Advanced Materials Series

Graphene Materials

Fundamentals and Emerging Applications

Edited by

Ashutosh Tiwari

Mikael Syväjärvi

Scrivener Publishing

WILEY

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Co-published by John Wiley & Sons, Inc. Hoboken, New Jersey, and Scrivener Publishing LLC, Salem, Massachusetts.
Published simultaneously in Canada.

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Cover design by Russell Richardson

Library of Congress Cataloging-in-Publication Data:

ISBN 978-1-118-99837-3

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

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Scrivener Publishing
100 Cummings Center, Suite 541J
Beverly, MA 01915-6106

Advanced Materials Series

The Advanced Materials Series provides recent advancements of the fascinating field of advanced materials science and technology, particularly in the area of structure, synthesis and processing, characterization, advanced-state properties, and applications. The volumes will cover theoretical and experimental approaches of molecular device materials, biomimetic materials, hybrid-type composite materials, functionalized polymers, supramolecular systems, information- and energy-transfer materials, biobased and biodegradable or environmental friendly materials. Each volume will be devoted to one broad subject and the multidisciplinary aspects will be drawn out in full.

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Preface

Graphene materials constitute probably the most focused arena of materials research in the present decade because of their involvement with fundamental phenomena from the fields of physics, chemistry, biology, applied sciences and engineering. As the first atomic-thick two-dimensional crystalline material, graphene has continuously created a wonderland in nanomaterials and nanotechnology. A number of methods have been developed for the preparation and rendering functional of single-layered graphene nanosheets, the essential building blocks for the bottom-up architecture of various graphene materials. They possess unique physico-chemical properties including large surface area, good conductivity and mechanical strength, high thermal stability and desirable flexibility. Altogether they create a new type of super-thin phenomenon, highly attractive for a wide range of applications. The electronic behaviour in graphene such as Dirac fermions obtained due to the interaction with the ions of the lattice has led to the discovery of novel miracles like Klein tunneling in carbon based solid state systems and the so-called half-integer quantum Hall effect due to a special type of Berry phase. This book entitled, **Graphene Materials: Fundamentals and Emerging Applications** proposes a detailed up-to-date chapters on the processing, properties and technology developments of graphene materials including multifunctional graphene sheets, surface functionalization, covalent nanocomposites, reinforced nanoplatelets composites etc. for a wide range of applications.

Graphene has created a profound interest in two-dimensional materials properties. Graphene oxide has shown to be possible to reproduce in large quantities, but still the properties for its fabrication needs to be understood in order to have reproducible material quality. Still it is not clear what type of two dimensional materials will be best for various applications. Other two dimensional materials may be better suited regarding certain applications, and therefore should be understood more in detail. In addition, hybrids and two dimensional materials can results in extended properties.

Chapter 1 presents fabrication of graphene oxide and two dimensional materials, like tin selenides, SnS_2, MnO_2, NO BN, MoS_2 and WS_2, the latter which can tune electrical properties from metallic and semiconducting by changing the crystal structure and the amount of layers, but it may also act as a lubricant material for use in high temperature and high pressure applications. In comparison, MoS_2 is one of the transition metal dichalcogenides and applicable as battery, electrochemical capacitor, memory cell, catalysts, and composite. The chapter also introduces the concept of WS_2 nanosheets hybridized with reduced graphene oxide nanosheets to achieve a good catalytic activity.

Novel features may be obtained combining graphene nanosheets and graphene oxide with other new nanomaterials such as magnetic nanoparticles, carbon dots, carbon nanotubes, nanosemiconductors, quantum dots. The requirement is that the graphene surfaces must be rendered functional. The noncovalent and covalent functionalization of graphene nanosheets and graphene oxide are presented in **Chapter 2**. Noncovalent functionalization involves hydrophobic, π-π, Van der Waals, and electrostatic interactions. In this, there is a physical adsorption of suitable molecules on the graphene surface. Covalent functionalization can take place at the end of the sheets and/or on the surface. The combination of inorganic nanoparticles with graphene oxide may be either as a pre-graphenization (graphene oxide is mixed with the nano particles) or post-graphenization (where nanosheets and graphene oxide are prepared separately) process. The functionalized graphene nanosheets may be applied into three-dimensional porous graphene networks that have large surface areas, good conductivity and mechanical strength, high thermal stability and flexibility.

In **Chapter 3**, the most widely-used methods for assembling three-dimensional porous graphene networks and their structural characteristics are presented. Examples are given of their applications in sensors and energy devices. Graphene-based composites have a large specific surface area, porous structure, and fast electron transport kinetics, providing unique physicochemical properties that are mechanically robust, with high conductivity and thermal stability combined with fast mass and electron transport properties. The challenges lie in controlling pore size and functionality so as to enjoy flexibility in the development of frameworks for mechanically robust materials while maintaining structural integrity, stability and conductivity.

Graphene-based nanocomposites may act as both graphene filler and polymer host. These are known for their enhanced performance in many applications such as flexible packaging, structural components for transportation or energy storage, memory devices, hydrogen storage and printed electronics. Polymers covalently reinforced with graphene may be best when homogeneously dispersed in the matrix with a strong filler/polymer interface without phase segregation, especially in direct covalent binding between polymers and graphene. The *grafting-from* (graphene as a macromolecular initiator for growing polymer brushes from its surface) and *grafting-to* (combining graphene and polymers through a chemical reaction) approaches to bind polymers to graphene are presented in **Chapter 4**.

In **Chapter 5**, metal matrix composites, often used in aerospace and automobile industries, are investigated using graphene and magnesium matrix composites reinforced with graphene nanoplatelets. The mechanical properties of Mg-graphene composites show that there is a poor response of graphene nanoplatelet additions on tensile strength of pure Mg matrix, while addition of graphene nanoplatelets into Mg alloys matrix leads to significant improvement in mechanical strength. In addition, there is higher tensile failure strain in the synergetic effect of graphene and carbon nanotubes in the Mg-1Al alloy matrix relative to those reinforced with individual graphene nanoplatelets and multi-wall carbon nanotubes.

The increase in energy saving need pushes the graphene to be explored in batteries and supercapacitors. Graphene with its electron transfer behavior and unique two-dimensional surface is acknowledged as a potential electrode material. This becomes attractive since graphene improves conductivity, charge rate, energy capacity. The excellent chemical stability, high electrical conductivity, and large surface area of graphene makes it attractive in reduction of volume expansion of electrode materials in lithium batteries and graphene-based supercapacitors which may exhibit high storage capacity, fast energy release, quick recharge time, and a long lifetime. **Chapter 6** furnishes insights in intrinsic challenges of poor kinetics, large volume expansion, and dissolution of polysulfides in the electrolyte in graphene based batteries, and V_2O_5/reduced graphene oxide nanocomposites, Co_3O_4 nanoplates/reduced graphene oxide composites and graphene/NiO as well as graphene–MnO_2 hybrids together with some other material approaches as electrode materials for supercapacitors. The poor stability of conducting polymers during charging/discharging is a major challenge in high power supercapacitors. In addition, the low conductivity of conducting polymer also results in high ohmic polarization and a declining reversibility and stability.

Chapter 7 presents conducting polymers including polypyrrole, polyaniline and polyethenedioxythiophene with superior electrical conductivity and large pseudo capacitance have aroused great interest as electrode materials for supercapacitors as a consequence of their high conductivity and fast redox electroactivity.

Chapter 8 deals with ZnO/graphene nanocomposite-based bulk hetero-junction solar cells, deliberating upon carrier diffusion length, recombination losses, device architect limitations, efficient charge separation and transport to respective electrodes and possible restriction of organic photovoltaic efficiency, dielectric constant value and charge carrier mobility.

Bimetallic nanocatalysts may give a large surface excellent dispersion and high degrees of sensitivity. **Chapter 9** describes hierarchically-structured platinum–ruthenium nanoparticles incorporated in three-dimensional graphene foam as electrode materials for fuel cells with enhanced performance by decreasing particle size, increasing number of active sites for methanol or ethanol, and increasing the resistance against CO poisoning, as well as detection of H_2O_2 in biosensing by Pt active binding sites that are able to interact with H_2O_2 to enhance the catalytic activity of the H_2O_2 detection. Graphene and graphene-based nanocomposites may be platforms for electrochemical sensing and biosensing. These can lead to biosensors with superior analytical performance, high sensitivity, low detection limit, high precision, high specificity, low working potentials and prolonged stability.

Direct electrochemical detection or enzymeless sensing of glucose is feasible using nanocomposites of graphene decorated with metal nano particles and nanowires that can be operated at low applied potentials. In particular, graphene with exposed edge-like planes offers several advantages over other electrode materials for the catalytic oxidation of the DNA bases, as described in **Chapter 10**. This has also been used to demonstrate how graphene can be used as a biocompatible substrate to enhance cell adhesion and growth to form a basis for the detection of cells.

Chapter 11 describes graphene approaches that have been adopted for improving the performance of graphene nanomaterials-based miniaturized electrochemical biosensors that may be binding of various enzymes. This may lead to utilizing graphene as a transducer in bio-field-effect transistors, electrochemical, impedimetric, electrochemiluminescence, and fluorescence biosensors, as well as biomolecular labels. Further on, graphene-nanostructured biosensors have broad applicability for environmental monitoring purposes, particularly in toxic gases, heavy metal ions and organic pollutants detection.

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February 2015

Foreword

Graphene is a monolayer of carbon atoms in a densely-packed two-dimensional (2D) honeycomb crystal structure. It can be considered a building block of three-dimensional (3D) graphite, quasi one-dimensional (1D) carbon nanotubes and quasi zero-dimensional (0D) fullerenes. Graphene is a semi-metal with a tiny overlap between the valence and the conduction band (zero-gap semiconductor). Graphene was not known to exist in an isolated form until 2004. Before that, it was known to exist only in the 1D or 0D form, or even better known in its 3D structure as graphite, which consists of graphene sheets with strong in-plane bonds and weak van der Waals-like coupling between layers. Moreover, it was presumed, that a single 2D graphene sheet would be thermodynamically unstable. Only in 2004, researchers from Manchester — Kostya Novoselov and Andre Geim — demonstrated that it is indeed possible to realize stable single and few layer graphene sheets. They were awarded the Nobel Prize in Physics 2010 for groundbreaking experiments regarding the two-dimensional material graphene. Graphene was first obtained by delicately cleaving a sample of graphite with sticky tape.

The direct observation of the isolated graphene monolayer has sparked exponentially growing interest. Just a few years were enough to gather several scientific communities to investigate the properties of this unusual material. About 3500 scientific articles were published in 2010. Owing to its peculiar electronic behavior under magnetic field and at low temperature, graphene has attracted the curiosity of mesoscopic physicists. The investigation and tailoring of its transport properties from macroscopic to molecular scales captures a large share of the current research effort. Materials scientists have rapidly grabbed some of the assets of graphene and are already exploring the ways of incorporating graphene into applied devices and materials.

Because of its linear energy–momentum dispersion relations, which cross at the Dirac point, graphene holds open great promise for future electronics technology as well as fundamental physics applications. Two of the most extraordinary properties of graphene are its absolute two-dimensionality and the behavior of its charge carriers as Dirac particles, which obey the Dirac equation rather than usual Schrödinger equation. As a result, many well-known effects in the field of solid state physics are expected to be modified.

Graphene's exceptional electronic properties (e.g. high carrier mobility) along with transparency make it an extremely attractive material candidate for a wide range of applications - in electronics, optoelectronics, sensing and fundamental studies of the way electrons behave when confined in two dimensions. Concomitantly, the light weight, mechanical strength and high conductivity of graphene are perfectly suited for composite and light polymer materials.

Graphene can be fabricated by many different ways: from exfoliation to chemical synthesis and thermal decomposition of SiC exploiting solid, liquid or vapor phase. The thinnest-ever crystal graphene is a versatile material promising many applications for mankind's benefit. These will contribute to the solution of existing acute problems related to health, energy saving and ecology. Depending on targeted applications different types of graphene are used. In this book, the reader will find useful information on most of these aspects.

November 27, 2014
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Linköping, Sweden

Rositsa Yakimova is Professor Emerita in material science, Linköping University. She is an internationally recognized expert in the field of semiconductor crystal and nanostructure growth. Since 1993 she has had a substantial contribution to the development of the sublimation growth process of SiC. Her major efforts recently have been in research of graphene on SiC. Yakimova has pioneered a novel method for fabrication of large area uniform epitaxial graphene on SiC and since 2008 she is leading the research of graphene on SiC at Linköping University.

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