Converting Nanoparticles by Surface Modification and Chemomechanical Processing

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Abstract

Inorganic Nanoparticles can be understood as carriers of interesting functions like UV absorption, porous structure provision, or photocatalytic activity. However, to make these functions available and useful in real world products, additional features are needed with respect to functionality, reactivity, viscosity, solid content, solvent, and pH value. Chemical modification of the surface of nanoparticles can help to meet these requirements. Stabilization of nanoparticle dispersions in the medium of the application is a basic requirement for a nanoadditive system. Starting from agglomerated powders, chemomechanical processing may be used for deagglomeration and simultaneous functionalization of nanoparticles.

Nanoparticle dispersions

Using nanoparticles in applications is rewarding because the resulting composition is not a mere mixture but a microscopically homogeneous composition with respect to e.g., optical, mechanical, chemical, electrical, or magnetic properties. Nanoparticle technology as enabling technology is therefore a versatile tool for the materials community.

In industrial applications, however, it is important to note that nanoparticles are quite often simply the carrier of a specific function which is sought to be introduced into a material; the focus is on the function rather than on the nanoparticle. The usual method is to disperse nanoparticles into the product to obtain the final product formulation as a stable functional colloid. Whereas the production of a dispersion of nanoparticles in water or a solvent may be a difficult task in itself, dispersing nanoparticles in complex product formulations is even more challenging. The interaction with the additional components as well as downstream processing has to be taken into account. However, less complex nanoparticle (pre-)dispersions may serve as a convenient means to introduce the nanoparticles. In fact, also in this case, the side requirements of the final product have to be considered right at the start of nanoparticle processing.

Nanoparticles are used to render printing substrates suitable for photo-quality ink-jet printing. As a side requirement, the particle formulation can only be applied as coating if its viscosity is sufficiently low. As an additional requirement, the particles of the formulation have to provide a cationic surface charge. In another example, nanoscaled Zincoxide may be dispersed and stabilized in organic media to provide sustainable UV protection of inks. Apart from transparency, the protection efficiency is controlled by the state of dispersion in the ink.

In these examples, the raw materials of nanopowders must be converted into usable materials by chemical surface modification and chemomechanical processing.

Chemical Surface Modification

The surface of a particle system has a great influence on its properties. As an example the surface energy, and thus its wettability, varies with the composition of the surface. Apart from the chemical composition, the overall surface energy is additionally influenced by the surface morphology, which is at different length scales controlled by the size respectively the curvature, the packing, shape, and the roughness of the particles. The surface of inorganic oxides comprises mostly of OH-functions of different concentration. Consequently, untreated inorganic oxide particles are usually hydrophilic.

The chemistry of nanoparticles can be compared to molecular chemistry rather than to the behavior of micron-size particles [1]. We consequently understand nanoparticles as molecules with reactive groups at the surface. Using molecular bifunctional additives these groups are accessible to a chemical reaction (Figure 1). Examples of suitable reagents include a wide range of chemicals like e.g. silanes, boranes, carboxylic acids, (di-, tri-,…) amines, β-diketones, and other chelating agents.

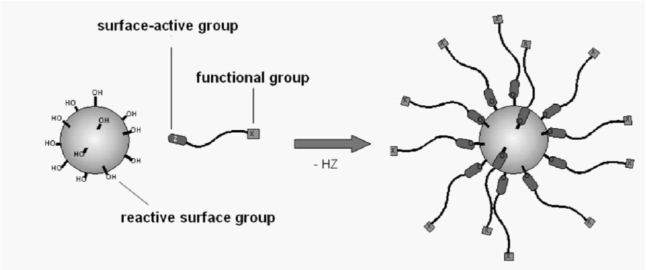

***Figure 1**. Chemical Reaction between inorganic nanoparticles and bifunctional surface modifiers.*

The second function of the molecular additive is also chosen according to the application. It can render the particle hydrophobic by alkyl groups, or even oleophobic by fluoro-alkyl groups. Also, chemical reactivity may be induced by introducing e.g., amino-groups, C=C-double bonds, alcohol- or epoxy groups. The surface modifier controls the isoelectric point (IEP), polarity, and reactivity of the particles as well as solid content and viscosity of the dispersion.

Generally, a complete coverage of the surface is not necessary for surface modification. Rather, the concentration of attached modifier is a parameter in itself to control the properties of the colloid. As an example, the concentration of amino groups at the surface of Titania particles control the zeta potential of the system, where a higher concentration of amino groups increases the positive charge of the particles in an acidic medium. Figure 2 shows the Zeta potential of untreated and aminosilane-treated TiO_2 in an aqueous acidic medium. The positive charge of TiO_2 at $pH < pH_{IEP}$ is increased. In addition, the pH_{IEP} has been shifted from about 6 to about 9.5.

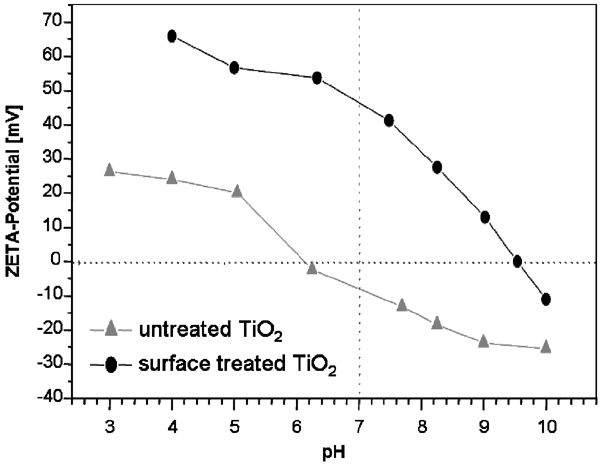

***Figure 2**. Zeta potential of untreated TiO_2 and TiO_2 treated with aminosilane (TiO_2: Degussa P25).*

Theorectically, only chemistry limits the scope of chemical surface modification. In practice, custom synthesis of a specific molecule is economically feasible only for applications of high volume. However, this situation is usually no real limitation because of the wide variety of commercially available molecular modifiers.

Dispersion of Nanoparticles

Colloids are highly dispersed systems with large specific surface areas. Figure 3 depicts the specific surface area as a function of the particle size. Nanoscaled systems often feature internal surfaces in the order of 50-500 m^2/ml which need to be chemically controlled to obtain stable and functional dispersions.

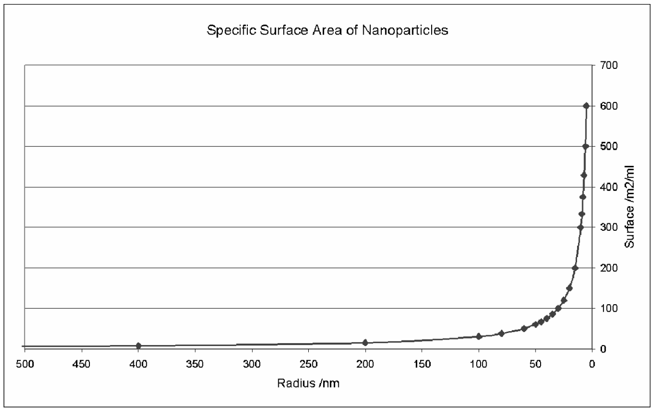

***Figure 3**. Specific Surface Area vs. Particle Size.*

General stabilization mechanisms for dispersions and colloids are well known [2]. The mechanisms are based on changing the surface of the particles. For stabilizing micron-sized particles in a liquid, a variety of organic polymers is available. The general concept comprises in specific groups or segments of a macromolecule to attach at the particles' surface. At the same time, the molecule comprises segments with a good compatibility to the medium.

Colloids in an aqueous medium can be electrostatically stabilized if the pH value is adjusted accordingly. The mechanism is fast and efficient. However, many commercial products do not allow this approach as the pH value is a figure given from the application. As a consequence, steric and electrosteric stabilization mechanisms are used more frequently for product formulations. Figure 4 summarizes the different stabilization mechanisms for colloids.

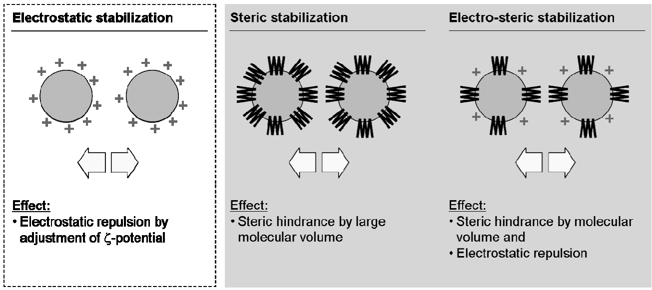

***Figure 4**. Stabilization Mechanisms for Colloids. From left to right: Electrostatic, Steric, Electro-Steric Stabilisation.*

As an important parameter, the interparticle distance should be considered when stabilizing particles (Figure 5). The distance between two particles is decreasing with decreasing particle size. As an example, this interparticle distance in a dispersion of sub-µm (0.5 µm) particles at a concentration of 30 vol.-% is comparable to the distance in a nanoparticle dispersion at a concentration only well below 10 vol.-%. The interparticle distance is basically the contiguous space available for stabilization, functionalization, and the rest of the product formulation. Therefore, substituting micron-sized particles with nanoparticles influences the whole product formulation and mainly its viscosity. Consequently, we have to reflect size considerations when using surface modifier molecules.

As a general rule we find that it is helpful to employ smaller surface modifier molecules as the particles get smaller. This concept of ‘small molecule surface modification’ contrasts the classical usage of oligomeric dispersants.

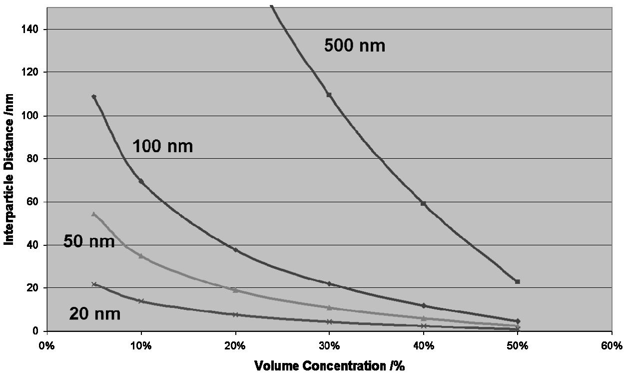

***Figure 5**. Interparticle Distance vs. concentration for particles of different size.*

Chemomechanical Processing

If agglomerated powders are used as starting material, a deagglomeration step and thus an additional feature in the process is necessary. This can be done using chemomechanical processing and agitator bead mills are a versatile tool in this process. Chemomechanical processing can be understood as carrying out chemical surface modification, which is mandatory in nanoparticle processing, under well-defined mechanical conditions [3].

Because many parameters influence the selection of the agitator bead mill, there is no standard equipment which can be used in all cases. For instance product viscosity, cooling options for temperature sensitive products, availability of materials for the grinding chamber (the stator) and the rotor (e.g. ceramics like ZrO_2, Al_2O_3 or SiC, polymers like PU, PA or PFA, steel), sensitivity of the product with respect to contamination, chemically aggressive products, bead size and thus grinding media separation as well as flow rate need to be considered for the best choice of equipment.

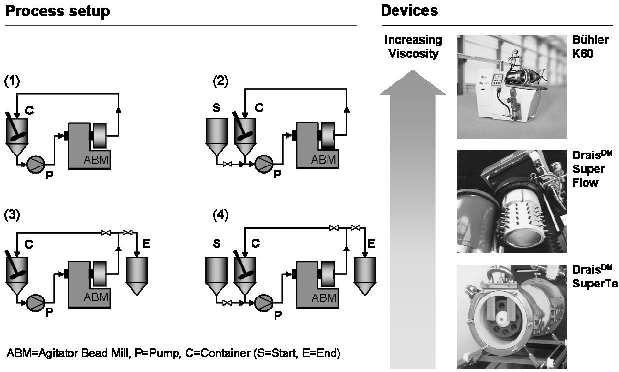

***Figure 6**. Chemomechanical Process: Different agitator bead mills and different set-ups. ABM: Agitator Bead Mill, C: Container, P: Pump, S: Start, E: End.*

Agitator bead mills expand the parameter space for optimizing the process of manufacturing functional colloids. As an example, the deagglomeration and particle stabilization process can be advantageously influenced by using ultra-fine grinding media of between 0.3 mm down to 20 microns. It takes a special bead mill design that allows most efficient and versatile means to handle such small grinding media in the processing zone. Figure 7 pictures a simplified schematic of a proprietary novel mill design [4], type MicroMedia®, specifically developed for the optimized use of micro beads. The energy is introduced by rotor pegs in a unique double-helical arrangement. This set-up results in centrifuging the beads in the active outer milling annulus. The product is treated while flowing axially through the highly turbulent layer of centrifuged beads. The screen on top of the inner stator is efficiently kept clear from beads. Consequently it merely functions as a protection device in case the mill is being operated beyond the range of optimum parameters.

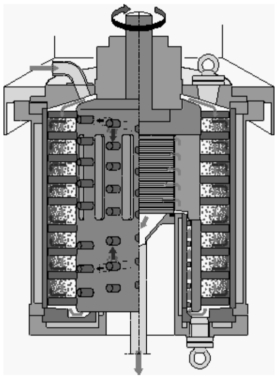

***Figure 7**. Simplified schematic drawing of novel mill concept MicroMedia®.*

Exceptionally high flow rates are possible in combination with beads down to 20 µm and for a product viscosity well exceeding several hundred mPa·s. The MicroMedia® concept allows for linear scale-up to large production size mills.

Examples

Cationically modified Silica

Silica is probably the nano-particle of widest application today. It is used in colloidal as well as in agglomerated form. The iso-electric point of SiO_2 is at ca. pH 2, i.e. SiO_2 in aqueous medium is negatively charged and thus anionically stabilized at $pH > 2$. However, in several applications like printing media, textile finishes, and for deposition on ceramic surfaces a positive charge of particles is required or advantageous. E.g., aqueous dispersions of untreated silica with PVA (polyvinylalcohol) lead to inconveniently high viscosities and negatively charged dyestuffs cannot attach to untreated SiO_2. In turn, untreated silica doesn’t deposit well onto negatively charged surfaces like fabrics or glass. If silica is to be used in these applications, the charge needs to be reversed. This has been accomplished by different methods, e.g., doping with metal oxides at the production step, charge reversal with metal salts and subsequent silanisation, or treatment with cationic organic polymers.

We propose a direct chemical surface modification of silica using aminosilanes and optionally further silanes to balance the chemical composition of the surface (Figure 8) [5]. As an example, chemomechanical processing of fumed silica (Aerosil) with 3-aminopropyltriethoxysilane yields at pH 4 a stable aqueous dispersion of cationically stabilized silica. As the viscosity of the dispersion is a crucial parameter, we kept the solid content at 20 wt.-% to keep the viscosity below 100 mPa·s (100 centipoise). The dispersion can be mixed with binders e.g., PVA, to give a low viscous paint. In principle, such a composition can be used as paper coating for ink-jet printing media, although the final composition will contain further components.

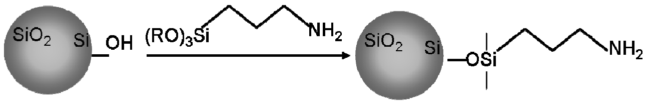

***Figure 8**. Reaction of silica nanoparticles with aminosilane (schematic).*

Zincoxide as mineral UV absorber

Nanoscaled mineral UV absorbers such as Fe_2O_3, TiO_2, or ZnO, are advantageous if diffusion processes of the UV absorber are unwanted and/or a sustainable UV protection is needed. Due to the particulate structure of the absorbers, diffusion of the agents practically does not occur in contrast to molecular UV absorbers. Mineral UV absorbers enhance the sustainability also, however, because they are not photolytically destroyed and consequently do not fade even under harsh UV conditions and/or over long periods of time.

Table 1: BET of nanoscaled Zincoxide and dispersion states in typical solvents for coatings (volume distribution).

ZnO	
BET	37 m²/g
Dispersed: d_{90} in 2-butanone	95 nm
Dispersed: d_{90} in Butylacetate	105 nm

The starting material is a powder of agglomerated ZnO of nanoscaled primary particles with a primary particle size of ca. 30 nm (Table 1). When processing the material chemomechanically into organic solvents the use of explosion-proof equipment is mandatory. We obtained dispersions of 40 wt.-% concentration with a viscosity below 100 mPa·s (100 centipoise). The dispersions exhibit a particle size d_{90} of about 100 nm with a mean particle size of ca. 30-50 nm, which allows formulation of highly efficient transparent UV protection coatings.

Conclusion

We emphasize the importance of chemical surface modification of nanoparticles to make them applicable in industrial applications. Surface modification controls many properties such as viscosity, functionality and stability, relevant for the downstream production process and/or the product itself. For the dispersion of nanoparticles in liquid matrices, chemical surface modification is mandatory. Agglomerated nanopowders can be conveniently processed by chemomechanical processing using agitator bead mills. Novel design concepts allow the full use of the parameter space by making small bead handling feasible.

References

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Author Biography

Steffen Pilotek received his Dipl.-Chem. and Dr. rer. nat. from the Universität Bielefeld (Germany, 1999). Following a research position at the Institute for New Materials (INM, Saarbrücken) he joined the nanotechnology group of Bühler AG (Switzerland) in 2002. Since 2007 he works for Buhler Inc. (U.S.A.) as Business Development Director Particle Technology (PARTEC).

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