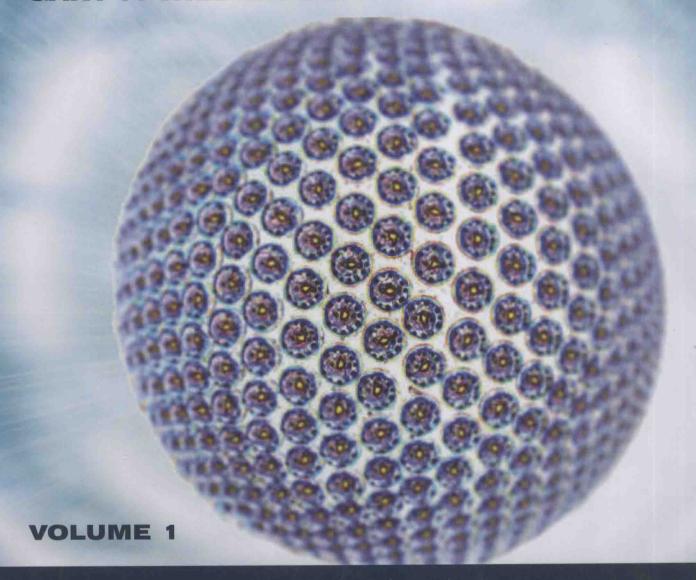
DAVID L. ANDREWS
GREGORY D SCHOLES
GARY P. WIEDERRECHT



COMPREHENSIVE NANOSCIENCE AND TECHNOLOGY

NANOMATERIALS



COMPREHENSIVE NANOSCIENCE AND TECHNOLOGY

Editors-in-Chief

David L. Andrews

School of Chemical Sciences, University of East Anglia, Norwich, UK

Gregory D. Scholes

Department of Chemistry, University of Toronto, Toronto, ON, Canada

Gary P. Wiederrecht

Center for Nanoscale Materials, Argonne National Laboratory, Argonne, IL, USA



School of Chemical Sciences, University of East Anglia, Norwich, UK

Zeev Valentine Vardeny

University of Utah, Salt Lake City, UT, USA

Duncan H. Gregory

University of Glasgow, Glasgow, UK

Thomas Nann

University of East Anglia, Norwich, UK





Academic Press is an imprint of Elsevier 32 Jamestown Road, London NW1 7BY, UK 30 Corporate Drive, Suite 400, Burlington MA 01803, USA 525 B Street, Suite 1900, San Diego, CA 92101-4495, USA

First edition 2011

Copyright © 2011 Elsevier B.V. All rights reserved

The following articles are US Government works in the public domain and are not subject to copyright:

QUANTUM DOTS: THEORY, SURFACE NANOPHOTONICS THEORY, COLLOIDAL SEMICONDUCTOR

NANOCRYSTAL-ENABLED ORGANIC/INORGANIC HYBRID LIGHT EMITTING DEVICES

Notice

No responsibility is assumed by the publisher for any injury and/or damage to persons or property as a matter of products liability, negligence or otherwise, or from any use or operation of any methods, products, instructions or ideas contained in the material herein. Because of rapid advances in the medical sciences, in particular, independent verification of diagnoses and drug dosages should be made

British Library Cataloguing in Publication Data

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

Library of Congress Control Number: 2010935386

ISBN: 978-0-12-374390-9

For information on all Elsevier publications visit our website at elsevierdirect.com

Printed and bound in Spain

11 12 13 14 10 9 8 7 6 5 4 3 2 1

Working together to grow libraries in developing countries

www.elsevier.com | www.bookaid.org | www.sabre.org

ELSEVIER

BOOK AID

Sabre Foundation

Editorial: Donna De Weerd-Wilson, Fiona Geraghty Production: Laura Jackson

COMPREHENSIVE NANOSCIENCE AND TECHNOLOGY

Editors-in-Chief Biographies



David Andrews is Professor of Chemical Physics at the University of East Anglia, where he leads a theory group conducting wide-ranging research on fundamental photonics, fluorescence and energy transport, nonlinear optics and optomechanical forces. He has 250 research papers and ten other books to his name, and he is a regularly invited speaker at international meetings. In North America and Europe he has organized and chaired numerous international conferences on nanoscience and technology. Professor Andrews is a Fellow of the Royal Society of Chemistry, the Institute of Physics, and the SPIE – the international society for optics and photonics. In his spare time he enjoys relaxing with family and friends; he also is a keen painter of the British landscape. His other interests generally centre on music, art and graphics, and writing.



Greg Scholes is a Professor at the University of Toronto in the Department of Chemistry. His present research focuses on elucidating the principles deciding electronic structure, optical properties, and photophysics of nanoscale systems by combining synthesis, theory, and ultrafast laser spectroscopy. Recent awards honoring his research achievements include election to the Academy of Sciences, Royal Society of Canada in 2009, the 2007 Royal Society of Canada Rutherford Medal in Chemistry, a 2007 NSERC Steacie Fellowship, the 2006

Canadian Society of Chemistry Keith Laidler Award, and an Alfred P. Sloan Fellowship (2005–2006). Dr. Scholes serves as a Senior Editor for the Journal of Physical Chemistry and Associate Editor for the Journal of Nanophotonics. He enjoys basketball, hiking, photography, family and friends.



Gary Wiederrecht is the Group Leader of the Nanophotonics Group in the Center for Nanoscale Materials at Argonne National Laboratory. His research interests center on the photochemistry and photophysics of nanoparticles and periodic assemblies, hybrid nanostructures, photochemical energy conversion, and nonlinear optical responses resulting from photoinduced charge separation. His experimental expertise is in the areas of ultrafast optical spectroscopy and scanning probe microscopy, including near-field scanning optical microscopy. He has received an R&D100 award, the Department of Energy Young Scientist Award, and the Presidential Early Career Award for Scientists and Engineers. He has authored or co-authored approximately 80 peer-reviewed research articles, and works collaboratively with scientists around the world. He enjoys traveling, nature, and spending time with his family.

VOLUME EDITORS

Alexandre Bouhelier

Insititut Carnot de Bourgogne, Université de Bourgogne, Dijon, France

Frank Caruso

The University of Melbourne, Parkville, VIC, Australia

Duncan H. Gregory

University of Glasgow, Glasgow, UK

Brent P. Kreuger

Hope College, Holland, MI, USA

Thomas Nann

University of East Anglia, Norwich, UK

Teri W. Odom

Northwestern University, Evanston, IL, USA

John C. Polanyi

University of Toronto, Toronto, ON, Canada

John A. Rogers

University of Illinois, Urbana, IL, USA

Takao Someya

The University of Tokyo, Tokyo, Japan

Yugang Sun

Center for Nanoscale Materials, Argonne National Laboratory, Argonne, IL, USA

Rienk Van Grondelle

VU University, Amsterdam, The Netherlands

Zeev Valentine Vardeny

University of Utah, Salt Lake City, UT, USA

Gilbert C. Walker

University of Toronto, Toronto, ON, Canada

List of Contributors to Volume 1

Y. Chao

University of East Anglia, Norwich, UK

R. R. Cooney

McGill University, Montreal, QC, Canada

D. Dorfs

Istituto Italiano di Tecnologia, Genoa, Italy

B. Engels

University of Würzburg, Würzburg, Germany

A. Falqui

Istituto Italiano di Tecnologia, Genoa, Italy

R. F. Fink

University of Würzburg, Würzburg, Germany

C. Frandsen

Technical University of Denmark, Kongens Lyngby, Denmark

C. Giannini

CNR-Istituto di Cristallografia (IC), Bari, Italy

A. Govindaraj

Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, India

M. F. Hansen

Technical University of Denmark, Kongens Lyngby, Denmark

F. Hubenthal

Universität Kassel, Kassel, Germany

S.-H. Jang

University of Washington, Seattle, WA, USA

A. K.-Y. Jen

University of Washington, Seattle, WA, USA

P. Kambhampati

McGill University, Montreal, QC, Canada

R. Krahne

Istituto Italiano di Tecnologia, Genoa, Italy

S. Kudera

Max Planck Institute for Metals Research, Stuttgart, Germany

G. Lanzani

Italian Institute of Technology, Milano, Italy

W. Liu

University of Würzburg, Würzburg, Germany

X. Liu

National University of Singapore, Singapore

L. Lüer

Madrid Institute for Advanced Studies, IMDEA Nanociencia, Madrid, Spain

H. S. Majumdar

Abo Akademi University, Turku, Finland

S. Majumdar

Abo Akademi University, Turku, Finland

L. Manna

Istituto Italiano di Tecnologia, Genoa, Italy

L. Maus

Max Planck Institute for Metals Research, Stuttgart, Germany

Z. Mi

McGill University, Montreal, QC, Canada

S. Mørup

Technical University of Denmark, Kongens Lyngby, Denmark

Y. Nosaka

Nagaoka University of Technology, Nagaoka, Japan

M. Ohtsu

The University of Tokyo, Tokyo, Japan

R. Österbacka

Abo Akademi University, Turku, Finland

W. J. Parak

Philipps Universität Marburg, Marburg, Germany

J. Pfister

University of Würzburg, Würzburg, Germany

R. C. Polson

University of Utah, Salt Lake City, UT, USA

C. N. R. Rac

Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, India

M. Remskar

Jozef Stefan Institute, Ljubljana, Slovenia

V. Settels

University of Würzburg, Würzburg, Germany

J. Shinar

Ames Laboratory, USDOE and Iowa State University, Ames, IA, USA

R. Shinar

Iowa State University, Ames, IA, USA

Z. V. Vardeny

University of Utah, Salt Lake City, UT, USA

S. R. C. Vivekchand

Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, India

N. Vukmirović

Lawrence Berkeley National Laboratory, Berkeley, CA, USA

F. Wang

National University of Singapore, Singapore

L.-W. Wang

Lawrence Berkeley National Laboratory, Berkeley, CA, USA

T. Yatsui

The University of Tokyo, Tokyo, Japan

G.-C. Yi

Seoul National University, Seoul, Republic of Korea

D. Zanchet

Laboratório Nacional de Luz Síncrotron, Campinas-SP, Brazil

M. Zanella

Philipps Universität Marburg, Marburg, Germany

H.-M. Zhao

University of Würzburg, Würzburg, Germany

Contents of All Volumes

Volume 1

Nanomaterials

- 1.01 Electronic Structure of Organic Materials Investigated by Quantum Chemical Calculations
- 1.02 Carbon Nanotubes: Electronic Structure and Spectroscopy
- 1.03 Laser Action in Organic Semiconductors
- 1.04 An Overview of Organic Light-Emitting Diodes and their Applications
- 1.05 Organic Spintronics
- 1.06 Structured Organic Non-Linear Optics
- 1.07 Quantum Dots: Theory
- 1.08 Quantum Dots: Synthesis and Characterization
- 1.09 Core-Shell Nanocrystals
- 1.10 Inorganic Nanowires
- 1.11 Inorganic Nanotubes beyond Cylindrical Matter
- 1.12 ZnO Nanorods and their Heterostructures for Electrical and Optical Nanodevice Applications
- 1.13 Noble Metal Nanoparticles: Synthesis and Optical Properties
- 1.14 Magnetic Nanoparticles
- 1.15 Colloidal and Self-Assembled Quantum Dots for Optical Gain
- 1.16 Optical Properties of Nanostructured Silicon
- 1.17 Solar Cells and Photocatalysts
- 1.18 Rare-Earth Doped Upconversion Nanophosphors

Volume 2

Biological Nanoscience

- 2.01 Nanoparticles for Photodynamic Therapy
- 2.02 Energy Transfer in Photosynthetic Light-Harvesting Complexes: From Spectroscopy to Quantitative Models
- 2.03 Photonic Nanoparticles for Cellular and Tissular Labeling
- 2.04 DNA-Conjugated Nanomaterials for Bioanalysis
- 2.05 Förster Resonance Energy Transfer
- 2.06 Chemistry and Materials Development of Protein-Based Nanoparticles
- 2.07 Tissue Engineering
- 2.08 Engineering Biomimetic Membranes with Hydrogels
- 2.09 Protein Nanomechanics
- 2.10 Biological Imaging Using Near-Field Scanning Optical Microscopy
- 2.11 Single-Molecule and Nanoscale Approaches to Biological Signaling
- 2.12 Solar Energy Conversion Natural to Artificial

Volume 3

Nanostructured Surfaces

- Catalysis by Supported Gold Nanoparticles
- Directed Assembly of Nanostructures 3.02
- Bio-Mediated Assembly of Ordered Nanoparticle Superstructures 3.03
- Chiral Molecules on Surfaces 3.04
- Optics of Metallic Nanostructures 3.05
- Surface Nanophotonics Theory 3.06
- Constructing and Enhancing the Superior LED: Photonic Crystal and Photonic Band-Gap 3.07 Structures for Light Extraction and Emission Control
- 3.08 Liquid-Crystalline Nanostructured Optical Metamaterials
- 3.09 Nanostructures and Surface-Enhanced Raman Spectroscopy
- Nanostructured Superconductors with Efficient Vortex Pinning 3.10
- Second Harmonic Generation in Nanostructures 3.11
- 3.12 Tribology of Nanostructured Surfaces
- 3.13 Nanotribology and Nanoscale Materials Coatings for Lubricants
- Functionalization and Solubilization of Carbon and Inorganic Nanostructures 3.14

Volume 4

Nanofabrication and Devices

- 4.01 Scanning Probe-Based Lithography for Production of Biological and Organic Nanostructures on Surfaces
- 4.02 Electron Beam Lithography of Nanostructures
- Sub-Micrometer Patterning Using Soft Lithography 4.03
- 4.04 Status of UV Imprint Lithography for Nanoscale Manufacturing
- Picoliter Printing 4.05
- 4.06 Molecular Printboards: From Supramolecular Chemistry to Nanofabrication
- 4.07 Colloidal Semiconductor Nanocrystal-Enabled Organic/Inorganic Hybrid Light **Emitting Devices**
- 4.08 The Use of Aluminum Nanostructures in Plasmon-Controlled Fluorescence Applications in the Ultraviolet Toward the Label-Free Detection of Biomolecules
- Quantum Dot Solar Cells 4.09
- 4.10 Femtosecond-Laser-Induced Periodic Self-Organized Nanostructures
- 4.11 Nanofluidics
- 4.12 Molecular Machines and Motors
- 4.13 Superhydrophobicity at Micron and Submicron Scale
- 4.14 Organic Electronic Devices with Water-Dispersible Conducting Polymers
- III-V and Group-IV-Based Ferromagnetic Semiconductors for Spintronics 4.15
- 4.16 Electronic Properties of Alkanethiol Molecular Junctions: Conduction Mechanisms, Metal-Molecule Contacts, and Inelastic Transport
- 4.17 Nanoscale Transistors
- 4.18 Spin-Based Data Storage
- 4.19 Optical Holographic Data Storage

Volume 5

Self-Assembly and Nanochemistry

- 5.01 Porous Metal-Organic Frameworks
- 5.02 Ligands for Nanoparticles
- Assembly of Nanoparticles 5.03
- 5.04 Periodic Mesoporous Materials: Holes Filled with Opportunities

- Self-Assembled Monolayers 5.05
- 5.06 Nanocrystal Synthesis
- Self-Assembly of Nanoparticle Building Blocks 5.07
- Chemical Processing of Assembled Block Copolymers 5.08
- 5.09 Biotemplated Semiconductor Nanocrystals
- 5.10 Polymer-Layered Silicate Nanocomposites
- 5.11 Mesogens and Mesophases
- Layer-by-Layer Assembled Capsules for Biomedical Applications 5.12
- Functionalized Fullerenes: Synthesis and Functions 5.13
- Microemulsion Preparative Methods (Overview)
- 5.15 Nanotechnology, Society, and Environment

Subject Index

Preface

Volume 1: Nanomaterials

This volume considers the enormous and significant changes that have occurred in the recently emergent and now rapidly maturing fields of organic and inorganic nanomaterials. Neatly bridging the gap between nanoscience and nanotechnology, such materials now find application from functional materials in electronics, photonics and spintronics, through energy conversion and storage materials to structural materials and nanocomposites. The themes explored in this volume are dominated by the former two categories of nanomaterials and the fertile border territory between nanoscale condensed matter physics, chemical nanoscience, and nano-fabrication and nano-engineering.

The field of organic optoelectronics has progressed enormously in recent years as a result of frenetic activity in many research groups around the world. Major advances have been made both in the fields of device science and fabrication, as well as in the underlying chemistry, physics, optics, and materials science. The impact of this field continues to influence many adjacent disciplines - and especially nanomaterial technology, the focus of this volume. The first six chapters demonstrate how advances in organic optoelectronic materials have inspired a vital and growing interest in fundamental organic materials research - notably in connection with carbon nanotubes - that could potentially revolutionize a range of future applications. Examples in the area of organic nonlinear optics are discussed by Jang and Jen (Chapter 1.06). It is expected that the present worldwide funding in this field will stimulate a major research and development effort in organic materials research for lighting, photovoltaics, spintronics, and other optoelectronic applications. Organic light-emitting diodes (OLEDs), described by Shinar and Shinar (Chapter 1.04), were introduced to the scientific community about two decades ago and permeated to the market about ten years later. A bright future awaits organic white-light-emitting diodes, which are emerging as viable replacements for the classic Edison-type light bulb. It is salutary to remember that laser action in organics, a subject addressed by Polson and Vardeny (Chapter 1.03), was first revealed as recently as 1996. The initial enthusiasm paved the way for current, realistic expectations on the fabrication of current-injected organic laser action.

Until a few years ago, electron spin was ignored in organic electronics. However, in 2002, with the achievement of substantive magnetoresistance in a two-terminal organic device at room temperature, a new field was born, namely organic spintronics (Chapter 1.05). The associated technology of spin-based electronics, where carrier spin is used as information carrier in addition to charge, offers opportunities for a new generation of electronic devices that combine standard microelectronics with spin-dependent effects arising from interactions between the carrier spin and externally applied magnetic fields. Adding the spin degree of freedom to more conventional charge-based electronics should substantially increase the functionality and performance of electronic devices.

Semiconductor nanocrystals (or quantum dots) play a dominant role in the field of inorganic nanomaterials. Their size-dependent optical properties and the wide variety of available materials and synthesis methods make them ideal candidates for the study of mesoscopic phenomena. Moreover, they have a broad range of applications in fields as diverse as bioimaging or lasing. Four chapters of this volume are dedicated to semiconductor nanocrystals and their properties: Vukmirović and Wang (Chapter 1.07)

introduce the theory. The following chapter (Chapter 1.08) on wet-chemical synthesis and characterization has a strong emphasis on the frequently used II_B/VI semiconductors. Manna *et al.* cover all of the relevant synthesis methods, including timely approaches such as continuous flow synthesis or thermospray methods. This chapter is concluded with a comprehensive discussion on the most important characterisation methods. The epitaxial growth of additional shells onto quantum dots (and other nanoparticles) is an important field in its own right.

Building on the fundamentals introduced in the previous contribution, Parak et al. (Chapter 1.09) describe methods for the growth of inorganic shells onto (primarily semiconductor) nanocrystals. They particularly focus on the physical properties of different types of semiconductor core/shell structures, which differ significantly from core-only nanocrystals. Finally, the important issue of shape control is discussed. Next, Kambhampati et al. (Chapter 1.15) discuss semiconductor nanocrystals. Their chapter is primarily dedicated to the optical and physical properties of quantum dots, and also takes into account assemblies of these nanoparticles. The chapter concludes by introducing devices to use/characterize quantum dot-based structures. Silicon nanostructures differ slightly from typical quantum dots, since their optical properties are not dominated by band-gap luminescence, but by defect photoluminescence. Chao (Chapter 1.16) discusses the fabrication and properties of both, porous silicon and silicon nanoparticles. As with II_B/VI quantum dots, optical properties dominate the physics of these particles.

The role of anisotropy in inorganic nanomaterials is never more profoundly exhibited than in the existence of nanowires and nanotubes. Rao et al. (Chapter 1.10) discuss the multitude of inorganic compounds that can now be synthesized as solid (filled) one-dimensional structures on the nanoscale. Examples are drawn from elemental and alloyed metals through oxides to nitrides, chalcogenides, and beyond. The importance of the evolving approaches of the synthetic chemist in this ongoing discovery process are highlighted as are the many characterization techniques and tools now available that have made this discovery possible. Finally, the myriad of useful, and at times unexpected, properties from such structures are discussed in depth. These range, for example, from high tensile strength fibers, through conducting wires, nanoscaled arrays of photovoltaics and electrode materials, to light-emitting diodes and nanocomposites. The special case of inorganic nanotubes is considered in the chapter by Remskar (Chapter 1.11). The author draws initial parallels with the carbon nanotubes which preceded documented inorganic examples only by a year or so. The chapter highlights that, despite ostensible similarities, the growth mechanisms of inorganic nanotubes are profoundly different from their carbon brethren. Further, the compositional range afforded by combining many different elements across the periodic table in nanotubular forms, gives rise to a wide range of contrasting properties that might find potential application as lubricants, inert reaction vessels, or drug delivery systems.

Four more chapters of this volume are dedicated to specific inorganic nanoparticles. Yi et al. (Chapter 1.12) focuses on the extraordinary opportunities afforded by zinc oxide nanorods for electrical and optical nanodevice applications – significant examples including field-effect transistors and logic gates. Chapter 1.13 then deals with noble metal nanoparticles, Chapter 1.14 with magnetic nanocrystals, and Chapter 1.18 with rare-earth doped particles. Hubenthal starts Chapter 1.13 with a comprehensive introduction to the optical properties specific for metal nanoparticles. The synthetic methods for these particles include both top-down and bottom-up approaches, the latter further subdivided into gas-phase and wet-chemical methods. A variety of applications is envisaged. Magnetic nanoparticles also have a high potential for commercial applications – they are already used in many fields, such as contrast agents for magnetic resonance imaging. Mørup et al. (Chapter 1.14) introduce and discuss the properties of these materials, including important issues such as superparamagnetism, magnetic fluctuations, and anisotropy. This chapter concludes with a discussion of several applications of magnetic nanocrystals and their occurrence in nature.

With much of the synthetic effort in nanoscience relating directly or indirectly to solar energy, it is not surprising to find solar cell and photocatalytic objectives driving much of the current effort in both bottom-up and top-down nanostructure fabrication. Nosaka (Chapter 1.17) surveys a field in which numerous nanotechnological motifs are already deployed, including dye and plasmon sensitization, and the incorporation of quantum-well and quantum-dot components. Up-converting nanoparticles have a huge potential for applications in bioimaging, cancer therapy and electro-optics, although the preparation of highly luminescent

up-converting nanoparticles is still challenging. Wang and Liu (Chapter 1.18) give a comprehensive overview of synthesis methods and applications of this class of nanomaterials. The chapter especially highlights current challenges such as colour tuning and surface modification.

The range of topics in this volume attests to the grand breadth and scale of research and development activity in the field of nanomaterials. We gladly record our indebtedness to the numerous experts who have shared their vision of this rapidly growing area of nanoscience and technology.

Duncan H. Gregory, Thomas Nann, Zeev Valentine Vardeny and David L. Andrews

Foreword

Nanotechnology and its underpinning sciences are progressing with unprecedented rapidity. With technical advances in a variety of nanoscale fabrication and manipulation technologies, the whole topical area is maturing into a vibrant field that is generating new scientific research and a burgeoning range of commercial applications, with an annual market already at the trillion dollar threshold. The means of fabricating and controlling matter on the nanoscale afford striking and unprecedented opportunities to exploit a variety of exotic phenomena such as quantum, nanophotonic, and nanoelectromechanical effects. Moreover, researchers are elucidating new perspectives on the electronic and optical properties of matter because of the way that nanoscale materials bridge the disparate theories describing molecules and bulk matter. Surface phenomena also gain a greatly increased significance; even the well-known link between chemical reactivity and surface-to-volume ratio becomes a major determinant of physical properties, when it operates over nanoscale dimensions.

Against this background, this comprehensive work is designed to address the need for a dynamic, authoritative, and readily accessible source of information, capturing the full breadth of the subject. Its five volumes, covering a broad spectrum of disciplines including material sciences, chemistry, physics, and life sciences, have been written and edited by an outstanding team of international experts. Addressing an extensive, cross-disciplinary audience, each chapter aims to cover key developments in a scholarly, readable, and critical style, providing an indispensible first point of entry to the literature for scientists and technologists from inter-disciplinary fields. The work focuses on the major classes of nanomaterials in terms of their synthesis, structure, and applications, reviewing nanomaterials and their respective technologies in well-structured and comprehensive articles with extensive cross-references.

It has been a constant surprise and delight to have found, among the rapidly escalating number who work in nanoscience and technology, so many highly esteemed authors willing to contribute. Sharing our anticipation of a major addition to the literature, they have also captured the excitement of the field itself in each carefully crafted chapter. Along with our painstaking and meticulous volume editors, full credit for the success of this enterprise must go to these individuals, together with our thanks for (largely) adhering to the given deadlines. Lastly, we record our sincere thanks and appreciation for the skills and professionalism of the numerous Elsevier staff who have been involved in this project, notably Fiona Geraghty, Megan Palmer, Laura Jackson, and Greg Harris, and especially Donna De Weerd-Wilson who has steered it through from its inception. We have greatly enjoyed working with them all, as we have with each other.

David L. Andrews Gregory D. Scholes Gary P. Wiederrecht