



# **Metal Oxide-Based Nanofibers and Their Applications**

**A volume in Metal Oxides**

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# Preface to the series

The field of synthesis, study, and application of metal oxides is one of the most rapidly progressing areas of science and technology. Metal oxides are among the most ubiquitous compound groups on earth, having a large variety of chemical compositions, atomic structures, and crystalline shapes. In addition, metal oxides are known to possess unique functionalities that are absent or inferior in other solid materials. In particular, metal oxides represent an assorted and appealing class of materials, properties of which exhibit a full spectrum of electronic properties from insulating to semiconducting, metallic, and superconducting. Moreover, almost all the known effects, including superconductivity, thermoelectric effects, photoelectrical effects, luminescence, and magnetism, can be observed in metal oxides. Therefore metal oxides have emerged as an important class of multifunctional materials with a rich collection of properties, which have great potential for numerous device applications. Specific properties of the metal oxides, such as the wide variety of materials with different electrophysical, optical, and chemical characteristics, their high thermal and temporal stability, and their ability to function in harsh environments, make metal oxides very suitable materials for designing transparent electrodes, high-mobility transistors, gas sensors, actuators, acoustical transducers, photovoltaic and photonic devices, photocatalysts and heterogeneous catalysts, solid-state coolers, high-frequency and micromechanical devices, energy-harvesting and storage devices, nonvolatile memories, and many other applications in the electronics, energy, and health sectors. In these devices, metal oxides can be successfully used as sensing or active layers, substrates, electrodes, promoters, structure modifiers, membranes, and fibers, that is, they can be used as active and passive components.

Among other advantages of metal oxides are the low fabrication cost and robustness in practical applications. Furthermore, metal oxides can be prepared in various forms, such as ceramics, thick film, and thin film. For thin film deposition, deposition techniques can be used that are compatible with standard microelectronic technology. The last factor is very important for large-scale production because the microelectronic approach promotes low cost for mass production, offers the possibility of manufacturing devices on a chip, and guarantees good reproducibility. Various metal oxide nanostructures, including nanowires, nanotubes, nanofibers, core-shell structures, and hollow nanostructures also can be synthesized. As is known, the field of metal oxide nanostructured morphologies (e.g., nanowires, nanorods, and nanotubes) has become one of the most active research areas in the nanoscience community.

The ability to create a variety of metal oxide-based composites and the ability to synthesize various multicomponent compounds significantly expand the range of

properties that metal oxide–based materials can have, making metal oxides truly versatile multifunctional materials for widespread use. Small changes in their chemical composition and atomic structure can be accompanied by spectacular variations in properties and behavior. Even now, advances in synthesizing and characterizing techniques are revealing numerous new functions of metal oxides.

Taking into account the importance of metal oxides for progress in microelectronics, optoelectronics, photonics, energy conversion, sensors, and catalysis, a large number of various books devoted to this class of materials have been published. However, one should note that some books from this list are too general, some books are collections of various original works without any generalizations, and some were published many years ago. However, during the past decade, great progress has been made in the synthesis of metal oxides as well as their structural, physical, and chemical characterization and application in various devices, and a large number of papers have been published on metal oxides. In addition, until now, many important topics related to metal oxides study and application have not been discussed. To remedy the situation in this area, we decided to generalize and systematize the results of research in this direction and to publish a series of books devoted to metal oxides.

The proposed book series, *Metal Oxides*, is the first one to be devoted solely to the consideration of metal oxides. We believe that combining books on metal oxides in a series could help readers in finding required information on the subject. In particular, we plan that the books in our series, which will have clear specialization by content, will provide interdisciplinary discussion for various oxide materials with a wide range of topics, from material synthesis and deposition to characterizations, processing, and device fabrications and applications. This book series is being prepared by a team of highly qualified experts, which guarantees its high quality.

I hope that our books will be useful and easy to use. I hope that readers will consider this book series to be like an encyclopedia of metal oxides that will enable readers to understand the present status of metal oxides, to evaluate the role of multifunctional metal oxides in the design of advanced devices, and then, on the basis of observed knowledge, to formulate new goals for further research.

The intended audience of the present book series is scientists and researchers who are working or planning to work in the field of materials related to metal oxides, that is, scientists and researchers whose activities are related to electronics, optoelectronics, energy, catalysis, sensors, electrical engineering, ceramics, biomedical designs, and so on. I believe that this *Metal Oxides* book series will also be interesting for practicing engineers or project managers in industries and national laboratories who would like to design metal oxide–based devices but don't know how to do it or how to select the optimal metal oxides for specific applications. With many references to the vast resource of recently published literature on the subject, this book series will serve as a significant and insightful source of valuable information, providing scientists and engineers with new insights for understanding and improving existing metal oxide–based devices and for designing new metal oxide–based materials with new and unexpected properties.

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I believe that this *Metal Oxides* book series will be very helpful for university students, postdoctorate scholars, and professors. The structure of these books offers a basis for courses in the field of material sciences, chemical engineering, electronics, electrical engineering, optoelectronics, energy technologies, environmental control, and many others. Graduate students could also find the book series to be very useful in their research, for understanding features of metal oxide synthesis, and for study and applications of this multifunctional material in various devices. We are sure that all of them will find the information useful for their activity.

Finally, I thank all contributing authors and book editors who have been involved in the creation of these books. I am thankful that they agreed to participate in this project and for their efforts in the preparation of these books. Without their participation, this project would have not been possible. I also express my gratitude to Elsevier for giving us the opportunity to publish this series. I especially thank the team at the editorial office at Elsevier for their patience during the development of this project and for encouraging us during the various stages of preparation.

**Ghenadii Korotcenkov**

# Preface to the volume

In the last few decades the scientific community has progressively shifted its research interest toward the infinitely small: the nanoworld. The trend has opened the unprecedented opportunity to have a detailed picture of the world at the atom level and the unrivaled prospect of tuning and controlling the properties of the materials as never before. At the nanoscale, atoms interact and combine to determine the specific properties of materials (e.g., chemical, physical, electronic, magnetic, optical).

The targeted manipulation of materials at this scale makes it possible to significantly enhance existing properties while new exotic ones can be induced. The behavior of materials can be controlled by controlling the chemical composition (atom by atom) and by confining one or more dimensions into the nanoscale range. Several advanced compositions shaped into novel nanostructures have been engineered and proven to possess superior emerging properties compared to their bulk counterparts. At the same time, a significant number of structures with one or more dimensions in the nanoscale range have emerged in many fields with proven enhanced properties or even entirely new properties. The list includes superior nanomaterials in the 10- to 100-nm scale. This range is above the atom-to-atom size domain. However, these materials still have exceptional properties and unique compositional and microstructural features. Some prominent examples are nanoparticles, nanosheets, nanocages, nanotubes, nanowires, and nanofibers. Many others are expected to be introduced with various shapes and heterostructures. Heterostructures combine two or more nanomaterials with complementary functionalities to enable nanodevices.

Nanofibers are a class of quasi-one-dimensional materials with cross-sectional diameters ranging from tens to hundreds of nanometers and a few tens of micrometers in length. These peculiar dimensional characteristics offer the merits of an extremely high aspect ratio and surface-area-to-volume ratio. In addition, nanofibers are typically arranged into thick membranes or substrates with a wide-open and well-interconnected porous network that offer further potential to significantly affect performance. The relationship between structure and composition is an essential aspect for efficient tuning of properties and performances of the materials. As one of the main strengths, nanofibers are easily fabricated with a sizable and simple spinning system that is flexible for different materials processing, such as ceramic, polymers, metals, and even hybrid materials.

Among the materials, metal oxides exhibit a rich spectrum of properties that can potentially solve many technological challenges, from lower energy consumption to renewable energy sources. Their success is mainly due to compositional diversity,

easy tunability of the chemical and physical properties, facile synthesis, high stability, low cost, and environmental friendliness.

When metal oxides are shaped into nanofibers, devices with enhanced performances and emerging behaviors are designed to meet the specific requirements of many different applications. The tuning of specific properties can be attained by manipulating either the chemistry and the structural parameters of the nanofibers (e.g., diameters and crystallite size). In the last decades, many metal oxides have been synthesized in the shape of nanofibers and explored for their applications in diverse fields, such as purification of liquids and gases; remediation of water and air pollutants; sensors; and energy generation, conversion, and storage.

This book provides an overview of the current state of developments, challenges, and perspectives of metal oxide nanofibers. It comprises three main sections covering the synthesis with its related critical aspects and applications in topical areas.

The first section deals with the theoretical and experimental aspects of synthesis and methodologies. The focus is on the control of the microstructure, composition, and shape of nanofibrous metal oxides. The section includes electrospinning and other methods to synthesize nanofibers in either random or allied fashion. The section also includes the safety aspects associated with the fabrication and handling of nanofibers.

The second and third sections emphasize applications of metal oxide nanofibers in diverse technologies, focusing on the relationship between the peculiar structural, morphological, and compositional features of the nanofibers with the performances in specific fields of applications. Specifically, the second section deals with the applications of metal oxide nanofibers in sensors (e.g., biosensing, gas, and vapor sensors) and water and air purification (e.g., catalyst and filter for the abatement of pollutants). The third section discusses energy generation and storage technologies (e.g., piezoelectric, solar cells, solid oxide fuel cells, lithium-ion batteries, supercapacitors, and hydrogen storage).

The book results from the contributions of several eminent worldwide experts along with their collaborators. The editors highly appreciate their time and effort, without which the book would not have been possible. The book will be relevant for students, young research scientists working with metal oxide nanofibers, engineers, and technology developers. The editors have done their best to cover all the areas of great interest in the field of metal oxides. The intent is to transfer the current enthusiasm about metal oxide nanofibers to as large a readership as possible. The editors hope that the book will serve this purpose. Finally, the editors would like to thank the editorial team at Elsevier for the opportunity to publish this book and for the valuable support, patience, and persuance, which were essential for finalizing it.

**Debora Marani and Vincenzo Esposito**

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# 12 - Metal oxide nanofibers in solar cells

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## Abstract

The motivation to improve the performance of sensitized photovoltaic (PV) cells by enhancing both the surface area and carrier diffusion properties of its photoanode had drawn attention toward utilizing metal oxide nanofibers (NFs). Owing to the anisotropic carrier transport characteristic, NFs had surpassed the nanoparticles analog in achieving higher photoconversion efficiency (PCE) in sensitized PV while preserving the benefit of high surface area. However, the higher density of delocalized trap states in nanostructured materials, compared to the bulk materials, hampered further improvement in the PCE of NF-based sensitized PV cells. This chapter offers a brief explanation of the photoconversion mechanism of sensitized PV cells,

followed by a discussion of the importance of utilizing metal oxide NFs as the charge extractor for this specific application. Details on the formation of delocalized trap states and how it impairs the carrier diffusion coefficient are provided. Some techniques for eradicating the effect brought about by the delocalized trap states are offered and reviewed, and challenges for future development of metal oxide NF-based sensitized PV cells are discussed.

## Keywords

Photoanode; DSSCs; Fermi level; sintering; doping; p-type; n-type; composite; band-bending



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