

**Supplementary Information for**

**High-yield exfoliation of the three-dimensional graphite into two-dimensional graphene-like sheets**

Eun-Kyoung Choi,<sup>†,‡</sup> In-Yup Jeon,<sup>†,‡</sup> Seo-Yoon Bae,<sup>‡</sup> Hwa-Jung Lee,<sup>‡</sup> Hyeon Suk Shin,<sup>‡</sup>

Liming Dai<sup>§</sup> and Jong-Beom Baek<sup>\*,‡</sup>

*School of Energy Engineering, Ulsan National Institute of Science and Technology*

*(UNIST), 100, Banyeon, Ulsan, 689-897 South Korea*

*Department of Chemical Engineering, Case Western Reserve University,*

*10900 Euclid Avenue, Cleveland, Ohio 44106, USA*

\* Corresponding author. E-mail: [jbbaek@unist.ac.kr](mailto:jbbaek@unist.ac.kr)

† Authors contributed equally.

‡ Ulsan National Institute of Science and Technology

§ Case Western Reserve University

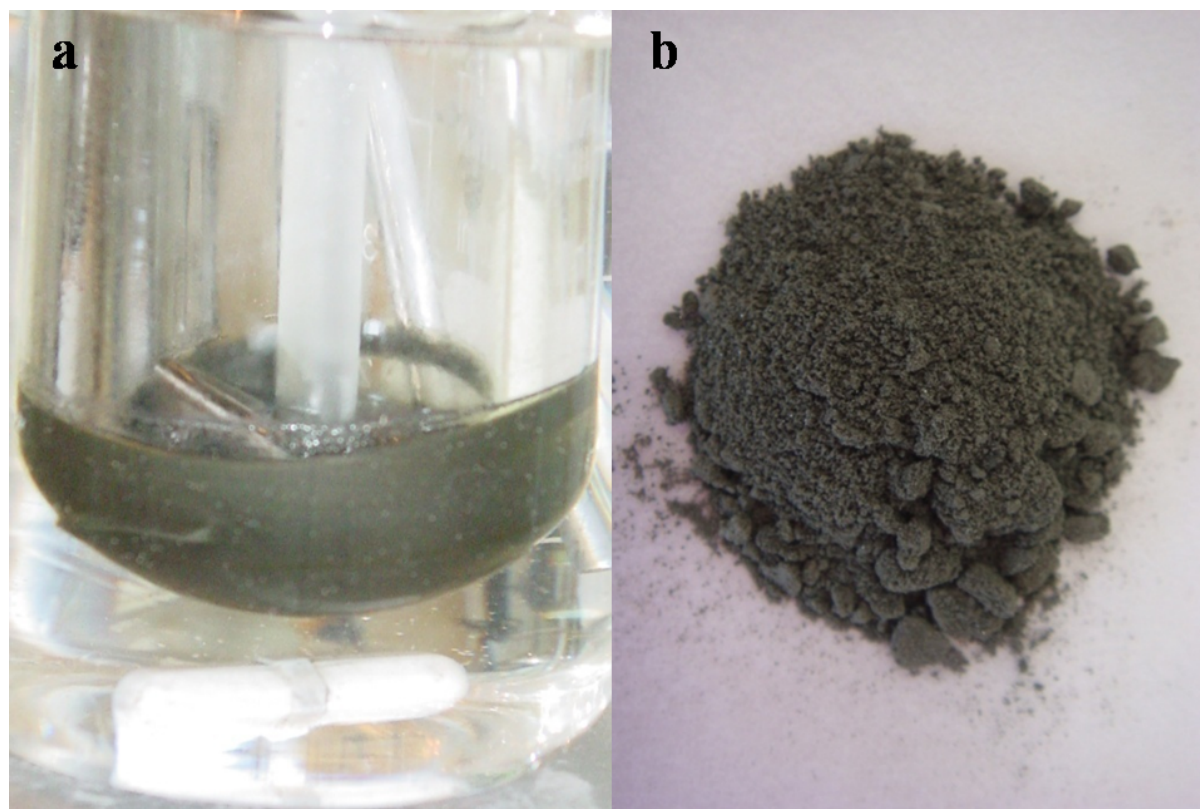
## Experimental

**Materials.** All reagents and solvents were purchased from Aldrich Chemical Inc. and used as received, unless otherwise mentioned. 4-Aminobenzoic acid as a reactive molecular wedge was purified by recrystallization from water. Graphite was obtained from Aldrich Chemical Inc. and used as received.

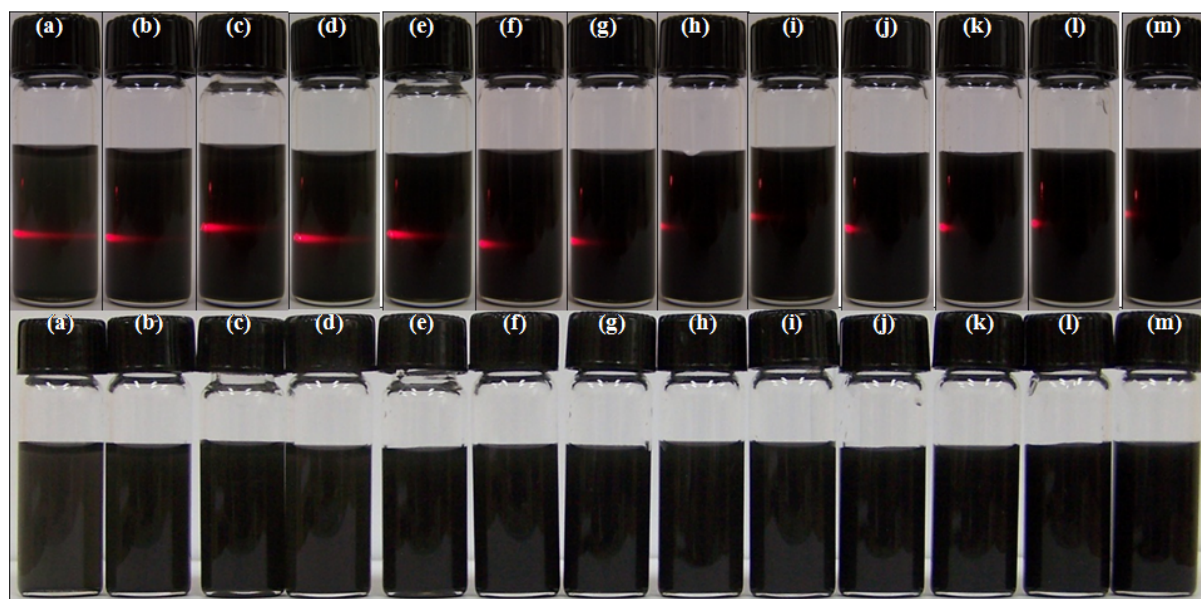
**Instrumentations.** Infrared (FT-IR) and FT-Raman spectra were recorded on a Bruker Fourier-transform spectrophotometer IFS-66/FRA106S. UV-vis spectra were obtained from a Perkin-Elmer Lambda 35 UV-vis spectrometer. Fluorescence experiments were conducted with a Perkin-Elmer LS 55 fluorometer. The applied excitation wavelength was the UV-absorption maximum. Thermogravimetric analysis (TGA) was conducted in air and nitrogen atmospheres at a heating rate of 10 °C/min using a TA Hi-Res TGA 2950 thermogravimetric analyzer. The field emission transmission electron microscope (FE-TEM) images were taken on a FEI Tecnai G2 F30 S-Twin under an operating voltage of 200 kV. The samples for electron microscopy were prepared by dispersion in *N*-methyl-2-pyrrolidone (NMP). X-ray photoelectron spectroscopy (XPS) was performed on Thermo Fisher K-alpha. Elemental analysis (EA) was conducted with Thermo Scientific Flash 2000. Atomic force microscopy (AFM) analysis was conducted with Veeco Multimode V. The resistance of film was measured by four point probe method using Advanced Instrument Technology (AIT) CMT-SR1000N with Jandel Engineering probe at room temperature. The film was prepared by

filtration with membrane (Whatman Anodisc 47, 0.2  $\mu\text{m}$ ), and the conductivity values were the averages of 10 measurements.

**Procedure for the Functionalization of Graphite with 4-Aminobenzoic Acid in Polyphosphoric Acid (PPA)/Phosphorous Pentoxide ( $\text{P}_2\text{O}_5$ ).** Graphite was functionalized with 4-aminobenzoic in a 250 mL resin flask equipped with a high-torque mechanical stirrer, the nitrogen inlet and outlet. Into the flask, 4-aminobenzoic acid (0.5 g, 3.6 mmol), graphite-mesh (0.5 g), PPA (83%  $\text{P}_2\text{O}_5$  assay: 20.0 g) and  $\text{P}_2\text{O}_5$  (5.0 g) were placed and stirred under dry nitrogen purge at 130  $^\circ\text{C}$  for 72h. The initially black mixture became lighter and viscous as the functionalization onto graphite progressed. At the end of the reaction, the color of the mixture turned tanned brown, and water was added into the flask. The resultant tanned brown precipitate was collected by suction filtration, Soxhlet-extracted with water for three days, and then with methanol for three more days. Finally, the sample was dried over phosphorus pentoxide under reduced pressure (0.5 mmHg) at 100  $^\circ\text{C}$  for 72h to give 0.74 g (79% yield) of tanned brown powder. Anal. Calcd. for  $\text{C}_{26.70}\text{H}_6\text{NO}$ : C, 89.90%; H, 1.70%; N, 3.93%; O, 4.48%. Found: C, 86.41%; H, 1.54%; N, 3.81%; O, 6.02%.

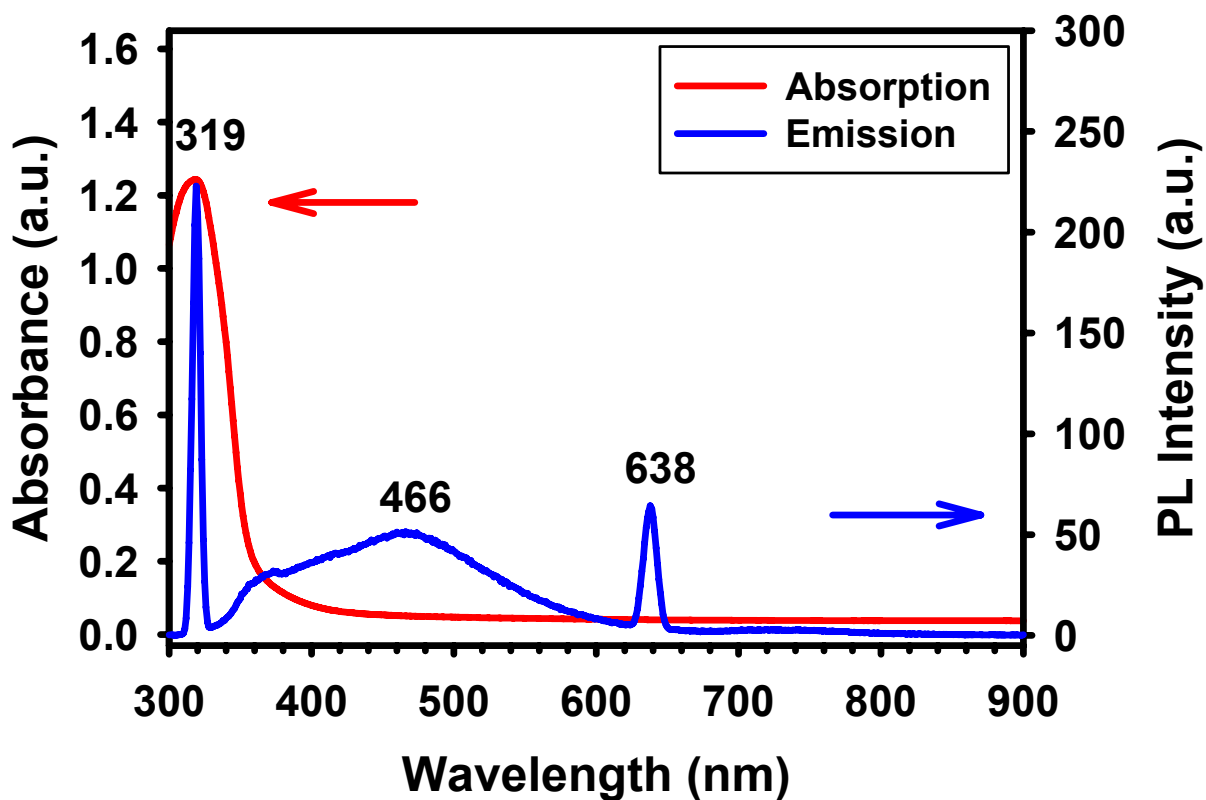


**Fig. S1** (a) (b) digital photograph of reaction flask at the final stage of reaction between graphite and 4-ABA in PPA/P<sub>2</sub>O<sub>5</sub> medium; (b) digital photograph of isolated 4-aminobenzoyl-functionalized graphite (graphite-g-ABA, EFG) after complete work-up procedure (see Experimental part).



**Fig. S2** EFG solutions in NMP with different concentrations (mg/3 mL) with (top) without (bottom) a red beam from hand-held laser pointer: (a) 0.20; (b) 0.25; (c) 0.30; (d) 0.35; (e) 0.40; (f) 0.45; (g) 0.50; (h) 0.55; (i) 0.60; (j) 0.65; (k) 0.70; (l) 0.75; (m) 0.80.

With handheld laser beam, the depth of laser light penetration is an indication of the concentration and homogeneity of EFG in NMP. Above the concentration of 0.80 mg/3 mL (0.27mg/mL), visually discernable precipitations were monitored (Fig. S2, top row). Without handheld laser beam, the colors of the same sample solutions from left to right turn from deep brown to dark black as concentrations increased (Fig. S2, bottom row).



**Fig. S3** UV-vis absorption and fluorescence spectra of EFG solution in NMP.

EFG shows absorption peak centered at 319 nm. When it was excited with 319 nm, EFG solution displayed emission peak maximum at 466 nm (The peaks at 319 and 638 nm are excitation wavelength (319 nm) and its twice wavelength ( $2 \times 319 \text{ nm} = 638 \text{ nm}$ ), respectively).

Generally, carbon materials are known to be strong excimer quencher not to show emission (Guldi, D. M.; Hungerbühler, H.; Asmus, K.-D. *J. Phys. Chem.* **1995**, *99*, 9380). In the case of the EFG, a broad peak centered at 466 nm was detected at low concentration. This behavior could reflect that the organic wedge molecules onto the edges of graphite were covalently attached, since optical quenching of EFG was minimized by ABA moieties.

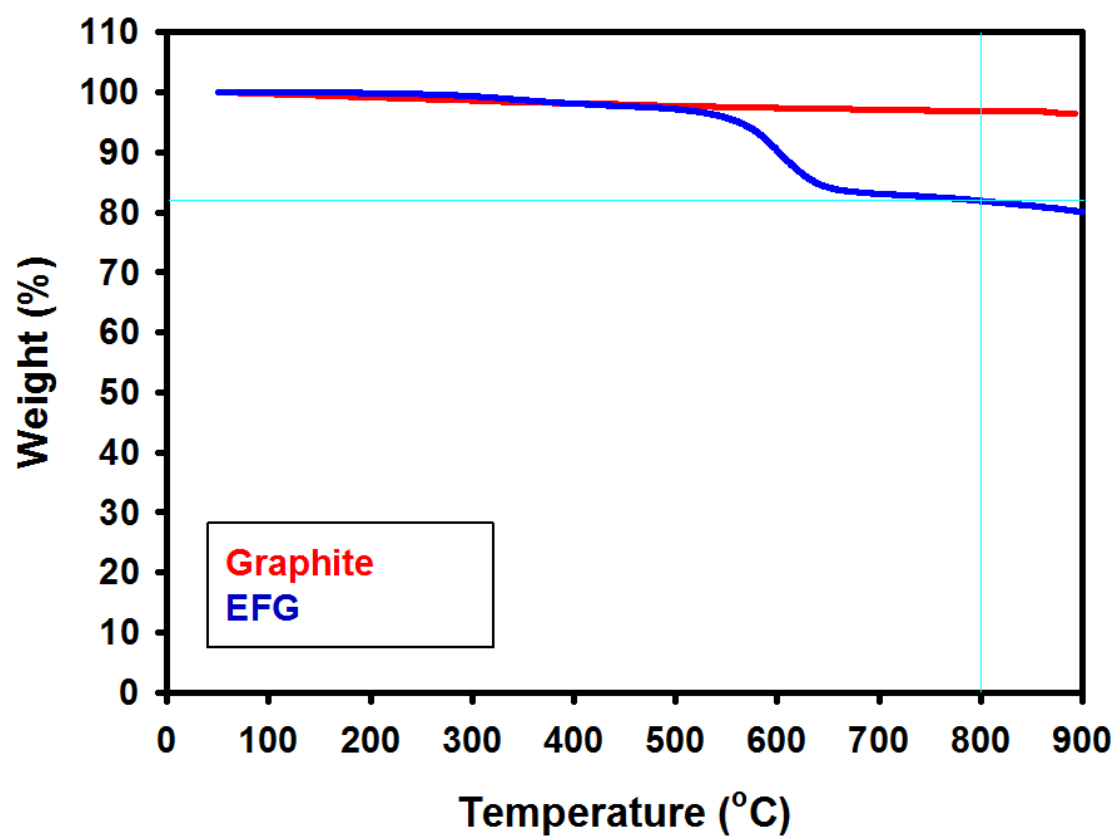
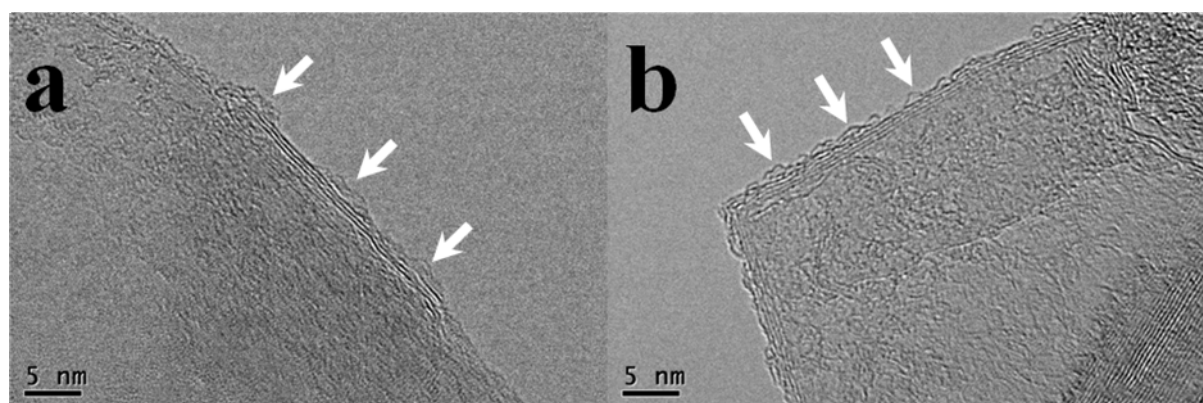


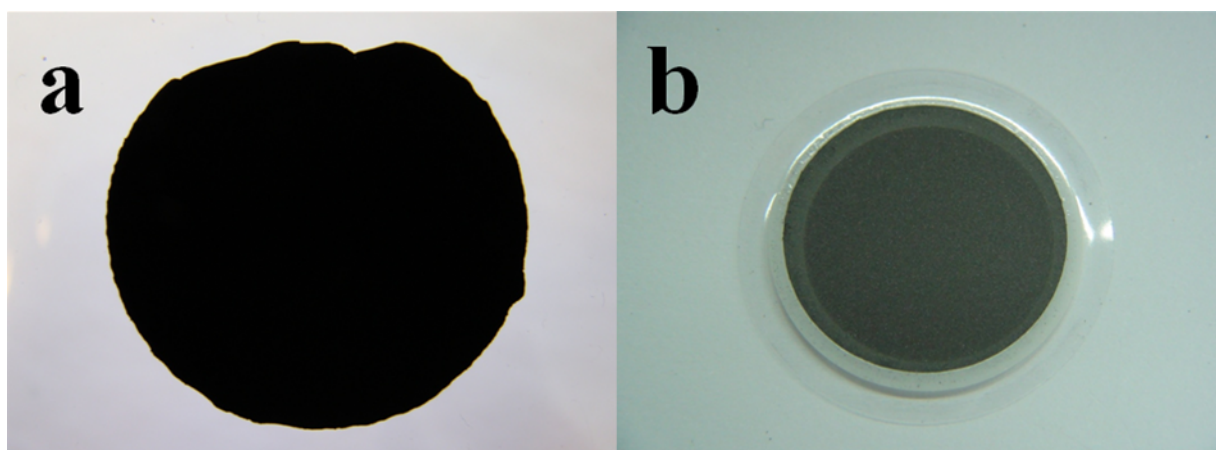
Fig. S4 TGA thermograms obtained with ramping rate of 10 °C/min in nitrogen.



**Fig. S5 TEM images obtained from EFG after dispersion in NMP: (a) three layers of graphene-like sheets; (b) four layers of graphene-like sheets.**

ABA moiety in graphite-g-ABA could be randomly observed at the edge of three and four layers of graphene-like sheets (Fig. S5a and S5b, arrows). Many TEM images were randomly taken from different locations and most of them showed that graphene-like sheets consisted of less than five stacks of graphene layers.





**Fig. S6 Photographs of sample films cast from NMP solutions: (a) as-prepared free-standing EFG film; (b) pristine graphite film.**

**Table S1. Elemental analysis and XPS surface composition data for samples.**

Sample		Elemental Analysis				XPS		
		C (%)	H (%)	N (%)	O (%)	C (%)	N (%)	O (%)
Pristine Graphite	Calcd	100.00	0.00	0.00	0.00	100.00	0.00	0.00
	Found	97.64	BDL*	0.085	0.0046	85.05	BDL*	14.92
Graphite, PPA/P <sub>2</sub> O <sub>5</sub> treated	Calcd	100.00	0.00	0.00	0.00	--	--	--
	Found	97.85	0.022	BDL*	BDL*	--	--	--
EFG	Calcd	89.90	1.70	4.48	3.93	89.90	4.48	3.93
	Found	86.41	1.55	3.81	6.02	74.81	6.65	18.54

\* BDL=Below detection limit.

Theoretical C content for pristine graphite is assumed to be 100%, if the amount of edge  $sp^2$ C-H contribution is ignored. Elemental analysis of pristine graphite shows CHNO contents of 97.64, 0.00, 0.085 and 0.0046%, respectively. However, the surface chemical compositions obtained from XPS analyses show some amount of oxygen located on the graphite surface. The result indicates that the composition of graphite surface should be consisted with oxygenated groups such as carbonyl (C=O), carboxylic acid (COOH), lactone (O-C=O) and anhydride (O=C-O-C=O).

The difference between pristine graphite and PPA/P<sub>2</sub>O<sub>5</sub> treated graphite is CH contents. The C content of PPA/P<sub>2</sub>O<sub>5</sub> treated graphite is marginally increased compared to pristine graphite. A small amount of H is detected, but the amount could still be in experimental error range. Thus, unlike strong acid treatment such as HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub>, PPA/P<sub>2</sub>O<sub>5</sub> treatment itself does not chemically alter graphite.

The theoretical CHNO values of EFG are calculated based on final yield by assuming that the amount of graphite is constant and an estimated ABA amount. Experimental CHN values obtained from EFG are slightly lower than calculated values, while O content is higher than calculated one. Similar to pristine graphite, this is due to preexisting oxygenated groups.

On the basis of elemental and XPS analysis, two important characteristics could be drawn from pristine graphite and EFG. Most of chemical groups are present on the edge of graphite and ABA groups are also most likely attached on the edge of EFG.