

Reduction of graphite oxide using alcohols†‡

Daniel R. Dreyer,^a Shanthi Murali,^b Yanwu Zhu,^b Rodney S. Ruoff^b and Christopher W. Bielawski^{*a}

Received 17th August 2010, Accepted 27th September 2010

DOI: 10.1039/c0jm02704a

A method for reducing graphite oxide using a variety of commercially available alcohols is described. The carbon products were found to exhibit high C : O ratios (up to 30 : 1, as determined by elemental combustion analysis), high conductivities (up to 4600 S m⁻¹), and good specific capacitances (up to 35 F g⁻¹) when tested as electrode materials in ultracapacitors.

Introduction

Because of its remarkable electronic, optical, mechanical, and catalytic properties, graphene has emerged as a material of great interest.^{1–9} Although relatively few methods for preparing graphene on large scales have been demonstrated, one of the most promising is based on the chemical reduction of graphite oxide (GO).^{10–12} Since Boehm and co-workers' early report, methods which reduce GO^{13,14} using various chemical reagents have been central to the synthesis and manipulation of single- and multi-layered carbon species.¹² Typically, strong reductants such as anhydrous hydrazine,¹⁵ hydrazine monohydrate,¹⁰ or sodium borohydride^{16,17} are used to transform aqueous dispersions of GO or its exfoliated monolayer, graphene oxide, into a highly reduced material that resembles graphene. A persistent challenge surrounding these methodologies, however, is achieving high extents of reduction. It is known that GO exhibits a C : O ratio of approximately 2 : 1¹⁸ and exposure of this material to one or more of the aforementioned chemical reductants often affords a carbon product with a C : O ratio as high as 15 : 1.¹² Although pristine graphene should theoretically exhibit an infinite C : O ratio, recent calculations suggest that achieving ratios of 16 : 1 or higher may be difficult because of the relative inertness of the partially reduced product.¹⁹ While combining the use of chemical reductants with thermal annealing has been shown to increase the C : O ratio of the reduced product to 250 : 1 or higher,²⁰ multi-step procedures are required. Hence, the development of a convenient method that uses a safe and non-toxic reductant to effectively reduce GO and graphene oxide in a single step is warranted.

Recently, we reported that GO may be used to catalyze the oxidation of a variety of benzylic and aliphatic alcohols. In our preliminary study, it was believed that atmospheric oxygen may have functioned as the terminal oxidant.¹ Regardless, in light of these results, we envisioned that alcohols may serve as effective reductants for GO. Further inspiration stemmed from reports

which detailed the use of hydroquinone as a reducing agent for graphene oxide.^{21,22} In these studies, it was surmised that hydroquinone (a diol) was likely oxidized to quinone (a diketone). Hence, we reasoned that other activated alcohols (*e.g.*, benzyl alcohol) may also undergo oxidation and ultimately reduce GO as well as graphene oxide in the process. Indeed, as described herein, we have found that a variety of inexpensive, relatively non-toxic alcohols effectively reduce GO and graphene oxide, and afford carbon products with higher conductivities and higher C : O ratios than those obtained using strong reductants (*e.g.*, hydrazine) that have been previously used for such purposes (Scheme 1).

Results and discussion

In our initial report,¹ we found that heating 200 wt% GO in benzyl alcohol (BnOH) for 24 h at 100 °C under an atmosphere of air resulted in partial reduction of the carbon material. The C : O ratio increased from approximately 2 : 1 (measured for the GO starting material) to 7 : 1 in the product, as determined by elemental combustion analysis; likewise, the powder conductivity increased from 2 × 10⁻⁵ S m⁻¹ to 15 S m⁻¹, respectively, as measured by a two-point probe technique performed on powder samples.¹⁰ Absorbances in the FT-IR spectrum attributable to the O–H, C=O and epoxide groups in the starting material were attenuated or completely disappeared, and the absorbances associated with aromatic and olefinic species became distinguishable in the isolated carbon product. As a further indicator that the GO was successfully reduced, the isolated product could not be re-dispersed in water or other polar solvents, even upon prolonged sonication and heating.¹⁰ Despite these promising results, neither the C : O ratio nor the powder conductivity of the reduced GO product were as high as has been demonstrated with other reductants, such as hydrazine.¹⁰ However, the inherent advantages of this reduction method (*e.g.*, low temperature, low cost, and relatively low toxicity) were encouraging and prompted us to explore the process in greater detail.

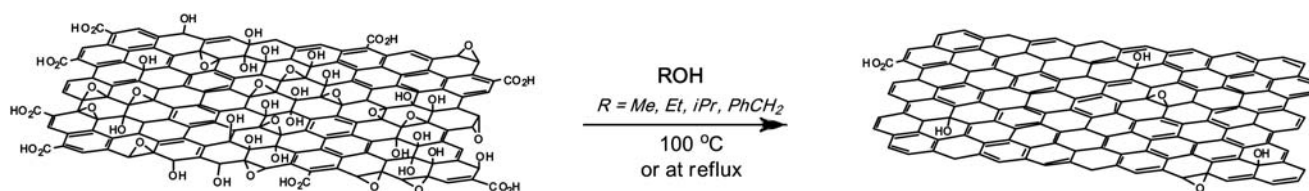
Our first modification of the aforementioned reduction method was to increase the volume of BnOH used. Decreasing from 200 wt% of GO in benzyl alcohol to 10 wt% under otherwise identical conditions resulted in a product that exhibited a C : O ratio of 15 : 1 and a conductivity of 2200 S m⁻¹. The increase in volume of BnOH used in this variation of the reduction reaction proved to be important as it is believed that the oxidation process (and subsequently the reduction of the GO)

^aDepartment of Chemistry and Biochemistry, The University of Texas at Austin, 1 University Station, A5300, Austin, TX, 78712, USA. E-mail: bielawski@cm.utexas.edu; Fax: +1-512-471-5884; Tel: +1-512-232-3889

^bDepartment of Mechanical Engineering and the Texas Materials Institute, 1 University Station, C2200, Austin, TX, 78712, USA

† Electronic supplementary information (ESI) available: Additional experimental details and characterization data. See DOI: 10.1039/c0jm02704a

‡ This paper is part of a *Journal of Materials Chemistry* themed issue on Chemically Modified Graphenes. Guest editor: Rod Ruoff.



Scheme 1 The reduction of graphite oxide or graphene oxide using alcohols under mild conditions afforded highly reduced carbon products.

may be catalytic in alcohol.¹ As such, the use of small amounts of BnOH may be insufficient to drive the reaction to completion; rather, excess reductant may be necessary to achieve maximal reduction.

In an effort to further improve the extent of reduction, aliquots of GO were heated in the presence of even larger volumes of GO and for longer periods of time. In particular, a mixture of 200 mg of GO in 25 mL of BnOH (0.8 wt% GO) was stirred for 5 days at 100 °C. § The resulting dispersion was then poured into ethanol to facilitate precipitation, and the product was collected *via* filtration and dried under vacuum. ¶ The conductivity of this material was measured to be 4600 S m⁻¹ (Table 1) and the C : O ratio was found to be 30 : 1. To the best of our knowledge, this C : O ratio is the highest reported for any material obtained *via* the chemical reduction of GO or graphene oxide. In further support of an effective reduction reaction, FT-IR analysis of the BnOH-reduced product showed a significantly attenuated peak at 3400 cm⁻¹ (Fig. 1), which was consistent with a near-complete disappearance of hydroxyl functionality, as well as water. However, the surface area of the product was found to be relatively low (9.6 m² g⁻¹ as determined using the BET method;²³ see Fig. S1–S5 and Table S2, ESI†) and comparable to the surface area measured for (non-reduced) GO as well as materials prepared by the reduction of graphene oxide with hydroquinone or NaBH₄.^{22**}

We believe the origin of the low surface area observed in the product of the aforementioned reduction reaction may be understood in terms of the kinetics, as well as the compatibility of GO and reduced graphite oxide with BnOH. While the reduction

proceeds rapidly (minutes, upon heating) when hydrazine or other strong reductants are used on aqueous dispersions of graphene oxide, the reduction of GO using BnOH was found to proceed much slower (hours). This sluggishness may afford opportunities for the reduced lamellae to restack in solution, forming small, graphite-like agglomerates, as supported by the relatively large particles observed by scanning electron microscopy (SEM). These images (Fig. S12–S14, ESI†) showed thick, agglomerated particles on the order of tens of microns in diameter, rather than the isolated monolayers (either lamellar or crumpled) often observed when other reductants are used. Since both the oxidized and reduced products were found to form appreciably stable dispersions in BnOH, transient exfoliation followed by reduction and agglomeration may be occurring during the reaction. However, we cannot discount the possibility that the alcohols intercalated into the stacked structure of GO (as has previously been demonstrated²⁴), reduced the lamellae without effectively exfoliating the carbon, and then were expelled as their oxidized analogues (*e.g.*, aldehydes and acids).

As shown in Fig. 2, transmission electron microscopy (TEM) revealed that the recovered, BnOH-reduced GO was largely unexfoliated and exhibited a lamellar morphology (consistent

Table 1 Characterization of the products obtained by reducing graphite oxide using various alcohols^a

	MeOH	EtOH	iPrOH	BnOH
BET surface area ^b /m ² g ⁻¹	5.8	35.9	10.4	9.6
C : O ratio ^c	4.0 : 1	6.0 : 1	6.9 : 1	30 : 1
Powder conductivity ^d /S m ⁻¹	3.2 × 10 ⁻⁵	1.8 × 10 ⁻⁴	1019	4600
I _d /I _g ratio ^e	1.15	1.10	1.25	1.20
Interlamellar spacing ^f /Å	8.11, 3.74	7.02, 3.90	3.75	3.54
Specific capacitance ^g /F g ⁻¹	—	—	2.8	35

^a Material prepared by heating GO in neat alcohol (indicated in table) at 8 mg mL⁻¹ for 5 days at 100 °C (or at reflux) in an open vessel with an attached condenser. The product was isolated by precipitation into EtOH followed by filtration. ^b Measured using nitrogen as the adsorbate. ^c Determined *via* elemental combustion analysis. ^d Determined using a two point probe technique (ESI†). ^e Determined from the relative peak heights in the Raman spectra. ^f Determined *via* powder X-ray diffraction (25 °C). As seen in Fig. S11 (ESI†), two diffraction peaks were observed for the products reduced by MeOH and EtOH. ^g Determined using cyclic voltammetry (scan rate: 25 mV s⁻¹) and a galvanostatic charge–discharge technique (current: 10 mA) on a two-plate apparatus (Fig. S21, ESI†) with KOH as the electrolyte. Ultracapacitor cells fabricated using carbons obtained by reduction of GO with methanol and ethanol showed negligible capacitance under these conditions.

§ While such prolonged reaction periods may not be practical, this experiment was designed to explore the potential of using alcohols as non-conventional reductants of GO.

¶ Greater than 95% of the BnOH was found to be unreacted and was successfully recovered after the reaction *via* distillation. Given the low vapor pressure and low flammability of BnOH, this reduction method is highly scalable and relatively safe, and we have performed reactions analogous to those reported herein on scales greater than 2.5 g without incident.

|| In an effort to improve the surface area, an aqueous dispersion of graphene oxide was prepared^{37,38} by sonicating 100 mg of GO for 3 h in 100 mL of water at room temperature, followed by addition of 10 mL of BnOH (no precipitation was observed). After heating the resulting stable dispersion at reflux for 5 days, the product precipitated from solution. The material was isolated by vacuum filtration and did not show an improvement in the extent of reduction (as determined by elemental combustion analysis; C : O ratio = 10.4 : 1) or surface area (as determined by the BET method; 15.1 m² g⁻¹). However, benzaldehyde and benzoic acid were observed (as confirmed by ¹H NMR spectroscopy) to phase separate, indicating that aqueous dispersions of graphene oxide share similar catalytic properties as GO.¹

** For comparison, carbon materials with surface areas of 300–700 m² g⁻¹ are commonly observed when hydrazine is used as the reductant of aqueous dispersions of graphene oxide.^{3,18}

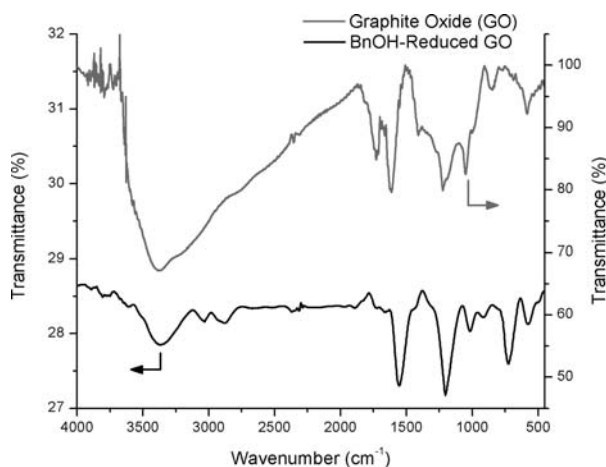


Fig. 1 Overlaid FT-IR spectra (KBr) of GO (gray, top) and reduced graphite oxide obtained by reduction with benzyl alcohol (black, bottom).

with SEM imagery). Furthermore, structural disorder was evident from the lattice fringe patterns seen in the diffraction pattern (Fig. 2 inset; see ESI† for an enlargement of the pattern, as well as additional high resolution imagery). These results were in contrast with those observed in other solution-phase reduction processes, where crumpling and agglomeration of the reduced materials altered most of the lamellar structure.¹⁰ Moreover, Raman analysis revealed an I_D/I_G ratio of 1.20 (Fig. 3), which was consistent with a substantial degree of disorder in the restacked system.²⁵ The morphological differences between the BnOH-reduced GO and materials obtained *via* the reduction of GO using other methods may be due to the dissimilar rates of the reduction reactions involved, as described above.

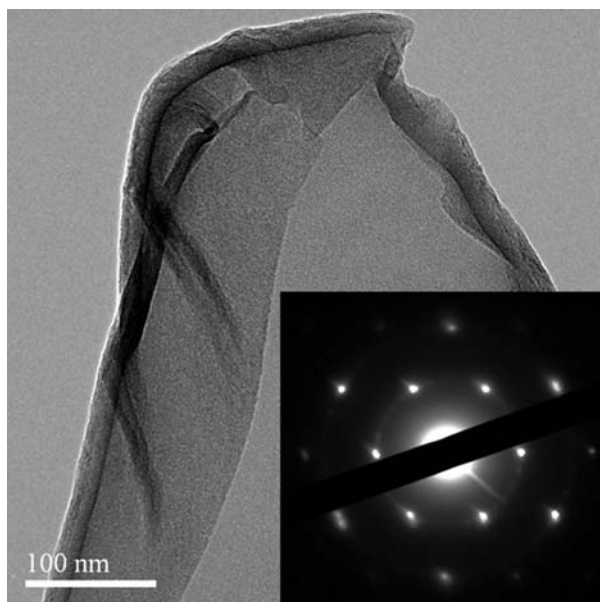


Fig. 2 High resolution TEM image and diffraction pattern (inset) of the material obtained by the reduction of GO with benzyl alcohol. Sheet-like graphitic stacking was observed from the diffraction pattern (see ESI† for an enlargement).

Under the aforementioned conditions (200 mg of GO in 25 mL of alcohol [0.8 wt% GO] heated at 100 °C for 5 days), benzaldehyde and benzoic acid¹ were observed by NMR spectroscopy, suggesting that the reduction process involved BnOH. However, since elevated temperatures were required, thermally mediated processes may also contribute to the reduction.²⁶ To investigate, a series of control experiments was performed wherein GO was heated under otherwise identical conditions in a variety of non-alcoholic solvents, including propylene carbonate (PC), water, anisole, benzonitrile, and diphenyl ether. These five solvents were chosen for their structural and/or chemical similarities (*e.g.*, solubility parameters [δ_D , δ_P , δ_H]²⁷) to BnOH, and for their chemical inertness to GO (confirmed by ¹H NMR spectroscopy). The C : O ratios and powder conductivities determined for the products obtained after 5 days of heating GO in these solvents at 100 °C were indicative of inferior reduction processes compared to BnOH (see Table S4, ESI†). Water and PC proved to be the most effective solvents, though the carbon products obtained from these reactions were measured to possess C : O ratios of only 4.3 : 1 and 4.8 : 1 and powder conductivities of 149.7 and 96.8 S m⁻¹, respectively. These results suggested to us that although thermal effects may be partially responsible for the reduction of GO and graphene oxide, BnOH was critical to obtaining high extents of reduction under these conditions.

After determining that BnOH was effective in reducing GO, efforts shifted toward exploring the potential of other widely available alcohols, including methanol (MeOH), ethanol (EtOH), and isopropanol (iPrOH), to function similarly. Key characterization data obtained from the respective reduced materials (prepared by heating 200 mg of GO in 25 mL of the alcohol [1.0 wt%] to reflux for 5 days) are summarized in Table 1. In all tested metrics (surface area, C : O ratio, powder conductivity, I_D/I_G ratio, and specific capacitance), the three non-aromatic alcohols studied proved to be less effective in facilitating the reduction of GO when compared to BnOH, though the carbon material reduced in the presence of iPrOH exhibited a relatively high C : O ratio and conductivity. Notably, GO was found to disperse in iPrOH (but not MeOH or EtOH), suggesting

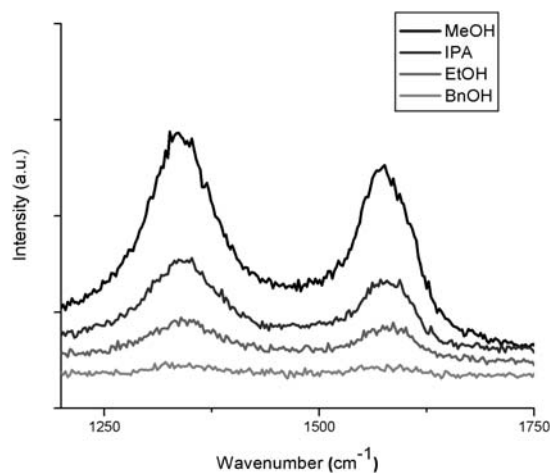


Fig. 3 Raman spectra of materials obtained by the reduction of GO in methanol (black, top), isopropanol (IPA) (dark gray, 2nd from top), ethanol (gray, 2nd from bottom) and benzyl alcohol (light gray, bottom).

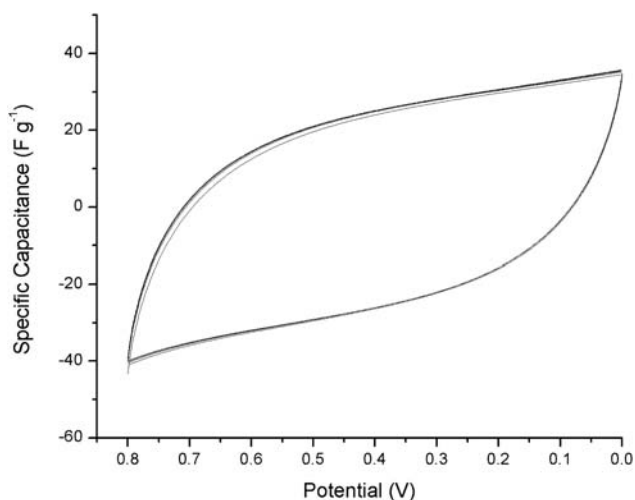


Fig. 4 Cyclic voltammogram (25 mV s^{-1}) of an ultracapacitor incorporating electrodes fabricated from GO reduced by benzyl alcohol. A specific capacitance of *ca.* 35 F g^{-1} was calculated from these data.

GO and *i*PrOH may be compatible with each another, and thus facilitate a more efficient reduction process.

To explore the structural properties (in particular, the interlayer spacing and stacking behavior) of the materials obtained *via* the reduction of GO using various alcohols, a series of powder X-ray diffraction (PXRD) analyses (Fig. S11, ESI†) was performed. The diffraction pattern for the material obtained *via* the reduction of GO with BnOH revealed an interlamellar *d*-spacing of 3.54 \AA , a value consistent with a highly reduced product.^{22,28,29} PXRD analyses of the MeOH-reduced GO ($8.11, 3.74 \text{ \AA}$) and EtOH-reduced GO ($7.02, 3.90 \text{ \AA}$) suggested to us that a mixture of reduced and non-reduced products was present (the larger *d*-spacings were consistent with non-reduced GO³⁰), though these alcohols may be inserting into the interlamellar space.²⁴ The diffraction pattern obtained from the PXRD analysis of the material prepared by reducing GO with *i*PrOH exhibited a similar interlayer *d*-spacing as the BnOH-reduced GO material (3.75 \AA).

To demonstrate that the aforementioned alcohol-reduced products may be implemented in useful applications, electrodes were fabricated from the materials obtained *via* the reduction of GO using *i*PrOH and BnOH, and incorporated into two-electrode ultracapacitors using methods previously reported.³¹ The specific capacitance was quantified using both cyclic voltammetry (scan rate: $5\text{--}100 \text{ mV s}^{-1}$; Fig. 4) and galvanostatic charge–discharge measurements (current: $5\text{--}20 \text{ mA}$; Fig. S21, ESI†) using aqueous KOH as the electrolyte. Specific capacitances as high as 35 F g^{-1} were measured for samples reduced by *i*PrOH and BnOH, and higher values are expected if the surface areas of the materials can be improved.†† These specific capacitances are consistent with those that have been reported for other ultracapacitors which contain carbons obtained either by the

chemical^{31,32} or thermal³³ reduction of GO, or other carbon allotropes such as carbon nanotubes.^{34–36}

Conclusions

In conclusion, we have shown that the treatment of GO with various alcohols under mild conditions afforded highly reduced products. Though low surface areas were measured *via* the BET method (and confirmed by TEM and SEM), bulk powder conductivities as high as 4600 S m^{-1} and C : O ratios as high as 30 : 1 were obtained when BnOH was used as a neat reductant. These results are surprising given that alcohols are not commonly used as reductants and such atypical reactivity may reflect chemical pathways unique to GO, and, perhaps, other chemically modified graphenes or carbon materials.¹ The development of an increased understanding of these processes as well as the exploration of other reductants that may also facilitate access to reduced carbon-based materials is underway.

Acknowledgements

This work was generously supported by the National Science Foundation (DMR-0907324), the Robert A. Welch Foundation (F-1621) and Graphene Energy, Inc.

References

- 1 D. R. Dreyer, H.-P. Jia and C. W. Bielawski, *Angew. Chem., Int. Ed.*, 2010, **49**, 6813–6816.
- 2 Y. Zhu, S. Murali, W. Cai, X. Li, J. W. Suk, J. R. Potts and R. S. Ruoff, *Adv. Mater.*, 2010, **22**, 3906–3924.
- 3 C. N. R. Rao, A. K. Sood, K. S. Subrahmanyam and A. Govindaraj, *Angew. Chem., Int. Ed.*, 2010, **48**, 7752–7777.
- 4 D. R. Dreyer, R. S. Ruoff and C. W. Bielawski, *Angew. Chem., Int. Ed.*, 2010, DOI: 10.1002/anie.201003024.
- 5 F. Kim, J. Luo, R. Cruz-Silva, L. J. Cote, K. Sohn and J. Huang, *Adv. Funct. Mater.*, 2010, **20**, 2867–2873.
- 6 D. Wei and Y. Liu, *Adv. Mater.*, 2010, **22**, 3225–3241.
- 7 K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva and A. A. Firsov, *Science*, 2004, **306**, 666–669.
- 8 M. J. Allen, V. C. Tung and R. B. Kaner, *Chem. Rev.*, 2010, **110**, 132–145.
- 9 Y.-H. Lu, M. Zhou, C. Zhang and Y.-P. Feng, *J. Phys. Chem. C*, 2009, **113**, 20156–20160.
- 10 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.
- 11 A. Bagri, C. Mattevi, M. Acik, Y. J. Chabal, M. Chhowalla and V. B. Shenoy, *Nat. Chem.*, 2010, **2**, 581–587.
- 12 S. Park and R. S. Ruoff, *Nat. Nanotechnol.*, 2009, **4**, 217–224.
- 13 H. P. Boehm, A. Clauss, G. Fischer and U. Hofmann, in *Proceedings of the Fifth Conference on Carbon*, Pergamon Press, 1962, pp. 73–80.
- 14 H. P. Boehm, A. Clauss, G. O. Fischer and U. Hofmann, *Z. Naturforsch., B: Anorg. Chem. Org. Chem. Biochem. Biophys. Biol.*, 1962, **17**, 150–153.
- 15 V. C. Tung, M. J. Allen, Y. Yang and R. B. Kaner, *Nat. Nanotechnol.*, 2009, **4**, 25–29.
- 16 Y. Si and E. T. Samulski, *Nano Lett.*, 2008, **8**, 1679–1682.
- 17 H.-J. Shin, K. K. Kim, A. Benayad, S.-M. Yoon, H. K. Park, I.-S. Jung, M. H. Jin, H.-K. Jeong, J. M. Kim, J.-Y. Choi and Y. H. Lee, *Adv. Funct. Mater.*, 2009, **19**, 1987–1992.
- 18 D. R. Dreyer, S. Park, C. W. Bielawski and R. S. Ruoff, *Chem. Soc. Rev.*, 2010, **39**, 228–240.
- 19 D. W. Boukhalov and M. I. Katsnelson, *J. Am. Chem. Soc.*, 2008, **130**, 10697–10701.

†† Frequency response analysis (FRA) performed on the ultracapacitor incorporating BnOH-reduced GO as the electrode material revealed a cell resistance of 0.20 \Omega at 62 kHz and 0.51 \Omega at 15 kHz (see Fig. S22 (ESI†) for the respective Nyquist plot), consistent with other highly reduced graphene-like materials used as electrodes.³¹

- 20 W. Gao, L. B. Alemany, L. Ci and P. M. Ajayan, *Nat. Chem.*, 2009, **1**, 403–408.
- 21 G. Wang, J. Yang, J. Park, X. Gou, B. Wang, H. Liu and J. Yao, *J. Phys. Chem. C*, 2008, **112**, 8192–8195.
- 22 A. B. Bourlinos, D. Gournis, D. Petridis, T. Szabó, A. Szeri and I. Dékány, *Langmuir*, 2003, **19**, 6050–6055.
- 23 S. Brunauer, P. H. Emmett and E. Teller, *J. Am. Chem. Soc.*, 1938, **60**, 309–319.
- 24 A. V. Talyzin, B. Sundqvist, T. Szabó, I. Dékány and V. Dmitriev, *J. Am. Chem. Soc.*, 2009, **131**, 18445–18449.
- 25 A. C. Ferrari, *Solid State Commun.*, 2007, **143**, 47–57.
- 26 Y. Zhu, M. D. Stoller, W. Cai, A. Velamakanni, R. D. Piner, D. Chen and R. S. Ruoff, *ACS Nano*, 2010, **4**, 1227–1233.
- 27 C. M. Hansen, *Hansen Solubility Parameters: a User's Handbook*, CRC Press, Hoboken, NJ, 2007.
- 28 E. Yoo, J. Kim, E. Hosono, H.-s. Zhou, T. Kudo and I. Honma, *Nano Lett.*, 2008, **8**, 2277–2282.
- 29 O. C. Compton, D. A. Dikin, K. W. Putz, L. C. Brinson and S. T. Nguyen, *Adv. Mater.*, 2010, **22**, 892–896.
- 30 D. A. Dikin, S. Stankovich, E. J. Zimney, R. D. Piner, G. H. B. Dommett, G. Evmenenko, S. T. Nguyen and R. S. Ruoff, *Nature*, 2007, **448**, 457–460.
- 31 M. D. Stoller, S. Park, Y. Zhu, J. An and R. S. Ruoff, *Nano Lett.*, 2008, **8**, 3498–3502.
- 32 K. Zhang, L. L. Zhang, X. S. Zhao and J. Wu, *Chem. Mater.*, 2010, **22**, 1392–1401.
- 33 Y. Zhu, S. Murali, M. D. Stoller, A. Velamakanni, R. D. Piner and R. S. Ruoff, *Carbon*, 2010, **48**, 2118–2122.
- 34 A. G. Pandolfo and A. F. Hollenkamp, *J. Power Sources*, 2006, **157**, 11–27.
- 35 P.-C. Chen, G. Shen, S. Sukcharoenchoke and C. Zhou, *Appl. Phys. Lett.*, 2009, **94**, 043113.
- 36 R. H. Baughman, A. A. Zakhidov and W. A. de Heer, *Science*, 2002, **297**, 787–792.
- 37 J. Shen, Y. Hu, M. Shi, X. Lu, C. Qin, C. Li and M. Ye, *Chem. Mater.*, 2009, **21**, 3514–3520.
- 38 Y. Zhu, S. Murali, W. Cai, X. Li, J. W. Suk, J. R. Potts and R. S. Ruoff, *Adv. Mater.*, 2010, **22**, 3906–3924.