

Azo addition to exfoliated graphene: a facile and high yield route to functionalized graphene†

Cite this: *RSC Advances*, 2013, 3, 17689

Received 28th May 2013,
Accepted 1st August 2013

DOI: 10.1039/c3ra42591f

www.rsc.org/advances

Xiaoyong Zhang, Mingsong Han, Shu Chen, Lin Bao, Ling Li and Weijian Xu*

A facile and high yield method for the covalent functionalization of graphene through the free radical addition of a commercially available polymerization initiator, 2,2'-azobisisobutyronitrile (AIBN), has been successfully realized. The obtained material was determined to have 1 isobutyronitrile group substituent per 50 carbon atoms.

Graphene, a one-atom-thick two dimensional (2D) flat sheet of sp^2 bonded carbon atoms arranged in a hexagonal lattice, has attracted enormous attention in recent years.¹ Owing to its special 2D structure, the unprecedented physical properties of graphene, such as quantum hall effect at room temperature,² tunable band gap,³ ultrahigh electron mobility,⁴ very high mechanical strength⁵ and high elasticity,⁶ have made it one of the most promising future materials. Graphene sheets have been used for the creation of energy storage materials,⁷ biological and chemical sensors,⁸ and semiconductor electronics.⁹ Despite the potential and versatility of graphene in various applications, there are still two major challenges on the intrinsic gapless band-structure and no appreciable solubility in both organic and aqueous solvents¹⁰ prior to its transfer into successful practical applications. Chemical functionalization of graphene is one of the many approaches to address the above mentioned challenges of graphene since the structural, physical, chemical and electronic properties of graphene could be modified through functionalization to suit specific applications.¹⁰ Successful chemical functionalization would result in the opening of the band gap near the Fermi level of graphene, so that graphene would be converted to a semiconductor,¹¹ which ultimately enables graphene to be the most promising successor to silicon as a material for micro-/nano-electronic and photonic applications. Furthermore, by varying the groups which are covalently bonded on the graphene sheets, modification of graphene's solubility in both organic and aqueous

solvents could be easily realized.¹² As such, chemical functionalization could effectively pave the way towards the usage of graphene in practical applications. In contrast to its strained counterparts, fullerenes and carbon nanotubes (CNTs) which exhibit a curved surface, graphene is less reactive because it is a planar sheet.¹³ As a result, only a few functionalizations of carbon allotropes have been successfully applied to graphene chemistry, such as diazonium salt addition,¹⁴ aryne addition,¹⁵ nitrene addition,^{12,16} 1,3-dipolar cycloaddition,¹⁷ Claisen rearrangement,¹⁸ Diels–Alder cycloaddition,^{19,20} dichlorocarbene addition²¹ and zwitterion intermediate cycloaddition.²² Those methods to functionalize graphene mainly involve the rehybridization of sp^2 to sp^3 carbons and insert covalent functionalized groups mainly localized on the basal plane and the edges.¹⁷ However, the above mentioned approaches usually require relatively demanding reaction conditions, such as high temperature,^{12,17} long reaction time,¹⁷ anaerobic conditions²² or complicated procedures.²⁰ A growing number of applications would profit from the availability of a facile and high yield method to produce high-quality functionalized graphene in large quantities.

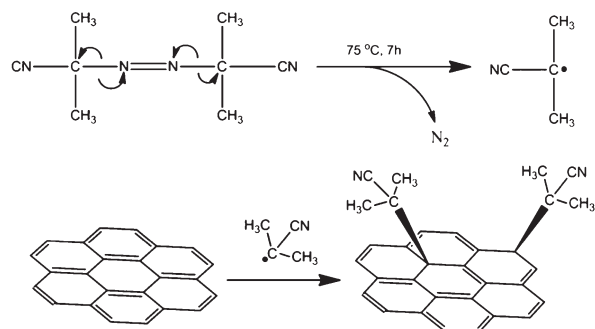
It has been shown that both fullerenes and CNTs could be easily functionalized by azo addition, generated *in situ* by the thermal decomposition of AIBN.^{23,24} Likewise, the radical group can be readily anchored to the surface of graphene. Although AIBN has been reported to trigger the growth of polymer chains on the surface of graphene,²⁵ the interaction between graphene and AIBN has been seldom explored.

In this communication, we prove the covalent functionalization of graphene with AIBN as depicted in Scheme 1.

The starting material, graphene (GR), was obtained from graphite exfoliation by the method explored by our group and reported in a previous paper.²⁶ The functionalization was carried out based by a facile and high yield method. GR was dispersed in *N*-methyl-2-pyrrolidone (NMP) (100 mL, 0.60 mg mL⁻¹) and used to carry out the reaction. AIBN (1.68 g) was added into the dispersed GR, then the mixture was heated at 75 °C under magnetic stirring for 7 h. After the reaction, the dark slurry was filtered through a 0.22 µm PTFE (Teflon) membrane. The filter cake was purified by multiple filtration–redispersion cycles with

College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, P.R. China. E-mail: weijianxu59@gmail.com; Fax: +86-731-88821549

† Electronic supplementary information (ESI) available: Preparation of the graphene dispersion. EDX spectrum and atomic concentration data in the XPS spectrum of f-GR. Photograph of the dispersion of GR and f-GR in various solvents. See DOI: 10.1039/c3ra42591f



Scheme 1 The synthetic route to functionalized graphene (f-GR).

alcohol, *N,N*-dimethylformamide (DMF) and acetone in order to avoid the possible adsorption of AIBN on the surface of graphene, and then dried for one day, yielding a fine dark powder of functionalized graphene (f-GR). A control experiment was carried out by just mixing graphene with AIBN to prepare a mixture (c-GR) to examine the possible adsorption of AIBN on the surface of graphene. All the products were dried in a vacuum oven at 30 °C for 3 days before detection. Evidence of the successful functionalization was provided by using a variety of characterization techniques, including Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, thermogravimetric analysis (TGA), and high-resolution transmission electron microscopy (HR-TEM).

The FTIR spectra of GR, f-GR and c-GR are shown in Fig. 1. Compared to GR, the f-GR spectrum shows two new peaks at 2998 and 2886 cm^{-1} which are assigned to the stretching and in-plane bending vibrations of the C-H bonds of the alkyl groups, respectively. Besides, a new peak appears at 2240 cm^{-1} corresponding to the stretching vibration of the C≡N group of isobutyronitrile. At the same time, it is obvious that the spectra of f-GR and c-GR are different. Peaks at 1230 and 1456 cm^{-1} are observed in the spectra of c-GR due to the presence of the C-N bond stretch and azo group¹⁴ of AIBN, but have disappeared in the

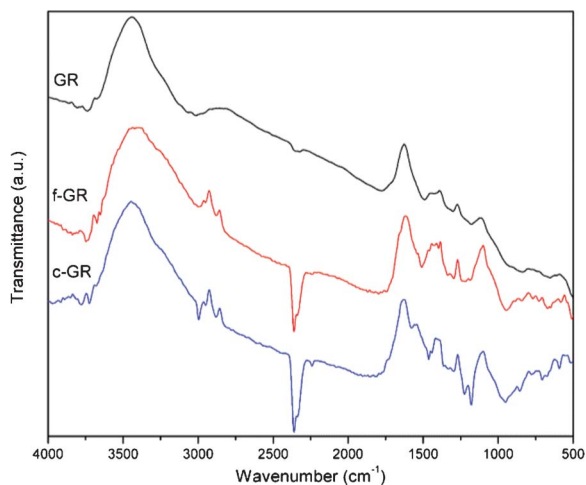


Fig. 1 FTIR spectra of GR, f-GR, and c-GR.

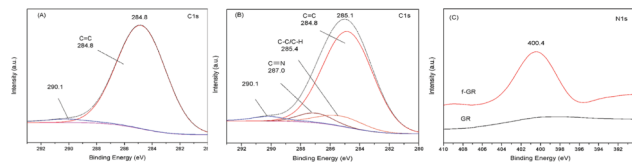


Fig. 2 XPS core level spectra of (A) C 1s of GR, (B) C 1s of f-GR and (C) N 1s of GR and f-GR.

spectrum of f-GR as a result of the decomposition of AIBN when it reacts with graphene. The evolution of these peaks indicates the covalent attachment of isobutyronitrile groups on the surface of graphene.

X-ray photoelectron spectroscopy was employed to confirm the detailed elemental composition on the surface of GR and f-GR. The curve-fitted C 1s core level spectra for GR and f-GR are shown in Fig. 2 (A) and (B), respectively. A peak (284.8 eV) with slight tailing towards higher binding energies corresponding to C=C is observed in GR. However, compared with GR, f-GR gives a high intensity peak at 285.1 eV with a little shift of 0.3 eV, which is attributed to the presence of C-C/C-H (285.4 eV) and C≡N (287.0 eV). Also, a sp^2 -hybridized carbon $\pi^* \leftarrow \pi$ shake-up (290.1 eV) is observed in Fig. 2 (A) and (B).²⁷ Apart from that, the obvious presence of the N 1s (400.4 eV) peak on f-GR in Fig. 2 (C), further ascertains the success of the covalent functionalization.

Raman spectroscopy was used to obtain structural information on f-GR. Fig. 3 shows the Raman spectra of GR, f-GR and c-GR. The I_D/I_G ratio of GR, c-GR and f-GR are 0.21, 0.39 and 0.61 on average, respectively. The ratio of GR is low. Compared to GR, we do not observe a significant change for c-GR, even though the I_D/I_G ratio is a little larger, probably because of the presence of AIBN. However, for f-GR, there is an obvious increment of the I_D/I_G ratio, accompanied by blue-shifting of the G band. Such increment of the I_D/I_G ratio and blue-shifting have been previously identified as a result of an increasing amount of sp^3 carbon atoms,²⁸ which indicates the successful covalent functionalization.

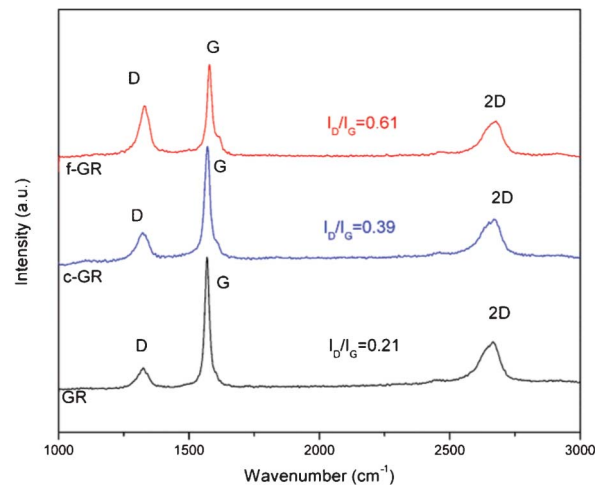


Fig. 3 Raman spectra of GR, c-GR and f-GR.

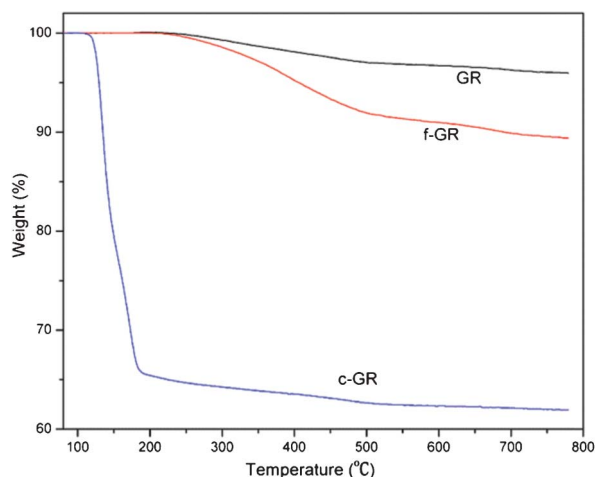


Fig. 4 Thermogravimetric analysis of GR, f-GR and c-GR.

The presence of isobutyronitrile groups on the graphene sheets was further analyzed by TGA. TGA was performed at a $20\text{ }^{\circ}\text{C min}^{-1}$ rate under helium. Fig. 4 shows a comparison of the weight loss of GR, f-GR and c-GR. GR displays a little weight loss, which is possibly due to defects caused by sonication, and retains more than 97% weight fraction even when the temperature is up to $800\text{ }^{\circ}\text{C}$. In the curve for f-GR, there is a rapid decrease of weight when the temperature is between $220\text{ }^{\circ}\text{C}$ and $500\text{ }^{\circ}\text{C}$. TGA can provide a quantitative estimation of the functionalization degree. The f-GR curve in Fig. 4 indicates a weight loss of 10%, which is calculated to be 1 isobutyronitrile group substituent per 50 carbon atoms, which agrees with the results from XPS (Fig. S1, ESI†) and EDX (Fig. S2, ESI†). In order to demonstrate that covalent bonds have been formed between graphene and AIBN, c-GR was also tested. As shown in the Fig. 4, c-GR has a heavy weight loss from $110\text{ }^{\circ}\text{C}$. When the temperature is above $200\text{ }^{\circ}\text{C}$, the weight shows little change, which is similar to the TGA spectra of AIBN,²⁴ proving that we have successfully prepared f-GR.

In addition, HR-TEM was utilized to characterize the morphology of GR and f-GR to provide evidence of the successful functionalization. Since GR was obtained without any stabilizer, we could observe aggregation of the graphene sheets as shown in Fig. 5. However, for f-GR, little aggregation is observed since chemical modification on the sp^2 carbon lattice of the graphene improves the dispersibility.

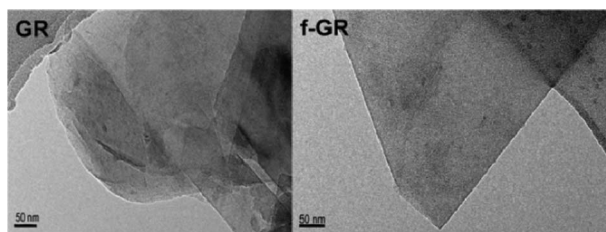


Fig. 5 TEM images of GR and f-GR.

In conclusion, we have reported a facile and high yield method to functionalize exfoliated graphene by azo addition. The characterization and analyses have fully confirmed that the radical groups from the thermal decomposition of AIBN in NMP solution were covalently grafted on the graphene surface. Our studies show that AIBN, which is commercially available, is capable of opening the π -bonds of graphene. Therefore, during fabrication of graphene-polymer composites with the initiator AIBN, it should be considered that the free radicals thermally decomposed from AIBN not only trigger the growth of polymer chains, but also react themselves with graphene. Future work could use other azo radical initiators to functionalize graphene in order to attach various functional groups onto the surface of graphene, which are expected to tune the band gap energy, improve the solubility of graphene and provide high-performance graphene-based materials.

Notes and references

- 1 A. K. Geim and K. S. Novoselov, *Nat. Mater.*, 2007, **6**, 183–191.
- 2 K. S. Novoselov, Z. Jiang, Y. Zhang, S. V. Morozov, H. L. Stormer, U. Zeitler, J. C. Maan, G. S. Boebinger, P. Kim and A. K. Geim, *Science*, 2007, **315**, 1379–1379.
- 3 M. Y. Han, B. Ozyilmaz, Y. B. Zhang and P. Kim, *Phys. Rev. Lett.*, 2007, **98**, 206805.
- 4 A. K. Geim, *Science*, 2009, **324**, 1530–1534.
- 5 J. S. Bunch, A. M. van der Zande, S. S. Verbridge, I. W. Frank, D. M. Tanenbaum, J. M. Parpia, H. G. Craighead and P. L. McEuen, *Science*, 2007, **315**, 490–493.
- 6 C. Lee, X. D. Wei, J. W. Kysar and J. Hone, *Science*, 2008, **321**, 385–388.
- 7 M. S. Goh and M. Pumera, *Electrochem. Commun.*, 2010, **12**, 1375–1377.
- 8 A. Bonanni and M. Pumera, *ACS Nano*, 2011, **5**, 2356–2361.
- 9 M. E. Ramon, A. Gupta, C. Corbet, D. A. Ferrer, H. C. P. Movva, G. Carpenter, L. Colombo, G. Bourianoff, M. Doczy, D. Akinwande, E. Tutuc and S. K. Banerjee, *ACS Nano*, 2011, **5**, 7198–7204.
- 10 L. Yan, Y. B. Zheng, F. Zhao, S. J. Li, X. F. Gao, B. Q. Xu, P. S. Weiss and Y. L. Zhao, *Chem. Soc. Rev.*, 2012, **41**, 97–114.
- 11 E. Bekyarova, M. E. Itkis, P. Ramesh, C. Berger, M. Sprinkle, W. A. de Heer and R. C. Haddon, *J. Am. Chem. Soc.*, 2009, **131**, 1336–1337.
- 12 X. Xu, W. Lv, J. Huang, J. Li, R. Tang, J. Yan, Q. Yang, J. Qin and Z. Li, *RSC Adv.*, 2012, **2**, 7042.
- 13 D. R. Dreyer, S. Park, C. W. Bielawski and R. S. Ruoff, *Chem. Soc. Rev.*, 2010, **39**, 228–240.
- 14 J. R. Lomeda, C. D. Doyle, D. V. Kosynkin, W. F. Hwang and J. M. Tour, *J. Am. Chem. Soc.*, 2008, **130**, 16201–16206.
- 15 X. Zhong, J. Jin, S. W. Li, Z. Y. Niu, W. Q. Hu, R. Li and J. T. Ma, *Chem. Commun.*, 2010, **46**, 7340–7342.
- 16 T. A. Strom, E. P. Dillon, C. E. Hamilton and A. R. Barron, *Chem. Commun.*, 2010, **46**, 4097–4099.
- 17 M. Quintana, K. Spyrou, M. Grzelczak, W. R. Browne, P. Rudolf and M. Prato, *ACS Nano*, 2010, **4**, 3527–3533.
- 18 W. R. Collins, W. Lewandowski, E. Schmois, J. Walish and T. M. Swager, *Angew. Chem., Int. Ed.*, 2011, **50**, 8848–8852.
- 19 S. Sarkar, E. Bekyarova, S. Niyogi and R. C. Haddon, *J. Am. Chem. Soc.*, 2011, **133**, 3324–3327.

- 20 J. Yuan, G. Chen, W. Weng and Y. Xu, *J. Mater. Chem.*, 2012, **22**, 7929.
- 21 Chun Kiang Chua, Adriano Ambrosi and M. Pumera, *Chem. Commun.*, 2012, **48**, 5376–5378.
- 22 X. Zhang, W. R. Browne and B. L. Feringa, *RSC Adv.*, 2012, **2**, 12173.
- 23 W. T. Ford, T. Nishioka, F. Qiu, F. D'Souza, J. P. Choi, W. Kutner and K. Noworyta, *J. Org. Chem.*, 1999, **64**, 6257–6262.
- 24 X. Wang, S. Li, Y. Xu, L. Wan, H. You, Q. Li and S. Wang, *Appl. Surf. Sci.*, 2007, **253**, 7435–7437.
- 25 J. Long, M. Fang and G. H. Chen, *J. Mater. Chem.*, 2011, **21**, 10421–10425.
- 26 Y. Z. Xiong, H. Chen, E. Ou, J. Qian, C. Peng, Y. Xiong and W. Xu, *Chem. Lett.*, 2012, **41**, 606–608.
- 27 Y. Liu, Z. L. Yu, Y. M. Zhang, D. S. Guo and Y. P. Liu, *J. Am. Chem. Soc.*, 2008, **130**, 10431–10439.
- 28 L. G. Cancado, A. Jorio, E. H. M. Ferreira, F. Stavale, C. A. Achete, R. B. Capaz, M. V. O. Moutinho, A. Lombardo, T. S. Kulmala and A. C. Ferrari, *Nano Lett.*, 2011, **11**, 3190–3196.