Photocatalytic Hydrogen Generation from Water/Methanol Mixtures Using Halogenated Reconstituted Graphene

Rafael Ballesteros-Garrido, Herme G. Baldoví, Marcos LaTorre, Mercedes Alvaro, Hermenegildo Garcia*

Electronic Supplementary Information

S1. Experimental details

All reagents were purchased from commercially firms and were employed without extra purification. Raman spectra were recorded at ambient temperature with a 514 nm laser excitation at 2 W power on a *Renishaw In Via* Raman spectrometer equipped with a CCD detector. The Raman signal was accumulated over 5 min without any sing of sample thermal decomposition. Different areas of the sample were monitored using a confocal microscope (10×10 μm^2). IR spectra were recorded with a Brucker ATR spectrometer. TEM images were recorded in a Philips CM300 FEG system with an operating voltage of 100 kV. SEM images were recorded with a JEOL JSM6300. XPS spectra were recorded on a SPECS spectrometer equipped with a Phoibos 150 9MCD detector using a non-monochromatic X-ray source (Al and Mg) operating at 200 W. The samples were evacuated in the prechamber of the spectrometer at 1×10^{-9} mbar. The materials were exfoliated in water by sonication. The third harmonic (355 nm) output of a Nd-YAG laser (7ns FWWHP, 350 mW) was used as irradiation source for the photocatalytic hydrogen production tests. The photorreactor was a cylindrical quartz vessel (55mL total volume) with an inlet and outlet bearing independent valves that has a manometer to determine the pressure. The system was purged with a flow of argon for 30 min before irradiation to ensure the absence of oxygen. The photocatalytic solution (30 mL) containing 30 v/v% of methanol as sacrificial electron donor was continuously stirred during irradiation. All the experiments were performed at the same laser energy and using optically matched solutions of the photocatalyst at the laser wavelength (0.2 absorbance at 355 nm).The experiments were carried out at room temperature and the percentage of hydrogen evolved in the photorreactor during the irradiation was determined by gas chromatography (GS_MOL 15 meters column ID 0.55 mm TCD from J&W Scientific). Experiments were carried out in duplicated with an estimated error of 5%. Apparent quantum yields were calculated from the number of moles of hydrogen formed at 2 h multiplied by two divided by the number of photons emitted in this time. The number of photons was calculated multiplying the power of the laser (350mW) by the time in seconds and divided by the energy of one single photon of 355 nm. At the end of the reaction, some degree of aggregation was visually observed as evidenced by the appearance of some black precipitate. The absence of X^- in the aqueous solutions after the photocatalytic runs was determined by adding to the clear supernatant after the irradiation and removal of (X)G, 1 M aqueous solution of $AgNO_3$ (for **(Cl)G** Kps 1.77×10^{-10} M^{-2}, **(Br)G** Kps 5.35×10^{-13} M^{-2} and **(I)G** Kps 8.52×10^{-17} M^{-2}) or $CaCl_2$ (for **(F)G** Kps 3.45×10^{-11} M^{-2}) and no observing the evolution of any precipitate after 8 h. This indicates that the concentration of halides must be below the corresponding solubility products. Laser flash photolysis (LFP) experiments were performed by using a QswitchedNd:YAG laser (Quantel Brilliant, 355 nm, 20 mJ per pulse, 5 ns fwhm) coupled to a mLFP-111 Luzchem miniaturized equipment. This transient absorption spectrometer includes a ceramic xenon light source, 125 mm monochromator, Tektronix 9-bit digitizer TDS-3000 series with 300 MHz bandwidth, compact photomultiplier and power supply, cell holder and fiber optic connectors, fiber optic sensor for laser-sensing pretrigger signal, computer interfaces, and a software package developed in the LabVIEW environment from National Instruments. The LFP equipment supplies 5 V trigger pulses with programmable frequency and delay. The rise time of the detector/digitizer is ~3 ns up to 300 MHz (2.5 GHz sampling). The monitoring beam is provided by a ceramic xenon lamp and delivered through fiber optic cables. The laser pulse is probed by a fiber that synchronizes the LFP system with the digitizer operating in the pretrigger mode. All transient spectra were recorded using 10 mm × 10 mm quartz cells with a capacity of 4 mL and were bubbled for 30 min with Ar beforesignal acquisition. The absorbance of the samples was 0.2 at the laser excitation wavelength (355 nm).

S.2: Preparation of (F)G, (Cl)G, (Br)G, (I)G and rG,

(F)G was synthesized by a simple hydrothermal reaction of GO dispersion in wáter and HF (water solution 40%). 25 mL GO dispersion (2 mg/mL) was ultrasonicated for 2 h. The mixture was transferred into a 50mL Teflon-lined autoclave, 312 μL of HF were added. The reaction mixture was maintained at 150 ºC for 30 h. The autoclave was cooled to room temperature. At last, the product was filtered using nylon membrane (0.2 μm pore) and washed with ultrapure wáter (3 times 20 mL). The crude black powder was dried under vacuum at 70 ºC.

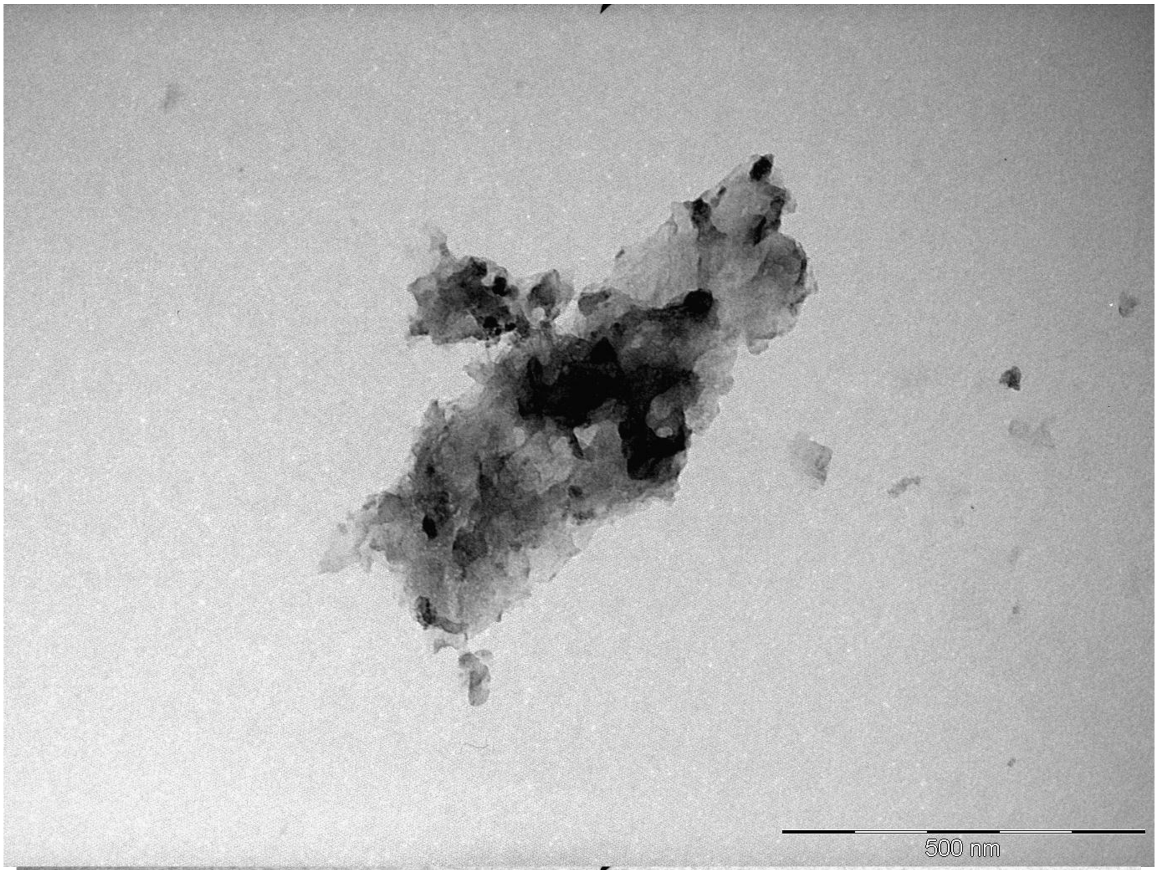
(Cl)G was synthesized by a simple hydrothermal reaction of GO dispersion in wáter and HCl (water solution 37%). 25 mL GO dispersion (2 mg/mL) was ultrasonicated for 2 h. The mixture was transferred into a 50 mL Teflon-lined autoclave, 850 μL of HCl were added. The reaction mixture was maintained at 150 ºC for 30 h. The autoclave was cooled to room temperature. At last, the product was filtered using nylon membrane (0.2 μm pore) and washed with ultrapure water (3 times 20 mL). The crude black powder was dried under vacuum at 70 ºC.

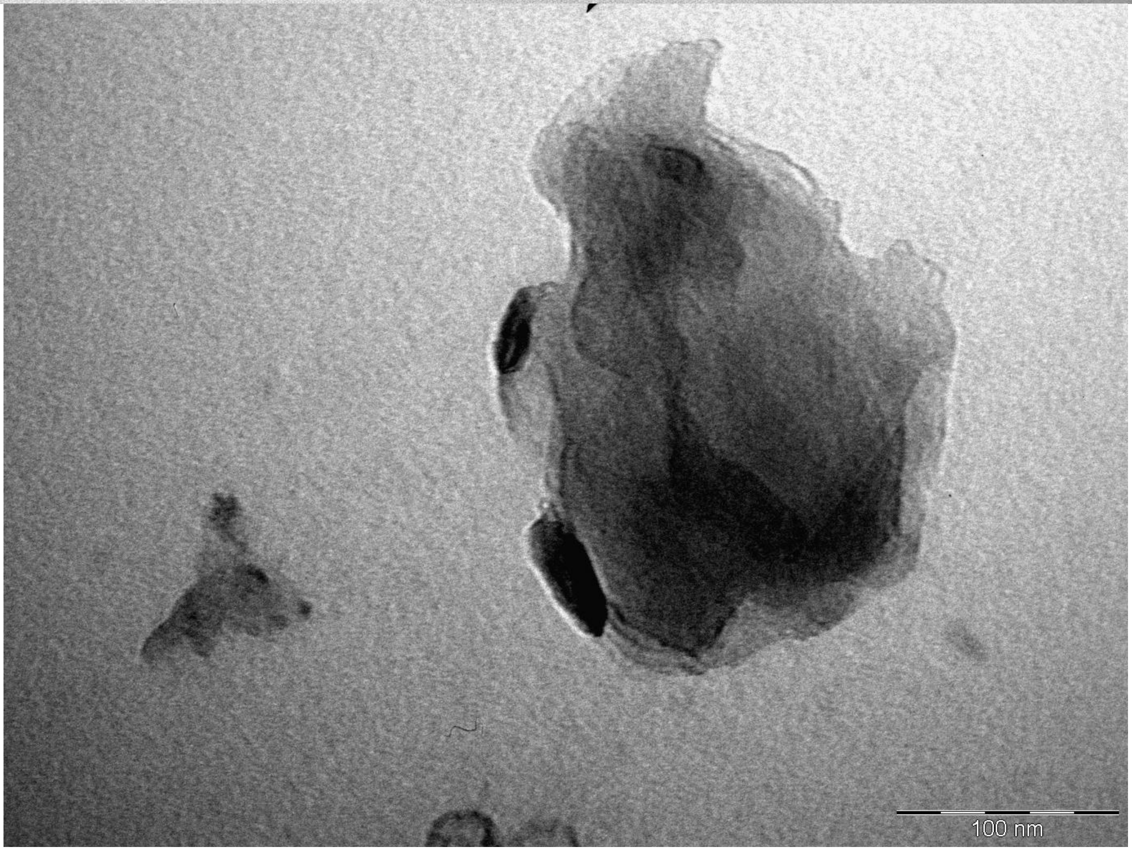
(Br)G was synthesized by a simple hydrothermal reaction of GO dispersion in wáter and HBr (water solution 33%). 25 mL GO dispersion (2 mg/mL) was ultrasonicated for 2 h. The mixture was transferred into a 50 mL Teflon-lined autoclave, 1.5 mL of HBr were added. The reaction mixture was maintained at 150 ºC for 30 h. The autoclave was cooled to room temperature. At last, the product was filtered using nylon membrane (0.2 μm pore) and washed with ultrapure water (3 times 20 mL). The crude black powder was dried under vacuum at 70 ºC.

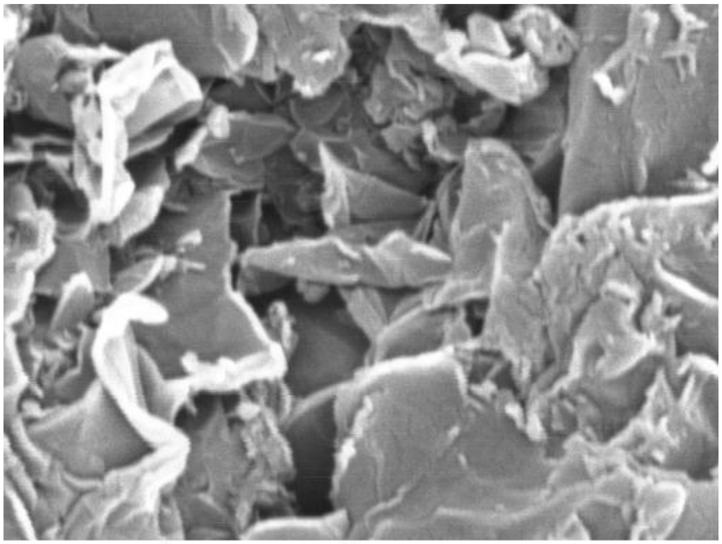
(I)G was synthesized by a simple hydrothermal reaction of GO dispersion in wáter and HI (water solution 57%). 25 mL GO dispersion (2 mg/mL) was ultrasonicated for 2 h. The mixture was transferred into a 50 mL Teflon-lined autoclave, 1.8 μL of HI were added. The reaction mixture was maintained at 150 ºC for 30 h. The autoclave was cooled to room temperature. At last, the product was filtered using nylon membrane (0.2 μm pore) and washed with ultrapure water (3 times 20 mL). The crude black powder was dried under vacuum at 70 ºC.

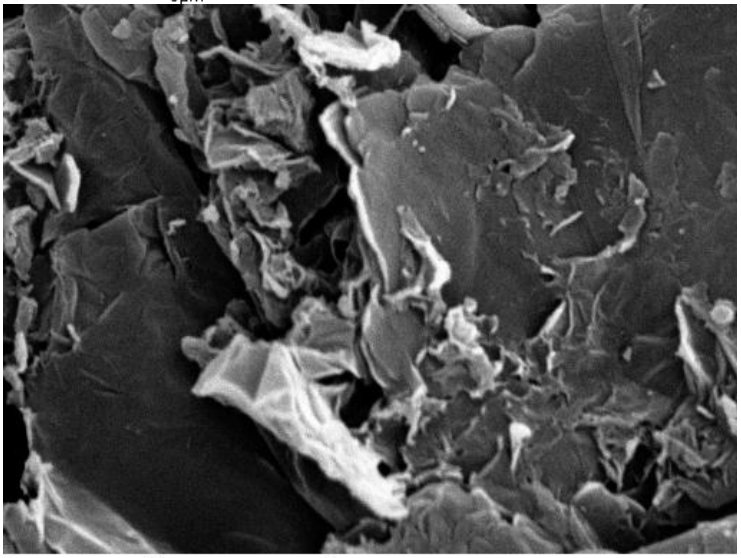
rG was synthesized by a simple hydrothermal reaction of GO dispersion in water. 40 mL GO dispersion (2 mg/mL) was ultrasonicated for 2 h. The mixture was transferred into a 50mL Teflon-lined autoclave and maintained at 150 ºC for 30 h. The autoclave was cooled to room temperature. At last, the product was filtered using nylon membrane (0.2 μm pore) and washed with ultrapure wáter (3 times 20 mL). The crude black powder was dried under vacuum at 70 ºC.

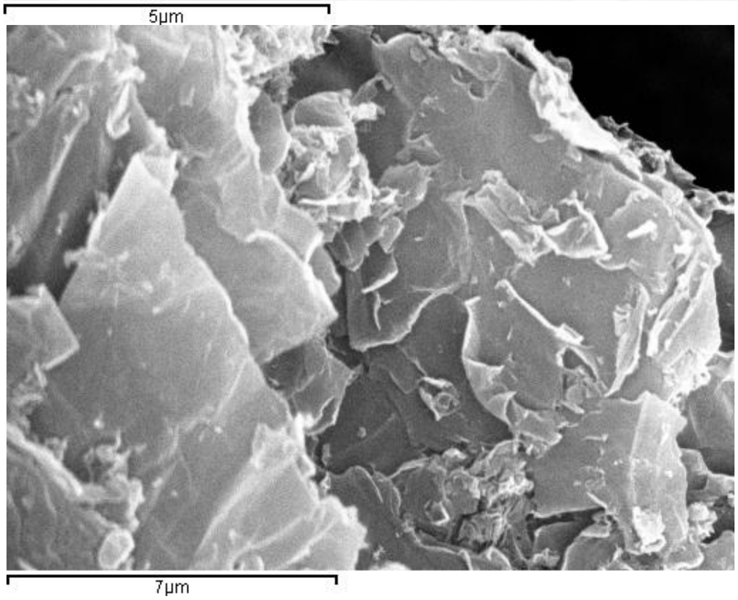
S.3: Selected TEM and SEM Images (F)G:



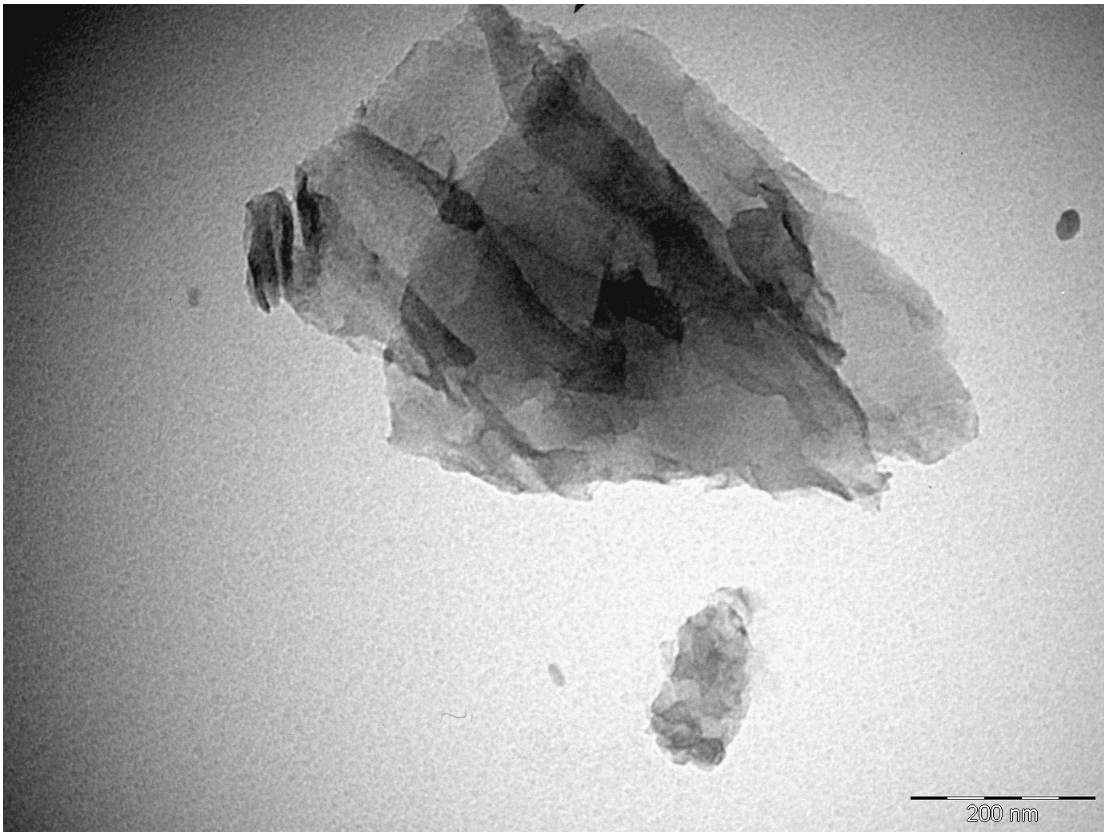


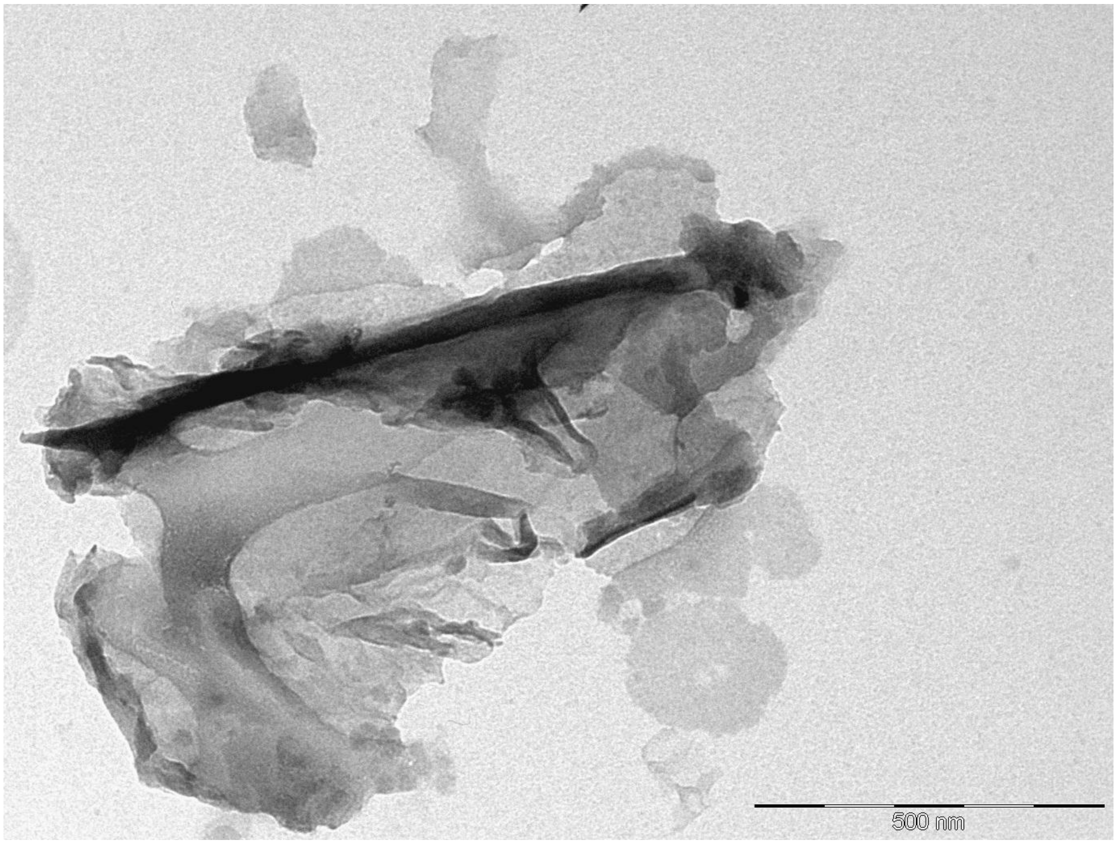

3μm

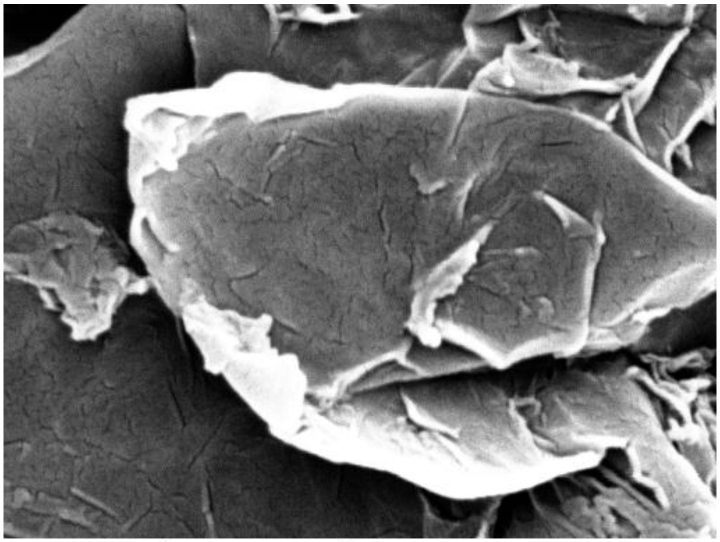

5μm


7μm

(Cl)G:



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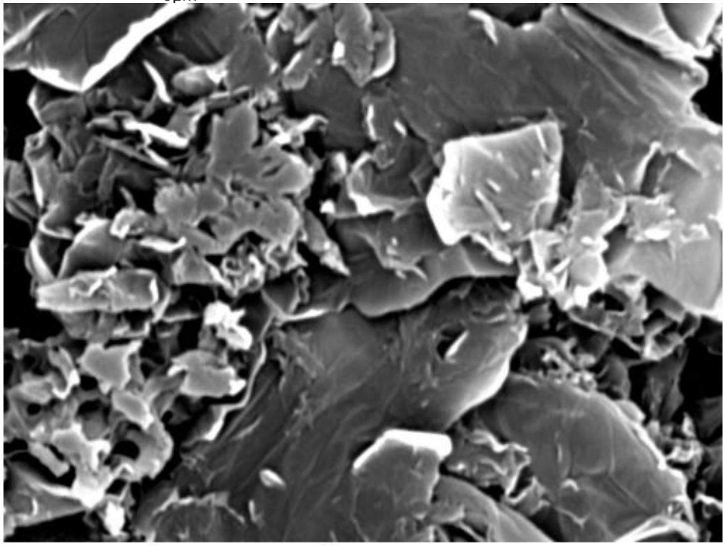
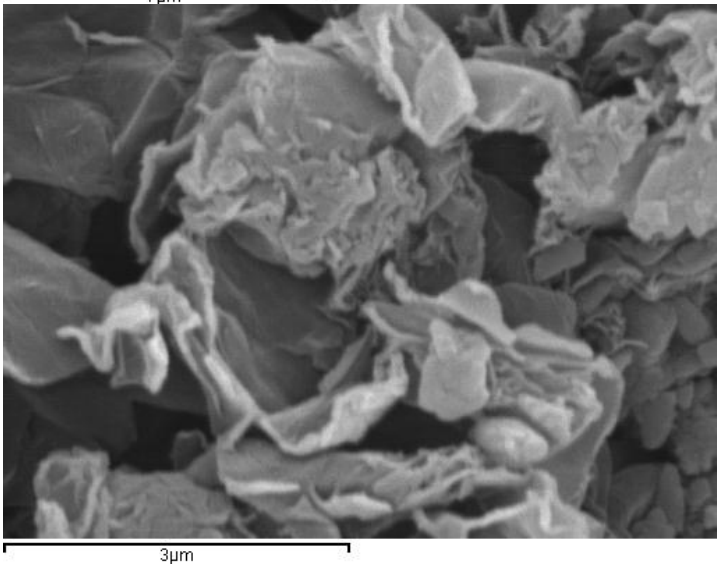
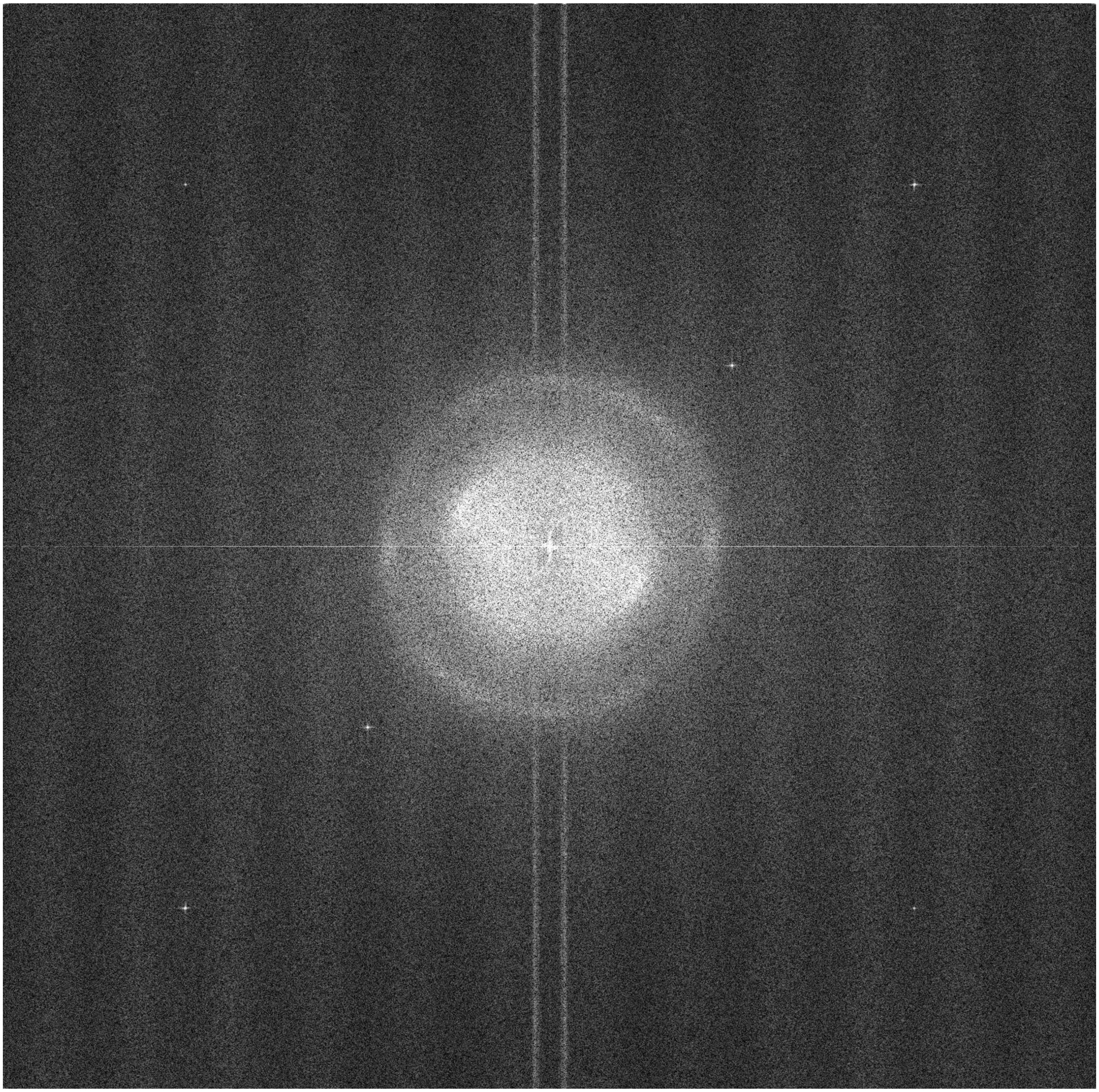
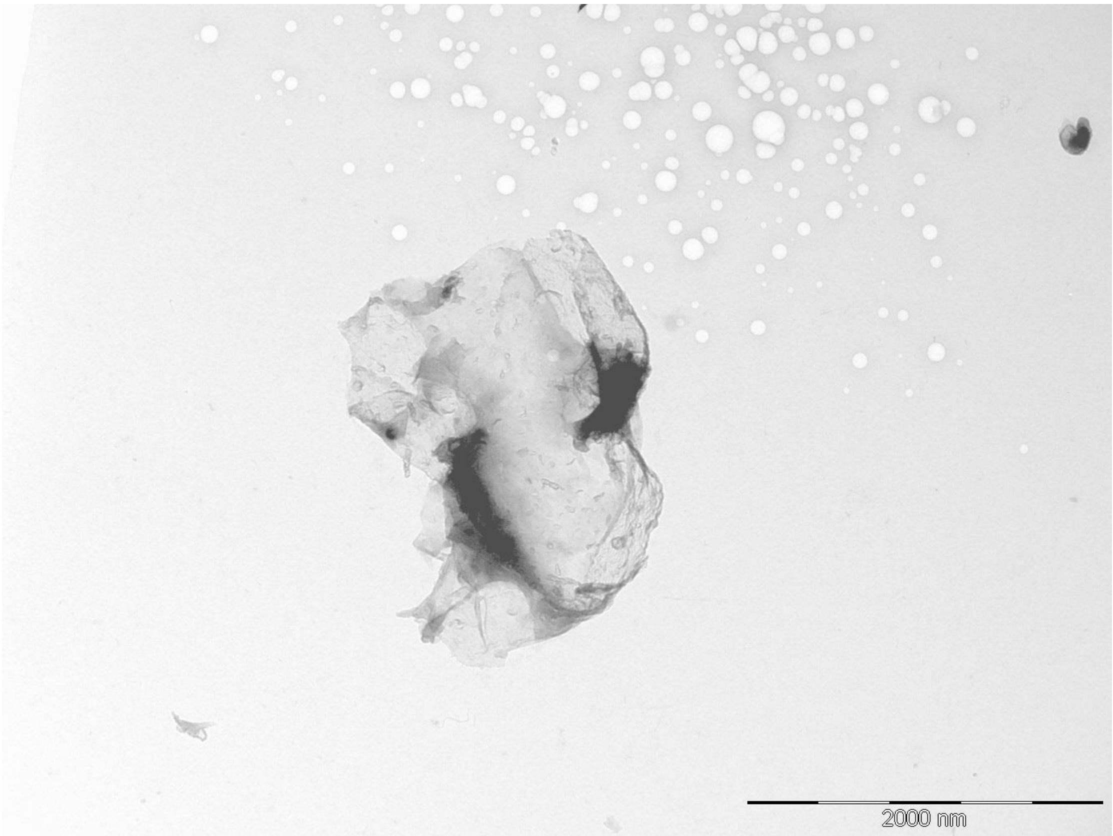

7μm

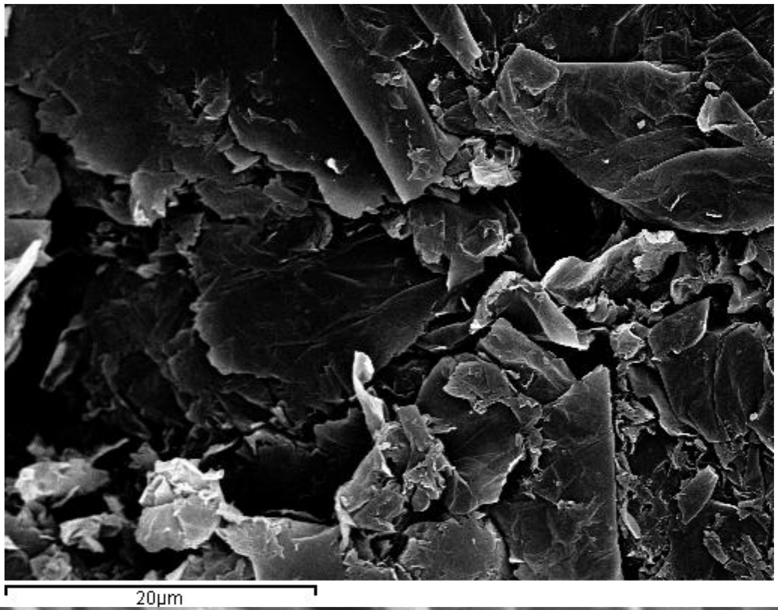

3μm

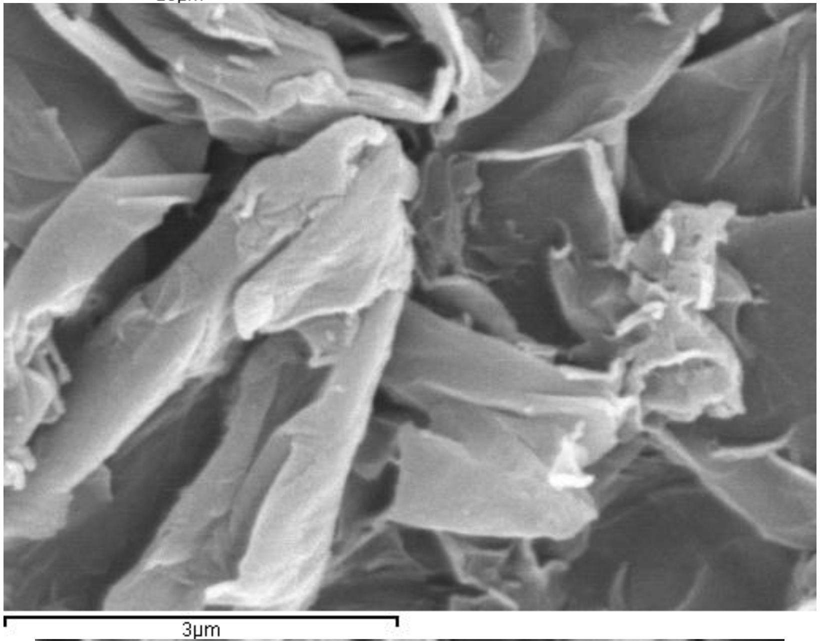
Electron diffraction pattern for **(Cl)G**



(Br)G




20μm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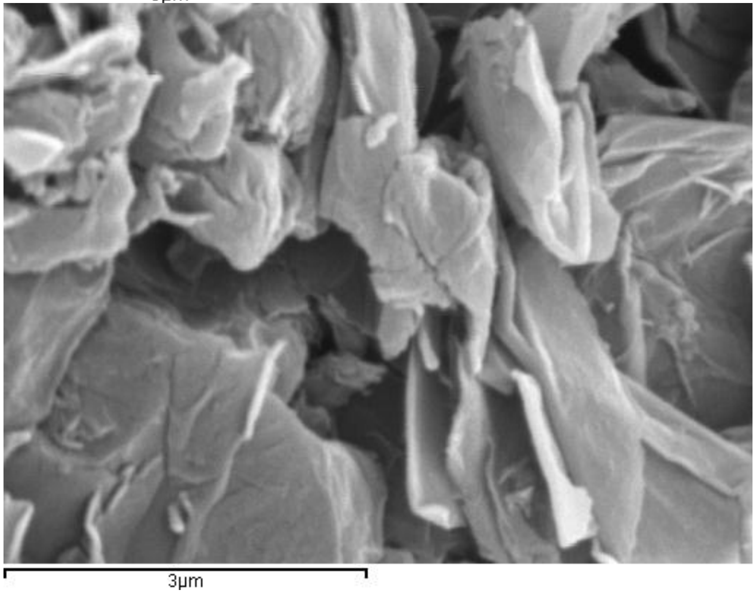
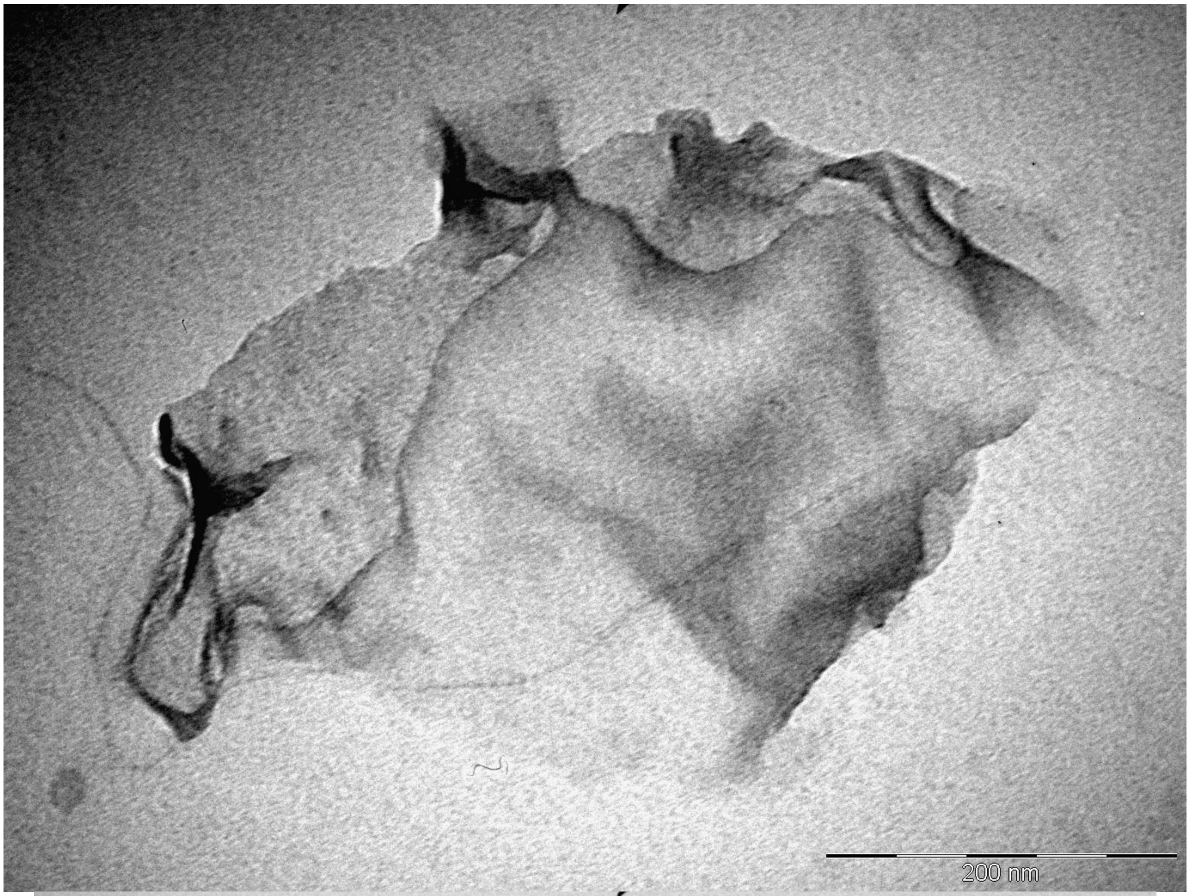
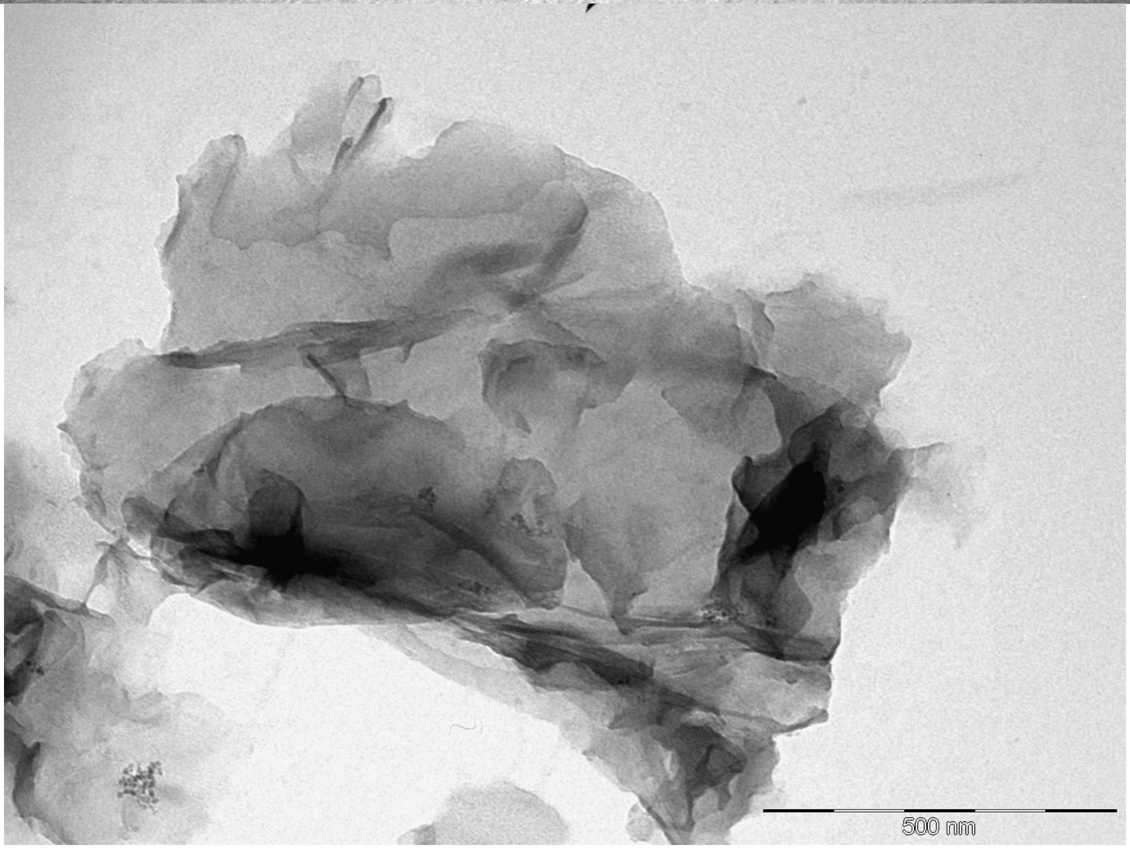
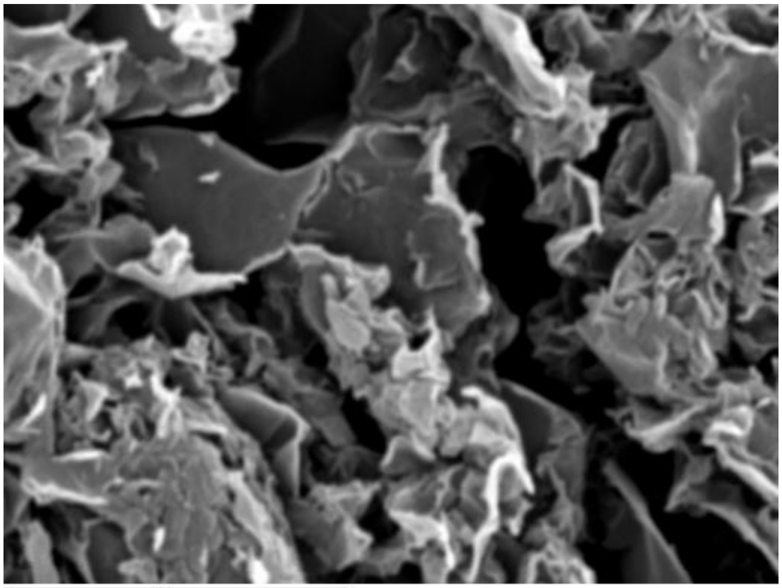
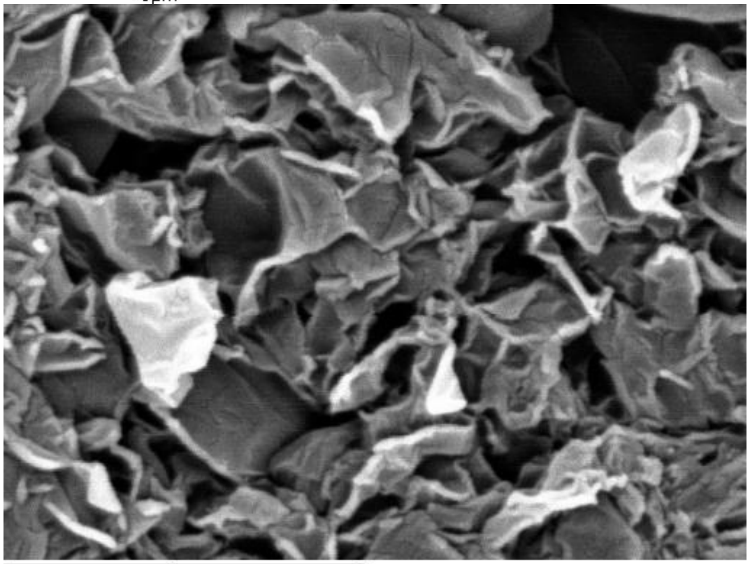

3μm

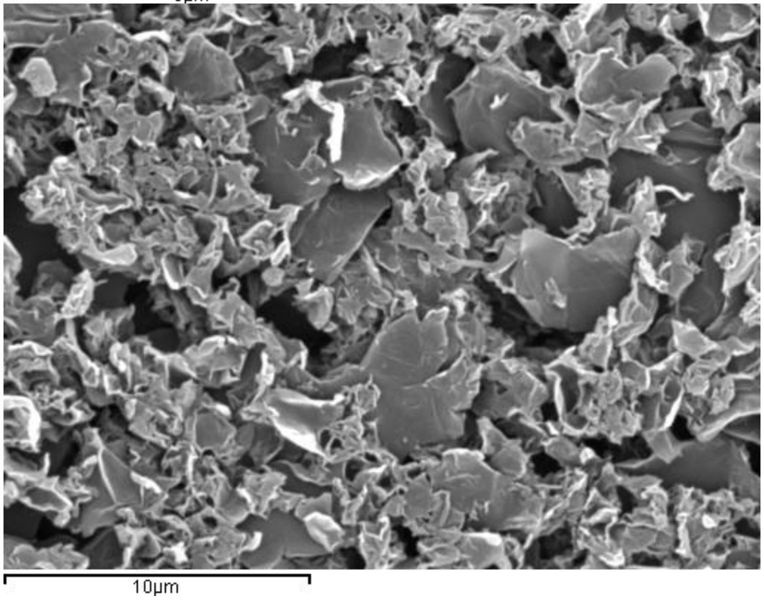
(I)G



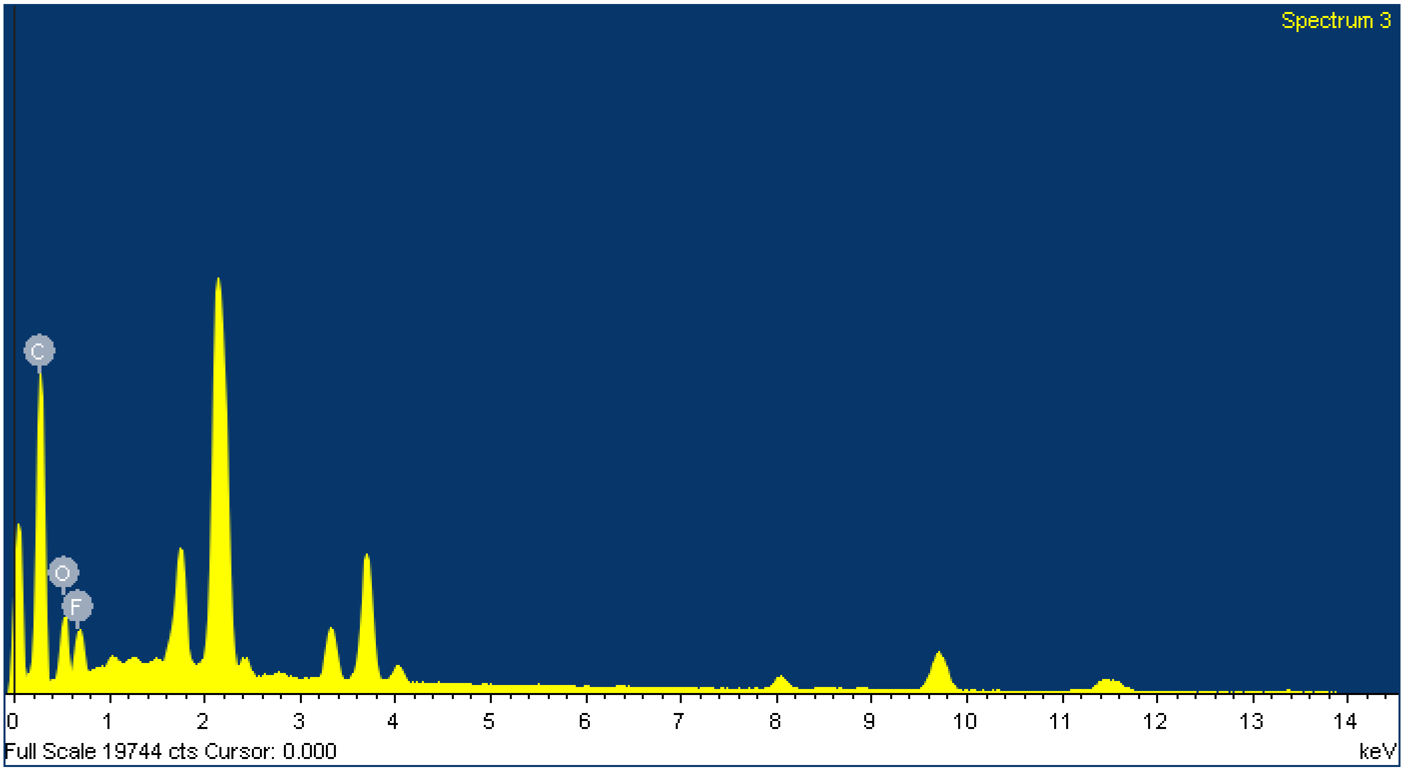



5μm


3μm

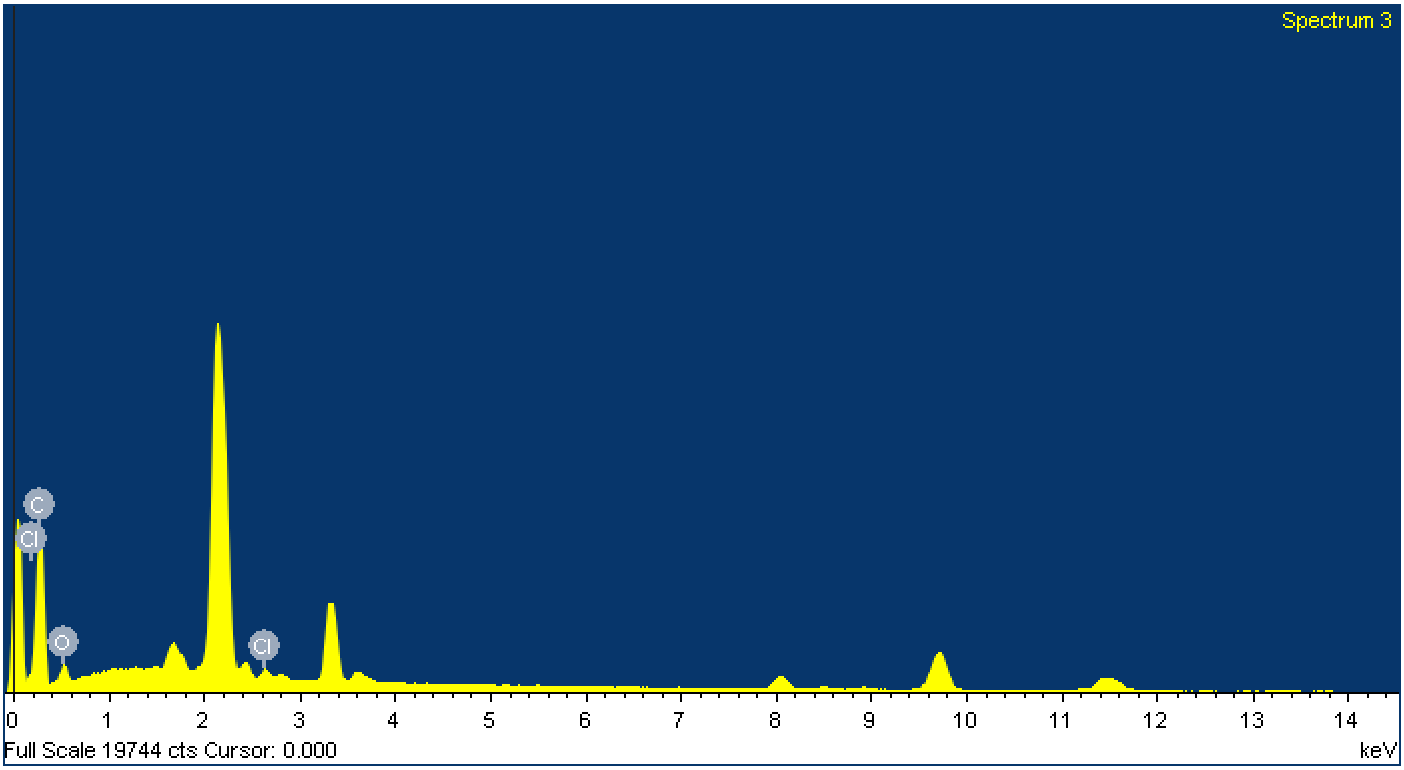

10μm

S.4: EDX: (F)G



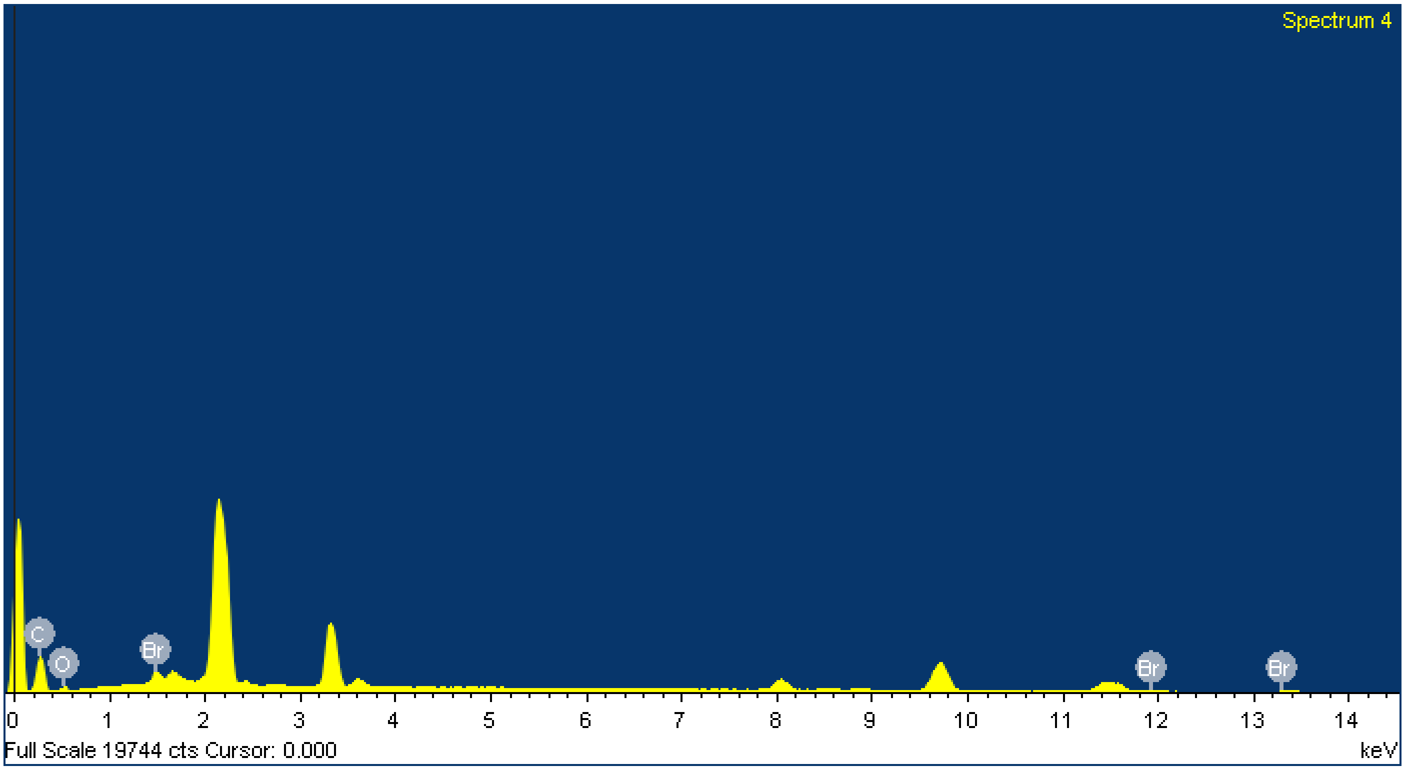
Element	Weight%	Atomic%
C K	58.21	66.64
O K	22.89	19.67
F K	18.90	13.68
Totals	100.00	

EDX: **(Cl)G**



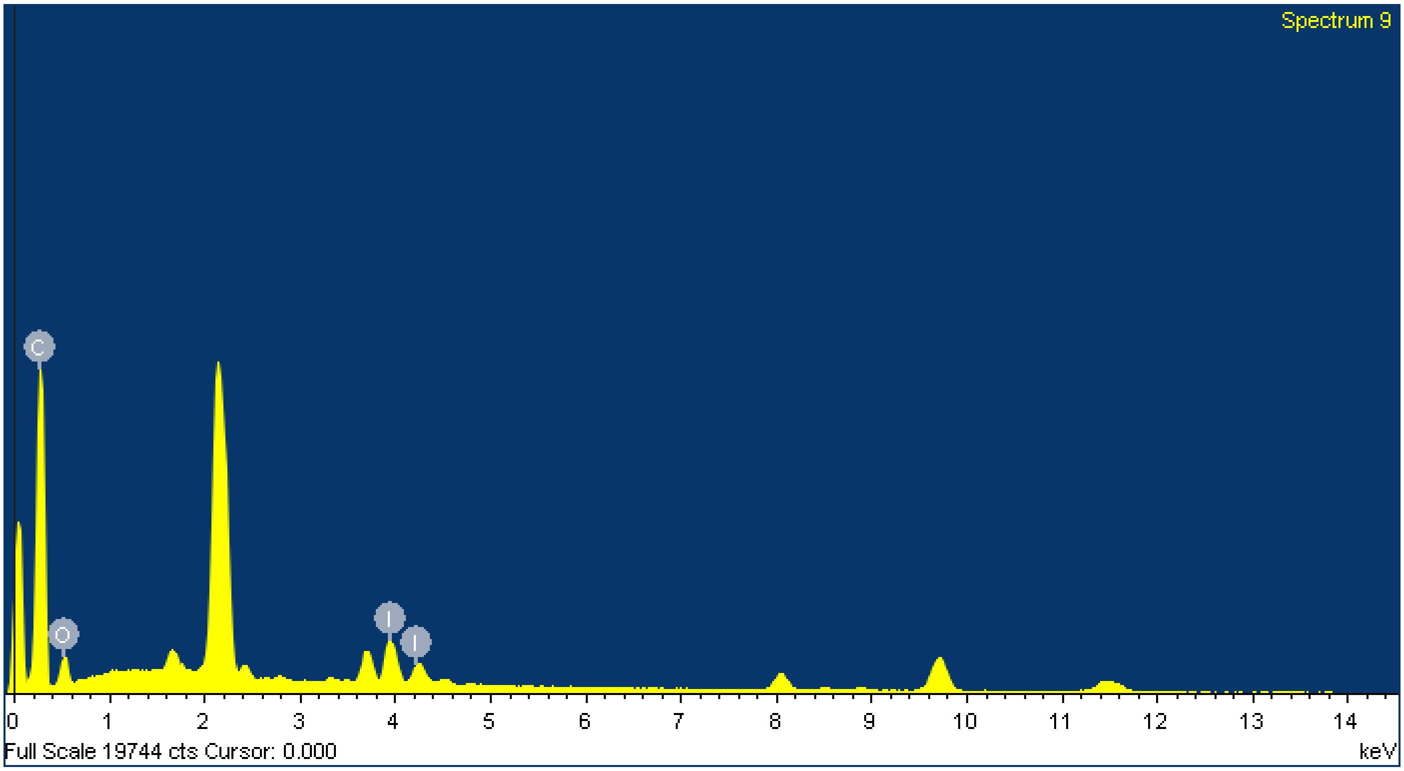
Element	Weight%	Atomic%
C K	75.95	81.34
O K	22.51	18.10
Cl K	1.54	0.56
Totals	100.00	

EDX: **(Br)G**



Element	Weight%	Atomic%
C K	74.36	83.27
O K	18.46	15.52
Br L	7.18	1.21
Totals	100.00	

EDX: **(I)G**

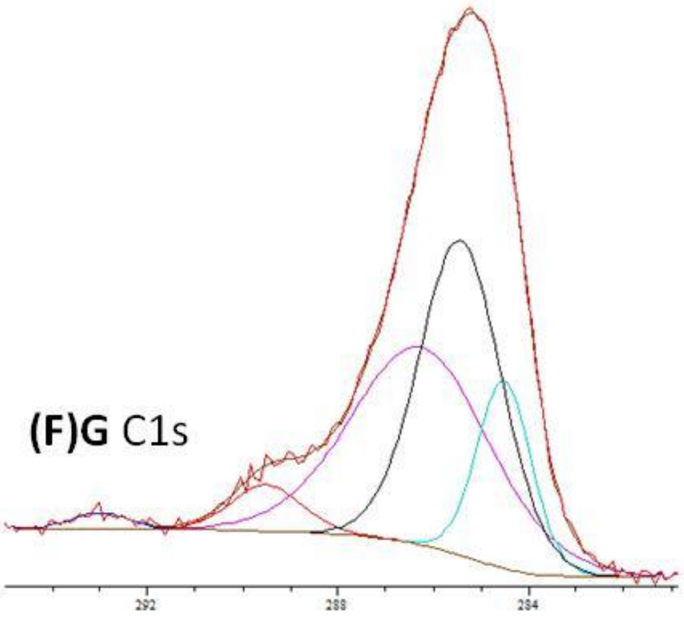


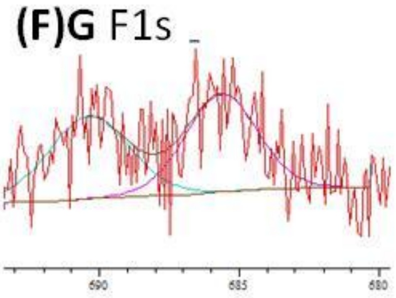
Element	Weight%	Atomic%
C K	68.85	83.20
O K	16.69	15.14
I L	14.46	1.65
Totals	100.00	

S.5. XPS:

(F)G

C1s	C=C	284.5	10.30%
C1s	C-C, C-O	285.3	50.60%
C1s	C=O	286.5	32.80%
C1s	C-F	289.5	4.85%
C1s	C-F2 /π-π*	292.9	1.36%





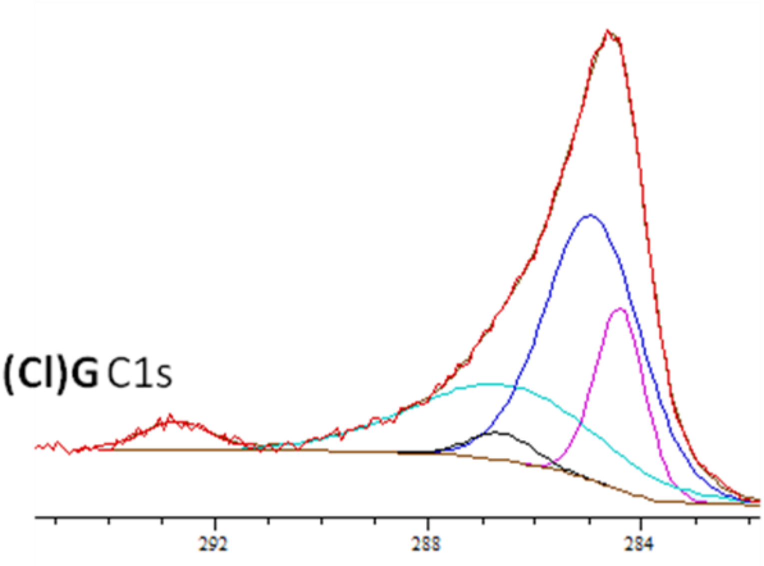
F content calculated by correlation of C1s and E.A. = 4.38 %

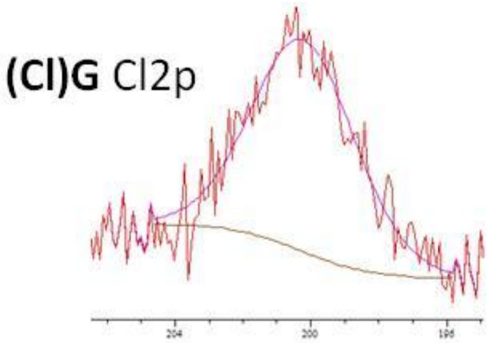
Ratio C/F = 16.6

Carbon-fluorine eV values were determined according to Z. Wang J. Wang, Z. Li, P. Gong, X. Liu, L. Zhang, J. Ren, H. Wang and S. Yang, *Carbon*, 2012, **50**, 5403,

(Cl)G

C1s	C=C	284.4	17,29%
C1s	C-C,C-O	285.9	48.80%
C1s	C=O	286.5	27.02%
C1s	C-Cl	286.7	3.59%
C1s	π-π*	292.65	3.29%





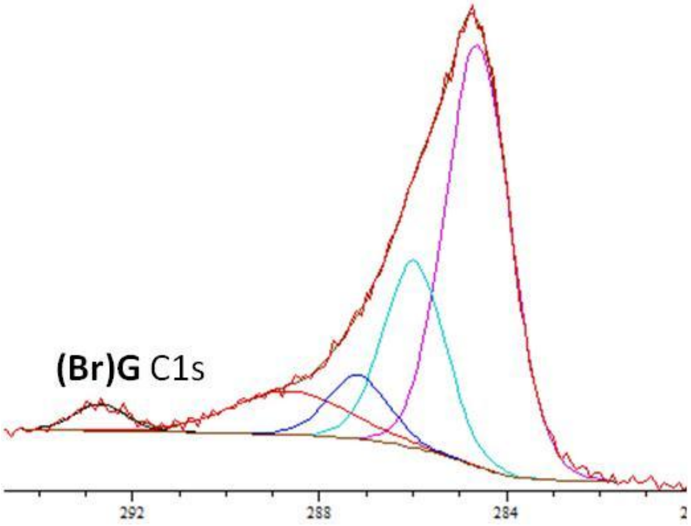
Cl content calculated by correlation of C1s and E.A. = 2.28 %

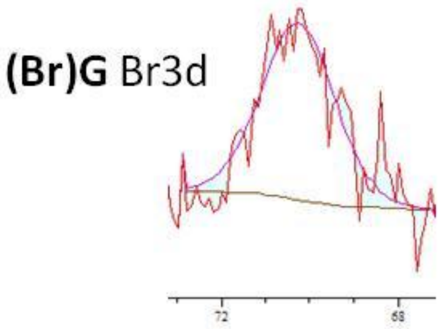
Ratio C/Cl = 85

Carbon- Chlorine eV values were determined according to H.L. Poh, P. Simek, Z. Sofer and M. Pumera, *Chem. Eur. J.*, 2013, **19**, 2655.

(Br)G

C1s	C=C	284.61	55.66%
C1s	C-C,C-O	285.97	23.39%
C1s	C=O	288.6	10.27%
C1s	C-Br	287.17	7.82%
C1s	p-p*	292.7	2.88%





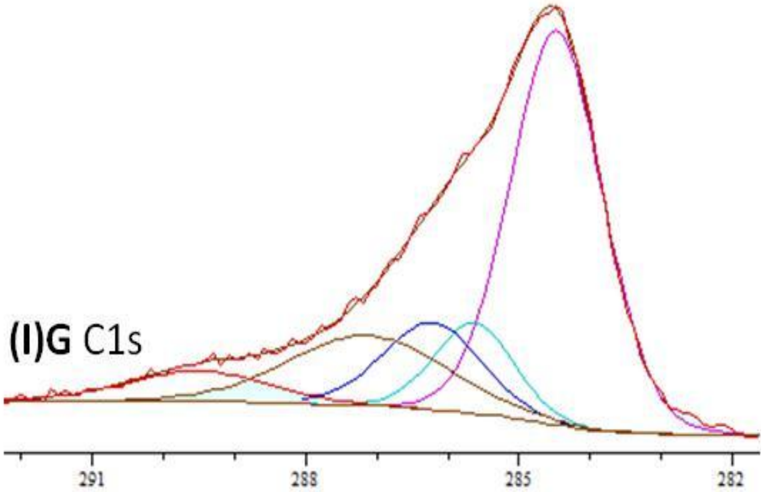
Br content calculated by correlation of C1s and E.A. = 5.36 %

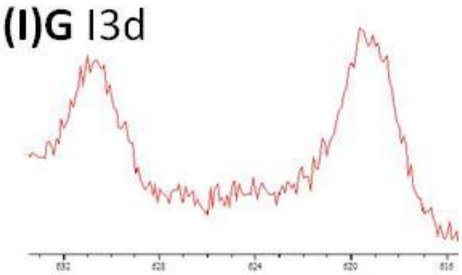
Ratio C/Br = 42

Carbon- Bromine eV values were determined according to H.L. Poh, P. Simek, Z. Sofer and M. Pumera, *Chem. Eur. J.*, 2013, **19**, 2655.

(I)G

C1s	C=C	284.47	54.11%
C1s	C-C	285.63	10.70%
C1s	C-O	286.22	12.69%
C1s	C=O	287.12	16.40%
C1s	C-I	289.5	6.10%





I content calculated by correlation of C1s and E.A. = 4.33 %

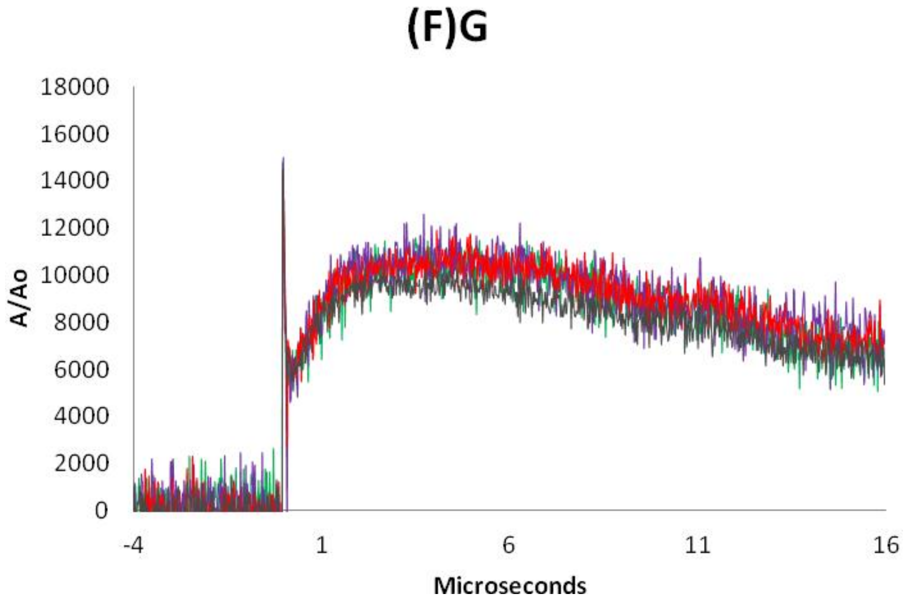
Ratio C/I = 109.

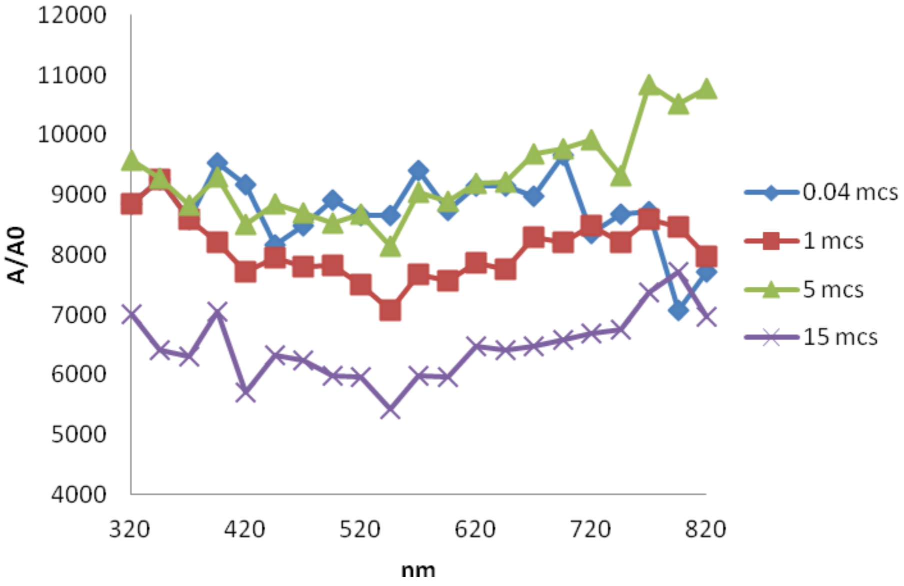
Carbon- Iodine eV values were determined according to H.L. Poh, P. Simek, Z. Sofer and M. Pumera, *Chem. Eur. J.*, 2013, **19**, 2655.

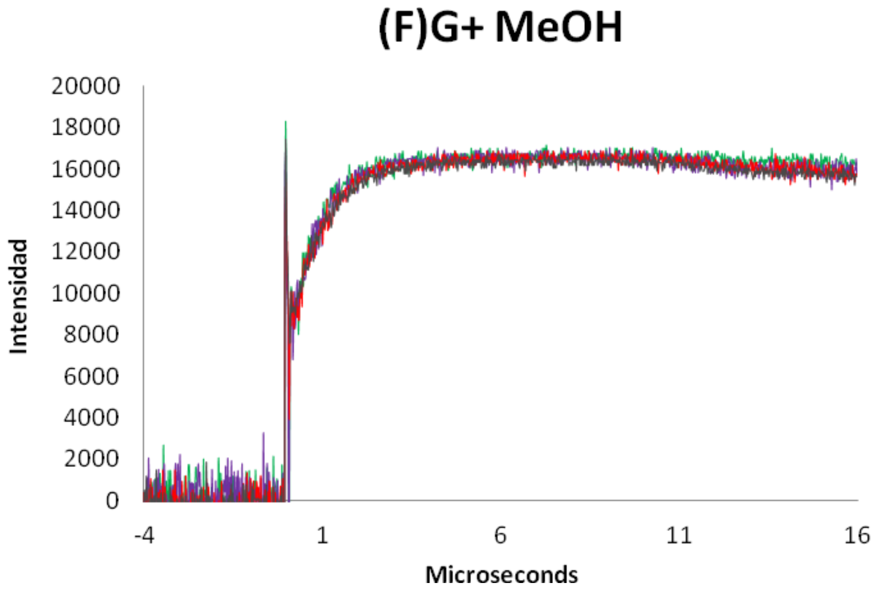
C1s/O1s ratios:

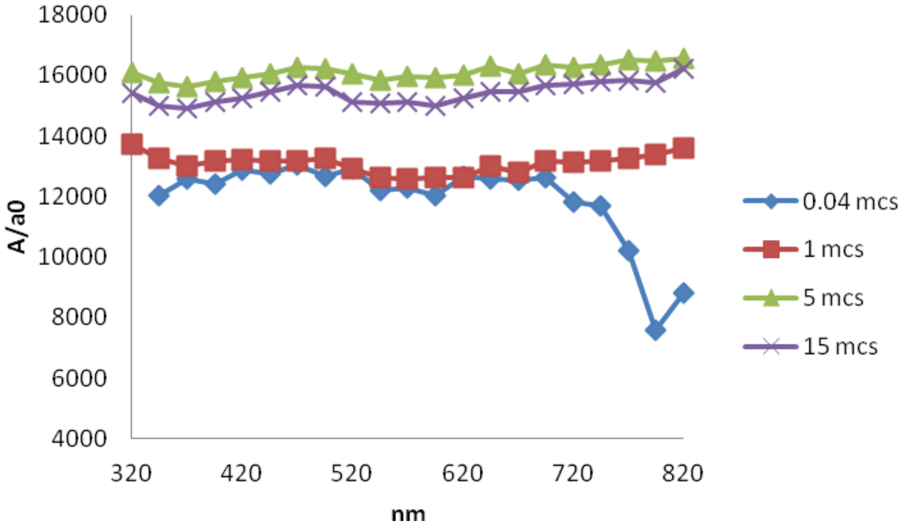
(F)G	**Peak**	**ratio (%)**
C1s	285.2	46.69
O1s	532.5	53.31
(Cl)G	**Peak**	**ratio (%)**
C1s	284.64	54.88
O1s	532.02	45.12
(Br)G	**Peak**	**ratio (%)**
C1s	284.7	56.98
O1s	532.89	43.02
(I)G	**Peak**	**ratio (%)**
C1s	284.49	58.74
O1s	532.91	41.26

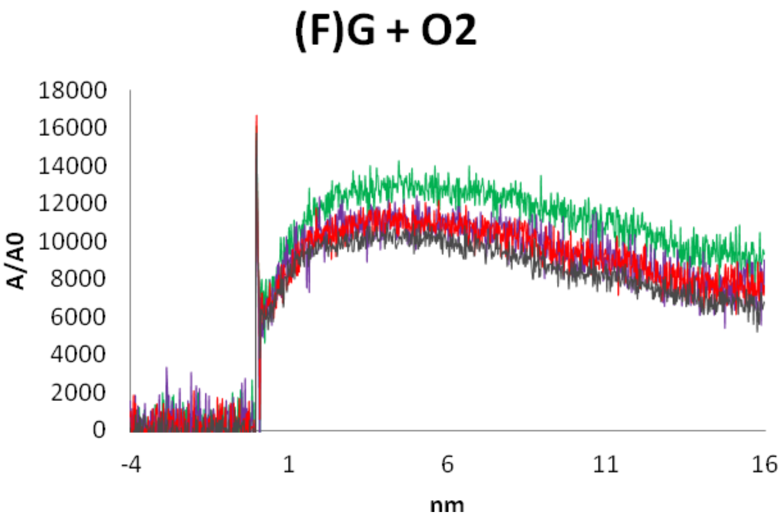
S.6: LASER FLASH PHOTOLYSIS





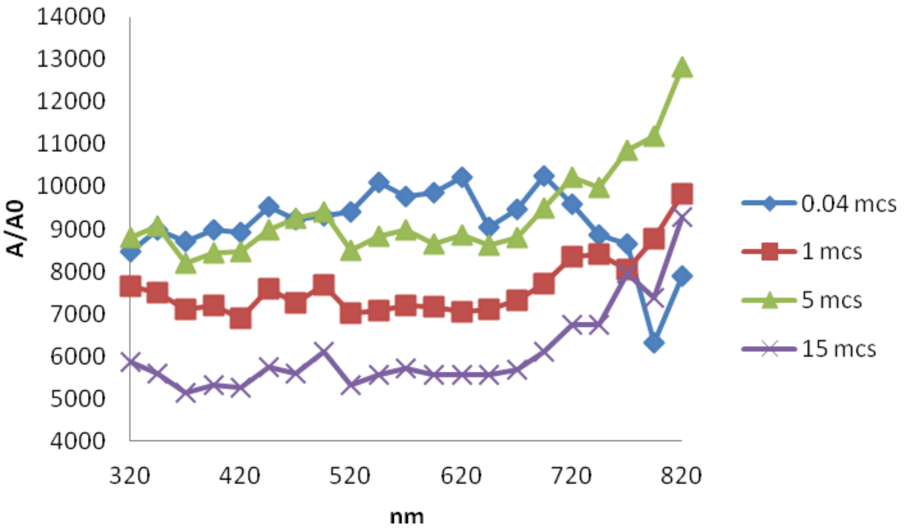

(F)G+ MeOH
Intensidad
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-4
1
6
11
16
Microseconds


A/a0
18000
16000
14000
12000
10000
8000
6000
4000
320
420
520
620
720
820
nm
0.04 mcs
1 mcs
5 mcs
15 mcs



(F)G + O2

A/A0
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-4
1
6
11
16
nm



A/A0
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
320
420
520
620
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nm
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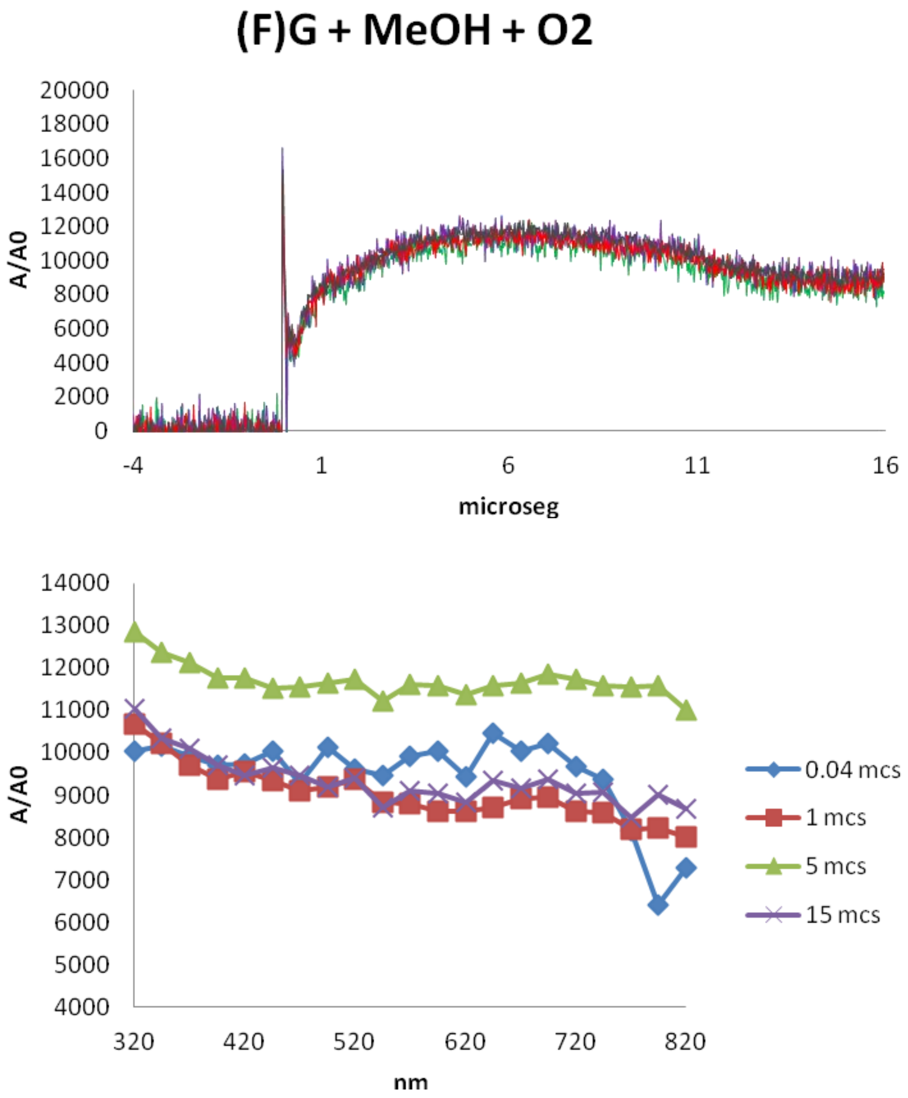
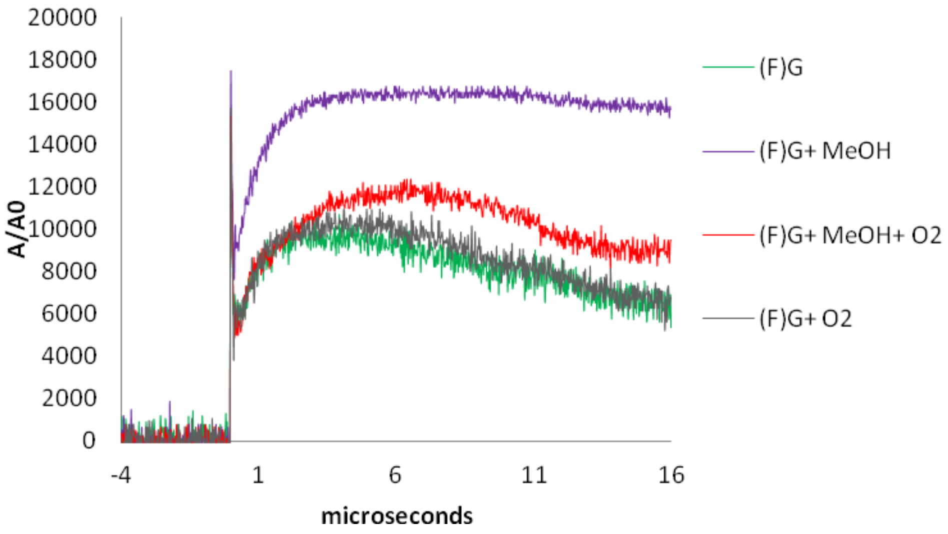
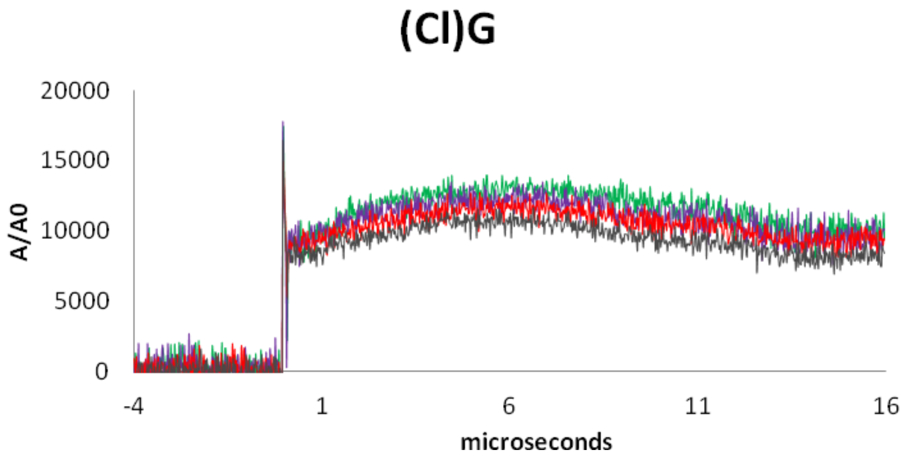
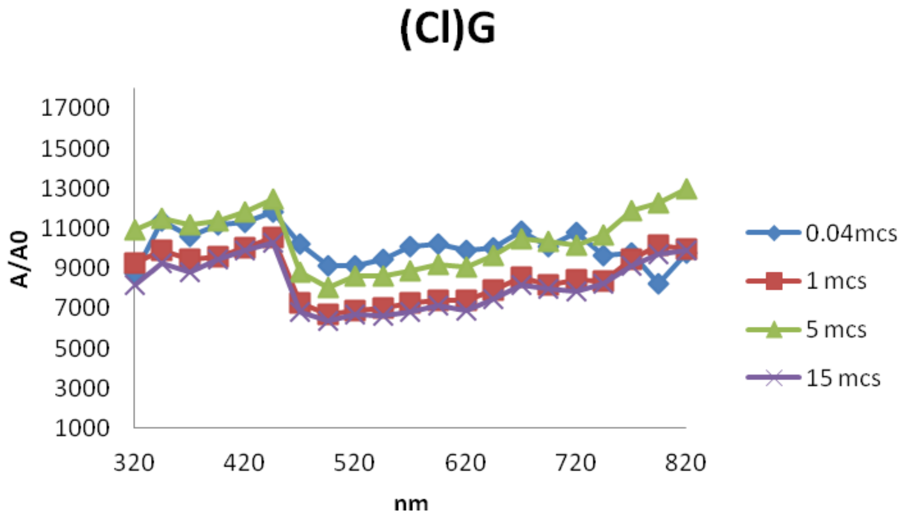
1 mcs
5 mcs
15 mcs

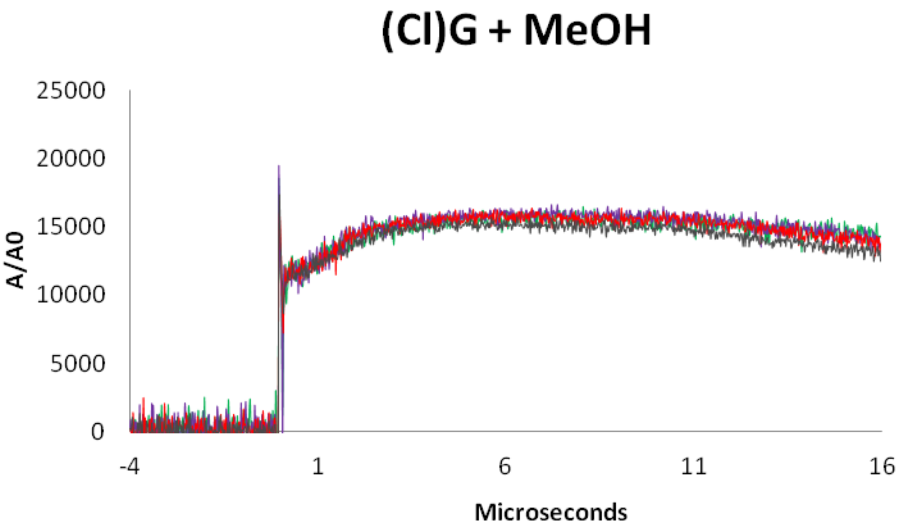

(F)G + MeOH + O2
A/A0
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-4
1
6
11
16
microseg
A/A0
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
320
420
520
620
720
820
nm
0.04 mcs
1 mcs
5 mcs
15 mcs

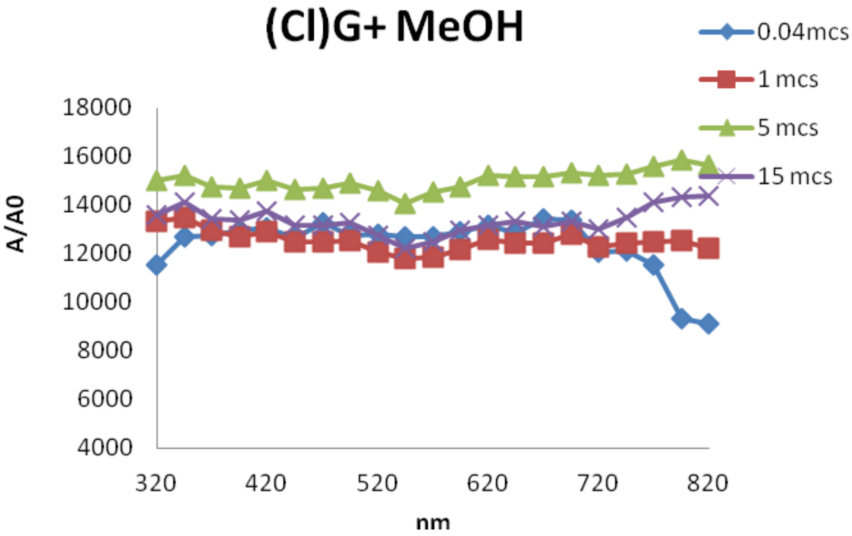
Decays Recorded at 745 nm:

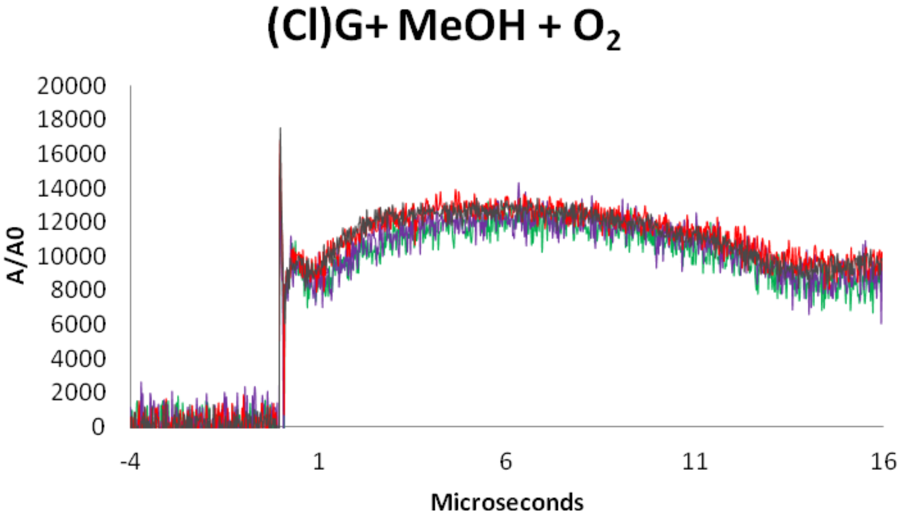


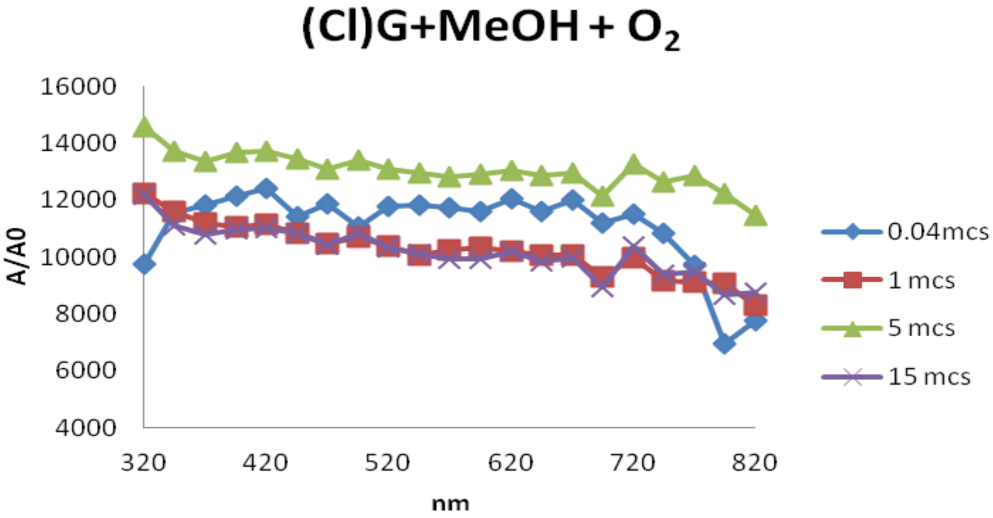

(Cl)G
A/A0
20000
15000
10000
5000
0
-4
1
6
11
16
microseconds

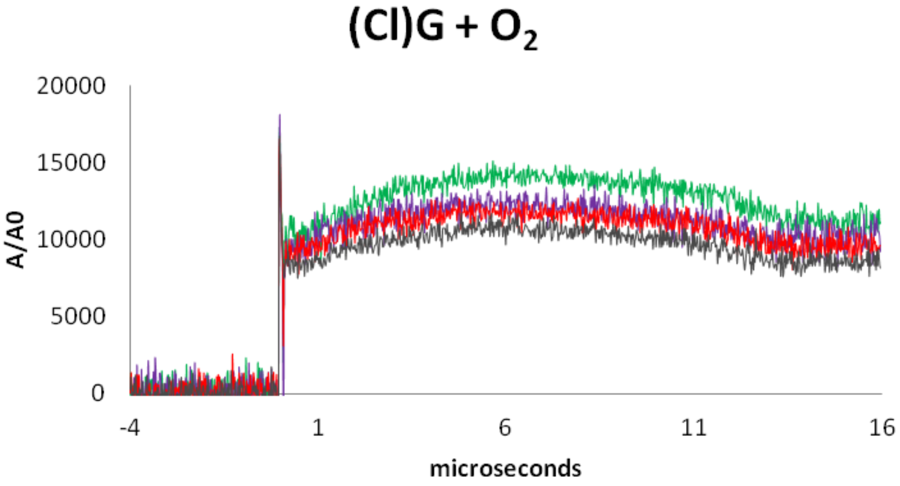

(Cl)G
A/A0
17000
15000
13000
11000
9000
7000
5000
3000
1000
320
420
520
620
720
820
nm
0.04mcs
1 mcs
5 mcs
15 mcs

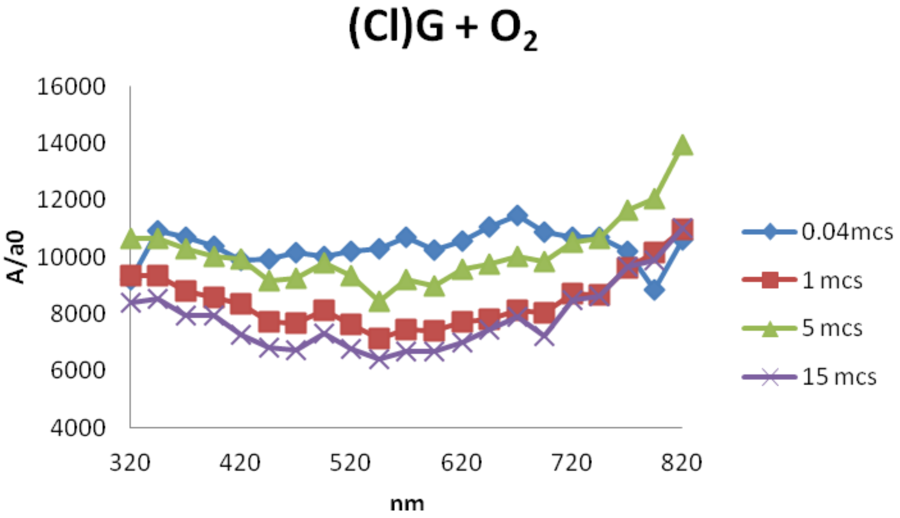

(Cl)G + MeOH
A/A0
25000
20000
15000
10000
5000
0
-4
1
6
11
16
Microseconds


(Cl)G+ MeOH
0.04mcs
1 mcs
5 mcs
15 mcs
A/A0
18000
16000
14000
12000
10000
8000
6000
4000
320
420
520
620
720
820
nm

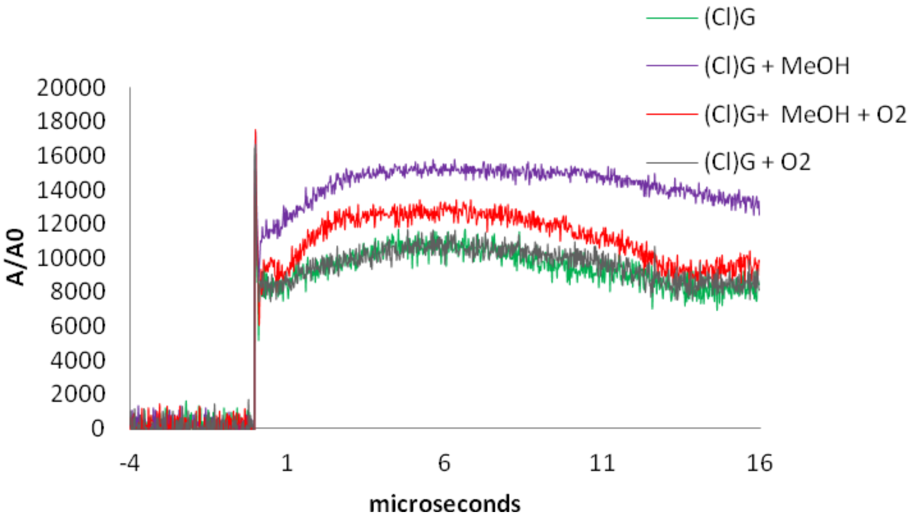

(Cl)G+ MeOH + O_2
A/A0
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-4
1
6
11
16
Microseconds


(Cl)G+MeOH + O_2
A/A0
16000
14000
12000
10000
8000
6000
4000
320
420
520
620
720
820
nm
0.04mcs
1 mcs
5 mcs
15 mcs


(Cl)G + O_2
20000
15000
10000
5000
0
A/A0
-4
1
6
11
16
microseconds

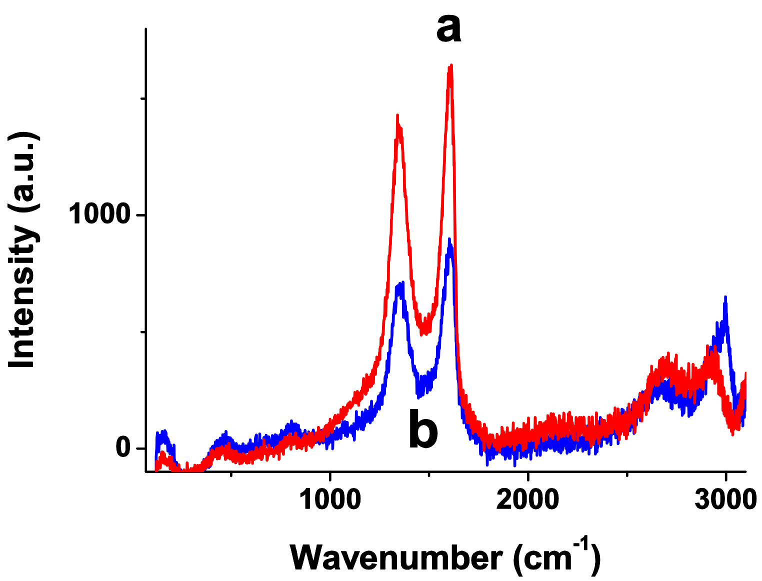

(Cl)G + O_2
16000
14000
12000
10000
8000
6000
4000
A/a0
320
420
520
620
720
820
nm
0.04mcs
1 mcs
5 mcs
15 mcs

Decays Recorded at 745 nm:



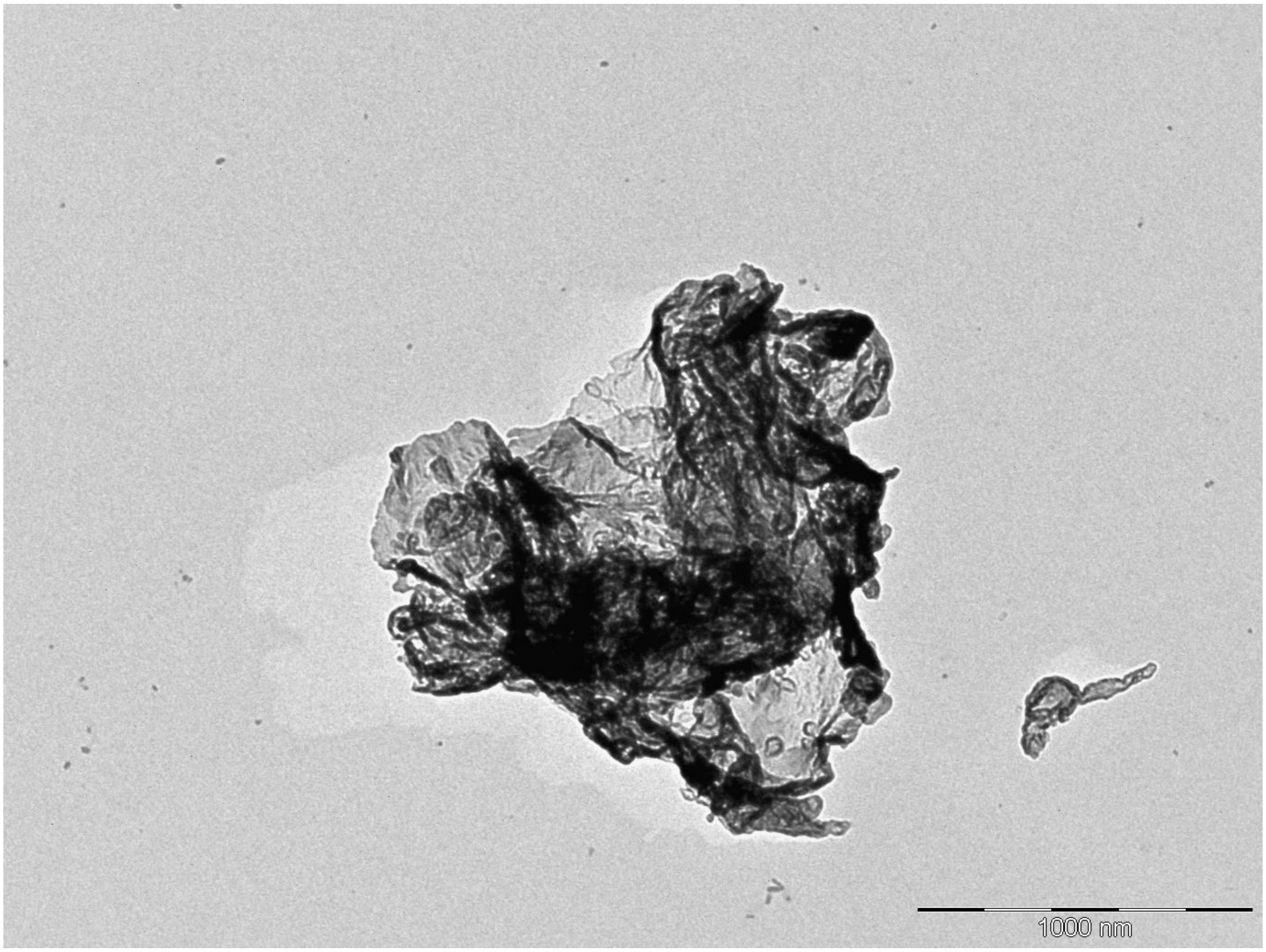
S.7 Stability of **(Cl)X** under irradiation (see conditions in the experimental section)

Raman spectra of **(Cl)G** before (a) and after 6 h irradiation (b).

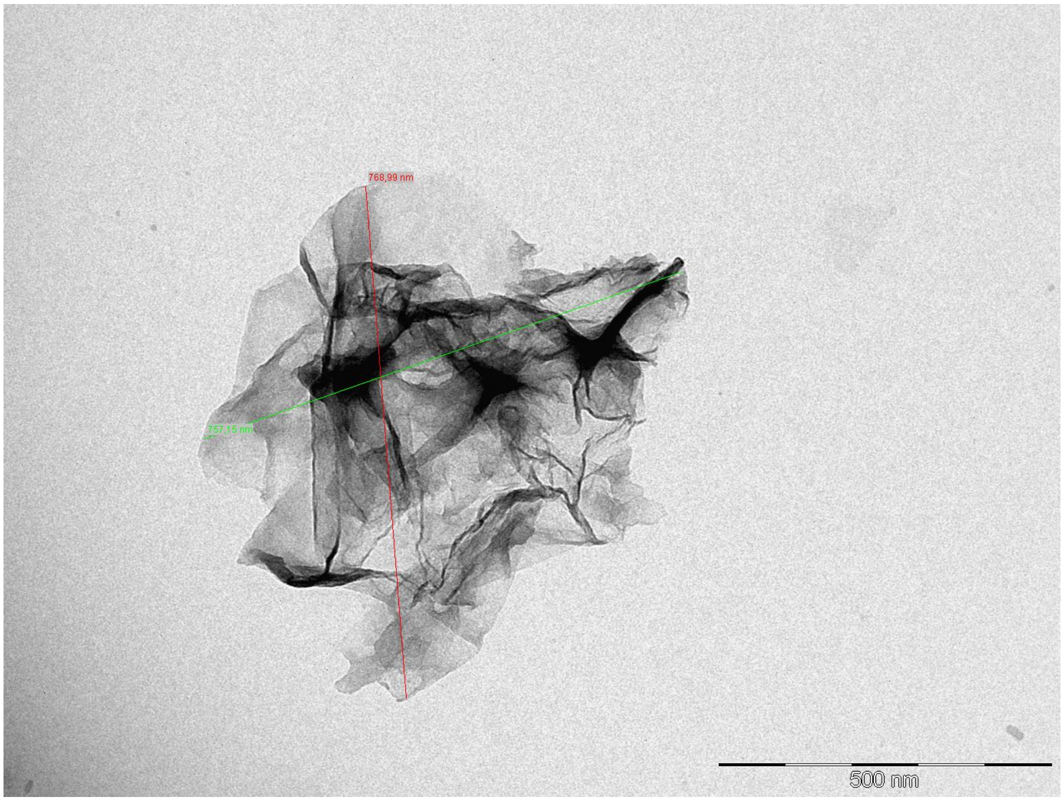


Set of TEM images of **(Cl)G** sample before (a), and after 1 (b), 3 (c) and 6 h (d) irradiation.

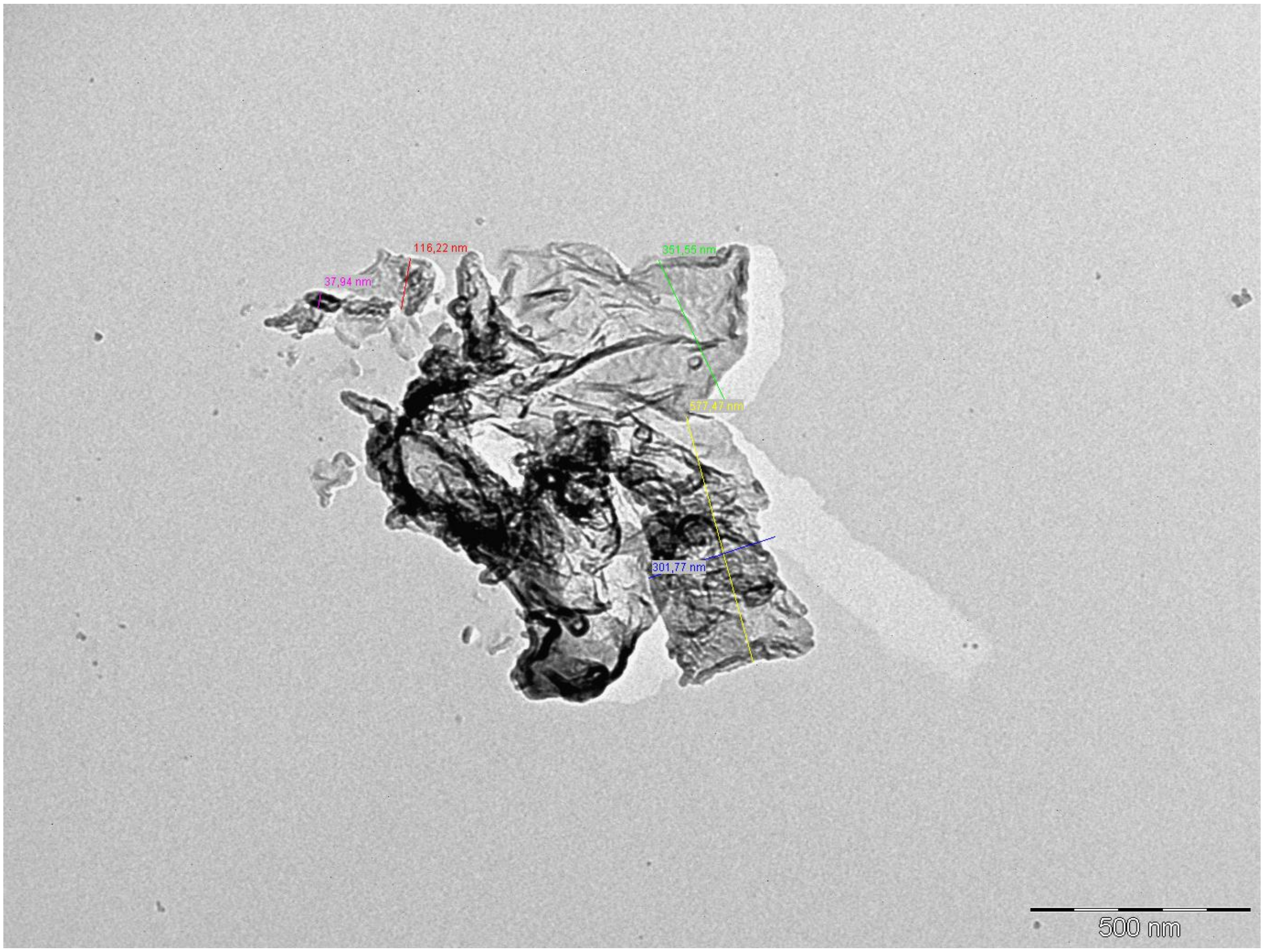
a)



b)



c)



d)