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Characterisation and Functionalisation
of Mechanically Fractured Graphene
Nanoribbons

A thesis presented in partial fulfilment of the requirements for
the degree of

Master of Science
in
Nanoscience

at Massey University, Manawatū
New Zealand

Samuel James Brooke
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Abstract

Graphene has been heralded as the supermaterial of the future, boasting incredibly high electron mobility, thermal conductivity, and physical strength – all contained within the world’s first true 2D material, only a single atom thick. Graphene nanoribbons (GNRs) broaden this potential further by demonstrating width-dependent band gaps due to confinement effects. In addition, the ability to define the edge geometry and dimensions of GNRs allows control over self-assembly of these novel carbon nanostructures. GNR synthesis has been broadly explored in literature, demonstrating both relatively high yields and atomic-scale precision. Rarely, however, are these two criteria achieved in the same technique. Longitudinal unzipping of carbon nanotubes (CNTs) generates large quantities of nanoribbon material at the expense of quality, while techniques such as chemical vapor deposition (CVD) and bottom up synthesis achieve truly astounding quality, but lack scalability.

Recently, the synthesis of highly ordered GNRs with tunable dimensions and unique geometries has been demonstrated using mechanical fracturing of a block of graphite via simple microtomy techniques. This method offers a top-down approach to GNR synthesis providing highly ordered structure on a much larger scale than efforts to date. In this work, this technique has been altered to use a dry-cut method, and the structural and chemical properties of the material obtained therein have been extensively characterised, demonstrating increased quality, structural order, and quantities obtainable. Further, this work has demonstrated the functionalisation of these dry-cut materials both chemically via simple organic chemistries, and non-covalently utilising filamentous bacteriophage as a route towards biofunctionalisation.
Acknowledgements

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I would like to acknowledge Ashley Way, for providing me with computational data, Ewan Fisher for running SEIRAS on all my samples, and Haidee Dykstra for her contributions from, and complex analysis of, the Raman data obtained from these mechanical fracturing techniques. Additionally, I would like to thank Callum Hill and Harry Deare for their efforts in refining the SLIPSERS protocols, which were invaluable during my final data collections.

Lastly, I would like to thank my friends and family for supporting me throughout the project, particularly in the last months. I would not have come this far without them.
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<tr>
<td>2D</td>
<td>Two-dimensional</td>
</tr>
<tr>
<td>3D</td>
<td>Three-dimensional</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>CA</td>
<td>Cysteamine</td>
</tr>
<tr>
<td>CHCl₃</td>
<td>Chloroform</td>
</tr>
<tr>
<td>CNT(s)</td>
<td>Carbon nanotube(s)</td>
</tr>
<tr>
<td>CTAB</td>
<td>Cetyltrimethylammonium bromide</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical Vapor Deposition</td>
</tr>
<tr>
<td>DCC</td>
<td>N,N'-dicyclohexylcarbodiimide (catalyst)</td>
</tr>
<tr>
<td>DCM</td>
<td>Dichloromethane</td>
</tr>
<tr>
<td>DMAP</td>
<td>4-dimethylaminopyridine (catalyst)</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethylformamide</td>
</tr>
<tr>
<td>EDC</td>
<td>1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (catalyst)</td>
</tr>
<tr>
<td>EtOH</td>
<td>Ethanol</td>
</tr>
<tr>
<td>FET</td>
<td>Field effect transistor</td>
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<td>GNB(s)</td>
<td>Graphene nanoblock(s)</td>
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<td>GNR(s)</td>
<td>Graphene nanoribbon(s)</td>
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<td>Graphene nanoribbons, cysteamine modified</td>
</tr>
<tr>
<td>GNR-MPA</td>
<td>Graphene nanoribbons, 3-mercaptopropionic acid modified</td>
</tr>
<tr>
<td>GO</td>
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</tr>
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<td>GQD(s)</td>
<td>Graphene quantum dot(s)</td>
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</table>
H₂O  Water
H₂O₂  Hydrogen peroxide
H₂SO₄  Sulfuric acid
H₃PO₄  Phosphoric acid
HEPES  4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (buffer)
HOPG  Highly oriented pyrolytic graphite
I_D:I_G  Ratio of intensities of D band to G band
IPA  Isopropyl alcohol
IR  Infrared spectroscopy
KMnO₄  Potassium permanganate
LiAlH₄  Lithium aluminium hydride
LPE  Liquid-phase exfoliation
MD  Molecular dynamics
MeCN  Acetonitrile
MPA  3-mercaptopropionic acid
MQ  Milli-Q® > 18 MΩ grade H₂O
MWNT(s)  Multi-walled carbon nanotube(s)
NaBH₄  Sodium borohydride
NHS  N-hydroxysuccinimide (catalyst)
PDC  Pyridinium dichromate
Phage  Filamentous bacteriophage
PMMA  Poly(methyl methacrylate)
Raman  Raman spectroscopy/microscopy
rpm  Revolutions per minute
SDBS  Structural Database for Organic Compounds
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>SEIRS</td>
<td>Surface enhanced infrared spectroscopy</td>
</tr>
<tr>
<td>SLIPSERS</td>
<td>Slippery liquid-infused porous surface-enhanced Raman scattering</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>UV-vis</td>
<td>Ultraviolet/visible spectroscopy</td>
</tr>
<tr>
<td>ZYA</td>
<td>High-grade HOPG with mosaic spread of $0.4^\circ \pm 0.1^\circ$</td>
</tr>
<tr>
<td>ZYB</td>
<td>Medium-grade HOPG with mosaic spread of $0.8^\circ \pm 0.2^\circ$</td>
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<td>$\Delta G$</td>
<td>Change in Gibbs energy</td>
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<td>$\Delta S$</td>
<td>Change in entropy</td>
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<tr>
<td>$\kappa$</td>
<td>Thermal conductivity in Wm$^{-1}$K$^{-1}$</td>
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