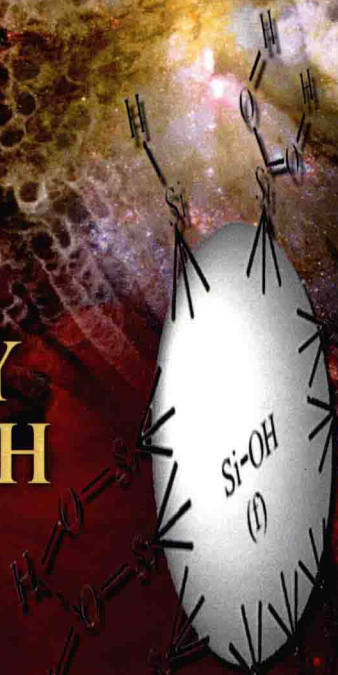


New Developments in Metal Oxides Research



**ISTVAN NAGY
ADAM BALOGH**
EDITORS



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NEW DEVELOPMENTS IN METAL OXIDES RESEARCH

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ADAM BALOGH
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PREFACE

In this book, the authors present current research in the study of metal oxides. Topics discussed include the preparation of titania nanoparticles and relationships between procedures and properties; metal oxides as water retention materials of low humidity proton exchange membrane applications; computational materials design of d^0 ferromagnetism in metal oxides; application of transition metal oxides in tandem organic optoelectronics; and catalytic oxidation of VOCs using lanthanum, nickel and lanthanum-nickel oxides.

Chapter 1 – Recent literature on methods for preparation of titania nanoparticles is reviewed. It is shown that in addition to the method chosen (hydrolysis, solvolysis, sol-gel, hydrothermal or solvothermal), the precise nature of the titanium precursor, and the experimental conditions (e. g., relative concentration of reagents, calcination temperature, the presence of additives, etc.) play an outstanding role on the properties (mainly crystalline phase, morphology and size) of the titania prepared.

Chapter 2 – Polymer electrolyte membrane fuel cells (PEMFCs) operating at elevated temperature have attracted considerable attention in recent years because they could benefit from enhanced tolerance to impurity of the fuel gas, improved water and heat management, and increased reaction rates at both cathode and anode compared with PEMFCs operating below 80°C. One of great technical challenges in high temperature PEMFC systems is proton exchange membranes (PEMs), which should maintain reasonable proton conductivity and good mechanical stability at high temperature. This has led researchers' interest to membranes impregnated with nano-structured hygroscopic metal oxides that can act as water retention materials in membranes. The incorporation of hydrophilic nanobuilding blocks of metal

oxides as fillers comes in the form of nanoparticles, nanowires, and nanotubes depending on the synthetic route and processing techniques. This chapter covers an unprecedented review of water retention and transport properties of metal oxides and metal oxide based materials for elevated temperature polymer electrolyte membrane. It provides an ideal introduction, preparations and characterization techniques as well as an overview of recent progress on metal oxide nanostructures and their applications as water retention materials for elevated temperature polymer electrolyte membranes.

Chapter 3 – d^0 ferromagnetism refers to a new class of magnetism in which the ferromagnets contain no magnetic elements. This class has attracted significant interest for spintronics applications. To present a unified picture of d^0 ferromagnetism, this chapter summarizes a series of computational materials design and first-principles investigations of d^0 magnetism with a focus on the host materials of alkaline-earth metal oxides. The electronic structures of materials, such as N- or cation-vacancy-doped MgO , CaO and SrO are described, with a specific focus on how the electronic structures are correlated with the magnetic properties. Additionally, the significant need for a methodology that goes beyond local density approximation has been noted for the investigation of d^0 ferromagnetism. The chemical trends of the calculated exchange interactions and Curie temperatures are reviewed, and a recent proposal on the self-organization of dopants and their potential contribution to d^0 ferromagnetism is discussed.

In this context, the underlying mechanism for room-temperature d^0 ferromagnetism from recent reports is also discussed. A brief summary on the materials design of dilute magnetic semiconductors doped with 4d or 5d transition metals is provided to introduce an important finding that has significantly contributed to the creation of this novel field.

Chapter 4 – Owing to the ease of processing and potential for inexpensive fabrication on low-cost substrates, organic optoelectronics have generated intense research efforts towards the realization of efficient organic light-emitting diodes (OLEDs) for flat-panel displays and solid-state lighting, organic photovoltaic cells (OPVs) for low-cost solar energy generation, thin-film field-effect transistors and photodetectors for large-area detector arrays. For all of these organic devices, optimization of charge injection/extraction and carrier transport is critically important towards their technological success. Efficient injection or extraction requires low energetic barriers, while competent transport demands highly conductive transport layers.

During the last few years, transition metal oxides (TMOs) such as molybdenum tri-oxide (MoO_3), vanadium pent-oxide (V_2O_5) or tungsten tri-

oxide (WO_3) have been extensively used for improved charge injection and extraction in organic optoelectronic devices, due to their advantages of excellent electric properties, high optical transparency, and good environment stability. Generally, TMOs can realize efficient p-type doping of organic hole-transport layers, charge generation layers for tandem OLEDs, charge recombination layers for tandem OPVs because of their unique electronic properties. It is now recognized that a more complete knowledge on electronic structures of TMOs, especially the energy level alignments in TMO-organic interfaces is of pronounced importance for the resulting interpretation of their role as functional constituents in organic electronics.

In this chapter, recent advances in understanding the interfacial energetics, chemical properties, and electrical behavior of TMO-based intermediate connectors used in tandem OLEDs and OPVs are reviewed, which are the typical examples of TMO applications in organic optoelectronics. Current understanding of the operating mechanisms that control and limit the charge generation or recombination process is presented. The specific properties of the resulting materials and their role as functional layers in organic devices are addressed. Recent efforts towards interface engineering of TMO/organic interfaces are also discussed. The physical insights provide guidance for identification of new materials and device architectures for high-performance devices.

Chapter 5 – Volatile organic compounds (VOC) are harmful environmental pollutants originated from stationary and mobile sources, such as painting, printing, petroleum refineries, fuel storage and motor vehicles. As some VOCs are dangerous to human health and to the environment, their emissions are regulated.

Catalytic oxidation to CO_2 and water is an environmentally friendly technology for VOC abatement. It requires low temperatures (around 250-500 °C) and causes less NO_x formation, compared to conventional thermal oxidation, which requires high operation temperatures (650-1100 °C).

Metal oxides can be used as heterogeneous catalysts for VOC oxidation. Commonly used catalysts include manganese, copper, nickel and iron oxides. It has been reported that although metal oxide based catalysts are less active than supported precious metals in oxidizing VOC streams, they are generally more resistant to poisoning phenomena. However, mixed oxides can show good activities in catalytic oxidation of VOCs, thus being good candidates for this application.

In this work, single oxides of lanthanum and nickel were used. Mixed oxide samples of La-Ni-O synthesized by an evaporation method, with La-Ni

ratios of 1:1 and 1:2 were also evaluated. Catalyst samples were characterised by N₂ adsorption at -196 °C, temperature programmed reduction, scanning electron microscopy and X-ray diffraction. The materials were tested in the oxidation of ethyl acetate, a compound widely used as a solvent in printing operations, glues, nail polish removers, etc.

It was found that the mixed oxide was much more active than the single oxide catalysts, allowing 100 % conversion of the VOC into CO₂ at ~250 °C, with no formation of CO. Full conversion was not achieved by any of the single oxides, and CO was detected. The La:Ni 1:2 sample was more active than the 1:1 analogue. The 1:2 mixed oxide had a much larger surface area and also easier reducibility than the 1:1 sample. Both mixed oxides had larger surface area and higher reducibility than the single components, which can explain their improved performance.

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Chapter 1

PREPARATION OF TITANIA NANOPARTICLES AND RELATIONSHIPS BETWEEN PROCEDURES AND PROPERTIES

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ABSTRACT

Recent literature on methods for preparation of titania nanoparticles is reviewed. It is shown that in addition to the method chosen (hydrolysis, solvolysis, sol-gel, hydrothermal or solvothermal), the precise nature of the titanium precursor, and the experimental conditions (e. g., relative concentration of reagents, calcination temperature, the presence of additives, etc.) play an outstanding role on the properties (mainly crystalline phase, morphology and size) of the titania prepared.

Keywords: Titania preparation, pre-shaped morphology, anatase, rutile, brookite, hydrothermal, solvolysis, sol-gel

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1. INTRODUCTION

The structure and microstructure exhibited by a material depends, in addition to its chemical composition, on the method followed to prepare it. To select an adequate preparation procedure is relevant as its control and optimization permits to influence and to tailor the properties shown by the solid finally prepared and its performance.

Due to its biological and chemical inertness, strong photooxidation power, cost effectiveness and long thermostability against photo and chemical degradation, titania is one of the major heterogeneous photocatalysts. The most important polymorphs of titania are brookite, anatase and rutile. Brookite is orthorhombic ($a = 5.4558 \text{ \AA}$, $b = 9.1819 \text{ \AA}$ and $c = 5.1429 \text{ \AA}$), while anatase and rutile are orthogonally (crystal parameters $a = 3.7845 \text{ \AA}$, $c = 9.5143 \text{ \AA}$ for anatase and $a = 4.5937 \text{ \AA}$, $c = 2.9587 \text{ \AA}$ for rutile). Other forms are also known, for instance, akagoeite, with a monoclinic structure ($a = 4.606 \text{ \AA}$, $b = 4.986 \text{ \AA}$, $c = 4.933 \text{ \AA}$, $\beta = 99.17^\circ$). All three brookite, anatase and rutile are constituted by $[\text{TiO}_6]$ octahedra, linked together by sharing edges or corners; different packing of these octahedra leads to the three different crystal forms. The stability decreases in the order rutile > anatase > brookite; as a result, synthesis of brookite is difficult and for practical applications, rutile and anatase are almost exclusively used. The transition temperature between one phase and another depends on the nature of the precursor used for their synthesis, the presence of impurities, reaction atmosphere and particle size [1]. The stability of a given phase depends on the surface characteristics of the material. As a consequence, even from nanoparticles with the same particle size, but prepared following different procedures, the phase transformation or the particle size increasing rate can be controlled, due to the differences in the surface properties related to the synthesis procedure used. The anatase-rutile transformation takes place between 600 and 900 °C [1, 2]. As the temperature is increased, the size of the anatase particles increases too, the transformation to rutile also occurring in an irreversible way. The transformation mechanism proceeds via nucleation and growing [3], favoured by the presence of nucleation sites. The rutile particles grow at a faster rate than the anatase ones. The size increase can be explained by the displacement of the grain boundaries by atomic diffusion when several particles coalesce. In this process, the lower the size of the particles being aggregated, the larger the growing rate of the particles.

The different stability of the main titania phases, namely, anatase, rutile and brookite, can be explained on the basis of polymorphism effects, surface

energy, and the presence of water and other impurities [4]. Both anatase and rutile have the same entropy (50.6 ± 0.6 and $49.9 \pm 0.3 \text{ J mol}^{-1}$ for rutile and anatase, respectively, at 298 K) [5], the differences between both arising from enthalpy values. On plotting the enthalpy against the specific surface area, straight lines are obtained for each phase, the zero intercept being the enthalpy of the bulk and the slope the change in surface energy between the phases. The surface enthalpies calculated for rutile, brookite and anatase are 2.2 ± 0.2 , 1.0 ± 0.2 , and $0.4 \pm 0.1 \text{ J m}^{-2}$, respectively. As a result, rutile is stable for specific surface areas below $7 \text{ m}^2 \text{ g}^{-1}$ (particle size larger than 200 nm), brookite between 7 and $40 \text{ m}^2 \text{ g}^{-1}$ (particle size 40 – 200 nm) and anatase for specific surface areas above $40 \text{ m}^2 \text{ g}^{-1}$, corresponding to a particle size below 40 nm.

Transition metal oxides usually exhibit different practical properties and applications not only attending to their intrinsic crystal structure and chemical composition, but also depending on the crystal size and morphology, specially if the material is micro- or nano-structured, thus showing a large specific surface area (an important point in heterogeneous catalysts) or short solid state diffusion paths (an interesting feature in electrochromic devices and batteries [6, 7]). Moreover, one dimensional architectures such as nanorods, nanowires and nanotubes play prominent roles in functional devices due to their dimensionality and quantum confinement phenomena. Different nanostructures can be obtained by chemical or electrochemical methods, the most popular ones being template, sol-gel and hydrothermal approaches, producing nanoparticles shaped as nanorods, nanowires and nanotubes.

The photocatalytic activity of titania is related to the specific nature of the faces exposed [8]; this is reasonable, since the surface energy, the chemical surface states and the number and energy states of defect sites mostly depend on the atomic arrangement of the crystal face. Consequently, efforts have been made to prepare titania particles with a given crystal structure and a predetermined morphology; for instance, the presence of chloride or perchlorate during nucleation favours the formation of rodlike rutile, and octahedral and decahedral anatase, respectively [9-12]. For monodimensional nanostructured crystals, the space charge region is well defined along the longitudinal direction of the crystals, and thus photogenerated electrons can flow in the direction of the crystal length; increased delocalization of electrons in these crystals leads to a decrease in electron-hole recombination probability and, consequently, larger numbers of electrons and holes will exist on the active sites of the nanocrystal surface, if compared to spherical particles. The primary crystal size of photocatalysts determines both the photoconversion efficiency and the specific surface area, which are essential to a good

photocatalyst; actually, it has been demonstrated that an optimal TiO_2 particle size exists to maximize photocatalytic oxidation rates [13].

During photocatalysis, titania is activated by a UV photon, which results in the excitation of an electron from the valence band (VB) to the conduction band (CB). On migrating to the surface, the photogenerated electrons and the holes may act as reducing or oxidizing agents. If electron accepting species are adsorbed on the surface of the particle, they will capture the photogenerated electrons, becoming reduced; on the contrary, the photogenerated holes may accept electrons from donor species, which will then result oxidized. These processes will depend on the red-ox potentials of the participating species. As a result, species such as H_2O_2 , O_2 or O^{2-} are formed, as well as radical species, depending on the accepting species. These processes compete with *recombination reactions* of the electron-hole pairs, which may occur on the surface or in the bulk of the particle; they are favoured by the presence of crystalline defects. The efficiency can be increased by the presence of metals [14, 15]. The role of the loaded metal is trapping and subsequently transferring of photoexcited electrons onto the photocatalyst surface and decreasing the recombination of electron-hole pairs [16].

It is rather difficult to define the physical properties which will optimize the photocatalytic efficiency. Solids with a large specific surface area, able to adsorb a large number of species, will give rise to larger charge transfer rates and high photocatalytic activity. However, defects concentration is rather high in the particle surface, favouring recombination of the electron-hole pairs. High temperature treatments usually improve the crystallinity of the material, removing defects, but also favour aggregation of the particles and decrease their specific surface area.

Best photocatalytic activity results are usually observed with anatase, probably due to its larger specific surface area, pore structure and low particle size [17, 18]. However, some studies have demonstrated that anatase-brookite, brookite-rutile and specially anatase-rutile mixtures are beneficial on the charge transfer processes, due to properties such as particle size, surface structure or development of new electronic states located close to the band gap [19].

Although most of the reports on photocatalytic activity of titania has been addressed to remove organic pollutants, it has been also applied to oxidize As^{3+} to As^{5+} [20,21], a prior step in arsenic removal because As^{5+} adsorbs more strongly than As^{3+} on a solid phase. The first report on the antibacterial properties of anatase was published in 1985 [22], and after that anatase TiO_2

has attracted an increasing interest in inactivation of bacteria, molds, viruses and even cancer cells [23-29].

One of the main drawbacks of titania as a photocatalyst is the large value of its band gap, 3.0 and 3.2 eV, respectively, for the rutile and anatase crystalline phases; as a consequence, numerous efforts have been made to extend the activity of TiO_2 into the visible region to improve the efficiency of TiO_2 , such as dye-sensitization, or doping with non metal atoms or transition metals, although detrimental effects have been also pointed out [30]. These studies are outside the general scope of this review, although some comments are made on some of these procedures.

Titania has been also used in organic/inorganic nanocomposites, where ideally the titania particles should not aggregate in an organic matrix.

Due to its opacity, titania nanoparticles are also used in commercial sunscreen products, mixed with organic reagents to adjust the sun protection factor [31]; the most widely organic component is *p*-amino benzoic acid, which absorbs UV-B radiation (320-290 nm) and is transparent to the UV-A radiation (400-320 nm). By supporting this reagent on titania nanoparticles it has been claimed that the protection can be extended to a broader spectrum [32].

Mesoporous TiO_2 has also attracted much attention due to its high surface-to-volume ratio, displaying a large concentration of active sites, to be used in photocatalysis and photoelectrical chemical conversion; however, it is a challenge to prepare these solids without phosphorous (from the precursors used), and a tridentate ligand – triethanolamine – has been used in some cases [33], as well as surfactants, triblock polymers, etc.

The increasing use of titania nanoparticles in every day more and different fields has also given rise to concerns about their possible negative effect on the human body; it has been confirmed, however, that titania nanoparticles prepared by spark ignition, having a crystallite size close to 4 – 5 nm in the anatase form, did not disintegrate in lung tissue [34].

To advance in the optimization of the use of titania, nanostructures fulfilling a series of requirements, such as defined crystal phases, degree of crystallinity, shape of the elemental crystallites and their size, as well as suitable chemical modification of its surface, need to be developed [35].

We have reviewed here the methods described in recent literature to prepare nanostructured titania particles or shape-controlled titania nanoparticles, as well as, when data are available, the influence of the shape, morphology and size on the catalytic performance. We cover the period starting roughly in 2007, when Chen and Mao published a review on titanium

dioxide nanomaterials for different uses [36]. Other relevant reviews recently published have been dedicated to solar water splitting [37], colloidal strategies for preparing hybrid nanocrystals [38] and to the growth and functionality of titania nanotubes [39]. The performance of dye-sensitized solar cells has been also correlated with the morphology and chemical composition of titania [40]. Only those methods which we can considered to be “classical” or conventional are here reviewed, while other (for instance, the use of titania nanotubes, ionic liquids, combustion-assisted methods, anodization, or the use of titanium complexes) are not considered. In this review, the procedures to prepare titania are clasified according to the process followed (e. g., hydrolysis, hydrothermal processes, sol – gel); these methods have been used for long time to produce titania photocatalysts and we summarize here the results from many articles; within a given method the procedures are classified according to the titanium precursor used (inorganic and organic) and then, the studies are roughly ordered by their publication date. Special attention is paid to the experimental procedure (although details concerning amounts of reactants are generally avoided), the aim of the study, and the performance in a given reaction, if available and provided by the authors. However, a sharp and clear division between the methods cannot be done, as in some cases combined methods (for instance, sol – gel and ultrasounds treatment) are applied simultaneously.

2. HYDROLYSIS AND SOLVOLYSIS METHODS

Hydrolysis is probably one of the most widely methods used to prepare titania nanoparticles; the problem, however, is that usually a high temperature calcination step is required to obtain crystallised materials, so giving rise to sintering of the particles and a decrease in the specific surface area.

2.1. Inorganic Precursors

2.1.1. *Titanium Tetrachloride*

Vapour phase hydrolysis of TiCl_4 below $550\text{ }^\circ\text{C}$ was used by Xia et al. [41] to prepare titania nanoparticles in a specially designed aerosol reactor, where TiCl_4 vapour reacted with water vapour to produce a TiO_2 aerosol at atmospheric pressure, collecting the product by thermophoresis and filtration. A thermal treatment at a heating rate of $8\text{--}10\text{ }^\circ\text{C min}^{-1}$ rendered the final crystallized titania powders. In the temperature range $360\text{--}550\text{ }^\circ\text{C}$ and using a