Environmental Chemistry for a Sustainable World

Nandita Dasgupta · Shivendu Ranjan Eric Lichtfouse *Editors*

Environmental Nanotechnology Volume 1



Environmental Chemistry for a Sustainable World

Volume 14

Series editors

Eric Lichtfouse, CEREGE INRA, Aix en Provence Cedex 04, France Jan Schwarzbauer, RWTH Aachen University, Aachen, Germany Didier Robert, CNRS, European Laboratory for Catalysis and Surface Sciences, Saint-Avold, France

Other Publications by the Editors

Books

Environmental Chemistry http://www.springer.com/978-3-540-22860-8

Organic Contaminants in Riverine and Groundwater Systems http://www.springer.com/978-3-540-31169-0

Sustainable Agriculture Volume 1: http://www.springer.com/978-90-481-2665-1 Volume 2: http://www.springer.com/978-94-007-0393-3

Book series

Environmental Chemistry for a Sustainable World http://www.springer.com/series/11480

Sustainable Agriculture Reviews http://www.springer.com/series/8380

Journals

Environmental Chemistry Letters http://www.springer.com/10311

Agronomy for Sustainable Development http://www.springer.com/13593

More information about this series at http://www.springer.com/series/11480

Nandita Dasgupta • Shivendu Ranjan Eric Lichtfouse Editors

Environmental Nanotechnology

Volume 1



Editors Nandita Dasgupta Nano-Food Research Group, Instrumental and Food Analysis Lab, Industrial Biotechnology Division, School of Bio Science and Technology VIT University Vellore, Tamil Nadu, India

Eric Lichtfouse CEREGE INRA Aix en Provence Cedex 04, France Shivendu Ranjan R&D and Technology Development, E-Spin Nanotech Pvt Ltd, SIDBI Incubation Center IIT-Kanpur Kanpur, Uttar Pradesh, India

 ISSN 2213-7114
 ISSN 2213-7122
 (electronic)

 Environmental Chemistry for a Sustainable World
 ISBN 978-3-319-76089-6
 ISBN 978-3-319-76090-2
 (eBook)

 https://doi.org/10.1007/978-3-319-76090-2
 ISBN 978-3-319-76090-2
 (eBook)

Library of Congress Control Number: 2018939755

© Springer International Publishing AG, part of Springer Nature 2018

This work is subject to copyright. All rights are reserved by the Publisher, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in any other physical way, and transmission or information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed.

The use of general descriptive names, registered names, trademarks, service marks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

The publisher, the authors and the editors are safe to assume that the advice and information in this book are believed to be true and accurate at the date of publication. Neither the publisher nor the authors or the editors give a warranty, express or implied, with respect to the material contained herein or for any errors or omissions that may have been made. The publisher remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Printed on acid-free paper

This Springer imprint is published by the registered company Springer International Publishing AG part of Springer Nature.

The registered company address is: Gewerbestrasse 11, 6330 Cham, Switzerland

We dedicate this book to those who are affected by environmental hazards. We hope that this book may be a small contribution to improving their quality of life.



Think Environment – Think Nanomaterials –Dr. Nandita Dasgupta

Preface

Nanotechnology will modify the environment both in a positive and negative way. On the one hand, new nanomaterials are promising for reducing greenhouse gases, cleaning toxic wastes and building alternative energy sources. On the other hand, some toxic nanoparticles enter and disrupt ecosystems. Therefore, research should focus on the sustainable use of nanomaterials to avoid environmental contamination. This book presents the environmental benefits of nanomaterials in agriculture, water purification and nanomedicine. This book is the first of several volumes on Environmental Nanotechnology, which will be published in series *Environmental Chemistry for a Sustainable World*.



Food, Agriculture and Water

Hadef introduces the classification, structure and properties of nanomaterials in Chap. 1. This chapter also highlights the diverse applications of nanomaterials, including energy, environment, nanomedicine, sensors, nanoelectronics, textile, food and agriculture. Chapters 2 and 5 discuss the applications of nanomaterials in food and agriculture. Mousa and El-Hady review nanomaterials in food processing, packaging and safety in Chap. 2. They discuss, in particular, nanodelivery systems of bioactive food components. In Chap 5, Chandrika et al. present nanomaterials in agriculture, with applications such as nanopesticides, nanofertilizers, controlled-delivery devices, water and soil management and precision agriculture.

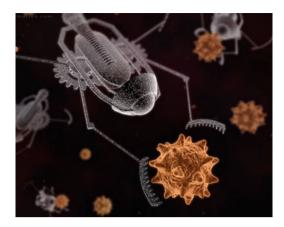


Source: International Food Information Council Foundation. http://www.foodinsight.org/articles/questions-and-answers-about-food-biotechnology

Medicine, Energy and Pollutants

Simeonidis explains the potential application of nanoparticles for water treatment in Chap. 3, with a special emphasis on the removal of heavy metals. In Chap. 4, Kuswandi reviews the nanomaterials used as biosensors for the detection of micropollutants. Chapter 6 by Rahman et al. discusses clay-polymer nanocomposites and its applications in various fields, ranging from automobile to biomedical. Dasari et al. review nanostructured photovoltaics as a medium of alternative energy in Chap. 7. Lateef et al. explain emerging applications of metallic nanoparticles for the management of blood coagulation disorders in Chap. 8. Osmani et al. in Chap. 9 describe cyclodextrin-based nanosponges in drug delivery and nanotherapeutics. In Chap. 10, Borzenkov et al. give an update on the application of gold nanoparticles in tissue engineering.

Preface



Source: Slaw.me http://slaw.me/naotechnology-size-does-matter-article-by-eliza beth-fiend/

Thanks for reading

Vellore, Tamil Nadu, India Vellore, Tamil Nadu, India Aix en Provence Cedex 04, France Nandita Dasgupta Shivendu Ranjan Eric Lichtfouse

Contents

1	An Introduction to Nanomaterials	1
2	Nano-food Technology and Nutrition	59
3	Nanoparticles for Heavy Metal Removal from Drinking Water Konstantinos Simeonidis, Carlos Martinez-Boubeta, Paula Zamora-Perez, Pilar Rivera-Gil, Efthimia Kaprara, Evgenios Kokkinos, and Manassis Mitrakas	75
4	Nanobiosensors for Detection of Micropollutants	125
5	Nanotechnology Prospects and Constraints in Agriculture Kella Poorna Chandrika, Anupama Singh, Madhu Kiran Tumma, and Praduman Yadav	159
6	Surface Modification of Advanced and Polymer Nanocomposites . Maliha Rahman, Farhan Zahin, Md Abid Shahriar Rahman Saadi, Ahmed Sharif, and Md Enamul Hoque	187
7	Photovoltaics and Nanotechnology as Alternative Energy Mallika Dasari, Rajesh P. Balaraman, and Punit Kohli	211
8	Nanomedical Applications of Nanoparticles for Blood Coagulation Disorders Agbaje Lateef, Sunday Ayotunde Ojo, Joseph Adetunji Elegbede, Paul Oluwadamilare Akinola, and Emmanuel Olufemi Akanni	243

9	Cyclodextrin Nanosponges in Drug Delivery and		
	Nanotherapeutics	279	
	Riyaz Ali Osmani, Parthasarathi Kulkarni, Shringari Manjunatha,		
	Vishakante Gowda, Umme Hani, Rudra Vaghela, and Rohit Bhosale		
10	Gold Nanoparticles for Tissue Engineering	343	
	Mykola Borzenkov, Giuseppe Chirico, Maddalena Collini,		
	and Piersandro Pallavicini		
Ind	ex	391	

xii

Contributors

Emmanuel Olufemi Akanni Division of Hematology, Department of Medical Laboratory Science, LAUTECH College of Health Sciences, Osogbo, Osun State, Nigeria

Paul Oluwadamilare Akinola Laboratory of Industrial Microbiology and Nanobiotechnology, Department of Pure and Applied Biology, Ladoke Akintola University of Technology, Ogbomoso, Nigeria

Rajesh P. Balaraman Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, IL, USA

Rohit Bhosale Department of Pharmaceutics, JSS College of Pharmacy, JSS University, Mysuru, Karnataka, India

Mykola Borzenkov Nanomedicine Center, Department of Medicine and Surgery, Department of Physics, University of Milano-Bicocca, Milan, Italy

Kella Poorna Chandrika ICAR-Indian Institute of Oilseeds Research, Hyderabad, Telangana, India

Giuseppe Chirico Nanomedicine Center, Department of Medicine and Surgery, Department of Physics, University of Milano-Bicocca, Milan, Italy

Maddalena Collini Nanomedicine Center, Department of Medicine and Surgery, Department of Physics, University of Milano-Bicocca, Milan, Italy

Mallika Dasari Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, IL, USA

Joseph Adetunji Elegbede Laboratory of Industrial Microbiology and Nanobiotechnology, Department of Pure and Applied Biology, Ladoke Akintola University of Technology, Ogbomoso, Nigeria

Deia Abd El-Hady Chemistry Department, Faculty of Science, University of Jeddah, Jeddah, Saudi Arabia

University of Jeddah Center for Scientific and Medical Research, Jeddah, Saudi Arabia

Vishakante Gowda Department of Pharmaceutics, JSS College of Pharmacy, JSS University, Mysuru, Karnataka, India

Fatma Hadef Département de Physique, Faculté des Sciences, Université 20 Août 1955-Skikda, Algeria

Umme Hani Department of Pharmaceutics, College of Pharmacy, King Khalid University, Asir-Abha, Saudi Arabia

Md Enamul Hoque Department of Biomedical Engineering, Military Institute of Science and Technology (MIST), Mirpur Cantonment, Dhaka, Bangladesh

Efthimia Kaprara Department of Chemical Engineering, Aristotle University of Thessaloniki, Thessaloniki, Greece

Punit Kohli Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, IL, USA

Evgenios Kokkinos Department of Chemical Engineering, Aristotle University of Thessaloniki, Thessaloniki, Greece

Parthasarathi Kulkarni Department of Pharmaceutics, JSS College of Pharmacy, JSS University, Mysuru, Karnataka, India

Bambang Kuswandi Chemo and Biosensors Group, Faculty of Pharmacy, University of Jember, Jember, Indonesia

Agbaje Lateef Nanotechnology Research Group (NANO+), Ladoke Akintola University of Technology, Ogbomoso, Nigeria

Laboratory of Industrial Microbiology and Nanobiotechnology, Department of Pure and Applied Biology, Ladoke Akintola University of Technology, Ogbomoso, Nigeria

Shringari Manjunatha Defence Food Research Laboratory (DFRL), Ministry of Defence, Mysuru, Karnataka, India

Carlos Martinez-Boubeta Integrative Biomedical Materials and Nanomedicine Laboratory, Department of Experimental and Health Sciences, Pompeu Fabra University, Barcelona, Spain

Manassis Mitrakas Department of Chemical Engineering, Aristotle University of Thessaloniki, Thessaloniki, Greece

Rasha M. A. Mousa Home Economic Department, Faculty of Specific Education, Assiut University, Assiut, Egypt

Biochemistry Department, Faculty of Science, University of Jeddah, Jeddah, Saudi Arabia

Sunday Ayotunde Ojo Laboratory of Industrial Microbiology and Nanobiotechnology, Department of Pure and Applied Biology, Ladoke Akintola University of Technology, Ogbomoso, Nigeria

Riyaz Ali Osmani Department of Pharmaceutics, JSS College of Pharmacy, JSS University, Mysuru, Karnataka, India

Piersandro Pallavicini Department of Chemistry, University of Pavia, Pavia, Italy

Maliha Rahman Department of Materials and Metallurgical Engineering, Bangladesh University of Engineering and Technology (BUET), Dhaka, Bangladesh

Pilar Rivera-Gil Freelancer, Bilbao, Spain

Md Abid Shahriar Rahman Saadi Department of Materials and Metallurgical Engineering, Bangladesh University of Engineering and Technology (BUET), Dhaka, Bangladesh

Ahmed Sharif Department of Materials and Metallurgical Engineering, Bangladesh University of Engineering and Technology (BUET), Dhaka, Bangladesh

Konstantinos Simeonidis Department of Chemical Engineering, Aristotle University of Thessaloniki, Thessaloniki, Greece

Anupama Singh Division of Agricultural Chemicals, ICAR-Indian Agricultural Research Institute, New Delhi, India

Madhu Kiran Tumma PBRD Asia Specific Millet India, Pioneer Hibrid Pvt Ltd, Hyderabad, India

Rudra Vaghela Department of Pharmaceutics, JSS College of Pharmacy, JSS University, Mysuru, Karnataka, India

Praduman Yadav ICAR-Indian Institute of Oilseeds Research, Hyderabad, Telangana, India

Farhan Zahin Department of Materials and Metallurgical Engineering, Bangladesh University of Engineering and Technology (BUET), Dhaka, Bangladesh

Paula Zamora-Perez Integrative Biomedical Materials and Nanomedicine Laboratory, Department of Experimental and Health Sciences, Pompeu Fabra University, Barcelona, Spain

About the Editors



Dr. Nandita Dasgupta has vast working experience in Micro/Nanoscience and is currently working at LV Prasad Eye Institute, Bhubaneswar, India. She has exposure of working at university, research institutes, and industries including VIT University, Vellore, Tamil Nadu, India; CSIR-Central Food Technological Research Institute, Mysore, India; Uttar Pradesh Drugs and Pharmaceutical Co. Ltd., Lucknow, India; and Indian Institute of Food Processing Technology (IIFPT), Thanjavur, Ministry of Food Processing Indus-

tries, Government of India. At IIFPT, Thanjavur, she was involved in a project funded by a leading pharmaceutical company, Dr. Reddy's Laboratories, and have successfully engineered microvehicles for model drug molecules. Her areas of interest include Micro/Nanomaterial fabrication and its applications in various fields – medicine, food, environment, agriculture, and biomedical.

She has published six edited books and one authored book in Springer, Switzerland, and two with CRC Press, USA. She has finished a contract for three book volumes in Elsevier, one volume with Wiley, two book volumes in CRC Press, and one volume in RSC (UK). She has authored many chapters and also published many scientific articles in international peer-reviewed journals. She has received the Certificate for 'Outstanding Contribution' in Reviewing from Elsevier, Netherlands. She has also been nominated for advisory panel for Elsevier Inc., Netherlands. She is the associate editor of *Environmental Chemistry Letters* – a Springer journal of 3.59 impact factor – and also serving as editorial board member and referee for reputed international peer-reviewed journals. She has received several awards and recognitions from different national and international organizations.



Dr. Shivendu Ranjan has expertise in Micro/Nano (Bio)technology and is currently working as Head R&D and Technology Development at E-Spin Nanotech Pvt. Ltd., SIDBI Incubation Center, IITKanpur, India. He has founded and drafted the concept for the first edition of the "VIT Bio Summit" in 2012, and the same has been continued till date by the university. He has worked in CSIR-CFTRI, Mysuru, India; UP Drugs and Pharmaceutical Co. Ltd., India; and IIFPT, Thanjavur, MoFPI, Govt of India. At IIFPT, Thanjavur, he was involved in a project funded by a leading pharmaceutical company,

Dr. Reddy's Laboratories, and have successfully engineered microvehicles for model drug molecules

His research interests are multidisciplinary and include: Micro/Nanobiotechnology, Nano-toxicology, Environmental Nanotechnology, Nanomedicine, and Nanoemulsions. He is the associate editor of *Environmental Chemistry Letters* – a Springer journal of 3.59 impact factor – and an editorial board member in *Biotechnology and Biotechnological Equipment* (Taylor and Francis). He is serving as executive editor of a journal in iMed Press, USA, and also serving as editorial board member and referee for reputed international peer-reviewed journals. He has published six edited books and one authored book in Springer, Switzerland, and two with CRC Press, USA. He has recently finished his contract of three volumes of book in Elsevier, two volumes in CRC Press, and one with Wiley and RSC (UK). He has published many scientific articles in international peer-reviewed journals and has authored many book chapters as well as review articles. He has bagged several awards and recognitions from different national as well as international organizations.



Eric Lichtfouse born in 1960, is a geochemist working on carbon sequestration and climate change at the European Centre of Research and School in Environmental Geosciences. He has invented the ¹³C-dating method allowing to measure the dynamics of soil organic molecules. He has published about 100 articles in organic synthesis, petroleum geochemistry, environmental chemistry, food chemistry, soil science and phytoremediation. He is Chief Editor and Founder of the journal *Environmental Chemistry Letters*, the book series *Sustainable Agriculture Reviews* and *Environ*-

mental Chemistry for a Sustainable World and the magazine *Publier La Science*. His book *Scientific Writing for Impact Factor Journals* contains the micro-article, a new tool to identify the novelty of experimental results. He got awards in analytical chemistry and in science editing. He is also a triathlete who got the Bronze Medal in age groups at the World ITU Cross Triathlon Championships. He has qualified for the Word Ironman, Ironman 70.3 and XTerra Championships, finished 5 times in the top 3 of French Triathlon and Duathlon Championships, and completed 17 ironman competitions.

Chapter 1 An Introduction to Nanomaterials



Fatma Hadef

Contents

1.1	Introduction and Historical Background						
1.2	The N	anoworld	5				
	1.2.1	Lotus Leaves (Self Cleaning)	6				
	1.2.2	Gecko Feet (Adhesive Materials)	7				
1.3	Nanor	naterials	8				
	1.3.1	Definitions	9				
	1.3.2	Classifications	10				
	1.3.3	Structure of Nanomaterials	17				
1.4	Proper	rties: The Physics at the Nanoscale	19				
	1.4.1	Confinement Effect	19				
	1.4.2	Surface Effects	20				
	1.4.3	Thermal Properties	21				
	1.4.4	Optical Properties	23				
	1.4.5	Magnetic Properties					
1.5	Nanor	naterials Synthesis Procedures					
	1.5.1	Bottom-Up Procedures	27				
	1.5.2	Top-Down Procedures	27				
1.6	Applic	cations	28				
	1.6.1	Energy	28				
	1.6.2	Environment	32				
	1.6.3	Nanomedicine	33				
	1.6.4	Sensors	35				
	1.6.5	Nanoelectronics	36				
	1.6.6	Food Industry	38				
	1.6.7	Textile Industry	40				
	1.6.8	Agriculture	42				
1.7		usion	43				
Refe	References						

F. Hadef (🖂)

Département de Physique, Faculté des Sciences, Université 20 Août 1955-Skikda, Skikda, Algeria

[©] Springer International Publishing AG, part of Springer Nature 2018

N. Dasgupta et al. (eds.), *Environmental Nanotechnology*, Environmental Chemistry for a Sustainable World 14, https://doi.org/10.1007/978-3-319-76090-2_1

Abstract Nanotechnology can be defined as the systematic study of materials that have properties critically dependant on length scales on the order of nanometers. Such novel and improved properties make nanoscale materials promising candidates for a wide range of applications that are expected to improve our lifestyles. Here, I review different aspects of nanotechnology. This paper describes first, definitions and classifications of nanomaterials reported in published research works. Then, I disscuss the most enhanced properties of manufactured nanomaterials. This will be followed by a description of the synthesis methods being used to obtain nanostructured materials. Nanotechnology applications in the energy, environment, nanomedicine, sensors, nanoelectronics, textile, food and agriculture fields are discussed in the last section.

1.1 Introduction and Historical Background

The first Industrial Revolution, at the end of eighteenth century, has triggered the development of technological research and the obtention of novel materials (Fajardo et al. 2015). The challenges today are the miniaturation of devices and instruments; smaller volume, lesser power consumption but greater performance. The progression relies upon the searching out new desirable materials and the ability of making tiny structures with high precision. However, the development is not so smooth and easy. One of the most brilliant methods created to answer such condition is the nanotechnology (Fajardo et al. 2015; Huyen 2011). In recent years, research involving nanoscale materials has generated a great deal of interest from scientists and engineers. They view nanotechnology as the revolutionary technology of the twenty-first century (The Royal Society 2004).

Visualize printing all 24 volumes of the Encyclopaedia Britannica on the head of a pin. In 1959, Richard Feynman articulated this reality in an insightful address at the annual meeting of the American Physical Society. In what became a prophetic speech, "There's plenty of room at the bottom" (Feynman 1960). It was a masterly and provocative talk in which the problem of manipulating and controlling things on a small scale was discussed to its extreme limits. Points considered, several of which contained sound predictions, included: information on a small scale, comparisons with the biological systems, miniaturization by evaporation, making small machines, arranging the atoms one by one the way we want (Ferro and Saccone 2008). The tunable material properties that nanotechnology can provide were stated in Norio Taniguchi's paper in 1974 where the term "nanotechnology" was first used in a scientific publication to explain precision engineering in semiconductor processes (Taniguchi 1974). However, the growing interest in nanosciences and nanotechnology emerged during the 1980s with the invention of the scanning tunnelling microscope by Binning and Rohrer. They received the Nobel Prize in Physics in 1986 (Binnig and Rohrer 1986). It was also used in the development of the atomic force microscope, invented by Calvin Quate and Christoph Gerber (Khun 2015). They

provided atomic resolution, three orders of magnitude better than the diffraction limit of optical microscopes, which more than fulfilled Feynman's request to make the electron microscope 100 times better (Roduner 2006). In 1985, fullerene, which is shaped like a ball and just 1 nm in diameter, was discovered by Kroto et al. (1985). In 1986, Eric Drexler published a book titled "Engine of Creation" which disseminates his provocative ideas on molecular nanotechnology to a general audience outside the scientific community (Drexler 1986). In 1991, Sumio Iijima discovered carbon nanotubes, which are tube shaped materials whose diameter measures on the nanometer scale (Iijima 1991). Ahead of schedule in 1995, S.Y. Chou and coworkers firstly proposed the nanoimprint lithography concept in Nanostructure Laboratory of University of Minnesota. Dr. T. Sasaki from National Institute of Research discovered nanosheets and investigation of nanosheets in photocatalytic activity in 1996 (Bashir and Liu 2015). As a strategic and distinct area of scientific inquiry, nanotechnology research began in the United States with the establishment of the National Nanotechnology Initiative (NNI) in 2001 (Eckelman et al. 2008). Actually, scientific journals that are focused specifically on nanotechnology have been started including: International Journal of Nanotechnology, Nano Letters, Journal of Nanoscience and Nanotechnology, Journal of Nanoparticle Research...etc. (Eckelman et al. 2008).

The term nanotechnology is derived from a Greek word 'nano' meaning 'dwarf', hence it relates to materials of very small size ranges (Nikalje 2015). Indeed, it is the creation of materials, components, devices and/or systems at near atomic or molecular levels. Usually, one of the dimensions of nanoproducts is between 1 and 100 nm length in scale. This emerging technology involves fabricating, imaging, measuring, modeling, and manipulating matter at individual atoms, molecules, or particles to significantly improve the physical, chemical, physico-chemical, and biological properties of materials and devices, for various purposes (Asmatulu et al. 2010). This definition has two parts. One is the part about engineering at dimensions of 1-100 nm, and the other is about properties of materials at the nanoscale that enable their use for novel applications. The size range that holds so much interest is typically from 100 nm down to the atomic level, because it is in this range that materials have radically different properties from their bulk counterparts. The main reasons for this change in behavior are an increased relevance of surface and interfacial area (Wardak et al. 2008). On the other hand, nanotechnology, is a new paradigm in fundamental thinking and understanding about the physical universe, where the bottom up approach is the norm and not an exception. In this new approach, one has to think in terms of atoms and how they interact to make useful materials, structures, devices and systems (Raza and Raza 2013; Rocco 2007; Rocco et al. 2011) (Fig. 1.1).

Nanotechnology has been moving from the laboratory environment into applications and consumer products for some time now (Barakat and Jiao 2011). Actually, nanotechnology is a highly multidisciplinary field, bringing together many fields, including: electrical and mechanical engineering, physics, chemistry, and biosciences. It will radically affect all these disciplines and their application areas. Economic impact is foreseen to be comparable to information technology and telecom

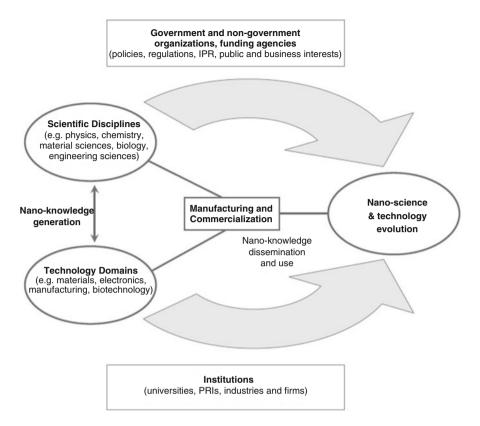


Fig. 1.1 General framework of nanoscience and technology evolution (Reproduced from Islam and Miyazaki 2010 Copyright (2010) Elsevier)

industries (Ermolov et al. 2007). As a result, demand has risen significantly for a workforce capable of supporting this promising technology (Barakat and Jiao 2011). The nanotechnology will create the new horizons for the human world and their promises have been realized to deliver the greatest scientific and technological advances in several areas including: environment, energy, health and medical care, information, communications, and electronics (Daryoush and Darvish 2013). This article addresses to fill current knowledge of manufactured nanomaterials, by providing a comprehensive review of recent developments in the nanotechnology field. It highlights the various definitions, classifications, fundamental properties and synthesis routes of nanomaterials. The review also focuses onto their potential applications in many fields.

1.2 The Nanoworld

The nanoworld is not new. Many important functions of living organisms take place at the nanoscale. The human body uses natural nanoscale materials such as proteins and other molecules, to control the body's many systems and processes. A typical protein such as hemoglobin, which carries oxygen through the bloodstream, is 5 nm in diameter (National Nanomaterial Initiative 2010).

Nanometal particle inclusions have been used for a long time, for example the famous Lycurgus Cup from fourth century AD, which was probably carved in Rome (Fig. 1.2). It appears red by reflexion and green by transmission (Daniszewska et al. 2006). The reason for this dichroism was unknown until detailed SEM analysis of the cup was performed in 1990. It was found that it was due to the presence of nanosized particles of silver (66.2%), gold (31.2%) and copper (2.6%), up to 100 nm in size, embedded in the glass. Light absorption and scattering by these nanoparticles determines the different colours (Filipponi and Sutherland 2013). Another application of alloy nanoparticles is lustered pottery, which shows shining surfaces with particular optical properties. Lustering is one of the most sophisticated techniques used to decorate majolica. It was developed in Iraq and was then introduced in Italy via Spain. The studies showed that the beautiful iridescent reflections of various colors (especially gold and ruby-red) were obtained from a thin metallic film containing silver, copper, and other substances such as iron oxide and cinnabar. The differences in the luster nanostructures suggest how they are affected by not only the chemical composition of the recipes used but also the technological processes used (Pienpinijtham and Thongnopkun 2015).

The existence of nanomaterials has been known for centuries; examples of which are the carbon black, fumed silica, titania; their industrial applications dated since the 1900s (Charitidis et al. 2014). Nanomaterials are, also in the environment (Klaine et al. 2008):

Fig. 1.2 The Lycurgus cup dates from the Roman empire (British Museum)



- 1. In urban atmospheres: diesel- and gasoline-fueled vehicles and stationary combustion sources have for many years contributed particulate material throughout a wide size range, including nanoparticles, amounting to more than 36% of the total particulate number concentrations (Shi et al. 2001).
- 2. In aquatic systems: colloid is the generic term applied to particles in the 1–100 nm size range. Aquatic colloids comprise macromolecular organic materials, such as humic and fulvic acids, proteins, and peptides, as well as colloidal inorganic species, typically hydrous iron and manganese oxides.
- 3. In soils: natural nanoparticles include clays, organic matter, iron oxides, and other minerals that play an important role in biogeochemical processes.

Nanomaterials are in nature. We see hundreds of examples of nanoscience under our eyes daily. Natural nanomaterials are of interest not only to understand the amazing properties of biological materials but also to gather inspiration for the design and engineering of new materials with advanced properties (Filipponi and Sutherland 2013). These natural nanomachines are inspiring in their own right, and their existence and the detailed study of their mode of operation have driven efforts to mimic them using artificially designed and constructed systems – this is called bioinspired nanotechnology or biomimetic nanotechnology (Ramsden 2016).

1.2.1 Lotus Leaves (Self Cleaning)

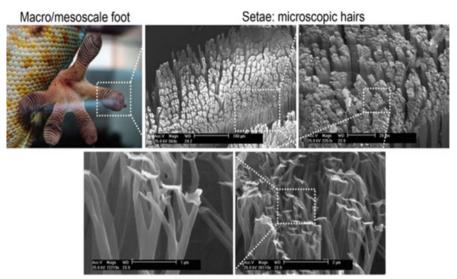
In recent times there has been new understanding about how the hydrophobic (water hating) and hydrophilic (water loving) surfaces work. This effect has been there for millions of years and now scientists call it as the Lotus effect. Lotus (Nelumbo nucifera Gaertn) is an important freshwater aquatic plant within the family Nelumbonaceae (Fig. 1.3). Lotus is also commonly known as sacred lotus or Indian lotus (Zhu 2017). This flower, a symbol of beauty, has a superficial hydrophobic molecular layer made of nanometric-sized hairs on which the tiny water droplets slide, removing any dust particles; as a result the flower retains its shape (Nouailhat 2008). In fact, The surface properties of the lotus leaf were first investigated by Wilhelm Barthlott. In 1997, he published an important paper where he described for the first time the 'Lotus effect' (a term that he later copyrighted) responsible for the self-cleaning properties of the lotus leaves (Filipponi and Sutherland 2013). This self-cleaning behavior, called superhydrophobicity, is useful for many modern applications, including stain-resistant paints and roof tiles as well as coatings for fabrics and other surfaces that need to stay dry and repel dirt. Scientists are also studying this effect for lab-on-a-chip applications, in which hydrophobic and hydrophilic materials can be used to control the flow of liquids through microfluidic components (Risbuda and Bartl 2013; Ressine et al. 2007).



Fig. 1.3 Lotus flowers and leaves (Reproduced from Guo 2009 Copyright (2009) Springer)

1.2.2 Gecko Feet (Adhesive Materials)

Scientific interest in the gecko began when, more than 2000 years ago, the Greek philosopher Aristotle first coined the phrase "like the Gecko lizard" (Aristotle 1918). Since then, this lizard's amazing ability to climb walls and run on ceilings has inspired a wealth of research studies, many of which have proposed reasons for the gecko's amazing adhesive abilities (Greiner 2010). Gecko feet is one of the attractive examples since these animals can climb vertical surfaces without the need of cleaning their feet (Hansen and Autumn 2005). It was not until the 1960s that the German anatomist, Uwe Hiller made a major breakthrough when, using electron microscopy, he revealed the bristle - like, hierarchical structure of the gecko' stoe pads (Hiller and Blaschke 1967; Hiller 1968) that today, are recognized as being responsible for the animal's climbing abilities (Greiner 2010). The gecko foot has a series of small ridges called scansors which contain numerous projections called setae. Each seta is about 100 µm long and has a diameter of about 5 µm. There are about half a million of these setae on the foot of a gecko. Each seta is further subdivided into about a thousand 200 nm-wide projections called spatulae (Fig. 1.4). As a result, the total surface area of the gecko's feet is enormous. The gecko spatulae are very flexible, so they essentially mould themselves into the molecular structure of any surface. The result is a strong adhesion which is entirely due to van der Waals forces (Filipponi and Sutherland 2013). Researchers are experimenting with using gecko tape on the feet of climbing robots (Kunkel Microscopy).



Spatulae: nanoscale tips

Fig. 1.4 Multi-scale combined hierarchical gecko foot hairs. As shown, millions of fine microscopic foot hairs (setae) on the attachment pads split into hundreds of nanoscale ends (spatulae) (Reproduced from Jeong and Suh 2009 Copyright (2009) Elsevier)

1.3 Nanomaterials

Nanomaterials and nano-manufactured goods represent areas of scientific research and industrial applications in full expansion (Gaffet 2011). Size reduction can lead to a whole range of new physico-chemical properties and a wealth of potential applications (Lehn 2006). These propertites strongly depends on size, shape, surface area and structure of particles. Nanomaterials can exist in single, fused, aggregated or agglomerated forms with spherical, tubular, and irregular shapes (Kumar and Kumbhat 2016). The major advantages of nanomaterial over bulk material include decrease in melting point and surface area, increase in dielectric constant and mechanical strength (Maddineni et al. 2015; Dasgupta et al. 2016; Ranjan et al. 2016; Pulimi and Subramanian 2016). In addition, size of nanoparticles enables them to absorb exceptionally on to other material (Dasgupta et al. 2015; Ranjan et al. 2015, 2016). Because of all these unique behaviour and properties, nanoparticles have wider application in textiles, clothing, and cosmetics, pharmaceutical, electronic and paint industry. Also, they are widely used for development of health care products and remediation of contaminated environment (Pulimi and Subramanian 2016).

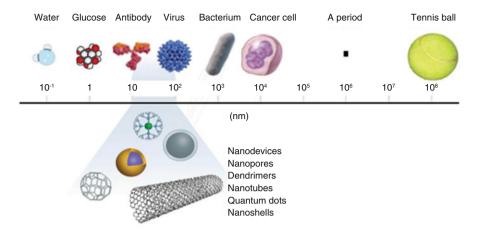


Fig. 1.5 A size comparison of nanoparticle with other larger-sized materials (Reproduced from Amin et al. 2014 Copyright (2014) Hindawi publishing corporation)

1.3.1 Definitions

Nanomaterials, once called by Paul Ehrlich as "Magic Bullets" (Kreuter 2007), are one of the most studied materials of the century that gave birth to a new branch of science known as nanotechnology (Nasir Khan et al. 2017). Nanomaterials are chemical substances or materials that are produced or used at a very small scale. In fact, the term material refers to an almost infinite number of constituents, collectivelly displaying an averaged statistical behavior. Therefore the behavior of nanomaterials is dominated by particular interface effects and exhibit characteristics affected by size and the limited number of constituents (Bahrami 2007).

But what is a nanometer? A nanometer is a thousandth of a micron and a micron is a thousandth of a millimeter, so a nanometer is a millionth of a millimeter or 10^{-9} m (Fig. 1.5). To date, there is no uniformly accepted definition of what in fact constitutes a 'nanomaterial'. To be classified as a nanomaterial, the material must be less than 100 nm in size in at least one direction. In 2008 and 2010, the International Standardization Organization has provided overarching technical definitions for nanotechnology-related terms: 'Nanomaterial' is defined as material with any external dimension in the nanoscale or having internal or surface structure in the nanoscale, with 'nanoscale' defined as the size range from approximately 1 to 100 nm (ISO/TS 27687 2008; ISO/TS 80004-1 2010). The European Commission has defined a nanomaterial as "Nanomaterial" means a natural, incidental, or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range 1-100 nm (Official Journal of the European Union 2011). The definition, adopted in 2011, aims to provide a reference for determining whether a material should be considered as a nanomaterial for legislative and policy purposes in the European Union. This latter is the only definition that includes natural or accidentally occurring nanoparticles, whereas all other definitions are restricted to 'intentionally produced, manufactured, or engineered nanomaterials (Cefic 2012).

The following microstructural features are considered to be the main factors on which the properties of the nanostructured materials are defined (Lemoine 2000):

- 1. Fine grain size and size distribution (less than 100 nm).
- 2. Presence of interfaces (grain boundaries, heterophase interfaces, free surface).
- 3. Interactions between constituent domains.

1.3.2 Classifications

A nanomaterial is a broad name given to all types of materials found at the nanoscale. Several names have been given to these new materials; nanostructured, nanometer-sized, ultrafine-grained ...etc. They can be naturally occurring or chemically, mechanically, physically, or biologically synthesized with various structures (Saleh 2016). Nanomaterials can be classified based on different parameters including their origin (natural or anthropogenic); chemical composition (organic and inorganic); formation (biogenic, geogenic, anthropogenic, and atmospheric); size, shape, and characteristics; and applications in research and industry (Salah and Gupta 2016).

1.3.2.1 Classification of Nanomaterials Based on Their Origin

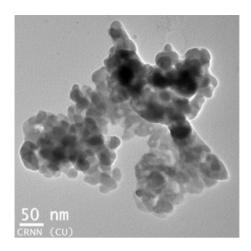
Nanomaterials can be of two types (Filipponi and Sutherland 2013):

- 1. Non-intentionally made nanomaterials, which refers to nano-sized particles or materials that belong naturally to the environment (e.g. proteins, viruses, nanoparticles produced during volcanic eruptions, ...etc.) or that are produced by human activity without intention (e.g. nano-particles produced from diesel combustion).
- 2. Intentionally made nanomaterials, which refers to nanomaterials produced deliberately through a defined fabrication process.

1.3.2.2 Classification of Nanomaterials Based on Chemical Composition

On the basis of their chemical composition, they can be classified into various categories, Metal-based materials are mainly composed of metals (e.g, silver, gold, and copper nanoparticles). Metal oxide nanomaterials are made of metal and oxygen, such as titania, silica, and alumina...etc. (Saleh and Gupta 2016).

Fig. 1.6 Particle distribution of CdTe nanoparticles from TEM micrograph (Reproduced from Das et al. 2016 Copyright (2016) Elsevier)



1.3.2.3 Classification of Nanomaterials Based on Dimensionality

Nanomaterials with structural features at the nanoscale can be found in different forms. The materials of interest include metals, amorphous and crystalline alloys, semiconductors, oxides, nitride and carbide ceramics in the form of clusters, thin films, multilayers, and bulk nanocrystalline materials. According to this concept, nanomaterials can be classified as follows:

1.3.2.3.1 Zero-Dimensional (0-D)

They are crystalline clusters of a few hundred to a few thousand atoms with sizes of ranging from 2 to 100 nm (Wani 2015) (Fig. 1.6). Nanoparticles have been used in glass making since Mesopotamian and Roman times. However, it is only recently that nanoparticles and materials have been knowingly and deliberately manufactured (Royal Society of Chemistry 2011). In general, there are two broad types of nanoparticles: incidental and engineered. Incidental airborne nanoparticles (diameters less than 100 nm), also referred to as ultrafine particles, are common in indoor air. Engineered nanoparticles, on the other hand, are manufactured materials, and there are a growing number of concerns about the potential hazards associated with these particles (Jordan et al. 2014). Engineered nanoparticles cover a broad range of compounds, including both inorganic (elemental metals, metal oxides, metal salts, and aluminosilicates) and organic (fullerenes, micelle-like amphiphilic polyurethane particles, and dendrimers) compounds (Filella 2012).

Man-made/engineered nanoparticles have well-known applications in wide range of fields with the increasing demand in material science, electronic devices, biomedical research, food industry etc. Within the biomedicine industry, nanoparticle application has expanded to the areas of diagnostics and therapeutic purposes. The nano product demands in medicine and the pharmaceutical industry is expected to rise by over 17% each year and at a much higher rate in the food industry (Jones and Grainger 2009, Jain et al. 2016). Metal nanoparticles are mainly used for drug delivery systems. These metals include silver AgNP, gold AuNP, titanium dioxide TiO_2 NP, and silica SiO₂.

Many techniques, including both top-down and bottom-up approaches, have been developed and applied for the synthesis of nanoparticles. The most traditional preparation method for nanoparticle synthesis is the sol-gel method (Brinker and Scherer 1990; Rajendran and Sen 2017). This technique allows the addition of all the dispersants in one synthetic step. In the spray-drying technique, a homogenized precursor solution and relevant additives are sprayed within a specially designed chamber at temperatures at or above the boiling point of the solvent leading to the quick formation of metallic nanoparticles. The ablation of a solid source with a pulsed laser can also yield nanoparticles, but the formation mechanism is at present not very clear. A micronsized aerosol droplet may also yield nanoparticles by evaporating a solute-containing droplet. Electrospray systems are often applied as droplet generators, as they produce very small droplets being quite monodisperse in comparison to other spray processes (Kruis 2001). Recently much attention was focused on green and biological synthesis of metallic nanoparticles using plants and microorganisms (Kumar et al. 2012, 2015; Kumar and Sen 2013).

Quantum Dots

Quantum dots or QDs, also known as nanocrystals, are another form of nanomaterial and are a specific type of semiconductor. They are 2-10 nm (10-50 atoms) in diameter (Salamon et al. 2010). The optical properties of nanocrystals are defined by their size and surface chemistry and they differ drastically from those of the bulk solids (Mohapatra et al. 2012). Indeed, QDs of the same element, are clusters of atoms less than tens of nanometers in size that emit different colors depending on their specific particle size (Kang 2010). In structure, quantum dots consist of a metalloid crystalline core and a 'cap' or 'shell' that shields the core. QDs cores can be formed from a variety of metal conductors such as semiconductors, noble metals and magnetic transition metals (Allsopp et al. 2007). The shells are also formed of a variety of materials. Therefore, not all quantum dots are alike and they cannot be considered to be a uniform group of substances (Hardman 2006). As quantum dots have such a small size they show different properties to bulk material. Hence the 'tunability', for example, sensitivity to different wavelengths of light, can be adjusted by the number of atoms or size of the quantum dot. They are typically made from CdSe, ZnS or CdTe compounds (Salamon et al. 2010). Quantum dots can be used for LEDs and solid-state lighting, displays, photovoltaics, transistors, quantum computing, medical imaging, biosensors, among many others (Material Matters 2012).

Fullerene

The first 0D graphite allotrope molecule to be discovered, and the family's namesake, buckminsterfullerene (C_{60}) (Fig. 1.7), was prepared in 1985 by Richard Smalley, Robert Curl, James Heath, Sean O'Brien, and Harold Kroto at Rice University. They named the molecule Buckminsterfullerene in honor of the

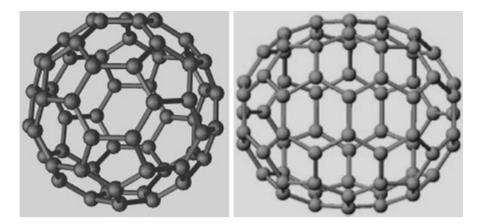


Fig. 1.7 The structures of C_{60} and C_{70} molecules (Reproduced from Wang 2015 Copyright (2015) Elsevier)

American architect R. Buckminster Fuller who introduced geodesic structures in architecture (Kroto et al. 1985). Its existance had been predicted before, in 1970, by the Japanese theoretician Eiji Ozawa (Ozawa et al. 1993). Fullerene or C_{60} is soccer – ball – shaped molecule, with a diameter around 1 nm, consisting of 20 hexagonal and 12 pentagonal rings as the basis of an icosahedral symmetry closed cage structure. In fullerenes, all the carbon atoms are sp² hybridized but they are not arranged on a plane like in graphite (Connell 2006; Meyyappan 2005). The unique morphology of these nanostructures possess large surface area to volume ratio and is suitable for a wide variety of applications (Cherusseri and Kar 2015). More than thirty higher fullerenes including C_{70} , C_{76} , C_{78} , C_{84} , C_{90} and C_{94} and their derivatives are synthesized along with C_{60} (Diederich et al. 1991).

1.3.2.3.2 One-Dimensional (1-D)

The second class of nanoscale materials, referred to as 1-D nanostructures, is reserved for those materials that have nanoscale dimensions that are equivalent in all but one direction (Balaz 2008). They are generally well understood and technologically advanced (The Royal Society 2003). One-dimensional nanoscale materials, such as nanowires and nanofibers, are extremely attractive as main elements for the first action of the sensors (Fig. 1.8). These nanoscale materials offer significant advantage over bulk or thin-film planar devices (Abdelsalam and Abdelaziz 2014). Nanofibers are slightly larger in diameter than the typical nanomaterial definition, though still invisible to the naked-eye. Their size ranges between 50 and 300 nm in diameter and are generally produced by electro spinning in the case of inorganic nanofibers or catalytic synthesis for carbon nanotubes. Nanofibers can be electrostatically aligned and biochemically aligned (Kumar and Kumbhat 2016). Similar to nanofibers are nanowires. In these systems, one dimension exceeds by an order of magnitude the

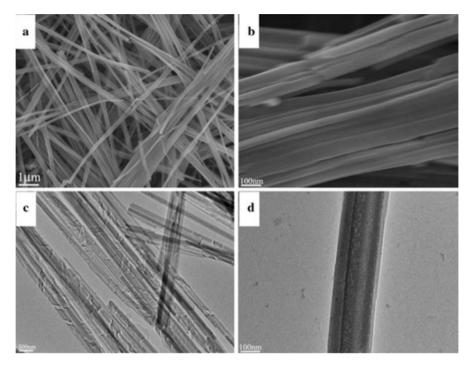


Fig. 1.8 SEM images (a and b) and TEM images (c and d) of FeC_2O_4 nanowires (Reproduced from Du et al. 2010 Copyright (2010) Springer International Publishing)

other two dimensions, which are in the nano-range (Gubin 2009). This class of nanomaterials can be potentially used in nanophotonics, laser, nanoelectronics, solar cells, resonators and high sensitivity sensors (Chellammal 2013).

Carbon Nanotubes

The discovery of carbon nanotubes is most often attributed to Sumio Iijima and his 1991 publication in Nature (Iijima 1991). Carbon nanotubes (CNTs, also called buckytubes in earlier days) are elongated cylindrical fullerenes with diameters of nanometers and lengths of microns even millimeters (Ren et al. 2013). There are two basic types of CNTs: single-wall carbon nanotubes, SWCNTs, which are the fundamental cylindrical structure and multi-wall carbon nanotubes, MWCNTs, which are the fundamental cylinders (Fig. 1.9), having interlayer spacing close to that of the interlayer distance in graphite (0.34 nm) (Ajayan 2000). The walls of these tubes are constructed of a hexagonal lattice of carbon atoms and capped by fullerene-like structures (Ong et al. 2010).

The electrical conductivity of SWNTs may vary from metallic to semiconducting, depending on the way a graphene sheet is folded. For metallic SWNTs, the electrical conductance may exceed silver or copper by three orders of magnitude. Another electronic application for CNTs is for next-generation field-effect transistor, FET