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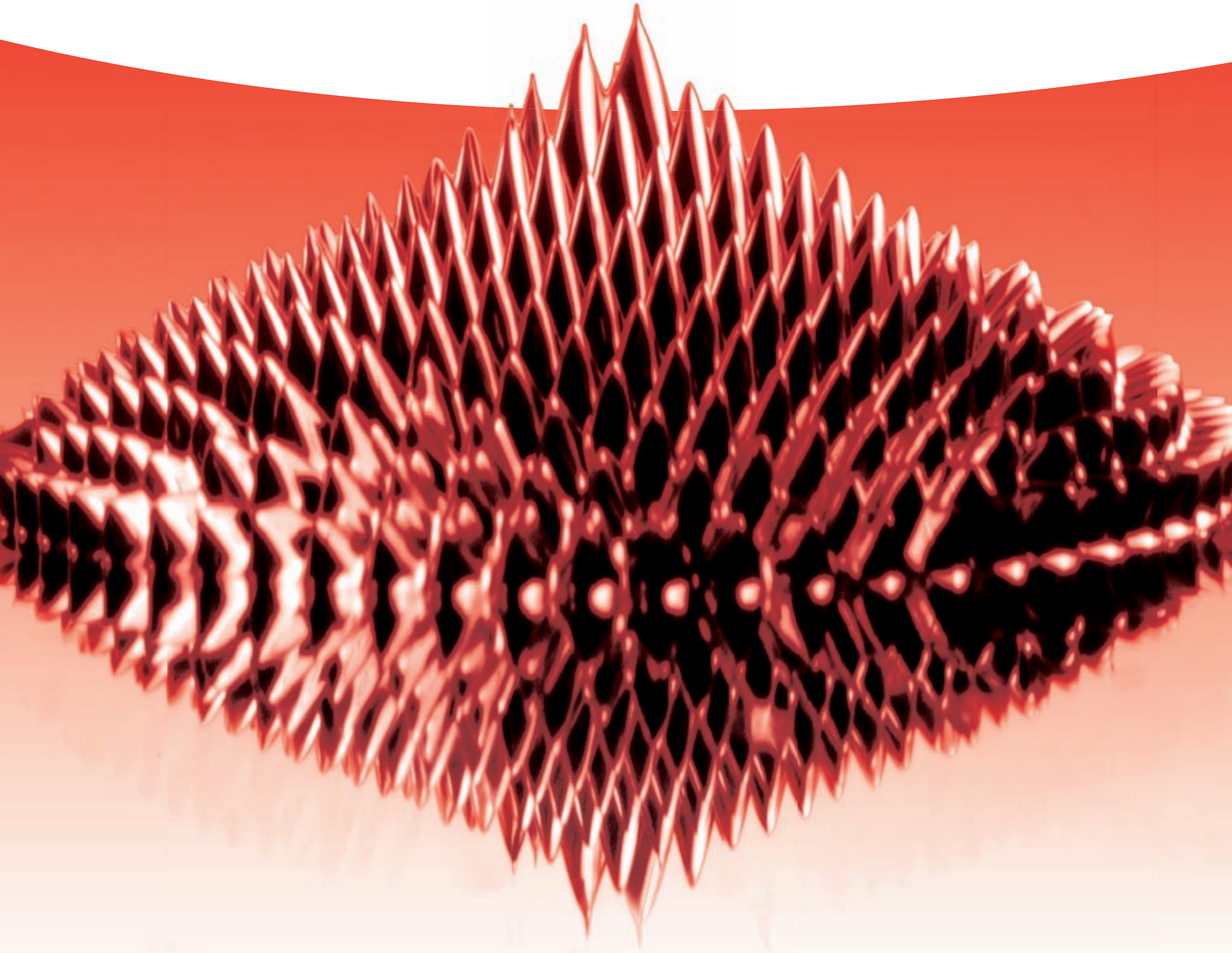
Dieter Vollath

Nanomaterials

An Introduction to Synthesis, Properties, and Applications

Second Edition



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Contents

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*

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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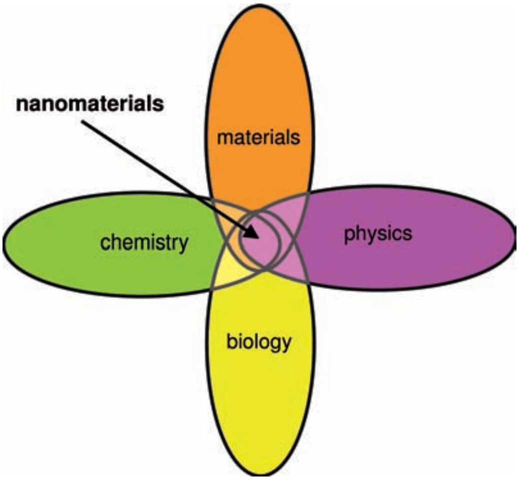

Figure 1.1 A basic understanding of physics and chemistry, and some knowledge of materials science, is necessary to understand the properties and behavior of nanomaterials. As many applications are connected with biology and medicine, some knowledge of these areas is also required.

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.

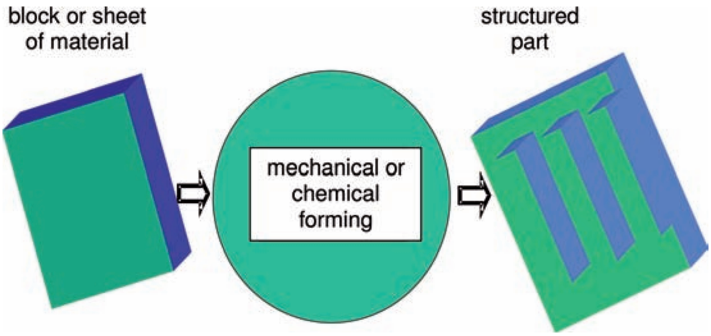

Figure 1.2 Conventional goods are produced via top-down processes, starting from bulk materials. The intended product is obtained by the application of mechanical and/or chemical processes.

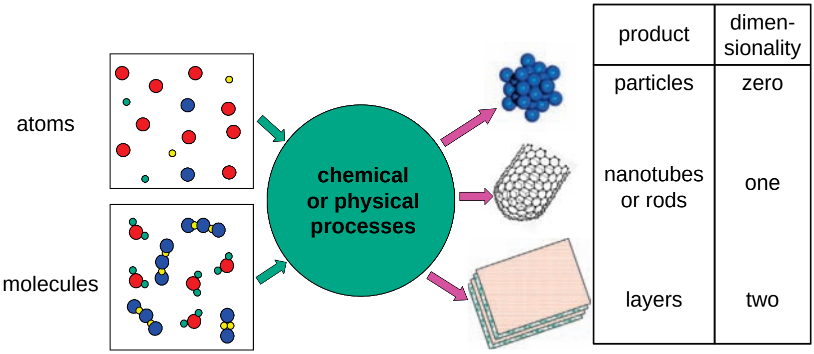

Figure 1.3 Nanotechnologies are usually connected to bottom-up processes and are characterized by the use of atoms or molecules as building blocks. Bottom-up processes result in particles, nanotubes, nanorods, thin films, or layered structures. These products are also characterized by their dimensionality,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

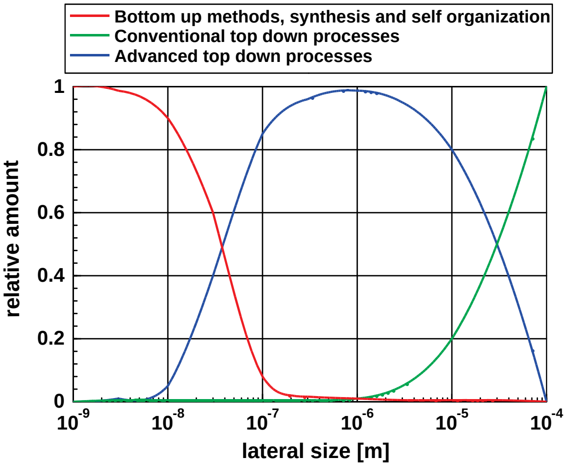

Figure 1.4 Estimated lateral limits of different structuring processes. Clearly, the size range of bottom-up and conventional top-down processes is limited. New, advanced top-down processes expand the size range of their conventional counterparts and enter the size range typical of bottom-up processes.

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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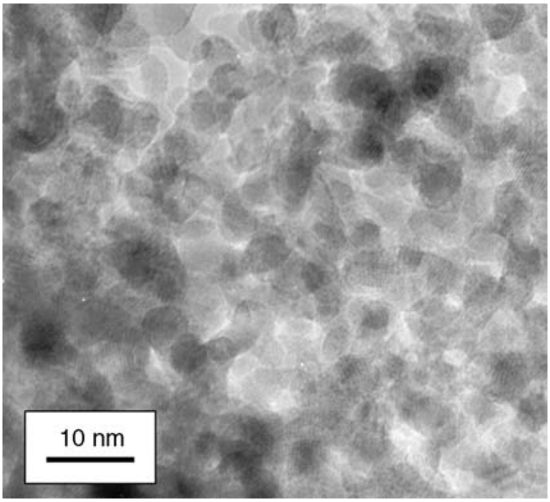

Figure 2.1 Electron micrograph of zirconia (ZrO_2) powder. This material has a very narrow grain size distribution; this may be important as the properties of nanomaterials depend on grain size [1].

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.

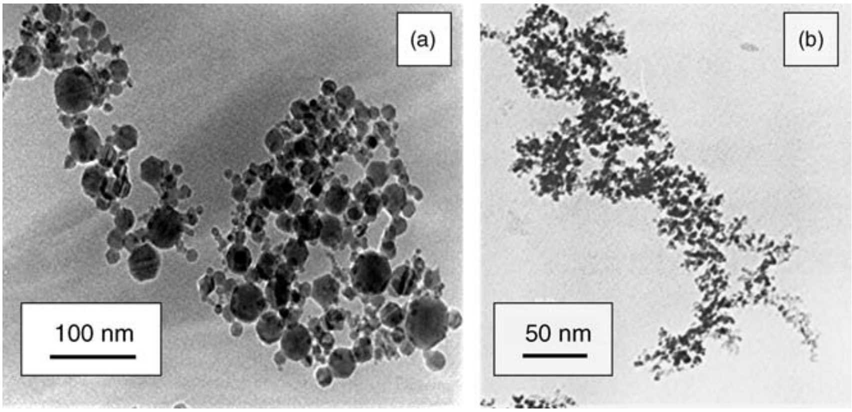

Figure 2.2 Two types of nanoparticulate Fe_2O_3 powder. (a) Industrially produced nanomaterial with a broad particle size distribution; this is typically used as a pigment or for UV protection. (Reprinted with permission of Nanophase Technologies, Romeoville, IL, USA; www.nanophase.com.) (b) Nanoparticulate 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.

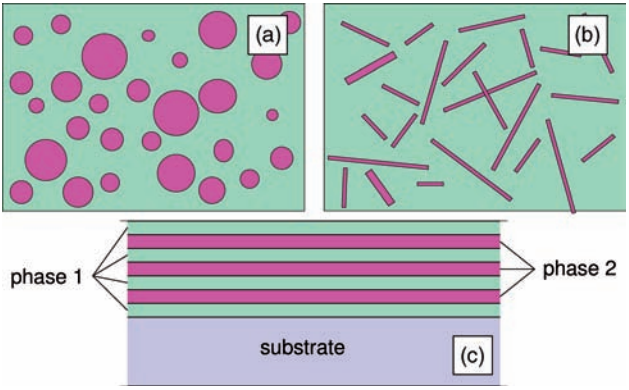

Figure 2.3 Three basic types of nanocomposite. (a) Composite consisting of zero-dimensional particles in a matrix; ideally, the individual particles do not touch each other. (b) One-dimensional nanocomposite consisting of nanotubes or nanorods distributed in a second matrix. (c) Two-dimensional nanocomposite 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.

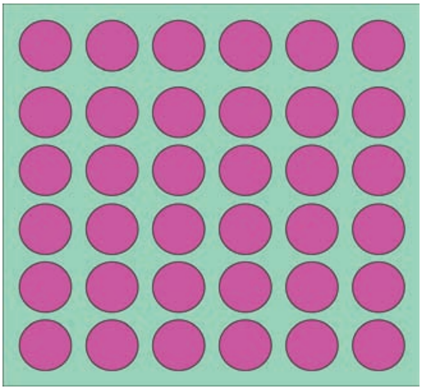

Figure 2.4 Perfectly ordered zero-dimensional nanocomposite; this type of composite is generally made via a self-organization processes.

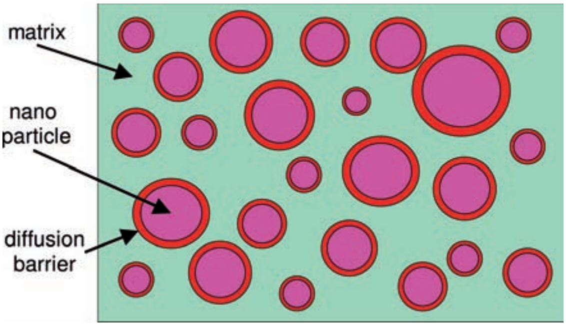

Figure 2.5 Advanced zero-dimensional nanocomposite. Here, a diffusion barrier surrounds each particle. This type of material is required if the nanoparticle and matrix are mutually soluble.

The oldest, and most important, type of nanocomposite is that which has more or less spherical nanoparticles. An example is the well-known "gold ruby glass," which consists of a glass matrix with gold nanoparticles as the second phase (see also Section 9.5 and Figure 9.32). This material was first produced by the Assyrians in the seventh century BC and reinvented by Kunkel in Leipzig in the seventeenth century. It is interesting to note that the composition used by the Assyrians was virtually identical to that used today. This well-known gold ruby glass needed a modification of nanocomposites containing a second phase of spherical nanoparticles. In many cases, as the matrix and the particles exhibit mutual solubility, a diffusion barrier is required to stabilize the nanoparticles; such an arrangement is shown in Figure 2.5. In the case of gold ruby glass, the diffusion barrier consists of tin oxide. In colloid chemistry, this principle of stabilization is often referred to as a "colloid stabilizer."

A typical electron micrograph of a near-ideal nanocomposite, a distribution of zirconia nanoparticles within an alumina matrix, is shown in Figure 2.6. Here, the

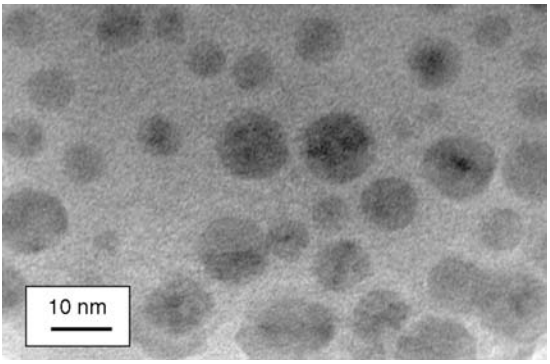

Figure 2.6 Transmission electron micrograph of a zero-dimensional nanocomposite, showing composite zirconia particles embedded in an alumina matrix. The specimen was produced from zirconia particles coated with alumina. The image was taken from an ion beam-thinned sample. There is a high probability that these particles do not touch each other as they are in different planes [3]. (Reproduced by permission of Springer).

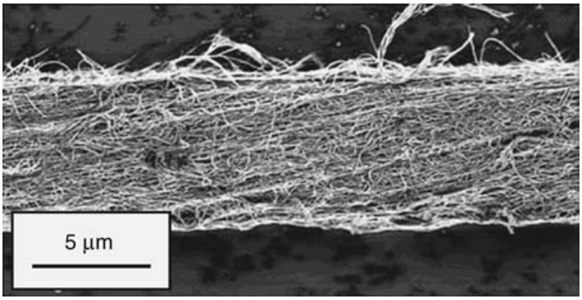

Figure 2.7 Electron micrograph of a composite fiber consisting of polymer-bound carbon nanotubes. These fibers have good electrical conductivity and high tensile strength [4] (Reproduced by permission of The Royal Chemical Society).

material was sintered and the starting material alumina-coated zirconia powder; the particles remained clearly separated.

Composites with nanotubes or nanorods are used for reinforcement or to introduce electric conductivity to the polymer. Most important in this context are composite fibers consisting of well-aligned carbon nanotubes, which are bound with a polymer. Such materials may have good electrical conductivity and high tensile strength. A micrograph of a typical example is displayed in Figure 2.7.

When producing nanocomposites, the central problem is to obtain a perfect distribution of the two phases; however, processes based on mechanical blending never lead to homogeneous products on the nanometer scale. Likewise, synthesizing the two phases separately and blending them during the stage of particle formation never leads to the intended result. In both cases, the probability that two or more particles are in contact with each other is very high and normally in such a mixture the aim is 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 n particles with volume concentration c are touching each other is $p_n = c^n$. Then, assuming a concentration of 0.30, the probability of two touching particles is 0.09; for three particles it is 0.027. The necessary perfect distribution of two phases is obtained only by coating the particles of the active phase with the distance holder phase. In general, this can be achieved by either of the two following approaches:

- Synthesis of a metastable solution and precipitation of the second phase by reducing the temperature (Vollath and Sickafus, unpublished results). A typical example is shown in Figure 2.8a, which shows amorphous alumina particles within which zirconia precipitation is realized. As the concentration of zirconia in the original mixture was very low, the size of these precipitates is small (less than 3 nm). Arrows indicate the position of a few of these precipitates. One of the precipitates is depicted at higher magnification in Figure 2.8b, where the lines visible in the interior of the particle represent the lattice planes. This is one of the most elegant processes for synthesizing ceramic/ceramic nanocomposites as it leads to extremely small particles, although the concentration of the precipitated phase may be low (in certain cases, this may be a significant disadvantage).

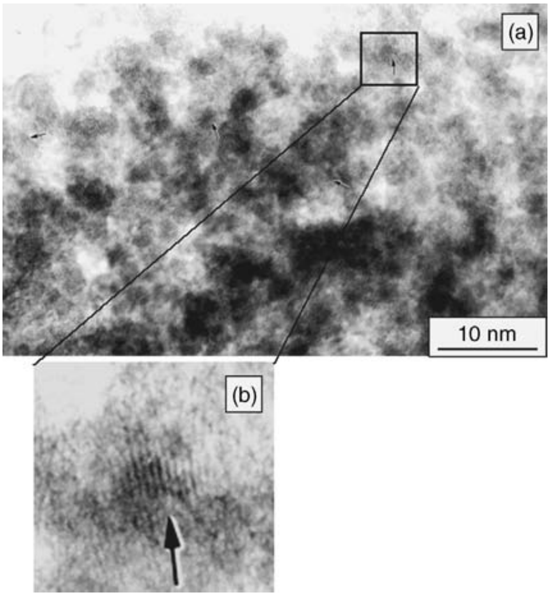

Figure 2.8 Electron micrograph of a nanocomposite consisting an amorphous alumina matrix and precipitated crystallized zirconia particles. (a) Within the amorphous alumina, the crystallized zirconia precipitations are indicated by arrows. (b) One of the precipitations shown at a higher magnification. The precipitation sizes range between 1.5 and 3 nm; such precipitation occurs because zirconia is insoluble in alumina at room temperature (Vollath and Sickafus, Los Alamos National Laboratories, USA; unpublished results).

- The most successful development in the direction of nanocomposites was that of coated particles, as both the kernel and coating material are distributed homogeneously on a nanometer scale. The particles produced in a first reaction step are coated with the distance-holder phase in a second reaction step. Two typical examples of coated nanoparticles are shown in Figure 2.9. In Figure 2.9a, a ceramic–polymer composite is shown in which the core consists of iron oxide (γ-Fe_2O_3) and the coating of poly(methyl methacrylate) (PMMA). The second example, a ceramic–ceramic composite, uses a second ceramic phase for coating; here, the core consists of crystallized zirconia and the coating consists of amorphous alumina. It is a necessary prerequisite for this type of coated particle that there is no mutual solubility between the compounds used for the core and the coating. Figure 2.9b shows three alumina-coated zirconia particles, where the center particle originates from the coagulation of two zirconia particles. As the process of coagulation was incomplete, concave areas of the zirconia core were visible. However, during the coating process these concave areas were filled with alumina, such that the final coated particle had only convex surfaces. This led to a minimization of the surface energy, which is an important principle in nanomaterials.

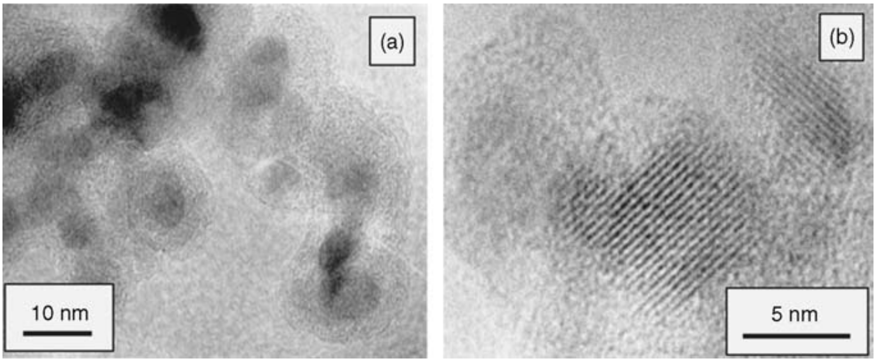

Figure 2.9 Nanocomposite particles. Electron micrographs depicting two types of coated particle. (a) The particles consist of a γ-Fe_2O_3 core and are coated with PMMA [5]. (b) Crystallized zirconia particles coated with amorphous alumina [6] (Reproduced by permission of Elsevier).

The properties of a densified solid may also be adjusted gradually with the thickness of the coating. Depending on the requirements of the system in question, the coating material may be either ceramic or polymer. In addition, by coating nanoparticles with second and third layers, the following improvements are obtained:

- The distribution of the two phases is homogeneous on a nanometer scale.
- The kernels are arranged at a well-defined distance; therefore, the interaction of the particles is controlled.
- The kernel and one or more different coatings may have different properties (e.g., ferromagnetism and luminescence); this allows a combination of properties in one particle that would never exist together in nature (bifunctional materials [2]) In addition, by selecting a proper polymer for the outermost coating it is possible to adjust the interaction with the surrounding medium (e.g., hydrophilic or hydrophobic coatings may be selected).
- During densification (i.e., sintering) the growth of the kernels is thwarted, provided that the core and coating show no mutual solubility. An example of this is shown in Figure 2.6.

These arguments confirm that coated nanoparticles, first described by Vollath and Szabó [3,6], represent the most advanced type of nanocomposite because they allow:

- Different properties to be combined in one particle.
- Exactly adjusted distances to be inserted between directly adjacent particles in the case of densified bodies.

Today, coated particles are widely used in biology and medicine [2], although for this it may be necessary to add proteins or other biological molecules at the surface of the particles. Such molecules are attached via specific linking molecules and accommodated in the outermost coupling layer. A biologically functionalized particle is shown schematically in Figure 2.10, where the ceramic core is usually either magnetic or luminescent. Recent developments in the combination of these

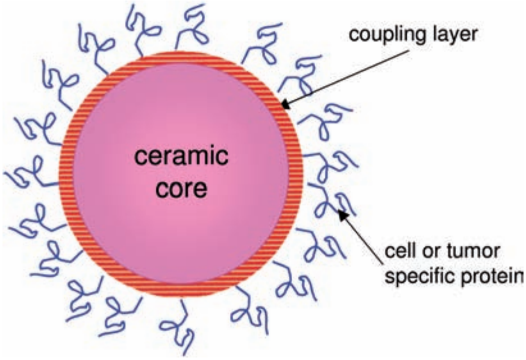

Figure 2.10 Nanocomposite particle for application in biology or medicine. The ceramic core may be magnetic or luminescent. The cell- or tumor-specific proteins at the surface, which are necessary for application, require a coupling layer, as typically they cannot be attached directly to the ceramic surface.

two properties have utilized a multishell design of the particles. In the design depicted in Figure 2.10, the coupling layer may consist of an appropriate polymer or a type of glucose, although in many cases hydroxylated silica is also effective. Biological molecules such as proteins or enzymes may then be attached at the surface of the coupling layer.

2.2
Elementary Consequences of Small Particle Size

Before discussing the properties of nanomaterials, it may be advantageous to describe some examples demonstrating the elementary consequences of the small size of nanoparticles.

2.2.1
Surface of Nanoparticles

The first and most important consequence of a small particle size its huge surface area; in order to obtain an impression of the importance of this geometric variable, the surface over volume ratio should be discussed. So, assuming spherical particles, the surface a of one particle with diameter d is $a = \pi d^2$ and the corresponding volume v is $v = d^3\pi/6$. (Within this book, in all thermodynamic considerations quantities related to one particle are written in lower case characters, whereas for molar quantities upper case letters are used.) Therefore, one obtains for the surface/volume ratio:

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

This ratio is inversely proportional to the particle size and, as a consequence, the surface increases with decreasing particle size. The same is valid for the surface per mole A, a quantity that is of extreme importance in thermodynamic considerations:

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

where N is the number of particles per mole, M is the molecular weight, and ρ is the density of the material. Similar to the surface/volume ratio, the area per mole increases inversely in proportion to the particle diameter; hence, huge values of area are achieved for particles that are only a few nanometers in diameter.

It should be noted that as the surface is such an important topic for nanoparticles, Chapter 3 of this book has been devoted to surface and surface-related problems.

2.2.2
Thermal Phenomena

Each isolated object – in this case a nanoparticle – has a thermal energy of kT (k is the Boltzmann constant and T is the temperature). First, let us assume a property of the particle that depends for example on the volume v of the particle; the energy of this property may be $u(v)$. Then, provided that the volume is sufficiently small such that the condition:

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

is fulfilled, one may expect thermal instability. As an example, one may ask for the particle size where thermal energy is large enough to lift the particle. In the simplest case, one estimates the energy necessary to lift a particle of density ρ over the elevation x: $u(v) = \rho v x = kT$. Assuming a zirconia particle with a density of $5.6 \times 10^3\,\mathrm{kg\,m^{-3}}$, at room temperature the thermal energy would lift a particle of diameter 1100 nm to a height equal to the particle diameter d. If one asks how high might a particle of 5 nm diameter jump, these simple calculations indicate a value of more than 1 m. Clearly, although these games with numbers do not have physical reality, they do show that nanoparticles are not fixed, but rather are moving about on the surface. By performing electron microscopy, this dynamic becomes reality and, provided that the particles and carbon film on the carrier mesh are clean, the specimen particles can be seen to move around on the carbon film. On occasion, however, this effect may cause major problems during electron microscopy studies.

Although the thermal instability shown here demonstrates only one of the consequences of smallness, when examining the other physical properties then an important change in the behavior can be realized. Details of the most important phenomenon within this group – superparamagnetism – are provided in Chapter 8. In the case of superparamagnetism, the vector of magnetization fluctuates between different "easy" directions of magnetization and these fluctuations may also be observed in connection with the crystallization of nanoparticles. In a more generalized manner, thermal instabilities leading to fluctuations may be characterized graphically, as shown in Figure 2.11.

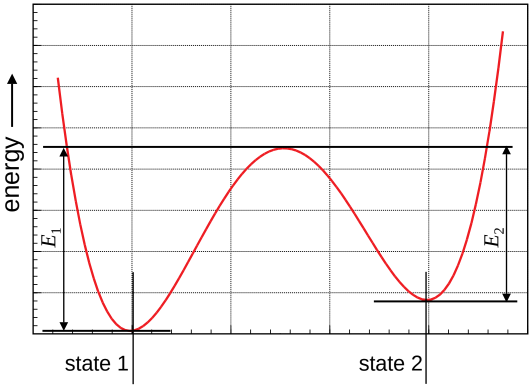

Figure 2.11 Graphical representation of the energy barrier, showing the energy necessary to jump from state 1 to state 2 and vice versa.

Provided that the thermal energy kT is greater than the energies E_1 and E_2, the system fluctuates between both energetically possible states 1 and 2. Certainly, it does not make any difference to these considerations if E_1 and E_2 are equal or more than two different states are accessible with thermal energy at temperature T.

The second example describes the temperature increase by the absorption of light quanta. Again, a zirconia particle with density $\rho = 5.6 \times 10^3\,\mathrm{kg\,m^{-3}}$, a heat capacity $C_p = 56.2\,\mathrm{J\,mol^{-1}\,K^{-1}}$ equivalent to $c_p = 457\,\mathrm{J\,kg^{-1}\,K^{-1}}$, and, in this case, a particle diameter of 3 nm is assumed. After the absorption of one photon with a wavelength, λ, of 300 nm, a photon, which is typical for the UV-range, the temperature increase ΔT is calculated from $c_p \rho v \Delta T = h\nu = \eta(c/\lambda)$ (c is the velocity of light and h is Planck's constant) to 18 K. Being an astonishingly large value, this temperature increase must be considered when interpreting optical spectra of nanomaterials with poor quantum efficiency or composites with highly UV-absorbing kernels.

2.2.3
Diffusion Scaling Law

Diffusion is controlled by the two laws defined by Fick. The solutions of these equations, which are important for nanotechnology, imply that the mean square diffusion path of the atoms $\langle x \rangle^2$ is proportional to Dt, where D is the diffusion coefficient and t is the time. The following expression will be used in further considerations:

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

Equation (2.4) has major consequences, but in order to simplify any further discussion it is assumed that $\langle x \rangle^2$ is proportional to the squared particle size. The angular brackets $\langle\,\rangle$ denote the mean value. Conventional materials usually have grain sizes of around 10 μm and it is well known that at elevated temperatures these materials require homogenization times of the order of many hours. When considering materials with grain sizes of around 10 nm (which is 1/1000 of the conventional grain size), then according to Eq. (2.4) the time for homogenization is reduced by a factor of $(10^3)^2 = 10^6$. Hence, a homogenization time of hours is reduced to one of milliseconds; the homogenization occurs instantaneously. Indeed, this phenomenon is often referred to as "instantaneous alloying." It might also be said that ". . . each reaction that is thermally activated will happen nearly instantaneously" and therefore it is not possible to produce or store nonequilibrium systems (which are well known for conventional materials) at elevated temperature. While this is an important point in the case of high-temperature, gas-phase synthesis processes, there are even more consequences with respect to synthesis at lower temperatures or the long-term stability of nonequilibrium systems at room temperature. The diffusion coefficient D has a temperature dependency of $D = D_0 \exp(-Q/RT)$, with the activation energy Q, the gas constant R, and the temperature T. The quantity D_0 is a material-dependent constant. However, on returning to the previous example, for a material with 10 µm grain size, we can assume a homogenization time of 1000 s at a temperature of 1000 K, and two different activation energies of 200 kJ mol^{-1} (which is typical for metals) and 300 kJ mol^{-1} (which is characteristic for oxide ceramics). The homogenization times for the 10-µm and 5-nm particles are compared in Table 2.1. In terms of temperature, 1000 K for gas-phase synthesis, 700 K for microwave plasma synthesis at reduced temperature, and 400 K as a storage temperature with respect to long-term stability, were selected. The results of these estimations are listed in Table 2.1.

The data provided in Table 2.1 indicate that, under the usual temperatures for gas-phase synthesis (1000 K and higher), there is no chance of obtaining any nonequilibrium structures. However, when considering microwave plasma processes, where the temperatures rarely exceed 700 K, there is a good chance of obtaining nonequilibrium structures or combinations of such materials. A temperature of 400 K represents storage and synthesis in liquids, and at this temperature, the 5-nm particles are stable; however, from the point of thermal stability, it should be straightforward to synthesize nonequilibrium structures. However, according to Gleiter, diffusion coefficients up to 20 orders of magnitude larger than those for

Table 2.1 Relative homogenization time (s) for 5-nm nanoparticles at activation energies of 200 and 300 kJ mol^{-1} compared to 10-µm material at 1000 K[a)].

Particle size	**Activation energy (kJ mol^{-1})**	**Temperature (K)**		
		1000	**700**	**400**
10 µm	300	10^3	5.0×10^9	2.8×10^{26}
	200	10^3	2.9×10^7	4.3×10^{18}
5 nm	300	2.4×10^{-4}	1.3×10^3	7.0×10^{19}
	200	2.4×10^{-4}	7.3×10^0	1.1×10^{12}

a) Assumed homogenization time = 1000 s.

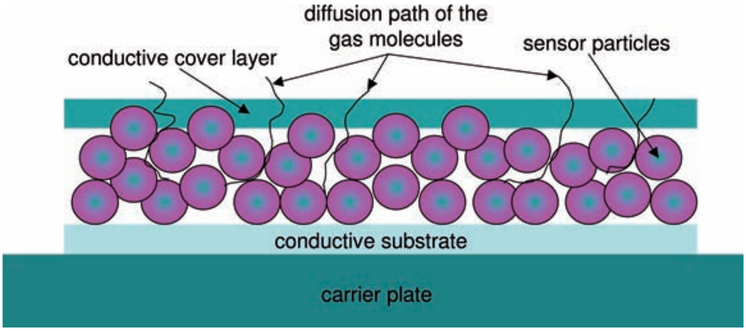

Figure 2.12 General layout of a gas sensor based on nanoparticles. The sensor comprises a layer of sensing nanoparticles placed on a conductive substrate and the whole system is covered with a gas-permeable electrode. Time control is via diffusion in the open pore network; the influence of bulk diffusion through the grains is negligible.

single crystals of conventional size were occasionally observed for nanomaterials [7]. Diffusion coefficients of such magnitude do not allow the synthesis and storage of nonequilibrium nanoparticles under any conditions. It should be noted that the above discussion is valid only in cases where transformation from the nonequilibrium to the stable state is not related to the release of free energy.

The possibility of near-instant diffusion through nanoparticles has been exploited technically, the most important example being the gas sensor. This is based on the principle that changes in electric conductivity are caused by changes in the stoichiometry of oxides, variations of which are often observed for transition metals. The general design of such a sensor is shown in Figure 2.12.

This type of gas sensor is set up on a conductive substrate on a carrier plate and the surface of the conductive layer covered completely with the oxide sensor nanoparticles. Typically, for this application, nanoparticles of TiO_2, SnO_2, and Fe_2O_3 are used. A further conductive cover layer is then applied on top of the oxide particle; it is important that this uppermost layer is permeable to gases. A change in the oxygen potential in the surrounding atmosphere causes a change in the stoichiometry of the oxide particles, which means that the oxygen/metal ratio is changed. It is important that this process is reversible, as the oxides are selected to show a large change in their electric conductivity as they change stoichiometry. The response of a sensor made from conventional material with grains in the micrometer size range, compared to a sensor using nanomaterials, is shown in Figure 2.13. Clearly, the response of the nanoparticle sensor is faster and the signal better but, according to Eq. (2.4), one might expect an even faster response. In a sensor using nanoparticles (see Figure 2.13) the time constant depends primarily on the diffusion of the gas molecules in the open-pore network and through the conducting cover layer.

The details of a gas sensor, which was developed following the design principle shown in Figure 2.12 is illustrated in Figure 2.14. Here, the top electrode was a sputtered porous gold layer and a titania thick film was used as the sensing material.

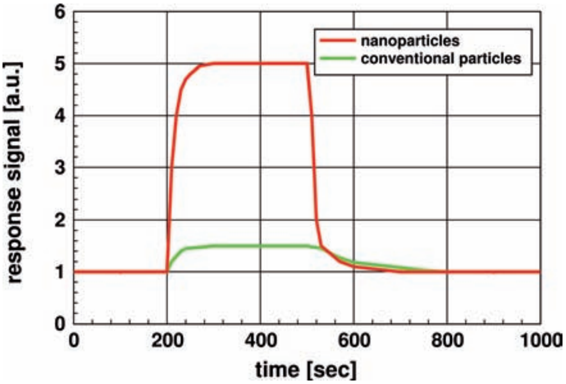

Figure 2.13 Comparative response over time of two gas sensors utilizing a conventional material with grain size either in the micrometer or nanometer range (www.boulder.nist.gov/div853/Publication%20files/NIST_BCC_Nano_Hooker_2002.pdf).

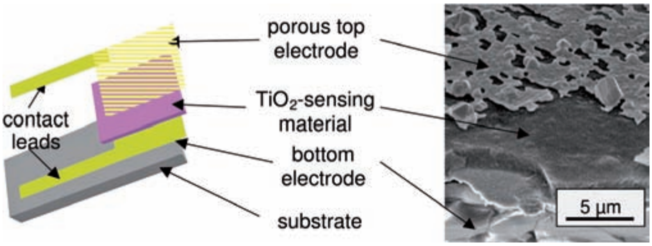

Figure 2.14 Gas sensor following the design principle shown in Figure 2.12 (Cho and Hahn, TU Darmstadt, private communication). The titania-sensing particles are placed on a gold electrode and the top electrode is gas permeable (this is clearly visible in the image at the right-hand side of the figure).

A further design for a gas sensor applying platinum bars as electrical contacts is shown in Figure 2.15. Although this design avoids the response-delaying conductive surface layer, the electrical path through the sensing particles is significantly longer. However, it would be relatively straightforward to implement this design in a chip.

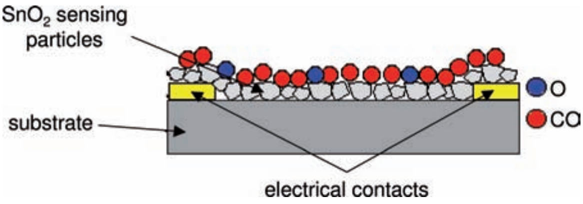

Figure 2.15 Sensor design applying platinum bars as electrical contacts. The sensing nanoparticles (e.g., SnO_2) are located between these contacts. The molecules to be detected (in this example oxygen and CO) are shaded dark and light gray, respectively. (Note the molecules and nanoparticles are not drawn to the same scale.)

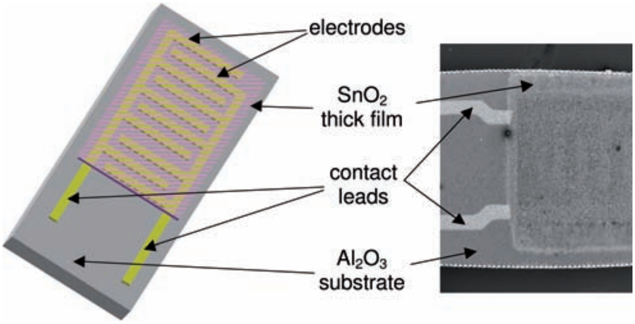

Figure 2.16 Gas sensor in which a SnO_2 thick film made from nanoparticles is applied as the sensing element (Barunovic and Hahn,TU Darmstadt, private communication).

An experimental sensor using the design principles explained above is shown in Figure 2.16; this design uses SnO_2 as the sensing material, while the contacts and contact leads are made from platinum.

The response of this sensor is heavily dependent on the size of the SnO_2 particles used as the sensing material, there being a clear increase in the sensitivity of detection for carbon monoxide (CO) with decreasing grain size (see Figure 2.17). Such behavior may occur for either of two reasons: (i) that there is a reduced diffusion time, according to Eq. (2.3) and (ii) that there is an enlarged surface, thereby accelerating exchange with the surrounding atmosphere.

For the successful operation of a thick-film sensor, it is a necessary prerequisite that the sensing layer be prepared from nanoparticles consisting of a highly porous structure that allows a relatively rapid diffusion of the gas to be sensed. A scanning electron microscopy image of the characteristic structure of such a SnO_2 thick-film

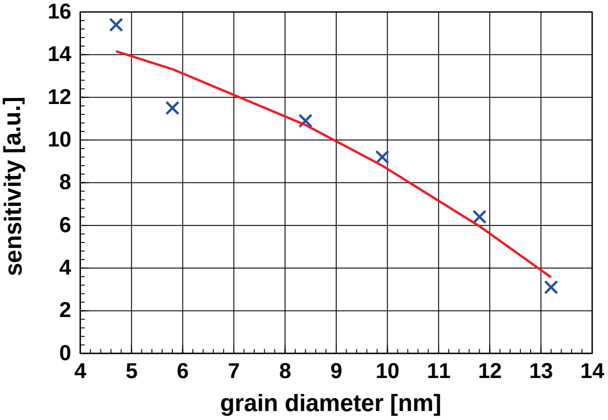

Figure 2.17 Sensitivity of CO determination of a gas sensor designed according to Figure 2.16. A significant increase in sensitivity is achieved with decreasing grain size (Barunovic and Hahn, TU Darmstadt, private communication).