

Tailored nanoscaled TiO₂ dispersions for photocatalytic applications

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ABSTRACT

We present the production of photocatalytic TiO₂ dispersions in water and organic solvents for various applications as well as an application of such dispersions in a self cleaning transparent hard coat. TiO₂ dispersions in water may be used in aqueous systems, whereas TiO₂ in organic solvents can be integrated into suitable binders including screen printing pastes. We stress the importance of dispersion quality with respect to the application to produce efficient photocatalytic materials. Apart from the photocatalytic effect itself which is intrinsic to TiO₂, the main challenges comprise the chemical degradation of the matrix and the particle integration into a suitable matrix. We use the chemomechanical process to produce nanoscaled dispersions of inorganic oxides from agglomerated nano powders. This process allows for a tailored surface modification reaction under well-defined mechanical stress conditions. Colloids of extremely fine TiO₂ can be produced by wet-chemical synthesis.

Keywords: nanoparticle, dispersion, titania, anatase, photocatalysis.

1 INTRODUCTION

Titania is a versatile and highly interesting material for the cleantech community. It has been thoroughly investigated as the active in dye-doped photovoltaic cells to produce electrical from solar energy. In addition, the use of the photocatalytic activity of nanoscaled titania nanoparticles is intriguing.[1] Photocatalysts may be used to oxidize pollutants in air and water to less toxic species, e.g. in wastewater treatment and air purification systems. Photocatalytic coatings on equipment and in architecture contribute to a higher overall sustainability by reducing the cleaning effort, extending cleaning cycles, and reducing the amount of chemically aggressive cleaners. By functional protection, they allow for a longer serviceable lifetime.

Even though the photocatalytic effect of nanoscaled titania has been known for a long time it is still a challenge to make the effect useful in everyday applications. The photocatalytic effect itself is intrinsic to TiO₂. There have been discussions about which of the crystalline phases

(anatase, rutile, and brookite) is the most active. Usually, nanoscaled anatase is considered as the most active phase.

It is highly important, however, to design the photocatalyst such that a large fraction of the catalytic surface area is accessible. Nano powders intrinsically have a large specific surface, however, agglomeration usually reduces the accessible area. Thus, processing has an immediate effect on efficiency. At the same time, sufficiently dispersed nanoscaled particles allow to produce transparent materials.

We present various photocatalytic TiO₂ dispersions in water and organic solvents produced by top-down and bottom-up methods. Dispersing nanoparticles needs special attention since colloidal systems are very sensitive to change within a formulation. Dispersing and stabilizing nanoparticles is therefore the enabling technology to provide efficient nanoparticle additives, so we are starting the discussion with a focus on dispersion technology.

2 NANOPARTICLE DISPERSIONS

For functional nanoparticle additives, the key parameter comprises the degree of dispersion within the final formulation. In this paragraph, we briefly summarize the basics of colloidal dispersion technology as needed in the context of this paper. We have discussed the topic of processing nanopowders into functional colloids previously and refer the interested reader for a more detailed discussion [2].

Nanopowders have a high specific surface area of up to several hundred m²/ml which needs to be chemically stabilized to produce a stable dispersion. In principle, stabilization mechanisms are well known [3]. Colloids can be stabilized by electrostatic, steric, or electrosteric means. Particularly in aqueous media, electrostatic stabilization is fast and efficient. However, for many products the pH value cannot be freely chosen and consequently steric and electrosteric stabilization mechanisms are used in addition or instead if it comes to stabilizing particles in complex formulations.

The chemistry of nanoparticles can be rather compared to molecular chemistry than to the behavior of micron-size particles [4]. The surface of titania is covered with OH-functions, the density of which varies with the production

method of the specific material. Generally, high-temperature methods provide a lower density of functional groups compared to a wet-chemical precipitation procedure. Using molecular bifunctional additives, these groups are accessible to a chemical interaction and the desired stabilization can be achieved.

It is most effective to carry out the surface modification reaction at the instant a new interface is generated. When particles are synthesized wet-chemically, surface modifiers can be used to limit particle growth and thus control particle size. Likewise, when agglomerated nanopowders are dispersed into functional colloids using mechanical force, the surface modification reaction is most efficiently carried out at the time when the powders are deagglomerated.

Processing nanopowders into nanoparticle dispersions requires a deagglomeration step. Buhler has developed the chemomechanical process which is a surface modification reaction under well-defined mechanical stress conditions. We have found the use of agitator bead mills useful for the deagglomeration of commercially available nanopowders. Because many parameters influence the selection of the agitator bead mill, there is no standard equipment which can be used in all cases. Technical as well as economical considerations have an important impact on the best choice of equipment like, e.g. product viscosity, cooling options for temperature sensitive products, contamination by grinding media and/or the grinding chamber, bead size, targeted particle fineness and the flow rate.

When manufacturing dispersions with particle sizes below 100 nm the energy input into the product tends to be high. In the case of inorganic oxides, even if only loosely agglomerated, the specific energy requirement to overcome the inter-particle interaction is typically in the range of 1 to 10 kWh/kg product.

3 TITANIA DISPERSIONS

3.1 Wet-chemically synthesized TiO₂

As explained in the previous section, surface chemistry can be used to control the particle size of wet-chemically controlled colloids. We have used specific surface modifiers to stabilize colloidal titania in water and in xylene as examples of solvents of highly different polarity (Table 1).

TiO ₂	
Dispersed: d ₉₀ in Water	< 8 nm
Dispersed: d ₉₀ in Xylene	12 nm

Table 1: Dispersion states of nanoscaled Titania in solvents of different polarity (volume distribution).

Figure 1 shows the particle size distribution of the titania colloid in water which has only a small dispersity (d₉₀ – d₁₀) of ca. 6 nm.

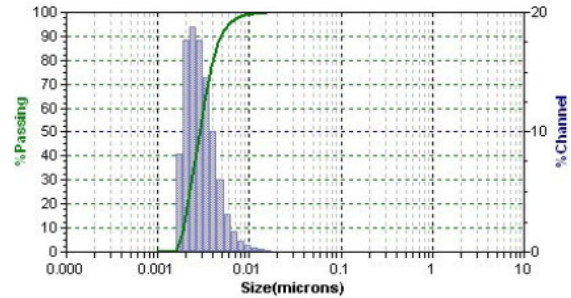


Figure 1: Volumetric particle size distribution of an aqueous anatase colloid (DLS).

For a surface area determination, the material was dried at 300° C. The resulting powder had a BET surface area of ca. 150 m²/g. We have scaled-up the synthesis of the aqueous colloid to industrial volumes to ensure a consistent property profile including the particle size distribution. As a result, we can produce the colloid up to 10 metric tons annually with the current specifications.

3.2 Chemomechanically dispersed TiO₂

When agglomerated titania nano powder is processed into a dispersion, the specific process parameters determine the properties of the titania dispersion. As an example, we have dispersed Degussa Evonik P25 into water. The agglomerated powder has a surface area of ca. 50 m²/g (ca. 200 m²/ml). Chemomechanical processing doesn't change the surface area (as determined by N₂-BET), however dispersing leads to a higher fraction of surface area accessible by molecules larger than nitrogen. The process provides a stable dispersion of the powder at a d₉₀ < 100 nm. It is interesting to note that the dispersion has a very low viscosity of just 3 mPa·s. Table 2 summarizes the properties of the dispersion.

solid content	35 wt.-%
solid content	12 vol.-%
dynamic viscosity (100 s ⁻¹)	3 mPa·s
density	1.3 g/ml
particle size d ₉₀	< 100 nm

Table 2: Characteristic data of a chemomechanically synthesized dispersion of nanoscaled TiO₂ in water.

Chemomechanical processing allows for a tailoring of the surface chemistry. Thus, using the same process but different surface modifiers, it was possible to disperse agglomerated titania into xylene with d₉₀ < 70 nm. The viscosity of this dispersion is somewhat higher than that of the aqueous dispersion but still low. A specific second-tier advantage of chemomechanical processing comprises the relatively easy scalability of the production to industrial

volumes. Scaling parameters for milling equipment are well established and can be used. As xylene is a flammable solvent, the large scale production of this dispersion requires a suitable production environment. We have set up an explosion proof production workshop where we safely and consistently carry out 100 kg+ batch production of the material. Table 3 summarizes the properties of the dispersion.

solid content	40 wt.-%
solid content	13 vol.-%
dynamic viscosity (100 s ⁻¹)	42 mPa·s
density	1.3 g/ml
particle size d ₉₀	< 70 nm

Table 3: Characteristic data of a chemomechanically synthesized dispersion of nanoscaled TiO₂ in xylene.

For several applications – like Graetzel cell manufacturing, sensors and other electronic applications – patterning of the Titania active is required. Screen printing processes have been used as they allow the deposition of rather thick films in one step. Screen printing inks require a high loading of active as well as a shear thinning and/or thixotropic rheology of the ink. Using the chemomechanical process we have realized a dispersion of nanoscaled titania in a screen-printing compatible (high-boiling) solvent mixture of diglycol butyl ether and ethylene glycol at a solid content of 56 wt.-%. Combination with a suitable binder system like binders based on cellulose derivatives should provide a screen printable titania ink. Table 4 summarizes the properties of the dispersion.

solid content	56 wt.-%
solid content	26 vol.-%
dynamic viscosity (100 s ⁻¹)	900 mPa·s
density	1.8 g/ml
particle size d ₉₀	ca. 150 nm

Table 4: Characteristic data of a chemomechanically synthesized dispersion of nanoscaled TiO₂ in DGBE/EG.

3.3 Photocatalytic Hardcoats

A challenge in photocatalytic coatings is the “binder-dilemma”: Under UV irradiation, the material oxidizes organic matter without difference. So if the active particles are fixed to a substrate using some kind of organic binder or carrier, this matrix will be ultimately destroyed by the photocatalytic effect, as well. As a result, the composite or coating destroys itself.

The company Clariant has developed an elegant approach to overcome this challenge: Clariant uses an inorganic coating system based on polysilazanes. The coating formulation provides a hard, clear and very dense, glass-like inorganic film that is unaffected by the photocatalytic effect. We have developed a tailored titania dispersion for the specific polysilazane coating formulation of Clariant to introduce the photocatalytic activity into the coating. The surface of the titania particles was chemically tailored to produce a highly compatible functional colloid that can be easily mixed with the coating formulation. The resulting coatings are highly transparent.

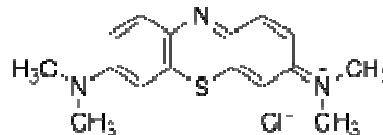


Figure 2: Chemical Structure of methylene blue.

The efficiency of the photocatalytic effect of the coatings was evaluated by photo-degradation studies. In a first evaluation, the photo-degradation of methylene blue (Figure 2) in aqueous solution was monitored using UV-Vis spectroscopy over time. The solution was placed on aluminum substrates that were coated with the photocatalytic hardcoat, and irradiated with 1 mW/cm² UV-A black light. For comparison, the same experiment was carried out without irradiation, as well. In each case, the concentration of the dye was calculated from the absorption data. Figure 3 shows the concentration of methylene blue over time with irradiation as well as in the dark.

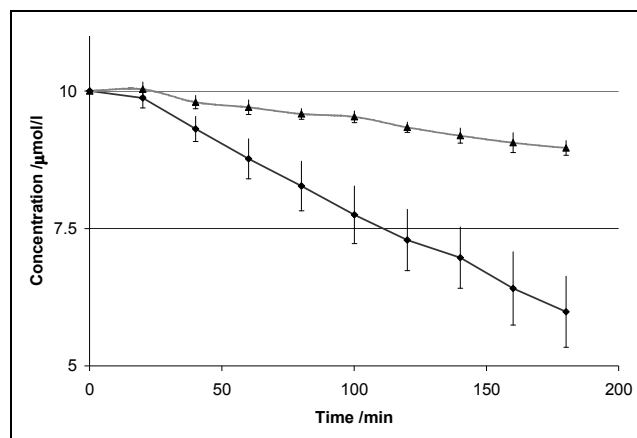


Figure 3: Degradation of methylene blue by photocatalytically active coating in light (solid line) and dark (dashed line) conditions.

After an initialization phase of ca. 20 min, the photocatalytic degradation of methylene blue is about linear. The effect is quite pronounced at a rate of ca. 1.5 µM/h.

In a second evaluation, methyl stearate was used as substrate in the photo-degradation. In contrast to methylene blue, methyl stearate is not soluble in water but in organic solvents. Using methyl stearate as a non-polar probe extends the scope of the activity profile of the photocatalytic coating.

As in the previous evaluation, coated aluminum substrates were used. A 5 mM solution of methyl stearate in n-hexane was placed on the substrates for 23 h with and without irradiation. After this period, the residual amount of the stearate was collected and quantitatively determined using GC. Figure 4 shows the amount of methyl stearate that was degraded during the 23 h-period with irradiation as well as in the dark.

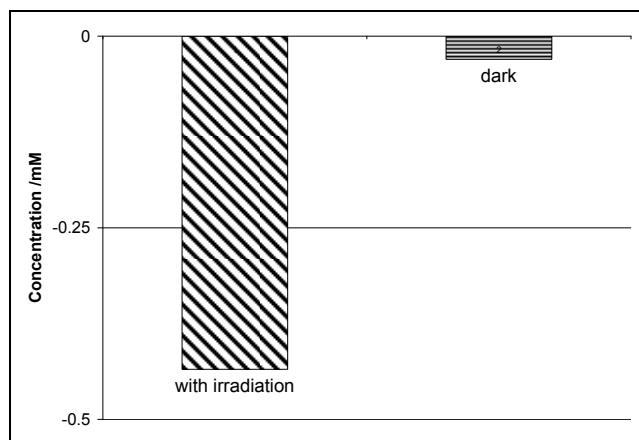


Figure 4: Degradation of methyl stearate in 23 hrs by photocatalytically active coating with irradiation (left) and in the dark (right).

Negative values indicate degraded methyl stearate.

Under irradiation, the provided methyl stearate dissipated almost completely. In stark contrast, in dark conditions only ca. 7% of the compound was lost. With a rate of almost 20 $\mu\text{M}/\text{h}$ the photo-degradation of methyl stearate is even stronger than the photo-degradation observed for methylene blue.

As this long-term stable transparent hard coating provides functional protection, we expect that this coating will have a major impact on overall sustainability.

4 SUMMARY

For photocatalytic applications, the photocatalyst TiO_2 needs to be present in a highly dispersed state to provide a highly accessible catalytically active surface. Depending on the actual application, different TiO_2 dispersions in water or organic solvents are required. The chemomechanical process allows a direct approach to produce titania nanoparticle dispersions with tailored surface modification for commercially available nanopowders. In a bottom-up approach, ultra-fine titania particles are available by wet-chemical synthesis. In an application example, we have presented the photo-degradation performance of a

transparent hard coat containing tailored photoactive titania dispersions.

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