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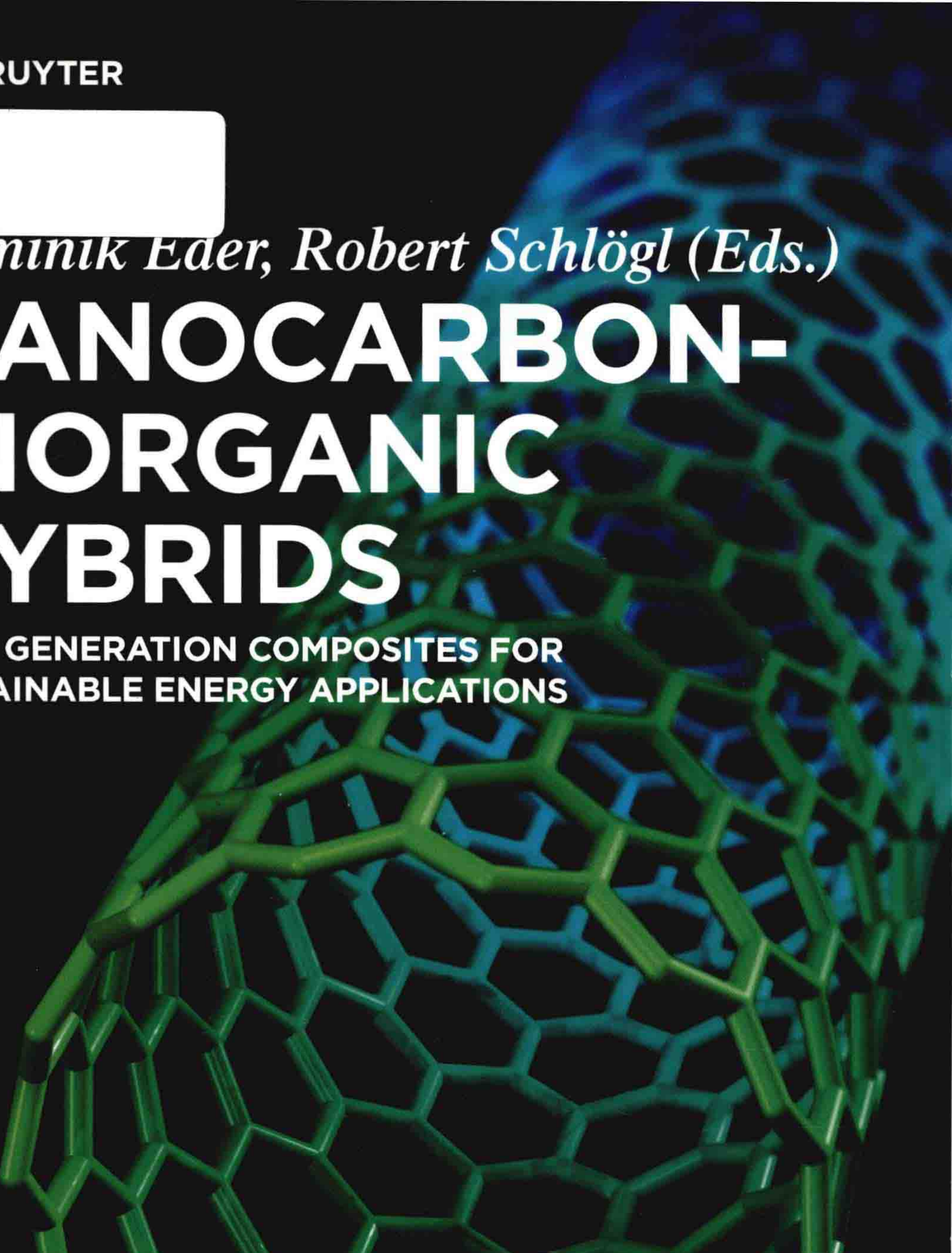

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Next Generation Composites for Sustainable Energy Applications

Edited by
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ISBN 978-3-11-026971-0
e-ISBN 978-3-11-026986-4
Set-ISBN 978-3-11-026987-1

Library of Congress Cataloging-in-Publication Data
A CIP catalog record for this book has been applied for at the Library of Congress.

Bibliographic information published by the Deutsche Nationalbibliothek
The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available in the Internet at http://dnb.dnb.de.

Cover image: Simone Brandt/gettyimages/creative
Typesetting: PTP-Berlin, Protago-TEX-Production GmbH, Berlin
Printing and binding: Hubert & Co. GmbH & Co. KG, Göttingen
♾Printed on acid-free paper
Printed in Germany

MIX
Papier aus verantwortungsvollen Quellen
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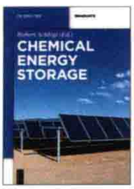

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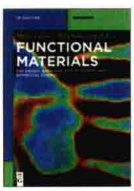

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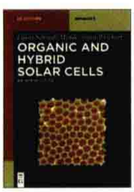

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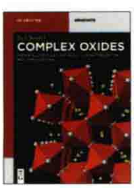

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ISSN 1869-8778

Preface

Today's world is facing major challenges that directly affect our modern life. The demand for energy is expected to double by the year 2050. As a consequence of increased energy utilization the need is growing to protect our environment from the adverse effects of pollution and the destruction of natural habitats. To ensure sufficient supply of clean water and air and to nourish the growing population without conflicts and poverty are additional global challenges. In this arena, the transformation of the fossil energy system into a sustainable operation and the technical increase of energy efficiency are key objectives of chemical sciences with their ability to create novel fuels, materials and processes of molecular transformations. Using the energy of sunlight to split water into hydrogen as a clean energy source and storing energy in batteries and supercapacitors are two popular examples of energy science. Both challenges critically involve the availability of novel carbon materials. Carbon is the most versatile chemical element for designing molecules and materials. It enables us to address a wide range of functional characteristics by varying the assembly of only one type of atoms interacting with each other in essentially only two binding modes, i.e. sp^2/sp^3 hybridization.

The unlimited number of combinations of the two basic bonding motives allows the realization of molecular and supra-molecular properties limited only by our imagination. Hetero-atomic additions to the carbon backbone give additional chemical and structural diversity that needs exploitation in interface-controlled material science applications. The interplay between combining building blocks of carbon and decorating the products with hetero-elements forms the basis of a knowledge-based carbon material science. A critical strategy of material design is to combine carbon with other materials with diverging properties into spatial arrangements that create synergistic functions. Such materials, known as composites, were developed for carbon-based systems with the maturation of polymer science and are implemented today in numerous products ranging from materials for packaging, dental and medical use, energy production and storage, to structural materials for lightweight applications.

Nanocarbon composites are multiphase materials, in which a nanostructured *filler* (*i.e.* particles, whiskers, fibers, nanotubes or lamellae) is dispersed in an organic (*i.e.* polymer) or inorganic (*i.e.* carbon, ceramic or metal) *matrix*. In the last few years, carbon in the form of nanotubes (CNTs) in addition to nanostructured fibers or as graphene has attracted wide interest as a filler for nanocomposites. Typical application profiles are a high electrical conductivity in transparent conducting polymers or a remarkable fracture toughness reinforcing ceramics such as hydroxyapatite for bone replacement. Nanocomposites have a considerable impact on large-scale industrial applications of lightweight structural materials in aerospace and e-mobility, of electrically conducting plastics for electronic applications or as packaging materials with reduced gas permeability for foodstuff and air-sensitive goods.

Nanocarbon hybrids are a new class of composite materials in which the carbon nanostructures are compounded with thin layers of metals, semiconductors, inorganic glasses or ceramics. The carbon component gives ready access for gases and fluids to a large fraction of the inner surface area of the inorganic compound. In addition, a large interface between two materials with different bulk properties allows for the design of materials with interface-dominated properties. Their special appeal arises from charge and energy transfer through this interface, giving rise to transport properties different from the linear combination of the respective bulk properties. Although still at an early stage of research, such hybrid materials have demonstrated potential in applications concerning energy conversion and environmental protection. These include improved sensitivities in bio/chemical sensors, increased energy densities in batteries and larger capacities in supercapacitors, higher currents in field emission devices, more efficient charge separation and thus superior activities in photocatalysts and improved efficiencies in photovoltaics.

This book is dedicated exclusively to the family of nanocarbon hybrids covering a multidisciplinary research field that combines materials chemistry and physics with nanotechnology and applied energy sciences. It provides both introductory material on fundamental principles as well as reviews of the current research. Therefore, this book should be helpful for Master and PhD students wishing to become familiar with a modern field of knowledge-driven material science as well as for senior researchers and industrial staff scientists who explore the frontiers of knowledge.

The **first part of this book** introduces the concept of nanocarbons as building blocks. It establishes a scientific foundation for their subsequent use in hybrids and composites. *Chapter 1* provides a concise introduction into the world of carbon nanotubes (CNTs), explaining their unique structural characteristics, synthesis routes and key characterization techniques. It summarizes the profile of exceptional properties of CNT. *Chapter 2* concentrates on the synthesis and characterization of graphene-based materials, including single-layer and few-layer graphene as well as graphene oxide and its chemically/thermally reduced counterpart. The chapter further demonstrates that the dispersion of nanocarbons remains a key challenge for their implementation into hybrids. Chapters 3 and 4 are dedicated to the post-synthesis processing of nanocarbons. In particular, *Chapter 3* focuses on the chemical functionalization of CNTs, providing examples for a whole range of covalent and noncovalent functionalization routes. *Chapter 4* offers a comprehensive review on doping and filling of CNTs and the effect of defects on the hybridization of CNTs with polymers.

The **second part of this book**, comprising Chapters 5 to 10, is dedicated to the synthesis of nanocarbon hybrids and composites. *Chapter 5* begins by identifying the general synthesis routes towards nanocarbon hybrids, which can be categorized into *ex situ* (*i.e.* "building block") and *in situ* approaches, and comparing their advantages and disadvantages on the basis of some of the most intriguing recent results. In general, the *ex situ* route is a two-step process in which the inorganic compound is synthesized first, taking advantage of the existing wealth of knowledge in synthesizing nanomaterials (*i.e.* structure-property relationship). In a second step, the inorganic compound is linked to the nanocarbon surface via covalent, noncovalent or electrostatic interactions. In the *in situ* approach the inorganic or polymeric compound is grown on the (modified) nanocarbon surface from molecular precursors via (electro)chemical, vapor-based or physical deposition techniques, exploiting the stabilizing effects of nanocarbon as templates and as local heat sinks.

The examples discussed in *Chapter 5* cover a wide range of synthetic aspects, yet concentrate on hybrids involving CNTs, while *Chapter 6* summarizes recent developments on the hybridization of graphene-based materials. *Chapter 7* on the other hand introduces sustainable carbon materials made from hydrothermal carbonization (HTC) as promising candidates for hybrid materials. *Chapter 8* then combines nanocarbons with polymers and documents that engineering the interfaces is a challenge that is equally important in the synthesis of nanocarbon hybrids and of carbon composites. The book section is concluded by *Chapters 9 and 10*, which are dedicated to specific examples of hybrids. Chapter 9 describes hybrids whose components are all carbon based, such as CNTs hybridized with graphene, while Chapter 10 discusses the incorporation of graphene oxide into metal-organic framework structures (MOFs).

The **third part of the book** highlights the potential of nanocarbon hybrids for various important applications, particularly concerning environmental and sustainable energy applications. These include electrode materials in batteries and electrochemical capacitors (*Chapters 11 and 12*), sensors and emitters in field emission devices (*Chapter 13*), electrocatalysts in fuel cells (*Chapter 14*), supports for heterogeneous catalysts (*Chapter 15*), next-generation photocatalysts (*Chapter 16*), as well as active compounds in electrochromic and photovoltaic applications (*Chapters 17 and 18*). All these chapters discuss the benefits of nanocarbon hybrids in the respective application, identify major challenges and critically review the present state of research with the most intriguing recent developments. Finally, *Chapter 19* elaborates on the importance of defects and edge atoms in graphene-based hybrid materials.

This book illustrates that nanocarbon hybrid materials are an exciting new class of multi-purpose composites with great potential to become the next-generation energy materials. The synergistic effects in nanocarbon hybrids are manifold and it is clear that a detailed fundamental understanding of their origins will be essential to exploit the options given by combining classes of materials with diverging properties.

We foremost express our deepest thanks to our colleagues who spent considerable time and effort in writing the chapters in this book. We hope that this book will be useful to those interested in the subject of nanocarbon hybrids from many different perspectives and that it will establish a sound foundation for future research. We further would like to thank Julia Lauterbach and Karin Sora of De Gruyter Publishers for their tireless support and guidance. It is a particular pleasure to acknowledge the students of the Münster group for their invaluable help in proof-reading.

June 2014 Dominik Eder and Robert Schlögl

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