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Metal Oxide Nanoparticles in Organic Solvents

Synthesis, Formation, Assembly
and Application

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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 save 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

Preface

“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-

ganic 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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