

The Real Graphene Oxide Revealed: Stripping the Oxidative Debris from the Graphene-like Sheets**

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Graphene oxide (GO) provides a potential route to large quantities of graphene, is cheap to make in bulk quantities, and easy to process.^[1] It is also a starting point for further functionalization to create chemically modified graphenes (CMGs), for example, for use in composite materials,^[2] for light harvesting,^[3] or as sensors.^[4] GO is derived from the exfoliation of graphite oxide, the structure of which, despite over one hundred years of investigation, is still subject to debate.^[1b,5] Understanding the chemical and physical structure of GO is a necessary step towards its controllable functionalization for CMGs and complete reduction back to graphene.

Depending on the starting material and oxidative conditions, the composition of GO can vary significantly, but extensive study has resulted in a number of accepted properties.^[1b] Fully oxidized GO forms stable aqueous suspensions and has an atomic C/O ratio of roughly 2:1. The dominant surface functional groups are epoxides and alcohols, with carboxylic acids and other keto groups on the edges. GO is thermally unstable; heating it to more than around 80 °C in air or under vacuum changes the composition and increases the C/O ratio. Recent high-resolution STM^[6] and TEM^[7] studies have concluded that the degree of functionalization is highly heterogeneous with nanometer-scale, predominantly graphitic islands observable amongst disordered/amorphous regions.

The oxidation and subsequent functionalization of carbon nanotubes (NTs) has been studied extensively over the last two decades. Recently it has been shown that oxidation debris,^[8] also termed fulvic acids,^[9] adheres to NTs after oxidation. This debris of ill-defined composition is stably complexed to the NTs, but can be removed by washing with base, which significantly changes the apparent degree and type of NT oxidation. The oxidative debris was found to make up almost a quarter of the mass of oxidized NTs.^[8a] Similar results have been found for the oxidation of carbon fibers.^[10] As the relative surface area increases from carbon fibers to nanotubes to graphene, so may the oxidative debris be expected to have a greater effect. However, we are not aware of any studies that determine to what extent oxidative debris is present on GO.

Herein, we show that GO, as produced by the Hummers method, is composed of functionalized graphene sheets decorated by strongly bound oxidative debris, which acts as a surfactant to stabilize aqueous GO suspensions.

Graphene oxide was prepared by a modified Hummers method,^[11] and characterization of the resultant material by AFM and TEM showed complete exfoliation.^[12] The as-produced GO (aGO) was washed by centrifuging, discarding the supernatant, and resuspending at least ten times. The effect of treating this aGO with a number of different concentrations of NaOH is demonstrated in Figure 1.

At high concentration (1M NaOH) the initially clear brown suspension rapidly separates into a black aggregation and an essentially colorless supernatant solution. At lower concentration (e.g. 0.01M) the GO darkens over time to a stable black suspension. Heating the aGO in a low concen-

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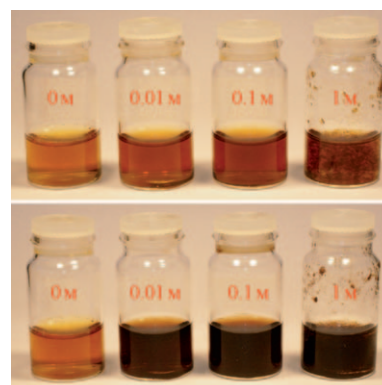


Figure 1. Photograph of 0.5 mg mL⁻¹ aGO suspensions in NaOH (concentrations as marked) within 30 s of the addition of the NaOH (top), and after three hours (bottom).

tration of NaOH at reflux for one hour has a similar effect as mixing with a high concentration of NaOH. By contrast, heating the aGO in distilled water at reflux has no readily discernible effect.

After heating in NaOH at reflux, the black aggregate was separated from the supernatant by centrifugation, reprotonated with HCl of an equivalent concentration to the NaOH, washed with distilled water and dried under vacuum. The resultant base-washed GO (bwGO) is a black powder that cannot be resuspended in water by either vigorous stirring or sonication. The supernatant liquid was also reprotonated and dried to give a white powder: we show later this material contains oxidative debris, hence we refer to it as OD. The mass of the bwGO and OD were determined independently, and compared to control samples prepared in the same way using distilled water instead of NaOH. The mass of bwGO was found to be $(64 \pm 2)\%$ of the mass of aGO added; that is, a mass loss of roughly one third had occurred, which was not observed in the control samples, heated at reflux in water. Crucially, the mass of OD attributable to aGO was found independently to be $(30 \pm 9)\%$, whilst no measurable mass was found after drying the supernatant obtained from aGO heated at reflux in water. We must conclude that washing with base has separated the aGO into two parts, bwGO and OD, and that by mass they are present in a ratio of roughly 2:1.^[12]

Figure 2 shows the thermogravimetric analysis (TGA) of aGO, bwGO, and OD. aGO shows an initial mass loss which has been attributed to absorbed water, a mass loss at around

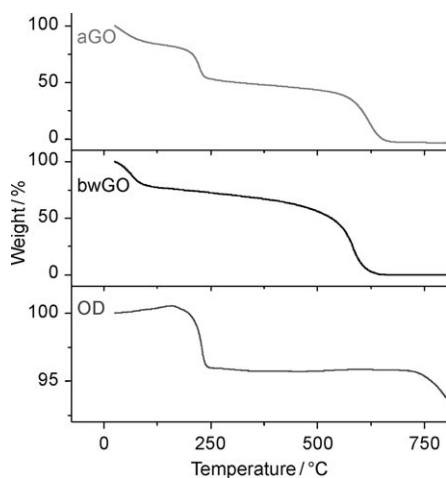


Figure 2. Thermogravimetric analysis in air of as-produced GO (aGO) and the two components after base washing; the black precipitate (bwGO), and the remaining, water-soluble fraction (OD).

200°C which has previously been explained to be due to the decomposition of functional groups, and a mass loss at around 600°C which has been attributed to sublimation or burning of the damaged graphitic regions.^[13] The ratio of the mass loss at 600°C to that at 200°C is roughly 2:1. TGA of bwGO shows a significantly reduced mass loss at around 200°C and complete mass loss at around 600°C. A significant low-temperature mass loss at around 200°C is seen for OD, but none at around 600°C, which suggests there are no graphitic regions in this

fraction (note that the OD material contains NaCl, hence only a small fraction of its total mass is lost).^[12] These results suggest that the mass loss at about 200°C from the aGO is in fact due to the oxidative debris; a similar conclusion was drawn from the TGA of oxidized NTs.^[8b]

The FTIR absorption spectrum of aGO shows a broad feature at 3000 to 3800 cm^{-1} , $\nu(\text{C}-\text{OH}, \text{COOH}, \text{H}_2\text{O})$, and several sharper bands between 1000 and 1800 cm^{-1} . These lower frequency bands have variously been ascribed to epoxide, hydroxy, carboxy, and ketone groups, as well as sp^2 -hybridized C–C bonding.^[8a,14] The FTIR spectrum of OD is similar to that of aGO, whilst the spectrum of bwGO is comparatively featureless, apart from around 1630 cm^{-1} , where an absorption peak is seen in the spectra of aGO and bwGO but not of OD. We tentatively assign this band to the in-plane vibrations of sp^2 -hybridized C–C bonding. From these infrared (IR) data we conclude that OD is heavily covalently functionalized with similar groups to aGO, whilst the degree of functionalization is decreased in bwGO (Figure 3).

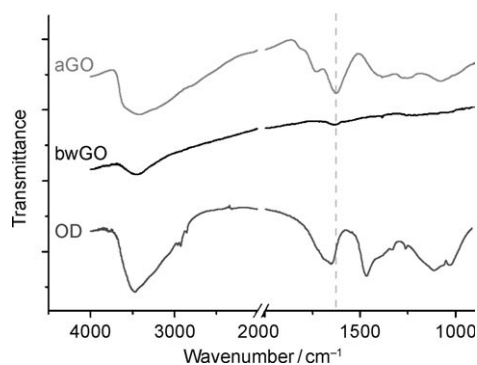


Figure 3. FTIR absorption spectra of as-produced GO (aGO), bwGO, and OD. The dashed gray line marks the band at around 1630 cm^{-1} .

A solution of the OD material passes through a 0.22 μm filter membrane leaving no residue behind, which indicates that no large graphene-like sheets are in this component. High-resolution mass spectrometry of the OD indicated the presence of highly oxidized small fragments such as $\text{C}_{19}\text{H}_{35}\text{O}_6$ and $\text{C}_{18}\text{H}_{33}\text{O}_9$, similar to the oxidative debris found on NTs.^[9] The OD material cannot therefore just be the by-products of deoxygenation of the graphene-like sheets, as this would give only small molecules such as H_2O and CO_2 .

Whilst it has been known for some time that the addition of base to graphite oxide changes the color, and that acidification does not reverse the color change (resulting instead in coagulation), the proposed explanation that the base deaggregates the graphite oxide cannot be valid for already exfoliated graphene oxide.^[15] A recent study on the effect of alkaline conditions on graphene oxide also found a fast irreversible color change, which was attributed to a deoxygenation.^[16] In that study, TGA and XPS of the resultant black, graphene-like material gave similar results as those reported herein; the analysis did not indicate whether the mass had changed or attempt to characterize the solution left behind.

Given the functionalities accepted as being present in GO (alcohols, epoxides, ketones, and carboxy groups) we do not expect any irreversible chemical reaction to take place upon heating at reflux under mildly basic conditions. Certainly, reductions are impossible. Instead, by analogy with oxidized carbon nanotubes, we suggest that GO actually consists of two distinct components noncovalently complexed together: the majority by mass being large functionalized graphene-like sheets (which becomes the bwGO) together with small, more highly oxidized, fragments or debris (the OD). The mass balance, TGA, FTIR, and mass spectrometry results reported here demonstrate that low-molecular-weight, heavily functionalized carbon-based fragments are left in solution after a base wash. The control experiments using aGO heated at reflux in water show that these fragments are not present in a separable form without the base wash, and so must initially be firmly adhered.

Previous studies have shown that graphene oxide can be cut into progressively smaller fragments by repeated or prolonged oxidation.^[17] However, here we have relatively large sheets; any smaller isolated fragments have been removed by the washing process during the synthesis of GO. Thus, we can distinguish between covalently functionalized graphene sheets (as usually understood by the term graphene oxide) and the noncovalent functionalization of these sheets by the OD.

We believe that, in acidic or neutral conditions, the debris is strongly adhered to the graphene-like sheets of GO by a combination of π - π stacking and hydrogen bonds. The interaction between the oxidative debris and underlying covalently functionalized graphene sheet under basic conditions becomes repulsive because of the negative charge on the deprotonated debris.^[9] Once separated, it would appear that the two components cannot be recombined, and hence the original structure is metastable. We find that this oxidative debris makes up roughly a third of the mass of aGO, slightly higher than the 17–24% reported for multiwalled carbon nanotubes.^[8b] The oxidative debris has been shown to have a significant impact on the chemical properties of NTs. It is thus important to study the properties of base-washed GO.

Although not soluble in water, bwGO could be temporarily dispersed by sonication to form an unstable and clearly aggregated suspension. TEM analysis of bwGO deposited from this suspension showed the presence of large sheets, up to micrometers in diameter, similar in size to those seen in aGO (Figure 4a). Although the bwGO material is aggregated and crumpled, it is clearly sheetlike in nature. Selected-area electron diffraction analysis of the bwGO shows two sharp rings corresponding to intralayer d spacings of 0.213 nm and 0.123 nm, as expected.^[11] Ring patterns are formed rather than distinct spots as the sheets are overlapping and wrinkled. The inner ring is more intense than the outer, which is consistent with exfoliated graphene-like sheets rather than AB-stacked graphitic material.^[12]

A less aggregated, although still unstable, suspension could be formed by sonicating bwGO in *N*-methylpyrrolidone (NMP). XPS analysis of bwGO deposited from NMP is given in Figure 5a. The C 1s XPS spectra of aGO (Figure 5a) is consistent with previous reports.^[18] The peak at around

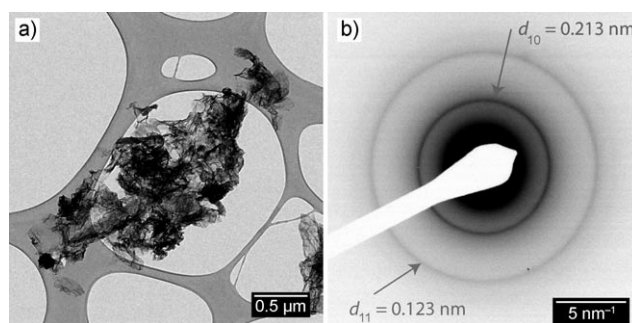


Figure 4. a) Brightfield TEM image of bwGO (the light gray structure is the lacy carbon support film), b) corresponding selected-area electron diffraction pattern.

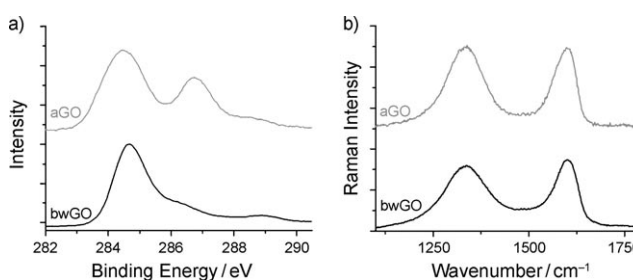


Figure 5. a) C 1s XPS spectra of aGO and bwGO. b) Raman spectra of aGO and bwGO obtained by laser excitation at a wavelength of 633 nm.

284.5 eV arises from carbon atoms that have C–C bonds, whilst the higher binding energy components, which are greatly reduced in bwGO, primarily arise from carbon atoms that have C–O bonds. This finding is consistent with the O 1s spectra and enables the C/O ratio to be calculated: here C/O = 2:1 for aGO and C/O = 4:1 for bwGO. The degree of oxidative functionality is clearly reduced in the bwGO compared to that in the aGO, but is still significant.

Raman spectroscopy is an important diagnostic tool for the analysis of graphite-like materials such as graphene and NTs.^[19] Their strong Raman response is due to resonant enhancement by C–C π states; the response of more disordered carbon-based materials is weaker. Mixed samples show Raman responses dominated by the less amorphous, more ordered, graphitic material. The “quality” of graphite-like samples is often studied through analysis of the “D” peak at around 1300 cm^{-1} , which is due to breathing modes in C–C ring structures and whose presence is indicative of defects, and the “G” peak at around 1600 cm^{-1} , which is due to C(sp²)–C(sp²) bond stretching vibrations. Figure 5b shows Raman spectra from this region for aGO and bwGO under laser excitation at a wavelength of 633 nm. As expected, aGO shows broad D and G peaks,^[18a] with a ratio of integrated peak intensities of D/G = 1.9:1. The bwGO shows an almost identical response, with D/G = 1.9:1. Raman spectra from OD show no evidence of D or G peaks. Together with the XPS and TEM results, this finding confirms that the bwGO consists of oxidatively functionalized graphene-like sheets and suggests that the sheets themselves are not altered significantly by the base wash.

Vacuum filtration of bwGO from a suspension in NMP onto an alumina filter membrane gave a shiny black film. Preliminary results on films 0.5–1 μm thick indicate the bwGO is conducting, with a conductivity on the order of 10^0 – 10^1 S m^{-1} . This is roughly five orders of magnitude more conducting than aGO, and only an order of magnitude less than values reported for GO reduced by chemical or low-temperature thermal treatments.^[1a] Such a dramatic enhancement in the conductivity as a result of the removal of oxidative debris is surprising. It is possible that the comparatively strong noncovalent interaction between the debris and the GO sheets, combined with the highly electronegative functional groups on the debris and the single-atom thick graphene lattice, is sufficient to alter the electronic structure.

Whilst, to our knowledge, no other research groups have suggested that oxidative debris is an important component of as-produced GO, some evidence supporting this hypothesis can be seen in previous reports. For example, in high-resolution TEM studies prior to imaging, GO is typically heated to remove/reduce amorphous material, which otherwise masks the graphene-like lattice.^[7] Even after heating, amorphous regions cover a significant fraction of the area, with only nanometer-sized “clean” regions evident between them. Electron diffraction studies of GO without prior heating show that the hexagonal graphene-like lattice is retained,^[11,20] thus supporting the interpretation that the amorphous regions are predominantly oxidative debris bound to the GO sheets. Recent reports have demonstrated that structures similar to those expected in the oxidative debris are effective as surfactants for graphene (directly from graphite powder),^[21] and for chemically reduced graphene oxide.^[22] The oxidative debris clearly has a strong affinity for the graphene-like sheets of GO, and is an effective surfactant for GO; if it can be purified in large quantities it may act as an effective surfactant for the direct dispersion of graphene from graphite.

In conclusion, therefore, these results suggest that the as-produced GO consists of functionalized graphene-like sheets to which oxidative debris is strongly adhered. The graphene-like sheets are oxidized, but at a much lower level than current models for GO suggest (Figure 6). This OD–bwGO complex appears to be indefinitely stable in water, but the removal of the oxidative debris can simply be effected with a base wash, whereupon the more highly functionalized debris dissolves fully into water to leave a suspension of functionalized sheets. The separation of the highly oxidized OD from

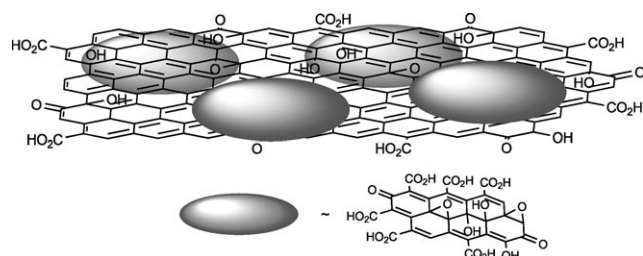


Figure 6. Schematic representation of aGO: large oxidatively functionalized graphene-like sheets with surface-bound debris. Note that the graphene-like sheets extend further than depicted.

the aGO to give bwGO corresponds to a net reduction of the graphene-like material. We have yet to find a method of recombining the debris and graphene-like material, which suggests to us that the original structure is metastable. The importance of the oxidative debris is demonstrated by the change in the properties of aGO after its removal: unlike as-produced GO, the resultant base-washed graphene oxide is not easily suspended in water and is conducting.

Our results suggest that models for the structure of graphene oxide need revisiting. The oxidative debris non-covalently attached to as-produced GO has important implications for the synthesis and application of CMGs, particularly where direct covalent functionalization of the graphene lattice is required.

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