CERAMIC NANOPARTICLE TECHNOLOGIES FOR CERAMICS AND COMPOSITES

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ABSTRACT

Nanoparticles provide interesting processing routes and material properties for many composites. For the fabrication of ZrO_2 nanoparticles, a precipitation process followed by a hydrothermal treatment has been developed. For surface modification and deagglomeration to the primary particle size, a ball milling process and a kneading process have been developed, leading to agglomerate-free particle systems between 6 and 10 nm. For photo induced diffusion, double bond containing modifiers have been used and a process for holographic pattern formation has been developed. The ZrO_2 nanoparticle systems have been used in compounding technologies for polycarbonate, showing a strong increase of the compressive strength and for the formation of ceramic membranes by a tape casting and lamination technology.

INTRODUCTION

The fabrication of nanoparticles has become of very broad spread interest for scientists and also for industry. Many types of particles are offered on the market, for example, derived by spray pyrolysis (Degussa) or similar techniques (Nanophase Inc. Ltd.). The fabrication of nanoparticles by other routes like chemical precipitation, laser pyrolysation, plasma techniques or flame spray techniques is laid down in numerous papers which, for example, are represented to a great deal in the powder conferences [1, 2, 3], and literature cited herein [4, 5, 6, 7]. However,

the utilization in industrial applications of nanoparticulate system is still on a very low level. One of the main reasons for this is the fact that material costs are still very high and second, processing techniques suitable for the end user, that means the manufacturer of the final products are not available or not yet developed. This includes the whole route from the particle fabrication, the particle handling, the particle processing to materials, components and systems. One of the difficulties is related to the particle to particle interaction by van der Waals and chemical forces which are a function of the particle diameter, the increase of which is a quadratic function of the particle diameter.

For this reason, it seems to be of interest to use colloidal chemical routes including surface modification in order to tailor the particle surface chemistry for appropriate processing. Basic considerations already have been published in [8, 9, 10, 11]. In these papers, it could be shown that nanoparticle fabrication by precipitation in analogy to the sol-gel process [12] advantageously can be used to fabricate nanoparticles with controlled surface chemistry. In this paper, two alternative routes are described for the fabrication of nanoparticles also on a large scale, and some examples of the utilization of such nanoparticles using very specific surface modification is given.

EXPERIMENTAL
Nanoparticle fabrication
For powder preparation, a precipitation process under controlled particle growth condition has been used as described elsewhere [13]. A solution of zirconium n-propoxide in ethanole was added drop wise to an aqueous ammonia solution (pH > 12) containing 10 wt.% of the surface modifying agent, bifunctional amines, β-diketones or amino carbonic acids (e.g. β-Alanine) with respect to the oxide. The weight ratio of precursor and water phase was 1 : 1.

Crystallisation of the nanoparticles
The so prepared suspensions were treated at 250 °C and 80 bar for 30 minutes in a continuous working flow reactor. The resulting powder was washed to remove the no longer required processing additives and freeze-dried.

Two routes have been used for the surface modification and deagglomeration:

a) One kilogram of the freeze dried powder, organic acids (10-15 wt.% with respect to the oxide) as surface modifiers and 80 ml water were mixed and kneaded in a water cooled laboratory double-Z-kneader (Linden LK II 1) for 4 hours. During the kneading process agglomerates in the high viscous paste were deagglomerated due the high shear forces of the rotor blades. A reagglomeration is prevented through the presence of the very reactive surface modifier, which is passivating the newly generated particle surface. After the kneading process water was added to get a fully dispersed suspension with low viscosity; this suspension

was freeze dried. Particle size distributions of the resultant suspensions were determined by dynamic laser light scattering (UPA).

b) The chemo mechanical comminution reactions were carried out in a water cooled Drais Perl Mill PML-H/V equipped with a zirconia milling chamber (volume: 1 litre) and a zirconia rotor. 1700 g zircon milling balls (diameter 0.3-0.4 mm) were utilized for the experiments. Distilled water, surface modifier (formic acid [5 wt.%], acetic acid [10 wt.%], 3-oxabutanic acid [10 wt.%], 3,6-dioxaheptanic acid [10 wt.%], 3,6,9-trioxadecanic acid [15 wt.%], N-(2-hydroxy-ethyl)ethylendiamine-N,N',N'-triacetic acid (HEDTA) [15 wt.%], N-(2-hydroxyethyl)-imino-diacetic acid (ethanoldiglycine) [15 wt.%], N,N-bis(2-hydroxy-ethyl)glycine (bicine) [15 wt.%] and 6-aminohexanic acid [15 wt.%]) and the hydrothermal produced zirconia (BET 150 m^2/g) were premixed and mechanical stirred for 30 min. Values in brackets are wt.% surface modifier used with respect to the oxide. These suspensions were milled for 4 h. Particle size distributions of the resultant suspensions were determined by dynamic laser light scattering (UPA) [14].

ZrO$_2$ holographic sol preparation

Methacryloxypropyl trimethoxysilane (MPTS, I) was used as matrix material in combination with zirconium propoxide (II) complexed with methacrylic acid (MA, III). In the first step, 24.80 g of MPTS is hydrolysed and condensed by a slow addition of 2,70 g of 0.5 N HCL. The water content is monitored by Karl-Fischer titration to determine the time at which water content reaches its minimum. In a second step, 4,57g of zirconium propoxide is complexed with 1.72 g of III. The complexed Zr alkoxide was mixed with the partially condensed silane under stirring conditions, and 0.54 g water (50 % of the amount necessary for stoichiometric hydrolysis) was added. As plastisizer, 33.04 g of TEGDMA (triethylene glycol dimethacrylate) was added. In order to initialise photopolymerization, 0.01 mole of the photoinitiator Irgacure 184 was added per mole of C=C double bond. After stirring for 4 hours, ethanol was added as solvent to adjust the viscosity of the solution. All this experiments were carried out under UV and blue light exclusion in order to prevent undesired photopolymerisation. The diameter of the ZrO$_2$-particles, which are formed by the in-situ condensation of the ZR/MA in the MPTS matrix, was measured in the liquid phase by photon correlation spectroscopy (Laser Goniometer ALV/SP-125 #10).

Slurry for tape casting

A slurry with a solid content of 50 wt.% is made by mixing 50 wt.% ZrO$_2$, 6,25 wt.% TODS (12,5 wt.% respective to ZrO$_2$), 7,5 wt.% polyvinyl alcohol PVA 4-88 (15 wt.% respective to ZrO$_2$), 2,25 wt.% glycerol (30 wt.% respective to PVA) and 34 wt.% water.

RESULTS AND DISCUSSION

All experiments were based on the precipitation of ZrO_2 from zirconium propoxide as described in the experimental. The processing route is schematically shown in figure 1. As shown elsewhere by X-ray diffraction [15], the ZrO_2 nanoparticles are completely non-crystalline. The particle size of the amorphous precipitates in the process for the holographic systems was about 4 nm, as measured by photon correlation spectroscopy. The hydrothermal processing was carried out by the newly developed process shown in figure 2. In this process, the precipitated amorphous slurry was crystallized in a continuously working tubular reactor. This reactor with an inner volume of 25 liters is constructed in a modular arrangement of 27 stainless steel coils (each 7 m in length). The maximum working temperature is 500 °C. The pressure, produced by a high pressure membrane pump, can be chosen from 10 bars to 220 bars. The hydrothermal treatment time is controlled by the flow rate of the suspension. The production capacity is depending on the solid content of the suspension and the required treatment time. A water-based amorphous suspension with 10 wt. % solid content was pumped with a flow rate of 50 liters/h trough the heated coil reactor at a temperature of 250 °C. On that condition the production capacity of the reactor for zirconia is 5 kg/h. The obtained fully crystalline suspension is weakly agglomerated with a primary crystal size of 9 nm (determined by X-ray powder diffraction) and a BET-surface of 150 m^2/g. After removing of the no longer required processing additives by a washing step, the suspension was freeze dried (Christ, Epsilon 2-60) for further use. In figure 1 the flow chart of the process is shown. The core unit is the tubular reaction chamber having a total length of about 190 m (figure 2). The precipitation takes place in the mixing chamber b.
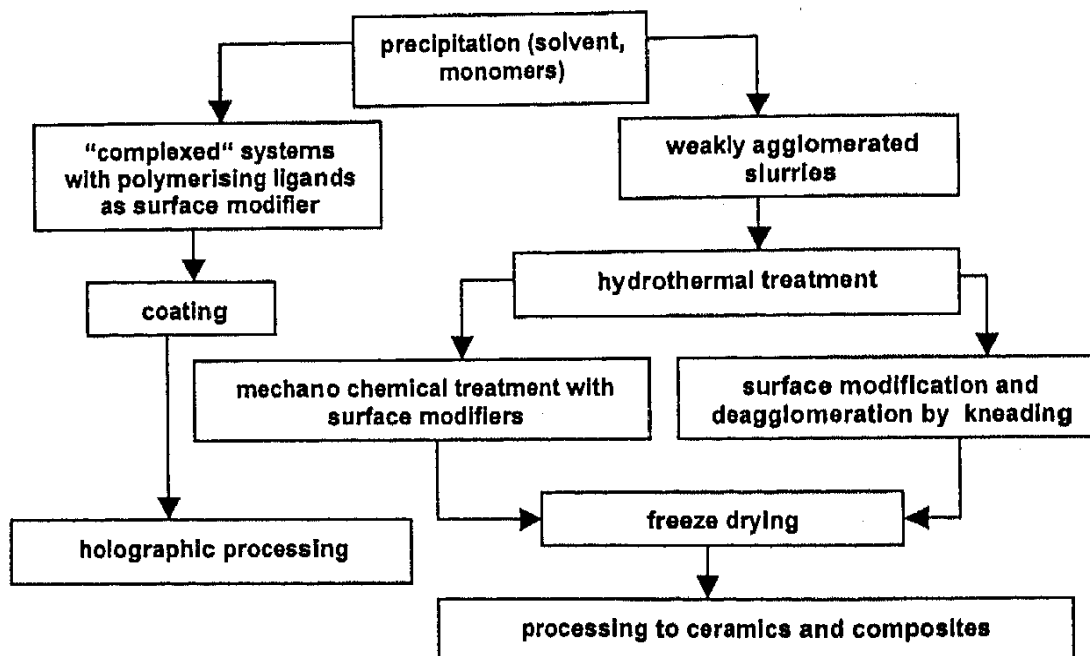

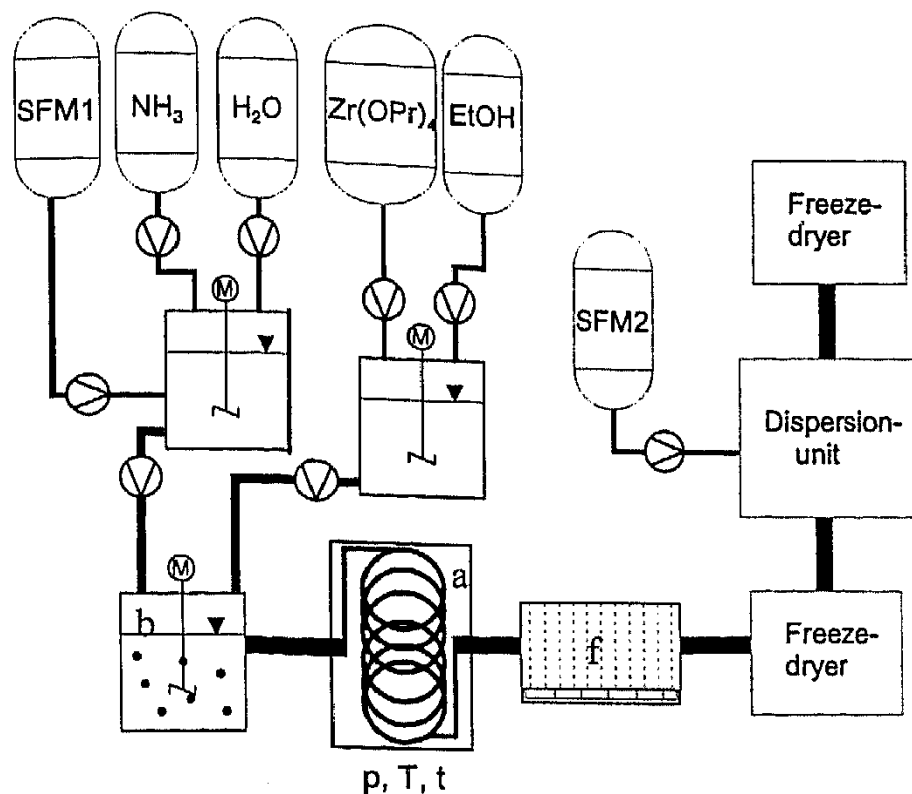Fig. 1. Scheme of the different processing routes for ZrO_2 nanoparticles

Fig. 2. Scheme of the hydrothermal process in a continuously working tubular reactor; a: reaction tubes; b: precipitation chamber; SFM 1, 2: surface modifier addition; f: filtering unit

The particle size can be manipulated by altering the processing parameters of the hydrothermal treatment. By prolongation of the reaction time the particle size was influenced as shown in figure 3 in a narrow particle size range of 7 to 10 nm. Even the process of particle growth is slow under the chosen conditions. First experiment by changing other variables in the overall reaction allowed an acceleration up to the factor of four (to be published in detail later).

Two different methods for the deagglomeration and surface modification were utilized in this study, kneading and milling. For an effective kneading process a paste able to be kneaded is needed. This means, that an optimised paste has to have a sufficiently high viscosity, high cohesion and low adhesion. If these criteria are fulfilled, as it is achieved by the device described in the experimental part, it is possible to separate the agglomerated particles due the high shear forces, which are provided by the kneader rotors. Because of the generation of heat the kneading process is limited by the cooling capacity of the kneader to avoid temperatures above the boiling point of the solvents. For deagglomeration, 1 kg of the freeze dried powder, 10-15 wt. % surface modifier and 80 ml water were filled into the kneader. After 4 hours of kneading the following particle size distribution (d_{10}, d_{50} und d_{90} values represent the volume fractions) of the zirconia powder

could be achieved: $d_{10} = 10$ nm, $d_{50} = 13$nm, and $d_{90} = 17$ nm. The surface modified powder is fully dispersable in water and can be used e.g. for tape casting or for compounding into polymers.

As second route for deagglomeration and surface modification a ball milling process was investigated. The combination of the SMSM-concept (Small Molecule Surface Modification) [11] with the technology of wet grinding enables the production of ZrO_2 colloids from neat powders. In contrast to conventional milling additives small molecules with specific functional groups are utilized, tailoring the particle surface chemistry for appropriate processing.
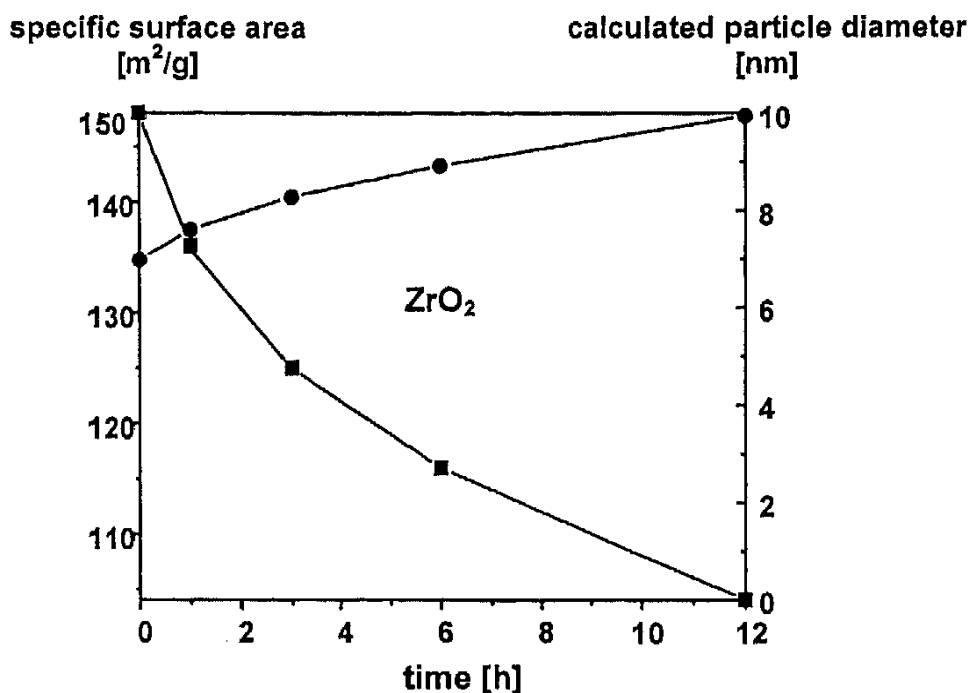

Fig. 3. Particle growth with time during hydrothermal treatment

The chemo mechanial comminution reaction in this study was carried out in a drais ball mill according to the laboratory set up shown in figure 4.

As starting material, the agglomerated zirconia, fabricated by the former mentioned hydrothermal process has been used. Water based suspensions of ZrO_2 and the surface modifiers listed in the experimental were subject to the mechanical comminution reaction leading to highly transparent and stable colloids. During this milling process high mechanical stress (shear and impact force) by the moving milling balls is introduced to the powder breaking down the agglomerates. In the present of a surface modifier strong bonds simultaneously were formed to the fresh produced surfaces. The resultant saturation of the reactive surface groups prevents the reagglomeration of the powder. For this type of reaction it is of high
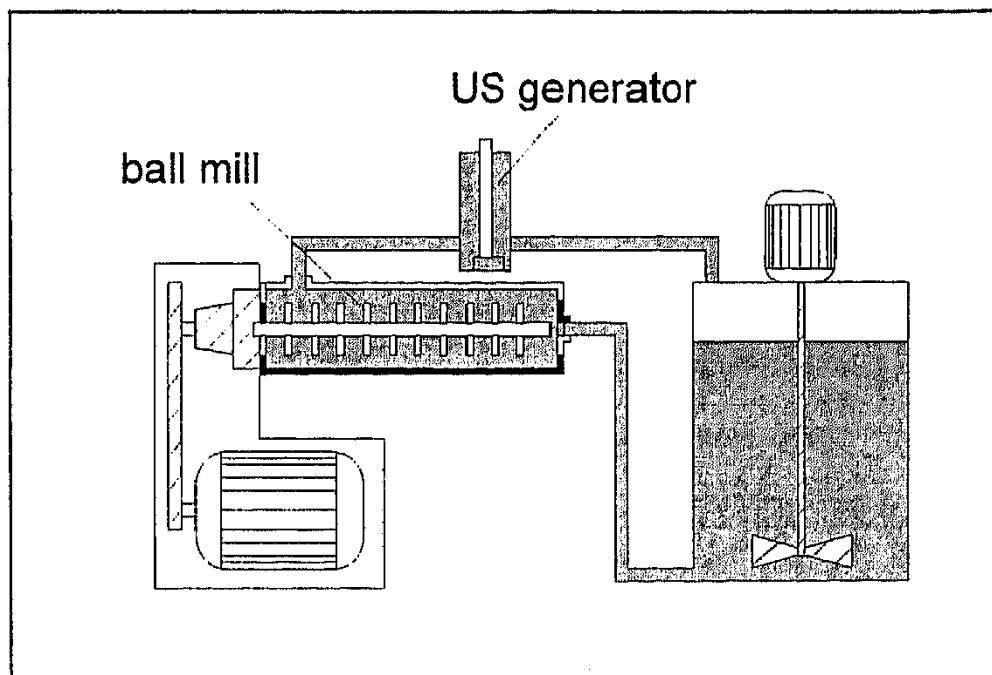
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Fig. 4. Scheme of the ball mill device using an ultra sonic generator in the flow system

importance to utilize relatively small molecules, because the process is diffusion controlled. The second requirement for the surface modifier is to produce good stable bonds to the particle surface.

Surface modifiers used in these investigations are listed in table I as well as the achieved particle sizes after 4h of milling. The best result has been obtained by N-(2-hydroxyethyl)iminodiacetic acid where a d_{50} value of 11 and a d_{90} value of 14 nm has been realized. Although the values obtained from 3,6,9-trioxadecanic acid (TODS) are very reasonable. Based on the availability, most experiments have been carried out with 3,6,9-trioxadecanic acid. Still the performance of formic acid can be described as sufficient. However it was a little bit surprising, because of the very small size of formic acid we had expected a much better dispersion state. This is still under investigation. A systematic examination on the surface modifier concentration dependency of the comminution reaction was carried out for the TODS surface modifier. The concentration of TODS was varied in 5 wt.% steps from 5 to 15 wt.%. There is a clear connection between the concentration of the modifier und the results obtained by the grinding process. 15 wt.% TODS are required to accomplish the best particle size reduction during the grinding (table II).

In the case of the surface modifier TODS [15 wt.%] the chemo mechanical comminution reaction was also monitored by taking specimens of the suspension every hour. These measurements clearly indicate (figure 5) a particle size

Table I. Surface modifier and obtained particle size (d_{10}, d_{50} und d_{90}- value of the volume distribution) by the grinding process (grinding time 4h)

	Surface modifier	d_{10} [nm]	d_{50} [nm]	d_{90} [nm]
alkylcarboxylic acids	formic acid	12	17	46
	acetic acid	10	13	27
ethercarboxylic acids	3-oxabutanic acid	9	12	33
	3,6-dioxaheptanic acid	9	13	24
	3,6,9-trioxadecanic acid	9	11	23
amino acids	N-(2-hydroxyethyl)ethylendiamine-N,N',N'-triacetic acid	10	13	32
	N-(2-hydroxyethyl)iminodiacetic acid	9	11	14
	bicine	8	10	19
	6-aminohexanic acid	11	15	33

reduction during the grinding according to expectations reaching a minimum after 5 h (d_{10} = 9 nm, d_{50} = 11nm, and d_{90}= 20 nm).

Table II. Obtained particle size (d_{10}, d_{50} und d_{90}- value of the volume distribution) by the grinding process with 5,10, 15 wt.% TODS as surface modifier.

wt.% TODS	d_{10}	d_{50}	d_{90}
5	36	72	155
10	12	47	135
15	9	11	23

After the strong decrease of the particle size during the first hour to d_{10} = 14 nm, d_{50} = 48 nm, and d_{90}= 185 nm, practically no effective size reduction occurred after 4 h of grinding (only reduction of d_{90} value in the 5th hour from 23 to 20 nm, d_{10} and d_{50} value are unchanged). Compared to the d_{90} value, the d_{50} and also the d_{10} displayed a much weaker dependency of the milling time. The d_{10} value is to a large extent independent of the milling time and is approximately identical with the primary crystal size of 9 nm.
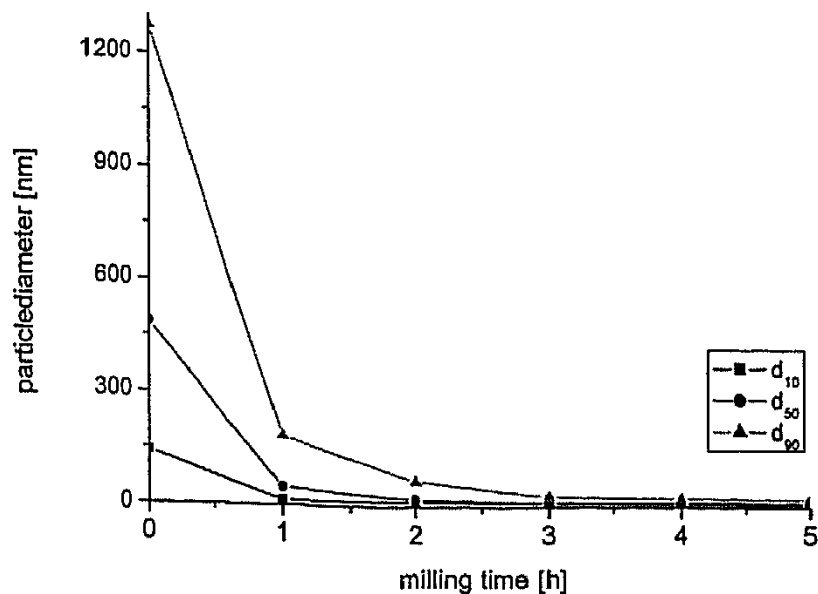
Fig. 5. Time dependence of the d_{10}, d_{50} and d_{90} values on the volume distribution

As stated before for a efficient surface modification, it is of high importance to get good chemical bonds of relatively small molecules to the surface. This is shown in figure 6 for TODS where it can be clearly seen that the CO frequency (free acid) is shifted to lower wave numbers in the bonded case. This confirms that a strong chemical bond is formed, which is necessary to maintain the surface modification in the further processing steps.
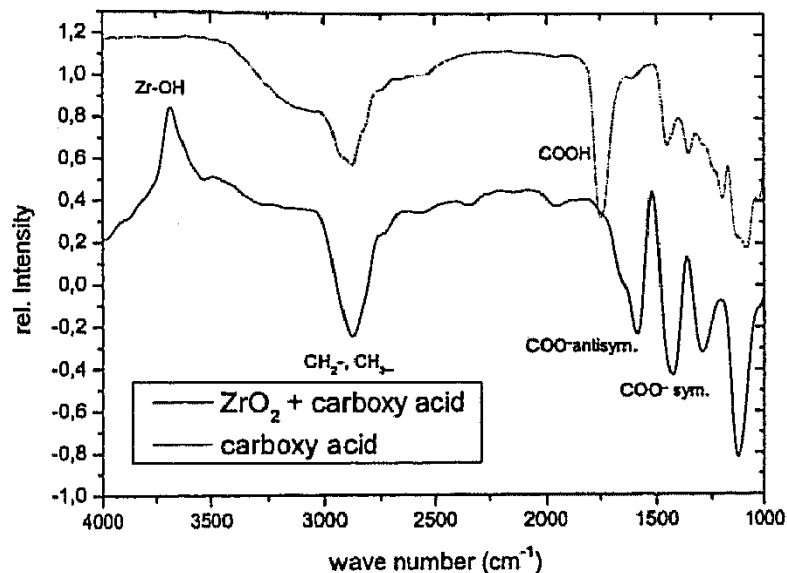

Fig. 6. DRIFT-spectroscopy of a surface modified zirconia sample (15 wt.% TODS) and the pure surface modifier (upper curve); the pure TODS is measured in transmission mode

To broaden the field of functional surface modifiers sorbic acid [10 wt.%], a unsaturated carboxylic acid was also tested. The viscosity of the water based suspension increases extremely after a short milling time so that the test could not be continued. This might be attributed to the low solubility of sorbic acid in water. To overcome this drawback the dispersion media was changed to ethanol with 1,5 wt.% water. In contrast to the former observation, no increase in viscosity took place and a comparable particle size distribution to the water based systems could be obtained after 6 hours of grinding (d_{10} = 9 nm, d_{50} = 11 nm, d_{90} = 14 nm).

Tape casting

Zirconia powders as derived from the hydrothermal processing and the subsequent surface modification have been used for the fabrication of ceramic membranes. For this reason, a tape casting process has been developed. A slurry with a solid content of 50 wt.% was made by mixing 50 wt.% ZrO_2, 6,25 wt.% TODS (12,5 wt.% respective to ZrO_2), 7,5 wt.% polyvinylalcohole PVA 4-88 (15 wt.% respective to ZrO_2), 2,25 wt.% glycerol (30 wt.% respective to PVA) and 34 wt.% water. The solid content of the resulted slurry was 50 wt.% (15 vol.%). After tape casting and subsequently drying the green density of the tape reached 79 wt.% (42 vol.%). The casted tapes have been dried and can be stored in the form of rolls. For the fabrication of the membrane, the zirconia separation layer has been laminated on top of a porous support, for example, alumina and sintered at 1000°C to a micro or nanoporous film. In figure 7, the cross section of a membrane fabricated by this technology is shown.
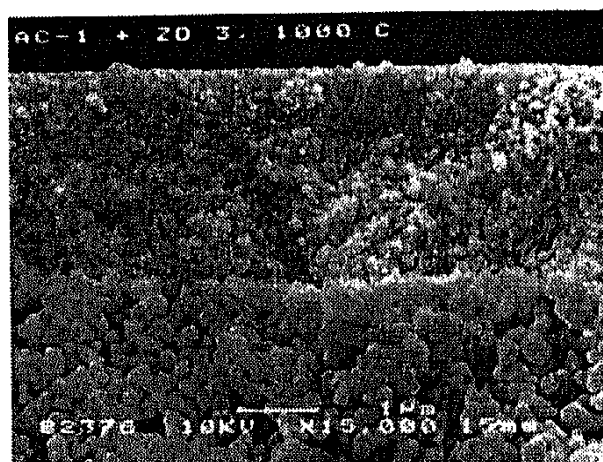

Fig. 7. SEM-micrograph of a nanoscaled zirconia membrane layer on a porous alumina support

The advantage of this type of membrane fabrication is two-fold. First, the membrane can be fabricated independently and the green membrane tape can be stored for a long time, and second, the flatness of these membranes is much higher than the conventional technology by sol-gel dip-coating. A first state about the separation behaviour is shown in table III.

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Table III. Gas phase separation behaviour of the nanofiltration membrane

Temperature	H_2-Permeation	Permselectivities
25 °C	$7*10^{-5}$ mol/Pa*s*m²	H_2 / Air: 3,2 (independent of the temperature)
200 °C	$5,5*10^{-5}$ mol/Pa*s*m	H_2 / CO_2: 3,6 (independent of the temperature)

Polymer Compounding

The fabrication of polymer matrix compounds has been carried out by using surface modified zirconia particles by trioxadecanic acid (12.5 wt.% trioxadecanic acid on zirconia with 9 nm primary particle size). This has been used to stabilize polycarbonate in a melt compounding process. The effect on the compressive strength is shown in figure 8. The bars of 20 x 20 x 100 mm³ in size have been put under an axial pressure of 100 MPa. As one can see, the unstrengthened polycarbonate is completely deformed whereas the polycarbonate filled with 5 wt .% of ZrO_2 does not deform at all.
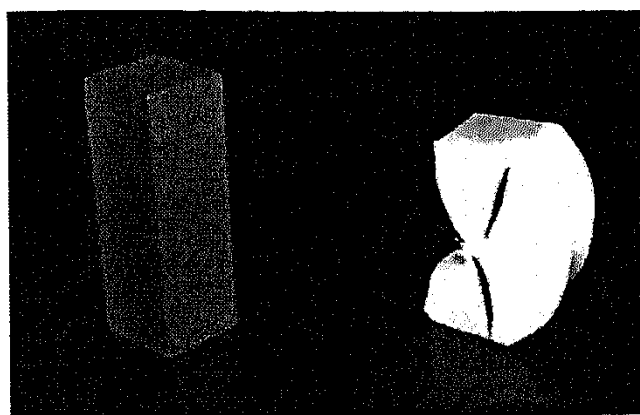

Fig. 8. Comparison of two PC bars of identical dimensions in the pressure test

The effect of the surface modifier for the homogeneity of the particle dispersion is shown in figure 9. Whereas the unmodified zirconia cannot be dispersed in the melt compounding process (using a Werner & Pfleiderer two screw extruder), the surface zirconia modified by TODS (see above) is homogeneously dispersed. The polycarbonate granules were melted in the extruder and the surface modified zirconia nanoparticles have been added the polycarbonate melt as in the conventional compounding process as a powder.
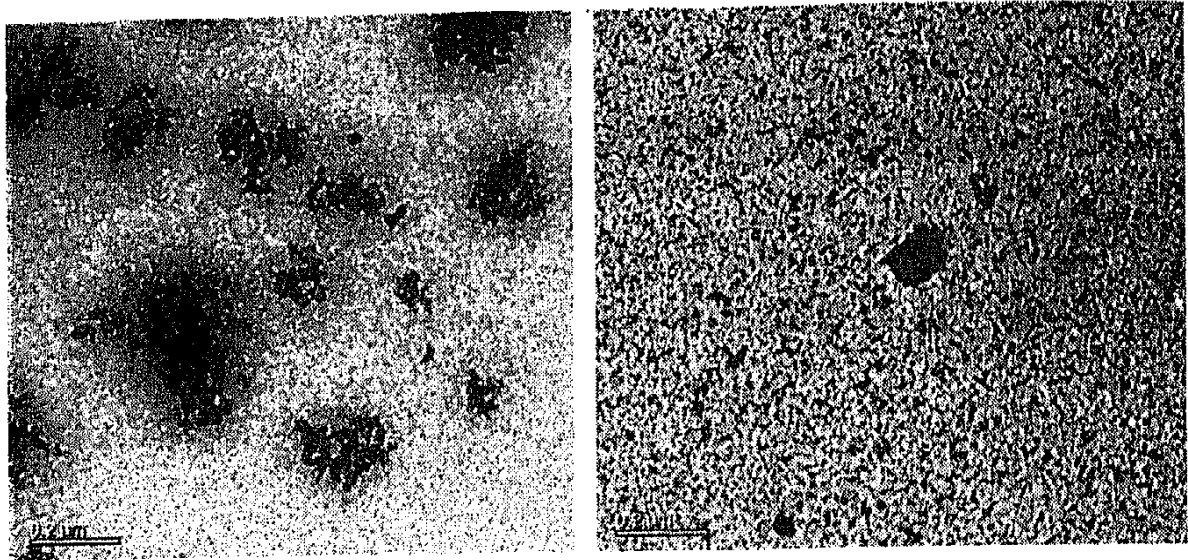
Fig. 9. Transmission electron micrograph (TEM) of unmodified (left) and modi
fied (right) zirconia in the polymer

The photo induced diffusion
Amorphous zirconia nanoparticles prepared according to the experimental part,
suspended in prehydrolysed MPTS, have been irradiated through a mask or by
two wave mixing as described in [15]. In figure 10, the scheme of the process is
shown and in figure 11, the diffractive pattern which has been obtained by the up
concentration of the zirconia nanoparticles. The lines have be verified by EDX,
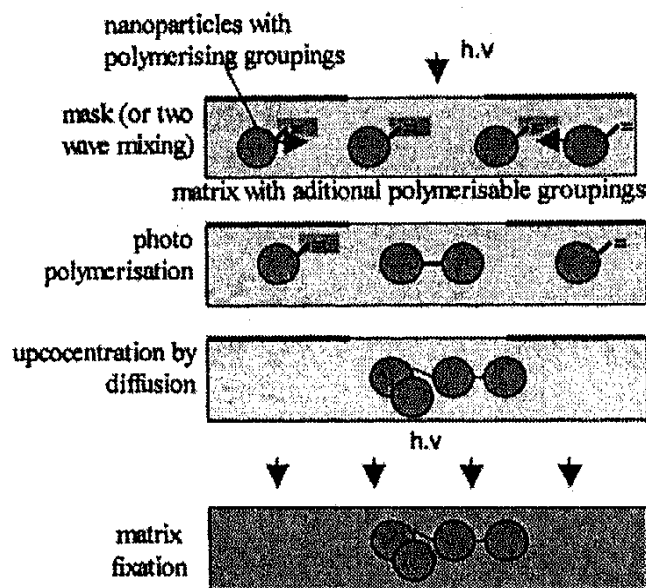
shown in figure 11. By two wave mixing process of a concentric with a planar wave, fresnel lenses have been written using this technology. In the meanwhile, an industrial process has been developed for the fabrication of light guiding films by a continuous process, where the photo induced micropaterning is carried out online after the wet web coating of the patternable nanocomposite films on a carrier plastic foil.
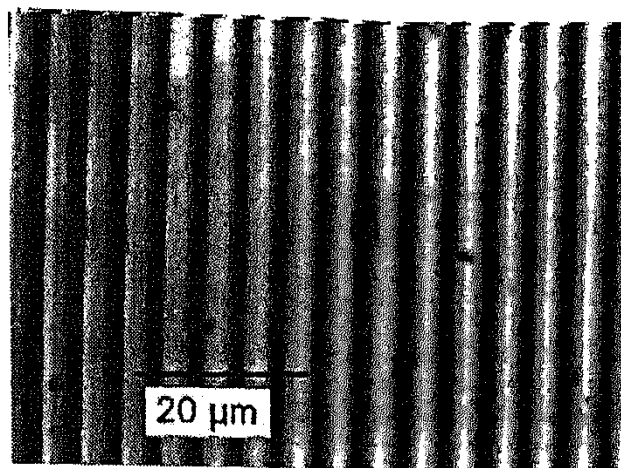

Fig. 11. Diffraction Patterns obtained by the ZrO_2 holographic process

CONCLUSION

One of the most important conclusion of this work is, that the processing of nanoparticles is strongly facilitated by the appropriate surface modification. This includes fabrication as well as processing to films and composites. Especially if optical systems are envisaged, a homogeneous dispersion is indispensable to reduce Rayleigh scattering. This process as shown with zirconia can be generalized and used also for other nanoparticles.

ACKNOWLEDGEMENT

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