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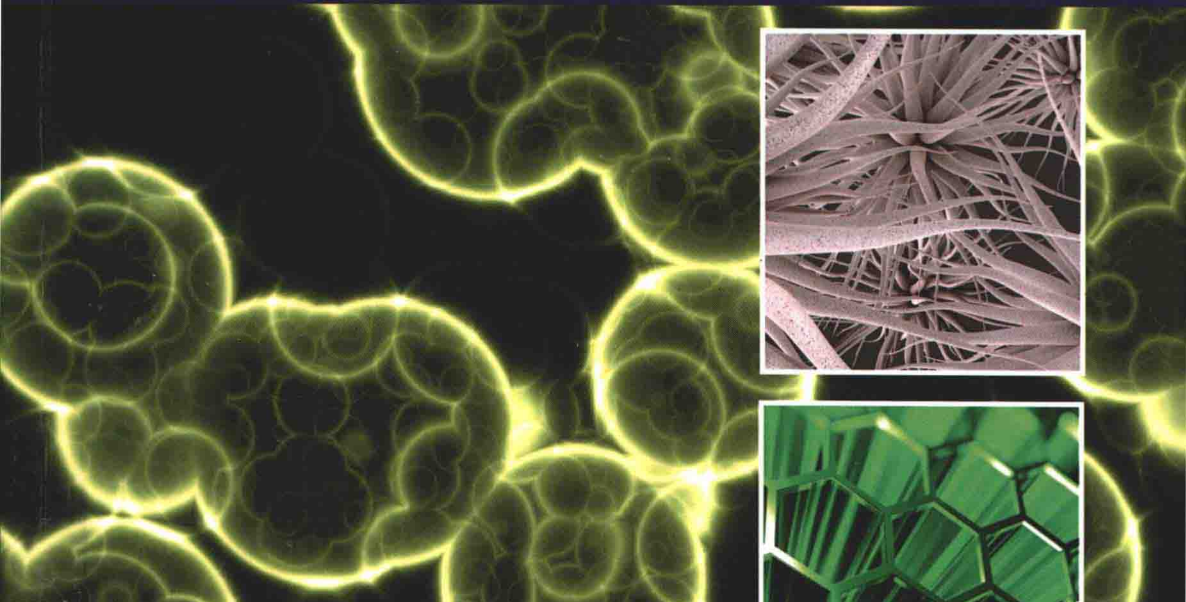
Nanoscience and the Environment



Edited by
Jamie R. Lead
Eugenia Valsami-Jones

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Edited by

Jamie R. Lead
SmartState Center for Environmental Nanoscience and Risk,
Department of Environmental Health Sciences,
Arnold School of Public Health, University of South Carolina,
Columbia, South Carolina, USA

Eugenia Valsami-Jones
School of Geography, Earth and Environmental Sciences,
University of Birmingham, Birmingham, United Kingdom

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Volume 7

Nanoscience and the Environment

FRONTIERS OF NANOSCIENCE

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Contributors

Numbers in Parentheses indicate the pages on which the author's contributions begin.

Mohammed Baalousha (1), School of Geography, Earth and Environmental Sciences, University of Birmingham, Birmingham, United Kingdom, and Center for Environmental Nanoscience and Risk, Department of Environmental Health Sciences, Arnold School of Public Health, University of South Carolina, Columbia, South Carolina, USA

Marie-Noële Croteau (157), U.S. Geological Survey, Menlo Park, California, USA

Kenneth A. Dawson (127), Centre for BioNano Interactions, University College Dublin, Dublin 4, Ireland

Eli S. Goldberg (89), Institute for Chemical and Bioengineering, ETH Zürich, Zürich, Switzerland

William How (1), School of Geography, Earth and Environmental Sciences, University of Birmingham, Birmingham, United Kingdom

Farhan R. Khan (157), Department of Environmental, Social and Spatial Change, Roskilde University, Roskilde, Denmark

Jamie R. Lead (1, 127), SmartState Center for Environmental Nanoscience and Risk, Department of Environmental Health Sciences, Arnold School of Public Health, University of South Carolina, Columbia, South Carolina, USA, and School of Geography, Earth and Environmental Sciences, University of Birmingham, Birmingham, United Kingdom

Stacey M. Louie (55), Center for Environmental Implications of Nanotechnology, and Department of Civil and Environmental Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania, USA

Gregory V. Lowry (55), Center for Environmental Implications of Nanotechnology, and Department of Civil and Environmental Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania, USA

Samuel N. Luoma (157), John Muir Institute of the Environment, University of California, Davis, and U.S. Geological Survey, Menlo Park, California, USA

Iseult Lynch (127), School of Geography, Earth and Environmental Sciences, University of Birmingham, Birmingham, United Kingdom

Rui Ma (55), Center for Environmental Implications of Nanotechnology, and Department of Civil and Environmental Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania, USA

Antonia Praetorius (89), Institute for Chemical and Bioengineering, ETH Zürich, Zürich, Switzerland

Martin Scheringer (89), Institute for Chemical and Bioengineering, ETH Zürich, Zürich, Switzerland

Kristin Schirmer (195), Department of Environmental Toxicology, Eawag, Swiss Federal Institute of Aquatic Science and Technology, P.O. Box 611, Duebendorf, and School of Architecture, Civil and Environmental Engineering (ENAC), EPF Lausanne, Lausanne, and Department of Environmental Systems Science, Institute of Biogeochemistry and Pollutant Dynamics, ETH Zürich, Zürich, Switzerland

Eugenia Valsami-Jones (1, 127), School of Geography, Earth and Environmental Sciences, University of Birmingham, Birmingham, and Earth Sciences, Natural History Museum, London, United Kingdom

Preface

Nanoscience, generally defined as the science of materials ranging between approximately 1 and 100 nm in at least one dimension, has become a hugely important area of research and development (R&D) in recent years. In this range, novel size-dependent properties manifest themselves and many exciting technological applications have emerged with perhaps more yet to come. As a result, there has been an exponential explosion in R&D funding (see Chapter 1), along with publications, patent applications, products on the market, and other metrics which capitalize on the novel uses of nanoscience. Interestingly, many of the commercial uses are currently fairly low technology, but the increasing sophistication in development and application means that there is potential for growth in more sophisticated nanomaterials, nanosystems, and nanodevices in a range of sectors including medicine and health, energy production, environmental remediation, and elsewhere. These sophisticated materials will tend to be more highly structured, more tightly constrained, and often smaller and dispersible; these properties will tend to increase mobility, bioavailability, and toxicity. Such properties will therefore likely increase the use and importance of nanomaterials as a social and economic driver, but will also likely lead to greater potential hazard and exposure to humans and to the environment.

The trade-off between utility and benefit of nanotechnology and its potential implications for human and environmental health is often seen as a major complication and potential limitation on the spread and general acceptance of the technology. For instance, potential hazards and risks might be perceived, misunderstood, and inflated. The consequent fallout might retard acceptance and uptake of new and important technologies. However, it is also possible to see this problem as illusory, except in the very short term; long-term sustainability of a technology depends upon its safety (however defined) and that this safety is seen to be openly investigated. Environmental and health issues which might arise are hopefully of less importance because knowledge is greater and, as there is greater transparency, general distrust is reduced. Therefore, it is possible to argue convincingly that commercial sustainability is increased by open research into environmental and human health consequences. In addition, the development of new knowledge and understanding is an important "good" in its own right, quite separate from the pragmatic gains produced.

From all of these arguments, it is clear that research into the fate and effects of nanomaterials in the environment is essential in both health and technology sectors. This book aims to summarize the current state of the art in relevant areas. Chapter 1 gives a grounding and overview of the many issues involved in a broadly defined "environmental nanoscience" including discussions of history, nomenclature and definitions, environmental processes, and related areas, setting the scene for the more detailed chapters that follow, on topics of particular current interest. Chapter 2 gives an account of the chemical, physical, and biological transformations which might occur once nanomaterials are released into the environment. The persistence of nanomaterials is governed by the nature of the particle and the nature of the environmental conditions, but changes might occur via processes such as microbial degradation, agglomeration, and dissolution. Chapter 3 surveys the current knowledge regarding the modeling of fate and behavior processes in the environment, a particularly important theme, considering the logistical difficulties of experimentally determining all potential behaviors, while Chapter 4 examines a particular transformation process relevant to fate and behavior, the development of an "eco-corona." In human toxicology, the development of a more widely known protein corona is important on nanomaterial contact with biological macromolecules and alters protein and nanomaterial behavior. In the environment, development of an eco-corona, primarily due to natural organic macromolecules, is an important process which may significantly alter physicochemical processes (e.g., aggregation, dissolution, sulfidation), while also altering biouptake processes. Chapter 4 therefore nicely leads into Chapter 5, which considers biouptake and bioaccumulation mechanisms of nanomaterials, giving evidence of nanospecific uptake of metal-based nanomaterials, separate from that of dissolution. Finally, Chapter 6 discusses the potential mechanisms of toxicity, taking this slightly unusual perspective on toxicology to attempt to draw out more fundamental understanding of toxicity. Taken as a whole, the book serves as an introduction to environmental nanoscience and nanoecotoxicology and a detailed discussion of some of its key current issues.

We would like to thank various funding bodies for supporting the editors specifically for this book and in their general research, equally important to the quality of this volume. In particular, the UK Natural Environment Research Council, the European Union Framework Programs, and the Center for Environmental Nanoscience and Risk, USA have played a pivotal role in the editors' research. In addition, we would like to thank the authors for their interest, timely submissions, and great effort in producing the individual chapters that form this book. Lastly, we would like to thank the publishing team whose patience and help was essential to completion of this book.

Jamie R. Lead
Eugenia Valsami-Jones

Contents

Chapter 1

Overview of Environmental Nanoscience

Mohammed Baalousha*,†, William How*, Eugenia Valsami-Jones* and Jamie R. Lead*,†

*School of Geography, Earth and Environmental Sciences, University of Birmingham, Birmingham, United Kingdom

†Center for Environmental Nanoscience and Risk, Department of Environmental Health Sciences, Arnold School of Public Health, University of South Carolina, Columbia, South Carolina, USA

1 INTRODUCTION

Nanoscience involves the understanding of processes and properties occurring at the lowest size range possible for matter to exist before reaching atomic dimensions. In its current form, where technological advances have enabled imaging, manipulation, and control of matter at the nanoscale, it is a relatively new field of science and can be dated to a number of key events including the discovery of the electron microscope in the 1930s, the scanning probe microscope in the 1970s, and the later discoveries of the carbon-based nanomaterials (NMs) such as C_{60}, carbon nanotubes (CNTs) and, most recently, graphene. In addition to these technological developments, the concepts of nanoscience have been developed, and the Richard Feynman essay (there is a plenty of room at the bottom; Feynman, 1992) is often cited as a key staging post. Nanotechnology is generally defined as the spatial scale of 1–100 nm where novel, size-dependent properties are often exhibited. The products of such manipulations are often small structures within the nanoscale range, known as NMs or nanoparticles (NPs). Matter at the nanoscale often displays novel properties, and thus finds new applications in a wide range of consumer products to enhance efficiency, reduce harmful emission, and reduce waste (see examples in Table 1.1). Nanotechnology is expected to bring huge benefits to humans and the environment in areas such as medicine, clean energy, and environmental remediation, but not without potential risks. Understanding the environmental and human health impacts of NMs is therefore important for two reasons, in addition to the fundamental importance of curiosity-led scientific discovery. First, understanding the risks will help to ensure the

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TABLE 1.1 Examples of Nanomaterials, Their Novel Properties, and Their Potential Applications

Nanomaterial	Product Group	% of Total Use
TiO_2	Cosmetics (including sunscreens)	70–80
	Coatings and cleaning agents	<20
	Plastics	<20
	Paints	10–30
	Cement	1
	Others	<10
ZnO	Cosmetics (including sunscreens)	70
	Paints	30
CeO_x	Chemical mechanical planarization	45–80
	Fuel catalyst	1–50
	UV coatings, paints	5–10
CNTs	Composites and polymer additives	20
	Materials	80
	Composites	50
	Batteries	50
Fullerenes	R&D	80
Ag	Paints, coatings, and cleaning agents	10–30
	Textiles	30–50
	Consumer electronics and conductivity	10–20
	Cosmetics	20
	Medtech	20
	Antimicrobial coatings	80–100
Quantum dots	Light conversion for LED/OLED	90
	Lab use for imaging	10

Taken from Piccinno et al. (2012).

protection of the environment and health, and second, such knowledge will safeguard the sustainable development of the nanotechnology industry, which is expected to be a significant global economic driver.

Understanding the environmental and human health impacts of NMs is a highly multidisciplinary area of research requiring knowledge of physics, chemistry, biology, and social sciences. The purpose of this book is to provide a critical analysis of the state of the art of NMs in the environment including synthesis, characterization, fate, behavior and transformations, exposure, biouptake, and toxicity. This chapter gives an overview of our knowledge on NMs in the environment as a preamble to the more detailed analysis in subsequent chapters. Chapter 2 discusses the currently available knowledge on the transformations of NMs in environmental systems including processes such as interactions with natural organic macromolecules, sulfidation, oxidation, and aggregation. Chapter 3 reviews the current efforts on modeling the environmental fate and exposure of NMs. Chapter 4 reviews the available knowledge on the formation and characterization of natural organic matter and protein macromolecular corona and its implications in nano(eco)toxicology. Chapter 5 discusses the biouptake and bioaccumulation of NPs, while Chapter 6 discusses mechanisms of nanotoxicity as they are currently understood.

2 HISTORY: FROM EMPIRICAL USE TO DISCOVERIES

This section discusses the key events in the development of NMs and nanotechnologies and for more details the readers are referred to other sources (DiscoverNano, 2014; NNI, 2014; Tolochko, 2009).

NMs have been used early in known human history, well before the current development of nanotechnology, but without the understanding and control that characterizes our current technological and intellectual capabilities. Such NMs were based on craftsman's empirical understanding and manipulation of materials. For instance, "soluble" gold appeared around the fifth to fourth century B.C. in Egypt and China and has been used for both aesthetic and curative purposes. Colloidal gold and silver were used in a range of artifacts, a notable example being the Lycurgus Cup, a fourth century drinking vessel, possibly made in Rome, of dichroic glass, that is, a glass which looks opaque green in normal light, but translucent red when lit from the inside. The effect is thought to be the result of light scattering by the dispersed gold and silver NPs within the glass. In the sixth to fifteenth centuries, stained glass windows in European cathedrals were colored by gold chloride and other metal oxide and chloride NPs. Later on, "Luster" ceramic glazes were used in the Islamic world during the ninth to seventeenth centuries, and later in Europe, and contained silver, copper, or other metallic NPs (DiscoverNano, 2014; NNI, 2014). During the thirteenth to eighteenth centuries, "Damascus" saber blades contained CNTs and cementite nanowires—an ultrahigh carbon steel formulation that gave them strength, resilience, the ability to hold a keen edge and visible moire pattern in the steel that give the blades their name (Reibold et al., 2006).

More recently (seventeenth to twenty-first centuries), the advancement in colloidal chemistry laid out the basics for the synthesis of NMs and consequently enabled the development of nanotechnology in the shape we now know and provided the fundamental understanding of nanoscience and nanotechnology. For instance, the philosopher and medical doctor Francisci Antonnii published a book (1618) which is considered as the first book about colloidal (nanoparticulate) gold. The German chemist Johann Kunckel published a book (1676) where he talked about "drinkable gold that contains metallic gold in neutral, slightly pink solution that exert curative properties for several diseases" and concluded that "gold must be present in such a degree of comminution that it is not visible to the human eye" (Lagaly et al., 2002; Wilson, 2008). In 1818, Jeremias Benjamin Richters observed the formation of pink or purple solutions of fine gold and yellow solutions when the particles have aggregated (Daniel and Astruc, 2004), and in 1857, Faraday reported the formation of red solutions of gold by the reduction of an aqueous solution of $AuCl_4^-$ using phosphorus in CS_2 (DiscoverNano, 2014; Faraday, 1857; NNI, 2014). Shortly after that, in 1861, the term "colloid" (of which NPs are the smallest fraction) was coined by Thomas Graham, who is known as the founder of colloidal chemistry (Graham, 1861; Mokrushin, 1962).

The basic concept of nanotechnology, as we know and practice it today, was first introduced in 1959 by the Nobel Prize winner physicist Richard Feynman. In his talk at the 29th annual meeting of the American Physical Society, Richard Feynman said "the principles of physics as far as I can see, do not speak against the possibility of manoeuvring things atom by atom. It is not an attempt to violate any laws; it is something, in principle, that can be done; but in practice it has not been done because we are too big" (Feynman, 1992). However, the term "nanotechnology" was not used until 1974 when Norio Taniguchi, Tokyo Science University Professor, used the term "nanotechnology" to describe the precision of manufacture of materials at the nanometer scale (Taniguchi, 1974). Then in 1980, Eric Drexler published his book *Engines of Creation*, which brought the term "nanotechnology" into the popular public domain.

Alongside the conceptual and popular understanding of nanoscience, scientific and technological progress during the twentieth century paved the way toward the development of nanotechnology as we know it today. In particular, the development of microscopy techniques and the scientific understanding of the nature of electrons and electron optics played a major role in advancing our understanding of matter. In 1872, Ernst Abbe suggested that resolving detail in an object is limited approximately by the wavelength of the light used in imaging in optical microscopes, which limits the resolution of an optical microscope to few hundreds of nanometers. The development of ultraviolet microscope in the early twentieth century by August Köhler and Moritz Rohr improved resolving power by about a factor of two because of the shorter wavelength of UV light compared to visible light used in optical microscopes.

In 1926, the physicist Han Busch laid out the foundations of geometrical electron optics after demonstrating that electric and magnetic fields could act as particle lenses. Nearly at the same time, the French physicist de Broglie