Supporting Information

Covalent modification of exfoliated fluorographite with nitrogen functionalities

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SI1. Experimental section

Synthesis of aminofluorographite (AFGr).

The synthesis of AFGr was carried out in two steps. First fluorographite (250mg; *Graphite fluoronitad polymer,* Aldrich) was exfoliated by sonicating it in N,N-dimethylformamide (50 mL) for 1h, followed by stirring the mixture overnight at room temperature. Afterwards, the mixture was left to settle down for 6 h, after which a clear grey dispersion was obtained, with some solid deposit precipitated out. The grey dispersion (ex-FGr) was separated from the solid and used without further modification in the next step. The second step was the nucleophilic substitution with sodium amide (Sigma Aldrich), for which 250 mg of sodium amide was added to the dispersion containing ex-FGr and the mixture was stirred for one week at room temperature. The product was collected by centrifugation and washed with water until pH 7. The resultant AFGr was obtained as a black solid.

Experimental techniques

SEM and EDX. SEM characterization was performed on a ZEISS Supra 55-VP field emission SEM, operated at 10 kV, using the inlens secondary electron detector. EDX data were recorded on a Zeiss SUPRA 55-VP FEGSEM with an EDAX Genesis analytical system.

X-ray photoelectron spectroscopy (XPS). The x-ray photoemission spectroscopy (XPS) data were collected at the Warwick Photoemission Facility, University of Warwick, more details of which are available at http://go.warwick.ac.uk/XPS. The samples investigated in this study were deposited on to electrically-conductive carbon tape, mounted on to a sample bar and loaded in to a Kratos Axis Ultra DLD spectrometer with a base pressure of ~ 2 x 10^{-10} mbar.

XPS measurements were performed in the main analysis chamber, with the sample being illuminated using a monochromated Al Kα x-ray source. The measurements were conducted at room temperature and at a take-off angle of 90° with respect to the surface (i.e. normal emission). The core level spectra were recorded using a pass energy of 20 eV (resolution approx. 0.4 eV). The spectrometer work function and binding energy scale were calibrated using the Fermi edge and $3d_{5/2}$ peak recorded from a clean Ag foil prior to the commencement of the experiments. The data were analysed in the CasaXPS package, using Shirley backgrounds and mixed Gaussian-Lorentzian (Voigt) lineshapes. For compositional analysis, the analyser transmission function has been determined using Ag, Au and Cu foils to determine the detection efficiency across the full binding energy range.

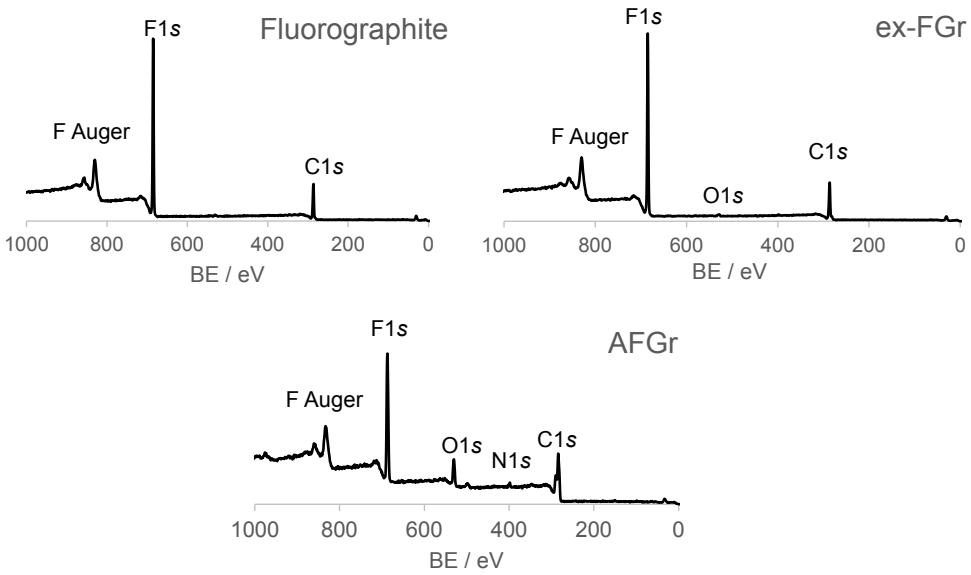
Transmission electron microscopy (TEM). For TEM imaging and diffraction a Jeol 2000Fx was used at an accelerating voltage of 200 kV.

Thermogravimetric analysis (TGA). TGA was recorded on a Mettler-Toledo TGA/DSC1 system at a heating rate of 10 K/min from 25-800 °C under air.

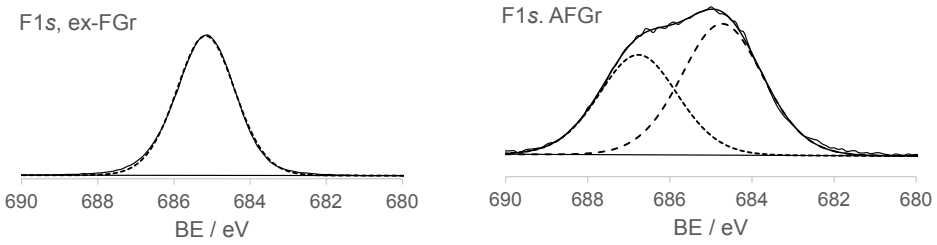
Raman spectroscopy. Raman spectra were recorded with a Renishaw InVia micro-Raman system using a 633 nm laser excitation. A confocal microscope with 50x lens was used to record spectra with a spatial resolution of ~2 μm.

% At	**% C**	**% F**	**% O**	**%N**	**%Na**
FGr	56 (±2)	44 (±1)	-	-	-
Ex-FGr	70 (±2)	22 (±3)	7.3 (±1.7)	-	-
AFGr	70 (±4)	19 (±3)	6.5 (±0.8)	2.5 (±0.4)	1.6 (±0.5)

SI2. EDX compositional analysis of pristine FGr, ex-FGr and AFGr



(a)



(b)

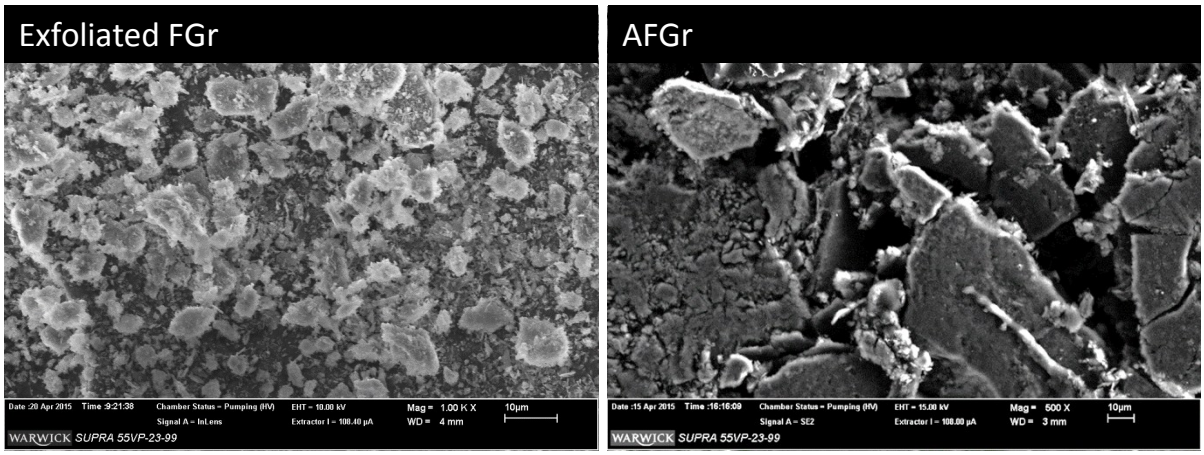
	%C	%F	%O	%N	Na
Fluorographite	58.6	40.7	0.7	-	-
ex-FGr	42.2	56.6	1.2	-	-
AFGr	52.6	34.6	8.9	2.1	1.8

(c)

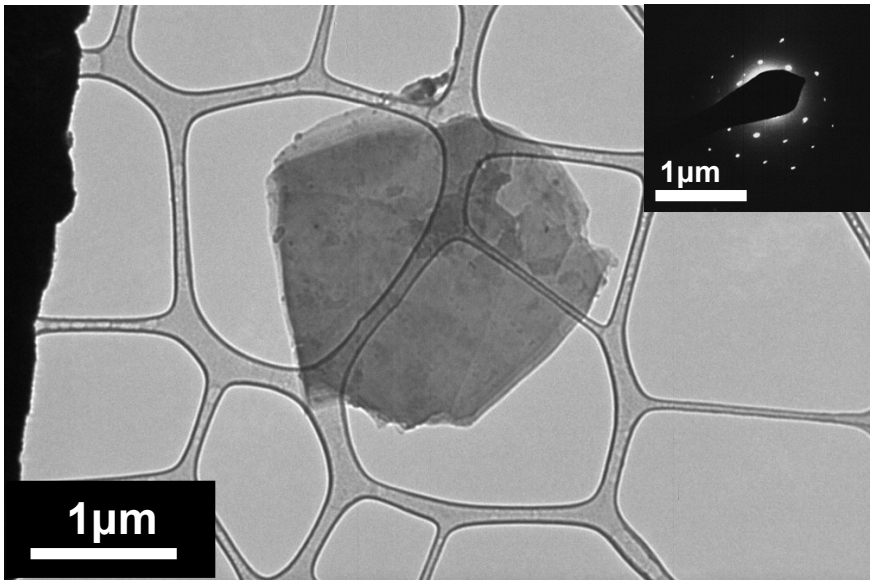
C 1*s* bond deconvolution (%at)						
	C=C 284.2 eV	C sp^3 285.8 eV	C-C-F / ionic C-F 287.5 eV	Covalent C-F 288.4 eV	H_2N-C-F / CF_2 291.0 eV	CF_3 293.3 eV
ex-FGr	12 %	-	69 %	18 %	1 %	-
AFGr	21 %	12 %	24 %	12 %	24 %	7 %

(d)

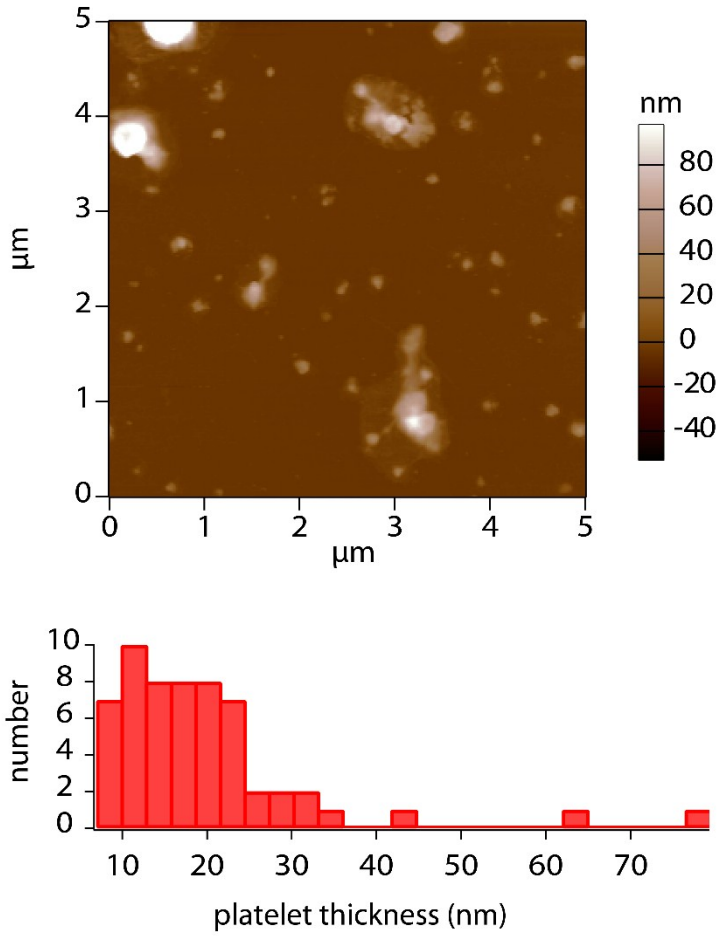
SI3. a) Survey XPS spectra of fluorinated graphite, exfoliated FGr in DMF and AFGr. As shown, after chemical functionalization a new signal corresponding to nitrogen appears, and the oxygen content increases. b) F 1*s* XPS spectra of ex-FGr and AFGr. c) Table summarizing the atomic composition of FGr and AFGr as calculated from the XPS analysis. d) Summary of C atomic composition as obtained from the deconvolution of high resolution C 1*s* XPS spectra of ex-FGr and AFGr.



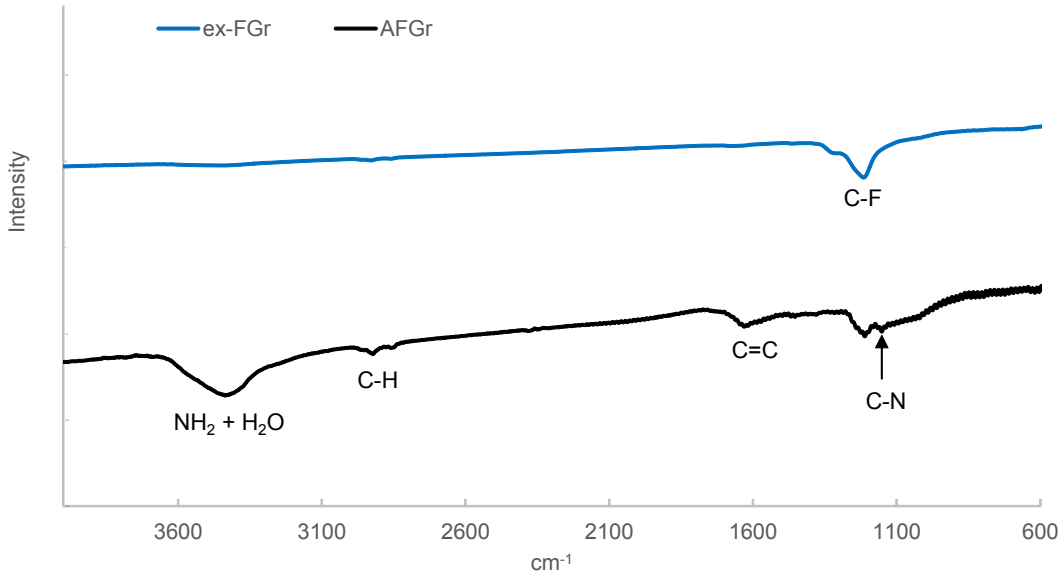
SI4. SEM images of ex-FGr and AFGr showing important morphological changes after exfoliation.



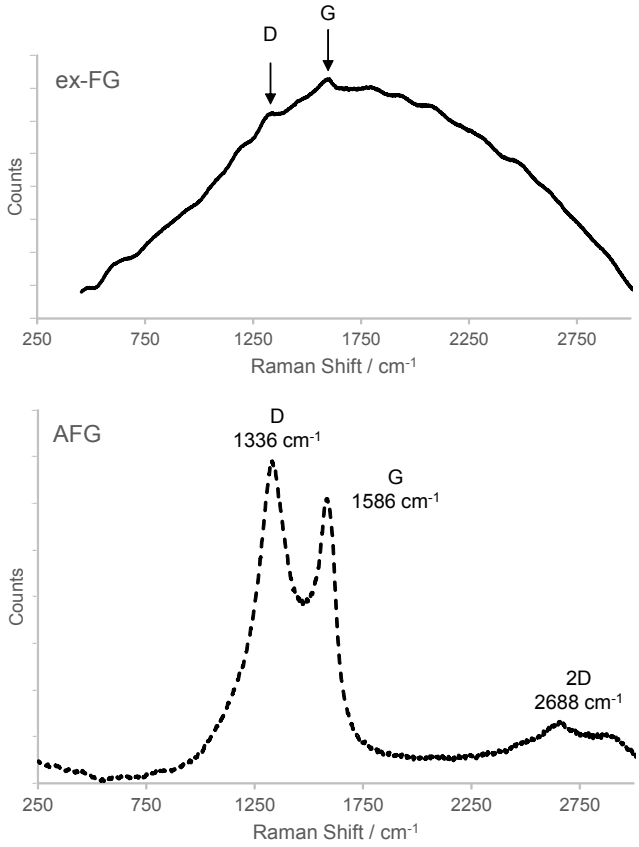
SI5. Bright-field TEM image of the synthesized AFGr. *inset,* selected area electron diffraction pattern showing a hexagonal pattern characteristic of graphite. The intensities of the diffraction peaks, and in the bright-field image, indicate that this is few-layer graphite rather than monolayer material.



SI 6. AFM images of AFGr acquired over a silicon substrate.

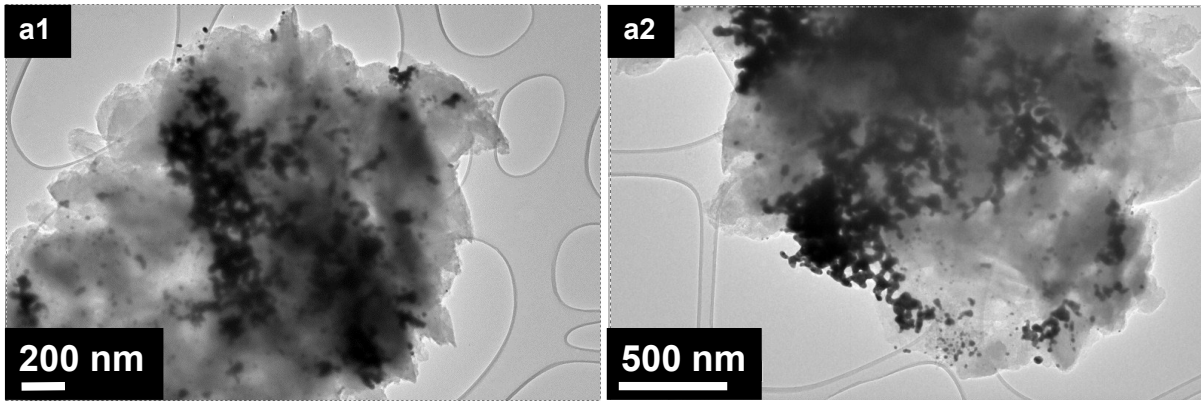


SI 7. FT-IR of ex-FGr (blue line) and AFGr (black line)

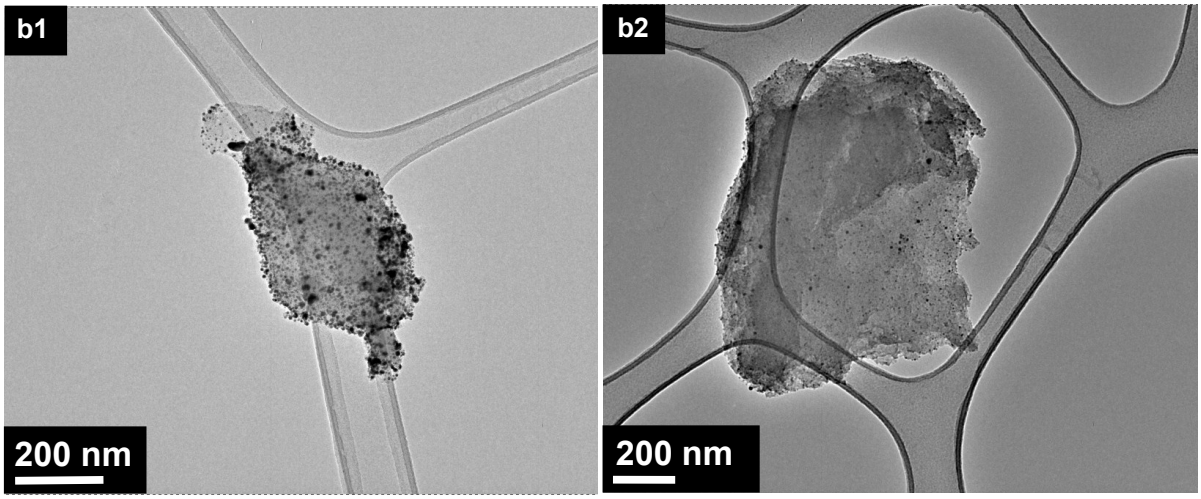


(a)

SI8. Raman spectra recorded at 633nm of ex-FGr (*top,* solid line) and AFGr (*bottom,* dashed line). As shown, ex-FGr exhibits a strong fluorescence, but the D and G peaks typical of graphitic-like materials can still be distinguished.

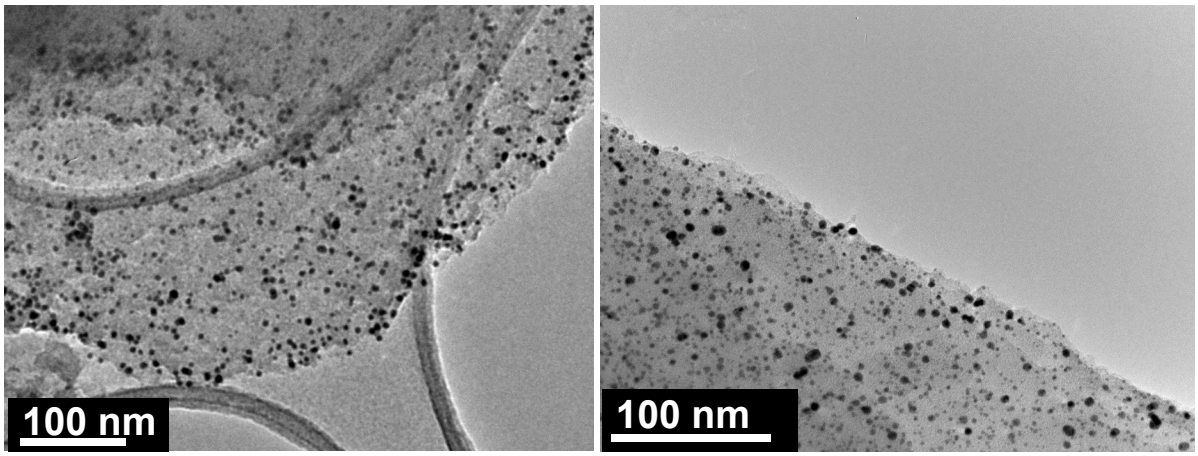


(a)



(b)

SI9. Additional TEM images of (a) ex-FGr-AuNPs and (b) AFGr-AuNPs.



SI10. TEM showing a magnified view AFGr-AuNPs. As shown, well-dispersed AuNPs with sizes between 3-6 nm are obtained.

This ESI file was updated on 20th January 2020 and replaces the original file first published on 30th June 2015. The word “sodium azide” has been corrected to “sodium amide” in the text. This change does not affect the results or conclusions of the article and the details provided in the main text are correct.