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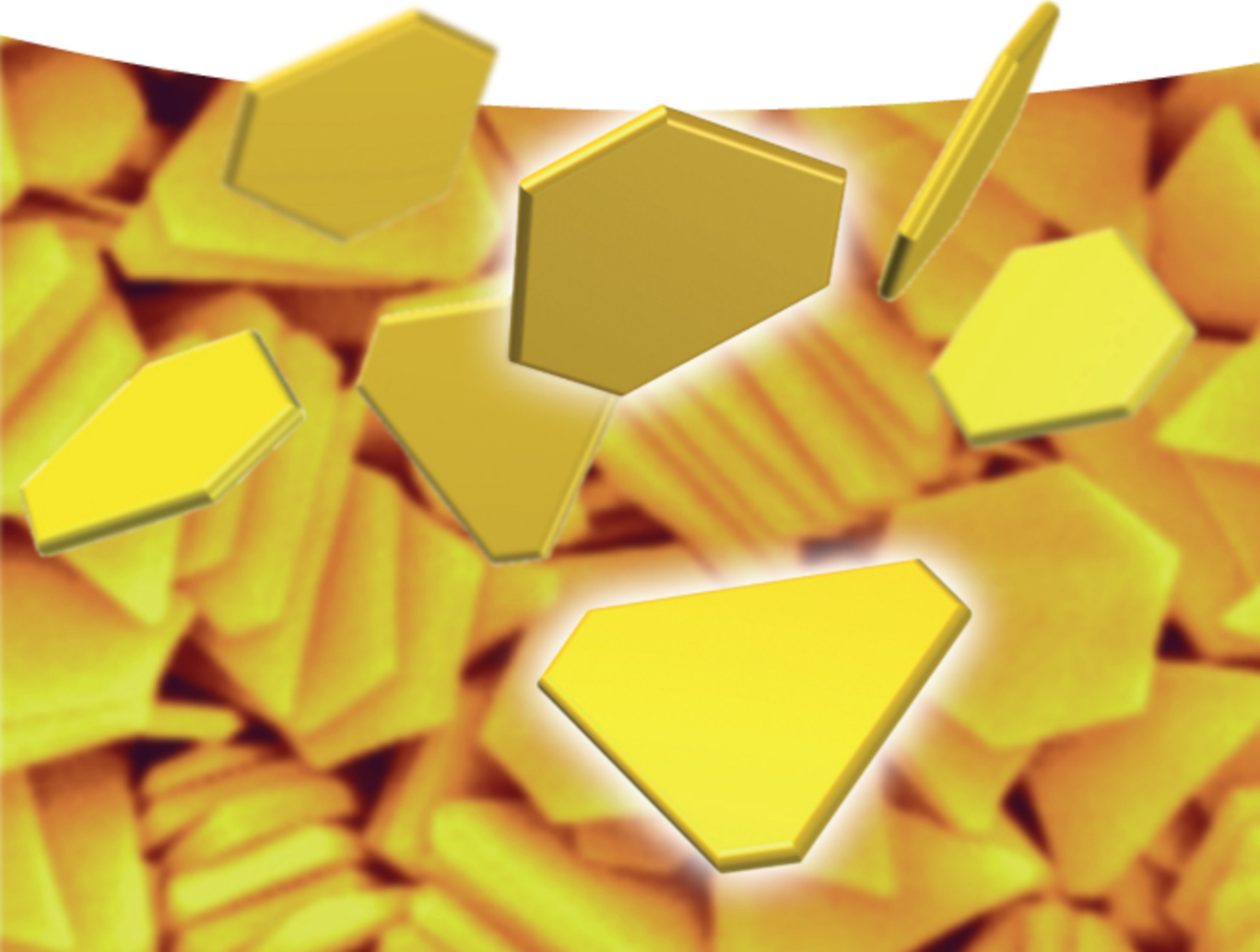
An Introduction for Beginners



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Contents

Preface

This book is really two books. It gives an introduction to the topics connected to nanoparticles, nanocomposites, and nanomaterials on a descriptive level. Wherever 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.

Stutensee, June 2013 *Dieter Vollath*

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 cm = 6×10^{-2} m and compare it with a particle with diameter of 6 nm = 6×10^{-9} 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

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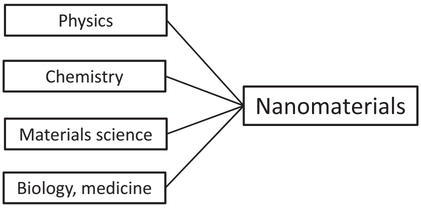

Figure 1.1 To understand and apply nanomaterials, besides knowledge on materials science, a basic understanding of physics and chemistry is necessary. As many applications are connected to biology and medicine; knowledge in these fields are also of advantage.

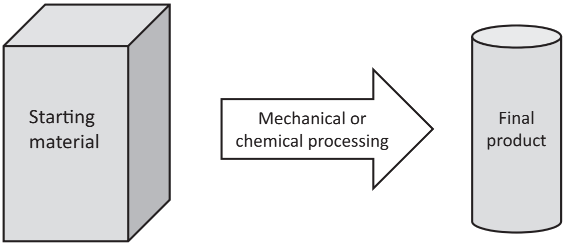

Figure 1.2 Conventional goods are produced by top-down processes, which start from bulk material. Using mechanical or chemical processes, the intended product is obtained.

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

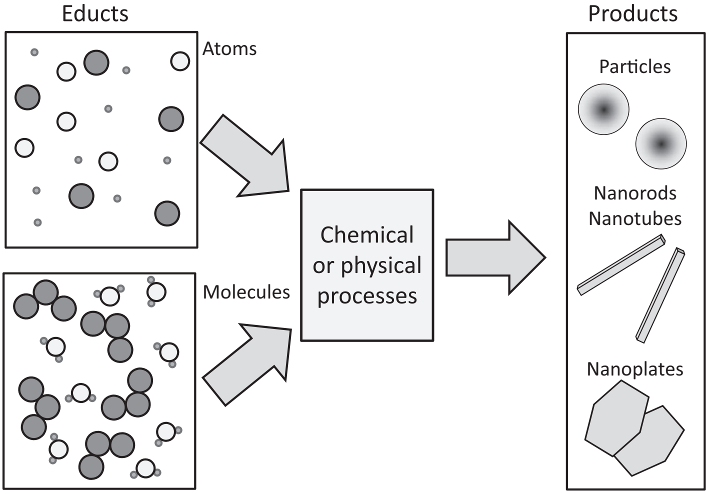

Figure 1.3 Chemical synthesis as bottom-up process. Bottom-up processes are characterized by the use of atoms or molecules as educts. Products are particles, nanotubes or nanorods, or layered structures.

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

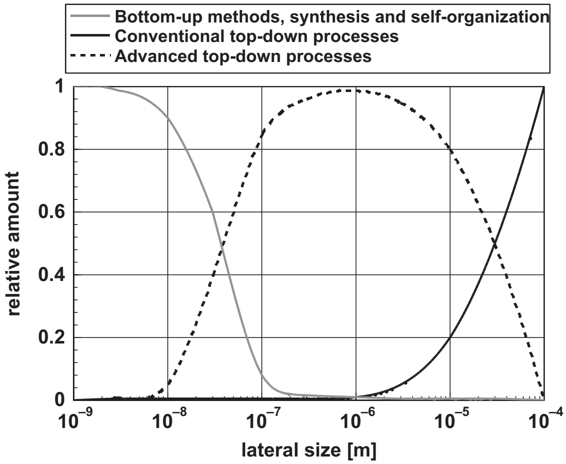

Figure 1.4 Estimated lateral limits of different structuring processes. The size range of bottom-up and conventional top-down processes is limited. New, advanced top-down processes expand the size range of conventional ones and enter the size range typical for bottom-up processes.

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 magnetoception. In plants the phenomenon of self-cleaning of leafs 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.

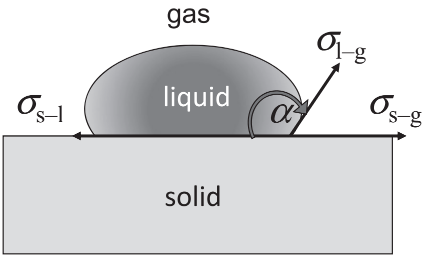

Figure 1.5 Equilibrium of surface stresses at a contact between a solid and a liquid.

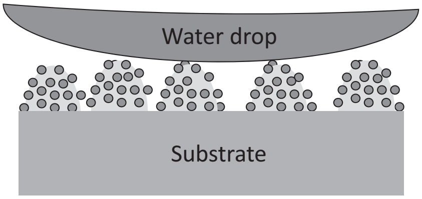

Figure 1.6 Contact situation in the case of the *Lotus* effect. Due to the corrugated surface, one has the impression of a huge contact angle α. However, looking at the points of contact of the individual particles, it is obvious that there is nothing special there, one finds the standard values.

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

$$\sigma_{s-g} - \sigma_{s-l} = \sigma_{l-g} \cos\alpha. \tag{1.1}$$

The quantities in Eq. (1.1), σ_{s-g} describe the surface stresses at the interface between the solid and the gas phase, σ_{s-l} the surface stress between the solid and the liquid phase, σ_{l-g} the one between liquid and the gas pas phase, and α 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 (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 Fe_2O_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

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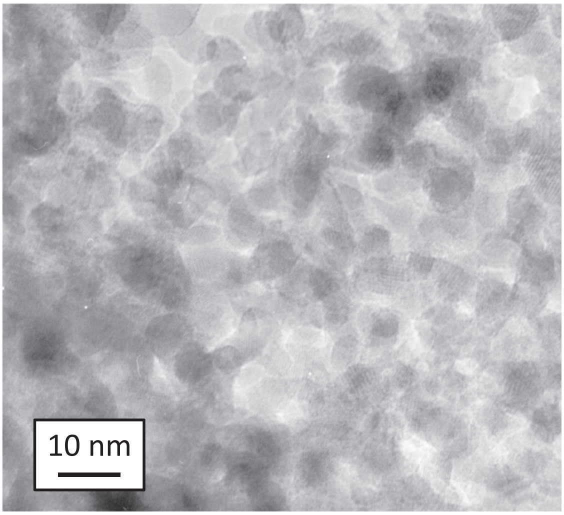

Figure 2.1 Electron micrograph of zirconia, ZrO_2 powder. A very narrow distribution of grain sizes is characteristic of this material. In many cases, this is predicated as important, because the properties of nanomaterials depend on the grain size [1].

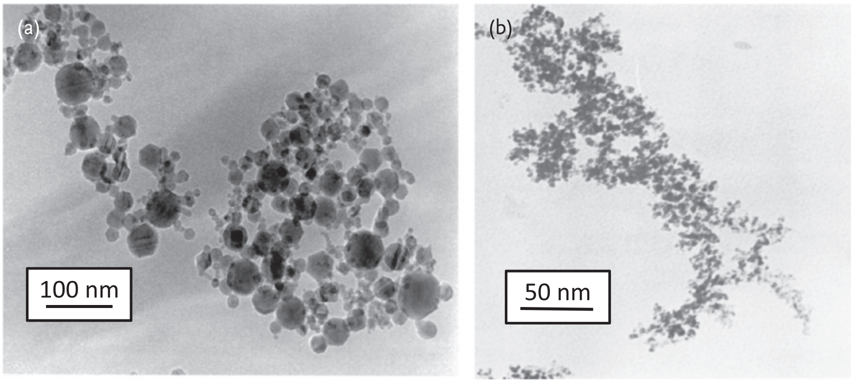

Figure 2.2 Two extremely different types of nanoparticulate Fe_2O_3 powder. (a) Industrially produced nanomaterial with broad particle size distribution, typically of application as pigments or UV-protection. Courtesy Nanophase, Nanophase Technologies Corporation, 1319 Marquette Drive, Romeoville, IL 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

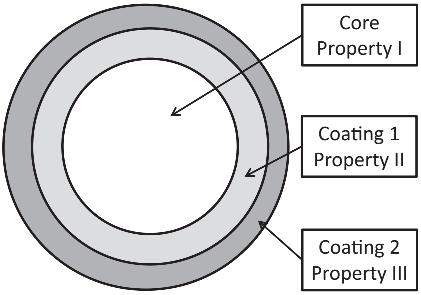

Figure 2.3 Typical design of a core–shell nanocomposite particle. The properties of the core and coating 1 are, in most cases, selected to the demand of the physics (e.g., magnetic and luminescence); the second coating is selected in view of the interaction with the surrounding medium (e.g., hydrophilic or hydrophobic) [2].

may change the properties significantly. Certainly, this is senseless in view of the technical applications.

The two problems described above and to exploit these very special properties of nanoparticles, composite particles of the core–shell type, with a second phase acting as distance holder were developed. The necessary distance depends on the phenomenon to be suppressed; it may be smaller, in the case of tunneling of electrons between particles, and is larger in the case of dipole–dipole interaction. Furthermore, such composite particles can be designed in a way to combine different "incompatible" properties, such as magnetism and luminescence. The typical design of these particles is depicted in Figure 2.3.

The core–shell composite design, as depicted in Figure 2.3 is typical for advanced applications, for example, in medicine or biotech. Such a core–shell nanocomposite consists of a core, carrying the property, which demand the largest volume, for example, magnetism. The property of Coating 1, is the case of a bifunctional particle, for example, luminescence. The outermost layer, Coating 2 in Figure 2.3 has to mediate with the surrounding medium. Therefore, in most cases, it is either hydrophilic or hydrophobic. In many medical applications, the outermost layer may consist of a protein or enzyme, which is characteristic for a specific type of cells.

Typical examples for coated particles are shown in Figures 2.4a–c. In Figure 2.4a, a ceramic core (ZrO_2), which is coated with a ceramic layer (Al_2O_3), an amorphous one, is displayed. In Figure 2.4b, the ceramic core (Fe_2O_3) is coated with a polymer (PMMA). This type of composite is often used as a special magnetic material. As a third variety, a ceramic particle (TiO_2) decorated with a metal (Pt) is displayed in Figure 2.4c. Coating of ceramic particles with thin metallic layers is, because of the relation in the surface energy, in most cases impossible. Instead of a coating, one obtains a decoration of the core with metallic clusters. This type of composite is often used as a catalyst.

Most interesting are the particles displayed in Figure 2.4a, as they show an important phenomenon, characteristic of nanomaterials. This figure shows three coated ceramic particles. The particle in the center of the figure originates from

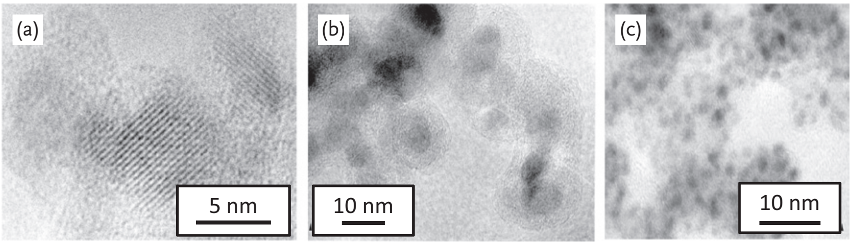

Figure 2.4 Three typical examples of nanocomposite particles. In (a), a crystallized ceramic core (ZrO_2) is coated with an amorphous ceramic layer (Al_2O_3). It is also possible (b) to coat a ceramic core (Fe_2O_3) with a polymer. Coating a ceramic core (TiO_2) with a thin metal (Pt) layer (c) is impossible because of the difference in the surface energies. In such a case, tiny metal clusters decorate the ceramic particles [1, 3].
(a, b: Reproduced with permission by Elsevier; c: Vollath, Szabó unpublished results.)

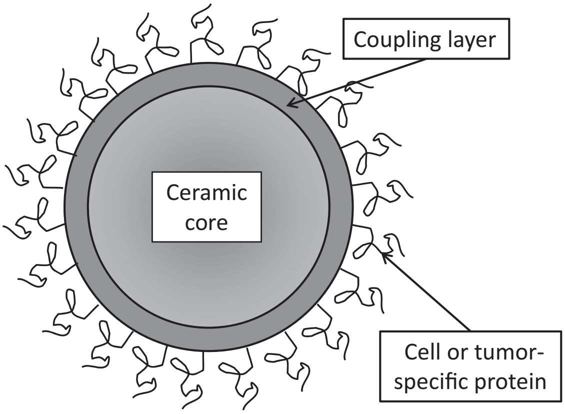

Figure 2.5 Nanocomposite particle for application in biology or medicine. The ceramic core may be magnetic, luminescent, or even bifunctional. The cell or tumor-specific proteins or enzyme at the surface, necessary for coupling of the particle at the intended type of cells, need a coupling layer as; in general, these molecules cannot be attached directly at the ceramic surface.

coagulation of two zirconia particles. As the process of coagulation was incomplete, there are concave regions of the zirconia core visible. During the coating process, these concave areas were filled with alumina; therefore, finally, the coated particle has only convex surfaces. This minimizes surface energy; an important principle acting in any type of nanomaterial.

As already mentioned above, multifunctional particles are widely used in biology and medicine. For this application, it is necessary to add proteins or other biological molecules, which are characteristic of cells, where the particle should attach at the surface of the particles. Biological molecules are attached at the particles only via specific types of molecules, accommodated in the outermost coupling layer [4]. The development of these coupling layers is one of the crucial points for this application. Figure 2.5 displays such a biologically functionalized particle. The

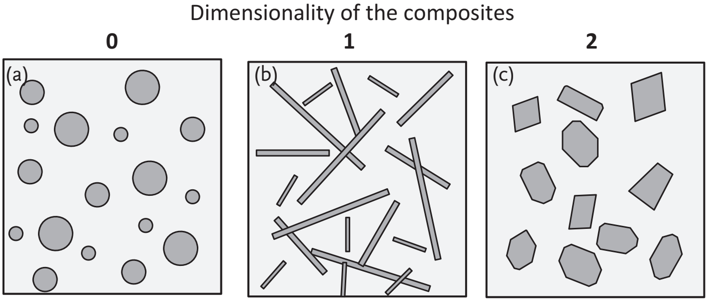

Figure 2.6 Three basic types of nanocomposites. (a) Composite consisting of zero-dimensional particles in a matrix. In the ideal case, the individual particles are not touching each other. (b) One-dimensional nanocomposite consisting of nanotubes or nanorods distributed in a second, in general, polymer matrix. (c) Two-dimensional nanocomposite consisting of platelets embedded in a second matrix.

ceramic core, usually, is either magnetic or luminescent, or multifunctional. In the design depicted in Figure 2.5, the coupling layer may consist of an appropriate polymer or a type of glucose; however, in many cases, hydroxylated silica is sufficient, too. At the surface of the coupling layer, the biological molecules, such as proteins or enzymes are attached.

Bulk 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. Figure 2.6 displays the most important three different types of nanocomposites. The types differ in the dimensionality of the second phase. This phase may be zero-dimensional, isolated nanoparticles, one-dimensional, consisting of nanotubes or nanorods, or two-dimensional composites with platelets as second phase; one may also think of stacks of layers. In most cases, such composites are close to zero-dimensional ones. However, some of them with polymer matrix have existing mechanical and thermal properties; therefore, they are used primarily in the automotive industry. In particular, the latter ones will be discussed in detail in Chapter 11.

A typical electron micrograph of a nearly ideal nanocomposite, a distribution of zirconia (ZrO_2) nanoparticles in an alumina (Al_2O_3) matrix is displayed in Figure 2.7. This figure displays a micrograph of a sintered material. The starting material was alumina-coated zirconia powder. It is obvious that the particles remain separated. For products of this type, it is essential that there is no mutual solubility between the core and coating. After sintering of the powder, consisting of coated nanoparticles, the coating will form the matrix.

Looking at applications, one will find zero-dimensional composites of the type depicted in Figure 2.4a quite often in connection to magnetic materials. One- and two-dimensional nanocomposites are often found in applications where high mechanical strength is demanded. Looking at carbon nanotubes (one-dimensional)

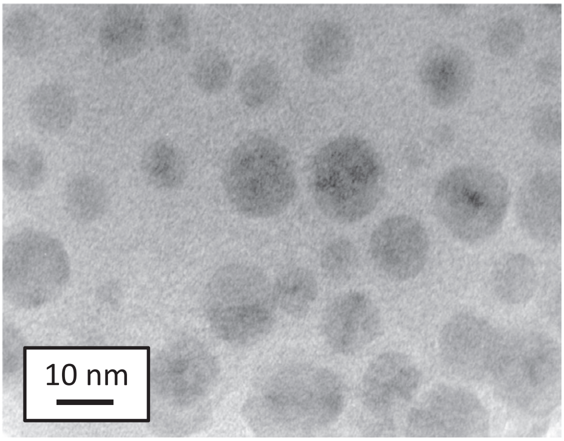

Figure 2.7 Transmission electron micrograph of a zero-dimensional nanocomposite. It depicts a composite zirconia particles embedded in an alumina matrix. The specimen was produced from zirconia particles coated with alumina. This micrograph was taken from an ion-beam-thinned sample. It is essential to realize that there is a high probability that particles are not touching each other, because they are lying in different planes [3]. (Reproduced with permission by Springer.)

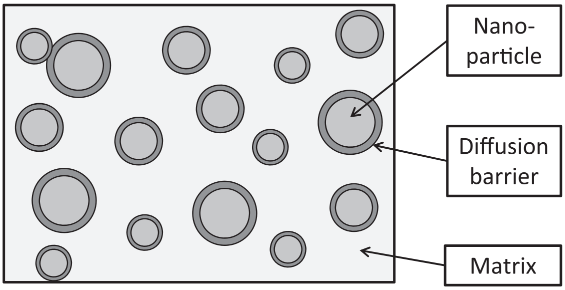

Figure 2.8 Zero-dimensional nanocomposite. To avoid dissolution in the matrix, the particles are coated with a diffusion barrier.

or graphene (two-dimensional) as a filler, a very important application is found in the field of optically transparent electrical conductors. Because of the large aspect ratio of these particles, electrical conductivity is obtained already with extremely small concentrations of these particles.

Practically, the composites, as depicted in Figures 2.4a,b exist primarily using a polymer matrix. In all the other cases, there is the possibility that there is a mutual solubility between the nanoparticles and the matrix. To avoid dissolution of the particles, often it is necessary to coat the particles with a diffusion barrier. This situation is depicted in Figure 2.8.

Figure 2.8 displays the oldest, man-made type of nanocomposite with more or less spherical nanoparticles. This composite is realized in the well-known gold-ruby glass. It consists of a glass matrix with gold nanoparticles as second phase.

However, as gold can be dissolved in the glass matrix, a diffusion barrier is necessary. In the case of gold-ruby glass the diffusion barrier consists of tin oxide. In colloid chemistry, this principle of stabilization is well known as “colloid stabilization”. This material was produced for the first time by the Sumerians in the seventh century BC and re-invented by *Kunkel* in Leipzig in the seventeenth century. It is interesting to note that the composition used by the Sumerians was practically identical to the one reinvented by *Kunkel* and that is used nowadays.

Furthermore, the properties of a bulk solid made of coated nanoparticles may be adjusted gradually with the thickness of the coating. Depending on the requirements of the application, the coating material may be ceramic or polymer. Coating nanoparticles with a second and third layer leads to the following improvements:

- The distribution of the two phases is homogenous on a nanometer scale.
- The kernels are arranged in a well-defined distance. Therefore, the interaction of the particles is controlled.
- The kernel and one or more different coatings may have different properties. This allows the combination of properties in one particle that are never found together in nature. Additionally, by selecting a proper polymer for the outermost coating, it is possible to adjust the interaction with the surrounding medium.
- During densification, i.e. sintering, the growth of the kernels is thwarted, provided core and coating show no mutual solubility. An example for this is depicted in Figure 2.7.

These arguments demonstrate that the most advanced type of nanocomposites are coated nanoparticles. They allow not only the combination of different properties in one particle, but also in bulk materials.

In addition to the composites displayed in Figures 2.6 and 2.7, one observes nanocomposites with regular well-ordered structure, as displayed in Figure 2.9.

In general, self-organization processes in the case of spherical filler particles or mechanical stretching are appropriate mechanisms to create this type of composite, if the filler particles are one- or two-dimensional. Successful realization of self-organization processes, leading to structures as depicted in Figure 2.9a, requires particles nearly identical in size.

2.2
Elementary Consequences of Small Particle Size

2.2.1
Surface of Nanoparticles

The first and most important consequence of the small particle size is the huge surface area. To get an impression of the importance of this geometric

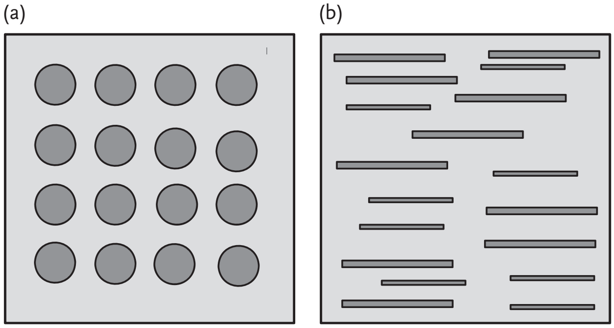

Figure 2.9 Typical examples of ordered nanocomposites. In the case of a zero-dimensional filler (a), it is necessary that the particles are more or less equal in size; whereas, in the case of one- or two-dimensional fillers, in general, the particles have different size; however, they are oriented in parallel.

variable of nanoparticles, the surface over volume ratio is discussed. Simple calculations show that the ratio surface / volume is inversely proportional to the diameter of the particle. Similar to the surface over volume ratio for one particle, in molar quantities, this ratio is inversely proportional to the particle diameter, too.

Box 2.1 Surface of Particles

Assuming spherical particles with the diameter d, the surface area a of one particle is given by

$$a = \pi d^2.$$

The volume v of this particle is

$$v = \frac{\pi}{6} d^3.$$

The surface/volume ratio R

$$R = \frac{a}{v} = \frac{6}{d}. \tag{2.1}$$

This ratio is inversely proportional to the particle size. The surface A per mol, a quantity important in thermodynamics, is

$$A = na = \frac{M}{\rho \frac{\pi d^3}{6}} \pi d^2 = \frac{6M}{\rho d}, \tag{2.2}$$

with n the number of particles per mol, M the molecular weight, and ρ the density of the particles.

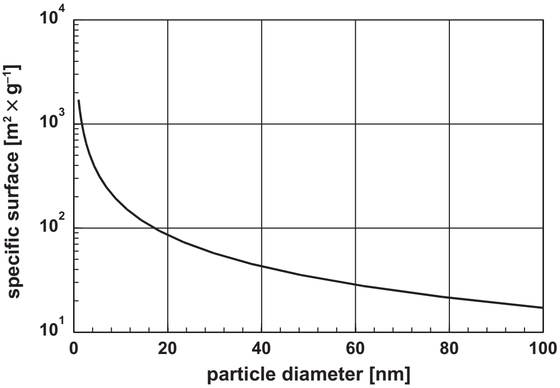

Figure 2.10 Theoretical dependency of the specific surface area of the particle diameter. Due to the agglomeration of the particles, experimentally these values are not realized.

To get an idea about the magnitudes of surfaces that may be expected in case of nanoparticles, Figure 2.10 displays the theoretical surface of one gram of a powder consisting of spherical particles with a density of $3.5 \times 10^3\,\mathrm{kg\,m^{-3}}$ (alumina).

In Figure 2.10, the surface is given in the non-SI unit $\mathrm{m^2\,g^{-1}}$. This unit is applied because this is the only unit that is generally accepted for the specific surface area. In general, the specific areas visible in Figure 2.10 are never realized experimentally. The reason for this discrepancy is found in the agglomeration of the particles. The influence of this phenomenon increases with decreasing particle diameter, as the influence of the *van der Waals* forces increases too. (*Van der Waals* forces are weak interactions between molecules or small particles having their origin in quantum dynamics. These forces are neither covalent nor based on electrostatic or dipolar interaction.) Experimentally, the largest values are measured with activated charcoal in the range of $2000\,\mathrm{m^2\,g^{-1}}$ and finely dispersed amorphous silica with values up to $600\,\mathrm{m^2\,g^{-1}}$.

The surface is such an important topic for nanoparticles that there is a full chapter devoted to surface and surface-related problems (see Chapter 3).

2.2.2
Thermal Phenomena

Each isolated object, in this case a nanoparticle, has a thermal energy, which is directly proportional to the temperature. Furthermore, each object tries to be in a state where the energy is a minimum. Generally, this is a stable state. Certainly, energetically speaking, there are other states with higher energy possible. The energy difference between the state of lowest energy and the next one may depend for example, on the mass of the particle. As the mass of the particle decreases with particle diameter, there is the possibility that, starting at a sufficiently high temperature, the thermal energy gets larger than the difference between the two neighboring states. Now the system is no longer stable, and the system fluctuates.

Box 2.2 Thermal Instability

Thermal energy u_{th} of an isolated particle is given by

$$u_{\text{th}} = kT,$$

with k the *Boltzmann* constant and T the temperature.

Assuming an energy that depends on the volume of the particle $u(v)$. The system is no longer stable, it fluctuates, if the condition

$$u(v) \le kT \tag{2.3}$$

is fulfilled.

A simple example: The energy necessary to lift a particle with the density ρ the elevation x.

$$u(v) = \rho v x.$$

This particle moves around thermally and jumps up to a height x, if the condition

$$\rho v x \le kT \quad \text{or} \quad T \ge \frac{\rho v}{k} x$$

is fulfilled.

Schematically, this situation is depicted in Figure 2.11.

Looking at thermal instabilities (fluctuations), one can design a simple example. One can ask for the size of a zirconia particle ($\rho = 5.6 \times 10^3\,\text{kg m}^{-3}$) that could be lifted at room temperature to a height equal to its diameter. The answer is somewhat surprising, the diameter of 1100 nm. If one asks, how high could a particle

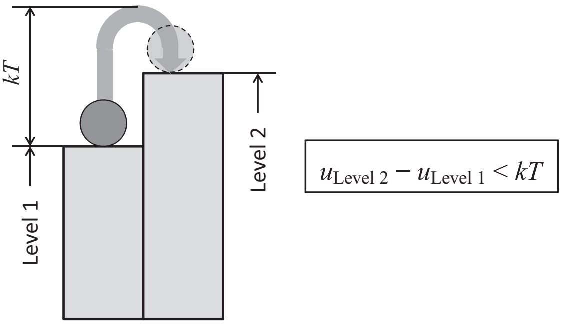

Figure 2.11 Schematic visualization of thermal fluctuation. In this case, the thermal energy is larger than the energy difference between level 1 and level 2.

of 5 nm diameter jump these simple calculations lead to a height of more than one meter. Certainly, these games with number do not have physical reality; however, they indicate that nanoparticles that are not fixed at a surface are moving around. Doing electron microscopy, this dynamic becomes reality. Provided the particles and the carbon film on the carrier mesh are clean, the particles of the specimen move around like ants on the carbon film. This makes electron microscopy difficult.

The thermal instability presented here, demonstrates a simple consequence of smallness; however, other physical properties may change significantly and this may lead to new properties. The most important phenomenon of this group, superparamagnetism, will be described in Chapter 8 on magnetic properties. Fluctuations are also observed in connection with phase transformation, for example, melting and crystallization of nanoparticles.

2.2.3
Diffusion Scaling Law

Diffusion is controlled by the two *Fick*'s laws. Solutions of these equations, important for nanotechnology, say that the squared mean diffusion path of the atoms is proportional to the time. In other words: Assuming the particle diameter as the diffusion path, doubling of the diameter leads to a four-fold time needed for diffusion.

Box 2.3 Scaling Law of Diffusion

Mathematically, diffusion is described by the two laws of *Fick,* a set of two partial differential equations. The solution, important for the considerations connected to nanoparticles says:

$$\langle x \rangle^2 \propto Dt. \tag{2.4}$$

The brackets $\langle\ \rangle$ stand for the mean value of an ensemble; the quantity x stands for the diffusion path; therefore, $\langle x \rangle^2$ is the mean square of the diffusion path, D is the diffusion coefficient and t the time. Generally, the diffusion coefficient depends exponentially on the temperature,

$$D \propto \exp\left(-\frac{q}{kT}\right), \tag{2.5}$$

which means that the diffusion will get faster with increasing temperature. The quantity q is the activation energy.

This scaling law for diffusion has dramatic consequences when applied to nanomaterials. As an example, the homogenization time necessary in the case of conventional and nanomaterials are compared. Conventional materials usually have grain sizes of around 10 μm. It is well known that at elevated temperatures, these materials need homogenization times in the range of many hours. Looking at materials with grain sizes around 10 nm, which is 10^{-3} of the conventional grain size, according to the scaling law of diffusion Eq. (2.3) the time for homogenization is reduced by a factor of $(10^3)^2 = 10^6$. This means that the homogenization time of hours, for conventional materials, is reduced to milliseconds; for nanomaterials. Lastly, this says that homogenization is virtually instantaneous. This phenomenon is often called "instantaneous alloying". One may also say: Each thermally activated reaction will happen nearly instantaneously. Therefore, it is not possible to produce nonequilibrium systems of nanomaterials, well known for conventional materials, at elevated temperatures.

The possibility of nearly instantaneous diffusion through nanoparticles is exploited technically. The most important example is the gas sensor applying the variation in the electric conductivity due to changes in the stoichiometry of oxides. (The stoichiometry describes the ratio oxygen / metal.) Variations of stoichiometry are often observed in oxides of transition metals. Because of the small particle size, any change in the oxygen potential in the surrounding atmosphere changes the stoichiometry of the sensing particles immediately. In contrast to conventional gas sensors, the time response is now controlled by the gas diffusion through the narrow channels in between the nanoparticles. Figure 2.12 displays the general design of such a sensor.

Such a gas sensor is set up on a conductive substrate on a carrier plate. The surface of this conductive layer is covered completely with the oxide sensor nanoparticles. Transition-metal oxides, well suited for this purpose are example, TiO_2, SnO_2, Fe_2O_3. On the top of the oxide particle layer, the counterelectrode, a gas-permeable conductive layer is applied. Variations in the oxygen potential in the surrounding atmosphere changes the stoichiometry of the oxide, and, therefore, the electrical conductivity. This process is reversible.

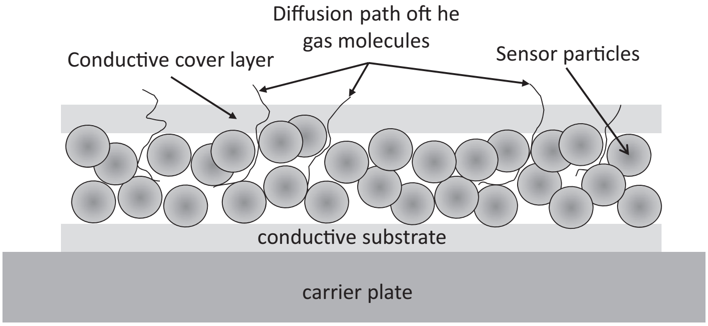

Figure 2.12 General layout of a gas sensor based on nanoparticles. This gas sensor consists of a layer of sensing nanoparticles, in most cases SnO_2, placed on a conductive substrate. The whole system is covered with a gas-permeable electrode. The diffusion within the nanosized grains is no longer time controlling, it is rather the diffusion in the open-pore network in-between the grains.