

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 and easy to process.[1, 2] It is also a starting point for further functionalisation to create chemically modified graphenes (CMGs) e.g. for use in composites, light-harvesting, or as sensors. Understanding the chemical and physical structure of GO is a necessary step towards its controllable functionalisation for CMGs and potential complete reduction back to graphene.

Here we will provide compelling evidence 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. We will also show that the physical and chemical properties of the as-produced GO are strongly influenced by this oxidative debris.[3]

Upon the addition of NaOH as-produced graphene oxide (aGO) rapidly separated into a black aggregation and an essentially colorless supernatant, Figure 1. The black aggregate was separated and analysed; TEM and AFM showed it to contain graphene-like single sheets (we subsequently refer to it as base-washed GO, or bwGO). The supernatant was also dried and analysed; it showed a similar FTIR spectrum to aGO but contained no graphene-like sheets. We will show that this material contains oxidative debris, and refer to it as OD. Careful and independent measurement of the masses revealed that 64 ± 2 % of the mass of aGO can be attributed to bwGO, and 30 ± 9 % to OD. We conclude that base-washing separates aGO into two-parts, bwGO and OD, and that by mass they are present in a ratio of roughly 2:1. XPS analysis showed the C:O ratio increased from 2:1 for aGO to 4:1 for bwGO, with no discernible change in the Raman spectra, Figure 2. It was not possible to resuspend the bwGO in water. bwGO is conducting with a conductivity of order 10^0 - 10^1 S m⁻¹.

These results strongly 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 3. 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, leaving a suspension of functionalized sheets. The importance of the oxidative debris is demonstrated by the change in 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 functionalisation of the graphene lattice is required.

References

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[3] J. P. Rourke *et al.*, *Angew. Chem. Int. Ed.* **accepted for publication**, (2011)

Figures

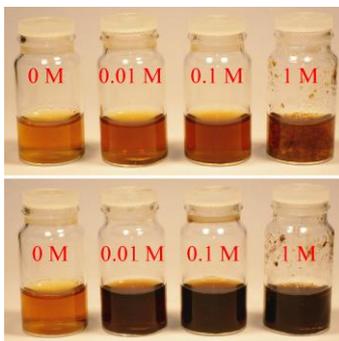


Figure 1. Photograph of 0.5 mg ml⁻¹ aGO suspension in NaOH (concentrations as marked) within 30 s of addition of the NaOH (top), and after three hours (bottom).

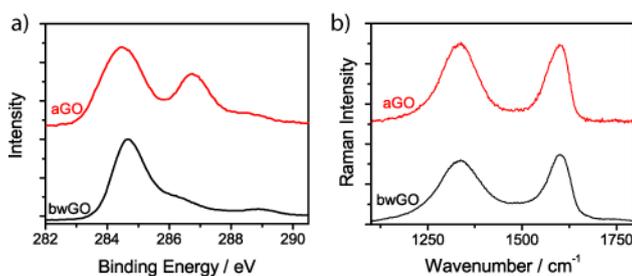


Figure 2. a) C 1s XPS spectra of as-produced GO (aGO) and base-washed GO (bwGO). b) Raman spectroscopy of aGO and bwGO using 633 nm laser excitation.

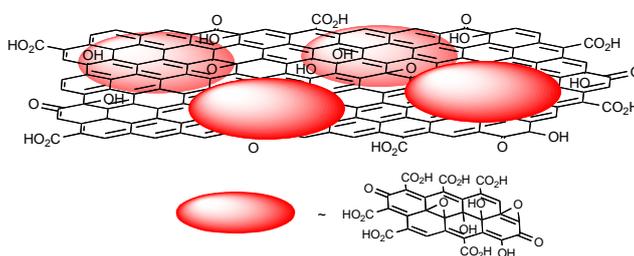


Figure 3. A diagrammatic representation of aGO; large oxidatively functionalized graphene-like sheets with surface bound debris. Note that the graphene-like sheets extend further than depicted.