

Graphene Oxide Flower-like Microstructures from Carbon Nanotubes

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To date, graphene has been prepared by a range of methods, including hydrothermal,¹ oxygen plasma treatment² and electrochemical exfoliation of graphite in ionic liquids.³ However, the most facile large scale method of GO production is the prolonged ultrasonication of graphite or carbon nanotubes (CNTs) in various solvents.^{4,5} Using this technique the exfoliation of graphite or unzipping of CNTs can produce aromatic carbon sheets which are functionalized with -OH, -COOH and epoxy moieties, called graphene oxide (GO).⁶ Significantly, select solvents such as *N*-methylpyrrolidone (NMP) exhibit strong interactions with sp² carbon nanostructures, including CNTs⁷ and graphene.⁸ Therefore exfoliation or unzipping is possible because the energy required for this is balanced by the solvent-graphene interaction for solvents whose surface energies match that of graphene.⁸ By capitalizing on this interaction, this work produced GO by the unzipping of single-wall carbon nanotubes (SWCNTs) in NMP. Further we will report on the controlled generation of graphene oxide (GO) flower-like microspheres (Figure 1) by self-assembly of solutions of GO in *N*-methylpyrrolidone (NMP) on glass and silicon slides and propose a mechanism for this self-assembly.⁹

Firstly, the GO precursor was prepared in a simple, easily scalable process employing the ultrasonication of SWCNTs at ambient conditions. We found that GO was not obtained by this approach when the concentration of SWCNTs in NMP exceeds 0.3 mg/mL. The GO microspheres were characterized using Raman scattering spectroscopy which showed a disorder-induced first order scattering or "D2-scattering" band¹⁰ at approximately 1447 cm⁻¹ related to the direct result of disorder induced graphene edge effects,¹⁰ or in this case the formation of C=O moieties. UV-Visible spectroscopy showed that the GO in NMP exhibited a blue luminescence at 406 nm (3.1 eV) when excited at 300 nm. Eda et al.¹¹ calculated the band gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of a single benzene ring to be approx. 7 eV, which decreased down to approx. 2 eV for a cluster of 20 aromatic rings. The GO mono-layers reported in this work have a band gap of around 3.1 eV suggesting that they have sp² domains that are approximately 15 aromatic rings surrounded by sp³ localized states.

Lastly, the GO microspheres were tested for a photoelectric response when deposited onto n-type silicon (Figure 1). Results indicated that even though the fill factor (~0.28) was low a short circuit photocurrent density of 8 μ A and an open circuit photovoltage of 65 mV was observed. It is also expected that the morphology of the GO flowers will provide outstanding light trapping functionality compared to flat graphene/GO sheets. In light of this and the recent reports of graphene-on-silicon solar cells a more detailed investigation of the light harvesting ability of this material is warranted. Furthermore, the successful fabrication of these GO hierarchical morphologies provides more complex forms with extremely high surface-to-volume ratios for potentially new catalytic or scaffolding applications.

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Figures

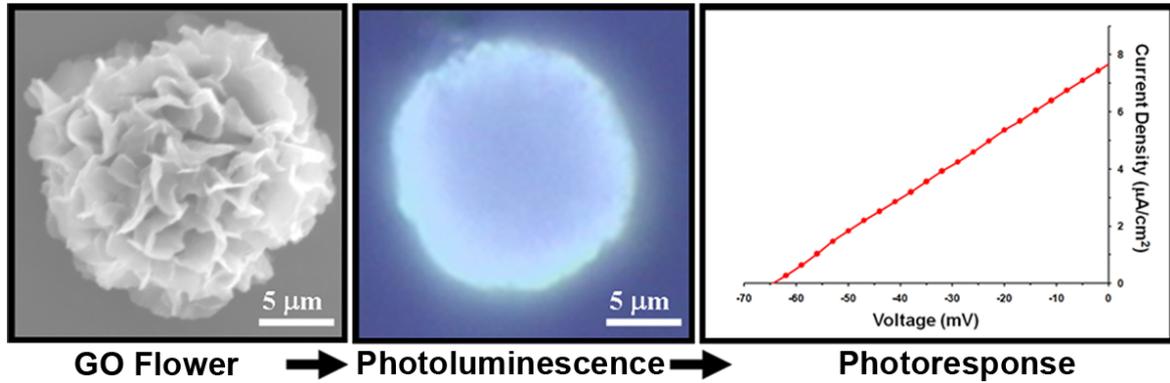


Figure 1: Left - Scanning electron micrograph of self-assembled graphene oxide deposited from a solution of graphene oxide in N-methylpyrrolidone (NMP) on n-type silicon; Middle – optical image under white light in a Raman microscope; and Right - current density ($\mu\text{A}/\text{cm}^2$) versus voltage (mV) curves obtained from the self-assembled graphene oxide on n-type silicon.