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Facile and Ecofriendly Fluorination of Graphene Oxide

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A one-pot, facile and ecofriendly approach to the fabrication of covalently fluorinated graphene using mild reaction conditions is reported. This straightforward and efficient strategy allows fluorine groups to be covalently and stably anchored onto graphene to produce single-layer functionalized graphene sheets from a graphene oxide precursor.

Key Words : Graphene oxide, Flourination, Functionalization, Eco-friendly

Introduction

Graphene is an emerging carbon material consisting of planar monolayer hexagonal sp^2 hybridized carbons. This unique 2-dimensional structure results in unique properties, such as high carrier mobility, a high Young's modulus, and high thermal conductivity. All of these properties make graphene a promising material for various applications.[1-4] Heteroatomic doping on the surface of graphene by both wet chemistry and chemical vapour deposition (CVD) techniques has led to breakthrough applications in energy storage devices and electronics, but recent reports have been limited to polymeric and biological materials.[5-8]

Fluorination is one of the most efficacious chemical techniques to modify the physiochemical properties of carbon materials, since further substitution can be readily accomplished.[9-11] To date, the fluorination of carbon nanomaterials has been carried out at very high temperatures and pressures using very toxic fluorinating agents such as elemental fluorine gas, TbF_4, XeF_2, and CF_4 plasma.[12-17] There are a number of difficult challenges posed particularly with wet chemistry approaches to fluorination since elemental fluorine and common electrophilic fluorinating agents have various concerns such as limited thermal stability, high toxicity, corrosion, the need for special handling, and environmental issues. The one-pot synthesis scheme we propose consistently yielded functionalized graphenes with different C/O and C/F ratios, which we term fluorinated graphene (FG). Graphene oxide (GO), derived from graphite by decoration with oxygen functional groups, readily decomposes and is transformed into complicated aggregates under heat treatment at high temperature, a conventional condition for the fluorination of carbon.

The aim of this study was to develop a fluorination reaction of carbon sheets at lower temperature and under favorable conditions for a scalable, high throughput process. We found that the simple mixing of GO and hexafluorophosphoric acid (HPF_6), which can be handled safely and efficiently, easily generated fluorinated graphene (FG). Our systematic investigation of the fluorination of GO demonstrated that carbon sheets could be effectively functionalized with fluorine, and the level of GO reduction could be simultaneously controlled by the temperature of the reaction.

Experimental

Graphene powders were purchased from Bay Carbon (USA, SP-1). Hexafluorophosphoric acid (HPF_6, 65 wt %) obtained from Aldrich. GO was synthesized by the modified Hummers' method as reported elsewhere.[18]

GO in NMP at a concentration of 0.5 mg/mL was sonicated at room temperature for 30 minutes to obtain a completely exfoliated, monolayer GO dispersion. 2.0 mL of GO suspension was transferred to a Teflon bottle, and 1.0 mL of HFP6 was added. The mixture was stirred using a magnetic stirrer at three different temperatures (50 °C, 100 °C and 160 °C) for 24 h. The final product was obtained by successively washing with excess NMP and THF. Products were characterized by X-ray photoelectron spectroscopy (XPS, ESCSA 2000), Raman spectroscopy (LabRam HR Ar-ion laser 514 nm, Jobin-Yvon, Longjumeau, France), transmission electron microscopy (TEM, JEM 2100F, JEOL, Tokyo, Japan), AFM XE-70 (Park Systems, Korea) and Thermal analyzer (Q50, TA Instruments, USA).

Results and Discussion

Figure 1 shows the scheme for preparing fluorinated graphene sheets using GO as precursor and the mild fluorinating agent hexafluorophosphoric acid. Fluorinated graphene (FG) produced by reactions run at temperatures of 50, 100, and 160 °C are designated FG-50, FG-100, and FG-160, respectively. Raman spectroscopy detected slight changes in the structure of graphene sheets before and after chemical

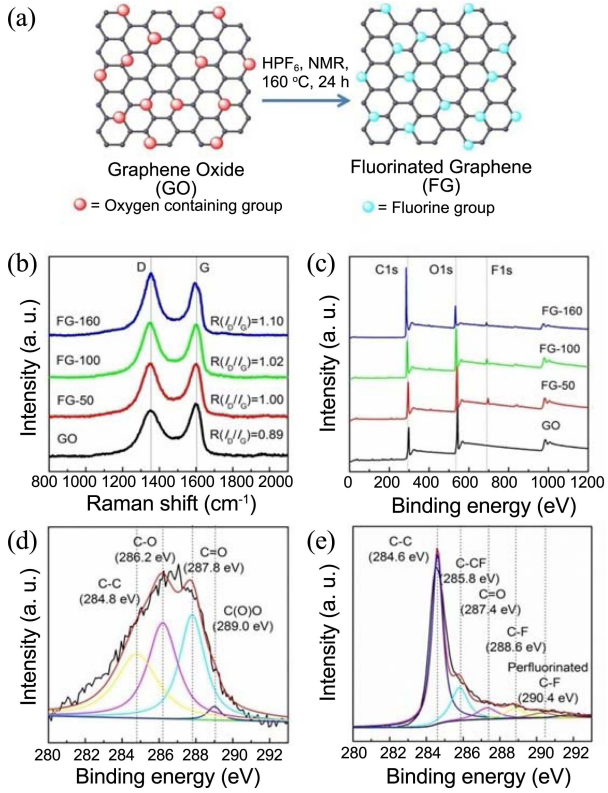


Figure 1. Schematic of the fluorination of graphene (a). Characterization of fluorinated graphene. (b) Raman spectra, (c) Wide-scan XPS spectra of graphene oxide and fluorinated graphene, (d) C 1s spectra of GO, and (e) C 1s spectra of FG-16.

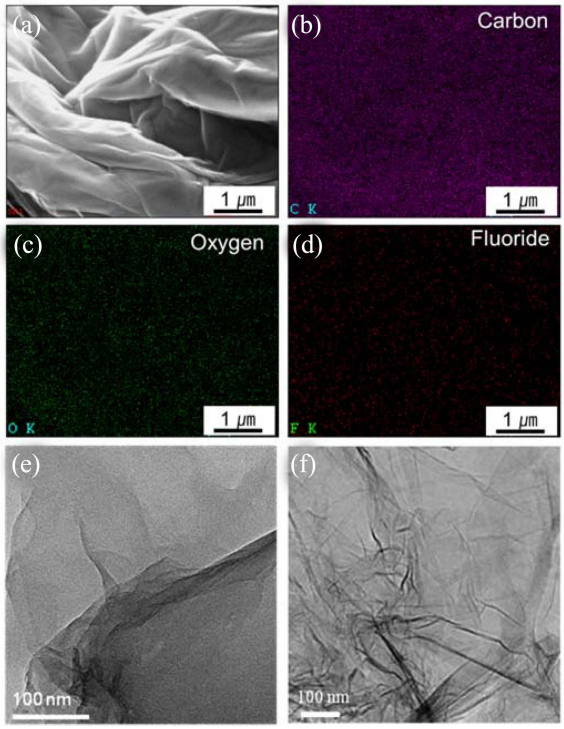


Figure 2. SEM images of fluorinated graphene (FG-160) (a). Elemental mapping of FG-160: (b) carbon, (c) oxygen, (d) fluorine. TEM image of GO (e) and FG-160 (f).

reaction; Figure 1(a) shows the Raman spectra of GO and fluorinated graphene (FG). The GO and FG-50 spectra contained a G-band at 1581 cm^{-1} and a D-band at 1354 cm^{-1} with an I_D/I_G of 0.89 and 1.0, respectively.

The broad G-band in the FG-100 and FG-160 spectra was shifted to lower wavelength and had a considerably increased I_D/I_G intensity ratio (1.02 and 1.10) compared to that of GO. These changes indicate that electronic conjugation in the fluorinated graphene was regained from GO reduction and chemical functionalization had taken place and imply a decrease in the average size of the sp^2 domains upon the functionalization and reduction of GO.[19,20]

The extent of fluorination was quantitatively determined by thermogravimetric analysis (Figure S1). GO was less thermally stable than FG. GO displayed an initial weight loss around 100 °C, which is associated with evaporation of water adhered to the π-stacked structure.[21]

The main weight loss occurred around 200 °C due to degradation of oxygen-containing functional groups accompanied by the generation of CO_2, CO, and H_2O.[21]

At temperatures between 200 and 500 °C, GO was thermally stable due to the carbonization effect under a N2 atmosphere, and above 500 °C, decomposition of the carbon structure occurred. However, with FG-50 and FG-100, degradation started at 160 °C, which was associated with decomposition of fluorine groups as well as oxygen containing groups. In contrast, the FG-160 sample was highly thermally stable due to high levels of reduction as well as fluorination.[19]

Wide-scan X-ray photoelectron spectra (XPS) of the surface of fluorinated graphenes contained two strong peaks at 281.0 eV (C 1s) and 532.9 (O 1s) and a weak peak at 691.0 eV (F 1s) as shown in Figure 1(b). The observation of an F 1s peak around 691.0 eV indicates that fluorine groups were introduced to the graphene structure via reaction with the mild fluorinating reagent. Furthermore, a high-resolution C 1s spectrum of GO (Figure 1(c)) showed four carbon types corresponding to C-C (284.6 eV), C-O (286.2 eV), carbonyl C=O (287.8 eV), and carboxylate O-C=O (290.0 eV), which indicate the presence of oxygen-containing groups including hydroxyl, epoxy, carbonyl, and carboxylic acid on the surface or edge of the GO. However, in the case of fluorinated graphenes, a peak at 284.6 eV is ascribed to non-grafted carbon, a peak around 288.6 eV is attributed to carbon atoms covalently bonded to fluorine atoms (C-F), the shoulder at 285.8 eV corresponds to carbon atoms positioned near CF groups (C-CF), and the peak observed at 287.4 eV corresponds to the C=O group, all of which support the successful fluorination of graphene (Figure 1(d)).[17]

From the XPS and EDX spectra the highest fluorine content was determined to be 3.27 atomic% and 4.3 weight%, respectively, for the FG-160 sample (Figure S2 and Table S1).

Morphological differences between GO and FG were observed by SEM and TEM. Surface analysis of FG was also carried out using SEM micrographs in conjunction with energy dispersive X-ray spectroscopy (EDS) elemental mapp-

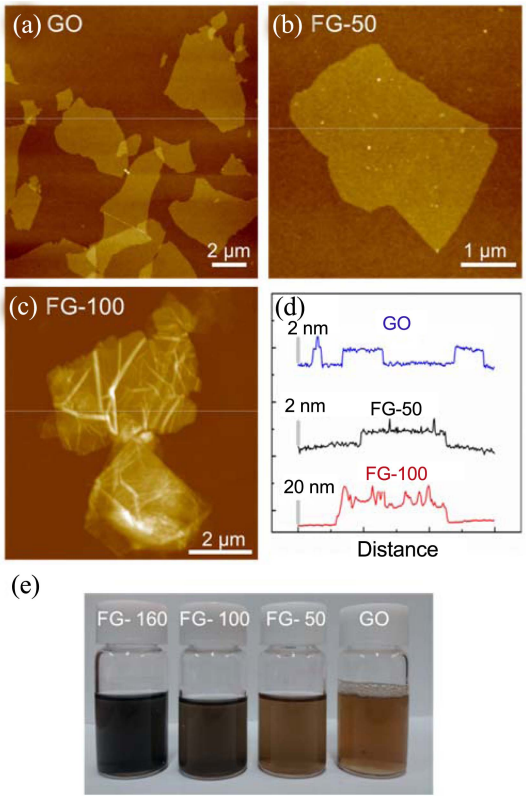


Figure 3. AFM images of graphene oxide (a), FG-50 (b), FG-100 (c) and thickness profile (d). The solubility test of GO and FG (e).

ing (Figure 2(a)). EDS elemental mapping can be used to locate elemental composition variations in SEM micrographs. Three EDS mapping images, colored maroon (carbon) (Figure 2(b)), dark green (oxygen) (Figure 2(c)), and red (fluorine) (Figure 2(d)), show that fluorine groups are uniformly distributed on the surface of the graphene sheets. TEM images of GO and chemically reduced graphene (Figure 2(e) and (f)) exhibit a large, folded graphene structure. Figure 3 shows AFM images and height profiles of fluorinated graphenes drop-casted on silicon wafers. AFM analysis confirmed that the starting GO sheets were entirely single layered with a thickness of approximately 1.2 nm. At a low fluorination temperature, the FG sheets were still single layered, as seen in Figure 2(b), indicating the effectiveness of low temperature fluorination to prepare monolayered graphene decorated with fluorines. As the temperature was increased to 100 °C, graphene sheets stacked together due to the effect of partial deoxygenation during the fluorination reaction.

The AFM image in Figure 3(c) clearly shows the crumpled, rippled sheet morphology. However, when the fluorination temperature was increased to 160 °C, the resulting FG particles were largely stuck together, and it became difficult to characterize the material by AFM. Furthermore, FG was highly soluble in THF, an organic solvent with a low boiling point, as shown in Figure 3(e). The good dispersion of FG powder was readily achieved through simple sonication in THF solvent, even with material produced in the higher temperature synthetic process at 160 °C. The color of the suspension of FG in Figure 3(e) varied with reaction temperature from brown to black.

Conclusion

In conclusion, we have developed a facile and versatile methodology for the fluorination of graphene sheets using mild reaction conditions. This strategy allows fluorine to be covalently introduced onto graphene, resulting in fluorinated graphene sheets. The functionalized graphene mostly remained in individually separated single layers. The fluorine functionalized graphene had much better chemical and thermal stability than GO and can be further modified by different chemical reactions. The resulting functionalized graphene had excellent dispersibility and processability in solvents. This general strategy could be extended to the preparation of many other distinctive types of functionalized carbon nanomaterials, thus opening a new horizon in the field of functional graphene materials.

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References

1. Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorievo, I. V.; Firsov, A. A. *Science* **2004**, *306*, 666.
2. Kim, Y. A.; Fujisawa, K.; Muramatsu, H.; Hayashi, T.; Endo, M.; Fujimori, T.; Kaneko, K.; Terrones, M.; Behrends, J.; Eckmann, A.; Casiraghi, C.; Novoselov, K. S.; Saito, R.; Dresselhaus, M. S. *ACS Nano* **2012**, *6*, 6293.
3. Geim, A. K.; Novoselov, K. S. *Nat. Mater.* **2007**, *6*, 183.
4. Balandin, A. A.; Ghosh, S.; Bao, W.; Calizo I.; Desalegne, T.; Miao, F.; Lau, C. N. *Nano Lett.* **2008**, *8*, 902.
5. Mathkar, A.; Narayanan, T. N.; Alemany, L. B.; Cox, P.; Nguyen, P.; Gao, G.; Chang, P.; Romero-Aburto, R.; Mani, S. A.; Ajayan, P. M. *Part. Part. Syst. Charact.* **2012**, *30*, 266.
6. Wang, X.; Li, X.; Zhang, L.; Yoon, Y.; Weber, P. K.; Wang, H.; Guo, J.; Dai, H. *Science* **2009**, *324*, 768.
7. Liu, Z.; Robinson, J.; T.; Sun, X.; Dai, H. *J. Am. Chem. Soc.* **2008**, *130*, 10876.
8. Hwang, J. O.; Park, J. S.; Choi, D. S.; Kim, J. Y.; Lee, S. H.; Lee, K. E.; Kim, Y. H.; Song, M. H.; Yoo, S.; Kim, S. O. *ACS Nano* **2012**, *6*, 159.
9. Ahmad, Y.; Disa, E.; Dubois, M.; Gurin, K.; Dubois, V.; Zhang, W.; Bonnet, P.; Masin, F.; Vidal, L.; Ivanov, D. A.; Hamwi, A. *Carbon* **2012**, *50*, 3897.
10. Kwon, S.; Ko, J. H.; Jeon, K. J.; Kim, Y. H.; Park, J. Y. *Nano Lett.* **2012**, *12*, 6043.
11. Lee, W. H.; Suk, J. W.; Lee, J.; Hao, Y.; Park, J.; Yang, J. W.; Ha, H. W.; Murali, S.; Chou, H.; Akinwande, D.; Kim, K. S.; Ruoff, R. S. *ACS Nano* **2012**, *6*, 1284.
12. Wheeler, V.; Garces, N.; Nyakiti, L.; Myers-Ward, R.; Jernigan, G.; Culbertson, J.; Eddy, C., Jr.; Gaskill, K. *Carbon* **2012**, *50*, 2307.

13. Wang, Z.; Wang, J.; Li, Z.; Gong, P.; Liu, X.; Zhang, L.; Ren, J.; Wang, H.; Yang, S. *Carbon* **2012**, *50*, 5403.
14. Asanov, I. P.; Bulusheva, L. G.; Dubois, M.; Yudanov, N. F.; Alexeev, A. V.; Makarova, T. L.; Okotrub, A. V. *Carbon* **2013**, *59*, 518.
15. Walter, A. L.; Jeon, K. J.; Bostwick, A.; Speck, F.; Ostler, M.; Seyller, T.; Moreschini, L.; Kim, Y. S.; Chang, Y. J.; Horn, K.; Rotenberg, E. *Appl. Phys. Lett*. **2011**, 98.
16. Shen, B.; Chen, J.; Yan, X.; Xue, Q. *RSC Adv.* **2012**, *2*, 6761.
17. Maiti, J.; Kakati, N.; Lee, S. H.; Yoon, Y. S. *J. Fluorine Chem*. **2012**, *135*, 362.
18. Cote, L. J.; Kim, F.; Huang, J. *J. Am. Chem. Soc*. **2008**, *131*, 1043.
19. He, H.; Gao, C. *Chem. Mater*. **2010**, *22*, 5054.
20. Yadav, S. K.; Yoo, H. J.; Cho, J. W. *J. Polym. Sci. Pol. Phys.* **2013**, *51*, 39.
21. Pan, Y.; Bao, H; Sahoo, N. G.; Wu, T.; Li, L. *Adv. Funct. Mater.* **2011**, *21*, 2754.