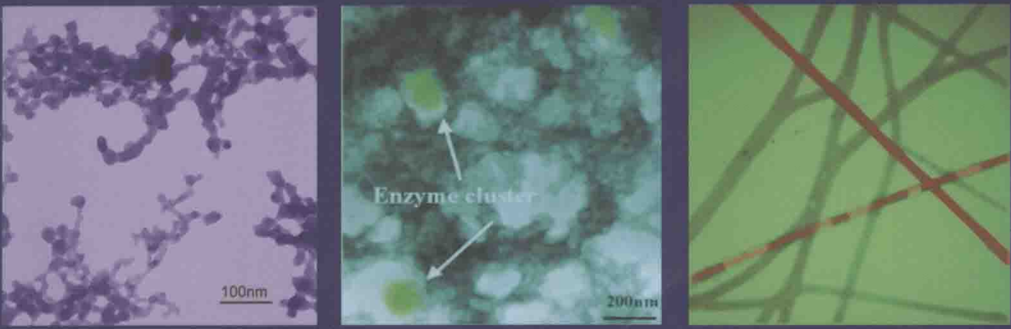

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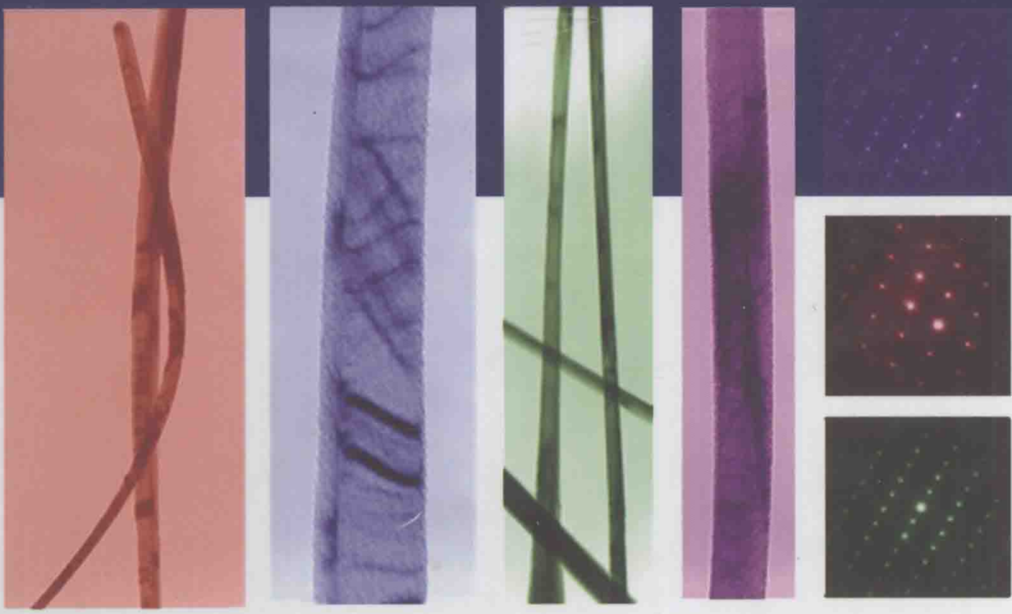

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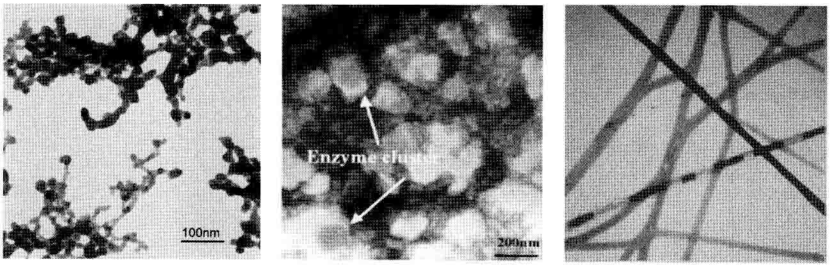

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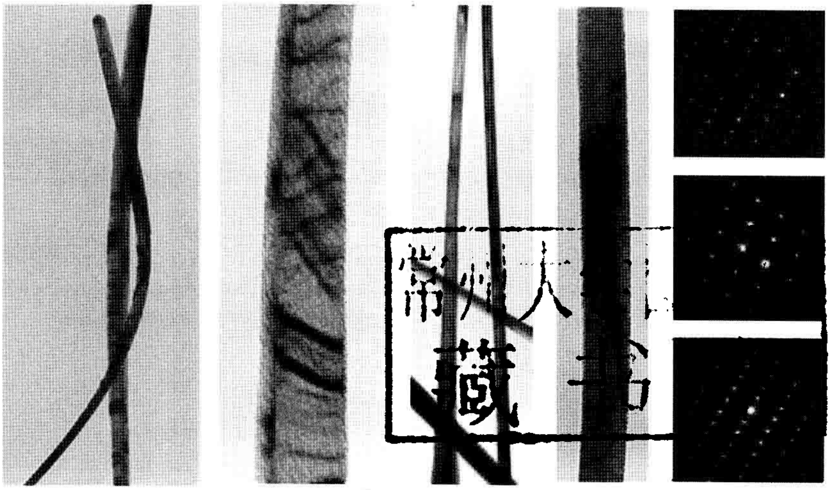

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Nanomaterials for Chemical Sensors and Biotechnology

This book is dedicated to the loving memory of my parents, Georgios and Ekaterini Gouma. They are dearly missed...

Preface

Upon embarking on an independent research career one faces the challenge of choosing a topic within his/her field to study in depth so as to make new and significant contributions to science, engineering or medicine. The authors' earlier involvement with the characterization of colloidal 3D networks of metal oxide (titania) nanoparticles and their thin films had suggested that these exhibit catalytic properties far superior to those of their micro-sized equivalents. Heating the nanostructures at temperatures that were considered "safe" for larger particles, the nano-entities would undergo a phase transformation and coarsen abnormally (due to oriented attachment) losing their nanostructure advantage. Studying the gas sensing properties of ceramic nanomaterials, was the beginning of a learning path to the wonders of nanotechnology.

Sol-gel 3D nanomaterials led to 2D nanobelts and from there to 1D nanowires that can detect just a few molecules of a specific gas with high selectivity. Nanomaterials synthesis methods from the conventional: electrodeposition, physical or chemical vapor deposition (PVD, CVD) to the exotic: laser ablation, flame spray synthesis, and the latest nanomanufacturing craze: electrospinning, have all been used in the authors' research and are discussed in this text. Ceramic materials were combined with biomolecules to make novel bio-doped composites and resistive biosensing platforms for the rapid screening/determination of pathogens and biothreats; and electroactive polymer transducers were introduced for enabling ion to electron transport. Nanofiber mats became the ultimate "active" and "smart" structures for bio-chemo-sensing and actuating, ultimately leading to 3D scaffolding architectures for implants.

So, this is the journey that you are invited along through the contents of this book. The hope is that you'll find the adventure as thrilling and fulfilling as the author has felt it (and she is still finding it) to be, with a strong belief that nanotechnology has the potential to lead to breakthrough materials and devices that will change our lives immensely for the better. Non-invasive diagnostics, personalized and telemetric medicine applications, skin, bone, and organ regeneration, ubiquitous environmental monitoring, novel energy sources, are a few of the promises that are becoming realized with time. It is with great anticipation that the impact of the advances described in this book on the human life and welfare in our lifetime is envisioned.

This book involves some part of each of the sciences, engineering and medicine fields: nanomaterials, nanotechnology for chemical /bio-chemical sensing, and nanomedicine, i.e. the application of nanomaterials in biotechnology. The fundamental principle that has enabled the recent progress in each of these fields is that materials at the nanoscale (sized between 1–100 nm) behave in a different manner than their bulk form, exhibiting size dependent properties. It has only been in the last 10–15 years that this notion was introduced to the research communities and it has still to catch up with the general population. There are graduate college students who have never heard of nanomaterials even today. There is a layman population who's read science fiction novels about nano-robots and other scary products of nanotechnology, feeling confused about this new science. And there is a real need for advanced technologies to protect the human health and welfare as well as the environment.

The above became the stimulus that led the author to introduce a new course on Nanostructured Sensor Materials and Devices to the academic curriculum of her department a few years ago so as to introduce materials science and engineering students to this exciting world of nanostructures and miniaturized machines. This endeavor became a learning experience for her too, which led to the book that you are holding in your hands (or browsing in your electronic reader).

Acknowledgments

This book resulted from the collective effort of my research group at the Center for Nanomaterials and Sensor Development at the State University of New York, Stony Brook over the past 5 years to produce new knowledge on the synthesis, manufacturing, characterization, and testing of novel nanomaterials for sensors and biotechnology. Funded by a NSF award for Nanoscale Interdisciplinary Research Teams, a whole new research activity on novel nanomaterials flourished, producing breakthrough results, such as the "extreme" aspect ratio single crystal semiconducting nanowires or the first handheld NO breathanalyzer for monitoring oxidative stress. There are many people responsible for the successes presented here, starting from the Program Manager at the NSF's Ceramics Program, Dr. L. Madsen, who became a mentor to the me early on, to the undergraduate and graduate students who carried out the various research projects, to the collaborators and visiting scientists joining this adventure. In particular, thanks go to Dr. A. Prasad Kapaleeswaran who first produced a *selective ammonia sensor based on nanomaterials*, Dr. M. Karadge who skillfully produced CuO *nanogrids*, Ms. K. Sawicka who won a finalist position at the National Inventors' Competition for her work on *electrospun bio-nanocomposites*. The nanocomposites work is covered in chapter 4, parts of which are reproduced with permission from the Journal of Nanoparticle Research. Mrs. S. Gadre who worked on *bio-doped (non-transparent) metal oxides*; Chapter 3 is reproduced by permission of the American Ceramic Society based on a review of the field of ceramic hybrids. Continuing on, Dr. K. (Iyer) Kalyanasundaram is acknowledged for her major contribution to the development of an *electronic olfaction system based on nanosensors*, as well as for making *selective nanoprobes for signaling metabolites*. Parts of Chapter 2, which describes resistive metabolite sensing by nanomaterias, are reproduced with permission from the publisher of "Science and Technology of Chemiresistive Gas Sensors" book. It was Dr. L. Wang who produced the first *handheld detector for selective acetone measuring in exhaled breath*. Mr. D. Han and Mr. K. Ramachandran both had significant contributions in preparing *electrospun 3D scaffolds for tissue engineering* and Dr. A. Bishop-Haynes produced *electroactive polymers for nanomedicine* applications. Mr. R. Xue assisted with the editing of this book. Collaborators Abroad: Professor S. Pratsinis and Dr. A. Teleki (ETH Zurich, Switzerland), Professor G. Sberveglieri and Dr. E. Comini (Univ. of Brescia, Italy), Professor H. Doumanidis (Univ. of Cyprus), Dr. C. Balazsi and Dr. J. Pfeifer (Hungarian Academy of Sciences), Dr. H. Haneda, and Dr. N. Ohashi (NIMS, Japan) have also supported and contributed to the work presented in this book in one way or another and are greatly appreciated. Furthermore, US-based collaborators from academia, industry and from National and Defense Laboratories, Professor S.A. Akbar (The Ohio State University), Dr. M. Frame (SUNY Stony Brook), Dr. G. Gaudette (WPI), Dr. D. Kubinski and Dr. J. Visser (Ford SRL), and Dr. H. Scheuder-Gibson (Natick Army Laboratories), have also been instrumental to the success of our research and are dearly acknowledged. In closing, sincere thanks are due to my maternal grandmother, Mrs. Pelagia Micha, for the unconditional love, support, guidance and insight she has always offered to me, to my spouse, Antonios Michailidis, for his encouragement to bring this book to completion, and especially to my beloved child, Nectarios (Aris), who brought new light and happiness to my life and new meaning to my work. Sincere thanks and God bless you all.

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Glossary

Alternative energy: Forms of energy sources other than conventional fuels, such as solar power, wind power, nuclear power, etc.
Artificial organ: Man-made device implanted into the human body intending to replace a natural organ
Band gap, for semiconductors: It is the energy difference between the bottom of the conduction band and the top of the valence band, i.e. the energy range where no electron states exist
Bio-doped material: Composites of biomolecules and other inorganic or organic materials, such as ceramics or polymers where the biological component retains/enhances it's functionality
Biosensor: An electronic device that receives a biochemical signal and converts it to a measurable output
Ceramic: Inorganic, non-metallic solid; metal oxides are the most common ceramic materials
Cell: The smallest unit of an organism
Conducting polymer: An organic material that (inherently) exhibits electrical conductivity
Data processing: The mathematical process converting a set of data into useful information
Debye length: The distance in the crystal over which significant charge separation may occur
Depletion layer: The region in a (doped-)semiconductor that is depleted from electric charge due to external effects (i.e. chemisorption of gas molecules on the material's surface)
Drug delivery vehicle: Novel materials allowing therapeutic agents to be stored and released in a controlled manner
ECM: Extracellular matrix-the nature's scaffold for tissue, bone, and organ growth
Electronic energy levels: Regions of specific energy on which electrons are distributed in an atom
Electronic Nose System: Sensor materials, device architecture, intelligent signal processing routines
Electronic olfaction system: Intellligent chemical sensor array system for odor classification
Electrochemoactuator: A device that converts a chemical stimulus (energy) to a physical output (charge transfer / change in electrical resistance)
Electrospinning: A manufacturing process producing non-woven fiber mats through the application of a strong electric field to a polymer-based solution or melt

Entrapment: The encapsulation of organic species in a porous material
Hybrid material: Organic-inorganic composite
Implant: A material (natural or synthetic) that is used to replace damaged tissue/bone
Magneli phases: Families of non-stoichiometric oxides first discovered by Magneli
Metal oxide: A ceramic material consisting by one or more metal cations and oxygen ions
Nanobelt: 2D nanostructure
Nanomanufacturing: Any process producing nanomaterials
Nanowire: 1D nanostructure
Pattern recognition: Software that categorizes data sets according to specified criteria
Polymorph: A phase of the material with distinct crystallographic configuration from another with the same chemical composition
Polymorphism: The effect of a material existing in different crystallographic arrangements
Reaction kinetics: Chemical kinetics (dynamics) of a process, such as diffusion profile, etc
Resistive gas detection: The process in which a chemical stimulus is converted to changes in the electrical conductance resistance of a gas sensitive material
Scaffold: The structural basis for cell growth, proliferation, and differentiation
Tissue engineering: The art of bone/tissue/organ regeneration
VOC: Volatile organic chemical compounds

Contents Summary

Chapter 1, the Introduction to the book, deals with the definitions of the important, keyword terms used throughout this book such as nanomaterials, sensors, biotechnology, and nanomedicine. Chapter 2 introduces resistive gas detection and the effect of nanostructures in obtaining extreme gas sensitivity and for stabilizing non-equilibrium phases offering gas specificity. Furthermore, key processing methods of chemosensing nanomaterials are discussed, and emphasis is paid to nanowire fabrication and use. Case studies of nanosensor technologies are presented. Chapter 3 introduces hybrid (organic-inorganic) nanomaterials–that is bio-doped metal oxide nanosystems for chemosensing. This is a new class of materials expecting to impact not only bio-related diagnostics but also a plethora of other fields, from environmental monitoring and remediation to alternative energy. Next, in Chapter 4, the nanomanufacturing technique of electrospinning is covered in some detail, as it is a unique processing technology that enables the formation of almost all nanomaterials used in sensing and biotechnology, from semiconductor nanowires to drug delivery vehicles and artificial scaffolds for organ growth. Chapter 5 is where nanomedicine applications of nanomaterials are presented, including electronic olfaction systems and breath analyzers, the 3D fibrous scaffold approach for tissue engineering and the polymeric electro-chemo-actuators. The book concludes with an overview and insights for the future.

Contents

Chapter One

Introduction

1.1 DEFINITIONS

Learning about nanomaterials for sensors requires that the keyword terms be defined up front. Naturally, the first important term that needs to be determined is *nanomaterial*. What is this? Most people familiar with the term will respond: the material that has at least one dimension to be between 1–100 nm in size (whereas 1nm equals 10^{-9}m. Fair enough you might say; but this is only one part of the definition. According to the **NNI** (National Nanotechnology Initiative) the material that has at least one nano-dimension has to also exhibit size-dependent properties, to be called a nanomaterial. Aluminun nanocrystals have a melting point that drops (i.e. the solid to liquid transition temperature decreases) with decreasing grain size of the material. Similarly, TiO_2 (titanium dioxide or titania) is known to transform from anatase to rutile at 1200°C when in bulk form; however, this transition occurs at temperatures as low as 400°C for 10 nm nanocrystals of anatase. Furthermore, the nature of the later transition (a "massive"-type transformation involving oriented attachment) results in bulk microcrystals of rutile. When a nanocrystalline anatase film was first used as a CO sensor operating at 400°C it behaved as a bulk rutile sensor, because it had transformed to bulk rutile crystals. It was this unexpected result that introduced the author to the surprises of *nanoscience* and *nanotechnology*.

To stay within the theme of this section, nanoscience is the study of materials systems and phenomena involving nanomaterials; whereas nanotechnology is the engineering of nanomaterials and miniaturized devices based on them. Combining nano-science and nano-engineering with medicine, the new field of *nanomedicine* has evolved, defined as medical diagnosis, monitoring, and treatment at the level of single molecules or molecular assemblies that provide structure, control, signaling, homeostasis, and mobility in cells. It is a very important research direction in order to understand the cellular mechanisms in living cells, and to develop advanced technologies for the early diagnosis and treatment of various diseases.

This book focuses on two key applications of nanomaterials: **sensors** (bio-/chemical detectors, in particular) and **biotechnology** (regenerative

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nanomedicine, and non-invasive diagnostics). Sensors are devices that receive a physical, chemical or biological input (stimulus) and which provide an output signal in response to this stimulus. They consist of an active element (detector) and a transducer. The active element in the work reported in this book is a nanomaterial, organic, inorganic, or composite/hybrid. The transducer converts the receiving information (chemical composition of gas or bio-related compound) to another measurable signal (e.g. change in electrical resistance). Thus, there are myriads of different sensor technologies for gas detection alone. The focus will remain on resistive type sensors, as they are the most promising in terms of rapid response to the presence of the chemical analyte of interest, the most versatile and economic to fabricate, and the only ones having the potential to be selective to the gas of interest in the presence of interfering compounds. The active elements for these are either ceramics, or (mostly electroactive) polymers, or a combination of both. Biotechnology, within the context of this book, addresses the need for biodetectors, bio-mimicking synthetic skin, bone, and organ implants, chemomechanical actuators, and artificial olfaction-based non-invasive diagnostic kits.

REFERENCES

[1] National Nanotechnology Initiative (www.nano-gov).
[2] American Academy of Nanomedicine (www.aananomed.org).