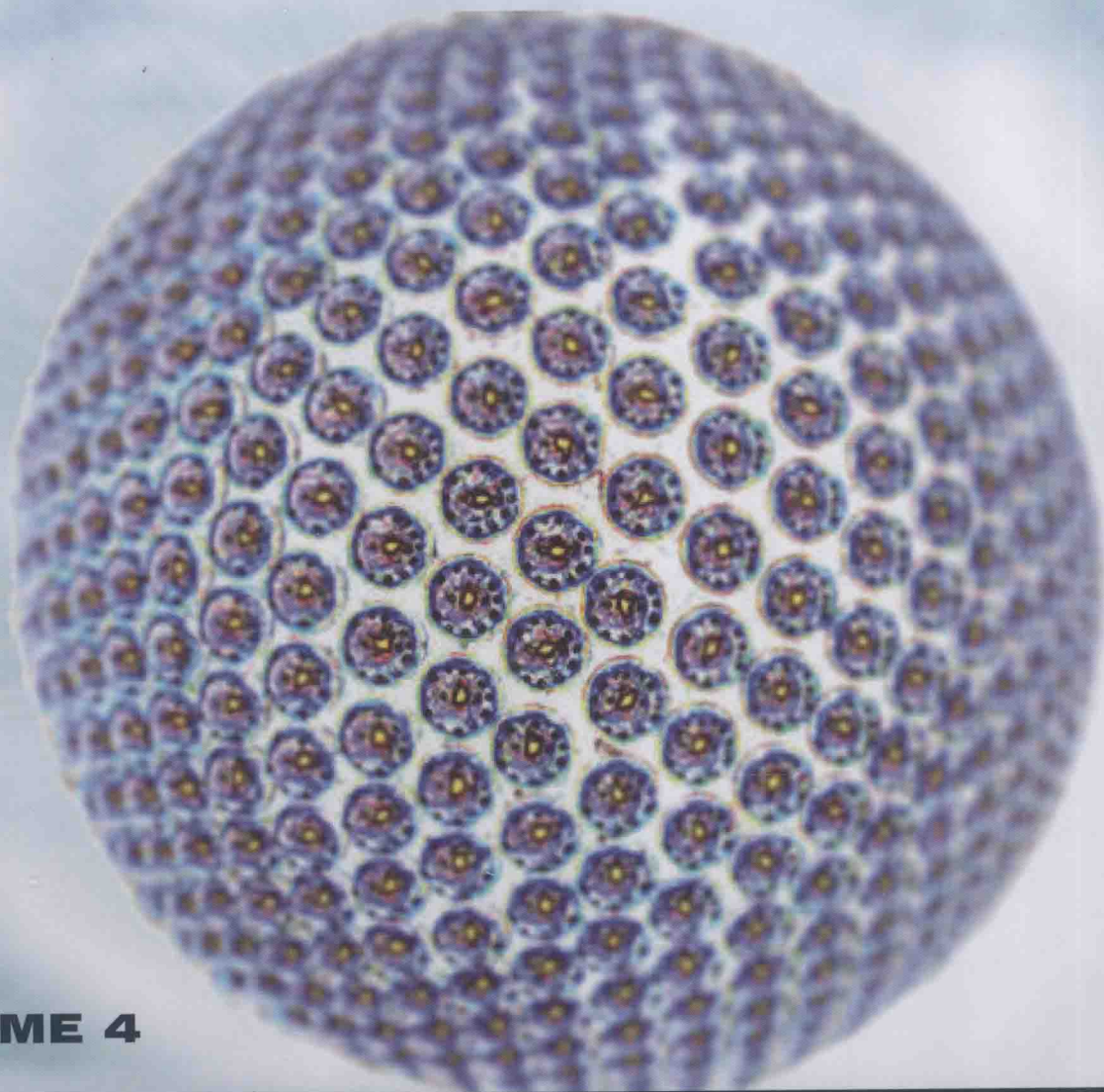


**DAVID L. ANDREWS  
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GARY P. WIEDERRECHT**



**VOLUME 4**

**COMPREHENSIVE  
NANOSCIENCE  
AND TECHNOLOGY**

**NANOFABRICATION  
AND DEVICES**



# COMPREHENSIVE NANOSCIENCE AND TECHNOLOGY

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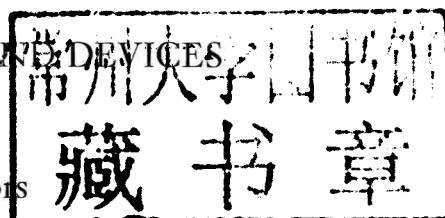
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Volume 4

NANOFABRICATION AND DEVICES



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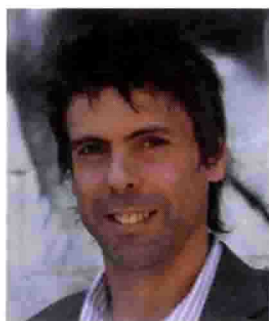
# **COMPREHENSIVE NANOSCIENCE AND TECHNOLOGY**

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# 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

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# Preface

## Volume 4: Nanofabrication and Devices

Nanofabrication is leading the way toward solving technological challenges of great importance. This is due to several reasons. In some cases, nanostructuring a material simply produces an improved critical device parameter, such as the greater speed of a nanoscale transistor. In other cases, however, new device possibilities are derived from the onset of new physical phenomena at the nanoscale. In fact, nanofabrication advances have produced stunning physical and chemical discoveries and phenomena that have no analog in larger-scale structures. One example of new phenomena is the confinement of electronic states in semiconductor materials to produce quantized electronic transitions rather than band-structure behavior that typifies bulk semiconductors. Entirely new optical and electronic behavior is produced in such materials compared to their bulk semiconductor counterparts, with proposed applications in sensing, lighting, energy conversion, medical diagnostics, to name only a few. Perhaps most important of all for applications related to nanostructuring is the extreme tunability of physical and chemical characteristics. By changing the size, shape, composition, or local environment, very large changes in the properties of the nanoscale materials are achieved. Thus, it is possible in nanoscale materials to tune and optimize material properties to a greater degree for a desired application than with bulk materials. The reasons for this control are varied, but can relate to the large change of surface-to-volume ratio with nanoparticle size, the transition between bulk and confined electronic states, or changes in the surface structure of a nanoparticle, for example.

The importance of nanoscale materials for solving technological problems has never been more important. For example, entirely new architectures in electronic integrated circuitry will likely be needed soon, simply because silicon transistors are approaching sizes that will rely on the transport of a single electron. Furthermore, enormous engineering challenges are present at this length scale, as the high density of transistors create tremendous heat loads and the lithography requires ever more complex and costly fabrication tools. As transistors scale down to the 10 nm length scale, nanofabrication advances have enabled totally different materials to be explored as next-generation transistors. These include carbon nanotube or graphene-based transistors, or even single molecule transistors. Nanofabrication is also proving critical for next-generation energy conversion and storage devices, such as nanostructured lithium in batteries for improved recharging and power delivery properties. The high surface-to-volume ratio of nanoparticles relative to bulk materials is also proving important for new, efficient catalytic processes.

All of the grand goals for nanoscience are dependent upon reliable ways to fabricate nanostructures. The challenges to nanofabrication are many, beginning with the incredibly broad range of applications, materials, and geometries that have been proposed for nanoscale structures. Applications include nanoelectronics, nanophotonics, nanomechanics, nanocatalysis, nanoantennae, and nanosensors. Materials are needed that possess almost every conceivable range of properties: metallic to insulating, hard to soft, inert to reactive, luminescent to quenched, crystalline to glassy – the list goes on. As a result, an immeasurable number of elements, compounds, and alloys have been subject to nanostructuring and nanofabrication tools. Add to this the range of geometrical nanostructures required: disks, rods, holes, pyramids, etc., and a range of tunability in the degree of interaction between nanoparticles to be isolated or closely coupled. The degree of long-range ordering, either random or periodic, can also be a critical consideration, as well as whether that ordering extends in one, two, or three dimensions. It is clear that nanofabrication is a daunting task.

The range of nanofabrication routes toward these structures is almost as diverse as the materials, applications, and geometries needed for next-generation applications. The approaches can begin to be compartmentalized by separation into either a top-down or bottom-up approach. Top-down fabrication refers to methods where one begins with a macroscopically dimensioned material, such as a thin film, into which is placed nanostructured defects. Top-down thus refers to approaches such as electron beam lithography (EBL) or focused ion beam lithography (FIB). In these cases, either focused electrons or ions are used to carve nanostructures out of larger structures. Alternatively, in the bottom-up approach, one begins to assemble nanostructures from smaller units. Examples include colloidal synthesis, where frequently the colloids are literally assembled from single ions in solution that are chemically neutralized so as to produce an aggregation process resulting from a sudden lack of solubility of the now neutral atom. Such processes are frequently used for the creation of plasmonic metal nanoparticles or semiconductor quantum dots. Bottom-up assembly also refers to the assembly of larger hierarchical structures, where, for example, colloids self-assemble into larger structures for a particular purpose. These can be for diverse applications such as the creation of three-dimensionally periodic photonic band-gap structures or periodic structures for the study of charge transport processes at the nanoscale.

Equally important to the patterning steps described above are the deposition methods. In many cases, it is not enough to produce a pattern from top-down or bottom-up methods. In these cases, the patterned material simply serves as a template for the deposition of the true nanostructured material of interest. This is frequently the case for photonic crystals where, for example, the self-assembled colloids serve only as a template for the high refractive index material that is deposited in the interstitial regions of the template. Another example is plasmonic nanostructures, where metal is deposited into the EBL patterned holes in polymer films.

This book describes the recent work of true leaders in the fields of nanofabrication and devices. The work described herein covers both the bottom-up and top-down lithography approaches. In the top-down category, Tennant and Bleier (Chapter 4.02) describe the state-of-the-art in electron beam lithography, while Her (Chapter 4.10) describes novel optical methods to create nanostructured materials. Approaches to soft lithography and patterning nanostructures reliably and over large areas is described in the chapters by Geissler (Chapter 4.03) and Sreenivasan *et al.* (Chapter 4.04). Routes that have great potential in manufacturing, such as inkjet printing, are described in the chapter by Sirringhaus *et al.* (Chapter 4.05). In the bottom-up category, methods that produce nanostructures with elegant long-range order are described. These include directed assembly (Macleod and Rosei Chapter 3.02, Volume 3), bio-mediated assembly (Luo *et al.*, Chapter 3.03, Volume 3) and patterned molecular binding (Reinhoudt *et al.*, Chapter 4.06) methods. Important nanofabrication methods toward next-generation nanoscale applications and devices are also described. These include routes toward optically active structures with applications in catalysis (Baddeley and Held, Chapter 3.04, Volume 3) and nanoscale molecular motors and devices (Credi, Chapter 4.12; Lee *et al.*, Chapter 4.16). Applications such as superhydrophobicity (Krupenkin *et al.*, Chapter 4.13), organic electronic devices (Loo *et al.*, Chapter 4.14), energy conversion (Kamat *et al.*, Chapter 4.09), light emitting devices (Kafafi *et al.*, Chapter 4.07), nanofluidics (Daiguji, Chapter 4.11), and optical data storage (Dhar *et al.*, Chapter 4.19) are described. Extraordinary advances in enabling advanced technologies, such as nanoscale transistors (Li and Hwang, Chapter 4.17) and spin-based data storage (Ozatay *et al.*, Chapter 4.18) are also presented.

It is certain that the impact of nanoscale devices and nanofabrication on our lives will grow dramatically in the coming years with the rise of nanotechnology. It is also clear that scientists and engineers working from many different directions and finding their inspiration from biological, chemical, and physical sources, are all contributing greatly toward this end. Thus, it is our belief that readers from all fields will find material of interest in this multidisciplinary topic, and perhaps even find additional inspiration to invent next-generation nanoscale devices and the nanofabrication methods and tools to create those devices.

Gary P. Wiederrecht

# 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 indispensable first point of entry to the literature for scientists and technologists from interdisciplinary 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



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