Dispersion of alkyl-chain-functionalized reduced graphene oxide sheets in nonpolar solvents

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Dispersion of Alkyl-Chain-Functionalized Reduced Graphene Oxide Sheets in Nonpolar Solvents

Jean-Philippe Tessonnier and Mark A. Barteau*

INTRODUCTION

Graphene is a rapidly expanding field of research that covers diverse topics including electronics,1,2 composites,3 energy storage,4,5 and catalysis.6,7 While cutting-edge work is carried out in all these areas, more practical challenges regarding the synthesis, handling, and processing of graphene remain. The exfoliation of graphite or graphite oxide is the most reliable and energy efficient method to produce, respectively, graphene and reduced graphene oxide (RGO) on a large scale.8 Graphite readily exfoliates in organic solvents having a surface tension of approximately 40 mJ m⁻², for example, in N-methylpyrrolidone (NMP) or orthodichlorobenzene (ODCB), using sonication.9–11 For solvents having a lower surface tension (e.g., ethanol, \(\gamma = 22.4 \text{ mJ m}^{-2}\)), flocculation of the graphene sheets occurs relatively rapidly unless a polymer is added to stabilize the suspension.12 Coleman’s group investigated suitable solvents using Hansen’s solubility theory, which is widely used to predict solvent–polymer interactions.11,13–15 They demonstrated that best solvents have dispersive, polar, and H-bonding components of the cohesive energy density within certain well-defined ranges.15 Choi et al. extended this approach to RGO and obtained very similar results, despite the presence of residual oxygen on the surface and the higher defect density compared to graphene.16 Therefore, the same solvents can be used to prepare both graphene and RGO suspensions with similar efficiency.16

Suspensions of single graphene or RGO sheets can be easily prepared if their concentration is kept low (<1 mg mL⁻¹).17 Stable graphene inks with much higher concentrations, up to 63 mg mL⁻¹, have been obtained but with the limitation that the flakes contain three to five sheets each, which is still sufficient for many applications.14

To date, the general strategy has aimed at finding the best solvent to achieve stable suspensions, regardless of the future application. It appears that the best solvents tend to be polar organic ones with high boiling points, such as NMP or N,N-dimethylformamide (DMF).16,18 However, many applications impose constraints on the choice of the solvent in terms of cost, toxicity, or integration in the production process.

We report here on a general method to chemically modify RGO depending on the target application and its constraints. Specifically, we developed a technique to disperse RGO sheets in nonpolar aprotic organic solvents such as toluene and alkanes, which are known to yield unstable suspensions but which are commonly used in organic chemistry and polymer synthesis, for example.13,16,18,19

EXPERIMENTAL SECTION

Grafting Procedure. In a typical experiment, 100 mg of thermally reduced graphene oxide (Vor-X BK86X from Vorbeck Materials) was placed in a 50 mL round-bottom flask. The RGO material was outgassed under dynamic vacuum at 120 °C overnight using an oil bath to remove any adsorbed moisture. The flask was then flushed with argon (Argon 5.0, Keen Compressed Gas), and 20 mL of extra dry toluene was added (Acros Organics). The suspension was tip-sonicated for 15 min (Branson Sonifier 200) in order to disperse the sheets. The mixture was then transferred to a 250 mL round-bottom flask under Ar. The 100 mL of dry toluene and 20 mL of n-butyl lithium (n-BuLi, 2.6 M in toluene, Acros Organics) were added. The mixture was stirred at room temperature under Ar for 2 h in order for the n-BuLi to react with the RGO sheets and activate the surface. A total of 11 mL of 1-bromodecane (Acros Organics) was added, and the mixture was kept at room temperature for another 1 h before starting heating to 70 °C in an oil bath. After 4 h at 70 °C, the mixture was allowed to cool down to room temperature (≈1 h). The mixture was subsequently transferred into a 500 mL round-bottom flask containing 50 mL of...
cold methanol to neutralize the excess n-BuLi. A series of liquid phase extractions was performed with distilled water (1 L in total) to complete the neutralization and remove the LiBr formed during the reaction. The organic phase was recovered, filtered, and washed with 200 mL of fresh toluene and 200 mL of methanol. Finally, the recovered powder was dried at 60 °C overnight.

**Characterization.** Specific surface areas were determined from N₂ adsorption—desorption at liquid nitrogen temperature (77 K) using a Micromeritics ASAP 2020 sorptometer. Prior to measurement, the samples were outgassed for 8 h under vacuum at 120 °C to remove moisture. The total surface area was calculated using the BET equation.

Thermogravimetric-mass spectrometric (TG-MS) measurements were performed with a Mettler-Toledo TGA/DSC 1 instrument connected to a Pfeiffer ThermoStar mass spectrometer. The sample (∼4 mg) was placed in a 150 μL alumina crucible. After inserting the sample, the instrument was purged with N₂ until reaching a low and steady O₂ signal in the MS (m/z = 32). The sample was then ramped from room temperature to 900°C at 5°C min⁻¹ in N₂. The evolved gases were analyzed with the MS.

1H nuclear magnetic resonance (NMR) spectra were acquired on a Bruker 400 MHz instrument. Chemical shifts were measured relative to the signal of residual chloroform (7.26 ppm) in the deuterated solvent.

Attenuated total reflectance Fourier transform infrared spectrometric (ATR-FTIR) measurements were performed using a Nicolet 8700 spectrometer equipped with an MCT-B detector and a Specac Golden Gate heated ATR stage with single reflection diamond crystal. Typically, 32 scans were accumulated with a resolution of 4 cm⁻¹. UV–visible spectra were obtained with a Jasco V-550 spectrometer.

Raman spectra were obtained using a Kaiser Holospec 1.4 spectrograph equipped with a Roper EEV CCD array detector. Excitation at 532 nm was supplied by using a Coherent DPSS 532 laser spectrograph equipped with a Roper EEV CCD array detector.

**RESULTS AND DISCUSSION**

Following the approach of Coleman et al., RGO disperses in solvents having similar cohesive energies. More precisely, RGO and the solvent must both have similar Hildebrand solubility parameters and similar Hansen solubility parameters (HSP), with

$$\delta_T^2 = \delta_D^2 + \delta_P^2 + \delta_H^2$$  \hspace{1cm} (1)

where $\delta_T$ is the Hildebrand solubility parameter, and $\delta_D$, $\delta_P$, and $\delta_H$ are the Hansen solubility parameters corresponding, respectively, to dispersive, polar, and H-bonding components.

Suitable solvents for graphene are characterized by $\delta_T \approx 23$ MPa¹/², $\delta_D \approx 18$ MPa¹/², $\delta_P \approx 9.3$ MPa¹/², and $\delta_H \approx 7.7$ MPa¹/² (Table 1). Values corresponding to polar and H-bonding components are slightly higher for graphene than for fullerene or graphitized carbon fibers (Table 1), which is probably due to the presence of polar oxygen-containing groups on the surface. It was demonstrated experimentally and theoretically that when graphene is exposed to air, O₂ and H₂O react with defect sites and oxygen atoms bind to the edges (ether groups) and on the surface (as epoxy groups “hopping” on the basal plane). Therefore, it is likely that HSP values for RGO are similar to those determined for graphene, and the latter were used in the present work. This assumption is consistent with the experimental observation that stable suspensions of RGO and graphene are obtained with the same solvents.

Toluene and alkanes are poor solvents for RGO because of their lower polar and H-bonding cohesive energies. Following Hansen’s solubility concept of “like dissolves like”, RGO dispersion in nonpolar aprotic solvents can be significantly improved if suitable groups are attached to the surface. We tested this hypothesis by grafting decyl groups (−C₂₉H₅₉), as decane exhibits similar HSP values to toluene and most alkanes (Table 2).

Thermally reduced graphene oxide sheets were dispersed in a water–toluene (50:50 v:v) mixture and compared with the initial RGO. Figure 1a shows that the pristine RGO remains close to the water–toluene interface, which is consistent with the dual hydrophilic–lipophilic character of the RGO surface. Although RGO was produced by thermal reduction and exfoliation of graphene oxide, oxygen-containing functional groups are still present at defect sites (C/O = 16–19), thus increasing the polarity of the RGO surface. This observation is consistent with previous works which demonstrated that RGO can be dispersed in water and in polar solvents but not in nonpolar aprotic organic solvents such as toluene.

In contrast, the alkyl-grafted material moved immediately to the toluene phase and a rather stable CₓHᵧ-RGO suspension was achieved, which confirms the change in the surface properties upon grafting (Figure 1b). In addition, CₓHᵧ-RGO readily dispersed in toluene without the need for any sonication treatment (Figure 1c). The stability of the suspension was found to depend on the CₓHᵧ-RGO concentration and varied between 6 h and several days, which is sufficient for most applications.

Several groups previously demonstrated that it is possible to disperse RGO sheets in nonpolar solvents by employing cationic surfactants. Liang et al. in particular developed a simple method based on amphiphilic molecules carrying a positive charge (NR₄⁺). They demonstrated that the surfactant binds to deprotonated carboxylic groups (COO⁻) present on the RGO surface and that the sheets were transferred to the organic phase (chloroform) by simple shaking. Although the method is simple and efficient, it requires a high number of COO⁻ groups on RGO surfaces, meaning that the reduction of GO must be carefully controlled. In addition, although the technique was efficient to disperse RGO sheets in chloroform, nonpolar solvents such as toluene did not

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**Table 1. Hansen Solubility Parameters for Various Carbon Materials**

<table>
<thead>
<tr>
<th>material</th>
<th>$\delta_D$ (MPa¹/²)</th>
<th>$\delta_P$ (MPa¹/²)</th>
<th>$\delta_H$ (MPa¹/²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>graphene</td>
<td>18 (15–21)</td>
<td>9.3 (3–17)</td>
<td>7.7 (2–18)</td>
</tr>
<tr>
<td>fullerene</td>
<td>19.7</td>
<td>2.9</td>
<td>2.7</td>
</tr>
<tr>
<td>carbon black</td>
<td>17.9</td>
<td>12.3</td>
<td>11.3</td>
</tr>
<tr>
<td>carbon fiber (polar)</td>
<td>13.4</td>
<td>17.8</td>
<td>14.2</td>
</tr>
<tr>
<td>carbon fiber (nonpolar)</td>
<td>17.2</td>
<td>3.4</td>
<td>2.0</td>
</tr>
</tbody>
</table>

*Values in parentheses correspond to the range of acceptable HSP values for graphene exfoliating solvents.*
Toluene and heptane yielded large RGO agglomerates. For C10-methanol, ethanol, or water, or with end-functionalized polymers to suspend RGO in benzene.16 Chloroform yielded very stable suspensions. Surprisingly, C10-dispersibility in solvents with low polar and H-bonding (RGO also dispersed in methanol and ethanol, although their dispersibility in common solvents (Table 2). RGO was found to easily disperse in solvents with HSP values for C10-RGO but also acted as a spacer, hindering the sheets’ reagglomeration. In general, the flocs formed were relatively loose. It was possible to fully redisperse C10-RGO in all the tested organic solvents by thermal convection and Brownian motion, by placing the vial on a hot plate at 70 °C for 5 min (Figure 2 and Supporting Information). In summary, by grafting the alkyl chains, the dispersibility of RGO and C10-RGO were ranked depending on their ability to disperse and form stable suspensions with the listed solvents: (+++) disperses and forms stable suspensions, (+) disperses but settles after several hours, (+) disperses but settles within 1 h, (−) disperses but settles within minutes, (−−) does not disperse, (−−−) immiscible.

**Table 2. Dispersibility of RGO and C10-RGO in Solvents with Various Hansen Solubility Parameters**

<table>
<thead>
<tr>
<th>solvent</th>
<th>δP (MPa1/2)</th>
<th>δH (MPa1/2)</th>
<th>(δP + δH)</th>
<th>dispersibility</th>
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<tr>
<td>DMSO13</td>
<td>18.4</td>
<td>16.4</td>
<td>10.2</td>
<td>26.6</td>
</tr>
<tr>
<td>DMF13</td>
<td>17.4</td>
<td>13.7</td>
<td>11.3</td>
<td>25.0</td>
</tr>
<tr>
<td>CHCl313</td>
<td>17.8</td>
<td>3.1</td>
<td>5.7</td>
<td>8.8</td>
</tr>
<tr>
<td>ethanol13</td>
<td>15.8</td>
<td>8.8</td>
<td>19.4</td>
<td>28.2</td>
</tr>
<tr>
<td>methanol18</td>
<td>15.1</td>
<td>12.3</td>
<td>22.3</td>
<td>34.6</td>
</tr>
<tr>
<td>H2O13</td>
<td>15.5</td>
<td>16</td>
<td>42.3</td>
<td>58.3</td>
</tr>
<tr>
<td>toluene20</td>
<td>18</td>
<td>1.4</td>
<td>2</td>
<td>3.4</td>
</tr>
<tr>
<td>heptane30</td>
<td>15.3</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>decane20</td>
<td>15.7</td>
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Figure 1. (a) RGO and (b) C10-RGO dispersions in water–toluene 50:50, with a concentration of 0.05 mg/mL(water+toluene). (c) C10-RGO dispersion in toluene without sonication. The C10-RGO concentration is 0.1 mg/mL.

allow an efficient transfer process.25 Similarly, Choi et al. used end-functionalized polymers to suspend RGO in benzene.16 Stable suspensions were obtained for polymer concentrations of 0.4 and 0.7 wt % but lower or higher concentrations led to a reagglomeration of the sheets. In addition, as the work of Liang et al., the sheets need to bear a high number of COO− groups, which is a significant drawback for both techniques. Our approach offers a more efficient and more versatile solution, as the alkyl chains are grafted on a variety of O-containing groups (see below). Therefore, our grafting technique can be employed on any RGO material, independent of the reduction process employed.

The dispersibility of RGO and C10-RGO was further tested for common solvents (Table 2). RGO was found to easily disperse in solvents with 9 < (δP + δH) < 27, in good agreement with Park et al.18 Solvents with (δP + δH) > 27 such as methanol, ethanol, or water, or with (δP + δH) < 9 such as toluene and heptane yielded large RGO agglomerates. For C10-RGO, the grafted alkyl chains significantly improved the dispersibility in solvents with low polar and H-bonding cohesive energies, such as toluene and heptane, but also chloroform yielded very stable suspensions. Surprisingly, C10-RGO also dispersed in methanol and ethanol, although their (δP + δH) values are significantly higher (34.6 and 28.2, respectively). In contrast, RGO suspensions in both alcohols were only stable for ≈1 h: the sheets typically formed large flocs and settled within a few hours. Thus, it appears that the grafted alkyl chains modified the HSP values for C10-RGO but also acted as a spacer, hindering the sheets’ reagglomeration. In general, the flocs formed were relatively loose. It was possible to fully redisperse C10-RGO in all the tested organic solvents by thermal convection and Brownian motion, by placing the vial on a hot plate at 70 °C for 5 min (Figure 2 and Supporting Information). In summary, by grafting the alkyl chains, the dispersibility of RGO and C10-RGO were ranked depending on their ability to disperse and form stable suspensions with the listed solvents: (+++) disperses and forms stable suspensions, (+) disperses but settles after several hours, (+) disperses but settles within 1 h, (−) disperses but settles within minutes, (−−) does not disperse, (−−−) immiscible.

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Thermogravimetric analysis performed in N2 coupled with mass spectrometry (TG-MS) confirmed the presence of alkyl groups and their chemical bonding to the surface (Figure 3). TG-MS analysis of the RGO material showed a weight loss of only 3% in the range 150–500 °C, which is consistent with the synthesis method employed.22,23 Here, graphite oxide was thermally treated at ca. 1000 °C for a few seconds in order to exfoliate and reduce the sheets simultaneously. At high temperature, oxygen-containing functional groups such as carboxylic acids, phenols, ketones, and so forth decompose into CO and CO2,26,27 which leads to the exfoliation.23 However, the shortness of the treatment does not allow the reconstruction of the carbon backbone. A high number of structural defects are still present in the material,26,27 which react with O2 and H2O upon exposure to air. TG-MS data indicate that most oxygen on the surface is involved in phenol, ketone and ether groups (decomposition temperature > 600 °C).26,27,30 C10-RGO showed a much higher weight loss, 19%, between 150 and 500 °C. The main fragments detected over this temperature range were m/z = 43, 41, 57, 71, 85, which is consistent with the decomposition and fragmentation of decyl groups. In addition, the onset temperature and the fact that the removal of alkyl chains occurs over a 350 °C range confirm that the groups are chemically anchored and not simply adsorbed, and that they are grafted over a variety of chemically different defect sites of the RGO sheets.

Many techniques have been developed over the past few years to chemically modify GO and RGO.31 The most popular one involves the use of diazonium compounds. Although this approach is efficient and can be used on any carbon material, it breaks the π electron system and therefore significantly modifies the electronic and optical properties of the sheets. In contrast, n-BuLi only reacts with existing defects such as aromatic protons (at edges) or oxygen-containing groups already present on the surface.52 Organolithium compounds are known to react with various groups, including alcohols,
epoxides, or ketones, all of which exist on RGO surfaces as a result of reoxidation when exposed to air.27 As shown in Scheme 1, the basic and nucleophilic properties of n-BuLi both play a significant role in activating the oxygen-containing groups. Grafting occurs either by C–C coupling (1) or by C–O coupling following the Williamson reaction (2–4). It is worth noting that, despite the variety of chemically different sites, grafting of decyl groups can occur on each of them, which

Figure 2. Dispersibility of RGO (top) and C₁₀-RGO (bottom) in DMSO, DMF, CHCl₃, ethanol, methanol, water, toluene, heptane, and decane (from left to right). The RGO and C₁₀-RGO concentration is 1 mg/mL. The pictures show the redispersion of both materials using Brownian and convective motions, by simply placing each vial on a hot plate at 70 °C for 5 min.

Figure 3. TG-MS data obtained for C₁₀-RGO. The TG curve of RGO is included for information. Data were acquired when heating both samples in N₂. These show the amount and thermal stability of the grafted decyl groups.
makes it a very polyvalent and efficient grafting technique. Considering the initial C/O ratio of 16 for the commercial RGO product employed here (the high end value for the residual oxygen concentration) and a weight loss of 19 wt % for the amount of grafted decyl groups (corresponding to the weight loss between 150 and 500 °C in the TG-MS results), it was calculated that decyl groups were grafted on approximately 1/3 of the oxygen-containing groups. This yield is relatively high if we consider that the presence of graphene stacks of a few layers in thickness is difficult to avoid and that some of the oxygen groups might not be accessible during the grafting procedure. Based on these results, we also estimate that the C_{10}-RGO stacks contain three layers at most (if one assumes that all the accessible oxygen groups react during the grafting reaction), which is sufficient for most applications. Based on these results, we also estimate that the C_{10}-RGO stacks contain three layers at most (if one assumes that all the accessible oxygen groups react during the grafting reaction), which is sufficient for most applications. A similar estimate of the number of layers was obtained by comparing the specific surface area measured for the dry C_{10}-FGS powder (415 m²/g) with the theoretical surface area of graphene (2630 m²/g). If the contribution of grafted alkyl chains to the sample mass is taken into account, the maximum number of layers in each stack is calculated to be 5. However, it should be noted that the number of stacked layers was calculated for the dry powder and that some restacking may occur after synthesis, during filtration and drying. Therefore, the number of stacked layers estimated from TG-MS and nitrogen physisorption should be seen as an upper limit, and it is likely that the actual C_{10}-FGS sheet thicknesses are less than 5 for suspensions.

Very stable, high concentration (4 mg mL⁻¹) suspensions were obtained in CDCl₃, which made the acquisition of liquid phase ¹H NMR spectra of the suspended material possible (Supporting Information). Obviously, the peaks were broader and less defined due to anisotropic interactions resulting from the lack of mobility of the sheets at high concentration. Therefore, the number of stacked layers estimated from TG-MS and nitrogen physisorption should be seen as an upper limit, and it is likely that the actual C_{10}-FGS sheet thicknesses are less than 5 for suspensions.

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The successful attachment of the decyl groups was also confirmed by ATR-FTIR (Figure 4). New peaks were observed in the spectrum of C_{10}-RGO at 1457–1375 and 2954–2852 cm⁻¹, which correspond respectively to C–H bending and stretching vibrations, in good agreement with the spectrum of decane. The shape, position, and intensity of other bands did not change significantly in comparison to the spectrum of the starting material and are characteristic of thermally reduced GO.

UV–visible as well as Raman spectra were also acquired for both materials in order to probe any change in the structure of the graphene sheets upon functionalization. The UV–visible spectra of RGO and C_{10}-RGO suspensions in ethanol showed a
high absorption in the entire spectral region, which is characteristic of reduced graphene oxide suspensions (Figure 5).24 The mass attenuation coefficients for RGO and C10-RGO (taking into account the contribution from the grafted alkyl chains) were found to be 45 and 41 mg cm−1, respectively, at 660 nm. Both values are close to the attenuation coefficient measured for microcrystalline graphite suspensions10 (42 mg cm−1 at 660 nm) which indicates that the sheets are highly reduced and that the electronic conjugation did not change significantly upon grafting. The spectra also showed broad absorption peaks with maxima at 275 nm, which is also characteristic for reduced graphene oxide suspensions.3,24 Raman spectra of RGO and C10-RGO were acquired at an excitation wavelength of 532 nm (Figure 6). Two first-order bands were observed in the 1000–1800 cm−1 region, which correspond to vibrations of carbon atoms at defect sites (D band, ≈1340 cm−1) and vibrations of carbon atoms in the ideal graphitic lattice (G band, ≈1585 cm−1).33 The difference spectrum, calculated by subtracting both spectra, reveals that the G band became sharper and the D band intensity decreased slightly upon grafting. This observation implies a small increase in the size of the sp2 domains. It is also worth noting that the G band shifted from 1583 to 1589 cm−1, which is characteristic of debundling in the case of single-wall carbon nanotubes14–36 and of a better exfoliation of the graphene layers for RGO.16

**CONCLUSIONS**

In summary, we developed a new approach based on Hansen’s solubility theory to chemically modify RGO depending on the constraints of the target application. Specifically, we designed a grafting technique to attach decyl groups on a variety of defect sites already present on RGO surfaces. As a result, graphene sheets which were initially polar could be dispersed in nonpolar aprotic solvents such as toluene. We found that the attached alkyl chains also act as spacers which improve the exfoliation of the sheets and prevent the sheets from reagglomerating. As a result, it became possible to disperse RGO in several low boiling point solvents such as chloroform as well as in green solvents such as ethanol. We believe that this technique could be particularly useful for the further processing of defect-engineered graphene sheets, that is, materials where the nature and density of defects is tuned to achieve particular electronic and optical properties.37

**ASSOCIATED CONTENT**

Supporting Information

1H NMR spectrum of C10-RGO as well as a video showing the redispersion of C10-RGO by simple heating. This material is available free of charge via the Internet at http://pubs.acs.org.

**AUTHOR INFORMATION**

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**Notes**

The authors declare no competing financial interest.

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