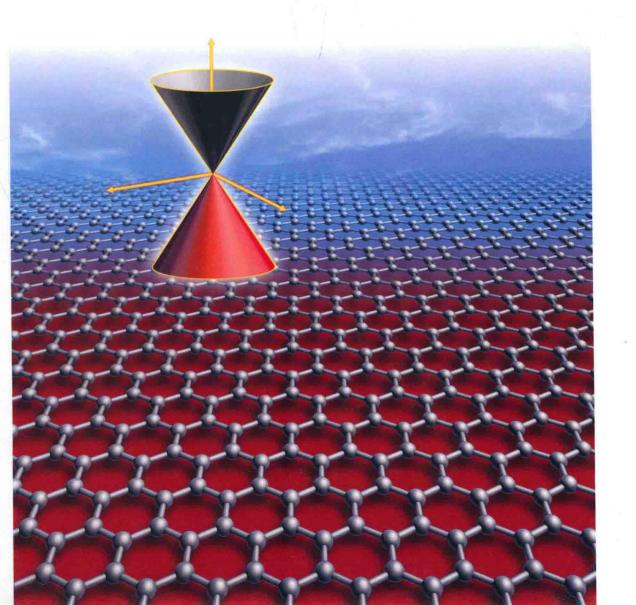
# Graphene

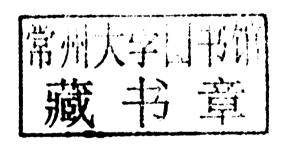
Synthesis, Properties, and Phenomena



Edited by C. N. R. Rao and A. K. Sood

# Graphene

Synthesis, Properties, and Phenomena





WILEY-VCH Verlag GmbH & Co. KGaA

#### The Editors

Prof. Dr. C. N. R. Rao Chemistry of Materials Unit Jawaharlal Nehru Centre Jakkur P.O. Bangalore 560 064 India

Prof. Dr. A. K. Sood Indian Institute of Science Department of Physics Bangalore 560 012 India All books published by Wiley-VCH are carefully produced. Nevertheless, authors, editors, and publisher do not warrant the information contained in these books, including this book, to be free of errors. Readers are advised to keep in mind that statements, data, illustrations, procedural details or other items may inadvertently be inaccurate.

Library of Congress Card No.: applied for

#### British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library.

#### Bibliographic information published by the Deutsche Nationalbibliothek

The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available on the Internet at <a href="http://dnb.d-nb.de"><a href="http://dnb.d-nb.de">http://dnb.d-nb.de</a>.

© 2013 Wiley-VCH Verlag & Co. KGaA, Boschstr. 12, 69469 Weinheim, Germany

All rights reserved (including those of translation into other languages). No part of this book may be reproduced in any form – by photoprinting, microfilm, or any other means – nor transmitted or translated into a machine language without written permission from the publishers. Registered names, trademarks, etc. used in this book, even when not specifically marked as such, are not to be considered unprotected by law.

Print ISBN: 978-3-527-33258-8 ePDF ISBN: 978-3-527-65115-3 ePub ISBN: 978-3-527-65114-6 mobi ISBN: 978-3-527-65113-9 oBook ISBN: 978-3-527-65112-2

Cover Design Formgeber, Eppelheim
Typesetting Laserwords Private Limited,
Chennai, India
Printing and Binding Markono Print Media
Pte Ltd, Singapore

Edited by C. N. R. Rao and A. K. Sood

Graphene

#### Related Titles

Martin, N., Nierengarten, J.-F. (eds.)

Supramolecular Chemistry of Fullerenes and Carbon Nanotubes

2012

ISBN: 978-3-527-32789-8

Jorio, A., Dresselhaus, M. S., Saito, R., Dresselhaus, G.

Raman Spectroscopy in Graphene Related Systems

2011

ISBN: 978-3-527-40811-5

Kumar, C. S. S. R. (ed.)

Carbon Nanomaterials

Series: Nanomaterials for the Life Sciences (Volume 9)

2011

ISBN: 978-3-527-32169-8

Saito, Y. (ed.)

Carbon Nanotube and Related Field Emitters

**Fundamentals and Applications** 

2010

ISBN: 978-3-527-32734-8

Krüger, A.

Carbon Materials and Nanotechnology

2010

ISBN: 978-3-527-31803-2

Guldi, D. M., Martín, N. (eds.)

Carbon Nanotubes and Related Structures

Synthesis, Characterization, Functionalization, and Applications

2010

ISBN: 978-3-527-32406-4

#### **Preface**

Graphene is a fascinating subject of recent origin, its first isolation being made possible through micromechanical cleavage of a graphite crystal. Since its discovery, graphene has caused great sensation because of its unusual electronic properties, and scientists from all over the world have been working on the varied facets of graphene. Thus, there has been much effort to synthesize both single-layer and few-layer graphenes by a number of methods. A variety of properties and phenomena have been investigated, and many of the studies have been directed toward understanding the physical and chemical properties of graphene. Raman spectroscopy has been particularly useful in unraveling various aspects of graphene. A graphene field-effect transistor, a basic building block of nanodevices, is a single-element laboratory to study electron-phonon interactions using Raman scattering. The low-frequency electrical noise or the flicker noise in graphene devices defines the figure of merit of a device and has contrasting behavior for single- and bilayer-graphene devices. Magnetic properties have been of equal interest with the indication that graphene may be ferromagnetic at room temperature, exhibiting magnetoresistance. Graphene nanoribbons have attracted attention because of their unique electronic structure and properties. Graphene also provides a playground for exploring many quantum field related phenomena such as Klein tunneling, antilocalization, zitterbewegung, vacuum collapse by Lorenz boost and so on. Suspended graphene devices have been used to study nanoscale electromechanics and quantum Hall effect.

A variety of applications of graphene have come to the fore. Its use in supercapacitors and batteries has been explored. Other properties of graphene, which are noteworthy, are those that enable its use in nanoelectronics, field emission and catalysis. Biological aspects of graphene have been investigated by a number of workers, with emphasis on its toxicity and its possible use for drug delivery.

In this book, we have tried to cover many of the salient aspects of graphene, which are of current interest. Although the book mostly deals with graphene, we have included some material on graphene-like inorganic layered materials. It is possible, however, that some topics have been left out owing to constraints on the size of the book and possible errors in judgement. We trust that the

# XIV | Preface

book will be useful to students, teachers, and practitioners, and serves as an introduction to those who want to take part in the exciting developments of this subject.

June 2012

C.N.R. Rao A.K. Sood

#### List of Contributors

#### Ganapathy Baskaran

The Institute of Mathematical Sciences C.I.T. Campus Chennai 600 113 Tamil Nadu India

and

Perimeter Institute for Theoretical Physics 31 Caroline Street North Waterloo Ontario Canada N2L 2Y5

#### Santanu Bhattacharya

Indian Institute of Science Department of Organic Chemistry Bangalore 560 012 Tala Marg Karnataka India

and

The Chemical Biology Unit Jawaharlal Nehru Centre for Advanced Scientific Research Bangalore 560 064 Jakkur Karnataka India

#### Biswanath Chakraborty

Indian Institute of Science Department of Physics Bangalore 560012 Karnataka India

#### Mandar M. Deshmukh

Tata Institute of Fundamental Research Department of Condensed Matter Physics and Materials Science Homi Bhabha Road Mumbai 400005 India

## M. Samy El-Shall

Virginia Commonwealth University Department of Chemistry Richmond VA 23284-2006 USA

and

King Abdualziz University Department of Chemistry Jeddah 21589 Kingdom of Saudi Arabia

#### Toshiaki Enoki

Tokyo Institute of Technology Department of Chemistry Ookayama Meguro-ku Tokyo 152-8551 Japan

#### Arindam Ghosh

Indian Institute of Science Department of Physics C.V. Raman Avenue Bangalore 560012 Karnataka India

#### Srijit Goswami

Indian Institute of Science Department of Physics C.V. Raman Avenue Bangalore 560012 Karnataka India

#### Vidya Kochat

Indian Institute of Science Department of Physics C.V. Raman Avenue Bangalore 560012 Karnataka India

#### Manzoor Koyakutty

Amrita Vishwa Vidyapeetham University Amrita Centre for Nanosciences and Molecular Medicine Elamakkara Kochi 682041 Kerala India

#### Urmimala Maitra

Iawaharlal Nehru Centre for Advanced Scientific Research International Centre for Materials Science Chemistry and Physics of Materials Unit, and CSIR Centre of Excellence in Chemistry Jakkur P.O. Bangalore 560 064 Karnataka India

#### H. S. S. Ramakrishna Matte

Jawaharlal Nehru Centre for Advanced Scientific Research International Centre for Materials Science Chemistry and Physics of Materials Unit, and CSIR Centre of Excellence in Chemistry Jakkur P.O. Bangalore 560 064 Karnataka India

#### Shantikumar Nair

Amrita Vishwa Vidyapeetham University Amrita Centre for Nanosciences and Molecular Medicine Elamakkara Kochi 682041 Kerala India

#### Atindra Nath Pal

Indian Institute of Science Department of Physics C.V. Raman Avenue Bangalore 560012 Karnataka India

#### Ganganahalli Kotturappa Ramesha

Indian Institute of Science Department of Inorganic and Physical Chemistry Bangalore 560 012 Karnataka India

#### C. N. R. Rao

Jawaharlal Nehru Centre for Advanced Scientific Research International Centre for Materials Science Chemistry and Physics of Materials Unit, and CSIR Centre of Excellence in Chemistry Jakkur P.O. Bangalore 560 064 Karnataka India

#### Suman K. Samanta

Indian Institute of Science Department of Organic Chemistry Bangalore 560 012 Tala Marg Karnataka India

#### Srinivasan Sampath

Indian Institute of Science Department of Inorganic and Physical Chemistry Bangalore 560 012 Karnataka India

#### Biplab Sanyal

Uppsala University Department of Physics and Astronomy Box-516 75120 Uppsala Sweden

#### Sharmila N. Shirodkar

Theoretical Sciences Unit Jawaharlal Nehru Centre for Advanced Scientific Research Srirampura Cross Jakkur P.O. Bangalore 560 064 Karnataka India

#### Vibhor Singh

Tata Institute of Fundamental Research Department of Condensed Matter Physics and Materials Science Homi Bhabha Road Mumbai 400005 India

#### A. K. Sood

Indian Institute of Science Department of Physics Bangalore 560012 Karnataka India

#### Abhilash Sasidharan

Amrita Vishwa Vidyapeetham University Amrita Centre for Nanosciences and Molecular Medicine Elamakkara Kochi 682041 Kerala India

## Umesh V. Waghmare

Theoretical Sciences Unit Jawaharlal Nehru Centre for Advanced Scientific Research Srirampura Cross Jakkur P.O. Bangalore 560 064 Karnataka India

# Contents

1	Synthesis, Characterization, and Selected Properties of Graphene 1
	C. N. R. Rao, Urmimala Maitra, and H. S. S. Ramakrishna Matte
1.1	Introduction 1
1.2	Synthesis of Single-Layer and Few-Layered Graphenes 4
1.2.1	Mechanical Exfoliation 5
1.2.2	Chemical Exfoliation 5
1.2.3	Chemical Vapor Deposition 8
1.2.4	Arc Discharge 8
1.2.5	Reduction of Graphite Oxide 10
1.3	Synthesis of Graphene Nanoribbons 12
1.4	Selected Properties 15
1.4.1	Magnetic Properties 15
1.4.2	Electrical Properties 19
1.4.2.1	Supercapacitors 22
1.4.2.2	Photovoltaics and Photodetectors 24
1.4.2.3	Field Emission and Blue Light Emission 25
1.4.3	Molecular Charge Transfer 25
1.4.4	Decoration with Metal and Oxide Nanoparticles 28
1.4.5	Surface Area and Gas Adsorption 30
1.4.6	Mechanical Properties 32
1.4.7	Quenching of Fluorescence of Aromatics 34
1.4.8	Chemical Storage of Hydrogen and Halogens 36
1.5	Inorganic Graphene Analogs 39
	References 40
2	Understanding Graphene via Raman Scattering 49
	A. K. Sood and Biswanath Chakraborty
2.1	Introduction 49
2.2	Atomic Structure and Electronic Structure of Graphene 49
2.3	Phonons and Raman Modes in Graphene 51

l		
	2.4	Layer Dependence of Raman Spectra 57
	2.4.1	G-Band 57
	2.4.2	2D-Band 57
	2.4.3	D-Band 59
	2.4.4	Combination Modes in the Range 1650–2300 cm <sup>-1</sup> 59
	2.4.5	Low-Frequency Modes 61
	2.5	Phonon Renormalization Due to Electron and Hole Doping of
		Graphene 61
	2.5.1	Optical Phonon Mixing in Doped Bi- and Multilayer
		Graphene 66
	2.5.2	Charge Inhomogeneity and p-n Junction in the FET Channel Probed
		by Raman Spectroscopy 68
	2.6	Raman Spectroscopy of Graphene Edges and Graphene
		Nanoribbons 70
	2.6.1	Effect of the Edge Orientation on the G-Band 70
	2.6.2	Effect of the Edge Orientation on the D-Band 72
	2.6.3	Raman Spectroscopy of Graphene Nanoribbons 73
	2.7	Effect of Disorder on the Raman Spectrum of Graphene 74
	2.8	Raman Spectroscopy of Graphene under Strain 77
	2.9	Temperature and Pressure Dependence of Raman Modes in
		Graphene as Nanometrological Tools 83
	2.10	Tip-Enhanced Raman Spectroscopy of Graphene Layers 85
	2.11	Conclusions 86
		Acknowledgments 87
		References 87
	3	Physics of Quanta and Quantum Fields in Graphene 91
		Ganapathy Baskaran
	3.1	Introduction 91
	3.2	Dirac Theory in 3 + 1 Dimensions: A Review 93
	3.3	Band Structure of Graphene: Massless Chiral Dirac Electrons in $2 + 1$
		Dimensions 95
	3.3.1	Phase Vortices of Bloch States in k-Space 99
	3.4	Anomaly – A Brief Introduction 100
	3.4.1	Anomalous Commutator in $(1 + 1)$ Dimensions 101
	3.4.2	Axial Anomaly in $(1 + 1)$ , $(3 + 1)$ Dimensions 102
	3.5	Graphene and 2 + 1-Dimensional Parity Anomaly 105
	3.6	Zitterbewegung 107
	3.7	Klein Paradox 110
	3.8	Relativistic-Type Effects and Vacuum Collapse in Graphene in
		Crossed Electric and Magnetic Fields 111
	3.9	Prediction of Spin-1 Quanta from Resonating Valence Bond
		Correlations 116
	3.10	Majorana Zero Mode from Two-Channel Kondo Effect in
		Graphene 120

VI | Contents

3.11	Lattice Deformation as Gauge Fields 125
3.12	Summary 127
	Acknowledgment 127
	References 127
4	Magnetism of Nanographene 131
	Toshiaki Enoki
4.1	Introduction 131
4.2	Theoretical Background of Magnetism in Nanographene and
	Graphene Edges 134
4.3	Experimental Approach to Magnetism of Nanographene 139
4.3.1	Magnetic Structure of Edge-State Spins in Nanographene 139
4.3.2	Magnetism of $\sigma$ -Dangling Bond Defects in Graphene 143
4.4	Magnetic Phenomena Arising in the Interaction with Guest Molecules
	in Nanographene-Based Nanoporous Carbon 146
4.4.1	Magnetic Switching Phenomenon 146
4.4.2	Helium Sensor 152
4.5	Summary 154
	Acknowledgment 155
	References 155
5	Physics of Electrical Noise in Graphene 159
	Vidya Kochat, Srijit Goswami, Atindra Nath Pal, and Arindam Ghosh
5.1	Introduction 159
5.1.1	Single-Layer Graphene 159
5.1.1.1	Effective Tight-Binding Hamiltonian: Sublattice and Valley
	Symmetry 161
5.1.1.2	Valley and Sublattice Pseudospin 161
5.1.1.3	Chirality 162
5.1.1.4	Berry Phase and Absence of Backscattering 162
5.1.2	Bilayer Graphene 163
5.1.2.1	Biased Bilayer Graphene 164
5.1.3	Multilayer Graphene 165
5.1.4	Disorder and Scattering Mechanism in Graphene 166
5.1.4.1	Coulomb Impurity Scattering 167
5.1.4.2	Phonon Scattering 169
5.1.4.3	Electron–Hole Puddles at Low Density 169
5.2	Flicker Noise or " $1/f$ " Noise in Electrical Conductivity of
	Graphene 169
5.2.1	Microscopic Origin of 1/f Noise in Graphene 173
5.2.2	Effect of Bandgap on Low-Frequency Noise in Bilayer Graphene 175
5.2.3	Shot Noise in Graphene 178
5.3	Noise in Quantum Transport in Graphene at Low Temperature 179
5.3.1	Quantum Transport in Mesoscopic Graphene 179
5.3.2	Universal Conductance Fluctuations in Graphene 184

VIII	Contents	
	5.4	Quantum-Confined Graphene 188
	5.4.1	1D Graphene–Nanoribbons (GNRs) 188
	5.5	Conclusions and Outlook 193
		References 193
	6	Suspended Graphene Devices for Nanoelectromechanics and for the Study of Quantum Hall Effect 197 Vibhor Singh and Mandar M. Deshmukh
	6.1	Introduction 197
	6.2	Quantum Hall Effect in Graphene 198
	6.3	Fabrication of Suspended Graphene Devices 200
	6.4	Nanoelectromechanics Using Suspended Graphene Devices 201
	6.5	Using Suspended Graphene NEMS Devices to Measure Thermal Expansion of Graphene 203
	6.6	High-Mobility Suspended Graphene Devices to Study Quantum Hall Effect 206
		Acknowledgments 208
		References 208
	7	Electronic and Magnetic Properties of Patterned Nanoribbons:  A Detailed Computational Study 211
	7.1	Biplab Sanyal Introduction 211
	7.1	
	7.2	Experimental Results 212 Theory of GNRs 214
	7.3.1	Tight-Binding Method 214
	7.3.1	First Principles Studies 217
	7.3.2	Hydrogenation at the Edges 219
	7.4.1	Stability of Nanoribbons 219
	7.4.2	Dihydrogenated Edges 219
	7.5	Novel Properties 226
	7.6	Outlook 231
	7.0	Acknowledgements 231
		References 231
	8	Stone–Wales Defects in Graphene and Related Two-Dimensional Nanomaterials 235
	0.1	Sharmila N. Shirodkar and Umesh V. Waghmare Introduction 235
	8.1	
	8.2	Computational Methods 236
	8.3	Graphene: Stone–Wales (SW) Defects 237
	8.3.1	Structural, Electronic, Magnetic, and Vibrational Properties of Graphene with SW Defect 238
	8.3.1.1	Structural Changes at an SW Defect 238
	8312	Interaction between SW Defects 239

8.3.1.3	Electronic Structure of Graphene and Effects of SW Defects 239
8.3.1.4	Magnetization due to Topological Defects 245
8.3.1.5	Effects on Vibrational Properties 246
8.3.2	Lattice Thermal Conductivity of Graphene with SW Defect 252
8.3.2.1	Theoretical Model 252
8.3.2.2	$\kappa$ : Results 253
8.3.3	Discussion 254
8.4	$C_{1-x}(BN)_{x/2}$ : C-BN Interfaces 255
8.4.1	SW Defect at the C–BN Interface 256
8.4.2	Discussion 259
8.5	Two-Dimensional MoS <sub>2</sub> and MoSe <sub>2</sub> 259
8.5.1	Point Defects 259
8.5.2	Stacking Faults 261
8.5.3	IR Radiation Absorption 261
8.5.4	Discussion 265
8.6	Summary 265
	Acknowledgments 266
	References 266
9	Graphene and Graphene-Oxide-Based Materials for Electrochemical Energy Systems 269
	Ganganahalli Kotturappa Ramesha and Srinivasan Sampath
9.1	Introduction 269
9.2	Graphene-Based Materials for Fuel Cells 270
9.2.1	Graphene-Based Catalyst Support for Small Molecule Redox
0.2.2	Reactions 271
9.2.2	Graphene-Oxide-Based Proton Conducting Membranes 278
9.2.3	Graphene-Based Biofuel Cells 279
9.3	Graphene-Based Supercapacitors 280
9.4	Graphene in Batteries 289
9.5	Conclusions and Future Perspectives 296 References 297
10	Heterogeneous Catalysis by Metal Nanoparticles Supported on
	Graphene 303
	M. Samy El-Shall
10.1	Introduction 303
10.2	Synthesis of Graphene and Metal Nanoparticles Supported on
	Graphene 304
10.2.1	Chemically Converted Graphene by Microwave-Assisted Chemical
	Reduction of Graphene Oxide 304
10.2.1.1	Metal Nanoparticles Supported on Graphene by Microwave Synthesis 307

x	Contents	
	10.2.2	Laser-Converted Graphene by Laser Reduction of Graphene Oxide 308
	10.2.2.1	Laser-Assisted Photoreduction of Graphene Oxide in Different Solvents 313
	10.2.3	Photochemical Reduction of Metal Ions and Graphene Oxide 315
	10.2.3.1	Photoreduction of Gold Ions and GO in Different Solvents 315
	10.2.3.2	Photoreduction of Silver Ions and GO in Different Solvents 316
	10.2.3.3	Mechanism of Photocatalytic Reduction 318
	10.3	Pd/Graphene Heterogeneous Catalysts for Carbon–Carbon Cross-Coupling Reactions 319
	10.3.1	Pd/Graphene Catalysts Prepared by Microwave-Assisted Chemical Reduction of GO 319
	10.3.1.1	Catalytic Activity and Range of Utility 320
	10.3.1.2	Catalyst Recyclability 322
	10.3.2	Pd/PRGO Catalysts Prepared by Laser Partial Reduction of GO 323
	10.3.2.1	Laser Synthesis of Pd Nanoparticles on Structural Defects in Graphene 323
	10.3.2.2	Mechanism of Partial Reduction of GO and Defect Generation 325
	10.3.2.3	Application of Pd/PRGO Nanocatalysts to Suzuki Reaction 326
	10.3.2.4	Recyclability of the Pd/PRGO Nanocatalysts in Suzuki Reaction 328
	10.3.2.5	Applications of the Pd/PRGO Catalyst A to Heck and Sonogashira Reactions 329
	10.4	CO Oxidation by Transition-Metal/Metal-Oxide Nanoparticles Supported on Graphene 330
	10.5	Conclusions and Outlook 334
		Acknowledgment 335
		References 335
	11	Graphenes in Supramolecular Gels and in Biological Systems 339 Santanu Bhattacharya and Suman K. Samanta
	11.1	Introduction 339
	11.1.1	Overview of 2D-Nanomaterials 339
	11.1.2	Overview of Physical Gels 339
	11.1.3	Different Types of Graphenes, Their Preparation, Functionalization,
		and Gelation 340
	11.2	Toward the Gelation of GO 341
	11.2.1	Effect of pH on the Gelation of GO 342
	11.2.2	Effect of the Dimension of GO toward Gelation 343
	11.2.3	Cross-Linker (Small Molecule/Polymer)-Induced GO Gels 343
	11.2.4	Cation-Induced GO Gels 345
	11.2.5	Surfactant-Induced GO Gels 346
	11.2.6	Ionic-Liquid-Induced GO Gels 347
	11.2.7	Gelation of Hemoglobin by GO and Sensing 347