Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

In-situ synthesis of g-C_3N_4 /$Ti_3C_2T_x$ nano-heterostructures for enhanced photocatalytic H_2 generation via water splitting

Amol B. Tambe,[1] Sudhir S. Arbuj, [1,]* Govind G. Umarji,[1] Sulbha K. Kulkarni,[1] Bharat B. Kale[1,2,]*

[1]Centre for materials for Electronics Technology (C-MET), Minister of Electronic and Information Technology Off Pashan Road, Panchwati, Pune-411008, Maharashtra, India.

[2]MIT World Peace University (MIT-WPU), Paud Rd, Kothrud, Pune, Maharashtra 411038.

E-mail: sudhir1305@gmail.com / bbkale1@gmail.com

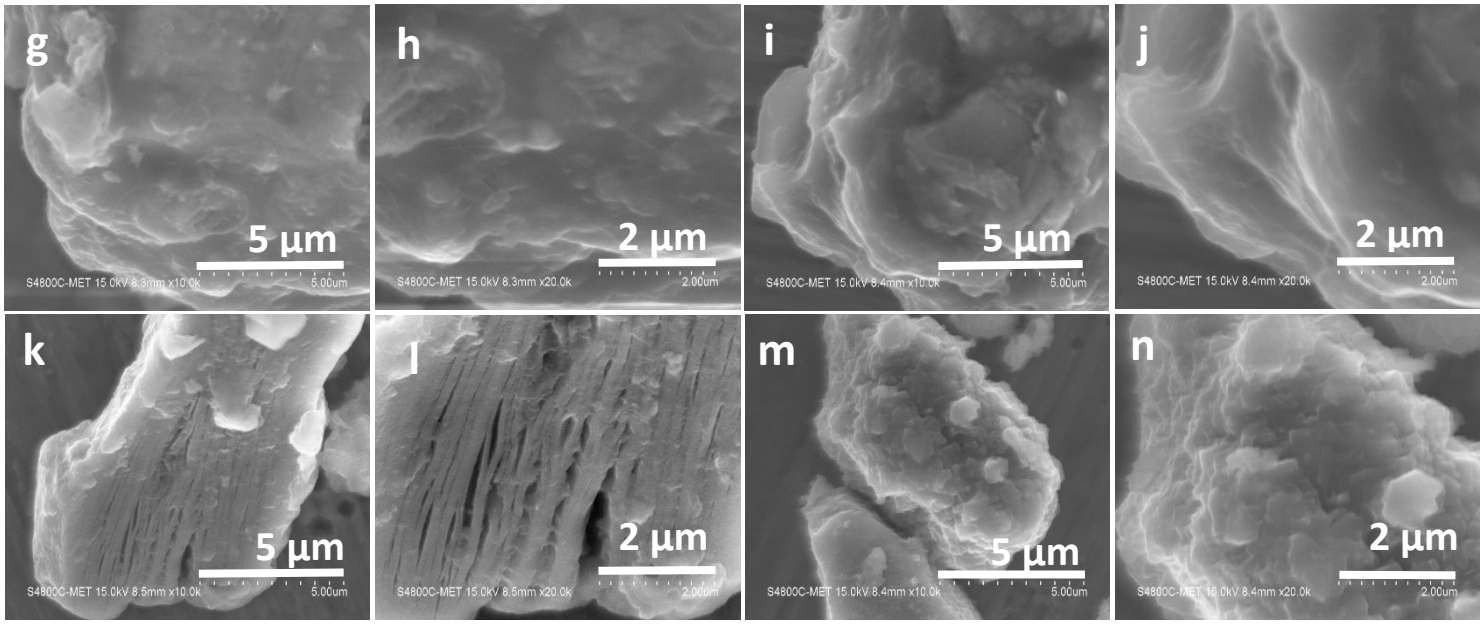

Fig.S1 *FESEM image of gCT-1(g, h), gCT-0.50(i, j), gCT-0.25(k, l), and gCT-0.05(m, n).*

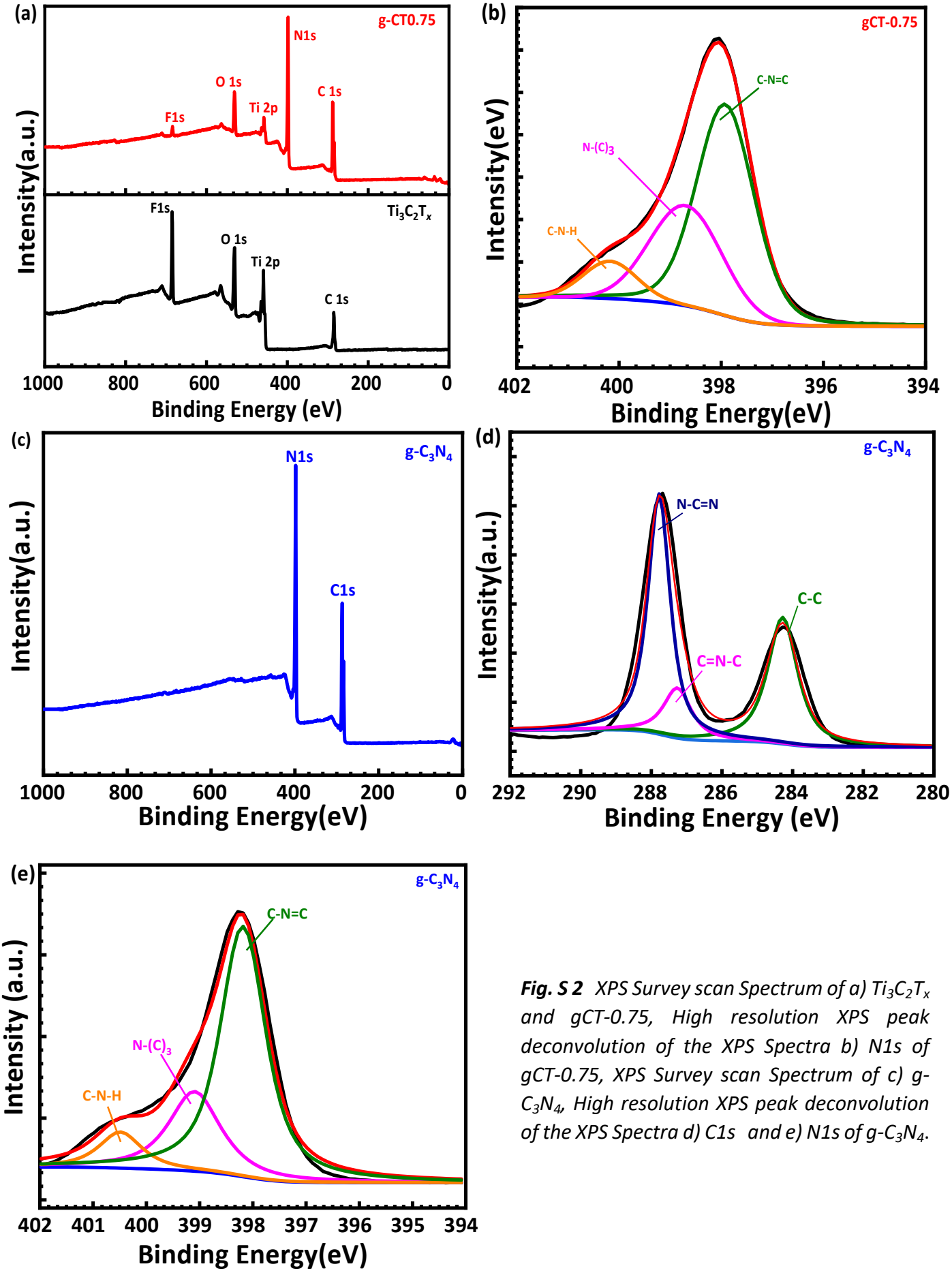

Fig. S 2 *XPS Survey scan Spectrum of a) $Ti_3C_2T_x$ and gCT-0.75, High resolution XPS peak deconvolution of the XPS Spectra b) N1s of gCT-0.75, XPS Survey scan Spectrum of c) g-C_3N_4, High resolution XPS peak deconvolution of the XPS Spectra d) C1s and e) N1s of g-C_3N_4.*

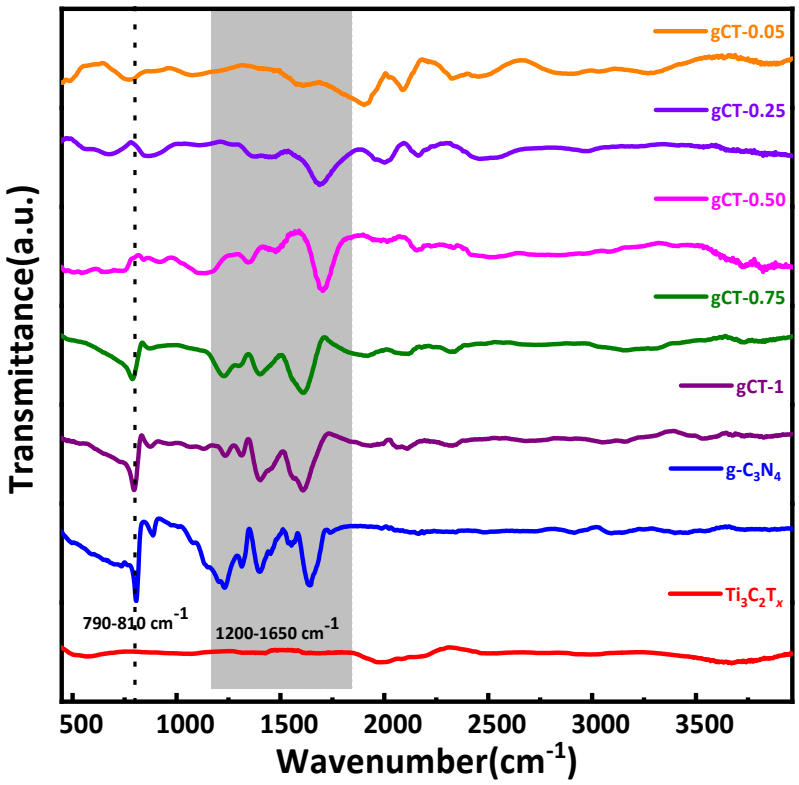

Fig.S3 *FTIR Spectra of $Ti_3C_2T_x$, g-C_3N_4, gCT-1, gCT-0.75, gCT-0.50, gCT-0.25, and gCT-0.05.*

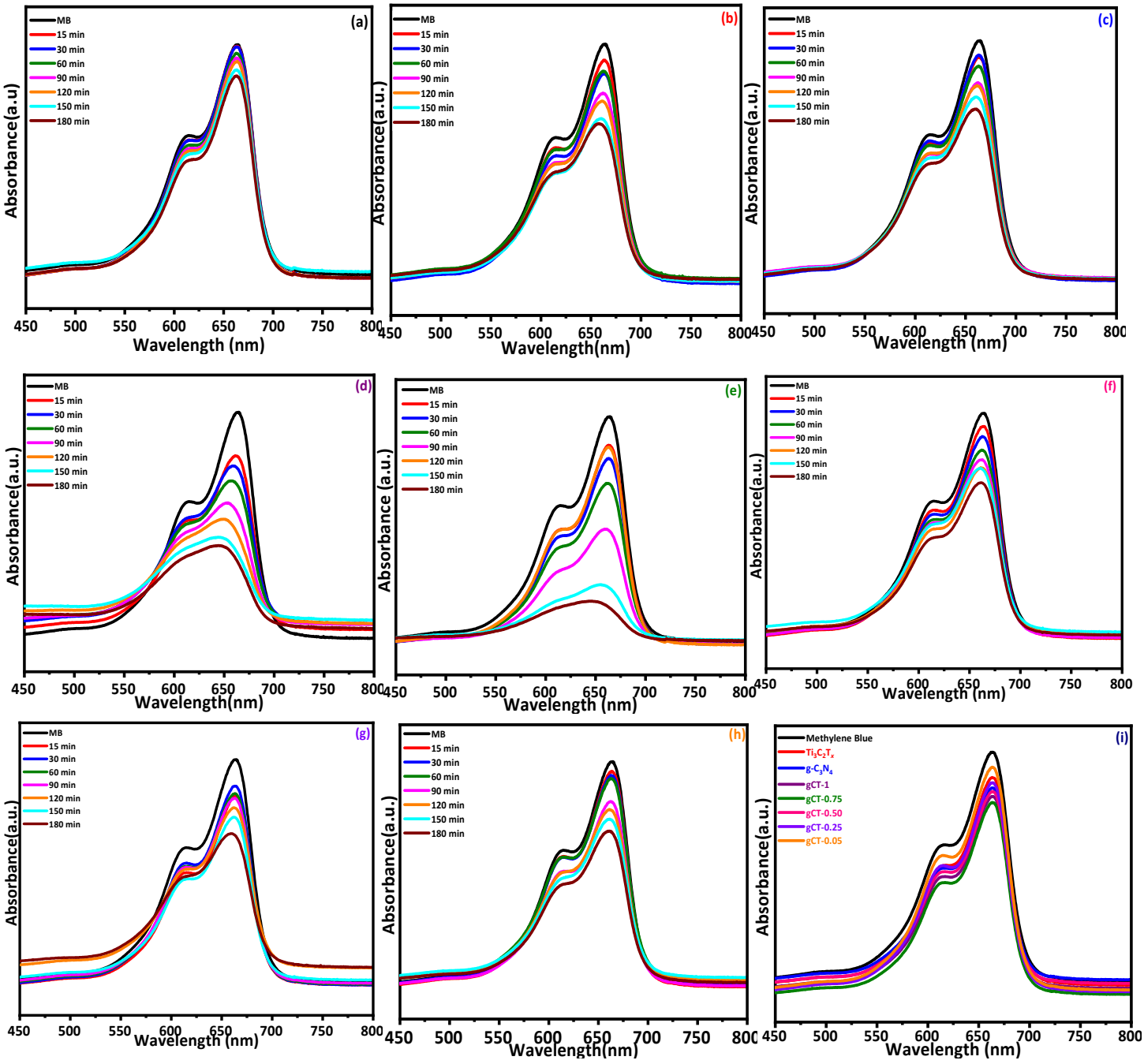

Fig. S4 *UV-Vis Absorbance spectra of (a) MB degradation under UV-Visible light (b) $Ti_3C_2T_x$, (c)g-C_3N_4 ,(d) gCT-1, (e)gCT-0.75, (f) gCT-0.50, (g) gCT-0.25 , (h) gCT-0.05 and (i) UV-Vis absorbance spectra of MB degradation under dark condition using $Ti_3C_2T_x$,g-C_3N_4 and its nano-heterostructure.*

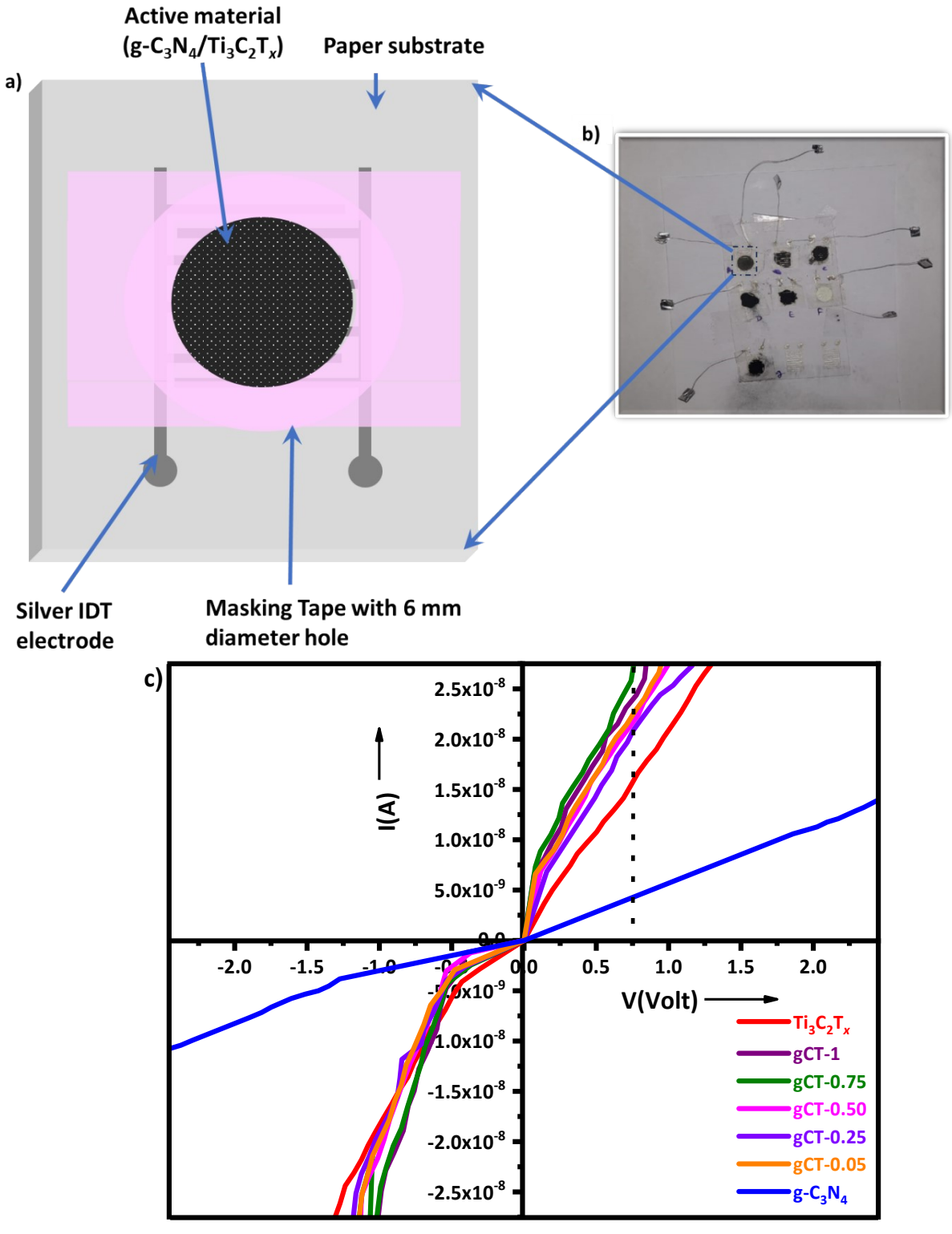

Fig. S5 *a) photo conductivity sample measurement design, b) Actual sample deposited, c) current –Voltage characteristics of $Ti_3C_2T_x$, g-C_3N_4, gCT-1, gCT-0.75, gCT-0.50, gCT-0.25, and gCT-0.05.*

Table S1 *XPS peak fitting results of a) $Ti_3C_2T_x$, b) gCT-0.75, c) g-C_3N_4*

a)	Region	B.E.(eV)	FWHM(eV)	Assigned	References
		454.6(460.3)	0.7	Ti-C	1
		455.4(461.3)	0.8	Ti^{2+}	2
	$Ti2p_{3/2}(2p_{1/2})$	456.3(462.3)	1.3	Ti^{3+}	3
		459.1(464.0)	1.6	Ti-O	1
		461.5(466.8)	2.5	C-Ti-T_x	2
		464.9	1.9	$TiO_{2-X}T_x$	1
		281.6	1.0	C-Ti	2
		284.4	1.1	C-Ti-T_x	1
	C 1s	285.0	1.0	C-C	2
		286.1	1.6	CH_x/C-O	1
		288.4	1.4	C-F/-COO	2
		529.9	1.1	TiO_2	1
		530.7	1.1	Ti-O_x	2
	O1s	531.8	1.2	Ti-OH	1
		533.2	1.6	Ti-H_2O	2
	F 1s	684.7	1.3	C-Ti-T_x	1
		685.7	1.5	C-F	2

b)	Region	B.E.(eV)	FWHM(eV)	Assigned	References
		454.3(460.0)	1.0	Ti-C	1
		455.9(461.8)	1.5	Ti^{2+}	2
	$Ti2p_{3/2}$	457.7(463.7)	1.6	Ti^{3+}	3
	$(2p_{1/2})$	458.2(464.1)	1.2	Ti-O	1
		460.9(465.9)	2.6	C-Ti-T_x	2
		463.8	1.6	$TiO_{2-X}T_x$	1
		281.0	0.5	C-Ti	2
		284.5	1.2	C-C	1
	C 1s	286.8	1.8	C-N=C	2
		287.8	1.2	N-C=N	1
		397.9	0.9	C-N=C	1
	N 1s	398.8	1.5	N-$(C)_3$	1
		400.2	1.4	C-N-H	1
		529.3	1.2	TiO_2	1
		530.5	1.3	Ti-O_x	2
	O1s	531.4	1.0	Ti-OH	1
		532.4	1.1	Ti-H_2O	2
	F 1s	683.8	1.5	C-Ti-T_x	1
		685.4	1.9	C-F	2

c)	Region	B.E.(eV)	FWHM(eV)	Assigned	References
		284.2	1.0	C-C	1
	C 1s	286.8	0.9	C-N=C	2
		287.8	0.8	N-C=N	1
		398.2	0.9	C-N=C	1
	N1s	399.1	1.2	N-$(C)_3$	1
		400.5	0.9	C-N-H	1

Table *S2.* *Time Resolved Photoluminescence (TRPL) fitting parameters about fast PL lifetime (τ_1),slow PL lifetime(τ_2), and average lifetime(τ_{ave}) for $Ti_3C_2T_x$, gCT-0.75, g-C_3N_4 .*

Catalyst	A_1 (%)	τ_1 (ns)	A_2 (%)	τ_2 (ns)	τ_{ave} (ns)
$Ti_3C_2T_x$	91.3042	0.6801	8.9214	3.9214	1.8290
gCT-0.75	84.0100	0.9723	15.9900	4.5923	2.7656
g-C_3N_4	90.2382	0.7682	9.7618	4.0123	1.9390

Table S3 *Photocatalytic Hydrogen generation (µmole of H_2 in 4h) of prepared $Ti_3C_2T_x$, g-C_3N_4, gCT-1, gCT-0.75, gCT-0.50, gCT-0.25, and gCT-0.05.*

Time(h)	Amount of H_2 generated in µmol/0.1g						
	$Ti_3C_2T_x$	g-C_3N_4	gCT-1	gCT-0.75	gCT-0.50	gCT-0.25	gCT-0.05
1	14.50	212.22	350.11	482.36	309.89	290.24	266.16
2	33.18	429.41	716.26	947.78	633.21	555.23	520.12
3	49.89	642.83	1040.65	1410.36	948.98	830.36	760.20
4	74.90	860.98	1410.21	1912.25	1296.23	1150.32	1021.23

Table S4 *Photocatalytic Hydrogen production using MXene/g-C_3N_4*

S. No.	Photocatalyst	Light Source	Amount (mg)	Scavenger	Photocatalytic activity H_2 generation	Ref.
1	Ti_3C_2/g-C_3N_4	200 W Hg lamp	30	triethanolamine	72.3 µmol $gcat^{-1}h^{-1}$	1
2	g-C_3N_4@Ti_3C_2 QDs	300 W Xe arc lamp	10	triethanolamine	5111.8 µmol g^{-1} h^{-1}	2
3	g-C_3N_4/$Ti_3C_2T_x$	350 W xenon lamp	30	triethanolamine	88 µmol /g.cat./h	3
4	2Dg-C_3N_4/2D TiO_2	300 W Xenon lamp source	30	triethanolamine	1840.83 mmol g^{-1} L^{-1}	4
5	g-C_3N_4/Ti_3C_2/Pt	300 W Xe lamp	30	methanol	5100 µmol h^{-1} g^{-1}	5
6	P doped g-C_3N_4/ Ti_3C_2	Xe lamp 300 W	10	TEOA	3600.5 µmol h^{-1} g^{-1}	6
7	gCT-0.75	400 Mercury Vapour lamp	20	Methanol	1912.25 µmol h^{-1} 0.1g^{-1}	This work
8	g-C_3N_4/Ti_3C_2	300 W Xe lamp (λ > 420 nm)	50	TEOA	116.2 µmol h^{-1} g^{-1}	7
9	Ti_3C_2/O-doped g-C_3N_4	300 W Xe lamp	10	TEOA	25124 µmol h^{-1} g^{-1}	8
10	CCNT-TO-0.6	Xenon lamp 300 W	30	TEOA	1840.8 µmol h^{-1} g^{-1}	9
11	BNCN20	Xenon lamp 300 W (λ > 420 nm)	10	TEOA	1941.7 µmol h^{-1} g^{-1}	10

Table S5. *Hydrogen evolution rates $Ti_3C_2T_x$, g-C_3N_4, gCT-1, gCT-0.75, gCT-0.50, gCT-0.25, and gCT-0.05 and their corresponding apparent quantum yield (AQY).*

S.No.	Catalyst	Amount of H_2 generated in (µmol/0.1g)	AQY(%)[a]
1	$Ti_3C_2T_x$	74.90	0.2
2	g-C_3N_4	860.98	1.4
3	gCT-1	1410.21	2.3
4	gCT-0.75	1912.25	3.1
5	gCT-0.50	1296.23	2.1
6	gCT-0.25	1150.32	1.9
7	gCT-0.05	1021.23	1.7

a = the % AQE calculated using the H_2 generation values for 0.1 g catalyst per h.[11]

Table S6 *Amount of MB remain of prepared $Ti_3C_2T_x$, g-C_3N_4, gCT-1, gCT-0.75, gCT-0.50, gCT-0.25, and gCT-0.05.*

Time(min)	MB	$Ti_3C_2T_x$	g-C_3N_4	gCT-1	gCT-0.75	gCT-0.50	gCT-0.25	gCT-0.05
0	100	100	100	100	100	100	100	100
15	90.58	87.99	81.27	80.28	74.84	80.78	80.50	80.23
30	88.98	83.75	76.77	64.51	60.49	67.71	73.32	74.59
60	86.96	77.54	70.25	54.20	50.59	57.84	62.59	65.20
90	85.72	67.14	60.68	42.95	39.8	46.61	52.79	53.13
120	83.39	59.54	53.60	33.42	30.10	37.56	41.85	48.68
150	82.66	56.95	45.68	21.95	16.43	31.56	36.47	41.95
180	81.60	47.69	36.91	15.30	8.30	21.72	27.41	32.60

Table S7 *Photocatalytic MB degradation $Ti_3C_2T_x$/g-C_3N_4.*

S.No.	Photocatalyst	Light source	Amount (mg)	Dye	Dye con(µm)	Photocatalytic activity %Dye degradation	Ref.
1	facile modification of g-C_3N_4	400W halogen lamp	80	MB	20	85.5	12
2	C_3N_4/Cu_2O	400 W sodium vapor lamp	50	MB	10	81	13
3	MXene/g-C_3N_4	500 W halogen lamp	50	MB	20	69.9	14
4	gCT-0.75	400 Mercury Vapour Lamp	50	MB	30	91.7	This work
5	$Ti_3C_2T_x$/alkalized-C_3N_4	300 W Xe lamp	10	MB	20	77	15

Photoconductivity Measurements by I-V

To support the higher photocatalytic activity of gCT-0.75, the photoconductivity measurements of $Ti_3C_2T_x$, g-C_3N_4, gCT-1, gCT-0.75, gCT-0.50, gCT-0.25, and gCT-0.05 were carried out and the obtained current-voltage characteristics are depicted in (Supporting information Fig. S5 c). For photoconductivity measurement, the construction schematic is illustrated in (Supporting information Fig. S5 a). $Ti_3C_2T_x$ nanostructured powder films deposited on pre-patterned silver (CI1001, ECM USA) inter-digited electrode (jet-printed using Nordson PICO Pulse contact dispensing valve printer) on paper (Substrate). The inter-electrode spacing of 200 µm between electrodes was maintained with a total path length of 30 mm. The 6 mm open diameter mask was pasted on the pre-patterned silver electrode to ensure the same area of powder films deposited for each photoconductivity measurement. The dispersed powder concentration was maintained the same for all samples throughout the photoconductivity measurement experiment (Supporting information Fig. S5 b). The measurements were performed using a kelvin probe connected to spring-loaded pressure contacts at room temperature. The entire setup was maintained in the metallic chamber (shield) in order to reduce the electrical noise effect. [16,17] I-V measurements were carried out using Keithley 4200 semiconductor characterization system (SCS) integrated with photo-emission system (1000 W xenon lamp and 1.5AM (air mass ratio). All sample measurements were taken with voltage bias from -2.5 V to + 2.5 V under the illumination of light for all synthesized sample. [18,19] The $Ti_3C_2T_x$, gCT-1, gCT-0.50, gCT-0.25,and gCT-0.05 show relatively less photocurrent (in the range of 2.42-1.38 X 10^{-8} A) compared to gCT-0.75 as shown in the range of 2.73 X 10^{-8}A) at applied bias of 0.75 V. The ~2 time's enhanced photoconductivity is observed for the gCT-0.75 than the other prepared catalyst and ~ 6 times than that of g-C_3N_4 (4.23 X 10^{-9}A). This photoconductivity result is in accordance with the higher photocatalytic performance of gCT-0.75 among prepared catalysts.

References

1. T. Su, Z. D. Hood, M.Naguib, L. Bai, S. Luo and C. M. Rouleau,I. N. Ivanov, H. Ji and Z. Qin ZiliWu, *Nanoscale*, 2019, **11**, 8138-8149.
2. Y.Li, L.Ding, Y. Guo, Z. Liang, H. Cui, and J. Tian, *ACS Appl. Mater. Interfaces.* 2019,**11** (44), 41440-41447.
3. Y.Sun, D. Jin, Y. Sun, X. Meng, Y. Gao, Y. D.Agnese, C.Gang and X.Wang, *J. Mater. Chem. A*,2018,**6**, 9124-9131.
4. J. Liu , H. Zhou , J. Fan and Q. Xiang, *Int. J. Hydrog. Energy*, 2022, **47**, 4546-4558.
5. X. An, W. Wang, J. Wang, H. Duan, J. Shi, X. Yu, *Phys. Chem. Chem. Phys.* 2018, **20**, 11405-11411.
6. Z. Ai, Y. Shao, B. Chang, L. Zhang, J.Shen, Y. Wu, B.Huang and X. Hao, *Appl. Catal., B* 2019, **259**, 118077.
7. J. Li, L. Zhao, S. Wang, J. Li, G. Wang and J. Wang, *Appl. Surf. Sci.*, 2020,**515**, 145922.
8. P. Lin, J. Shen, X. Yu, Q. Liu, D. Li and H. Tang, *Ceram. Int.*, 2019, **45**, 24656-24663.
9. J. Liu, H. Zhou, J. Fan and Q. Xiang, *Int. J. Hydrog. Energy*, 2022, **47**(7), 4546-4558.
10. H. Dang, S.Mao, Q. Li, M. Li, M. Shao, W. Wang and Q. Liu, *Catal. Sci. Technol*., 2022, **12**, 5032.
11. T. Su, Z.D. Hood, M. Naguib, L. Bai, S. Luo, C.M. Rouleau, I.N. Ivanov, H. Ji, Z. Qin and Z.Wu, *ACS Appl. Energy Mater.,* 2019, **2**,4640-4651.
12. F.Changa, Y. Xiea, C. Li, J. Chena, J. Luoa, X. Hub, J.Shen, *Appl. Surf. Sci*., 2013,**280**, 967-974.
13. G. R. Surikanti, P. Bajaj,and M. V. Sunkara, *ACS Omega,* 2019, **4**(17), 17301-17316
14. M.Nasri , M.Samsudin , A.Tahir and S. Sufian , *Energies*, 2022, **15**, 955.
15. Y. Xuanying , Y. Jili, T. Haifang, D. Yi, H. Bashir, Y.Kai , C. Yuqing, Liu Xia, *J. Colloid Interface Sci.*, 2020, **571**, 297-306.
16. M. Zhang, J Qin,S.Rajendran, X. Zhang and R. Liu, *Chem.Sus.Chem.,*2018,11, (24), 4226-4236.
17. H. Yu, H. Ma, X. Wu, X.Wang, J.Fan and J.Yu, *Solar Photocatalysis*,2021,5,(2),2000372.
18. J. Liu, H. Zhou, J. Fan and Q. Xiang, *Int.J.Hydrog.Energy*., 2022,47, 7, 4546-4558.
19. N. Jawale, S. Arbuj, G.Umarji, M. Shinde, B. Kale and S.B. Rane, *RSC Adv.,*2023, 13, 2418-2426.