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Graphene Oxide

Sulfur-Functionalized Graphene Oxide by Epoxide Ring-Opening**

Helen R. Thomas, Alexander J. Marsden, Marc Walker, Neil R. Wilson, and Jonathan P. Rourke**

Abstract: *The treatment of graphene oxide (GO) with potassium thioacetate followed by an aqueous work-up yields a new material via the ring-opening of the epoxide groups. The new material is a thiol-functionalized GO (GO-SH) which is able to undergo further functionalization. Reaction with butyl bromide gives another new material, GO-SBu, which shows significantly enhanced thermal stability compared to both GO and GO-SH. The thiol-functionalized GO material showed a high affinity for gold, as demonstrated by the selective deposition of a high density of gold nanoparticles.*

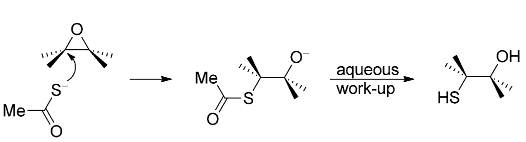
Graphene itself has many outstanding properties:[1] it is exceptionally electrically[2] and thermally[3] conductive, transparent,[4] elastic,[5] highly impermeable,[6] extremely strong,[5b] and yet is the thinnest[6b] 2D material ever obtained. However, its poor solubility and difficult processability in both water and organic solvents make it a less than ideal material to work with. The development of chemically modified graphenes (CMGs) is thus a topic of great interest to many researchers as this will allow the properties of graphene to be tailored for specific applications such as optoelectronics,[7] energy storage,[8] sensors,[9] and catalysts[10] as well as increasing the ease with which it can be processed.

Graphite derivatives such as graphene oxide (GO) provide an excellent platform for the development of CMGs. GO is cheap and easy to make in bulk quantities and can be manipulated chemically[11] due to its high solubility in many common solvents, such as water. It is possible to reduce graphene oxide back to a more graphene-like material by thermal[12] or chemical[13] means.

Functionalization is, in theory, possible through each of the four groups known to be present on the surface of GO: carboxylic acid, ketone/aldehyde groups, hydroxy groups and epoxides.[14] The carboxylic acid groups in particular have been extensively exploited for chemical modification in the development of CMGs.[15] Edge site ketones[16] and surface hydroxy[17] groups have also been studied, but work on surface epoxide functionalization is less extensive. Nucleophilic attack on the epoxide groups of GO has been previously demonstrated with nitrogen nucleophiles,[18] and more recently with carbon nucleophiles.[19] These ring opening reactions leave reactive groups on the GO surface, which can then be utilized for further chemistry. The selective reduction of epoxides has also been recently studied.[20] Given our earlier results,[21] in which we identified that around one third of the mass of GO is actually highly oxidized, low molecular weight, oxidative debris (OD) with the same functional groups as GO itself, it is entirely possible that some of these groups functionalized the OD, rather than the graphene-like sheets.

To the best of our knowledge, the use of sulfur nucleophiles for the ring-opening of epoxides on the surface of GO has so far been unexplored, and here we show how we replaced epoxide functionalities on the GO surface with reactive thiol groups. We also show that these surface thiol groups can undergo chemical modification by the attachment of alkyl chains (which substantially enhances the thermal stability of the material) or by the attachment of gold nanoparticles (which can be directly imaged by TEM).

Potassium thioacetate is a convenient source of nucleophilic sulfur[22] and introduces a group that can be subsequently elaborated to reveal a thiol group. When applied to GO, we would expect such a nucleophile to selectively attack the epoxide groups. We found that under reasonably mild conditions (50°C, 5 h) reaction with GO occurred, giving a material that contained covalently bound sulfur. To avoid the possibility of side reactions, the OD is removed from the as-produced GO (aGO) by a basic wash to give base-washed GO (bwGO) prior to reaction. Our reaction work-up included an aqueous step, which we would expect to result in the hydrolysis of the thioacetate to leave just surface-bound thiol groups. Extensive washing of the material after work-up removes all unreacted reagents [Eq. (1)].



(1)

Nucleophilic attack may occur at the electrophilic carbon atoms of an epoxide, or at a carbon double bond adjacent to the epoxy group. Both reaction pathways will cause ring-opening of an epoxide, relieving strain, but note that, while

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[*] H. R. Thomas, Dr. J. P. Rourke
Department of Chemistry, University of Warwick
Coventry, CV4 7AL (UK)
E-mail: j.p.rourke@warwick.ac.uk

A. J. Marsden, Dr. M. Walker, Dr. N. R. Wilson
Department of Physics, University of Warwick
Coventry, CV4 7AL (UK)
E-mail: neil.wilson@warwick.ac.uk

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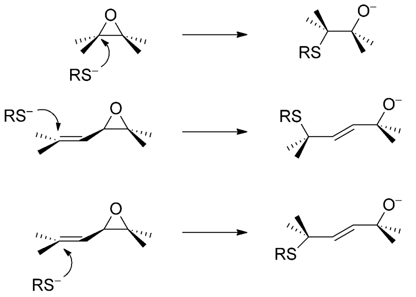
the direct S_N2 opening of the epoxide requires the incoming nucleophile to approach from the opposite face of the epoxide, attack at a double bond (an S_N2' reaction) allows for the nucleophile to attack at either the same face as the epoxide or at the opposite one [Eq. (2)].



(2a)

(2b)

(2c)

aGO will have epoxides on both sides of the graphene-like sheet, so ultimately it does not matter which reaction pathway is followed and we would expect thiol groups and hydroxy groups on both sides of the sheet. We do not know the relative rates of the S_N2 and S_N2' reactions at GO, but it is entirely feasible that the S_N2' reaction dominates.[23]

We denote the new material that we were able to collect following this reaction as GO-SH and used energy-dispersive X-ray (EDX), X-ray photoelectron spectroscopy (XPS), FTIR, Raman, TEM, and solid-state NMR (ssNMR) spectroscopy as well as thermogravimetric analysis (TGA) to characterize it. The new material resembles bwGO in that it is much darker than aGO and it still exhibits an appreciable solubility in dimethyl sulfoxide (DMSO), unlike hydrazine-reduced GO.[21b]

Both XPS and EDX (Figure 1 and Figure S1 in the Supporting Information, SI) confirm the presence of carbon, oxygen, and sulfur in GO-SH with close agreement between the atomic percentages; both techniques indicate a sulfur incorporation of around 4 atom %. This equates to an attached sulfur for every group of nine or so graphitic rings, which is slightly lower than the one suggested for the epoxide concentration.[19] Because the binding energy of carbon with a C−S bond is very similar to that of carbon with a C−C(sp^3) bond, the C 1s XPS spectrum (Figure 1 a) cannot be used to prove the presence of such a low atomic percentage of S-bound species. However, the S 2p spectrum (Figure 1 b) can be used to show exactly this. The S 2p spectrum is fitted with $2p_{3/2}$ components at 161.9 eV (lower binding energy component of spin-orbit split doublet, assigned to a S−S bond), 163.5 eV and 164.5 eV (H−S−C and R−S−C), and 168.0 eV (S−O),[24] with the dominant contribution from the H−S−C. Thus the majority of the sulfur present is shown to be covalently attached to carbon and hydrolyzed to a thiol group. A small amount of sulfur is present as R−S−C, which is presumably due to a number of unhydrolyzed MeCOS−C groups. An inert atmosphere was used to prevent unwanted oxidation impurities,[25] however, the spectrum indicates that a small fraction of the S is present in the form of S−S and S−O bonds.

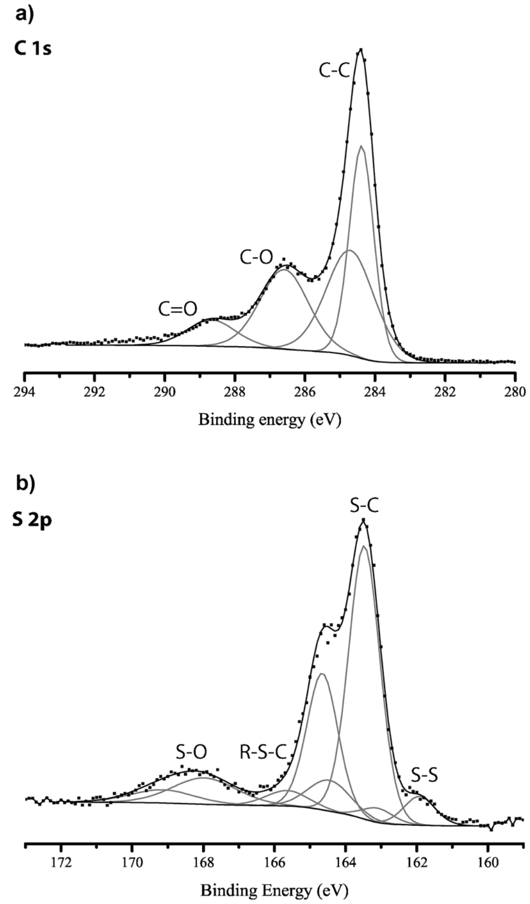


Figure 1. XPS spectra of GO-SH: a) C 1s and b) S 2p. The experimental data is shown as points with the underlying lines showing the fitted peaks (assignations as labeled).

While FTIR spectra (Figure S4 in the SI) of bwGO show clear bending and stretching vibrations of OH hydroxy, C=O carbonyl/carboxyl, C−O epoxy and alkoxy, and C=C aromatic groups, the FTIR spectrum of GO-SH (Figure S5 in the SI) shows a clear decrease in both OH and C−O epoxy groups. The functionalization of the bwGO material causes a decrease of its hygroscopic nature, and thus the noticeable decrease in hydrogen-bonded OH groups may be due to a loss of adsorbed water, or might be the result of reduction (see later). A weak S−H stretching band would be expected between 2600 and 2550 cm^{-1}, but unfortunately we were unable to detect it; presumably it is obscured by the broad OH absorbance. Raman spectra (Figure S8 in the SI) of GO-SH are similar to bwGO, suggesting that there is little, if any, change to the graphene-like backbone.

Figure 2 shows the ^{13}C solid-state NMR spectrum of GO-SH. The dominant peak is the characteristic sp^2 C−C peak at around 125 ppm together with much weaker peaks at 72 ppm (C−OH) and 61 ppm (C−O−C).[26] A carbon atom with a thiol group would be expected to exhibit a resonance at around 30–40 ppm lower than one with an oxygen atom attached, and the small peak at around 26 ppm could be caused by these carbon atoms (this peak is substantially enhanced in the cross polarized spectrum, see Figure S10 in the SI).

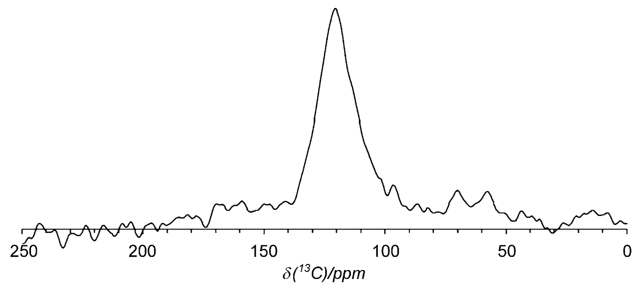


Figure 2. ssNMR ^{13}C MAS spectrum of GO-SH.

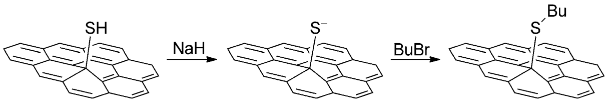
The intensity of the signal for the carbon atoms with hydroxide and epoxide groups attached is greatly reduced in GO-SH, compared to both aGO and bwGO.[21b] We propose that this decrease in intensity is due to a combination of epoxide-opening reactions and chemical reduction. Thioacetates might not be a chemist's first choice of reducing agent, but their reducing properties do have synthetic utility in certain areas of organic chemistry.[27] Thus, we find that if we measure the elemental composition of the GO-SH as a function of reaction time (bwGO with thioacetate), we see an increase in the proportion of sulfur up to about five hours, before it starts to decrease. At the same time, we see a steady decrease in the proportion of oxygen, with the result that after 60 h reaction the material produced has essentially no sulfur and has a C/O ratio similar to that obtained after a 24 hour hydrazine reduction.[21b]

Thermogravimetric analysis (TGA, Figure S15 in the SI) shows that GO-SH is distinctly less hygroscopic than bwGO, which is indicated by the low mass loss at around 100 °C. Similar to chemically reduced GO samples, there is little mass loss below 500 °C with the major mass loss coming from the decomposition of the graphene-like sheets at higher temperature. This single mass loss for GO-SH also provides further evidence of the covalent functionalization: if the thioacetate reactant had simply been adsorbed to the surface of the GO material, we would expect to see a mass loss corresponding to its desorption at a temperature lower than 500 °C.

Finally, TEM analysis confirms the monolayer graphene-like structure of GO-SH (Figure 3). The sheets have flatly deposited, without coagulation, and are visible in the bright-field TEM image (Figure 3 a) stretched across holes in the lacy carbon support. Although the sheets are almost electron-transparent, they can be discerned in images due to the occasional crease or fold, see for example just above the dashed circle. Electron diffraction patterns from individual GO-SH sheets show hexagonal arrays of diffraction spots, such as the diffraction pattern in Figure 3 b which was taken from the area in Figure 3 a marked by the dashed circle. The inner hexagon of spots are more intense than the outer ones, as shown by the line profile given in Figure 3 c, which is taken from the dashed box in Figure 3 b. The diffraction patterns are thus characteristic of a material with a monolayer graphene-like backbone, indistinguishable from those of graphene oxide.[28]

Thus, all characterization data gathered provides evidence for surface functionalization by epoxide-opening using a sulfur nucleophile, with subsequent hydrolysis yielding a clean graphene-like material with surface thiol groups (GO-SH). To provide additional evidence for this result we set about chemically functionalizing the GO-SH.

The surface thiols of GO-SH should be nucleophilic in their own right and amenable to further reaction with electrophiles. Thus we deprotonated GO-SH using sodium hydride at room temperature under an inert atmosphere, and subsequently reacted with bromobutane: the intention being to synthesize a thioether-functionalized GO [Eq. (3)].



(3)

After an aqueous work-up, characterization evidence from EDX, XPS, FTIR, TGA, TEM, and ssNMR techniques indicated that C_4 (butyl) alkyl chains have been covalently attached to the surface through sulfur to form the CMG material we denote GO-SBu. EDX and XPS (Figure S2 in the SI) show the proportion of sulfur to be at slightly lower levels than GO-SH, as would be expected after the incorporation of additional carbon atoms. FTIR (Figure S6 in the SI) shows a clear C–H stretching band at around 2920 cm^{-1} and TEM (Figure S18 in the SI) shows the new material is still fully exfoliated. Physically the new material looks very similar to GO-SH and retains good solubility in DMSO. Solid-state NMR is very illuminating and provides direct evidence for an S-Bu chain attached to the surface (Figure 4): four new carbon resonance signals typical of aliphatic carbon atoms are now seen, with the resonance at 39 ppm having a chemical shift appropriate for the S–CH_2 group. TGA (Figure S16 in the SI) shows a significant ($\approx$125 K) enhancement of the thermal stability of GO-SBu compared with GO-SH with

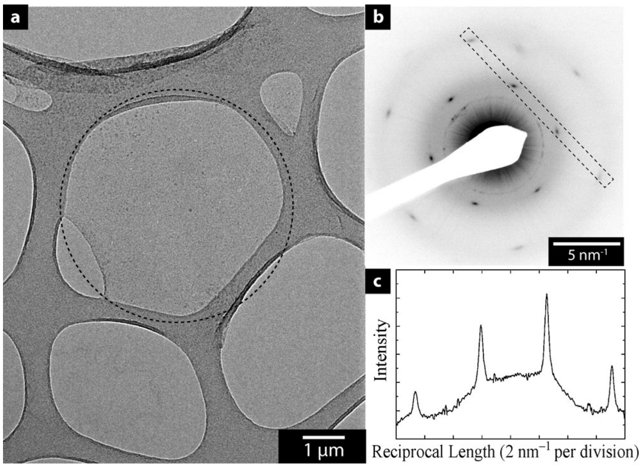


Figure 3. TEM analysis of GO-SH. a) Bright-field TEM image showing a sheet of GO-SH suspended across a hole in a lacy carbon support grid. b) A selected area diffraction pattern from the dashed region in (a). c) Line profile as marked on the diffraction pattern showing that the outer diffraction peaks are less intense than the inner ones, consistent with a monolayer graphene-like material.

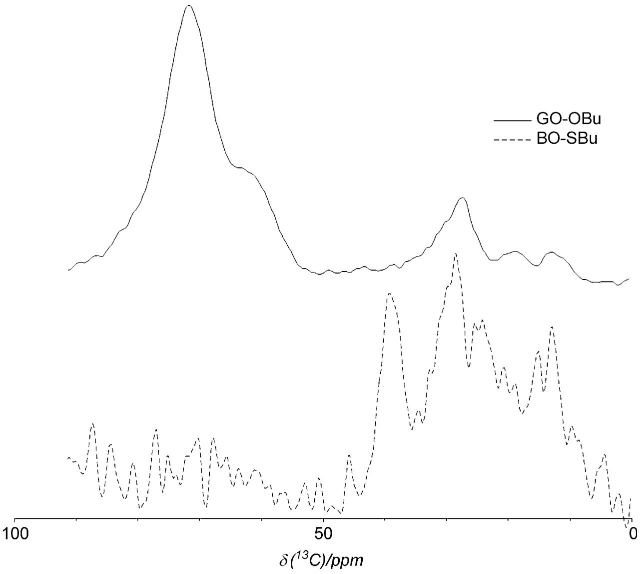


Figure 4. Partial ssNMR ^{13}C CPMAS spectra of GO-OBu (full line) and GO-SBu (dashed). Full spectra are available in the SI (Figures S12 and S14).

a decomposition temperature of around 600 °C. Presumably this is due to the capping of SH groups, preventing a decomposition pathway that is initiated at these reactive centers. Previous reports on the decomposition of GO have highlighted the changes that take place at defect sites and the chemical reactions that take place at functional groups such as the hydroxy groups.[12,26b,29] While not exactly analogous, it is not unreasonable to expect the decomposition of our new GO-SH material to follow similar pathways, with the SH taking the role of the OH group.

As a control, we used the same conditions and reacted bwGO with sodium hydride followed by bromobutane. Now, if any reaction were to occur, it should be one that yields a normal ether GO-OBu. FTIR of the new material showed some remaining OH stretches, but also new peaks, which are consistent with an alkoxy chain at 2950 cm^{-1} (Figure S7 in the SI). The solid-state NMR shows a conclusive difference to GO-SBu. Figure 4 shows the spectrum of GO-OBu and it shows new aliphatic resonances at different chemical shifts to those of GO-SBu. Thus, GO-SBu has carbon resonance signals at 39, 28, 24, and 13 ppm, whereas GO-OBu only has peaks at 27, 19, and 13 ppm with the first carbon in the chain, the O−CH$_2$ group, expected to resonate between 60 and 70 ppm. This final peak will be obscured by the residual C−OH and epoxide carbon atoms still present. We therefore conclude that we have, in both cases, functionalized the GO surface with alkyl chains, but at different points of attachment. It is hard to be sure, but the attachment of alkyl chains to the thiol groups in GO-SH seems to be essentially complete, whereas the NMR and FTIR spectra clearly indicate that unreacted OH groups remain present in the GO-OBu material. Thus it would appear that further functionalization by reaction of surface thiol groups is substantially easier than by reaction of surface hydroxy groups, which is in line with the increased nucleophilicity of an SH compared with an OH.[30]

TGA (Figure S17 in the SI) shows a smaller enhancement of the thermal stability of GO-OBu compared with bwGO (≈50 K) than was seen with GO-SBu compared with GO-SH, presumably due to the incomplete capping of reactive OH groups.

The deposition of gold nanoparticles (AuNPs)[31] on our GO-SH provides further evidence for our synthesis of thiol-functionalized GO materials and for the changes of the functional properties that this synthesis creates.[32] GO-SH was deposited on a lacy carbon TEM support grid which was then placed in a solution of HAuCl$_4$. NaBH$_4$ was added to reduce the HAuCl$_4$, generating gold nanoparticles. The grid was then rinsed with both water and acetone and dried in air on a filter paper. Figure 5 shows the TEM image of the resultant material, with Au nanoparticles generated in situ on the GO-SH sheets. Low magnification images (Figure 5 a and Figure S19a in the SI) show a homogeneous deposition of nanoparticles on the GO-SH sheets. Diffraction and EDX analysis (Figures S19b and S19d in the SI) confirm that they are gold nanoparticles, and this is further confirmed by SEM analysis (Figure S3 in the SI). Note that the deposition is selective to the GO-SH; some large particles are observed on the lacy carbon support film (Figure S20 in the SI), but these appear to have been formed in solution and deposited on the support film during drying. Control experiments showed that no Au nanoparticles were deposited on bwGO without thiol functionalization (Figure S20 in the SI), consistent with previously published results on gold deposition on chemically modified graphene.[33]

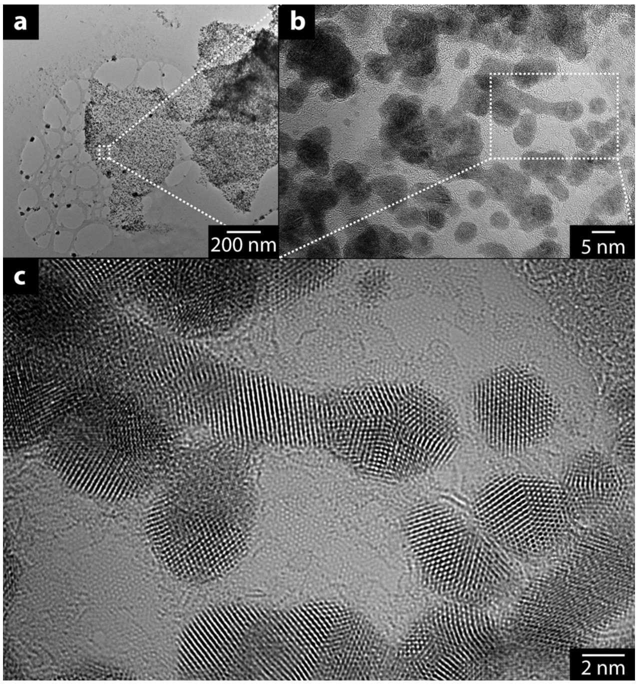


Figure 5. HR-TEM image of AuNPs deposited on GO-SH (GO-SAu). a) Low magnification bright field TEM image of GO-SAu sheets on a lacy carbon support. b,c) Successively higher magnification images of the same region, with (b) the area marked by the dashed box in (a), and (c) the area marked by the dashed box in (b).

Higher magnification images (Figure 5 b and c) show that a high density of small nanoparticles are formed. The nanoparticle sizes range from small clusters of Au atoms through to agglomerations of coalesced nanoparticles, but the typical size of isolated nanoparticles is 5–10 nm. The nucleation density is very high; due to the obvious coalescence of many smaller particles to form larger ones, the nucleation density is difficult to quantify, but certainly the spacing between nanoparticles is typically of the order of a few nanometers. The high-resolution images resolve the crystalline lattice of the Au nanoparticles, but there is no evidence for any preferred orientation of the Au lattice relative to the underlying graphene-like lattice, which can also be seen in the high-resolution images. The morphology of the nanoparticle deposition is very different from what would be expected on graphene or graphene oxide. The interaction between gold and graphene is weak, such that gold nanoparticles normally form a droplet-like morphology.[34] Here, the nanoparticles are often elongated and branched, characteristic of a high density of nucleation, with coalescence of clusters without subsequent rearrangement. This indicates a much stronger interaction between the gold and GO-SH, consistent with the presence of thiol groups on the graphene oxide surface. The uniformity of deposition and high density of nanoparticles indicates that the thiol groups must be homogeneously distributed across the graphene oxide sheets.

In conclusion, we have demonstrated the functionalization of GO using a sulfur nucleophile to selectively open epoxy groups on the basal plane. Though we have only demonstrated the reaction of the surface thiol groups with alkyl halides, there are many electrophiles that could react, allowing extensive functionalization of the GO surface. For example the popular thiol–ene "click" reaction can be used to, amongst other things, graft polymer chains onto the thiol groups.[35] Thus, we anticipate our new GO-SH material will provide a convenient route into making CMGs with a wide variety of chemical and physical properties. The robust anchoring of gold nanoparticles also indicates the possibility of anchoring other metal nanoparticles to the GO surface, facilitating both catalytic and electrochemical reactions.[36] Finally, the increased robustness of the GO-SBu is of considerable relevance as it is achieved without the loss in solubility, that is the case when GO is chemically reduced.

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[1] K. S. Novoselov, *Angew. Chem.* **2011**, *123*, 7123; *Angew. Chem. Int. Ed.* **2011**, *50*, 6986.
[2] I. Meric, M. Y. Han, A. F. Young, B. Ozyilmaz, P. Kim, K. L. Shepard, *Nat. Nanotechnol.* **2008**, *3*, 654.
[3] A. A. Balandin, S. Ghosh, W. Bao, I. Calizo, D. Teweldebrhan, F. Miao, C. N. Lau, *Nano Lett.* **2008**, *8*, 902.
[4] K. P. Loh, Q. Bao, G. Eda, M. Chhowalla, *Nat. Chem.* **2010**, *2*, 1015.
[5] a) A. Sakhaee-Pour, *Solid State Commun.* **2009**, *149*, 91; b) C. Lee, X. D. Wei, J. W. Kysar, J. Hone, *Science* **2008**, *321*, 385.
[6] a) J. S. Bunch, S. S. Verbridge, J. S. Alden, A. M. van der Zande, J. M. Parpia, H. G. Craighead, P. L. McEuen, *Nano Lett.* **2008**, *8*, 2458; b) V. Berry, *Carbon* **2013**, *62*, 1.
[7] J. Wu, H. A. Becerril, Z. Bao, Z. Liu, Y. Chen, P. Peumans, *Appl. Phys. Lett.* **2008**, *92*, 263302.
[8] D. Yu, L. Dai, *J. Phys. Chem. Lett.* **2009**, *1*, 467.
[9] G. Lu, L. E. Ocola, J. Chen, *Nanotechnology* **2009**, *20*, 445502.
[10] G. M. Scheuermann, L. Rumi, P. Steurer, W. Bannwarth, R. Mülhaupt, *J. Am. Chem. Soc.* **2009**, *131*, 8262.
[11] D. R. Dreyer, S. Park, C. W. Bielawski, R. S. Ruoff, *Chem. Soc. Rev.* **2010**, *39*, 228.
[12] R. Larciprete, S. Fabris, T. Sun, P. Lacovig, A. Baraldi, S. Lizzit, *J. Am. Chem. Soc.* **2011**, *133*, 17315.
[13] P. Cui, J. Lee, E. Hwang, H. Lee, *Chem. Commun.* **2011**, *47*, 12370.
[14] T. M. Swager, *ACS Macro Lett.* **2012**, *1*, 3.
[15] a) L. M. Veca, F. Lu, M. J. Meziani, L. Cao, P. Zhang, G. Qi, L. Qu, M. Shrestha, Y.-P. Sun, *Chem. Commun.* **2009**, 2565; b) J. Shen, M. Shi, H. Ma, B. Yan, N. Li, Y. Hu, M. Ye, *J. Colloid Interface Sci.* **2010**, *352*, 366; c) M. B. Avinash, K. S. Subrahmanyam, Y. Sundarayya, T. Govindaraju, *Nanoscale* **2010**, *2*, 1762; d) H. Hu, X. Wang, J. Wang, F. Liu, M. Zhang, C. Xu, *Appl. Surf. Sci.* **2011**, *257*, 2637; e) C. Xu, X. Wang, J. Wang, H. Hu, L. Wan, *Chem. Phys. Lett.* **2010**, *498*, 162.
[16] a) D. W. Chang, E. K. Lee, E. Y. Park, H. Yu, H.-J. Choi, I.-Y. Jeon, G.-J. Sohn, D. Shin, N. Park, J. H. Oh, L. Dai, J.-B. Baek, *J. Am. Chem. Soc.* **2013**, *135*, 8981; b) Z. Sun, S.-i. Kohama, Z. Zhang, J. Lomeda, J. Tour, *Nano Res.* **2010**, *3*, 117.
[17] a) Y. Liu, R. Deng, Z. Wang, H. Liu, *J. Mater. Chem.* **2012**, *22*, 13619; b) W. R. Collins, W. Lewandowski, E. Schmois, J. Walish, T. M. Swager, *Angew. Chem.* **2011**, *123*, 9010; *Angew. Chem. Int. Ed.* **2011**, *50*, 8848; c) S. A. Sydlik, T. M. Swager, *Adv. Funct. Mater.* **2013**, *23*, 1873; d) T. A. Pham, N. A. Kumar, Y. T. Jeong, *Synth. Met.* **2010**, *160*, 2028; e) Y. Zhang, L. Ren, S. Wang, A. Marathe, J. Chaudhuri, G. Li, *J. Mater. Chem.* **2011**, *21*, 5386.
[18] a) Z. Lin, Y. Liu, C.-p. Wong, *Langmuir* **2010**, *26*, 16110; b) H. Yang, C. Shan, F. Li, D. Han, Q. Zhang, L. Niu, *Chem. Commun.* **2009**, 3880; c) H. Yang, F. Li, C. Shan, D. Han, Q. Zhang, L. Niu, A. Ivaska, *J. Mater. Chem.* **2009**, *19*, 4632; d) A. B. Bourlinos, D. Gournis, D. Petridis, T. Szabó, A. Szeri, I. Dékány, *Langmuir* **2003**, *19*, 6050; e) M.-C. Hsiao, S.-H. Liao, M.-Y. Yen, P.-I. Liu, N.-W. Pu, C.-A. Wang, C.-C. M. Ma, *ACS Appl. Mater. Interfaces* **2010**, *2*, 3092.
[19] W. R. Collins, E. Schmois, T. M. Swager, *Chem. Commun.* **2011**, *47*, 8790.
[20] C. K. Chua, M. Pumera, *Chem. Eur. J.* **2014**, *20*, 1871.
[21] a) J. P. Rourke, P. A. Pandey, J. J. Moore, M. Bates, I. A. Kinloch, R. J. Young, N. R. Wilson, *Angew. Chem.* **2011**, *123*, 3231; *Angew. Chem. Int. Ed.* **2011**, *50*, 3173; b) H. R. Thomas, S. P. Day, W. E. Woodruff, C. Vallés, R. J. Young, I. A. Kinloch, G. W. Morley, J. V. Hanna, N. R. Wilson, J. P. Rourke, *Chem. Mater.* **2013**, *25*, 3580.
[22] a) F. Effenberger, S. Gaupp, *Tetrahedron: Asymmetry* **1999**, *10*, 1765; b) N. Park, K. Park, M. Jang, S. Lee, *J. Org. Chem.* **2011**, *76*, 4371.
[23] a) R. M. Magid, *Tetrahedron* **1980**, *36*, 1901; b) C. S. V. Houge-Frydrych, A. Marsh, I. L. Pinto, *J. Chem. Soc. Chem. Commun.* **1989**, 1258.
[24] B. J. Lindberg, K. Hamrin, G. Johansson, U. Gelius, A. Fahlman, C. Nordling, K. Siegbahn, *Phys. Scr.* **1970**, *1*, 286.
[25] G. A. Bagiyan, I. K. Koroleva, N. V. Soroka, A. V. Ufimtsev, *Russ. Chem. Bull.* **2003**, *52*, 1135.
[26] a) W. Cai, R. D. Piner, F. J. Stadermann, S. Park, M. A. Shaibat, Y. Ishii, D. Yang, A. Velamakanni, S. J. An, M. Stoller, J. An, D.

Chen, R. S. Ruoff, *Science* **2008**, *321*, 1815; b) W. Gao, L. B. Alemany, L. Ci, P. M. Ajayan, *Nat. Chem.* **2009**, *1*, 403.

[27] a) T. Rosen, I. M. Lico, D. T. W. Chu, *J. Org. Chem.* **1988**, *53*, 1580; b) N. Rakotomanomana, J. M. Lacombe, A. A. Pavia, *Carbohydr. Res.* **1990**, *197*, 318; c) N. Shangguan, S. Katukojvala, R. Greenburg, L. J. Williams, *J. Am. Chem. Soc.* **2003**, *125*, 7754.

[28] N. R. Wilson, P. A. Pandey, R. Beanland, R. J. Young, I. A. Kinloch, L. Gong, Z. Liu, K. Suenaga, J. P. Rourke, S. J. York, J. Sloan, *ACS Nano* **2009**, *3*, 2547.

[29] A. Bagri, C. Mattevi, M. Acik, Y. J. Chabal, M. Chhowalla, V. B. Shenoy, *Nat. Chem.* **2010**, *2*, 581.

[30] a) R. G. Pearson, H. Sobel, J. Songstad, *J. Am. Chem. Soc.* **1968**, *90*, 319; b) T. B. Phan, M. Breugst, H. Mayr, *Angew. Chem.* **2006**, *118*, 3954; *Angew. Chem. Int. Ed.* **2006**, *45*, 3869.

[31] a) J. P. Hermes, F. Sander, T. Peterle, R. Urbani, T. Pfohl, D. Thompson, M. Mayor, *Chem. Eur. J.* **2011**, *17*, 13473; b) V. G. Yarzhemsky, C. Battocchio, *Russ. J. Inorg. Chem.* **2011**, *56*, 2147.

[32] T. Nakamura, T. Ohana, Y. Hagiwara, T. Tsubota, *Phys. Chem. Chem. Phys.* **2009**, *11*, 730.

[33] C. Bosch-Navarro, E. Coronado, C. Martí-Gastaldo, *Carbon* **2013**, *54*, 201.

[34] P. A. Pandey, G. R. Bell, J. P. Rourke, A. M. Sanchez, M. D. Elkin, B. J. Hickey, N. R. Wilson, *Small* **2011**, *7*, 3202.

[35] A. B. Lowe, *Polym. Chem.* **2010**, *1*, 17.

[36] a) K. Jasuja, J. Linn, S. Melton, V. Berry, *J. Phys. Chem. Lett.* **2010**, *1*, 1853; b) Y. Li, W. Gao, L. Ci, C. Wang, P. M. Ajayan, *Carbon* **2010**, *48*, 1124; c) T.-F. Yeh, J.-M. Syu, C. Cheng, T.-H. Chang, H. Teng, *Adv. Funct. Mater.* **2010**, *20*, 2255; d) X. Chen, G. Wu, J. Chen, X. Chen, Z. Xie, X. Wang, *J. Am. Chem. Soc.* **2011**, *133*, 3693; e) D. Chen, H. Feng, J. Li, *Chem. Rev.* **2012**, *112*, 6027.