

Nano-Engineered Spacing in Graphene Sheets for Hydrogen Storage

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Hydrogen has the great potential to serve as a clean and efficient energy carrier which may replace nonrenewable fossil fuels to reduce CO₂ emissions and air pollution, especially in hydrogen-fueled vehicles.^{1,2} However, to develop the onboard high-capacity storage of hydrogen fuel remains a significant challenge.^{3–5} There have been many efforts made to use gas adsorbent materials as the media for facile and reversible hydrogen storage, such as activated carbons^{6,7} and metal organic frameworks.^{8,9} The metal organic frameworks show high uptake but suffer from being of exceedingly low density, which compromises volumetric targets. While carbon material densities are sufficiently high, typically the maximum excess hydrogen physisorption capacity of carbon adsorbents is ~1 wt % H₂ per 500 m²/g specific surface area at 77 K and ~40 bar, according to the “Chahine rule”.^{10,11} To further enhance the hydrogen uptake capacity, it is essential to search for

novel adsorbents with engineered nanospaces¹² or to modify the surface of adsorbents with heteroatom-doping^{13–15} or functional groups¹⁶ to polarize H₂ molecules. For instance, three-dimensional (3-D) nanoengineered carbon scaffolds of organic-cross-linked single-walled carbon nanotube fibers have enhanced hydrogen physisorption capacity compared to typical carbon materials.^{17,18}

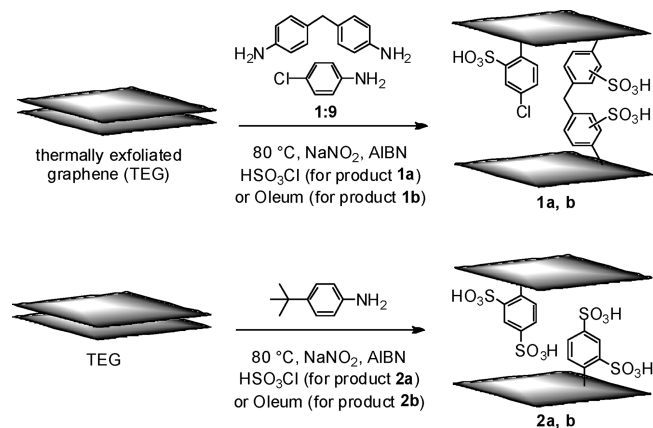
Graphene, a 2-D carbon nanomaterial, has attracted much recent interest.^{19,20} Theoretical calculations^{21–23} show that graphene and graphene-based pillared nanostructures may have great potential for hydrogen storage. Recent experimental results indicated that the hydrogen uptake capacity of thermally exfoliated graphene (TEG) derived from graphite oxide^{24,25} increases linearly with the surface area: ~0.5 wt % H₂ per 500 m²/g specific surface area at 77 K and 1 bar.²⁶ But TEG materials still need further improvement in hydrogen uptake which could be afforded by the insertion of proppants to build engineered nanospaces. Here we report an efficient method for the facile organic functionalization and cross-linking of TEG to produce carbon scaffolds with enhanced hydrogen storage capacity at 77 K and 2 bar when compared to original TEG material and normal carbonaceous adsorbents.

The original TEG material was obtained by rapidly heating graphite oxide (GO, synthesized by Hummers method²⁷) to 1000 °C in 1 min under a H₂/Ar (50 sccm/500 sccm) gas flow. Then the TEG was annealed at 1000 °C in the H₂/Ar gas flow for 15 min. In this modified procedure, H₂ was introduced to remove most of the oxygen content. As shown in Scheme 1, the process of preparing functionalized and cross-linked TEG (f-TEG) involves the dispersion and diazonium modification of graphene sheets in the super acids chlorosulfonic acid or oleum, which have been shown to be good solvents for dispersion

- (1) The Department of Energy (DOE) Office of Energy Efficiency and Renewable Energy's Fuel Cell Technologies Program: Hydrogen Storage. <http://www1.eere.energy.gov/hydrogenandfuelcells/storage/> (2009).
- (2) Satyapal, S.; Petrovic, J.; Read, C.; Thomas, G.; Ordaz, G. *Catal. Today* **2007**, *120*, 246.
- (3) Felderhoff, M.; Weidenthaler, C.; von Helmolt, R.; Eberle, U. *Phys. Chem. Chem. Phys.* **2007**, *9*, 2643.
- (4) Morris, R. E.; Wheatley, P. S. *Angew. Chem., Int. Ed.* **2008**, *47*, 4966.
- (5) Eberle, U.; Felderhoff, M.; Schuth, F. *Angew. Chem., Int. Ed.* **2009**, *48*, 6608.
- (6) Dillon, A. C.; Heben, M. J. *Appl. Phys. A: Mater. Sci. Process.* **2001**, *72*, 133.
- (7) Strobel, R.; Garche, J.; Moseley, P. T.; Jorissen, L.; Wolf, G. *J. Power Sources* **2006**, *159*, 781.
- (8) Rosi, N. L.; Eckert, J.; Eddaoudi, M.; Vodak, D. T.; Kim, J.; O'Keefe, M.; Yaghi, O. M. *Science* **2003**, *300*, 1127.
- (9) Rowsell, J. L. C.; Yaghi, O. M. *Angew. Chem., Int. Ed.* **2005**, *44*, 4670.
- (10) Benard, P.; Chahine, R. *Int. J. Hydrogen Energy* **2001**, *26*, 849.
- (11) de la Casa-Lillo, M. A.; Lamari-Darkrim, F.; Cazorla-Amoros, D.; Linares-Solano, A. *J. Phys. Chem. B* **2002**, *106*, 10930.
- (12) Kitagawa, S.; Kitaura, R.; Noro, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334.
- (13) Deng, W. Q.; Xu, X.; Goddard, W. A. *Phys. Rev. Lett.* **2004**, *92*.
- (14) Yoon, M.; Yang, S. Y.; Hicke, C.; Wang, E.; Geohagan, D.; Zhang, Z. Y. *Phys. Rev. Lett.* **2008**, *100*.
- (15) Chung, T. C. M.; Jeong, Y.; Chen, Q.; Kleinhammes, A.; Wu, Y. *J. Am. Chem. Soc.* **2008**, *130*, 6668.

- (16) Stein, A.; Wang, Z. Y.; Fierke, M. A. *Adv. Mater.* **2009**, *21*, 265.
- (17) Leonard, A. D.; Hudson, J. L.; Fan, H.; Booker, R.; Simpson, L. J.; O'Neill, K. J.; Parilla, P. A.; Heben, M. J.; Pasquali, M.; Kittrell, C.; Tour, J. M. *J. Am. Chem. Soc.* **2009**, *131*, 723.
- (18) Biswas, M. M.; Cagin, T. *J. Phys. Chem. B* **2010**, *114*, 13752.
- (19) Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. *Science* **2004**, *306*, 666.
- (20) Stankovich, S.; Dikin, D. A.; Dommett, G. H. B.; Kohlhaas, K. M.; Zimney, E. J.; Stach, E. A.; Piner, R. D.; Nguyen, S. T.; Ruoff, R. S. *Nature* **2006**, *442*, 282.
- (21) Patchkovskii, S.; Tse, J. S.; Yurchenko, S. N.; Zhechkov, L.; Heine, T.; Seifert, G. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 10439.
- (22) Henwood, D.; Carey, J. D. *Phys. Rev. B* **2007**, *75*.
- (23) Dimitrakakis, G. K.; Tylianakis, E.; Froudakis, G. E. *Nano Lett.* **2008**, *8*, 3166.
- (24) Schniepp, H. C.; Li, J. L.; McAllister, M. J.; Sai, H.; Herrera-Alonso, M.; Adamson, D. H.; Prud'homme, R. K.; Car, R.; Saville, D. A.; Aksay, I. A. *J. Phys. Chem. B* **2006**, *110*, 8535.
- (25) McAllister, M. J.; Li, J. L.; Adamson, D. H.; Schniepp, H. C.; Abdala, A. A.; Liu, J.; Herrera-Alonso, M.; Milius, D. L.; CarO, R.; Prud'homme, R. K.; Aksay, I. A. *Chem. Mater.* **2007**, *19*, 4396.
- (26) Ghosh, A.; Subrahmanyam, K. S.; Krishna, K. S.; Datta, S.; Govindaraj, A.; Pati, S. K.; Rao, C. N. R. *J. Phys. Chem. C* **2008**, *112*, 15704.
- (27) Hummers, W. S.; Offeman, R. E. *J. Am. Chem. Soc.* **1958**, *80*, 1339.

Scheme 1. Functionalization and Cross-Linking of TEG Sheets in Chlorosulfonic Acid and Oleum



and diazonium functionalization of carbon nanotubes and graphene.^{28,29} Typically, TEG (24 mg, 2 mequiv carbon) and chlorosulfonic acid or oleum (40 mL; oleum had 20% free SO₃) were placed in a 100 mL round-bottom flask and cup-horn sonicated for 30 min. In a glass vial, 4,4'-methylenedianiline (0.040 g, 0.2 mmol) and 4-chloroaniline (0.230 g, 1.8 mmol) were dissolved in chlorosulfonic acid or oleum (15 mL), and the solution was added to the TEG suspension. Then sodium nitrite (0.347 g, 5.0 mmol) and 2,2'-azobis(2-methylpropionitrile) (AIBN, 0.082 g, 0.5 mmol) were slowly added, and the TEG suspension was stirred at 80 °C for 6 h. After cooling to room temperature, the mixture was carefully quenched over ice and filtered over a poly(tetrafluoro)ethylene membrane (0.22 μm pore size), and then the filter cake was sequentially rinsed with water, acetone, and ether. After washing, the f-TEG products were dried at 80 °C in a vacuum oven at 30 mmHg. The products **1a** and **1b** were prepared by the diazonium reaction in chlorosulfonic acid and oleum, respectively. Alternatively, *tert*-butylaniline (0.77 mL, 2.0 mmol) was used as the reagent instead of 4,4'-methylenedianiline and 4-chloroaniline for comparative experiments; products **2a** and **2b** (in chlorosulfonic acid or oleum, respectively) were obtained by this alternative process, where *tert*-butyl loss in the acid and arylsulfonation was expected.

The samples were characterized by scanning electron microscopy (SEM, FEI Quanta 400 ESEM FEG). In contrast to the disordered fluffy conglomerates of the original TEG sheets (Figure 1a), f-TEG sheets formed layered stacking structures as shown in Figure 1b (also see Supporting Information, page S1). The organic aryl groups grafted to both sides of the f-TEG sheets served as spacers to establish interstitial gaps between the graphene planes, thus providing nanometer-sized pores for the physisorption of H₂ molecules. This kind of propped 3-D layered carbon nanostructure with interlayer spacing has been predicted to increase hydrogen uptake capacity.^{18,21,23}

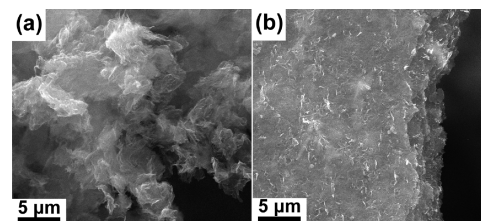


Figure 1. SEM images of (a) original TEG sheets and (b) layered-stacking structure of organic cross-linked f-TEG product **1a**. The other products **1b**, **2a**, and **2b** (as shown in Supporting Information, page S1) have the same layered-stacking structure as product **1a**.

The degree of functionalization was determined by X-ray photoelectron spectroscopy (XPS, PHI Quantera SXM, see Supporting Information, page S2). The XPS analysis of f-TEGs detected chlorine and sulfur from the grafted chloro-aryl groups and sulfonic-aryl groups, respectively; no sodium peaks were detected, which indicates the sodium salts were completely removed from the f-TEG. After reaction with the diazonium salts derived from 4,4'-methylenedianiline and 4-chloroaniline (products **1a** and **1b**), the presence of Cl was detected, indicating that the graphene sheets had been successfully functionalized. High-resolution XPS of products **1a** and **1b** showed the atomic percentages of chlorine as 1.7% and 0.8%, respectively. Meanwhile, S2p peaks were detected in all four products: **1a**, 6.3%, **1b**, 2.2%, **2a**, 4.2%, and **2b**, 1.7%, indicating that the aryl rings were sulfonated to varying degrees by the super acid solvents; the degree of sulfonation was higher in chlorosulfonic acid than in oleum. The functionalized aryl groups can serve as inter-layer spacers between graphene sheets while the sulfonic acid groups could generate partial charge transfer with the graphene planes. Both could be good factors for increasing adsorption of H₂ to the surface of f-TEG sheets.¹⁶

Fourier transform infrared spectroscopy (FTIR, Nicolet 6700 FTIR Instrument) was used to detect the characteristic absorbance of functional groups grafted on graphene sheets, as shown in Supporting Information, page S3. The FTIR spectra show the asymmetric stretch at 1175 cm⁻¹ and the symmetric stretch at 1033 cm⁻¹ of the -SO₃H groups. The peaks at 1130 cm⁻¹ can be assigned to the in-plane bending vibrations of phenyl rings substituted with sulfonate groups. These absorption peaks can be ascribed to the functionalized sulfonated aryl groups. The wide bands at ~1460 and 1650 cm⁻¹ are due to C=C stretching. The two peaks at ~680 and 668 cm⁻¹ are characteristic bands of out-of-plane skeleton bending vibrations and out-of-plane bending vibration of the C-H in the benzene rings.

Thermogravimetric analysis (TGA) was performed on TEG and the f-TEGs to further confirm the degree of functionalization. The samples were heated to 110 °C for 1 h to remove any remaining water or solvents and then cooled to room temperature. Subsequently, the samples were heated to 850 at 1 °C/min under Ar flow. The overall weight loss of original TEG was less than 2%, indicating that most of the surface groups were removed by thermal

(28) Hudson, J. L.; Casavant, M. J.; Tour, J. M. *J. Am. Chem. Soc.* **2004**, *126*, 11158.

(29) Behabtu, N.; Lomeda, J. R.; Green, M. J.; Higginbotham, A. L.; Sinitiskii, A.; Kosynkin, D. V.; Tsentlovich, D.; Parra-Vasquez, A. N. G.; Schmidt, J.; Kesselman, E.; Cohen, Y.; Talmon, Y.; Tour, J. M.; Pasquali, M. *Nat. Nanotechnol.* **2010**, *5*, 406.

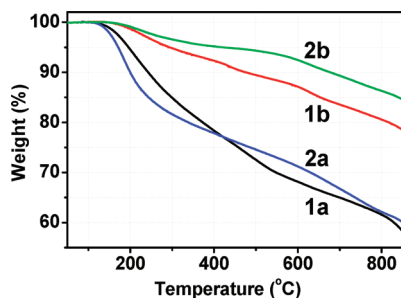


Figure 2. TGA analysis of f-TEG products.

exfoliation. As shown in Figure 2, the weight loss of the f-TEGs was as follows: **1a**, 42%; **1b**, 21%; **2a**, 40%, and **2b**, 15%. The weight loss of **1a** and **2a** was higher than in product **1b** and **2b**. The data show that the degree of functionalization in chlorosulfonic acid is higher than in oleum, and this is consistent with the results of XPS data and the recorded solubility of graphene in those solvents.²⁹

Specific surface areas and gravimetric hydrogen uptake capacities of original TEG and f-TEG materials were recorded at the National Renewable Energy Laboratory (NREL). The hydrogen uptake data were collected with a custom-built high-precision system that recorded hydrogen uptake at 77 K and 2 bar while simultaneously heat-treating and recording BET surface areas without being exposed to air.^{17,30} The BET surface area of original TEG was found to be as high as 550 m²/g. The cross-linked f-TEG products **1a** and **1b** had surface areas of ~440 m²/g, while the surface areas of **2a** and **2b** were 260 m²/g and 350 m²/g, respectively, which indicates the interlayer cross-linkers derived from 4,4'-methylenedianiline provide better propping effects than simple functional groups derived from substituted aniline. The hydrogen uptake capacities per unit surface area were obtained by plotting the surface area versus hydrogen uptake, as shown in Figure 3. The hydrogen uptake of TEG was ~1.0 wt % per 500 m²/g at 77 K and 2 bar, which is comparable to a previous report (about 0.5 wt % H₂ per 500 m²/g specific surface area at 77 K and 1 bar).²⁶ The hydrogen uptake of f-TEGs at 77 K and 2 bar were as follows: **1a**, 1.6 wt %; **1b**, 1.4 wt %; **2a**, 1.4 wt %, and **2b**, 1.1 wt %. The hydrogen uptake per unit surface area of f-TEG products is ~1.9 wt % per 500 m²/g at 77 K and 2 bar, demonstrating an improvement compared to original TEG and the typical value of carbon materials as provided by the "Chahine rule" at 77 K and 40 bar; normally, the hydrogen uptake of carbon adsorbents increases an additional 20–35% if the pressure is raised from 2 to 40 bar (we did not have enough product to do

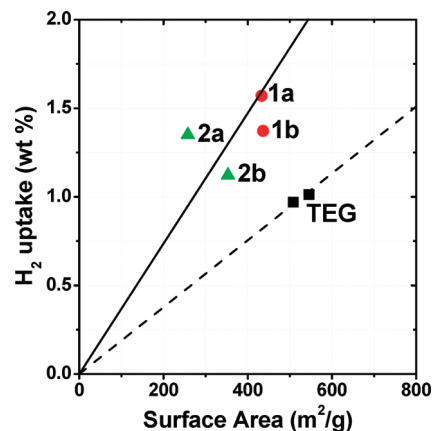


Figure 3. Specific surface area determined from nitrogen BET at 77 K versus hydrogen uptake capacity at 77 K and 2 bar. The data of different materials are represented by different symbols: black squares, original TEG; red circles, products **1a** and **1b**; and green triangles, products **2a** and **2b**. The solid line is the fit and extrapolation from the data of f-TEG products. The dashed line correlates to the data of original TEG.

the test at 40 bar). Hence, the hydrogen uptake of f-TEGs is expected to be substantially higher if we project the saturation surface excess values at higher pressures.^{10,11,17,26} The results indicates the binding of hydrogen on graphene can be greatly improved with the aid of cross-linkers and functional groups. The hydrogen uptake of the f-TEGs propped up by cross-linkers (**1a** and **1b**) was higher than the f-TEGs functionalized by substituted phenyl groups (**2a** and **2b**), which indicates the hydrogen adsorption capacity can be affected by the variety of organic spacers and interlayer spacing (theoretically calculated interlayer spacings of products **1a** and **2a** are, respectively, ~0.96 nm and ~0.76 nm).^{18,21} Also, the higher degree of functionalization proved to increase the hydrogen uptake.

In summary, a facile functionalization and cross-linking of TEG using an in situ diazonium reaction in super acids has been successfully achieved. The degree of functionalization was monitored by XPS, FTIR, and TGA. The f-TEG products show enhanced hydrogen uptake capacities compared with the original TEG, which can be attributed to the propping of the functional groups on f-TEG sheets and the charge transfer of sulfonic addends with the graphene planes of the f-TEG sheets. The hydrogen uptake enhancement of TEG by organic cross-linking demonstrates a possible route to further increase the hydrogen storage capacity of graphene materials.

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Supporting Information Available: Additional SEM images, XPS analysis, and FTIR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

(30) Simpson, L. J.; Parilla, P. A.; Blackburn, J. L.; Gennett, T. G.; Gilbert, K. E. H.; Engtrakul, C.; Dillon, A. C.; Heben, J. M. In *Global Progress Toward Clean Energy: Proceedings of the 17th NHA Annual Hydrogen Conference, 12–16 March 2006, Long Beach, California* (DVD-ROM); National Hydrogen Association: Washington, DC, 2006; p 14.