Chemical routes to nanostructured materials

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Chemical synthesis has been used to fabricate polymerisable nanoparticles. Agglomerate free, well crystallised particles have been obtained by hydrothermal treatment and by using surface modifiers. Polymerisable liquids are used as modifiers to obtain polymerisable particles. Suspensions of these particles were used to carry out dip and spin on coating processes, either for optical applications or for superhard coatings. For optical purposes, a wet coating antireflection technology has been developed. The superhard coatings have been developed for polycarbonate plastic glazing for automobiles. These coatings are employed on top of nanocomposite (Nanomer) hard coatings and are cured by UV polymerisation. They show abrasion resistance of 1·5 haze after 1000 taber abrador cycles, a value which is similar to glass.

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Introduction

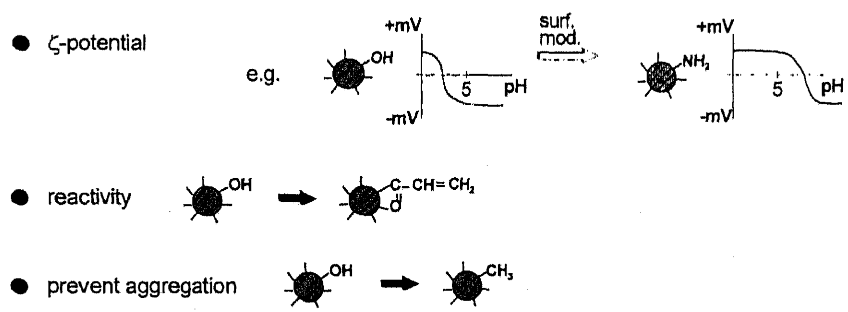
Nanostructured materials have gained a high significance during the last decade. They are mainly investigated by using nanoparticles which have been synthesised through gas or vacuum phase reactions.[1-7] One of the drawbacks of these materials is that agglomeration has been very difficult to control. The fabrication of nanostructured materials by wet chemistry involves the same problems as those known to be involved in the sol–gel route, i.e. it is very difficult to control agglomeration of sol particles during the gelation to prevent the production of hard agglomerates.[8] This is because of strong particle–particle interaction involving the formation of various types of chemical bonds, such as ionic bonds, hydrogen bonds, or strong dipole interactions. To overcome these problems, particle–particle interaction has to be reduced to Van der Waals forces or bonds that are easily overcome in an appropriate media. One example would be ionic bonds in liquid media with high ionic strength. For this reason, a surface modification of the nanoparticles would be an appropriate means.

To tailor the properties of nanoparticles by surface modification, the surface modifier has to be carefully selected. The role of modification is shown in Fig. 1. The surface modification, for example, can affect the surface charges of nanoparticles. A suitable surface charge is indispensable for maintaining the stability of colloidal solutions at a given pH value. This is of great importance for the processing of nanoparticles in liquid systems (which resembles a colloidial system), since at the point of zero charge, flocculation or aggregation takes place. The second important topic is that by surface modification, the reactivity of the particles can be tailored in many ways. For example they can be made polymerisable, or reactive to form bonds to organic molecules like monomers, biochemical molecules, or to spacers. The same principle is of importance if nanoparticles are to be compounded into polymers in order to get sufficient dispersion. If the surface is modified by unreactive groupings, hard agglomerates can be avoided totally. To reduce particle–particle interaction it is of high importance for dispersing nanoparticles in liquids, e.g. for optical coatings in order to avoid light scattering. Based on this idea, many new materials for optics will be possible. As shown elsewhere,[9] nanoparticles also can be used in matrix systems to catalyse reactions (for example, epoxide polymerization by boehmite)[10] to form poly(ethylene oxide) networks for hard coatings on polycarbonate and CR 39 (eye glass lenses).[11]

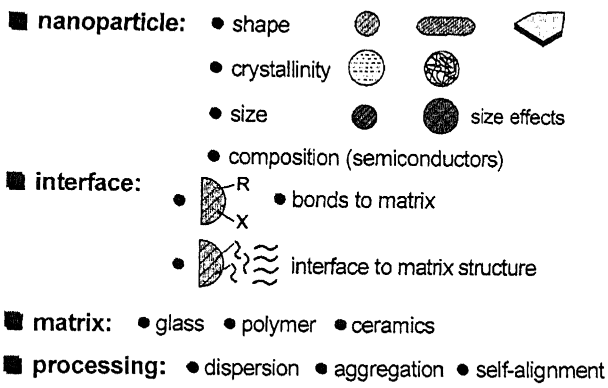
The composition and shape of the nanoparticles also can be used for tailoring materials. Figure 2 summarises four main uses of nanoparticles in materials tailoring, including selforganising effects, e.g. for the fabrication of gradient materials. Gradients also can be obtained with nanoparticles, e.g. by electrophoretic means with subsequent polymerization of the matrix, two wave mixing for holograms,[12] or thermodynamical effects as shown in low surface free energy coatings.[13]

Material development and application

One of the most interesting questions in connection with nanoparticles, is how to make a material form these



1 Overview of effect of surface modification of nanoparticles



2 General survey about tailoring materials through nanoparticles

finely divided systems. As mentioned above, agglomeration and aggregation are the crucial points in these systems. As one knows from the sol–gel process, colloids can easily be processed to gels but the solid content of the gels is low and they are porous.[14] By organic modification of these gels, densification can be carried out at low temperatures but the organic content of these systems is rather high, in general more than 50 wt-%.[15] The problem therefore is whether it is possible or not to end up with high inorganic contents without using easy to process high temperatures in order to maintain properties. For this reason, investigations have been carried out to photopolymerise nanoparticles. The surface modification of nanoparticles by polymerizing groupings is a well established method to incorporate nanoparticles into polymers.[16–20] Recent investigations have shown that nanoparticles coated with monomolecular layers of polymerisable molecules can be used for the formation of layers with surprisingly high densities. For this reason particulate sols from TiO_2, zirconia, or silica have been fabricated by hydrolysis and condensation of appropriate alkoxides as shown in Fig. 3. Another way is to fabricate sols by redispersing nanopowders.[21]

These particulate sols with particle diameters of 5–10 nm have been subsequently treated with epoxy or methacryloxy silanes at room temperatures for several hours. This leads to a surface modification of the particles by the silanes. The thickness of the layer is estimated to be in the range of several angstroms only. This means that the contribution to the particle volume of this coating is low. The modified sols can be used for coating techniques in the same way as the unmodified sols (for dip and spin coating). After the addition of UV initiators (irgacure type Ciba) the coatings can be UV polymerised to solid layers. Investigations of the density of the coatings through refractive index measurements lead to the conclusion that the ceramic density is, in the case of TiO_2 or ZrO_2, at >90%. Investigations by high resolution electron microscopy show that an almost dense microstructure in these coatings are obtained (Fig. 4).

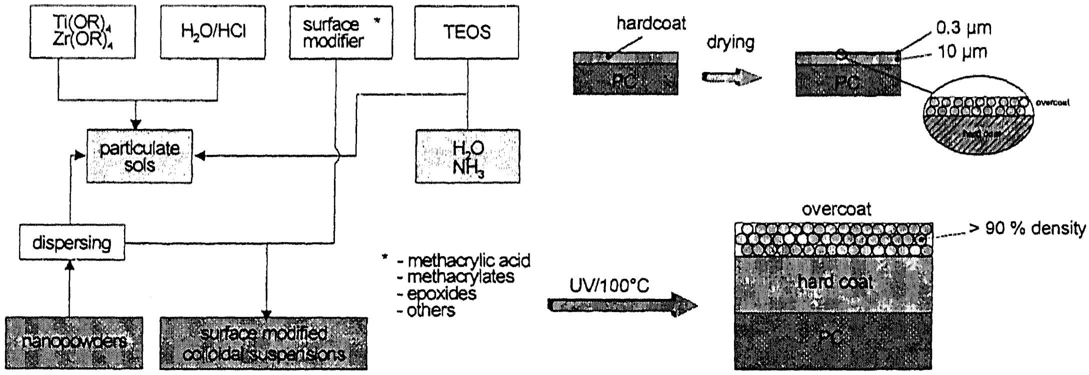
The crystallinity of the system is very high and in this case shows a pure anatase structure. The refractive index of the systems is up to 1·95. These systems now can be used for the fabrication of interference layers since the difference to silica containing nanoparticulate coatings with a refractive index of 1·46 is sufficient to tailor optical coatings.[22]

Based on these results, wet coating technology for the fabrication of antireflective (AR) coatings on eye glass lenses has been developed since, on plastic eye glass lenses in general, hard coatings by a wet coating technique have to be employed anyway. The new technology opens up the possibility to fabricate in a rational way entire reflective coatings on eye glass lenses with one and the same technology. In the most cases, hybrid technologies are still used which involve the application of hard coatings by wet chemistry followed by a vacuum technique for the fabrication of all the reflective layers.

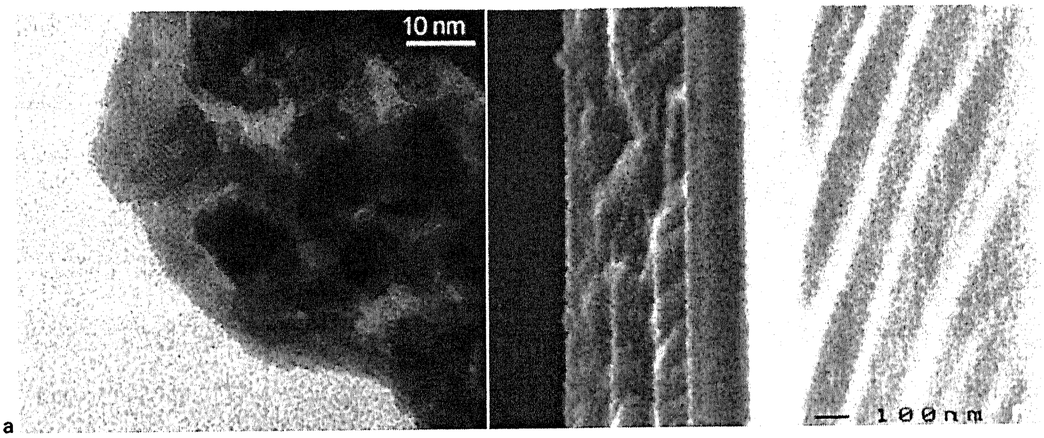
The scratch resistance of the AR coatings directly deposited on plastics is fair but not excellent. However, if the AR coatings are deposited on hard coatings, the scratch resistance is improved remarkably. This also has been used to improve the abrasion resistance of hard coatings on plastics and metals substantially (from 2–4% haze after 1000 cycles taber abrader down to 1·5%), which is the value obtained by float glass. The additional effect of the top coating is attributed to the high density of the coating and the tapered modulus of elasticity ranging from the low value of plastic substrates (~200 MPa), to the hard coat (about 1–3 GPa), to the overcoat of an estimated modulus close to glass.

Conclusions

This example of material development of nanocomposites (nanomers) shows that there is a huge potential in the fabrication of new and innovative materials for the future. The possibility of choosing any type of nanoparticles (ceramics, semiconductors, metals, and others) opens up a very interesting field for new material fabrications. In combination with appropriate processing techniques and tailoring of the interface, a new generation of nanostructured materials becomes accessible.



3 Process to produce surface modified particulate sols[10] for layers with high densities and sequence of coating for fabrication of ultrahard coatings



4 *a* high resolution TEM micrograph of cross-section of a TiO_2 layer; *b* five layer stack of different compositions for AR coating for eye glasses: TiO_2, TiO_2-SiO_2, and SiO_2

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