1 What is sol-gel and nanotechnology?

1.1 Definitions

According to W. Ostwald, colloids are a field which is only for practical reasons separated within the larger field of dispersed systems.[7]

Definitions are important because they allow that a topic can be discussed without misunderstandings. When talking about sol-gel and nanotechnology this seems to be especially important, because nanotechnology is no scientific field on its own, but rather a conglomerate of almost all scientific disciplines, ranging from chemistry and physics over materials science to e.g. medicine.

The BMBF (the German Ministry of education and research) defines the term nanotechnology as follows: “Nanotechnology describes the production, analysis and application of structures, molecular materials, inner interfaces and surfaces exhibiting at least one critical dimension or production tolerance smaller than 100 nm. The nanoscale nature of the components of the system alone is responsible for the new functions and properties to improve existing or develop new products”[3].

The second part of this definition is very important, because it separates nanotechnology from many products which contain nanoparticles by nature or by accident, or those products where the nanostructures are not relevant for the value at use. Nanotechnology thus incorporates the knowledge about structure-property relationships and the deliberate production of particles or structure in the nanoscale.

Figure 1.1: Nanoparticles put into perspective of other materials and technologies
Now it becomes clear, that nanotechnology cannot be a defined market or a precisely defined industry. Nanotechnology rather is an artificially designed scientific discipline, which covers different materials and processes, as well as simply a description of a dimension in material- and process development.

The sol-gel process is one aspect of nanotechnology. It describes the preparation of nano-scaled objects like e.g. particles and their processing to nanostructured materials. One process step thereby includes the solidification of a liquid nanoparticle dispersion (sol) by interparticulate forces to a gel.

Figure 1.1 can help to put nanoparticles into perspective of other materials or technologies. The gray shading illustrates the relevant dimensions for the sol-gel process and nanotechnology. Some further definitions are shown in Figure 1.2.

With regard to a consistent definition, it can be problematic that almost every material contains nanoparticles or consists of nanostructures, if you just look close enough with suitable microscopes. Therefore, the second part of the nanotechnology definition refers to the special, deliberate property profile which is caused by the nanostructures (compare “Health, safety and environmental aspects of nanoparticles”, Chapter 7).

In order to be able to talk effectively about sol-gel- and nanotechnology, some further definitions are necessary. The german norms “ISO” help us out with useful descriptions. According to ISO TC 24/SC 4, TC 146, TC 209:

**Particle**

A very small piece of material with defined physical limits.
Definitions

Aggregate

A collection of particles with strong interparticulate bonds (covalent or even sintered necks), whose resulting surface area is significantly smaller than the calculated sum of the surface areas of its components.

Agglomerate

A collection of weekly bonded particles or aggregates, whose surface area is comparable to the sum of the calculated surface areas of its components.

The term “monodisperse”, in contrary to “polydisperse” describes a group of particles which are homogeneous with regard to their size and shape. Officially a special limit does not exist, but ±10 % variation seems to be a suitable value. Monodispersity in most cases is a desired property of the dispersion, because it allows a more precise control of the properties of the material which is to be synthesized. This is important, especially for the preparation of transparent nanocomposites or coatings to avoid haziness caused by larger particles or agglomerates.

1.2 Historical and actual facts

“It’s a pity that even now, colloidal chemistry has become an almost unmanageable field of science” (W. Ostwald 1927).

Nano- and sol-gel technology are not new and since centuries are used to prepare materials with extraordinary properties. Gold-ruby glass for example is one of the oldest nanomaterials. Described already by the sumerians in 700 BC, German chemist Kunkel rediscovered this ancient technology [4]. Nano gold particles are responsible for the beautiful red color.

Figure 1.3: Illustration of different forms of nanomaterials

Nanoobjects:

- Bulkmaterial
- 1-dimension: coatings, platelets
- 2-dimensions: fibers
- 3-dimensions: nanoparticles

Nanostructured materials:

- Nanocomposite
- Core/shell particle

Figure 1.3: Illustration of different forms of nanomaterials
Their agglomeration is prevented by addition of SnO₂ to the liquid glass melt. In 1900 Zsigmondy described monodisperse gold particles as the basis for this technology [5].

Another example are carbon nanotubes, which can be found e.g. in the multiply folded steel blades of Japanese master forgers. In this case nanotechnology was used without knowing the structure-property relationships. Today’s discussion tends to use the term nanotechnology only in these cases, where knowingly and deliberately nanostructures are used to develop materials with new properties.

In 1947 for the first time Taniguchi proposed the term nanotechnology for these applications [6]. Decades before him, Ostwald already described the “world of the neglected dimensions” in a lecture series around the year 1910. He focused on materials ranging in size from 1 to 100 nm known as colloids, materials, which are not held back by conventional filters. Still today, his book is a fascinating source of inspiration, describing some early commercial applications of nanotechnology [7].

A decisive breakthrough for today’s popularity of chemical nanotechnology however was besides others the work of Schmidt et al who dealt with the synthesis and applications of organically modified inorganic materials [8, 87]. These materials, which are often referred to as “ormocers”, “ormosils”, or “ceramers”, open up a new world full of possibilities for materials science by combining organic polymers with inorganic building blocks. Some of them are described in more detail in the following pages.

### 1.2.1 Nanotechnology as part of our daily life

We cannot avoid coming into contact with nanotechnology, because nanotechnology is a universal building principle of nature, even more so, it is a basis for our existence. It makes sense to look at the deliberate and coincidental points of contact with nanotechnology in our lives to better understand the breadth and the nature of nanotechnology.

**A typical day with nanotechnology**

We start the day with a refreshing shower in the nanocoated easy-to-clean shower cabin, put on our silver nanoparticle impregnated socks and impregnated stain-proof tie. On our way to work, we drive with fuel-saver tires, reinforced with nanoscaled carbon black and silica.

During the drive with our new car with a scratch-proof clear coat due to silica nanoparticles we produce exhaust gases loaded with nanoscaled carbon black, even though they had been purified by our noble metal nanoparticles containing catalyst. At work, we use the newest CPU made by “26 nm technology” and print our documents with laser printers using nanostructured toner particles.

After work we relax with a tennis match, of course with the carbon nanotubes reinforced new racket. Finally at home at candlelight we read the novel “prey” from Michael Crichton [9] and shiver at the thought of wild swarms of nanoorganisms turning the world into a gray goo. During reading, we inhale the nanoparticle soot produced by the candle flame. While brushing our teeth at the evening of this busy day with a toothpaste containing nano-apatite which remineralizes our teeth, we look in the mirror and see the most perfect nanomachine of all - ourselves, because most processes in our body run on the nanoscale [10].

The different reports and estimations of the current and future market potential of nanotechnology were collected in fall 2011 by the German BMBF (Ministry of education and research). They outbid each other in euphoria and differed by billions of euro – why [11–13]?
Nanotechnology is, as already discussed before, no market of its own, therefore it is difficult to draw a line. Today’s computer processors are without doubt nanotechnology, proudly Intel advertises its 22 nm architecture.

What turnover can now be accredited to nanotechnology? That of the processor, the motherboard, or that of the whole computer? How this question is answered will significantly affect the market potential of nanotechnology which is published.

Of the whole computer, only a tiny fraction is nanotechnology, however a decisive one. This opens up the question how to generate turnover and profit with nanotechnology. This is occasionally called the “nano-trap”[14].

A practical example can be an easy-to-clean coating of shower cabins. Calculated from the typical raw materials, a 100 nm thick coating, applied at 0.1 g/m² causes € 2 – € 5 material costs when an area of 10 m² is coated. An end customer however pays a premium of up to 250 € per shower cabin, thereby generating a value of roughly € 25,000 per kilogram nanocoating which is kept by the producer or seller of the shower cabin.

For a material producer it should be difficult to get a significant piece of that cake if the technology and the application are not thoroughly protected by patents or other hurdles. At the end, the major part of the generated value stays with the producer or seller, in spite of the fact that the R&D of that nanotechnology coating might have been a risky venture, burning a lot of money. These and further problems in realizing the full monetary potential of nanotechnology innovations led to the discrepancy between the high expectations and the so far realized commercial success.

Meanwhile, a more realistic approach to the market potential of nanotechnology is favored. Not nanotechnology by itself, but rather the achievable and affordable customer advantage is in the focus.

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**Figure 1.4: Changes of “breakthrough”-technologies in the public perception over time**

*Source (picture): Sumba, www.piqs.de*
This situation is nothing specific. Not only nanotechnology, but almost every new technology breakthrough in the beginning causes euphoria about the limitless opportunities. With time, market participants realize that not the technology itself can be sold, but only economically sound problem solutions for a paying customer.

A consequence is, that the high expectations cannot be fulfilled and disappointment arouses. Sooner or later the new technology gets absorbed and integrated into current product development cycles and a market pull for the new problem solutions develops. It is this stage of development, nanotechnology is in today.

### 1.3 Nanotechnology in the development of paints and coatings

Nanotechnology has already been used in the development of paints and coatings since a long time. Many pigments exhibit dimensions in the nanoscale and water-based coating resins consist of nanosized polymer droplets. So it is not surprising that the German organization of the coatings industry (VdL) describes the future perspective of nanotechnology like this: “Nanotechnology is a key technology of the future and gains more and more importance also in the fields of paints and coatings. The improvement of conventional coatings and the realization of new functions with the help of nanotechnology will increase in the following years”[353].

Before nanomaterials can be used in the development of coatings, they have to be synthesized first. The problems and possibilities of the manifold synthesis processes are discussed in the next Chapter 2.
2 Synthesis of nanomaterials

“The colloidal state is a universal state of matter” Wolfgang Ostwald wrote in 1922. Nanotechnology describes only a dimension, therefore in principle almost all materials can be brought into a nanoscaled state. During the synthesis of nanomaterials, three critical success factors are important and shown in Figure 2.1.

The synthesis of nanomaterials with defined specifications in many cases is difficult, because structure-property relationships are not known and must be determined in large-scale series experiments. After their synthesis, agglomeration of nanoparticles has to be prevented in order to make use of their specific properties. The third important point is the adaption of nanomaterials to their environment. Nanoparticles usually are not synthesized directly in the medium they are used in at a later stage of the process and the transfer requires a suitable surface modification.

In the following chapters, step by step the critical success factors for the synthesis of nanoparticle dispersions are discussed, starting with the synthesis. Two basic routes are known to synthesize nanomaterials. Either something big is broken down into smaller pieces or something very small is grown in a controlled way to yield nanoparticles. These approaches are known as top-down and bottom-up synthesis pathways.

![Figure 2.1: Critical parameters of success during the synthesis of nanomaterials](image)

![Figure 2.2: Top-down und bottom-up approach for the synthesis of nanomaterials](image)
2.1 **Top-down processes**

During a top-down synthesis, bigger structures are broken down to smaller structures by energy-intensive processes like milling. In order to protect the particles from agglomeration, the generated new surfaces have to be coated with significant amounts of surface modifiers. For 20 nm sized particles, up to 15 weight% are necessary. Smaller particles due to their larger surface can need even more.

During milling, more and more energy is put into the system in the form of freshly generated surfaces. At some point in time, the tendency of the system to reduce its energy content by agglomeration becomes so dominant, that longer milling does not lead to a further decrease of particle size.

A disadvantage of top-down processes is the high energy consumption. For dispersing an agglomerated, coarse powder into a nano-dispersion, ball mills of some kilowatts per hour are necessary, which need up to 10 hours to break down the bigger particles. During this process, a contamination of the nanoparticles by the mill has to be taken into account.

![Milling](image)

**Figure 2.3:** Surface modifiers are necessary to avoid the formation of agglomerates during milling.

![ZrO₂ colloidal dispersion](image)

**Figure 2.4:** Transparency of zirconium dioxide dispersions as a function of milling time in a high energy mill. Source: Bühler AG
Example 1: Preparation of a ZrO₂ (zirconium dioxide) nanoparticle dispersion by milling

1,000 ml of distilled water, 400 g of zirconium dioxide (BET surface 150 ± 10 m²/g) and 60 g of 3,6,9-trioxadecanic acid are placed in a reaction vessel and mixed for 30 minutes while stirring. The obtained mixture is milled in an agitating ball mill for 4 hours (Drais Perl Mill PML-H/V, 1,700 g milling balls, zirconium silicate, ball diameter 0.3 to 0.4 mm, continuous operation in circular mode). The colloid obtained in this way contains particles with an average particle diameter of \(d_{50} = 0.0118 \mu m\) (UPA).

Avoiding agglomeration

During milling, the decisive point to avoid agglomeration is to occupy the newly generated surfaces quickly with a surface modifier. Trioxadecanic acid is such a modifier with an exceptionally strong affinity to metal oxide surfaces, which also is used to control the wet chemical synthesis of other oxides, like e.g. ITO.

15 to 20 weight% surface modifier, in relation to the weight of the nanoparticles is a common value. This large amount of organic contamination is carried through all the following process steps and usually has to be removed at some point. Also, a contamination by the material of the mill should be considered.

Example 2: Preparation of an ITO indium tin oxide nanoparticle dispersion

140 g indium (III) chloride (0.63 mol, anhydrous), 18 g tin (IV) chloride · 5 H₂O and 5.6 g caprolactam were added to 1,400 ml water and stirred. After a clear solution had been formed, this was heated to 50 °C. Once this temperature had been reached, 105 ml ammonium hydroxide solution (25 %) were added dropwise under vigorous agitation. The produced suspension was stirred for a further 24 hours at a temperature of 50 °C. A further 280 ml ammonium hydroxide solution were then added to the mixture for full precipitation.

A white deposit consisting of indium hydroxide was formed, which was centrifuged off (30 min at 4000 rpm). The powder was dried in a vacuum drying oven at 190 °C until a slight yellowing of the powder could be determined. The dried powder was finely ground in a mortar, spread out in crystallising trays and placed in a forming gas oven. The oven was evacuated, then flooded with nitrogen. The oven was heated at a heating rate of 250 °C/hour to 250 °C with a nitrogen flow of 200 l/h. This temperature was maintained for 60 minutes under a forming gas atmosphere at a gas flow of 300 l/h. The oven then cooled to room temperature under a nitrogen atmosphere (duration approx. 5 hours). This resulted in dark blue ITO powder.

A mortar mill is charged with 25 g of a mixture of 50 % by weight ethylene glycol, 50 % by weight diethylene glycol monobutylether, and 5.6 g of 3,6,9-trioxadecanic acid. 75 g of ITO powder are added slowly, and milling is carried out for 2 hours. This results in a dark blue suspension of high viscosity which is homogenized on a roller bed for approximately 20 minutes. The resulting suspension is redispersed in ethanol by introducing 43 g of the suspension thus obtained into 57 g of ethanol and stirring.

Separation of the ethanol produces ITO powders which are dispersible in ethanol to a particle size of less than 20 nm. The primary particle size is 10
to 11 nm, the specific surface area 70 m²/g. Isoelectric point: 7.2. The tin content is usually 8 mol-%. From these powders it is possible to apply sol-gel layers which, at a film thickness of 400 nm with a baking temperature of 550 °C, are able to realize a transmission > 90 % and a surface resistance of 160 Ω/square on glass.

**ITO indium tin oxide nanoparticle dispersion**

When synthesizing nanoparticles via controlled wet chemical methods, it is important to avoid the formation of irreversible aggregates. One possibility is to use surface modifiers right from the beginning during the precipitation step. Thereby the newly generated surfaces are immediately covered by the modifier and agglomeration as well as aggregation is reduced to a great extent.

The use of caprolactam in this example is such a case. The co-precipitation of the ITO yields agglomerated nanoparticles which can be redispersed to primary particle size, because their active surface had been covered and growth had been stopped by the surface modifier. A further effect is that the size of the primary particles can be controlled by the amount of the surface modifier if the adsorption on the surface is strong enough (compare Figure 3.18, page 49) [63].

If thermally treated nanoparticle agglomerates have to be dispersed, strong shear forces are necessary. In this example the thermal treatment was used to foster crystallization and thus a three roll mill is necessary to break down the aggregates. As pointed out before, the newly generated surfaces have to be protected again with a surface modifier. Trioxadecanic acid is a very effective modifier which coordinates with its carbonic acid function and the ether oxygen atoms to the surface of the nanoparticles.

The first step in the nanoparticle synthesis of the example is the solubilizing, diluting and heating of indium and tin chloride. Under these conditions, already hydrolysis and formation of chloride-stabilized seed particles takes place (compare Table 2.2, page 25). It is not known if this step is decisive for the product quality, however it is important to understand, that even the smallest detail like the dilution of the salt solution can be very important for the final product.

### 2.2 Bottom-up processes

Bottom-up processes use atoms, ions or molecules to build up the nanoparticles via physical or chemical processes. A rough segmentation can be done via the phase in which the reaction takes place, so gaseous, fluid and solid state processes are distinguished. Table 2.1 shows examples of several known bottom-up processes.