THIN FILMS FOR OPTICS AND PHOTONICS THROUGH NANOPARTICLE TECHNOLOGY

Helmut Schmidt, P. W. Oliveira, M. Mennig
Leibniz-Institut für Neue Materialien, Im Stadtwald, Geb. 43 A, 66123 Saarbrücken, Germany

1. INTRODUCTION

Nanoparticles have become of interest for many reasons. Numerous papers have been issued about the fabrication of nanoparticles since the book of Gleiter has been published in the 80's [1], where first very interesting results have been discussed about materials made from nanoparticles derived by gas phase reactions. For the fabrication of nanoparticles, many routes have been investigated, such as gas phase reactions, e. g. flame pyrolysis as used by Degussa for large scale production or the fabrication of nanoparticulate silica sols as used and produced by many chemical companies like Clariant or Bayer. In the scientific literature, numerous precipitation methods in liquid phases have been presented [2]. In our own work, it was shown that the surface modification of nanoparticles opens up very interesting routes for obtaining processing properties based on these nanoparticles which can be used for obtaining new materials like coatings and composites [3,4,5,6].

These investigations have shown that it is possible to modify surfaces of nanoparticles, e.g. by reactive silanes which then allow to react these particles according to the reactivity of the ligands. These ligands are polymerizable or polycondensable, but also may change the surface polarity and reduce particle to particle interaction, so that the dispersibility of the particles becomes much higher than without these modifications. The stabilization of colloidal systems, in general, is carried out by surface charges as used in the sol-gel process [7]. It is well established that gelation takes place at the point of zero charge where the repulsion forces of the particles are low so that they can react with each other. If the surface is covered with non-reactive ligands or ligands which do not react at the point of zero charge, a substantially better dispersion takes place, opening up new processing possibilities. In this paper, several routes based on this approaches are summarized with respect to new applications.

2. BASIC CONSIDERATION

In figure 1 the different effects of surface modification on the ζ-potential are schematically shown.

As one can see, the ζ-potential by appropriate surface modification can be changed in various ways. Once with respect to the height of the ζ-potential as a function of pH and second the point of zero charge is varying by the type of the ligand (OH groups, basis or assets). In addition to this, in figure 1 (equation 1), the influence of thermodynamic parameters ΔG_n and ΔG_D (free energy of nucleation and diffusion) as well as the interfacial energy σ are shown. This means that the nucleation frequency can be controlled by σ and σ can be influenced by ligands able to react with the surface. This also means that the surface modifiers also can be used for influencing the particle growth reaction or even the shape. In addition to this, it easily can be seen that the surface reactivity of the particles may change drastically by these ligands. In the following, in a few examples it is demonstrated how this can be utilized for the preparation of interesting materials for optics or photonics. As already mentioned in the introduction, the most
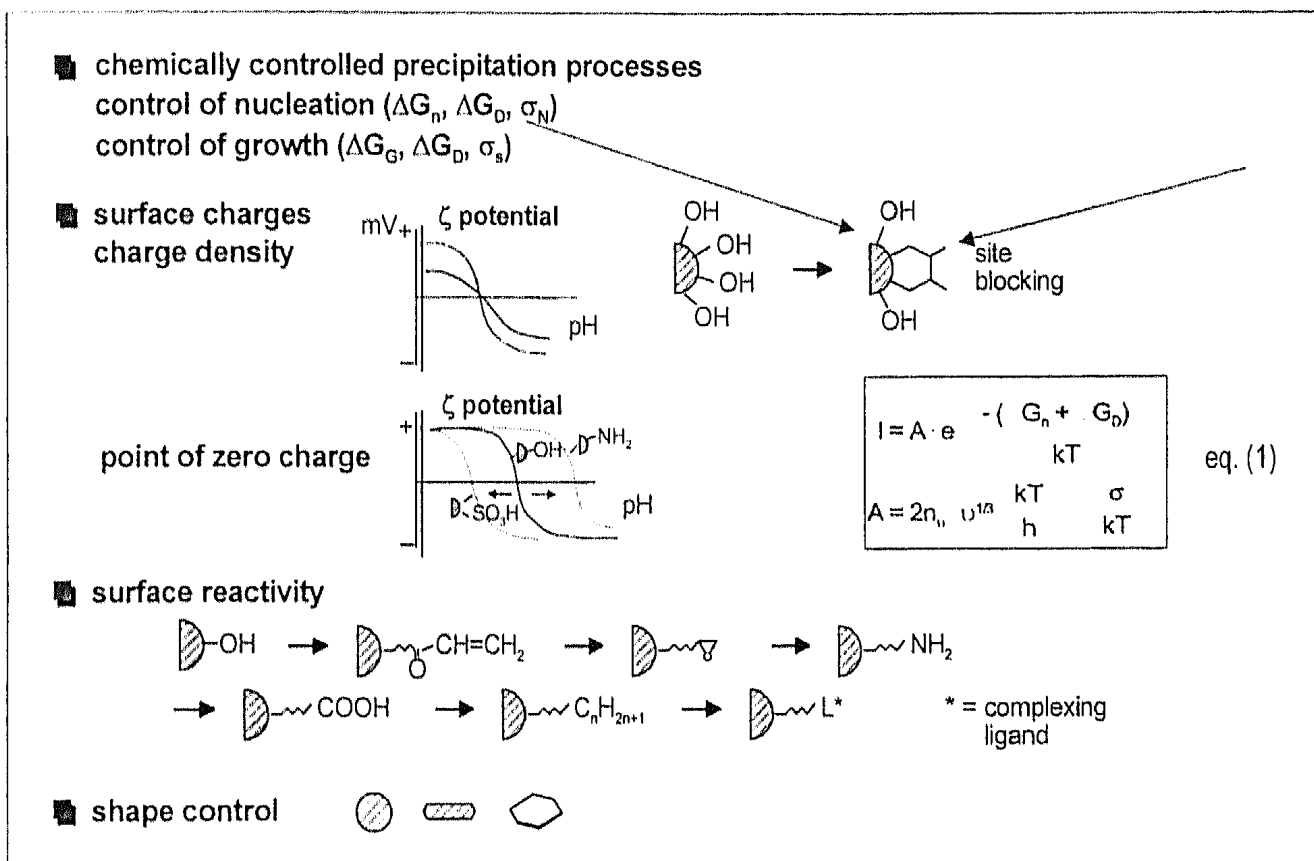
- chemically controlled precipitation processes
  control of nucleation (ΔG_n, ΔG_D, σ_N)
  control of growth (ΔG_G, ΔG_D, σ_s)

- surface charges
  charge density

  ζ potential (mV vs pH)

- point of zero charge

  ζ potential

  $$I = A \cdot e^{\frac{-(G_n + G_D)}{kT}}$$

  $$A = 2n_v \cup^{1/3} \frac{kT}{h} \frac{\sigma}{kT}$$

  eq. (1)

- surface reactivity

  $\bigcirc$-OH → $\bigcirc\sim\!\!_O^{}\!$-CH=CH$_2$ → $\bigcirc\sim\!\!\triangledown$ → $\bigcirc\sim\!$NH$_2$

  → $\bigcirc\sim$COOH → $\bigcirc\sim$C$_n$H$_{2n+1}$ → $\bigcirc\sim$L*

  * = complexing ligand

- shape control

Figure 1: Effect of surface modification on the ζ-potential of small particles

important part for the utilization of nanoparticles in optical applications is that they have been dispersed perfectly in the matrix to be used. It is well-known from the Rayleigh scattering formula that particle sizes have to be in the lower nm range in order to lead to transparent systems. For this reason, the surface free energy between the particle and the matrix has to be at its minimum, otherwise the aggregation would be the preferred reaction; as a consequence, this leads to light scattering. As a rough rule, it can be said that in optical films, the light scattering can be neglected if the particle size is below 1/20 of the wave length to be utilized. In figure 2, several agglomerate-free nanoparticle systems are shown. The process for preparation is described elsewhere [8]. All these particles are surface modified and by this, can be kept free from agglomeration. Through a second step, a hydrothermal processing, the particles can be obtained in a well crystallized form as shown in figure 2 with the examples of ITO which leads to almost theoretical density even if the particle size is in the lower nm range.

3. EXPERIMENTAL

3.1 Holography
Synthesis of the ZrO$_2$ containing holographic sol

Methacryloxypropyl trimethoxysilane (MPTS,I) was used as matrix material in combination zirconium propoxide (ZR,II) complexed with methacrylic acid (MAS,III). In a first step, 24,8 g of MPTS is hydrolysed and condensated during a slow addition of 2,7 g of 0.5 N HCL. The water content is followed by Karl-Fischer titration to determine the time after water content has minimized. In a second step, 4,57g of Zirconium propoxide is complexed with 1.72 g of methacrylic

acid. In the used alkoxide precursor, the Zr-alkoxide content was 70 weight%. The complexed Zr alkoxide was mixed with the controlled condensated silane under stiring and 0.54g
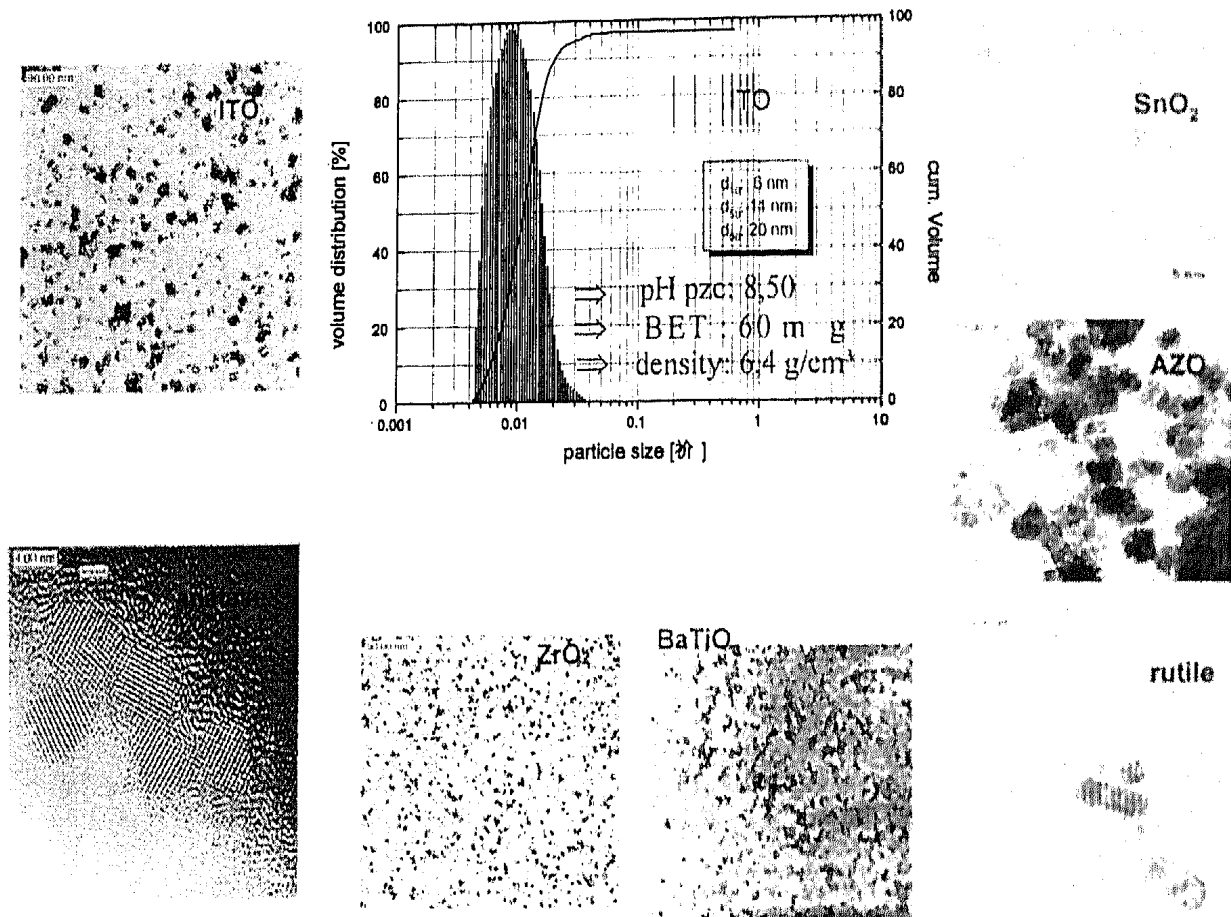

Figure 2: Examples for nanoparticles prepared by chemical precipitation routes

water (half stechiometric) was added. In order to initialize photopolymerization in further processing steps, a 0.01 mol of photoinitiator Irgacure 184 pro mol C=C have been added. After stiring for 4 hours,ethanol or an other alcohol can be added as solvent to adjust the viscosity of the solution. The diameter of the ZrO_2-particles, which are formed by the in-situ condensation of the ZR/MAS in the MPTS matrix is measured in the sol state by photon correlation spectroscopy to be about 4 nm. No particles can be detected for both the pure MPTS matrix nor for the complexed ZR/MAS system before mixing.

Films on glass, silica or other substrates with 0.5 to 10 μm of thickness were prepared by dip coating (speed from 0.3 to 6 mm/s). The system was photopolymerised using a 60 mJ (by 351,1 nm) or thermally polymerised at 80 °C for 10 min. The two-wave mixing experiment was carried out with a laser beam of wavelength 351 nm (from an Ar^+-laser) and is described elsewhere [9]. Concentration profiles of Zr/MA were determined by EDX analysis.

3.2 AR coating on glass
High refractive index coating sol (TiO₂ sol)

2.1 g of tetraisopropylorthotitanat was slowly dropped in to a mixture of isopropanol with 0.981 g con. HCl (37 wt%/H₂O) and 0.205 g water under stirring at 25 ^{0}C. The solution has been stirred 24 hours at 25 ^{0}C. To silanise the surface of the formed TiO₂-nanoparticles 2g GPTS were mixed with 200 g TiO₂-sol under refluxe and vigorous stirring at 50 ^{0}C for 5 hours. The photoinitiator UVI 6974 (Union Carbide) is not soluble in isopropanol. A part of isoproponol (10g) was removed from the sol by vacuum destilation at 14 mbar and 25 °C and 14 g of 2-isopropoxyethanol were added. To produce films with different refractive index GPTS hydrolyzed with 0.1 N HCl and 2 wt% of UVI 6974 (in relation to the GPTS species) were added to the particulate sol.

3.3 Low refractive index coating sol (SiO₂ sol)

The SiO₂ nanoparticles were synthesized by base catalyzed hydrolyses and condensation of tetraethoxysilane (TEOS) mixed with an aqueous solvent. 670 ml TEOS were mixed with 1058 ml deionised water and 1980 ml ethanol to give a homogeneous solution. 4,043 ml NH₃, 25% in water, were added under vigorous stirring at 25 °C. The mixture was heated up to 50 °C under refluxe under stirring for two days until no more residual TEOS was present. This silica sol was concentrated by vacuum distillation to 30 wt% of SiO₂ in water. After adding 2-propanol and 0.5% glucose as stabilizer, the sol was concentrated by vacuum destillation to 30 wt% of SiO₂ and the water was removed to 0.3 wt%. (Karl Fischer tritation). The silanisation of the SiO₂-nanopartiles was carried out with the mixture of 3.94 g of SiO₂-nanoparticles with 1 g of GPTS. The GPTS was slowly dropped in to the SiO₂-sol at refluxe and the mixture was stirred at 50 °C during 5 hours. 2 wt% of UVI 6974 (in relation to the GPTS species) were added to the TiO₂ particulate sol.

3.4 Stack fabrication

The stack of middle (mixture of 60 wt%. Of SiO₂-sol with 40 wt%. of TiO₂-sol), high and low refractive index layers was calculated theoretically by a multilayer simulation program (TF Calc-HS 3.1). Based on Landau Levy's equation, the dip coating parameters were established that the calculated thicknesses in the fired layers have been achieved.

Coatings were prepared by dip coating on float glass with a speed of 3 to 6 mm/s, drying at 25° C for 1 min and fixed by UV-exposure of 2.5 J/cm² after each individual coating step. The densification of the stack was carried out by thermal treatment at 450 °C for 15 min.

4. RESULTS AND DISCUSSIONS

In figure 3, the scheme is shown how a crosslinking reaction between surface modified nanoparticles may take place. E. g., methacryloxy modified particles (a) can be crosslinked by radical photo initiators. The requirement for this is that the particles are diffusible in the matrix, so that the double bonds can reach each other. Similar mechanism can be assumed with epoxy groups. In this case, ionic photo initiators can be used. For both reactions, initiators are commercially available.
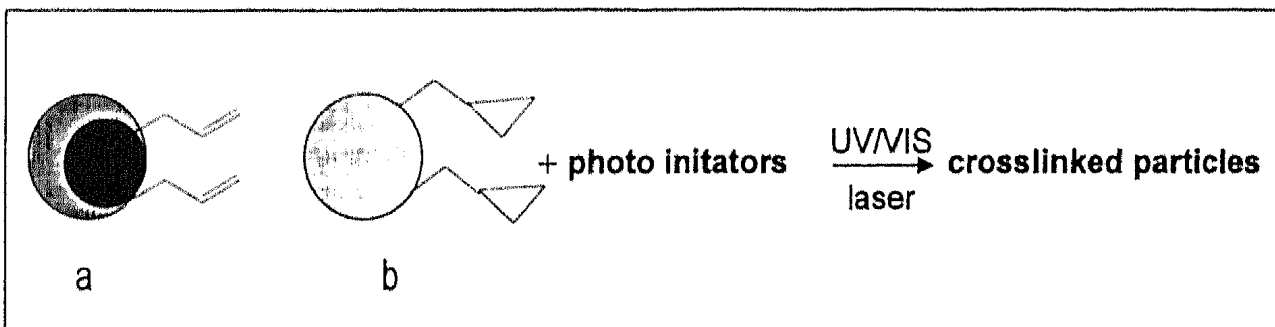

Figure 3: Scheme of the reaction of surface modified nanoparticles

In figure 4, it is schematically shown how the photopolymerization process is assumed to take place if a mask or a two wave mixing process with light fluctuations is drawn. These schematics show in case the process takes place as assumed that a photo induced upconcentration of nanoparticles takes place. If the refractive index of the matrix is different from the nanoparticles, holographic pattern can be written by this process.
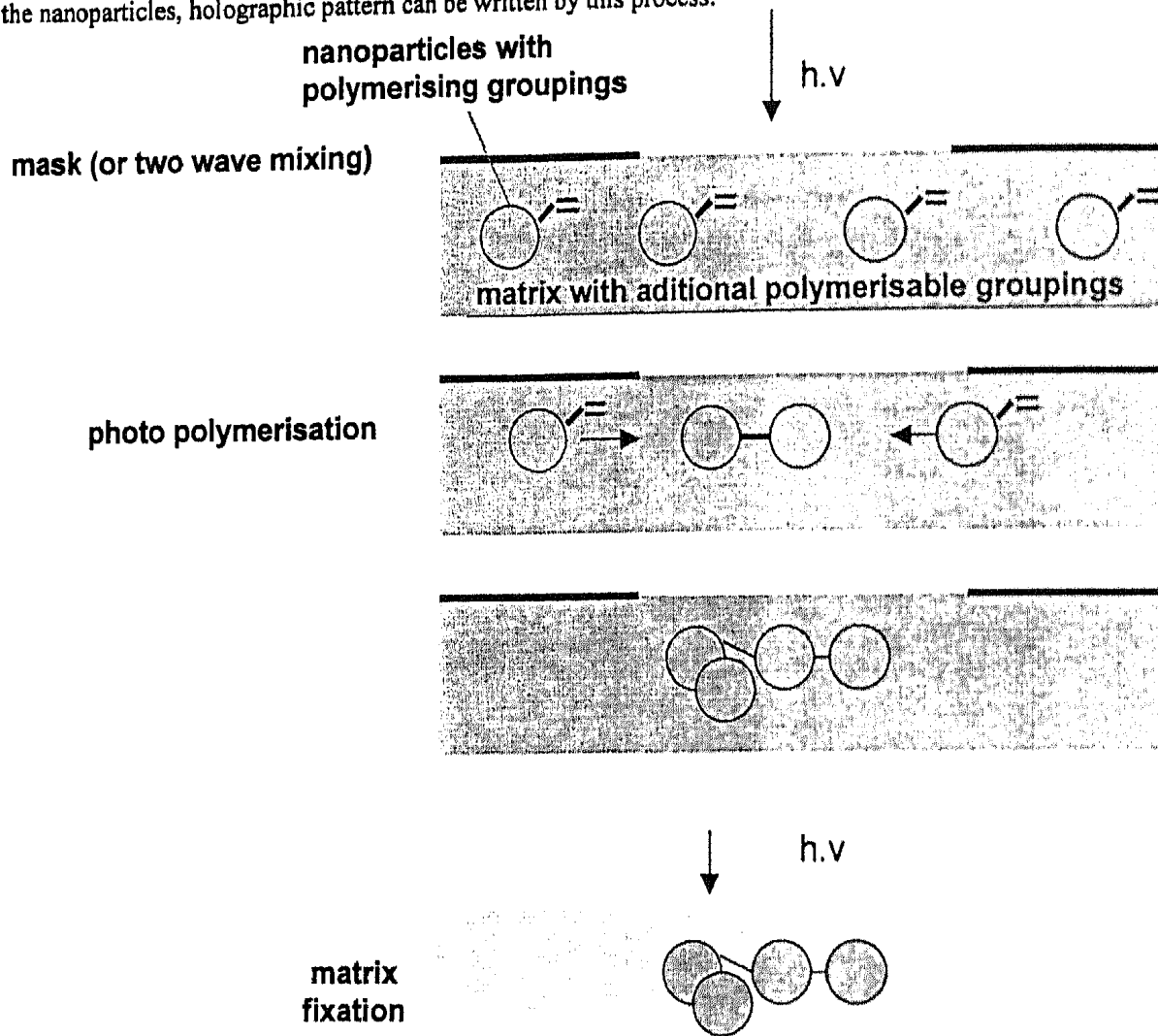

nanoparticles with polymerising groupings

h.v

mask (or two wave mixing)

matrix with aditional polymerisable groupings

photo polymerisation

h.v

matrix fixation

Figure 4: Schematics of the photo induced upconcentration of nanoparticles

In figure 5, the results of these experiments are shown. By using a two wave mixing device as described above, parallel waves as well as concentric waves can be generated. In the lower part of figure 5, the result of writing of a defractive grating is shown. On the right side, the EDX analysis has been carried out and one clearly can see that the distance of the defractive gradient lines is similar to that of the fluctuation of the tantalum signal. In this case, Ta_2O_5 nanoparticles have been used as refractive index increasing nanoparticles. In order to stabilize the film, methacrylates have been added to the system which then are used to freeze the patterns by full area polymerization of the film. The defractive efficiency at 630 nm has been determined to 95%. The use of concentric waves leads to fresnel lenses which can be produced down to sizes of 0.05. This experiments show that the assumptions of photo induced nanoparticle diffusion

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works rather well. With this techniques, also wave guides have been written within planar films. If the matrix is a hybrid matrix with a high content of inorganics, these systems also can be fired to purely inorganic coatings.
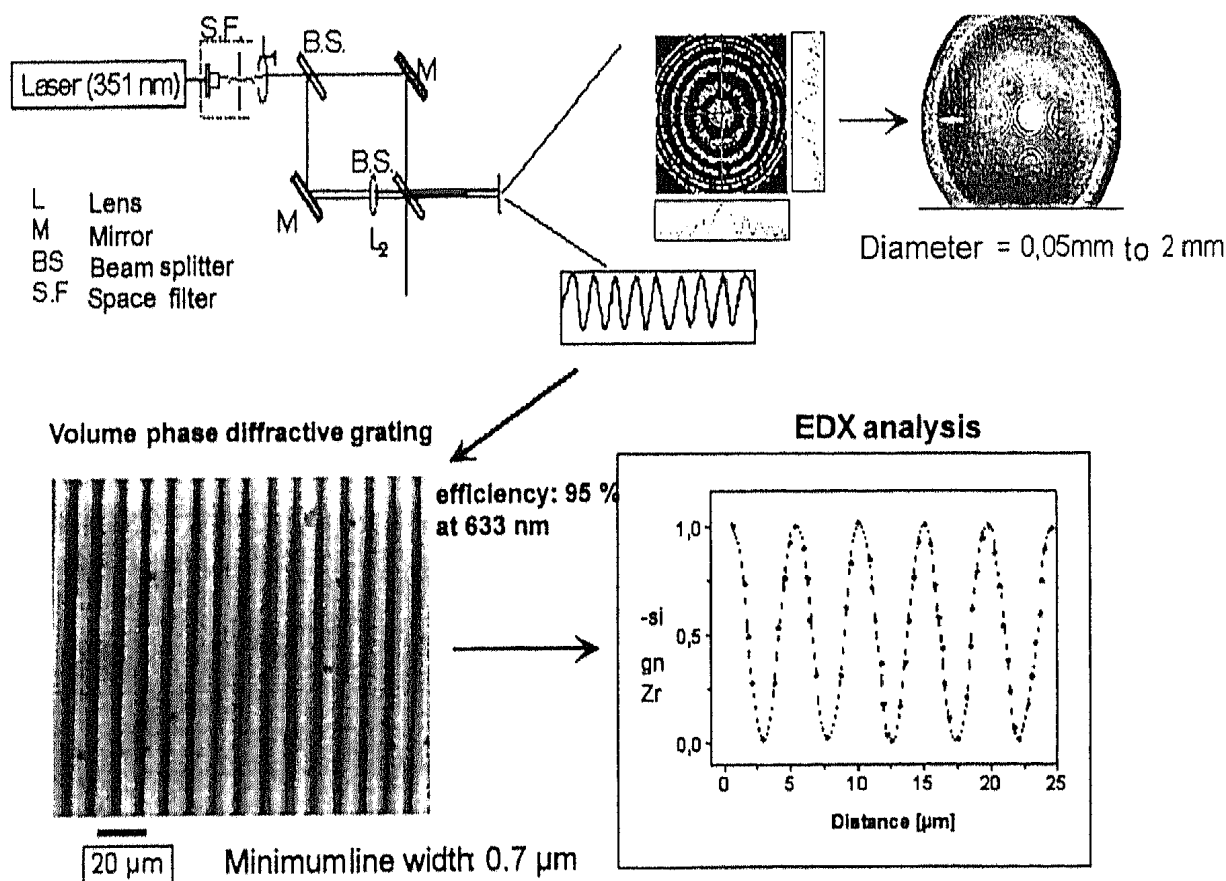

L   Lens
M   Mirror
BS   Beam splitter
S.F Space filter

Diameter = 0,05mm to 2 mm

Volume phase diffractive grating

efficiency: 95 %
at 633 nm

EDX analysis

20 µm   Minimum line width 0.7 µm

Figure 5: Process of writing volume phase holograms by two wave mixing

Whereas the experiments described above have been performed in films which have still a rather low viscosity, investigations have been carried out to test the diffusability of zirconia nanoparticles, surface modified with a methacryloxy group in dried film. In figure 6, the plastic foil roller coating system is shown which leads to a continuous technology. After the coating, the coated foil is dried by infrared irradiation. After employing a mask with appropriate patterns, during UV irradiation step the holographic pattern formation by photo induced diffusion takes place. After the UV irradiation step, final curing by infrared irradiation is carried out. This leads to so-called light guiding or diffuser foils, a system which has been developed to a large scale technology. The experiments show that by appropriate surface treatment, nanoparticles can be used for generating interesting optical effect by photo induced diffusion.

The photo polymerization of nanoparticles also can be used advantageously for passive optics, in multi layer systems if $\lambda/4$ layers can be prepared with different refractive indexes. In figure 7, nanoparticle systems surface modified in the case of SiO_2 with methacryloxy ligands and in the case of TiO_2 with epoxy ligands are shown. Epoxy ligands are preferable in the case of TiO_2 since methacryloxy ligands lead to intensively yellow coloured systems. These nanoparticulate dispersions have been used for the coating of glass surfaces. After the wet coating step, the UV curing step takes place and the system becomes mechanically stable and chemically stable.

photopolymerizable ligands ⟶ high refractive index nanoparticles with diffusion in gradient field of their chemical potential
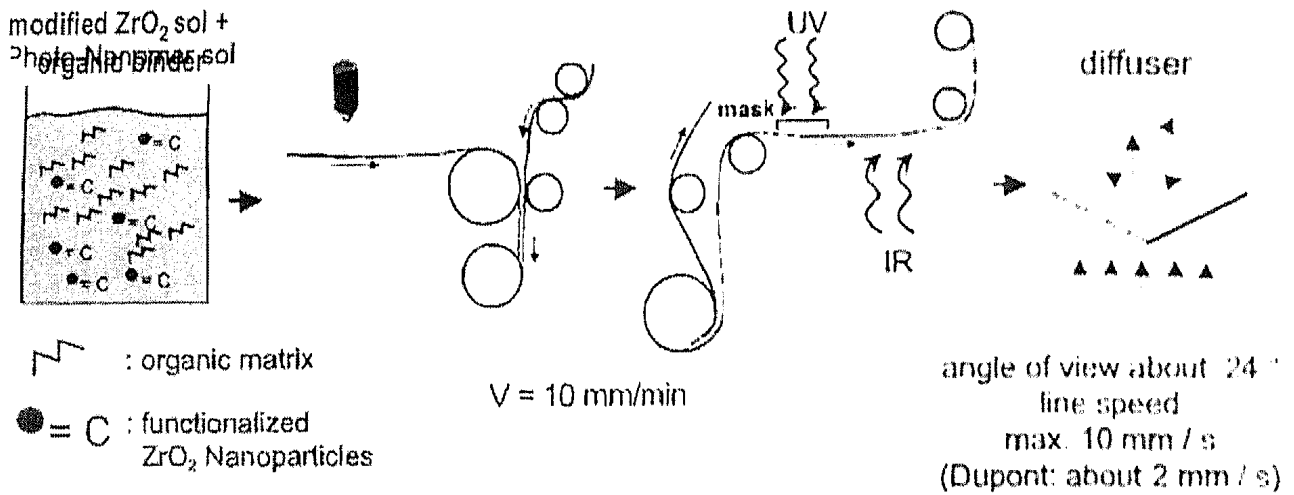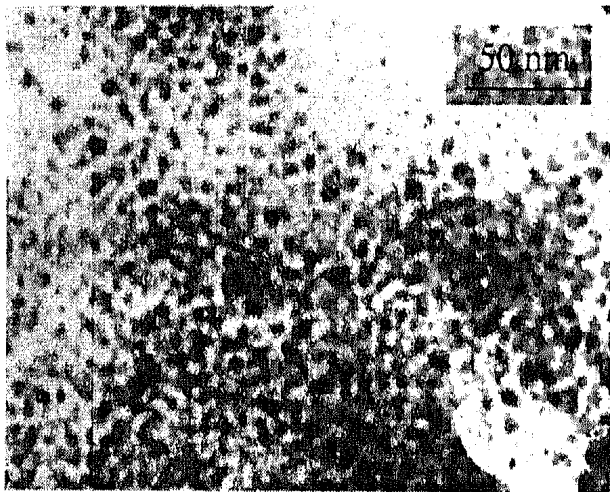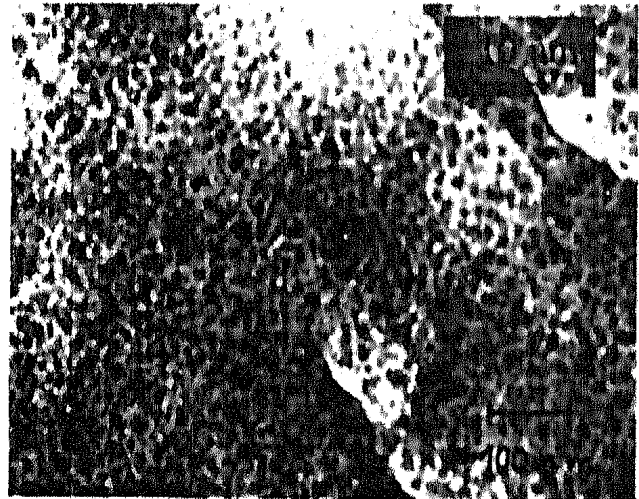⟶ formation of Δn-micropatterns by UV-mask irradiation

modified ZrO$_2$ sol +
organic binder

$\leadsto$: organic matrix

● = C : functionalized ZrO$_2$ Nanoparticles

V = 10 mm/min

UV

mask

IR

diffuser

angle of view about 24°
line speed
max. 10 mm / s
(Dupont: about 2 mm / s)

Figure 6: Continuous fabrication of light guiding foils

SiO$_2$

TiO$_2$

Figure 7: Surface modified TiO$_2$ and SiO$_2$ nanoparticulate systems

The next coating step can be employed immediately after the previous coating. Up to five layers have been employed on both sides of glass plates and only one firing step is necessary. In figure 8, the layers are shown on a 5 layer system. It easily can be seen that the uniformness of the layers is very good.

This technology has been used to fabricate antireflective, automotive windscreens as shown in figure 9. One clearly can see the difference between the coated and the uncoated part. It could be shown that the dip coating process which was used for this technology, leads to extremely precise coating thickness, so that rest reflectance is the same over the whole area.
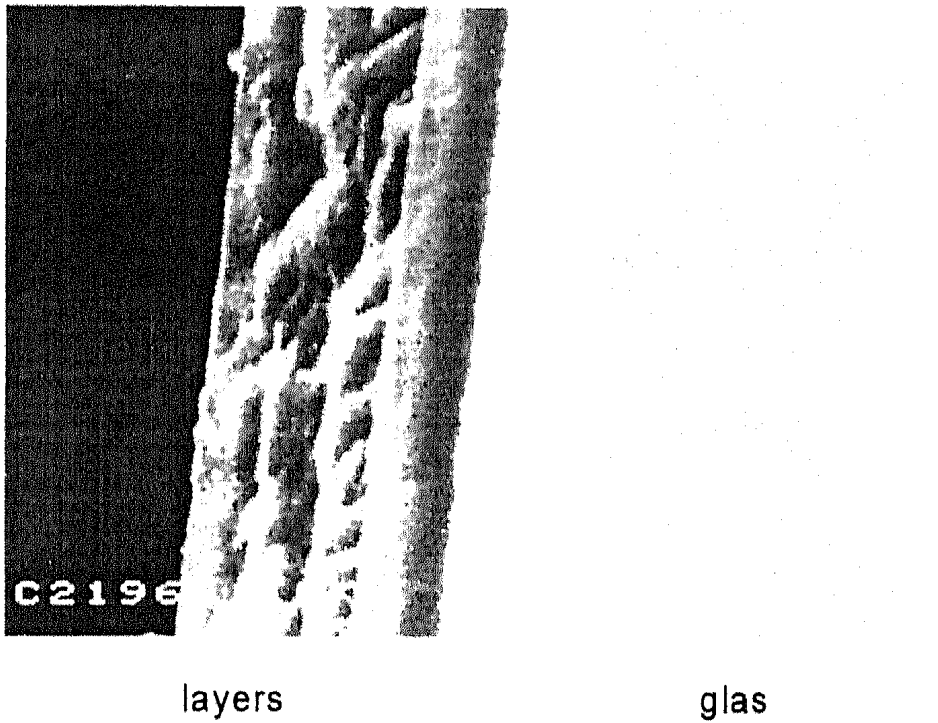

layers   glas

Figure 8: Cross section of a 5 layer dielectric stack under HR-SEM

For technology purposes, these systems also can be fired during the bending process of the glass pane.

Due to the possibility of photopolymerization, this technology can be used on plastic like polycarbonate or even TAC foils, too. In figure 10, the result of a wet web coating technology of an antireflective three layer coating on TAC is shown.
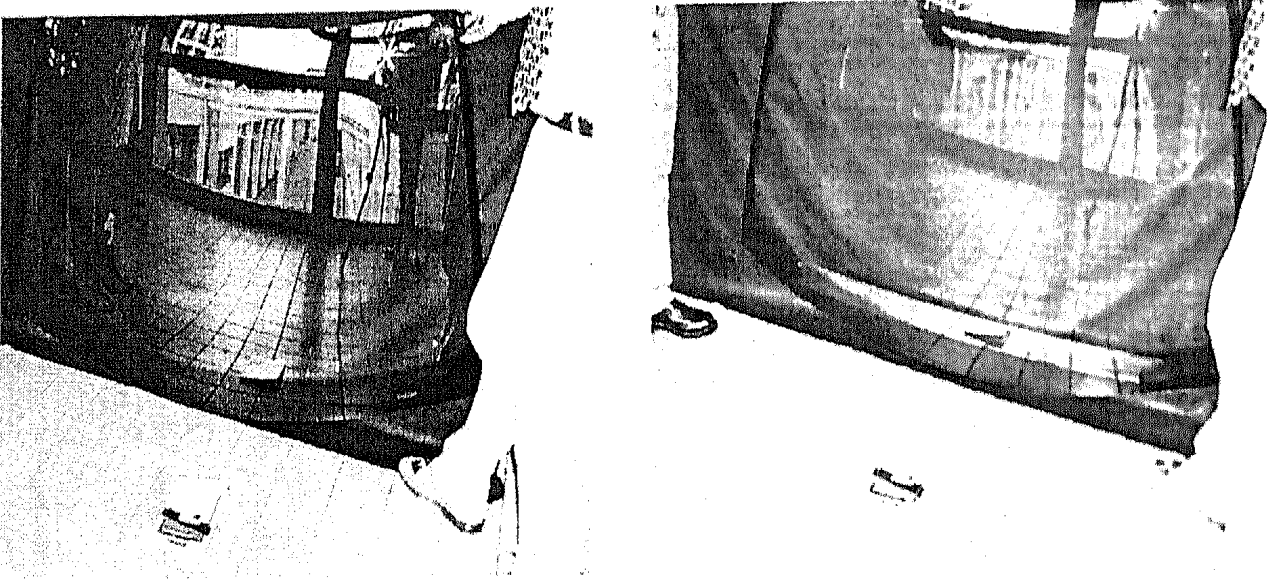
Figure 9: Antireflective windscreen by high precision dip coating based on the polymerisable nanoparticle technology
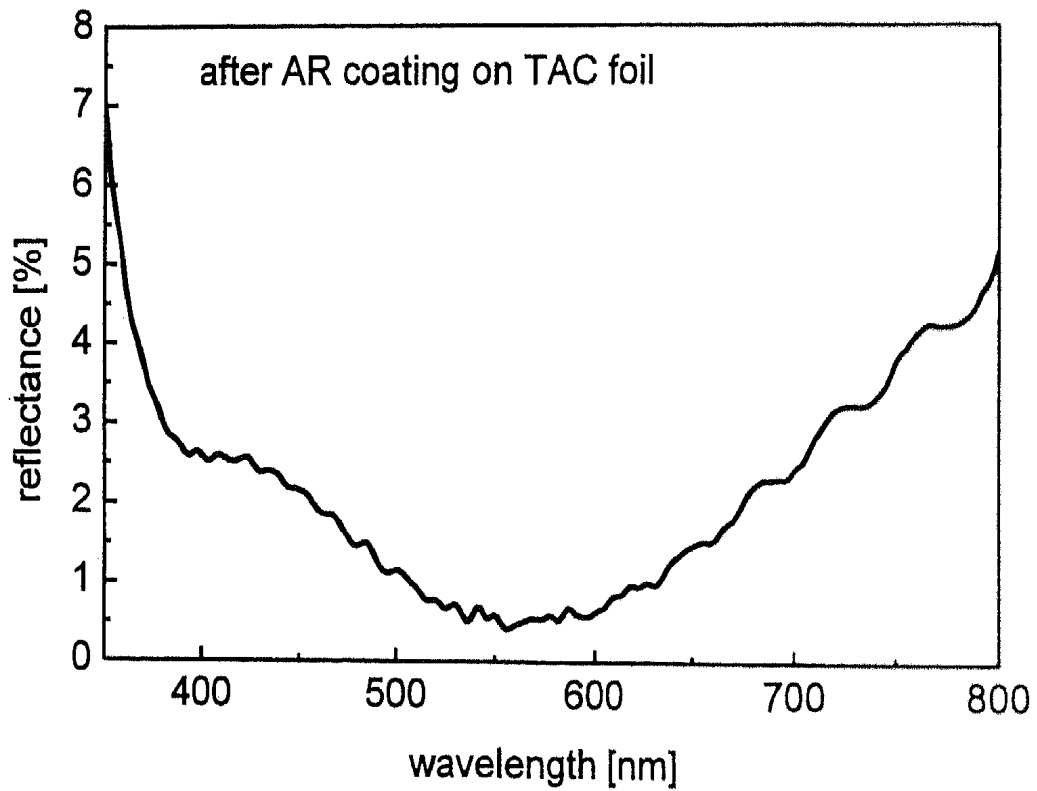
uncoated coated

Figure 10: Three layer antireflective coating on TAC produced by wet web coating

5. CONCLUSION

The utilization of chemically processed nanoparticles advantageously can be carried out if surface modification is used. Since this is a generalizable reaction route, many interesting applications in optics and photonics may become possible, especially if the mobility of the nanoparticulate systems is exploited. Since the diffusion rates of nanoparticles as determined by [5] is in the range of organic molecules, this process is rather fast and can be used for tailoring refractive index profiles for many optical purposes. By firing, these systems may become purely inorganic and for this reason, very resistant against environmental impact.

6. ACKNOWLEDGEMENT

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