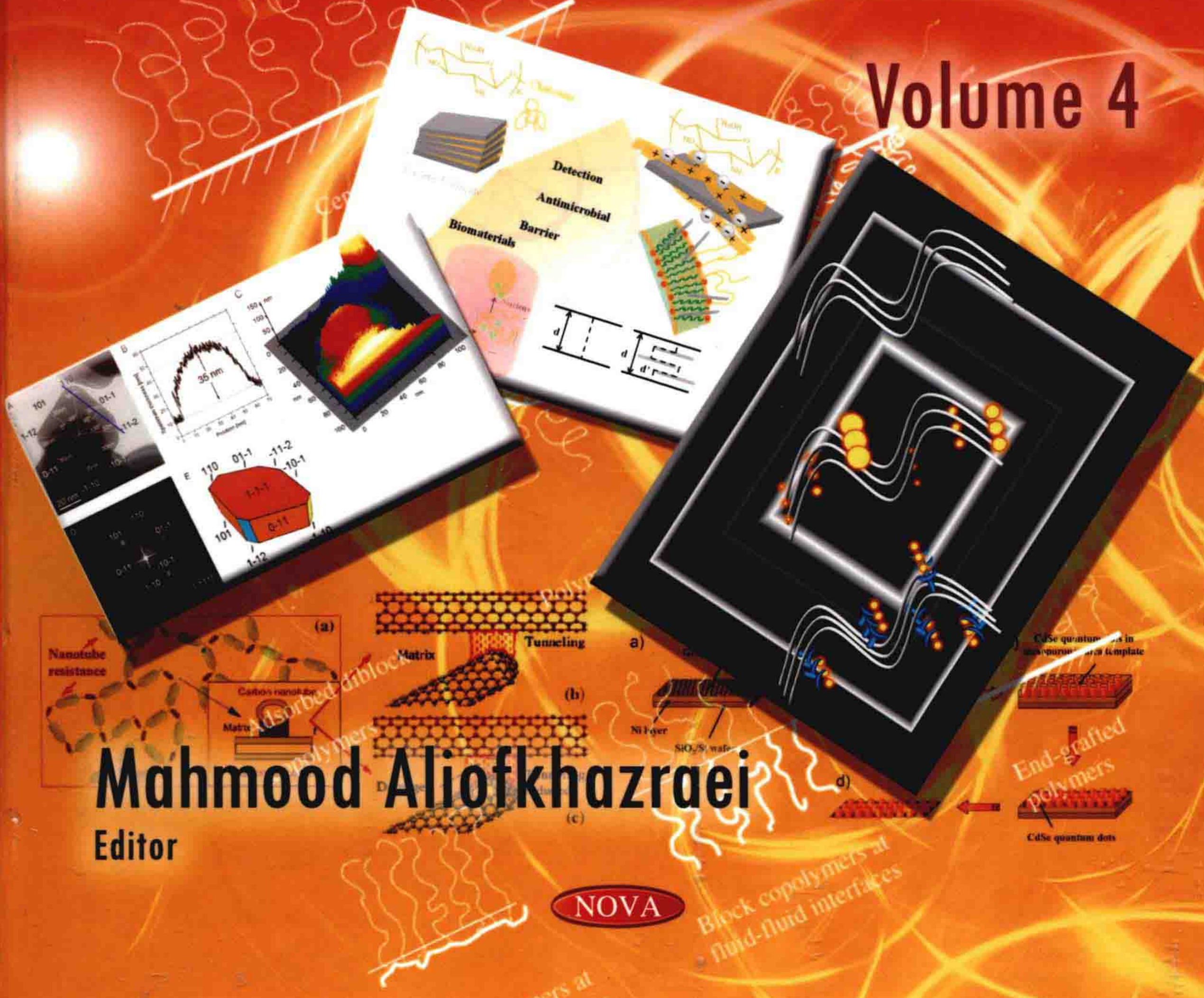
Nanotechnology Science and Technology

Handbook of Functional Nanomaterials

Properties and Commercialization

Volume 4



Mahmood Aliofkhazraei
Editor

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NANOTECHNOLOGY SCIENCE AND TECHNOLOGY

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PROPERTIES AND COMMERCIALIZATION

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PREFACE

This is the fourth volume of the handbook of functional nanomaterials (4 volume set). Functional nanomaterials appear in our daily lives. These materials mainly include nanocomposites, nanopowders, nanoparticles and nanocoatings. Nanotechnology enables the creation of structures that do not exist in nature, those which cannot be produced by conventional chemistry. Some advantages of this technology are the synthesis of stronger, more adjustable materials, as well as lower costs. Nanotechnology is (1) scientific and research development at the atomic, molecular, or macromolecular levels in a dimension range of 1 to 100 nm, (2) the fabrication and application of the structures, equipment, and systems which involve unique characteristics and new applications because of their small or medium dimensions, (3) and the potential for (materials and processes) the control and management of atomic scales. This research aims to create and exploit the structures and systems which involve unique applications due to their small dimensions. The main difference between nanotechnology and other technologies is found within the dimensions and properties of the materials and structures applied to this technology. As a matter of fact, the main difference between these two types of technologies is the presence of base elements, which are indeed the same nanoscale elements with different properties in their nanoscale and larger states. Due to the developed properties of the very fine powders including surface chemistry, compressive properties, optical characteristics, and synthetic reactions, as well as an increasing demand for fine powders in industries, a very fine fragmentation is applied in many materials such as: minerals, ceramics, dyes, chemicals, microorganisms, pharmaceuticals and paper manufacturing. This volume mainly discusses the properties and commercialization of functional nanomaterials. Some of the functional nanomaterials that were discussed in this volume are graphene-based nanocomposites, nanoporous materials, ionic liquids-carbon nanotube nanocomposites, carbon nanotube/nanofiber cement-based composites, titania nanostructured materials, nanostructured multilayer films, ZnO nanostructures, biomolecular nanoconjugates, functionalized magnetic nanoparticles, nano latex materials, semiconductor quantum dots, mesoporous silica-based sensors and keratin nanomaterials. There are 21 chapters in this volume. Each one includes examples of these interesting materials, supported with appropriate figures for better clarification.

Chapter 1 - Highly ordered TiO_2 nanorod and nanowirearrays and other nanostructures were prepared. Those ordered nanostructures present different optical, electrical and photocatalytic properties compared with those bulk materials and unordered nanostructure. The nanorod array shows a reversible electrochromism in lithium-ion-containing organic electrolyte. The coloration and bleaching throughout a visible range can be switched on and off within some seconds. The nanowire array shows photoluminescence phenomenon at room temperature regardless of its indirect transition nature compared with bulk TiO_2. Those ordered nanostructures also show much higher photocatalytic activity when photo degrading organic pollutants.

Chapter 2 - Carbon nanotubes (CNTs) have been the focus of intense research since their discovery in 1991. Their high mechanical strength and chemical stability, excellent electrical conductivity and electro catalytic activity have made CNT a promising material for fabrication of electrochemical biosensors. This chapter reviews the author's recent research work on fabrication of carbon nanotube based multilayer thin films using the solution based layer-by-layer self-assembly technique. The techniques used to disperse CNT in water, the electrochemical behaviour of the composite films and the film application in electrochemical sensing small biomolecules are discussed in detail.

Chapter 3 - Solution-phase synthesis methods have become the main approaches to prepare ZnO photo anodes with various nanostructures for the use in dye-sensitized solar cells (DSSCs). These methods show several advantages, include their simplicity, low cost, and suitability for large-area preparation. This chapter mainly reviewed the author's recent researches about solution-phase synthesized ZnO nanostructures for the photo anodes of DSSCs. The effects of ZnO-based photo anodes with different morphologies, prepared by solution-phase methods, on the performance of DSSCs are discussed, and some of the relevant literatures were also discussed. The future aspects for improving the conversion efficiency of ZnO-based DSSCs are also mentioned in the end of this chapter.

Chapter 4 - Nano-dimensioned titania is attracting increasing interest, owing to its unique physiochemical properties, and widespread applications – solar energy conversion, sensors, photochromic devices, photo catalysis, and environmental remediation. The performance for a given application depends on the crystalline structure, morphology, and size of the material.

In this chapter, the authors report the synthesis – via an aqueous sol-gel method – of nanostructured titania, and Ag-doped-titania. The optical and photochromic properties of the powders were investigated by diffuse reflectance spectroscopy; while quantitative phase analysis was performed by means of the Rietveld-RIR method, performed using X-ray powder diffraction data. The photocatalytic activity of the prepared samples was assessed in liquid–solid phase, under UV- and visible-light irradiation, monitoring the degradation of an organic dye. Antibacterial tests were also performed, against both Gram-positive and Gram-negative strains – *MRSA* and *E. coli*, respectively.

Chapter 5 - In early stages of biomaterials development, the main focus was on mimicking the physical properties of damaged tissues. However, attention has shifted to the interaction of cells and materials. By the time, it has been proved that the material surface chemistry and physical properties have a defining impact for various applications. In this regard, functional nanomaterials can act as essential components of a variety of biological applications. By having the basic knowledge required to design advanced biomaterials that closely mimic the host tissues, recently developed nanofabrication techniques and devices help us to achieve reproducible and high throughput products. It is envisioned that precise engineering at nanoscales enable us to control the elements for realized advanced biomaterials. This chapter reviews the important role of factional nanomaterials in tissue engineering and regenerative medicine.

Chapter 6 - Nanocomposites are multiphase materials containing dissimilar components at the nanometer scale. The properties of nanocomposites depend not only on the properties of their individual parents but also on their morphology and interfacial characteristics. Regarding to the unique properties of carbon nanotubes (CNTs) and ionic liquids (ILs), their combination produces efficient nanocomposites for developing biosensors and biomedical devices. The author's research works represented a dual role for RTIL/CNTs nanocomposites: CNTs play as a promoter for protein electron transferring at electrode surface, while RTIL plays as a biocompatible matrix by which the native structure of enzyme could be preserved. The authors have developed different types IL/CNTs nanocomposites and used them for studying the direct electrochemistry of proteins and development of different biosensors.

Chapter 7 - From the nexus of the fields of cell and molecular biology and nanomaterials has emerged a new field, "biomolecular nanotechnology". In recent years the authors and many other investigators have discovered that nanomaterials can have profound effects on the function of biological molecules. In particular the author's interest has been the effects of nanomaterials on proteins and RNA. In initial studies the authors have focused on biocompatible nanoparticles, such as gold (GNP) or nanomaterials derived of the bio-elements zinc and manganese. For example the authors have demonstrated interactions between GNP, Zinc oxide (ZnO) and Manganese oxide (MnO) nanomaterials with albumin and protamine proteins, and with thrombin enzyme, on the basis of dynamic light scattering (DLS) spectroscopy where the authors observed shifts in the size and surface charge of the nanomaterials as a function of their association to the proteins. The nanomaterials function to stabilize or enhance the biochemical activity of enzymes which the authors have shown for the widely used Luciferase enzyme and are working to extend to other enzymes of considerable commercial and research interest. More recently the authors have formed nanoconjugates between these nanomaterials and protamine or polyamidoamine (PAMAM) dendrimer and demonstrated their biological capacity for the delivery of genes or splice switching oligomers (SSOs). This chapter will summarize these techniques for characterizing biomolecular nanoconjugates and for determining their functional effects on biochemical or biological activity.

Chapter 8 - Aqueous sequestration of dissolved toxic metal species has been a strategic target for scientific research since the development of quantitative methods of detection. Traditional technologies mainly include reductions and adsorption with zero-valent metals and their oxides. Adsorption-based platforms are incapable of selection bias, unable to differentiate between similar oxidation states, and are difficult to separate and recycle. Magnetic nanoparticles have been the focus of multidisciplinary research efforts for the removal of aqueous toxic metals since they can be magnetically separated from the treated water. This makes the toxic metals easier to isolate and allows for regeneration of the nanoparticles, reducing cost and resource consumption. Smaller magnetic nanoparticles above specific temperatures are superparamagnetic which broadens their applicability. Adsorption is enhanced by the increased surface to volume ratio compared to bulk materials and ease of isolation under applied magnetic fields. Surface functionalization with various organic and inorganic compounds capable of preferential interactions with specific metals and metalloids improves the selection bias and enhances the utility of the filtration technology. This chapter will focus on the basic chemistry of magnetic iron oxides and highlight functionalization techniques, including the use of organosilanes, designed to remove specific metals and metalloid ions from aqueous solutions through covalent bonding (chemisorption). Current functionalization platforms including the use of organosilanes will also be examined.

Chapter 9 - During the last decade, there has been a major increase in the interest of nanostructured materials in advanced technologies such as biomedical and dental technology. Nanostructured materials are associated with a variety of uses within the biomedical field, for example, nanoparticles in drug-delivery system, in biomaterial science and diagnostic systems and in regenerative medicine.

By definition, a biomaterial is a nondrug substance that is ideal for inclusion in systems that replace or extend the function of bodily tissues or organs. The key factors in the clinical success of any biomaterial are its biocompatibility and biofunctionality, both of which are related directly to tissue/implant interface interactions.

Nanocomposites can be described as a heterogeneous combination of two or more materials, in which at least one of those materials should be on a nanometer-scale. By using the composite approach, it is possible to manipulate the mechanical properties such as strength and modulus of the composites closer to those of natural bone, with the help of secondary substitution phases.

Currently, the most common composite materials used for clinical applications are those selected from a handful of available and well-characterized biocompatible ceramics and the combination with metals and polymers as composites and hybrids. This approach is currently being explored in the development of a new generation of nanocomposites with a widened range of biomedical and dental applications.

The aim of this chapter is to provide information relating to the use of nanocomposites for biomedical and dental applications.

An overview on the basis of biomaterials will be followed by some of past and present research into the use of nanocomposites in biomedical and dental applications.

Chapter 10 - Carbon nanotubes (CNT) have excellent physical properties including mechanical, electrical and thermal behaviors and good chemical stability. Moreover, they possess unique hollow tube structure, nanoscale diameter and high aspect ratio. These make CNT become excellent nanoscale fillers for fabricating self-sensing and self-damping cement-based composites, which can help us develop intelligent infrastructure with elegantly integrated sensing and damping abilities, thus increasing the safety, durability, serviceability and sustainability of infrastructure structures. The self-sensing and self-damping cement-based composites have great potential in the field of structural health monitoring for concrete structures, traffic detection, and structural vibration control. In this chapter, the authors systematically introduce researches on self-sensing and self-damping CNT cement-based composites, with attentions to their fabrication, measurement, self-sensing and self-damping performances and generation mechanisms, and application in traffic detection.

Chapter 11 - The spectra of magnetoplasma waves, zero sound and spin waves in electron gas on a surface of a nonferromagnetic nanotube in longitudinal magnetic field are considered. The initial spectrum of the electron energy is assumed to be parabolic, and the electron-electron interaction is taken into account within the framework of random phase approximation. For a great number of filled sub bands the frequencies of waves in degenerate electron gas experience oscillations of the type of de Haas-van Alphen and Aharonov-Bohm with changing the parameters of nanotube and magnetic flux.

The spectra of waves on nanotube surface with a super lattice in magnetic field are considered. The oscillation characteristics are determined by the ratio of the Fermi energy to the miniband width. For large values of the ratio, the beating pattern appears in wave's frequency dependence on the nanotube parameters. These oscillations are not present if the ratio is sufficiently small.

Chapter 12 - Graphene, an expeditiously rising star on the horizon of materials science in electronic, optical and catalytic fields, has become one of the most exciting topics of research in recent years. This one-atom-thick fabric of carbon uniquely combines extreme mechanical strength, exceptionally high electronic and thermal conductivities, impermeability to gases, as well as many other supreme properties, all of which make it highly attractive for application in electrochemical energy devices, such as solar cells, photodetectors, light emitting devices, ultrafast lasers, optical sensing, and metamaterials. In this chapter, the authors attempt to review the methods of graphene preparation and summarize the recent research and development on graphene-based energy conversion and storage: photo catalysts, super-capacitors and lithium ion batteries. First, the origin of graphene and preparation will be simply introduced. Then, the synthesis and applications of graphene-based materials will be described in detail. As the authors know, graphene has a multitude of striking properties that make it an exceedingly attractive material for various applications, many of which will emerge over the next decade. However, one of the most promising applications lies in exploiting its peculiar photoelectronic properties which are governed by its electrons obeying a linear dispersion relation. This leads to the observation of half integer quantum hall effect and the absence of localization. The focus then centers on current synthesis strategies for graphene and their applications in terms of energy conversion and storage are highlighted. Finally, a brief outline of potential future work is given to conclude this chapter.

Chapter 13 - Cavitation plays an important role in the synthesis of nanoparticles. Both chemical and physical effects of cavitation have prominent effects in the preparation of different shapes, structures and sizes of inorganic particles and nano latex. Further, it is a versatile technique for the preparation of monodisperse nanoparticles with uniform particle size distribution. In this book chapter, an ultrasound assisted synthesis of polymer nanoparticles such as poly methyl methacrylate (PMMA), poly butyl acrylate (PBA) and PMMA-co-Styrene/MMT is reported. The ultrasound assisted synthesis of inorganic intercalated nanoparticles such as nanoclay and ZnO doped nanocomposite nanoclay is discussed. The application of sonochemically synthesized nano clay, nanoclay-ZnO and ZnO nanocontainers in waste water treatment and coatings are also reported.

Chapter 14 - TiO_2 nanostructures offer many applications in solar energy production, photo-catalysis, water splitting, drug delivery, bone implants, the color and paint industry, sensors, hydrogen storage, antibacterial surface coatings and opened a new area in modern industry and medicine. Tuning and controlling of the optimized growth of TiO_2 nanostructures regarding the substrate and the chemical environment and physical properties of TiO_2 nano-materials is considered as the crucial issue for using TiO_2 nanostructures in different devices. This Chapter is devoted to description of the synthesis and application of different TiO_2 nanostructures likeTiO_2 nano-tubes, nano-rods, nano-particles, nano-wires and nano-sheets which are prepared by different methods such as anodization, hydrothermal, sol-gel and chemical vapor deposition, physical vapor deposition and electrochemical deposition. An introduction to the physical basis, optimization and control of the growth, tuning of the physical properties of TiO_2 nanostructures, and a review of TiO_2 nano-structure based devices is also given.

Chapter 15 - This chapter provides an overall picture for luminescent transparent bulk nanocomposites and on the construction, key properties and advanced applications in photonic, optoelectronic materials and devices as well as sensing. Here, the authors generalize the relativity of the properties of the nanocomposites with the incorporation of luminescent nanomaterials in highly processable, transparent bulk polymeric, inorganic and organic-inorganic matrices. Because of the various combinations of material types and the large extent of the topic, this chapter will mainly focus on luminescent nanomaterials embedded in matrices and luminescent nanocomposites copolymerized by novel polymerizable nanomaterials. Finally, some future trends and perspectives in this research area are outlined.

Chapter 16 - Internal reflection features caused by the surface plasmon resonance in nanoscale films containing defect tin dioxide clusters in the stoichiometric dielectric matrix are studied by the method of polarization modulation of electromagnetic radiation. The angular and spectral characteristics of reflectances R_s^2 and R_p^2 of *s*- and *p*-polarized radiation and their polarization difference $\rho = R_s^2 - R_p^2$ are measured in the wavelength range $\lambda = 400$–1600 nm. The experimental characteristics $\rho(\theta, \lambda)$ (θ is the radiation incidence angle) obtained represent the optical property features associated with the film structure and morphology. Surface plasmon polaritons and local plasmons excited by *s*- and *p*-polarized radiation are detected; their frequency and relaxation properties are determined. The structural sensitivity of the technique for studying the surface plasmon resonance for tin dioxide films is shown.

Chapter 17 - With the discovery of novel properties of matters at their nanoscale sizes, almost the entire materials science has been reoriented towards exploring the so called 'nanomaterials' including the growth, characterizations and possible applications. The chemical methods of growth based on 'bottom up' approach have been popular, easier, and simpler and are explored maximum in different new forms. The other costlier, tedious and well known methods of epitaxial growth have been in use since very long. The author will discuss the use of most common, simpler and yet least explored method of vacuum physical vapor deposition for the growth of semiconductor quantum dots on any substrate which can also be termed as the 'bottom-up' approach of growth. A brief description of relevant nucleation and growth models for this process is presented for understanding and appreciating this method. The experimental details of growth and characterizations are presented for some III-V and Iodide semiconductors investigated in the author's laboratory.

Chapter 18 - Porous silicon, porous alumina and porous titania obtained by etching silicon and anodising aluminium and titanium, respectively, have become three popular materials in many scientific disciplines as a result of their outstanding set of properties and cost-competitive fabrication processes. To understand the electrochemical processes that take place during the etching of silicon and anodisation of aluminium and titanium is a key factor to control and modify the structure of these porous materials. This makes it possible to produce many innovative and versatile pore architectures by some electrochemical approaches (e.g. straight and well-defined pores, cone-like, funnel-like, modulated, serrated-like, hierarchical, three-dimensional, tip-like, etc.). All this opens a new window towards smart designs of nanoporous materials, which have multiple applications in many research fields as biotechnology, medicine, optics, electronics, chemistry and so on.

This chapter reports about the most important aspects of electrochemical etching and anodisation of silicon, aluminium and titanium as well as some electrochemical approaches used to modify their porous structure for subsequent technological applications.

Chapter 19 - There is a constant demand for the development of new optical sensors with improved sensor performance. Therefore, over recent years structurally well-defined mesoporous silica materials with high specific surface areas, tuneable pore sizes and well-ordered pore size distribution, have become very attractive for the fabrication of optical sensors. In this chapter the authors firstly present the properties of mesoporous silica materials and provide a brief description on the analytical aspects of optical sensors. A survey of the recently developed mesoporous silica sensors, which include articles from the year 2008 until recently, is critically discussed. It was shown that mesoporous silica-based sensors represent a good alternative to classical sol-gel materials that can improve the limit of detection, response times, and selectivity properties.

Chapter 20 - Increasing awareness of environmental issues and associated demand from consumers for non-petrochemical-derived materials has led to a surge of interest in new bio-based materials. Keratins are fibrous proteins with excellent inherent potential for extraction and reconstruction into new biomaterials. This chapter discusses the utilisation of keratins and their derivatives in nanomaterial and nanotechnology applications, including such emerging areas as keratin nanofibres, stimuli-responsive keratin nanomaterials, and keratin-based nanocomposites and advanced fibres. The current state of each of these areas is reviewed, along with relevant application examples.

Chapter 21 - Graphene has a honeycomb crystal lattice structure with densely packed carbon atoms. The sp^2 bond between these atoms is an excellent property of this layered material. Graphene paper/sheet is a thin-film paper made of functionalized graphene Nano flakes, which has very high strength and flexibility compared to many other materials currently used by industries. The strong interlayer sp^2 bonds and interlayer crosslinking between the layers help maintain better load transfer and electrical and thermal conductivity more effectively. When incorporated with polymeric composites, graphene paper can vastly improve the mechanical, thermal, and electrical properties of composites and can be used in various applications, such as batteries, super capacitors, and several other electronic and telecommunication devices. This book chapter discusses the fabrication techniques; mechanical, electrical, and thermal properties; structural defects; and applications of graphene and graphene thin films.

CONTENTS

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Chapter 1

PREPARATION AND APPLICATION OF TITANIA WITH ORDERED NANOSTRUTURES

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ABSTRACT

Highly ordered TiO_2 nanorod and nanowire arrays and other nanostructures were prepared. Those ordered nanostructures present different optical, electrical and photocatalytic properties compared with those bulk materials and unordered nanostructure. The nanorod array shows a reversible electrochromism in lithium-ion-containing organic electrolyte. The coloration and bleaching throughout a visible range can be switched on and off within some seconds. The nanowire array shows photoluminescence phenomenon at room temperature regardless of its indirect transition nature compared with bulk TiO_2. Those ordered nanostructures also show much higher photocatalytic activity when photodegrading organic pollutants.

INTRODUCTION

As one of the most important semiconductors, TiO_2 has drawn much attention due to its high photocatalytic activities and the key role in the injection process of a photochemical solar cell. TiO_2 is widely applied in many fields such as environmental purification, utilization of solar energy and electrochromic electrodes. Since Fujishima et al. first discovered the phenomenon of photocatalytic splitting of water on TiO_2 electrodes exposed to UV irradiation in 1972 [1], TiO_2 has become one of most studied material as photovoltaics and photocatalyst to decompose and oxidize various organic and/or inorganic chemicals in waste and emission by its strong oxidation activity based on OH radicals [2]. The optical properties of anatase TiO_2 materials have been a subject of intensive research. These researches mostly focus on the properties of bulk, thin film and particle samples of unordered titania [3, 4]. Indeed, ordered quasi-one-dimensional nanostructural systems are the smallest dimensional structures that can be used for optical excitations and efficient transport of electrons, and thus there has been increasing interest in such nanostructures. They are expected to be critical to the function and integration of nanoscale devices.

Many transition-metal oxide materials such as WO_3 and TiO_2 can be electrochemically changed to a redox state due to its intense electronic absorption. Such nature can be used to be electrochromic devices that are able to change their optical properties reversibly. They result from charge insertion and extraction induced by an external voltage. In spite of a slow response time and low coloration efficiency of TiO_2 as electrochomic materials, it is still very attractive due to its excellent photoelectrochemical and photocatalytic activity and thus its potential application in electrochromic devices. Many efforts have been done to improve its performance, including its morphology modifying into ordered nanostructure. In this chapter, a novel ZnO-nanorod-array-templating technology was attempted to fabricate TiO_2 nanorod array in a large scale on ITO substrates. This nanorod array showed a reversible electrochromism in lithium-ion-containing organic electrolyte. The coloration and bleaching throughout a visible range can be switched on and off within some seconds.

Photoluminescence is a nondestructive and high-sensitivity technique widely used to investigate the photo-physicochemical properties of transition-metal oxide semiconductors. It can supply information such as the separation and recombination of photoinduced electrons and holes and surface oxygen vacancies related to band structure. Therefore, the study of photoluminescence of ordered TiO_2 nanostructure will help us to understand the effect of structure on the optical and electric properties and hence its photocatalytic activities. It is difficult to observe any photoluminescence phenomenon at room temperature for bulk TiO_2 due to its indirect transition nature [5]. However, some special nanocrystal TiO_2 have been reported to exhibit broad PL related to the surface states and band structure at room temperature [6-8]. In this chapter, highly ordered anatase TiO_2 nanowire arrays with diameter of about 20, 35 and 60 nm were prepared within the pores of anodic aluminium oxide (AAO) templates by a cathodically induced sol-gel method. The spectra of absorption and photoluminescence of titania nanowire arrays were employed to characterize the optical and electric properties.

TiO_2 has become a very attractive photocatalytic material due to its strong oxidizing power, nontoxicity, and long-term photostability. Therefore it is used in pollution control, including air cleaning and wastewater treatment. However, when using TiO_2 powder to photodegrade pollutants in waste water, separation problems may be encountered by the following repeated utilization. At the same time it also suffers the problems of the low photo-degradation efficiency. Therefore many efforts including the preparation of films with highly ordered structures have been done to improve the surface area and electron transport. In this chapter, the photocatalytically degradation of dye solutions by TiO_2 films prepared by different methods, including sol-gel, electrochemically induced sol-gel and electrophoretic deposition (EPD) were compared to investigate the effects of nanostructure on photocatalytic activities.