CHEMICAL ROUTES TO NANOSTRUCTURED CERAMICS AND COMPOSITES

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1. Introduction

The sol-gel process represents a chemical synthesis route to fabricate oxidic materials like glasses and ceramics. It is characterized that molecular, oligomeric or colloidal systems can be used as precursors. The synthesis reaction is mainly based on a hydrolysis and condensation reaction. Through the condensation reaction metal oxygen metal bonds are formed leading to a three-dimensional network. While in silica systems in the majority of the cases under acid catalysis a more or less polymeric type of network is built up, in most other cases like alumina, titania, zirconia the first condensation step leads to colloidal systems which may be amorphous or partially crystalline like in titania. The gel formation takes place by aggregation of colloidal particles or further growth of polymer networks [1].

The growth reaction is an interesting step since after exceeding the critical nuclei size the nuclei grow to particles in chemical environment, which, and this is a prerequirement, has to have a decreasing value of the free energy. There is a competition between the interaction of the components of the chemical environment of the growing particle with molecular units getting deposited or reacted to the surface causing particle growth. The competing components may be solvents, molecules, protons, hydroxyl ions or other components of the reacting system. If the free energy of the absorption step or one of the components is lower than that of the deposition of further molecular units of the growing system, the growth reaction stops. This model would allow to influence the growth reaction to stop it or even to reverse it by addition of components with the desired surface reactivity, and it further leads to the possibility of stopping the particle growth at a desired diameter.

The basic principle is used for stabilizing sols by proper choice of pH values, leading to surface charges with repulsion forces through building up a surface potential [2]. From these stabilized sols, gelation can be carried out by destabilization of the sols, for example, by pH change to the isoelectric point. At this point, rapid condensation by surface hydroxyls takes place, leading to a not densely packed system, a two-phasic gel with a solvent or a gas phase in the pores.

The uncontrolled particle-to-particle interaction is one of the major problems of sol-gel processing. Due to the low solid content of gels, it is extremely difficult to fabricate

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large-dimensional monoliths or coatings in films exceeding one μm in thickness. In fig. 1, it is schematically shown how gels are formed by destabilization of particulate sols.
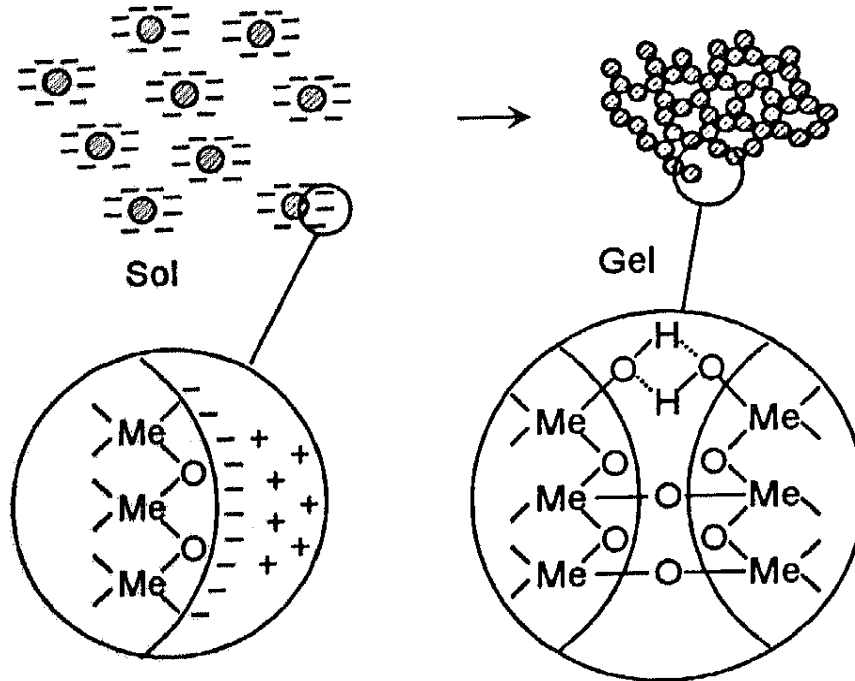

Figure 1. Schematics of the gelation of electric charge stabilized sols.

For these reasons, if sols will be used for the fabrication of ceramics or composites, it is of great importance to control the particle-to-particle interaction in a way that uncontrolled agglomeration to low-density gels or uncontrolled agglomeration to clusters can be avoided during composite fabrication.

There is a variety of reasons why small particle processing is of interest for material development and properties. In the case of ceramics it is well-known that the sintering temperature is a function of the particle size and can be decreased substantially with small particulate systems. Moreover, if it is possible to reduce sintering temperatures in a way that the densification takes place at temperatures where grain growth can be avoided, there is a good chance to "separate" densification from microstructure formation, which would lead to new perspectives for ceramic processing. In addition to this, nano-scale additive systems can be coupled to micron or sub-micron ceramic powders by proper surface chemistry tailoring, leading to a homogeneous distribution of additives and a variety of interesting processing perspectives through grain boundary engineering. Last not least, nanocrystalline materials are interesting from the functional ceramic point of view as well as from the structural ceramic point of view, the expectation of new electronic properties [3] and defect-free microstructures interesting for mechanical properties from the option to tailor through a special type of microstructure in nanocomposites with extraordinary mechanical properties, as shown by Niihara [4].

Another interesting point is related to the size of the particles. If the particle size in a composite, for example, can be kept below the Rayleigh scattering limit (which is about 1/20 of the applied wavelength and, in addition to this, depends on the refractive index difference between the particle and the matrix), composite systems can be developed for optical purposes where the solid state properties of the particulate system define to a great deal the material properties together with the matrix. The electronic properties related to small particulate size are another interesting perspective, for example, quantum effects, if semiconductor nano-scale particles or metal particles are used. For this reason, these composites have interesting application potentials. The key point for the preparation is to control the particle-to-particle interaction as well as the interface of the particle to the matrix environment, since this interface, due to the large surface area of small particles, plays an important role for the material properties.

The sol-gel process seems to be an ideal method for the preparation and utilization of small particles if the surface properties can be controlled in a satisfying way. For the synthesis the growth process is the most important reaction, and there is no basic difference between the formation of amorphous structure by a condensation process or a crystalline structure by a precipitation process, since both processes follow the same basic rules. For this reason, it will not be distinguished between the precipitation of nano-scale particles from solution and the sol-gel-based formation of colloidal sols by condensation. Through "extension of sol-gel processing" the preparation of metal colloids or semiconductor colloids can be included. For preparing metal colloids from the oxidized state, e.g. from metal salts, a reduction process has to be included into the precipitation step, of course.

2. Basic Principle and Requirements

As pointed out above, systems with small particles are interesting for a variety of reasons if the specific properties of these particles can be utilized in materials. In the case of ceramic processing, it is the low-temperature sintering and the separation of densification and crystal growth. For optical properties based on colloids, in fig. 2 some examples are given and, of course, combinations of these properties are very interesting, too, for example, high transparency with good surface-mechanical properties.

However, as pointed out above, it is necessary to keep the particle size at a very low state if light scattering shall be avoided. In fig. 3, the results of the calculation are given [5], showing the optical transparency as a function of particle size and refractive index difference. For this calculation a glass of 1 cm in thickness was assumed, containing 1 vol.-% of scattering particles with two different refactive indices.

Optical Properties

♦ = Oxide
(surface hardness,
passive,n_o)

● = Semiconductors
(active, χ^3)

✿ Dyes
(n_o, χ^2,
photochromic)

● = Metal
(active: χ^3
passive: E)

○ = Laser
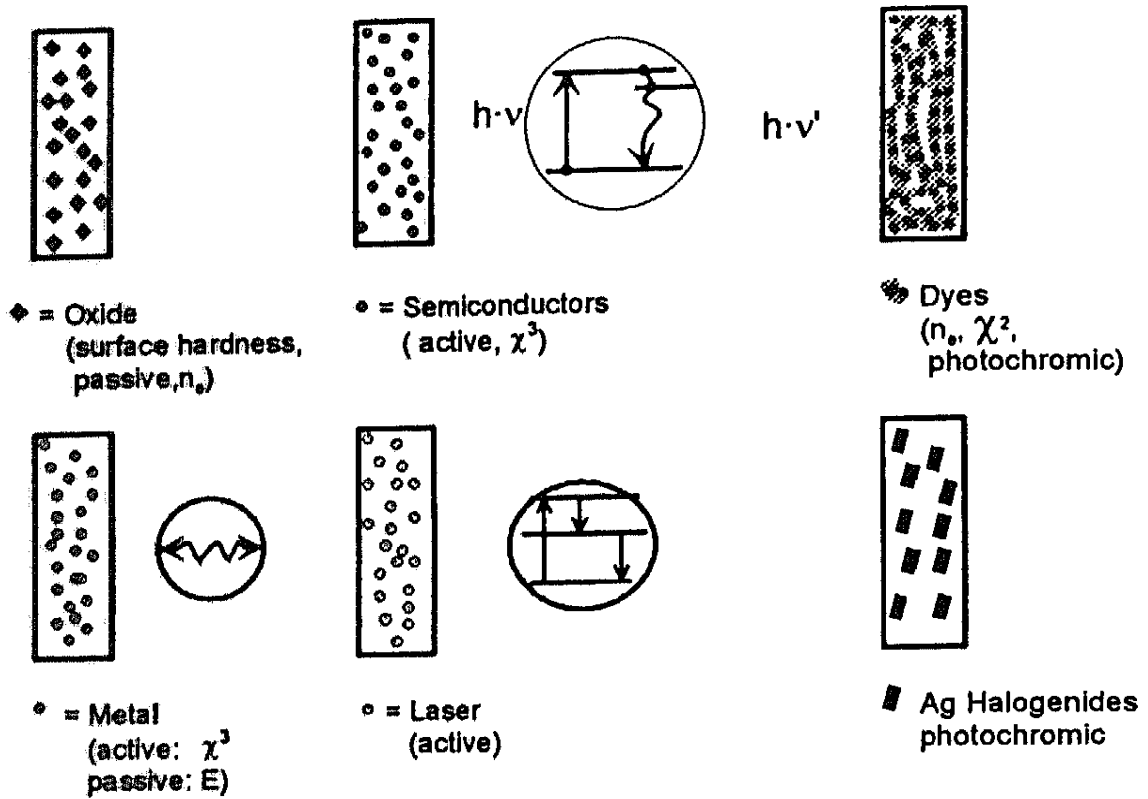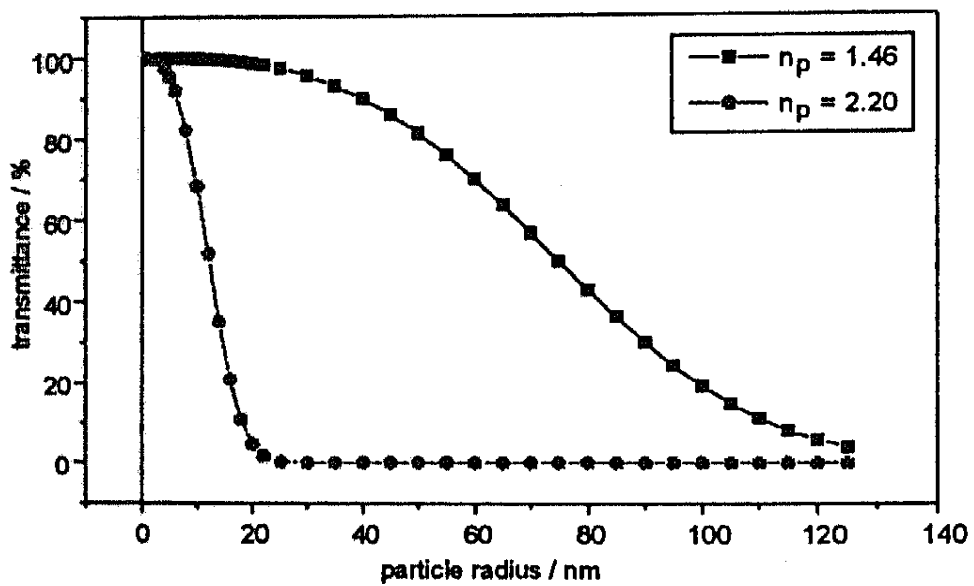(active)

▮ Ag Halogenides
photochromic

Figure 2. Examples for optical properties to be obtained with small particles.

transmittance of glass (thickness 1 cm, refractive index 1.50), containing non absorbing, scattering particles (volume fraction 1 %) with different refractive index as function of particle size, calculated for 500 nm wavelength

Figure 3. Calculated values of transmission reduction by Rayleigh scattering, from particles in glass [after 5].

As one can see, in the case of n = 2.20, the particle size has been kept on a level below 3 nm; in the case of n = 1.46, the particle size can be up to 20 nm without remarkable scattering losses.

The problem of stabilization of suspension is an important question in ceramic processing, and different approaches are used. The simplest one is the electrostatic stabilization where by use of appropriate pH values electric charges are established on the surface of ceramic particles. The stabilization requires high concentrations of soluble ionic compounds which are, in general, not very useful for the ceramic system, for example, if low alkaline contents are required. For this reason the electrosteric surface modification is chosen, which can be performed by the absorption of organic polyelectrolytes on the surface of ceramic particles. These polymeric compounds have to be burned out during firing. In other cases organic polymers are used to wrap up the particles, for example, in the case of ceramic injection moulding. Due to the fact that all these surface-controlling agents show repulsion forces which range from several up to 10 nm, their use is restricted to particle sizes in the μm or upper sub-μm range since the "volume" they require becomes extremely large if one reduces the particle size to the lower nm range. In this case this type of surface modification would lead to extremely low solid contents, as it already has been pointed out for electric charge stabilized sols.

To solve these problems, a new concept for surface modification of nano-scale particles has to be developed which protects the particles from co-condensation and which, in addition to this, can control the growth reaction during the particle synthesis. In fig. 4 a schematic is given to demonstrate the described situation. For nanoparticles, the reaction of small molecules with relatively stable surface bonds to keep the equilibrium on the absorbed side is necessary.

several nm

electrostatic with
ionic componds

several to
more than 10 nm

electrostatic with
polymer electrolytes

10 to 20 nm

steric with
polymers

~1 nm

small molecule
surface modification

• active site
•◁⌇∿ small molecule
with specific
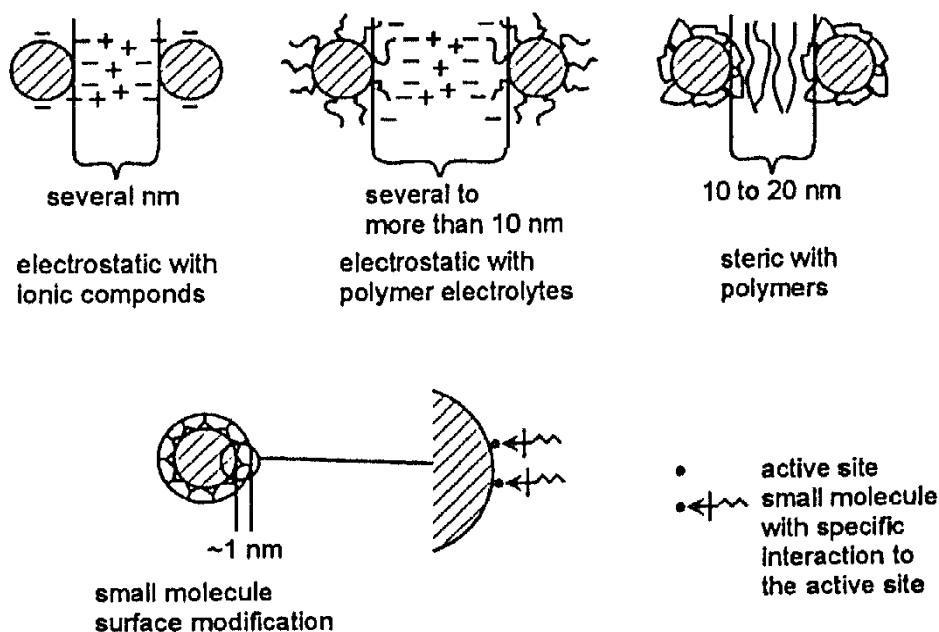interaction to
the active site

Figure 4. Comparison of the required volume of different types of sol stabilizations.

As one can see, the conventional types of surface modification lead to systems with low volume fractions of solids in case of nanoparticles but is suitable for μm particles. The advantage is the good adhesion due to the large number of adsorptive site per macromolecule. If the conception of small-molecule surface modification is used, one has to ensure that at least a large part of the molecules used for surface modification present in the system is adsorbed on the surface. In this case, one has to establish a selective interaction of the active site of the molecule with the active site of the surface. This requires a specific development for each system. On the other hand, this concept can also be used for tailoring growth reaction or even for stabilizing two-phasic systems, such as microemulsion systems. The concept becomes even more attractive if bifunctional molecules for surface modification are used. The second function not blocked by adsorption can be used for further reaction, for example, with double bonds for polymerization. This leads to a new type of particulate precursor with organic function, for example, "polymerizable colloids". The principle is shown in fig. 5
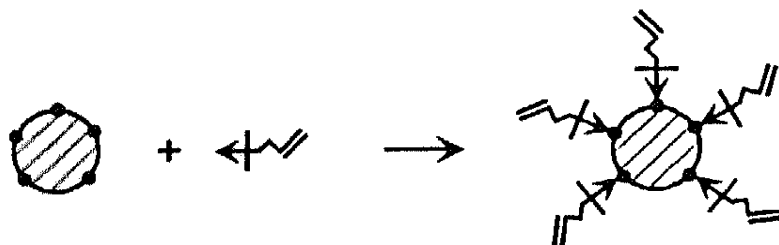

Figure 5. Formation of "polymerizable colloids" by bifunctional molecule surface modification of colloids.

If non-polar groupings are used, there exists a good chance to avoid agglomeration and at the same time obtain high package densities of sols or gels.

In the following, the described basic principles are used to synthesize nano-scale particulate systems with controlled surface reactivity or to process nano-scale particles to bulk materials or parts.

3. Synthesis and Processing of Nano-Scale Systems

3.1 OXIDIC COLLOIDS

One of the basic possibilities of controlling the particle size during the sol-gel process is to use a diphasic system where the reacting or precipitating phase is dispersed within a carrier phase. In general, the stability of this system is very low if no means are employed to use the interface free energy. This can be carried out by bifunctional molecules having strong interaction with both faces, such as tensides or emulsifiers [6, 7]. It has been shown that thermodynamically stabilized microemulsion systems of the water-in-oil emulsion type can be used for carrying out precipitation processes in the very small particles of several nm in diameter. If appropriate emulsifiers are chosen, the emulsion system then is turned into a suspension system without losing its basic characteristics, that means the stabilizing molecules still remain adsorbed on the

particle surface, avoiding agglomeration completely. Even after solvent removal, the systems can easily be redispersed, and the emulsifiers can be burned off under controlled atmosphere without leading to agglomeration. Thus, zirconia powders have been prepared with 5 - 20 nm in diameter, completely redispersable with a means [6, 7].

In a variation of this route, the carrier phase can be avoided if an aqueous emulsion of the emulsifier is added to the aqueous precursor system, and after this a pH value is established, leading to precipitation, e.g. pH 9 in case of ZrO_2. As shown in [6], precipitation takes place in a way that the emulsifier micelles are dissolved and the emulsifier molecules are absorbed on the growing particle, avoiding agglomeration completely. With this method, zirconia powders have been prepared in the nanometer range with a volume yield up to 110 g oxide powders per liter. In fig. 6 a flow chart comparing the microemulsion route with the controlled precipitation route is given.
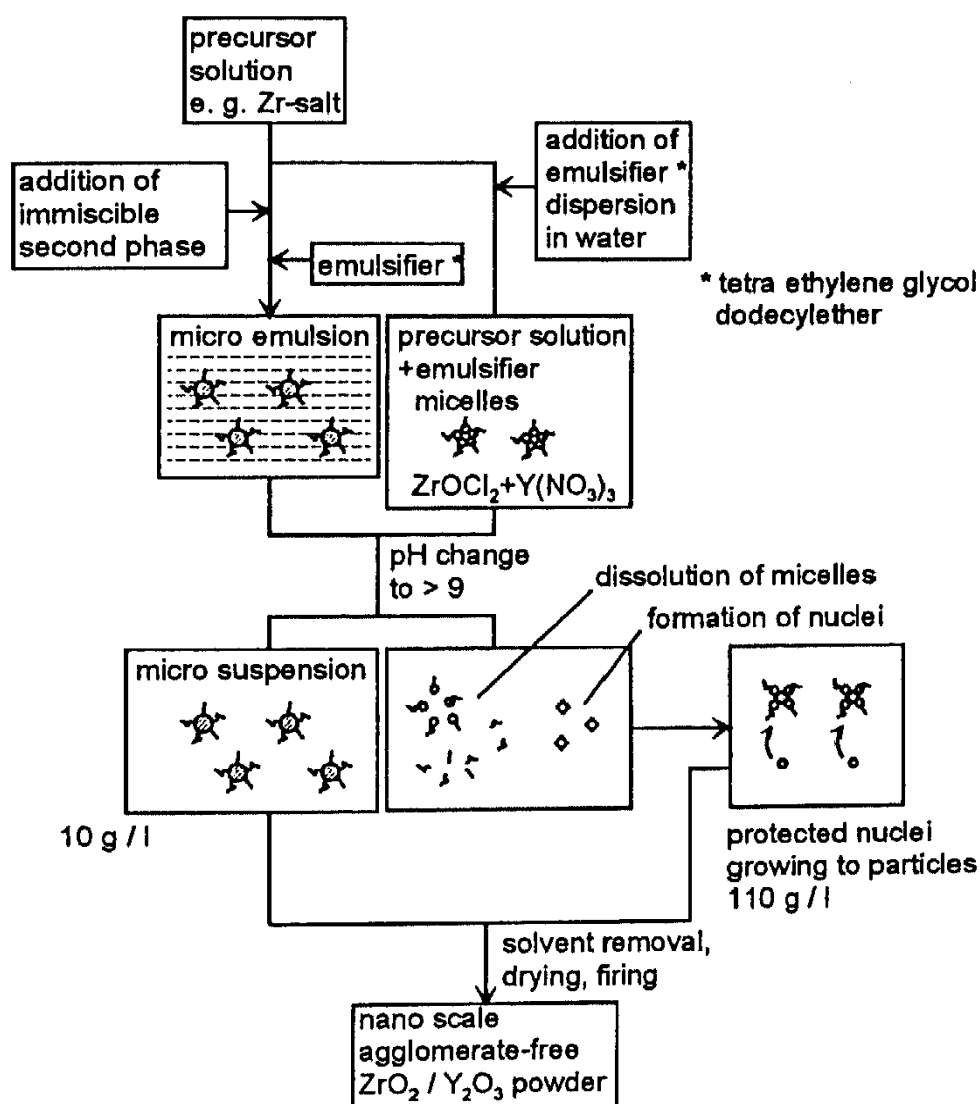

Figure 6. Schematics of the microemulsion and the controlled precipitation route for the synthesis of nano-scale oxidic particles.

The main difference between the microemulsion and the controlled growth route is the volume yield, which is substantially higher than with the microemulsion route. In fig. 7 the X-ray diffraction patterns of microemulsion derived and controlled growth route derived powders are given.
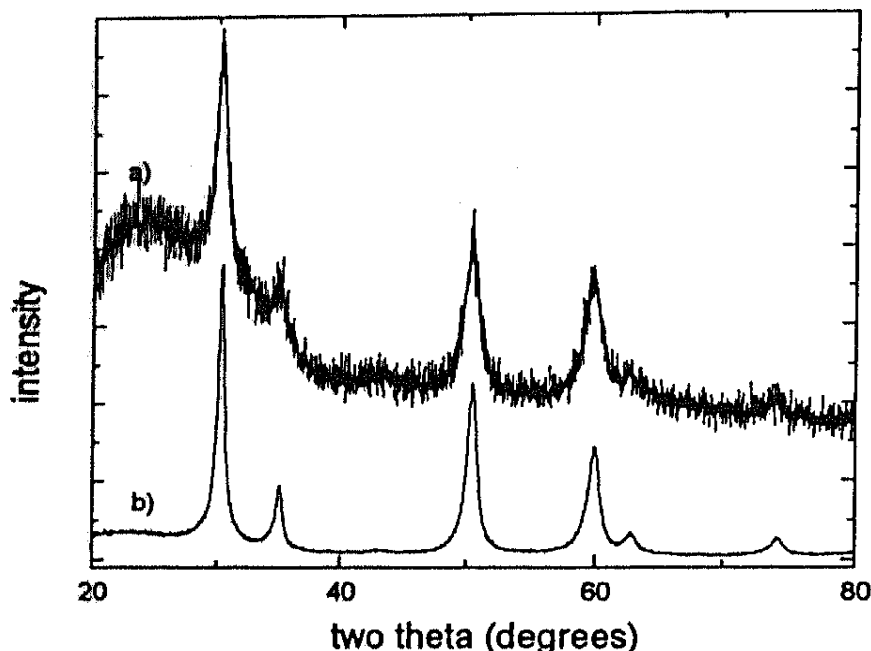

Figure 7: X-ray diffraction patterns of $5Y_2O_3$ /ZrO_2 nano powders derived from microemulsions (a, 8 nm) and controlled precipitation (b, 16 nm) [after 6, 7].

As one can see, both powders are well crystallized. The line width can be used for calculating the particle size according to Scherer's equation, which is in the case of the microemulsion 8 nm and for the controlled growth powders 16 nm.

In a very similar way, alkoxides in connection with carboxylic acids can be used for nanoparticle synthesis. As described in detail elsewhere [8], zirconia alkoxides have been reacted with methacrylic acid, leading to a mixed alkoxide carboxylide. Hydrolysis and condensation of this system lead to particulate systems with zirconia covered with methacrylic acid, as schematically shown in fig. 8.
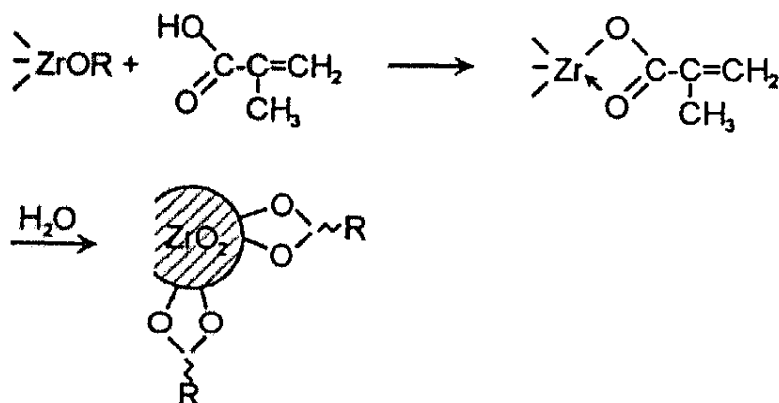

Figure 8. Formation of ZrO_2/methacrylic (ma) acid colloids by complexation of Zr alkoxides with ma and subsequent hydrolysis [after 8].

The zirconia particles can be obtained in the crystallized form after incorporating them into sol-gel inorganic-organic matrices, as proved by electron diffraction (fig. 9) which shows that most of the zirconia is monoclinic. It has to be mentioned that the crystallization takes place at temperatures below 120 °C. NMR and IR studies show that after hydrolysis and precipitation the methacrylic acid-to-zirconia bond is unchanged. This has to be interpreted that the methacrylic acid is bond to 2 nm-sized colloids in a similar way as it is bond to alkoxides (colloidal complex).
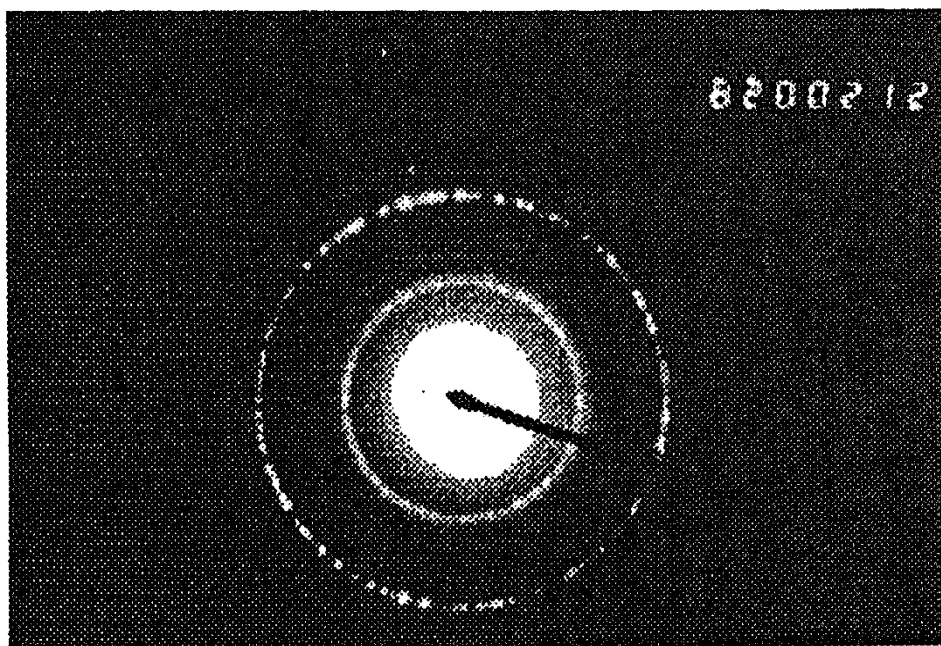
Electron diffraction pattern of nano-crystalline ZrO_2
particles of ZrO_2 / methacrylate nanocomposites

Figure 9. Electron diffraction pattern prepared from Ormocer films containing ZrO_2 colloids (monoclinic ZrO_2)
[after 8].

This principle has been successfully applied for a variety of other systems like chromia, magnetite, PZT and barium titanate.

3.2 METAL COLLOIDS

Metal colloid-containing systems can be prepared by a sol-gel reaction from metals to be reduced under mild conditions by organic molecules, especially noble metals like palladium, platinum, gold, silver, but also for copper. For example, it is well-known that gold can be reduced by ketones under light exposure from Au^{3+} to Au^0. However, the colloids formed by this process tend to aggregate and cannot be controlled very easily in size. Stabilization of the oxidized form by complex formation with amines, as already shown in [9], leads to the possibility of processing these ionic compounds to stable Au colloids and, if bifunctional ligands, for example amino silanes, are used for bulk materials or films. Similar reactions can be carried out with silver, Pd or Cu and (without a reduction step) with semiconductor quantum dots like CdS. If Cl⁻ is

introduced into these systems [9-13], photochromic layers can be obtained. In fig. 10, the general reaction scheme for the fabrication of colloidal metal particle-containing coating systems is shown.

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┌──────────────────────────────┐
│ AuPdCu / ammine complexes    │
└──────────────────────────────┘
              │
              ▼
┌──────────────────┐        ┌─────────────────────────────────┐
│ stable Au colloids├──────►│ addition of methacryloxy silane │
└──────────────────┘        └─────────────────────────────────┘
                                             │
                                             ▼
┌──────────┐    ┌─────────┐       ┌──────────┐
│ χ³ systems│◄──│ curing  │◄──────│ coating  │
└──────────┘    └─────────┘       └──────────┘

┌──────────────────────────┐
│ Ag / ammine complexes    │
└──────────────────────────┘
              │
              ▼
┌──────────────────────┐
│ stable molecular      │       colloid formation by
│ systems preventing    ├────►  heat → conductive
│ precipitation during  │       tracks
│ processing            │
└──────────────────────┘
       │ + Cl / Br
       ▼
┌──────────────┐
│ photochromic │
│ layers       │
└──────────────┘

┌──────────────────────────────┐
│ Cd / SH or ammine complexes  │
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              │
              ▼
┌──────────────────┐
│ stable colloids  │
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│ fluorescent activity├────►│ addition of methacryloxy silane │
│ to be tailored      │     └─────────────────────────────────┘
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┌──────────────────┐    ┌─────────┐    ┌──────────┐
│ fluorescent films│◄───│ curing  │◄───│ coating  │
│ χ³ films         │    └─────────┘    └──────────┘
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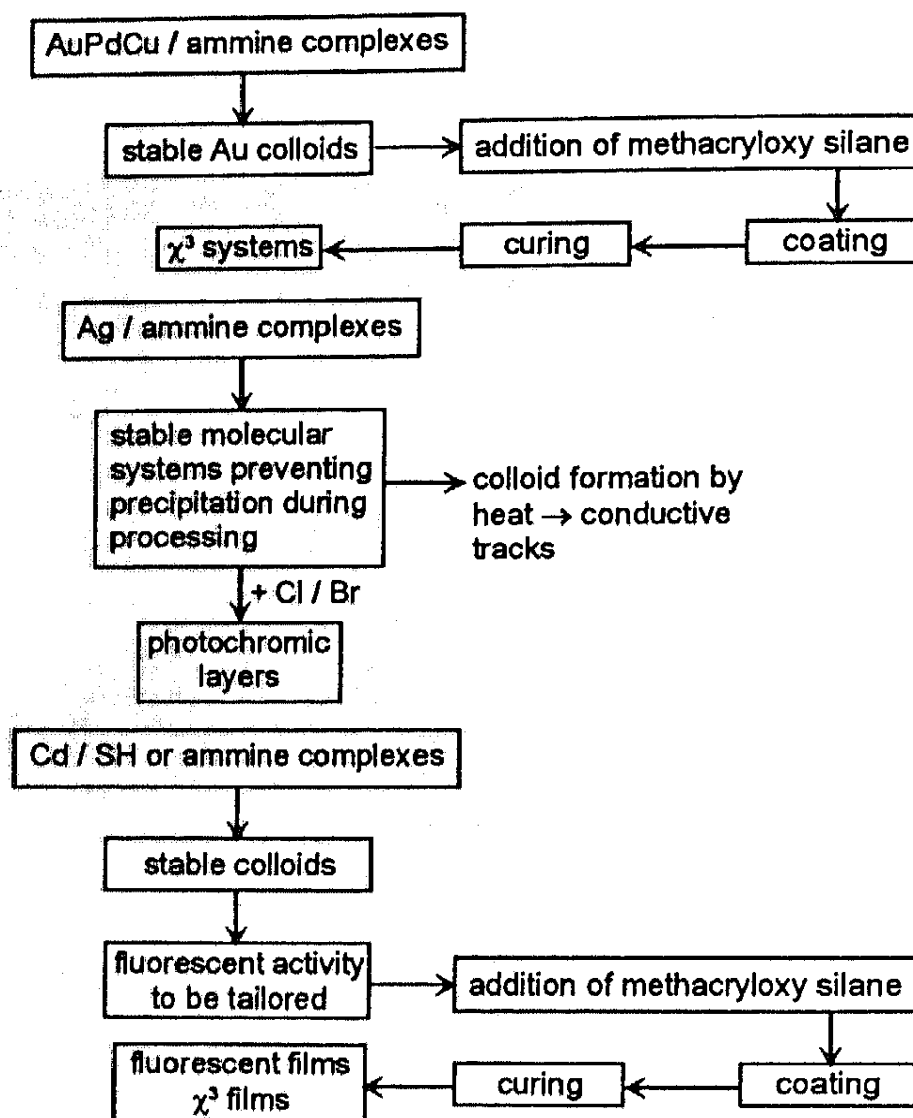
Figure 10. General reaction schemes of the fabrication of metal and semiconductor colloid containing films [after 9 - 12].

It is of importance that the colloids can be transferred into the solid state. Another possibility is to transfer the ionic complex into the solid system and to carry out colloid formation under controlled temperature conditions, as shown in [9 - 11]. It is surprising that the colloid size can be controlled by the metal-to-amino ligand ratio. It could be shown that with increasing complex ligand concentration, the colloid size decreases. Optical spectra, as shown for Pd [11] prove that the ionic state can be transformed into the solid phase, as schematically shown in fig. 11, the ligand concentration seems to influence nucleation with the tendency of higher ligand concentrations leading to a higher nuclei concentration. With these principles it was possible to develop metal-containing, highly transparent composites with particle sizes between several and 20 nm.
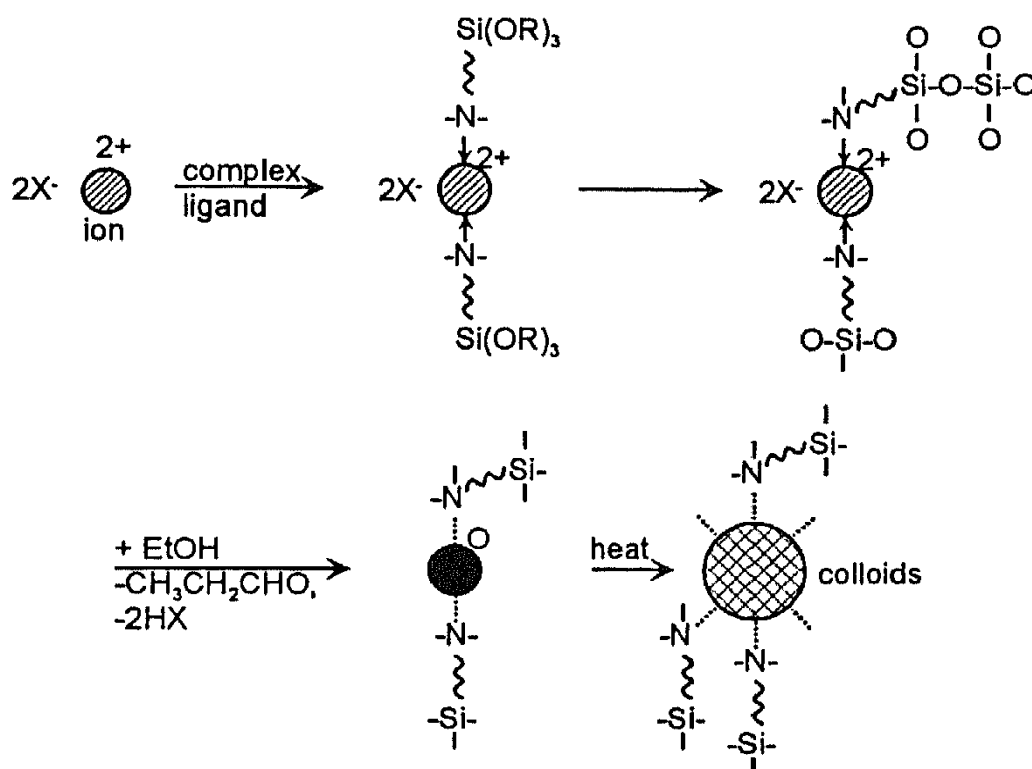
Figure 11. Schematics of processing Au colloid containing inorganic-organic composite films by colloid growth during curing.

Using this approach, it was also possible to avoid reduction in the case of silver and to form silver halide containing nanocomposites with photochromic behavior, too. In order to form the silver halide, organofunctional silanes with fluorinated alkyl groups were used. These groups have the property to release chlorine at about 200 °C, reacting with the reduced silver under ambient conditions [12]. These coatings can be darkened by UV light and bleached at slightly elevated temperatures.

Summarizing, one can say that the control of the reactivity of metal ions by appropriate ligands and using these ligands as matrix formers, metal colloids can easily be incorporated into sol-gel matrices, showing high optical transparency.

3.3 SURFACE MODIFICATION OF NANOPARTICLES FOR PROCESSING

As already pointed out above, the interesting properties of nano-scale powders should be successfully exploited for ceramic processing, it is necessary to end up with green bodies with high package densities. The small molecule surface modification approach should be an adequate means for achieving this target. In order to prove this, boehmite was chosen as a model system, which was redispersed by refluxing in acids to primary particle sizes of 15 to 20 nm. After redispersing, the boehmite was treated with carbo-

xylic acids, and it could be shown that a surface compound was formed [14], showing similar molecular structures by IR investigation as aluminum acetates (fig. 12).
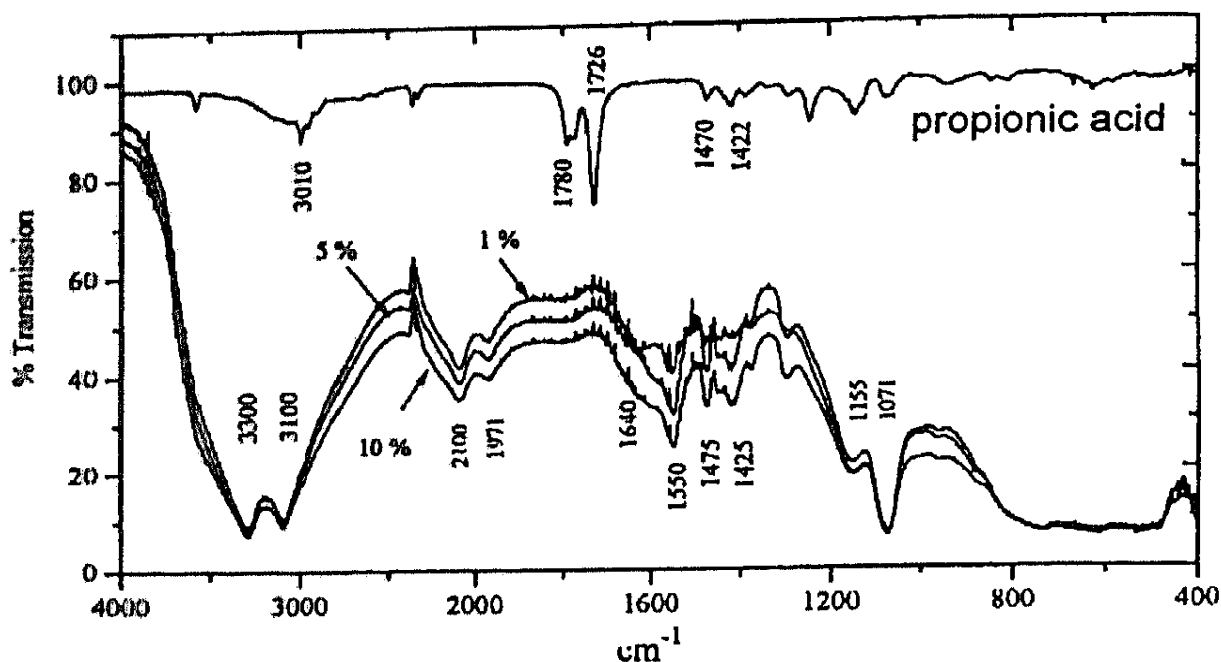

Figure 12. IR spectra of boehmite/propionic acid surface compounds compared to propionic acid with 1, 5 and 10 wt.% of propionic acid.

The surface compound is rather stable and cannot be destroyed by simple washing. This type of colloidal sols show very interesting properties since they do not exhibit a gel point. By increasing the solid contents, the viscosity increases, too, but never reaches gel-like rigidity. These systems remain plastic. With solid contents of 40 to 50 % by volume, extrusion processes can be carried out, leading to translucent systems (fig. 13).

Figure 13. Translucent green body of modified boehmite.

After drying the solid content of this type of "gels" is up to about 60 % by volume, which is extraordinarily high for gels. Extruded tubes can be fired to alumina ceramics despite the fact that boehmite is not a very suitable starting compound for alumina.

Untreated gels show gelation at about 20 % of solid content by volume, which can be shifted to higher solid contents only by high concentrations of nitric acid.

Following this concept, titanium nitride produced by H. C. Starck company by the chemical vapour reaction process, available with particle sizes of about 40 nm, was treated with a diamino grouping-containing chelating ligand. Guanidino proprionic acid was found to be a very stable complex former for Ti_4^+ and can be used to stabilize the TiN colloids. Pressure filtration of these systems leads to green bodies with about 60 % of green density by volume.

4. Material Development

4.1 COMPOSITE PREPARATION AND APPLICATION

Based on the synthesis of zirconia methacrylic acid (ma)/methacryloxy silane composites based on the preparation of zirconia methacrylate complexes with subsequent nanoparticle formation have been carried out. One of the very important questions is the stability of the methacrylic acid zirconia colloid bond, especially under the influence of water vapour, since for an appropriate material development high stabilities are necessary in most cases. A series of investigations have been carried out to optimize the solid content without agglomeration or gelation. By NMR and IR investigations [8] it could be shown that relatively high concentrations (up to 50 mole%) of zirconia can be incorporated into these systems if the water content during hydrolysis of zirconia can be kept low, especially if the free water is transformed into hydroxyles of the silanes before the addition of zirconia/ma complex. During the hydrolysis the silanole concentration of the methacryloxy silane undergoes a maximum, leading to a minimum content of free water [8]. The mixing of the complexed zirconia alkoxide with a reacting silane at its maximum SiOH content leads to clear and transparent nanocomposite sols. During hydrolysis, by IR no frequences attributed to the free methacrylic acid can be detected. The results are proved by ^{13}C NMR. After preparing coatings from these systems, even two weeks water treatment do not show any traces of free methacrylic acid after polymerization of methacrylic acid to the methacryloxy groups of the silane. Polymerization at 120 °C leads to conversion rates of 95 % [15].

A variety of systems and components have been produced from this basic system. They have been used for waveguide fabrication, for micropatterning, for photolithography and direct laser writing as well as for embossing two-microlens arrays [16, 17]. A survey is given in fig. 14.
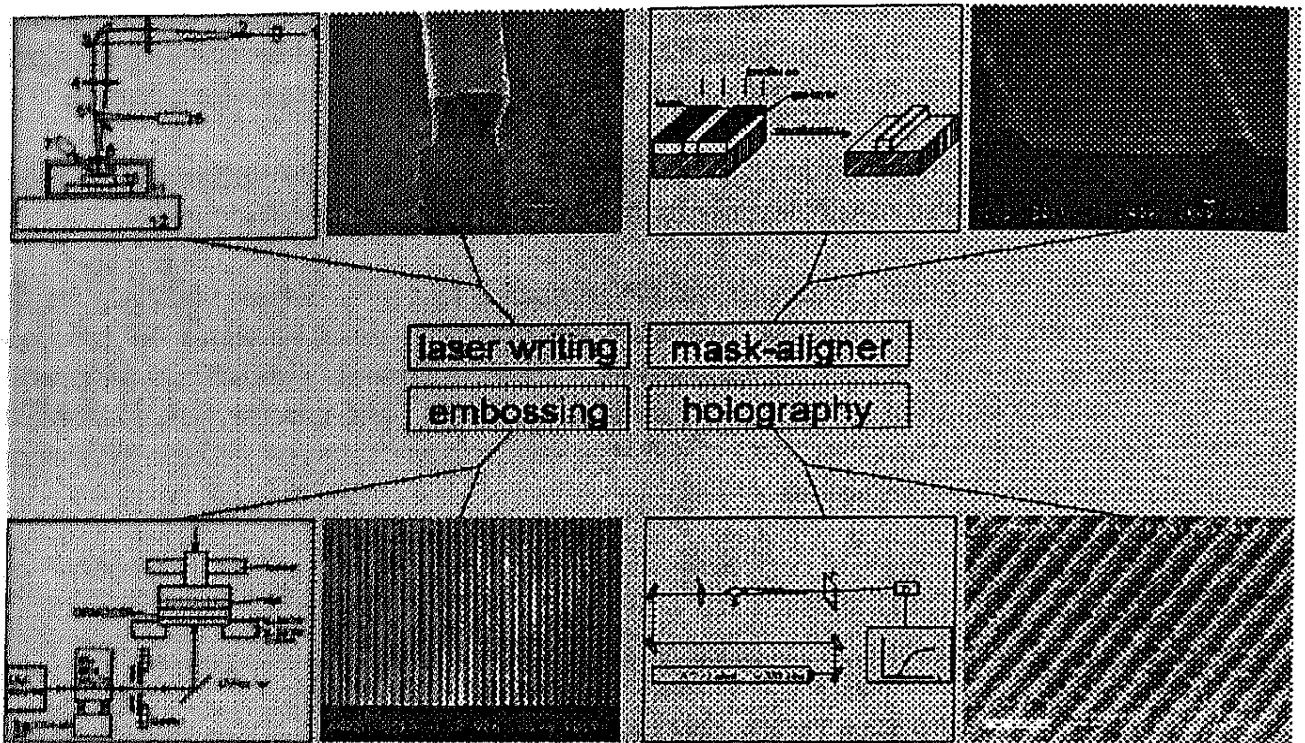
Figure 14. Schematics of the fabrication of micropatterning with different methods and SEM micrographs with patterned surfaces. 1-12: laser writing device. 1: light source; 2: beam expander; 3-5: mirrors and filter; 6: microscope; 7-12: xy device under clean conditions with observation window.

Fig. 15 gives a survey over the materials already developed by nanocomposite and colloidal processing [after 15 - 17].
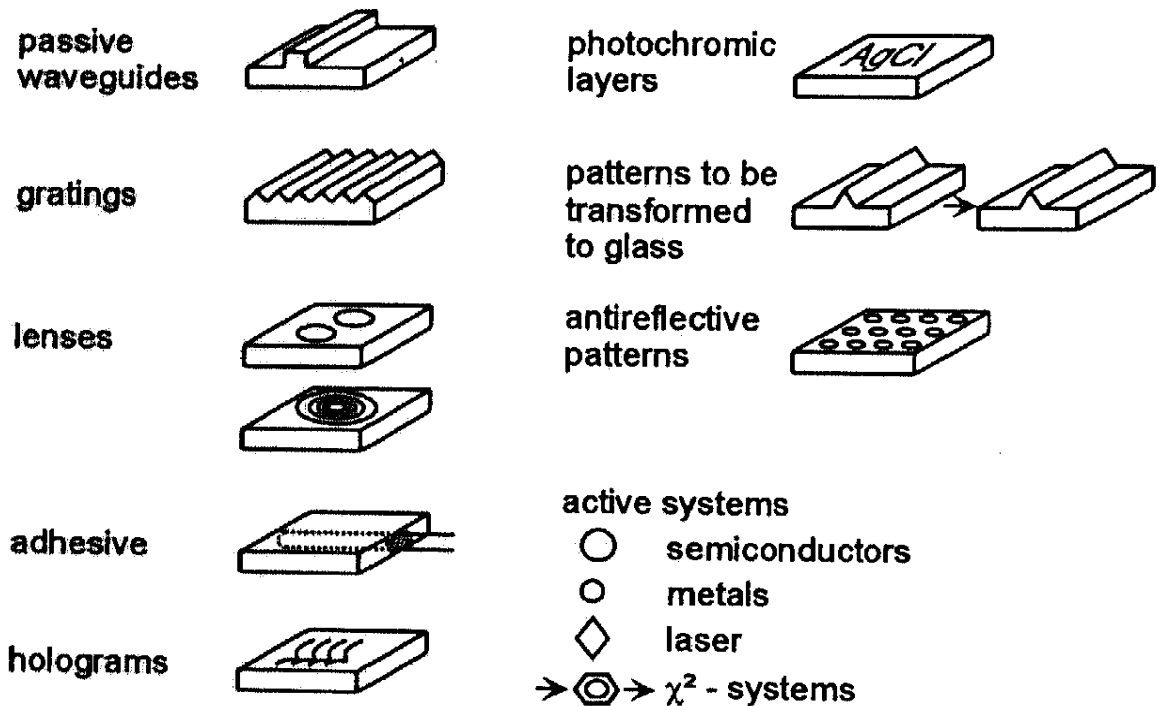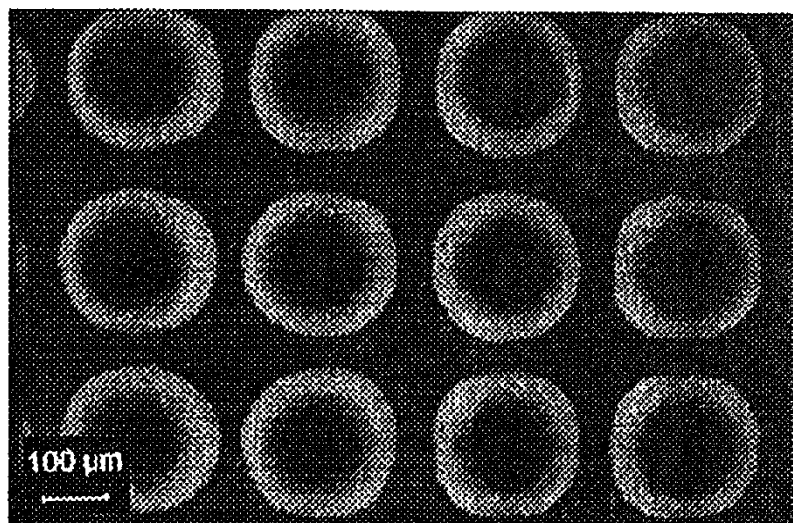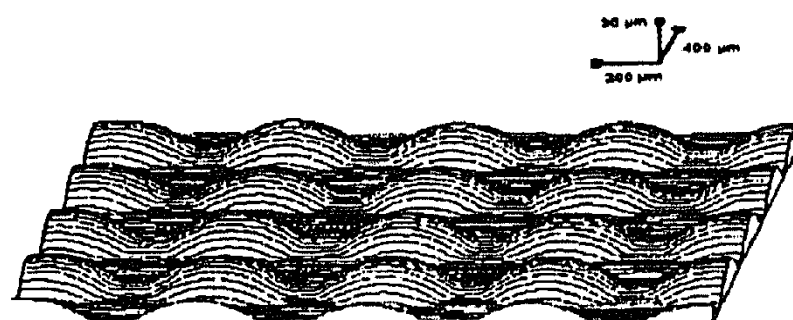

Figure 15. Survey over a series of materials developed by nanocomposite technology.

Fig. 16 shows the SEM micrograph as well as a profilometer plot fabricated from a ZrO_2/ma/methacryloxy silane nanocomposite by embossing with a metal stamp and UV curing during embossing.

Micrograph of an sperical lens array in an organic-inorganic composite material

Three dimensional profile of the lens array of the same sample

Figure 16. SEM micrograph and profilometer plot of an embossed microlens array from a ZrO_2/(ma) methacryloxy silane nanocomposite.

To this basic system, additional functions can be added. This can be done, for example, through additional functional silanes. If silanes with perfluorinated side chains are used in low concentrations, coatings with gradient functions can be synthesized [18]. Due to the thermodynamic rules, the system tends to reduce its interface free energy or surface free energy, and the fluorinated groupings are transported to the surface of the coating while the polar groups diffuse to the interface as long as the substrate has sufficient polarity (for example, metals, ceramics, glasses or most of polymers). This type of coatings shows high transparency, remarkable scratch resistance and adheres to many substrates. The surface free energy is in the range of 18 N/m^2 (polytetrafluoro ethylene: 19 N/m^2). These surfaces can be used for antisoiling surfaces, antisticking surfaces, and are very interesting for many applications. The process is

shown schematically in fig. 17. the gradient formation has been clearly shown by ESCA profiling.
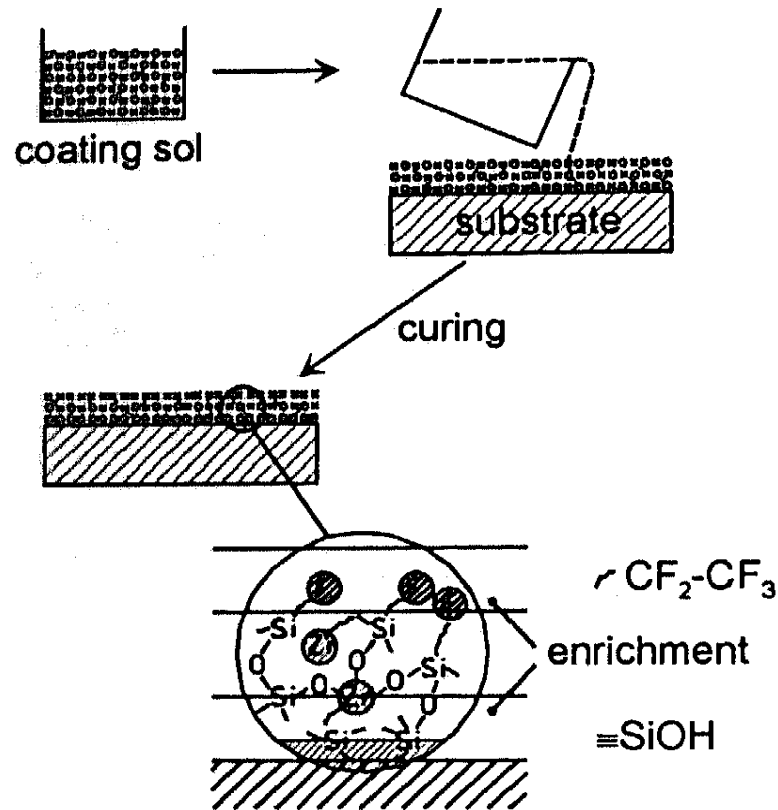

Figure 17. Formation of a low surface free energy formation in a nanocomposite coating. ZrO$_2$ particle size: about 2 nm.

As shown elsewhere, scratch-resistant coatings can be obtained from epoxy silanes with a variety of alkoxides [19]. As shown by Kasemann [20], the hardness of this type of coatings can be increased substantially if nano-scale boehmite is added to the epoxy group-containing system. The main reason for the increased surface hardness is the fact that boehmite acts as a catalyst for the polymerization of epoxides. In the described system, starting from epoxy silane, TEOS, aluminum isopropylate, by carrying out hydrolysis and condensation of the precursors to a viscous liquid after the addition of boehmite nanoparticles, the polymerization of the epoxy group of the silane is completed leading to a structure that boehmite nanoparticles are wrapped up into a network of polyethylene oxide chains.

In this system, aluminum-oxygen-silicon bonds are formed from the boehmite surface to the silane in addition to the epoxy polymerization, as proved by ^{29}Si solid-state NMR . The excellent surface properties are attributed to the flexible suspension of the nanoparticles in the system. The system is completely transparent and can be used for coating plastic surfaces. It is used for CR^{39} eye glass lens protection [21].

If during hydrolysis and condensation the epoxy goup of these systems is opened to glycole groupings and tensides are embedded in these materials when applied as coatings, scratch-resistant antifogging coatings with long-term controlled release beha-

vior over several years can be obtained. It is assumed that if the surface gets in touch with water vapour and a water condensation process takes place through the penetration of the water vapour into the coating surface, the diffusion of tensides to the surface is activated, leading to a complete spreading of water in form of a film on the surface, so that the transparency is maintained [8].

In the way described in chapter 3, copper, gold and palladium containing composite materials have been synthesized [9 - 11]. In all these types of synthesis processes it could be shown that the concept of surface molecule-controlled growth can be applied very successfully and that the particle size can be controlled by the concentration of the surface-modifying ligands. In addition to this, these ligands can be used for incorporating the colloid-forming component in a molecular or atomic state into a backbone and grown to appropriate particle sizes. These composites are intensely coloured due to the high coefficient of extinction of the colloids (in the range of 10^6) and, in case of gold, show very high χ^3 non-linear susceptibilities of about 10^{-6} esu. In fig. 18, the various preparation techniques for nanocomposites are summarized.

Separate synthesis of inorganic components

microemulsion techniques
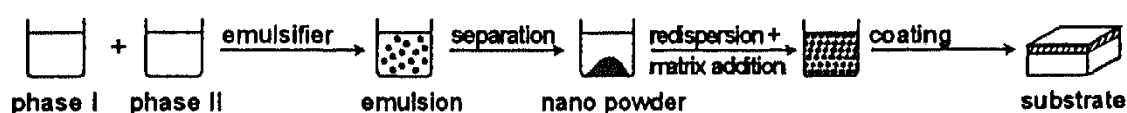
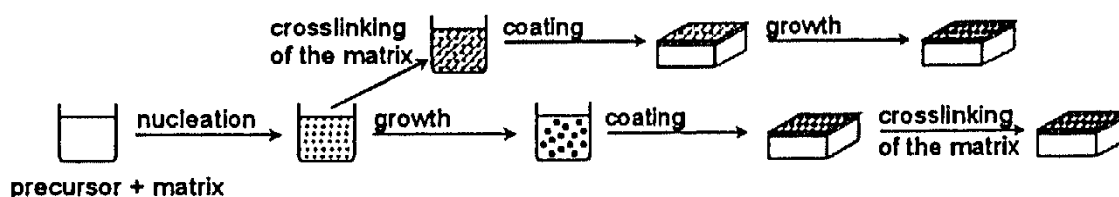**controlled growth**
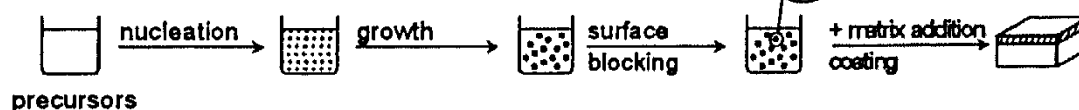
"in-situ" - synthesis

Figure 18. Different routes to nanocomposites.

These investigations show that using the described approach, a variety of composites with interesting properties can be synthesized. One of the main features of these composites is that they can be prepared with homogeneities leading to high optical transparency, but at the same time are particulate systems with properties related to the solid-state properties of the inorganic phase.

5. Ceramic Processing

As already indicated above, this concept can also be used for processing of nano-scale particles to ceramics. If the small-molecule surface modification concept is used, high solid content green bodies can be fabricated where the gelation takes place only after shaping. This could be shown for boehmite as a model system, but also for titanium nitride. The surface modification of titanium nitride [22] leads to slips allowing the fabrication of green bodies with green densities of about 60 % by volume, which can be sintered to coatings and bulk material at temperatures between 1100 and 1300 °C. The most interesting fact is that these green bodies can be densified below 1300 °C and no grain growth takes place. This is quite unusual since grain growth is driven by thermo-dynamics which begins as soon as the transport mechanisms in a system gets into a range where atomes or molecules can diffuse (which is an indispensable prerequire-ment for densification). The result of this investigation is summarized in fig. 19, where one can see clearly that grain growth only takes place after densification is almost finished.
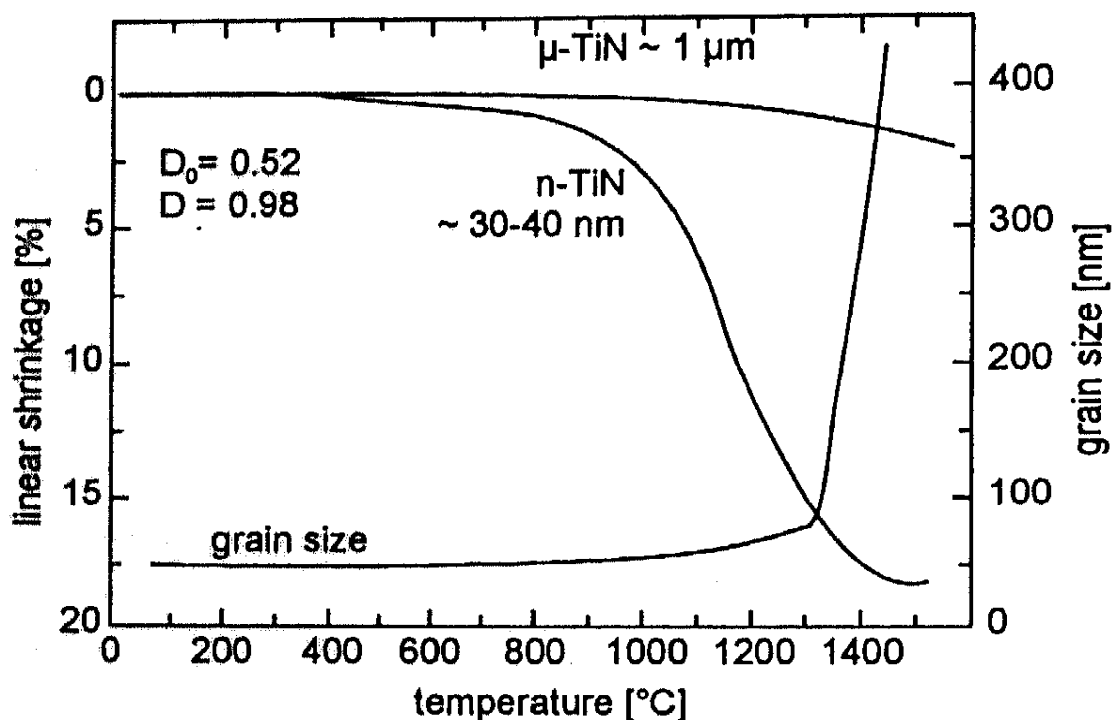

Figure 19. Densification and grain growth of nano TiN as a function of temperature compared to µm TiN [after 22].

One of the possible interpretations is that, due to the nano-scale phase, the high volume fraction of the interface, having a lower order than the crystalline "core", leads to a rearrangement of this "shell" without affecting the crystalline core.

The property of the systems has already been used for plastic deformation of titanium nitride at 1100 °C [14], which can be interpreted with the same assumption as described above and the nano slips have been used for dip-coating processes (fig. 20 and 21), also fully densified at 1100 °C up to several µm in this thickness on Al_2O_3. Above 1300 °C, a rapid grain growth takes place as expected.

hot pressing of n-TiN

P = 20 MPa
T = 1150 °C
t = 30 min

n-TiN green body

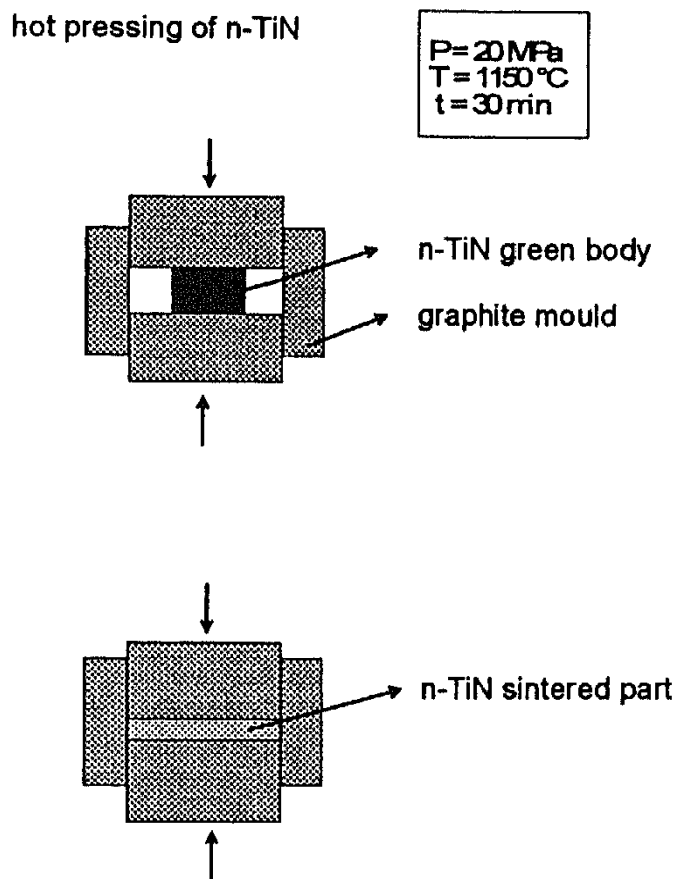graphite mould

n-TiN sintered part

Figure 20. Hot pressing with plastic deformation of a TiN nano green body fabricated by a nano processing route [after 14].
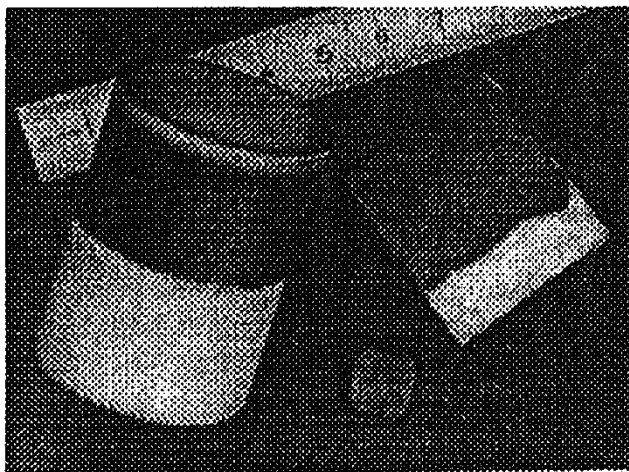

Figure 21. Dip-coated TiN, sintered at 1100 °C on Al₂O₃.

The results show that it is possible to separate densification from grain growth by nano processing.

If the effects found in the titanium nitride system can be generalized to other ceramic systems, it should be possible to end up with hot or "warm" pressing tech-

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niques, leading to low-defect ceramic bodies with the option of tailoring the micro-structure by additional grain growth after densification.

6. Conclusion

Small particle processing is an interesting feature for a variety of materials synthesis since small particles show interesting properties, for example, quantum size effects, plasmon frequences or low light scattering on the one side and interesting processing properties for ceramics on the other side. The key part for a successful material development, however, is the control of the particle surface to avoid agglomeration or gelation, leading to inhomogeneities or low-density materials, very difficult to be processed to parts and components. The concept of small-molecule surface modification in combination with multifunctional ligands leads to an interesting perspective for the fabrication of nanocomposites as well as ceramic nanoprocessing.

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