Characterisation and Functionalisation of Mechanically Fractured Graphene Nanoribbons

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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.

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Abbreviations

2D	Two-dimensional
3D	Three-dimensional
AFM	Atomic force microscopy
CA	Cysteamine
$CHCl_3$	Chloroform
CNT(s)	Carbon nanotube(s)
CTAB	Cetyltrimethylammonium bromide
CVD	Chemical Vapor Deposition
DCC	N,N'-dicyclohexylcarbodiimide (catalyst)
DCM	Dichloromethane
DMAP	4-dimethylaminopyridine (catalyst)
DMF	Dimethylformamide
EDC	1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (catalyst)
EtOH	Ethanol
FET	Field effect transistor
GNB(s)	Graphene nanoblock(s)
GNR(s)	Graphene nanoribbon(s)
GNR-CA	Graphene nanoribbons, cysteamine modified
GNR-MPA	Graphene nanoribbons, 3-mercaptopropionic acid modified
GO	Graphene oxide
GO-CA	Graphene oxide, cysteamine modified
GONR(s)	Graphene oxide nanoribbon(s)
GONR-CA	Graphene oxide nanoribbons, cysteamine modified
GQD(s)	Graphene quantum dot(s)

H_2O	Water
H_2O_2	Hydrogen peroxide
H_2SO_4	Sulfuric acid
H_3PO_4	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
$KMnO_4$	Potassium permanganate
$LiAlH_4$	Lithium aluminium hydride
LPE	Liquid-phase exfoliation
MD	Molecular dynamics
MeCN	Acetonitrile
MPA	3-mercaptopropionic acid
MQ	Milli-Q® $>$ 18 MΩ grade H_2O
MWNT(s)	Multi-walled carbon nanotube(s)
$NaBH_4$	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

SEIRS	Surface enhanced infrared spectroscopy
SLIPSERS	Slippery liquid-infused porous surface-enhanced Raman scattering
TEM	Transmission electron microscopy
THF	Tetrahydrofuran
UV-vis	Ultraviolet/visible spectroscopy
ZYA	High-grade HOPG with mosaic spread of $0.4° \pm 0.1°$
ZYB	Medium-grade HOPG with mosaic spread of $0.8° \pm 0.2°$
ΔG	Change in Gibbs energy
ΔH	Change in enthalpy
ΔS	Change in entropy
κ	Thermal conductivity in $Wm^{-1}\ K^{-1}$