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At the Cutting Edge: Structural Analysis and Chemical Modification of the Edges of Mechanically Cleaved Graphene Nanoribbons

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Abstract

The first decade of the new carbon nanomaterial graphene has been a time of great discovery and excitement as the exceptional properties of this material were uncovered and its promise for numerous applications realised. The unique properties of graphene, including its exceptional electronic structure, are now well-established, and investigations into how these properties can be manipulated and exploited are rapidly taking off. This research contributes to the emerging field by exploring the structure and chemistry of the edges of mechanically cleaved graphene nanoribbons; groundwork for the future development of edge-modified nanoribbons that could be used to form self-assembled graphene nanoribbon composite structures with potential for devices in solar energy conversion. For this purpose, a Raman microscope was built that enabled for various aspects of the structure of graphene nanoribbons to be probed, in particular the geometry and smoothness of the edges, which have important implications for the specific reactivity of the edge carbon atoms. Chemical approaches for the specific functionalisation of the edges of the nanoribbons were developed, involving reactions tailored to the reactive groups present at the edges, and these were found to be highly successful and selective.

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List of Acronyms and Abbreviations

In order of appearance:

CVD	Chemical vapour deposition
GO	Graphene oxide
BZ	Brilluoin zone
QHE	Quantum Hall effect
FET	Field effect transistor
LED	Light-emitting diode
ITO	Indium Tin oxide
SAM	Self-assembled monolayer
DOS	Density of states
GNR	Graphene nanoribbon
CNT	Carbon nanotube
HOPG	Highly-oriented pyrolytic graphite
HNF	Holographic notch filter
VBG	Volume Bragg grating
VHG	Volume holographic filter
PTR	Photo-thermo-refractive
BNF	BragGrate TM notch filter
BPF	BragGrate TM bandpass filter
OD	Optical density
NA	Numerical aperture
OPSL	Optically pumped semiconductor laser
MFD	Mode field diameter
PM	Polarisation maintaining
PMMA	Poly(methyl) methacrylate
GNB	Graphite nanoblock
AFM	Atomic force microscopy
TEM	Transmission electron microscopy
IPA	Isopropanol
SDS	Sodium dodecylsulfate
CMC	Critical micelle concentration
THF	Tetrahydrofuran
r-GNR	Reduced GNR
4-ABA	4-aminobenzoic acid
EDC	1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide
DMAP	4-Dimethylaminopyridine

DMSO	Dimethyl sulfoxide
f-GNR	functionalised GNR
SA	Sulfanilic acid
NHS	N-Hydroxysuccinimide
DMF	Dimethylformamide
FTIR	Fourier transform infrared
ATR	Attenuated total reflection
S:N	Signal-to-noise
HDFT	Heptadecafluoro-1-decanethiol
KK	Kramers-Kronig
SERS	Surface-enhanced Raman spectroscopy
CTAB	Cetyltrimethylammonium bromide
Agnp	Silver nanoparticle
PE	Polyethylene
XPS	X-ray photoelectron spectroscopy
TA	Terephthalic acid
TMA	Trimesic acid
BTB	Benzene 1,3,5-tribenzoic acid
EDA	Ethylenediamine
TFA	Trifluoroacetic acid
4-NA	4-nitroaniline
PDOS	Phonon density of states
iTO	In-plane transverse optical
iLO	In-plane longitudinal optical
DR	Double resonance
PAH	Polycyclic aromatic hydrocarbon
NMP	N-methyl-pyrrolidone
SDBS	Sodium dodecylbenzenesulfonate
BDE	Bond dissociation energy
OTS	Octadecyltrichlorosilane
hBN	Hexagonal Boron nitride
STM	Scanning tunnelling microscopy
TERS	Tip-enhanced Raman spectroscopy
AE	Activated ester
4-NBA	4-nitrobenzoic acid
RhB	Rhodamine B
SP	Sulfophenyl
NP	Nitrophenyl
SPR	Surface plasmon resonance

R6G

HATN

TCNQ

F4-TCNQ

Rhodamine 6G

hexaazatriphenylene

7,7,8,8-tetracyanoquinodimethane

2,3,5,6-tetrafluoro-7,7,8,8-
tetracyanoquinodimethane