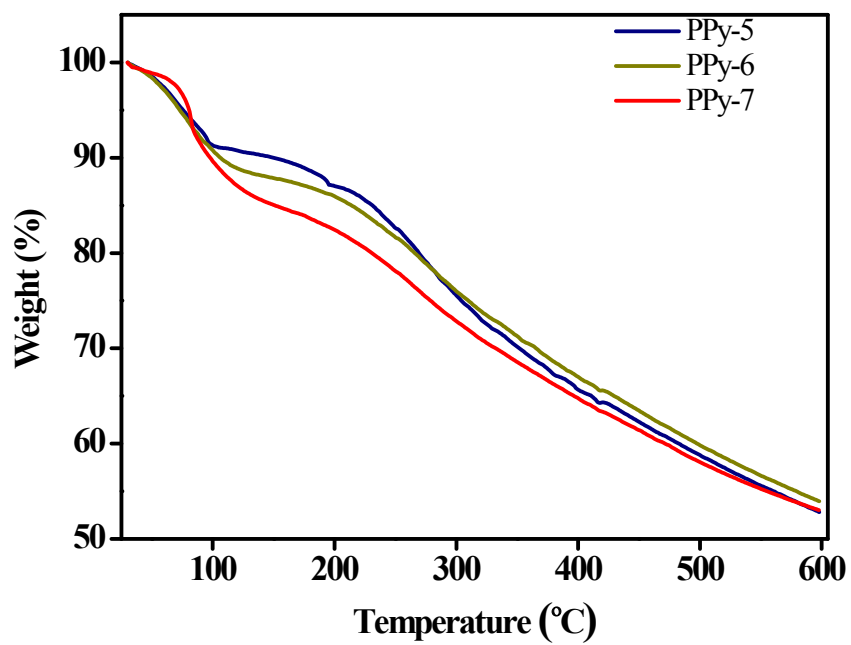


Figure S2: TGA spectra of PPy-5, 6 and 7.

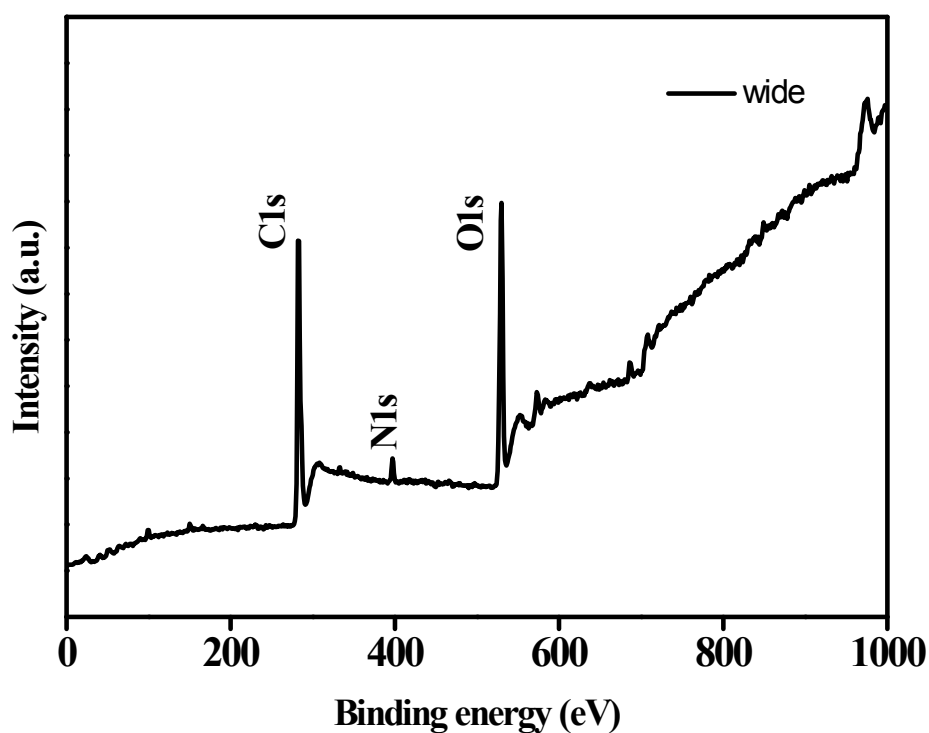


Figure S3: XPS wide angle spectra of Polypyrrole

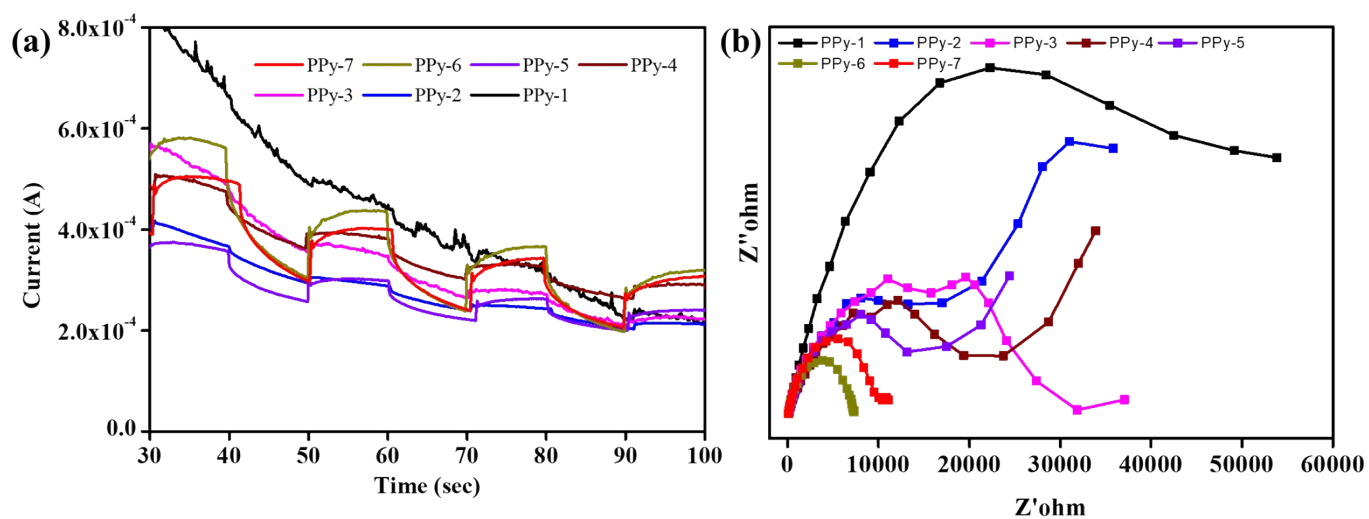


Figure S4: a) Transient photocurrent measurement b) Nyquist plot for different concentrations of oxidizing agent in polypyrrole.

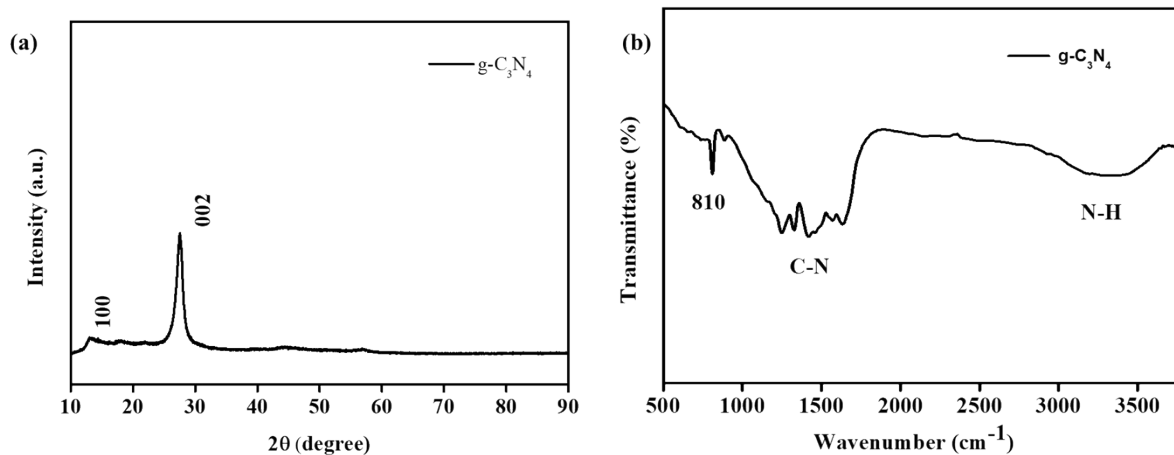


Figure S5: a) XRD b) FT-IR spectra of g-C₃N₄

Table S1: Comparison table.

Catalysts	Cocatalysts	Light Source	Sacrificial agents	H ₂ Evolution Rate (μmol g ⁻¹ h ⁻¹)	Ref
g-C ₃ N ₄ -P3HT	Pt	300 W xenon lamp λ > 420 nm	TEOA	609.9	1
g-C ₃ N ₄ /Ti ₂ C	-	300 W xenon lamp λ > 420 nm	TEOA	950	2
g-C ₃ N ₄ /CuO/Co	-	300 W xenon lamp λ > 420 nm	TEOA	93.8	3
g-C ₃ N ₄ /InVo4	Pt	300 W xenon lamp λ > 420 nm	Methyl Alcohol	212	4
g-C ₃ N ₄ /P25	Au	300 W xenon lamp λ > 420 nm	Methanol	219	5

$g\text{-C}_3\text{N}_4/\text{MoS}_2$	Pt	300 W xenon lamp $\lambda > 420 \text{ nm}$	Methanol	231	6
$g\text{-C}_3\text{N}_4/\text{TiO}_2$	Pt	300 W xenon lamp $\lambda > 420 \text{ nm}$	TEOA	329	7
$g\text{-C}_3\text{N}_4/\text{SrTiO}_3$	Pt	250 W iron doped metal halide ($\lambda \geq 420 \text{ nm}$)	oxalic acid	440	8
$\text{WO}_3/g\text{-C}_3\text{N}_4/\text{Ni(OH)}_x$	-	300 W xenon lamp $\lambda > 420 \text{ nm}$	TEOA	576	9
$g\text{-C}_3\text{N}_4/\text{Cu(OH)}_2$	-	300 W xenon lamp $\lambda > 420 \text{ nm}$	Methanol	48.7	10
$g\text{-C}_3\text{N}_4/\text{Ag}$ quantum dots	-	300 W xenon lamp $\lambda > 420 \text{ nm}$	Methanol	200	11
$g\text{-C}_3\text{N}_4/\text{Fe}_2\text{O}_3$	Pt	350 W xenon lamp $\lambda > 420 \text{ nm}$	TEOA	398	12
$g\text{-C}_3\text{N}_4/\text{PPy}$	Pt	300 W xenon lamp $\lambda > 420 \text{ nm}$	TEOA	1851.8	This Work

AC conductivity (s) and dielectric constant was calculated using equation 1 and 2

$$\tan \delta (\omega) = \frac{\varepsilon''(\omega)}{\varepsilon'(\omega)}$$

$$\varepsilon'(\omega) = \frac{Cd}{\varepsilon_0 A} \text{-----}(1)$$

$$\sigma = \varepsilon_0 \varepsilon' \omega \tan \delta \text{-----}(2)$$

Where, C is the measured capacitance in Farad, Thickness and cross-sectional area of the PPy pellet was represented as d and A, respectively. ε_0 is defined as permittivity of free space ($8.85 \times 10^{-12} \text{ F m}^{-1}$). ε' are the real parts of dielectric constant. $\omega = 2\pi f$ is the angular frequency and f is the applied frequency

Reference:

1. M. Luo, H. Gong, W. Yang, F. He, Y. Cao, Y. Zhang, Y. Zhang, K. Liu, H. Cao and H. Yan, , *Int. J. Hydrogen Energy*, 2019, **44**, 7108-7117.
2. M. Shao, Y. Shao, J. Chai, Y. Qu, M. Yang, Z. Wang, M. Yang, W. F. Ip, C. T. Kwok and X. Shi, *J. Mater. Chem. A*, 2017, **5**, 16748-16756.
3. P. Karthik, T. N. Kumar and B. Neppolian, *Int. J. Hydrogen Energy*, 2020, **45**, 7541-7551.
4. B. Hu, F. Cai, T. Chen, M. Fan, C. Song, X. Yan and W. Shi, *ACS Appl. Mater. Interfaces*, 2015, **7**, 18247–18256.

5. W. Zhao, L. Xie, M. Zhang, Z. Ai, H. Xi, Y. Li, Q. Shi and J. Chen, *Int. J. Hydrogen Energy*, 2016, **41**, 6277–6287.
6. L. Ge, C. Han, X. Xiao and L. Guo, *Int. J. Hydrogen Energy*, 2013, **38**, 6960–6969.
7. J. Ma, X. Tan, T. Yu and X. Li, *Int. J. Hydrogen Energy*, 2016, **41**, 3877–3887.
8. Xu, G. Liu, C. Random and J. T. Irvine, *Int. J. Hydrogen Energy*, 2011, **36**, 13501-13507.
9. K. He, J. Xie, X. Luo, J. Wen, S. Ma, X. Li, Y. Fang and X. Zhang, *Chinese J Catal*, 2017, **38**, 240-252.
10. X. Zhou, Z. Luo, P. Tao, B. Jin, Z. Wu and Y. Huang, *Mater. Chem. Phys*, 2014, **143**, 1462-1468.
11. T. Chen, W. Quan, L. Yu, Y. Hong, C. Song, M. Fan, L. Xiao, W. Gu and W. Shi, *J. Alloys Compd*, 2016, **686**, 628-634.
12. Q. Xu, B. Zhu, C. Jiang, B. Cheng and J. Yu, *Sol. RRI*, 2018, **2**, 1800006.