Handbook of Nanostructured Materials and Nanotechnology

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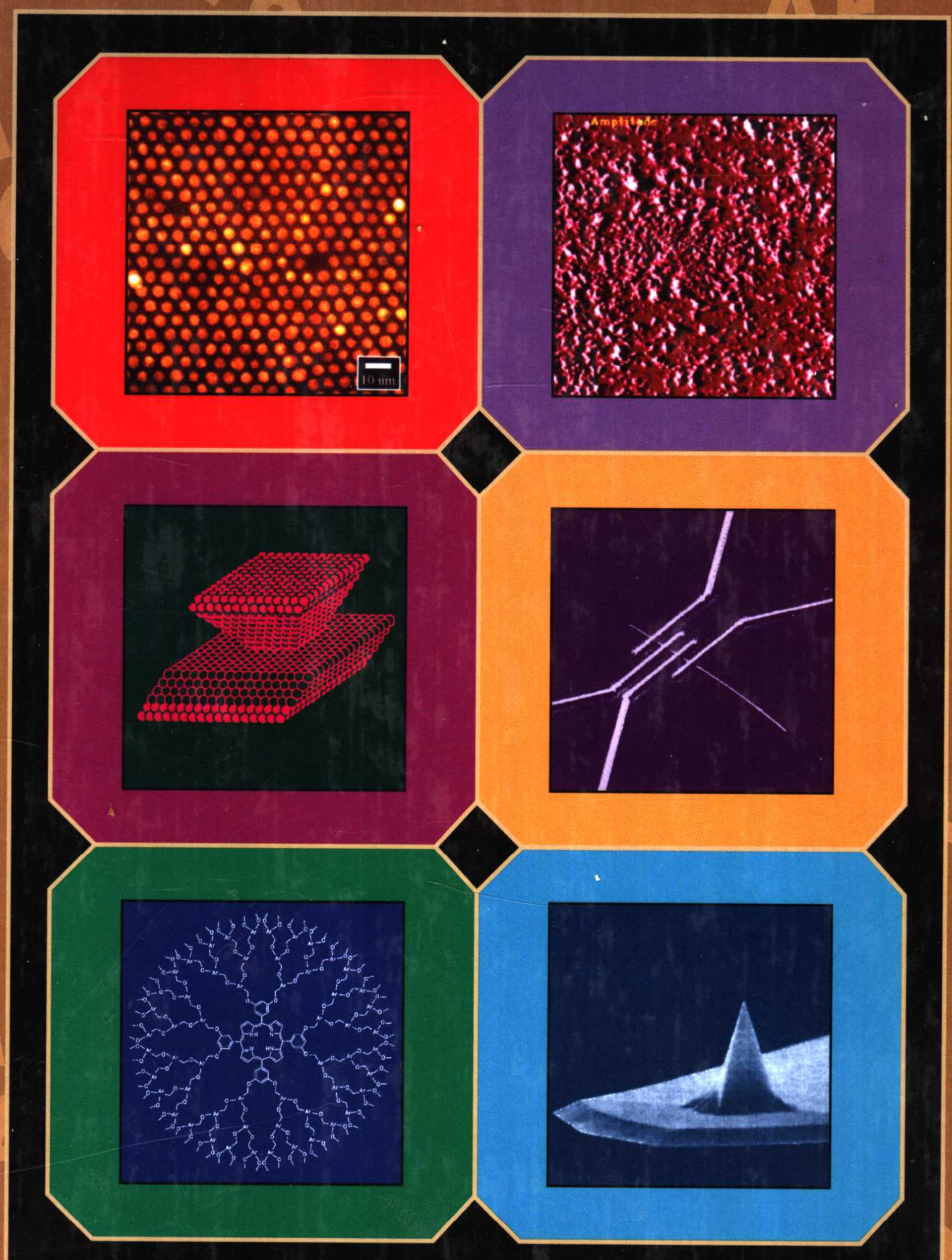
Organics, Polymers, and Biological Materials



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Edited by Hari Singh Nalwa

Foreword by George A. Olah, Nobel Laureate

Handbook of Nanostructured Materials and Nanotechnology

Volume 5

Organics, Polymers, and Biological Materials

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To my children,
Surya, Ravina and Eric

Foreword

Nanostructured materials are becoming of major significance and the technology of their production and use is rapidly growing into a powerful industry. These fascinating materials whose dimension range for 1–100 nanometer (1 nm = 10^{-9} m, i.e., one billionth of a meter) include quantum dots, wires, nanotubes, nanorods, nanofilms, nanoprecision self assemblies and thin films, nanosize metals, semiconductors, biomaterials, oligomers, polymers, functional devices, etc. etc. It is clear that the number and significance of new nanomaterials and application will grow explosively in the coming twenty-first century.

This dynamical fascinating new field of science and its derived technology clearly warranted a comprehensive treatment. Dr. Hari Singh Nalwa must be congratulated to have undertaken the task to organize and edit such a massive endeavor. His effort resulted in a truly impressive and monumental work of fine volumes on nanostructured materials covering synthesis and processing, spectroscopy and theory, electrical properties, and optical properties, as well as organics, polymers, and biological materials. One hundred forty-two authors from 16 different countries contributed 62 chapters encompassing the fundamental compendium. It is the merit of these authors, their contributions coordinated most knowledgeably and skillfully by the editor, that the emerging science and technology of nanostructured materials is enriched by such an excellent and comprehensive core-work, which will be used for many years to come by all practitioners of the field, but also will inspire many others to join in expanding its vistas and application.

Professor George A. Olah
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Nobel Laureate Chemistry, 1994

Preface

Nanotechnology is the science and engineering of making materials, functional structures and devices on the order of a nanometer scale. In scientific terms, "Nano" means 10^{-9} where 1 nanometer is equivalent to one thousandth of a micrometer, one millionth of a millimeter, and one billionth of a meter. In Greek, "nanotechnology" derives from the *nanos* which means dwarf and *technologia* means systematic treatment of an art or craft. Nanostructured inorganic, organic, and biological materials may have existed in nature since the evolution of life started on Earth. Some evident examples are micro-organisms, fine-grained minerals in rocks, and nanosize particles in bacterias and smoke. From a biological viewpoint, the DNA double-helix has a diameter of about 2 nm (20 angstrom) while ribosomes have a diameter of 25 nm. Atoms have a size of 1–4 angstrom, therefore nanostructured materials could hold tens of thousands of atoms all together. Moving to a micrometer scale, the diameter of a human hair is 50–100 μm. Advancements in microscopy technology have made it possible to visualize images of nanostructures and have largely dictated the development of nanotechnology. Manmade nanostructured materials are of recent origin whose domain sizes have been precision engineered at an atomic level simply by controlling the size of constituent grains or building blocks. About 40 years ago, the concept of atomic precision was first suggested by Physics Nobel Laureate Richard P. Feynman in a 1959 speech at the California Institute of Technology where he stated, "*The principles of physics, as far as I can see, do not speak against the possibility of maneuvering things atom by atom* ...". Research on nanostructured materials began about two decades ago but did not gain much impetus until the late 1990s. Nanotechnology has become a very active and vital area of research which is rapidly developing in industrial sectors and spreading to almost every field of science and engineering. There are several major research and development government programs on nanostructured materials and nanotechnology in the United States, Europe, and Japan. This field of research has become of great scientific and commercial interest because of its rapid expansion to academic institutes, governmental laboratories, and industries. By the turn of this century, nanotechnology is expected to grow to a multibillion-dollar industry and will become the most dominant technology of the twenty-first century.

In this handbook, nanostructures loosely define particles, grains, functional structures, and devices with dimensions in the 1–100 nanometer range. Nanostructures include quantum dots, quantum wires, grains, particles, nanotubes, nanorods, nanofibers, nanofoams, nanocrystals, nanoprecision self-assemblies and thin films, metals, intermetallics, semiconductors, minerals, ferroelectrics, dielectrics, composites, alloys, blends, organics, organominerals, biomaterials, biomolecules, oligomers, polymers, functional structures, and devices. The fundamental physical and biological properties of materials are remarkably altered as the size of their constituent grains decreases to a nanometer scale. These novel materials made of nanosized grains or building blocks offer unique and entirely different electrical, optical, mechanical, and magnetic properties compared with conventional micro or millimeter-size materials owing to their distinctive size, shape, surface chemistry, and topology. On the other hand, organics offer tremendous possibilities of chemical modification by tethering with functional groups to enhance their responses. Nanometer-sized organic materials such as molecular wires, nanofoams, nanocrystals, and dendritic molecules have been synthesized which display unique properties compared with their counterpart conventionally sized materials. An abundance of scientific data is now available to make useful comparisons between nanosize materials and their counterpart microscale or bulk materials. For example, the hardness of nanocrystalline copper increases with decreasing grain size and 6 nm copper grains show five times hardness than the conventional copper. Cadmium selenide (CdSe) can yield any color in the spectrum simply by controlling the size of its constituent grains. There are many such examples in the literature where physical properties have been remarkably improved through nanostrucure maneuvering. Nanostructured materials and their base technologies have opened up exciting new possibilities for future applications in aerospace, automotive, cutting tools, coatings, X-ray technology, catalysts, batteries, nonvolatile memories, sensors, insulators, color imaging, printing, flat-panel displays, waveguides, modulators, computer chips, magneto-optic disks, transducers, photodetectors, optoelectronics, solar cells, lithography, holography, photoemitters, molecular-sized transistors and switches, drug delivery, medicine, medical implants, pharmacy, cosmetics, etc. Apparently, a new vision of molecular nanotechnology will develop in coming years and the twenty-first century could see technological breakthroughs in creating materials atom by atom where new inventions will have intense and widespread impact in many fields of science and engineering.

Over the past decade, extraordinary progress has been made on nanostructured materials and a dramatic increase in research activities in many different fields has created a need for a reference work on this subject. When I first thought of editing this handbook, I envisaged a reference work covering all aspects of nanometer scale science and technology dealing with synthesis, nanofabrication, processing, supramolecular chemistry, protein engineering, biotechnology, spectroscopy, theory, electronics, photonics, and other physical properties as well as devices. To achieve this interface, researchers from different disciplines of science and engineering were brought together to share their knowledge and expertise. This handbook, written by leading international experts from academia, industries, and governmental laboratories, consists of 62 chapters written by 142 authors coming from 16 different countries. It will provide the most comprehensive coverage of the whole field of nanostructured materials and nanotechnology by compiling up-to-date data and information.

Each chapter in this handbook is self-contained with cross references. Some overlap may inevitably exist in a few chapters, but it was kept to a minimum. It was rather difficult to scale the overlap that is usual for state-of-the-art reviews written by different authors. This handbook illustrates in a very clear and concise fashion the structure-property relationship to understand a broader range of nanostructured materials with exciting potential for future electronic, photonic, and biotechnology industries. It is aimed to bring together in a single reference all inorganic, organic, and biological nanostructured materials currently studied in academic and industrial research by covering all aspects from their chemistry, physics, materials science, engineering, biology, processing, spectroscopy, and technology to applications that draw on the past decade of pioneering research on nanostructured materials for the first time to offer a complete perspective on the topic. This handbook should serve as a reference source to nanostructured materials and nanotechnology. With over 10,300 bibliographic citations, the cutting edge state-of-the art review chapters containing the latest research in this field is presented in five volumes:

Volume 1: Synthesis and Processing
Volume 2: Spectroscopy and Theory
Volume 3: Electrical Properties
Volume 4: Optical Properties
Volume 5: Organics, Polymers, and Biological Materials

Volume 1 contains 13 chapters on the recent developments in synthesis, processing and fabrication of nanostructured materials. The topics include: chemical synthesis of nanostructured metals, metals alloys and semiconductors, synthesis of nanostructured coatings by high velocity oxygen fuel thermal spraying, nanoparticles from low-pressure and low-temperature plasma, low temperature compaction of nanosize powders, kinetic control of inorganic solid state reactions resulting from mechanistic studies using elementally modulated reactants, strained-layer heteroepitaxy to fabricate self-assembled semiconductor islands, nanofabrication via atom optics, preparation of nanocomposites by sol-gel methods: processing of semiconductors quantum dots, chemical preparation and characterization of nanocrystalline materials, rapid solidification processing of nanocrystalline metallic alloys, vapor processing of nanostructured materials and applications of micromachining to nanotechnology. The contents of this volume will be useful for researchers particularly involved in synthesis and processing of nanostructured materials.

Volume 2 contains 15 chapters dealing with spectroscopy and theoretical aspects of nanostructured materials. The topics covered include: nanodiffraction, FT-IR surface spectrometry of nanosized particles, specification of microstructure and characterization by scattering techniques, vibrational spectroscopy of mesoscopic systems, advanced interfaces to scanning-probe microscopes, microwave spectroscopy on quantum dots, tribological experiments with friction force microscopy, electron microscopy techniques applied to study of nanostructured ancient materials, mesoscopic magnetism in metals, tools of nanotechnology, and nanometrology. The last five chapters in this volume describe computational technology associated with the stimulation and modeling of nanostructures. The topics covered are tunneling times in nanostructures, theory of atomic-scale friction, theoretical aspects of strained-layer quantum-well lasers, carbon nanotube-based nanotechnology in an integrated modeling and stimulation environment, and wavefunction engineering: a new paradigm in quantum nanostructure modeling.

Volume 3 has 11 chapters which exclusively focus on the electrical properties of nanostructured materials. The topics covered are: electron transport and confining potentials in semiconductor nanostructures, electronic transport properties of quantum dots, electrical properties of chemically tailored nanoparticles and their applications in microelectronics, design, fabrication and electronic properties of self-assembled molecular nanostructures, silicon-based nanostructures, semiconductor nanoparticles, hybrid magnetic-semiconductor nanostructures, colloidal quantum dots of III-V semiconductors, quantization and confinement phenomena in nanostructured superconductors, properties and applications of nanocrystalline electronic junctions, and nanostructured fabrication using electron beam and its applications to nanometer devices.

Volume 4 contains 10 chapters dealing with different optical properties of nanostructured materials. The topics include: photorefractive semiconductor nanostructures, metal nanocluster composite glasses, porous silicon, 3-dimension lattices of nanostructures, fluorescence, thermoluminescence and photostimulated luminescence of nanoparticles, surface-enhanced optical phenomena in nanostructured fractal materials, linear and nonlinear optical spectroscopy of semiconductor nanocrystals, nonlinear optical properties of nanostructures, quantum-well infrared photodetectors and nanoscopic optical sensors and probes. The electronic and photonic applications of nanostructured materials are also discussed in several chapters in Volumes 3 and 4.

All nanostructured organic molecules, polymers, and biological materials are summarized in Volume 5. This volume has 13 chapters that include: Intercalation compounds in layered host lattices-supramolecular chemistry in nanodimensions, transition-metal-mediated self-assembly of discrete nanoscopic species with well-defined shapes and geometries, molecular and supramolecular nanomachines, functional nanostructures incorporating responsive modules, dendritic molecules: historical developments and future applications, carbon nanotubes, encapsulation and crystallization behavior of materials inside carbon nanotubes, fabrication and spectroscopic characterization of organic nanocrystals, polymeric nanostructures, conducting polymers as organic nanometals, biopolymers and polymers nanoparticles and their biomedical applications, and structure, behavior and manipulation of nanoscale biological assemblies and biomimetic thin films.

It is my hope that *Handbook of Nanostructured Materials and Nanotechnology* will become an invaluable source of essential information for academic, industrial, and governmental researchers working in chemistry, semiconductor physics, materials science, electrical engineering, polymer science, surface science, surface microscopy, aerosol science, spectroscopy, crystallography, microelectronics, electrochemistry, biology, microbiology, bioengineering, pharmacy, medicine, biotechnology, geology, xerography, superconductivity, electronics, photonics, device engineering and computational engineering.

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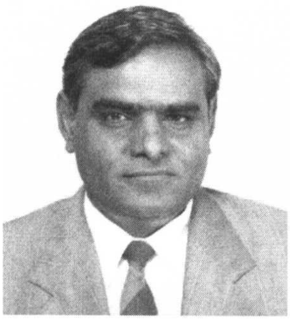
This handbook could not have reached fruition without the marvelous cooperation of many distinguished individuals who contributed to these volumes. I am fortunate to have leading experts devote their valuable time and effort to write excellent state-of-the-art reviews which led foundation of this handbook. I deeply express my thanks to all contributors. I am very grateful to Dr. Akio Mukoh and Dr. Shuuichi Oohara at Hitachi Research Laboratory, Hitachi Ltd., for their kind support and encouragement. I would like to give my special thanks to Professor Seizo Miyata of the Tokyo University of Agriculture and Technology (Japan), Professor J. Schoonman of the Delft University of Technology (The Netherlands), Professor Hachiro Nakanishi of the Tohoku University (Japan), Professor G. K. Surya Prakash of the University of Southern California (USA), Professor Padma Vasudevan of Indian Institute of Technology at New Delhi, Professor Toskiyuki Watanabe, Professor Richard T. Keys, Dr. Christine Peterson, and Dr. Judy Hill of Foresight Institute in California, Rakesh Misra, Krishi Pal Reghuvanshi, Rajendra Bhargava, Jagmer Singh, Ranvir Singh Chaudhary, Dr. Hans Thomann, Dr. Ho Kim, Dr. Thomas Pang, Ajit Kelkar, K. Srinivas, and other colleagues who supported my efforts in compiling this handbook. Finally, I owe my deepest appreciation to my wife, Dr. Beena Singh Nalwa, for her cooperation and patience in enduring this work at home; I thank my parents, Sri Kadam Singh and Srimati Sukh Devi, for their moral support; and I thank my children, Surya, Ravina, and Eric, for their love.

I express my sincere gratitude to Professor George A. Olah for his insightful Foreword.

Hari Singh Nalwa

About the Editor



Dr. Hari Singh Nalwa has been working at the Hitachi Research Laboratory, Hitachi Ltd., Japan, since 1990. He has authored over 150 scientific articles in refereed journals, books, and conference proceedings. He has 18 patents either issued or applied for on electronic and photonic materials and their based devices. Dr. Nalwa has published 18 books, including *Ferroelectric Polymers* (Marcel Dekker, 1995), *Handbook of Organic Conductive Molecules and Polymers, Volumes 1–4* (John Wiley & Sons, 1997), *Nonlinear Optics of Organic Molecules and Polymers* (CRC Press, 1997), *Organic Electroluminescent Materials and Devices* (Gordon & Breach, 1997), *Handbook of Low and High Dielectric Constant Materials and Their Applications, Volumes 1–2* (Academic Press, 1999), and *Advanced Functional Molecules and Polymers, Volumes 1–4* (Gordon & Breach, 1999).

Dr. Nalwa is the founder and Editor-in-Chief of the *Journal of Porphyrins and Phthalocyanines* published by John Wiley & Sons and serves on the editorial board of *Applied Organometallic Chemistry, Journal of Macromolecular Science-Physics, International Journal of Photoenergy*, and *Photonics Science News*. He is a referee for the *Journal of American Chemical Society, Journal of Physical Chemistry, Applied Physics Letters, Journal of Applied Physics, Chemistry of Materials, Journal of Materials Science, Coordination Chemistry Reviews, Applied Organometallic Chemistry, Journal of Porphyrins and Phthalocyanines, Journal of Macromolecular Science-Physics, Optical Communications*, and *Applied Physics*.

He is a member of the American Chemical Society (ACS), the American Association for the Advancement of Science (AAAS), and the Electrochemical Society. He has been awarded a number of prestigious fellowships in India and abroad that include National Merit Scholarship, Indian Space Research Organization (ISRO) Fellowship, Council of Scientific and Industrial Research (CSIR) Senior fellowship, NEC fellowship, and Japanese Government Science & Technology Agency (STA) fellowship. Dr. Nalwa has been cited in the *Who's Who in Science and Engineering, Who's Who in the World*, and *Dictionary of International Biography*. He was also an honorary visiting professor at the Indian Institute of Technology in New Delhi.

He was a guest scientist at Hahn-Meitner Institute in Berlin, Germany (1983), research associate at University of Southern California in Los Angeles (1984–1987) and State University of New York at Buffalo (1987–1988). He worked as a lecturer from 1988–1990 in the Tokyo University of Agriculture and Technology in the Department of Materials and Systems Engineering. Dr. Nalwa received a B.Sc. (1974) in biosciences from Meerut University, a M.Sc. (1977) in organic chemistry from University of Roorkee, and a Ph.D. (1983) in polymer science from Indian Institute of Technology in New Delhi, India. His research work encompasses ferroelectric polymers, electrically conducting polymers, electrets, organic nonlinear optical materials for integrated optics, electroluminescent materials, low and high dielectric constant materials for microelectronics packaging, nanostructured materials, organometallics, Langmuir-Blodgett films, high temperature-resistant polymer composites, stereolithography, and rapid modeling.

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