Supplementary Information

An Investigation into the Stability of Graphitic C_3N_4 as a Photocatalyst for CO_2 Reduction

Francesca R. Pomilla[1, 2, 3], Maria A. L. R. M. Cortes[4], Jeremy W. J. Hamilton[4], Raffaele Molinari[1], Giuseppe Barbieri[3], Giuseppe Marcì* [2], Leonardo Palmisano[2], Preetam K. Sharma[4], Alan Brown [4], John A. Byrne[4]

1. Department of Environmental and Chemical Engineering, University of Calabria

Via Pietro Bucci, 87036 Rende CS, Italy

2. "Schiavello-Grillone" Photocatalysis Group. Dipartimento di Energia, Ingegneria dell'informazione e modelli Matematici (DEIM), Università di Palermo Viale delle Scienze, 90128 Palermo, Italy

3 Institute on Membrane Technology (ITM-CNR), National Research Council c/o University of Calabria, Cubo 17C, Via Pietro Bucci, 87036 Rende CS, Italy

4 NIBEC, Ulster University, Newtownabbey, BT37 0QB, UK

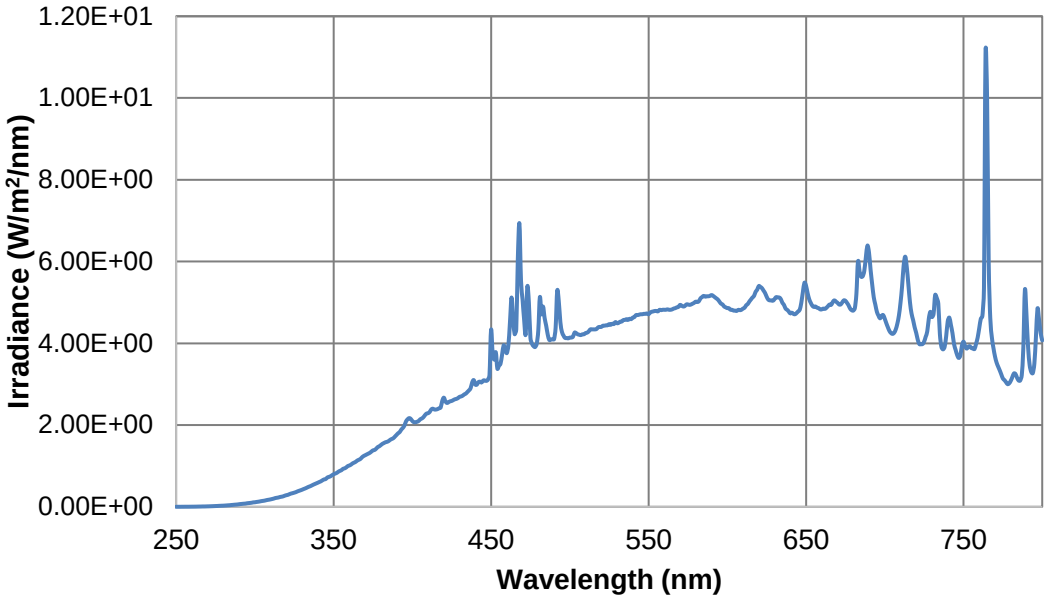


Figure S1 - Measured irradiance from 100W Xe lamp with IR filter.

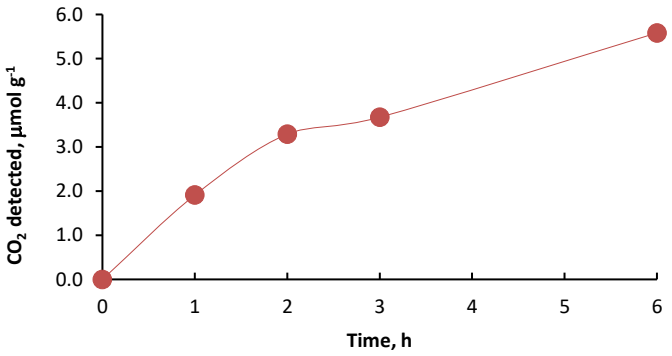


Figure S2 – Amount of CO_2 released in a batch reactor under irradiation at ambient pressure and N_2 atmosphere.

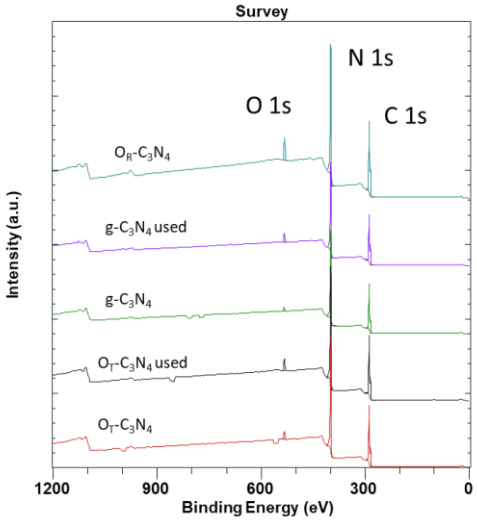
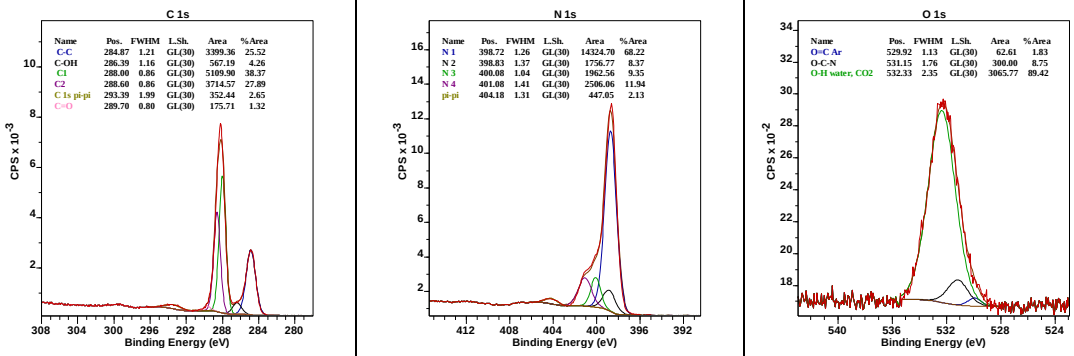
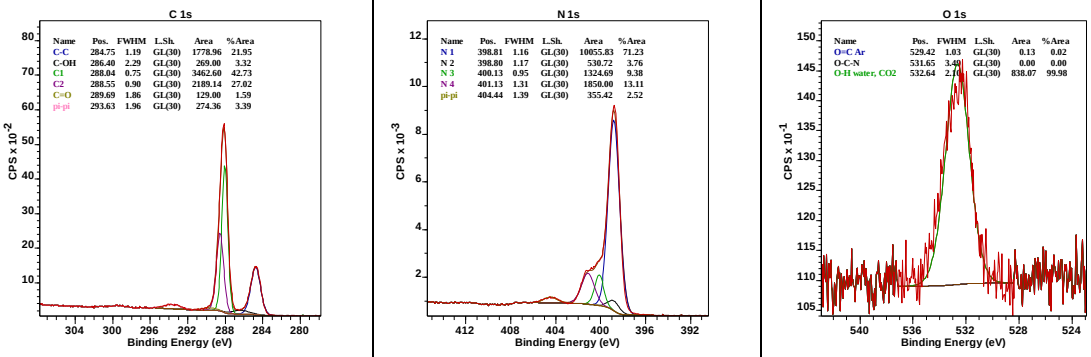


Figure S3 – Representative XPS survey analysis.

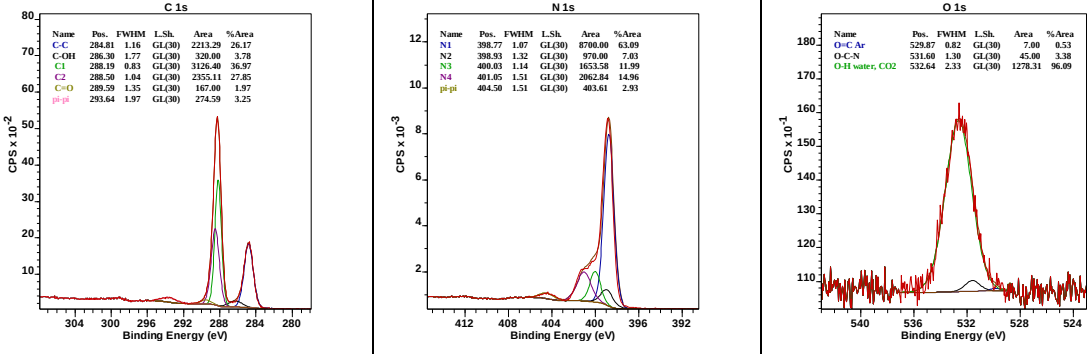
a


C 1s
Name Pos. FWHM L.Sh. GL(30) Area %Area
C-C 284.87 1.21 GL(30) 3399.36 25.52
C-OH 286.39 1.16 GL(30) 567.19 4.26
C1 288.00 0.86 GL(30) 5109.90 38.37
C2 288.60 0.86 GL(30) 3714.57 27.89
C 1s pi-pi 293.39 1.99 GL(30) 352.44 2.65
C=O 289.70 0.80 GL(30) 175.71 1.32
CPS x 10-3
Binding Energy (eV)
N 1s
Name Pos. FWHM L.Sh. GL(30) Area %Area
N 1 398.72 1.26 GL(30) 1432470 68.22
N 2 398.83 1.37 GL(30) 1756.77 8.37
N 3 400.08 1.04 GL(30) 1962.56 9.35
N 4 401.08 1.41 GL(30) 2506.06 11.94
pi-pi 404.18 1.31 GL(30) 447.05 2.13
CPS x 10-3
Binding Energy (eV)
O 1s
Name Pos. FWHM L.Sh. GL(30) Area %Area
O=C Ar 529.92 1.13 GL(30) 62.61 1.83
O-C-N 531.15 1.76 GL(30) 300.00 8.75
O-H water, CO2 532.33 2.35 GL(30) 3065.77 89.42
CPS x 10-2
Binding Energy (eV)

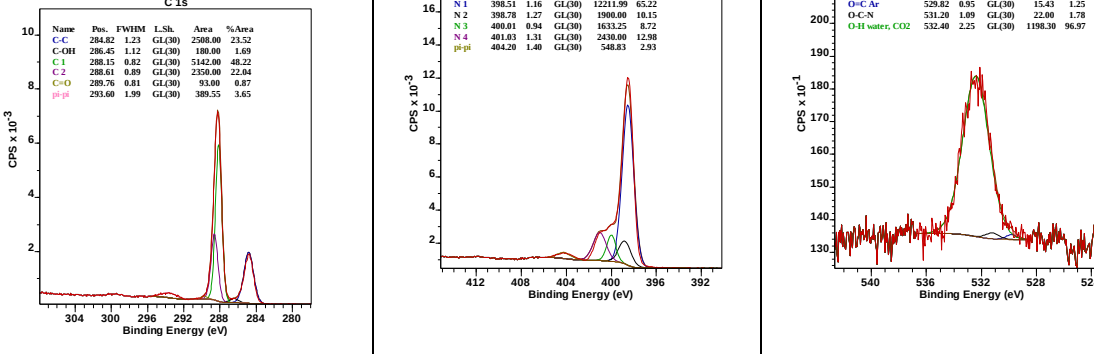
b


C 1s
Name Pos. FWHM L.Sh. GL(30) Area %Area
C-C 284.75 1.19 GL(30) 1778.96 21.95
C-OH 286.40 2.29 GL(30) 269.00 3.32
C1 288.04 0.75 GL(30) 3462.60 42.73
C2 288.55 0.90 GL(30) 2189.14 27.02
C=O 289.69 1.86 GL(30) 129.00 1.59
pi-pi 293.63 1.96 GL(30) 274.36 3.39
CPS x 10-2
Binding Energy (eV)
N 1s
Name Pos. FWHM L.Sh. GL(30) Area %Area
N 1 398.81 1.16 GL(30) 10055.83 71.23
N 2 398.80 1.17 GL(30) 530.72 3.76
N 3 400.13 0.95 GL(30) 1324.69 9.38
N 4 401.13 1.31 GL(30) 1850.00 13.11
pi-pi 404.44 1.39 GL(30) 355.42 2.52
CPS x 10-3
Binding Energy (eV)
O 1s
Name Pos. FWHM L.Sh. GL(30) Area %Area
O=C Ar 529.42 1.03 GL(30) 0.13 0.02
O-C-N 531.65 3.49 GL(30) 0.00 0.00
O-H water, CO2 532.64 2.10 GL(30) 838.07 99.98
CPS x 10-1
Binding Energy (eV)

c


C 1s
Name Pos. FWHM L.Sh. GL(30) Area %Area
C-C 284.81 1.16 GL(30) 2213.29 26.17
C-OH 286.30 1.77 GL(30) 320.00 3.78
C1 288.19 0.83 GL(30) 3126.40 36.97
C2 288.50 1.04 GL(30) 2355.11 27.85
C=O 289.59 1.35 GL(30) 167.00 1.97
pi-pi 293.64 1.97 GL(30) 274.59 3.25
CPS x 10-2
Binding Energy (eV)
N 1s
Name Pos. FWHM L.Sh. GL(30) Area %Area
N1 398.77 1.07 GL(30) 8700.00 63.09
N2 398.93 1.32 GL(30) 970.00 7.03
N3 400.03 1.14 GL(30) 1653.58 11.99
N4 401.05 1.51 GL(30) 2062.84 14.96
pi-pi 404.50 1.51 GL(30) 403.61 2.93
CPS x 10-3
Binding Energy (eV)
O 1s
Name Pos. FWHM L.Sh. GL(30) Area %Area
O=C Ar 529.87 0.82 GL(30) 7.00 0.53
O-C-N 531.60 1.30 GL(30) 45.00 3.38
O-H water, CO2 532.64 2.33 GL(30) 1278.31 96.09
CPS x 10-1
Binding Energy (eV)

d


C 1s
Name Pos. FWHM L.Sh. GL(30) Area %Area
C-C 284.82 1.23 GL(30) 2508.00 23.52
C-OH 286.45 1.12 GL(30) 180.00 1.69
C 1 288.15 0.82 GL(30) 5142.00 48.22
C 2 288.61 0.89 GL(30) 2350.00 22.04
C=O 289.76 0.81 GL(30) 93.00 0.87
pi-pi 293.60 1.99 GL(30) 389.55 3.65
CPS x 10-3
Binding Energy (eV)
N 1s
Name Pos. FWHM L.Sh. GL(30) Area %Area
N 1 398.51 1.16 GL(30) 12211.99 65.22
N 2 398.78 1.27 GL(30) 1900.00 10.15
N 3 400.01 0.94 GL(30) 1633.25 8.72
N 4 401.03 1.31 GL(30) 2430.00 12.98
pi-pi 404.20 1.40 GL(30) 548.83 2.93
CPS x 10-3
Binding Energy (eV)
O 1s
Name Pos. FWHM L.Sh. GL(30) Area %Area
O=C Ar 529.82 0.95 GL(30) 15.43 1.25
O-C-N 531.20 1.09 GL(30) 22.00 1.78
O-H water, CO2 532.40 2.25 GL(30) 1198.30 96.97
CPS x 10-1
Binding Energy (eV)

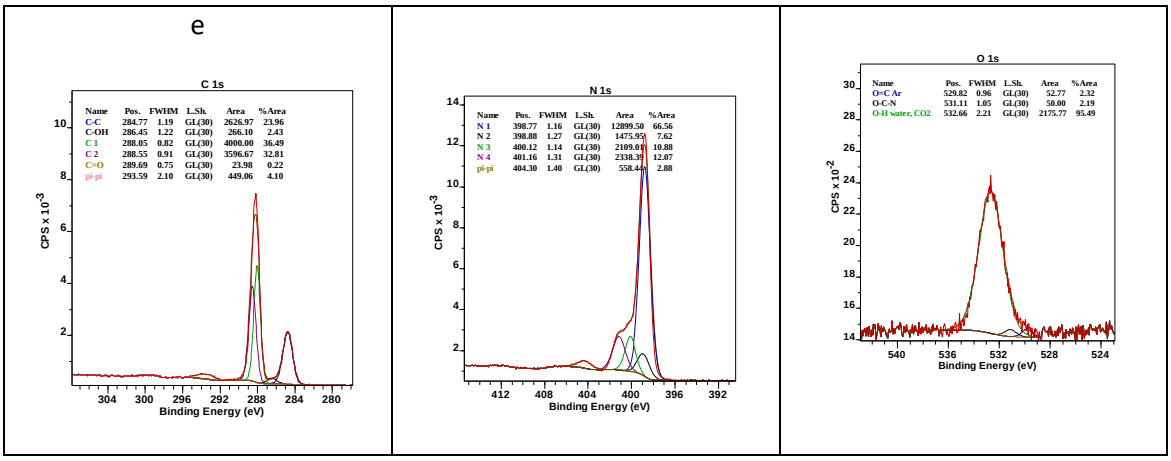


Figure S4 – Representative C, N and O XPS analysis of a)$O_RC_3N_4$, b) g-C_3N_4, c) g-C_3N_4used, d)O_T-C_3N_4 and e) O_T-C_3N_4 used .

Table S1 - Formal Quantum Yield (QY) and CO generated by all sample used and reused after 5 hours of irradiation time in presence of CO_2 and water.

Samples	**QY %**	**ppm**	**μmol g^{-1}**
C_3N_4 R1	0.0132	18.9	13.0
C_3N_4 R2	0.0042	6.00	4.10
O_T-C_3N_4 R1	0.0118	16.9	11.7
O_T-C_3N_4 R2	0.0057	8.10	5.60
O_R-C_3N_4R1	0.0035	5.10	3.50
O_R-C_3N_4R2	0.0020	2.80	1.90