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TOPICAL REVIEW

Dispersion and surface functionalization of oxide nanoparticles for transparent photocatalytic and UV-protecting coatings and sunscreens

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Abstract

This review describes recent efforts on the synthesis, dispersion and surface functionalization of the three dominating oxide nanoparticles used for photocatalytic, UV-blocking and sunscreen applications: titania, zinc oxide, and ceria. The gas phase and liquid phase synthesis is described briefly and examples are given of how weakly aggregated photocatalytic or UV-absorbing oxide nanoparticles with different composition, morphology and size can be generated. The principles of deagglomeration are reviewed and the specific challenges for nanoparticles highlighted. The stabilization of oxide nanoparticles in both aqueous and non-aqueous media requires a good understanding of the magnitude of the interparticle forces and the surface chemistry of the materials. Quantitative estimates of the Hamaker constants in various media and measurements of the isoelectric points for the different oxide nanoparticles are presented together with an overview of different additives used to prepare stable dispersions. The structural and chemical requirements and the various routes to produce transparent photocatalytic and nanoparticle-based UV-protecting coatings, and UV-blocking sunscreens are described and discussed.

Keywords: dispersion, functionalization, synthesis, nanoparticles, zinc oxide, titanium dioxide, cerium dioxide, coatings, sunscreens, photocatalysis, transparency

1. Introduction

Successful implementation and optimized utilization of functional nanoparticles into commercial products ranging

Content from this work may be used under the terms of the Creative Commons Attribution-NonCommercial-ShareAlike 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI. from catalysts, polishing media and magnetic fluids to cosmetics and sunscreens requires robust and cost-effective dispersion and surface functionalization routes [1]. Indeed, the ability to prepare and handle concentrated and colloidally stable dispersions of nanoparticles in aqueous or non-aqueous media is important both in intermediate process steps and for the performance of the final product [2, 3]. This review describes recent efforts in the dispersion and surface

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functionalization of the three dominating oxide nanoparticles used for photocatalytic [4–6], UV-blocking [7–9], and sunscreen applications: titania, zinc oxide, and ceria [10].

Titanium dioxide and zinc oxide are wide bandgap semiconductors, which are transparent in the visible and absorb in the UV range. Upon UV irradiation, the photogenerated charge carriers can be used to generate a current, induce chemical reactions or emit light [11, 12], One consequence of this process is photocatalysis, which can be defined as the light-induced degradation of organic molecules, driven by the formation of reactive radical species on the surface of the photocatalytic material (e.g. $O_2^{-\bullet}$ and OH^{\bullet} on illuminated TiO_2) [13, 14]. The radical formation also results in an increase in the surface density of hydroxyl groups that may change the wetting characteristics of TiO_2 [15, 16]. The photocatalytic activity increases with decreasing particle size [17-20] due to an increase in the specific surface area, down to a critical particle size, which is about 10 nm for titania, below which the wide bandgap and the high probability for electron/hole surface recombination results in a loss of photoactivity under visible light [21].

Transparent, self-cleaning titania coatings on glass are today widely used and sold under several trade [22]. These coatings combine photocatalytic names breakdown of absorbed organic dirt [23] with light-induced superhydrophilic surface properties [24] that promote water to evenly wet and rinse away the decomposition products. The titania films are normally applied by dip coating of an organic precursor followed by heat treatment to remove the organic residue and form the desired anatase phase. With the commercial success of self-cleaning glass in window frames of high-rise buildings, there is a growing interest in applying photocatalytic and self-cleaning coatings to the façades of buildings and to other construction materials in urban areas. This will not only keep the surfaces clean but also reduce the concentrations of harmful pollutants in the city air, such as NO_x and other airborne contaminants (e.g. volatile organic compounds, VOCs) [25]. The anti-bacterial properties of photocatalytic coatings are also attractive as a means to mitigate the problem of persistent bacteria, mainly in hospitals [26]. In many cases, it is not possible to subject the facade or building material to the thermal treatment needed to transform a traditional sol-gel coating to a transparent anatase film. Hence, alternative low-temperature routes where transparent films can be formed directly, e.g. from dispersions containing photocatalytic nanoparticles, are needed.

Transparent UV-absorbing or UV-blocking coatings [8, 9] have two main applications at present: as a UV-protecting lacquer for wooden surfaces, and as a UV-barrier coating deposited onto the surface of polymer-based products or devices to reduce the ageing of the polymer or internal components encased inside the polymer-based device. Transparent UV-blocking coatings are at an earlier stage of development compared to the established photocatalytic and self-cleaning coatings, but industrial interest is rapidly increasing with growing demands for durability without compromising the esthetic appearance of the underlying

material. The limited thermal resistance of wood and most polymers means that UV-blocking coatings are normally produced directly from dispersions of UV-absorbing nanocrystals without a subsequent heating step.

Nanoparticle-based sunscreen formulations are already available commercially. Efficient utilization of the broad absorption in the UVB and UVA regions of titanium dioxide and zinc oxide in transparent sunscreens requires not only that the particle size be reduced far below the wavelength of visible light but also that agglomeration be minimized. The development of formulations of nanosized nanoparticles of titanium dioxide and zinc oxide with minimized light scattering in the visible region [27, 28], together with reports on allergic reaction to some organic UV attenuators [29], have resulted in a rapid increase of titania and zinc oxide in sunscreens. Currently, most of the commercial sunscreens incorporate titanium dioxide, zinc oxide, or both.

This review attempts to provide an overview of the fundamental principles of deagglomeration and stabilization of nanoparticles as well as describe the main processing steps for the production of photocatalytic and UV-blocking coatings and sunscreens, illustrated in figure 1. The main synthesis methods producing titania, zinc oxide and ceria nanoparticles are reviewed with a focus on recent liquid state studies that generate non-agglomerated powders. Agglomeration is often the major cause of poor performance and limited transparency. The deagglomeration process is described in detail and the challenges related to handling nanopowders are highlighted together with examples on primary titania nanoparticles. The main particle interactions-van der Waals, electrical double layer, and polymer induced forces-in dispersions of nanoparticles are described and important parameters for the three oxides, like the Hamaker constant and isoelectric point, are tabulated. Organic additives that are both efficient dispersants and can also serve to improve the compatibility of the inorganic particles with an organic matrix are identified.

The requirements for transparency of thin films are described and guidelines are presented for how the particle size or aggregates affect the transparency. The various methods used to deposit nanoparticle-containing films onto a substrate are briefly described with a discussion on the importance of the colloidal stability and rheological properties. The influence of the coating formulation and the post-processing treatment on the performance of photocatalytic coatings is illustrated by numerous examples from the literature. The structural and chemical requirements and the various routes to produce transparent nanoparticle-based UV-protecting coatings and UV-blocking sunscreens are described and discussed. An outlook discussing not only the technical performance but also concerns related to distributing nanoparticles in the environment is presented. Finally, the future prospects are described and promising materials, such as multifunctional coatings and hybrid films, are identified.

2. Synthesis of TiO₂, ZnO and CeO₂ nanoparticles

Oxide nanoparticles can be produced by several methods, which can be broadly classified by the physical state of



Figure 1. Schematic illustration of the main processing steps involved in the formation of transparent coatings containing oxide nanoparticles.

the carrier or continuous media (gas or liquid). Gas-phase methods have in general a higher output capacity and lower production costs compared to liquid-phase routes. Hence, most of the commercially available oxide nanopowders intended for large-scale applications are produced by gas-phase techniques, which form nanocrystals with a high yield and high purity [30, 31]. A noteworthy example is the Aeroxide P25 titania (anatase/rutile) powder used primarily for photocatalytic applications [32]. However, oxide nanopowders produced in the gas phase are often heavily aggregated, which can severely limit the utilization of the inherent properties, pose substantial processing challenges and complicate the dispersion and functionalization of the nanoparticles [33–36]. Indeed, films and coatings produced from aggregated gas-phase powders are often hazy, with poor adhesion to the substrate [37, 38].

In contrast to gas-phase reactions, where agglomeration is inherent and impossible to avoid, it is possible to design liquid-phase synthesis routes that also keep the particles colloidally stable as they grow. The production of non-agglomerated particles with a narrow size distribution [39, 40] is typically achieved by adding organic additives that adsorb (weakly) onto the surface of the growing particles and simultaneously provide a means to control the growth rate and the extent of agglomeration [41, 42]. Liquid-phase synthesis methods are also able to yield dispersed nanoparticles that can be functionalized *in situ*. However, the low concentration of reactants and the associated need to process large volumes of solvents, and time-consuming post-treatment routes are restricting and hampering the commercial introduction of liquid-phase-synthesized nanopowders for large-scale applications.

The liquid-phase synthesis of TiO₂, ZnO and CeO₂ nanoparticles has been described extensively in a number of reviews [43–46]. Some recent work has also reported the preparation of mesoporous TiO₂, ZnO and CeO₂ particles [47–49]. Here, we will present a concise account of synthesis routes for non-aggregated crystalline TiO₂, ZnO and CeO₂ nanoparticles. The methods were selected based on the demonstrated formation of non-aggregated particles smaller than 50 nm and a potential for up-scaling through the utilization of relatively concentrated precursor solutions (above 0.1 mol1⁻¹).

Three polymorphs of TiO₂ have been identified at atmospheric pressure: rutile, anatase and brookite. Anatase is metastable and tends to transform into rutile upon heating, typically above 600 °C for bulk anatase [50, 51]. Brookite is metastable too and is rarely the main phase in synthetic powders; it has thus been less studied than the two other phases. Whereas rutile is the stable polymorph (in bulk form), anatase and brookite become thermodynamically stable when the crystal size decreases and are quite common in fine-grained powders [52]. Anatase has often been identified as the most photoactive phase of TiO₂ [53, 54] with some notable exceptions [55, 56], suggesting that comparison of the photocatalytic efficiency of anatase and rutile is not straightforward.

The synthesis of titania nanoparticles has been the subject of a very large research activity [12, 43]. The large free energy of formation of titania is reflected in the high reactivity of most titania precursors, making it difficult to design synthesis routes with a high degree of size and shape control. Moreover, nanoparticles synthesized at near-ambient temperature are often amorphous or poorly crystallized in the anatase form [57, 58]. Thus, significant efforts have been made to reduce the reactivity of the precursor and to improve the crystallinity [59, 60].

Figure 2 shows transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images of TiO₂ nanoparticles produced by different chemical routes. The hydrolysis and condensation of tetrabutyl orthotitanate Ti(O-^tBu)₄ at low temperature (60 °C) can be controlled in the presence of acetylacetone and paratoluene sulfonic acid, yielding anatase nanocrystals of 7 nm [61]. Carboxylic acids are also commonly used to reduce the reactivity of the precursors and stabilize the particles. Barbé *et al* [62] obtained anatase nanoparticles from the hydrolysis of titanium tetraisopropoxide (TTIP) with acetic acid, which results in a sol of acetate-capped particles that can be autoclaved without agglomeration. Oleic acid has been used as solvent to produce anatase nanorods from concentrated TTIP solutions with amines as crystallization promoters and shape-directing agents [63, 64]. Benzyl alcohol is a versatile reaction medium that can act as both a solvent and capping agent. Niederberger showed that the reaction between titanium tetrachloride and benzyl alcohol [65] yields anatase nanocrystals with a diameter of about 15 nm.

Zinc oxide precursors are less reactive than their titania counterparts and the formation of the oxide nanoparticles typically proceeds through a series of intermediate compounds [44]. Hence, the as-synthesized particles often consist of a mixture of zinc hydroxide species that are sensitive to the water content and to ageing [44, 70]. Figure 3 shows some examples of ZnO nanoparticles prepared by different routes. Aqueous synthesis of spheroidal wurtzite ZnO nanoparticles can be achieved at near room temperature using zinc nitrate and tris(hydroxymethyl)aminomethane, which is a polydentate ligand that adsorbs strongly on the particles, inhibiting crystal growth [71]. Concentrated zinc oxide nanocrystal suspensions can be obtained by adding a base (LiOH, NaOH or tetramethylammonium hydroxide) to zinc acetate dihydrate dissolved in alcohol [72-74]. The acetate-capped nanoparticles obtained by this sol-gel method exhibit photoluminescence both in the near UV (370 nm) and in the visible range (500-550 nm), the former being related to excitonic emission and the latter to the presence of oxygen vacancies on the surface. The visible emission might be problematic for some applications and can be quenched by a thermal post-treatment or copper doping [44]. Alkylamines are often used as a base and shape-directing agent for the formation of rod-like ZnO particles or oriented films [75, 76]. The solvothermal reaction between zinc acetate and ethanol at 120 °C results in wurtzite nanocrystals, formed upon the release of hydroxide ions during the formation of ethylacetate [77]. Teardrop-shaped wurtzite nanocrystals can be obtained from the controlled dissolution-precipitation of ZnO in a mixture of oleic acid, octadecene and hexadecylamine [78]. Bullet-shaped wurtzite nanoparticles were obtained from the thermal decomposition of zinc stearate in 1-octadecene in the presence of a small amount of octadecylamine [79].

Cerium dioxide (CeO₂) in a loosely aggregated form is frequently produced by precipitation of cerium salts (e.g. cerium nitrate or cerium sulfate) in liquid media at elevated temperature. While the precipitation conditions (temperature, solvent, counter ions and final pH of the reaction), can have a profound effect on the size and shape of the cerium oxide nanoparticles, it is impossible to avoid agglomeration unless surfactants are introduced during the precipitation process [80]. Sometimes, synthesis is performed under mechanical disintegration (ball-milling). Mechanical-chemical processes may not only deagglomerate the nanoparticles but also have an influence on the reaction kinetics and the crystallization behaviour [81]. Interestingly, the use of both NH₄OH and H₂O₂ results in the formation of intermediate species (e.g. $Ce(OH)_x(OOH)_{4-x}$), which transform into weakly-agglomerated nanosized ceria upon heating [82].

Efforts to develop easy and scalable liquid-state synthesis routes of ceria have included a range of batch



Figure 2. TEM and SEM images of titania nanoparticles synthesized by different chemical routes (a) Anatase nanocrystals obtained by hydrothermal treatment in acetic acid of amorphous electrospun TiO₂ nanofibers. Reprinted with permission from Dai *et al* [66], O (2009) American Chemical Society [66]. (b) Anatase nanocrystals synthesized in benzyl alcohol, after annealing at 450 °C; reprinted with permission from Niederberger *et al* [65], O (2002) American Chemical Society. (c) Acetate-capped anatase particles synthesized through hydrothermal treatment of titanium isopropoxide at 230 °C; reprinted from Barbé *et al* [62], O (1997), with permission from John Wiley and Sons. (d) Tetramethylammonium-capped anatase particles synthesized by hydrothermal treatment of a titanium isopropoxide; reprinted from Chemseddine *et al* [67], O (1999), with permission from John Wiley and Sons. (e) Tetramethylammonium-capped anatase nanoparticles produced by hydrothermal synthesis. Reprinted with permission from Yang *et al* [68], O (2001), John Wiley and Sons. (f) Aeroxide P25 aggregated nanocrystals synthesized by flame pyrolysis. Reprinted with permission from Faure *et al* [69], O (2010) Elsevier.

and continuous methods [45, 83–90]. Ceria nanoparticles can be produced in aqueous media by generating the precipitating agents *in situ*, e.g. by the slow decomposition of chemicals like urea [91–96], ammonium carbonate [97], or hexamethylenetetramine (HMTA), but are often loosely aggregated [20, 98, 99]. The decomposition of these salts can have a double effect on preventing agglomeration through

(i) bridging of the metal ions and (ii) their decomposition into ammonia, carbamates, and aldehydes, which can result in electrosteric repulsion between the particles.

The simultaneous synthesis and surface modification of loosely aggregated dispersible CeO_2 nanoparticles has been achieved in continuous flow reactors [100–105]. Figures 3(e) and (f) show examples of both water dispersible and solvent



Figure 3. TEM micrograph of ZnO and CeO₂ nanoparticle produced by various routes. (a) Wurtzite ZnO nanoparticles precipitated in aqueous solution at pH 8 and 37 °C. Reprinted from Bauermann *et al* [71] © (2006) American Chemical Society. (b) ZnO wurtzite nanocrystals formed by solvothermal reaction in ethanol (scale bar 200 nm) [77]; (c) bullet-shaped ZnO nanocrystals wurtzite nanocrystals prepared by thermal decomposition of zinc stearate in 1-octadecene in the presence of octadecylamine. Reprinted from Jana *et al* [79] © (2004) American Chemical Society. (d) TEM and corresponding high-resolution-TEM images of CeO₂ nanoparticles synthesized from cerium (IV) and ammonium carbonate aqueous solutions under reflux conditions. Reprinted from Sutradhar *et al* [97] © (2011) American Chemical Society. (e) Hydrophilic ceria nanoparticles synthesized from ammonium cerium (IV) nitrate in water by supercritical flow method at 400 °C. Reprinted from Slostowski *et al* [100] © (2012) American Chemical Society. (f) Hydrophilic ceria nanoparticles synthesized from the Ce(CO₃)₂ · 3H₂O + NH₄OH + H₂O₂ system using acetic acid in water by a hydrothermal method and corresponding electron diffraction pattern. Reprinted from Tok *et al* [86], © (2007), with permission from Elsevier.

dispersible nanoparticles synthesized by supercritical flow synthesis in water. The process is also suitable for the production of complex and composite metal oxide nanoparticles [103].

3. Deagglomeration of nanoparticles

Full utilization of the inherent properties of nanoparticlebased materials usually requires that the powders be deagglomerated down to a size that either represents the individual nanocrystallites or the smallest, primary, agglomerates. Minimization of the flaw size is, e.g., essential to obtain a high reliability and high strength, and transparency and other optical properties are highly sensitive to the presence of inhomogeneities with sizes in the order of the wavelength of the electromagnetic radiation of interest.

Most large-scale nanoparticle synthesis routes yield powders that are either weakly or strongly agglomerated. Agglomeration is commonly observed in nanopowders that have been produced in the gas phase or dried from the liquid phase, as shown for titania in figure 4. Indeed, agglomeration is inevitable during gas-phase synthesis, due to the ubiquitous attractive van der Waals interactions between the particles in the gas phase [106]. If the synthesis temperature is high, partial sintering may reinforce the agglomerates by forming so-called inter-particle necks [32–34]. Agglomeration is also driven by the capillary forces generated by drying a dispersion; this effect is more pronounced for aqueous dispersions of hydrophilic nanoparticles, e.g. oxides. Moreover, the contact points between the grains may act as nucleation sites for the condensation of dissolved material, which leads ultimately to the formation of necks between the grains resulting in so-called 'hard' agglomerates.

Deagglomeration proceeds through the break-up of bonds between single nanoparticle crystallites in the aggregates. The adhesive interparticle forces that both cause the crystallites to aggregate and keep them together can be reduced by creating a repulsive interaction or simply by keeping the surfaces of the nanoparticles separated by an adsorbed adlayer that acts as a spacer. Milling, high-shear mixing and ultrasonication are commonly used to break down agglomerates. Upon milling, the mechanical impact between the particles and the grinding media result in both the breakup of agglomerates and the reagglomeration of particles, which broadens the particle size distribution. It is well known from experiments that the size reduction rates decrease with decreasing particle size [107], e.g., due to the decrease of inertial and hydrodynamic forces and the increase of aggregate strength with decreasing particle



Figure 4. The effect of high-pressure deagglomeration on the morphology and size of the aggregates of flame-made TiO₂ particles; (A) as synthesized large agglomerates and aggregates, (B) smaller aggregates after high-pressure deagglomeration through a nozzle (1400 bar). Reprinted from *Powder Technology* Teleki *et al* [34], \bigcirc (2008), with permission from Elsevier.

size [30, 66, 108]. In practice, this means that the milling efficiency is significantly reduced at particle sizes below 500 nm and further size reduction requires long milling times at very high collision speeds, which may increase the risk of contamination and unwanted phase transitions [109, 110].

Milling, even at very large energy inputs, is best suited for deagglomeration of 'soft' agglomerates that are held together by physical interparticle bonds, i.e. van der Waals, hydrogen, electrostatic bonds, but less well suited to deagglomerate so-called 'hard' nanoparticle aggregates that are bonded together by interparticle necks [111, 112]. Figure 4(b) shows that even high-pressure deagglomeration is not able to fully deagglomerate TiO₂ nanoparticles, which strongly suggests that this gas-phase-produced material contains hard agglomerates [111, 112].

Chemical approaches can complement mechanical routes to deagglomerate hard agglomerates. Chemical deagglomeration focuses on controlled dissolution of the interparticle necks by subjecting the nanoparticle aggregates to weakly aggressive conditions. Laarz et al [113] showed how controlled dissolution of the silica necks between silicon nitride nanoparticle solutions could be accomplished by subjecting the material to alkaline solutions. Chemical deagglomeration of oxide nanoparticles requires it to be possible to dissolve or chemically attack the necks without dissolving or deteriorating the nanocrystals. Hence, differences in solubility between the interparticle necks and the 'bulk' nanocrystals should be utilized to chemically deagglomerate the nanoparticles. The difference in curvature between the neck and the nanocrystal and possible differences in degree of crystallinity could be sufficient to select conditions where the necks dissolve while the nanocrystal remains unaffected. The three oxides of interest in this review display significant differences in their degree of inertness in aqueous media, related, e.g., to the ionic potential of the metal cations [71]. Thus, the solubility of ZnO in water depends strongly on the pH, and is high below pH 7 or above pH 13, while CeO_2 and, in particular, TiO_2 are relatively inert [114–116].

4. Stabilization and surface functionalization of nanoparticle dispersions

The utilization of photoactive and UV-blocking nanoparticles in transparent coatings and films relies on the ability to avoid agglomeration and to adapt and optimize the film forming and deposition processes to ensure that the nanosized functional particles are distributed either homogeneously or in desired patterns [117]. Providing robust methods to prepare colloidally stable dispersions in polar or non-polar media is of pivotal importance and a process that requires a fundamental understanding of the nature and magnitude of the interparticle forces [3]. Controlling the compatibility between the nanoparticles and the matrix, either polymeric or inorganic, is also very important in order to tune the microstructure of the final material.

4.1. Nanoparticle interactions

Interparticle forces play a pivotal role in determining the rheology and light-scattering behavior of nanoparticle dispersions. For example, concentrated nanoparticle dispersions can be transformed from an easily pourable liquid to a stiff paste by changing the interparticle forces from repulsive to attractive. Flocculation or aggregation will induce the formation of large clusters or aggregates that will scatter light. The ability to control and manipulate the sign of particle interactions represents a first step towards optimized nanoparticle processing. The dominating interparticle forces in most nanoparticle systems are the van der Waals, double layer (electrostatic), and steric (polymeric) forces, as shown in figure 5. We will give a brief account of these interactions



Figure 5. Schematic illustration of the main mechanisms for stabilization of nanoparticle dispersions, assuming positively charged surfaces.

with relevant examples for the three oxide systems of interest in this review.

The van der Waals or dispersion force is an electrodynamic interaction that arises as a consequence of the interactions between fluctuating or permanent dipoles between molecular and macroscopic bodies (i.e. nanoparticles in this context) in close proximity [3, 118, 119]. The magnitude of the van der Waals (vdW) pair interaction energy, V_{vdW} , scales with the value of the Hamaker constant A [120], and decreases with the separation distance, *s*. The exact form of the distance scaling depends on the geometry of the interacting particles, the pair interaction for two spheres of radius *r*, is shown in equation (1).

$$V_{\rm vdW} = -\frac{Ar}{12s}.$$
 (1)

The Hamaker constant is material dependent and increases with the contrast in dielectric properties between the particles and the solvent. It is possible to directly measure the van der Waals forces between inorganic particles using atomic force microscopy and also to estimate the magnitude of *A* from optical data using Lifshitz theory [121, 122]. Table 1 provides estimates of the Hamaker constants for oxide nanoparticles interacting in three commonly used solvents: water, isopropanol and hexane. The Hamaker constant for TiO₂ is significantly larger than the Hamaker constant for CeO₂, and ZnO.

Colloidally stable nanoparticle dispersions require that some type of interparticle repulsion is introduced to overcome

Table 1. Material-dependent parameters involved in the colloidal interactions between CeO_2 , TiO_2 and ZnO nanoparticles.

			•	
Material	Water	Isopropanol	Hexane	IEP [123]
CeO ₂	41	46	35	6.5
TiO ₂	60	79	59	6.4
ZnO (wurtzite)	26	30	19	8.6

^a Non-retarded symmetrical Hamaker constants, calculated using a previously reported methodology [124, 125]. The oscillator parameters of CeO₂ in the ultraviolet range ($C_{UV} = 4$ and $\omega_{UV} = 6.77 \times 10^{15}$ rad s⁻¹) were calculated from ellipsometry measurements [126], and the Ce–O stretching vibration was chosen for the relaxation frequency of the infrared oscillator ($C_{IR} = \varepsilon_r - C_{UV} - 1 = 18$ and $\omega_{IR} = 1.04 \times 10^{14}$ rad s⁻¹) [127, 128]. Published dielectric properties were used to construct the complex dielectric response functions of water, isopropanol and hexane [129–131].

the ever-present van der Waals attraction. In a stable system, the maximum attractive interparticle energy should be sufficiently small, in the order of $1 - 2k_BT$, to allow thermal motion or agitation to readily break all particle–particle bonds. Below, we will describe the two most common methods of stabilizing a nanoparticle dispersion; either by creating an electrical double layer at the solid–liquid interface or by adsorbing polymers or surfactants on the nanoparticle surfaces.

Table 2. List of additives for the dispersion of CeO₂, TiO₂ and ZnO.

	CeO ₂	TiO ₂	ZnO
Aqueous dispersions	Nitrate at pH < 3 [140] Acetylacetone [141] Phosphonate-PEG up to pH 9 [149] PAA at pH 6–9 [80, 144]	Citrate at neutral pH [152] Alkylammonium at high pH [67, 68, 153] PAA below the IEP [143] PVA [154, 155] PAM [142]	Sulfate below the IEP [115] PAA below the IEP [114] Poly(methyl methacrylate) (PMMA) [156]
Alcoholic dispersions		Acetylacetone [23, 61] HPC [157]	Acetate [72, 73, 158] PVP [150, 151] HPC [159]
Non-aqueous dispersions	Propylamine [160] Oleic acid [161, 162] Phosphonate-PEG [163] Sulfonated acrylate copolymer [164] Fluorinated non-ionic surfactants [165]	OLOA 370 (amine-based) [166] Oleic acid [167] Tert-butylphosphonic acid [168] Dodecylbenzenesulfonic acid [169]	Alkylamine [161, 170] Oleic acid [161]

Figure 6. TiO₂ particles prepared without (A) and with HPC (B). Reprinted from Park *et al* [157], \bigcirc (1997), with permission from John Wiley and Sons.

Electrical double layer interactions originate from the accumulation of counter ions near a charged surface. A net charge may build up on the surfaces of nanoparticles in liquids through various mechanisms such as the dissociation of surface groups, the specific adsorption or dissolution of ions, and the presence of crystalline defects [132]. The dissociation of surface hydroxyl groups is the main charging-up mechanism for metal oxide surfaces in water and depends on the pH:

$$M - OH_2^+ \xrightarrow{H_3O^+} M - OH \xrightarrow{OH^-} M - O^-.$$

The pH at which the net surface charge is neutral is called the isoelectric point (IEP), and is typically close to pH 6.5 for CeO₂ and TiO₂, while the surface of ZnO is more alkaline with an IEP at pH 9, as shown in table 1 [123]. The adsorption of charged molecules with a high affinity for the surface can also be used to increase the surface charge. The range of these interactions is defined by the Debye length κ^{-1} and strongly decreases with increasing ionic strength *I*:

$$\kappa^{-1} = \left(\frac{\varepsilon_r \varepsilon_0 k_{\rm B} T}{2N_{\rm A} e^2 I^2}\right)^{1/2},\tag{2}$$

where ε_r is the dielectric constant of the solvent, ε_0 the permittivity of vacuum, k_B the Boltzmann constant, T the

temperature, N_A Avogadro's number and e the elementary charge. A high concentration of free ions will screen the repulsive double layer interactions and decrease their range. Therefore, electrical double layer stabilization, or electrostatic stabilization as it is frequently but somewhat erroneously called, is not recommended for the deposition of particles onto a substrate from evaporating aqueous suspensions. The ionic strength will increase upon drying, which may lead to agglomeration when the critical coagulation concentration is reached. Electrical double layer interactions can also be used to stabilize particles suspended in low-polar solvent ($\varepsilon_r < 11$) [133]. Widegren and Bergström showed how the effective pH can be controlled and measured in ethanol and demonstrated that colloidally stable dispersions can be produced [134].

In many nanoparticle systems, it is not possible to create a stable dispersion simply by controlling the pH. Hence, addition of suitable surfactants or polymeric dispersants is commonly used to provide a so-called polymer-induced or steric stabilization. Polymer-induced interactions arise when the adsorbed surfactants or polymers have segments or chains that protrude into the solvent and thus provide a protective adlayer on the nanoparticle surfaces. Several conditions should be fulfilled for efficient steric stabilization: the adsorbed layer should be thick enough to screen the attractive van der Waals interaction, the adsorbed molecules should be strongly adsorbed and cover the entire nanoparticle surface, the segments protruding into the solvent should be in so-called good solvent conditions [135]. The polymer layers induce an increase in the pair-interaction energy when the adsorbed segments overlap at short separation distances [136]. For metal oxide nanoparticles, the high surface density of hydroxyl groups is commonly used as the specific surface groups that are targeted for the adsorption groups of the surfactants or the polymer dispersants. High surface coverage is typically achieved through hydrogen-bonding moieties (e.g. ethers, alcohols and acrylamides), acid-base reactions (e.g. carboxylic acids) or electrostatic interactions (e.g. phosphates and carboxylates) [137, 138]. Even if the affinity of each individual segment for the particle surface is low, the multiplicity of anchoring groups in the whole polymer chain provides a strong adsorption [139].

4.2. Stabilization and surface functionalization of oxide nanoparticles

Colloidal dispersions of metal oxide particles can be stabilized by electrical double layer interactions, e.g., by adjusting the pH away from the pH value of the IEP (table 1). Sometimes, simple ions can also promote the colloidal stability. Nitrate and acetate ions were found to specifically adsorb onto the surface of CeO₂, and enhance the colloidal stability below pH 3 [140, 141]. Due to the presence of hydroxyl groups on the surfaces of most oxides, similar additives can be used to stabilize aqueous dispersions of CeO₂, TiO₂ and ZnO, differing mainly in the pH conditions at which they are efficient. A list of organic additives displaying an affinity for the surfaces of the three oxides is provided in table 2. By combining the adsorbing moieties listed in the table with various steric moieties, stable dispersions can be prepared in a wide range of solvents [135].

Polyelectrolytes are frequently used as dispersants of metal oxide nanoparticles. The term electro-steric stabilization is often used to describe how polyelectrolytes act as dispersants (figure 6). Electrosteric stabilization is a combination of a pure electrostatic repulsion and a polymer-induced repulsion. If the polyelectrolyte adsorbs in a flat conformation, the polymeric repulsion is short range, and the stabilization mechanism is mainly electrostatic. With thicker adsorbed layers, having chains protruding into the solution, the polymeric contribution will become more important. In addition to the steric contribution, there is always an electrostatic contribution since the adsorption of a highly charged polyelectrolyte on a weakly charged, amphoteric oxide surface usually results in an increase of the net surface charge density. Dispersants containing carboxylic groups (e.g., polyacrylic acid (PAA) and polyacrylamide (PAM)) interact with the surface through electrostatic interactions and H-bonding. Such dispersants have been used successfully to stabilize TiO2 and ZnO below their IEP [114, 142, 143].

It has been found that anionic, predominantly carboxylic acid-based polyelectrolytes have a significantly stronger interaction with metal oxide surfaces compared to other functional groups. The efficient stabilization of CeO₂ by the addition of PAA at pH values between pH 6 and pH 9, has been related to the favorable interaction between the negatively charged carboxylate groups on the PAA and the weakly positively charged hydroxyl groups on the ceria surface [80, 144]. Amines were found to have an overall weak affinity for TiO₂ and ZnO in water [145, 146]. Polyethers, which are commonly used as binders, have a low affinity for the surfaces of TiO₂ and ZnO and presumably interact primarily by hydrogen bonding [147, 148]. Combining polyether chains with a strongly adsorbing head group has resulted in efficient dispersants in water, e.g. phosphonated polyethlene glycol (PEG) for dispersions of CeO_2 [149]. The strongly adsorbed PEG-based dispersant provides a steric layer that is able to extend the stability range of the original ceria dispersion (that was stable only below pH 3) up to pH 9.

High-molecular weight polymers are commonly used as binders to enable handling and drying without cracking. However, sometimes the binder can also act as a dispersant, e.g., in recent studies on ZnO, where polyvinyl pyrrolidone (PVP), was found to be a better stabilizing agent than PVA and improved the optical properties significantly [150, 151].

The adsorption of additives on hydroxylated metal oxide surfaces in non-aqueous systems relies on the same anchoring groups as the aqueous systems. In water–alcohol mixtures, acetate groups or ethers containing hydroxyl groups such as hydroxypropylcellulose (HPC) can be used as dispersant [73, 157, 159]. As can be seen in figure 6, HPC prevents the aggregation of TiO₂ nanoparticles.

Propylamine is beneficial for the dispersibility and film-forming ability of ZnO in chlorobenzene and chloroform, without preventing electron-transfer processes between the nanoparticles [160, 170]. An amine-based dispersant has also been reported for TiO₂ in styrene and hexane [166].

5. Transparent photocatalytic and UV-absorbing coatings

This section will describe the requirements for transparency and provide guidelines for how the refractive index difference and the size of particles or aggregates control the degree of transparency of thin coatings and films. The various methods used to deposit nanoparticle-containing films onto a substrate are briefly described with a discussion on the importance of the colloidal stability and rheological properties for the preparation of transparent photocatalytic and UV-absorbing coatings.

5.1. Requirements for transparency

Transparent materials are characterized and defined by a small or insignificant loss in intensity of transmitted light. The transmittance of the sample can thus be defined as $T = I/I_0$, where I_0 is the intensity of the incident light and I is the intensity of the transmitted light. This transmittance will be limited by a number of events, which will reduce T. These events, illustrated in figure 7, consist of (i) surface *reflection*, (ii) *scattering* and (iii) *absorption*.



Figure 7. Schematic illustration of the main mechanisms affecting the transparency of a material.

The coefficient of reflection, often defined as the reflectivity, R, of a given material can be calculated from equation (3) [171]

$$R = \left(\frac{\tilde{n} - 1}{\tilde{n} + 1}\right)^2,\tag{3}$$

where \tilde{n} is the complex refractive index, i.e. $\tilde{n} = n + i\kappa$, with n the refractive index and κ the extinction coefficient. In the absence of absorption, i.e. $\kappa = 0$, the reflectivity becomes $R = \left(\frac{n-1}{n+1}\right)^2$. In the absence of scattering, the transmittance is lowered only by the reflection at the sample's front and back surfaces, and can be expressed as $T = (1 - R)^2$.

The scattering and absorption of light propagating in a solid has been observed to follow an exponential law as shown in equation (4) [172]

$$\frac{I(x)}{I_0} = \exp\left(\frac{4\pi i (\tilde{n} - 1) x}{\lambda}\right),\tag{4}$$

where I(x) is the intensity of the beam at a depth x and λ is the wavelength of the incident light. Considering that the refractive index \tilde{n} is a complex quantity, equation (4) can thus be expanded as

$$\frac{I(x)}{I_0} = \exp\left(\frac{4\pi i(n-1)x}{\lambda}\right) \exp\left(\frac{-4\pi\kappa x}{\lambda}\right).$$
 (5)

The previous equation shows that the light attenuation can be separated into scattering and absorption, which are represented by the first and second factor of equation (5), respectively. Using an analogy to the Lambert–Beer law, equation (5) can be modified into

$$\frac{I(x)}{I_0} = \exp(-(\alpha_{abs} + \alpha_{scat})x), \tag{6}$$

where α_{abs} and α_{scat} are the absorbance and scattering of the material, respectively. These can be expressed as a function of the number of absorbing/scattering centers per unit volume, N, and the absorbance and scattering cross-sections, C_{abs} and C_{scat} , respectively:

$$\alpha_{\rm abs} = NC_{\rm abs} = N\pi r^2 \chi_{\rm abs},\tag{7}$$

$$\alpha_{\rm scat} = NC_{\rm scat} = N\pi r^2 \chi_{\rm scat},\tag{8}$$

where *r* is the radius of the scattering center, and χ the efficiency factor for either absorbance or scattering.

The efficiency factors can be described under Mie's formalism as:

$$\chi_{\rm abs} = A_1 \beta + A_2 \beta^3 + A_3 \beta^4 + \dots, \tag{9}$$

$$\chi_{\text{scat}} = A_4 \beta^4, \tag{10}$$

where $\beta = \frac{2\pi r}{\lambda}$ and the coefficients A_i depend on *n* and κ [173].

In the special case when $\kappa = 0$, $A_1 = A_2 = A_3 = 0$, the transmittance of light across a given material can be reduced to

$$T = (1 - R)^2 \exp(-(\alpha_{\text{scat}})x), \qquad (11)$$

where, in the interval $n\beta < 1$, with

$$A_4 = \frac{8}{3} \left(\frac{n^2 - 1}{n^2 + 2}\right)^2 \left[1 + \frac{6}{5}\beta^2 \left(\frac{n^2 - 2}{n^2 + 2}\right) + \dots\right], \quad (12)$$

Rayleigh's expression of scattering is obtained [173].

All the materials of interest in this review, i.e., titanium dioxide (rutile, brookite, and anatase), zinc oxide, and cerium oxide, are transparent in the visible region. The optical transmittance can thus be estimated using equation (11) and using the reported refractive indices $n_{\text{TiO}_2}^{\text{rutile}} = 2.62$, $n_{\text{TiO}_2}^{\text{anatase}} = 2.54$, $n_{\text{CeO}_2} = 2.2$, $n_{\text{ZnO}} = 2.02$ at $\lambda = 589.3$ nm [174, 175]. Figure 8 shows how the reflectivity and scattering (calculated using equation (11)) affect the transmittance of films composed of CeO₂, TiO₂ and ZnO nanoparticles with different particle sizes and refractive indices.

The scattering component has the most dramatic effect on the transmittance, where small deviations of the particle size $(\alpha_{\text{scat}} \propto r^6)$ or of the wavelength of the incident light $(\alpha_{\text{scat}} \propto \lambda^4)$ result in very large changes. Scattering is significantly reduced if nanoparticles with diameters below $\approx 10\%$ of the wavelength are used, relating to $\beta < 0.2 - 0.3$, and preferably $\beta < 0.1$. This effect is reduced if the contrast in refractive index between the particle and the matrix is small. Hence,



Figure 8. The dependence of transmittance of films containing nanoparticles of different particle size and refractive index. (Top) Decrease of transmittance of a film due to changes in reflectivity with the refractive index of the film calculated according to the first term in equation (11). (Middle) Decrease of transmittance of a film containing nanoparticles of different diameters: 20 nm (solid line), 50 nm (dashed line), and 100 nm (dotted line). The curves are calculated using a wavelength $\lambda = 589.3$ nm, a volume fraction of 1, and a film thickness $x = 0.5 \,\mu$ m according to the second term in equation (11). (Bottom) Decrease of transmittance of a film due to both reflection and scattering using both terms according to the second term in equation (11).



Figure 9. Examples of liquid phase deposition methods; (a) dip coating; (b) spin coating and (c) spray coating.

the lower refractive index of ZnO ($n_{ZnO} = 2.02$) compared to CeO₂ ($n_{CeO_2} = 2.2$) and TiO₂ ($n_{TiO_2} = 2.6$) is beneficial but the particle size has to be minimized and the number density of particles above about 100 nm has to be very small to achieve a high transparency of the films. The reflectance of the films is independent of the particle size or the film thickness and is only determined by the refractive index, i.e. the composition of the film. This parameter is difficult to tune but one possible way to avoid a strong film reflectance is to introduce nanosized porosity, which would result in a lower effective refractive index while avoiding excessive scattering.

5.2. Deposition of photocatalytic coatings

Deposition of nanoparticle suspensions onto a substrate of choice is a widely used method to produce nanostructured coatings [176]. The deposition methods producing thin films can be classified into gas phase (e.g. chemical vapor deposition (CVD), sputtering) or liquid phase (e.g. dip coating, spin coating, spray coating) methods [177]. Gas phase methods continue to be important for deposition on glass and metals [22, 178, 179], while liquid phase deposition methods are widely used for deposition onto polymeric and heat sensitive substrates [180, 181]. The liquid phase deposition of precursor solutions or nanoparticle dispersions [117, 182–186] offers several advantages, such as simple equipment, mild deposition conditions, and flexibility in tuning the properties of the films, that may be difficult to achieve using gas-phase deposition methods.

Dip coating and spin coating are suitable methods for the application of uniform and thin films onto flat substrates. In the dip-coating method (figure 9(a)), the substrate is immersed in the dispersion and then withdrawn at a constant speed under controlled temperature and atmospheric conditions [187–189]. The thickness of the film can be controlled by the withdrawal speed [190, 191]. If the dispersion has a Newtonian behavior in the relevant shear rate range, the thickness can be calculated by the Landau–Levich equation

$$h = 0.94 \times \frac{(\eta U)^{\frac{2}{3}}}{\gamma_{l_{v}}^{\frac{1}{6}}\sqrt{\rho g}},$$
(13)

where *h* is the coating thickness, η the dynamic viscosity, *U* the substrate withdrawal speed, γ_{lv} the liquid-vapor surface

tension, ρ the density and g the gravity [192]. The dip-coating method is generally characterized by a high optical quality and a homogeneous thickness of the coatings [193].

The spin coating process (figure 9(b)) relies on centrifugal forces to spread the liquid phase evenly across a spinning substrate. The solvent is usually volatile and therefore evaporates during the spinning process [188]. The thickness of the film obtained by the spin-coating method depends on the rotation speed and the viscosity of the liquid phase. Newtonian liquids result in a uniform thickness, while the shear-thinning behavior commonly observed in particulate sols and gel-forming systems, results in spin-coated films that are thicker near the centre than at the edges. The thickness of an initially uniform film during spin-off is described by

$$h(t) = \frac{h_0}{\sqrt{1 + \frac{4\rho\omega^2 h_0^2 t}{3n}}},$$
(14)

where h_0 is the initial thickness, t is the time, ω the angular velocity, ρ the density and η the dynamic viscosity.

High-boiling solvents with a high viscosity are commonly used for liquid phase deposition to suppress crack formation during drying and thermal post-processing, and to minimize the number of coating cycles [194]. Alternatively, the addition of hydrated compounds (e.g. trehalose) that swell when the solvent is removed can reduce the induced tensile stresses in the coatings during evaporation [195, 196]. Finally, polymers are commonly added to act both as plasticizers and to improve the wetting of the substrate. Uniform coatings have been prepared using, e.g., PEG [62], methylcellulose (MC) [197], hydroxypropoyl cellulose (HPC) [184, 198, 199], and block co-polymers [200, 201]. The spray coating process (figure 9(c)) offers some advantages over dip and spin coating, e.g. high deposition speed and a significant flexibility in the shape of the substrate [193, 202]. However, the spray-coating method offers limited control of the uniformity of thickness.

The choice of substrate material, such as glass, ceramics, metals and polymers, has a profound influence on the deposition parameters and the properties of the coating. The most widely used material has been borosilicate glass due to its transparency, chemical and thermal stability, low cost and well-known optical properties. However, the non-crystalline nature of glass and the associated diffusion of Na⁺ and Ca²⁺ from the borosilicate glass substrate into a deposited titanium oxide layer have been shown to result in a drop of the photoactivity [203, 204]. This can be prevented by coating the substrate with a SiO₂ or Al₂O₃ barrier layer prior to the deposition of the TiO₂ film [26, 117, 205, 206], or by treating the substrate and the coating with sulfuric acid [207, 208].

Coating of stainless steel used for construction and architectural design with transparent photocatalytic coatings offers a way to reduce corrosion and discoloration of façades, bridges and other structures. Such photocatalytic coatings applied to large constructions in cities could also contribute to a reduction in harmful airborne substances. Steel is a relatively inert material that is not altered during the deposition process except under extremely harsh chemical and thermal conditions [209]. Steel, like other metallic substrates, can also be used for electrophoretic deposition of nanoparticles [203]. Coating of ceramic substrates has also been studied for construction and indoor applications [14, 210]. Similar to glass, coatings on ceramics can be heat treated at high temperature, which gives the coatings good adhesion properties [211, 212].

Alternative deposition methods using, e.g., nanoparticle dispersions have been developed for heat-sensitive substrates such as polymers or organic fibers [213, 214]. Many of the low-temperature deposition techniques suffer from poor adhesion of the coating to the substrate. The introduction of anionic hydrophilic groups by layer-by-layer impregnation, plasma etching, ion or UV irradiation, chemical etching or silanization can improve the mechanical adhesion of the films [215–222]. The uniformity and adhesion of deposited particle-based coatings can be significantly improved by using a layer-by-layer approach [223–226].

Attempts have been made to improve the properties of the coatings by embedding the particles in a matrix [117, 227-231]. The use of an inorganic matrix such as silica improves the optical transmittance, enhances the photoactivity and may also introduce superhydrophilic properties to the coatings [176, 224, 232-235]. In addition, the use of a silica matrix was found to prevent phase transitions and grain growth of the nanoparticles upon thermal post-treatment, and to improve the mechanical properties of the films [224, 236, 237]. Organic additives have been used as pore-forming agents (PFA). Pore formation increases the photoactivity of the coatings by increasing the surface area, but reduces the transparency; hence, the porosity and the pore size needs to be tuned [238, 239]. Long-chain non-ionic surfactants, such as PEG [239–242], diethyleneglycol (DEG) [183], Tween 20 and Triton X-100 [208, 243, 244] have been used as pore-forming agents and subsequently leached out by hot water treatment [245]. Mesoporous photocatalytic coatings have been obtained using cationic surfactants [246] and diblock [247, 248], or triblock copolymers [200, 201, 249, 250]. The rich structural polymorphism of block copolymers results in organic-inorganic cooperative self-assembly and yields ordered micro-mesoporous coatings upon removal of the organic component [251]. Finally, silica-based sol-gel coatings made by incorporation of pre-formed N-doped nanoparticles [252] have also been reported recently (for use as thin coatings on glass substrates), and have been shown to be highly active photocatalytic coatings under irradiation at 390 nm (figure 10).

An alternative approach has been to embed pre-formed titanium dioxide nanoparticles in a titanium dioxide matrix prepared by in situ hydrolysis of titanium alkoxide precursors. In recent years, this alternative sol–gel approach has been used both in the case of commercial P25 nanoparticles [253] and in the case of other pre-synthesized nanoparticles of 4-5 nm in size [254] for coating glass or silicon substrates (by either spin or dip coating), which were then heat treated up to 300-400 °C. In the latter case, the mesoporous coatings were found to display higher than expected activities, which were attributed to a synergic interaction between the crystalline and amorphous components.



Figure 10. SEM images of TiO₂ films deposited on glass (a) without PEG, (b) with PEG (200 g mol⁻¹), showing reduced crack formation and increased porosity [257].



Figure 11. Preparation of a UV-protective clear coating containing inorganic nanoparticles.

Other more interesting sol-gel matrices for photocatalytic films embedding pre-formed or commercial (e.g. Hombikat, 5nm) titanium dioxide nanoparticles are those based on silica-zirconia [255] resulting from the hydrolysis of the zirconium and organosilane precursors. One added advantage in this case is the need for lower thermal treatment temperatures (about 100 °C), which make the process attractive for use on metallic substrates such as aluminum. Furthermore, these ZrO_x : SiO_x coatings, applied on glass and aluminum surfaces by dip coating, have been shown to possess high photocatalytic and biocidal activity.

Finally, a recent report [256] has found that commercial titanium dioxide nanoparticles (about 25 nm in size) combined with PTFE can be sputtered (by radio frequency magnetron sputtering) onto substrates (such as quartz or structured Ti) and then heated at relatively mild temperatures (about $100 \,^{\circ}$ C), to yield novel superhydrophobic surfaces with photocatalytic properties. These coatings display superhydrophobic rather than the usual superhydrophilic properties, commonly found in inorganic titania coatings, which widens the range of possible products that can be developed by incorporation of photocatalytic nanoparticles in different types of coating matrices.

5.3. UV-absorbing coatings

Transparent UV-absorbing or UV-protective clear coatings are primarily used as UV-protecting lacquer for wooden surfaces, and as a UV-barrier coating on polymer-based products or devices. The limited thermal resistance of wood and most polymers requires that UV-blocking coatings are produced directly from a dispersion that contains the UV-absorbing nanoparticles and the organic binder/matrix, schematically depicted in figure 11. Important considerations for the preparation of transparent UV-protective clear coatings are similar to the transparent photocatalytic coatings. However, because the UV-protective clear coatings are often significantly thicker than the photocatalytic coatings, issues related to scattering and absorption become very important. The UV-protective clear coatings are normally required to be colorless, which means that the light absorption in the visible range of the inorganic semiconducting nanoparticles and the organic additives should be negligible [176, 258–262].

Semiconducting nanoparticles such as TiO₂, ZnO, SrTiO₃, CeO₂, WO₃, Fe₂O₃, GaN, Bi₂S₃, CdS and ZnS are photoactive and UV absorbing due to their electronic structures, characterized by a filled valence band and an empty conduction band [263]. However, a high photoactivity can also result in photocatalytic behavior, which brings about the production of unwanted reaction products and the possible degradation of the continuous phase the nanoparticles are dispersed in. Zinc oxide nanoparticles show a lower photocatalytic performance than TiO_2 but are luminescent, radiating light in the visible region upon UV irradiation [264, 265]. Recent work has suggested that CeO₂ could be an interesting UV-absorbing additive in transparent UV-protective clear coatings due to a lower photocatalytic activity and a bandgap closer to the visible region compared to TiO_2 . However, CeO_2 is frequently doped with divalent or trivalent cations to reduce the photocatalytic activity [107].



Figure 12. Charge carrier formation (electron e^- and hole h^+) and recombination in TiO₂ and CeO₂ by UV light irradiation (adapted from [269]).

Yabe and Sato [107] suggested that the resulting low photocatalytic activity of doped ceria may be related to the oxygen vacancies.

The processes of charge separation and recombination in both TiO_2 and CeO_2 are schematically illustrated in figure 12. The photocatalytic activity of TiO_2 can be suppressed, e.g., by surface modification with organic or inorganic compounds which prevents the recombination of the charge carriers with adsorbed species [266, 267]. CeO_2 can be used without surface modification and is considered as a better candidate for UV absorption in the cosmetic and coating formulations [268]. Due to strict VOC regulations in the European Union, aqueous coating formulations using latex binders are preferred to solvent-based coatings.

Dispersions of CeO₂ nanoparticles with diameters of 10-20 nm have been used to prepare UV-absorbing and abrasion-resistant nanocomposite coatings on polycarbonate substrates [165]. The nanocomposite coatings were prepared by dispersing the nanoparticles into a matrix based 3-glycidoxypropyltrimethoxysilane. The on CeO₂-based UV-protective clear coatings enhanced the scratch and abrasion resistance and the hardness of the polycarbonate substrate. Polyurethane nanocomposite films containing nanosized ceria functionalized with a phosphonated poly(oxyalkene) as UV absorber have also been studied [163].

6. Nanoparticle-based sunscreens

Sunscreen (sometimes called sunblock) formulations have traditionally included a variety of organic and inorganic compounds with absorption bands in various regions of the UV–visible spectrum. The UV radiation from the sun is often divided into three different classes that relate to the response of the skin: UVC (270–290 nm), UVB (290–320 nm), and UVA, which is subdivided into UVA2 (320–340 nm) and UVA1 (340–400 nm). Many different

UV-absorbing ingredients, primarily organic-based, have been developed and used in sunscreen formulations since the 1940s. Table 3 presents a summary of the different FDA-approved ingredients in sunscreen formulations. In this review, we focus on sunscreens that utilize UV-absorbing inorganic nanoparticles, primarily titanium dioxide and zinc oxide, as the active ingredient.

The high refractive index and the broad absorption in the UVB and UVA regions of titanium dioxide and zinc oxide particles have been utilized in early and modern sunscreens and sunblock formulations [270, 271]. The early use of a white zinc paste that consists of suspensions of micrometer sized zinc oxide particles in an oil-based medium on the skin was indeed an effective (but less attractive) sunscreen simply due to the pronounced light scattering in the visible region together with the UV absorption. However, the preparation of transparent sunscreens in the 1990s required that the particle size is reduced (see section 5.1) and that agglomeration is minimized. In the case of titanium dioxide, due to its very high refractive index, smaller particles are required whereas a somewhat larger particle size can be tolerated for zinc oxide.

Sunscreens can be formulated as sticks, ointments, gels, or aerosols with the dominating form being oil-in-water or water-in-oil emulsions, i.e. a mixture of two immiscible liquids. Emulsions offer a cost-effective and versatile formulation suitable for simple adjustment of the hydrophilic and hydrophobic UV-blocking organic components to tailor the rheology and the sun protection factor (SPF) [272]. Emulsions are also cosmetically desired as they can make the skin smooth and avoid the greasy feeling of purely oil-based sunscreens [29]. Many of the active ingredients are normally dissolved or dispersed in the hydrophobic oil phase. Titanium dioxide and zinc oxide in sunscreen formulations are usually coated with a dispersant, e.g. dimethicone (polydimethylsiloxane, PDMS) to be able to generate stable oil-based dispersions (see figure 13). The major drawbacks with emulsions relate to their thermodynamic instability that eventually results in phase separation. Emulsions also provide a good medium for microbial attack, which needs to be suppressed by suitable preservatives. Sunscreen formulations contain additives to provide long-term stability. Most of these additives are either emulsifiers or thickeners. Emulsifiers reduce the interfacial tension between the oil and water phase and also adsorb and form an interfacial film on the emulsion drops that act as a barrier against coalescence. Emulsifiers are typically amphiphilic molecules like fatty acid soaps and nonionic ethoxylated surfactants. However, liquid crystal and particle-stabilized emulsions can also be used and provide very stable emulsions (see below). Thickeners increase the viscosity of the continuous phase, which reduces the coalescence rate and segregation rate. Commonly used thickeners include alginates, natural gums, cellulose derivatives, fatty alcohols, and inorganic materials like bentonite, laponite, and fumed silica. In the following subsections, we will give examples of nanoparticle-based formulations of both oil-in-water and water-in-oil type sunscreens.

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Table 3. FDA-approved ^a active sunscreen ingredients [272].							
FDA-approved active sunscreen ingredient	Maximum FDA-approved concentration (%)	Peak absorption wavelength (nm)	Range of protection (nm)	Protection provided (UVB/UVA)			
Inorganic							
Titanium dioxide	25.0	Varies	290-350	UVB, UVA2			
Zinc oxide	25.0	Varies	290-400	UVB, UVA1			
Organic UVB							
PABA	15.0	283	260-313				
Padimate O	8.0	311	290-315				
Octinoxate (octyl methoxycinnamates)	7.5	311	280-310				
Cinoxate	3.0	290	270-328				
Octisalate (octyl salicylate)	5.0	307	260-310	UVB			
Homosalate	15.0	306	290-315				
Trolamine salicylate	12.0	260-355	269-320				
Octylocrylene	10.0	303	287-323				
Ensulizole (phenylbenzimidazole sulfonic acid)	4.0	310	290-340				
Organic UVA							
Oxybenzone	6.0	290, 325	270-350	UVB, UVA2			
Sulisobenzone	10.0	366	250-380	UVB, UVA2			
Dioxybenzone	3.0	352	206-380	UVB, UVA2			
Meradimate (menthyl anthranilate)	5.0	336	200-380	UVA2			
Avobenzone	3.0	360	310-400	UVA1, UVA2			
Ecamsule (terephthalydene dicamphor	10.0	345	295-390	UVA1, UVA2			
sulfonic acid [Mexoryl SX])							

^a FDA approved as of 7 December 2009.



Figure 13. TEM images of commercial sunscreen formulations containing (A) 10% titanium dioxide (T-Lite SF-S) and (B) 9% ZnO (Z-Cote) prepared as oil-in-water emulsions. Scale bar 200 nm. Reprinted from Gamer *et al* [273], © (2006), with permission from Elsevier.

6.1. Oil-in-water formulations

Oil-in-water formulations are emulsions with water as the continuous media with an oil-based dispersed phase. The active ingredients, including the nanoparticles, are normally dispersed or dissolved in the oil phase and the final composition can thus be adjusted by either varying the concentration in the oil phase and the relative concentration of the oil phase in the emulsion (i.e. the oil/water ratio). One of the practical advantages of this type of emulsion is that the oil content can be kept low. The nanoparticles also need to be functionalized with hydrophobic adlayers using, e.g., the techniques and additives discussed in section 4.2. This section contains a summary of some oil-in-water sunscreen formulations.

Monteiro-Riviere *et al* [274] prepared a titanium dioxide-based sunscreen formulation consisting of 10% TiO₂ nanoparticles (T-Lite SF, rutile nanocrystals with a primary

size of 14-16 nm) coated with dimethicone/methicone copolymer. The treatment was only partially successful and resulted in the formation of agglomerates with a mean size of 200 nm with a relatively broad distribution. Hydrated silica and aluminum hydroxide were included as well, probably as thickeners. In comparison, a zinc oxide-based formulation was also prepared using 5% ZnO with a significantly larger particle size of 140 nm and a specific surface area of $12-24 \text{ m}^2 \text{ g}^{-1}$ that was coated with triethoxycaprylsilane resulting in a stable dispersion in the non-polar medium. Gamer et al [273] have also compared zinc oxide and titanium dioxide-based formulations. They prepared two titanium dioxide oil-in-water formulations of 10% T-Lite SF-S and T-Lite SF. The T-Lite SF-S titanium dioxide particles were needle-like with dimensions of $30-60 \times 10$ nm and coated with silica (2-5 wt%) and methicone (4.5-6.5%). The T-Lite SF titanium dioxide particles had the same dimensions as in



Figure 14. Stability of formulated sunscreens. (A) Representative P25 absorbance spectra before and after 1 h UV exposure. (B) Representative SF absorbance spectra before and after 1 h UV exposure. (C) Comparison of percentage change in area under the curve for formulated sunscreens from initial value after 1 h UV exposure. Only the sunscreen formulated with P25 shows significant reduction in the area under the curve, P < 0.05. Reprinted from Tyner *et al* [276], © (2011), with permission from John Wiley and Sons.

T-Lite SF-S but were coated with methicone (3.5-5.5%) only. They prepared a zinc oxide-based formulation containing 10.3 wt% zinc oxide (Z-Cote) where the primary particles and loose agglomerates were present exclusively in the water phase with a substantial fraction of the primary particles being often adsorbed at the oil/water interface of the emulsion droplets. Bennat and Müller-Goymann [275] prepared commercial TiO₂ dispersions either in octyl palmitate or in water. The dispersions contained about 40% nanosized TiO₂ and 1–2% of the polyelectrolyte, sodium polyacrylate. Formulations containing 5% TiO₂

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were manufactured using sodium carboxymethylcellulose (thickener), PEG 4000, lecithin (emulsifier) and two different silicon oils (dimethicone 100 and silicon oil AR 20 S, respectively).

Tyner et al [276] showed that stable sunscreen formulations containing 5 wt% titania can be prepared using TiO₂ particles with different surface properties (see figure 14): (i) uncoated nanosized titanium dioxide (Degussa Aeroxide P25); (ii) titanium dioxide coated with aluminum hydroxide/dimethicone copolymer (BASF T-Lite SF); and (iii) titanium dioxide treated with aluminum hydroxide (Ishihara Tipaque CR-50). The versatile formulation consisted of three different phases in addition to the titanium dioxide particles: phase A (dibutyl adipate, cocoglycerides, sodium cetearyl sulfate (cationic emulsifier), lauryl glucoside (nonionic emulsifier), polyglyceryl-2 dipolyhydroxystearate, glycerin, cetearyl alcohol, C₁₂₋₁₅ alkyl benzoate, octyl methoxycinnamate, and tocopheryl acetate; phase B glycerin, allantoin, xanthan gum (thickener), disodium EDTA, magnesium aluminum silicate and water; *phase* C phenoxyethanol, methylparaben, ethylparaben, butylparaben, propylparaben, and isobutylparaben. Sadrieh and coworkers [277] followed up on this work and formulated sunscreens using an improved procedure. Phase A (dibutyl adipate, C12–15 alkyl benzoate, cocoglycerides, sodium cetearyl sulfate, lauryl glucoside, polyglyceryl-2 dipolyhydroxystearate, glycerine, cetearyl alcohol, octyl methoxycinnamate, tocopheryl acetate) was heated to 80 °C. The titanium dioxide was added to phase A and homogenized for 3 min. Phase B (glycerin, disodium ethylenediaminetetraacetic acid (EDTA), allantoin, xanthan gum, magnesium aluminum silicate, water) was heated to 80° C and mixed with *phase A* (with the titanium dioxide) by vigorous stirring. The homogenized mixture was cooled to about 40 °C. Phase C (phenoxyethanol, methylparaben, ethylparaben, butylparaben, propylparaben, isobutylparaben) was added and then homogenized to yield the emulsion.

Zvyagin et al [278] used a formula which includes 19 wt% 26-30-nm mean size ZnO particles with preservatives phenoxyethanol (0.3 wt%) and hydroxybenzoates of (0.3 wt%) suspended in caprylic capric triglycerides (liquid crystal formulation). Cross et al [279] prepared (i) a ZnO dispersion with 60 wt% of siliconate-coated ZnO in caprylic capric triglyceride (ZinClearS_60CCT), (ii) a typical oil-in-water emulsion sunscreen with 20 wt% ZnO (using ZinClear_40CCT). Türkoglu and Yener [280] made formulations with 5 or 10% TiO₂ and/or ZnO using three different surfactants (2.7% cetyl trimethyl ammonium chloride, 1.5% sodium lauryl sulfate (anionic emulsifier) and 1.5% polysorbate 80, and 3.0% triethanolamine stearate). The rest of the formulation consisted of 64.2% water, 5% glycerol, 10% petrolatum, 2.5% isopropyl palmitate, 7% stearyl alcohol, 2.5% dimethicone, 0.5% sodium chloride, 0.3% methyl and propyl parabens. Villalobos-Hernández and Müller-Goymann [281] investigated the use of carnauba wax (thickener) and cetyl oleate (emulsifier) for the dispersion of TiO_2 , $BaSO_4$ or $SrCO_3$. The suspensions were produced by dispersing the lipid phase into the aqueous phase using high-pressure homogenization. The lipid phase was composed of inorganic content 2-6 wt%, decyl oleate 5%, and carnauba wax 5-10% whereas the aqueous phase consisted of 1% Tween 80 (emulsifier) simethicone 0.01%, methylisothiazoline 0.0285% (added as preservative), and water. Those substances were mixed together by melting the wax at 90 ± 5 °C and applying magnetic stirring during 30 min at a rate of 300 rpm. The aqueous phase was prepared by dispersing the components at a speed rate of 300 rpm. Semenzato et al [282] studied the UV-attenuating properties and the rheology of different emulsions. All emulsions were prepared according to the following formula: steareth-2 (3%); steareth-21 (2%); cetearyl alcohol (3%); mineral oil (17%); preservative (0.1%); inorganic sunscreen (5%); and water. The powder was pre-dispersed in the hot oil phase $(70 \,^{\circ}\text{C})$ under vigorous stirring using a turbine mixer for 10 min; then the emulsion was prepared by adding the powder dispersed in oil to the aqueous phase under vigorous stirring for 5 min. The emulsions contained: (i) no inorganic component; (ii) 5% TiO₂, inorganic-treated (iii) 5% ZnO; and (iv) TiO₂, organic-treated (hydrophobized).

6.2. Water-in-oil formulations

Most metal oxide nanoparticles are hydrophilic and contain hydroxyl surface groups that develop a surface charge when immersed in water. This hydrophilicity is exploited in water-in-oil formulations where the inorganic nanoparticles are readily dispersed in an aqueous medium. Below is a summary of some water-in-oil sunscreen formulations.

Dussert et al [283] investigated emulsions containing titanium dioxide, zinc oxide, and iron oxides. The emulsions contained decyl oleate (thickener), cyclomethicone and dimethicone copolyol (emulsifier), glycerin, cyclomethicone, C12-15 alkyl benzoate, mineral oil and caprylic/capric triglyceride (emulsifier), sodium chloride, octyldodecanol, phenoxyethanol, methylparaben, butylparaben, ethylparaben, propylparaben, petrolatum, quaternium-18 hectorite (thickener), polypropylene glycol (PPG) myristyl ether, tocopheryl acetate, glyceryl stearate, glyceryl laurate, PEG-30 dipolyhydroxystearate, silica, ozokerite, disodium EDTA, xanthan gum (thickener), o-cymen-5-ol, magnesium ascorbate, beta-carotene, orange oil and rosemary oil, lecithin and tocopherol and ascorbyl palmitate and hydrogenated tallow glyceride citrate.

Schulz *et al* [284] compared formulations that utilized (i) the hydrophobization of T805 titanium dioxide (Degussa, particle size 20 nm) with trimethyloctylsilane, (ii) Eusolex T-2000 titanium dioxide (Merck, mean size of 10–15 nm) coated with Al_2O_3 (8–11%) and SiO₂ (1–3%), and (iii), a hydrophilic dispersion of titanium dioxide (Tioveil AQ-10P, Solaveil, needle-shaped with a mean particle size of 100 nm) in water and propylene glycol, with alumina (4.25%) and silica (1.75%) as thickeners. The water-in-oil emulsions contained water, caprylic triglyceride, glycerin, butylene glycol, glyceryl stearate, octyldodecanol, dicaprylyl ether, cyclomethicone, stearic acid, trisodium EDTA, cetearyl alcohol, carbomer, lanolin alcohol and 4% ultra-fine titanium dioxide in either of the above-mentioned variants. Mavon

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et al [285] designed a broad-spectrum UV water-in-oil emulsion containing water, glycerin, dimethicone, ethylhexyl methoxycinnamate, isododecane, cyclomethicone, C12-15 alkyl benzoate, PEG-30 dipolyhydroxystearate, decyl glucoside, dodecyl glycol copolymer, magnesium aluminum silicate, preservatives, zinc oxide, tocopheryl acetate, o-cymen-5-ol, xanthan gum and 3% ultrafine TiO₂ (T805, Degussa, Germany) with a mean particle size of 20 nm (the TiO₂ was hydrophobically coated with trimethyloctylsilane) and 8% methylene bis-benzotriazolyl tetramethylbutylphenol in a dispersion of decyl glucoside. Beasley et al [286] prepared formulations of water-in-oil emulsions using 5% PEG-12 dimethicone cross-polymer as the emulsifier and containing either 3% avobenzone, 5% ZnO (Z-Cote HPl; BASF) or 5% TiO₂ (TNP50M170; Kobo Products, Inc.,) as single sunscreen active ingredients. The oil phase additionally comprised 12% cyclopentasiloxane, 4% bis-hydroxyethoxypropyl dimethicone, and 7.0-31.5% di-isobutyl adipate. The water phase contained 5% propylene glycol and 0.5% sodium chloride, which was added to the oil phase under constant mixing to give final compositions.

6.3. Human risk

A great deal of work is also being dedicated to investigating the risk posed to humans by nanosized nanoparticles [287]. Several recent investigations report that the inorganic TiO₂ and ZnO nanoparticles do not penetrate into the dermis [272–279, 283–285, 288]. However, the penetration distance varies with the state of the formulation; those encapsulated into liposomes that have a relative deeper penetration [275]. In a recent review paper, authors from the major cosmetic companies indicate that the risk for humans from the use of nanosized titanium dioxide and zinc oxide is negligible [289]. Nevertheless, although the authors did not find evidence of transdermal absorption, a recent report indicated that UV-damaged skin is more permeable to nanoparticles [274]. Moreover, an increased amount of ⁶⁸Zn has been found in blood and urine after exposure to ⁶⁸Zn-enriched zinc oxide-containing sunscreens [290].

7. Future prospects

Some of the early and commercially most important applications of nanoparticles like mechanochemical planarization, catalysis and sunscreens were realized through the development of efficient and cost-effective ways to formulate and process the nanoparticles. In this review, we have also shown how the applications of nanoparticles as part of photocatalytic and UV-absorbing coatings or as an ingredient in sunscreens rely on adequate strategies for stabilizing and functionalizing nanoparticles prior to their incorporation into an organic, inorganic or hybrid material, as well as for the final processing of the nanoparticle-containing product.

These successful cases give important guidance for the introduction and development of new, large-scale applications of nanoparticles. There is a need to develop versatile production routes that minimize or avoid the formation of hard, covalently bonded aggregates. Indeed, the inability to deagglomerate commercial nanoparticles to a sufficient extent to utilize the inherent size-specific properties is one of the major obstacles to introducing promising nanoparticles in prospective applications. In addition, many of the potential applications require that monodisperse nanoparticles with well-defined shapes can be produced in large quantities at moderate cost. While liquid-based colloidal routes have significant advantages over gas-phase routes with respect to size, shape and agglomeration control, the liquid-state routes are limited by poor yield and high cost. Development of cost-efficient colloidal nanoparticle production routes in aqueous media could open up more mundane application areas for the introduction of tailored nanoparticles.

The surface chemistry of nanoparticles needs to be much better understood. The surfaces of nanoparticles may differ significantly from the surface chemistry of larger, more well-characterized colloidal particles. Recent work that utilizes highly focused synchrotron light and high-resolution electron microscopy techniques is giving pivotal information on, e.g., the nucleation and growth of nanoparticles [291, 292]. The rapid method development will certainly also provide important information on the highly dynamic surface chemistry and elucidate the mechanisms for efficient surface functionalization.

Finally, further development of new additives and innovative routes for the processing and preparation of stable dispersions of functionalized nanoparticles will be of pivotal importance for enabling and promoting new nanoparticle-based applications. Recent examples include, e.g., the functionalization of titanium dioxide nanoparticles for subsequent application in transparent nanocomposites [287]. Other types of nanoparticles, such as lipid nanoparticles, have also been successfully functionalized for use in cellophane biocompatible hybrid films [288].

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