Nanoscience

Nanoparticulate Functional Materials
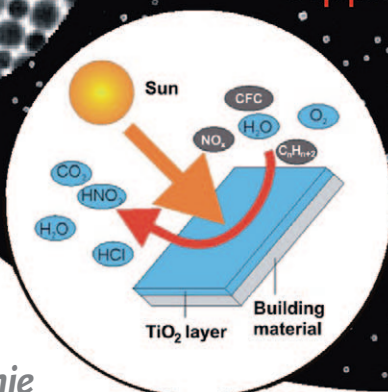
Helmut Goesmann and Claus Feldmann*

*Dedicated to Professor Martin Jansen on the
occasion of his 65th birthday*

Nanocomposite

Particle size
Agglomeration
Surface functionalization

... Nanoparticles ...

Properties
Function
Application

Sun · CFC · H₂O · O₂ · NO₅ · C₅H₅₊₂ · CO₂ · HNO₃ · H₂O · HCl

TiO₂ layer · Building material

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Chemie

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*N*anoparticulate functional materials offer manifold perspectives for the increasing miniaturization and complexity of technical developments. Nanoparticles also make a major contribution to utilization of materials that is sparing of natural resources. Besides these obvious aspects, however, the importance of nanoparticles is due to their fundamentally novel properties and functions. These include photonic crystals and efficient luminophors, single particles and thin films for electronic storage media and switching elements, magnetic fluids and highly selective catalysts, a wide variety of possibilities for surface treatments, novel materials and concepts for energy conversion and storage, contrast agents for molecular biology and medical diagnosis, and fundamentally novel forms and structures of materials, such as nanocontainers and supercrystals. Creating high-quality nanoparticles requires that numerous parameters, involving the particle core and surface, colloidal properties, and particle deposition, are taken into consideration during synthesis of the material. An appropriate characterization and evaluation of the properties requires the incorporation of a wide range of expertise from widely differing areas. These circumstances are what challenges and appeals to the nanoscientist.

From the Contents

1. Introduction

Even the mere number of publications on nanoparticles (NPs) appearing annually makes it obvious that the field has achieved substantial importance on the one hand and a certain degree of maturity on the other. The term "nanoparticle" (at first termed "small particles") first appeared in the 1980s.[1] Even after few years, the number of publications increased incredibly (1990: ca. 20, 1995: ca. 300, 2000: ca. 2100).[2] In total, this development corresponds to epidemic growth,[3] which is now experiencing initial saturation at a very high level (2008: ca. 16000 publications).[2] Similar growth with a certain delay can be seen in the sales volumes of industrial products and the totals of government subsidies. So overall, it is quite an active research field of great current interest, in which sometimes euphoric expectations are placed.

With all these expectations of a scientific topic that is very much in fashion, the question arises as to what the current situation of nanoparticles as an aspect of the "nanosciences" or "nanotechnology" is and what value is being created for modern society now and in the future. Out of the broad field of nanosciences and nanotechnology, this Review selects nanoparticulate functional materials and summarizes the main research activities of recent years. The emphasis is on the special properties and functions of NPs and their importance for science and technology, which is illustrated and assessed by selected examples. First, we will delimit the term "nanoparticles" and discuss some fundamental considerations of their historical development, general synthesis concepts, and special properties. Next, the properties and functions of nanoparticulate functional materials are discussed in detail and subdivided into optical, electronic/electrical, magnetic, and catalytic properties. The improve-

ment of materials and surface finishing, which are of great commercial relevance, as well as the visionary field of "nanocontainers", molecular particles, and particulate crystals, are also presented.

Overall, the materials discussed below and their properties range as widely as the nanosciences themselves. The pronounced interdisciplinary nature—with contributions from chemistry, physics, biology, materials sciences, all the way to engineering and medicine—is perhaps one of the most striking features of the nanosciences, compared to many classical disciplines, and is vital to the development of nanotechnological products. The breadth of the topic makes a clear limitation of this Review an absolute necessity. Therefore, we will only consider chemical synthesis as the portal to high-quality nanoparticles in as much as it lays the foundation for the quality and formation of the desired properties of the material. Furthermore, with respect to specific synthesis concepts, we refer the reader to a number of current reviews.[4] In accordance with the title, nanorods and nanotubes,[5] as well as organic nanoparticles and inorganic–organic composites,[6] will only be discussed in certain individual cases. Here, too, we refer the reader to current

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review articles. And finally, even for the topics presented below, there is such a large number of original papers that it is necessary to restrict ourselves to fundamental aspects and current highlights.

2. What Are "Nanoparticles"?

This introductory section serves to introduce the reader to the topic and is intended to make it accessible even to the nonspecialist. First, we will classify the concept "nano" and present some milestones of the historical development, important synthesis concepts, and the special properties of nanoparticles.

2.1. General Classification

The term "nano" is derived from the Greek word for "dwarf", "nanos". This etymology, and its placement on the metric scale ($1\,\text{nm} = 10^{-9}\,\text{m}$), make it clear that tiny dimensions not visible to the naked eye, beyond the normal limits of our observation, are involved. Approaching it from familiar terrain may make the "nanoworld" more easily accessible (Figure 1). The diameters of hairs, cells (such as red blood
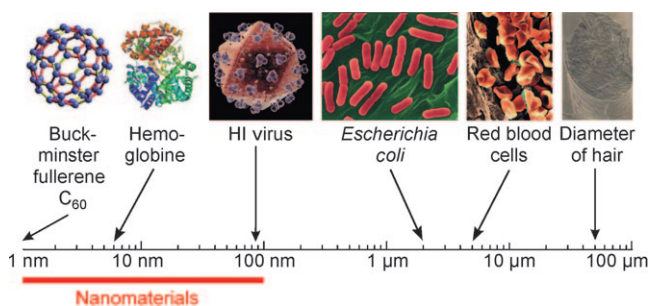

Figure 1. Length scale for classifying nanoparticles.

cells), bacteria (such as Escherichia coli), viruses (such as the HI virus), or molecules (such as hemoglobin or the buckminsterfullerene C_{60}) can serve as path marks here. On this length scale, bodies with lateral dimensions less than 100 nm are

typically termed nanoparticles. This classification is somewhat arbitrary, but it is largely established in the scientific literature and also covers well the range in which specific properties of materials become size-dependent and differ from those of three-dimensional infinite solids.

Characteristic of nanoparticles, besides their small size, is their vast surface area. A simple thought experiment will serve to illustrate this concept (Figure 2). Take a cube with
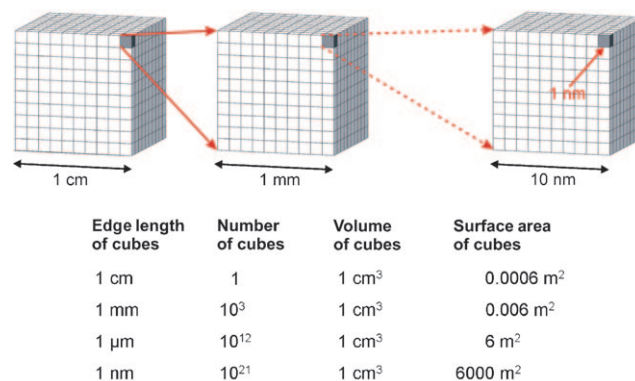

Edge length of cubes	Number of cubes	Volume of cubes	Surface area of cubes
1 cm	1	1 cm^3	0.0006 m^2
1 mm	10^3	1 cm^3	0.006 m^2
1 µm	10^{12}	1 cm^3	6 m^2
1 nm	10^{21}	1 cm^3	6000 m^2

Figure 2. Surface area of NPs: a simple model.

edges 1 cm in length—roughly the size of a sugar cube—at divide it step by step into cubes with edges 1 nm in length. While the sum of the volumes remains the same, the number of individual cubes and their total surface area increases dramatically. The surface area of the 10^{21} "nanocubes", at 6000 m^2, amounts to roughly the area of a football field (ca. 7000 m^2)—created from a single sugar cube! Compared to an infinite three-dimensional solid (aptly expressed by the term "bulk"), with nanoparticles we may expect that their physicochemical properties are strongly influenced, if not indeed dominated, by the surface. Unsaturated bonding sites and unoccupied coordination sites will play a major role, compared to a highly ordered crystalline solid.

The increasing number of weakly bound surface atoms is directly reflected in changes in the physicochemical properties. A prominent example of this phenomenon is the lowering of the melting point as the number of surface atoms increases. This behavior was first observed experimen-

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Claus Feldmann studied chemistry (degree in 1991) at the University of Bonn, where he obtained his doctorate in inorganic solid-state chemistry in 1994 under Martin Jansen. After postdoctoral study with Hans-Georg von Schnering at the Max-Planck-Institute for Solid-State Research in Stuttgart, he moved to industry (Philips Research Laboratories), where he worked in the field of luminescence research. At the same time, he completed his habilitation at RWTH Aachen on the subject of nanomaterials. In 2003, he was appointed to Chair I in Inorganic Chemistry at the University of Karlsruhe. His research interests include the synthesis, characterization, and properties of solids and nanomaterials.

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tally in the 1950s and 1960s for tin by Takagi and Wronski[7] and is particularly well-documented for gold nanoparticles[8] (Figure 3). A further example is the drastic increase in the chemical reactivity of nanoparticles as the particle diameter decreases, a phenomenon which is well known for pyrophoric iron.[9]
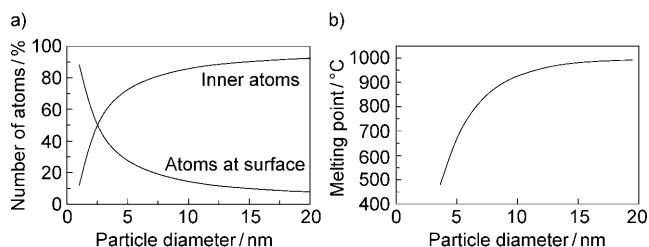
Figure 3. a) Number of surface and inner atoms as a function of particle diameter and b) correlation between particle diameter and melting point of gold NPs (modified reproduction of ref. [8b]).

2.2. Nanoparticles in Retrospect

In fact, the historical roots of nanoparticles date back far beyond their current intensive scientific study. This is true of both the deliberate manufacture and the utilization of nanoparticles. A few illustrative examples suffice as documentation. The dyeing of glass by freshly precipitated colloidal solutions of gold was already known in late Greco-Roman times.[10] Red-violet hues are typical, but also purple and wine-red variations, which have found wide use in glass and porcelain manufactories since the eighteenth century (Figure 4). The surprising variety of colors is due to colloidal
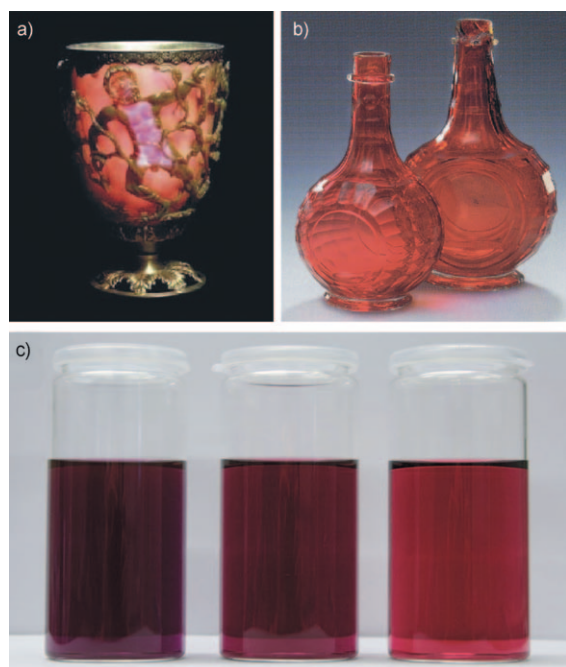
Figure 4. a) Late Roman Lycurgus cup, b) baroque ruby glass, and c) colloidal Au NPs (modified reproduction of (a) and (b) from ref. [19]).

gold particles with typical diameters ranging from 1 to 50 nm, and the correlation of the particle size with the plasmon resonance which causes the color.[11] The optical absorption as a physical property of the gold nanoparticles is thus size-dependent and differs from the bulk property—a finding that is now known as a quantum size effect.[12] The names of Cassius and Faraday stand for the deliberate synthesis of such gold nanoparticles and the description of their properties.[13] The colored nanoparticles of gold that can be obtained by the reduction of alkaline metal tetrachloroaurates(III) with tin(II) chloride, which are still known as "purple of Cassius", also make it clear that it can be very simple to obtain nanoparticles.[14] It was Faraday who recognized the connection between the color and the size of the particles (Figure 4).[15] Today, gold nanoparticles are manufactured industrially and are still used for dyeing glass as well as finding applications as biomarkers (see Section 3.1) or catalysts (see Section 6.1).

Suntan lotion as protection against ultraviolet radiation is another application for nanoparticles that has been commercially significant for quite a long time.[16] The TiO_2 or ZnO nanoparticles (diameter 30–80 nm) contained in suntan lotion can serve as a simple example of the optical transparency of thin layers of nanoparticles when the size of the nanoparticles is well below the wavelength of visible light (380–780 nm).[17] While a thick layer of suntan lotion appears milky white because of diffuse multiple scattering at the nanoparticles, a thin layer on the skin is transparent and no longer visible to the human eye. Generally speaking, this optical transparency can be achieved more readily the smaller the particle diameters are (Figure 5). A third field of applications for
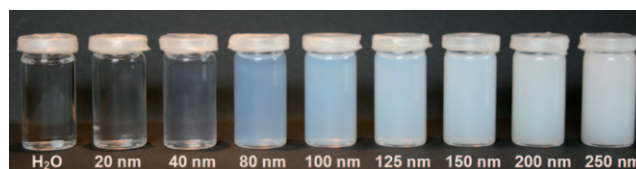
Figure 5. Suspensions with SiO_2 NPs of various sizes and partial blue tint from Rayleigh scattering (modified reproduction of ref. [20]).

nanoparticles worth mentioning is heterogeneous catalysis.[18] Since the catalyzed reaction occurs only on the surface, the available catalyst surface area correlates directly with the turnover of material. And especially in the case of the noble metals, the cost advantage of nanoparticles is obvious. In retrospect, heterogeneous catalysis is one of the first examples of a major industrial relevance of nanoparticles.[18a]

The examples cited make it clear that nanoparticles acquired commercial and technical importance at a very early date, sometimes without knowledge of the sizes involved and their significance. The scientific basis for systematic study and description of nanoparticles was first established with colloid chemistry at the beginning of the twentieth century. Some of its important pioneers were Michael Faraday, Thomas Graham, Marian Smoluchowsky, Richard Zsigmondy, and Wilhelm and Wolfgang Ostwald.[21] Many of the concepts they developed can be applied directly to nanoparticles. With

respect to the scale of sizes, nanoparticles can certainly be regarded as examples of particularly small colloids. On the other hand, nanoparticles require synthesis strategies and display properties that go well beyond classical colloid chemistry. Another milestone is the development of effective analytical methods, without which observation and specific study of nanoparticles is not possible. Of outstanding importance for this field are the techniques of electron microscopy and force-field microscopy.[22] These methods form the basis for nanometer-scale manipulators, analytical in situ techniques, and three-dimensional holographic imaging methods that are available today.[23]

But to assess modern nanoparticles properly, it must be said that, despite all scientific progress, the degree of structuring, complexity, and functionality that occurs in nature has not been reached yet. This is obviously true of all living creatures and each individual cell. But opals with a comparatively simple structure and the highly complex SiO_2 structure of diatoms make it apparent that nature is also a good model in the field of inorganic nanostructures (Figure 6). However, nature has one essential parameter at its disposal in abundance, of which scientists only have a limited amount: time.
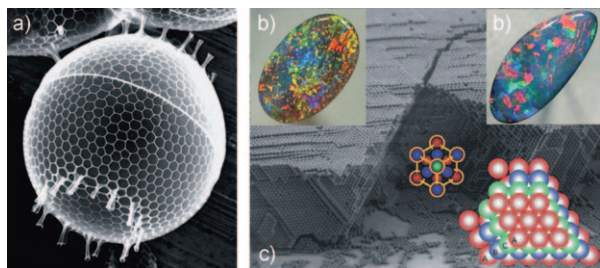

Figure 6. Inorganic nanostructures in nature: a) SiO_2 frustule of diatoms and b,c) natural opals: photos (b) and electron-microscope image (c; modified reproduction of ref. [24]).

2.3. Special Properties of Nanoparticles

Those properties of nanoparticles which differ from the properties of the bulk material are of particular interest. Otherwise, the importance of nanoparticles would be limited to the aspects of savings in materials and expenses, and of miniaturization, which are indeed of the greatest importance commercially. The differences between nanoparticles and bulk material can be assigned qualitatively to three subgroups:

1) Surface-dependent particle properties: These are properties which in principle the bulk material also displays, but which only become dominant in nanoparticles owing to the high surface-to-volume ratio. Typical examples are the higher turnover of nanoparticle catalysts already mentioned (see Section 6.1), the higher chemical reactivity of nanoparticles (e.g. pyrophoric iron),[9] soil-repellent surfaces (e.g. Lotus effect, Section 7.1), the surface conductivity of nanoparticulate oxides (e.g. the Grätzel cell, Section 4.3), and in general numerous thin-film applica-

tions (e.g. thin-film capacitors, Figure 7, Sections 4.2, 4.3, and 7.1).
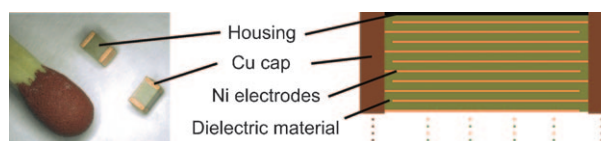
Figure 7. Photograph and schematic depiction of thin-film capacitors, which are composed in alternating layers of 200 electrodes (e.g. Ni) and 200 dielectric layers (e.g. $BaTiO_3$).

2) Size-dependent particle properties: Many properties of nanoparticles are directly related to their small size. Among these are optically transparent layers (e.g. pigments, thin-film electrodes, coatings; Sections 3.1, 4.2, 4.3, and 7.1), interference effects (e.g. Bragg stacks, photonic crystals; Section 3.2), superparamagnetic nanoparticles (Section 5.1), and applications in molecular biology and medicine (Figure 8, Sections 3.1, 3.3, and 5.2).
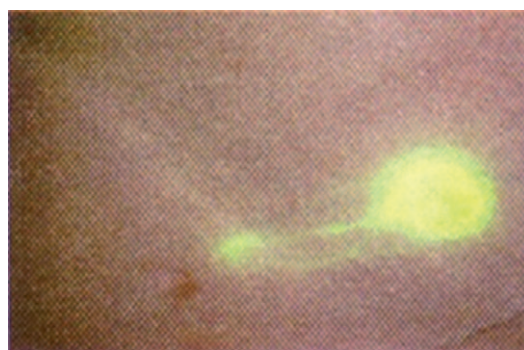

Figure 8. Detection of a lymph-gland carcinoma by optical imaging with NIR quantum dots (modified reproduction of ref. [25]).

3) Size-dependent quantum effects: If the electronic structure of nanoparticles is influenced directly by their size, the phenomena are called size-dependent quantum effects. These are due to the transition from an atom or molecule with defined energy levels to the dispersed bands of collective ensembles of atoms and finally of the bulk material. Prominent examples are the shift of the plasmon resonance of gold nanoparticles discussed above (Sections 2.2 and 3.1) and the size-dependent color and luminescence of semiconductor quantum dots (Figure 9, Section 3.3).[26]

2.4. Approaches to the Synthesis of Nanoparticles

There are a wide variety of synthetic methods for obtaining nanoparticles, which can be divided into three groups: 1) grinding methods (wet and dry grinding, reactive grinding, etc.);[27] 2) gas-phase methods (chemical vapor deposition (CVD), laser ablation deposition (LAD), sputtering techniques, etc.);[28] 3) liquid-phase syntheses (forced hydrolysis, hydrothermal synthesis, sol-gel process, micro-
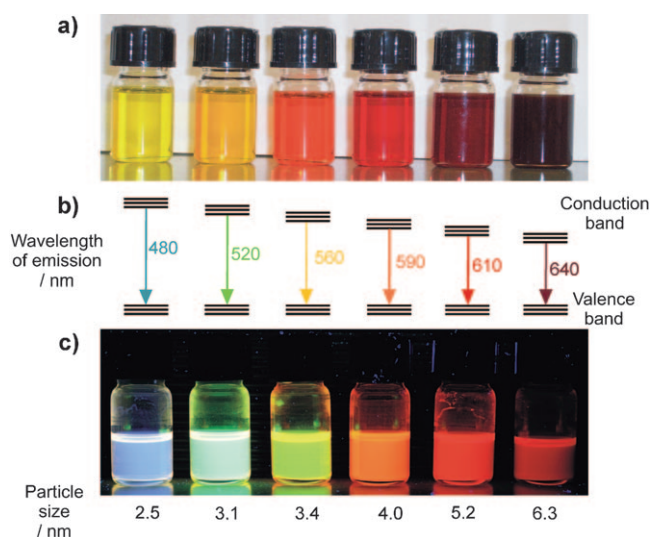
Figure 9. CdSe semiconductor quantum dots as nanoscale lumino-phors: a) Surface color of suspensions in toluene in visible light. b) Schematic diagram of band gap and emission color as a function of particle size. c) Light emission of suspensions in toluene when excited with UV light.

emulsion method etc.).[4, 29] Besides the particle size itself, other aspects must be taken into account for high-quality nanoparticles. These include a size distribution that is as monodisperse as possible, effective suppression of agglomeration processes, and well-directed control of the surface functionalization. Furthermore, the boundary conditions of specific compositions and the requirements of specific properties of the material limit the potentially applicable synthesis methods.

In general, when grinding processes are employed, appreciable agglomeration and contamination by material abraded from the grinding body must be expected. Very small particles (diameter < 50 nm) are usually only obtainable to a limited degree. For technical processes, grinding methods are extremely important, as they allow even large quantities of substance to be obtained inexpensively. Gas-phase methods are typically employed as continuous processes that provide crystalline nanoparticles with largely noncovered surfaces. However, owing to the high synthesis temperatures (above 500 °C), such approaches may result in the formation of hard aggregates that are difficult to separate into primary particles. Also, the formation of complex multinary phases can be hindered or even prevented by segregation processes at high temperatures. Since gas-phase reactions are usually subject to thermodynamic control, the production of compounds that are metastable under synthesis conditions is only possible to a limited degree.

In liquid-phase syntheses, particle size and agglomeration behavior can usually be controlled effectively. The reactive surfaces can be saturated with functionalized organic molecules as stabilizers immediately after nucleation. Typically, these stabilizers are long-chain alkyl compounds, tensides, or polymers.[30] With the aid of such stabilizers, it is possible to control the shape of nanoparticles, permitting a wide variety ranging from simple spheres through lenticular and rod-

shaped forms to nanoparticle tetrahedra, octahedra, cubes, or stellate shapes.[4b, 31] However, the use of high-molecular-weight organic stabilizers can be a disadvantage if they have undesired effects on the properties and function of the nanoparticles after completion of the synthesis. For example, the quantum yield of luminescent nanoparticles (Section 3.3), the conductivity of thin-film electrodes (Sections 4.2 and 4.3), or the catalytic activity of nanoparticles (Sections 6.1 and 6.2) can be reduced considerably by unsuitable surface functionalization. It is possible to burn out organic stabilizers, but this requires temperatures above 500 °C and usually results in the formation of agglomerates, which either may still be separable into primary particles if appropriate force is applied, or may not be physically separable at all.

Because many nanoparticles of varying compositions and a wide range of sizes, shapes, surface functionality, and material properties can be obtained well by liquid-phase methods, most of the nanoparticulate functional materials presented below are prepared in this way. In accordance with this importance, we discuss some boundary conditions in more detail; many aspects apply in principle to gas-phase syntheses, as well. As current reviews of liquid-phase syntheses of nanoparticles are available,[4, 29] our discussion is focused more on fundamental aspects. Starting from a homogeneous liquid phase, the synthesis of high-quality nanoparticles, that is, those with a defined diameter, almost monodisperse size distribution, and small degree of agglomeration, can in general be limited to two major boundary conditions: 1) precisely directed control of nucleation and nucleus growth; 2) effective suppression of agglomeration processes.

According to the model of LaMer and Dinegar, nucleation is an endothermic process (Figure 10).[32] The splitting of
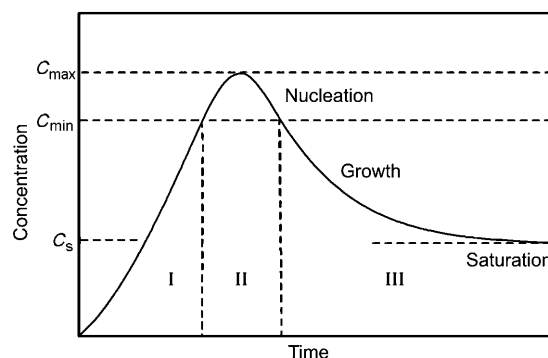
Figure 10. LaMer and Dinegar's model to describe nucleation and nucleus growth (modified reproduction of ref. [32]).

bonds in the initial compounds, the removal of solvate shells, and overcoming the surface tension of the solvent require energy. Nucleus growth and Ostwald ripening, on the other hand, are exothermic processes that release the enthalpy of formation of the solid, such as lattice binding energy.[33] Therefore, the formation of infinite solids is always energetically favored over nanoparticles with their large surface areas, unsaturated bonding sites, and unoccupied coordination sites.[34] The agglomeration of the nanoparticles is also

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energetically favored, as it minimizes surface areas and saturates the bonding and coordination sites (Figure 11).

In principle, the synthesis of nanoparticles is not difficult, especially if the resultant solid is of low solubility. Everyone
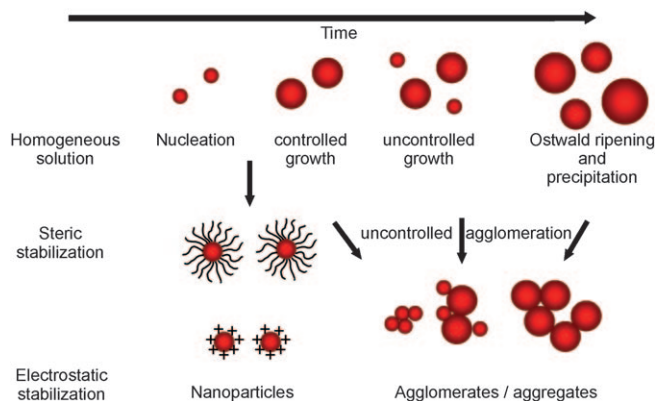
Figure 11. Growth and stabilization of nanoparticles.

who has taken a laboratory course in qualitative or quantitative chemistry will remember a precipitation reaction whose product runs through every filter (e.g. CdS, AgBr). Although not desired at that point, the precipitate is very likely to consist of nanoparticles.[35] At this point, the range of methods of the nanoscientist comes into play, in order to control reactions and equilibria in the desired way (Figure 11). To prevent a premature switch from nucleation to nucleus growth, the addition of a certain amount of activation energy (e.g. by performing the reaction at a higher temperature) is helpful. It is also useful to establish a high degree of supersaturation in the homogeneous phase and to reduce it again by nucleation as directly and exclusively as possible. The "hot injection" method, a standard synthesis for obtaining quantum dots developed by Bawendi and co-workers (Section 3.3), illustrates the potential of this strategy impressively (Figure 11).[36] And finally, the particle surfaces should be saturated immediately after nucleation by electrostatic or steric stabilization to protect the nanoparticles from further growth or agglomeration (Figure 11).[37] Electrostatic stabilization can be achieved by targeted adsorption of ions (H$^+$, OH$^-$, SO$_4^{2-}$, NO$_3^-$, RCOO$^-$, RSO$_3^-$, R$_4$N$^+$, etc.) on the particle surface. Steric stabilization is realized by adsorption of long-chain organic molecules (e.g. oleyl amine, oleic acid, trioctyl phosphine, trioctyl phosphine oxide). Both options are standard methods in colloid chemistry.[30] And finally, nucleus growth and agglomeration can also be controlled by complete separation of the reaction spaces. In principle, such control is possible by high dilution but can also be achieved by continual removal of the nanoparticles already formed (such as in microfluidic continuous-flow devices).[38]

3. Color, Reflection, and Luminescence

We begin our review of nanoparticulate functional materials with their optical properties, as the wide range of

materials and properties can be illustrated particularly impressively here. They range from absorptive pigments through reflecting Bragg stacks and photonic crystals to luminophors and luminescent biomarkers.
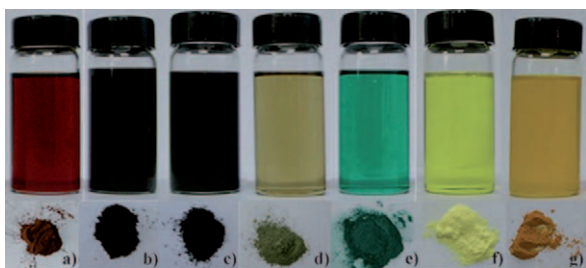
3.1. Transparent Pigments

The basic importance of nanoparticulate pigments for coloring is obvious. However, in this case as in many others, merely replacing conventional bulk-material pigments by nanomaterials is usually out of the question, simply because of the higher manufacturing costs. Nanoparticles are relevant if their use offers options beyond those of a bulk material. In the case of classical pigments, the optical transparency of particulate thin films is such an advantage.[39] Thus substrates such as glass or plastic are colored after embedding of or coating with pigment nanoparticles, but they remain optically transparent (Sections 2.2, 4.2, and 7.1). And the advantages of inorganic pigments over organic dyes, namely their temperature and ultraviolet stability, are retained.[39] Nanoscale pigment particles therefore play an important role, especially for vehicle paint coatings, as color filters in displays, for coloring plastics, and in cosmetics.[40] These also include UV-absorbing nanoparticles such as ZnO or TiO$_2$ in plastics or suntan lotion, which are discussed elsewhere as non-colored materials. (Sections 2.2, 7.1, and 7.2).[16]

As far as the materials properties of the pigment nanoparticles are concerned, their crystallinity requires particular attention. All kinds of defects in the solid state (i.e. defect sites; contaminations; inclusions; domain, grain, or phase boundaries; noncrystalline regions) directly affect the electron excitation and transfer processes, and compromise properties of the material such as color, luminescence (Section 3.3), or electrical conductivity (Section 4.2) compared to the bulk material. A good specific example of this phenomenon is the pigment CoAl$_2$O$_4$, known as "Thénard's blue". If noncrystalline regions, secondary phases such as Co(OH)$_2$ or Al(OH)$_3$, or internal surfaces in the form of grain boundaries exist, they are associated with slight changes in the bond distances and angles. And if the latter differ from those of the crystalline bulk material, the energy split of the d orbitals of the Co^{2+} ion is affected, which in turn is the cause of the color.[41] As a result, CoAl$_2$O$_4$ no longer displays its characteristic brilliant blue color but acquires a reddish-blue or greenish-blue hue. As the crystallinity of the material generally depends on the synthesis temperature, especially liquid-phase syntheses at temperatures over 300 °C require special measures. Noncrystalline nanoparticles, however, can form even at the high temperatures of gas-phase syntheses (over 500 °C), for example if the dwell time in the hot reactor zone is very short.[28] In liquid-phase syntheses, highly crystallized pigments can be obtained by polyol-mediated synthesis, by hydrothermal synthesis and subsequent separation of the ligand-stabilized nanoparticles using phase transfer, or by decomposition of single-component precursors ("single-source precursors"; Figure 12).[42]

Metal nanoparticles whose plasmon resonance falls in the visible range of the spectrum are also interesting as pigments

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Figure 12. Nanoparticulate pigments in cyclohexane (0.1 g in 20 mL) and as powder: a) α-Fe$_2$O$_3$, b) Fe$_3$O$_4$, c) CoFe$_2$O$_4$, d) ZnCo$_2$O$_4$, e) Cr$_2$O$_3$, f) BaCrO$_4$, g) PbCrO$_4$ (modified reproduction of ref. [42c]).

Figure 14. Detection of the nicotine metabolite benzoyl ecgonine in latent fingerprints: a) White-light and b) fluorescent photograph after incubation of anti-benzoyl-ecgonine antibody-functionalized nanoparticles (Au or γ-Fe$_2$O$_3$) and secondary antibodies with red fluorescence (modified reproduction of ref. [48]).

(Section 2.2).[13] With regard to chemical and physical stability, gold and silver are particularly suitable. If the particle size, shape, and surface functionalization are precisely controlled, hues across the entire visible spectrum can be achieved (Figure 4).[43] A method described by Yin and co-workers is especially elegant, in which silver nanoparticles are first produced by simple reduction of AgNO$_3$ with NaBH$_4$ in an aqueous phase. The form of these nanoparticles, and thus their color, can subsequently be deliberately modified by ultraviolet radiation (Figure 13).[44]
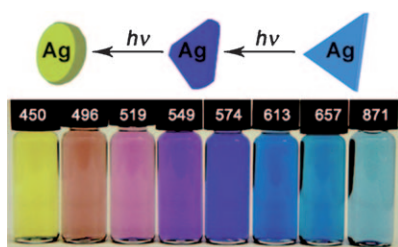
Figure 13. The shape and color of silver nanoparticles can be modified deliberately by UV radiation (modified reproduction of ref. [44]).

Gold and silver nanoparticles have now achieved considerable importance in biosensing, as they can considerably enhance the emission of molecules adsorbed onto the particle surface by means of fluorescence resonance energy transfer (FRET). By excitation of the plasmon resonance, the metal particles act as "nanoantennae". The resulting photoluminescence can be detected by fluorescence spectroscopy or surface-enhanced Raman scattering (SERS) with sensitivity up to a single photon.[45] Such plasmonic nanosensors offer outstanding perspectives for molecular biology, thus enabling detection of sugars, peptides, enzymes, DNA, hormons, and tumor markers, but also of viruses and cells.[46] Even intracellular gene regulation has been directly observed with the aid of oligonucleotide-functionalized gold nanoparticles.[47] Overall, the use of plasmonic nanoparticles in molecular biology is gaining substantially in scope, and the diagnostic techniques thus made possible are gaining in complexity. Another example of an application is described by Russell and co-workers: the immunological detection of nicotine metabolites in latent fingerprints (Figure 14).[48] This approach may well produce a simple test for drug abuse or handling of explosives. In a current paper, Ras et al. describe
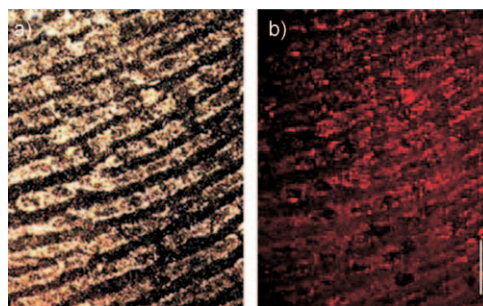
solvatochromic effects of silver nanoparticles, which can be used to distinguish between solvents such as water or methanol or to identify solvent mixtures.[49] On the basis of the success with single particles, the arrangement of plasmonic nanoparticles in the form of supercrystals may well provide a wide variety of options for molecular diagnostics and optoelectronics (Sections 3.2, 4.1, and 8.3).[50] In this context it should be noted that, in addition to their plasmonic properties, gold and silver nanoparticles may also be used in medicine as X-ray contrast media.[51]

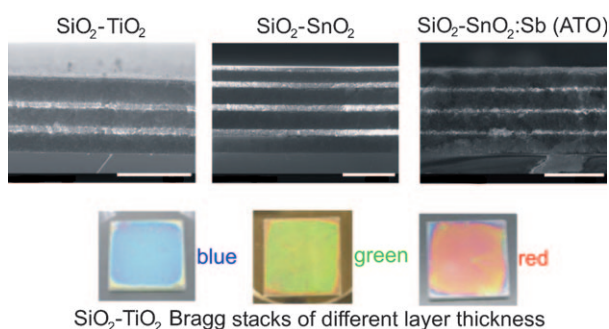### 3.2. Bragg Stacks and Photonic Crystals

In addition to coloration by absorption of light, color effects can also arise from structural interference at nanoparticles. Colloidal particles in the form of Bragg stacks have attracted some attention in this respect.[52] If nanoparticles with different indices of refraction (e.g. TiO$_2$ $n = 2.5$ and SiO$_2$ $n = 1.5$) are deposited alternatingly with a defined layer thickness, the resulting "distributed Bragg reflectors" (DBR) have an intensive "structure-based" color, owing to structural interference. The first-order wavelength (λ_{max}) in reflection depends on the difference of the indices of refraction (n_A, n_B) of the materials used (A, B) and on the respective thickness of the layers (d_A, d_B); it can be determined according to Bragg's law [Eq. (1)].[53]

$$\lambda_{max} = 2\,(n_A\,d_A + n_B\,d_B) \tag{1}$$

Since the relevant layer thicknesses are less than 100 nm, nanoparticles are necessary to produce them (typically by means of spin-coating). It is particularly appealing that with Bragg stacks, various colors can be produced with materials that are themselves colorless (Figure 15).[54] Furthermore, the color can be altered by adsorption of molecules onto the surface of the porous, nanoparticulate matrix if this adsorption is accompanied by a change in the refraction indices or the thickness of the layers.[55] In this way, novel gas sensors or biosensors can be created, for example. Further work by Ozin et al. has shown that the color of Bragg stacks can also be altered by mechanical pressure or by applying electrical

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Figure 15. Structural color of Bragg stacks with different composition and layer thickness; scale bars 1 μm (modified reproduction of ref. [54]).

fields.[56] The possible applications here range from pressure sensors (e.g. for registering fingerprints) to electrochromic displays. And when organic fluorescent dyes, such as rhodamine, are incorporated into Bragg stacks, stimulated emission can be observed after pulsed excitation.[57] The emission wavelength of the resultant one-dimensional laser can be tuned through wide ranges by varying the thickness of the layers or the kind of materials employed.

Besides layered Bragg stacks, modulation of optical density can also be achieved in three dimensions. The aristotype here is the opal, with its three-dimensionally periodic arrangement of monodisperse particles of SiO_2 for closest spherical packing, first described by Sanders (Section 2.2, Figure 5).[58] The refraction of light at the SiO_2–air or SiO_2–water phase boundary (natural opals can contain large amounts of water, which is incorporated between the SiO_2 particles) results in structural colors from interference, which depend on the wavelength of the light, the diameter of the SiO_2 particles, and the angle of observation. In natural opals, while individual domains with diameters of a few hundred micrometers are highly ordered, they are slightly tilted with respect to other domains, resulting in facetted coloring (Figure 6).[24,59] According to the structural principle of the opals, the synthesis of the material aims for a controlled "crystallization" of monodisperse nanoparticles with a high index of refraction to form what are called "photonic crystals", which are highly relevant for optical waveguides, optical memory stores, thresholdless lasers, or optical data processing.[60] An optical band gap, similar to the electronic band gap of semiconductors, is observed (i.e. electromagnetic waves that cannot penetrate into the photonic crystal in a certain range of wavelengths). Photonic crystals are technologically interesting especially if a complete band gap exists (i.e. 100% reflection), which requires a difference in index of refraction greater than 2.8 (e.g. $n(TiO_2)$: 2.9; $n(InP)$: 3.4; cf. $n(SiO_2)$: 1.5).[61] For use in modern optoelectronics, the optical band gap should also lie in the visible part of the spectrum, which requires periodically arranged nanoparticles with diameters less than 350 nm.

Highly-ordered photonic crystals can be obtained in a bottom-up approach by targeted self-organization of individual nanoparticles. This method requires, besides nanoparticles that are as monodisperse as possible, an appropriate surface
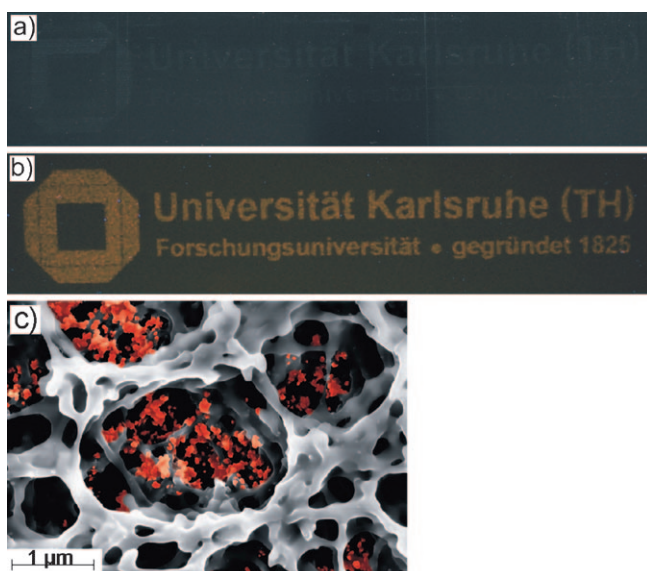
functionalization and a controlled removal of the dispersion medium as slowly as possible. The difficulty is in achieving a three-dimensionally perfect growth of the photonic crystals up to a size of a few millimeters.[62] Even individual lattice imperfections would cause a fault in the periodicity and would be visible to the naked eye as scattering centers.

Photonic crystals have already been created by bottom-up methods, but to date, their reproducibility and size is only of limited use for optoelectronic applications. We should mention here that top-down approaches to obtaining photonic crystals are also known. A two-dimensional modulation of the optical density was created for the first time by mechanical drilling or chemical etching in silicon wafers. These structures, named "yablonovites" after their discoverer,[63] show a partially forbidden band in the microwave or radio-wave region.[64] By means of holographic lithography or direct laser writing as a top-down method, Wegener and co-workers have been able to harden selectively photosensitive polymer matrices with dimensions of a few millimeters and three-dimensional structuring on the nanometer scale.[65] The templates remaining after the nonhardened portions have been dissolved out can then be filled with almost any inorganic material. After complete removal of the template (such as by thermal erosion), the highest quality of photonic crystals to date is obtained. To modify the optical properties, defects can even be incorporated into the matrix in a controlled fashion, which would enable wavelength-specific readouts of optical data.[66] In addition to photonic crystals composed of materials with a high dielectric constant, three-dimensionally periodic arrays have also been implemented with metal or magnetic nanoparticles by top-down methods; these are called metamaterials.[67]

Although top-down methods for obtaining "crystallized" nanoparticle arrays are particularly successful at present, the self-organization of colloidal nanoparticles by bottom-up approaches does offer fascinating possibilities, which we will return to in Section 8.3 with the concepts of "particulate crystals" or "supercrystals".

3.3. Luminophors and Luminescent Biomarkers

Besides the optical properties of absorption and reflection, nanoparticles can also display luminescence. And in principle, nanoparticulate luminophors are of interest for all applications of classical bulk luminophors (i.e. fluorescent lamps, light-emitting diodes, emissive displays, tomographs, image plate detectors).[68] As in the case of pigment nanoparticles, luminophor nanoparticles also only become technically relevant if they offer a decisive advantage over the bulk materials (cf. Section 3.1). Thus luminophor nanoparticles can also be used as optically transparent but luminescent if suitably excited thin layers for marking purposes (e.g. advertising or emergency lighting), or as a security feature (e.g. on banknotes, securities, or identification documents) in or on a wide variety of substrates, such as glass, plastic, or paper (Figure 16).[39] However, luminophor nanoparticles have found their most notable application as luminescent markers in molecular biology and medical diagnosis and

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Figure 16. Transparent layer with LaPO$_4$:Eu nanoparticles on black cardboard a) in daylight, b) under UV light, and c) an electron microscopic image of this layer with LaPO$_4$:Eu nanoparticle (marked red for better visibility) between the paper fibers (modified reproduction of ref. [70]).

therapy; we will return to this topic at the end of this section.[69]

For the practical suitability of nanoparticle luminophors, numerous parameters usually play a role (e.g. absorption and emission characteristics, decay time, chemical or physical stability, costs and reproducibility of manufacture, toxicity of the materials). The weighting of these aspects depends on the specific material and the background of the application and cannot be discussed in more detail here. However, the quantum yield, as a central figure of merit for high-quality luminophors, will be considered in more detail, especially since it can be used to directly illustrate the challenges to material selection and synthesis planning. The quantum yield (here QA) is defined as the ratio between emitted ($N_{emission}$) and absorbed photons ($N_{absorption}$).[71] Its maximum possible value is 100 %, except for multiple-photon luminophors [Eq. (2)].

$$QA = N_{emission}/N_{absorption} \qquad (2)$$

A quantum yield of less than 100 % simply means that some of the electrons in excited states relax without radiation through competing dissipation processes. Technical bulk luminophors accordingly have very high quantum yields (over 80 %).[72] The quantum yield is drastically reduced by any kind of defect in the crystal lattice (cf. Section 3.1) that permits relaxation without radiation.[73] For such dissipation processes, even defects with concentrations of a few hundred parts per million play a major role, and they have even greater weight the longer the lifetime of the excited states is and the farther the excited electrons can travel in the solid state (e.g. via band states, dipole–dipole interactions, or superexchange).[74] And high-energy molecular vibrations (e.g. O−H, N−H, C=O, C≡N, and C=N valence vibrations) can also

lead to nonradiative decay. But even highly crystallized, high-purity, water-free luminophor nanoparticles have a decisive intrinsic defect compared to the bulk material: the surface (cf. Section 2.1). Unsaturated bonding and unoccupied coordination sites result in the surface of the nanoparticles being coated with a layer of adsorbate, which may consist of moisture or solvent molecules. But even an advantageous functionalization of the nanoparticle surfaces from the point of view of colloidal stability by organic molecules or polymers may cause a drastic reduction in quantum yield, owing to molecular vibrations. Both aspects, the surface and surface coating, cause the quantum yield of nanoparticle luminophors to be considerably less than that of bulk-material luminophors, usually at values less than 40 %, unless additional measures are taken (e.g. core–shell structures).

Generally speaking, luminophor nanoparticles can be assigned to three classes of materials: 1) semiconductor quantum dots, 2) doped materials, and 3) organic–inorganic hybrids. Quantum dots such as CdS or CdSe may be considered the most prominent representatives, and they are discussed in a number of current reviews.[75] Major developments are represented by the now well-established syntheses in high-boiling-point, strongly coordinating solvents such as trioctyl phosphine (TOP) and trioctyl phosphine oxide (TOPO). These methods permit both precise control of the size and also effective saturation of the particle surfaces.[76] Such protocols have been extended to other high-boiling-point, coordinating solvents, such as pyridine, oleyl amine, tetradecylphosphonic acid (TDPA), and hexadecylamine (HDA), to make the choice of source materials easier and in particular to replace alkyl metal compounds such as [Cd(CH$_3$)$_2$] by CdO, CdCO$_3$, or Cd(CH$_3$COO)$_2$.[77] By now, a large variety of II–VI, III–V, and IV–IV semiconductor quantum dots (composition MX with M = Zn, Cd, Hg, Sn, Pb, Al, Ga, In; X = S, Se, Te, N, P, As, Sb, and Si, Ge) can be obtained.[78] Owing to the correlation of particle size and luminescence, emission colors over the entire visible spectrum, up into the infrared, can be achieved with only one chemical composition (cf. Section 2.3, Figure 9).

Another milestone was the synthesis of core–shell semiconductor quantum dots. In this case, the luminescent core (e.g. CdSe) is surrounded with a nonluminescent shell (e.g. ZnS) and thus separated completely from the surrounding liquid phase.[79] A precondition is that the lattice spacing of the two materials is very similar (i.e. differs by less than 5 %) so that the core and shell merge without defects at the inner phase boundary. It is also a good idea if the conduction band of the shell material is at a somewhat higher energy level and the valence band at a somewhat lower level than in the core material (known as a "Type 1 structure"). Then excited electrons and holes cannot leave the core and are inside a quasi-surfaceless zero-dimensional solid. CdSe@ZnS (E_g(CdSe): 1.74 eV, E_g(ZnS): 3.61 eV) or InP@ZnS (E_g(InP): 1.35 eV, E_g(ZnS): 3.61 eV) are perfect examples of this concept.[80]

The synthesis of high-quality core–shell quantum dots is by no means easy and requires effective control of nucleation and nucleus growth. This control is now possible with various synthesis paths.[78–80] Precise control of the size is essential for

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the emission properties of the quantum dots. An example of gradual and precise growth is shown by Weller and co-workers for CdS@HgS with interplay between the precipitation and redissolution of CdS and the precipitation of HgS, precisely controlled by means of the differing solubility products (Figure 17).[87] With values of 60–90%, quantum
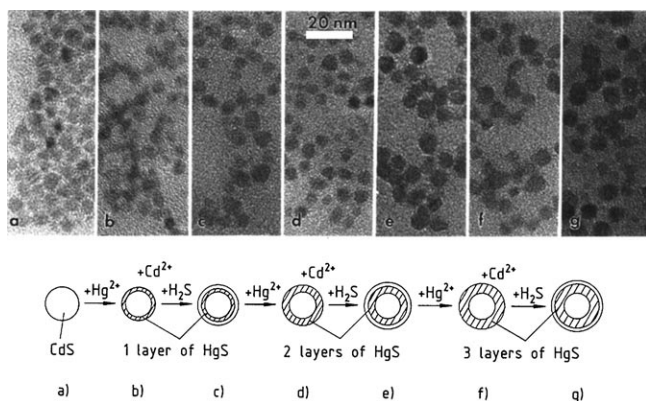

Figure 17. Directed growth of CdS@HgS quantum dots by controlled precipitation and redissolution of CdS and precipitation of HgS in conjunction with an increase in particle diameter from approximately a) 5.0 nm to g) 7.8 nm (modified reproduction of ref. [87]).

dots with a core–shell structure currently have the highest quantum yields for luminophor nanoparticles.[81] However, the increasing complexity of the synthesis and composition of the materials is accompanied by small amounts of the substance and high production costs. And finally, the inherent toxicity of the materials and the sensitivity of the quantum dots to hydrolysis and oxidation, especially over lengthy periods and at increased temperatures, restricts their use.[82] To get around these limitations, extensive work on surface functionalization has been performed, so that the quantum dots, which, owing to the synthesis, occur in nonpolar media, can be dispersed in water-based liquid phases. Moreover, their physicochemical stability and biocompatibility is improved.[83] The use of SiO_2 as a shell on classical II–VI semiconductor quantum dots offers interesting aspects. And by suitable surface functionalization, effective control of the shape can be achieved, including the synthesis of spherical, wedge-shaped, cylindrical, or rod-shaped quantum dots.[84] Furthermore, different emission colors and high quantum yields (i.e. 50–60%) can now also be achieved with less toxic surface-functionalized Si[85] or ZnO[86] nanoparticles.

In addition to quantum dots, solids doped with rare-earth metals or transition metals have also proven to be effective as luminophor nanoparticles. The cause of the emission in this case is the luminescence of individual elementary or molecular ions.[73] Thus no quantum effect is involved but rather a transition between energy states localized at the luminescent center. Concrete examples of high-quality luminophor nanoparticles with different emission colors are $CaWO_4$ (blue),[88] $LaPO_4$:Ce,Tb (green),[89] Zn_2SiO_4:Mn (green),[90] ZnS:Mn (yellow),[91] $Y_3Al_5O_{12}$:Ce (yellow),[92] YVO_4:Eu (red),[93] $(Y,Gd)BO_3$:Eu (red),[94] and Y_2O_3:Eu (red).[95] Examples

with high quantum yield (greater than 50%) continue to be concentrated on relatively few materials, such as $LaPO_4$:Ce,Tb, ZnS:Mn, and YVO_4:Eu. The luminescence mechanism often includes parity-forbidden f→f or d→d transitions, which are partially permitted only because of the reduced symmetry of the solid.[73] Since the decay is correspondingly long (i.e. a few microseconds up to a few milliseconds), permitted competing processes can lead to nonradiative relaxation and thus to a decisive reduction in the quantum yield. Therefore, much the same requirements apply to doped luminophor nanoparticles as to quantum dots. These include high purity and crystallinity of the host lattice and the shielding of the luminescent core by a nonluminescent shell in the form of core–shell structures. Prominent examples are ZnS:Mn@ZnO, $LaPO_4$:Ce,Tb@LaPO_4, and LaF_3:Eu@LaF_3.[96]

Inorganic–organic hybrid materials form the third category of nanoparticle luminophors. An organic fluorescent dye (phenoxazine, Nile red, rhodamine, indocyanine green, fluorescein, etc.) is enclosed in a nanoparticulate inorganic matrix. SiO_2 and calcium phosphate may be considered the most common materials.[97] Nanoparticulate hybrid materials are usually produced by microemulsion techniques in which the organic fluorescent dye is first dissolved in the micelles and subsequently incorporated into the inorganic matrix, for example by hydrolysis of tetraethylorthosilicate. The bond between the matrix and the fluorescent dye is usually based on hydrogen bonds. The molar concentration of fluorescent dye is typically less than 1%, so that the number of luminescent centers per nanoparticle is less than for quantum dots and doped nanoparticles. On the other hand, the low toxicity and the simple synthesis, requiring neither highly crystalline solids nor core–shell structures, are advantages. In a direct development from nanoparticulate hybrid luminophors, an inorganic cation (e.g. the formal building unit $(ZrO)^{2+}$) can be precipitated with an organic fluorescent dye (e.g. flavin mononucleotide, FMN) in the form of slightly soluble nanoparticles. This approach was demonstrated recently in the example of the mixture series $ZrO(HPO_4)_x$-$(FMN)_{1-x}$ ($x = 0–1$).[98] With the composition ZrO(FMN) in particular, biocompatible nanoparticles with molar quantities of fluorescent dye that luminesce intensively are obtained by simple precipitation in water (Figure 18).
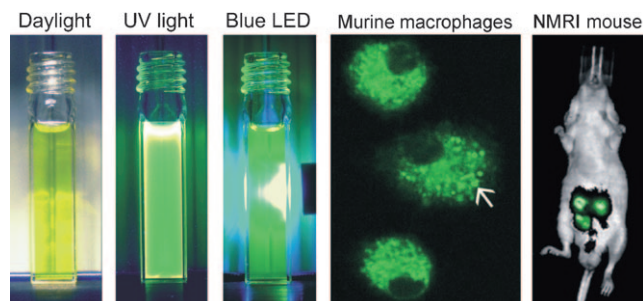
Figure 18. Aqueous suspension of ZrO(FMN) nanoparticles in daylight, excited with UV light, and excited with light from a blue LED, as well as in vivo application in bone marrow cells and mice (modified reproduction of ref. [98]).

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All the nanoparticulate luminescent materials mentioned above now find a broad range of uses in molecular biological and medical research.[99] These range from non-invasive in vivo whole-body diagnosis to in vitro examination of individual organs or cells (cf. Section 2.3).[100] An example is the optical in vivo imaging of a prostate carcinoma by means of antibody-functionalized CdSe@ZnS quantum dots (Figure 19).[101] In vivo distinguishing of cell compartments
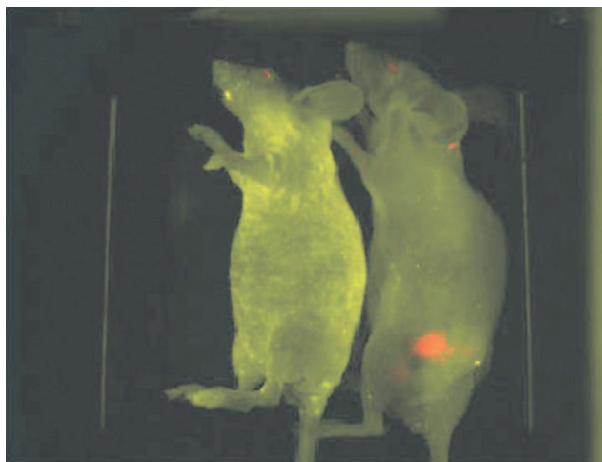
Figure 19. In vivo detection of a prostate cancer in a mouse model before and after adding antibody-marked CdSe@ZnS quantum dots (modified reproduction of ref. [101]).

is also possible.[102] This method was demonstrated, for example, by Bhatia and co-workers with NLS-peptide-functionalized CdSe@ZnS quantum dots (NLS: nuclear localization sequence), which can be specifically localized in the nucleus of fibroblasts (Figure 20).[103] Recently, Krauss and
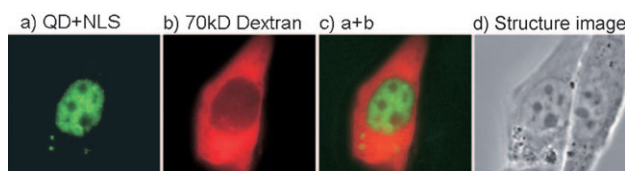
Figure 20. NLS-peptide-functionalized CdSe@ZnS quantum dots for specific in vivo imaging of the nucleus of fibroblasts: a) luminescence of NLS-peptide-functionalized quantum dots, b) 70 kDa rhodamine–dextran as control, c) summed image (a + b), d) structure image in bright field (modified reproduction of ref. [103]).

co-workers demonstrated for (Zn,Cd)Se@ZnSe that the detrimental "blinking", that is, the noncontinuous emission intensity characteristic of quantum dots, can be corrected.[104] They attribute their promising results to the fact that the potential curve of the quantum dots is flatter than in classical core–shell quantum dots, owing to a mixture series of CdSe and ZnSe with corresponding concentration gradients between the core and the shell.

The general preconditions for broad application of luminophor nanoparticles in molecular biology and medicine are: 1) high biocompatibility, 2) material that can be obtained

easily and inexpensively, 3) simple detection, and 4) the presence of a highly specific emission that does not overlap with the autofluorescence of tissue and cells. The latter can be achieved very elegantly if, as with $NaYF_4$:Yb,Er nanoparticles, a longer-wave laser excitation (980 nm) leads to a shorter-wave emission (540 nm) by means of two-photon absorption ("upconversion").[105] By exchange of the rare-earth ions (e.g. with Er, Yb, or Tm), other emission colors can be achieved, and by setting up core–shell structures (e.g. $NaYF_4$:Yb,Er@SiO_2) high quantum yields are attained.[106] Of interest for medical applications are also luminophor nanoparticles such as $LaPO_4$:Er, NdF_3@SiO_2,[107] whose emission lies in the near-infrared window (700–1100 nm), in which tissue shows only weak absorption.[99, 108]

4. Single Particles and Particle Ensembles in Electronics

This section describes both the electronic properties of single particles and the electrical properties of particle ensembles, typically in the form of structured thin films.
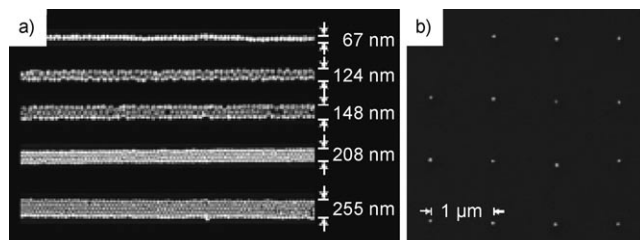
4.1. Single-Particle Studies

Studies of single particles are directed at a general characterization of the material and the fundamental gain of knowledge. Single particles are typically contacted through thin tips in electron and atomic force microscopes.[23] Quantum dots and metal nanoparticles in particular are ideal objects for studying the size-dependent transition from atom or molecule to the collective atom ensemble of the solid state (cf. Sections 2.3, 3.3, and 8.2).[12] Owing to its chemical inertness and good availability, nanoparticulate gold has been and is being studied intensively. The optical properties, that is, color, position of the plasmon resonance frequency, and light emission, are one aspect (cf. Sections 2.2, 3.1). But other physicochemical properties also offer surprises in the border region between the atom and the solid state.[12, 109] For example, it has been demonstrated by microwave spectroscopy that gold nanoparticles with a diameter of 4 nm have an electrical conductivity a factor of 10^7 smaller than that of the bulk material.[110] Similarly, it is reported for copper that nanoparticles with diameters less than 3 nm are nonmetallic.[111] It is to be expected that the surface and surface functionalization will prove to be decisive here, too. For example, the direct-current conductivity of dithiol-functionalized gold particles with diameters of 4 nm in a thin film depends on the chain length of the adsorbed thiol.[112]

Of fundamental importance is the use of single particles as an electronic circuit element. For example, electronic storage and switching elements have been created whose function depends on the presence or absence of a single electron. Such an approach would enable a dramatic increase in the recording density or a substantial miniaturization of electronic components. In principle, such effects have been known since the late 1990s and have contributed much to the basic understanding of electron states in single particles. Thus

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single-electron transistors (SETs) have been realized with CdSe quantum dots.[113] But the studies remained limited to single particles, which naturally restricts the technical implementability. Ordered two-dimensional structures, on the other hand, were previously only accessible by lithographic structuring methods. But now it is also possible to print nanoparticles directly with single-particle resolution using suitable stamp masterforms.[114] Both particulate conductor paths and periodic particle patterns on silicon or polymers can be implemented (Figure 21). Alternatively, by lithographic

Figure 21. Printing Au nanoparticles a) as a particulate conductor path or b) as a highly ordered periodic pattern with single-particle resolution (modified reproduction of ref. [114]).

direct writing (DPN: dip-pen nanolithography) chemical substances or nanoparticles can be deposited precisely with a resolution of a few nanometers, and thus "written" by means of force-field microscopic techniques.[115] Such arrays may be of great importance in the future as flexible light emitters, electronic memory units, and circuit elements or as sensors.[116]

4.2. Particulate Thin-Film Electrodes

Thin-film electrodes include transparent conductive oxides (TCO),[117] with In_2O_3:Sn (ITO: indium tin oxide) as the most prominent representative, and classical metal electrodes (e.g. Cu, Ag, Au).[118] Thin-film electrodes already find wide employment in flat-panel displays, solar cells, and membrane keyboards or as radio-frequency distributor (RFD) tags, thin-film transistors, and ultra-high-frequency (UHF) antennas.[119] In general, their use is driven by aspects of miniaturization, weight reduction, and savings in material and costs. In conventional processes, thin films are precipitated onto a thermally stable substrate by gas-phase methods and then structured lithographically (cf. Section 2.4).[28,120] This approach requires vaporizable precursors and the use of vacuum processes and thermal methods. Suitable substrates are usually limited to glass, ceramics, or metal. And finally, the lithographic structuring causes high losses of material (up to 90% of the precipitated material).

Nanoparticulate thin-film electrodes act in two ways: 1) simultaneous precipitation and structuring with only negligible loss of material by printing techniques (e.g. ink-jet, offset, screen, relief, or gravure printing); 2) the ability to use thermally labile and flexible substrates such as plastic or paper.[121] Both aspects are extremely interesting, especially for simple, inexpensive electrical components. However, a

prerequisite for printing structured particle thin films is the availability of dispersible, non-agglomerated nanoparticles in the form of printing inks. The electrical properties of the printed thin films should match as closely as possible those of the films obtained conventionally by gas-phase precipitation. And with regard to the electrical conductivity of the nanoparticles, their crystallinity is of the utmost importance (cf. Sections 3.1 and 3.3). In addition, in printed layers the electrical contact between the nanoparticles is essential. In this light, thermal processing is usually necessary after the printing process to increase the crystallinity of the nanoparticles, to remove residual moisture or hydroxide, or to burn out organic stabilizers. For the most commonly used ITO, temperatures of 300–500 °C under oxidizing conditions (e.g. in the air) with a subsequent reduction stage (e.g. in a reducing gas) at 200–300 °C are typical. Such post-processing procedures naturally preclude plastic and paper as substrates.[117] The direct preparation of highly crystalline ITO nanoparticles by nonhydrolytic sol–gel syntheses or syntheses in ionic liquids or high-boiling-point alcohols is now possible.[122] With suitable surface functionalization, printed thin films with electrical resistivities of 1×10^{-2} to 5×10^{-2} Ω cm can be produced directly without thermal post-processing steps.

Besides the electrical properties, the choice of material with respect to toxicity, cost, and availability of the material is extremely important. The use of classical TCO materials such as CdO or SnO_2:Sb (ATO) is now greatly restricted.[123] Furthermore, an inexpensive alternative to In_2O_3:Sn (ITO) would be desirable.[117] Possible candidates include ZnO:Al (AZO), ZnO:In (IZO), or SnO_2:F (FTO), which are also readily available as nanoparticles. However, their conductivities are generally about an order of magnitude smaller than those of ITO, and the reproducibility of the material is still not as good. Finally, in liquid-phase syntheses in particular, the large difference in radius between Zn^{2+} (0.76 Å, C.N. [4]) and Al^{3+} (0.53 Å, C.N. [4]) is reflected in the fact that Al^{3+} is not incorporated into the ZnO lattice, or only to a limited degree.[124] Fluoride-doped TCOs would appear at first to be advantageous, owing to the similar ion radii ($r(O^{2-})$: 1.24 Å, $r(F^-)$: 1.17 Å, C.N. [4]), but the high mobility of the fluoride ions in oxidic lattices is a disadvantage.[125] Based on ZnO nanoparticles, it was also recently possible to produce thin films having a reproducible hysteresis with conductivity varying by a factor of 10^5, and thus displaying diode behavior.[126]

There has been good success with silver nanoparticles as printed, structured metal electrodes. However, the high cost of the material and the biocidal properties of silver are disadvantages (Section 7.1). Copper, which would otherwise be preferred, displays a too great a tendency to oxidation, so that the conductivity of printed films drops rapidly.[118,127] As in the case of transparent conductive oxides, metallic thin films are usually precipitated by gas-phase methods and then structured lithographically.[128] Both solutions of organometallic compounds,[129] which are converted into metals thermally or with suitable reducing agents, and functionalized metal nanoparticles in suspension are available as printable precursors.[127] The resulting metal thin films display conductivities similar to those of the bulk metals. However, the

precursors, which are often expensive, and the use of organic solvents are disadvantages. The use of thermal processes also has its problems, as thermal decomposition products may have poisonous or corrosive effects. A decisive advance in this respect was achieved by Lewis et al.[130] Starting with Ag nanoparticles with diameters of approximately 5 nm dispersed in ethylene glycol in proportions of up to 70% by weight, they succeeded in printing flexible silver wires with diameters of approximately 10 μm even onto large-area substrates by ink-jet printing (Figure 22).
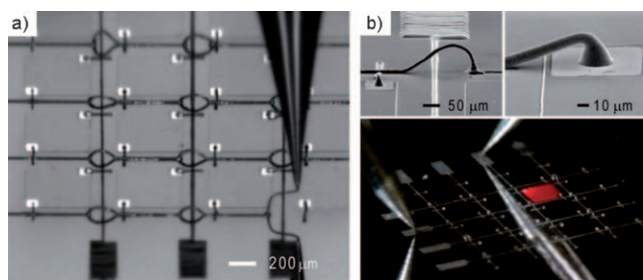
Figure 22. a) Ink-jet printing of Ag wires onto GaAs LED chips and b) bonding onto gold platelets based on Ag nanoparticles in ethylene glycol (modified reproduction of ref. [130]).

4.3. Particle Layers for Energy Conversion and Storage

Here too, the significance of nanoparticles lies mainly in miniaturization and savings in materials, but the high mobility of electrons and ions in nanoparticulate materials is an additional positive factor. An example which by now is classical but remains current is the dye-sensitized solar cell (also known as the Grätzel cell, after its inventor; Figure 23).[131] While bulk TiO_2 may be considered a typical
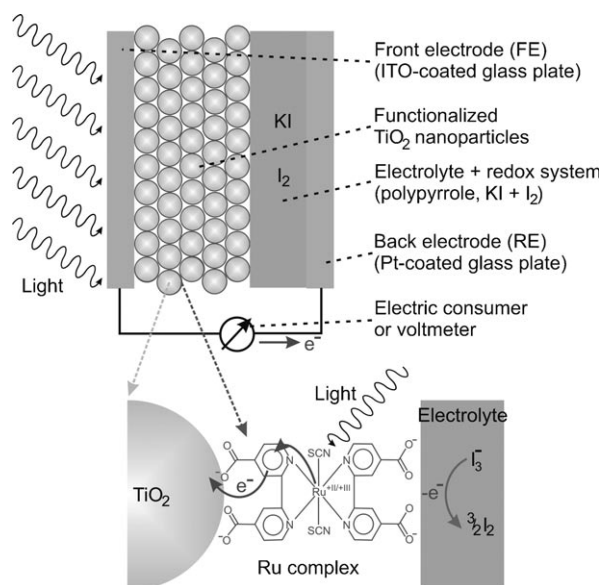
***Figure 23.*** Schematic and mode of operation of a dye-sensitized solar cell.

nonconductor, efficient electron transport occurs through the large surface area of the TiO_2 nanoparticles (30–80 nm diameter). This property of the TiO_2 particles is a major factor in the functioning of the transparent and flexible dye-sensitized solar cell, which presently achieves efficiencies of about 15%. In a current paper, Hagfeldt and co-workers show that Bragg stacks (cf. Section 3.2) consisting of SiO_2 and TiO_2 nanoparticles show promise in increasing the light absorption, and thus the efficiency, still further.[132]

Other design concepts for thin-film solar cells also make use of nanoparticles. For example, printable, flexible solar cells as modules on plastic foil are under intensive study. The highest efficiencies (up to 12%) have been achieved with Si nanoparticles,[133] Cu(In,Ga)S₂ nanoparticles (CIGS: copper indium gallium selenide),[134] or CdSe quantum dots[135] as the light-absorbing component. Quantum dots are of particular interest, as solar cells can be produced whose light absorption occurs in different areas of the spectrum, owing to the correlation of particle size and band gap (cf. Sections 2.3, 3.3). In what are known as stacked or tandem solar cells, in which quantum dots with different absorption are arranged in layers, optimum exploitation of the different energies of the photons in the solar spectrum would be possible, theoretically permitting efficiencies up to 30%.[136] Quantum dots can also serve as emitters in light-emitting diodes. If the nanoparticles are embedded between an ITO and a polymer electrode (e.g. poly(phenylenevinylene), PPV), completely transparent sheet LEDs can be constructed.[137]

Besides solar cells, nanoparticles are also used in lithium ion batteries,[138] fuel cells, and supercapacitors ("super caps").[139] Here too, the large surface area of nanoparticulate materials is of the greatest importance to enable faster diffusion and thus a faster turnover. For example, the charging and discharging speeds of lithium ion batteries can be increased considerably. Nanoparticulate cathode materials such as $LiMO_2$ (M: Mn, Fe, Co, Ni), $Li_xV_2O_5$, $LiTiS_2$, or $LiFePO_4$ are therefore the subjects of intensive research.[140] As anode materials, besides the traditional graphite intercalations, lithium alloys such as $Li_{4.4}Si$, $Li_{4.4}Sn$, or Li_xB are enjoying increasing attention, since they potentially exceed the capacity of conventional graphite electrodes ($855\ mA\,h\,cm^{-3}$) considerably, with values up to $1750\ mA\,h\,cm^{-3}$.[141] At present, the relatively large volume changes during the charging cycles, which limit the service life of the systems, present a problem in utilizing nanoparticles. The latest developments also have the goal of printable microbatteries and three-dimensional battery architectures. Here, too, nanostructured materials ranging from nanoparticles to nanorods and nanotubes are of great importance.[142]

In the case of fuel cells (SOFC: solid-oxide fuel cell), the employment of nanoparticulate cathode materials such as $LaFeO_3$ (LSF), $LaMnO_3$ (LSM), $LaCoO_3$ (LSCo), or $LaFe_{0.8}Co_{0.2}O_3$ (LSCF), especially at the three-phase boundary between the solid electrolyte (typically YSZ: yttria-stabilized zirconia), cathode material, and gas phase, leads to a higher turnover or lower process temperatures (Figure 24).[143] At present, the service life is limited by sintering effects of the nanoparticles. Both for lithium ion batteries and for fuel cells, nanomaterials are currently in the

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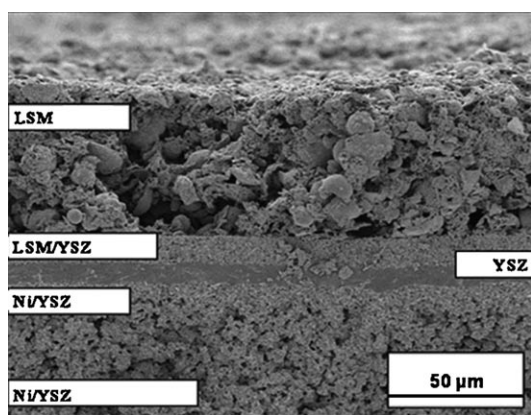
Figure 24. Cross section of a fuel cell with LSM–YSZ composite cathode, YSZ solid electrolyte, and Ni–YSZ composite anode (modified reproduction of ref. [143]).

research and development stage. Although further optimization of the material is necessary for real technical implementation, the advantages and future benefits of nanomaterials are already beyond question.

Nanoparticles of a wide variety of compositions are already in use for a range of sensing activities (e.g. detection of reducing or oxidizing gases, biosensing). Because of the large number of design concepts and applications, we refer the reader to current reviews.[144] Concrete examples based on the plasmon resonance of metal nanoparticles (Section 3.1), Bragg stacks (Section 3.2), nanoparticulate luminophors (Section 3.3), transparent conductive oxides (Section 4.2), or magnetic nanoparticles (Section 5.2), are presented elsewhere. But with respect to future energy supplies, nanoparticles may also be useful for completely different concepts. For example, de Jong and co-workers show that the activation energy of H_2 desorption for complex metal hydrides such as $NaAlH_4$ as a hydrogen storage material depends substantially on the particle size. A value of 116 kJ mol^{-1} for particle sizes of 1–10 μm contrasts with a value of 58 kJ mol^{-1} for particle sizes of 2–10 nm.[145] These results give hope that the current high desorption temperatures (200–500 °C) for complex-hydride hydrogen storage units might be reduced to less than 100 °C.[146]

4.4. Thermoelectric Materials

In a thermoelectric converter, heat is converted into electrical energy.[147] For example, electricity can be generated from the waste heat of power plants or engines, thus increasing the efficiency of combustion processes considerably. Thermoelectric materials experienced a first surge of innovation in the Apollo space missions of the 1960s. But widespread technical use has not yet occurred, as efficiency remains low and suitable materials are lacking.

The efficiency of thermoelectric materials is expressed by the dimensionless factor of merit ZT [Eq. (3)], which incorporates the Seebeck coefficient (S), the electrical conductivity (σ), the thermal conductivity (κ), and the temperature (T, in K).[147]

$$Z = S^2 \, \sigma \, T \, \kappa^{-1} \qquad (3)$$

High-quality thermoelectric materials feature high Seebeck coefficients and high electrical but low thermal conductivity. At present, the most promising approach to increasing the efficiency or ZT values is considered to be the nanostructuring of known or novel thermoelectric materials. In the 1990s, Dresselhaus et al. predicted that ZT values for metals (e.g. Bi) or semiconductors (e.g. Bi_2Te_3) would increase drastically at small particle sizes, owing to the change in the band structure.[148] This prediction was verified in 2001 by Venkatasubramanian et al. for epitaxially grown Bi_2Te_3–Sb_2Te_3 multilayer systems, which display ZT values of about 2.4 at room temperature.[149] The cause of this increase in the factor of merit, which is about 1.0 for bulk Bi_2Te_3, is a considerably reduced thermal conductivity, which results from the scattering of phonons at the numerous interfaces of the layers, which are up to 5 nm thick (Figure 25). In addition, electrons that only move within a layer cause an increase in electrical conductivity, owing to quantum effects. The two effects together contributed to a significant increase in the ZT values.
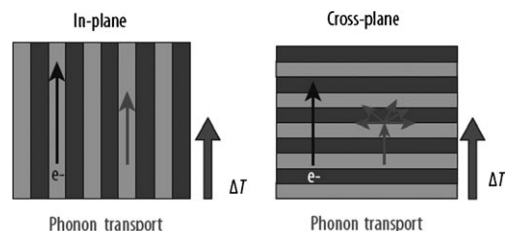
Figure 25. Mode of operation of thermoelectric multilayer structures: a) In in-plane transport, the increase in electrical conductivity owing to quantum effects dominates. b) In cross-plane transport, thermal conductivity is reduced by increased phonon scattering at the interfaces (modified reproduction of ref. [150]).

The theory-based optimization and the refinement of synthesis and characterization techniques have led to promising results for nanostructured layers.[151] Harman et al. found ZT values of 1.6 for Pb(Se,Te) quantum dots that were embedded in a PbTe matrix.[152] Similar nanostructured composites have been realized with Sb_2Te_3 and Bi_2Te_3 nanoparticles, providing ZT values of the same magnitude.[153] The synthesis methods employed are melt-spinning processes or hydrothermal methods. Furthermore, ErAs nanoparticles can be embedded in epitaxially precipitated $In_{0.53}Ga_{0.47}As$ matrices, in which the nanoparticles act as scattering centers for phonons and halve the thermal conductivity of the composite.[154] Silicon in the form of nanowires or as nanoporous material also provides good ZT values,[155] and efficient thermoelectric material can be obtained simply and inexpensively from BiSbTe nanoparticles. These particles are pressed into blocks at elevated temperatures and have ZT values of 1.2 at room temperature and 1.4 at 100 °C.[156]

Even bulk materials display a nanostructuring which positively influences their thermoelectric properties, as a result of initially undesired segregation effects. The nano-

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particulate precipitates are embedded in a more or less ordered fashion in a thermoelectric matrix.[157] Kanatzidis and co-workers found such nanostructuring in the system $Ag_{1-x}Pb_mSbTe_{m+2}$. By spinodal segregation, composites are formed with nanoparticulate species of various compositions in the size range from 2 to 30 nm.[158] The large number of phase boundaries in the nanocomposites are responsible for the considerably reduced thermal conductivity and the associated increase in *ZT* values; the maximum is 2.2 for the composition $AgPb_{18}SbTe_{20}$.[159] Current papers report a comparatively simple synthesis of multiphase $PbTe–PtTe_2$ systems, which can be prepared with differing compositions depending on the ratio of concentrations of starting materials, in the size range from 40 to 100 nm.[160] The individual particles are made up of PbTe and $PtTe_2$ subunits with diameters of 4 to 12 nm. These dimensions are significantly smaller than the Bohr exciton radius for PbTe (46 nm), and lead by the associated quantum effects to a doubling of the Seebeck coefficient compared to bulk PbTe.[161]

Nanostructuring obviously represents a central key to efficient thermoelectric materials with high *ZT* values and has given many new impulses in recent years. However, the high cost of nanostructured semiconductor materials is still a problem.

5. Superparamagnetism and Magnetic Contrast Agents

Magnetic pigments of small size have been of the greatest significance in technology for decades, since the data packing density is directly related to the number of elementary magnets.[162] With the development of modern optical and electronic storage media, such as compact disks and flash memory sticks, classical magnetic pigments have gone somewhat out of fashion. But in connection with concepts such as magnetic fluids, magnetoseparation, and magnetothermal therapy, nanoparticulate magnetic pigments are currently experiencing a renaissance.[163]

5.1. Superparamagnetism

The concepts of ferromagnetism, ferrimagnetism, and antiferromagnetism, as well as paramagnetism and diamagnetism, are well known for classifying the magnetic properties of individual atoms and collective atom ensembles.[164] The concept of "superparamagnetism" appears at first confusing in this context, especially since the relevant materials are classical ferromagnets or ferrimagnets. To comprehend superparamagnetism, the question of the spatial dimensions of a magnetic domain is relevant. Both quantum-mechanical predictions and experimental findings (e.g. spin-polarized scanning tunneling microscopy and the magneto-optical Kerr effect) show mean critical domain diameters for elemental iron and magnetite of 10–20 and 110–130 nm, for example.[165] Depending on the orientation of the magnetization with respect to an external field, the respective domains expand or shrink in the bulk material. This process is endothermic and

becomes apparent as hysteresis as the external magnetic field vector rotates. If nanoparticles with dimensions less than the mean critical domain diameter are present, they have only one magnetic domain per particle. Above the blocking temperature, the magnetization of the nanoparticles thus follows the external field, with negligible retentivity and coercivity. The behavior now corresponds to that of a paramagnetic atom, but with an absolute magnetization a factor of 10^4 larger, which is expressed meaningfully by the term "superparamagnetism". Potential specific materials are elemental metals and alloys (e.g. Fe, Co, Ni, Co–Ni, Fe–Pt),[166] classical iron oxides (i.e. Fe_2O_3, Fe_3O_4),[167] but also ferrites with the composition MFe_2O_4 (M = Mn, Co, Ni, Zn).[168]

Like classical magnetic pigments, superparamagnetic nanoparticles can be used as magnetic storage media, with the magnetization of each individual particle serving to carry information.[169] For example, with a two-dimensional array of FePt particles of diameter 3 nm and with a lateral spacing of 6 nm, data packing densities of 15–20 terabits per square inch can theoretically be achieved.[170] Besides the high packing density, a blocking temperature (T_B) in the vicinity of the ambient conditions would be advantageous for practical use. Obviously, the arrangement and form of the nanoparticles play a decisive role here. Thus T_B rises with a chain-like arrangement of superparamagnetic γ-Fe_2O_3 nanoparticles from 80 K to about 120 K.[171] Cobalt particles with a hollow spherical structure even have a T_B of 180 K.[172]

Suspended in highly viscous fluids, superparamagnetic nanoparticles are used as a magnetic fluid or ferrofluid (Figure 26).[173] Such ferrofluids can be manipulated in a variety of ways by external magnetic fields. For example, their viscosity or speed and direction of flow can be altered in a controlled fashion. Magnetic fluids follow the external field very rapidly, and with negligible friction losses. These effects are currently utilized in special-purpose pumps, for rapid valve switching, and in the form of cooling and sealing fluids (Figure 26).
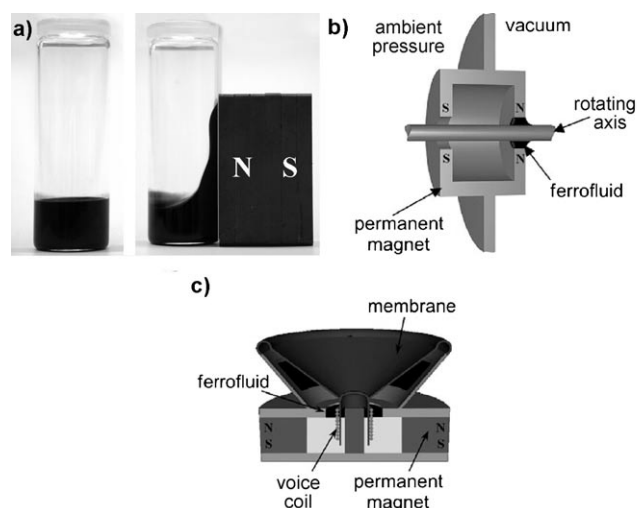

Figure 26. a) Magnetic fluid and b,c) applications as a seal around a rotating shaft (b) and as coolant in a loudspeaker (c) (modified reproduction of (a) and (b,c) from ref. [174] and [173]).

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By applying an external magnetic field, that is, by permanent magnets or electromagnetic coils, magnetic nanoparticles can be separated from a liquid phase easily and quickly. This so-called magnetoseparation offers an elegant method for separating both the magnetic nanoparticles themselves as well as substances that are docked onto the surface of the nanoparticles from a mixture of substances or a suspension. The extraction of catalysts (cf. Section 6.2), toxic or radioactive metals, pharmaceuticals, or even cells illustrates the effectiveness of this procedure.[175] A concrete example is the separation of traces of arsenic from drinking water. Dissolved arsenic (e.g. AsO_3^{3-}) can be adsorbed onto added γ-Fe_2O_3 or Fe_3O_4 nanoparticles and then removed by applying a magnetic field.[176] Further examples are the complex [$Ru(binap$-$PO_3H_2)(dpen)Cl_2$] (binap: 2,2′-bis(diphenyl phosphanyl)-1,1′-binaphtyl; dpen: 1,2-diphenylethylene diamine) immobilized on Fe_3O_4 nanoparticles as a catalyst for chiral hydrogenation of aromatic ketones[177] and the separation of proteins[178] and genes[179] with surface-functionalized iron oxide nanoparticles. But the docking of magnetic nanoparticles onto proteins, genes, or cells is suitable not only for extraction but also for their detection, with magnetic detection thus making detection sensitivities up to 10 pM possible. And if gold or silver nanoparticles are docked onto magnetic nanoparticles, heterodimers with Janus-faced properties are obtained,[180] which are detectable by both their magnetic and their optical properties (cf. Section 3.1).[181] Impressive examples are Ag–Fe_3O_4 or Fe_3O_4–Au–Fe_3O_4 ensembles (Figure 27), which are of interest for problems in molecular biology and medicine.[182]
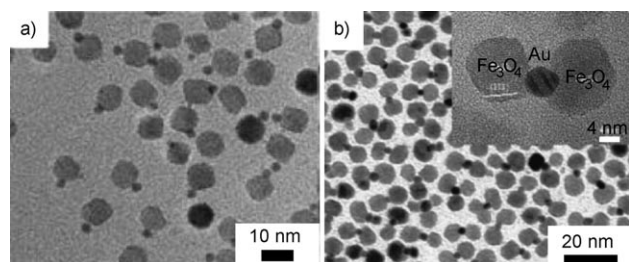
Figure 27. Heterodimeric Ag–Fe_3O_4 and Fe_3O_4–Au–Fe_3O_4 ensembles (modified reproduction of ref. [182]).

Besides the agglomeration tendency typical of nanoparticles, owing to their large surface area (Section 2.4), in the case of magnetic nanoparticles the attractive magnetic interactions encourage agglomeration. Therefore, the question of stabilization and surface functionalization is of particular importance. Coatings with tensides or polymers, SiO_2 or silicates, and with amorphous carbon have proven effective.[163,183] Furthermore, nanoparticles sensitive to oxidation, such as elemental iron, cobalt, nickel, or alloys, can be protected by deliberately building up passivating oxide layers or by depositing noble metals on the surface.[163,166,184] And finally, magnetic nanoparticles can not only be easily separated from a dispersion medium, as described above, but also just as easily redispersed after the external magnetic field is removed, if there is suitable surface stabilization.
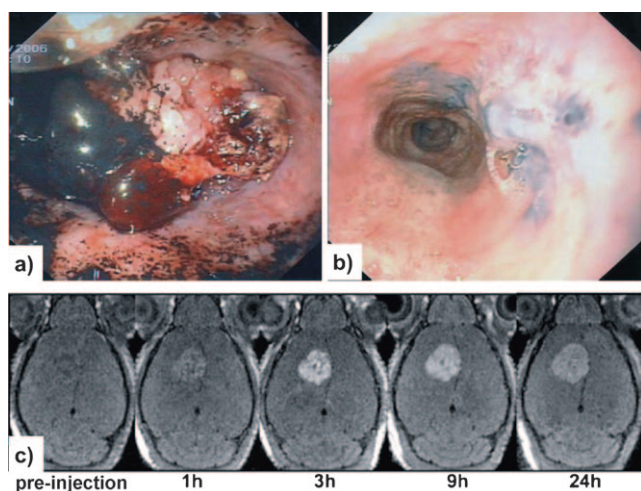
5.2. Magnetothermal Therapy and Magnetic Contrast Agents

Magnetic nanoparticles have proven to be especially promising in molecular biology and medicine, particularly superparamagnetic γ-Fe_2O_3, Fe_3O_4, and Fe particles. With suitable surface functionalization, for example with antibodies, it is possible to dock these nanoparticles in vivo specifically onto cells, such as tumor cells, or to infiltrate them into cells. The magnetic nanoparticles can then be detected in real time at the cellular level by means of magnetic resonance imaging (MRI).[185] The magnetic nanoparticles shorten the spin–spin relaxation time of the surrounding water molecules, which is accompanied by a substantial heightening of the contrast.[186] All told, magnetic contrast agents allow diagnostic access to clinical pictures, such as of breast and intestinal cancer, with previously unheard of resolutions, similarly to the luminescent biomarkers discussed above (Section 3.3).[187]

Besides in diagnosis, superparamagnetic particles have led to promising results in therapy, also mainly for tumors. In this approach, the fact that a fluctuating magnetic field causes a slight warming of magnetic nanoparticles is utilized. This heat derives from the realignment of the magnetization of the nanoparticles (Néel relaxation) and from friction forces of the nanoparticles rotating in the liquid phase. And if magnetic nanoparticles are present in high concentrations, they align themselves according to their magnetization. The energy input from an external alternating magnetic field interferes with this alignment and is also accompanied by the generation of heat (Brown relaxation).[163] Based on the interactions mentioned, "magnetothermal therapy" offers promising perspectives.[188] If, for example, γ-Fe_2O_3, Fe_3O_4, or Fe nanoparticles are applied in tumor tissue, they can be warmed by an external alternating magnetic field, thus producing a cytotoxic effect at temperatures above 40–42 °C in the adjacent tissue. The generally poorer thermoregulation of the tumor tissue and the high biocompatibility of the iron oxides also promote this process. Clinical studies show good success with glioblastomas, which are difficult to operate on, and with prostate and esophagus carcinomas (Figure 28). A particular advantage of magnetic nanoparticles lies in the combination of diagnosis and therapy. For example, MRI tomography can be used first to locate the tumor and then magnetothermal therapy used to treat it. Hybrid particles have also been described, which combine a core containing iron oxide and a polymer or SiO_2 shell surrounding it, which in turn contains active ingredients such as doxorubicin or HER2/neu antibodies. In this way, magnetic nanoparticles can even be targeted to a specific site by means of external magnetic fields, and the active ingredient can then be released.[189] Finally, Heeren et al. report on the in vivo observation of lipoprotein metabolism in real time, based on superparamagnetic γ-Fe_2O_3 nanoparticles.[190]

In addition to superparamagnetic iron oxides, other substances such as $MnFe_2O_4$, $ZnFe_2O_4$, MnO, and FeCo have also found use as magnetic contrast agents (Figure 28).[185,191] However, the advantage of the iron oxides remains their high biocompatibility. Besides superparamagnetic materials, paramagnetic nanoparticles are also

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Figure 28. Magnetothermal therapy: an esophagus carcinoma with injected γ-Fe$_2$O$_3$ nanoparticles a) before and b) 7 months after therapy. c) Magnetic resonance imaging of a breast tumor with herceptin-functionalized MnO nanoparticles (modified reproduction of (a,b) and (c) from refs. [188a] and [191a]).

employed in magnetic resonance imaging. Because of their high magnetic moment, rare-earth-metal compounds such as Gd$_2$O$_3$ are preferred for such applications.[192] After appropriate surface functionalization, targeted binding of the nanoparticles to tumor cells and thus diagnostic findings with high site resolution can be achieved in this case as well.

6. Nanoparticles in Heterogeneous Catalysis

It was in heterogeneous catalysis that nanoparticles first gained major industrial importance (see Section 2.2). As some reviews have been published,[18] we present current aspects of synthesis chemistry, environmentally relevant catalysis, photocatalysis, and analytical approaches and methodology.

6.1. Synthesis Chemistry

The deciding factor for the use of nanoparticles in catalysis is the large ratio of surface area to volume, with a large number of catalytically active centers at the surface and relatively few inactive inner atoms (cf. Section 2.1, Figure 2). In addition to the optimization of known catalysts by transfer to the nanoscale, increasing efficiency and selectivity is the subject of current research. But novel materials and considerable progress in analytical characterization have also contributed to a better understanding of the interactions between particle properties and catalytic activity.[193]

Noble metals in particular are predestined to be objects of studies aimed at better understanding, owing to the ease of obtaining them. They also continue to be very relevant commercially. Normally, noble-metal nanoparticles can be obtained by simple reduction of metal salts in the presence of suitable stabilizers. The nanoparticles, with typical diameters

of 1–20 nm, are then fixed to a substrate, such as SiO$_2$ or Al$_2$O$_3$. Polymer-functionalized and dendrimer-functionalized noble-metal nanoparticles have proven in recent years to be especially effective for numerous reactions.[194] Dendrimers serve as effective templates during nucleation, thus permitting the formation of nanoparticles with a controlled size and even a defined number of metal atoms. Since dendrimers are only weakly bound to the particle surface, nanoparticles functionalized in this way offer a good starting point for verification of the catalytic activity or selectivity in the case of differing particle sizes. This was demonstrated for the case of C−C bond formation in a Suzuki coupling with dendrimer-stabilized Pd nanoparticles.[195] Surprisingly, an increase in catalytic activity for sinking catalyst concentration is observed. Even in "homeopathic" concentrations of only 1 ppm Pd, turnover numbers (TON) of 540000 are achieved.[196] A similar correlation with particle size has also been observed for the selectivity in the hydrogenation of unsaturated alcohols.[197]

In addition to the size, the composition of nanoparticulate noble-metal catalysts of course plays a decisive role. For example, optimization of CO oxidation by variation of the Rh:Pt ratio in bimetallic nanoparticles is achieved at a uniform size of 9 ± 1 nm.[198] Furthermore, Zaera and co-workers have demonstrated the preferred hydrogenation of *cis*-alkenes for the case of unsaturated fats and connect this finding mechanistically with the presence of Pt(111) surfaces.[199] Somorjai and co-workers showed for the case of CO oxidation that core–shell structures with a platinum core and mesoporous SiO$_2$ shell display no major sintering effects even at temperatures of 750°C and that the catalytic activity is maintained even at high temperatures.[200] Overall, the approaches presented open new possibilities for rational design of catalysts.[201]

Gold, known for its inertness as a bulk material, has attracted much attention as a redox catalyst in nanoparticulate form.[13, 46a, 202] For example, the development of selective catalysts for the reduction of functionalized nitroaromatic compounds to aniline derivatives, which are important intermediates for pharmaceuticals, herbicide, numerous polymers, and fine chemicals, is of commercial significance.[203] The difficulty is the selective reduction of the nitro functionality in the presence of other reducible functional groups. Serna and Corma have shown that Au nanoparticles on TiO$_2$ or Fe$_2$O$_3$ substrates catalyze the hydrogenation of functionalized nitroarenes under mild reaction conditions with high selectivity. Thus, a new way of obtaining cyclohexanone oxime from 1-nitro-1-cyclohexene has been found.[204] It is also possible to prepare azo compounds starting from aniline derivatives and nitroaromatic compounds.[205] Likewise, nanoparticulate gold has proven to be an efficient catalyst for redox reactions of olefinic oxygenic hydrocarbons, such as alcohols and ketones, that preserve the olefin groups.[206]

As gold nanoparticles of different sizes and shapes are easy to obtain (Sections 2.2 and 4.1), they play a central role in furthering our understanding of size-dependent and shape-dependent catalytic properties. For example, polygonal gold nanoparticles can be prepared in situ by reduction with citric acid or citrates under mild conditions without using tensides

or templates at all. The particle size can be controlled by varying the concentrations of the starting materials. Furthermore, by adding metal ions such as Fe^{3+}, Ni^{2+}, and Cu^{2+}, an effective control of the nucleus growth and crystal habit can be achieved. Compared with spherical particles, polygonal gold species show an exceptionally high activity in the reduction of nitrophenols with complex boron hydrides, and also in the aerobic oxidation of various hexoses.[207]

Although gold nanoparticles without a substrate show very good catalytic properties in many redox reactions,[208] a description of the catalytic activity that is based exclusively on particle size and shape would be incomplete for particles on substrates. For example, in gold-catalyzed CO oxidation, carbon monoxide is obviously adsorbed onto the gold particles, but oxygen is adsorbed onto the CeO_2:La substrate.[209] Even the few examples listed here make it clear that catalysis with gold nanoparticles has made great progress. But overall, the study of the catalytically active species and of the interaction between substrate and catalyst is just beginning. These phenomena are the subject of intensive discussions.[210]

6.2. Environmentally Relevant Catalysis

By now, nanoparticulate catalysts have found what must be their most important role in environmentally relevant catalysis, which ranges from sewage and exhaust-gas treatment to photocatalytic dissociation of water. A major application of great commercial relevance is the scrubbing of exhaust gases from combustion engines. The three-way catalytic converters typically employed in motor vehicles all contain noble metals such as Pt, Pd, or Rh, which are applied to ceramic substrates such as Al_2O_3 or cordierite.[211] The formation of alloys and the oxidation behavior of the noble metals are the subjects of research aimed at increasing the activity and service life of the catalytic converters. In the case of Rh nanoparticles, Dosch et al. were recently able to observe for the first time the shape change of nanoparticles under in situ conditions, that is, in real exhausts at operating temperatures of 300 °C. On the basis of X-ray diffraction experiments with synchrotron radiation sources and with high-resolution transmission electron microscopes, the formation of an extremely thin oxide layer about three atoms thick is regarded as the cause of the change in shape (Figure 29).[212] From the energy perspective, the formation of this oxide layer on (001) and (100) surfaces is particularly favored, which correlates with the growth of the Rh particles under catalysis conditions.
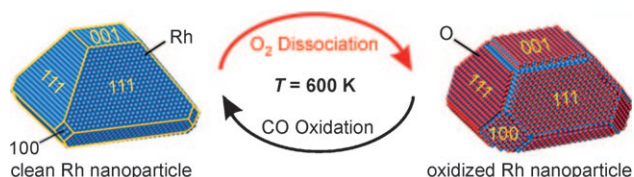
Besides treatment of exhausts, nanoparticulate catalysts are of importance for wastewater treatment, for example for environmentally friendly treatment of AOX-polluted sewage (AOX: absorbable organically bound halogens). These wastes can be removed selectively, even at very low concentrations of halogenated hydrocarbons, by reductive hydrodehalogenation on nanoparticulate palladium in the presence of a hydrogen donor, and converted into easily biodegradable substances (Figure 30). For this purpose, a mere 0.15 wt % palladium was applied to 20–30 nm large Fe_3O_4 particles, which can be isolated after the sewage treatment by simple magnetoseparation (Section 5.1).[213]
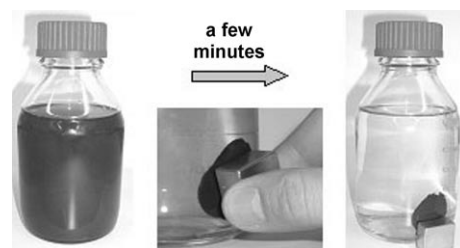
Figure 30. Magnetoseparation of Pd–Fe_3O_4 composite catalysts for treating AOX-polluted sewage (modified reproduction of ref. [213]).

6.3. Photocatalysis

Photocatalytic effects of coated surfaces have played an important role for many years, with an emphasis on self-cleaning, antimicrobial, and antifogging or antifouling properties (cf. Section 7.1).[214] A great variety of efforts are being made in this regard to increase the catalytic activity, especially making use of direct sunlight. The classical photocatalyst, titanium dioxide in the form of anatase, depends on ultraviolet radiation because of its large band gap (3.2 eV); however, in the presence of water it is very strongly oxidizing, forming hydroxyl radicals. Since TiO_2-coated surfaces also display photoinduced hydrophilicity, adsorbed substances can be rinsed off easily. Together, the two effects produce outstanding self-cleaning properties, thus making TiO_2 the most common photocatalyst for outdoor applications; it is used on roofing tiles, window panes, and on building façades in general (Figure 31). Here, too, the optical transparency of the nanoparticles in the visible spectrum is of decisive importance in preventing a dulling of the surfaces by scattering processes (cf. Sections 2.2, 3.1, and 7.1).

Figure 29. Changes in Rh nanoparticles with increasing (001) and (100) surfaces owing to the energetically favored formation of a film of oxide on these surfaces (modified reproduction of ref. [212]).
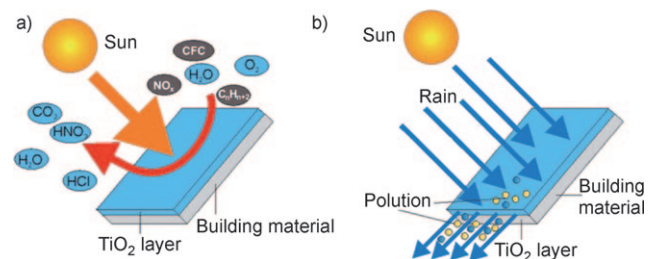

Figure 31. a) Photocatalytic and b) self-cleaning effects of TiO_2-coated façade surfaces (modified reproduction of ref. [215]).

Starting with the classical anatase, for the sake of higher catalytic activity it would be advantageous to extend the relevant absorption range for photocatalysis into the visible spectrum. In this context, composites with TiO_2 and MnO_2 nanoparticles[216] or also nanotubes[217] have proven quite promising. Alternatively, doped nanoparticles such as ZnS:Ni can be employed.[218] Finally, there are a number of approaches utilizing novel compounds that already function in the visible spectrum for photocatalysis.[219] For example, the mineral libethenite, $Cu_2(PO_4)OH$, displays high photocatalytic activity in the form of nanoparticles with diameters of about 20 nm.[220] Different particle sizes can be easily obtained by precipitation in an aqueous phase under variation of the pH value. $BiVO_4$ nanoparticles, which are synthesized under similar reaction conditions, show a clear correlation between particle size or shape and catalytic activity.[221] A similar situation is reported for $InNbO_4$ or Bi_2WO_6 nanoparticles that can be obtained by sol–gel synthesis.[222] The increased photocatalytic activity of the nanoparticles compared to the respective bulk materials is usually demonstrated by the decomposition behavior of organic dyes (e.g. methylene blue) compared to suitable reference materials (e.g. Degussa P25).

Besides the selection and optimization of the photocatalyst material itself, the interaction with the substrate is of great importance for technical applications (cf. Section 7.1). While thermally stable substrates can be coated and modified in a variety of ways, there are certain limitations for plastics. Polyethylene films can usually be coated with a stable, photocatalytically active surface by immersion in a TiO_2 suspension and subsequent thermal treatment at temperatures up to 180 °C.[223] But for many other plastics, this procedure is not suitable. In a novel method, the surfaces of TiO_2 nanoparticles were first functionalized with a fluororganic silane. After this functionalization, they can be applied to a wide variety of substrates by spray coating at 110 °C. On the basis of particles sized 4–6 nm, transparent TiO_2 layers with outstanding photocatalytic properties can be obtained.[224]

With regard to producing energy without CO_2 emissions, hydrogen is regarded as one of the most important energy media of the future. In this context, the direct utilization of sunlight for dissociation of water has become a focal point of photocatalysis. Although great progress has been made since photolytic dissociation of water was first observed in 1972 by Fujishima and Honda,[225] the efficiency of the catalysts known to date is far from sufficient for commercial use. Owing to its low material cost and high physicochemical stability, TiO_2 continues to be the most promising material, which can be improved still further by suitable modification. For example, nitrogen-doped TiO_2 nanoparticles show a visible absorption at wavelengths up to 600 nm in connection with increased catalytic activity.[226] Carbon-doped TiO_2 nanotubes even display a 20-fold greater efficiency than commercial reference substances (e.g. Degussa P25).[227] In recent work, $TiS_2@TiO_2$ core–shell structures were used to achieve good photocatalytic properties, but once again only in the ultraviolet range.[228] By replacing titanium with tungsten (about 30 %) in the shell, the catalytic properties can be improved further to a limited extent. Other subjects of study

are nanoparticulate TiO_2 films to which 1–5 nm sized, stabilized $IrO_2 \cdot n H_2O$ particles are applied. Here too, a photocatalytic dissociation of water in visible light can be observed, but with comparatively low efficiency.[229] And finally, Domen et al. have found a photocatalyst, a compound of the general composition $Ga_{1-x}Zn_x(N_{1-x}O_x)$ (x = 0–1), which absorbs in the visible spectrum, owing to its band gap (2.56 eV). Its catalytic activity, which is weak at first, can be increased considerably after modification with a mixture of nanoparticulate ruthenium and chromium oxide.[230] Current studies by Nocera and Kanan seem very promising. In this case the dissociation of water at a neutral pH value under standard conditions and with only a small overpotential of O_2 generation has been demonstrated with nanostructured, noncrystalline cobalt phosphate layers.[231] Taken together, the increasing understanding of the reaction mechanisms and the availability of novel substances give hope for efficient catalysts for photocatalytic dissociation of water in the future, and thus for an important contribution to future energy supplies.

7. Upgrading Materials and Surface Finishing

The modification and improvement of materials and their surfaces with the help of nanoparticles are fields of application which already have great industrial importance. These range from hardening, ultraviolet stabilization, and self-cleaning to materials for artificial bones and teeth.

7.1. Surface Finishing

The most investigated features of nanoparticles certainly include their mechanical properties,[232] owing to the work of Gleiter et al. in the 1980s, who predicted and also demonstrated that nanoparticles and bulk materials differ considerably in modulus of elasticity, hardness, and ductility.[233] From these beginnings, a broad range of applications has been developed, among which surface coatings play a major role. The use of nanoparticles in this area permits manifold optimization of materials for application-specific boundary conditions and enables broad modification of their properties.[39] Spherical nanoparticles are advantageous for achieving high packing densities in polymer matrices. Regarding the desired properties, careful adjustment of particle composition, size, and shape to the specific situation of the application is necessary, as well.

Polymer nanocomposites as transparent hard coatings have been commercially important for a long time (cf. Sections 2.2 and 3.1). There is a great need for improvement of the scratch resistance of clear paint coatings while maintaining their glossiness, transparency, and resistance to chemicals and environmental influences. Nanoparticles are predestined for such applications and can change the polymer structure of the matrix in composites, owing to their large specific surface area. For example, SiO_2 nanoparticles in polyurethane paints lead to greater scratch and wear resistance. A suitable surface treatment is essential for nano-

particle function and can be achieved by functionalization with unsaturated organic acids, for example. These are first bonded to the OH-terminated surfaces of the nanoparticles by esterification and then cross-linked with the organic matrix by UV-initiated radical polymerization.[234] In this way, up to 40 wt % nanoparticles can be incorporated into paint matrices. The resulting composite displays a significant increase in modulus of elasticity, Vickers hardness, and scratch resistance, while maintaining its optical transparency (Figure 32).[235] If
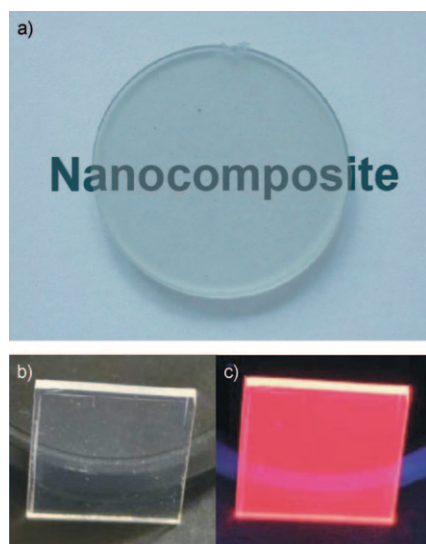
Figure 32. a) Transparent PMMA matrix with 20 wt % SiO_2 nanoparticles and b,c) PMMA matrix with YVO_4:Eu nanoparticles in daylight (b) and under UV excitation (c) (modified reproduction of (a) and (b,c) from refs. [235] and [242]).

instead silanes, silane-like oligomers, or polymers are used to functionalize the surface of SiO_2 nanoparticles, covalent siloxane bonds form, which are inert over wide ranges of pH value and temperature. Nanoparticles functionalized in this way can also be incorporated homogeneously into paints. In addition to increasing the scratch resistance, improved spreading of the laquer formulation is observed, which is due to lower surface tension.[236]

Particularly in automobile manufacturing, UV-hardening paints are gaining in importance for environmental reasons. Besides SiO_2 nanoparticles, Al_2O_3 nanoparticles are being employed increasingly for these applications. However, owing to the higher index of refraction ($n \approx 1.7$) compared to the polymer matrix, the use of Al_2O_3 even in low concentrations causes a certain haze of the paint film. If, however, γ-AlO(OH) nanoparticles ($n \approx 1.6$) with a diameter of 10 nm are used instead, even a proportion of 1 wt % leads to a substantial improvement of the mechanical properties of the polymer matrix without a reduction in glossiness and optical transparency.[236] Likewise, by incorporating SiO_2–PMMA core–shell nanoparticles (PMMA: polymethyl methacrylate) with diameters of 80–90 nm in a proportion of 5 wt % into PVC, a doubling of tear strength and fraction strain can be achieved.[237] And finally, the silicates montmorillonite and bentonite, termed nanoclays, are employed as functional filler

materials in plastics.[238] The idea here is also to improve the mechanical and thermal properties over the pure matrix;[239] the latter can consist of various polymers, such as polyethylene (PE), polyethylene terephthalate (PET), or polyamides (PA).[240] In addition to improving the mechanical properties of the nanoparticle composites, an optimized thermal behavior (e.g. with regard to flammability, melting behavior, decomposition temperature, and soot generation) is observed.[241]

Apart from embedding nanoparticles to increase the hardness and scratch resistance, luminescent nanoparticles can also be embedded in polymer matrices. In daylight, these appear completely transparent and colorless (cf. Sections 2.2, 3.1, and 3.3). Only with suitable excitation, such as under ultraviolet light, is the intensive luminescence of the nanoparticles seen. For a composite that is transparent as a whole, it is important that the nanoparticles be produced and embedded in the matrix without any agglomeration. Larger primary particles or agglomerates would stand out as clearly visible scattering centers, reducing the optical transparency of the polymers significantly. It makes sense to provide particles which are to be embedded in a hydrophobic or hydrophilic polymer with appropriate hydrophobic or hydrophilic surface functionalization during the synthesis. A particularly elegant method is to use monomer precursors as stabilizer and surface functionalization of the nanoparticles in the synthesis. Such particles can then be incorporated into the plastic directly during the polymerization reaction. In this way, for example, embedding of non-agglomerated luminescent YVO_4:Eu nanoparticles at up to 20 wt % in PMMA can be achieved (Figure 32).[242] And finally, the ultraviolet stability of plastics can also be improved by embedding TiO_2 or ZnO nanoparticles (cf. Section 2.2),[39,243] or an antistatic effect can be achieved by incorporating transparent conductive oxides (cf. Section 4.2).[244]

Paints and polymers may be the most advanced fields of application for nanoparticle composites, but nanoparticle-based improvement of properties is by no means limited to them. In engine building, where more and more components made of aluminum–silicon alloys are being used for the sake of weight reduction, ways to obtain harder and more corrosion-resistant surfaces are also being sought. One approach consists of surface modification of the materials with iron carbide or iron boride nanoparticles by thermal spray-coating. The formed vitreous layer, in which very hard particles of crystallite up to 500 nm large are embedded, is accompanied by a significant hardening and a considerable increase in corrosion resistance. Thus the friction losses of present-day engines could be reduced considerably and their service lives extended.[245]

The use of nanoparticles is also firmly established in the building industry.[215] For more than a decade, so-called "easy-to-clean" coatings have been on the market, which make cleaning building façades (e.g. plastics, ceramics, stone, or concrete) a great deal easier. These properties, known as the lotus effect, derive from the fact that it is not the smoothest surfaces, but on the contrary, ones that are textured on the nanometer scale, which are especially water- and dirt-repellent.[246] For this purpose, nanoparticles are embedded

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in a substrate matrix so that the resulting surface has numerous nanoscale knobs. These knobs ensure that droplets of water or particles of dirt have only minimal contact with the necessarily hydrophobic surface and can thus drip off or be rinsed off easily. The cause of the observed self-cleaning effect is the increase of the contact angle between water droplets and the wetted surface up to as much as 170°.[247] Today, self-cleaning surfaces also find use as protection against graffiti, in technical textiles, in analytical chemistry, and in medical technology.[248] Typically, organically functionalized metal oxide nanoparticles (e.g. SiO_2, Al_2O_3, ZrO_2) are applied to the substrate by immersion or spraying and subsequent heat treatment. By varying the initial components, their properties can be adjusted to the specific application conditions.[249] In addition to the self-cleaning effect obtained by the fractalization of surfaces (i.e. the lotus effect), hydrophilized surfaces, which result in a pronounced spreading of water films and thus to rapid runoff, display a similar "easy-to-clean" behavior. If, for example, ZrO_2 nanoparticles are incorporated into these surfaces, the scratch resistance of the layer can be increased at the same time.[250]

And finally, medical applications are an important field of surface modification and improvement with nanoparticles. Coatings with antibacterial effects are of great interest. This area remains a domain of silver, whose antiseptic and disinfecting action has been known for over 3000 years. Customized synthesis of silver nanoparticles offers a wide range of possible uses (cf. Section 3.1). For example, the adhesion and chemical stability can be improved by embedding silver nanoparticles in polymer matrices, with the high permeability of the polymer ensuring diffusion of silver ions to the surface and thus the development of the antibacterial properties.[251] Alternatively, amphiphilically coated silver nanoparticles can be covered with a mesoporous SiO_2 shell (Figure 33).[252] Besides silver, antibacterial effects are also reported with nanoparticles of other compositions, such as MgO.[253]

A particularly simple and inexpensive way of obtaining silver nanoparticles has proven to be a novel synthesis in vegetable oils. The nanoparticles obtained in this way can be transferred to biodegradable paints without agglomeration, thus lengthening the latters' shelf life.[254] A particularly efficient antibacterial effect is displayed by 1–2 nm large silver nanoparticles that are applied to 20–50 nm large calcium phosphate particles and embedded as a composite
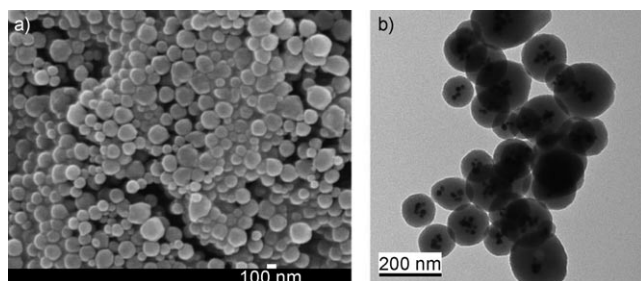
in polymer foils. The high antibacterial effect is evidently due to the fact that microorganisms need calcium as an essential element but under these conditions also take up the toxic silver nanoparticles.[255]

Besides the antibacterial effect, the opposite effect may also be desired, namely particularly easy linking of cells to surfaces. Considerable success has been achieved in the field of minute cavities in tooth enamel,[256] in the restoration of tissue and healing of wounds,[257] and in coating bone-substitute materials with calcium phosphate and apatite nanoparticles.[258] In the latter case, coating titanium implants with apatite nanoparticles promotes the connection and growth of bone marrow cells, as both the roughness of the coated surface and its composition are similar to the natural bone structure.

As the last example, we mention the use of nanoparticles for fireproofing, which involves both flame-retardant and thermally insulating effects. As a flame-retardant coating for flammable materials (e.g. plastics, wood, paper, textiles), metal phosphates are well known and have been used industrially for many years.[259] As an additional class of materials, polymer nanocomposites have recently found increasing interest. In this case, layered double hydroxides (LDH) of aluminum and magnesium are used; their flame-retardant effect as bulk materials has been known for a long time. Starting from this basis, Zammarano et al. achieved an important step with LDH epoxide nanocomposites, which are not only flame-retardant, but even self-extinguishing.[260]

To increase fire resistance, novel fireproofing systems can also be employed, which are applied in the form of paints or pastes to combustible or temperature-sensitive materials. If these contain, for example, SiO_2 or Al_2O_3 nanoparticles, when a fire breaks out, a ceramic layer foamed by combustion gases will form very rapidly and act as thermal insulation, thus considerably increasing the ignition temperature as well as the flashover temperature of the substrate beneath it (Figure 34).[215]

— fire-protection foam

— glass
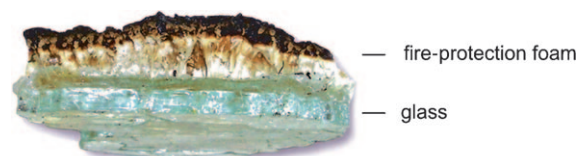
Figure 34. Fireproofing of glazing by coating based on SiO_2 nanoparticles, which form a stable foam in case of fire (modified reproduction of ref. [215]).

7.2. Improvement of Bulk Materials

Besides for modifying and improving surfaces, nanoparticles can also be incorporated into bulk materials, thus contributing to an optimization of the properties of the resulting composite. There are several reviews of this topic,[261] so our discussion can be brief. An already classical area of application is the use of nanoparticles in ceramic materials, for example to control their composition or their sintering and microstructure properties and to optimize their

Figure 33. Electron microscope images of mesoporous SiO_2 particles (a) with enclosed silver nanoparticles (b) (modified reproduction of ref. [252]).

mechanical and thermal properties.[262] Since nanoparticles are usually processed as dry powders, these must first be carefully disaggregated. This can be done in an aqueous phase with rotor–stator systems, high-pressure or ultrasonic homogenizers, or in ball mills (cf. 2.4).[27,263] The preparation of the nanoparticles has considerable influence on the properties of the subsequent nanoparticle-reinforced composite materials.[264]

Even simple template syntheses permit a wide range of variations in the manufacturing of macroporous ceramics of all sorts of shapes and compositions. With the aid of amphiphilic organic molecules, oxide nanoparticles (e.g. SiO_2, Al_2O_3, Fe_2O_3, Fe_3O_4) can be stabilized in emulsions, then dried and sintered and converted into macroporous ceramics with notable mechanical strength.[265] Owing to its mechanical properties, ZrO_2 is one of the most important oxide ceramics in this respect. Since its properties, as is well known, are closely related to the respective modification of the zirconium dioxide, the calcination temperature, possible doping, and particle size are particularly influential.[34] If ZrO_2 nanoparticles with diameters of about 5 nm are employed, the calcination provides almost quantitatively tetragonal ZrO_2 even at only 800 °C. As a consequence of the large specific surface area (cf. Section 2.1), the phase transition from monoclinic to tetragonal ZrO_2 thus occurs at a considerably lower temperature than in the bulk material (1170 °C).[266]

In addition to ceramic composites, metal-matrix nanocomposites (MMNC) are of increasing interest, especially in automobile and spacecraft manufacturing.[267] Besides the metallic matrix, these materials typically contain ceramic inclusions with particle diameters ranging from a few nanometers to a few hundred micrometers. The idea behind this approach is once again the optimization of the mechanothermal properties. For example, the hardness of Si–Al alloys can be increased by about 50 % by adding a mere 2 wt % SiC. As expected, the homogeneous dispersion of ceramic nanoparticles in molten metal proves to be a challenge.[39] Yang et al. achieved good results using ultrasonic probes at temperatures up to 100 °C above the solidification point of the respective molten charge. In this way, a practically homogeneous distribution of Al_2O_3 nanoparticles with diameters of about 10 nm in an aluminum matrix is achieved.[268] Provided that the nanoparticles are distributed homogeneously in the metallic matrix, these approaches may be expected to produce novel materials with very interesting mechanothermal and corrosive properties.

8. Nanocontainers, Molecular Particles, and Particulate Crystals

This last section goes deep into basic research but offers novel material shapes and structures and a visionary potential for the future, envisaging synthetic atoms, customized design of material properties, and even a formal extension of the periodic system.

8.1. Nanoparticulate Hollow Spheres

As a morphologically interesting class of substances, nanoparticulate hollow spheres have evoked manifold interest. The cavities enclosed in the hollow spheres are especially suitable as "nanocontainers" for inclusion, transportation, and targeted release of chemicals or pharmaceuticals. But nanoparticulate hollow spheres can also be of importance in light of other properties of the material, such as the large specific surface, the small specific weight, or the potentially high mechanical strength.[269]

Nanoparticulate hollow spheres are usually obtained by template methods. A prerequisite for this approach are practically monodisperse and non-agglomerated nanoparticles such as SiO_2,[270] metals (e.g. Fe, Bi, Ag, Au),[271] quantum dots (e.g. CdSe),[272] or polymer lattices,[273] which act as the template. A shell is subsequently precipitated onto these templates, and then the template is dissolved out through this shell. For SiO_2 templates, dissolution can be achieved with dilute hydrofluoric acid, for metal nanoparticles with oxidizing acids, and for lattices with nonpolar solvents or by burning out. Especially elegant is the reductive deposition of a more noble metal, such as gold, as the shell, while a less noble template, such as bismuth or silver, is simultaneously dissolved.[271] A prerequisite for template-based strategies, besides the availability of suitable templates, is the ability to dissolve the template out afterwards without damaging the shell. In addition to template methods, compact nanoparticles can in some cases be converted into nanoparticulate hollow spheres by Kirkendall ripening.[274]

With regard to exploiting the container functions, microemulsion techniques have turned out to be advantageous. Using these methods, various substances can be assembled as a crystalline shell around a micelle containing an aqueous or oil phase, which serves as a liquid template (Figure 35).[275] The size and wall thickness of the hollow spheres can be adjusted directly during synthesis by controlling the micelle
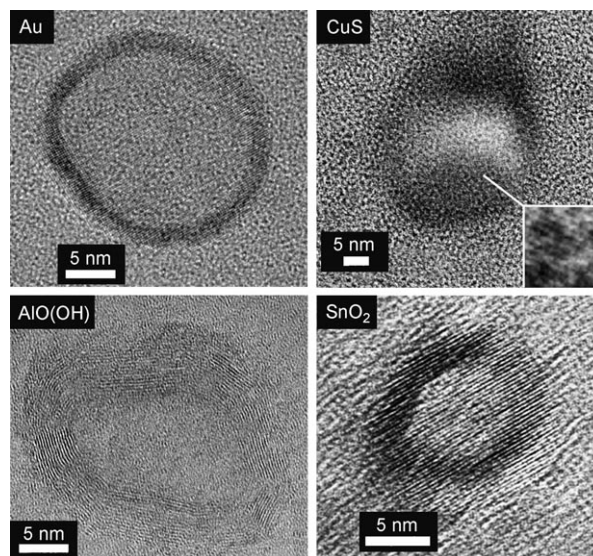
Figure 35. Nanoparticulate hollow spheres of various sizes and compositions (modified reproduction of ref. [276]).

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properties. Furthermore, a wide range of substances, such as inorganic salts, organic molecules, and biomolecules, can be dissolved in the micelles and enclosed after the synthesis of the wall of the hollow sphere. This approach has been verified for examples such as KSCN, $K_2S_2O_8$, phenylalanine, quercetin, and rhodamine.[276] The great variability of possible wall materials and ingredients proves to be the special strength of the microemulsion approach. In addition to simple hollow spheres, even rattle-like structures, in which a hollow sphere contains compact particles, can be obtained by various synthesis paths.[269] However, these structures must be considered mesoscopic, having dimensions which are sometimes considerably larger than 100 nm.

Initial studies have shown that nanoparticulate hollow spheres can have very interesting material properties. For example, SnO_2 or Si hollow spheres have proven to be promising electrode materials in lithium ion batteries (Section 4.3).[277] TiO_2 hollow spheres are very active photocatalysts (Section 6.3).[278] Au-, Pt-, or Pd-filled hollow spheres are suitable as catalysts and demonstrate a certain ability to store hydrogen.[279] And finally, hollow spheres can be employed as contrast agents in medicine or for transportation and targeted release of medications.[280] In many cases, however, the examples mentioned employ mesoscale hollow spheres. The mechanical properties are also extremely interesting. The high stability of spherical hollow objects under pressure is well known in the form of evacuable round-bottomed flasks. Alivisatos et al. were recently able to demonstrate a similar stability for CdS hollow spheres in situ. Despite considerable deformation, these withstood shear stresses up to 2.2 GPa.[281] Thus hollow spheres are also very promising as high-strength materials with a low specific weight.

8.2. Molecular Particles

The transition from atom or molecule to the solid state on the size scale of nanoparticles is scientifically fascinating. For example, molecules with a diameter of a few nanometers are now known whose core can be regarded as a segment of the crystalline structure of solids and whose shell consists of ligands which saturate this core.[282] On the one hand, these ligand-stabilized clusters correspond to very small nanoparticles, and on the other hand they form molecules of a defined composition and with a structure that can be determined by X-ray structure analysis. Starting with the prominent Au_{55} cluster in $[Au_{55}(PPh_3)_{12}Cl_6]$, which was presented in 1981 by Schmid et al.,[283] today the largest representatives of noble metals (e.g. $[Pd_{145}(CO)_x(PEt_3)_{30}]$ with $x \approx 60$)[284] and main-group metals (e.g. $[Ga_{84}(N-(SiMe_3)_2)_{20}Li_6Br_2(thf)_{20}]$),[285] as well as transition-metal oxides (e.g. $(Na_{48}[H_xMo_{368}O_{1032}(H_2O)_{240}(SO_4)_{48}]\cdot xH_2O$ with $x \approx 1000$)[286] and transition-metal chalcogenides (e.g. $[Ag_{490}S_{188}(StC_5H_{11})_{114}])$ are known.[287] Growing the crystals and the structural analysis of these compounds, some of which contain thousands of atoms, are a particular challenge, of course, especially if the ligand shell and particle core show a partial disorder. The latter is attributed, among other things, to an increased Laplace pressure in the interior of the particle

core.[287] To validate and understand the structures, high-resolution mass spectrometry and quantum mechanical calculations based on density function theoretical approaches have proven effective, in addition to single-crystal structural analysis. Besides large metal clusters, it is also possible to obtain "molecular alloys", with examples such as $[Cu_{40}Sb_{21}(PMe_3)_{16}]$ or $(PPh_4)_2[Bi_{10}Cu_{10}(SPh)_{24}]\cdot0.5DME$.[288]

With regard to their properties, cluster molecules of the transition-metal chalcogenides in particular display a behavior corresponding to that of quantum dots (cf. Section 3.3). For example, metal chalcogenide clusters also display luminescence; however, their emission wavelength is determined not by the diameter of the cluster core but by the respective ligand shell.[289] The inner diameter of the clusters can be determined by transmission electron microscopy and amounts to about 5 nm for $[Ag_{490}S_{188}(StC_5H_{11})_{114}]$, for example.[287] The inner ligand-free cluster core often has structure motifs that correspond to the elemental metals or the binary metal chalcogenides (e.g. M_2X with M: Cu, Ag; X: S, Se) in the solid (Figure 36). In some cases, the ligand shell can even be
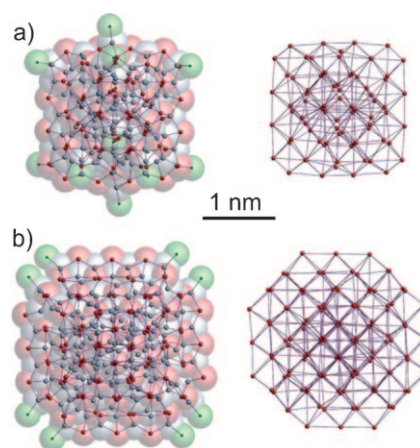
Figure 36. Structure of Ag-Se-P cluster cores in a) $[Ag_{114}Se_{34}(SetBu)_{46}(PtBu_3)_{14}]$ and b) $[Ag_{172}Se_{40}(SenBu)_{92}(dppp)_4]$ with the corresponding Se sublattices (Ag blue, Se red, P green, modified reproduction of ref. [282b]).

removed by thermal dissociation, forming "naked" nanoparticles. Fenske et al. demonstrated this for examples such as $[Cu_{26}Se_{13}(PEt_2Ph)_{14}]$, $[Cu_{44}Se_{22}(PEt_2Ph)_{18}]$, $[Cu_{70}Se_{35}(PEt_2Ph)_{23}]$, and $[Cu_{140}Se_{70}(PEt_2Ph)_{34}]$.[290] However, a certain aging of the originally 1–3 nm large cluster cores occurs, so that after the thermal dissociation, monodisperse α-Cu_2Se nanoparticles with a diameter of 15 nm are present.

Molecular particles can also serve as model substances for the fundamental understanding of elemental reactions and reaction mechanisms. Thus Schnöckel et al. showed for the example of aluminum clusters that the speed of oxygen oxidation depends on the spin state of the O_2 molecule and the number of aluminum atoms in the cluster.[291] For furthering our understanding, clusters such as $[Ga_{24}Br_{18}Se_2]$ can serve as a model for photoconductivity in GaSe. Aluminum or gallium clusters of various compositions contribute to our understanding of nucleation processes in metal

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vapors or of bonding conditions in clusters with magic electron numbers (such as jellium clusters).[292] Molecular particles also display properties that are typically found in bulk metals and alloys. For example, in the case of compounds with isolated $[Ga_{84}]^{4-}$ clusters, researchers were surprised to observe superconductivity, with a critical temperature of about 7 K.[293]

8.3. Particulate Crystals

In addition to the "molecular particles" discussed above, "particulate crystals", that is, three-dimensionally periodic arrangements of nanoparticles known as supercrystals, have opened entirely new perspectives in recent years.[294] We already discussed the crystallization of nanoparticles with a high index of refraction under the term "photonic crystals" in Section 3.2.[60] Now we turn to more complex arrangements in which nanoparticles of widely varying composition serve as lattice modules and form structures according to the pattern of close-packed crystal structures. As described for photonic crystals, here, too, a bottom-up approach requires a narrow size distribution of the nanoparticles (i.e. with deviations of less than 5% from the mean particle diameter) and precise control of the growth conditions. Supercrystals can now be obtained with nanoparticles of widely varying sizes and compositions. These can be oxides (e.g. SiO_2, ZnO, $BaCrO_4$), quantum dots (e.g. CdSe), main-group elements (e.g. Se), metals, or alloys (e.g. Ag, Au, Pd, Bi, FeCo; Figure 37).[295]
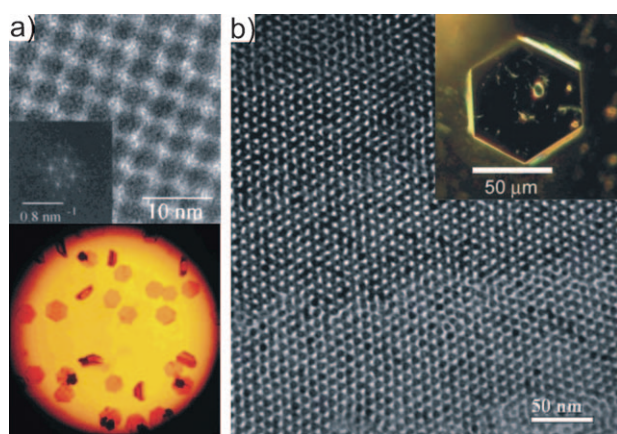
Figure 37. Supercrystals consisting of a) CdSe and b) Au nanoparticles (modified reproduction of (a) and (b) from refs. [295d] and [295f]).

Besides packings with one kind of particle, those with different particles are also known. In part, these follow known packing patterns and emulate the structures of ionic crystals or alloys, depending on the particle radii and the particle–particle interactions.[296] For example, Ag, Au, Pd, γ-Fe_2O_3, PbS, and PbSe nanoparticles of different sizes crystallize by cocrystallization in the NaCl, CsCl, AlB_2, $MgZn_2$, $MgNi_2$, Cu_3Au, Fe_4C, $CaCu_5$, CaB_6, $NaZn_{13}$, or other structure types (Figure 38).[297]

The challenge in creating such supercrystals is a well-directed crystallization of the nanoparticles, which requires, in addition to a monodisperse size distribution, defined surface functionalization and precise control of the conditions for nanoparticle self-organization.[294] As an alternative to methods based on a controlled, slow evaporation of the dispersion phase, particle deposition using electrical or magnetic fields has proven to be very successful.[298] Besides the aesthetic attraction of supercrystals, their properties give grounds for a variety of expectations, since the periodic arrangement of the nanoparticles is accompanied by a periodic alteration of the physicochemical properties in the particulate crystal. We already discussed this topic for the case of photonic crystals (cf. Section 3.2) and magnetic storage media (cf. Section 4.1). However, depending on the choice of nanoparticles, in principle the electrical conductivity, the density, thermal expansion, or work function can also alter periodically, thus resulting in an unforeseeable potential for customized design of materials and properties. In this construct, nanoparticles take the place of atoms and molecules not only structurally but also with respect to the material properties. These "synthetic atoms" can be regarded as an extension of the periodic system to the nanometer scale and even beyond. Periodic arrangements can now be achieved not only by cocrystallization of different nanoparticles but also with molecular clusters of differing composition. This approach has been demonstrated, for example, with $[Au_8(PPh_3)_8](C_{60})_2$ (Figure 39).[299] The compound crystallizes in the AlB_2 type and consists of cationic gold clusters and fulleride anions.

Overall, the examples of molecular particles and particulate crystals show how much the boundaries between classical molecular chemistry and classical solid-state chemistry are becoming blurred. We can only look forward with anticipation to the compounds, structures, and properties which will arise from this field in the future.

9. Quo Vadis Nanoparticles?

Nanoparticles now find a variety of industrial applications, in particular for modifying and upgrading a wide range of substrates and materials. These applications range from hardening and ultraviolet stabilization to self-cleaning or antimicrobial surfaces. Nanoparticles have also found a broad area of applications in heterogeneous catalysis, ranging from classical synthesis chemistry to photocatalysis. With model compounds, a fundamental understanding of catalytic reactions can be established. In many applications, nanoparticles are on the threshold of widespread use. Such areas include the use of luminescent, plasmonic, and magnetic nanoparticles in molecular biology and medical diagnosis and therapy. Nanoparticulate pigments and luminophors, transparent conductive oxides, and magnetic fluids should be mentioned in this context. In the field of functionalized thin films, nanoparticles are essential for the progressive miniaturization and sparing use of materials, which is of great importance for printed electronics in particular and ranges from flexible electronic circuit elements, light-emitting diodes, and visual display units to dye-sensitized solar cells and magnetic data-storage media. For obtaining high-quality nanoparticles, the synthesis of the material is of vital importance, as the quality of the
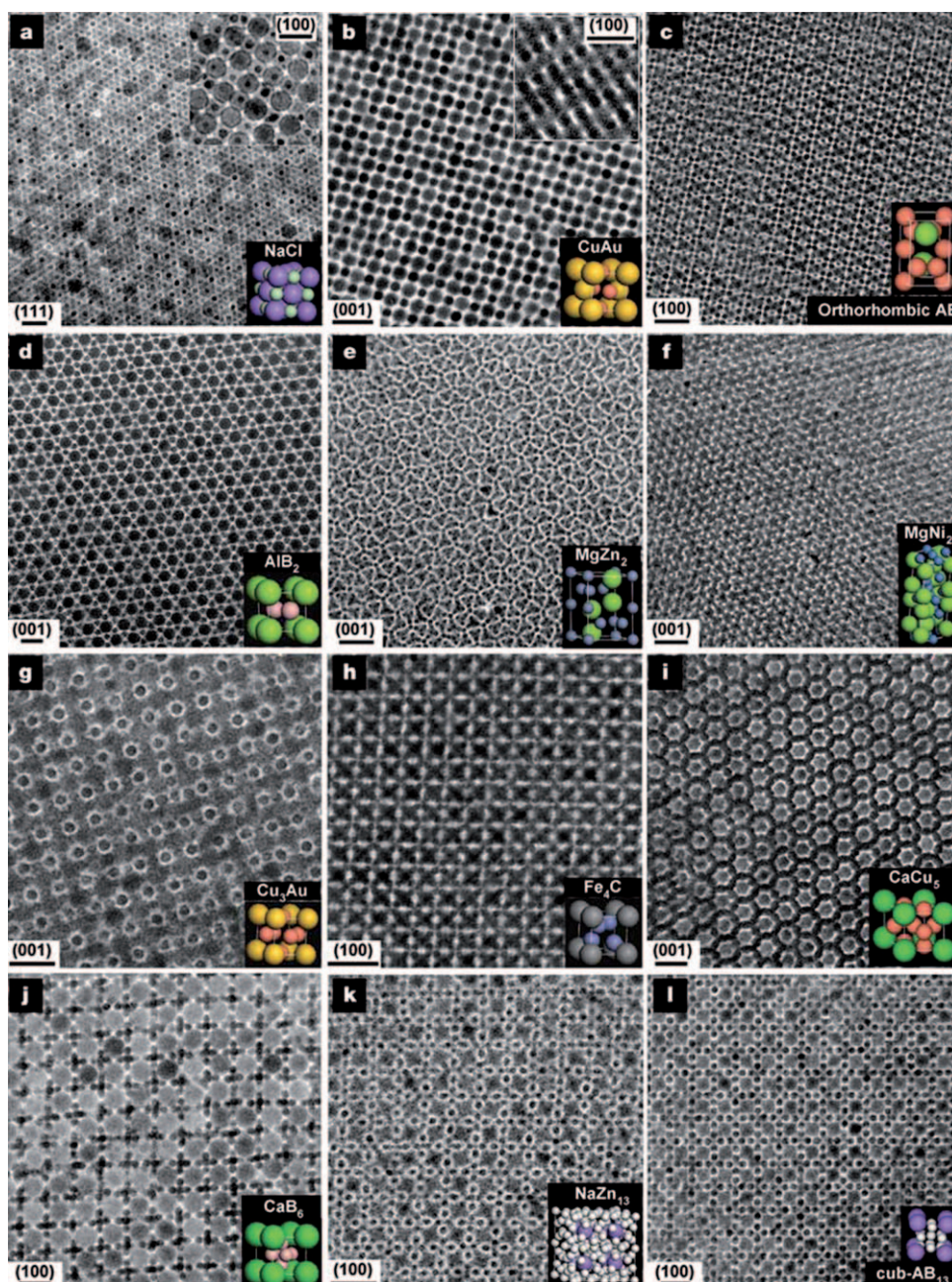
Figure 38. Cocrystallization of a) γ-Fe$_2$O$_3$ and Au nanoparticles (13.4 and 5.0 nm), b) PbSe and Au nanoparticles (7.6 and 5.0 nm), c) PbSe and Pd nanoparticles (6.2 and 3.0 nm), d) PbS and Pd nanoparticles (6.7 and 3.0 nm), e) PbSe and Pd nanoparticles (6.2 and 3.0 nm), f) PbSe and Pd nanoparticles (5.8 and 3.0 nm), g) PbSe and Au nanoparticles (7.2 and 4.2 nm), h) PbSe and Pd nanoparticles (6.2 and 3.0 nm), i) PbSe and Au nanoparticles (7.2 and 5.0 nm), j) PbSe and Pd nanoparticles (5.8 and 3.0 nm), k) PbSe and Ag nanoparticles (7.2 and 4.2 nm), l) PbSe and Pd nanoparticles (6.2 and 3.0 nm) to supercrystals with various packing arrangements (scale: a–c, e, f, i–l: 20 nm; d, g, h: 10 nm; modified reproduction of ref. [297]).

nucleus growth, stabilization and functionalization of surfaces). Many other aspects of chemistry, physics, biology, materials science, and disciplines such as engineering science or medicine play an important role. This high degree of interdisciplinarity is a characteristic feature of nanosciences and nanotechnology and contributes a great deal to the fascination of the field.

Although this Review is not intended to provide a technology impact assessment for nanoparticles, a brief evaluation seems appropriate. Like every novel area of research and every novel technology, nanosciences and nanotechnology evoke questions about their risks. Two aspects, however sweeping and simple, deserve consideration as part of an unprejudiced evaluation: 1) The "nanosciences" are already extremely varied and complex with respect to materials, syntheses, processing techniques, and properties. So there is little sense in subsuming this all under the overarching term "nanomaterial". 2) Belittling the risks is just as unhelpful as overdramatizing them, especially as long as no well-founded data are available; indeed, in view of the novelty of the research field, such data cannot be available yet. While some nanoparticles, such as Au, Ag, SiO$_2$, TiO$_2$, Al$_2$O$_3$, and Fe$_2$O$_3$, have been in industrial use for many years and are therefore well-known, novel nanoparticles can naturally only now be the subject of study.[300] However, a decided evaluation needs both time and money.

It seems beyond question that nanoparticles can and will make decisive contributions to future economic and social development. The discussed examples of solar cells, thermoelectric materials, lithium ion batteries, fuel cells, and photocatalytic dissociation of water show their contributions to new concepts of energy storage and conversion impressively. In

material properties and of the subsequent function is shaped here. In many cases, the complexity of the synthesis and the cost of the materials still present obstacles to the use of nanoparticles. The field of experimental parameters is very complex, comprising both classical synthesis parameters (e.g. kind of initial compounds, concentration, temperature control) and questions of colloid chemistry (e.g. nucleation and
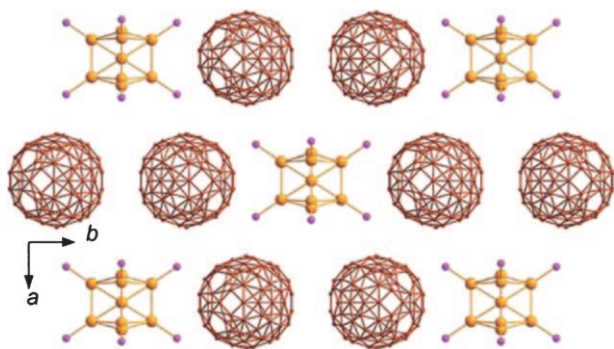
Figure 39. Crystal structure of [Au$_8$(PPh$_3$)$_8$](C$_{60}$)$_2$ with [Au$_8$(PPh$_3$)$_8$]$^{2+}$ cations and (C$_{60}$)$^-$ anions along [001] (shown without PPh$_3$ ligands for the sake of clarity; modified reproduction of ref. [299]).

molecular biology and medicine, entirely new perspectives for diagnosis and therapy, going down to the level of single cells and molecules, are opening up. Examples such as nano-containers, particulate molecules, and supercrystals show that fundamentally novel materials can be obtained, from which new properties and applications as well as targeted design of materials at the nanoscale can be expected. And finally, molecular particles and particulate crystals even allow us to envisage a formal extension of the periodic system with colloidal "superatoms". Surprises are preprogrammed and are the very essence of science.

Overall, this survey may be summed up aptly with a phrase by the Nobel laureate Richard Feynman, which was visionary at the time, has often been quoted since, and remains absolutely up-to-the-minute: "There is plenty of room at the bottom".[301] No doubt, we can add "still" and "tremendous".

[1] First reviews in: a) K. H. Bennemann, J. Koutecky, *Small Particles and Inorganic Clusters*, North Holland, Amsterdam, **1985**; b) M. D. Morse, *Chem. Rev.* **1986**, *86*, 1049; c) P. Jena, B. K. Rao, S. N. Khanna, *Physics and Chemistry of Small Clusters*, Plenum, New York, **1986**; d) A. Henglein, *Chem. Rev.* **1989**, *89*, 1861.

[2] The American Chemical Society, *Program package Scifinder*, Washington, **2009**.

[3] W. Goffman, V. A. Nevil, *Nature* **1964**, *204*, 225.

[4] Current reviews in: a) *The Chemistry of Nanomaterials* (Eds.: C. N. R. Rao, A. Müller, A. K. Cheetham), Wiley-VCH, Weinheim, **2004**; b) C. Burda, X. Chen, R. Narayanan, M. A. El-Sayed, *Chem. Rev.* **2005**, *105*, 1025; c) D. Vollath, *Nano-materials*, Wiley-VCH, Weinheim, **2008**.

[5] Current reviews in: a) G. A. Ozin, A. C. Arsenault, *Nano-chemistry*, RSC Publishing, Cambridge, **2005**, p. 167; b) M. C. Hersam, *Nat. Nanotechnol.* **2008**, *3*, 387; c) V. Sgobba, D. M. Vito, *Chem. Soc. Rev.* **2009**, *38*, 165.

[6] > Current reviews in: a) M. Ballauff, *Macromol. Chem. Phys.* **2003**, *204*, 220; b) A. C. Grimsdale, K. Müllen, *Angew. Chem.* **2005**, *117*, 5732; *Angew. Chem. Int. Ed.* **2005**, *44*, 5592; c) Q. Yuan, R. D. K. Misra, *Mater. Sci. Technol.* **2006**, *22*, 742; d) A. B. Descalzo, R. Martinez-Manez, F. Sancenon, K. Hoff-mann, K. Rurack, *Angew. Chem.* **2006**, *118*, 6068; *Angew. Chem. Int. Ed.* **2006**, *45*, 5924; e) K. Landfester, *Angew. Chem.* **2009**, *121*, 4556; *Angew. Chem. Int. Ed.* **2009**, *48*, 4488.

[7] a) M. Takagi, *J. Phys. Soc. Jpn.* **1954**, *9*, 551; b) C. R. M. Wronski, *Br. J. Appl. Phys.* **1967**, *18*, 1731.

[8] a) *Nanoscale Materials in Chemistry* (Ed: K. J. Klabunde), Wiley, New York, **2001**, S. 263; b) R. Alsfasser, C. Janiak, T. M. Klapötke, H. J. Meyer in *Moderne Anorganische Chemie* (Ed.: E. Riedel), de Gruyter, Berlin, **2007**.

[9] K. J. Klabunde, S. Winecki in *Nanoscale Materials in Chemistry* (Ed.: K. J. Klabunde), Wiley, New York, **2001**, p. 223.

[10] D. von Kerssenbrock-Krosigk, *Rubinglas des ausgehenden 17. und des 18. Jahrhunderts*, Verlag Philipp von Zabern, Mainz, **2001**.

[11] J. Z. Zhang, C. Noguez, *Plasmonics* **2008**, *3*, 127.

[12] E. Roduner, *Nanoscopic Materials: Size-Dependent Phenom-ena*, RCS Publishing, Cambridge, **2006**.

[13] P. P. Edwards, J. M. Thomas, *Angew. Chem.* **2007**, *119*, 5576; *Angew. Chem. Int. Ed.* **2007**, *46*, 5480.

[14] G. Jander, E. Blasius, *Lehrbuch der analytischen und präpar-ativen anorganischen Chemie*, Hirzel, Stuttgart, **2002**, p. 500.

[15] M. Faraday, *Philos. Trans. R. Soc. London* **1857**, *147*, 145.

[16] W. Umbach, *Kosmetik – Entwicklung, Herstellung und Anwen-dung kosmetischer Mittel*, Wiley-VCH, Weinheim, **1995**, p. 147.

[17] H. C. van de Hulst, *Light Scattering by Small Particles*, Dover Publications, New York, **1981**.

[18] Current reviews in: a) S. Abbet, U. Heiz, *Nanocatalysis* in *The Chemistry of Nanomaterials* (Eds.: C. N. R. Rao, A. Müller, A. K. Cheetham), Wiley-VCH, Weinheim, **2004**, S. 551; b) J. M. Thomas, R. Raja, *Top. Catal.* **2006**, *40*, 3; c) N. Shiju, G. Raveendran, V. Vadim, *Appl. Catal. A* **2009**, *356*, 1.

[19] a) Lycurgus beaker (late Roman, fifth–sixth century): British Museum, London; b) facetted carafes of ruby glass (Dresden, ca. 1715,): in the state art collection of the Grünes Gewölbe, Dresden; c) suspensions with gold nanoparticles: Susanne Ernst, Examensarbeit für das höhere Lehramt, University of Karlsruhe **2009**.

[20] S. Becht, Examensarbeit für das höhere Lehramt, University of Karlsruhe **2009**.

[21] a) W. Ostwald, *Z. Kolloidchem.* **1910**, *6*, 183; b) R. Zsigmondy, *Z. Kolloidchem.* **1912**, *198*, 217; c) H. D. Dörfler, *Grenzflächen und kolloid-disperse Systeme*, Springer, Berlin, **2002**.

[22] Current reviews in: a) J. Loos, *Adv. Mater.* **2005**, *17*, 1821; b) N. Tanaka, *Adv. Imaging Electron Phys.* **2008**, *153*, 385; c) D. A. Muller, *Nat. Mater.* **2009**, *8*, 263.

[23] Current reviews in: a) R. E. Dunin-Borkowski, T. Kasama, R. J. Harrison, *Nanocharacterisation* **2007**, 138; b) D. Wouters, U. S. Schubert, *Angew. Chem.* **2004**, *116*, 2534; *Angew. Chem. Int. Ed.* **2004**, *43*, 2480; c) M. Hosokawa, K. Nogi, M. Naito, T.

Yokoyama, *Nanoparticle Technology Handbook*, Elsevier, Oxford, **2007**.

[24] F. Fleischhaker, R. Zentel, *Chem. Unserer Zeit* **2007**, *41*, 38.

[25] S. Kim, Y. T. Lim, E. G. Soltesz, A. M. De Grand, J. Lee, A. Nakayama, J. A. Parker, T. Mihalijevic, R. G. Laurence, D. M. Dor, L. H. Cohn, M. G. Bawendi, J. V. Frangioni, *Nat. Biotechnol.* **2004**, *22*, 93.

[26] W. J. Parak, L. Manna, F. C. Simmel, S. Gerion, P. Alivisatos, *Quantum Dots* in *Nanoparticles* (Ed.: G. Schmid), Wiley-VCH, Weinheim, **2004**, p. 4.

[27] Current reviews in: a) A. P. Newbery, B. Q. Han, E. J. Lavernia, C. Suryanarayana, J. A. Christodoulou, *Mater. Process. Handb.* **2007**, *13*, 1; b) Q. Zhang, J. Kano, F. Saito, *Handb. Powder Technol.* **2007**, *12*, 509.

[28] Current reviews in: a) A. Gutsch, H. Mühlenweg, M. Krämer, *Small* **2005**, *1*, 30; b) D. Vollath, *Nanomaterials*, Wiley-VCH, Weinheim, **2008**, p. 71.

[29] Current reviews in: a) B. L. Cushing, V. L. Kolesnichenko, C. J. O'Connor, *Chem. Rev.* **2004**, *104*, 3893; b) T. Dwars, E. Paetzold, G. Oehme, *Angew. Chem.* **2005**, *117*, 7338; *Angew. Chem. Int. Ed.* **2005**, *44*, 7174; c) U. Jeong, Y. Wang, M. Ibisate, Y. Xia, *Adv. Funct. Mater.* **2005**, *15*, 1907; d) J. Park, J. Joo, S. G. Kwon, Y. Jang, T. Hyeon, *Angew. Chem.* **2007**, *119*, 4714; *Angew. Chem. Int. Ed.* **2007**, *46*, 4630; e) N. Pinna, M. Niederberger, *Angew. Chem.* **2008**, *120*, 5372; *Angew. Chem. Int. Ed.* **2008**, *47*, 5292.

[30] Current reviews in: a) T. F. Tadros, *Applied Surfactants*, Wiley-VCH, Weinheim, **2005**; b) *Biofunctionalization of Nanomaterials* (Ed.: C. S. S. R. Kumar), Wiley-VCH, Weinheim, **2005**.

[31] Current reviews in: a) Y. Yin, R. M. Rioux, C. K. Erdonmez, S. Hughes, G. A. Somerjai, A. P. Alivisatos, *Science* **2004**, *304*, 711; b) P. R. Selvakannan, M. Sastry, *Chem. Commun.* **2005**, 1684; c) Y. W. Jun, J. S. Choi, J. Cheon, *Angew. Chem.* **2006**, *118*, 3492; *Angew. Chem. Int. Ed.* **2006**, *45*, 3414; d) S. E. Skrabalak, J. Chen, L. Au, X. Liu, X. Li, Y. Xia, *Adv. Mater.* **2007**, *19*, 3177; e) D. Kim, J. Park, K. An, N. K. Yang, J. G. Park, T. Hyeon, *J. Am. Chem. Soc.* **2007**, *129*, 5812; f) X. Wang, H. Fu, A. Peng, T. Zhai, Y. Ma, F. Yuan, J. Yao, *Adv. Mater.* **2009**, *21*, 1636.

[32] V. K. LaMer, R. H. Dinegar, *J. Am. Chem. Soc.* **1950**, *72*, 4847.

[33] W. Ostwald, *Z. Phys. Chem.* **1879**, *22*, 289.

[34] A. R. West, *Solid State Chemistry and its Applications*, Wiley, Chichester, **1990**, p. 263.

[35] G. Jander, E. Blasius, *Lehrbuch der analytischen und präparativen anorganischen Chemie*, Hirzel, Stuttgart, **2002**, p. 131.

[36] a) C. B. Murray, D. B. Norris, M. G. Bawendi, *J. Am. Chem. Soc.* **1993**, *115*, 8706; b) C. de Mello Donegá, P. Liljeroth, D. Vanmaekelbergh, *Small* **2005**, *1*, 1152.

[37] a) D. Myers, *Surfaces, Interfaces and Colloids*, Wiley-VCH, Weinheim, **1999**; b) H. D. Dörfler, *Grenzflächen und kolloid-disperse Systeme*, Springer, Berlin, **2002**.

[38] Y. Song, J. Hormes, C. S. S. R. Kumar, *Small* **2008**, *4*, 698.

[39] Current review in: a) H. Althues, J. Henle, S. Kaskel, *Chem. Soc. Rev.* **2007**, *36*, 1454; b) P. M. Ajayan, L. S. Schadler, P. V. Braun, *Nanocomposite Science and Technology*, Wiley-VCH, Weinheim, **2003**.

[40] Reviews in: a) K. Bittler, W. Ostertag, *Angew. Chem.* **1980**, *92*, 187; *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 190; b) G. Buxbaum, *Industrial Inorganic Pigments*, VCH, Weinheim, **1993**; c) S. Schnittger, M. Sinha, *MRS Bull.* **2007**, *32*, 760.

[41] A. F. Hollemann, N. Wiberg, *Lehrbuch der Anorganischen Chemie*, de Gruyter, Berlin, **2007**, p. 1686.

[42] a) M. Veith, S. Mathur, C. Mathur, *Polyhedron* **1998**, *17*, 1005; b) C. Feldmann, *Adv. Mater.* **2001**, *13*, 1301; c) D. Wang, X. Liang, Y. Li, *Chem. Asian J.* **2006**, *1*, 91; d) D. Rangappa, T. Naka, A. Kondo, M. Ishii, T. Kobayashi, T. Adschin, *J. Am. Chem. Soc.* **2007**, *129*, 11061; e) N. El Habra, L. Crociani, C. Sada, P. Zanella, M. Casarin, G. Rossetto, G. Carta, G. Paolucci, *Chem. Mater.* **2007**, *19*, 3381.

[43] J. E. Millstone, S. J. Hurst, G. S. Metraux, J. I. Cutler, C. A. Mirkin, *Small* **2009**, *5*, 646.

[44] Q. Zhang, J. Ge, T. Pham, J. Goebl, Y. Hu, Z. Lu, Y. Yin, *Angew. Chem.* **2009**, *121*, 3568; *Angew. Chem. Int. Ed.* **2009**, *48*, 3516.

[45] a) A. V. Akimov, A. Mukherjee, C. L. Yu, D. E. Chang, A. S. Zibrov, P. R. Hemmer, H. Park, M. D. Lukin, *Nature* **2007**, *450*, 402; b) Z. Li, T. Shegai, G. Haran, H. Xu, *ACS Nano* **2009**, *3*, 637.

[46] Current reviews in: a) A. C. Daniel, D. Astruc, *Chem. Rev.* **2004**, *104*, 293; b) H. D. Hill, R. A. Vaga, C. A. Mirkin, *Anal. Chem.* **2007**, *79*, 9218; c) J. N. Anker, W. P. Hall, O. Lyandres, N. C. Shah, J. Zhao, R. P. van Duyne, *Nature* **2008**, *7*, 442; d) P. K. Jain, X. Huang, I. H. El-Sayed, M. A. El-Sayed, *Acc. Chem. Res.* **2008**, *41*, 1578.

[47] N. L. Rosi, D. A. Giljohann, C. S. Thaxton, A. K. R. Lytton-Jean, M. S. Han, C. A. Mirkin, *Science* **2006**, *312*, 1027.

[48] R. Leggett, E. E. Lee-Smith, S. M. Jickells, D. A. Russell, *Angew. Chem.* **2007**, *119*, 4178; *Angew. Chem. Int. Ed.* **2007**, *46*, 4100.

[49] I. Díez, M. Pusa, S. Kulmala, H. Jiang, A. Walther, A. S. Goldmann, A. H. E. Müller, O. Ikkala, R. H. A. Ras, *Angew. Chem.* **2009**, *121*, 2156; *Angew. Chem. Int. Ed.* **2009**, *48*, 2122.

[50] Current reviews in: a) A. Murray, W. L. Barnes, *Adv. Mater.* **2007**, *19*, 3771; b) J. Biener, G. W. Nyce, A. M. Hodge, M. M. Biener, A. V. Hamza, S. A. Maier, *Adv. Mater.* **2008**, *20*, 1211.

[51] J. F. Hainfeld, D. N. Slatkin, T. M. Focella, H. M. Smilowitz, *Br. J. Radiol.* **2006**, *79*, 248.

[52] a) Z. Wu, D. Lee, M. F. Rubner, R. E. Cohen, *Small* **2007**, *3*, 1445; b) M. C. Fuertes, F. J. Lopez-Alcaraz, M. C. Marchi, H. E. Troani, V. Luca, H. Miguez, G. J. D. A. Soler-Illia, *Adv. Funct. Mater.* **2007**, *17*, 1247.

[53] J. D. Joannopoulos, S. G. Johnson, J. N. Winn, R. D. Meade, *Photonic Crystals: Molding the Flow of Light*, Dover Publishing, New York, **1989**.

[54] L. D. Bonifacio, B. V. Lotsch, D. P. Puzzo, F. Scotognella, G. A. Ozin, *Adv. Mater.* **2009**, *21*, 1641.

[55] B. V. Lotsch, G. A. Ozin, Geoffrey, *Adv. Mater.* **2008**, *20*, 4079.

[56] a) G. A. Ozin, A. C. Arsenault, *Mater. Today* **2008**, *11*, 44; b) D. P. Puzzo, A. C. Arsenault, I. Manners, G. A. Ozin, *Angew. Chem.* **2009**, *121*, 961; *Angew. Chem. Int. Ed.* **2009**, *48*, 943.

[57] F. Scotognella, D. P. Puzzo, A. Monguzzi, D. S. Wiersma, D. Maschke, R. Tubino, G. A. Ozin, *Small* **2009**, *5*, 2048.

[58] J. V. Sanders, *Acta Crystallogr. Sect. A* **1968**, *24*, 427.

[59] F. Marlow, Muldarisnur, P. Sharafi, R. Brinkmann, C. Medive, *Angew. Chem.* **2009**, *121*, 6328; *Angew. Chem. Int. Ed.* **2009**, *48*, 6212.

[60] Current review in: a) Y. Xia, B. Gates, Y. Yin, Y. Lu, *Adv. Mater.* **2000**, *12*, 693; b) Z. Li, J. Yuan, Y. Chen, R. E. Palmer, J. P. Wilcoxon, *Adv. Mater.* **2005**, *17*, 2885; c) G. Schmid, U. Simon, *Chem. Commun.* **2005**, 697; d) P. V. Braun, S. A. Rinne, F. Garcia-Santamaria, *Adv. Mater.* **2006**, *18*, 2665; e) B. L. V. Prasad, C. M. Sorensen, K. J. Klabunde, *Chem. Soc. Rev.* **2008**, *37*, 1871.

[61] K. Busch, S. John, *Phys. Rev. E* **1998**, *58*, 3896.

[62] a) N. Tétreault, H. Miguez, G. A. Ozin, *Adv. Mater.* **2004**, *16*, 1471; b) D. J. Norris, E. G. Arlinghaus, L. Meng, R. Heiny, L. E. Scriven, *Adv. Mater.* **2004**, *16*, 1393.

[63] A. Blanco, E. Chomski, S. Grabtchak, M. Ibisate, S. John, S. W. Leonard, C. Lopez, F. Meseguer, H. Miguez, J. P. Mondia, G. A. Ozin, O. Toader, H. M. van Driel, *Nature* **2000**, *405*, 437.

[64] E. Yablonovitch, *Phys. Rev. Lett.* **1987**, *58*, 2059.

[65] D. C. Meisel, M. Diem, M. Deubel, F. Perez-Willard, S. Linden, D. Gerthsen, K. Busch, M. Wegener, *Adv. Mater.* **2006**, *18*, 2964.

These are not the final page numbers!

[66] P. V. Braun, S. A Rinne, F. Garcia-Santamaria, *Adv. Mater.* **2006**, *18*, 2665.

[67] W. A. Murray, W. L. Barnes, *Adv. Mater.* **2007**, *19*, 3771.

[68] Current reviews in: a) C. W. E. van Eijk, *Phys. Med. Biol.* **2002**, *47*, R85; b) C. Feldmann, T. Jüstel, C. R. Ronda, P. J. Schmidt, *Adv. Funct. Mater.* **2003**, *13*, 511; c) H. A. Höppe, *Angew. Chem.* **2009**, *121*, 3626; *Angew. Chem. Int. Ed.* **2009**, *48*, 3572.

[69] Current reviews in: a) G. M. Whitesides, *Nat. Biotechnol.* **2003**, *21*, 1161; b) X. Michalet, F. F. Pinaud, L. A. Bentolila, J. M. Tsay, S. Doose, J. J. Li, G. Sundaresan, A. M. Wu, S. S. Gambhir, S. Weiss, *Science* **2005**, *307*, 538; c) J. M. Klostranec, W. C. W. Chan, *Adv. Mater.* **2006**, *18*, 1953; d) R. C. Somers, M. G. Bawendi, D. G. Nocera, *Chem. Soc. Rev.* **2007**, *36*, 579; e) H. Hang, D. Yee, C. Wang, *Nanomedicine* **2008**, *3*, 83; f) Y. Xia, *Nat. Mater.* **2008**, *7*, 758.

[70] G. Bühler, C. Feldmann, *Appl. Phys. A* **2007**, *87*, 631.

[71] J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, Kluwer Academic, Norwell, **1999**.

[72] *Phosphor Handbook* (Eds.: S. Shionoya, W. M. Yen), CRC, Boca Raton, **1999**.

[73] G. Blasse, C. Grabmaier, *Luminescent Materials*, Springer, Berlin, **1994**.

[74] G. Blasse, A. Bril, *Philips Tech. Rundsch.* **1970/71**, *31*, 320.

[75] Current reviews in: a) S. J. Clarke, C. A. Hollmann, Z. Zhang, D. Suffern, S. E. Bradforth, N. M. Dimitrijevic, W. G. Minarik, J. L. Nadeau, *Nat. Mater.* **2006**, *5*, 409; b) M. K. So, C. Xu, A. M. Loening, S. S. Gambhir, J. Rao, *Nat. Biotechnol.* **2006**, *24*, 339; c) B. Nitzsche, F. Ruhnow, S. Diez, *Nat. Nanotechnol.* **2008**, *3*, 552.

[76] C. B. Murray, D. J. Norris, M. G. Bawendi, *J. Am. Chem. Soc.* **1993**, *115*, 8706.

[77] a) Z. A. Peng, X. Peng, *J. Am. Chem. Soc.* **2001**, *123*, 183; b) L. Qu, Z. A. Peng, X. Peng, *Nano Lett.* **2001**, *1*, 333; c) I. Mekis, D. V. Talapin, A. Kornowski, M. Haase, H. Weller, *J. Phys. Chem. B* **2003**, *107*, 7454.

[78] Current reviews in: a) T. Trindade, P. O'Brien, N. L. Pickett, *Chem. Mater.* **2001**, *13*, 3843; b) M. Green, *Curr. Opin. Solid State Mater. Sci.* **2002**, *6*, 355; c) *Nanoparticles* (Ed.: G. Schmid), Wiley-VCH, Weinheim, **2004**, p. 4, 50, 305; d) E. H. Sargent, *Adv. Mater.* **2005**, *17*, 515.

[79] P. Reiss, M. Protière, L. Li, *Small* **2009**, *5*, 154.

[80] a) M. A. Hines, P. Guyot-Sionnest, *J. Phys. Chem.* **1996**, *100*, 468; b) B. O. Dabbousi, J. Rodriguez-Viejo, F. V. Mikulec, J. R. Heine, H. Mattoussi, R. Ober, K. F. Jensen, M. G. Bawendi, *J. Phys. Chem. B* **1997**, *101*, 9463.

[81] a) L. P. Balet, S. A. Ivanov, A. Piryatinski, M. Achermann, V. I. Klimov, *Nano Lett.* **2004**, *4*, 1485; b) D. C. Pan, Q. Wang, S. C. Jiang, X. L. Ji, L. J. An, *Adv. Mater.* **2005**, *17*, 176; c) P. Reiss, J. Bleuse, A. Pron, *Nano Lett.* **2002**, *2*, 781; d) L. Li, P. Reiss, *J. Am. Chem. Soc.* **2008**, *130*, 11588; e) P. T. K. Chin, C. D. M. Doneaga, S. S. Bavel, S. C. J. Meskers, N. Sommerdijk, R. A. J. Janssen, *J. Am. Chem. Soc.* **2007**, *129*, 14880; f) A. Aharoni, T. Mokari, I. Popov, U. Banin, *J. Am. Chem. Soc.* **2006**, *128*, 257.

[82] a) Y. Su, Y. He, H. Lu, L. Sai, Q. Li, W. Li, L. Wang, P. Shen, Q. Huang, C. Fan, *Biomaterials* **2008**, *30*, 19; b) J. Curtis, M. Greenberg, J. Kester, S. Phillips, G. Krieger, *Toxicol. Rev.* **2006**, *25*, 245.

[83] M. S. Nikolic, M. Krack, V. Aleksandrovic, A. Kornowski, S. Förster, H. Weller, *Angew. Chem.* **2006**, *118*, 6727; *Angew. Chem. Int. Ed.* **2006**, *45*, 6577.

[84] Current reviews in: a) S. Kumar, T. Nann, *Small* **2006**, *2*, 316; b) G. D. Scholes, *Adv. Funct. Mater.* **2008**, *18*, 1157; c) N. Murase, P. Yang, *Small* **2009**, *5*, 800.

[85] a) R. D. Tilley, K. Yamamoto, *Adv. Mater.* **2006**, *18*, 2053; b) V. S. Y. Lin, *Nat. Mater.* **2009**, *8*, 252.

[86] a) A. B. Djurisic, Y. H. Leung, *Small* **2006**, *2*, 944; b) H. M. Xiong, D. G. Shchukin, H. Möhwald, Y. Xu, Y. Y. Xia, *Angew. Chem.* **2009**, *121*, 2765; *Angew. Chem. Int. Ed.* **2009**, *48*, 2727.

[87] A. Mews, A. Eychmüller, M. Giersig, D. Schooss, H. Weller, *J. Phys. Chem.* **1994**, *98*, 934.

[88] a) Y. Oaki, H. Imai, *Adv. Mater.* **2006**, *18*, 1807; b) Z. Wang, G. Li, Z. Quan, D. Kong, X. Liu, M. Yu, J. Lin, *J. Nanosci. Nanotechnol.* **2007**, *7*, 602; c) C. Li, C. Lin, X. Liu, J. Lin, *J. Nanosci. Nanotechnol.* **2008**, *8*, 1183; d) Y. Su, L. Li, G. Li, *J. Mater. Chem.* **2009**, *19*, 2316.

[89] a) K. Riwotzki, H. Meyssamy, H. Schnablegger, A. Kornowski, M. Haase, *Angew. Chem.* **2001**, *113*, 574; *Angew. Chem. Int. Ed.* **2001**, *40*, 573; b) G. Bühler, C. Feldmann, *Angew. Chem.* **2006**, *118*, 4982; *Angew. Chem. Int. Ed.* **2006**, *45*, 4864; c) K. Hickmann, K. Kömpe, A. Hepp, M. Haase, *Small* **2008**, *4*, 2136.

[90] a) S. Ahmadi, M. Haase, H. Weller, *Mater. Res. Bull.* **2000**, *35*, 1869; b) Y. C. Kang, H. D. Park, *Appl. Phys. A* **2003**, *77*, 529; c) A. Roy, S. Polarz, S. Rabe, B. Rellinghaus, H. Zahres, F. E. Kruis, M. Driess, *Chem. Eur. J.* **2004**, *10*, 1565; d) A. Manavbasi, J. C. LaCombe, *J. Mater. Sci.* **2007**, *42*, 252; e) M. Mai, C. Feldmann, *Solid State Sci.* **2009**, *11*, 528.

[91] a) A. A. Bol, A. Meijerink, *Phys. Rev. B* **1998**, *58*, R15997; b) N. Karar, F. Singh, B. R. Mehta, *J. Appl. Phys.* **2004**, *95*, 656; c) D. R. Jung, D. Son, J. Kim, C. Kim, B. Park, *Appl. Phys. Lett.* **2008**, *93*, 163118.

[92] a) R. M. Laine, J. Marchal, H. Sun, X. Q. Pan, *Adv. Mater.* **2005**, *17*, 830; b) P. A. Tanner, L. Fu, L. Ning, B. M. Cheng, M. G. Brik, *J. Phys. Condens. Matter* **2007**, *19*, 216213.

[93] a) A. Huignard, V. Buissette, A. C. Franville, T. Gacoin, J. P. Boilot, *J. Phys. Chem. B* **2003**, *107*, 6754; b) J. Liu, Y. Li, *Adv. Mater.* **2007**, *19*, 1118; c) F. Wang, X. Xue, X. Liu, *Angew. Chem.* **2008**, *120*, 920; *Angew. Chem. Int. Ed.* **2008**, *47*, 906; d) A. Zharkouskaya, H. Lünsdorf, C. Feldmann, *J. Mater. Sci.* **2009**, *44*, 3936.

[94] a) G. Pan, H. Song, L. Yu, Z. Liu, X. Bai, Y. Lei, L. Fan, S. Lu, X. Ren, *J. Nanosci. Nanotechnol.* **2007**, *7*, 593; b) Z. Li, J. Zeng, Y. Li, *Small* **2007**, *3*, 438; c) Y. Li, J. Zhang, X. Zhang, Y. Luo, S. Lu, X. Ren, X. Wang, L. Sun, C. Yan, *Chem. Mater.* **2009**, *21*, 468.

[95] a) G. Wakefield, E. Holland, P. J. Dobson, J. L. Hutchinson, *Adv. Mater.* **2001**, *13*, 1557; b) R. Schmechel, M. Kennedy, H. von Seggern, H. Winkler, M. Kolbe, R. A. Fischer, L. Xaomao, A. Benker, M. Winterer, H. Hahn, *J. Appl. Phys.* **2001**, *89*, 1679; c) X. Qin, Y. Ju, S. Bernhard, N. Yao, *J. Mater. Res.* **2005**, *20*, 2960; d) S. Yin, S. Akita, M. Shinozaki, R. Li, T. Sato, *J. Mater. Sci.* **2008**, *43*, 2234.

[96] a) K. Kömpe, H. Borchert, J. Storz, A. Lobo, S. Adam, T. Möller, M. Haase, *Angew. Chem.* **2003**, *115*, 5672; *Angew. Chem. Int. Ed.* **2003**, *42*, 5513; b) F. Meiser, C. Cortez, F. Caruso, *Angew. Chem.* **2004**, *116*, 6080; *Angew. Chem. Int. Ed.* **2004**, *43*, 5954; c) J. W. Stouwdam, F. C. J. M. van Veggel, *Langmuir* **2004**, *20*, 11763; d) J. S. Steckel, J. P. Zimmer, S. Coe-Sullivan, N. E. Scott, V. Bulovic, M. G. Bawendi, *Angew. Chem.* **2004**, *116*, 2206; *Angew. Chem. Int. Ed.* **2004**, *43*, 2154; e) N. Karar, G. Chander, S. M. Shivaprasad, *Appl. Phys. Lett.* **2004**, *85*, 5058.

[97] a) I. Sokolov, S. Naik, *Small* **2008**, *4*, 934; b) T. T. Morgan, H. S. Muddana, E. I. Altinoglu, S. M. Rouse, T. Tabakivic, T. Tabouillot, T. J. Russin, S. S. Shanmugavelandy, P. J. Butler, P. C. Eklund, J. K. Yun, M. Kester, J. H. Adair, *Nano Lett.* **2008**, *8*, 4108; c) H. Ow, D. R. Larson, M. Srivastava, B. A. Baird, W. W. Webb, U. Wiesner, *Nano Lett.* **2005**, *5*, 113.

[98] M. Roming, H. Lünsdorf, K. D. J. Dittmar, C. Feldmann, *Angew. Chem.* **2010**, *122*, 642; *Angew. Chem. Int. Ed.* **2010**, *49*, 632.

[99] Current review in: J. G. Fujimoto, D. Farkas, *Biomedical Optical Imaging*, Oxford University Press, Oxford, **2009**.

[100] a) M. De, P. S. Gosh, V. M. Rotello, *Adv. Mater.* **2008**, *20*, 4225; b) K. Douma, L. Prinzen, D. W. Slaaf, C. P. M. Reutlingsperger, E. A. L. Biessen, T. M. Hackeng, M. J. Post, M. A. M. J. von Zandvoort, *Small* **2009**, *5*, 544; c) R. Freeman, R. Gill, I. Shewky, M. Kotler, U. Banin, I. Willner, *Angew. Chem.* **2009**, *121*, 315; *Angew. Chem. Int. Ed.* **2009**, *48*, 309.

[101] X. Gao, Y. Cui, R. M. Levenson, L. W. K. Chung, S. Nie, *Nat. Biotechnol.* **2004**, *22*, 969.

[102] Current reviews in: a) P. Alivisatos, *Nat. Biotechnol.* **2004**, *22*, 47; b) V. Wagner, A. Dullaart, A. K. Bock, A. Zweck, *Nat. Biotechnol.* **2006**, *24*, 1211; c) K. Riehemann, S. W. Schneider, T. A. Luger, B. Godin, M. Ferrari, H. Fuchs, *Angew. Chem.* **2009**, *121*, 886; *Angew. Chem. Int. Ed.* **2009**, *48*, 872.

[103] A. M. Derfus, W. C. W. Chan, S. N. Bhatia, *Adv. Mater.* **2004**, *16*, 961.

[104] X. Wang, X. Ren, K. Kahen, M. A. Hahn, M. Rajeswaran, S. Maccagnano-Zacher, J. Silcox, G. E. Cragg, A. L. Efros, T. D. Krauss, *Nature* **2009**, *459*, 686.

[105] a) S. Heer, K. Kömpe, H. U. Güdel, M. Haase, *Adv. Mater.* **2004**, *16*, 2102; b) J. H. Zeng, J. Su, Z. H. Li, R. X. Yan, Y. D. Li, *Adv. Mater.* **2005**, *17*, 2119; c) S. Sivakumar, F. C. J. M. van Veggel, S. P. May, *J. Am. Chem. Soc.* **2007**, *129*, 620; d) F. Wang, X. Liu, *J. Am. Chem. Soc.* **2008**, *130*, 5642.

[106] Z. Li, Y. Zhang, S. Jiang, *Adv. Mater.* **2008**, *20*, 4765.

[107] a) G. A. Hebbink, J. W. Stouwdam, D. N. Reinhoudt, F. C. J. M. van Veggel, *Adv. Mater.* **2002**, *14*, 1147; b) X. F. Yu, L. D. Chen, M. Li, M. Y. Xie, L. Zhou, Y. Li, Q. Q. Wang, *Adv. Mater.* **2008**, *20*, 4118.

[108] P. Diagaradjane, J. M. Orenstein-Cardona, N. E. Colon-Casasnovas, A. Deorukhkar, S. Shentu, N. Kuno, D. L. Schwartz, J. G. Gelovani, S. Krishnan, *Clin. Cancer Res.* **2008**, *6*, 669.

[109] Current review in: G. Hodes, *Adv. Mater.* **2007**, *19*, 639.

[110] P. P. Edwards, S. R. Johnson, M. O. Jones, A. Porch, *Molecular Nanowires and other Quantum Objects*, Kluwer Academic Publishers, London, **2004**, p. 329.

[111] K. Chatterjee, B. Satpati, P. V. Satyam, D. Chakravorty, *J. Appl. Phys.* **2004**, *96*, 683.

[112] J. B. Pelka, M. Brust, P. Gierlowski, W. Paszkowicz, N. Schell, *Appl. Phys. Lett.* **2006**, *89*, 063110.

[113] D. L. Klein, R. Roth, A. K. L. Lim, A. P. Alivisatos, P. L. McEuen, *Nature* **1997**, *389*, 699.

[114] T. Kraus, L. Malaquin, H. Schmid, W. Riess, N. D. Spencer, H. Wolf, *Nat. Nanotechnol.* **2007**, *2*, 570.

[115] D. S. Ginger, H. Zhang, C. A. Mirkin, *Angew. Chem.* **2004**, *116*, 30; *Angew. Chem. Int. Ed.* **2004**, *43*, 30.

[116] a) L. Hou, Q. Hou, Y. Mo, J. Peng, Y. Cao, *Appl. Phys. Lett.* **2005**, *87*, 243504; b) A. L. Briseno, S. C. B. Mannsfeld, M. M. Ling, S. Liu, R. J. Tseng, C. Reese, M. E. Roberts, Y. Yang, F. Wudl, Z. Bao, *Nature* **2006**, *444*, 913; c) V. Shamanna, S. Das, Z. Celik-Butler, K. L. Lawrence, *J. Micromech. Microeng.* **2006**, *16*, 1984; d) S. A. Dayeh, D. P. Butler, Z. Celik-Butler, *Sens. Actuators A* **2004**, *118*, 49.

[117] Current review in: T. Minami, *Semicond. Sci. Technol.* **2005**, *20*, S35.

[118] Current reviews in: a) T. H. J. van Osch, J. Perelaer, A. W. M. de Laat, U. S. Schubert, *Adv. Mater.* **2008**, *20*, 343; b) R. Das, *Printed Electronics World*, **2008**, July 21st.

[119] a) R. A. Street, W. S. Wong, S. E. Ready, M. L. Chabinyc, A. C. Arias, S. Limb, A. Salleo, R. Lujan, *Mater. Today* **2006**, *9*, 32; b) D. H. Lee, Y. J. Chang, G. S. Herman, C. H. Chang, *Adv. Mater.* **2007**, *19*, 843.

[120] a) P. C. Andricacos, *Interface* **1999**, *28*, 32; b) J. Ederth, P. Heszler, A. Hultåker, G. A. Niklasson, C. G. Granqvist, *Thin Solid Films* **2003**, *445*, 199.

[121] Current reviews in: a) B. Michel, A. Bernard, A. Bietsch, E. Delamarche, M. Geissler, D. Juncker, H. Kind, J. P. Renault, H. Rothuizen, H. Schmid, P. Schmid-Winkel, R. Stutz, H. Wolf, *Chimia* **2003**, *56*, 527; b) B. J. de Gans, P. C. Duineveld, U. S. Schubert, *Adv. Mater.* **2004**, *16*, 203.

[122] a) J. Ba, D. F. Rohlfing, A. Feldhoff, T. Brezesinski, I. Djerdj, M. Wark, M. Niederberger, *Chem. Mater.* **2006**, *18*, 2848; b) G. Bühler, D. Thölmann, C. Feldmann, *Adv. Mater.* **2007**, *19*, 2224; c) E. Hammarberg, A. Prodi-Schwab, C. Feldmann, *Thin Solid Films* **2008**, *516*, 7437.

[123] R. G. Gordon, *MRS Bull.* **2000**, *25*, 52.

[124] a) M. Hilgendorff, L. Spanhel, C. Rothenhäusler, G. Müller, *J. Electrochem. Soc.* **1998**, *145*, 3632; b) J. H. Lee, B. O. Park, *Thin Solid Films* **2003**, *426*, 94; c) E. J. Luna-Arredondo, A. Maldonado, A. Asomoza, D. R. Acosta, M. A. Meléndez-Lira, L. M. de La Oliera, *Thin Solid Films* **2005**, *490*, 132; d) Z. Q. Xu, H. Deng, Y. Li, Q. H. Guo, Y. R. Li, *Mater. Res. Bull.* **2006**, *41*, 354.

[125] a) D. Burgard, C. Goebbert, R. Nass, *J. Sol-Gel Sci. Technol.* **1998**, *13*, 789; b) T. R. Giraldi, M. T. Escote, A. P. Maciel, E. Longo, E. R. Leite, J. A. Varela, *Thin Solid Films* **2006**, *515*, 2678; c) L. Li, L. Mao, X. Duan, *Mater. Res. Bull.* **2006**, *41*, 541.

[126] H. Faber, M. Burkhardt, A. Jedaa, D. Kälblein, H. Klauk, M. Halik, *Adv. Mater.* **2009**, *21*, 3099.

[127] a) B. K. Park, D. Kim, S. Jeong, J. Moon, J. S. Kim, *Thin Solid Films* **2007**, *515*, 7706; b) S. Gamerith, A. Klug, H. Scheiber, U. Scherf, E. Moderegger, E. J. W. List, *Adv. Funct. Mater.* **2007**, *17*, 3111; c) Y. Wu, Y. Li, B. S. Ong, *J. Am. Chem. Soc.* **2006**, *128*, 4202; d) Y. Wu, Y. Li, B. S. Ong, P. Liu, S. Gardener, B. Chiang, *Adv. Mater.* **2005**, *17*, 184; e) H. H. Lee, K. S. Chou, K. C. Huang, *Nanotechnology* **2005**, *16*, 2436.

[128] J. Rickerby, J. H. G. Steinke, *Chem. Rev.* **2002**, *102*, 1525.

[129] a) G. G. Rozenberg, E. Bresler, S. P. Speakman, C. Jeynes, J. H. G. Steinke, *Appl. Phys. Lett.* **2002**, *81*, 5249; b) Z. Liu, Y. Su, K. Varahramyan, *Thin Solid Films* **2005**, *478*, 275; c) P. J. Smith, D. Y. Shin, J. E. Stringer, B. Derby, N. Reis, *J. Mater. Sci.* **2006**, *41*, 4153.

[130] B. Y. Ahn, E. B. Duoss, M. J. Motala, X. Guo, S. I. Park, Y. Xiong, J. Yoon, R. G. Nuzzo, J. A. Rogers, J. A. Lewis, *Science* **2009**, *323*, 1590.

[131] Current reviews in: a) M. Grätzel, *Prog. Photovoltaics* **2006**, *14*, 429; b) H. J. Snaith, L. Schmidt-Mende, *Adv. Mater.* **2007**, *19*, 3187; c) M. Grätzel, J. R. Durrant, *Ser. Photoconvers. Sol. Energy* **2008**, *3*, 503.

[132] S. Colodrero, A. Mihi, L. Häggman, M. Ocana, G. Boschloo, A. Hagfeldt, H. Miguez, *Adv. Mater.* **2009**, *21*, 764.

[133] a) D. Timmerman, I. Izeddin, P. Stallinga, I. N. Yassievich, T. Gregorkiewicz, *Nat. Photonics* **2008**, *2*, 105; b) C. Y. Liu, Z. C. Holman, U. R. Kortshagen, *Nano Lett.* **2009**, *9*, 449.

[134] a) M. Nanu, J. Schoonman, A. Goossens, *Adv. Mater.* **2004**, *16*, 453; b) J. J. Nairn, P. J. Shapiro, B. Twamley, T. Pounds, R. von Wandruszka, T. R. Fletcher, M. Williams, C. Wang, M. G. Norton, *Nano Lett.* **2006**, *6*, 1218; c) S. Ahn, K. Kim, Y. Chun, K. Yoon, *Thin Solid Films* **2007**, *515*, 4036; d) J. Tang, S. Hinds, S. O. Kelley, E. H. Sargent, *Chem. Mater.* **2008**, *20*, 6906.

[135] a) C. Levy-Clemente, R. Tena-Zaera, M. A. Ryan, A. Katty, G. Hodes, *Adv. Mater.* **2005**, *17*, 1512; b) I. Robel, V. Subramanian, M. Kuno, P. V. Kamat, *J. Am. Chem. Soc.* **2006**, *128*, 2385.

[136] a) T. Takamoto, E. Ikeda, H. Kurita, M. Ohmori, *Appl. Phys. Lett.* **1997**, *70*, 381; b) D. J. Milliron, I. Gur, A. P. Alivisatos, *MRS Bull.* **2005**, *39*, 41; c) B. V. Andersson, N. K. Persson, O. Inganaes, *J. Appl. Phys.* **2008**, *104*, 124508/1; d) S. Wenger, S. Seyrling, A. N. Tiwari, M. Graetzel, *Appl. Phys. Lett.* **2009**, *94*, 173508/1.

[137] a) V. L. Colvin, M. C. Schlamp, A. P. Alivisatos, *Nature* **1994**, *370*, 354; b) W. K. Bae, J. Kwak, J. W. Park, K. Char, C. Lee, S. Lee, *Adv. Mater.* **2009**, *21*, 1690; c) J. Y. Kim, C. Ingrosso, V. Fakhfouri, M. Striccoli, A. Agostiano, M. L. Curri, J. Brugger, *Small* **2009**, *5*, 1051.

[138] Current reviews in: a) P. G. Bruce, B. Scrosati, J. M. Tarascon, *Angew. Chem.* **2008**, *120*, 2972; *Angew. Chem. Int. Ed.* **2008**, *47*,

2930; b) Y. Wang, G. Cao, *Adv. Mater.* **2008**, *20*, 2251; M. S. Whittingham, *MRS Bull.* **2008**, *33*, 411.

[139] a) A. S. Arico, P. Bruce, B. Scrosati, J. M. Tarascon, W. van Schalkwijk, *Nat. Mater.* **2005**, *4*, 366; b) Y. Shao, G. Yin, Z. Wang, Y. Gao, *J. Power Sources* **2007**, *167*, 235.

[140] P. Gibot, M. Casas-Cabanas, L. Laffont, S. Levasseur, P. Carlach, S. Hamelet, J. P. Tarascon, C. Masquelier, *Nat. Mater.* **2008**, *7*, 741.

[141] a) I. Amadei, S. Panero, B. Scrosati, G. Cocco, L. Schiffini, *J. Power Sources* **2005**, *143*, 227; b) P. L. Taberna, S. Mitra, P. Piozot, P. Simon, J. M. Tarascon, *Nat. Mater.* **2006**, *5*, 567; c) J. Hassoun, S. Panero, P. Simon, P. L. Taberna, B. Scrosati, *Adv. Mater.* **2007**, *19*, 1632; d) A. Timmons, J. R. Dahn, *J. Electrochem. Soc.* **2007**, *154*, A444.

[142] a) V. L. Pushparaj, M. M. Shaijumon, A. Kumar, S. Murugesan, L. Ci, R. Vajtai, R. J. Linhardt, O. Nalamasu, P. M. Ajayan, *Proc. Natl. Acad. Sci. USA* **2007**, *104*, 13574; b) G. Nagasubramanian, D. H. Doughty, *J. Power Sources* **2004**, *136*, 395; c) C. Wang, L Taherabadi, G. Y. Jia, M. Madou, X. T. Yeh, B. Dunn, *Electrochem. Solid-State Lett.* **2004**, *7*, A435; d) B. Dunn, *Chem. Rev.* **2003**, *104*, 4463; e) Y. K. Cho, R. Wartena, S. M. Tobias, Y. M. Chiang, *Adv. Funct. Mater.* **2007**, *17*, 379.

[143] J. M. Vohs, R. J. Gorte, *Adv. Mater.* **2009**, *21*, 943.

[144] Current reviews in: a) A. N. Shipway, E. Katz, I. Willner, *ChemPhysChem* **2000**, *1*, 18; b) M. E. Franke, T. J. Koplin, U. Simon, *Small* **2006**, *2*, 36.

[145] C. P. Balde, B. P. C. Hereijgers, J. H. Bitter, K. P. de Jong, *J. Am. Chem. Soc.* **2008**, *130*, 6761.

[146] a) S. Orimo, Y. Nakamori, J. R. Eliseo, A. Züttel, C. M. Jensen, *Chem. Rev.* **2007**, *107*, 4111; b) B. Bogdanovic, U. Eberle, M. Felderhoff, F. Schüth, *Scr. Mater.* **2007**, *56*, 813.

[147] *Handbook of Thermoelectrics* (Ed.: D. M. Rowe), CRC, Boca Raton, **1995**.

[148] a) L. D. Hicks, M. S. Dresselhaus, *Phys. Rev. B* **1993**, *47*, 12727; b) L. D. Hicks, M. S. Dresselhaus, *Phys. Rev. B* **1993**, *47*, 16631.

[149] a) R. Venkatasubramanian, T. Colpitts, B. O'Quinn, S. Liu, N. El-Masry, M. Lamvik, *Appl. Phys. Lett.* **1999**, *75*, 1104; b) R. Venkatasubramanian, E. Siivola, T. Colpitts, B. O'Quinn, *Nature* **2001**, *413*, 597.

[150] J. Sommerlatte, K. Nielsch, H. Böttner, *Phys. J.* **2007**, *6*, 35.

[151] G. Chen, M. S. Dresselhaus, G. Dresselhaus, J. P. Fleurial, T. Caillat, *Int. Mater. Rev.* **2003**, *48*, 45.

[152] T. C. Harman, P. J. Taylor, M. P. Walsch, B. E. LaForge, *Science* **2002**, *297*, 2229.

[153] a) W. Z. Wang, B. Poudel, J. Yang, D. Z. Wang, Z. F. Ren, *J. Am. Chem. Soc.* **2005**, *127*, 13792; b) S. S. Garje, D. J. Eisier, J. S. Ritch, M. Afzaal, P. O'Brien, T. Chivers, *J. Am. Chem. Soc.* **2006**, *128*, 3120; c) C. G. Jin, G. Q. Zhang, T. Qian, X. G. Li, Z. Yao, *J. Phys. Chem. B* **2005**, *109*, 1430; d) J. Y. Yang, W. Zhu, X. H. Gao, S. Q. Bao, X. Fan, X. K. Duan, J. Hou, *J. Phys. Chem. B* **2006**, *110*, 4599; e) W. D. Shi, J. B. Yu, H. S. Wang, H. J. Zhang, *J. Am. Chem. Soc.* **2006**, *128*, 16490; f) X. Tang, W. Xie, H. Li, W. Zhao, Q. Zhang, M. Niino, *Appl. Phys. Lett.* **2007**, *90*, 012102; g) W. Shi, L. Zhou, S. Song, J. Yang, H. Zhang, *Adv. Mater.* **2008**, *20*, 1892.

[154] W. Kim, J. Zide, A. Gossard, D. Klenov, S. Stemmer, A. Shakouri, A. Majumdar, *Phys. Rev. Lett.* **2006**, *96*, 045901.

[155] a) A. I. Boukai, Y. Bunimovich, J. Tahir-Kheli, J. K. Yu, W. A. Goddard, J. R. Heath, *Nature* **2008**, *451*, 168; b) J.-H. Lee, G. A. Galli, J. C. Grossman, *Nano Lett.* **2008**, *8*, 3750.

[156] B. Poudel, Q. Hao, Y. Ma, Y. Lan, A. Minnich, B. Yu, X. Yan, D. Wang, A. Muto, D. Vashaee, X. Chen, J. Liu, M. S. Dresselhaus, G. Chen, Z. Ren, *Science* **2008**, *320*, 634.

[157] H. Böttner, G. Chen, R. Venkatasubramanian, *MRS Bull.* **2006**, *31*, 211.

[158] I. U. Arachchige, J. Wu, V. P. Dravid, M. G. Kanatzidis, *Adv. Mater.* **2008**, *20*, 3638.

[159] K. F. Hsu, S. Lu, F. Guo, W. Chen, J. S. Dyck, C. Uher, T. Hogan, E. K. Polychroniadis, M. G. Kanatzidis, *Science* **2004**, *303*, 818.

[160] W. Zhou, J. Zhu, D. Li, H. H. Hng, F. Y. C. Boey, J. Ma, H. Zhang, Q. Yan, *Adv. Mater.* **2009**, *21*, 3196.

[161] F. W. Wise, *Acc. Chem. Res.* **2000**, *33*, 773.

[162] a) H. Hibst, *Angew. Chem.* **1982**, *94*, 263; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 270; b) R. Dronskowski, *Adv. Funct. Mater.* **2001**, *11*, 27.

[163] Current reviews in: a) A. H. Lu, E. L. Salabas, F. Schüth, *Angew. Chem.* **2007**, *119*, 1242; *Angew. Chem. Int. Ed.* **2007**, *46*, 1222; b) J. Dobson, *Nat. Nanotechnol.* **2008**, *3*, 139.

[164] H. Lueken, *Magnetochemie*, Teubner, Stuttgart, **1999**.

[165] a) E. C. Stoner, F. R. S. Wohlfarth, E. P. Wohlfarth, *Philos. Trans. R. Soc. London Ser. A* **1948**, *240*, 599; b) M. Bode, *Rep. Prog. Phys.* **2003**, *66*, 523; c) X. Batlle, A. Laberta, *J. Phys. D* **2002**, *35*, R15.

[166] a) J. Lin, W. Zhou, A. Kumbhar, J. Wiemann, J. Fang, E. E. Carpenter, C. J. O'Brien, *J. Solid State Chem.* **2001**, *159*, 26; b) E. E. Carpenter, *J. Magn. Magn. Mater.* **2001**, *225*, 17; c) C. J. O'Connor, J. A. Sims, A. Kumbhar, V. L. Kolesnichenko, W. L. Zhou, J. A. Wiemann, *J. Magn. Magn. Mater.* **2001**, *226*, 1915.

[167] a) J. Rockenberger, E. C. Scher, A. P. Alivisatos, *J. Am. Chem. Soc.* **1999**, *121*, 11595; b) M. Yin, S. O'Brien, *J. Am. Chem. Soc.* **2003**, *125*, 10180; c) W. W. Yu, J. C. Falkner, C. T. Yavuz, V. L. Colvin, *Chem. Commun.* **2004**, 2306; d) J. Park, E. Lee, N. M. Hwang, M. Kang, S. C. Kim, Y. Hwang, J. G. Park, H. J. Noh, J. Y. Kim, J. H. Park, T. Hyeon, *Angew. Chem.* **2005**, *117*, 2932; *Angew. Chem. Int. Ed.* **2005**, *44*, 2872.

[168] a) Y. Lee, J. Lee, C. J. Bae, J. G. Park, H. J. Noh, J. H. Park, T. Hyeon, *Adv. Funct. Mater.* **2005**, *15*, 503; b) Y. Mao, T. J. Park, S. S. Wong, *Chem. Commun.* **2005**, 5721; c) N. Bao, L. Shen, Y. Wang, P. Padhan, A. Gupta, *J. Am. Chem. Soc.* **2007**, *129*, 12374.

[169] S. Sun, C. B. Murray, D. Weller, L. Folks, A. Moser, *Science* **2000**, *287*, 1989.

[170] a) A. Ethirajan, U. Wiedwald, H. G. Boyen, B. Kern, L. Han, A. Klimmer, F. Weigl, G. Kästle, P. Ziemann, K. Fauth, J. Cai, R. J. Behm, A. Romanyuk, P. Oelhafen, P. Walther, J. Biskupek, U. Kaiser, *Adv. Mater.* **2007**, *19*, 406; b) C. Desvaux, C. Amiens, P. Fejes, P. Renaud, M. Respaud, P. Lecante, E. Snoeck, B. Chaudret, *Nat. Mater.* **2005**, *4*, 203; c) Z. Z. Bandic, D. Litvinov, M. Rooks, *MRS Bull.* **2008**, *33*, 831.

[171] K. Nakata, Y. Hu, O, Uzun, O. Bakr, F. Stellacci, *Adv. Mater.* **2008**, *20*, 4294.

[172] K. M. Nam, J. H. Shim, H. Ki, S. I. Choi, G. Lee, J. K. Jang, Y. Jo, M. H. Jung, H. Song, J. T. Park, *Angew. Chem.* **2008**, *120*, 9646; *Angew. Chem. Int. Ed.* **2008**, *47*, 9504.

[173] Current review in: S. Odenbach, *J. Phys. Condens. Matter* **2004**, *16*, R1135.

[174] C. Feldmann, *Solid State Sci.* **2005**, *7*, 868.

[175] a) S. Giri, B. G. Trewyn, M. P. Stellmaker, V. S. Y. Lin, *Angew. Chem.* **2005**, *117*, 5166; *Angew. Chem. Int. Ed.* **2005**, *44*, 5038; b) A. Fu, W. Hu, L. Xu, R. J. Wilson, H. Yu, S. J. Osterfeld, S. S. Gambhir, S. X. Wang, *Angew. Chem.* **2009**, *121*, 1648; *Angew. Chem. Int. Ed.* **2009**, *48*, 1620; c) C. Wang, J. Chen, T. Talavage, J. Irudayaraj, *Angew. Chem.* **2009**, *121*, 2797; *Angew. Chem. Int. Ed.* **2009**, *48*, 2759.

[176] C. T. Yavuz, J. T. Mayo, W. W. Yu, A. Prakash, J. C. Falkner, S. Yean, L. Cong, H. J. Shipley, A. Kan, M. Tomson, D. Natelson, V. L. Colvin, *Science* **2006**, *314*, 964.

[177] A. Hu, G. T. Yee, W. Lin, *J. Am. Chem. Soc.* **2005**, *127*, 12486.

[178] C. Xu, K. Xu, H. Gu, R. Zheng, H. Liu, X. Zhang, Z. Guo, B. Xu, *J. Am. Chem. Soc.* **2004**, *126*, 9938.

[179] I. Safarik, M. Safarikova, *Monatsh. Chem.* **2002**, *133*, 737.

[180] N. Zhao, M. Gao, *Adv. Mater.* **2009**, *21*, 184.

[181] H. Zeng, S. Sun, *Adv. Funct. Mater.* **2008**, *18*, 391.

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Angew. Chem. Int. Ed. **2010**, *49*, 2–36

[182] a) K. W. Kwon, M. Shim, *J. Am. Chem. Soc.* **2005**, *127*, 10269; b) W. L. Shi, H. Zeng, Y. Sahoo, T. Y. Ohulchanskyy, Y. Ding, Z. L. Wang, M. Swihart, P. N. Prasad, *Nano Lett.* **2006**, *6*, 875.

[183] a) D. K. Kim, M. Mikhaylova, Y. Zhang, M. Muhammed, *Chem. Mater.* **2003**, *15*, 1617; b) A. H. Lu, W. Lie, N. Matoussevitch, B. Spiethoff, H. Bönnemann, F. Schüth, *Chem. Commun.* **2005**, 98; c) M. Kim, Y. Chen, Y. Liu, X. Peng, *Adv. Mater.* **2005**, *17*, 1429.

[184] a) J. J. Park, J. Cheon, *J. Am. Chem. Soc.* **2001**, *123*, 5743; b) N. S. Sobal, M. Hilgendorff, H. Möhwald, M. Giersig, M. Spasova, T. Radetic, M. Farle, *Nano Lett.* **2002**, *2*, 621; c) H. G. Boyen, G. Kästle, K. Zürn, T. Herzog, F. Weigl, P. Ziemann, O. Mayer, C. Jerome, M. Möller, J. P. Spatz, M. G. Garnier, P. Oelhafen, *Adv. Funct. Mater.* **2003**, *13*, 359; d) M. Kim, Y. Chen, Y. Liu, X. Peng, *Adv. Mater.* **2005**, *17*, 1429.

[185] Current reviews in: a) Y. W. Jun, J. H. Lee, J. Cheon, *Angew. Chem.* **2008**, *120*, 5200; *Angew. Chem. Int. Ed.* **2008**, *47*, 5122; b) H. B. Na, I. C. Song, T. Hyeon, *Adv. Mater.* **2009**, *21*, 2133.

[186] a) R. Weissleder, A. Moore, U. Mahmood, R. Bhorade, H. Benveniste, E. A. Chiocca, J. P. Basilion, *Nat. Med.* **2000**, *6*, 351; b) M. Zhao, D. A. Beauregard, L. Loizou, B. Davletov, K. M. Brindle, *Nat. Med.* **2001**, *7*, 1241; c) J. R. McCarthy, K. A. Kelly, E. Y. Sun, R. Weissleder, *Nanomedicine* **2007**, *2*, 153.

[187] a) D. Vernimmen, M. Gueders, S. Pisvin, P. Delvenne, R. Winkler, *Br. J. Cancer* **2003**, *89*, 899; b) F. Hu, L. Wei, Z. Zhou, Y. Ran, Z. Li, M. Gao, *Adv. Mater.* **2006**, *18*, 2553; c) J. H. Lee, Y. M. Huh, Y. W. Jun, J. W. Seo, J. T. Jang, H. T. Song, S. Kim, E. J. Cho, H. G. Yoon, J. S. Suh, J. Cheon, *Nat. Med.* **2007**, *13*, 95.

[188] a) A. Jordan, K. Maier-Hauff, P. Wust, B. Rau, M. Johannsen, *Onkologe* **2007**, *13*, 894; b) R. B. Campbell, *Nanomedicine* **2007**, *2*, 649.

[189] a) N. Nasongkla, E. Bey, J. Ren, H. Ai, C. Khemtong, J. S. Guthi, S. F. Chin, A. D. Sherry, D. A. Boothman, J. Gao, *Nano Lett.* **2006**, *6*, 2427; b) J. Kim, J. E. Lee, J. Lee, Y. Jang, S. W. Kim, K. An, J. H. Yu, T. Hyeon, *Angew. Chem.* **2006**, *118*, 4907; *Angew. Chem. Int. Ed.* **2006**, *45*, 4789.

[190] O. T. Bruns, H. Ittrich, K. Peldschus, M. G. Kaul, U. I. Tromsdorf, J. Lauterwasser, M. S. Nikolic, B. Mollwitz, M. Merkel, N. C. Bigall, S. Sapra, R. Reimer, H. Hohenberg, H. Weller, A. Eychmüller, G. Adam, U. Beisiegel, J. Heeren, *Nat. Nanotechnol.* **2009**, *4*, 193.

[191] a) H. B. Na, J. H. Lee, K. An, Y. I. Park, M. Park, I. S. Lee, D. H. Nam, S. T. Kim, S. H. Kim, S. W. Kim, K. H. Lim, K. S. Kim, S. O. Kim, T. Hyeon, *Angew. Chem.* **2007**, *119*, 5493; *Angew. Chem. Int. Ed.* **2007**, *46*, 5397; b) W. S. Seo, J. H. Lee, X. Sun, Y. Suzuki, D. Mann, Z. Liu, M. Terashima, P. C. Yang, M. V. McConnell, D. G. Nishimura, H. Dai, *Nat. Mater.* **2006**, *5*, 971; c) J. H. Lee, Y. M. Huh, J. W. Jun, J. W. Seo, J. T. Jang, H. T. Song, S. J. Kim, E. J. Cho, H. G. Yoon, J. S. Suh, J. Cheon, *Nat. Med.* **2007**, *13*, 95; d) J. T. Jang, H Nah, J. H. Lee, S. H. Moon, M. G. Kim, J. Cheon, *Angew. Chem.* **2009**, *121*, 1260; *Angew. Chem. Int. Ed.* **2009**, *48*, 1234.

[192] a) J. L. Bridot, A. C. Faure, S. Laurent, C. Riviere, C. Billotey, B. Hiba, M. Janier, V. Josserand, J. L. Coll, L. V. Elst, R. Muller, S. Roux, P. Perriat, O. Tillement, *J. Am. Chem. Soc.* **2007**, *129*, 5076; b) M. Norek, E. Kampert, U. Zeitler, J. A. Peters, *J. Am. Chem. Soc.* **2008**, *130*, 5335; c) C. C. Huang, C. H. Su, W. M. Li, T. Y. Liu, J. H. Chen, C. S. Yeh, *Adv. Funct. Mater.* **2009**, *19*, 249.

[193] A. T. Bell, *Science* **2003**, *299*, 1688.

[194] D. Astruc, F. Lu, J. R. Aranzaes, *Angew. Chem.* **2005**, *117*, 8062; *Angew. Chem. Int. Ed.* **2005**, *44*, 7852.

[195] A. Suzuki in *Modern Arene Chemistry* (Ed.: D. Astruc), Wiley-VCH, Weinheim, **2002**.

[196] A. K. Diallo, C. Ornelas, L. Salmon, J. R. Aranzaes, D. Astruc, *Angew. Chem.* **2007**, *119*, 8798; *Angew. Chem. Int. Ed.* **2007**, *46*, 8644.

[197] S. Bhattacharjee, D. M. Dotzauer, M. L. Brüning, *J. Am. Chem. Soc.* **2009**, *131*, 3601.

[198] J. Y. Park, Y. Zhang, M. Grass, T. Zhang, G. A. Somorjai, *Nano Lett.* **2008**, *8*, 673.

[199] I. Lee, F. Delbecq, R. Morales, M. A. Albiter, F. Zaera, *Nature Mater.* **2009**, *8*, 132.

[200] S. H. Joo, J. Y. Park, C. K. Chia, Y. Yamada, P. Yang, G. A. Somorjai, *Nat. Mater.* **2009**, *8*, 126.

[201] A. J. Gellman, N. Shukla, *Nat. Mater.* **2009**, *8*, 87.

[202] A. S. K. Hashmi, G. J. Hutchings, *Angew. Chem.* **2006**, *118*, 8064; *Angew. Chem. Int. Ed.* **2006**, *45*, 7896.

[203] R. S. Downing, P. J. Kunkeler, H. van Bekkum, *Catal. Today* **1997**, *37*, 121.

[204] A. Corma, P. Serna, *Science* **2006**, *313*, 332.

[205] A. Grirrane, A. Corma, H. Garcia, *Science* **2008**, *322*, 1661.

[206] a) A. Abad, P. Concepción, A. Corma, H. García, *Angew. Chem.* **2005**, *117*, 4134; *Angew. Chem. Int. Ed.* **2005**, *44*, 4066; b) A. Corma, M. E. Domine, *Chem. Commun.* **2005**, 4042.

[207] H. Rashid, T. K. Mandal, *Adv. Funct. Mater.* **2008**, *18*, 2261.

[208] M. Comotti, C. Della Pina, R. Matarrese, M. Rossi, *Angew. Chem.* **2004**, *116*, 5936; *Angew. Chem. Int. Ed.* **2004**, *43*, 5812.

[209] R. J. Davis, *Science* **2003**, *301*, 926.

[210] a) C. T. Campbell, *Science* **2004**, *306*, 234; b) M. S. Chen, D . W. Goodman, *Science* **2004**, *306*, 252; c) N. Lopez, T. V. W. Janssens, B. S. Clausen, Y. Xu, M. Mavrikakis, T. Bligaard, J. K. Nørskov, *J. Catal.* **2004**, *223*, 232.

[211] Current review in: C. Brinkmeier, F. Opferkuch, U. Tuttlies, V. Schmeißer, J. Bernnat, G. Eigenberger, *Chem. Ing. Tech.* **2005**, *77*, 1333.

[212] P. Nolte, A. Stierle, N. Y. Jin-Phillipp, N. Kasper, T. U. Schulli, H. Dosch, *Science* **2008**, *321*, 1654.

[213] H. Hildebrand, K. Mackenzie, F. D. Kopinke, *Chem. Ing. Tech.* **2007**, *79*, 1461.

[214] a) D. Glöß, P. Frach, C. Gottfried, S. Klinkenberg, J. S. Liebig, W. Hentsch, H. Liepack, M. Krug, *Thin Solid Films* **2008**, *516*, 4487; b) M. R. S. Castro, E. D. Sam, M. Veith, P. W. Oliveira, *Nanotechnology* **2008**, *19*, 105704.

[215] T. Brockmann, P. Fontana, B. Meng, U. Müller, *Beton-Stahlbetonbau* **2008**, *103*, 446.

[216] M. Xue, L. Huang, J. Q. Wang, Y. Wang, L. Gao, J. Zhu, Z. G. Zou, *Nanotechnology* **2008**, *19*, 185604.

[217] C. A. Grimes, *J. Mater. Chem.* **2007**, *17*, 1451.

[218] J. H. Bang, R. J. Helmich, K. S. Suslick, *Adv. Mater.* **2008**, *20*, 2599.

[219] a) A. Ishikawa, T. Takata, J. N. Kondo, M. Hara, H. Kobayashi, K. Domen, *J. Am. Chem. Soc.* **2002**, *124*, 13547; b) H. G. Kim, D. W. Hwang, J. S. Lee, *J. Am. Chem. Soc.* **2004**, *126*, 8912.

[220] I. S. Cho, D. W. Kim, S. Lee, C. H. Kwak, S. T. Bae, J. H. Noh, S. H. Yoon, H. S. Jung, D. W. Kim, K. S. Hong, *Adv. Funct. Mater.* **2008**, *18*, 2154.

[221] J. Yu, A. Kudo, *Adv. Funct. Mater.* **2006**, *16*, 2163.

[222] a) L. Zhang, I. Djerdj, M. Cao, M. Antonietti, M. Niederberger, *Adv. Mater.* **2007**, *19*, 2083; b) L. W. Zhang, Y. J. Wang, H. Y. Cheng, W. Q. Yao, Y.-F. Zhu, *Adv. Mater.* **2009**, *21*, 1286.

[223] Y. Zhiyong, E. Mielczarski, J. Mielczarski, D. Laub, Ph. Buffat, U. Klehm, P. Albers, K. Lee, A. Kulik, L. Kiwi-Minsker, A. Renken, J. Kiwi, *Water Res.* **2007**, *41*, 862.

[224] H. Schmidt, M. Naumann, T. S. Müller, M. Akarsu, *Thin Solid Films* **2006**, *502*, 132.

[225] A. Fujishima, K. Honda, *Nature* **1972**, *238*, 37.

[226] C. Burda, Y. Lou, X. Chen, A. C. S. Samia, J. Stout, J. L. Gole, *Nano Lett.* **2003**, *3*, 1049.

[227] J. H. Park, S. Kim, A. J. Bard, *Nano Lett.* **2006**, *6*, 24.

[228] Y. Lin, S. Zhou, X. Liu, S. Sheehan, D. Wang, *J. Am. Chem. Soc.* **2009**, *131*, 2772.

[229] W. J. Youngblood, S.-H. A. Lee, Y. Kobayashi, E. A. Hernandez-Pagan, P. G. Hoertz, T. A. Moore, A. L. Moore, D. Gust, T. E. Mallouk, *J. Am. Chem. Soc.* **2009**, *131*, 926.

[230] K. Maeda, K. Teramura, D. Lu, T. Takata, N. Saito, Y. Inoue, K. Domen, *Nature* **2006**, *440*, 295.

[231] M. W. Kanan, D. G. Nocera, *Science* **2008**, *321*, 1072.

[232] C. C. Koch, *J. Mater. Sci.* **2007**, *42*, 1403.

[233] a) J. Karch, R. Birringer, H. Gleiter, *Nature* **1987**, *330*, 556; b) H. Gleiter, *Prog. Mater. Sci.* **1989**, *33*, 223.

[234] A. Brinkmann, Y. Wilke, V. Stenzel, *Farbe Lack* **2007**, *113*, 40.

[235] C. Gellermann, T. Ballweg, H. Wolter, *Chem. Ing. Tech.* **2007**, *79*, 233.

[236] a) W. Scholz, T. Sawitowski, *Eur. Coat. J.* **2005**, *10*, 52; b) T. Sawitowski, *Welt der Farben* **2008**, *5*, 8.

[237] A. Zhu, Z. Shi, A. Cai, F. Zhao, T. Liao, *Polym. Test.* **2008**, *27*, 540.

[238] U. Wagenknecht, B. Kretzschmar, P. Pötschke, F. R. Costa, S. Pegel, K. W. Stöckelhuber, G. Heinrich, *Chem. Ing. Tech.* **2008**, *80*, 1683.

[239] S. Sinha Ray, M. Okamoto, *Prog. Polym. Sci.* **2003**, *28*, 1539.

[240] a) Y. Ke, C. Long, Z. Qi, *J. Appl. Polym. Sci.* **1999**, *71*, 1139; b) J. W. Cho, D. R. Paul, *Polymer* **2001**, *3*, 1083; c) Z.-M. Liang, J. Yin, H.-J. Xu, *Polymer* **2003**, *5*, 1391; d) S. Y. A. Shin, L. C. Simon, J. B. P. Soares, G. Scholz, *Polymer* **2003**, *18*, 5317.

[241] a) S. Bourbigot, E. Devaux, X. Flambard, *Polym. Degrad. Stab.* **2002**, *2*, 397; b) S. Bourbigot, D. L. Vanderhart, J. W. Gilman, S. Bellayer, H. Stretz, D. R. Paul, *Polymer* **2004**, *22*, 7627; c) S. Nazaré, B. K. Kandola, A. R. Horrocks, *Polym. Adv. Technol.* **2006**, *17*, 294; d) S. Bourbigot, S. Duquesne, *J. Mater. Chem.* **2007**, *17*, 2283; e) S. Hotta, D. R. Paul, *Polymer* **2004**, *22*, 7639; f) X. Zhang, L. S. Loo, *Polymer* **2009**, *50*, 2643; g) S. Barus, M. Zanetti, M. Lazzari, L. Costa, *Polymer* **2009**, *50*, 2595; h) B. K. Kandola, G. Smart, A. R. Horrocks, P. Joseph, S. Zhang, T. R. Hull, J. Ebdon, B. Hunt, A. Cook, *J. Appl. Polym. Sci.* **2008**, *108*, 816; i) W. H. Awad, G. Beyer, D. Benderly, W. L. Ijdo, P. Songtipya, M. Jimenez-Gasco, E. Manias, C. A. Wilkie, *Polymer* **2009**, *8*, 1857.

[242] H. Althues, P. Simon, S. Kaskel, *J. Mater. Chem.* **2007**, *17*, 758.

[243] a) H. Lu, B. Fei, J. H. Xin, R. Wang, L. Li, *J. Colloid Interface Sci.* **2006**, *300*, 111; b) Y. Xing, X. Ding, *J. Appl. Polym. Sci.* **2007**, *103*, 3113.

[244] a) N. Al-Dahoudi, H. Bisht, C. Gobbert, T. Krajewski, M. A. Aegerter, *Thin Solid Films* **2001**, *392*, 299; b) X. Chen, C. Li, W. Shao, J. He, *J. Appl. Polym. Sci.* **2007**, *105*, 2783.

[245] K. Bobzin, F. Ernst, J. Zwick, T. Schlaefer, D. Cook, K. Nassenstein, A. Schwenk, F. Schreiber, T. Wenz, G. Flores, M. Hahn, *J. Therm. Spray Technol.* **2008**, *17*, 344.

[246] Z. Cerman, A. K. Stosch, W. Barthlott, *Biol. Unserer Zeit* **2004**, *5*, 290.

[247] a) T. Onda, S. Shibuichi, N. Satoh, K. Tsujii, *Langmuir* **1996**, *12*, 2125; b) R. Blossey, *Nat. Mater.* **2003**, *2*, 301.

[248] a) D. Hegemann, A. Fischer, *Vak. Forsch. Prax.* **2004**, *16*, 240; b) M. Fricke, V. Schädler, *Macromol. Biosci.* **2007**, *7*, 103.

[249] D. Frick, H. K. Pulker, *Vak. Forsch. Prax.* **2007**, *S1*, 21.

[250] F. Namavar, C. L. Cheung, R. F. Sabirianov, W. N. Mei, X. C. Zeng, G. Wang, H. Haider, K. L. Garvin, *Nano Lett.* **2008**, *8*, 988.

[251] D. Salz, D. M. Wagener, *Vak. Forsch. Prax.* **2005**, *4*, 191.

[252] M. Liong, B. France, K. A. Bradley, J. I. Zink, *Adv. Mater.* **2009**, *21*, 1684.

[253] S. Makhluf, R. Dror, Y. Nitzan, Y. Abramovich, R. Jelinek, A. Gedanken, *Adv. Funct. Mater.* **2005**, *15*, 1708.

[254] A. Kumar, P. K. Vemula, P. M. Ajayan, G. John, *Nat. Mater.* **2008**, *7*, 236.

[255] S. Loher, O. D. Schneider, T. Maienfisch, S. Bokorny, W. J. Stark, *Small* **2008**, *4*, 824.

[256] a) K. Yamagishi, K. Onuma, T. Suzuki, F. Okada, J. Tagami, M. Otsuki, P. Senawangse, *Nature* **2005**, *433*, 819; b) H. H. K. Xu, L. E. Carey, C. G. Simon, S. Takagi, L. C. Chow, *Dent. Mater.* **2007**, *23*, 433.

[257] J. D. Kretlow, S. Young, L. Klouda, M. Wong, A. G. Mikos, *Adv. Mater.* **2009**, *21*, 3368.

[258] a) B. Palazzo, M. Iafisco, M. Laforgia, N. Margiotta, G. Natile, C. L. Bianchi, D. Walsh, S. Mann, N. Roveri, *Adv. Funct. Mater.* **2007**, *17*, 2180; b) M. Goldberg, R. Langer, X. Jia, *J. Biomater. Sci. Polym. Ed.* **2007**, *18*, 241; c) Y. Cai, R. Ruikang, *J. Mater. Chem.* **2008**, *18*, 3775.

[259] a) K. I. Winey, R. A. Vaia, *MRS Bull.* **2007**, *32*, 314; b) A. R. Horrocks, B. K. Kandola, P. J. Davies, S. Zhang, S. A. Padbury, *Polym. Degrad. Stab.* **2005**, *88*, 3.

[260] M. Zammarano, M. Franceschi, S. Bellayer, J. W. Gilman, S. Meriani, *Polymer* **2005**, *46*, 9314.

[261] a) R. Chaim, M. Levin, A. Shlayer, C. Estournes, *Adv. Appl. Ceram.* **2008**, *107*, 159; b) S. C. Jong, *Adv. Eng. Mater.* **2007**, *9*, 639; c) H. Hofmann, *J. Eur. Ceram. Soc.* **2009**, *29*, 1235.

[262] M. Scheffler, P. Colombo, *Cellular Ceramics: Structure, Manufacturing, Properties and Applications*, Wiley-VCH, Weinheim, **2005**.

[263] a) M. Pohl, S. Hogekamp, N. Q. Hoffmann, H. P. Schuchmann, *Chem. Ing. Tech.* **2004**, *76*, 392; b) C. Sauter, H. P. Schuchmann, *Chem. Ing. Tech.* **2008**, *80*, 365.

[264] C. Schilde, C. Arlt, A. Kwade, *Chem. Ing. Tech.* **2009**, *81*, 1.

[265] I. Akartuna, A. R. Studart, E. Tervoort, L. J. Gauckler, *Adv. Mater.* **2008**, *20*, 4714.

[266] T. Schmidt, M. Mennig, H. Schmidt, *J. Am. Ceram. Soc.* **2007**, *90*, 1401.

[267] *Metal Matrix Composites: Custom-made Materials for Automotive and Aerospace Engineering* (Ed.: K. U. Kainer), Wiley-VCH, Weinheim, **2006**.

[268] Y. Yang, J. Lan, X. Li, *Mater. Sci. Eng. A* **2004**, *1–2*, 378.

[269] Current review in: X. W. Lou, L. A. Archer, Z. Yang, *Adv. Mater.* **2008**, *20*, 3987.

[270] a) R. H. A. Ras, M. Kemell, J. de Witt, M. Ritala, G. ten Brinke, M. Leskelä, O. Ikkala, *Adv. Mater.* **2007**, *19*, 102; b) R. Liu, P. Dong, S. L. Chen, *Chem. Lett.* **2005**, *34*, 548; c) X. Wang, Y. Li, *Angew. Chem.* **2003**, *115*, 3621; *Angew. Chem. Int. Ed.* **2003**, *42*, 3497.

[271] a) C. Xue, J. E. Millstone, S. Li, C. A. Mirkin, *Angew. Chem.* **2007**, *119*, 8588; *Angew. Chem. Int. Ed.* **2007**, *46*, 8436; b) S. Peng, S. Sun, *Angew. Chem.* **2007**, *119*, 4233; *Angew. Chem. Int. Ed.* **2007**, *46*, 4155; c) P. M. Arnal, M. Comotti, F. Schüth, *Angew. Chem.* **2006**, *118*, 8404; *Angew. Chem. Int. Ed.* **2006**, *45*, 8224; d) Y. Sun, Y. Xia, *J. Am. Chem. Soc.* **2004**, *126*, 3892; e) P. Selvakannan, M. Sastry, *Chem. Commun.* **2005**, 1684; f) Y. Xiong, B. Wiley, J. Chen, Z. Y. Li, Y. Yin, Y. Xia, *Angew. Chem.* **2005**, *117*, 8127; *Angew. Chem. Int. Ed.* **2005**, *44*, 7913.

[272] a) Y. Yin, C. K. Erdonmez, A. Cabot, S. Hughes, A. P. Alivisatos, *Adv. Funct. Mater.* **2006**, *16*, 1389; b) F. Teng, Z. Tian, G. Xiong, Z. Xu, *Catal. Today* **2004**, *93*, 651.

[273] a) J. Liu, A. I. Maaroof, L. Wieczorek, M. B. Cortie, *Adv. Mater.* **2005**, *17*, 1276; b) J. Han, G. Song, R. Guo, *Adv. Mater.* **2006**, *18*, 3140; c) X. W. Lou, C. Yuan, Q. Zhang, L. A. Archer, *Angew. Chem.* **2006**, *118*, 3909; *Angew. Chem. Int. Ed.* **2006**, *45*, 3825; d) X. Sun, Y. Li, *Angew. Chem.* **2004**, *116*, 3915; *Angew. Chem. Int. Ed.* **2004**, *43*, 3827.

[274] a) J. Yu, H. Ya, H. Guo, M. Li, S. Mann, *Small* **2008**, *4*, 87; b) T. Zhang, J. Ge, Y. Hu, Q. Zhang, S. Aloni, Y. Yin, *Angew. Chem.* **2008**, *120*, 5890; *Angew. Chem. Int. Ed.* **2008**, *47*, 5806; c) H. J. Fan, U. Gösele, M. Zacharias, *Small* **2007**, *3*, 1660; d) X. W. Lou, Y. Wang, C. Yuan, J. Y. Lee, L. A. Archer, *Adv. Mater.* **2006**, *18*, 2325.

[275] a) D. E. Zhang, Z. W. Tong, S. Z. Li, X. B. Zhang, A. Ying, Ailing, *Mater. Lett.* **2008**, *62*, 4053; b) X. Yu, C. Cao, H. Zhu, Q.

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⬊⬊ These are not the final page numbers!

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Angew. Chem. Int. Ed. **2010**, *49*, 2–36

Li, C. Liu, Q. Gong, *Adv. Funct. Mater.* **2007**, *17*, 1397; c) C. Zimmermann, M. Wanner, D. Gerthsen, C. Feldmann, *Small* **2007**, *3*, 1347; d) D. H. M. Buchold, C. Feldmann, *Nano Lett.* **2007**, *7*, 3489; e) Y. Ni, A. Tao, G. Hu, X. Cao, X. Wei, Yang, *Z. Nanotech.* **2006**, *17*, 5013.

[276] H. Gröger, F. Gyger, P. Leidinger, C. Zurmühl, C. Feldmann, *Adv. Mater.* **2009**, *21*, 1586.

[277] a) X. W. Lou, Y. Wang, C. Yuan, J. Y. Lee, L. A. Archer, *Adv. Mater.* **2006**, *18*, 2325; b) U. Kasavajjula, C. S. Wang, A. J. Appleby, *J. Power Sources* **2007**, *163*, 1003; c) X. W. Lou, M. L. Chang, L. A. Archer, *Adv. Mater.* **2009**, *21*, 2536.

[278] a) H. X. Li, Z. F. Bian, J. Zhu, D. Q. Zhang, G. S. Li, Y. N. Huo, H. Li, Y. F. Lu, *J. Am. Chem. Soc.* **2007**, *129*, 8406; b) X. B. Cao, L. Gu, L. Zhuge, W. J. Gao, W. C. Wang, S. F. Wu, *Adv. Funct. Mater.* **2006**, *16*, 896; c) Z. Y. Liu, D. D. Sun, P. Guo, J. O. Leckie, *Chem. Eur. J.* **2007**, *13*, 1851.

[279] a) P. M. Arnal, M. Comorri, F. Schüth, *Angew. Chem.* **2006**, *118*, 8404; *Angew. Chem. Int. Ed.* **2006**, *45*, 8224; b) C. M. Cobley, D. J. Campbell, Y. Xia, *Adv. Mater.* **2008**, *20*, 748; c) Y. E. Cheon, M. P. Suh, *Angew. Chem.* **2009**, *121*, 2943; *Angew. Chem. Int. Ed.* **2009**, *48*, 2899; d) H. Kobayashi, M. Yamauchi, H. Kitagawa, Y. Kubota, K. Kato, M. Takata, *J. Am. Chem. Soc.* **2008**, *130*, 1828.

[280] a) C. S. Peyratout, L. Dähne, *Angew. Chem.* **2004**, *116*, 3850; *Angew. Chem. Int. Ed.* **2004**, *43*, 3762; b) S. E. Skrabalak, J. Chen, L. Au, X. Lu, X. Li, Y. Xia, *Adv. Mater.* **2007**, *19*, 3177; c) K. M. L. Taylor, J. S. Kim, W. J. Rieter, H. An, W. Lin, W. Lin, *J. Am. Chem. Soc.* **2008**, *130*, 2154.

[281] Z. W. Shan, G. Adesso, A. Cabot, M. P. Sherburne, S. A. Syed Asif, O. L. Warren, D. C. Chrzan, A. M. Minor, A. P. Alivisatos, *Nat. Mater.* **2008**, *7*, 947.

[282] Current reviews in: a) H. Schnöckel, *Dalton Trans.* **2008**, 4344; b) J. F. Corrigan, O. Fuhr, D. Fenske, *Adv. Mater.* **2009**, *21*, 1867.

[283] a) G. Schmid, R. Pfeil, R. Boese, F. Bandermann, S. Meyer, H. G. M. Calis, J. W. A. van der Velden, *Chem. Ber.* **1981**, *114*, 3634; b) G. Schmid, *Chem. Soc. Rev.* **2008**, *37*, 1909.

[284] E. G. Mednikov, M. C. Jewell, L. F. Dahl, *J. Am. Chem. Soc.* **2007**, *129*, 11619.

[285] A. Schnepf, H. Schnöckel, *Angew. Chem.* **2001**, *113*, 733; *Angew. Chem. Int. Ed.* **2001**, *40*, 711.

[286] A. Müller, E. Beckmann, H. Bogge, M. Schmidtmann, A. Dress, *Angew. Chem.* **2002**, *114*, 1210; *Angew. Chem. Int. Ed.* **2002**, *41*, 1162.

[287] C. Anson, A. Eichhoefer, I. Issac, D. Fenske, O. Fuhr, P. Sevillano, C. Persau, D. Stalke, J. Zhang, *Angew. Chem.* **2008**, *120*, 1346; *Angew. Chem. Int. Ed.* **2008**, *47*, 1326.

[288] a) R. Ahlrichs, D. Fenske, M. McPartlin, A. Rothenberger, C. Schrodt, S. Wieber, *Angew. Chem.* **2005**, *117*, 4002; *Angew. Chem. Int. Ed.* **2005**, *44*, 3932; b) R. Ahlrichs, A. Eichhöfer, D. Fenske, K. May, H. Sommer, *Angew. Chem.* **2007**, *119*, 8402; *Angew. Chem. Int. Ed.* **2007**, *46*, 8254.

[289] a) S. Behrens, M. Bettenhausen, A. C. Deveson, A. Eichhöfer, D. Fenske, H. Lohde, U. Woggon, *Angew. Chem.* **1996**, *108*,

2360; *Angew. Chem. Int. Ed.* **1996**, *35*, 2215; b) H. Döllefeld, H. Weller, A. Eychmüller, *Nano Lett.* **2001**, *1*, 267.

[290] D. Cave, J. F. Corrigan, A. Eichhöfer, D. Fenske, C. M. Kowalchuk, P. Rösner, P. Scheer, *J. Cluster Sci.* **2007**, *18*, 157.

[291] R. Burgert, H. Schnöckel, A. Grubisic, S. T. Stokes, K. H. Bowen, G. F. Ganteför, B. Kiran, P. Jena, *Science* **2008**, *319*, 438.

[292] a) J. Hartig, F. Klöwer, J. Rinck, A. N. Unterreiner, H. Schnöckel, *Angew. Chem.* **2007**, *119*, 6669; *Angew. Chem. Int. Ed.* **2007**, *46*, 6549; b) R. Burgert, H. Schnöckel, *Chem. Commun.* **2008**, 2075; c) J. Hartig, A. Stößer, P. Hauser, H. Schnöckel, *Angew. Chem.* **2007**, *119*, 1687; *Angew. Chem. Int. Ed.* **2007**, *46*, 1658.

[293] D. Bono, A. Schnepf, J. Hartig, H. Schnöckel, G. J. Nieuwenhuys, A. Amato, L. J. de Jongh, *Phys. Rev. Lett.* **2006**, *97*, 077601.

[294] Current reviews in: a) H. Cölfen, M. Antonietti, *Angew. Chem.* **2005**, *117*, 5714; *Angew. Chem. Int. Ed.* **2005**, *44*, 5576; b) S. Sun, *Adv. Mater.* **2006**, *18*, 393; c) Y. Min, M. Akbulut, K. Kristiansen, Y. Golan, J. Israelachvili, *Nat. Mater.* **2008**, *7*, 527.

[295] a) C. B. Murray, C. R. Kagan, M. G. Bawendi, *Science* **1995**, *270*, 1335; b) C. E. Fowler, D. Khushalani, B. Lebeau, S. Mann, *Adv. Mater.* **2001**, *13*, 649; c) D. V. Talapin, E. V. Shevchenko, A. Kornowski, N. Gaponik, M. Haase, A. L. Rogach, H. Weller, *Adv. Mater.* **2001**, *13*, 1868; d) M. L. Kahn, M. Monge, E. Snoeck, A. Maisonnat, B. Chaudret, *Small* **2005**, *1*, 221; e) C. Desvaux, C. Amiens, P. Fejes, P. Renaud, M. Respaud, P. Lecante, E. Snoeck, B. Chaudret, *Nature* **2005**, *4*, 750; f) U. Jeong, Y. Xia, *Angew. Chem.* **2005**, *117*, 3159; *Angew. Chem. Int. Ed.* **2005**, *44*, 3099; g) N. Zheng, J. Fan, G. D. Stucky, *J. Am. Chem. Soc.* **2006**, *128*, 6550; h) Y. Wang, M. Ibisate, Z.-Y. Li, Y. Xia, *Adv. Mater.* **2006**, *18*, 471; i) F. Bai, D. Wang, Z. Huo, W. Chen, L. Liu, X. Liang, C. Chen, X. Wang, Q. Peng, Y. Li, *Angew. Chem.* **2007**, *119*, 6770; *Angew. Chem. Int. Ed.* **2007**, *46*, 6650.

[296] a) F. X. Redl, K. S. Cho, C. B. Murray, S. O'Brien, *Nature* **2003**, *423*, 968; b) C. Desvaux, C. Amiens, P. Fejes, P. Renaud, M. Respaud, P. Lecante, E. Snoeck, B. Chaudret, *Nat. Mater.* **2005**, *4*, 750; c) A. M. Kalsin, M. Fialkowski, M. Paszewski, S. K. Smoukov, K. J. M. Bishop, B. A. Grzybowski, *Science* **2006**, *312*, 420; d) E. V. Shevchenko, J. B. Kortright, D. V. Talapin, S. Aloni, A. P. Alivisatos, *Adv. Mater.* **2007**, *19*, 4183.

[297] E. V. Shevchenko, D. V. Talapin, N. A. Kotov, S. O'Brien, C. B. Murray, *Nature* **2006**, *439*, 55.

[298] Current reviews in: a) T. Ding, K. Song, K. Clays, C. H. Tung, *Adv. Mater.* **2009**, *21*, 1936; b) O. D. Velev, S. Gupta, *Adv. Mater.* **2009**, *21*, 1897; c) S. Acharya, J. P. Hill, K. Ariga, *Adv. Mater.* **2009**, *21*, 2959; d) K. J. M. Bishop, C. E. Wilmer, S. Soh, B. A. Grzybowski, *Small* **2009**, *5*, 1600.

[299] M. Schulz-Dobrick, M. Jansen, *Angew. Chem.* **2008**, *120*, 2288; *Angew. Chem. Int. Ed.* **2008**, *47*, 2256.

[300] Current review in: S. M. Hussain, L. K. Braydich-Stolle, A. M. Schrand, R. C. Murdock, K. O. Yu, D. M. Mattie, J. J. Schlager, M. Terrones, *Adv. Mater.* **2009**, *21*, 1549.

[301] R. P. Feynman, *Eng. Sci.* **1960**, *23*, 22.

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Reviews

Nanoscience

H. Goesmann,
C. Feldmann* ——————— ▮▮▮–▮▮▮

Nanoparticulate Functional Materials

At the very beginning was the dyeing of glass, a first application of nanoparticular functional materials (see picture). Today diverse perspectives for the increasing complexity of technical developments are offered. To prepare high-value nanoparticles a number of influences must be considered, and evaluation of particle properties requires the expertise of different fields. This background defines both the challenge and the attraction of nanoscience.

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