Electronic Supplementary Material (ESI) for Chemical Science.

Thermochemical Functionalisation of Graphenes With Minimal Framework Damage

Sheng Hu,[a] Zachary P. L. Laker,[b] Hannah S. Leese,[a] Noelia Rubio,[a] Martina De Marco,[a] Heather Au,[a] Mark S. Skilbeck,[b] Neil R. Wilson,[b] and Milo S. P. Shaffer*[a]

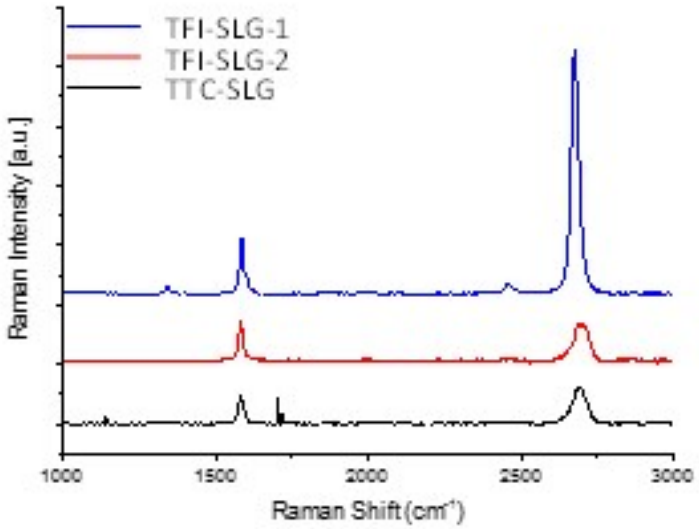

Figure S1. Raman spectra of TTC-SLG and TFI-SLG.

[a] Dr. S. Hu, Dr. H. S. Leese, Dr. N. Rubio, M. De Marco, H. Au, Prof. Dr. M. S. P. Shaffer
Department of Chemistry and London Centre for Nanotechnology
Imperial College London
London SW7 2AZ, UK
E-mail: m.shaffer@imperial.ac.uk
[b] Z. P. L. Laker, M. S. Skilbeck, Dr. N. R. Wilson
Department of Physics
University of Warwick
Coventry CV4 7AL, UK

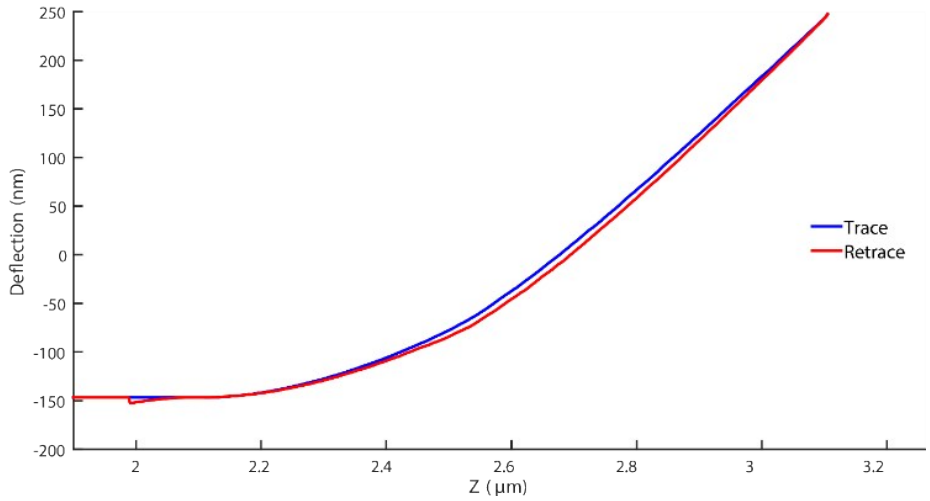

Figure S2. Trace/retrace curve from a typical AFM nano-indentation experiment for TFI-SLG.

Table S1. Comparison of IDD grafting over a panel of CNMs.

CNMs type	S_{BET} (m^2/g)	IDD Grafting			P(MMA) Grafting	
		Grafting Ratio (wt%)	Grafting Concentration (µmol/g)	Surface Grafting Density (µmol/m^2)	Grafting Ratio (wt%)	Repeating Units
GNPs (xGScience Grade GC750)	678	1.7	102	0.16	3.2	3.9
MWCNTs (Arkema, Graphistrength C100)	227	1.4	87	0.39	7.0	3.7
SWCNTs (HiPco)	526	3.3	202	0.38	3.7	3.8

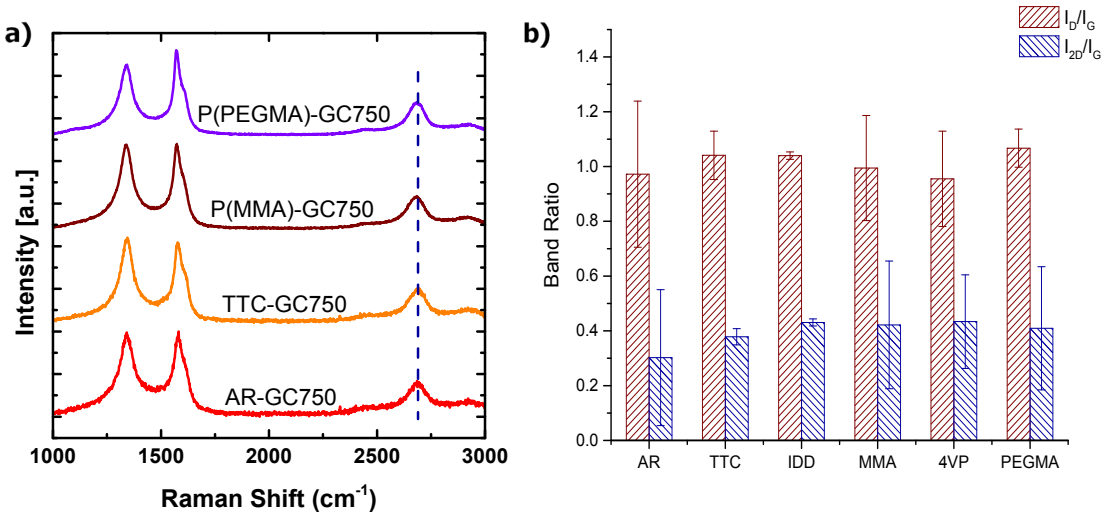

Figure S3. a) Example Raman spectra for AR- and f-GNPs and b) I_D/I_G, I_{2D}/I_G means and standard deviations from at least 100 independent spectra..

Calculation of the grafting concentration (given in C/N) determined by TGA and XPS analysis.

TGA

Taking P(4VP)-GNP as an example, the grafting ratio of P(4VP) determined by TGA was 4.2 wt% (ie P(4VP) within the whole product weight). Grafting ratio may also be defined relative to the carbon framework weight, but at low degrees of functionalization, the difference is not significant. The grafting concentration (μmol/g) was calculated from the micromoles of grafted 4VP per gram of framework graphene carbon. In this case, 0.042 /105.1 g/mol / (1 – 0.042) = 417 μmol/g. The grafting concentration, given in C/R can therefore be calculated as (1 g / 12.01 g/mol) / (417 × 10^{-6} mol) = 200 : 1.

To calculate the surface grafting concentration, the grafting concentration was normalised by the specific surface area (in this case, 678 m^2/g): i.e. 417 μmol/g / 678 m^2/g = 0.615 μmol/m^2. The surface area of one perfect hexagon carbon ring S_h (per two carbon atoms) has been reported to be 5.246 × 10^{-20} m^2, so the surface grafting concentration can also be presented as the ratio of surface carbon atoms to 4VP repeats: [1 m^2 / (5.246 × 10^{-20} m^2 / 2)] / (0.615 × 10^{-6} mol × 6.022 × 10^{23} mol^{-1}) = 103 :1.

XPS

From XPS, for the P(4VP)-GNP sample, the C & N contents were 94.7 at% and 3.7 at% respectively. The increased N content relative to the pristine materials (TTC-GNP with 0.4 at% N), the N amount was 3.3 at%. Considering the molecular formula of 4VP (C_7H_7N), and assuming the detected N were solely contributed by 4VP, the C from the 4VP would be 3.3 % × 7 = 23.1 %. Therefore the carbon content from graphene is 94.7 % - 23.1 % = 71.6 %. So the grafting concentration (given in C : R) is 71.6/3.3 = 22 : 1. The value indicates significantly more grafting than the TGA, presumably due to the surface sensitivity of XPS which does not probe the carbon at the centre of the 5-6 nm thick GNPs.

XRD

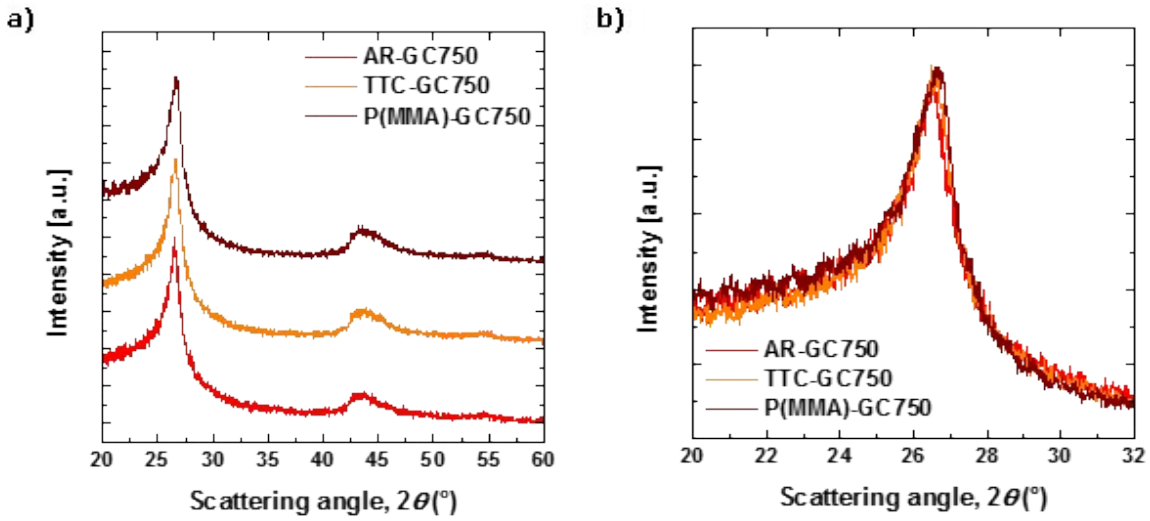

Figure S4. XRD analysis of AR-, TTC- and P(MMA)-GC750 GNPs showing the crystallinity and interlayer features of the materials. Diffractograms were normalized to the (002) peak intensity, and incident X-ray wavelength was 1.542 Å. The results show that the thickness and interlayer spacing of the GNPs are not significantly altered by the thermochemical grafting treatment which is expected only to modify the accessible surfaces. The thicknesses of the GNPs were estimated using the Scherrer approach, as summarized in Table S2. The values are consistent with the AFM measurements, but slightly larger than the manufacturer's data.

Table S2. Comparison of AR-, TTC- and P(MMA)-GC750 in terms of features revealed by XRD analysis (incident X-ray wavelength 1.542 Å).

Sample	(002) peak (°)	Theta (°)	GNPs interlayer distance (Å)	FWHM (002) at ca. 26°	Lc (nm)	No. of layers
AR-GC750	26.49	13.25	3.364	1.39	6.13	19
TTC-GC750	26.49	13.25	3.364	1.52	5.61	18
P(MMA)-GC750	26.56	13.28	3.356	1.58	5.40	17

SEM images of GC750 and GM5

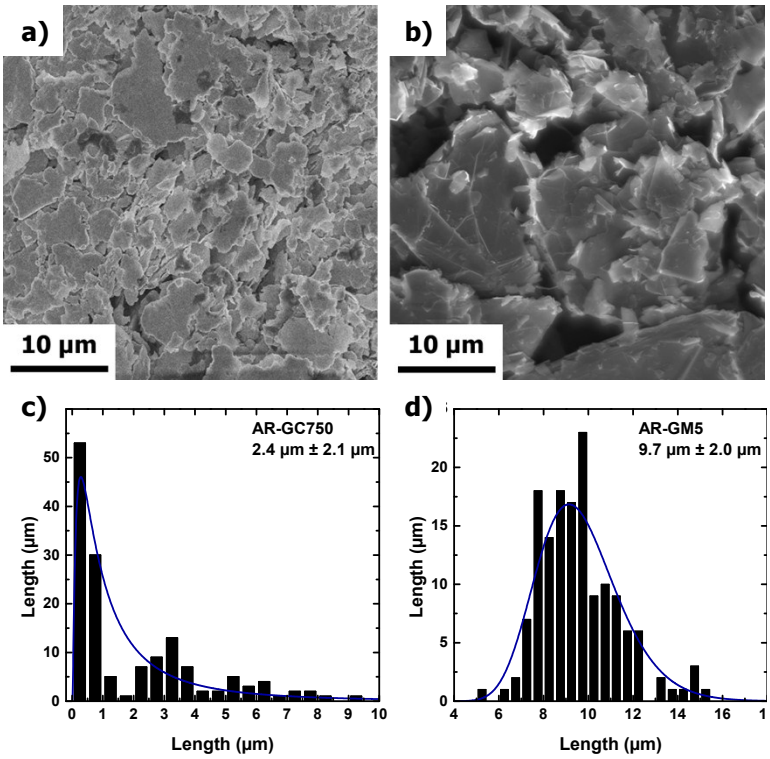

Figure S5. SEM images (a) GC750 and (b) GM5 GNPs showing the lateral morphology of the carbon sheets; size distribution of (c) GC750 and (d) GM5 GNPs, determined by image analysis.

Table S3. Comparison of GC750 and GM5 GNPs samples in terms of dimensions and BET surface area.

Sample	Product description	Flake size (µm)	Thickness* (nm)	BET surface Area (m^2/g)
GC750	Grade C 750 m^2/g	2.4 ± 2.1	1 - 2	678.0 ± 3.4
GM5	Grade M 5 µm	9.7 ± 2.0	6 - 8	100.8 ± 1.2

*** Data provided by manufacturer.**

Preliminary Functionalisation Results for GM5 GNPs

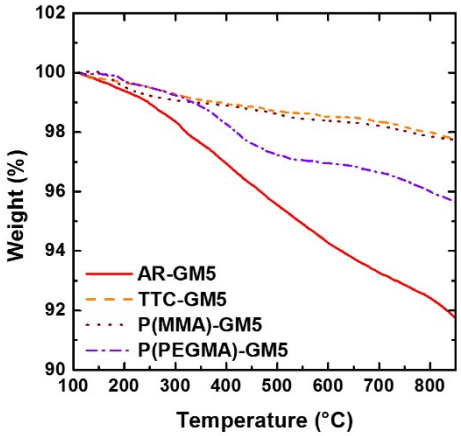

Figure S6. TGA weight loss profiles of AR, TTC and f-GM5 samples, heated under N_2 atmosphere.

Table S4. Grafting ratios in weight loss (wt%) and grafting concentration for AR-, TTC- and various *f*-GC5 samples. The degree of grafting is significantly lower for the GM5 samples, as expected given the lower accessible surface area.

Sample	Grafting Ratio (wt%)	Grafting Concentration (μmol/g)
AR-GM5	N/A	N/A
P(MMA)-GM5	< 0.2	0.2
P(PEGMA)-GM5	2.1	42