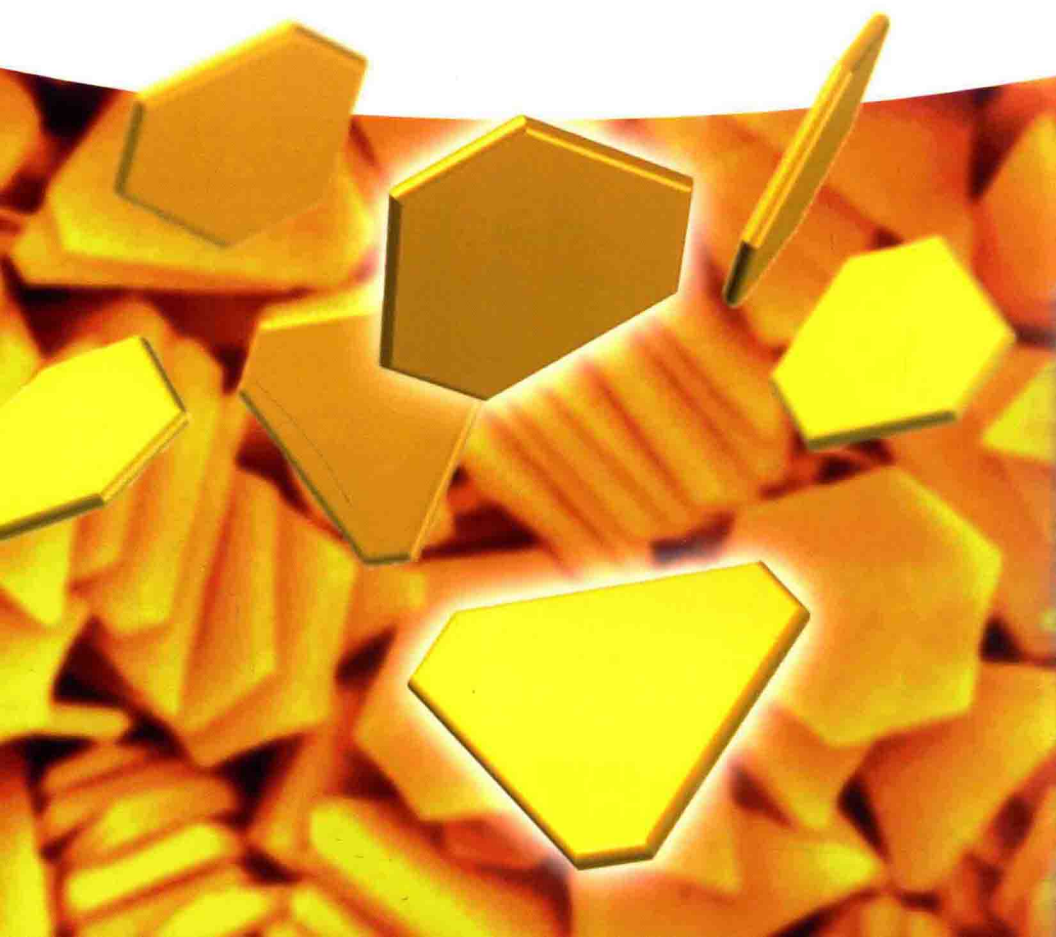


Dieter Vollath

# Nanoparticles – Nanocomposites – Nanomaterials

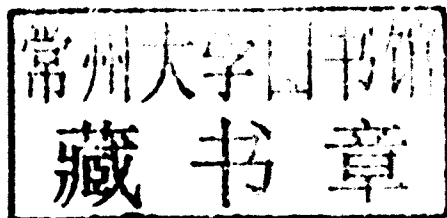
An Introduction for Beginners



*Dieter Vollath*

# **Nanoparticles – Nanocomposites – Nanomaterials**

An Introduction for Beginners



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## Preface

This book is really two books. It gives an introduction to the topics connected to nanoparticles, nanocomposites, and nanomaterials on a descriptive level. Whenever it seems appropriate, some topics are explained in more detail in separate boxes. It is not necessary to read these boxes; however, it may be interesting and helpful to the reader.

This textbook is intended for persons wanting an introduction into the new and exciting field of nanomaterials without having a formal education in science. It discusses the whole range from nanoparticles to nanocomposites and finally nanomaterials, explaining the scientific background and some of the most important applications. I want to provoke the reader's curiosity; he/she should feel invited to learn more about this topic, to apply nanomaterials and, may be, to go deeper into this fascinating topic.

This book is an excerpt from 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. This book is not written for scientists, so may be some physicists will feel unhappy about the simplifications that I made to explain complicated quantum mechanical issues.

I want to apologize for the selection of examples from the literature, as my selection of examples is, to some extent, unfair against those who discovered these new phenomena. Unfortunately, when a new phenomenon was described for the first time, the effect is only shown in principle. Later papers instead showed these phenomena very clearly. Therefore, the examples from later publications seemed more adequate for a textbook like this.

As the size of this book is limited, I had to make a selection of phenomena for presentation. Unavoidably, this selection is influenced by personal experience and preferences. I really apologize if a reader does not find information of interest for themselves or their company.

It is an obligation for me to thank my family, in particular my wife Renate, for her steady support during the time when I wrote this book and her enduring understanding for my passion for science. Furthermore, I have to thank Dr. Waltraud Wüst from Wiley-VCH for her steady cooperation.

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## 1

**Introduction**

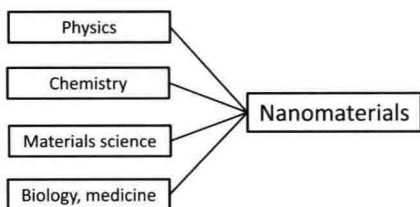
Everyone talks about nanomaterials. There are many publications, books and journals devoted to this topic. This is not surprising, as the economic importance is steadily increasing. Additionally, interested persons without specific education in one of these fields, have, at the moment, nearly no chance to understand this technology, its background and applications. This book fills this gap. It deals with the special phenomena found with nanomaterials and tries to give explanations, avoiding descriptions that are directed to specialists and need specialized education.

To get an idea about the actual size relations, think about a tennis ball, having a diameter of a little more than  $6\text{ cm} = 6 \times 10^{-2}\text{ m}$  and compare it with a particle with diameter of  $6\text{ nm} = 6 \times 10^{-9}\text{ m}$ . The ratio of the diameters of these two objects is  $10^7$ . An object  $10^7$  times larger than a tennis ball has a diameter of 600 km. This simple comparison makes clear: nanoparticles are really small.

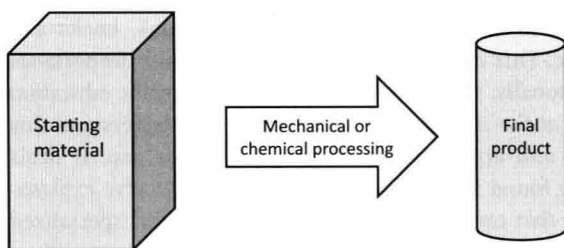
The difficulty with nanomaterials arises from the fact that—in contrast to conventional materials—knowledge of material science is not sufficient; rather some knowledge of physics, chemistry, and materials science is necessary. Additionally, as many applications are in the fields of biology and medicine, some knowledge in these fields is necessary to understand these important applications. Figure 1.1 demonstrates that science and technology of nanomaterials are influenced by materials science, physics, chemistry, and for many, economically most important applications, also of biology and medicine.

The number of additional facts introduced to materials science is not that large, therefore, this new situation is not that complicated, as it may look to the observer from the outside. However, the industrial user of nanomaterials, as a developer of new products, has to accept that the new properties of nanomaterials demand deeper insight to the physics and chemistry of the materials. Furthermore, in conventional materials, the interface to biotechnology and medicine depends on the application. This is different in nanotechnology, as biological molecules, such as proteins or DNAs are building blocks, quite often also for applications outside of biology and medicine.

The first question to be answered is: What are nanomaterials? There are two definitions. One, the broadest, says: nanomaterials are materials with sizes of the individual building blocks below 100 nm at least in one dimension. This definition



**Figure 1.1** To understand and apply nanomaterials, besides knowledge on materials science, a basic understanding of physics and chemistry is necessary. As many applications are connected to biology and medicine; knowledge in these fields are also of advantage.



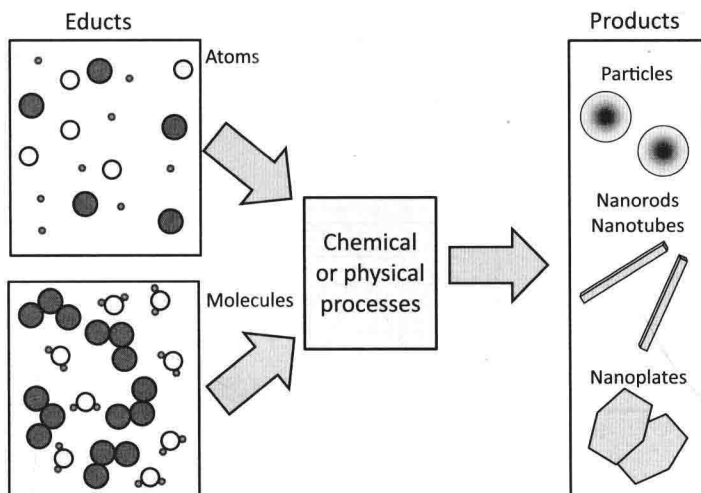
**Figure 1.2** Conventional goods are produced by top-down processes, which start from bulk material. Using mechanical or chemical processes, the intended product is obtained.

is quite comfortable, as it does not require deeper thoughts about properties and applications. The second definition is more restrictive. It says that nanomaterials are ones with properties inherently depending on the small grain size. As nanomaterials usually are quite expensive, such a restrictive definition makes more sense.

The main difference between nanotechnology and conventional technologies is the “bottom-up” approach preferred in nanotechnology, whereas conventional technologies usually prefer the “top-down” approach. The difference between these two approaches is explained for example, using the example of powder production. In this context, chemical synthesis is typical of the “bottom-up” approach; whereas, crushing and milling are techniques that may be classified as “top-down” processes. Certainly, there are processes, which may be seen as “in between”. A typical example is the defoliation of silicates or graphite to obtain graphene.

The expression “top-down” describes processes starting from large pieces of material to produce the intended structure by mechanical or chemical methods. As long as the structures are in a range of sizes accessible by mechanical tools or photolithographic processes, top-down processes have an unmatched flexibility in application. Figure 1.2 summarizes the basic features of top-down processes.

“Bottom-up” processes are, in general chemical processes starting from atoms or molecules as building blocks to produce nanoparticles, nanotubes or nanorods, thin films or layered structured. Using their dimensionality for classification, these

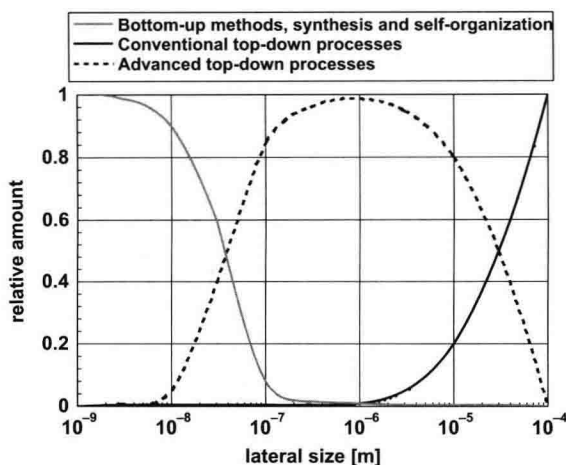


**Figure 1.3** Chemical synthesis as bottom-up process. Bottom-up processes are characterized by the use of atoms or molecules as educts. Products are particles, nanotubes or nanorods, or layered structures.

features are also called zero-, one-, or two-dimensional nanostructures. This is graphically demonstrated in Figure 1.3. Bottom-up processes give tremendous freedom in the composition of the resulting products; however, the number of possible structures to be obtained is comparatively small. Ordered structures are obtained by processes that are supplemented by self-organization of individual particles. Often, top-down technologies are described as subtractive ones, in contrast to additive technologies describing bottom-up processes.

Figure 1.4 shows the size ranges of the different processes applied in nanotechnology. Certainly, there is a broad range of overlapping, between the top-down and bottom-up technologies. Most interesting, there are improved top-down technologies, such as electron beam or X-ray lithography entering the size range typical for nanotechnologies. These improved top-down technologies obtain increasing importance, for example, in highly integrated electronic devices.

For industrial applications, the most important question is the price of the product in relation to the properties. As far as the properties are comparable, in most cases, nanomaterials and products applying nanomaterials are significantly more expensive than conventional products. This becomes problematic in cases where the increase in price is more pronounced than the improvement of the properties due to the application of nanomaterials. Therefore, economically interesting applications of nanomaterials are found primarily in areas where properties that are out of reach for conventional materials are demanded. Provided this condition is fulfilled, the price is no longer that important. However, in cases where nanomaterials are in direct competition to well-established conventional technologies, the price is decisive. This fierce price competition is extremely difficult for a young and expensive technology and may lead sometimes to severe, financial



**Figure 1.4** Estimated lateral limits of different structuring processes. The size range of bottom-up and conventional top-down processes is limited. New,

advanced top-down processes expand the size range of conventional ones and enter the size range typical for bottom-up processes.

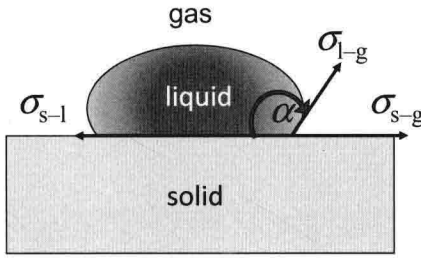
problems for newly founded companies. As a general rule one may say that in the case of nanomaterials one is rather selling “knowledge” than “tons”.

Nanoparticles are neither new nor unnatural. In nature, for example, some birds and mammals apply magnetic nanoparticles for navigation, a sense called magnetoreception. In plants the phenomenon of self-cleaning of leaves caused by nanoparticles at the surface, called the *Lotus* effect is well known and meanwhile technically exploited for self cleaning windows or porcelain ware for sanitary use (see Box 1.1). Man-made nanomaterials, in this case nanocomposites, have been known for more than 2500 years. The Sumerians already produced a red pigment to decorate their pottery. This pigment consisted of gold nanoparticles embedded in a glass matrix stabilized with tin oxide. In science, especially chemistry, suspensions of nanoparticles have been well known since the nineteenth century; however, at that time, this science was called colloid chemistry.

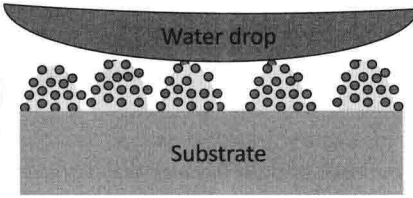
### Box 1.1 The Lotus Effect

As an example of a macroscopically observable phenomenon caused by nanostructures, the *Lotus* effect will be explained. It is well known that the leaves of the *Lotus* plant are always clean. This is caused by the fact that the *lotus* leaf can not be moistened, it is hydrophobic, each drop of water flows immediately off the leaf, picking up any dust, which is, in general, hydrophilic.

The *Lotus* effect is caused by an apparent increase of the contact angle between water and a solid surface. The undisturbed situation is depicted in Figure 1.5.



**Figure 1.5** Equilibrium of surface stresses at a contact between a solid and a liquid.



**Figure 1.6** Contact situation in the case of the *Lotus* effect. Due to the corrugated surface, one has the impression of a huge contact angle  $\alpha$ . However, looking at the

points of contact of the individual particles, it is obvious that there is nothing special there, one finds the standard values.

The contact angle, in the case of a water/solid interface, at a maximum of  $110^\circ$  is a result of the equilibrium of the surface stresses.

$$\sigma_{s-g} - \sigma_{s-l} = \sigma_{l-g} \cos \alpha. \quad (1.1)$$

The quantities in Eq. (1.1),  $\sigma_{s-g}$  describe the surface stresses at the interface between the solid and the gas phase,  $\sigma_{s-l}$  the surface stress between the solid and the liquid phase,  $\sigma_{l-g}$  the one between liquid and the gas phase, and  $\alpha$  is the contact angle. (To be mathematically exact, the surface stress is described by a vector in the tangential plane of the particle. However, for these simplified considerations, it is correct to work with the absolute values of these vectors.)

Assuming a corrugated surface with nanoparticles, as depicted in Figure 1.6, the situation conveys the impression of a larger contact angle. However, this is not correct, as the contact angle to each one of the nanoparticles has the correct value.



## 2

## Nanoparticles – Nanocomposites

## 2.1

## Nanoparticles

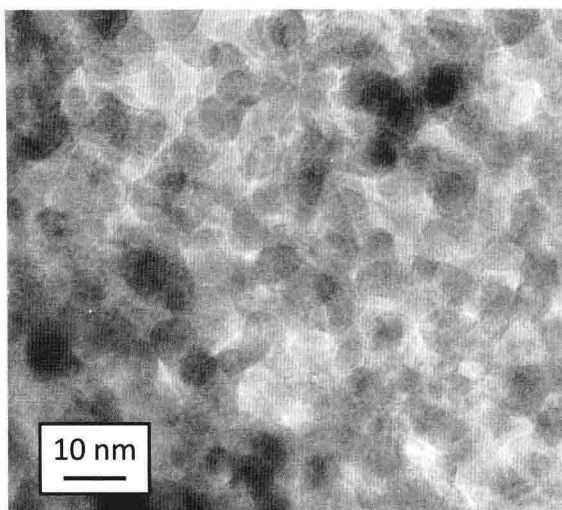
Nanoparticles may be classified as zero-dimensional, these are the nanoparticles per se, one-dimensional such as nanorods or nanotubes, and two-dimensional that are, in most cases, plates or stacks of plates. As a typical example of particles, Figure 2.1 displays an electron micrograph of zirconia ( $\text{ZrO}_2$ ) powder, zero-dimensional objects.

The particles depicted in Figure 2.1 show a size of ca. 7 nm. It is important to mention that the particles are in a very narrow range of sizes. This may be important, as many properties of nanomaterials are size dependent. On the other hand, many applications do not need such sophisticated material or they just need a broad variation of properties. Therefore, in many cases, cheaper materials with broader particle size distribution, as is depicted in Figure 2.2a, are necessary or, at least, sufficient. The material depicted in this figure shows particles in the size range from 5 to more than 50 nm. Such materials are perfectly suited for applications as pigments, UV-absorbers, etc.

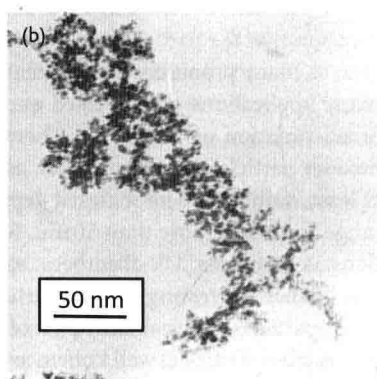
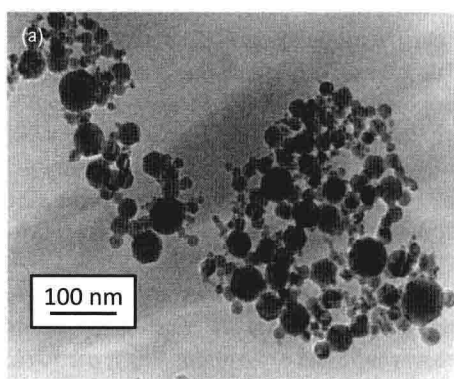
A further interesting class of particles may be described as clusters of extremely small particles. Typical examples of this type of materials are most of the amorphous silica particles, well known as “white soot”, and amorphous  $\text{Fe}_2\text{O}_3$  particles. Typically, particles of this type, as shown in Figure 2.2b, are applied as catalysts.

In producing bulk nanocomposites, the central problem is to obtain a perfect distribution of the particulate phase in the matrix. Processes based on mechanical blending or synthesizing the two phases separately and mixing during the step of particle formation, never lead to homogeneous products on the nanometer scale. Provided there are no preferences and the process of blending is random, the probability that two or more particles are touching each other and form a cluster is very high. Usually, in such a mixture, one wants to obtain a relatively high concentration of “active” particles, carrying the physical property of interest. Assuming, in the simplest case, particles of equal size, the probability  $p_n$  that a number of  $n$  particles with the volume concentration  $c$  are touching each other, is  $p_n = c^n$ . The consequences of this simple relation are severe: for example, assuming a concentration of 0.30, the probability of two touching particles is 0.09 and for





**Figure 2.1** Electron micrograph of zirconia,  $\text{ZrO}_2$  powder. A very narrow distribution of grain sizes is characteristic of this material. In many cases, this is predicated as important, because the properties of nanomaterials depend on the grain size [1].



**Figure 2.2** Two extremely different types of nanoparticulate  $\text{Fe}_2\text{O}_3$  powder. (a) Industrially produced nanomaterial with broad particle size distribution, typically of application as pigments or UV-protection. Courtesy Nanophase, Nanophase Technologies Corporation, 1319 Marquette Drive,

Romeoville, IL 60446. (b) Nanoparticulate powder consisting of clusters of amorphous particles with sizes around 3 nm. Catalysis is the most important field of application of this material with extremely high surface. Courtesy MACH I, Inc. 340 East Church Road, King of Prussia, PA 19406 USA.

three particles 0.027. Lastly, it is impossible to obtain the intended perfect distribution of two phases by blending. Further-reaching measures are necessary.

Except for properties related to grain boundaries, the special properties of nanomaterials are ones of single isolated particles that are altered or even lost in the case of interacting particles. Therefore, most of the basic considerations are related to isolated nanoparticles as the unavoidable interaction of two or more particles