Supporting Information

Refining and Validating Thermogravimetric Analysis (TGA) for Robust Characterization and Quality Assurance of Graphene Related 2D Materials (GR2Ms)

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Experimental conditions

Materials: Graphite in the form of graphite flakes obtained from a local graphite company (Uley, Eyre Peninsula, SA, Australia). Expanded graphite was supplied from Ceylone Graphene Techology, Sri Lanka. Carbon black material was provided by Acti-vated carbon (Haycarb) and biochar from Permachar SWCNT and MWCNT were supplied from Sigma, Sydney Australia. Graphene ribbons and graphene anions were synthesized in lab using procedures published in literature.

Characterizations: The morphology of GR2Ms used in this study was characterized using scanning electron microscope (FE-SEM, Quanta 450 FEG, FEI, USA) at operating voltage of 5 kV and transmission electron microscope (TEM, FEI Tecnai G2 Spirit at 120kV). Sample was sonicated for 30 minutes in ethanol before mounting on a silica wafer on a carbon tape and coated with 10 nm platinum for SEM imaging. Meanwhile, the sample was dispersed in ethanol via bath sonication to form a homogeneous dispersion before drop-casting on a Cu grid for TEM imaging.

Atomic force microscopy (AFM) image of GR2Ms was collected using an AFM NT-MDT Ntegra Solaris in tapping mode with a Si tip on the Si/SiO_2 substrate to measure the thickness and numbers of layers. FTIR (Nicolet 6700, Thermo Fisher) in the range of 500-4000 cm^{-1} was adopted to study the functional groups of GR2Ms. Raman spectroscopy (LabRAM HR Evolution, Horiba Jvon Yvon Technology, Japan) with a 532 nm laser (mpc3000) as the excitation source in the range of 500-3500 cm^{-1} was used to study the degree of defects of the GR2Ms. All the spectra were recorded at an integration time of 10 s for 3 accumulations using a 100× objective lens. XRD equipped with Cu X-ray tube (600 Miniflex, Rigaku, Japan) was conducted at 40 kV and 15 mA with 10° min^{-1} scan speed in the range of 2θ = 5- 80° to examine the interlayer spacing of GR2Ms.
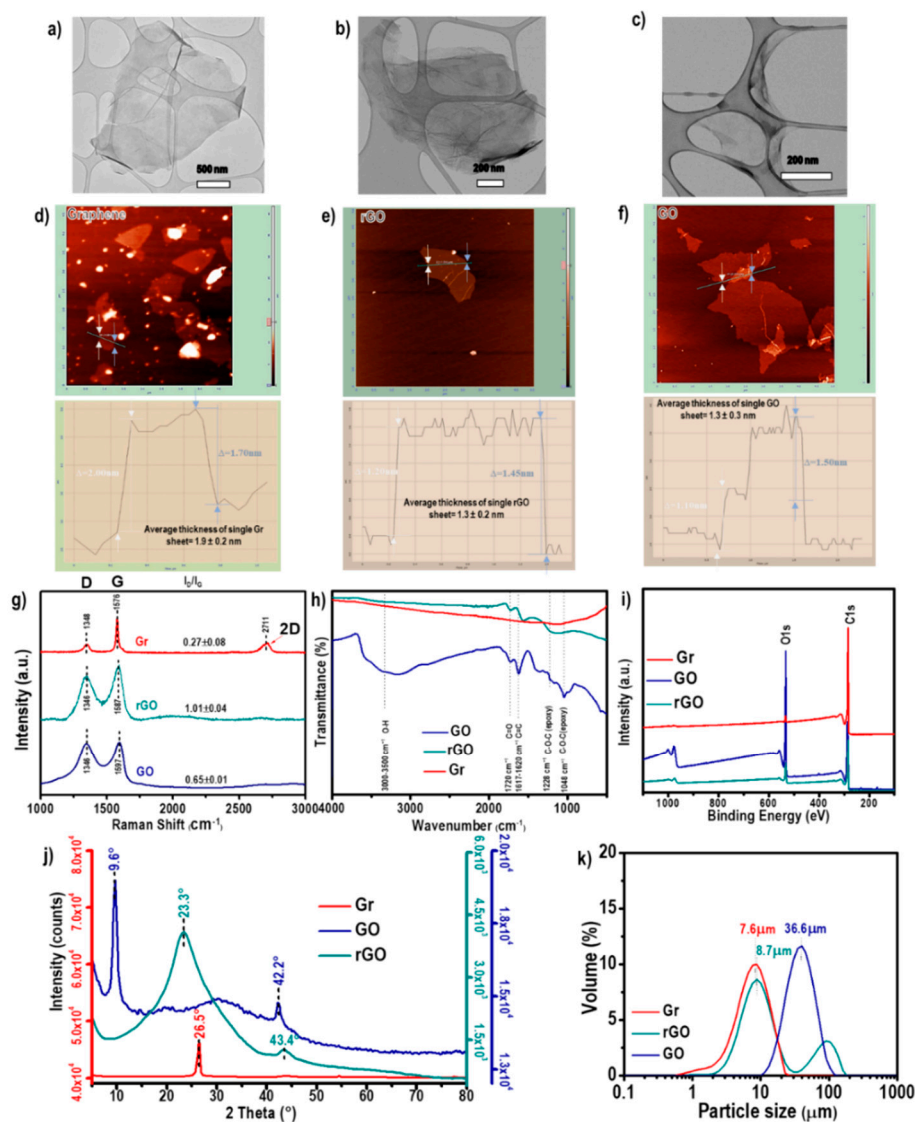
Results

Figure S1. Comparative characterization results of commercial graphene materials Gr (FLG), rGO, and GO used in this study showing their (a-c) TEM images, (d-f) AFM images with height profiles shown underneath for of FLG, rGO and GO. (g) Raman spectra, (h) FTIR spectra, (i) XPS survey spectra, (j) XRD and (k) particle size distribution, PSD-DLS plots (in terms of volume median diameter, d(0.5)v) More characterization details are presented in **Table S1**.

Table S1. Summary of characterization results for of FLG sample used in this study.

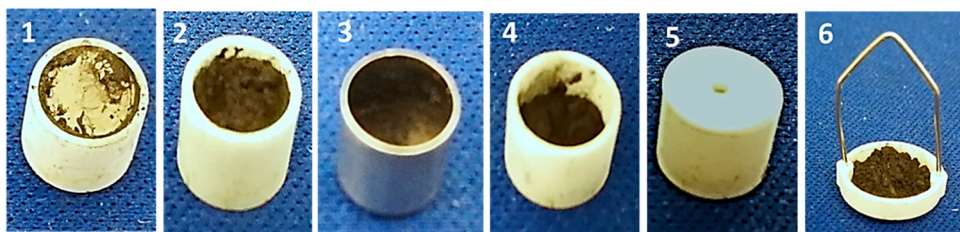| Sample	TEM (no. of layers)	AFM *Average thickness (± s.d. nm)	*Average PSD-LD, d(50)$_v$ (± s.d. μm)	Raman *Average I$_D$/I$_G$ (± s.d.)	XPS %C (± 0.3 at%)	XPS %O (± 0.3 at%)
FLG	3-5	1.9 ± 0.2	7.6 ± 0.01	0.27±0.08	97.7	2.4

Figure S2. Different type of crucibles explored for TGA measurement made from Platinum (3) and alumina (1,2, 4, 5 and 6); open (1, 2, 3, 4, 6) and closed with a hole (5) with further details included in Table S1.

Table S2. Details of the crucible/pan used in this study with respect to **Figure S2** with examples of loaded samples (free loaded and loosely packed powder and pressed samples).

From left to right	1	2	3	4	5	6
Crucible/pan Volume (µL)	70	70	70	70	70	100
Crucible/pan Material	alumina	alumina	platinum	alumina	alumina	alumina
Crucible/pan Lid	open	open	open	open	closed (with a hole)	open
Sample Mass (mg)	47.5 (pressed)	9.3 (loosely)	5.0 (loosely)	5.0 (loosely)	5.0 (loosely)	5.0 (loosely)

Table S3. Details of the crucible/pan used in this study at different heating rates. SD represents standard deviation; SE represents standard error.

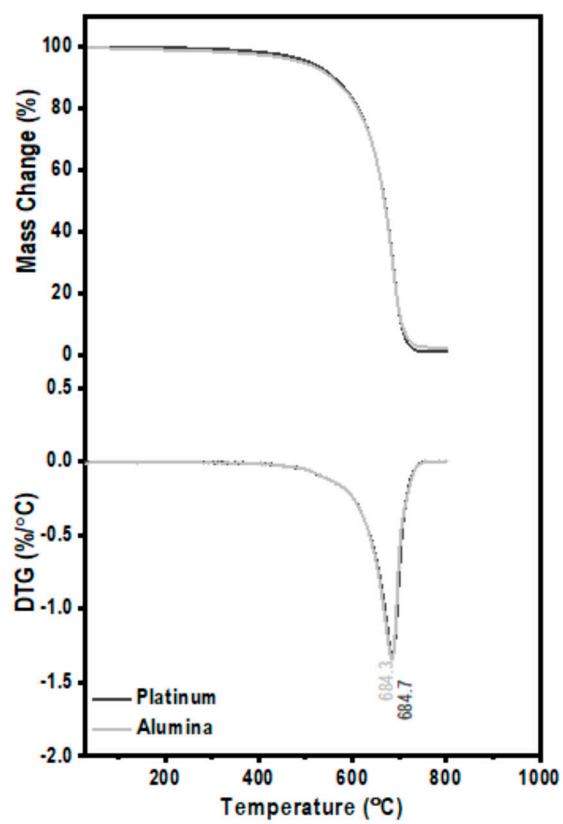| Crucible/pan		Heating rate (°C/min) / T_{max} (°C)		
		5 °C/min	10 °C/min	20 °C/min
with lid	Alumina (70uL)	686.6	724.3	788.0
without lid	Alumina (70uL)	684.3	704.2	724.3
	SD	1.6	14.2	45.0
	SE	1.2	10.1	31.9

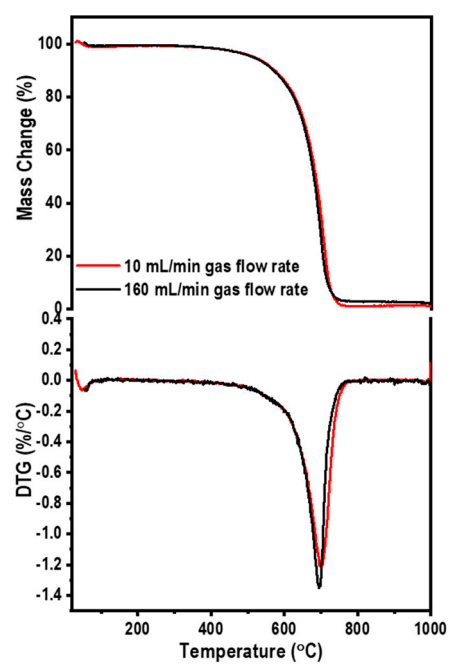**Figure S3.** Influence on the type of crucible (platinum vs alumina).

Figure S4. Influence of sample gas (O2) flow rate: 10 mL/min vs 160 mL/min.

Table S4. Details of the gas flow rates used with respect to **Figure S5**.

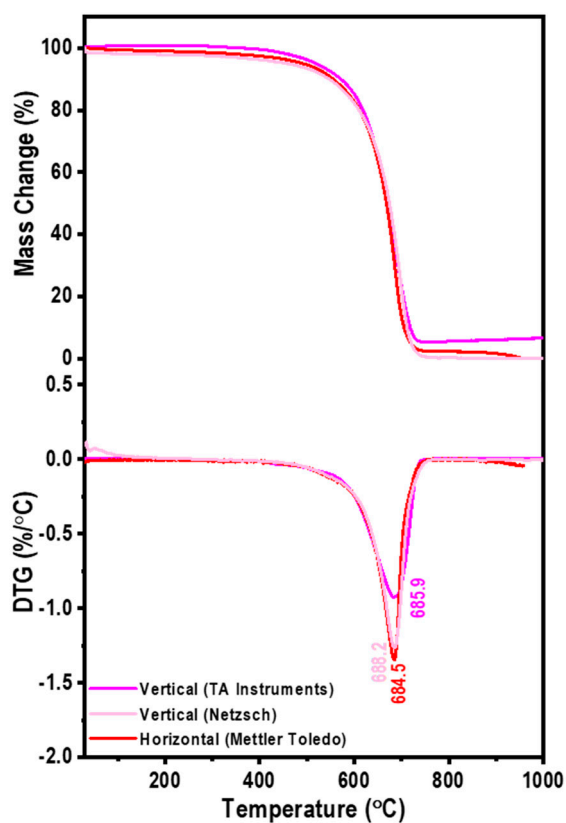| Balance gas Nitrogen flow rate (ml/min)	Crucible/pan	Sample gas O₂ Flow rate (ml/min)	Sample gas Nitrogen flow rate (ml/min)	O_2 (%)	Total Gass Flow rate (ml/min)	T_{max}
20	Alumina (70 μL) #4	10	0	33	30	700.3
20	Alumina (70 μL) #4	60	100	33	180	694.9

Figure S4. Influence of TGA instrument orientation.

Table S5. Details of the TGA instrument orientation used with respect to **Figure S4**.

Furnace orientation effect	Crucible/pan	T_{max} (°C)		Average T_{max} (°C)	SD	SE
		R1	R2			

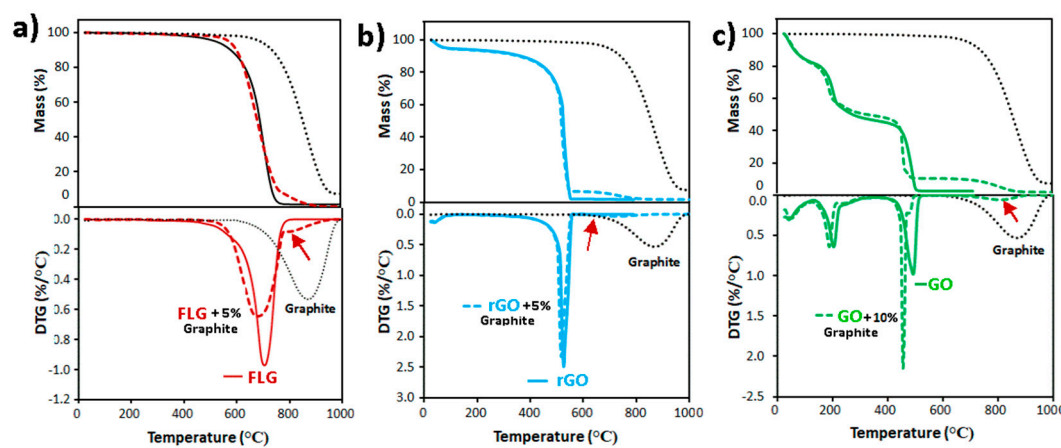|							
Horizontal (Mettler toledo)	**Side loading**	Alumina (70 uL) #4	684.3	684.7	684.5	0.3	0.2
Vertical (TA Instruments)	**Bottom loading**	Alumina (100 uL) #6	682.9	689.0	685.9	4.3	3.1
Vertical (Netzsch)	**Top loading**	Alumina (70 uL) #4	684.6	691.8	688.2	5.1	3.6

Figure S5. Comparative TG/DTG graphs, obtained by TGA optimized conditions, of GR2Ms (GO, rGO, FLG) mixed with 5-10% of graphitic particles with 5-10% concentrations which is common impurity in GR2Ms, showing ability of TGA method to detect these graphitic additions. .

Optimized TGA data processing protocol for quantitative analysis

For accurate determination of mass % of GR2Ms, plot the TG curve using the blank subtracted data. Plot a first derivate of TG (DTG) curve by performing a mathematical operation of first derivative of TG curve using instrument or external software (Origin, Matlab). Example of a DTG curve is depicted in **Figure S6**. Temperature of maximum mass change rates (T_{max}) for each step can be identified from the minimum points in negative DTG peaks (**Figure S6b**), which can be correlated to the zero crossover of the second derivative of TG (d2TG) curve. Plot a d2TG curve by performing a mathematical operation of d2TG curve using instrument or external software (Origin, Matlab) to define the starting point of a peak. Example of a d2TG curve is depicted in **Figure S6c**. Stack the TG, DTG and d2TG curves as shown in **Figure 6** and ensure that the temperature parameter is correctly scaled on the *x-axis* for the 3 graphs to allow the determination of accurate limits for each step. Determine the limits from the zero crossover of d2TG peaks (**Figure S6c**) for each step that can be correlated to the maximum points in the negative DTG peaks (**Figure S6b**) and the start and end of the mass change on TGA curve. If the two steps were so small that only a shoulder can be seen in the DTG curve and the d2TG curve did not vanish and only reached to a minimum, that minimum point can be used as the limit for the separation of steps. After establishing the limits, the mass change for the individual steps can be determined from the step height of the TG curve.
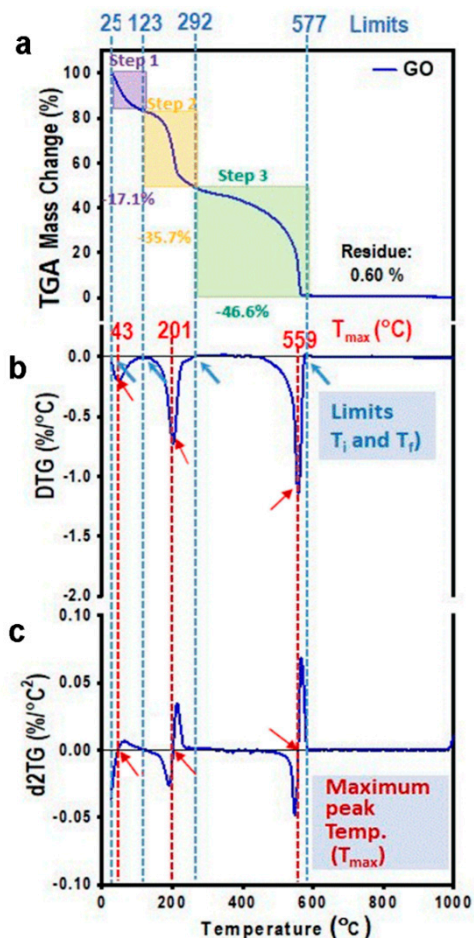
Figure S6. Example of   a) TG, b) DTG and c) d2TG graphs for GO showing the important parameters of the number of mass change steps (TGA/DTG)   giving the number of components present. T_{max} values identified from DTG and d2TG graphs for each step (component),   temperature limits identified from d2TG graph and used to determine limits (T_i and T_f)   for each step in TG graph to calculate mass % for each step (component). *T_i =initial temperature; T_f = final temperature.

Reference:

1. P. Lay Yap, F. Farivar, Å. K. Jämting, V. A. Coleman, S. Gnaniah, E. Mansfield, C. Pu, S. M. Landi, M. V. David, E. Flahaut, M. Aizane, M. Barnes, M. Gallerneault, M. D. Locatelli, S. Jacquinot, C. G. Slough, J. Menzel, S. Schmölzer, L. Ren, A. J. Pollard, D. Losic, International Interlaboratory Comparison (ILC) of Thermogravimetric Analysis (TGA) of Graphene Related 2D Materials, Anal. Chem, 2023, 95, 12, 5176–5186