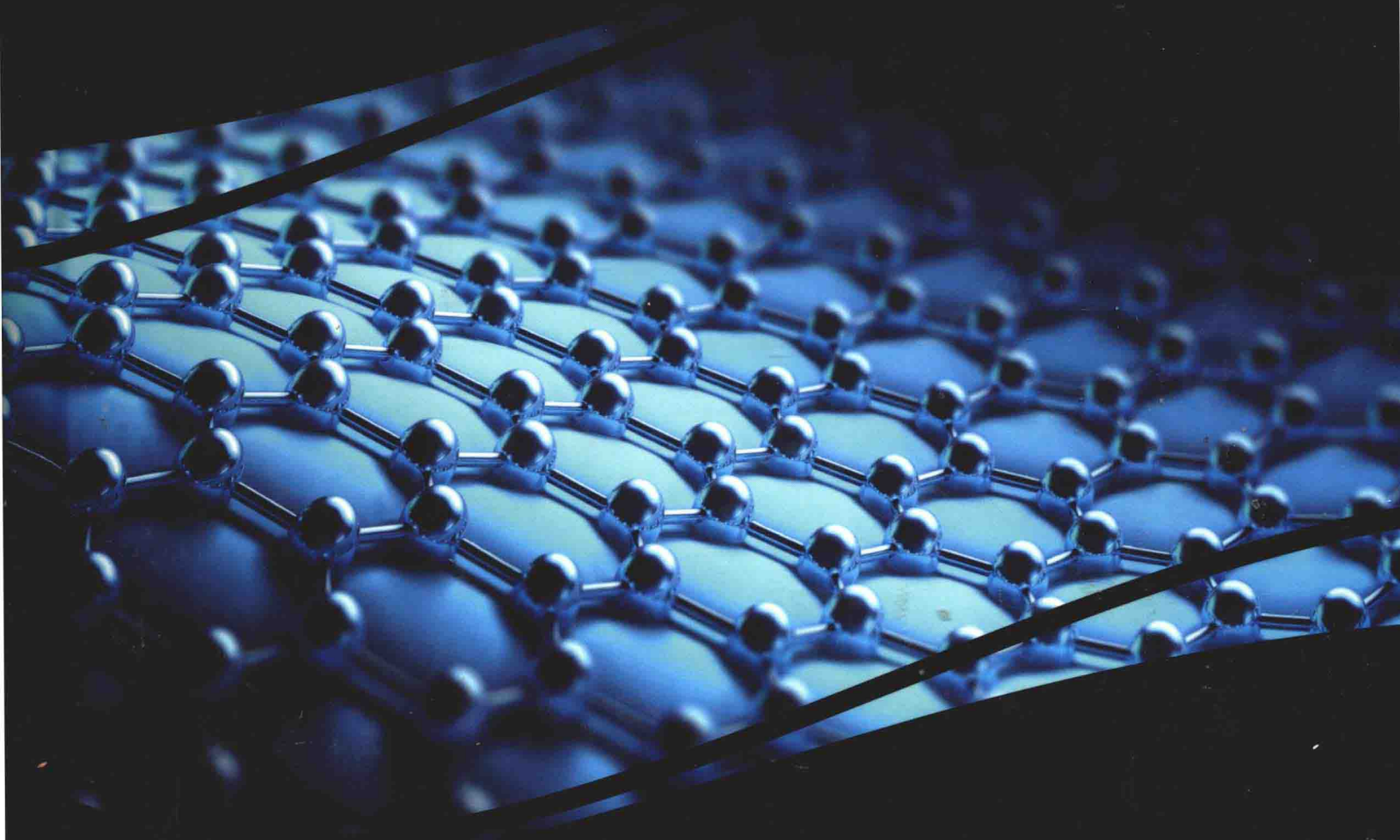
Premier Reference Source

Sustainable Nanosystems Development, Properties, and Applications



Mihai V. Putz and Marius Constantin Mirica

IGI GLOBAL
DISSEMINATOR OF KNOWLEDGE

Sustainable Nanosystems Development, Properties, and Applications

Mihai V. Putz
West University of Timişoara, Romania & Research and Development National Institute for Electrochemistry and Condensed Matter (INCEMC) Timişoara, Romania

Marius Constantin Mirica
Research and Development National Institute for Electrochemistry and Condensed Matter (INCEMC) Timişoara, Romania

A volume in the Advances in Chemical and Materials Engineering (ACME) Book Series

IGI GLOBAL
DISSEMINATOR OF KNOWLEDGE

www.igi-global.com

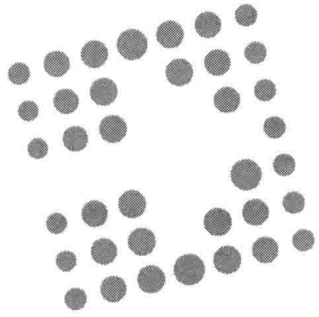
Published in the United States of America by
Engineering Science Reference (an imprint of IGI Global)
701 E. Chocolate Avenue
Hershey PA, USA 17033
Tel: 717-533-8845
Fax: 717-533-8661
E-mail: cust@igi-global.com
Web site: http://www.igi-global.com

Library of Congress Cataloging-in-Publication Data

Names: Putz, Mihai V., editor. | Mirica, Marius Constantin, 1974- editor.
Title: Sustainable nanosystems development, properties, and applications / Mihai V. Putz and Marius Constantin Mirica, editors.
Description: Hershey, PA : Engineering Science Reference, [2017] | Includes bibliographical references and index.
Identifiers: LCCN 2016012148| ISBN 9781522504924 (hardcover) | ISBN 9781522504931 (ebook)
Subjects: LCSH: Nanostructured materials. | Nanoelectronics. | Green electronics. | Green technology.
Classification: LCC TA418.9.N35 S885 2017 | DDC 620/.5--dc23 LC record available at https://lccn.loc.gov/2016012148

This book is published in the IGI Global book series Advances in Chemical and Materials Engineering (ACME) (ISSN: 2327-5448; eISSN: 2327-5456)

British Cataloguing in Publication Data
A Cataloguing in Publication record for this book is available from the British Library.



Advances in Chemical and Materials Engineering (ACME) Book Series

J. Paulo Davim
University of Aveiro, Portugal

ISSN: 2327-5448
EISSN: 2327-5456

Mission

The cross disciplinary approach of chemical and materials engineering is rapidly growing as it applies to the study of educational, scientific and industrial research activities by solving complex chemical problems using computational techniques and statistical methods.

The **Advances in Chemical and Materials Engineering (ACME) Book Series** provides research on the recent advances throughout computational and statistical methods of analysis and modeling. This series brings together collaboration between chemists, engineers, statisticians, and computer scientists and offers a wealth of knowledge and useful tools to academics, practitioners, and professionals through high quality publications.

Coverage

- Biomaterials
- Artificial Intelligence Methods
- Thermo-Chemical Treatments
- Materials to Renewable Energies
- Toxicity of Materials
- Heat Treatments
- Fatigue and Creep
- Multifuncional and Smart Materials
- Metallic Alloys
- Computational methods

IGI Global is currently accepting manuscripts for publication within this series. To submit a proposal for a volume in this series, please contact our Acquisition Editors at Acquisitions@igi-global.com or visit: http://www.igi-global.com/publish/.

The Advances in Chemical and Materials Engineering (ACME) Book Series (ISSN 2327-5448) is published by IGI Global, 701 E. Chocolate Avenue, Hershey, PA 17033-1240, USA, www.igi-global.com. This series is composed of titles available for purchase individually; each title is edited to be contextually exclusive from any other title within the series. For pricing and ordering information please visit http://www.igi-global.com/book-series/advances-chemical-materials-engineering/73687. Postmaster: Send all address changes to above address.

Titles in this Series

For a list of additional titles in this series, please visit: www.igi-global.com

Computational Approaches to Materials Design Theoretical and Practical Aspects
Shubhabrata Datta (Calcutta Institute of Engineering and Management, India) and J. Paulo Davim (University of Aveiro, Portugal)
Engineering Science Reference • copyright 2016 • 475pp • H/C (ISBN: 9781522502906) • US $215.00 (our price)

Green Approaches to Biocomposite Materials Science and Engineering
Deepak Verma (Graphic Era Hill University, Dehradun, India) Siddharth Jain (College of Engineering Roorkee, India and University of Alberta, Canada) Xiaolei Zhang (Queens University, Belfast, UK) and Prakash Chandra Gope (College of Technology, G.B.Pant University of Agriculure and Technology, Pantnagar, India)
Engineering Science Reference • copyright 2016 • 322pp • H/C (ISBN: 9781522504245) • US $165.00 (our price)

Position-Sensitive Gaseous Photomultipliers Research and Applications
Tom Francke (Myon, Sweden) and Vladimir Peskov (CERN, Switzerland)
Engineering Science Reference • copyright 2016 • 562pp • H/C (ISBN: 9781522502425) • US $240.00 (our price)

Research Perspectives on Functional Micro- and Nanoscale Coatings
Ana Zuzuarregui (CIC nanoGUNE Consolider, Spain) and Maria Carmen Morant-Miñana (CIC nanoGUNE Consolider, Spain)
Information Science Reference • copyright 2016 • 511pp • H/C (ISBN: 9781522500667) • US $215.00 (our price)

Emerging Research on Bioinspired Materials Engineering
Mohamed Bououdina (University of Bahrain, Bahrain)
Engineering Science Reference • copyright 2016 • 441pp • H/C (ISBN: 9781466698116) • US $215.00 (our price)

Petrochemical Catalyst Materials, Processes, and Emerging Technologies
Hamid Al-Megren (King Abdulaziz City for Science and Technology, Saudi Arabia) and Tiancun Xiao (Oxford University, UK)
Engineering Science Reference • copyright 2016 • 539pp • H/C (ISBN: 9781466699755) • US $225.00 (our price)

Applying Nanotechnology to the Desulfurization Process in Petroleum Engineering
Tawfik A. Saleh (Department of Chemistry, King Fahd University of Petroleum and Minerals, Saudi Arabia)
Engineering Science Reference • copyright 2016 • 555pp • H/C (ISBN: 9781466695450) • US $235.00 (our price)

Quantitative Structure-Activity Relationships in Drug Design, Predictive Toxicology, and Risk Assessment
Kunal Roy (Jadavpur University, India)
Medical Information Science Reference • copyright 2015 • 703pp • H/C (ISBN: 9781466681361) • US $295.00 (our price)

www.igi-global.com

701 E. Chocolate Ave., Hershey, PA 17033
Order online at www.igi-global.com or call 717-533-8845 x100
To place a standing order for titles released in this series, contact: cust@igi-global.com
Mon-Fri 8:00 am - 5:00 pm (est) or fax 24 hours a day 717-533-8661

Foreword

Dimensional analysis is based on the idea that length, mass, and time are fundamental parameters in all physical laws. During the first part of the 20th century, cm-gram-sec was the units for measuring these parameters, later changed to m-kg-sec units, compatible with the familiar macroscopic world. Physicists know about the simplifications in laws based on natural (Planck) units for length (1.616199×10^{-35} m), mass (2.17651×10^{-8} kg), and time (5.39106×10^{-44} s), but the numbers for length and time are incredibly small to be useful in everyday life.

Then Richard Feynman gave a lecture at Caltech in 1959 with the title "There's Plenty of Room at the Bottom" (freely available on the web) arguing that one could handle atoms one by one, opening the area of nanotechnology and nanorobots. The two challenging prizes for nanotechnology offered by Feynman were soon implemented experimentally. During the last four decades, K. Eric Drexler added to Feynman's concepts the idea of molecular manufacturing under computer control. At the end of the 20th century and the beginning of the 21st century, we have seen that indeed the numbers of transistors in dense integrated circuits doubled approximately every two years in agreement with Gordon E. Moore's Law.

Nowadays the International Union of Pure and Applied Chemistry in collaboration with the Union of Pure and Applied Physics have redefined the base units of the International System (SI) as follows: the meter is the length of the path travelled by light in vacuum during a time interval of 1/299792458 of a second, which in turn is the duration of 9192631770 periods of the radiation corresponding to the transition between the two hyperfine levels of the ground state of the cesium 133 atom. A new unit, the mole, is the amount of substance of a system which contains as many elementary entities as there are atoms in 0.012 kilogram of carbon 12. All these new definitions now refer to the nanoworld. Gerd Binnig and Heinrich Rohrer from IBM won the Nobel Prize for Physics in 1986 for inventing scanning tunneling microscope, and then Binnig, Quate and Gerber invented in 1986 the atomic-force microscope able to handle individual atoms. Adding the time dimension to these "descents to the bottom", Ahmed Zewail was awarded the 1999 Nobel Prize in Chemistry for his work on femtosecond chemistry.

A book reviewing past and future directions for the development of sustainable nanosystems is therefore welcome. The Editors have tried to group together authors from various countries working in areas related to the book's perspective. It is very likely that most of the developments will be based on carbon and possibly on a few other chemical elements centered on carbon and this fact is mirrored on titles of several chapters of the book. Readers with many different types of interests will be interested to learn forecasts about experimental and/or computational nanochemistry and related fields.

Alexandru T. Balaban
Texas A&M University – Galveston, USA

Preface

FACING SUSTAINABLE NANOSYSTEMS IN THE 21ST CENTURY

The present edited book endeavor is motivated by noticing the parallel evolution of Sciences on XX with the rising XXI: 1914 was the year when the general theory of relativity was still not published, and the quantum mechanics was just in its infancy by the 1913' Bohr paper on atomic structure, yet still waiting for the golden age of 20'-30' when the modern foundation of Physics and Chemistry was laid by the cornerstone contributions of Schrödinger, Hückel, Pauli, Pauling and their peers. ON chemical side instead, Lewis advanced on 1916 its cubic atom as the basic structural ingredient of molecules, from where the chemical bonding by electronic pair (the doublet) raised, while the full atomic cubic configuration (the octet rule) was naturally formulated, then extended by Langmuir (1919) contributions till the 60' Linnett's double quartet theory. Equally ground-breaking experiments as those advancing the chemical nano-structure determinations by X-ray diffraction, the Raman spectroscopy, by LASER applications, to the femtosecond chemistry just spanned the XX century with all its peaks towards the nowadays integrated nano-chemistry. So, where we are today? At near a century from Lewis's theory of chemical structure and "cocking" the XXI scientific revolution for when century anniversary from when the quantum mechanics expanded our world from 1927 ahead is anticipated! So 2027 is nearly knocking, and then with the rest of XXI fully of fundamental and applicative frontiers' expansions and "scientifically miracles" just ready to come! The signs are obvious from nowadays: the chemistry is no longer a self-contained discipline anymore; it becomes nano-chemistry, while physics merged with material sciences. Accordingly, at the middy of the second decade of XXI the modern mankind would like knowing the main concepts, trends and frontiers the science (fundamentals) and technology (applications) are preparing for the remaining growing century. Roughly the main XXI chapters can be identified as: organisms (living bodies), medicines (health and life prolongation), food (the earth supply), energy (life and environmental fuel and eco-nano-materials), and communication (spiritual needs).

Take for instance the photoelectrochemical effect: it just entered in its third century of study and applications from its discovery: it started with the Becquerel 1839 report of a photovoltage by an electrode under light action in the electrolytic solution; it passed on 1870 to 1900 when the selenium solid material featured the same effect, yet with 1% efficiency; it was 50 years later when Chapin while using silicon cell raised the efficiency to 6%, which was further increased (to 14% and then over 30% for GaAs multijunction) so that the so called inorganic photovoltaics were implemented satellites (starting with Vanguard I on March 1958) and other space-mission (including security) applications. Yet, they feature significant costs and relative fragility. Accordingly, the second generation of solar cells were designed, namely as based on organic and polymeric conjugated semiconducting materials; they appear

very promising due to ultra-fast optoelectronic response of carriers at donor-acceptor interface, by tunability of the energy gap by organic synthesis, by smooth integrability of plastic devices in every-day life and applications, and by the low-cost fabrication on large-scale; their study also opened the possibility of the so called dye-sensitized (DS) solar cell (SC) concept, commonly referred to as DSSC systems; nevertheless, the relatively low efficiency of photo-electricity conversion was boosted by the Graetzel employment (1991-2002) of the nanocrystalites TiO2 as thin films as electrode with Ru bipyridil complex as photosensiter to reach a solar conversion efficiency over 10% for air-mass (AM) 1.5, i.e. for non-vertical sun angle; the mesoporous surface of TiO_2 certainly contribute to the recorded enhancement in solar-to-energy conversion; with this we arrived to the third generation of photoelectrochemical solar cells - namely on those based on quantum dots (QD) sensitors (e.g. the oxides SnO2, ZnO, In2O3, NiO, Nb2O3, and their combined nanostructures as SnO2/ZnO, SnO2/MgO, etc.): they greatly use the quantum confinement attribute, that is their dimensions are directed by the action radius corresponding with the HOMO-LUMO (donor-acceptor) energy gap - which provides also the main current challenge regarding the quantum dots, i.e. the fine tuning of their synthesis since strongly depend on the critical size activating or inhibiting the solar cell electric circuit; this is the reason why, currently, the theoretical predictions of about tenths' order of conversion efficiency is practically registered around 5% output only; it is also why, and from where the present project is needed in assessing and designing reliable quantum dot sensitized solar cells (QDSSC) with sustainable (so renewable) energy. And still, more efficiency is required from quantum-dots science and technology towards combining low price in design, activation and production with increased efficiency and life-reliability: this is a typical example of what will become a sustainable nano-system.

In this context, and with this aim, the present book collects eminent contributions from active and recognized scholars from many continents gathered by the same passion in modeling and designing, either at fundamental research as well as by experimental development the sustainable lines for the next generation of eco-nano-materials being part of our every-day life, global economy and promising future.

The book breakdown chapters' structure flows as following.

Chapter 1 by Kori D. McDonald, Evelyn O. Ojo and Joel F. Liebman (What are the Structures of the Octet Rule obeying All-Carbon Species C_x ($2 \leq x \leq 7$ and larger x): A Pedagogical, Mathematical and Pictorial Study) discusses the possible structures for all-carbon species in which each carbon obeys the octet rule along introducing and then employed a new method, using the eigenvalues and eigenvectors of the structure's adjacency matrix and modified matrices, to guarantee structural uniqueness, names and better understanding of what was chemically reasonable and realizable for carbon-based produced structures.

Chapter 2 by István László, Ibolya Zsoldos and Dávid Fülep (Self Organizing Carbon Structures: Tight Binding Molecular Dynamics Calculations) reviews quantum chemical molecular dynamics calculations which selectively produce the buckminsterfullerene C_{60}, the C_{70}, the armchair and the zigzag nanotubes depending on the initial structure of patterns cut out from the graphene.

Chapter 3 by Ioan-Cezar Marcu, Adriana Urdă, Ionel Popescu, and Vasile Hulea (Layered Double Hydroxides-Based Materials as Oxidation Catalysts) focuses on the transition-metal-containing layered double hydroxides (LDHs)-based materials having potential applications in both catalytic selective oxidation for obtaining chemicals and intermediates, and complete oxidation as a promising valuable technology for the destruction of volatile organic compounds (VOCs).

Chapter 4 by Sorana D. Bolboacă and Lorentz Jäntschi (Characteristic Polynomial in Assessment of Carbon-Nano Structures) constructs and investigates from the topological point of view six dodecahe-

drane assemblies as multiple of five and respectively six structures; the investigation is conducted using characteristic polynomials, graph invariant encoding important properties of the graph of the chemical structure towards obtaining their spectra allowing in modeling/predicting the behavior of investigated assembly.

Chapter 5 by Marilena Ferbinteanu, Harry Ramanantoanina, and Fanica Cimpoesu (Case Studies in the Challenge of Properties Design at Nanoscale. Bonding Mechanisms and Causal Relationship) expose several cases relating the magnetic properties with methods of electron structure calculations and phenomenological models in the range of nanometers – there where many consecrated magnetic materials can be prepared at nano-scale granulation, such as oxides, with a bonding and exchange coupling mechanisms having the same causal engines as identified in coordination systems.

Chapter 6 by Zahra Khalaj, Majid Monajjemi, and Mircea V. Diudea (Main Allotropes of Carbon: A Brief Review) briefly reviews the introductory to some major allotropes: graphene, graphite, carbon nanotube, diamond and amorphous carbon; in addition, chemcial vapor deposition (CVD) techniques which mostly use for syntesizing these structures are also presented, while the influence of some important experimental parameters on growth of high quality diamond and diamond-like carbon (DLC) are equally investigated.

Chapter 7 by G.V. Zhizhin and M.V. Diudea (Space of Nanoworld) proposes a geometrical model to accurately describe the distribution of light points in diffraction patterns of quasicrystals; moreover, in supporting the idea of n-dimensional domains entangled within the three-dimensional Euclidean space, in minerals or synthetic chemicals, two series of small double-shell clusters are designed by operations on maps and their topological properties discussed.

Chapter 8 by Manoj Kumar, Pradip Kumar Jha, and Aranya B. Bhattacherje (Effects of Spin Orbit Interaction on Optical Properties for Quantum Dot and Quantum Wire) investigates the influence of external magnetic field on the optical absorption and refractive index changes for a parabolically confined quantum dot in the presence of Rashba spin orbit interaction; the results indicate the important influence of magnetic field on the peak positions of absorption coefficient and refractive index changes; the influence of external electric field and magnetic field on the optical absorption of a parabolic confinement wire is also studied.

Chapter 9 by Mihai V. Putz, Marina A. Tudoran, and Marius C. Mirica (Quantum Dots Searching for Bondots. Towards Sustainable Sensitized Solar Cells) reviews the relatively new technique of quantum-dots sensitizing the solar cells for optimum cost-efficiency of photovoltaics, while launching new concept of bonding-quantum dots – the so called bondots (abbreviated as $\not{D}$), founded on the Dirac quantum theory of coupling spinors; the associated analytics and basic illustration on paradigmatic chemical bonds are revealed, so paving the way for experimentally searching of at least doubling the photo-electric conversion in sustainable bondotic sensitized solar cells.

Chapter 10 by Mihai V. Putz, Marina A. Tudoran, and Marius C. Mirica (Bondonic Electrochemistry: Basic Concepts And Sustainable Prospects) reviews the main concepts of electrochemistry in a fundamental manner including the asymmetric currents approach in the galvanic cells; the whole electrochemical process is then combined with embedded the bondonic chemistry modeling the electronic charge transfer sensitizing the anode electrode and the overall photovoltaic effect through the electrolyte fulfilling the red-ox closed circuit; the resulted bondonic electrochemistry may be sustainable integrated with the fresh approach of sensitization of the solar cells by the bonding quantum dots (the bondots), see also the preceding chapter, towards a bondonic-bondotic photo-electrochemical integrated and cost-effective photo-current conversion.

Chapter 11 by Mihai V. Putz, Marina A. Tudoran, Marius C. Mirică, Mirela I. Iorga, Radu N. Bănică, Ştefan D. Novaconi, Ionel Balcu, Ştefania F. Rus, and Ana-Maria Putz (Sustainable Design of Photovoltaics: Devices and Quantum Information) reviews the main features of photo-electrochemistry processes from the perspective of devices phenomenology serving to sustainable design of photovoltaics, while providing the quantum insight in terms of data observability and interpretation; moreover, the bondonic information for molecules activated in mesoscopic scale are determined while combining their FT-IR spectra with photovoltaic fill factor and metrological quantum triangle (electron tunneling, Josephson effect and quantum Hall effect) towards challenging new perspective of sub-quantum interaction in condensed nano-matter.

Chapter 12 by Livia Petrescu, Speranta Avram, Maria Mernea, and Dan Florin Mihailescu (Up-Converting Nanoparticles, Promising Markers for Biomedical Applications) chapter reviews principal characteristics of up-converting nanoparticles and issues related to their use in biomedical applications referring to identification of optimal size suited for specific samples, prevention of aggregation, water stability/dispersibility, optical efficiency and biocompatibility.

Chapter 13 by V. Krasnoholovets (A Theoretical Study of The Refraction Index Of KDP Crystal Doped with TiO_2 Nanoparticles) studies a nonlinear response of an optical matrix formed by the K_2HPO_4 crystal doped with TiO_2 nanoparticles; the gigantic non-linear susceptibility $\chi^{(3)}$ responsible for the phenomenon of focusing of the laser beam is calculated by using the pseudospin model for the description of ferroelectric crystals and the expressions for nonlinear-susceptibility tensor components computed by other researchers.

Chapter 14 by Laurentiu Popescu, Adrian C. Robu, and Alina D. Zamfir (Sustainable Nanosystem Development for Mass Spectrometry. Applications in Proteomics and Glycomics) reviews the strategies, which allowed a successful development of nanotechnology for MS and the applications in biological and clinical research it presents the principles and technical developments of advanced nanosystems for electrospray and matrix-assisted laser desorption/ionization (MALDI) mass spectrometry (MS); equally the most important applications in clinical proteomics and glycomics are highlighted, while emphasizing that advanced nanosystems-MS has real perspectives to become a routine method for early diagnosis of severe pathologies.

Chapter 15 by Francisco Torrens and Gloria Castellano: (Graphene and Fullerene Clusters: Molecular Polarizability and Ion–Di/Graphene Associations) elaborates on how by varying the number of atoms, clusters show peaks indicative of particularly polarizable structures in agreement with alkalines polarizability and molar volume in the periodic table of the elements, along other challenges as interacting induced-dipoles polarization or smaller clusters not behaving like intermediate sizes, etc.

Chapter 16 by Ottorino Ori, Franco Cataldo, and Mihai V. Putz (Entropy of Nanostructures. Topological Effects on Schottky Vacancies Concentration in Graphenic Bidimensional HC(N) Lattices) describes the complex mechanisms leading to the formation of clusters of vacancies in 2D honeycomb HD lattices by a pure topological point of view, aiming to correlate the variation of specific topological invariants, sensible to vacancy concentration, to the structural evolution of the defective networks driven by the topo-therm dynamical Gibbs free energy.

Chapter 17 by Fatemeh Koorepazan-Moftakhar, Ali Reza Ashrafi, Ottorino Ori, and Mihai V. Putz (Atlas of ρ, ρ^E and TM-EC for Fullerenes Isomers) reports the topological efficiency index ρ, the parameter ρ^E and the Timisoara–eccentricity index (TM–EC) as reliable parameters for studying fullerenes on examples including at most 50 carbon atoms.

Chapter 18 by Margherita Venturi (Developing Sustainability: Some Scientific and Ethical Issues) reviews the main types of renewable energies in relation with currently available technologies, planet's emergencies and strategies towards sustainable development with the need in reintroducing the concepts of "enough" and "equity" while exploiting the know-how patrimony and good practices for the next generations.

The book appears therefore as truly complex and spanning both fundamental, theoretical, and experimental developments while advancing also innovative concepts to be further used, implemented and tested in synergic interconnection so fulfilling the integrated aims of nanosciences and technology in XXI century.

It is our editorial privilege knowing personally authors from each chapter contributing this indeed worthy book – an important ingredient in aggregating any challenging collection of high-level scientifically research and educational value; and also plus-value we would say as this book will consequently lead with new ideas, fundamental processes taking our interdisciplinary knowledge to the point the nano-matter may be controlled and may act in ecological-sustainable manner for present and next generations. So we thank all of them for their enthusiasm addressing the communicated chapters, ideas and necessary specialists' opinions. The wide spanning of affiliations through 3 continents (Europe, Asia, America) and from advanced or developing countries (Europe: Italy: with Rome and Bologna, Spain, Hungary, Russia, Ukraine, Romania: with Bucharest, Cluj and Timisoara; Asia: Iran and India; America: USA) assures the global interest and contribution to the global problem of eco-nano-technology, energy materials, intelligent materials, eco-life and smart functionalization and communication. Equally honorable is the Foreword provided by emeritus professor Alexandru Balaban from Texas A&M University at Galveston on the book overview and themes treated this way certifying once more the impact they have and will have in the forthcoming years and consolidating nano-sciences. Not less important is our pleasure thanking the IGI Publishing team since embracing the project from its incipient phase through all publisher in-house processing and world-wide advertising it by a top-publication product susceptible in becoming a referential one (and with possible forthcoming new editions) in the nano-science international literature of XXI century! Long life to macro-eco-systems by nano-sustainability!

Mihai V. Putz
West University of Timişoara, Romania & Research and Development National Institute for Electrochemistry and Condensed Matter (INCEMC) Timişoara, Romania

Marius C. Mirica
Research and Development National Institute for Electrochemistry and Condensed Matter (INCEMC) Timişoara, Romania

Table of Contents

Detailed Table of Contents