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Synthesis, Formation, Assembly and Application
To our wives Anja and Sabina
Foreword

Some scientists, especially those far off materials sciences, still perceive the prefix “nano” as a hype. To my opinion, this notation might describe the vigorous expansion phase of nanosciences and nanotechnology, but the hype meanwhile turned into real science, into real products and jobs.

Contrary to previous hyped topics, the nano-community was able to fill many promises with reality, at least to a larger extent, and this is why nanosciences are still flourishing, still growing, partly even beyond expectations of the educated experts.

A key part of nanosciences is nanoparticulate matter, including nanoparticles, nanorods, nanoplates, or even more complex tectonic assemblies. Exactly on these examples we can nicely illustrate what nanosciences really provides. Simply by finely dispersing common bulk materials down to the nanoscale, new properties can be observed: inert materials become catalysts, insulators become conductors, white substances become transparent, stable materials become combustible. It is known since the ancient world: Gold nanoparticles are shining red or blue, and the beauty of medieval church windows is based on the extraordinary color strength and the high thermal stability of those dispersions, exceeding ordinary dyes by some orders of magnitude.

There is more than only plasmonic color to be discovered: There is a whole new world out there in the nano cosmos, a world which already Wolfgang Ostwald about a hundred years ago named the “world of lost dimension”. Some colleagues even regard nanostructures as a new adjustable state of matter. This is due to the fact that atoms at surfaces behave differently to those in the bulk, and nanoparticles are literally dominated by those surfaces.

It is a safe prediction: The new questions to face while analyzing alternative energy cycles of society, communication technology, the desire for new catalysts for more efficient chemical reactions, new light sources, or better performing construction materials will only be answered by implementation of nanostructural aspects. There will be no real alternative or choice.

For many of those applications, appropriate nanostructures however do not yet exist, or their production is not sustainable so that “de novo” systems and
their synthetic pathways have to be designed from scratch. This is where the present book sets in: Both authors are most competent in this field, pioneers of a synthetic route towards metal oxide nanoparticles, which is meanwhile called “nonaqueous sol-gel route”. This technique not only turned out to be simple, convenient, scalable, mass efficient and rather sustainable, but it also was proven to be extremely flexible with respect to size and composition so that – within just a few years – an impressive number of binary, ternary and quaternary nanocrystalline oxides in a variety of sizes and morphologies could be assessed. This explosive development is nicely summarized and structured in this book, and this is why it is a timely endeavor.

The book not only reviews comprehensively the primary literature and observations, it also gives an actual description of current trends in the field and the still ongoing improvements of the technology, say by incorporation of microwave synthesis. Special emphasis is also put on the “social behavior” of nanoparticles, i.e., their ability to self-organize towards most complicated and aesthetically very appealing superstructures. If I look on some of those images, the word “emergence” is getting a real meaning even in the otherwise “dead” inorganic world. Some exemplary model cases delineating the properties and applications of nanoparticles are completing the story.

I think, the book is an excellent compendium both for the expert reader (due to the comprehensive, systematic presentation of the data) as well as a reading for students and laymen to get “infected” with the real fascination and potential of the “nanos”. Beside the wish for controlling and accessing the unknown, it is also the beauty of the found and the joy of the discovery which makes science so attractive. The following book is rich in that!

Potsdam,  
February 2009

Prof. Dr. Markus Antonietti
“Oxide Synthesis as Cornerstone of Nanoscience” – This statement was the title of a short Editorial we recently wrote for a special issue of the European Journal of Inorganic Chemistry on Metal Oxide Nanoparticles (Eur. J. Inorg. Chem. 2008, 825). Without any doubts, metal oxide nanoparticles play an outstanding role in many applications that are regarded as particularly promising within the broad area of Nanotechnology, e.g., nanophotonics, spintronics, energy storage and conversion, catalysis, or biomedical applications.

The great variety of structures and properties of metal oxides made this class of materials not only the primary target in solid state chemistry, but also represents a major inspiration for designing new materials on the nanoscale. It is therefore not surprising that a large number of synthesis methodologies have been reported for the size and shape-controlled synthesis of metal oxide nanostructures. One of the most versatile and fast developing approaches are nonaqueous or nonhydrolytic synthesis protocols, i.e., syntheses performed in organic solvents under exclusion of water. The main challenge we faced during writing this book was that we wanted to present both general and basic principles of metal oxide nanoparticle research as well as a rather exhaustive overview of the various metal oxide nanoparticles synthesized in organic solvents so far. We solved the problem in such a way that the main text explains the concepts on selected examples, whereas several tables list the various metal oxides synthesized via nonaqueous processes. We put great efforts in the preparation of these tables, i.e., we included all the literature we were aware of (until the end of 2008), offering a unique information source for chemists, physicists, materials scientists, and engineers to find the appropriate synthesis method for a targeted metal oxide with the desired properties.

The contents of the various chapters in this book were chosen based on a personal prioritization of the most fascinating topics in this research area. After a short and general excursion into the world of nanoparticles in Chapter 1, we discuss the basic principles of nonaqueous sol-gel chemistry in comparison with aqueous systems. Although water-based processes are generally preferred, in the case of metal oxide nanoparticle synthesis the use of or-
Organic solvents represents an advantageous alternative, which is elaborated in more detail in Chapter 2. Chapter 3 and 4 are fully dedicated to the synthesis of metal oxide nanoparticles and metal oxide-based organic-inorganic hybrids, involving surfactant-assisted (Chapter 3) and surfactant-free routes (Chapter 4). Chapter 5 presents the main chemical pathways leading to metal oxides in organic solvents. There is no doubt that in addition to the extensive synthesis work, also the assembly and positioning of nanoparticles in desired locations and across extended length scales as well as the in-depth investigation of the physical and chemical properties are key steps on the way to implement these materials into technological devices. We took these topics into account in Chapter 6, dealing with the assembly, Chapter 7 on the characterization and Chapter 8 on the properties and applications of metal oxide nanoparticles. The last Chapter of the book summarizes the current knowledge and the future challenges in the field of metal oxide nanoparticles prepared in organic solvents.

We are thankful to our current and past group members for their great scientific work and in particular to Guylhaine Clavel for proofreading the manuscript.

Zurich and Aveiro,
February 2009

Prof. Dr. Markus Niederberger
Prof. Dr. Nicola Pinna
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1.1 Fascination and Motivation of Nanoparticle Research

Research on nanoparticles, including synthesis, characterization of the structural, chemical and physical properties, assembly into 1-, 2- and 3-dimensional architectures extending over several lengths scales and with hierarchical construction principles, and application in various fields of technology, represents a fundamental cornerstone of nanoscience and nanotechnology. Many different synthesis techniques gave access to nanomaterials with a wide range of compositions, well-defined and uniform crystallite sizes, extraordinary and unprecedented crystallite shapes, and complex assembly properties. Although gas-phase processes are successfully employed for the low-cost production of large quantities of nanopowders [7, 12, 25], it seems that liquid-phase syntheses are more flexible with regard to the controlled variation of structural, compositional, and morphological features of the final nanomaterials. Liquid-phase routes include coprecipitation, hydrolytic as well as nonhydrolytic sol-gel processes, hydrothermal or solvothermal methods, template synthesis and biomimetic approaches [3]. However, often the synthesis protocol for a targeted material involves not just one, but a combination of several of these methods.

The synthesis of particles with control over size, shape and size distribution is not a special feature of nanoscience, but has been an integral part of colloid chemistry for decades. However, for quite a while, most efforts invested in the preparation of uniform, finely dispersed particles were essentially considered as due to the curiosity of colloid scientists, and, with the exception of polymer colloids (latexes), without any practical significance [14, 15]. With the advent of nanoscience this attitude has changed completely. Nowadays, there is no doubt about the fundamental role of uniform powders in many areas of science and technology. Parallel to the development of highly advanced analytical tools, enabling the characterization of small structures with atomic
resolution, the size of the targeted objects and devices decreased rapidly below the 100 nm limit. The preparation of nanostructures on such a small size scale makes great demands to the synthesis methodology and therefore it is a great challenge to develop a “synthetic chemistry” of nanoparticles that is as precise as that used to make molecules [27]. Two strategies are generally pursued to prepare nanostructures: the “top-down” approach, using physical methods such as photolithography and related techniques, and the “bottom-up” employing physical and chemical approaches. Miniaturization by lithographic techniques is mainly driven by microelectronics industry and has reached a level, at which feature sizes of around 10 nm can be generated [6, 26]. However, upon down-scaling the costs associated with lithography equipment and operating facilities rapidly increase, and the features achievable are on the one hand rather coarse and irregular on an atomic scale, and on the other hand difficult to extend onto non-planar surfaces or to 3D structures. The bottom-up approach, making use of both specific and non-covalent interactions (e.g. hydrogen bonding, electrostatic and van der Waals interactions) between molecules or colloidal particles to assemble discrete nanoscale structures, represents a valuable alternative on the way to further miniaturization of electronic devices and to the fabrication of complex 3D architectures [18, 28]. The use of nanoparticles as building blocks has the advantage that highly advanced synthesis methodologies provide control over crystallite size and shape with a precision well beyond that of top-down lithography. The bottom-up assembly of nanoparticles may prove to be a solution to the technological challenges faced by the semiconductor industry [13]. From a scientific point of view, the use of nanoparticles as “artificial atoms” to form 1-, 2- and 3-dimensional arrays extending over several length scales is particularly fascinating, because these superlattices are expected to have unprecedented and striking collective properties resulting from the interactions between the nanobuilding blocks that cannot be found in the individual constituents, thus opening up an almost indefinite playground to design novel multi-component materials [16, 22, 24, 29].

The availability of reproducible colloidal synthesis protocols for nanoparticles whose compositional, structural, morphological and surface characteristics are well-defined and uniform, is a prerequisite on the way to such complex superstructures. Research on the preparation of inorganic nanoparticles and nanostructures has always been, and still will be, at the heart of nanoscience for the next few years. The significance of nanoparticle synthesis is also reflected in the fact that many groundbreaking findings that can be regarded as milestones in the history of nanoscience are directly related to synthetic work, for example the discovery of carbon nanotubes [10], the synthesis of well-defined quantum dots [17], or the shape control of CdSe nanocrystals [19].

The size- and shape-dependent physical and chemical properties of semiconductor nanoparticles [9, 1, 2] as well as the increased surface-to-volume ratio of nanoscale materials in general raised expectations for a better performance of nanomaterials compared to their bulk counterparts in many ap-
1.2 Metal Oxides: Properties and Applications

Among all the functional materials to be synthesized on the nanoscale, metal oxides are particularly attractive candidates, from a scientific as well as from a technological point of view. The unique characteristics of metal oxides make them the most diverse class of materials, with properties covering almost all aspects of materials science and solid state physics. The great variety of structures and properties made them the primary target in solid state chemistry and still gives inspiration for designing new materials. The crystal structures range from simple rock salt to highly complex incommensurately modulated structures, and the nature of the metal-oxygen bonding varies from nearly ionic to covalent or metallic [20, 21]. Associated with such changes in structure and bonding, oxidic materials exhibit fascinating electronic and magnetic properties. Some oxides like RuO$_2$ or ReO$_3$ are metallic, whereas BaTiO$_3$ for example is an insulator. The magnetic properties found in oxides include ferro-, ferri- or antiferromagnetic behavior. Some oxides possess switchable orientation states as in ferroelectrics (e.g., titanates, niobates, or tantalates). Other fascinating classes of materials within the metal oxide family are the cuprate superconductors, the manganites showing colossal magnetoresistance, or multiferroics combining ferroelectricity and ferromagnetism within the same material (e.g., BiFeO$_3$, BiMnO$_3$). This exceptionally broad spectrum of properties makes (bulk) metal oxides a vital constituent in technological applications like gas sensing, medical science, electronics, ceramics, energy conversion and storage, and surface coatings, just to mention a few (Figure 1.1).
References


2.1 Introduction

The most widely used synthetic technique for bulk metal oxides has been the ceramic method, which is based on the direct reaction of powder mixtures. These reactions are completely controlled by the diffusion of the atomic or ionic species through the reactants and products. To bring the reaction partners sufficiently close together and to provide high mobility, these solid state processes require high temperature and small particle sizes. Although the harsh reaction conditions only lead to thermodynamically stable phases, preventing the formation of metastable solids, these approaches gave access to a large number of new solid compounds, enabling the development of structure-properties relationships. However, in comparison to organic chemistry, where highly sophisticated synthetic pathways are employed to make and break chemical bonds in a controlled way, the ceramic method is a rather crude approach. It is therefore no surprise that for the size- and shape-controlled synthesis of nanoparticles especially liquid-phase routes represent the most promising alternatives. In contrast to solid-state processes, but analogous to organic chemistry, “chimie douce” approaches offer the possibility to control the reaction pathways on a molecular level during the transformation of the precursor species to the final product, enabling the synthesis of nanoparticles with well-defined and uniform crystal morphologies and with superior purity and homogeneity [12]. Among the various soft-chemistry routes, sol-gel procedures were particularly successful in the preparation of bulk metal oxides (e.g., ceramics, glasses, films and fibers) [33, 20], and therefore they have also been applied for nanoparticle synthesis. But in spite of great efforts, the number of oxidic nanoparticles obtained by sol-gel chemistry is still rather small compared to the variety of compounds obtained via powder routes. It turned out that in many cases a synthesis protocol developed for a bulk metal oxide could not directly be adapted to its corresponding counterpart on the nanoscale. The reasons for this observation are manifold. Aqueous sol-gel
chemistry is quite complex, on the one hand due to the high reactivity of the metal oxide precursors towards water and the double role of water as ligand and solvent, and, on the other hand, due to the large number of reaction parameters that have to be strictly controlled (hydrolysis and condensation rate of the metal oxide precursors, pH, temperature, method of mixing, rate of oxidation, the nature and concentration of anions, ...) in order to provide good reproducibility of the synthesis protocol [33]. Another fundamental problem of aqueous sol-gel chemistry is that the as-synthesized precipitates are generally amorphous. The required post-synthetic annealing step to induce the crystallization process prevents any subtle control over crystal size and shape. For the preparation of bulk metal oxides these limitations play only a minor role, however, in the case of nanoparticle synthesis they constitute a major issue.

Nonaqueous (or non-hydrolytic) sol-gel processes in organic solvents, generally under exclusion of water, are able to overcome some of the major limitations of aqueous systems, and thus represent a powerful and versatile alternative [30, 40, 38, 37, 41]. The advantages are a direct consequence of the manifold role of the organic components in the reaction system (e.g., solvent, organic ligand of the precursor molecule, surfactants, or in situ formed organic condensation products). On the one hand they act as oxygen-supplier for the oxide formation and strongly determine the particle size and shape as well as the surface properties due to their coordination properties, and on the other hand the moderate reactivity of the oxygen carbon bond generally results in slower reaction rates. Altogether these parameters lead to the situation, where nonaqueous synthesis routes generally yield metal oxide nanoparticles with uniform, yet complex crystal morphologies, crystallite sizes in the range of just a few nanometers, and good dispersibility in organic solvents. Another important point is the fact that the chemistry of the oxygen-carbon bond is well-known from organic chemistry. This aspect is of utmost significance considering the fundamental role of organic reaction pathways in nonaqueous sol-gel chemistry approaches (cf. Chapter 5). Parallel to the formation of the inorganic nanoparticles, also the initial organic species undergo transformation reactions often following elementary mechanisms of organic chemistry [39]. Based on the identification and quantification of these organic by-products, it is possible to correlate the processes leading to these organic species by retro-synthetical analysis to the growth mechanisms of the oxide nanoparticles. The connection of organic chemistry with the synthesis of inorganic nanomaterials thus represents first, but fundamental steps towards a future rational synthesis design for inorganic nanoparticles.

We have to point out that many examples discussed in this book do not strictly follow the definition of sol-gel chemistry, i.e., the transformation of the molecular precursor does not exclusively proceed along the formation of a sol and then a gel. However, we denote any process as “sol-gel”, as long as the transformation of the molecular precursor into the final oxidic compound involves chemical condensation reactions in liquid-phase under mild condi-
tions. This definition allows us to draw comparisons between aqueous and nonaqueous sol-gel processes, highlighting the analogy between the mechanistic pathways found in both methods. We will also discuss some examples in this book that are not based on sol-gel chemistry, but on simple thermal decomposition of molecular precursors in liquid media. Furthermore, in the current literature the synthesis of metal oxides in organic solvents is typically denoted as “nonhydrolytic”. However, in some cases these procedures involve the use of hydrated metal oxide precursors and/or water is produced in situ, so that a hydrolytic reaction pathway cannot be excluded. Therefore, we prefer to name these routes as “nonaqueous sol-gel chemistry”.

2.2 Aqueous Sol-Gel Chemistry

The aqueous sol-gel process can shortly be defined as the conversion of a precursor solution into an inorganic solid via inorganic polymerization reactions induced by water. In general, the precursor or starting compound is either an inorganic (no carbon) metal salt (chloride, nitrate, sulfate, ...) or a metal organic compound such as an alkoxide. Metal alkoxides are the most widely used precursors, because they react readily with water and are known for many metals [47, 6]. Some alkoxides, which are widely used in industry, are commercially available at low cost (Si, Ti, Al, Zr), whereas other ones are hardly available, or only at very high costs (Mn, Fe, Co, Ni, Cu, Y, Nb, Ta, ...). In comparison to the preparation of silicates from silicon alkoxides, sol-gel processing of transition metal oxides has much less been studied, mainly due to the high reactivity of transition metal alkoxides.

In general, the sol-gel process consists of the following steps (Figure 2.1) [34]: i) Preparation of a homogeneous solution either by dissolution of metal organic precursors in an organic solvent that is miscible with water, or by dissolution of inorganic salts in water; ii) conversion of the homogeneous solution into a sol by treatment with a suitable reagent (generally water with or without any acid/base); iii) aging; iv) shaping; and v) thermal treatment/sintering. The first step in a sol-gel reaction is the formation of an inorganic polymer by hydrolysis and condensation reactions, i.e., the transformation of the molecular precursor into a highly crosslinked solid. Hydrolysis leads to a sol, a dispersion of colloidal particles in a liquid, and further condensation results in a gel, an interconnected, rigid and porous inorganic network enclosing a continuous liquid phase. This transformation is called the sol-gel transition. There are two possibilities to dry the gels. Upon removal of the pore liquid under hypercritical conditions, the network does not collapse and aerogels are produced. When the gel is dried under ambient conditions, shrinkage of the pores occurs, yielding a xerogel. One of the highly attractive features of the sol-gel process is the possibility to shape the material into any
desired form such as monoliths, films, fibers, and monosized powders, and subsequently to convert it into a ceramic material by heat treatment.

As mentioned before, the sol-gel processes can be classified into two different routes depending on the nature of the precursors: a) the precursor is an aqueous solution of an inorganic salt or b) a metal organic compound [33]. The inorganic route involves the formation of condensed species from aqueous solutions of inorganic salts by adjusting the pH, by increasing the temperature or by changing the oxidation state. But this method has several disadvantages. The aqueous chemistry of transition metal ions can be rather complicated because of the formation of a large number of oligomeric species, depending on the oxidation state, the pH or the concentration. The role of the counter anions, which are able to coordinate the metal ion giving rise to a new molecular precursor with different chemical reactivity towards hydrolysis and condensation, is almost impossible to predict. These ions can influence the morphology, the structure and even the chemical composition of the resulting solid phase. Also the removal of these anions from the final metal oxide product is often a problem. Many of these issues can be avoided by using metal alkoxides as precursors. They are often soluble in organic solvents, providing high homogeneity, and they can easily be converted to the corresponding oxide.

The sol-gel conversion of metal alkoxides involves two main reaction types: hydrolysis and condensation (Scheme 2.1). During hydrolysis, the alkoxide groups (-OR) are replaced via the nucleophilic attack of the oxygen atom of a water molecule under release of alcohol and the formation of a metal hydroxide. Condensation reactions between two hydroxylated metal species
leads to M-O-M bonds under release of water (oxolation), whereas the reaction between a hydroxide and an alkoxide leads to M-O-M bonds under release of an alcohol (alkoxolation).

\[ \text{M-O-M} \quad \xrightarrow{\text{H}_2\text{O}} \quad \text{M-O-M} + \text{ROH} \quad (2.1) \]

\[ \text{M-OH} + \text{HO-M} \quad \xrightarrow{\text{H}_2\text{O}} \quad \text{M-O-M} + \text{H}_2\text{O} \quad (2.2) \]

\[ \text{M-OR} + \text{HO-M} \quad \xrightarrow{\text{ROH}} \quad \text{M-O-M} + \text{ROH} \quad (2.3) \]

Scheme 2.1. Main reactions in the sol-gel process using metal alkoxides. Hydrolysis (Eq. 2.1) and condensation, involving oxolation (Eq. 2.2) and alkoxolation (Eq. 2.3).

Chemical aspects play an important role in studying and controlling the sol-gel process. The chemical reactivity of metal alkoxides towards hydrolysis and condensation depends mainly on the electronegativity of the metal atom, its ability to increase the coordination number, the steric hindrance of the alkoxy group, and on the molecular structure of the metal alkoxides (monomeric or oligomeric). The amount of added water in the hydrolysis step and how the water is added, determines, whether the alkoxides are completely hydrolyzed or not and which oligomeric intermediate species are formed. Additional parameters are the polarity, the dipole moment, and the acidity of the solvent.

The major problem of sol-gel methods based on the hydrolysis and condensation of molecular precursors is the control over the reaction rates. For most transition metal oxide precursors, these reactions are too fast, resulting in loss of morphological and also structural control over the final oxide material. Furthermore, the different reactivities of metal alkoxides make it difficult to control the composition and the homogeneity of complex multinary oxides by the sol-gel process. One possibility to decrease and to adjust the reactivity of the precursors is the use of organic additives like carboxylic acids, β-diketones or functional alcohols, which act as chelating ligands and modify the reactivity of the precursors [33, 21]. An alternative strategy involves the slow release of water by chemical or physical processes, allowing control over the local water concentration and thus, over the hydrolysis of the metal oxide precursors [9]. In spite of all these efforts, the strong sensitivity of aqueous sol-gel processes towards any slight changes in the synthesis conditions and the simultaneous occurrence of hydrolysis and condensation reactions makes it still impossible to fully control the sol-gel processing of metal oxides in aqueous medium.

More information and mechanistic details about the aqueous sol-gel processing of metal oxides can be found in several excellent books and reviews [33, 20, 7, 29].
2.3 Nonaqueous Sol-Gel Chemistry

In nonaqueous sol-gel chemistry, the transformation of the precursor takes place in an organic solvent under exclusion of water. In comparison to aqueous sol-gel chemistry, the list of potential precursors is longer and includes, in addition to inorganic metal salts and metal alkoxides, also metal acetates and metal acetylacetonates. Organometallic compounds are also frequently used, but then the process is rather based on thermal decomposition than sol-gel (remember: organometallic compounds are defined as having a direct metal-carbon bond, whereas metal organic compounds have a metal-hetero atom (usually oxygen) bond between the metal center and the organic ligand).

Nonaqueous sol-gel processes have a long history, although they never became as popular as their aqueous analogs. Early studies on nonaqueous sol-gel processes date back to the middle of the 19th century, when the reaction between various metal chlorides and alcohols were investigated. Ebelmen, for example, found that silicon tetrachloride forms silica gels in ethanol [14]. More than 80 years later, Dearing and Reid presented their work on “Alkyl Orthosilicates”, proposing an aqueous and nonaqueous route to silica gels, assuming that they might show “different absorptive power” [13]. Many other groups continued to work on this topic [42, 17, 16], including peculiar but interesting examples like the conversion of chlorosilanes to oligosiloxanes and of silicon and titanium tetrachloride to the respective oxide by refluxing in dimethylformamide [43], the reaction of silicon tetrachloride with benzaldehyde [49] and organic ethers [45], or the synthesis of silica-sodalite from nonaqueous systems [4]. Nevertheless, these publications were more or less isolated efforts without receiving much attention. However, in the middle of the 1980s, and more intense around the beginning of the 1990s, research on nonhydrolytic preparation routes to metal oxides became popular to a larger scientific community [9, 48, 19]. Two main research directions could be distinguished: One focusing on the preparation of metal oxide gels, the other on metal oxide powders. Several groups worked on the preparation of powders using metal alkoxides and alcohols [15, 23, 25] or inert organic solvents [25, 26, 24]. Especially the glycothermal method involving the reaction of metal alkoxides or acetylacetonates with 1,4-butanediol is a versatile approach to various metal oxides [31] and has recently been reviewed [22]. On the other side, in 1992 Corriu et al. published their work on monolithic silica, alumina, and titania gels, as well as on gels containing two metals [8, 11, 10]. In the same year, the synthesis of zinc oxide gels was presented, using zinc alkoxides as precursors and acetone as condensation agent [18]. Upon aging, the gels formed a precipitate, which contained 4 nm zincite nanocrystals. An analogous approach was later on used for TiO₂, BaO, and BaTiO₃ [3]. Following these examples, a large variety of metal oxide gels were synthesized and reported, including silica, alumina, titania, mixed Al/Si and transition metal oxides from the corresponding metal chlorides and metal alkoxides or ethers as oxygen donors [1, 2], metal ferrites from the metal nitrates and ethylene glycol.