Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Graphite Sulphate - A Precursor to Graphene

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Experimental Section

Methods.

Natural flake graphite, grade 3061, was obtained from Asbury Carbon. Sulphuric acid, hydriodic acid 57% in water and trifluoroacetic acid were obtained from Sigma-Aldrich® and used as received. Methanol was doubly distilled before use. Centrifugation was accomplished by a Sigma 4K15 centrifuge, Sigma Laborzentrifugen GmbH, Germany. Elemental analysis was performed by combustion and gas chromatographic analysis with a VarioMicro CHNS analyzer from Elementar Analysensysteme GmbH, Hanau, Germany. Thermogravimetric analysis (TGA) equipped with a mass spectrometer (MS) was accomplished on a Netzsch STA 409 CD instrument equipped with a Skimmer coupling to a QMS 422 mass spectrometer (MS/EI) with the following programmed time dependent temperature profile: 24-800 °C with 10 K/min gradient, and cooling to room temperature. The initial sample weights were about 6 to 7 mg and the whole experiment was accomplished under inert gas atmosphere with a He gas flow of 80 ml/min. Langmuir-Blodgett films were prepared using Langmuir-Blodgett Minitrough from KSV NIMA and films are prepared from MeOH/water mixtures on water as subphase at a pressure of 1.5 mN/m. These films were used for AFM imaging and scanning Raman microscopy (SRM). SRM was accomplished on a Horiba Jobin Yvon LabRAM Aramis confocal Raman microscope with an excitation wavelength of 532 nm. The spot size was about 1 µm using an Olympus LMPlanFl 100, NA 0.80 objective in back-scattering geometry. A silicon detector array charge coupled device (CCD) was used at -70 °C for gathering Raman spectra. The spectrometer was calibrated in frequency using crystalline graphite. A motorised x,y table was used to scan the sample area. The sample was mounted on the x,y table and it was ensured that the focus of the laser is constant within the scanned area. The increment of scanning was 2.5 µm, 0.25 s exposure time with a laser intensity of about 1 mW, grating 600, laser excitation 532 nm. For the analysis of Raman spectra, gathering and evaluation of statistical information, the preparation of histograms and creating SRM images was performed according to the published procedure.[1] Furthermore, the determination of the density of defects is also given in the supporting information of our earlier work and is based on the description of Lucchese et al. and Cançado et al..[2],[3],[4] Dispersions of oxidised graphite sulphate were sonicated in a glass-vial using a bath sonicater Sonorex Digital P10 from Bandelin, Germany. FTIR spectra of GO films were measured on a Bruker Tensor 27 FTIR spectrometer equipped with ZnSe windows under ambient conditions. About 1 ml of a dispersion of oxo-G_1 and oxo-$G_{\text{few-layer}}$, at a concentration of about 0.1 mg/ml, was dropped onto a ZnSe window (13 mm diameter) and dried under ambient conditions before measurement.

Experimental Details.

Potassium persulphate (3 g, 11 mmol) was added in portions to sulphuric acid (23 ml, 96%) at ambient conditions. Graphite (1 g, 83 mmol) was suspended after five minutes and the mixture was stirred for 16 h. Water (80 ml) was added under stirring in one portion and the temperature increased to 60 °C. Alternatively, water (100 ml) was added continuously by a syringe over a period of 16 h keeping the temperature < 10 °C. The reaction mixture was purified by centrifugation and redispersion in water (five times, neutral pH). An arbitrary amount of the slurry was suspended in a 1/1 mixture of water/methanol and sonicated by a bath sonicator for two minutes. The dispersion was centrifuged three times at 3000 U/min to yield the dispersion of oxo-G_1 and oxo-$G_{\text{few-layer}}$. Elemental Analysis: C 85.72, H 1.01, N 0.00, S 1.59. TGA (rt-800 °C): Δm, (%) = -13.3 %; TGA: Δm, (%); t_{range} (°C) = -1.3, rt-200; -11.8, 200-550; -0.2, 550-800. IR (ZnSe): $\tilde{\nu}$ = 3200, 2929, 1646, 1545, 1430, 1164, 1052 cm^{-1}. UV/Vis (H_2O/MeOH, 1/1): λ_{max} = 253, 318, 365 (sh) nm.

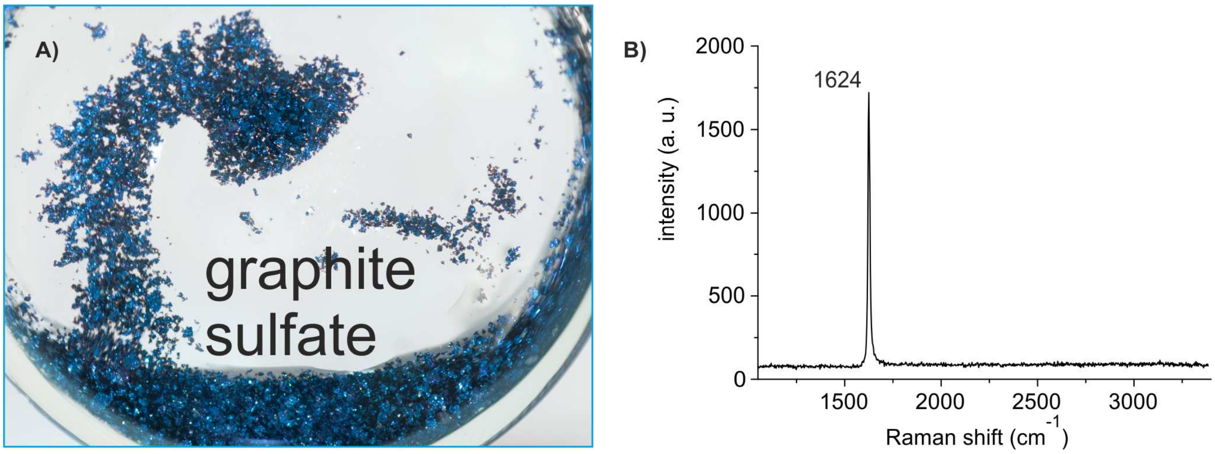

Figure S1. A) Image of blue stage 1 graphite sulphate / sulphuric acid in a glass vial; B) Raman spectrum of graphite sulphate (532 nm laser excitation), with the G peak at 1624 cm^{-1}.

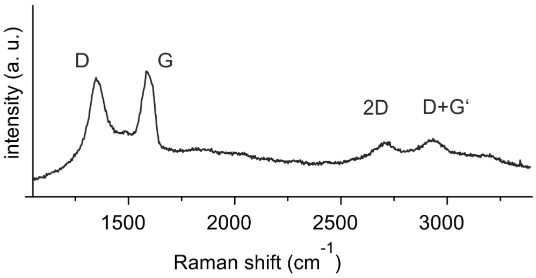

Figure S2. Raman spectrum of an oxidised graphite particle, showing a broad D, G, 2D and D+G' peak. There is no evidence for unoxidised graphite.

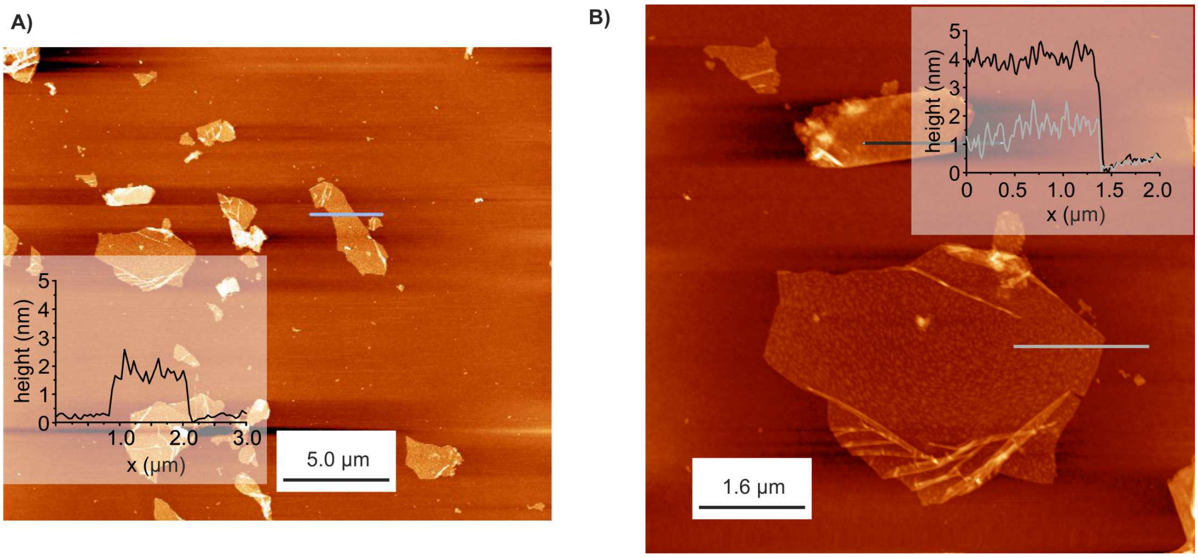

Figure S3. AFM images of delaminated oxo-G$_1$ and oxo-G$_{\text{few-layer}}$, with height-profiles along the grey lines or black line.

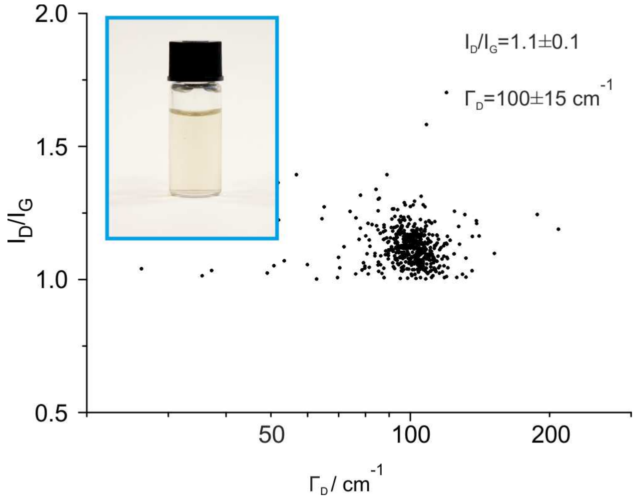

Figure S4. Statistical Raman microscopic (SRM) analysis of oxo-G_1 and oxo-$G_{few-layer}$; plot of I_D/I_G against Γ_D (full-width at half-maximum) illustrates the homogeneity of functionalization, with I_D/I_G=1.1±0.1 and Γ_D=100±15 cm^{-1}; inset: image of a dispersion of oxo-G_1 and oxo-$G_{few-layer}$. Raman spectra of G_1 with a similar I_D/I_G ratio as determined for oxo-G_1 and oxo-$G_{few-layer}$ is depicted in **Figure 2C**, however the Γ_D = 17 cm^{-1}. Thus, values of Γ_D=100±15 cm^{-1} and I_D/I_G=1.1±0.1 indicate a degree of functionalization on the %-scale and the sample appears quite homogeneous in Raman spectroscopy due to the standard deviation.

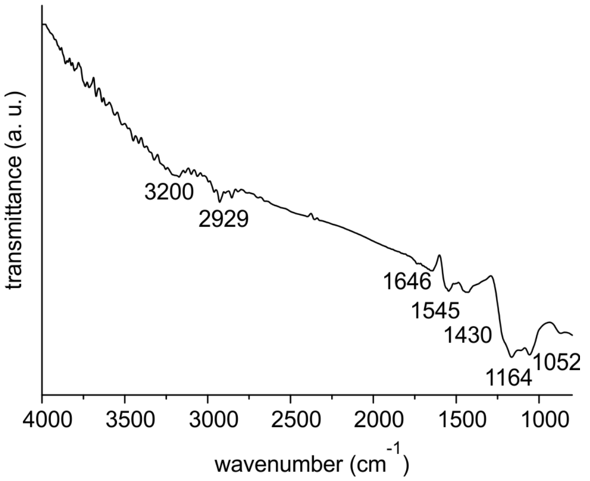

Figure S5. FTIR spectrum of a film of oxo-functionalised graphene and few-layer graphene on ZnSe.

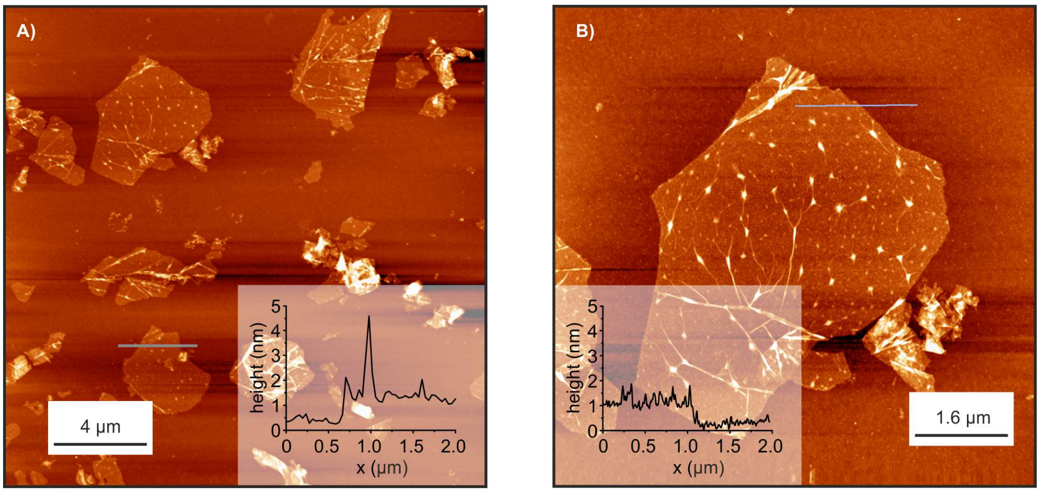

Figure S6. AFM images of G_1 and some $G_{few-layer}$ on 300 nm SiO_2 / Si wafers, obtained from oxo-G_1 and oxo-$G_{few-layer}$ by chemical reduction with HI/TFA.

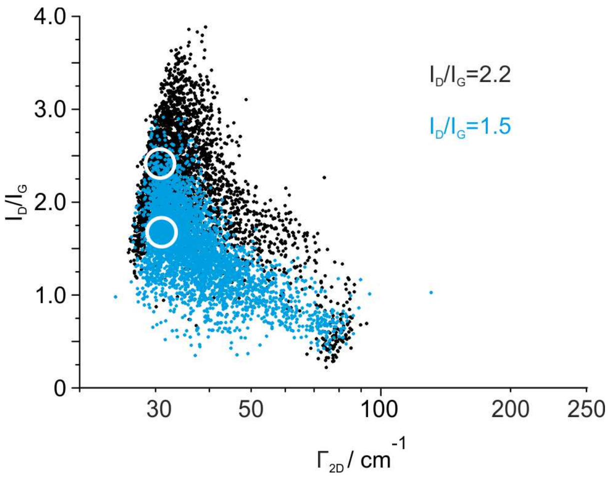

Figure S7. SRM analysis of G_1 derived from graphite sulphate by aqueous work-up at 60 °C (black) and aqueous work-up at < 10 °C (blue). Low I_D/I_G values of about 0.5 combined with Γ_{2D} of about 80 cm^{-1} originate from graphite particles with few defects and only edges of these flakes had been probed by the laser and thus, spectra could not be filtered by I_G.

Table S1. Elemental analysis of oxo-G_1 and oxo-$G_{\text{few-layer}}$; Molecular formula derived and degree of functionalization; italic values are calculated values, based on the assumption that C_{24}^+ unit is functionalized by 1 OH and 1 H_2O is non-covalently bound. However, covalent addition of H_2O to the carbon framework is not excluded, what is indicated by FTIR signal at 2929 cm^{-1}.

M (g/mol)	12	1	14	32	16	16	SUM
Element	C	H	N	S	O(sulphate)	O	
Mass (%)	85.72	1.01	0	1.59	*3.2*	*9.6*	*101.12*
Molar ratio	143	20	0	1	*4.0*	*12*	
C_{24}-unit	24	3.3	0	0.17	*0.7*	*2*	

Derived formula: $(C_{24}(OH)(H_2O))_n$ every 6 units one organosulphate.

It is proposed that one OH is bound on 24 C atoms, what results in a degree of functionalization of about 4%.

[1] S. Eigler, F. Hof, M. Enzelberger-Heim, S. Grimm, P. Müller, A. Hirsch, *J. Phys. Chem. C* **2014**, *118*, 7698-7704.
[2] S. Eigler, M. Enzelberger-Heim, S. Grimm, P. Hofmann, W. Kroener, A. Geworski, C. Dotzer, M. Rockert, J. Xiao, C. Papp, O. Lytken, H. P. Steinrück, P. Müller and A. Hirsch, *Adv. Mater.*, **2013**, *25*, 3583-3587.
[3] M. M. Lucchese, F. Stavale, E. H. M. Ferreira, C. Vilani, M. V. O. Moutinho, R. B. Capaz, C. A. Achete and A. Jorio, *Carbon*, **2010**, *48*, 1592-1597.
[4] L. G. Cançado, A. Jorio, E. H. M. Ferreira, F. Stavale, C. A. Achete, R. B. Capaz, M. V. O. Moutinho, A. Lombardo, T. S. Kulmala and A. C. Ferrari, *Nano Lett.*, **2011**, *11*, 3190-3196.