

Supplementary material

Chemical functionalization of graphene sheets by solvothermal reduction of suspension of graphene oxide in *N*-methyl-2-pyrrolidone

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Descriptions of Chemical, GO synthesis, Elemental composition of STRG reduced in nitrogen atmosphere, FT-IR spectra, XPS survey spectra and HRTEM of STRG, BET surface area of STRG-5.

1. Chemicals

Expandable graphite (Grade 1721) was kindly offered by Asbury Carbon. Concentrated sulfuric acid (H_2SO_4), potassium permanganate (KMnO_4), hydrochloric acid (HCl), hydrogen peroxide (H_2O_2), *N,N'*-dimethylformamide (DMF), propylene carbonate (PC), and 1-methyl-2-pyrrolidinone (NMP) were purchased from Aldrich. All chemicals were used as received without further purification.

2. Synthesis of GO

A small amount of expandable graphite was charged into a 1-L beaker and heated for 10 s in a microwave oven. The graphite expanded to about 150 times its original volume. Graphene oxide was synthesized from expanded graphite according to a modified Hummers method.⁵¹ Typically, 500 mL of concentrated H_2SO_4 was charged into a 3-L, three-necked flask equipped with a mechanical stirrer (Teflon impeller). The flask was put into an ice bath to chill to 0°C. Five grams of expanded graphite were gradually added under stirring to make a suspension. Then, 30 g of KMnO_4 was slowly added so that the temperature did not exceed 20°C. The temperature was then elevated to 35°C, and the suspension was stirred for 2 h. The flask was then chilled again in the ice bath, and 1 L of deionized

water was slowly added to maintain a temperature below 70°C. The mixture was stirred for 1 h and subsequently diluted with 5 L of deionized water. Fifty milliliters of H₂O₂ (30 wt%) was slowly added, and vigorous bubbles appeared as the color of the suspension changed from dark brown to yellow. The suspension was centrifuged and washed with 10% HCl solution four times, followed by centrifuging at 10,000 rpm and washings with deionized water to completely remove the acid until the pH of the GO dispersion reached 6. The as-synthesized GO dispersion was a paste. The concentration of GO was 1.0 wt%, which was determined after drying the GO dispersion at 80 °C under vacuum for 24 h.

3. Elemental composition of STRG reduced in nitrogen atmosphere

Table S1. Solvothermal reduction of graphene oxide suspension in nitrogen atmosphere

Sample	Carbon (wt%)	Oxygen (wt%)	Nitrogen (wt%)	Hydrogen (wt%)	C/O ratio	C/N ratio	C/H ratio
Graphene oxide	54.53	43.29	0	2.18	1.68	-	2.08
STRG-1	84.01	13.49	1.19	1.31	8.30	82.36	5.34
STRG-3	84.07	13.46	1.23	1.24	8.32	79.68	5.65

In order to confirm the assumption that graphene sheet was functionalized by free-radical generated when heating NMP in the presence of air, the solvothermal reduction of graphene oxide suspension was carried out in nitrogen atmosphere. The graphene oxide suspension was purged with nitrogen for 3 hours and subsequently heating the graphene oxide suspension under nitrogen purging condition. The elemental composition of STRG-x reduced in nitrogen atmosphere was given in table S1.

4. Thermal gravimetric analysis of STRG-x

STRG-x was characterized by thermal gravimetric analysis (TGA) under nitrogen atmosphere with a heating rate of 10 °C min⁻¹. As shown in Fig. S1 (a), graphene oxide is thermally unstable. Graphene oxide lost around 45 and 60 % of its weight when the temperature was increased to 300 and 900 °C, respectively. The main mass loss occurred at 175 °C which is assigned to the decomposition of labile oxygen functional groups.^{S2} By contrast, STRG-x lost only around 5 % of its weight at 300 °C indicating that most of labile oxygen functional groups were removed upon solvothermal reduction. The derivative of thermal gravimetric (DTG) curves of STRG-x show that the main

mass loss of STRG-x took place in range of 300-600 °C (Fig. S1 (b)), which could be attributed to the defunctionalization upon heating.^{S3,S4} The intensity of DTG peaks gradually increase with reduction time indicating that the functionalization of graphene sheet increased with reduction time, which is consistent with the elemental analysis result.

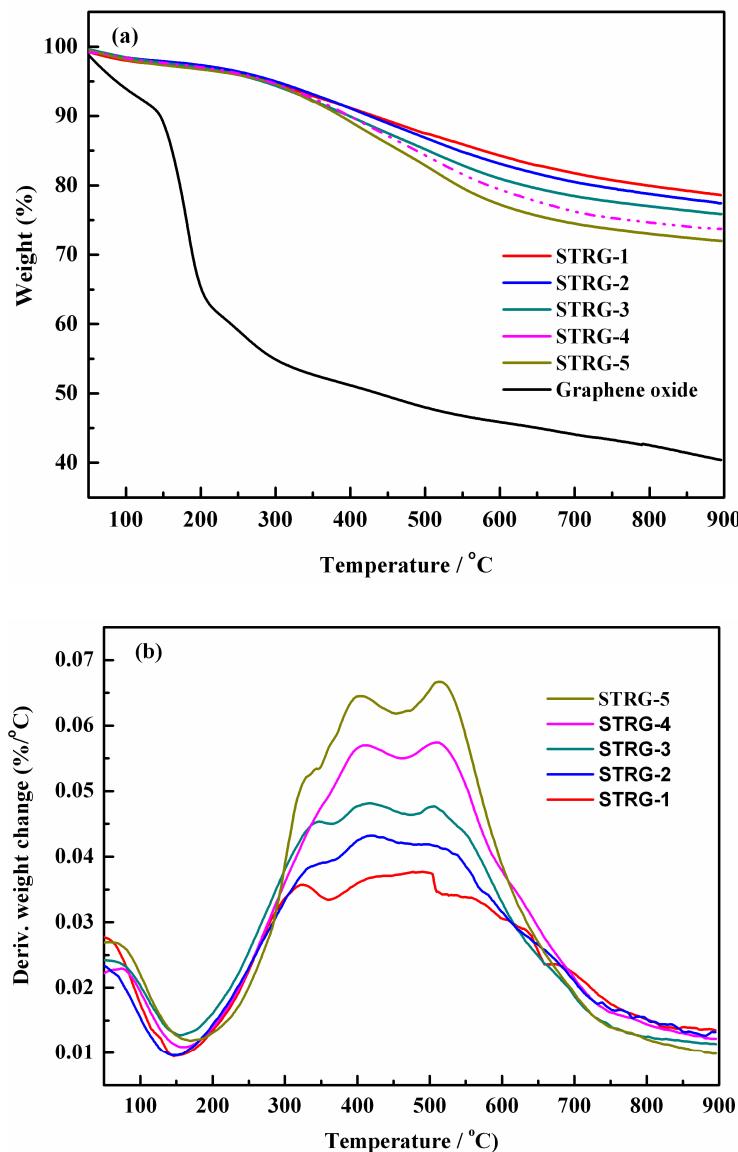
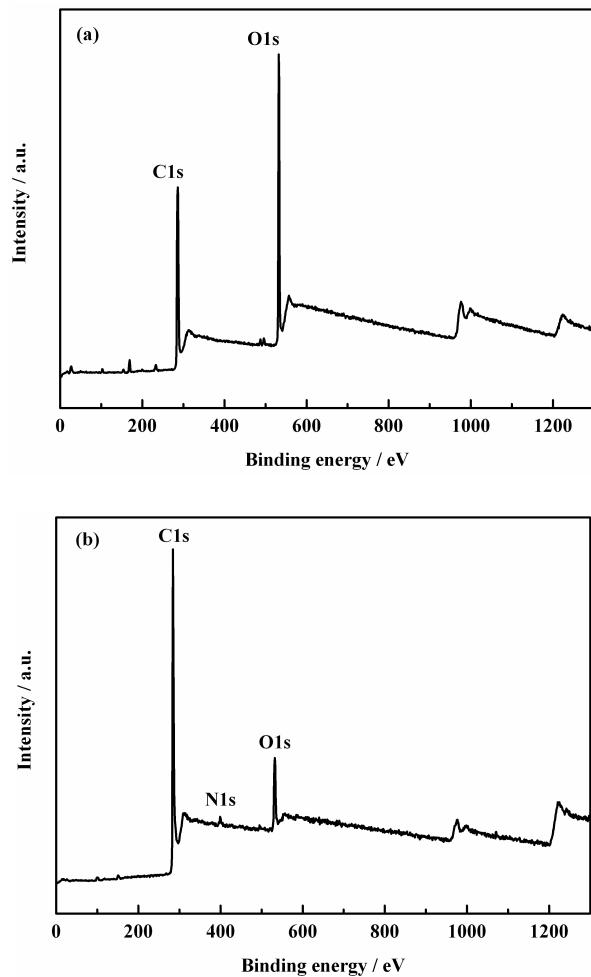


Figure S1. (a) TGA plots of graphene oxide and STRG-x, (g) DTG plots of STRG-x

5. XPS survey spectra of STRG



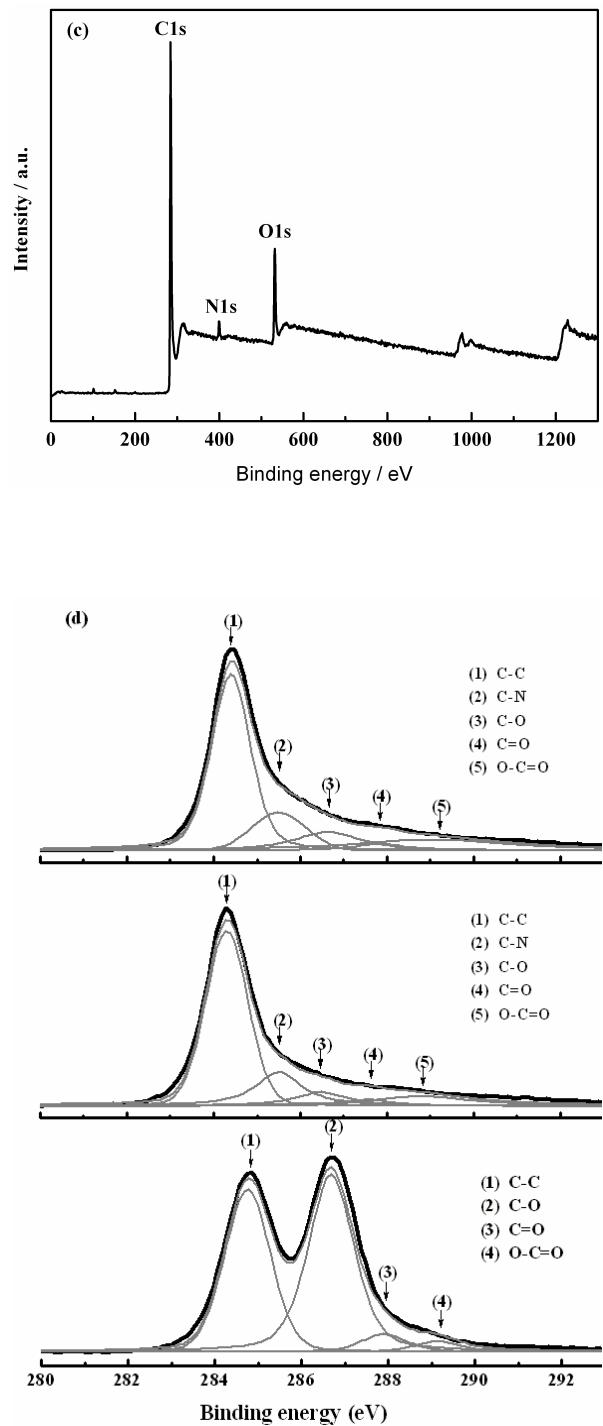


Figure S2. XPS survey spectra of (a) graphene oxide, (b) STRG-1 (c) STRG-5 and (d) C1s spectra of GO (bottom),
STRG-1 (middle) and STRG-5 (top)

The XPS spectra were used to further confirm the solvothermal reduction and functionalization of graphene oxide and STRG-x. Fig. S2 shows the survey and C1s XPS spectra of graphene oxide, STRG-1 and STRG-5. The C1s XPS spectrum of graphene oxide shows three peaks assigned to oxygen functional groups such as hydroxyl (286.6 eV), carbonyl (287.9 eV) and carboxylate (289.1 eV).^{S2,S5} After solvothermal reduction, the intensity of these peaks remarkably reduced, indicating that most of oxygen functional groups were successfully removed. The deconvolution of the C1s spectra of STRG-1 and STRG-5 show a new peak at 285.8 eV corresponding to C in the C-N bonds.^{S2,S6} The survey XPS spectra of STRG-1 and STRG-5 also display a small N1s peak at around 401 eV (Fig. S1 (b) & (c)), demonstrating that the graphene sheets were functionalized by NMP oxidation products during solvothermal reduction.

6. HRTEM of STRG

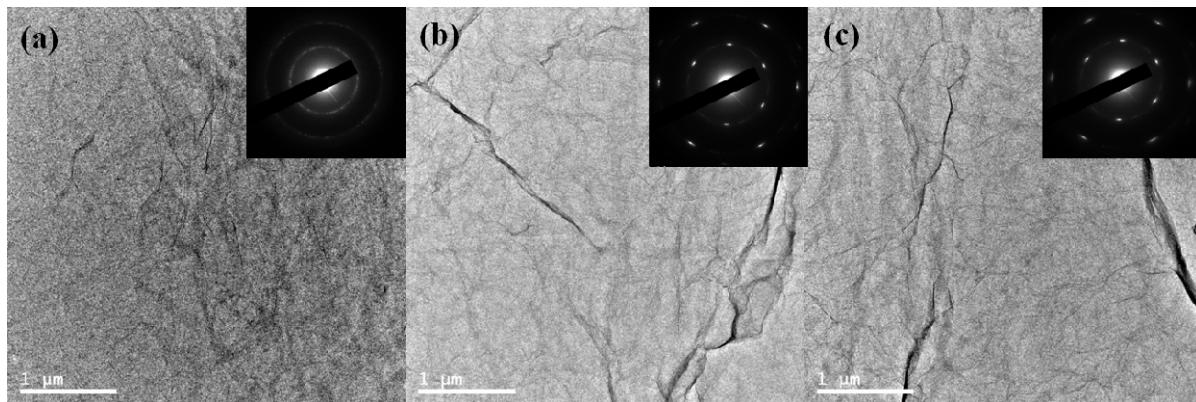


Fig. S3. TEM images with corresponding SAED (inset) of (a) GO, (b) STRG-1 and (c) STRG-5

The structure of STRG was characterized by high resolution TEM. As shown in Fig. 1, GO and STRG sheets have wrinkles and folded regions. The SAED showed the ring-like pattern consisting of many diffraction spots for each order of diffraction. These spots make regular hexagons with different rotation angles between such hexagons, indicating the essentially random overlay of individual graphene sheets.^{S7} The SAED patterns also exhibited the differences in crystallinity. The diffuse diffraction pattern of GO indicates an amorphous structure. The sharp diffraction pattern of STRG-1 indicates that STRG-1 has highly graphitic crystalline structure,^{S8} which is restored during the solvothermal reduction. Similarly, STRG-5 exhibited graphitic crystalline structure but the

crystallinity is not as high as STRG-1 due to the functionalization. The characterization of STRG by TEM has been added in supplementary information.

7. BET surface area of STRG-5

As described in manuscript, STRG was highly dispersed in polar organic solvents such as DMF, NMP, PC. The STRG suspensions in these solvents were stable for one month without noticeable precipitation. The high stability of STRG suspension indicates that the STRG was present almost entirely as individual sheets^{S97-S11}. Since STRG almost entirely exists in suspension as individual sheets, the surface area of STRG could reach the theoretical value, 2620 m²/g.^{S12} Fig. S4(a), (b) show the SEM image of free-standing paper and powder of STRG-5 prepared by two different methods: vacuum filtration and coagulation by HCl solution (1M) of STRG-5 suspension in DMF respectively. Surface area of free-standing paper and powder of STRG-5 determined by BET method using nitrogen gas adsorption yield surface area value of 28.64 (around 1% of theoretical value) and 269.76 m²/g (around 10% of theoretical value), respectively. Those values are quite different each other and it means that the surface area of dried STRG intimately depends on the processing method.

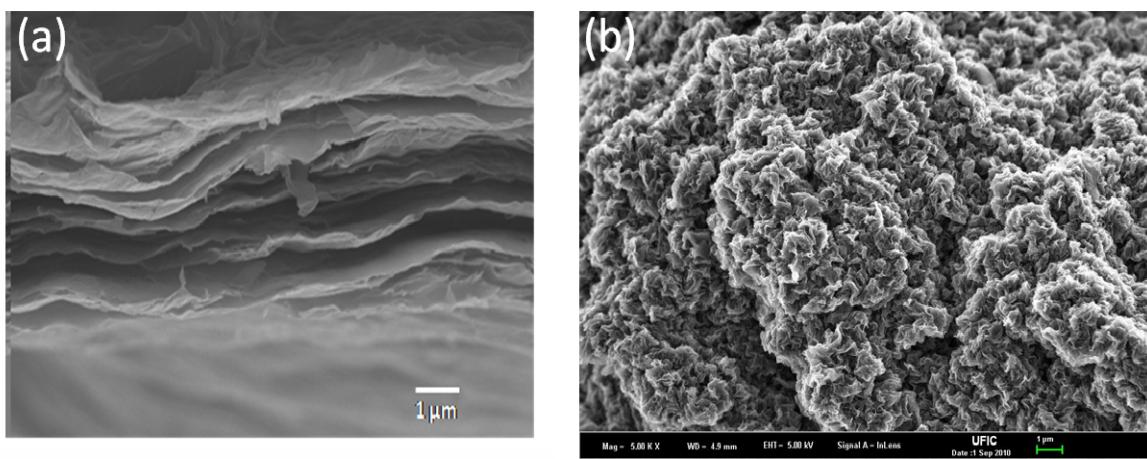


Fig. S4 (a) Cross-section SEM image of free-standing paper of STRG-5 and (b) SEM image of STRG-5 powder.

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