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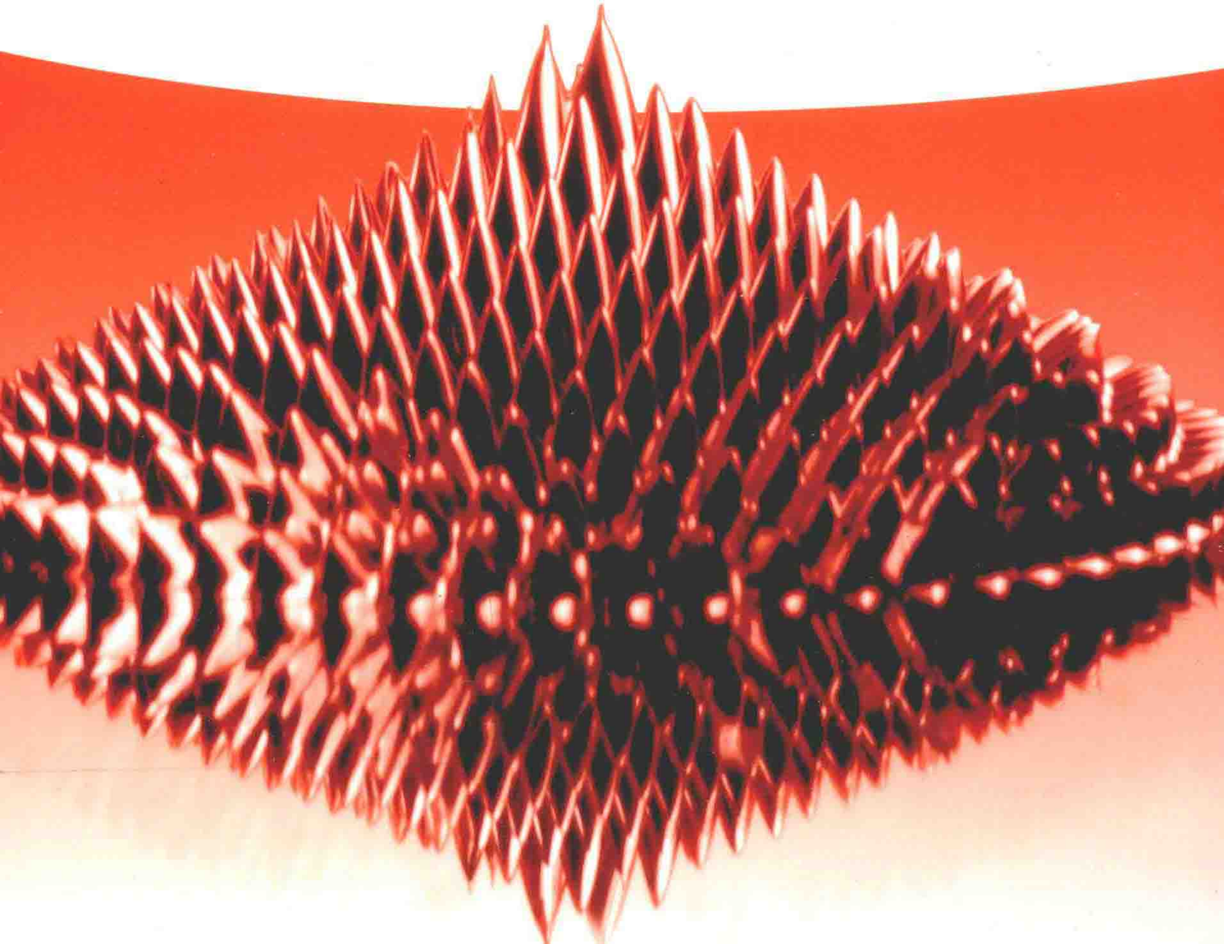
Nanomaterials

An Introduction to Synthesis, Properties, and Applications

Second Edition



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Preface

This book is an introduction to nanomaterials; one may consider it as an approach to a textbook. It is based on the course on Nanomaterials for Engineers that I give at the University of Technology in Graz, Austria, and on the courses that NanoConsulting organizes for participants from industry and academia. I want to provoke your curiosity. The reader should feel invited to learn more about nanomaterials, to use nanomaterials, and to want to go beyond the content of this book. However, even when it is thought of as an introduction, reading this book requires some basic knowledge of physics and chemistry. I have tried to describe the mechanisms determining the properties of nanoparticles in a simplified way. Therefore, specialists in the different fields may feel uncomfortable with the outcome, but I saw no other way to describe the mechanisms leading to the fascinating properties of nanoparticles for a broader audience.

I am fully aware of the fact that the selection of examples from the literature is, to some extent, biased against those who discovered these new phenomena. However, in most cases, where a new phenomenon was described for the first time, the effect is just shown in principle. Later papers only had a chance when they showed these phenomena very clearly. Therefore, from the viewpoint of a textbook, the later papers are preferred. I really apologize this selection of literature.

Many exciting phenomena and processes are connected with nanoparticles. However, the size of this book is limited and, therefore, I had to make a selection of the topics presented. Unavoidably, such a selection was inevitably influenced by personal experience and preferences. Again, I apologize if the reader does not find information on a field that is important for their company or institution.

I hope the reader will find this book inspiring, and will be motivated to go deeper into this fascinating field of science and technology.

This is now the second edition and I am so thankful for all the kind reviews of the previous edition in different journals. I have now reshuffled the chapters according to my current views. Some topics have been removed, because scientific or technological developments did not go as expected, and a few new and exciting topics have been added.

I want to thank my family, especially my wife Renate, for her steady support during the time when I wrote this book and her enduring understanding of my passion for science. Furthermore, I thank Dr. Waltraud Wüst from WILEY-VCH for her steady cooperation. Without her efforts, things would have been much more difficult for me.

Stutensee, June 2013 *Dieter Vollath*

Contents

1
Nanomaterials: An Introduction

Today, everybody is talking about nanomaterials, even advertisements for consumer products use the prefix "nano" as a keyword for special features, and, indeed, very many publications, books, and journals are devoted to this topic. Usually, such publications are directed towards specialists such as physicists and chemists, and the "classic" materials scientist encounters increasing problems in understanding the situation. Moreover, those people who are interested in the subject but who have no specific education in any of these fields have virtually no chance of understanding the development of this technology. It is the aim of this book to fill this gap. The book will focus on the special phenomena related to nanomaterials and attempt to provide explanations that avoid – as far as possible – any highly theoretical and quantum mechanical descriptions. The difficulties with nanomaterials arise from the fact that, in contrast to conventional materials, a profound knowledge of materials science is not sufficient. The cartoon shown in Figure 1.1 shows that nanomaterials lie at the intersection of materials science, physics, chemistry, and – for many of the most interesting applications – also of biology and medicine.

However, this situation is less complicated than it first appears to the observer, as the number of additional facts introduced to materials science is not that large. Nonetheless, the user of nanomaterials must accept that their properties demand a deeper insight into their physics and chemistry. Whereas for conventional materials the interface to biotechnology and medicine is related directly to the application, the situation is different in nanotechnology, where biological molecules such as proteins or DNA are also used as building blocks for applications outside of biology and medicine.

So, the first question to be asked is: "What are nanomaterials?" There are two definitions. The first – and broadest – definition states that nanomaterials are materials where the sizes of the individual building blocks are less than 100 nm, at least in one dimension. This definition is well suited for many research proposals, where nanomaterials often have a high priority. The second definition is much more restrictive and states that nanomaterials have properties that depend inherently on the small grain size; as nanomaterials are usually quite expensive, such a restrictive definition makes more sense. The main difference between nanotechnology and conventional technologies is that the "bottom-up" approach (see below) is preferred in nanotechnology, whereas conventional technologies usually use the "top-down"

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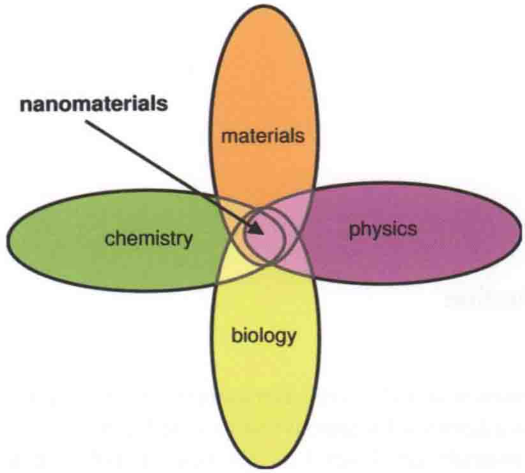

Figure 1.1 A basic understanding of physics and chemistry, and some knowledge of materials science, is necessary to understand the properties and behavior of nanomaterials. As many applications are connected with biology and medicine, some knowledge of these areas is also required.

approach. The difference between these two approaches can be explained simply by using an example of powder production, where chemical synthesis represents the bottom-up approach while crushing and milling of chunks represents the equivalent top-down process.

On examining these technologies more closely, the expression "top-down" means starting from large pieces of material and producing the intended structure by mechanical or chemical methods. This situation is shown schematically in Figure 1.2. As long as the structures are within a range of sizes that are accessible by either mechanical tools or photolithographic processes, then top-down processes have an unmatched flexibility in their application.

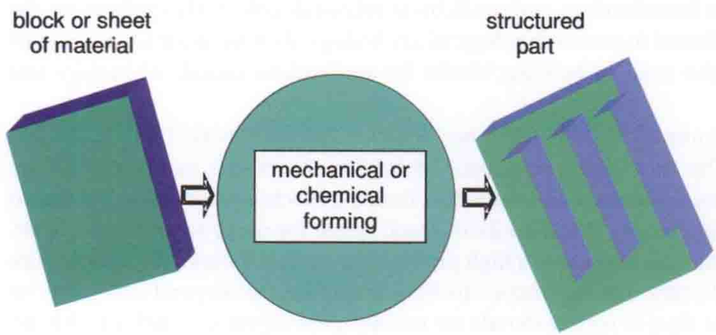

Figure 1.2 Conventional goods are produced via top-down processes, starting from bulk materials. The intended product is obtained by the application of mechanical and/or chemical processes.

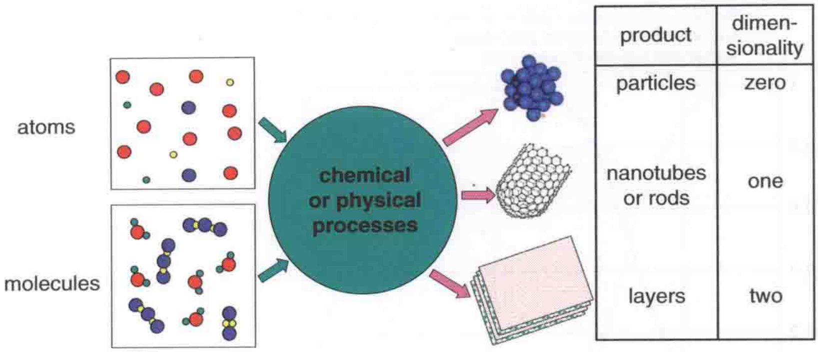

Figure 1.3 Nanotechnologies are usually connected to bottom-up processes and are characterized by the use of atoms or molecules as building blocks. Bottom-up processes result in particles, nanotubes, nanorods, thin films, or layered structures. These products are also characterized by their dimensionality, as is also indicated.

The situation is different in "bottom-up" processes, in which atoms or molecules are used as the building blocks to produce nanoparticles, nanotubes, or nanorods, or thin films or layered structures. According to their dimensionality, these features are also referred to as zero-, one-, or two-dimensional nanostructures (see Figure 1.3). Figure 1.3 also demonstrates the building of particles, layers, nanotubes, or nanorods from atoms (ions) or molecules. Although such processes provide tremendous freedom among the resultant products, the number of possible structures to be obtained is comparatively small. In order to obtain ordered structures, bottom-up processes (as described above) must be supplemented by the self-organization of individual particles.

Often, top-down technologies are described as being "subtractive," in contrast to the "additive" technologies that describe bottom-up processes. The crucial problem is no longer to produce these elements of nanotechnology; rather, it is their incorporation into technical parts. The size ranges of classical top-down technologies compared to bottom-up technologies are shown graphically in Figure 1.4. Clearly, there is a broad range of overlap where improved top-down technologies, such as electron beam or X-ray lithography, enter the size range typical of nanotechnologies. Currently, these improved top-down technologies are penetrating into increasing numbers of fields of application.

For industrial applications, the most important question is the product's price in relation to its properties. In most cases, nanomaterials and products utilizing nanomaterials are significantly more expensive than conventional products. In the case of nanomaterials, the increase in price is sometimes more pronounced than the improvement in properties and therefore economically interesting applications of nanomaterials are often found only in areas where specific properties are demanded that are beyond the reach of conventional materials. Hence, as long as the use of nanomaterials with new properties provides the solution to a problem that cannot be solved with conventional materials, the price becomes much less important. Another point is that as the applications of nanomaterials using

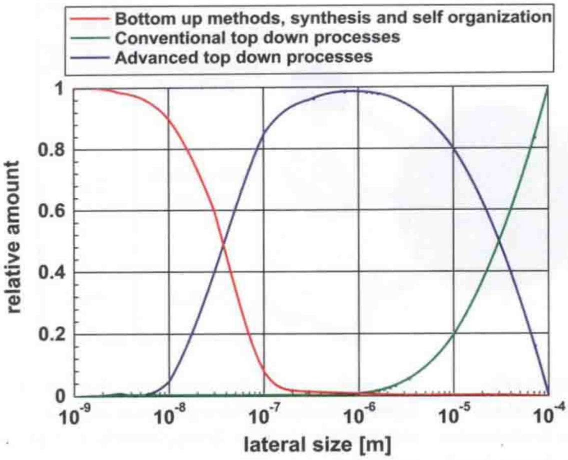

Figure 1.4 Estimated lateral limits of different structuring processes. Clearly, the size range of bottom-up and conventional top-down processes is limited. New, advanced top-down processes expand the size range of their conventional counterparts and enter the size range typical of bottom-up processes.

improved properties are in direct competition to well-established conventional technologies, they will encounter fierce price competition, and this may lead to major problems for a young and expensive technology to overcome. Indeed, it is often observed that marginal profit margins in the production or application of nanomaterials with improved properties may result in severe financial difficulties for newly founded companies. In general, the economically most successful application of nanomaterials requires only a small amount of material as compared to conventional technologies; hence, one is selling "knowledge" rather than "tons" (see Table 1.1). Finally, only those materials that exhibit new properties leading to novel applications, beyond the reach of conventional materials, promise interesting economic results.

Table 1.1 Relationship between the properties of a new product and prices, quantities, and expected profit (note that only those products with new properties promise potentially high profits).

Properties	Price		Quantity		Profits
	Low	High	Small	Large	
Improved	×	—	—	×	Questionable
New	—	×	×	—	Potentially high

2
Nanomaterials and Nanocomposites

2.1
Introduction

Nanomaterials may be zero-dimensional (e.g., nanoparticles), one-dimensional (e.g., nanorods or nanotubes), or two-dimensional (usually realized as thin films or stacks of thin films). As a typical example, an electron micrograph of zirconia powder (a zero-dimensional object) is shown in Figure 2.1.

The particles depicted in Figure 2.1 show a size of about 7 nm, characterized by a very narrow distribution of sizes. This is an important point, as many of the properties of nanomaterials are size-dependent. In contrast, many applications do not require such sophistication and therefore cheaper materials with a broader particle size distribution (see Figure 2.2a) would be sufficient. The material depicted in Figure 2.2a, which contains particles ranging in size from 5 to more than 50 nm, would be perfectly suited for applications such as pigments or ultraviolet (UV) absorbers.

A further interesting class of particles may be described as fractal clusters of extreme small particles. Typical examples of this type of material are most of the amorphous silica particles (known as "white soot") and amorphous Fe_2O_3 particles, the latter being used as catalysts (see Figure 2.2b).

Apart from properties related to grain boundaries, the special properties of nanomaterials are those of single isolated particles that are altered, or even lost, in the case of particle interaction. Therefore, most of the basic considerations are related to isolated nanoparticles as the interaction of two or more particles may cause significant changes in the properties. For technical applications, this proved to be negative and, consequently, nanocomposites of the core/shell type with a second phase acting as a distance holder were developed. The necessary distance depends on the phenomenon to be suppressed; it may be smaller in the case of the tunneling of electrons between particles, but larger in the case of dipole–dipole interaction. In this context, most important are bifunctional particles exhibiting a ferromagnetic core and a luminescent coating, as they are used medical applications [2]. Nanocomposites – as described in this chapter – are composite materials with at least one phase exhibiting the special properties of a nanomaterial. In general, random arrangements of nanoparticles in the composite are assumed.

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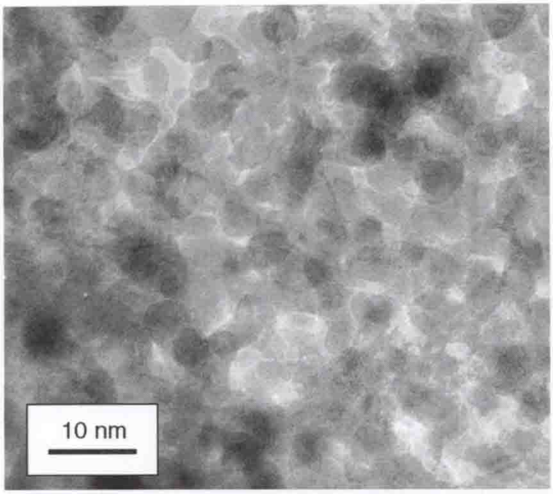

Figure 2.1 Electron micrograph of zirconia (ZrO_2) powder. This material has a very narrow grain size distribution; this may be important as the properties of nanomaterials depend on grain size [1].

The three most important types of nanocomposites are illustrated schematically in Figure 2.3. The types differ in the dimensionality of the second phase, which may be zero-dimensional (i.e., isolated nanoparticles), one-dimensional (i.e., consisting of nanotubes or nanorods), or two-dimensional (i.e., existing as stacks or layers). Composites with platelets as the second phase may be thought as two-dimensional.

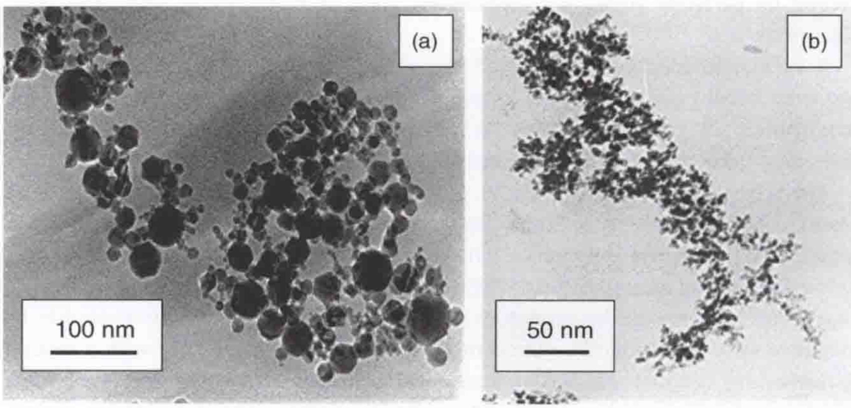

Figure 2.2 Two types of nanoparticulate Fe_2O_3 powder. (a) Industrially produced nanomaterial with a broad particle size distribution; this is typically used as a pigment or for UV protection. (Reprinted with permission of Nanophase Technologies, Romeoville, IL, USA; www.nanophase.com.) (b) Nanoparticulate powder consisting of fractal clusters of amorphous (about 3 nm) particles. (Reproduced by permission of MACH I Inc., King of Prussia, PA, USA; www.machichemicals.com.) As this material has an extremely high surface area, catalysis is its most important field of application.

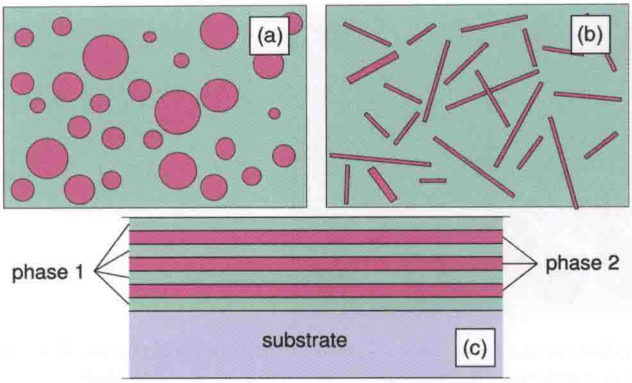

Figure 2.3 Three basic types of nanocomposite. (a) Composite consisting of zero-dimensional particles in a matrix; ideally, the individual particles do not touch each other. (b) One-dimensional nanocomposite consisting of nanotubes or nanorods distributed in a second matrix. (c) Two-dimensional nanocomposite built from stacks of thin films made of two or more different materials.

However, in most cases, such composites are close to a zero-dimensional state; some of those with a polymer matrix possess exciting mechanical and thermal properties, and are used to a wide extent in the automotive industry.

In general, nanosized platelets are energetically not favorable and therefore not often observed. However, a thermodynamically stable variety of this type of nanocomposite using polymer matrices is realized using delaminated layered silicates (these nanocomposites are discussed in connection with their mechanical properties in Chapter 11). In addition to the composites shown in Figure 2.3, nanocomposites with regular well-ordered structures may also be observed (see Figure 2.4). In general, this type of composite is created via a self-organization processes. The successful realization of such processes require particles that are almost identical in size.

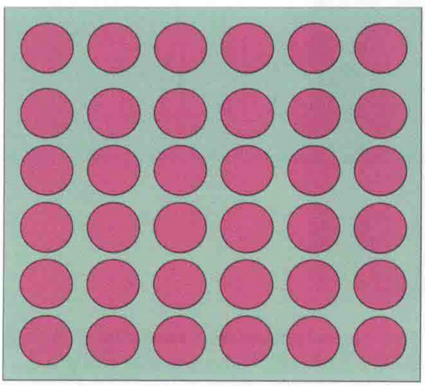

Figure 2.4 Perfectly ordered zero-dimensional nanocomposite; this type of composite is generally made via a self-organization processes.