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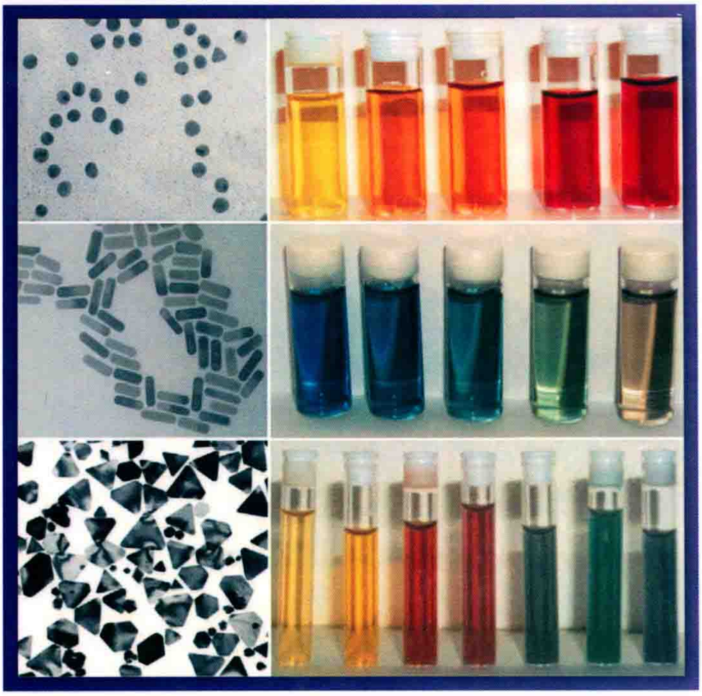

Edited by
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Michele Giordano • Antonello Cutolo

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Foreword

This book covers the rapidly growing field of optical chemical nanosensing, which is a new and exciting area of research and development within the larger field of optical chemical sensing and biosensing. Generally speaking, sensors are controlling our life to an extent that was not envisioned some 20 years ago and even today is not realized by many. An average-sized car typically has 20–50 sensors that control functions and warrant safety. All of them are usually so small or well hidden that they are virtually invisible and, thus, ignored. The temperature of refrigerators is kept fairly constant via sensors that switch the cooling system. Sensors record acceleration, position, and pressure and cause city lights to be turned on and off automatically. Physical sensors are true sensors in that they function in an unattended fashion, fully reversibly, and over long time spans without a need for maintenance. Malfunctions such as the loss of reversibility become obvious, for example, by the distinct smell of a refrigerator that has not been cooled for 10 days.

All physical sensors are small and mostly produced in large quantities. Chemical sensors and biosensors, by comparison, are much less established. Present day chemical sensors and biosensors are mainly of the electrochemical type, but optical sensors are also on the rise. They will cover more specific needs than physical sensors (which are almost ubiquitous), in particular in the medical field, in environmental sciences, marine sciences, and in bioprocess control, to give a few examples. Some chemical sensors (such as the oxygen sensor in a car's lambda probe in the catalytic converter) are expected to have very long lifetimes, while chemical sensors and biosensors for medical purposes often are not operated for more than 10 h in vivo. The glucose biosensor in an artificial pancreas (which, in my opinion, is the Holy Grail in biosensor research) is a notable exception. Moreover, in vivo sensors often are of the single use type for safety reasons.

Unlike physical sensors, the price of chemical sensors and biosensors in medical sciences is not a major issue, but their performance is extremely critical, not the least because existing sensors perform excellently. Typical examples are the pH electrode, the Clark electrode for oxygen, the many kinds of ion-selective electrodes for blood electrolytes, and the electrochemical biosensors for in vitro assays of glucose, lactate, or cholesterol.

Optical nanosensors will further widen the field. However, the design of such sensors requires new materials, new methods for their characterization, new optical sensing schemes in addition to established ones, new methods for creating nanosized structures, and new methods for their interrogation in a complex environment such as blood. New materials include the various kinds of Cd(II)- and Pb(II)-based quantum dots, fluorescent dots made from silica, semiconducting silicon, or carbon, upconverting nanoparticles (capable of converting IR light into visible light) or photonic crystals.

Such materials are not necessarily used in spherical shape, but are also in the form of nanosized fibers, films, elongated particles (rods), nanotubes, even flowers, or combinations thereof. There is also a particular need for improved methods for the characterization of nanomaterials (sensors included) because conventional methods such as IR, NMR, or mass spectrometry are not easily applicable here. TEM, SEM, SERS, and the like have therefore gained significant importance.

Nanosensors may also be considered as molecular machines that can provide valuable optical information, which, however, has to be read out and processed in a proper way so as to finally result in analytically useful information such as the concentration of a (bio)chemical. As a result, new sensing schemes and spectroscopies are needed to account for the fact that such sensors, because of their weak signals, need quite sophisticated methods, in particular if the response of a single nanosensor is to be detected. Fortunately, the use of nanometer-sized materials enables certain spectroscopic methods to be applied that work best on a micro- or nanoscale, examples being FRET, certain nonlinear spectroscopies, plasmonic resonance, effects of microring resonance, SERS, diffraction of light in photonic crystals, and the like.

Nanosized sensors enable the study of chemical and biochemical processes at a level and in dimensions that may not have been envisioned some 20 years ago. It has enabled and will enable a closer look at the cell and its function with unprecedented temporal and spatial resolution. In fact, imaging of cells with a spatial resolution of 2–10 nm has become true with fluorescent methods such as STED or STORM, spectroscopies that go far beyond the classical resolution of optical microscopy as defined by Abbe's law. However, it should also be emphasized here that the use of nanoparticles (that easily penetrate cells or even the blood/brain barrier) may imply certain risks that have not been investigated in adequate detail so far.

This book reflects ongoing research very well. Aside from new materials and spectroscopies, the progress made in micro- and nanofluidic devices (including lab-on-a-fiber technology) and nanofibers is also impressive. It is good to see that respective research not only has resulted in fundamental studies and new and generally applicable sensing platforms, but can already be applied to practical situations such as security, environmental monitoring, or detecting hazardous substances. Therefore, this book is a most valuable resource for anybody interested in this very exciting technology.

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Preface

Nanotechnology and nanoscale materials are new and exciting fields of research. Nowadays, only considering journal and conference papers, close to 100,000 scientific manuscripts are published yearly according to data extracted from ISI Web of Knowledge^{SM} and Scopus^{TM} databases. The inherent small size and the unique optical, magnetic, catalytic, and mechanical properties of nanostructured materials, which are not found in bulk materials, permit the development of novel devices and applications previously unavailable. One of the earliest implementations of nanotechnology has been the development of improved chemical and biological sensors. These optical chemical nanosensors can be generally defined as devices that transduce a chemical or biological event to an optical signal, having dimensions smaller than 1000 nm.

Remarkable progress has been made in the last few years in the design and fabrication of optical chemical nanosensors and their utilization worldwide. The emergence of this new technology is a continuous challenge since the new advances imply new applications and new questions to solve. The impact that will be made in the coming years by implementing novel sensing principles as well as new measurement techniques is unpredictable.

In fact, considering the broad field of sensors, what is exciting in sensor research and development today? This is a tough question because there are many significant innovations and inventions being made daily, and more than 200 new scientific studies are published every day related to sensors. Nevertheless, what seems clear is that there is an increasing interest in the practical utilization of nanotechnology in the sensors field and that the application of nanosensors to different types of molecular measurements is expanding rapidly. Therefore, micro- and nanotechnology, novel materials, and smaller, smarter, and more effective systems will play an important role in the future of sensors. The possibilities provided by nanosensor technology have just begun and will continue to revolutionize different key fields such as cellular biology or medicine, among others. For instance, further development of delivery techniques and new sensing strategies to enable quantification of an increased number of analytes are required to facilitate the access of medicaments to specific sites in organs and to deliver these drugs at a controlled and sustained rate to the site of action.

There are additional challenges in the sensors field, such as the promise of ubiquitous sensor systems, providing situational awareness at low cost. In order to fulfill this, there must be a demonstrated benefit that is only gained through further miniaturization. For example, new nanowire-based materials that have unique sensing properties can provide higher sensitivity, greater selectivity, and possibly enhance stability at a lower cost, and such advances are necessary to the sensor future. Nanosensors can improve the world through diagnostics in medical applications; improve health, safety, and security for people; and improve environmental monitoring. The seed technologies are now being developed for a long-term vision that includes intelligent systems that are self-monitoring, self-correcting and repairing, and self-modifying or morphing not unlike sentient beings.

The applications of these new optochemical nanosensors can also be extended to food safety, environmental monitoring, or homeland security among others. In fact, this book deals with the detection of bioterrorist threats, food security, virology, and explosive detection, as will be seen in the different chapters.

The book has been organized by topics of high interest. In order to offer a fast read of each topic, every chapter is independent and self-contained. On the other hand, since nanotechnology is an interdisciplinary field, some chapters overlap into others and are in some way related.

The book has been divided into three different parts: Basics, Research Advances, and Applications. In Part I, Fundamentals of Photonics (Chapter 1) is followed by a more specific Fundamentals of Optical Chemical Sensors (Chapter 2). The part concludes with Chapter 3, which provides a review on optochemical sensors. Part II opens with Chapter 4, Photoluminescent Nanosensors. The state of the art of cantilever-based sensors is covered in Chapter 5. Chapter 6 deals with nanostructured surface plasmon resonance sensors while Chapter 7 reviews fiber-optic nanosensors. Chapter 8 focuses on lab-on-fiber technology. The topics of micro/nanofibers for biochemical sensing, optofluidic sensor, and lab-on-chip nanostructured sensors are covered in Chapters 9 through 11, respectively. Chapters 12 through 14 describe photonic crystals, nanomaterials, and nanostructures and linear and nonlinear spectroscopy at nanoscale. Chapter 15 deals with plasmonic nanostructures and nano-antennas for sensing. The part concludes with Chapters 16 and 17, Overcoming Mass Transport Limitations with Optofluidic Plasmonic Biosensors and Particle Trapping and Optical Micro-Ring Resonators for Chemical Vapor Sensing. Part III begins with Chapter 18, which focuses on the detection of bioterrorist threats. This is followed by Chapter 19, which deals with food safety and security. Chapter 20 covers multifunctional fiber-optic nanosensors for environmental monitoring, and Chapter 21 reviews nano-optical sensors for virology. The book concludes with Chapter 22, Nano-Optical Sensors for Explosive Detection.

Editors

Andrea Cusano received his Laurea degree cum Laude in electronic engineering in 1998, from the University of Naples Federico II, Italy. In 2003, he defended his PhD thesis carried out in the Department of Electronic and Telecommunication Engineering at the University of Naples under the guidance of his tutor Professor Antonello Cutolo. His PhD thesis was entitled *Optoelectronic Sensors for Smart Materials and Structures.* In February 2002, while pursuing his PhD, he was engaged as a research fellow in the Department of Engineering at the University of Sannio to support Professor Antonello Cutolo in creating the Optoelectronic Division. From September 2002 to present, he has been professor for several courses in electronics in the Engineering Department at the University of Sannio. In December 2002, he started his service as permanent researcher at the University of Sannio. In December 2005, he won a national competition as associate professor (scientific area ING-INF/01) at the University of Sannio. His research interests are focused on optical sensors and nanotechnology.

Dr. Cusano is the cofounder of the following spin-off companies focused on the development of fiber-optic sensing systems for industrial applications: OptoSmart S.r.l. in 2005, MDTech in 2007, and OptoAdvance in 2011. He has published over 100 papers in prestigious international journals and more than 150 communications in well-known international conferences worldwide. He currently has four international patents in use in prestigious industrial companies (Ansaldo STS, Alenia WASS, OptoSmart, and MDTech) and more than 10 national patents.

Since 2011, he has been the editor in chief of the *Journal of Optics and Laser Technology* (Elsevier). He is also the associate editor of the *Journal of Sensors* (Hindawi), *The Open Optics Journal* (Bentham Science Publishers), *The Open Environmental & Biological Monitoring Journal* (Bentham Science Publishers), *Sensors and Transducers Journal* (IFSA), the *International Journal on Smart Sensing and Intelligent Systems*, and *Photonic Sensors* (Springer Verlag).

He is the coauthor of 30 chapters published in international books and invited papers in prestigious scientific international journals as well as international conferences. Cusano coedits two special issues on optical fiber sensors: "Special Issue on Optical Fiber Sensors" (*IEEE Sensors*, 2008) and "Special Issue on Fiber Optic Chemical and Biochemical Sensors: Perspectives and Challenges Approaching the Nano-Era" (*Current Analytical Chemistry*, Bentham, 2008).

He is also a coeditor of international books such as *Fiber Bragg Grating Sensors: Recent Advancements, Industrial Applications and Market Exploitation*, Bentham e-book, 2011; *Selected Topics on Photonic crystals and Metamaterials*, World Scientific (2011); and *Photonic Bandgap Structures: Technological Platforms for Physical Chemical and Biological Sensing*, Bentham Science Publishers (2012).

Cusano is a member of the technical program committee of several international conferences such as IEEE Sensors, International Conference on Sensing Technologies, the European Workshop for SHM, the European Workshop on Optical Fiber Sensors, the Asian-Pacific Optical Sensors, the International Conference on Applications of Optics and Photonics; and Bragg Gratings, Photosensitivity, and Poling (BGPP).

Cusano is a consultant for important companies of the Finmeccanica Group such as Ansaldo STS and Alenia WASS. He is also a consultant for CERN in Geneva, where he works on the development of innovative optical sensors for high-energy physics applications.

He has received many international recognitions and awards for his efforts in the development of innovative optical sensing systems. He was also principal investigator for many national projects and a consultant in many European projects.

Francisco J. Arregui is a professor at the Public University of Navarre, Pamplona, Spain. He was part of the team that fabricated the first optical fiber sensor by means of the layer-by-layer self-assembly method at Virginia Tech, Blacksburg, Virginia, in 1998. He is the author of about 300 scientific journal and conference publications, most of them related to optical fiber sensors based on nanostructured coatings. Professor Arregui has been an associate editor of *IEEE Sensors Journal*, the *International Journal on Smart Sensing and Intelligent Systems*, and the *Journal of Sensors*. He is also the editor of the book entitled *Sensors Based on Nanostructured Materials*. The *Journal of Sensors* (Hindawi) was founded in 2007 by Professor Arregui. He served as editor in chief of the journal between 2007 and 2011.

Michele Giordano received his master's degree in chemical engineering from the University of Naples Federico II in 1992. In the same year, he started a PhD course in materials engineering at the University of Naples Federico II and completed it in 1995. In 1998, he completed the formative track within the Institute for Composite Materials Technology (ITMC) of the National Research Council (CNR). Also, in 1998 he acquired a part-time position as a researcher at ITMC CNR, where he become a permanent researcher in 2001. From 2003 to present, he has been a lecturer at the University of Naples Federico II teaching a course on composite materials technology. Since 2005, he has served as a senior scientist at the Institute of Composite and Biomedical Materials (IMCB) CNR. In 2005, he cofounded the research spin-off company "OptoSmart," focused on the development of fiber-optic sensor systems. Since 2006, he has been responsible for the Composite Technology Unit of IMCB-CNR, coordinating the corporate CNR *commessa* project Polymers, composite and nanostructures technologies. In 2007, he cofounded a new research spin-off company, MDTech, conducting research in the field of optical systems for biomedical applications.

His research activities are within the area of engineering and materials science. In particular, his research focuses on nano- and macrocomposite materials, mainly polymer based, including multiscale design and processing of multifunctional composite materials, structural health management systems, and thin films engineering for sensing and optoelectronic applications. He is the author of more than 90 JRC journal papers, more than 130 international conference communications, and 8 book chapters.

Antonello Cutolo received his Laurea degree cum Laude in electronic engineering from the University of Naples Federico II in 1978 after a six months stint at the Fiat Research Center working on online characterization of mirrors for high-power laser systems.

After serving for one year in the Italian Air Force, he spent a year in the Department of Applied Mathematical Physics at the University of Copenaghen, working on propagation in nonlinear structures, soliton interaction, and Josephson structures. In particular, he found the theoretical limit of the bandwidth of finite size Josephson oscillators.

In 1982, he worked at the National Laboratories of Frascati (Rome) to build a free electron laser on the Adone storage ring, where he was in charge of the design and construction of the optical resonator.

In 1983, he was appointed researcher in the Department of Electronics at the University of Naples. From 1983 to 1986, he worked at the Photon Research Lab and at the Stanford Linear Accelerator Center (SLAC) of Stanford University (California) and in the Department of Physics at Duke University (North Carolina), where he designed and constructed a set of novel devices for increasing the peak power (cavity dumpers and mode lockers) and the tunability range (broadband output couplers and higher harmonic generators) of a free electron laser.

In 1987, he was appointed associate professor of quantum electronics at the University of Naples and in 1998, full professor of electronics and optoelectronics at the University of Sannio. He has founded and directed two laboratories of optoelectronics finalized to contactless characterization of electronics devices and materials, optical fiber sensors, nonlinear optics, and nanophotonics applications. Many of the results have found practical applications in the industry.

Professor Cutolo has been the main advisor of several projects in both basic and industrial research, which has led to many patents with large and small companies. He has tutored several students working on their PhD program. He has also published several books, more than 300 papers in international technical journals and conference proceedings, and has filed more than 20 patents both in Europe and in the United States.

He started a high-tech company (Optosmart, a spin-off from the University of Sannio and the Italian National Council of Research) that focused on the production of optical fiber sensor arrays for environment, structural health monitoring, railway security, harbor surveillance, and food quality control application.

In addition, he created the Optosonar Consortium finalized to the application of optical fibers to underwater security and monitoring. He has been a member of the scientific committee of Corista (Consortium for Research on Advanced Remote Sensing Systems) and is a member of the scientific committee of Confindustria.

Professor Cutolo has been chairman or co-chair of several national and international technical conferences, and he is the referee of several international scientific publications. His research interests include optoelectronic modulators and switching, optical characterization of semiconductor devices and materials, laser beam diagnostic, and nonlinear optical devices.

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