NANOCOMPOSITES FOR COATINGS AND OPTICS

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INTRODUCTION

The preparation of optical materials has to follow only one important requirement. The materials have to be transparent for the considered wavelength. In oder to obtain this, the phase dimension of these materials has to be considerably below the wavelength of the light to be used in order to avoid Rayleigh scattering. This simple requirement for a long time only could be fulfilled by glasses, single-crystals or some polymers the phase dimension of which is below 30 or 20 nm. With up-coming new technologies for the fabrication of dispersed materials with very small particle or pore sizes, a variety of new materials can be considered to be interesting for optics. One of the candidates are inorganic gels, for example produced by the sol-gel process [1, 2]. Depending on processing techniques, pores in gels can be made small enough to avoid light scattering, and if these pores are filled by components with optical functions, for example, lasing dyes [3], composite materials with high optical transparency and special functions can be produced.

Another example are solid particles, developed in inorganic or organic matrices [4, 5, 6]. Colloidal metals in glasses or organics, such as gold, silver or palladium can be of interest for reasons of intensive colours or non-linear effects. If the metal particle size is kept in the lower nano range, a transparency is not effected.

Summarizing, it is to say that if it is possible to keep the phase dimensions small, even composite materials can be of high optical transparency and, in addition to this, can show interesting optical effects. The focus of this paper is to show how to prepare various types of materials in small dimensions to prepare coatings, to incorporate them into optical transparent matrices and to fabricate passive or active optical components.

GENERAL PRINCIPLES

If small ceramic semiconductor or metal particles have to be fabricated, a variety of methods can be used. All these methods have to have in common that particles are

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produced which are completely agglomerate-free since agglomerates enlarge the phase dimension and lead to undesired light scattering. Methods for preparing nano-scale particles are gas phase reaction, which, in most cases, produces heavily agglomerated particles if the yield of the fabrication method is increased into technically relevant dimensions. Precipitation processes from the solution lead to nano-scale particles, too, but also suffer from heavy agglomeration if one has to work in high concentrations in order to increase the volume yield. Agglomerate-free nano-scale particles of different shape can be obtained in very diluted solution [7]. Agglomeration in precipitation processes from solution takes place very rapidly if the surface of the growing particles is highly reactive, and, for example, covered by OH groups.

To solve these problems, the concept of the small organic molecule surface modification has been developed, as shown in fig. 1.
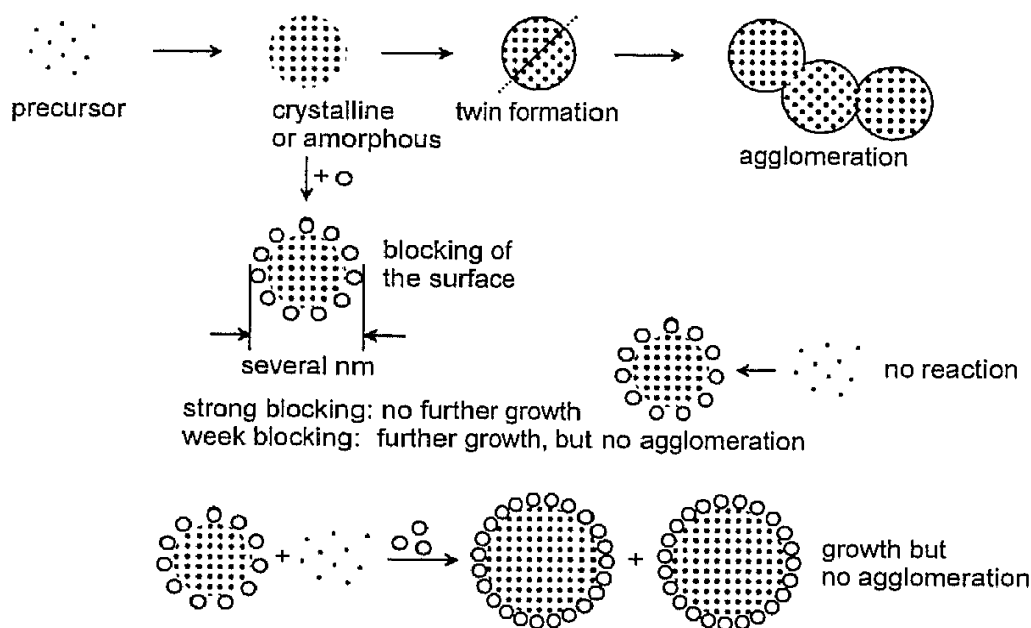
precursor   crystalline   twin formation
             or amorphous
             ↓ + o

             blocking of
             the surface

→   several nm   ←
strong blocking: no further growth
week blocking: further growth, but no agglomeration

                                    no reaction

                                    growth but
                                    no agglomeration

Figure 1. Concept of small organic molecule surface modification; ● inorganic units; o small organic molecules.

Precipitation from solution takes place after nucleation. The crystal is growing due to the decrease of the free energy of the system as long as the system is supersaturated, a status which can be maintained by reactions producing insoluble monomers (for example, by sol-gel techniques, e.g. hydrolysis of alkoxides such as titania, alumina and others). Since the particles are very small at the beginning, the surface free energy of the system is rather high, and the particles tend to reduce their surface free energy by growing together (for example, twin formation or agglomeration). If at a special state (for example, in the nano range) additives are added which react with the surface and are able to reduce the surface free energy to a level below the level obtained by the growing particle, the reaction simply stops, and no further growth takes place. If the bond to the surface is rather weak, a growth can take place, but agglomeration can be avoided by proper choice of the additives.

Chemistry provides a large number of means to modify the surface of small particles and, as is has been shown elsewhere [8, 4], complexing ligands can be used which still remain fixed to the surface after colloid formation. In fig. 2 this principle is illustrated.
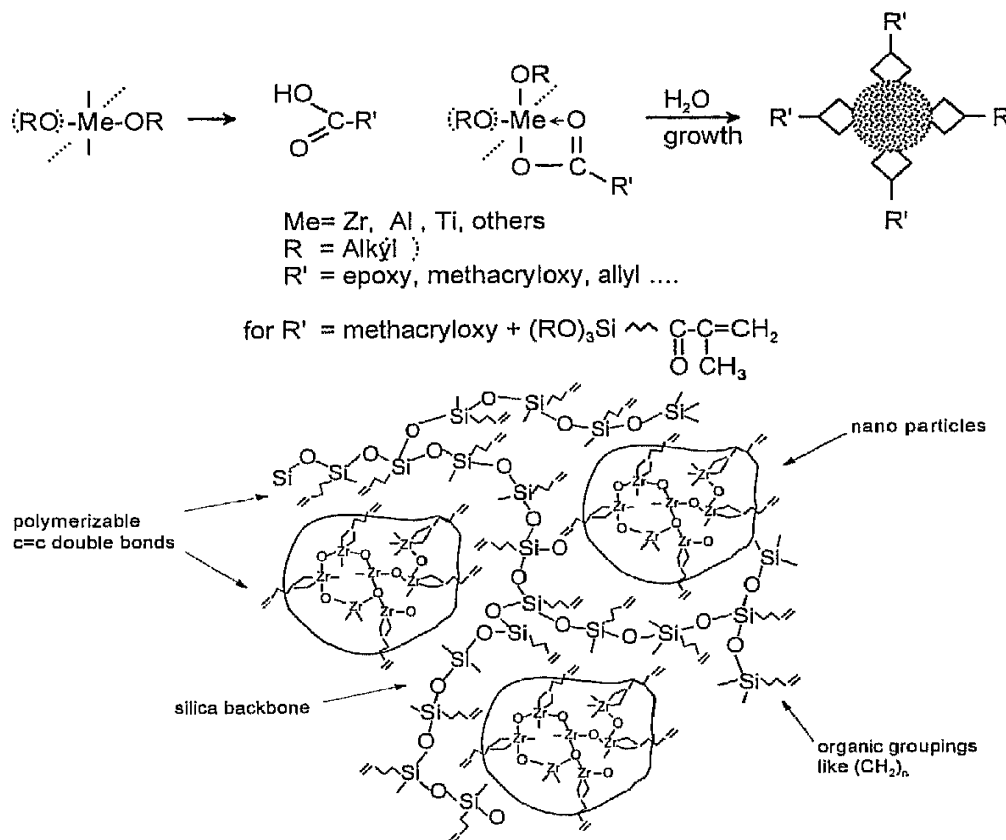
Me= Zr, Al, Ti, others
R = Alkyl
R' = epoxy, methacryloxy, allyl ....

for R' = methacryloxy + (RO)₃Si $\sim\sim$ $\underset{\underset{O\ \ CH_3}{||\ \ |}}{C-C=CH_2}$

polymerizable
c=c double bonds

silica backbone

nano particles

organic groupings
like (CH₂)ₙ

Figure 2. Schematics of the formation of ZrO_2 nanoparticles from Zr alkoxides using the controlled growth approach [after 4].

By proper choice of ligands, polymerization reactions can be used to cross-link the ligands to each other. If noble metals are used, for example, after crosslinking the metals can be reduced to atoms, and solid materials are obtained. In the case of ZrO_2, the particle size can be adjusted between 2 and 50 nm [9]. Similar results are obtained with metals from salts or complexes as far as they can be reduced. By heat treatment, for example, the nucleation process in $[AuX_4]^-$ complex containing ormocer films can be initiated, and metal clusters can be formed in polymeric matrices. In fig. 3, a gold colloid in an ormocer matrix [6] is shown. The particle diameter is about six nm.
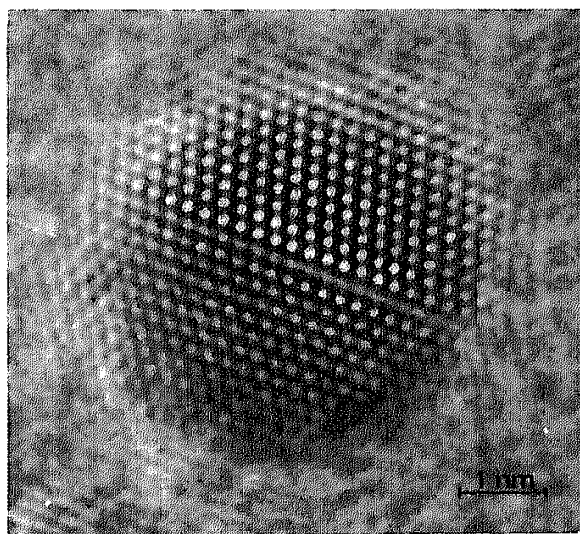

Figure 3. HRTEM micrograph from an Au cluster containing ormocer film [after 6].

What one can clearly see from this high-resolution TEM micrograph is the fact that close to the surface of the gold particle, the crystalline microstructure gets more and more disordered. In this case a twin formation has taken place.

The gold particles have been prepared from a gold amino complex where the amino group is linked to a silane (γ-ethylene aminopropyl triethoxysilane). The complex has been co-condensed with glycidyloxypropyl triethoxysilane, and the epoxide has been reacted to polyethylene oxide, forming a polyethylene oxide SiO_2 hybrid matrix. The only partially condensed system and polymerized to a viscous liquid was used for coatings. By heating up this film, the gold is reduced by organic molecules in the system (alcohols as solvents), and further heat treatments lead to nucleation and the gold colloid formation, and full condensation is obtained by this step, too. The gold colloid formation in ormocer films also has been observed by Mackenzie [5].

Another general principle is the use of sol-gel processes for small particle formation, as it has been shown with zirconia [10]. This principle can be used for other metal oxides, too, and, as it has been proved in the case of zirconia, crystalline particles are growing at temperatures around 120 °C, showing a monoclinic crystal structure. As shown in NMR and infrared studies, there are no indications that free methacrylic acid is present in the system. The CO frequency and the 13-C NMR signal show that methacrylic acid is still present in about the initial concentration. This result only can be interpreted that the methacrylic acid is bonded to the surface of the nanocrystalline particles. Similar results have been found with propionic acid for Al_2O_3 [8]. The particle size of the zirconia can be tailored by the concentration of the methacrylic acid and the reaction conditions like the water concentration. In other studies, it has been found that the colloidal particle size of gold or silver depends strongly on the ligand concentration, too. The influence of the ligand concentration on particle size depends strongly on the type of ligand.
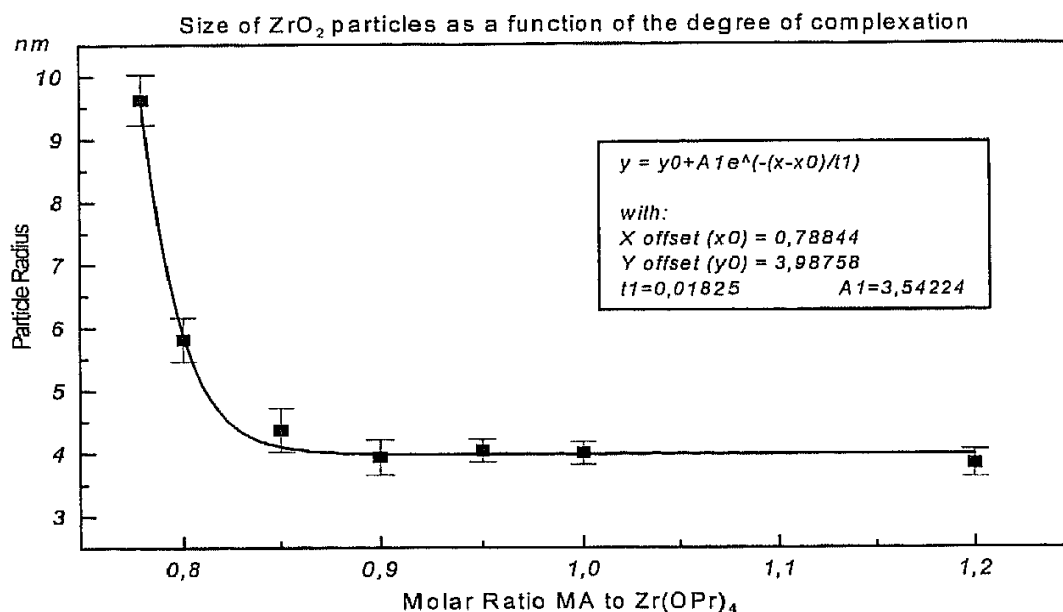

Figure 4. Dependence on colloidal particle size obtained by hydrolysis of Zr alkoxides in presence of methacrylic acid [after 9].

These results can be interpreted by a Gibbs free energy minimum, obtained by a specific surface coverage. It is assumed that through the interaction of the surface with the ligands a stabilization of the surface can be obtained and optimal surface coverage exists. If the optimal surface concentration is the driving force of the reaction, the particle size

produced by a reduction process depends on the ligand concentration. This approach the first time has been demonstrated on sol-gel derived alumina with ß-diketones. In this case, ethyl acetoacetate has been used as complexing ligands [11]. It has been shown elsewhere that acetylacetone also can be used for particle size control of ZrO_2 in the μm range [12] as well as in the nm range [9].

In connection with bifunctional ligands, the synthesis principle can be used to produce tailored particle sizes and at the same time to establish special surface reaction possibilities on the colloidal systems. If groups with double bonds are used, polymerization reactions can be carried out, for example, with methacrylates, and photolithographic processing becomes possible. Similar reactivities can be obtained with epoxides. If reactive silanes are used as a second function, the particles can be used as a new type of sol-gel precursor. The different type of reactivities leads to elegant ways to incorporate the colloidal particles into a variety of matrix systems (sol-gel derived glass systems, ceramic systems or composite systems).

The third type of the tailoring of the reactivity of colloidal particles is shown in fig. 5. Using colloidal SiO_2 and modifying it with $\equiv$Si-CH_3 leads to sols with substantially reduced particle-to-particle interaction.

→ dense layers
→ 3-5 mm thickness
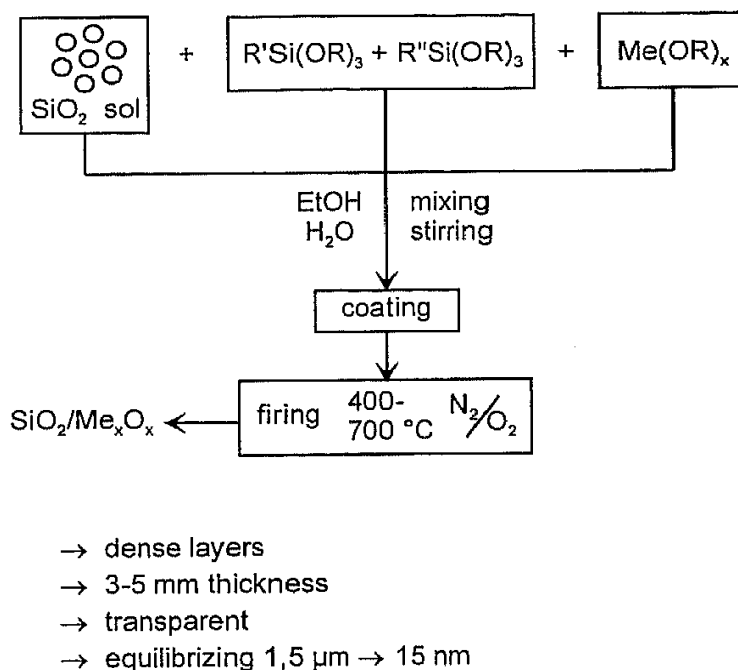→ transparent
→ equilibrizing 1,5 μm → 15 nm

Figure 5. Schematics of the surface modification of aqueous or alcoholic SiO_2 sols [after 13].

It shows the surface modification of colloidal silica particles in order to control the particle-to-particle interaction. This becomes of importance if high solid systems should be prepared, which, in general, is one of the drawbacks of sol-gel processing. If methyl groups are used as surface modifiers, it has been shown that high solid content low viscosity clear sols can be obtained [13]. As it has been shown recently [14], thick layers up to 30 μm can be produced in a one-step coating process, and patterning can be carried out by embossing. Using this technique, SiO_2 waveguides can be produced in a very easy way. The embossed layers can be cured to pure SiO_2 at comparingly low temperatures (500 - 700 °C). This low curing temperature is not quite well understood, but it is attributed to nano or sub-nano pores, obtained by the burn-out of methyl groups. In fig. 6 the schematics of the layer and micropatterning process is shown. The progress of layer

thickness is achieved by the increased solid content (> 50 wt. %), and the increased relaxation behavior due to the surface modification.
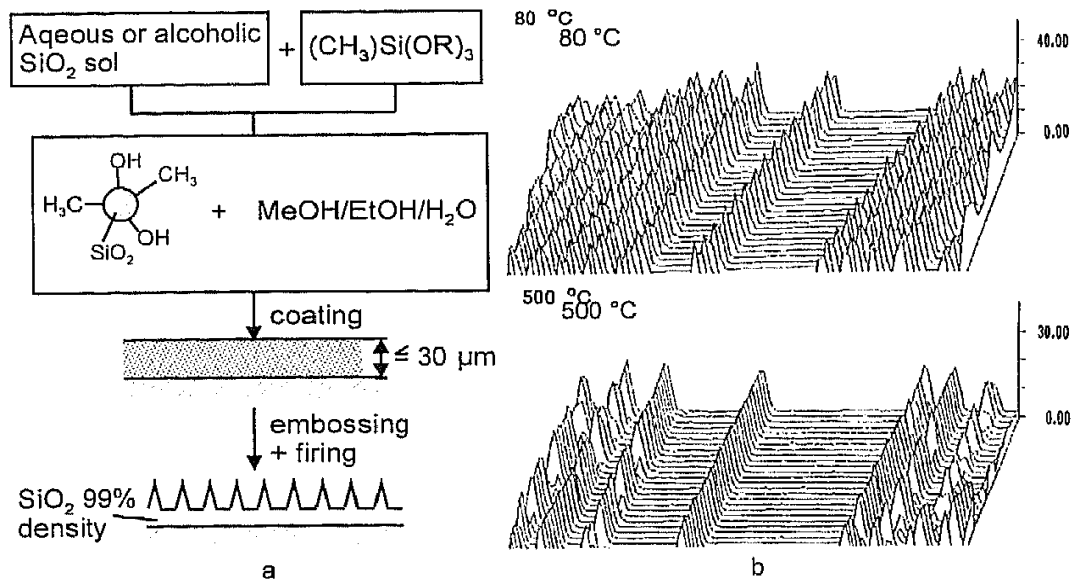

Figure 6. Schematics of the modification of the surface of SiO_2 particles and embossing of the non-cured films. After embossing the patterns can be cured to 99 % SiO_2 (according to the refractive index without changing their shape).

MATERIAL AND PROCESS DEVELOPMENT

The general approach of using interfacial thermodynamics to control the growth and the reactivity of colloidal particles can be used for many aspects. It can be used for controlling the particle-to-particle interaction, as already shown in the case of SiO_2. The extention of this principle to zirconia or titanium nitride has been investigated [15]. It could be shown that by appropriate surface modification, nano-scale titanium nitride (with particle sizes of about 30 nm) can be completely dispersed, and green densities of these "gels" by colloidal filtration of 60 % by volume after drying have been obtained. The titanium nitride surfaces covered by a very thin layer of titanium oxide, and for this reason, guanidino carbonate has been used as surface complex former forming strong bonds with Ti^{4+}. The surface modification with this short organic molecule firstly effects the complete dispersion of the agglomerated as received powder to the primary particle size and, secondly, reduces the particle-to-particle interaction to obtain high packing densities of 60 % of theory. These green compacts can be densified pressureless at temperatures of about 1250 - 1300 °C to almost complete density, and the most surprising effect is that almost no grain growth takes place. This seems to be contradictionary to the thermodynamics but has to be explained by a displacement mechanism of the atoms close to the surface, as known from nanocrystalline metals [16]. Due to the small particle size, the surface volume is remarkable and sufficient for a densification based on a displacement mechanism rather than on diffusion. By increasing the temperature above 1300 °C, rapid grain growth takes place, as to be expected. This leads to the possibility of separating "densification from crystal growth" and leads to an additional degree of freedom for processing ceramics. The principles of the surface modification of titanium nitride nanoparticles by guanidino carbonate is shown in fig. 7 as well as the effect of the surface modification on dispersion.
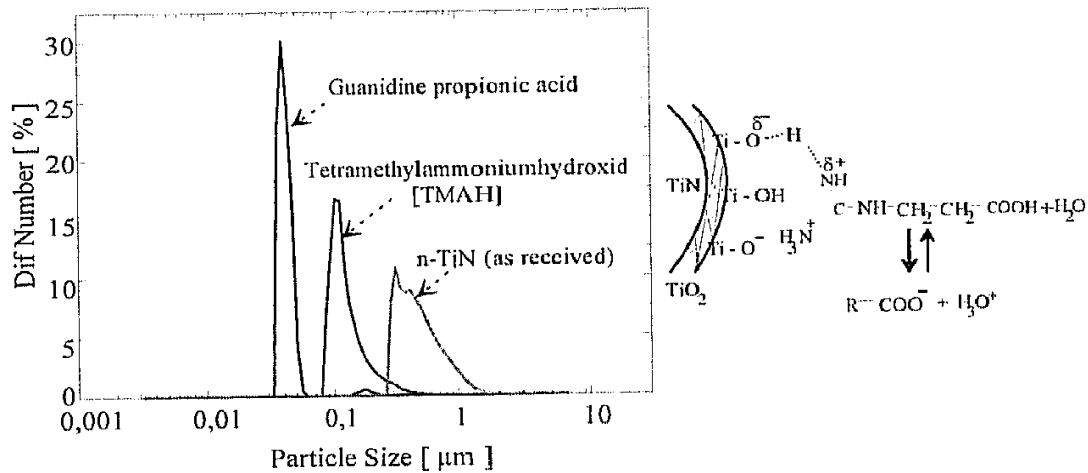
Figure 7. Surface modification of n-TiN by guanidino carbonate. The use of other ammines does not lead to complete dispersion [after 15].

The surface-modified sols also can be used for carrying out coatings, and in fig. 8 aluminum oxide coated by a titanium nitride sol is shown after densification in comparison to CVD coated Al_2O_3. The SEM micrograph shows the very fine crystal structure of the sol-gel coating compared to the CVD derived product. The irregular texture of the sol-gel coating is due to the aluminum oxide microstructure.
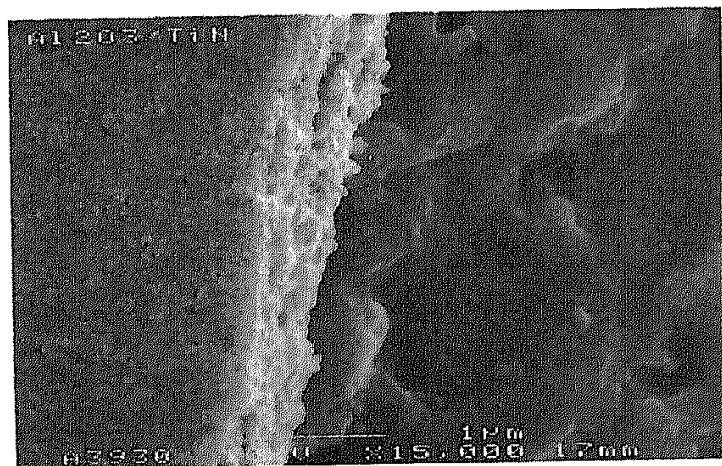

Figure 8. TEM micrograph of a sol-gel TiN coating on Al_2O_3 after 1,150 °C densification.

The described principle of handling nanoscale ceramic particles can be generalized and has been employed for zirconia [17] and alumina [18] processing.

As already described in the previous chapter, the surface modification of nano-scale particles also can be used for incorporating the particles into transparent matrices. Based on this principle, a variety of transparent coatings and optical materials have been developed. Depending on the desired properties, nano-scale particles can be used for a variety of purposes. For example, for the mechanical protection of optical components made from polymers, hard coatings are required. One of the major application areas are ophthalmics. Many investigations have been carried out to improve the scratch resistance of ophthalmic lenses. The deposition of inorganic coatings by vacuum or CVD techniques did not lead to satisfying results since the differences in the material properties between the coating (extremely brittle, but very hard) and matrix (ductile, but very soft) are not

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compatible. Liquid-phase hard coatings have been used for many years for the protection of ophthalmic lenses. It was of interest to investigate as far as nano-ceramic polymer matrix nanocomposites are able to improve the performance of liquid-phase hard coatings [19]. For these reasons, investigations are carried out to use alumina nanoparticles for the reinforcement of inorganic-organic composite matrix based on the ormocer principle. The results show that using this principle, a substantial improvement of the hard coatings could be obtained [20]. The effect is attributed to a very special structure of the material based on the fact that boehmite particles act as polymerization catalyst for the epoxide, forming a very special interface. Since the increase of hardness cannot be explained by the pure addition of the nano-scale filler, the effect is obtained by 5 % by volume only. The microstructure has been proved by IR and NMR analytics.
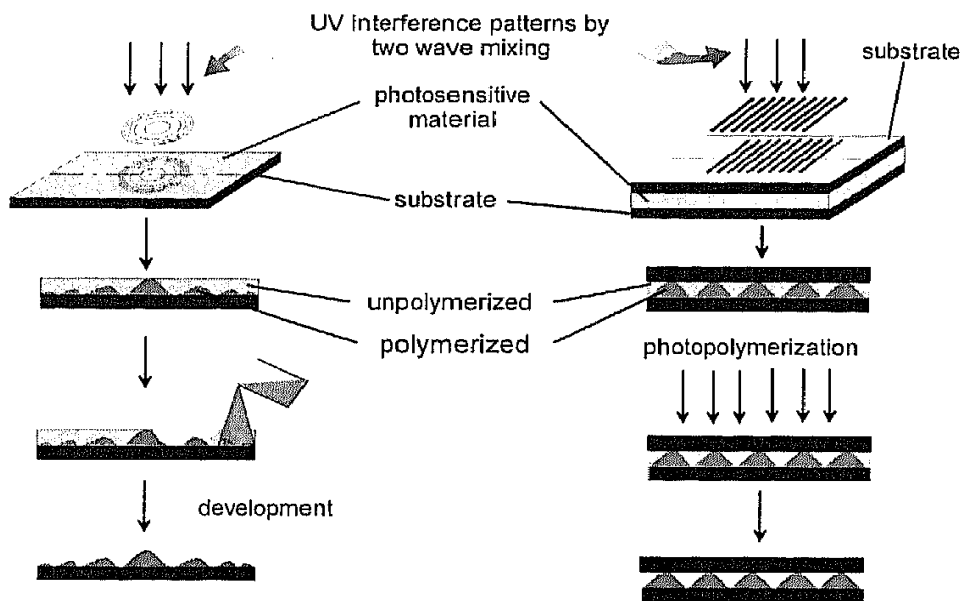
The development of new materials based on the principle of using nanoscale particles for maintaining the overall transparency of transparent matrices in composites can be extended by adding further components to the basic system. For example, if fluorinated silanes are added, a phase separation after coating takes place, leading to a gradient material with a high concentration of fluorinated groups at the surface. Using this approach, functional gradient materials have been prepared and components leading to a good adherence to substrates at the same time were obtained. This led to a surface similar to polyte-trafluorethylene (PTFE), with surface free energies between 18 and 20 mJ/m² but with high transparency and good adherence to various types of substrates (e.g. glass, metals and polymers) [21, 22]. These systems have been successfully used for antisoiling coatings on glass, on metals and on metals and on plastics. Another interesting area of application are demoulding processes, which is a wide field in thermoplastic materials' moulding.

For passive optical application by using nano-scale particles the refractive index can be tailored in a wide range. For example, using zirconia, it can be varied between 1.51 and 1.53. If titania is added, coating materials up to 1.70 can be obtained. Together with polymerizable ligands, as shown in fig. 2, radical photopolymerization can be applied as well as radical thermopolymerization. Both techniques can be used for micropatterning techniques, for example, for embossing of microlenses, waveguides or for using photo-lithography or laser writing, for the fabrication of diffractive gratings or coupling systems. By the use of the Colburn-Haines-effect [23], holograms can be written into these layers by two-wave-mixing. Holographic gratings or microfresnel lenses can be produced. Figs. 9a and 9b give a survey about the techniques already developed for photolithography, holographic techniques and microembossing.
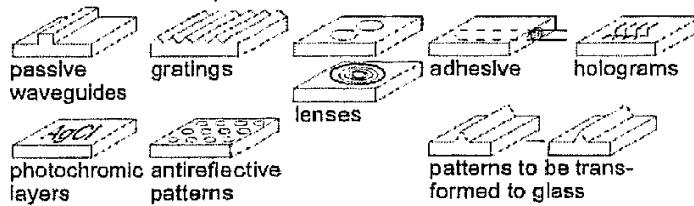
The described matrix materials also have been used as matrix materials for carrying additional optical functions, for example, semiconductor quantum dots or metal colloids for obtaining non-linear materials.

For the preparation of metal containing colloids the approach as described in the previous chapter has also been used. However, a reduction step has to be introduced, if one starts from salt solutions. This leads to several alternatives for the colloid synthesis. They can either be prepared in solution, by reduction, nucleation and growth in the presence of surface modifiers to stabilize the colloids and to control the particle size, or they can be introduced in an ionic complex form into a matrix system and then thermally be reduced in the presence of organic groupings, nucleated and grown in the already existing polymer or ormocer matrix. The different reaction routes are shown in figure 10.
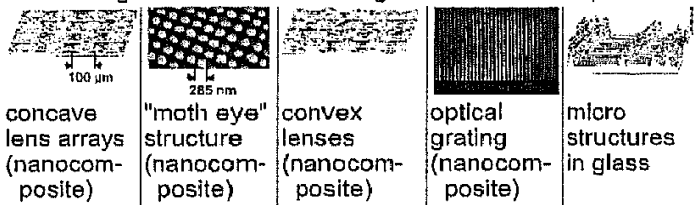
This route has been investigated for gold colloids [6], silver colloids [29], palladium colloids [30] and for copper-colloids [31]. One application simply to be verified is the use of these materials as coatings on glass substrates since the coefficient of extinction of the colloids is in the range of 10^5 up to 10^6 l · mole^{-1} · cm^{-1}. This means that even in film thicknesses of 200 nm and colloid contents of some vol.-%, optical densities up to 3 can be obtained. The reaction path is shown in fig. 11.

UV interference patterns by two wave mixing

photosensitive material

substrate

substrate

unpolymerized

polymerized

photopolymerization

development

O schematics of components

passive waveguides gratings lenses adhesive holograms

photochromic layers antireflective patterns patterns to be transformed to glass

O Embossing of microstructures in glass and nanocomposites

| concave lens arrays (nanocomposite) | "moth eye" structure (nanocomposite) | convex lenses (nanocomposite) | optical grating (nanocomposite) | micro structures in glass |

100 µm   285 nm

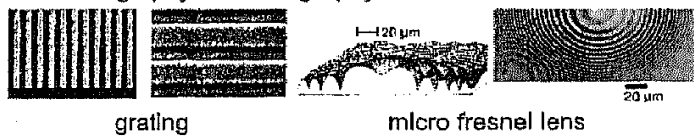O Photolithography and holography

grating   micro fresnel lens

Figure 9a. Schematics and SEM micrographs of micropatterned optical materials by holographic techniques; 9b: overview over components already fabricated by microtechniques [after 24 - 28].
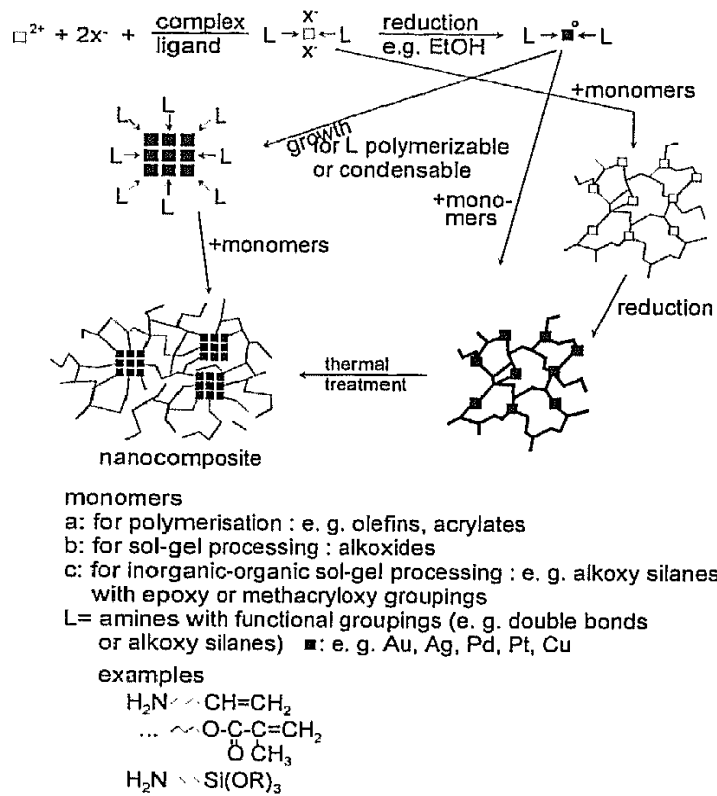
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Figure 10. Reaction routes for the formation of metal-colloids in polymerizable matrices.

monomers
a: for polymerisation : e. g. olefins, acrylates
b: for sol-gel processing : alkoxides
c: for inorganic-organic sol-gel processing : e. g. alkoxy silanes
   with epoxy or methacryloxy groupings
L= amines with functional groupings (e. g. double bonds
   or alkoxy silanes) ■: e. g. Au, Ag, Pd, Pt, Cu
   examples
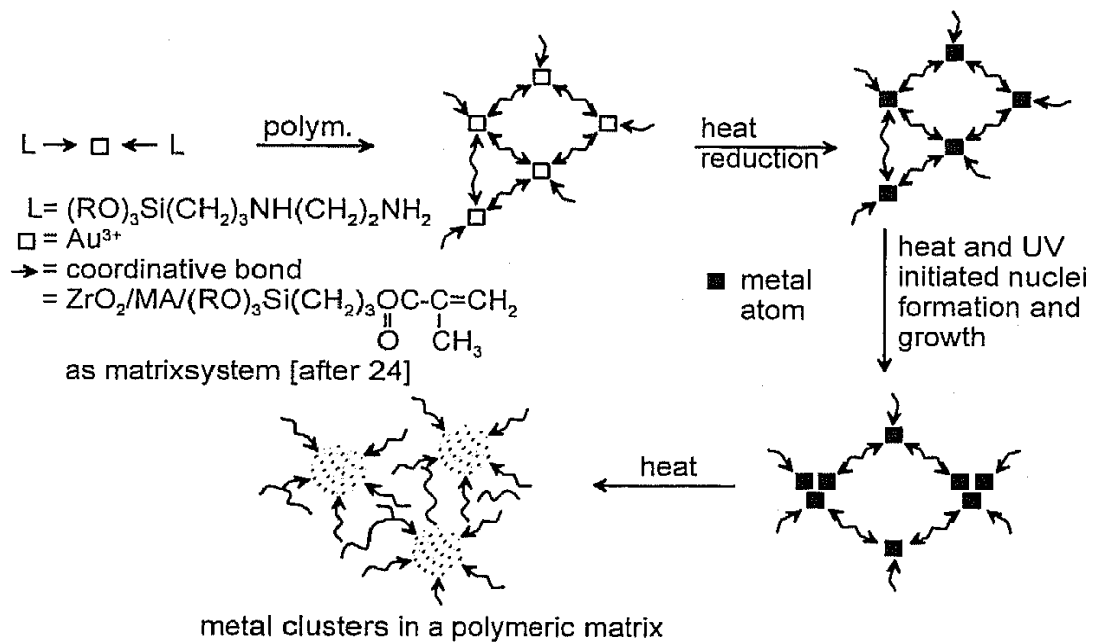

metal clusters in a polymeric matrix

Figure 11. Reaction path for the formation of Au colloids in an ormocer matrix [after 6].

It is well known that nanoscale Au particles show interesting χ^3 susceptibilities [5]. For verifying high non-linear optical effects the tailoring of the so-called local electric field factor has been used as an approach (fig. 12).

Local electric field factor: $\chi^{(3)} = p\, f_1^2\, |f_1|^2\, \chi^{(3)}_m$

$\chi^{(3)}$ = third order nonlinear susceptibility
        of the composite
$\chi^{(3)}_m$ = third order nonlinear susceptibility
        of the colloid
p = volume fraction of colloids
f_1 = local electric field factor

$$f_1 = \frac{3\varepsilon_d}{2\varepsilon_d + \varepsilon_m}$$

ε_d = dielectric function of the matrix
ε_m = dielectric function of the metal

homogeneous matrix

tailored interface:
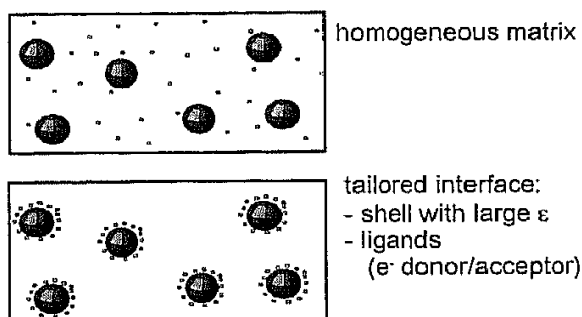- shell with large ε
- ligands
  (e⁻ donor/acceptor)

Figure 12. Schematics of the use of an enhanced local electric field factor to obtain high χ^3 susceptibilities [after 6, 32].

As pointed out in fig. 12, the local ecletric field factor is mainly defined by the dielectric function of the metal and the matrix. To increase the local electric field factor, the approach was followed to increase the electron density close to the metal colloid by appropriate ligands (amino, sulfido, cyano).

Investigations of the dependence of the χ^3 effect on the ligand show that amino ligands are much more effective than sulfido ligands. If the sulfido ligands are oxidized by heat treatment in air, resulting in sulfates, the χ^3 value decreases by several orders of magnitude. This is attributed to the fact that the sulfido ligands have a strongly decreased polarizability and do not contribute much to the local field factor. The highest χ^3 values have been obtained from amino-containing ligands. χ^3_m was up to $2\cdot 6\cdot 10^{-6}$, which is a rather high value. The χ^3 messurements have been carried out by a four-wave mixing process, as shown in figure 12, and in addition to this time depending experiments down to 7 ps have been carried out. In order to determine whether thermal effects are playing a role, the intensity dependence was investigated, showing no detectable dependence. Together with the time resolved experiments, it can be concluded that thermal effects do not play a role for the χ^3 susceptibilities.

Similar experiments have been carried out with Cu colloids [31]. By firing out the organics, two types of Cu colloids, depending on the atmosphere (reducing or oxidizing) are obtained: Cu clusters with and without oxide layers.

In fig. 14 the optical spectra and the χ^3 values of both types are shown.

The reduced form shows red and the oxidized form shows green colour. Green colour cannot be explained by the ionic absorbtion which would be far too less intensive and is attributed to the local electric field factor of the surrounding oxide.
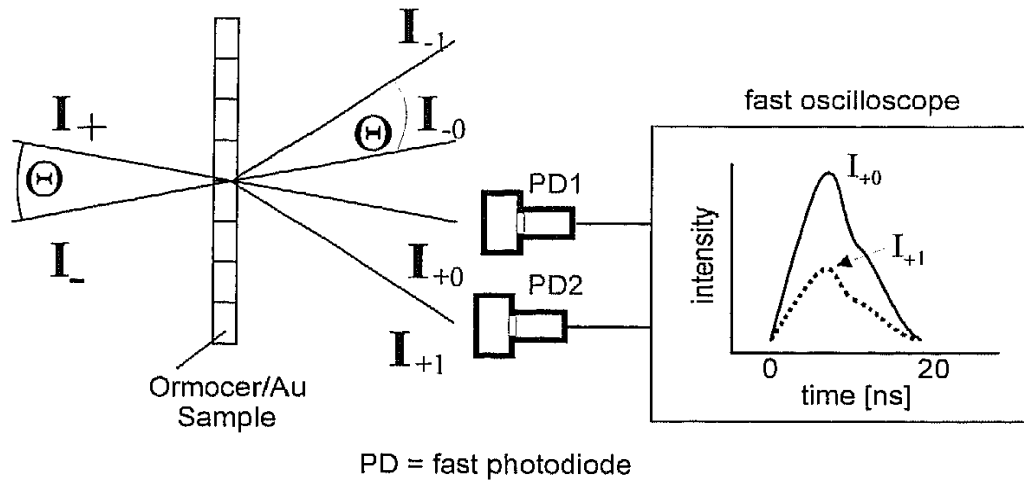
fast oscilloscope

PD1

PD2

Ormocer/Au
Sample

PD = fast photodiode

intensity

I_{+0}

I_{+1}

0   20
time [ns]

I_{-1}

I_{-0}

I_{+}

I_{-}

I_{+0}

I_{+1}

Figure 13. Schematics of the experimental χ^3 measurement set up and response curve.

$\chi^{(3)} = 1.4\ 10^{-6}$ esu
$\chi^{(3)}_m = 1.2\ 10^{-5}$ esu

$\chi^{(3)} = 3.1\ 10^{-6}$ esu
$\chi^{(3)}_m = 1.7\ 10^{-6}$ esu

CuO

reddish-brown

green

reference

absorbance

1,6

1,2

0,8

0,4

0,0

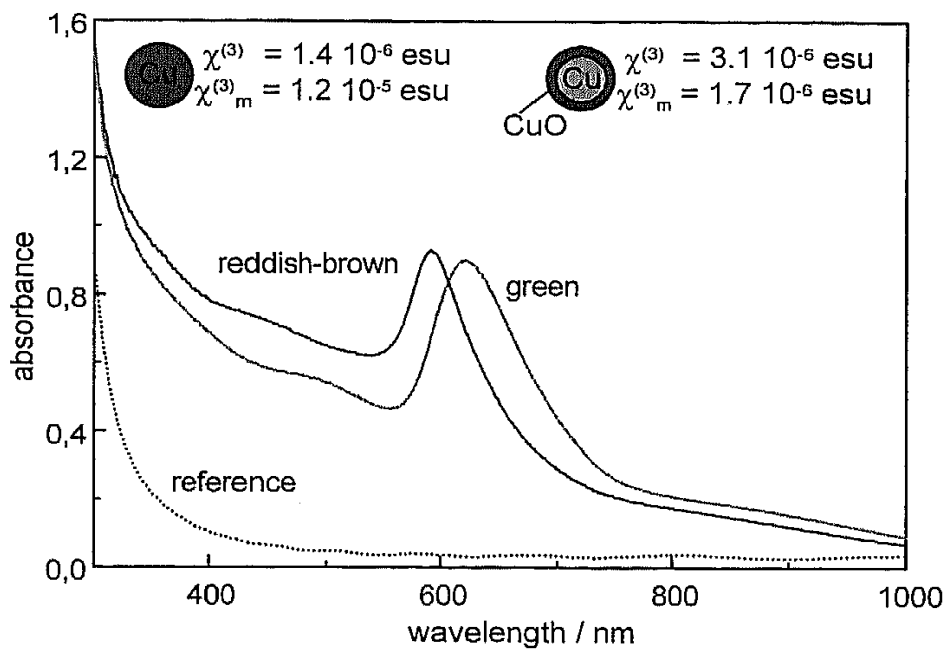400   600   800   1000

wavelength / nm

Figure 14. Optical spectra and χ^3 values of Cu colloids with and without oxide layer. $\chi^3_m = \chi^3$ metal.

Summarising one can say that using metal colloids together with selected ligands influencing the local electric field, non-linear optical properties can be increased remarkably.

One of the described effects of the tailoring of nano-sized particles is based on the reduction of interparticular interaction which leads to increased packing densities in compacts. It has been shown that increased packing densities can be used for monolithic processing, as in the case of ceramics. It can also be used for obtaining thick sol-gel films.

CONCLUSIONS

It could be shown that by using the surface thermodynamic approaches the control of growth and particle size of colloidal systems can be realized. In addition to this, it is possible to outfit the surface of the particles with organic groupings of different chemical properties and to immobilize them strongly on the surface by establishing chemical bonds. Based on these basic routes the colloidal particles can be used for advantageous processing of ceramics to films or inorganic-organic composites with interesting passive and active properties. With these techniques new routes for material synthesis have been opened, and the examples shown up to now only are scratching the surface.

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