

# 1 Introduction

## *1.1 Chemistry of Advanced Materials*

Stone, bronze, iron: civilization has always been defined by Man's relationship with materials [1]. Nowadays, materials have become such an integral part of our society, that they are often either underappreciated or even overlooked. But much of the technological progress is directly or indirectly dependent on the availability of advanced materials with improved functions. It is often forgotten, that there is much chemistry behind these investigations!

The definition of materials as "substances having properties which make them useful in machinery, structures, devices and products" clearly connects materials with function [1]. In general, solid materials are classified in five categories, based on both their chemical composition and their physical properties: metals, ceramics, polymers, semiconductors, and composites [2]. Composites consist of a combination of metals, ceramics, or polymers. They are designed to display new, unusual properties that are not found in any single material.

Being closely related to materials science, chemistry focuses on the atomic or molecular level, and materials science deals with macroscopic properties, however both together provide a proper understanding of how chemical composition, structure, and bonding of materials are related to the particular properties [3].

In the earlier days of civilization, especially in the production of metals, chemistry was only used empirically for the processing of materials, far from any understanding of the basic concepts. But many arising problems like pollution of the environment or the toxicity of different materials nowadays clearly reveal the need of a better understanding of the basic chemistry. It is becoming widely recognized that no new method for extracting or processing a material can be considered without good understanding of the real costs as well as its fate after its lifetime. A number of important aspects have to be investigated for example whether the required properties

can be achieved and maintained during the use of a material, whether the material is compatible with other parts of an assembly, whether a material can be easily recycled, whether a material causes environmental problems, and whether a material can be produced economically. Taking the fact into account that most of the processes during the life-cycle of a product are typically chemical reactions, it becomes obvious, that the solution of fundamental materials science problems is intimately interconnected with our knowledge in chemistry. Only a better understanding of the chemical concepts involved in materials life-cycle leads to substantial improvements in materials technologies. The understanding of the nano structure of materials will be an essential part of such an enterprise. But the complexity and interdisciplinary nature of material science and engineering requires effective cooperation between scientists and engineers from various disciplines.

This need for interdisciplinary co-operation was also considered at the ETH Zürich, when the TEMA (Templated Materials) project was established. This research project is focused on the development of materials that are synthesized or organized by the help of templates. It is a collaboration of groups from five different institutes [4,5]. In the group of Prof. Dr. A. Baiker, Catalysis and Chemical Reaction Engineering, the objectives of the project are the incorporation of organic templates, organometallic complexes and receptor templates for molecular recognition into inorganic host materials, in particular organically modified titania-silica aerogels as epoxidation catalysts and mesoporous ruthenium silica hybrid aerogels. In the laboratories of Nonmetallic Inorganic Materials of Prof. Dr. L. J. Gauckler, creation of ceramic structures in the micrometer range on surfaces and the fabrication of miniaturized functional devices is investigated. Also polymer scientists are involved in the TEMA project. The groups of Prof. Dr. U. W. Suter and Dr. W. R. Caseri deal with nanosized metal particles and the preparation of oriented structures or networks in polymers. Novel nanomaterials based on platinum  $\sigma$ -acetylide complexes of tetraethynylethenes, monodisperse poly(triacetylene) oligomers, and the incorporation of synthetic organic molecules, especially porphyrins with various central metal atoms, into aerogel materials during the formation process of the ceramic are objectives of Prof. Dr. Diederich's group in the Organic Chemistry Institute. In the Inorganic Solid State Chemistry group of Prof. Dr. R. Nesper, the template-directed

synthesis of structured transition metal oxides via sol-gel techniques is investigated, especially focused on the synthesis and microstructuring of vanadium oxide nanotubes. This work is part of the general TEMA project and of the latter specific enterprise.

## **1.2 Solid State Chemistry and Nanochemistry**

In general, research in solid state chemistry is concerned with investigations of syntheses, structures and properties of solids. The most important motivation is to understand, to predict, and to design the properties of solids with respect to both, chemical composition and their crystal and electronic structures. Of course, the first step is the synthesis of the required material. Three different categories of solid state synthesis can be distinguished depending on the motivation [6]:

- i) preparation of known compounds to investigate a specific property
- ii) synthesis of unknown members in a structurally related family in order to extend structure-property relations
- iii) synthesis of new classes of solids

Thus, solid state chemistry is mainly concerned with the development of new synthesis methods, new ways of identifying and characterizing materials and of describing their structure. In the last few years, the key direction of solid state chemistry lay in the search for new strategies of tailor-making materials with desired and controllable properties [7]. Although there have been major advances in the synthesis of solid materials due to many new chemical methods, we are still far away from a tailor-making of solid materials with specified structures/properties. Most of the discoveries of new solids still have been made by chance! Therefore, rational design and synthesis of novel materials have remained important objectives. The control over the composition is often possible, but still then there must be a way of producing materials in any required micro- and nanoscopic shape or form. At the same time, the characterization of materials

is a critical ingredient to progress, because it provides guidance for further research efforts [8].

In the last few years, solid state chemists started to exploit a combination of covalent and non-covalent interactions, i. e. they started to connect molecular chemistry, the chemistry of the covalent bond, with supramolecular chemistry, based on non-covalent, intermolecular forces (electrostatic interactions, hydrogen bonding, van-der-Waals forces). Molecular chemistry is concerned with uncovering and mastering the rules that govern the structures, properties, and transformations of molecular species, whereas the supramolecular chemistry is covering the structures and functions of organized entities of higher complexity formed by association of two or more chemical species held together by intermolecular forces [9]. These polymolecular assemblies may lead to supramolecular devices, defined as structurally organized and functionally integrated chemical systems built on supramolecular architectures [10].

From molecular to supramolecular chemistry, nanochemistry is the pursuit of this development of bottom-up synthesis of complex objects. The nanochemist's future goal is to built and organize nanoscale objects under mild and controlled conditions finally of one cluster of atoms or even one atom at a time instead of manipulating the bulk, thus, providing a reproducible method of preparing materials that are perfect in size and shape [11]. Nowadays, one would call this directed self-assembly. At present, nanochemistry is concerned with the development of novel methods for the synthesis and characterization of chemical systems within the size range of about 1 to 100 nm. The interest in nanoscale objects is due to the exhibition of novel electronic, optical, magnetic, transport, photochemical, electrochemical, catalytic and mechanical behavior, *depending on composition, size, and shape of the particles*. The physical properties of nanoparticles neither correspond to those of the free atoms or molecules making up the particle nor to those of the bulk solids with identical chemical composition [12]. It is astonishing, that many relevant phenomena at nanoscale are caused by the tiny size of the organized structure and by interactions at their predominant and complex interfaces [13]. *When the chemists are able to gain control over size and shape of the particles, further enhancement of material properties and device functions will surely be possible*. Each change in both, composition *or* size can lead to different physical and chemical properties, providing a large number of new materials. Interestingly, it is true

that the products of nanochemistry exhibit new and useful properties, but at the same time it is not necessarily a need for new starting materials: new applications and properties are rather a result of tailoring matter and subsequently arranging the components by means of chemical interactions, so, ideally, new properties can arise from a combination of inexpensive and environmentally harmless components [14].

At present the field of nanochemistry includes (i) nanoparticles, (ii) nanocrystalline materials, and (iii) nanodevices [15]. The most important aspect is still the development of new strategies for the synthesis of nanomaterials, particularly soft chemical routes. But the chemist not only has to be able to synthesize perfect, i.e., monodispersed and shape-defined objects having nanometer dimensions, but he also may have to position these objects in appropriately organized arrays. This may be tackled either by using lithographic techniques [16] or templating methods (molecular and supramolecular assembly processes [14,17], or deposition inside the void spaces of nanoporous host materials [18]). However, the templating methods may become the most favorable in the far run towards directed self-assembly.

All this reflects the desire of the chemists to deliberately control, to design, the synthesis of a particular solid-state structure [19].

### ***1.3 Nanomaterials, Nanodevices and Applications of Nanomaterials***

Nanomaterials are single-phase or multiphase polycrystals with a typical crystal size of 1 to 100 nm in at least one dimension. Depending on the dimensions they can be classified into (a) nanoparticles, (b) layered or lamellar structures, (c) filamentary structures, and (d) bulk nanostructured materials [15].

The properties of nanomaterials mainly depend on four features, namely (a) grain size and size distribution, (b) chemical composition, (c) presence of interfaces (grain boundaries, free surface), and (d) interactions between the constituent domains [20].

Due to the large surface/interface to volume ratio in nanophase materials, a wide variety of size-related effects can be introduced by controlling the size of the particles [21]:

- The density of dislocation, interface to volume ratio and the grain size strongly influence the mechanical properties.
- Quantum confinement, i. e., quantization of the energy levels of the electrons due to confined grain size, has applications in semiconductors, optoelectronics, and non-linear optics. Nanoclusters, so-called quantum dots for example can be developed to emit and absorb a specific wavelength of light by changing the particle diameters.
- The large amount of surface atoms increases the activity for catalytical applications.
- The magnetic properties of nano-sized particles depend on the large surface to volume ratio. Unlike bulk materials consisting usually of multiple magnetic domains, several small ferromagnetic particles can form only a single magnetic domain, giving rise to superparamagnetism. This behavior opens the possibility for applications in information storage.

Nanodevices may be defined as structurally organized and functionally integrated chemical systems in the dimension of nanometers. The components may be photo-, electro-, iono-, magneto-, thermo-, mechano-, or chemoactive, depending on whether they handle photons, electrons, or ions, respond to magnetic fields or to heat, undergo changes in mechanical properties, or perform a chemical reaction [9,10].

Areas of application that can be foreseen to benefit from the small size and organization of nanoscale objects include quantum electronics, nonlinear optics, photonics, chemoselective sensing, and information storage and processing [11], adsorbents, catalysis, solar cells [1], magnetic recording devices, superplastic ceramics, superhard metals, metastable alloys [12]...

### 1.4 Literature

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