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Book Review

NANOMATERIALS
An Introduction to Synthesis, Properties and Application

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The book focuses on the special phenomena related to nanomaterials and attempt to provide explanations which avoid – as far as possible any highly theoretical and quantum mechanical description. The difficulties with nanomaterials arise from the fact that, in contrast to conventional materials, a profound knowledge of materials science is not sufficient.

The book includes 11 chapters and a subject index. The authors give initially two definitions for nanomaterials. The first - and broadest - definition states that nanomaterials are those materials where the size of the individual building blocks are less then 100 nm, at least in one dimension. This definition is well suited for many research proposals, where nanomaterials have a high priority. The second definition is much more restrictive, and states that nanomaterials have properties which depend inherently on the small grain size and, as nanomaterials are usually quite expressive, such a restrictive definition makes more sense. The main difference between nanotechnology and conventional technologies is that the “bottom-up” approach is preferred in nanotechnology, whereas conventional technologies usually use the “top-up” approach. The difference between these two approaches can be explained simply by using an example of powder production, where the chemical synthesis represents the bottom-up approach, while the crushing and milling of chunks represents the equivalent top-down process.

Chapter 1 is an introductory part, which refers to nanomaterials and nanocomposites, elementary consequences of small particle size, surface of nanoparticles, thermal phenomena, diffusion scaling law.

Chapter 2, “Surfaces in Nanomaterials” presents some general consideration in nanomaterials, where the surface forms a sharp interface between a particle and its surrounding atmosphere, or between a precipitated phase and the current phase. These are free surface in the case of particulate materials, or grain boundaries in bulk material. Nanomaterials have large surfaces, a fact which can be demonstrated by using spherical particles as examples.

The origin of surface energy is explained by a mode which assumes that particles are produced by breaking a large solid piece of material into smaller parts. In order to achieve this, it is necessary to cut the bounds between the neighboring atoms.

Chapter 3, “Phase Transformation of Nanoparticles” focuses on thermodynamics of nanoparticles, heat capacity, phase transformations and coagulation, structures of nanoparticles, nanoparticle melting, structural fluctuations.

The simplest possible description is used, neglecting any influential factors required for an exact description of equilibria. Phase transformations are connected with changes in physical properties, and in most case it is the density of the material that is changing. Within the context of phase transformations of small particles, the majority of extensive studies have been conducted with respect to the melting of metal particles. Phase transformation might be caused by the temperature flash that occurs during the coagulation of two particles.

In the case of zirconia for example, the temperature of phase transformation was found to decrease with decreasing particle size, which led to the fact that tetragonal phase – a high temperature phase – is in fact found at room temperature. Additionally, in the case of particles with size less than 5 nm the cubic phase is quite often found. This phenomenon is not restricted to compounds with comparably simple structures; rather, it is also found in the case of more complex structures with typical examples being ferroelectric or antiferroelectric compounds. At high temperature, these compounds are cubic, however, by reducing the temperature a transformation occurs to the tetragonal perovskite structure, which is ferroelectric below the Curie point. The continuous transition from one phase to another (distorted) phase, in combination with an increase in the lattice parameter with decreasing particle size appears to be general, and was even observed for high-temperature superconductors.

Although until now those considerations that have been made were purely thermodynamic in nature, nanoparticles are so small that thermal fluctuations are in fact observed. Typical examples of those phenomena are superparamagnetism and its analogue, superferroelectricity, and electron microscopy studies on the melting of small metal nanoparticles have provided information on similar phenomena.

By determining the relative amounts of solid and melted particles as a function of the particle size, it is possible to calculate phase diagrams where two-phase regions caused by fluctuations are indicated.

Chapter 4, "Gas-Phase Synthesis of Nanoparticles" includes some fundamental considerations, inert gas condensation process, physical and chemical vapor synthesis processes, laser ablation process, the microwave plasma process, flame aerosol process, synthesis of coated particles.

The process of particle formation may be divided into four major steps: nucleation, condensation of atoms or molecules, coagulation by exchange of surface energy, agglomeration. Size limitation by charging the particle are observed at the microwave plasma process and special variants of the flame synthesis process, both of which are described later in the chapter. The most important – and certainly the oldest – process for synthesizing nanoparticles in the gas phase is that of inert gas condensation. This process applies thermal evaporation to a metal within a vacuum chamber filled with a small amount of inert gas.

The basic principle of the inert gas condensation process leads to many variants, as the systems employed differ in how the metal is introduced and subsequently evaporated. One of the most interesting possibilities is heating with an electron beam. The technical up-scaling of an inert gas condensation process may lead to the introduction of the elements that limit particle size growth. However, two possible measures exist by which particle size and particle size distribution may be controlled: (i) a reduction of the residence time of the particles in the reaction zone; and (ii) rapid cooling of the particles after they have left the reaction zone. For both measures the original diffusion-controlled process is not applicable. Rather it is necessary to replace transport via thermal diffusion with transport using a carrier gas. When used as a heat source for mass production, an electrical arc has many advantages and is utilized on a regular basis.

A system for powder production using the laser ablation process generally consists of two essential elements: the pulsed high-power laser, and with the optical focusing system and feeding device for the precursor. In order to produce larger quantities with this process, rotating targets and automatic wire feeding systems have been developed.

The processes of chemical and physical vapor synthesis, as well as laser ablation, are purely random processes; hence, the only means by which particle size and size distribution can be influenced are the concentrations of active species in the gas, the temperature and, most importantly, the rapid cooling (quenching) of the gas after leaving the reaction zone. This situation is entirely different from that of the microwave plasma process, where the particles originating in the plasma zone carry electric charges. As a consequence, the probability for coagulation and agglomeration is significantly reduced, as the collision parameter decreases with increasing particle size.

The mechanism of nanoparticle formation in the microwave plasma differs from, that of a chemical vapor synthesis in a tubular furnace, as the reactants are ionized and dissociated. This also allows lower reaction temperatures. Among all of the processes used to produce nanoparticulate powders, the flame aerosol process is the oldest. Additionally, it is the only one to be used for mass production in the kiloton range. Although this well-established industrial process has been used for many decades, the basic principles are still not well understood, not least because the processes of powder synthesis and particle formation take place at extremely high temperatures and over very short times.

Although many applications of nanomaterials require the use of nanocomposites, the impossibility of obtaining well-distributed nanocomposites simply by blending processes led to the development of coated nanoparticles.

The processes used for particle coating must fulfill a series of requirements. The first and most important point is that the particles remain individualized and are not agglomerated. This requires either extremely low particle concentrations in the gas atmosphere, or particles that carry electrical charges of equal sign. Additionally, the temperature in the coating step must be sufficiently low so as not to destroy the matter used for coating. This condition is of particular importance when the coating consists of organic compounds.

Chapter 5, "Magnetic Properties of Nanoparticles" refers to magnetic materials, superparamagnetic materials, susceptibility and related phenomena in superparamagnets, application of superparamagnetic materials, exchange-coupled magnetic nanomaterials.

Materials are classified by their response to an external magnetic field as diamagnetic, paramagnetic, or ferromagnetic. Although, in general, all materials show inherently diamagnetic properties, only those materials not showing paramagnetic or ferromagnetic behavior in addition are known as diamagnetic.

Superparamagnetic materials excel in zero remanence and coercitivity; moreover, superparamagnetism is limited to small nanoparticle. Superparamagnetism leads, as the vector of magnetization is fluctuating thermally, to a zero coercitivity. The explanation for this phenomen is found in the magnetic crystal anisotropy. Superparamagnetism is a property of isolated noninteracting particles. In a macroscopic material consisting of many particles, dipole-dipole interaction of the particles leads to magnetically large particles that are no longer superparamagnetic. Embedding the nanoparticles in a second, nonmagnetic, phase causes the particles to be spaced further apart, such that the interaction is reduced. This led to the production of nanocomposites. In order to ensure that a technical material is superparamagnetic, the individual particles should not touch each other.

The majority of successful applications of magnetic nanomaterials use particulars composites, with superparamagnetism being necessary for the application of magnetic particles, for two reasons:

- Superparamagnetic particles avoid magnetic clustering;
- Superparamagnetic particles may be either attracted or released by switching the magnetic field.

From an economic viewpoint, the most interesting applications of superparamagnetic nanoparticles are related to medicine and biology.

In general, these designs of particle may be applied to magnetic cell separation techniques. Further successful application is related to medical diagnostics. Superparamagnetic nanoparticles are used to enhance the contrast in nuclear magnetic resonance (NMR) imaging. One further potentially important application of superparamagnetic nanoparticles is that of magnetic refrigeration where, instead of using ozone-depleting refrigerants and energy-consuming compressors, nanocomposites moving in a magnetic field might be employed. The concept behind magnetic cooling dates back several decades, having been applied in low-temperature physics.

A further fascinating application of superparamagnetic particles, and one which is already widely used in technical products, is that of ferrofluids; these are stable suspensions of Superparamagnetic particles in a liquid. In order to avoid the particles coagulating magnetically, they are coated with a second distance-holder phase.

In order to obtain a nanosized regular structure in the final product, with perfect distribution of the two different magnetic phases, a well-ordered regular structure is necessary within the material before the annealing stage is started. The energy product of this composite magnetic material exceeds the theoretical possible maximal value for FePt by more than 50%.

Some extremely interesting applications of this class of materials involve soft magnetic materials. The constant of anisotropy of these materials, which in most cases are metallic, is more than an order of magnitude smaller than that for soft ferrites.

Chapter 6, “Optical Properties of Nanoparticles” refers to adjustment of the index of refraction, optical properties related to quantum confinement, quantum dots and other lumophores, metallic and semiconducting nanoparticles in transparent matrices, special luminescent nanocomposites, electroluminescence, photochromic and electrochromic materials, general consideration, photochromic materials, electrochromic materials, magneto-optic applications.

In view of technical applications, the optical properties of nanoparticles and nanocomposites are of major interest. Besides their economic importance, the scientific background of these properties is of fundamental importance in order to understand the behavior of nanomaterials.

In many applications, it is necessary to adjust the index of refraction of a polymer precisely to a given value. A typical example of this is the glue used to fix or connect optical glass fibers for information transmission. One way to do this is to add nanoparticles with an index of refraction which differs from that of the polymer.

The photocatalytic activity of the nanoparticles must not lead to a self-destruction of the composite system, and it is essential to check this point before fixing a combination of polymer matrix and nanoparticles. Nanoparticles which emit at different colors may be simultaneously excited with a single light source, making multiplexed detection of different biological targets possible. Additionally, the absorption spectra of organic compounds are relatively narrow in comparison to quantum dots exhibiting a broad absorption spectrum that range deep into the UV. The only major disadvantage here is the significantly larger size as compared to organic lumophore molecules.

At present, the economically most attractive application of luminescent nanoparticles is found in biotechnology and diagnostics. For this application, it is necessary to attach antibodies, peptides, or proteins at the surface of the particles. These compounds must be selected in such a way that they attach exactly at the intended receptor.

From an economics viewpoint, electroluminescence applications have an extremely high potential for technical applications among consumer products. In electroluminescent devices, light emission is stimulated by electric fields instead of energy-rich photons.

The main advantage of devices based on electroluminescent materials lies in the fact that, in contrast to liquid crystal devices (LCDs), an external light source is no longer necessary. Although today, most electroluminescent devices function with organic materials, these compounds (which are used as the starting materials for organic light - emitting diodes). Primarily, nanoparticles made from semiconducting materials or doped insulating particles are applied as luminescent materials. Therefore, perhaps the most interesting future application will be seen in flexible display technologies.

One further interesting optical application of ceramic/polymer nanocomposites is their use as magneto-optical materials. Within this context, the phenomena under question include the Faraday effect (rotation of the plane of polarization of light in transmission), and the Kerr effect (rotation of the polarization plane after reflection at the surface of magnetic materials).

A higher concentration of ferrite particles clearly increases optical absorption. Furthermore, the strong increase in absorption for shorter wavelengths is shifted significantly to shorter wavelengths when the concentration is reduced. This blue shift may be attributed to a smaller particle size or surface phenomena on the band gap.

Chapter 7, "Electrical Properties of Nanoparticles" discuss about fundamentals of electrical conductivity in nanotubes and nanorods, carbon nanotubes, photoconductivity of nanorods, electrical conductivity of nanocomposites.

One interesting method which can be used to demonstrate the steps in conductance is the mechanical thinning of a nanowire and measurement of the electrical current at a constant applied voltage. The important point here is that, with decreasing diameter of the wire, the number of electron wave modes contributing to the electrical conductivity is becoming increasingly smaller by well-defined quantized steps.

In electrically conducting carbon nanotubes, only one electron wave mode is observed which transport the electrical current. As the lengths and orientations of the carbon nanotubes are different, they touch the surface of the mercury at different times, which provides two sets of information: (i) the influence of carbon nanotube length on the resistance; and (ii) the resistances of the different nanotubes. As the nanotubes have different lengths, then with increasing protrusion of the fiber bundle an increasing number of carbon nanotubes will touch the surface of the mercury droplet and contribute to the electrical current transport.

For technical applications outside of electronics, the electrical conductivity of nanomaterials can best be exploited as the electric-conducting phase in nanocomposites. The electrical conductivity of nanocomposites depends on percolation, the theory of which treats the properties of two-phase mixtures consisting either of conducting and insulating phases, or of a solid and pores. In the latter case, percolation leads to the formation of a network of open pores.

Assuming an electric-conducting nanocomposite - a two-phase mixture consisting of an insulating and an electrical conductive phase - the percolation threshold describes, in simple terms, the concentration of conductors required for the onset of electrical conductivity. At concentrations below the percolation threshold, there is no electrical conductivity, whereas above the threshold conductivity is observed. The percolation threshold and electrical conductivity at saturation level are heavily dependent on the fabrication process.

Chapter 8, "Mechanical Properties of Nanoparticles" deals with bulk metallic and ceramic materials, influence of porosity, influence of grain size, superplasticity, filled polymer composites, particle-filled polymers, polymer-based nanocomposites filled with platelets, carbon nanotube-based composites.

The discussion of mechanical properties of nanomaterials is, in to some extend, only of quite basic interest, the reason being that it is problematic to produce macroscopic bodies with a high density and a grain size in the range of less than 100 nm. However, two materials, neither of which is produced by pressing and sintering, have attracted much greater interest as they will undoubtedly achieve industrial importance. These materials are polymers which contain nanoparticles or nanotubes to improve their mechanical behaviors, and severely plastic-deformed metals, which exhibit astonishing properties. However, because of their larger grain size, the latter are generally not accepted as nanomaterials. Experimental studies on the mechanical properties of bulk nanomaterials are generally impaired by major experimental problems in producing specimens with exactly defined grain sizes and porosities. Therefore, model calculations and molecular dynamic studies are of major importance for an understanding of the mechanical properties of these materials.

Filling polymers with nanoparticles or nanorods and nanotubes, respectively, leads to significant improvements in their mechanical properties. Such improvements depend heavily on the type of the filler and the way in which the filling is conducted. The latter point is of special importance, as any specific advantages of a nanoparticulate filler may be lost if the filler forms aggregates, thereby mimicking the large particles. Particulate-filled polymer-based nanocomposites exhibit a broad range of failure strengths and strains. This depends on the shape of the filler, particles or platelets, and on the degree of agglomeration. In this class of material, polymers filled with silicate platelets exhibit the best mechanical properties and are of the greatest economic relevance. The larger the particles of the filler or agglomerates, the poorer are the properties obtained. Although, potentially, the best composites are those filled with nanofibers or nanotubes, experience teaches that sometimes such composites have the least ductility. On the other hand, by using carbon nanotubes it is possible to produce composite fibers with extremely high strength and strain at rupture.

Among the most exciting nanocomposites are the polymer-ceramic nanocomposites, where the ceramic phase is platelet-shaped. This type of composite is preferred in nature, and is found in the structure of bones, where it consists of crystallized mineral platelets of a few nanometers thickness that are bound together with collagen as the matrix. Composites consisting of a polymer matrix and defoliated phyllosilicates exhibit excellent mechanical and thermal properties.

Chapter 9, "Nanofluids" analyses aspects regarding nanofluids for improved heat transfer, ferrofluids, general considerations, properties of ferrofluids, application of ferrofluids.

Nanofluids are stable suspensions of nanoparticles in a liquid. In order to avoid coagulation of the particles, the particles must be coated with a second distance-holder phase which, in most cases, consists of surfactants that are stable in the liquid. One typical application of nanofluids containing nanoparticles is as a coolant, since the addition of only a few volume percent of nanoparticles to a liquid coolant can significantly improve its thermal conductivity, yet have no negative influence on its heat capacity. In fact, the high heat capacity of nanoparticles can actually improve the heat capacity of a coolant. When considering the technical applications of these fluids, it is not only the heat capacity and thermal conductivity but also the rheological parameters that are of vital importance. One fascinating application of superparamagnetic particles - and one which already has been widely applied in technical products - is that of ferrofluids, which are a special type of nanofluids.

A ferrofluid is a stable suspension of superparamagnetic particles in a liquid. In order to avoid magnetic coagulation of the particles they must be-coated with a: second, distance-holder phase. Ferrofluids, as magnetic materials, may be used to transfer magnetic fields or to close magnetic circuits in a simple way, without the need for any complicated and shaped parts. Besides these possibilities, the variation of viscosity as a function of an external magnetic field represents one of the most striking properties of a ferrofluid. One of the commercially most successful applications-of ferrofluids in consumer products is in loudspeakers, where the ferrofluid plays three important roles: (i) it centers the voice coil within the magnet; (ii) it acts as a coolant for the voice coil, by removing the heat caused by Ohmic losses; and (iii) it acts as damping medium.

Further broad applications of ferrofluids are in the visualization of magnetic structures and domains. This is used extensively for the quality control of all types of magnetic storage devices, such as magnetic tapes, floppy disks, or magneto-optical disks. In materials sciences, the studies of magnetic domains in alloys, garnets, and minerals and the identification of small defects in steel and weldings are typical fields of application. In such cases, small external magnetic fields are often used to enhance the contrast. Within this context, many economically extremely interesting applications may be identified. For example, in medical diagnostics ferrofluids are applied to increase the contrast of nuclear magnetic resonance (NMR) imaging.

Chapter 10, "Nanotubes, Nanorods, and Nanoplates" discusses about conditions for the formation of rods and plates, layered structures, one-dimensional crystals, nanostructures related to compounds with layered structures, carbon nanotubes, nanotubes and nanorods from materials other than carbon, synthesis of nanotubes and nanorods.

Nanotubes, nanorods, and nanoplates are frequently observed. Whilst nanorubes and nanorods are often referred to as one-dimensional nanoparticles, nanoparticles and fullerenes, in contrast, are generally denominated as zero-dimensional structures. Althugh,nanorods and nanoplates are often found as more or less spherical or facetted particles, their one- or two-dimensionality is clearly visible. Notably, as very few routes of synthesis are available for the preferential delivery of aggregates that are not zero-dimensional, interest has centered on these specially shaped nanoparticles and continues to be promoted by the wide range of interesting physical properties associated with these structures. A possibility of obtaining nanorods and nanotubes is related to layered structures, where the crystal structure is built from layers held together;.with van-der Waals forces rather than by electrostatic attraction. Another possibility of obtaining nanotubes is to use compounds that crystallize in only one dimension. In theory, this is the most promising way to obtain long fibers, but unfortunately the importance of this route is negligible as the numbers of compounds coming into question is small. The modt important class of one-dimensional compounds is the class of silicates called allophanes.

For small particles of compounds crystallizing in layered structures, a minimum free energy can be achieved by reducing the number of dangling bonds by forming tubes; nanotubes are observed especially with this types of compound. The most prominent representative of this class of compound is graphite, although nanotubes consisting of boron nitride, the sulfides and selenides of molybdenum and tungsten, as well as many other compounds, have also been identified.

The formation of nanotubes is not limited to single graphene layers and, as for fullerenes, both "multiwall" and "single wall" nanotubes may be observed. The multiwall nanotubes consist of a series of coiled graphene layers, and can be depicted perfectly using electron microscopy. Potentially, a major application of nanotubes is as electron emitters. Electron emission in an electrical field requires a sharp tip, and the sharper the tip the lower the electrical voltage required for electron emission. This is because the electrical field at the tip controls electron field emission. Although single-wall nanotubes have the sharpest tip occurring in nature, in reality multiwall nanotubes are used as they are more readily available.

One further interesting application of carbon nanotubes exploits their electrical conductivity and large length-to-diameter ratios. Because of the huge aspect ratio, the amount of carbon nanotubes required to achieve electrical conductivity is very small, and it is possible to produce an optical transparent coating with relatively good electrical conductivity. It is also possible to fill the interior of carbon nanotubes with metals or other compounds. As in the case of coated nanoparticles, this strategy allows two different properties to be combined within one particle. These filled carbon nanotubes may have many exciting applications.

Chapter 11, "Characterization of Nanomaterials" includes aspects on global methods for characterization, specific surface area, X-Ray and electron diffraction, electron microscopy, general considerations, interaction of the electron beam and specimen, localized chemical analysis in the electron microscope, scanning transmission electron microscopy using a high-angle annular dark-field (HAADF) detector.

When considering characterization methods, it is very important to distinguish between methods that deliver values averaged over a large ensemble of particles, and those that provide information about a limited number of particles. The most important among the latter group of methods are those that are microscopic in nature. The behavior of nanomaterials is controlled by their global properties, which provide indications of how an ensemble behaves. However, in order to understand why an ensemble behaves in a certain way, it is necessary to utilize microscopic methods. Both, X-ray and electron diffraction techniques are used to study the crystal structure of specimens, and it is also possible to obtain information on the particle size in this way. Diffraction experiments may be conducted in transmission, usually in electron diffraction, or in reflection, as it is used primarily in X-ray diffraction techniques. In order to study the shape, size, and structure of nanoparticles, electron microscopy is the best-suited technique. Today, however, as electron microscopy is considered a broad science in its own right, within this chapter we will outline a few basic facts, aiming to avoid the impression that simply by reading these few pages it would be possible to interpret electron micrographs.

Nonetheless, the user of nanomaterials must accept that the properties of the latter materials demand a deeper insight into their physics and chemistry. Whereas, for conventional materials the interface to biotechnology and medicine is related directly to the application, the situation is different in nanotechnology, where biological molecules such as proteins or DNA are also used as building blocks for applications outside biology and medicine.

Each chapter ends with a list of References. Most of the images are colored and this fact improves significantly the understanding of various phenomena.

This valuable monograph addresses in particular the researchers who have to understand the special phenomena and potentials, with an average degree of details. It can also be use as a students course, since the nanomaterials are analyzed from an application – oriented perspective.

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