Electronic Supplementary Material (ESI) for RSC Advances

Effect of solvent on the uncatalyzed synthesis of aminosilane-functionalized graphene

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(Supporting Information)

1. Experimental details

The oxidation of graphite and the extent of exfoliation of GO is studied using X-ray diffraction (XRDX'Pert PRO MPD diffractometer, PANalytical). Scans at 2θ from 5 to 35° with 0.02° /sec step size at 40 KV voltage with an intensity of 20 Å using CuKα radiation of wavelength 1.5406 Å was conducted.

Transmission Electron Microscopy (TEM) was performed using FEI Tecnai G20 with 0.11 nm point resolution and operated at 200 kV. Samples were prepared by dispersing approximately 0.5 mg of graphene in 25 mL of dimethyl formamide by sonication at room temperature for 5 minutes. Two drops of the suspension were deposited on 400 mesh copper grids covered with thin amorphous lacey carbon film. The coupled Energy Dispersion Spectroscopy (EDS) X-ray analysis is used for elemental composition of TRG and f-TRG. Electron Energy Loss Spectroscopy (EELS) was acquired using post column energy filtered camera (Gatan Quantum 963). The energy resolution was measured to be 0.9 eV FWHM at the zero loss peak. Energy filtered TEM (EFTEM) mapping was applied to map the location of the elements on the surface of f-TRG by measuring core, post-edge and pre-edge losses of the respective elements using the "three-window method" technique[1]. EELS spectra of the aforementioned elements were also recorded at their respective core losses and the type of bonds were identified. Acquisition time necessary to obtain a good signal to noise ratio was 5 s for silicon $L_{2\text{-}3}$-edge, 10 s for carbon K-edge, 20 s for nitrogen K-edge and 30 s for oxygen K-edge.

XPS measurements were performed using SSX-100 system (Surface Science Laboratories, Inc.) equipped with a monochromated Al Kα X-ray source, a hemispherical sector analyzer (HSA) and a resistive anode detector. The base pressure was 4.0 x 10^{-10} Torr. During the data collection, the pressure was ca. 1 x 10^{-8} Torr. The X-ray spot size was 1x1 mm^2, which corresponded to an

X-ray power of 200 W. Each sample was separately mounted on a sample holder using a piece of double-sided carbon sticking tape. Care was taken to ensure the surface was fully covered by the samples. The survey spectra were collected using 150 eV pass energy and 1 eV/step. The atomic percentages were calculated from the survey spectrum using the ESCA 2005 software provided with the XPS system. The high resolution spectra were collected using 50 eV pass energy and 0.1 eV/step. For the high resolution data, the lowest binding-energy C 1s peak (presumably, C-C/ C-H peak) was set at 285.0 eV and used as the reference for all of the other elements. The curve fitting used a combination of Gaussian/Lorenzian function with the Gaussian percentages being at 80% or higher.

The electrical conductivity was measured by a custom made conductivity cell at the National Renewable Energy Laboratory (Golden, CO). A very small quantity of TRG (2-10 mg) was dispersed in 10 mL of a 3 to 1 water to isopropanol solution via 20 minutes of bath sonication followed by an additional 2 minutes of tip sonication to break any remaining clumps of TRG. About 1 mL of the dispersion was placed on a copper stub at a time and dried at 40° C in a drying oven (Despatch, model LBB1-23A-1). Subsequent layers of dispersed TRG were developed in this way until copper stub is completely covered with TRG layers. The complete coverage of the copper stub was obtained from ~8mL of pure TRG, and ~10mL of the f-TRG samples. The copper stub covered with a sample is loaded carefully in the custom made conductivity cell. The resistivity was measured using a multimeter (Wavetek 28XT, Accuracy: ±1% + 0.1 Ohm).

2. Characterization of TRG

The evidence of the complete exfoliation of graphite oxide has been obtained by XRD (Figure s1-a). The interlayer spacing in graphite has been observed to be 3.37Å from the single only intrinsic 002-peak at $\theta = 13.25$. Due to the presence of polar groups on GO from oxidation and because of the adsorbed water contents in GO, the 002-peak shifts to $\theta = 5.7$ (indicating the interlayer d-spacing of 0.78Å). The increased d-spacing is a clear evidence of expansion of graphite layers upon oxidation. In XRD of TRG, no interlayer spacing is observed indicating a complete exfoliation of GO. This confirms the production of no stacked structure and that we are not dealing with nanocrystalline graphite but with TRG. In addition, TEM image (Figure 1s-b) evidences the presence of overlapping layers of graphene. The transparent graphene sheets are clearly visible confirming that GO has been successfully exfoliated. However, the elastic corrugations and the scrolled or folded edges often result in different brightness in the surface of graphene [2].

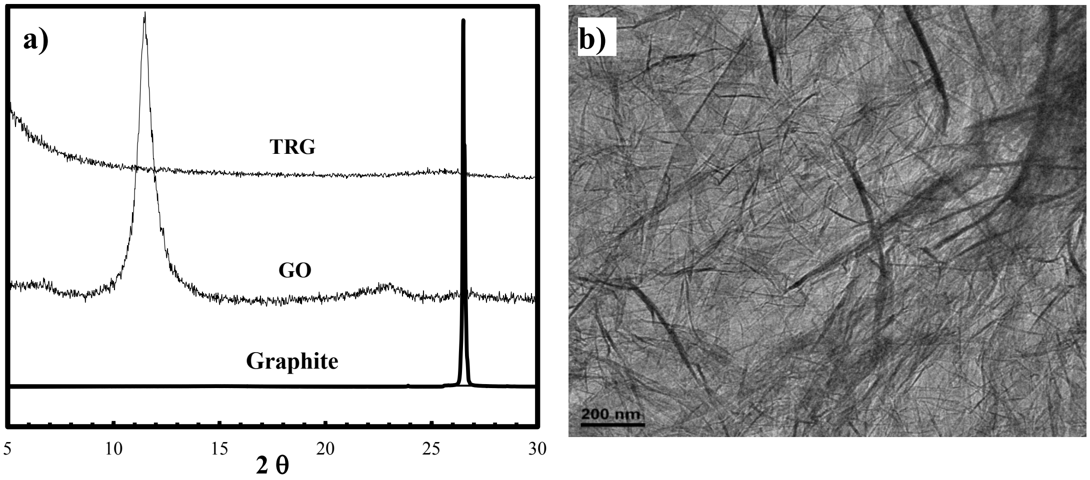

Figure s1 XRD spectra of graphite, graphite oxide (GO) and TRG (a), and TEM of pure TRG (b)

3. XPS spectra

Important insights into the reaction mechanism and the material structure come from the core-level binding energies (BEs) obtained from XPS high resolution spectra. Figure s2 shows the overall survey data of the pure and f-TRG samples. Clear differences between pure and f-TRG samples can be observed. The XPS spectra have been collected on dry TRG samples. In TRG overall survey, there has been no Si and N detected. Usually, the Si^{2p} is detectable between 95-110 eV whereas N^{1s} can be found between 400-407eV, depending upon the chemical environment of the molecule. As compared with pure TRG, both the f-TRG_p and f-TRG_s show the presence of Si^{2p} and N^{1s} originating from APTS, indicating the successful covalent functionalization of TRG with APTS.

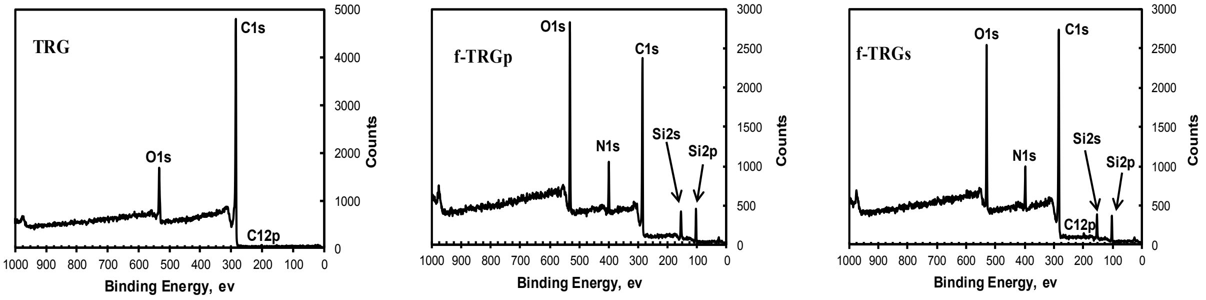

Figure s2 Overall XPS survey for the pure and f-TRG

The broad band in high resolution N^{1s} spectra of f-TRGp and f-TRGs fitted with two peaks at 399.95 eV (~400.0) and ~401.0 eV BE (Figure s3). The lower BE peak is assigned to aliphatic amine, imine or amide groups ($R\text{-}NH_2$, C=N, N-C=O) and the higher energy peak is assigned to positively charged quaternary nitrogen ($R\text{-}NH_3^+$). The latter peak might have resulted from the amine protonation by acidic groups on the surface of TRG[3].

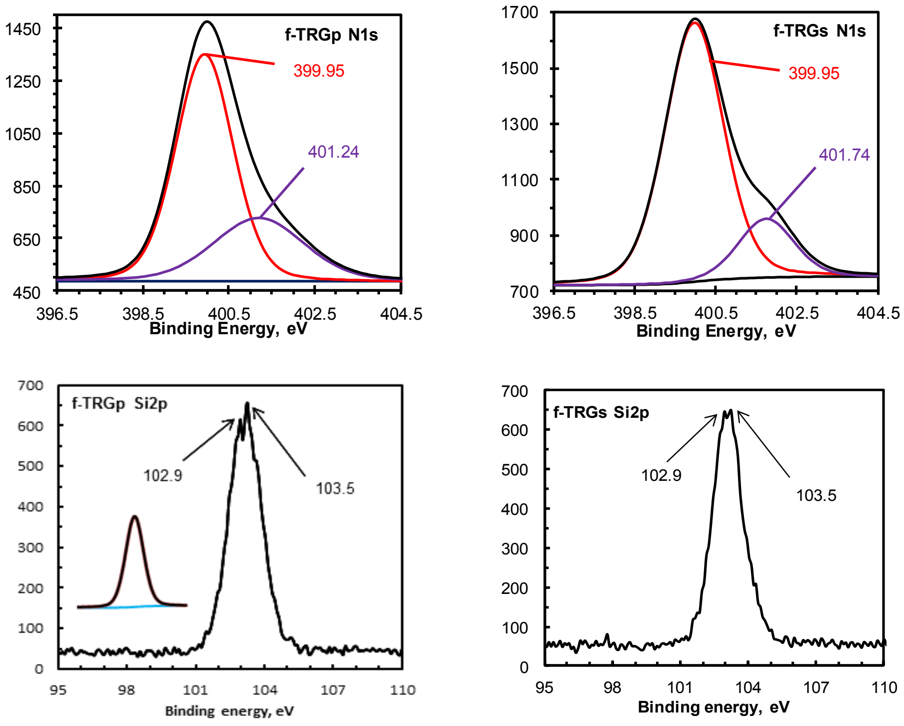

Figure s3 N^{1s} and S^{2p} high resolution XPS scans for TRG_p and TRG_s

In Si^{2p} region, the presence of bands confirms the grafting reaction of silane on TRG (Figure 3s). The Si^{2p} spectra of the two functionalized samples appear almost similar. The two shoulders are observed exactly at the same position for the functionalized samples. One small shoulder peak appears at 102.9 eV and the other at 103.5 eV. The peak at 103.5 eV is attributed to the development of a strong cage-like $Si\text{-}O_4$bonds[4] or Si-O-Si structure due to lateral polymerization, which affects the theoretical predictions of the product concentrations in silanization reaction. However, due to anhydrous conditions during the reaction, the lateral polymerization effects can be neglected[5]. The shoulder at 102.9 eV in both spectra can be attributed to N bonding with the carbon surface. However, when deconvoluted, the two peaks merge into one smooth peak at ~102-103 eV. This single peak contains the contributions from

$Si2p_{3/2}$ and $Si2p_{1/2}$ which cannot be resolved by non-monochromatic radiation as shown as inset in Figure s3 for Si in f-TRG_p. And therefore the single deconvoluted peak around 103 eV BE is assigned to Si-O bond. The relative contribution of each band in high resolution fitting is shown in Table s1. Table 1s High resolution fitting of functional groups in N^{1s} and Si^{2p} XPS scans

	N1s peaks		**Si2p peaks**	
	$R\text{-}NH_2$	$R\text{-}NH_3^+$	N-C	$Si\text{-}O_4$
f-TRG_p	399.95	401.24	102.9	103.5
f-TRG_s	399.95	401.74	102.9	103.5

4. EDS analysis

The EDS analyses were performed on selected thin areas of graphene sheets (Table s2). However, EDS shows a qualitative picture of the attached moieties which can be taken as a rough estimate for quantitative analysis.

Table s2 Averaged EDS results

	Atomic %	
	f-TRG_p	**f-TRG_s**
C(K)	73.98	74.98
N(K)	4.53	4.10
O(K)	13.53	14.39
Si(K)	7.89	6.27
S(K)	0.04	0.14
Cl(K)	0.01	0.10

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