Influence of Graphite Defect Density on Oxidation Behavior and π-electron Topology of Sub-stoichiometric Graphene Oxides

Zhi-Li Chen\(^b\), Li-Hong Zhao\(^b\), Roland G.-S. Goh\(^b\), Fong-Yu Kam\(^a\), Jie Song\(^a\), Wang-Zhi Chua\(^c\), Geok-Kieng Lim\(^b,d\), and Lay-Lay Chua\(^a,b\)

\(^a\) Department of Chemistry, National University of Singapore, Lower Kent Ridge Road, S117543, Singapore
\(^b\) Department of Physics, National University of Singapore, Lower Kent Ridge Road, S117542, Singapore
\(^c\) Hwa Chong Institution, 673 Bukit Timah Road, S269735, Singapore
\(^d\) DSO National Laboratories, 20 Science Park Drive, Science Park I, S118230, Singapore

Five commercial sources of natural (G1 and G3) and synthetic graphites (G2, G4 and G5) were investigated to study the role of defect density on their oxidative chemistry and properties of the functionalized graphene derivatives that are potentially suitable for optical or electronic applications. The starting graphites were characterized by Raman spectroscopy to yield the average mosaic size, and Fourier-transform infrared spectroscopy (FTIR) to yield the hydrogen concentration. These graphites were subjected to a Staudenmaier oxidation\(^1\), and the sub-stoichiometric graphene oxides (sub-GOx)\(^2,3\) obtained were characterized via thermogravimetry analysis (TGA) to evaluate their oxidation state. The latter reveals the amount of labile oxygen groups in the sub-GOx to vary as G1 < G2 – G4 < G5, in broad agreement with both elemental analysis and Raman results.

A method to “fingerprint” the Raman G-band was developed and used to evaluate their π-electron topology. We show that the more defective graphites are more readily oxidized to give smaller nano-graphene domains. These also tend to possess a higher non-benzenoid character.\(^4,5\) The π-electron topologies of benzenoid and non-benzenoid systems were also studied using quantum-chemical calculations at the semi-empirical PM3-MNDO level.

From the gathered findings, the most defective sub-GOx exhibits a higher activation energy for both electron and hole mobilities than the least defective sub-GOx, which gives sub-meV activation energies below 25 K. This suggests that the less defective G1 has given rise to a better sub-GOx with higher benzenoid character that can be thermally re-graphenized to a better graphene material with more extensive band-like transport. In contrast, more oxidized GOx re-graphenized to less perfect graphene material to give hopping transport. Therefore the defect type and density in the starting graphite play a crucial role in its chemistry that ultimately controls the electronic and optical properties of the derived functionalized graphenes.

References

Figures

Figure 1a. Raman spectroscopy of graphite G1–G5 obtained from commercial sources used for synthesis of graphene oxide.
Figure 1b. Transmission FTIR spectra of graphite G1–G5 dispersed in KBr pellet showing sp² νC–H stretch at 2972 cm⁻¹. Vibration arises from residual C–H (internal voids or fissions of graphene sheet) due to imperfect graphenization or impurities which further limit the lateral coherence and size of the mosaics.

Figure 2a. Thermogravimetry of the sub-GOx of G1–G5 obtained by modified Staudenmaier oxidation. The samples were equilibrated in N₂ glove box for 3 days before the analysis. The weight thermograms are plotted on the left axis and the derivative weight thermograms on the right.
Figure 2b. In-situ FTIR spectroscopy of a neat film of sub-GOx (from G1) on intrinsic Si wafer. The progressive pumping and heating time of a thin film of sub-GOx (i) showing the OH bend at 1325 cm⁻¹, C–OH stretch at 1200 cm⁻¹ and epoxy stretches at 1090, 950, 860 cm⁻¹, (ii) showing the OH stretch at 3745 cm⁻¹.

Figure 3a. Raman spectroscopy of sub-GOx of G1–G5 obtained by modified Staudenmaier oxidation. G band is fitted with several Gaussian spectra with peak centre at 1540 cm⁻¹, 1568 cm⁻¹, 1580 cm⁻¹ 1592 cm⁻¹ and 1642 cm⁻¹. The spectra have been offset for clarity.
Figure 3b. Transmission FTIR spectra of sub-GOx dispersed in KBr pellet. The broad absorption is due to π–π* electronic transition of the graphenities. The intensity of this background decreases across G1 > G2–G4 > G5, in agreement with the oxidation trend.
Figure 3c. Dependence of calculated vibration frequencies on type of termination edges in the π-electron network for (i) benzenoid and (ii) non-benzenoid structure.