Supplementary Information

Impact of Nitrogen Doping on Triazole-Based Graphitic Carbon Nitride-TiO_2 (P25) S-scheme Heterojunction for Improved Photocatalytic Hydrogen Production

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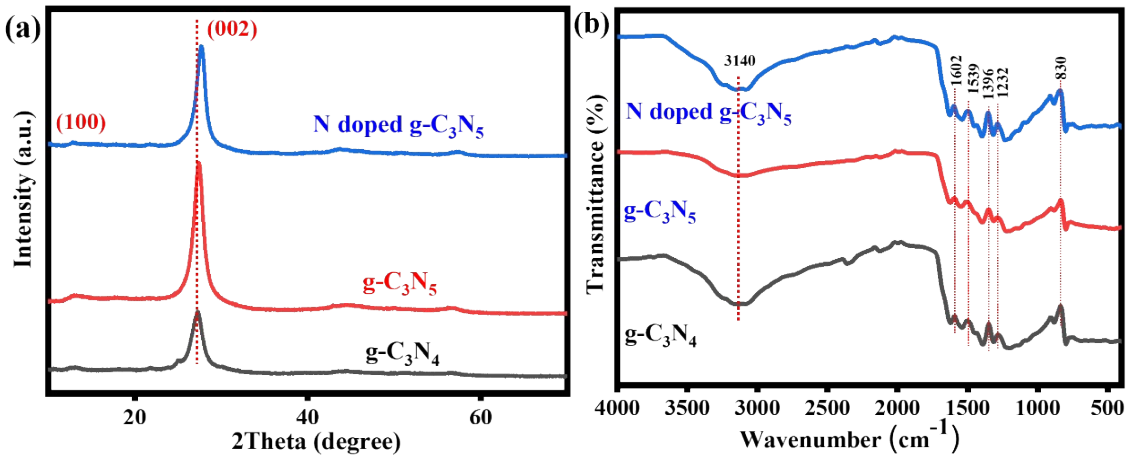

Fig. S1. Small angle XRD (a), and FTIR of the g-C_3N_4, g-CN (g-C_3N_5) and NCN (N-doped g-C_3N_5) samples (b).

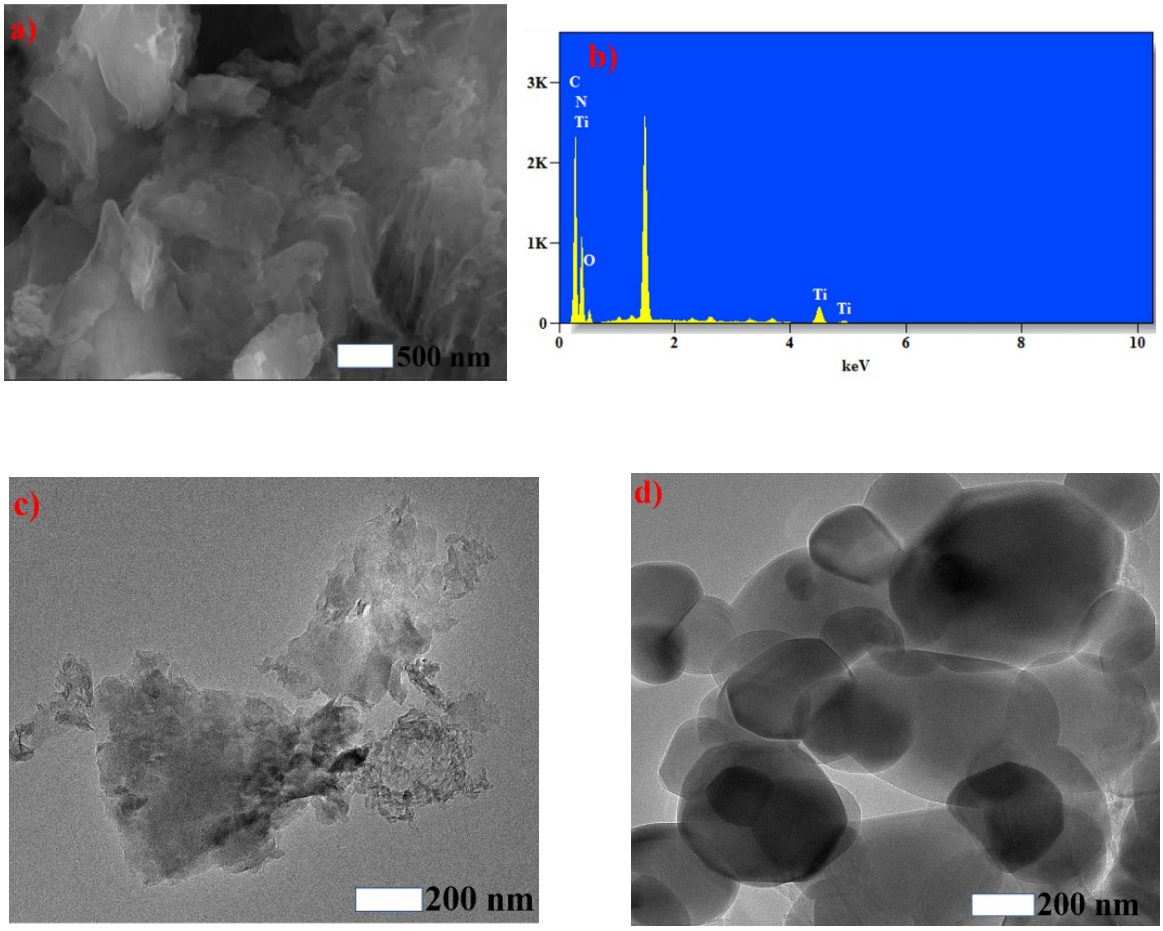

Fig. S2. SEM images of the g-CN (g-C_3N_5) (a), EDX analysis (b) and TEM images of the g-CN (g-C_3N_5) (c), TiO_2 (d).

Table S1: Elemental analysis of Scanning electron microscopy-energy

Samples	C	N	Ti	O
g-CN	38.12	60.88	---	---
NCN	35.29	64.20	---	---
TiO_2	---	---	39.87	60.13
$NCNT_5$	33.15	47.03	3.25	16.56

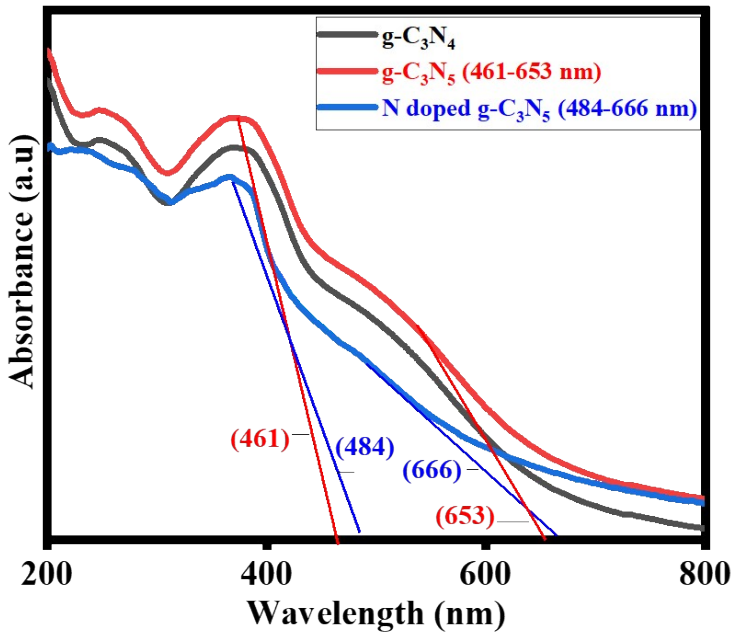

Fig. S3. UV-vis spectra of g-C_3N_4, g-CN (g-C_3N_5) and NCN (N-doped g-C_3N_5) samples (a).

Table S2

Samples code	τ1 (ns)	τ2 (ns)	B1	B2	τ_{av} (ns)
gCN	1.00E-09	7.00E-09	11.8861	0.4296	2.21
NCN	1.00E-09	4.80E-09	138.6623	7.2552	1.98
TiO_2	1.50E-09	6.00E-09	104.5315	6.0587	2.35
$NCNT_5$	2.00E-09	6.00E-09	63.0968	-1.9722	1.49

Density Functional Theory (DFT) Calculations:

Determining ground and excitation energies in polymer-type molecules presents a challenging task when utilizing density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations.[1] To ensure high accuracy in our results, we undertook a comprehensive analysis to determine the optimal function for our study. To accomplish this objective, we utilized three commonly employed functionals such as BP86, O3LYP, and B3LYP, with a 6-31+G* basis set for the ground state optimization extensively characterized experimentally.[2,3] To commence the optimization process for g-CN and NCN polymers, we utilize three repeating units (trimers) derived from the oligomers. Minimum

energy molecules were detected by frequency analysis, which yielded all positive frequencies. The O3LYP functional predicts the band gap values for g-CN and NCN molecules closest to the experimentally measured values than other functionals.

Table S3: Calculated HOMO, LUMO energies, and Band gap values at different DFT functionals. (All the values are in eV)

DFT Functionals (HF %)	Molecules	HOMO	LUMO	Band Gap	Band Gap (Experimental)
BP86 (0)	g-CN	-5.88	-4.11	1.77	-
	NCN	-5.50	-4.04	1.46	
O3LYP (20)	g-CN	-5.90	-3.18	2.72	2.02
	NCN	-5.73	-3.39	2.34	1.94
B3LYP (20)	g-CN	-6.61	-3.34	3.27	-
	NCN	-6.25	-3.26	2.99	

Table S4: Calculated absorption energies (in nm) and oscillator strengths (f) with different DFT functionals.

		DFT Functional (HF %)				
Molecules		**B3LYP (20)**	**PBE0 (25)**	**M06 (27)**	**M06-2X (54)**	**Experimental (Max. Absorption)**
g-CN	Absorption (in nm)	451	425	419	**390**	375 [Approximately] (461)
	Oscillator Strength (f)	0.0014	0.0008	0.0052	0.0140	-
NCN	Absorption (in nm)	500	456	449	**394**	365 [Approximately] (484)
	Oscillator Strength (f)	0.0004	0.0004	0.0007	0.0037	-

References

1 P. Li, C. Zhou, Y. Zhang, C. Chen, C. Zheng and R. Chen, *Physical Chemistry Chemical Physics*, 2022, **24**, 17686–17694.

2 J. Tirado-Rives and W. L. Jorgensen, *J Chem Theory Comput*, 2008, **4**, 297–306.

3 C. Adamo and V. Barone, *Journal of Chemical Physics*, 1999, **110**, 6158–6170.