

Supporting Information for

Radiation Induced Reduction: A Effect and Clean Route to Synthesize Functionalized Graphene

*Bowu ZHANG,^{a, b} Linfan LI,^a Ziqiang WANG,^a Siyuan XIE,^{a, b} Yujie ZHANG,^c Yue SHEN,^{a, b} Bo DENG,^a Ming YU,^a Qing HUANG,^a Chunhai FAN^a and Jingye LI^{a, *}*

^a Shanghai Institute of Applied Physics, Chinese Academy of Sciences, No. 2019, Jialuo Rd., Shanghai, 201800 (P. R. China)

^b Graduate University of the Chinese Academy of Sciences, No. 19A, Yuquan Rd., Beijing, 100049 (P. R. China)

^c Ningbo Institute of Material Technology & Engineering, Chinese Academy of Sciences, No. 519, Zhuangshi Rd., Ningbo, 315201 (P. R. China)

Corresponding Author: Fax&Tel: +86 21 39194505; E-mail: jingyeli@sinap.ac.cn

Experimental section

Preparation of graphene oxide (GO)

GO is synthesized from commercial graphite powder according to a modified *Hummer's method*.¹ In detail, 15 g of K₂S₂O₈, 15 g of P₂O₅ and 45 mL concentrated H₂SO₄ were mixed and heated to 80 °C. 30 g of graphite powder was added slowly to the mixture. The resultant mixture was cooled to room temperature over an interval of 6 hours and then carefully diluted with de-ionized water, filtered, and washed on the filter until the pH value of rinse water became 7. The product was dried in a vacuum oven at 45 °C. 5 g of the oxidized graphite powder was added to 115 mL of cold (0 °C) concentrated H₂SO₄. Subsequently, 15 g of KMnO₄ was slowly added with stirring and ice-cooling to make sure the temperature of the mixture solution below 20 °C. The solution was stirred at 35 °C for 2 hours and then cooled to room temperature. After that, 230 mL of de-ionized water was slowly added by keeping the temperature under 50 °C. The reaction was terminated by the addition of 700 mL of de-ionized

water and 12.5 mL of H₂O₂ solution (30 %), after which the colour of the mixture changed to bright yellow. The resultant mixture was filtered by PVDF membrane and filter-cake was washed with 1.25 L hydrochloric acid solution (1:10) and 1.0 L de-ionized water. The solid was suspended in de-ionized water and sonicated for 2 hours. The supernatant yellow-brown sol was subjected to dialysis for 3-5 days, followed by filtering and slightly drying at room temperature in a vacuum desiccator, forming a black and flexible paper-like material.

Supplementary Figures

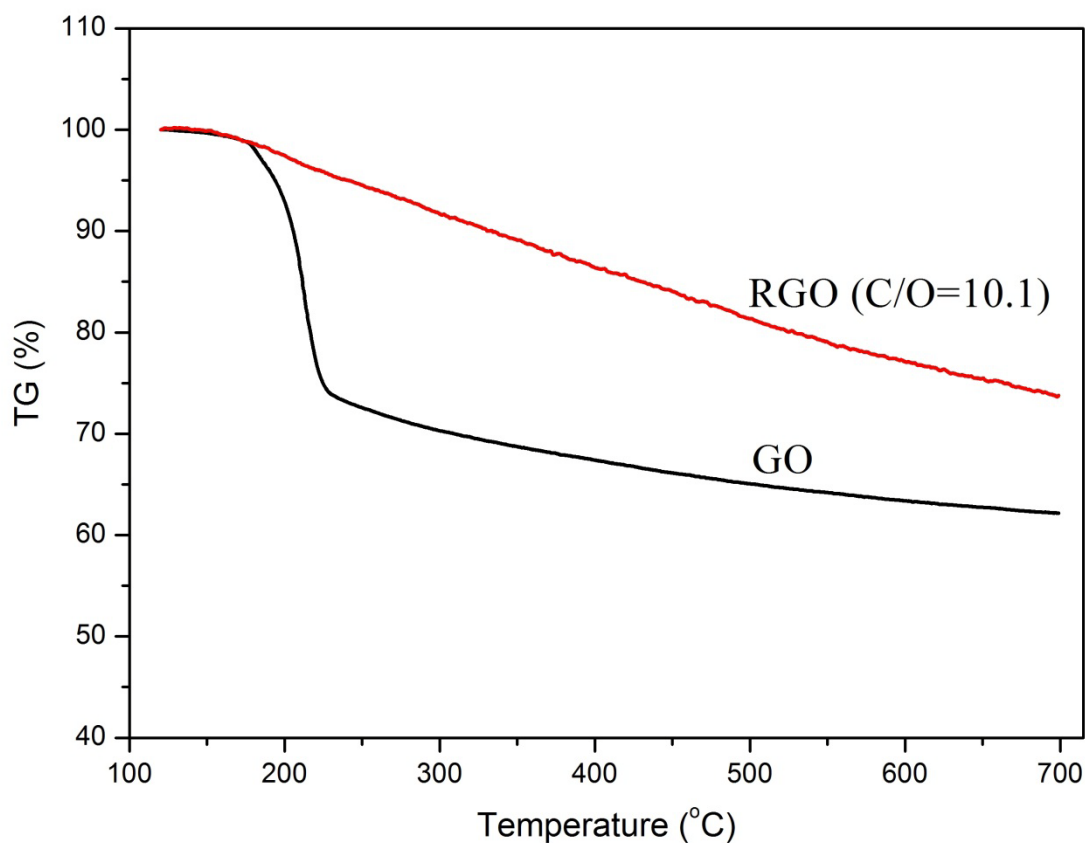


Figure S1 TGA curves of RGO and GO papers

The weight loss stage around 200 °C in the starting GO's TGA curves has disappeared in the curve of obtained RGO, which shows its enhanced thermal stability due to the removal of oxygen-containing groups² by γ -ray irradiation in ethanol/water.

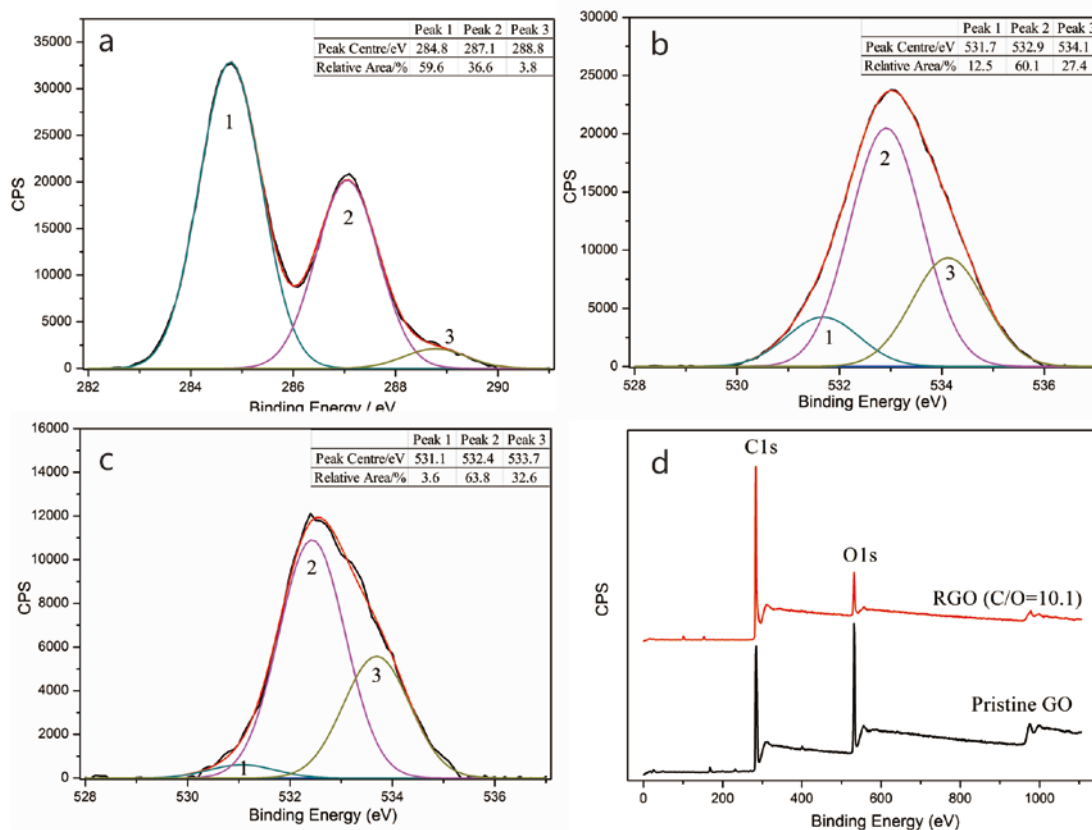


Figure S2 (a) and (b) show the XPS C1s and O1s spectra of GO; (c) the XPS O1s spectra of RGO; (d) the wide scan XPS spectra of GO and RGO.

Figure S2 (a) indicates the graphene sheet of GO was highly oxidized. **Figure S2** (b & c) shows three Gaussian peaks at 531.6 eV (C=O group), 532.8 eV (C-OH/C-O) and 534.1 eV (H₂O) in both GO and RGO samples. After the reduction, the intensity of C=O group (531.1 eV) is decreased extremely, and the total intensity of O peaks also decreased, which agree with the change of C1s spectra. **Figure S2** (d) shows RGO is highly pure, although a negligible silicon detected, which could be introduced from the glass containers. This is owing to the reactants used here are nonpersistent and volatilizable, which is easy to remove by membrane filtration and drying in simple and mild condition. It is conclusive that this process is a promising method to prepare chemically derived graphene comparing with other chemical reduction methods,³ and performs above other reduction methods by introducing an impurity-free result.

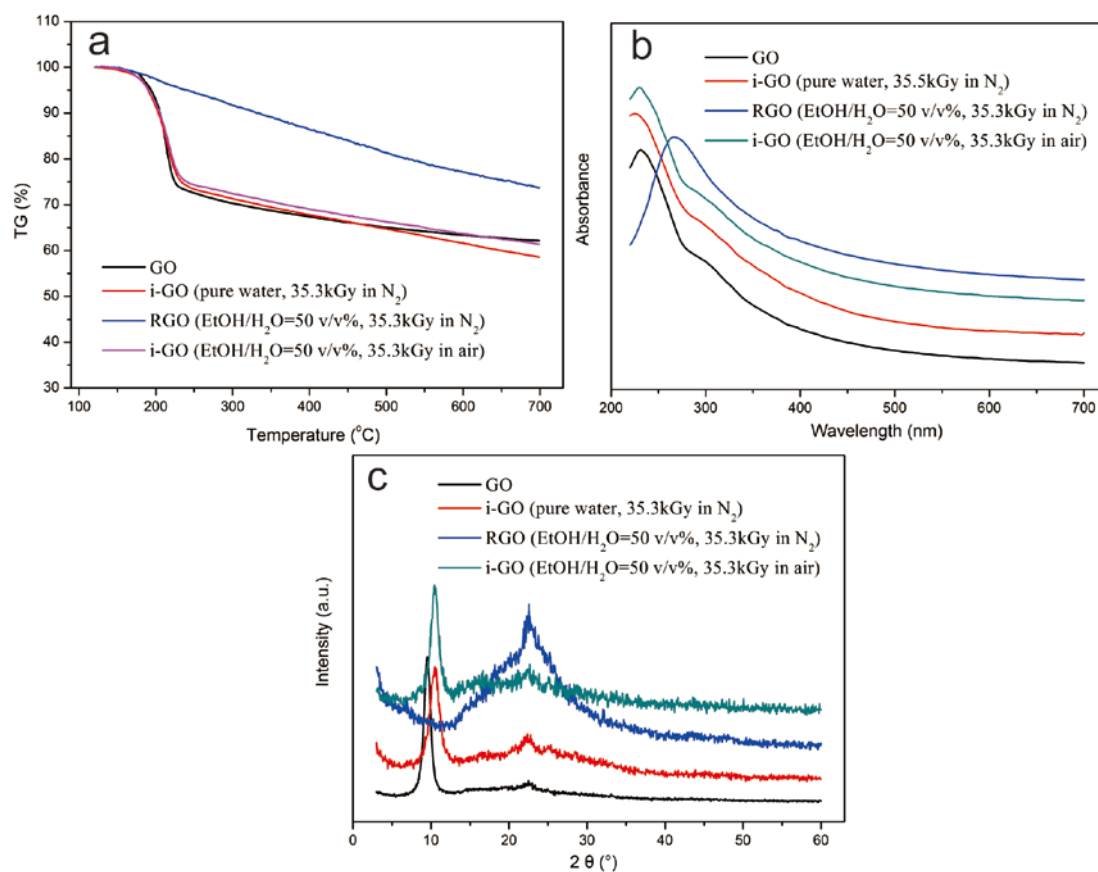


Figure S3. (a) TGA curves of GO and irradiated GO paper in different condition (dose rate: $0.882 \text{ kGy} \cdot \text{hr}^{-1}$); (b) UV-Vis spectra of GO and irradiated GO dispersion in different condition (dose rate: $0.882 \text{ kGy} \cdot \text{hr}^{-1}$), ethanol/water (50 v/v %) used as solvent. (c) XRD patterns of GO and irradiated GO dispersion in different condition (dose rate: $0.882 \text{ kGy} \cdot \text{hr}^{-1}$).

Figure S3 shows that both oxygen-free and alcohol-adding are the essential factors of GO reduction by γ -ray irradiation.

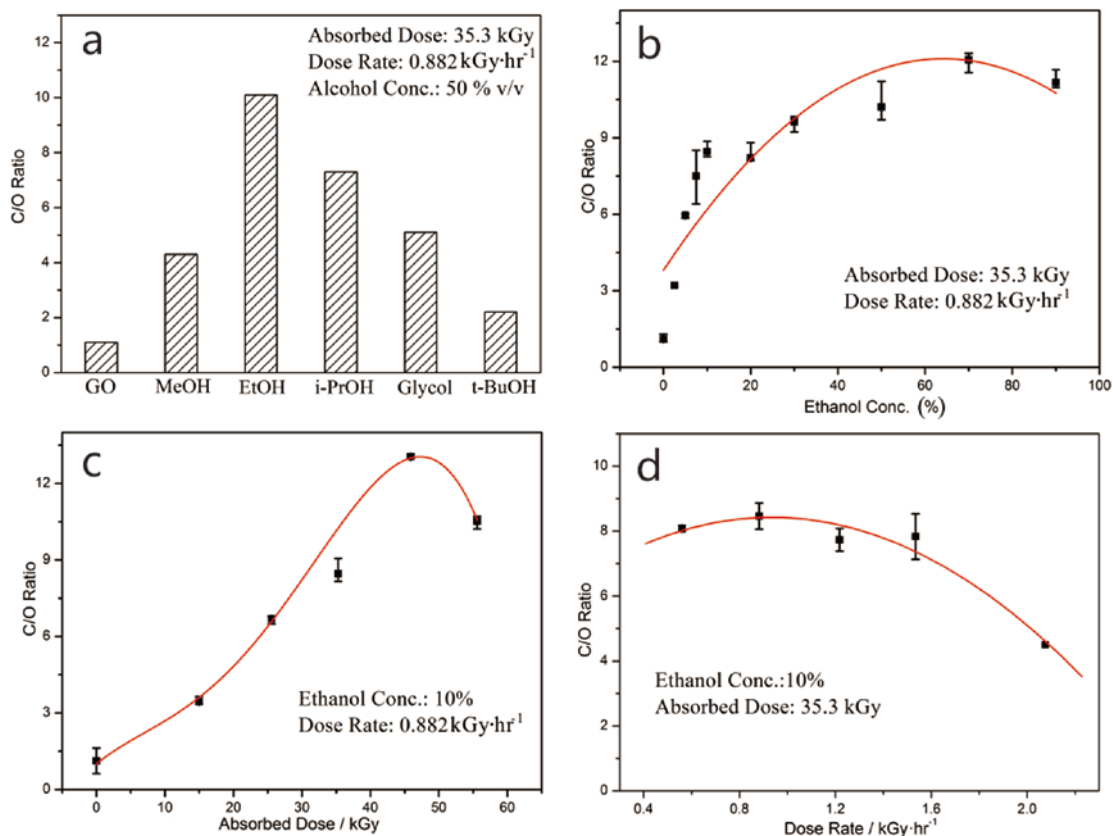
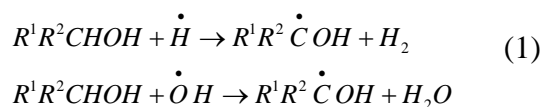


Figure S4 Plots of the C/O ratio of RGO obtained with reaction parameters: (a) different alcohols, (b) ethanol concentration, (c) adsorbed dose and (d) dose rate, when irradiated under the protection of a nitrogen atmosphere. The methanol, ethanol, isopropanol and tert-butyl alcohol are denoted as MeOH, EtOH, i-PrOH and t-BuOH, respectively.

Generally acknowledged, reactions of the $\cdot\text{H}$ and $\cdot\text{OH}$ radicals with alcohols, take place mainly at the α -carbon position, and produce reductive radicals as equation (1):⁴



Therefore, the different structure of alcohol molecules would affect the yield of reductive radicals. We compare the reduction level of GO by adding various alcohols and find ethanol is the best additive for this reduction system, while the tert-butyl alcohol is almost noneffective as **Figure S4 (a)** shows. This may be due to ethanol's radical processes mediate reactivity and steric size and provides sufficient time diffusion to approach GO sheets, while the tert-butyl alcohol is free α C-H and cannot scavenge the oxidative radicals, because of the nearly unavailable hydrogen

abstraction reaction with $\cdot\text{OH}$ radicals. In view of its best efficiency and nontoxicity, we choose ethanol as the subject investigated in this system.

Figure S4 (b) shows that the C/O ratio is a parabolic relation with the ethanol concentration of the blend solvent system. The radical reaction is a diffusion controlled reaction because of the high chemical reactivity,⁵ and good dispersibility of GO in the system is critical to higher reduction. However, the solubility of GO is good in water but poor in organic solvents, including ethanol,⁶ The increasing of ethanol concentration in system is favorable to the reduction due to more oxidative radicals eliminated, but turns against the reduction when exceeding 80% due to the poorer dispersibility of GO.

Figure S4 (c) presents the influence of the absorbed dose on the reduction. Obviously, greater absorbed dose contributes to more reductive radical species production, which is helpful to a higher reduction of GO. However, an extremely high absorbed dose could destroy the valence bonds of graphite layer and make it reacted with other molecules,⁷ which results in C/O ratio of RGO turning downwards.

Figure S4 (d) shows the influence of dose rate on the reduction. As to the fact mentioned above, the reduction of GO in an ethanol/water is a diffusion controlled radical reaction. The fast local reaction with GO will bring up aggregation and hinder the diffusion of radicals to GO sheets. Hence, a relative low dose rate is favored for higher reduced GO. The highest C/O ratio reaches 13 when the absorbed dose is 46.7 kGy at a dose rate of 0.882 kGy/h and ethanol concentration of 10 v/v %.

References:

1. W. S. Hummers and R. E. Offeman, *Journal of the American Chemical Society*, 1958, **80**, 1339-1339.
2. S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S. T. Nguyen and R. S. Ruoff, *Carbon*, 2007, **45**, 1558-1565.
3. D. Li, M. B. Muller, S. Gilje, R. B. Kaner and G. G. Wallace, *Nat Nanotechnol*, 2008, **3**, 101-105.
4. M. Simic, P. Neta and E. Hayon, *J. Phys. Chem.*, 1969, **73**, 3794-&.
5. B. G. Ershov, *Russ. Chem. Rev.*, 2004, **73**, 101-113.
6. J. I. Paredes, S. Villar-Rodil, A. Martinez-Alonso and J. M. D. Tascon, *Langmuir*, 2008, **24**, 10560-10564.
7. Z. Xu, L. Chen, L. Liu, X. Wu and L. Chen, *Carbon*, 2011, **49**, 350-351; Z. W. Xu, C. Y. Min,

L. Chen, L. S. Liu, G. W. Chen and N. Wu, *J. Appl. Phys.*, 2011, **109**; G. Compagnini, F. Giannazzo, S. Sonde, V. Raineri and E. Rimini, *Carbon*, 2009, **47**, 3201-3207.