SEIRAS of Functionalised Graphene Nanomaterials

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Abstract

Graphene exhibits many excellent properties, but many next-generation devices require post chemical treatment to introduce structural confirmations, defects or a particular impurity to obtain functionality. The understanding of these defects and the manifestation of desirable properties using chemical modification is a fundamental problem with low defect graphene as the small number of functional groups provides insufficient signal intensity for many characterisation techniques. Metallic nanoparticles are at the centre of plasmonics for enhancing optical signals. This work is a unique undertaking for the examination of novel Steglich esterification chemistry that is performable on graphene as well as providing insight into the native edge structure of as-produced graphene flakes using surface enhanced infrared reflection absorption spectroscopy (SEIRAS) to characterise covalently functionalised graphene materials.

Two methods of producing graphene flakes that are relatively low or high in defects have been developed to contrast the effect that inherent defects have on the macroscopic physical and spectroscopic properties. Ultraviolet-visible spectroscopy in conjunction with Raman, electron and atomic force microscopy was used to elucidate the origins and density of defects to draw conclusions on how graphene's macroscopic properties manifest from atomic level defects.

Discussions of infrared vibrational spectroscopy are carried out before an extension to SEIRAS where the use of near-field plasmon and phonon modes are attributed to observed optical enhancements. The experimental preparation is focused towards understanding the role nanoparticles play in SEIRAS of graphene and is discussed such that other graphene researchers can recreate SEIRAS for their graphene research. TEM is used to characterise

the variety of nanoparticle shapes and geometries as well as provide topological insights on nanoparticles adsorbed to flakes of graphene.

SEIRAS probes the defects native to graphene which confirms the presence of oxygen functionality. Steglich esterification reactions were utilised to successfully prepare a range of graphene materials with novel covalently bound functional groups as confirmed by SEIRAS. Covalent chemistry was extended to introduce a redox-active ferrocene derivative where SEIRAS was used to observe in real-time, the effect of interconversion of ferrocene to the ferrocenium cation.

The foundations for the development of graphene-based solid state solar cells was the final focus of this work. Development and production of a potential photo-active layer was explored with Cl-BODIPY as the basis chromophore. Production of a flexible, electrically conductive substrate from graphene flakes was carried out, and tunnelling electron microscopy (TEM) was used to characterise topological and morphological surface features. The focus here was on covalent and physical absorption to graphene flakes. SEIRAS was used to confirm nucleophilic substitution (covalent) modification while STEM was used to confirm the uniformity of BODIPY on the substrate and chlorine atomic mapping to confirm physisorption.

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Abbreviations and Symbols

AFM	Atomic force microscopy
ATR	Attenuated total reflectance
ATR-FTIR	Attenuated total reflectance Fourier transform infrared
CB	Conduction band
CVD	Chemical vapour deposition
DCC	N,N'-Dicyclohexylcarbodiimide
DOS	Density of states
E_D	Dirac point energy
ED	Ethylene diamine
EDC	1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide
E_F	Fermi level energy
E_g	Band gap energy
E_{local}	Local electric field intensity
EM	Electromagnetic
EPC	Electron-phonon coupling
eV	Electron volts
GO	Graphene oxide
HOPG	Highly orientated pyrolytic graphite
LB	Langmuir-Blodgett
NIR	Near infrared
PV	Photovoltaic
RAIRS	Reflection absorption infrared spectroscopy

SEIRAS	Surface enhanced infrared reflection absorption spectroscopy
SEIRASEC	Surface enhanced infrared reflection absorption spectroelectrochemistry
SEM	Scanning electron microscopy
SERS	Surface enhanced Raman spectroscopy
SP	Surface plasmon
SPR	Surface plasmon resonance
SSSC	Solid-state solar cell
THF	Tetrahydrofuran
UV-vis spec.	Ultraviolet-visible spectroscopy
VB	Valance band

Glossary of Graphene Materials

GN-Flake	Graphene flakes produced by graphite nanotomy at micron increments
GN-Flake-BO	GN-Flakes functionalised with Cl-BODIPY
GN-Flake-ED	GN-Flakes functionalized with Ethylenediamine
GN-Flake-NA	GN-Flakes functionalised with 4-Nitroaniline
GN-Flake-NB	GN-Flakes functionalised with 4-Nitrobenzoic acid
GN-Flake-SA	GN-Flakes functionalized with Sulfanilic acid
xFlakes	Flakes of graphene produced by electrochemical exfoliation
xFlake-BO	xFlakes functionalised with Cl-BODIPY
xFlake-ED	xFlakes functionalised with Ethylenediamine
xFlake-ED-Fe	xFlakes functionalised with Ethylenediamine then ferrocene
xFlake-NA	xFlakes functionalised with 4-Nitroaniline
xFlake-$NaBH_4$	xFlakes reduced over $NaBH_4$
xFlake-NB	xFlakes functionalised with 4-Nitrobenzoic acid
xFlake-paper	Graphene substrate produced by compacting xFlakes
xFlake-SA	xFlakes functionalised with Sulfanilic acid
xFlakes-$LiAlH_4$	xFlakes reduced over $LiAlH_4$
xFlakes-$NaBH_4$	xFlakes reduced over $NaBH_4$

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