

A new class of ER fluids is based on nonaqueous polyurethane dispersions. The dispersed phase consists of a specially developed polyurethane elastomer which solvates and stabilizes metal salts. The polymer network influences the mobility of the dissolved ions, allowing a surprising degree of control over the ER effect. The field strength dependence of the ER effect and the switching response correlate directly with the changes in the polymer structure. Electrorheological measurements in shear mode (as in common viscometers) and flow mode (as in shock absorbers) show that the ER effect depends on the shear geometry. Particle-based ER fluids can also use liquid crystals as the suspension medium. The liquid crystalline order can strongly increase the ER shear stress compared with an ER system made by the same particles but in a nonliquid crystalline medium.

A different type of ER fluid is based on homogeneous or single-phase ER fluids that usually consist of low-molecular weight or polymeric liquid crystals (see *Liquid Crystals: Overview* and *Liquid Crystalline Polymers: An Introduction*). Although the change in viscosity that can be obtained with liquid crystals in an electric field is typically smaller compared with other materials, homogeneous ER fluids have the advantage that they display no sedimentation or flocculation. The rheological behavior of liquid crystals depends on the director orientation and the theoretical basis for the mechanical properties is provided by the Leslie-Ericksen-Parodi theory. In polymeric liquid crystals different types can be distinguished: main-chain and side-chain liquid crystalline polymers, respectively. The mesogenic moieties are part of the polymer backbone in the former case, whereas they are located in the side chain of the macromolecule in the latter. This different polymer architecture influences the flexibility of the macromolecules and allows more precise control of the rheological properties of the entire system.

The ER response of side-chain liquid crystalline polysiloxanes can be modified by dilution with polydimethylsiloxane (PDMS). Increasing the molecular mass of the polymer backbone of the liquid crystalline polymer, the mesogenic group ratio (number of mesogenic groups per silicon), or the length of the spacer (which separates the mesogenic group from the polymer backbone) increases the strength of the ER effect. On the other hand, the miscibility of the liquid crystalline polymer with PDMS decreases, which eventually can lead to polymer-solvent phase separation and ER effect instability at elevated temperatures. Since the polymer-solvent interactions can be influenced by the chemical composition of the spacer, systems can be prepared where miscibility problems at high dilution can be avoided.

Homogeneous ER fluids composed of urethane-modified polyethers can display either a positive or negative ER effect depending on the structure. Systems prepared by the reaction of poly(propylene glycol) or

poly(tetramethylene glycol) as the polyether component with isocyanates such as *p*-chlorophenyl isocyanate or 1,5-naphthalene diisocyanate enable the influence of the displacement of hard and soft segments and the existence of branches on the ER effect to be quantified.

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Polymer-based Nanocomposites by Sol-Gel Routes, Applications of

The fabrication of inorganic nanoparticles by chemical means has become an interesting route to prepare many kinds of nanostructured materials. For example, sol-gel techniques, which have been used for over 60 years for making inorganic materials, can be considered as an interesting basis for the synthesis of nanoparticles, since sols as colloidal systems in general are composed of stabilized nanoparticles in solution. With a few exceptions, for example, SiO₂ sols prepared from alkoxide precursors at low pH-values, most sols are of particulate nature. These sols can be not only prepared from alkoxide precursors through the sol-gel process but through many precipitation reactions carried out outside of the point of zero charge. In these regimes, depending on pH and the chemical nature of the surface, particles absorb ions and develop surface charges which prevent aggregation, precipitation, or gel formation. In Fig. 1, some principles for the

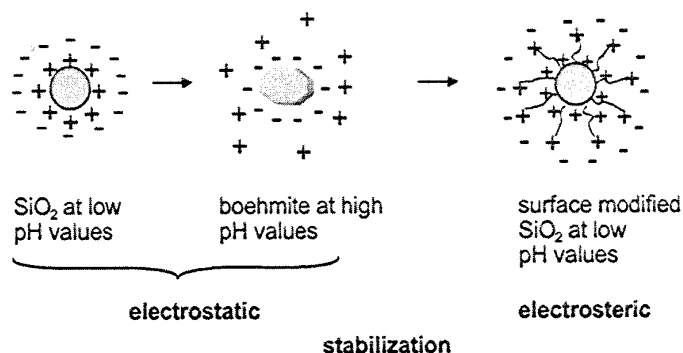


Figure 1
 Various types of stabilization of colloids.

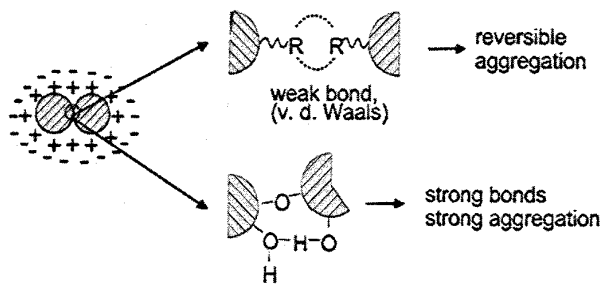


Figure 2 Aggregation mechanism for the formation of "hard."

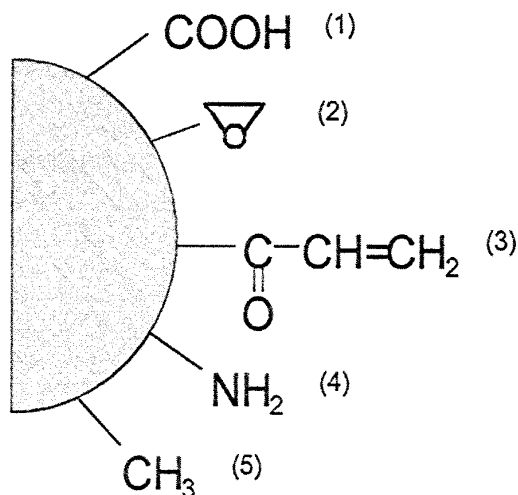


Figure 3 Various types of functional surface modification.

Table 1 Properties of nanoparticles depending on their small size

Surface area	interfacial phase catalytic properties sensor properties
Size effects	superparamagnetic or superferromagnetic properties
Quantum effects	semiconducting plasmon resonating NLO photocatalytic effects
Highly dispersed nanocomposites	abrasion resistance + transparency
Transparency	refractive index

stabilization of sols are shown. Whereas in aqueous solutions most of the precipitates carry surface groupings, for example OH-groups, which tend to react with each other by the formation of chemical or hydrogen bonds, the presence of surface modifiers which do not have groupings to form strong bonds can prevent irreversible aggregation even at the point of zero charge. In Fig. 1, several types of surface modification are shown. The electrostatic stabilization is very effective in diluted sols and outside of the point of zero

charge. In this case sols, stable over months, can be prepared. In the case of electrosteric stabilization, a surface is covered with groupings not able to form strong bonds to the next colloid, so that only van der Waals or weak polar forces are effective. In this case the aggregation leads to weak aggregates, which can be redispersed under appropriate conditions. The formation of strong and weak bonds is schematically shown in Fig. 2.

The preparation of surface-modified colloids is not only of interest for stabilization, but also for generating the desired reactivities of the colloids. In Fig. 3 several possibilities are shown. Acids (1) and bases (4) can be used to tailor an appropriate zeta-potential or to carry out condensation reactions to anhydrides, acid chlorides or acids. (2) and (3) (epoxides or methacrylates), represent polymerizable or polycondensable surface groupings which can be used for further reaction, for example, coupling reactions, but also for polymerizing the nanoparticles together with organic monomers in order to fabricate so-called polymer matrix nanocomposites. The alkyl group (5) represents a class of nonreactive groupings which can be used for reducing the particle-to-particle interaction, and also to adapt polar nanoparticles to nonpolar matrices. The combination of these surface-modifying principles with the inorganic nanoparticles' properties leads to a wide range of possible new composite materials. Nanoparticles by themselves have interesting properties, as shown in Tables 1 and 2. In Table 1, basic properties mainly resulting from the particle size are shown. One of the very interesting properties is the large surface area, especially together with matrix materials, since interfaces, for example, between inorganic surfaces and organic polymers in general have a structure different from the polymer matrix structure.

In Table 2, some examples for the relations between colloid types, functional groupings, materials, and basic properties are shown.

1. Fabrication of Nanoparticles

This is based on the rules of colloidal chemistry in connection with surface modifying agents, which at the same time act as thermodynamic stabilizers, and which not only prevent the reaction of the particles with each other, but also keep the particle size at a desired level during the colloid formation process (for example, precipitation). This approach has been successfully used for making various kinds of nanoparticles (Schmidt 1996, Schmidt and Nonninger 1998). This is schematically shown in Fig. 4. The figure also shows that by using small organic molecules, the volume fraction of the coating is rather low compared to the nanoparticle size. If the modifying agent is bifunctional, that means that not only is it linked to

Table 2
Examples of nanoparticle effects in nanostructured materials

Particles or chemical functions	Type of material	Properties/application
Ceramic nanoparticles (e.g., SiO ₂ , Al ₂ O ₃ , ZrO ₂)	polymer- or hybrid matrix-nanocomposites	refractive index: interference layers lenses; GRIN-lenses scratch resistance: coatings ion conductivity: smart windows
Ceramic or functional nanoparticles + functional groups (CF ₃ , ...loxy, epoxy, amino acids, etc.)	hybrid matrix nanocomposites; polymer matrix; nanocomposites with colloids linked to the matrix by polymerization	low surface energy coatings low refractive index coatings hard coatings smart coatings corrosion protection coatings
Metal colloids	glass matrix	colors; non-linear optics
Transition metal colloids	ceramics, glass matrix	colors, catalysts, sensors
Semiconductors (e.g., TiO ₂ , CdS)	coatings, glass matrix, hybrid matrix nanocomposites	refractive index tailored coatings photocatalytic coatings nonlinear optics holograms
Luminescent nanoparticles	ceramic coatings, polymer matrix	transparent luminescent security systems transparent chromophores
Transition metal nanoparticles	inorganic coatings	catalytic systems

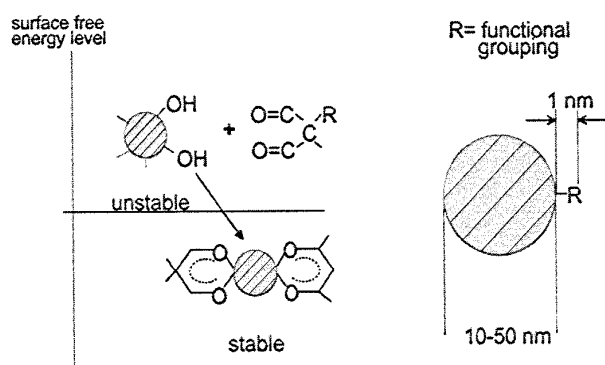


Figure 4
Thermodynamic effect of surface modification.

the surface by chemical bonds, as shown in Fig. 4 for complex bonds on oxidic particles by β -diketones, but the surface modification leads to the desired reactivities on the particle surface. In addition to this, and as also shown by Schmidt (1996) and Schmidt and Nonninger (1998), the desired crystallinity of the particles can be obtained by subsequent hydrothermal treatment. This means that using the chemical approach with appropriate surface modifiers, nanoparticles with desired surface reactivities can be produced and used as a basis for the nanocomposite fabrication. If these particles are combined with or dispersed in appropriate matrices, for example, in polymers, organic monomers or other hybrid sol-gel precursors such as organic alkoxy silanes, nanocomposites can be fabricated by many different routes.

If the nanoparticles are produced within a monomeric sol-gel or polymer precursor system, this is called the *in situ* route. If the nanoparticles are produced separately, isolated and then redispersed in appropriate matrix systems, it is called the *separate processing* route. These nanoparticles have also been introduced into a polymeric matrix by compounding processes, and these processes have been already successfully applied to transparent coatings or bulk materials (R. Nonninger: personal communication, 1998).

In the following section, a series of examples is given showing how the nanoparticle route can be used for various material developments.

2. Optical Applications

2.1 Smart Materials (Photochromics, Electrochromics, Luminescence)

So-called smart materials are causing more and more industrial interest for many reasons. Photochromic materials are very common in the field of bulk glass, e.g., for ophthalmic glasses. A new approach in this field is photochromic nanocomposite hard coatings as wet coating systems, using photochromic dyes. The photochromic effect of common dyes like spirooxazines or spiropyrans is based on a change of the conformation, which changes the size of the organic π -bond systems and hence the electron energy levels of the dye molecule. With an increase in size of the π -

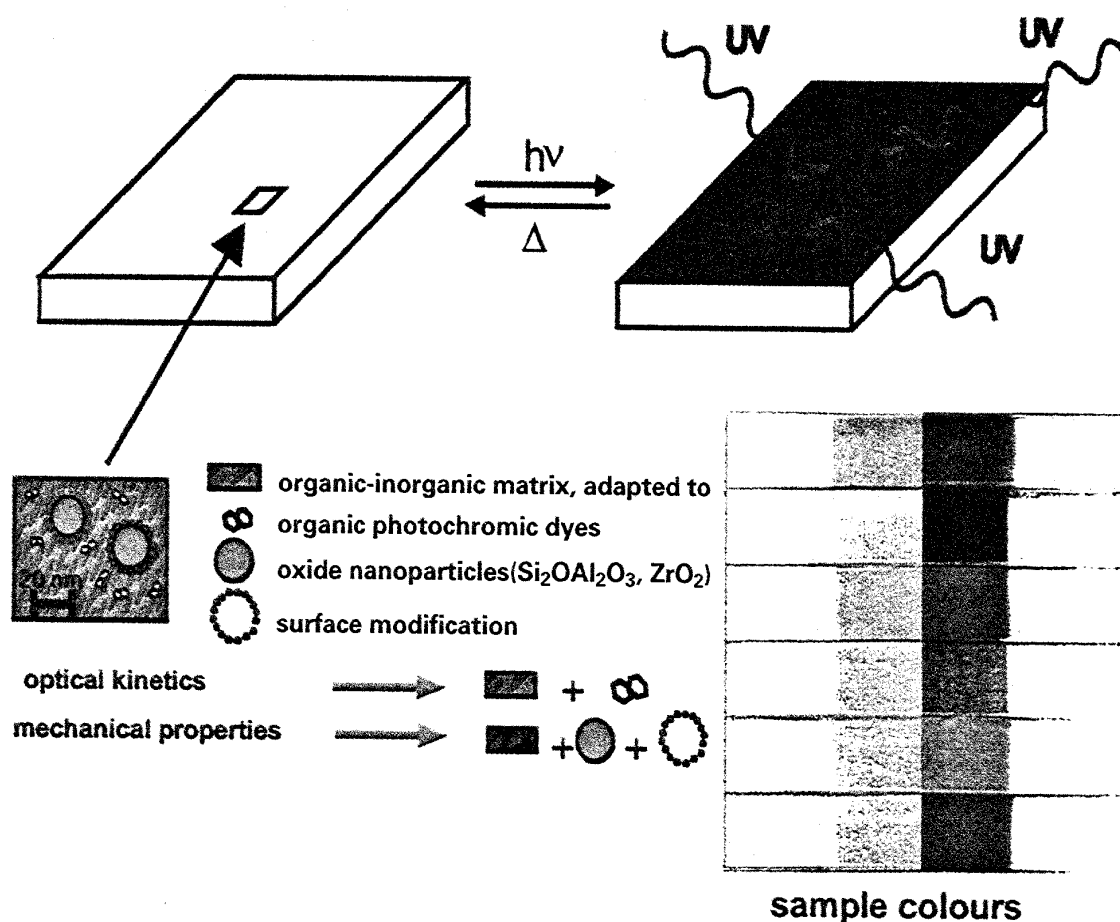


Figure 5 Photochromic coatings on glass without and with UV-irradiation (after Hou *et al.* 1994).

system, the energy levels for the excitation of the electrons decrease in number. This means that the absorption may be shifted from the UV into the visible. This conformation change requires a soft “host matrix system,” such as polymers with sufficient free volume. The more rigid the matrix system is, the more difficult it is for the molecule to change conformation. In order to use photochromic dyes in coatings, however, a high abrasion resistance is required. This in general can be obtained only by a very rigid matrix. In order to overcome these contradictory requirements, a nanocomposite coating material has been developed with ceramic nanoparticles—for example, from alumina or zirconia—which, when well dispersed in the matrix so as to obtain a good scratch resistance (where a soft matrix system made from polyacrylic components is synthesized in the voids between the nanoparticles), now provides sufficient flexibility for the photochromic dyes. The aim of the development is a photochromic coating material based on organic photochromic dyes with response times of seconds, which can be applied on transparent substrates (glass, polymers) or on non-transparent substrates (ceramics, polymers, paper) for the preparation of coatings with a thickness of 5–50 μm. The method is based on the incorporation of spirooxazines, pyrans, and fulgids

into the matrix of an organic–inorganic composite, which is prepared by a specially developed sol–gel process as described elsewhere (Fig. 5; Hou *et al.* 1994).

The result of this development is that by using UV radiation, a darkening of from 90% to 10% transmission can be reached. By further modification of the components of the matrix, the kinetic behavior of the photochromic dye can be adapted to different applications: glasses, pane glass, plastic foils (transparent and opaque), paper, ceramics, etc. The half-life times for darkening and fading ($t_{0.5}$) can be established anywhere between 2 s and 10 min. Due to the modularity of the network structure, different photochromic dyes can be integrated, resulting in neutral tints (gray or brown).

One of the superior features of nanoparticles and transparent matrices is that Rayleigh scattering can be neglected, if particle size and refractive index differences are appropriate. This is shown in Eqn. (1):

$$\gamma_{\text{ext}} = 32\pi^4 c \frac{n_p^2 - n_0^2}{n_p^2 + 2n_0^2} \frac{r^3}{\lambda^4} \quad (1)$$

where n_p is the refractive index, n_0 is the reflective index of the matrix, r is the particle radius, γ is the scattering

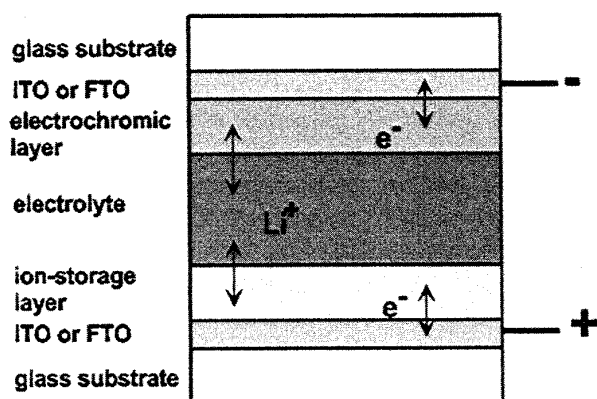


Figure 6
Schematic layout of an electrochromic (EC) device.

loss, λ is the wavelength, and c is a constant. From this equation a general rule can be deduced, which shows that if the particle size is below $1/20$ of the wavelength, Rayleigh scattering becomes very low and can be neglected in most cases, at least in thin films. From this point of view, nanocomposites or nanoparticulate thin films can be used for optical purposes. The second very interesting feature is that the physical, optical, or electronic properties connected to the crystalline or inorganic structure of a nanoparticle are still present, and can be used for obtaining specific properties.

A very interesting example of nanoparticle technology is smart windows or electrochromic windows, based on tungsten oxide. In Fig. 6, the multilayer system of an electrochromic cell is shown. The glass substrates are coated with transparent electronic layers, made from for example ITO or FTO, which are in direct contact with the electrochromic layer, which is made from tungsten oxide, vanadium oxide, molybdenum oxide, niobium oxide, or nickel oxide. Due to an electrochemical reduction, mixtures of different oxidation states can be obtained, leading to high absorption in the visible range. For compensating the charges, protons or lithium atoms have to be diffused into the electrochromic layers. On the other side of the cell a similar process takes place which, in general, does not lead to a change of the visible spectrum. In this case oxides like those of cerium or titanium can be used. This layer also has to show a certain storage capacity for the charge-compensating ions like protons or lithium. In order to avoid electronic shortcuts, an electronically isolating layer, having a high ionic conducting capacity, has to be used. For this reason, polymers with a sufficient solubility for lithium sols or acids are used (for example polyethylene oxide). These systems have been stabilized by the introduction of nanoparticles, for example zirconia. At their surfaces, lithium or protonic transport takes place advantageously. Moreover, the nanoparticles help to improve the mechanical properties of these materials, because at the same time they have to be used as adhesives for

gluing the layered systems together. It was demonstrated (Munro *et al.* 1998) that if the conductivity of the lithium containing nanocomposites reaches the region of about 10^{-4} S, and the electronic conductivity in the ceria, titania, and tungsten oxide system can be kept low, the switching behavior of such cells based on nanotechnologies is almost independent of the thickness of the ionic conductor, and systems up to 1 mm in thickness can be used.

This is very important for the production of large areas, since the planarity of large glass panes is very difficult to establish at the micrometer level. The chemical nanotechnology allows the production of cheap devices, because it has become possible to produce large area wet coatings, of optical quality, with very reproducible film thicknesses (Mennig *et al.* 1998b). The reversible variation in transmission of such cells reaches 70% (550 nm, bleached state) down to 21–25% (coloured state), with switching times t_{80} (t_{80} = time taken for 80% of transmission change): of 120 s (coloration), 70 s (bleaching) for EC-cells of $50 \times 80 \text{ cm}^2$. The benefits of this system are more comfort and energy saving in the architectural and automotive areas (e.g., air-conditioning costs in summer) and privacy effects.

By segmenting such an electrochromic device into pixels, and with an appropriate computer-controlled voltage supply, the fabrication of electrochromic displays becomes possible.

This opens up the possibility of the fabrication of large-area monochromatic displays between panes of glass, for example for displaying special sales offers in shop windows. Luminescent nanoparticles, such as those based on doped Eu^{3+} , have been developed, because there is a demand in industry for materials with high specific emission values. Interesting applications include photoluminescent displays, security tags on paper, plastic, luminescent textiles, etc. This development leads to materials in the form of redispersible nanoscaled powder, sols, coatings, and bulk materials, which present high luminescent emission under UV excitation. The main issue is the synthesis of rare-earth luminescent complexes (Eu^{3+} , Tb^{3+} , etc.), which perform the so-called antenna effect. These complexes can be incorporated into organic modified sols or attached on redispersible crystalline nanopowders. By this procedure, luminescent transparent coatings have been developed with thicknesses of up to $3 \mu\text{m}$ deposited on various glasses, polycarbonate, paper, or textiles.

2.2 Micropatterned Coatings

The fabrication of patterns in films is an interesting technology for many applications, such as the fabrication of holograms, the storage of information, the fabrication of microlens arrays, or even the micro-

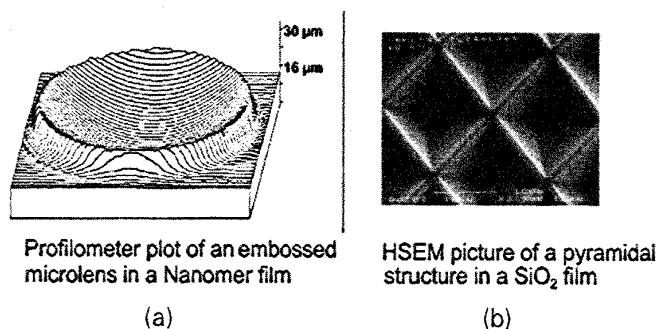


Figure 7

Lenses, produced by micropatterning of SiO₂ films.

electronic patterning and surface mounting device fabrication processes in microelectronics. Several basic techniques have to be distinguished. Etching techniques are very common in microelectronics. Patterning techniques using embossing require moldable systems, for example thermoplastic polymers. Embossing of sol-gel layers, as shown by Lukosz and Tiefenthaler (1983) and Tohge *et al.* (1994), requires very high pressures. In most cases, there are serious restrictions on using thermoplastic polymers, since it is difficult to obtain high precision patterns, due to the relaxation of the patterns as long as the polymer temperature is above the glass transition temperature T_g ; because of the limited film thicknesses, only patterns with a very low step height are possible. This means that it is very difficult to produce precise structures from pure inorganic systems like SiO₂, TiO₂, or glasses. In addition to this, polymers have low mechanical resistivity—for example, scratch resistance is poor.

The micropatterning of inorganic-organic nanocomposites in combination with UV-curing led to a process which allows the fabrication of micropatterns in a hard coating type of material, with a UV-curing

during the embossing step. The curing is based on the use of methacryloxysilane, which can be photo-cross-linked. Microlens arrays and refractive gratings have been developed using this approach. Another approach is based on the fact that SiO₂ nanoparticles coated with methyl groupings lead to gels with a remarkably increased relaxation behavior, and a film thicknesses of 20 μm and more are possible (Mennig *et al.* 1992). Due to the softness of these gels, they can be patterned with silicone rubber replicas and even curved shapes can be embossed. After embossing and densification at 500 °C, a transformation of the organically modified SiO₂ sol into almost pure SiO₂ glass (98% of the theoretical density) takes place. In Fig. 7(a), a profile of an embossed nanomer microlens is shown; in Fig. 7(b), a pyramidal structure of SiO₂ on glass as a light trap for the collection of light in solar collectors.

Through the application of a two-wave mixing process, holographic techniques have been developed. In this case, the intensity modulation of the incident light is used in a nanoparticle-containing film, with a nanoparticle surface modified with polymerizable groupings (Judeinstein *et al.* 1997). Before this, an inorganic backbone was built up in the system by hydrolysis and condensation, but care must be taken that no cross-linking of the nanoparticles to the system takes place. In the highly irradiated zones, the polymerizable nanoparticles are consumed by the polymerization process, and from the darker zones unpolymerized nanoparticles diffuse into the irradiated zones. By this technique an increase in concentration of nanoparticles in the irradiated zones takes place. If the nanoparticles show a higher refractive index than the matrix—for example, if zirconia or tantalum oxide nanoparticles are used—then volume phase holograms can be prepared. Meanwhile, the fabrication of the holograms by a two-way fixing process can be per-

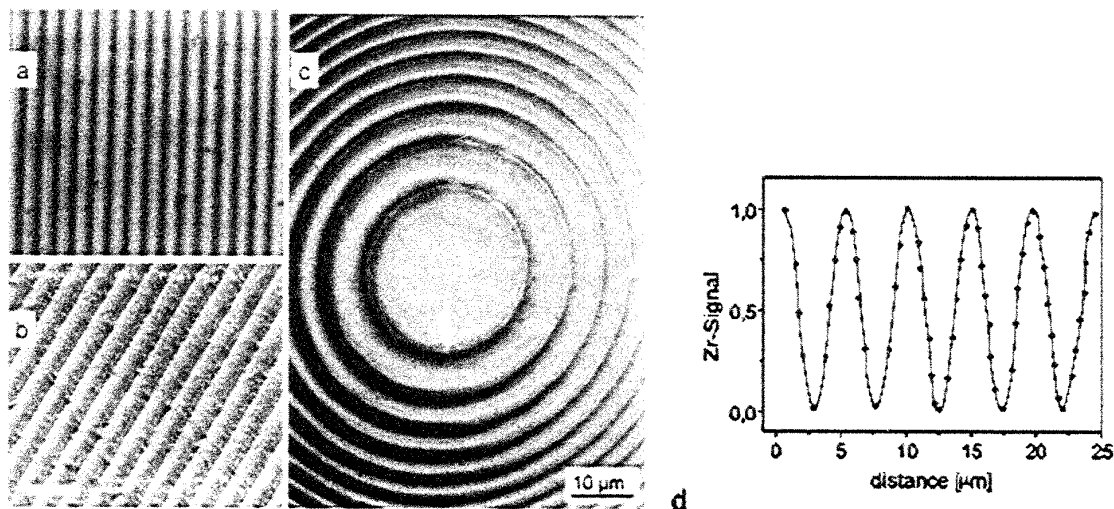


Figure 8

Microoptical component made by holographic process: (a) volume phase grating, (b) relief grating, (c) Fresnel lens, and (d) EDX line scan over a holographically fabricated diffractive grating according to (a).

formed within seconds, due to the high diffusion rates of the nanoparticles in the matrix. After the holographic process is finished, a fixation of the matrix by full-area photopolymerization takes place. In Fig. 8, some samples of the fabrication of such gratings are shown (diffraction gratings, Fresnel lenses). Alternatively, instead of being fixed after the holographic process, the gratings can be developed by dissolving the unirradiated areas. An EDX-pattern of a holographically fabricated refractive grating is also shown in Fig. 8. The concentration fluctuation of the tantalum oxide as a function of the two-wave mixing irradiation is clearly demonstrated.

As a variation of these “moving nanoparticles,” the nanoparticles also can be set into motion by electric fields, if the appropriate zeta potential is established in a non-fully-cross-linked matrix. Using this approach, gradient lenses up to 5cm in diameter have been developed (Oliveira *et al.* 1996).

2.3 Interference Coatings

The fabrication of interference coatings by sol-gel techniques on glass is very common for many purposes, for example anti-reflective coatings (AMIRAN 1998), and interference coatings on halogen bulbs. However, most of the coatings are produced by physical techniques like sputtering or waver condensation methods (such as for eyeglass lenses). This is because the technology for mass fabrication is considered to be more difficult than for physical techniques. One of the drawbacks of sol-gel techniques is that, in general, each coated layer has to be densified and prefired before the next layer can be employed. This means that a lot of time and energy has to be used in making multilayer coatings. For that reason, a technology has been developed which takes advantage of polymerizable nanoparticles, surface modified with methacrylic or epoxy groupings. Coatings fabricated from these sols can be photopolymerized a very short time after dipping or spraying, and are then insoluble against the next coating step. After the fabrication of an appropriate set of green layers, a one-step firing process can be employed on glass, which leads to multilayered interference systems. This is schematically shown in Fig. 9 with SiO_2 and TiO_2 .

Using this approach, a technology has been developed to produce anti-reflective layers for automotive glazings (Mennig *et al.* 1999). The technology can be employed also on plastics, as long as the photocuring process only is used. Due to the high package density of the “modified gels” (up to 90% of the theoretical density after UV-radiation), interference layers have also been obtained alternatively by using TiO_2 and SiO_2 . Such coatings can be produced also on conventional hard coatings, and then show extremely high abrasion resistance. It can be shown

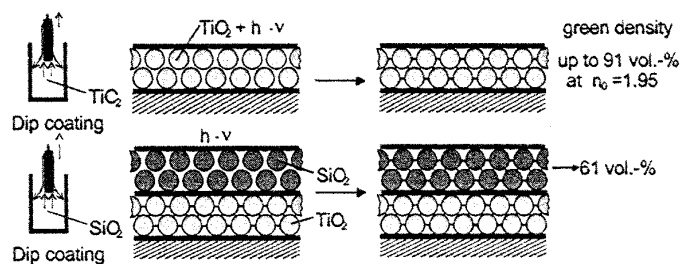


Figure 9

Scheme of the fabrication of interference layers by polymerizable nanoparticles (after Schmidt 1999).

also that the theoretical curves fit very well with the curves achieved in practice, by using the Landau-Lewich approach for calculating layer thicknesses. Taking into account the organic content, the calculations could be used for fired coatings on glass. This means that it is possible to design interference systems.

By using thicker layers, IR reflective coatings have been fabricated, which is an interesting approach for IR-shielding on plastics: for example, in the freezing industry. In this connection, it has to be mentioned that the dispersion of ITO nanoparticles, fabricated according to the processes described above, also leads to highly efficient IR-shielding coatings.

Using the nanocomposite approach, another type of anti-reflective coating was developed by the so-called “moth eye” process in nanometer surfaces combined with perfluorinated surfaces. The moth eye process leads to long-lasting anti-reflective systems only if the surface is equipped with easy-to-clean properties. Otherwise, the roughness in the nanometer range of the surface leads to dirt absorption filling out the voids and reducing the anti-reflective effect.

3. Functional and Mechanical Coatings

3.1 Hard Coatings

(a) *Thermally curable coatings.* The nanocomposite strategy for hard coatings is based on the fact that well-dispersed nanoparticles in hybrid matrices are considered to play a very important role in abrasion resistance. Schmidt *et al.* 1998 showed that boehmite particles, dispersed in an inorganic-organic hybrid network composed of epoxy silanes as basic components, catalyze epoxy polymerization at curing temperatures above 100°C , leading to a highly transparent, very scratch-resistant coating. These coatings are successfully employed for the fabrication of abrasion resistant CR-39 eyeglass lenses, and have been developed for hard coatings on polycarbonate. The coating leads to very high abrasion resistance (2% haze, or 98% transparency, after 1000 cycles of taber abrader). For this reason, the coating has currently been further developed for the use of poly-

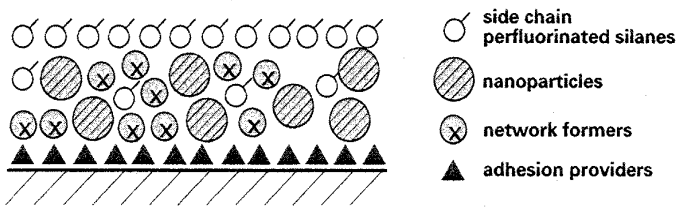


Figure 10
Scheme of a fluor gradient material.

carbonate for automotive glazing, substituting for inorganic glasses.

(b) *UV-radiation curable coatings.* If UV or electron beam curing is employed (by using photocurable organic groupings like epoxides or acrylics in conjunction with appropriate photoinitiators), photocurable hardcoatings are possible. Since these coatings are produced at low temperatures (around 60°C), the degree of inorganic network condensation is lower than in the case of temperature-cured hard coatings, leading in general to a lower abrasion resistance; but by using 10–15% of nanoparticles (by volume), the taber abrasion numbers are reduced also to about 7% after 1000 cycles, an extraordinarily high value for UV-cured hard coatings. Based on these results, a coating system for plastic lenses has been developed and an industrial process has been built up. Similar results have been obtained by electron beam curing.

By appropriate control of the drying conditions, a dry but uncured photocurable system is obtained, which has sufficient deformability to be used in deep drawing processes. By coating PMMA plates, deep drawing processes have been performed in which subsequent UV-curing leads to highly abrasion-resistant coatings on PMMA, and an industrial process has been developed.

3.2 Low Surface Free Energy Hard Coatings

Low surface free energy hard coatings are a very interesting area of application for hybrid matrix nanocomposites. As described elsewhere (Schmidt *et al.* 1991, Kasemann *et al.* 1992a, 1992b, Kasemann and Schmidt 1994), it could be shown that, based on interfacial thermodynamics, a self-alignment in layers takes place if side chain perfluorinated silanes are added, which increase in concentration at the surface as long as the concentration exceeds the critical micelle concentration. This leads to very low surface free energies of about 19 mJ m⁻² (20–22 mJ m⁻² with PTFE). The process is shown schematically in Fig. 10.

Based on this effect, various types of low surface free energy coatings have been developed (high- and low-temperature curing, UV curing, and two-component systems). All of these coatings form a gradient layer with an increased concentration of fluorine at the atmospheric side, as shown by ESCA or SNMS, and an adhesive layer to the substrates. Due to the

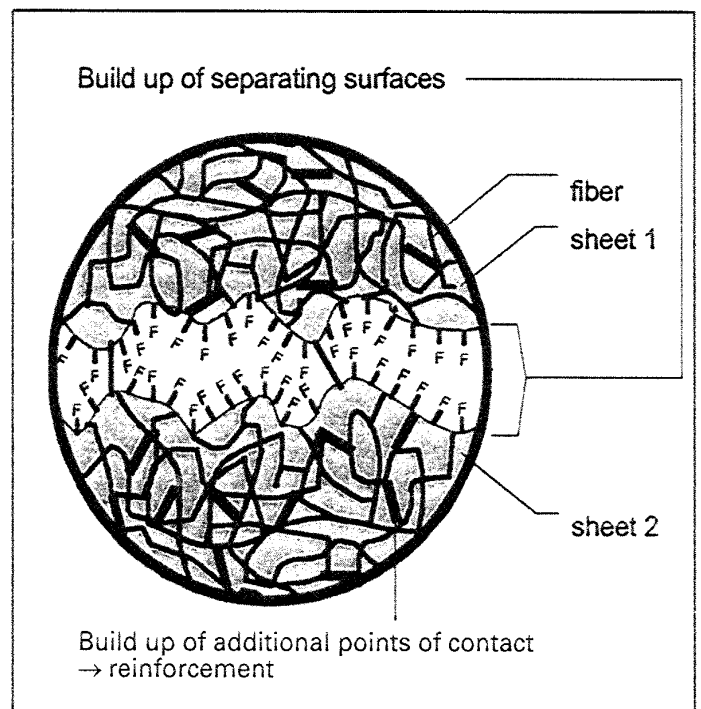
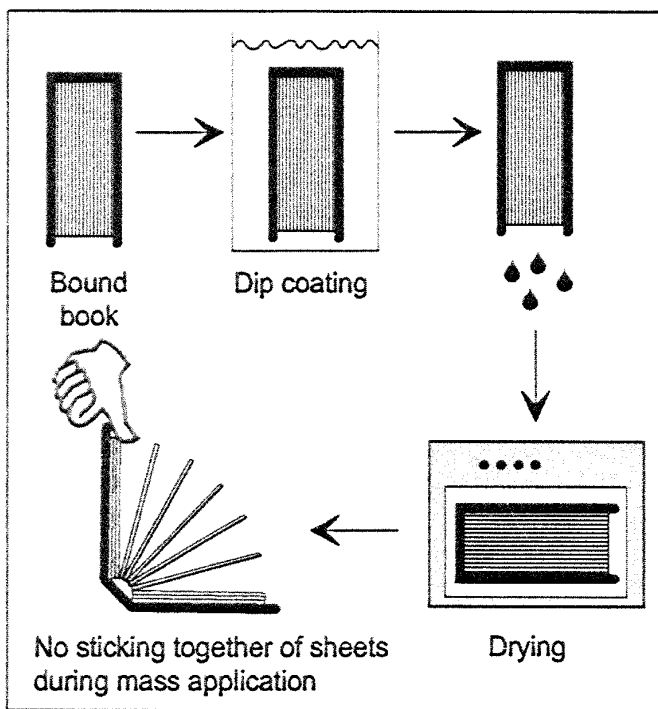


Figure 11
Scheme of paper coating: build-up of separating surfaces and reinforcement.

homogeneous distribution of nanoparticles, these systems can also be obtained with high transparency and high abrasion resistance. The contact angles of this type of coating with water are of the order of 110° , and with hexadecane in the range of $55\text{--}60^\circ$. If micro-patterned surfaces are used, the contact angles with water increase up to 160° , and with hexadecane up to 120° .

These surfaces can be obtained either by mechanical micropatterning or by the use of self-structuring effects based on appropriate nanoparticle sizes. Based on this technology, many industrial applications have been developed. These extend through anti-adhesive coatings; mold release coatings; zero-carryover coatings in capillaries, food technology, buildings and pavements; and anti-billposting coatings—all having the advantages of saving detergents and water. The coating material can be adjusted for glass, ceramics, enamel, polymers, and metals, with average thickness ranging from $1\text{--}5\mu\text{m}$. A special variation of the system is the easy-to-clean application and anti-graffiti protection in public areas (house and public building walls, monuments, railways, subway, traffic signs, etc.).

Similar coatings have been developed for mold release processes in metal molds for polyurethane, polyethylene and polystyrene foams. Other applications have been developed for anti-adhesive coatings in carpet production, for easy-to-clean windows, and for ceramic sanitary ware which has been commercialized extremely successfully (Duravit Wondergliss coatings).

Another very interesting development involves the restoration of historic books and papers. Due to the content of sulfuric acid of paper (starting about 150 years ago, as a consequence of the change in production technologies), the paper slowly deteriorates, by hydrolytic decay of the cellulose fibers. This leads to a weakening of the papers, so that in serious cases the paper sheets may even become powderized. Many attempts have been made around the world to solve this problem, for example by leaching out the acid (Batelle process), or by using plastic foils as support. In the first case no strengthening is added, and in the second case a single-sheet process has been used, by dismantling the book and then binding it after fixing the foil support. For these reasons, investigations have been carried out with the aim of combining both processes, using an infiltration process with a polymerizable resin which shows a "smart" behavior, by knowing that it has to reinforce the cellulose fibers but at the same time prevent two pages from sticking together. The problem has been successfully solved by using the self-aligning fluorinated type of coating, in combination with acrylic groupings and a thermally activated initiator, by simply impregnating the book with a reinforcing system, drying it at temperatures of about $60\text{--}80^\circ\text{C}$ (starting temperature of the radical initiator) and then drying it. The scheme of this process is shown in Fig. 11, the mechanism of the formation of

an anti-adhesive surface between two paper sheets is also depicted.

3.3 Photocatalytic Coatings

TiO_2 nanoparticles show photocatalytic activities, as has been known for a long time. Suspensions of TiO_2 have been used for photocatalytic water cleaning processes. Interesting applications of TiO_2 nanoparticles have been reported by Watanabe *et al.* (1999a, 1999b), in which TiO_2 is wet coated on ceramic tiles and sanitary ware for self-cleaning and microbicide purposes. Similar systems have been developed, based on work by Schmidt *et al.* 1995. Watanabe *et al.* 1999a showed that TiO_2 compositions have a self-cleaning effect on various substrates, especially on plastic foils, organic paints, and polycarbonate sheets.

Another area of catalytic applications is so-called non-selective catalysts, as used in oxidation catalysis. It could be shown that by the use of nanoparticulate SiO_2 -containing binder materials, transition metal oxides such as those of cobalt, nickel, and others show enhanced catalytic activities compared to systems made from pellets out of the pure oxides. This type of nanocomposite has been successfully used in exhaust systems for the deodorization of kitchens.

3.4 Conductive Coatings

Electrically conducting transparent coatings are of interest for the development of antistatic coatings, heat insulating coatings, electromagnetic shielding, and displays (touch screen panels). Polymer-based wet coatings again offer the possibility of cheap, large-area coating technologies, which up until now have not been achieved by sputter techniques. It could be shown that by use of the surface modified nanoparticle approach, thicker films and lower sheet resistances could be obtained, as compared to the classical sol-gel route. The development of transparent electrical conducting coatings of $\text{ZnO}:\text{Al}$ (AZO), $\text{SnO}_2:\text{Sb}$ (ATO), and $\text{In}_2\text{O}_3:\text{Sn}$ (ITO) with a defined sheet resistance, high optical transmission and good homogeneity, using the sol-gel process, led to coatings which can be obtained by dip- or spin-coating processes using stabilized sols. The sheet resistance can be adjusted by varying the layer thickness and the sintering temperature. These systems provide an adjustable sheet resistance ($\pm 2\%$) with high homogeneity of the thickness ($\pm 2\text{nm}$). The sheet resistance can be minimized, down to $150\text{--}200\Omega$ on float glass at 550°C for ATO and AZO, and on borosilicate and silica glass at $600\text{--}650^\circ\text{C}$. For an ITO double layer, the sheet resistance is below 200Ω , sintered at $900\text{--}1000^\circ\text{C}$ on silica glass. Substrate sizes of 1m^2 have already been dip coated. The temperature stability ranges up to

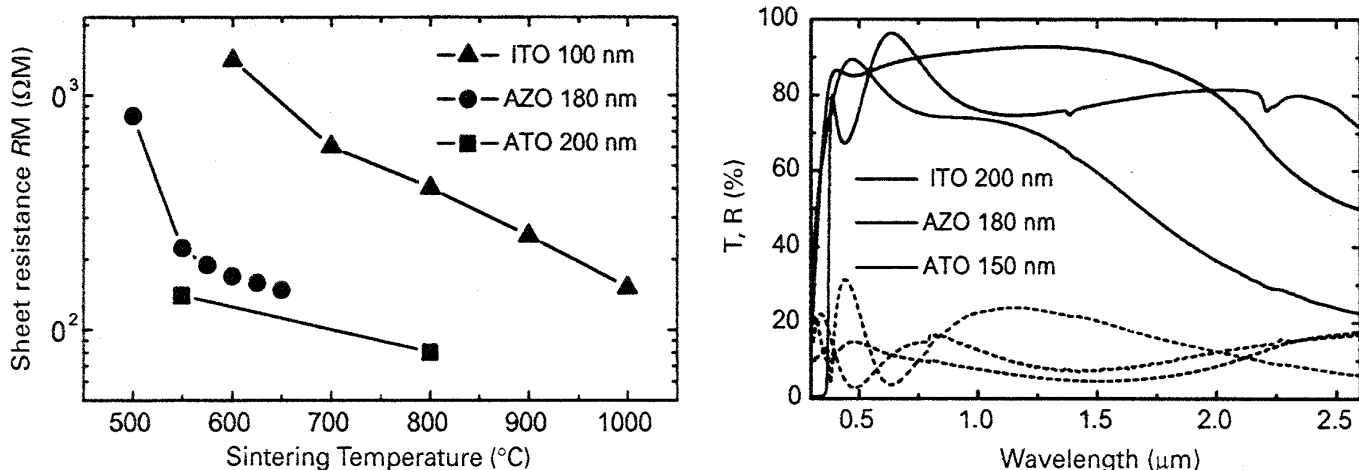


Figure 12

(left) Sheet resistance vs. sintering temperature of dip-coated SnO₂: Sb (ATO, 10 layers), In₂O₃ (ITO, 2 layers) and ZnO: Al (AZO, 10 layers) on silica glass; (right) transmission (—) and reflectance spectra (- -) of dip-coated ATO, AZO and ITO coatings.

800°C for ATO coatings, and up to 900°C for ITO coatings. In the visible range, a high transmission could be derived (Fig. 12).

3.5 Metal Colloid-containing Coatings

Metal colloids have been used for two different purposes. As known from gold ruby glass, metal colloids show high coefficients of extinction due to plasmon frequencies. The coefficients of extinction are up to 10⁶ l mol⁻¹ which even exceeds those of highly absorptive organic dyes. If these colloids are developed within a glass matrix by nucleation and growth, intensive colors can be obtained within thin sol-gel coatings. Based on this technology, an industrial process has been developed for the coloration of silicate eyeglass lenses, using different metals for different colors (gold colloids for red, silver colloids for yellow, copper colloids for green, and palladium colloids for brown). In the industrial process (Mennig *et al.* 1998b), a lead silicate glass matrix is doped with metal colloid precursors in a complexed form, and by a spin coating process a 200 nm thick coating is applied. After firing these coatings under reductive conditions, nucleation and growth take place, followed by the formation of the glass-like colored coatings. Mechanical properties of these coatings are similar to those of the substrate glass. Another interesting application of these particles is in non-linear optical materials based on gold particles (Mennig *et al.* 1994a). The fabrication of nanoparticle-containing coatings can be carried out by doping of the sol-gel precursors with gold complexes, and gold colloids can be grown in a glass matrix as well as in hybrid matrices. Other developments for materials with high χ^3 -nonlinear optical effects have been obtained by growing gold nanoparticles in hybrid matrices. For this process, precursor complexes from

aminosilanes with AuCl₃ were synthesized. After dispersing these complexes in TEOS and methacryloxysilane-containing systems, coating liquids were fabricated by hydrolysis and condensation. After coating and drying, photopolymerization of the methacrylic groupings was carried out. During this period a nucleation and growth process of gold particles took place, and gold particles of several nm in diameter were produced (Mennig *et al.* 1994b). The χ^3/α coefficient of $\chi^3/\alpha \approx 10$ (10⁻¹⁴ esum) could be obtained.

3.6 Coatings for Corrosion Protection

The possibility of the molecular design of polymer-based composites on the nanometer scale allows the adhesive forces to the substrate to be optimized. Various systems have been developed in order to stop corrosion processes on metallic substrates. The corrosion process itself occurs in the presence of an electrochemical couple, i.e., in the presence of metals that have a high tendency for the exchange of electrons. This setup is equivalent to an electrochemical cell, with electron donors and acceptors. Due to the change of the ionic state at the metal surface, chemical reactions take place (passivation). Metal oxides are formed, which lower the metallic properties of the components (strength, toughness, color, etc.). The transport of electrons takes place effectively in the presence of a polar liquid, e.g., water. Therefore, an effective corrosion protection system will prevent contact of water with the metal surface and so prevent electron transfer and the formation of corrosion products. Polymer-based nanocomposites have been developed which provide excellent adhesion forces, which can be tailored to various metals.

Additionally, anti-adhesive "easy-to-clean" properties can be built into these coatings. Many other systems have been developed, e.g., as tarnish

protection on silver, brass, and magnesium. The nanocomposite works without primer and has good adhesion to metals, offering high mechanical resistance at low coating thickness (approx. 5–10 μm). A special development is based on surface-modified SiO₂ nanoparticles, as described in Sect 3.2. These films can be densified at 500–600 °C. Highly scratch-, tarnish-, and corrosion-resistant coatings for stainless steel have been prepared. The coatings are 3–5 μm thick and very flexible. Another coating composition has led to anti-fingerprint coatings on stainless steel. Further advantages of this system lie in the application as an electrical isolation layer for high temperature applications on stainless steel, mild steel, copper, brass, and aluminum alloys. Compared to hardening of steel chromium plating, the glass coating shows an increased wear resistance. The decorative appearance of glossy steel surfaces is obtained up to 600 °C.

4. Hybrid Nanoparticles

4.1 Processing Aids

As described before, the surface modification of hybrid particles is one of the key issues in processing these particles to obtain desired materials and desired functions. In many cases, the particle consists of an inorganic core and an organic shell. These particles can also be defined as hybrid nanoparticles. This definition is used if the hybrid particle plays an important role in processing or in the final properties. In the field of ceramics, sintering temperature and mechanical performance play an important role. Many investigations have been devoted to reducing the sintering temperatures by reducing the particle size. However, in most cases the package density becomes a serious problem. For this reason, it was investigated how to use hybrid nanoparticles as ceramic precursors. As shown by Nass *et al.* (1995), with titanium nitride as an example, nanotitanium nitride coated with guanedinocarboxylic acid leads to package densities in colloidal shaping processes up to 60% by volume. These relatively densely packed matrices could then be densified to titanium nitride compacts or coatings at temperatures from 1200–1350 °C, showing that by hybrid nanoparticle processing, substantial reductions of sintering temperatures could be obtained; and it could be shown also that grain growth could be “separated” from the densification step. The grain growth takes place mainly above 1350 °C.

In the case of silicon carbide, it could be shown that nanometer-size carbon particles coated with carboxylic acids could be linked to silicon carbide surfaces containing amino groups, in such a way that wet processing did not lead to bleeding of the carbon black during slip casting. By using an appropriate concentration of carbon black, suitable for the stoichio-

metric reduction of the SiO₂, always present on silicon carbide particle surfaces, a slip casting processing route was developed which leads to near net-shaped large silicon carbide parts (Nass *et al.* 1994). Silicon carbide igniters based on this technology shows superior properties to those previously available (500 000 ignition cycles without rupture).

4.2 Medical Applications

Nanoparticles are interesting for medical applications for many reasons. One is that for *in vivo* applications they can be transported in the blood stream without any problems, can even pass important barriers and are not filtered out very easily. Moreover, with appropriate surfaces they may penetrate even cell membranes. Based on these considerations, amino-grouping-modified superparamagnetic iron oxide nanoparticles have been fabricated, and investigations have been carried out for transporting them into tumor cells (Lesniak *et al.* 1998). It has been shown that billions of nanoparticles penetrate tumor cells. By employing an alternative magnetic field, heat could be introduced into the cells and they could be selectively destroyed by heat. It was also shown (H. Jordan, personal communication 1998) that if the tumor cells divide, both daughter cells share the load of iron oxides.

Another technology is the use of SiO₂ nanoparticles, the surface charge of which is tailored by amino grouping modification in such a way that genes can be concentrated on top of the nanoparticles, leading to gene-plasmid clusters of about 80 nm in diameter. This is a substantial reduction from the original gene plasmids with a diameter of 200–250 nm. At this size, the nanoparticles could be used for the transfection of gene plasmids into cells with a very high transfection rate (Kneuer *et al.* 1999). The advantage of this technology is the fact that the SiO₂ is completely non-poisonous compared to polyethylene imines as gene carriers. An example of this coupling is the electrostatic bonding of glycoproteins (e.g., avidin) on top of a negatively charged SiO₂-nanoparticle. Avidin provides four sites for the chemical bonding of other groupings (like biotin/WGA-complexes) or DNA-fragments or genes (like WGA: wheat germ agglutinin). The aim of this approach is the destruction of cancer cells by pharmaceuticals. The coupling of biomolecules can be proved by electron microscope investigations.

Hydroxylapatite has been fabricated from nanoparticulate calcium phosphate precipitates and, using sol-gel binders, these nanoprecipitates have been used for fabricating thin films on titanium implants in thicknesses of about 5 nm. This thickness has great advantages compared to plasma- or flame-sprayed thick films, because it adheres very well on the surface

and no cracks are formed. First results in using these implants show that a very fast incorporation into the tissue takes place (Nonninger *et al.* 2001).

5. Conclusion

Nanoparticles are of great interest for many applications, either for use by themselves or by being processed to parts such as in ceramics, or by being used in the form of nanocomposites in various matrices. Because nanoparticles of many different compositions can be used, a wide range of properties can be developed for materials. Chemical fabrication routes for nanoparticles are very interesting, since they are mainly based on precipitation techniques which can be performed quite cheaply. One of the key issues is the surface modification of nanoparticles, since that is the crucial point in controlling aggregation. The application of these principles to the development of materials will be a very important and interesting prospect for the future.

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