

ACS SYMPOSIUM SERIES 1124

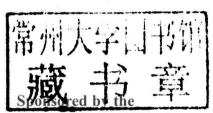
Sustainable Nanotechnology and the Environment: Advances and Achievements

Najm Shamim, Editor

U.S. Environmental Protection Agency Washington, DC

Virender K. Sharma, Editor

Florida Institute of Technology Melbourne, Florida



ACS Division of Industrial and Engineering Chemistry

American Chemical Society, Washington, DC Distributed in print by Oxford University Press



Library of Congress Cataloging-in-Publication Data

Sustainable nanotechnology and the environment: advances and achievements / Najm Shamim, editor, U.S. Environmental Protection Agency, Washington, DC, Virender K. Sharma, editor, Florida Institute of Technology, Melbourne, Florida; sponsored by the ACS Division of Industrial and Engineering Chemistry.

pages cm. -- (ACS symposium series; 1124)

Includes bibliographical references and index.

ISBN 978-0-8412-2784-2 (alk. paper)

1. Nanotechnology--Environmental aspects. 2. Nanostructured materials--Environmental aspects. 3. Sustainable engineering. 4. Sanitary engineering--Technological innovations. I. Shamim, Najm, editor of compilation. II. Sharma, Virender K., editor of compilation. III. American Chemical Society. Division of Industrial and Engineering Chemistry.

TD196.N36S87 2013 338.9'27--dc23

2012049658

The paper used in this publication meets the minimum requirements of American National Standard for Information Sciences—Permanence of Paper for Printed Library Materials, ANSI Z39.48n1984.

Copyright © 2013 American Chemical Society

Distributed in print by Oxford University Press

All Rights Reserved. Reprographic copying beyond that permitted by Sections 107 or 108 of the U.S. Copyright Act is allowed for internal use only, provided that a per-chapter fee of \$40.25 plus \$0.75 per page is paid to the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, USA. Republication or reproduction for sale of pages in this book is permitted only under license from ACS. Direct these and other permission requests to ACS Copyright Office, Publications Division, 1155 16th Street, N.W., Washington, DC 20036.

The citation of trade names and/or names of manufacturers in this publication is not to be construed as an endorsement or as approval by ACS of the commercial products or services referenced herein; nor should the mere reference herein to any drawing, specification, chemical process, or other data be regarded as a license or as a conveyance of any right or permission to the holder, reader, or any other person or corporation, to manufacture, reproduce, use, or sell any patented invention or copyrighted work that may in any way be related thereto. Registered names, trademarks, etc., used in this publication, even without specific indication thereof, are not to be considered unprotected by law.

Sustainable Nanotechnology and the Environment: Advances and Achievements

Foreword

The ACS Symposium Series was first published in 1974 to provide a mechanism for publishing symposia quickly in book form. The purpose of the series is to publish timely, comprehensive books developed from the ACS sponsored symposia based on current scientific research. Occasionally, books are developed from symposia sponsored by other organizations when the topic is of keen interest to the chemistry audience.

Before agreeing to publish a book, the proposed table of contents is reviewed for appropriate and comprehensive coverage and for interest to the audience. Some papers may be excluded to better focus the book; others may be added to provide comprehensiveness. When appropriate, overview or introductory chapters are added. Drafts of chapters are peer-reviewed prior to final acceptance or rejection, and manuscripts are prepared in camera-ready format.

As a rule, only original research papers and original review papers are included in the volumes. Verbatim reproductions of previous published papers are not accepted.

ACS Books Department



Preface

It has been ten years since Barbara Karn initially organized the symposium on Green Nanotechnology at the ACS Meeting under the Industrial & Engineering Chemistry Division. At the time, Barbara along with Tina Masciangioli, Wie-xian Zhang, Vicki Colvin, and Paul Alivisatos successfully put together an initial pioneering symposium consisting of relevant presentations and the fruits of this endeavor were published in the ACS Symposium book, entitled "Nanotechnology and the Environment: Applications and Implications". Later, Dr. Barbara Karn along with Dr. Stanislaus S. Wong continued the process of arranging these symposia till 2011. It was our great pleasure to organize the 10th symposium in 2012, particularly honoring Drs. Barbara Karn and Stanislaus Wong for their excellent contributions to the field of green nanotechnology.

Ten years has seen a tremendous advancement in the nanotechnology field, more so on the applications side than in nanoscience itself, although scientific progress in both has not been lagging behind.

We thought it fit to maintain the tradition and put together the contributions and papers of this latest symposium as chapters and to publish these as the following Symposium Book. We would be deluding ourselves if we thought that this symposium entirely captures the tremendous the length and breadth of scientific advancements in all disciplines related to nanotechnology. Neither one book nor many books can achieve this goal. But we are certain about one thing: This book makes a serious effort at bringing forth and synergistically combining the concepts of green chemistry, sustainability and nanotechnology and to some degree, should motivate scientists at all levels to think clearly and seriously about creating and optimizing novel and sustainable green approaches to nanotechnology.

The chapters in this book can be divided into three broad categories: 1) Advancement in research on pollution control through the green chemistry principles of nanotechnology; 2) Emergence of nanomaterials in widespread applications in various scientific fields, including but not limited to sensors and catalysts; 3) Extension of research into nanotechnology and green nanotechnology at a rapid pace. Review articles on the individual aspects of these diverse and complementary topics have become important resources for researchers, industry leaders, and regulators, both nationally and internationally. This book contains a few chapters associated with these particular themes, and provides glimpses of the many difficulties and challenges faced by those who seek to not only understand but also regulate the new nanomaterials.

Nanotechnology represents a unique field of science, and necessitates new and novel sustainable approaches to create usable end products for the market place with the primary goal of yielding less adverse effects upon both human health and the environment.



Acknowledgments

We would like to thank all the authors who graciously agreed at the ACS Conference in San Diego (March 2012) to convert their presentations to full chapters for this book. More so, they did not mind our repeated and sometimes nagging emails about completing the work in time. Without their research and efforts this book would be naught.

The ACS Editorial Staff: What an outstanding group of folks. Mr. Hauserman, Tim Marney, Mrs. Arlene Furman, and Mrs. Kathleen Squibb. The cooperation and outstanding professionalism kept Virender and I in line. The ACS even accepted our little excuses with a smile (We think).

We are indeed very thankful to the reviewers for this book who kindly donated their time and efforts to help us in the review process.

Virender thanks the support of Center of Ferrate Excellence at Florida Institute of Technology.

On a personal note, V. K. Sharma is happy that he met Dr. Barbara Karn in the University of Miami in 1987 and cherishes her friendship for the last 25 years. Both of us are very happy that they met and wish her the very best for enjoying the lovely moments of her life.

Contents

Pre	faceix	
Ack	nowledgments xi	
1.	Ten Years of Green Nanotechnology	
2.	Green Synthesis of Nanomaterials: Environmental Aspects	
3.	Greener and Other Approaches To Synthesize Fe and Pd Nanoparticles in Functionalized Membranes and Hydrogel	
4.	Nanostructured Materials for Environmentally Conscious Applications 59 Panagiotis Dallas, Antonios Kelarakis, and Emmanuel P. Giannelis	
5.	Nanomaterials in Agricultural Production: Benefits and Possible Threats? 7 Jie Hong, Jose R. Peralta-Videa, and Jorge L. Gardea-Torresdey	
6.	Nanotechnology for More Sustainable Manufacturing: Opportunities and Risks	
7.	Biological Synthesis of Silver Nanoparticles and Assessment of Their Bactericidal Activity	
8.	Reactive Peptide Nanofiltration	
9.	HCl Effect on Two Types of Ag Nanoparticles Utilizable in Detection of Low Concentrations of Organic Species	
10.	Stability and Toxicity of Silver Nanoparticles in Aquatic Environment: A Review	

Sub	Subject Index		
Aut	hor Index		
Indexes			
Editors' Biographies			
19.	Scientific and Regulatory Issues in Exposure Assessment of Conventional Metals vs Nanosized		
18.	Synthesis, Characterization, and Cyanide Photodegradation Over Cupric Oxide-Doped Zinc Oxide Nanoparticles		
17.	Stabilization of Fe ⁰ Nanoparticles with Silica for Enhanced Transport and Remediation of Hexavalent Chromium in Groundwater		
16.	Magnetically Recyclable Gold-Magnetite Nanocatalysts for Reduction of Nitrophenols		
15.	Visible-Light-Induced Activity of AgI-BiOI Composites for Removal of Organic Contaminants from Water and Wastewater		
14.	Hierarchical Hybrid K-OMS-2/TiO ₂ Nanofibrous Membrane for Water Treatment		
13.	Dye-Sensitized Photocatalyst: A Breakthrough in Green Energy and Environmental Detoxification		
12.	Chapter Green Nanotechnology: Development of Nanomaterials for Environmental and Energy Applications		
11.	Toxic PH ₃ Catalytic Decomposition and High Purity Phosphorus Production by Amorphous Co-Based Alloy Nanomaterials		

Chapter 1

Ten Years of Green Nanotechnology

Barbara Karn*,1 and Stanislaus S. Wong*,2

¹Program Director for Nano EHS, National Science Foundation, 4201 Wilson Blvd., Arlington, VA, 22230 ²Professor of Chemistry, Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York, 11794; Joint appointment with the Condensed Matter Physics and Materials Sciences Department, Brookhaven National Laboratory, Upton, New York, 11973 *E-mail: bkarn@nsf.gov (B.K.); stanislaus.wong@stonybrook.edu (S.S.W.)

> This Chapter examines a brief history of Green Nanotechnology during the last ten years. The field is both multi-disciplinary and inter-disciplinary, and, while it has made great strides for the past ten years, it is still evolving. important and positive aspect of Nanotechnology with respect to its latent impact upon research and applications is its deepening connection to both Green Chemistry and Sustainability. Although much work has gone into developing and strengthening this fruitful relationship, it has not caught up with other technical advances in Nanotechnology, Nevertheless, the convergence of three important fields of science, namely Nanotechnology, Green Chemistry, and Sustainability, could result in a novel and vital holistic area of study, namely Green Nanotechnology, with the potential for fewer societal issues. fewer hazardous reagents to deal with, and the generation of very efficient products associated with a reduced environmental footprint.

Introduction

"D'où venons nous? Que sommes nous? Où allons nous?" reads the inscription on Gaugin's 1897 painting. The quote is an appropriate framework for an introduction to Green Nanotechnology, examining its past, present and future.

Where Do We Come From? (D'où venons nous?)

Green Nanotechnology is a subset of nanotechnology itself. It couples the rigor of a legitimate scientific discipline with the fervent excitement and awesome responsibility for developing new opportunities for enhancing sustainability.

History

Nanotechnology is a relatively new discipline. Studies at the nanoscale were enabled by the practical development of instruments in the 1980s by talented visionaries including but not limited to Binnig, Roher, Gerber, and Quake working at IBM and beyond (1, 2). These included the scanning tunneling microscope and the atomic force microscope, which allowed scientists, for the first time, to "see" atoms, and furthermore, permitted them to controllably manipulate individual atoms and molecules. In doing so, this new and unprecedented capability enabled researchers to actually spatially move these chemical entities around on a substrate in a well-defined manner with the potential for not only probing novel properties but also conducting localized reactions.

Research at the nanoscale in the 1990s was supported by both government and industry. Research program directors at several government agencies noted that special phenomena were occurring at a size range, roughly between one and 100 nm. Realizing the game changing nature of research into matter at this length scale, these program directors convinced the science managers under the Clinton administration to form a National Nanotechnology Initiative (NNI) so as to coordinate funding among federal US agencies.

The NNI defines nanotechnology as the understanding and control of matter at the nanoscale, at dimensions between approximately 1 and 100 nanometers, where unique phenomena enable novel applications. Encompassing nanoscale science, engineering, and technology, nanotechnology involves imaging, measuring, modeling, and manipulating matter at this length scale. From the beginning, nanotechnology was different. In 1992, Eric Drexler stated: "Molecular nanotechnology promises a fundamental revolution in the way we make things. By bringing precise control to the molecular level...it can serve as a basis for (making) manufacturing processes cleaner, more productive, and more efficient than those known today." Nanotechnology also represented a paradigm shift in recognizing that special and often unexpected properties occur at the nanoscale due to the ultrasmall size of the material.

The NNI concept was formalized through the Nanotechnology Research and Development Act of 2003. The NNI vision denoted a future in which the ability to understand and control matter at the nanoscale can potentially lead to a revolution in understanding the underlying technology and industry that benefit society. In fact, the development of nanotechnology in its broadest and most altruistic sense seeks not only to improve the comprehension of nature through an increase in fundamental knowledge but also to provide yet another tool in tackling pressing basic global concerns of immense moral impact. As examples, the latter include providing for a clean water supply; ensuring food security and decent human shelter; improving transportation, power, and energy systems; and reducing the

weight of pollution and of greenhouse gases in industrial manufacturing processes in order to preserve a clean environment (3). To this end, not surprisingly, a lot of effort has been expended towards developing nanomaterials for the destruction of environmental pollutants as well as for remediation purposes. Other groups have sought to understand the role of the structure, shape, bandgap, size, morphology, and surface chemistry of the nanoparticles themselves in determining their formation and reactivity in a range of aquatic, air, and soil environments (4).

The four goals of the NNI include:

- (1) Advancing world-class nanotechnology research and development;
- (2) Fostering the transfer of new technologies into products for commercial and public benefit;
- (3) Developing and sustaining educational resources, a skilled workforce, and the supporting infrastructure and tools to advance nanotechnology;
- (4) Supporting the responsible development of nanotechnology. (5)

Green Nanotechnology 'sustains' the fourth goal. By either eliminating or minimizing harmful polluting substances in the synthesis of nanomaterials or using the products of nanotechnology to eliminate or minimize these pollutants in current chemical processes, Green Nanotechnology enables nanotechnology itself to develop in a responsible and more sustainable manner.

The efforts of the NNI federal expenditures work in concert with similar commercial outlays. As a result, many applications of nanotechnology are currently the focal point of extensive commercialization efforts with the potential for developing future markets that might be worth trillions of dollars (2). Sectors incorporating nanotechnology include but are not limited to food/agriculture, metallurgical additives and alloys, semiconductors/electronics/ computers, personal care products, energy/batteries, textiles, military applications, sporting goods, construction, medicine, as well as the automotive and chemical industries.

Commercial revenue impacted by nanotechnology spans three levels of the value chain – nanomaterials, nanointermediates, and nano-enabled products. Nanomaterials are those purposefully engineered materials that fit the NNI definition having dimensions between 1 and 100 nanometers and exhibiting unique properties, different from and potentially better than what is characteristic of the bulk. Carbon nanotubes, metal and metal oxide nanoparticles, quantum dots, graphene, dendrimers, and ceramic nanomaterials represent typical examples.

Nanointermediates incorporate nanomaterials which possess nanoscale features, but they are not the final products. Examples include solar cells, drug delivery systems, agricultural chemicals, sensors, lubricants, and catalysts. These nano-enabled products signify the end of the value chain, incorporating designed materials and intermediates that will be used as key components and constituents of aircraft, pharmaceuticals, phosphors, computer chips, sporting goods, automobiles, and so forth.

Each year, the NNI publishes a budget indicating expenditures of each participating agency in what are called Program Component Areas (PCA) (Table 1) (5). The 7th PCA deals with the environmental health and safety of

nanotechnology. That is, the focus is on discovering and addressing potential negative implications of nanotechnology before they can obstruct its sustainable development and progress. In this light, the NNI has held several workshops that have dealt with nanotechnology as well as its combined environmental and societal impact, both positive and negative. Early on, international meetings dealing with the responsible development of nanotechnology initiated productive conversations and set the stage for more detailed dialogues concerning both the potential applications and probable implications of nanotechnology with respect to the environment.

Table 1. NNI Program Component Areas (PCAs)

No.	Title	Description
1	Fundamental Nanoscale Phenomena and Processes	Discovery and development of fundamental knowledge pertaining to new phenomena in the physical, biological, and engineering sciences that occur at the nanoscale. Elucidation of scientific and engineering principles related to nanoscale structures, processes, and mechanisms.
2	Nanomaterials	Research aimed at the discovery of novel nanoscale and nanostructured materials and at a comprehensive understanding of the properties of nanomaterials (ranging across length scales, and including interface interactions). R&D leading to the ability to design and synthesize, in a controlled manner, nanostructured materials with targeted properties.
3	Nanoscale Devices and Systems	R&D that applies the principles of nanoscale science and engineering to create novel, or to improve existing, devices and systems. Includes the incorporation of nanoscale or nanostructured materials to achieve improved performance or new functionality. To meet this definition, the enabling science and technology must be at the nanoscale, but the systems and devices themselves are not restricted to that size.
4	Instrumentation Research, Metrology, and Standards for Nanotechnology	R&D pertaining to the tools needed to advance nanotechnology research and commercialization, including next-generation instrumentation for characterization, measurement, synthesis, and design of materials, structures, devices, and systems. Also includes R&D and other activities related to development of standards, including standards for nomenclature, materials, characterization and testing, and manufacture.

Continued on next page.