

Use of Chemistry as a Powerful Means for Synthesis and Processing of Nano Particles

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1. Introduction

The chemical synthesis of small particulate systems has become an interesting area of scientific activities since the potential of nano-scale systems has been demonstrated by the early work of Gleiter [1] and Henglein [2]. Colloidal systems in liquid phases with particle sizes in the lower nano range, however, have been known for centuries, and commercial applications of SiO₂ sols are known since the middle of the last century. It is a matter of fact that during each precipitation process from solution a growth reaction takes place and a nano size range is passed through. If the precipitation process is carried out far away from the point of zero charge (p. z. c.), the particles will be charged and prevented from agglomeration as long as the conditions for stability (e.g. critical distance, particle size versus precipitation) are not violated. This leads to stable sols, the concentration of which has to be kept rather low, as described in [3] and the references cited therein. Approaching the p. z. c., the interaction mechanisms get activated and gels (strong interaction) or precipitates (slow interaction) are formed. In fig. 1 the differences of charge stabilized and sterically stabilized systems during upconcentration are shown. In the charge stabilized systems, due to a strong interaction of surface groupings which are necessary to build up surface charges, in general, aggregates to be formed, are

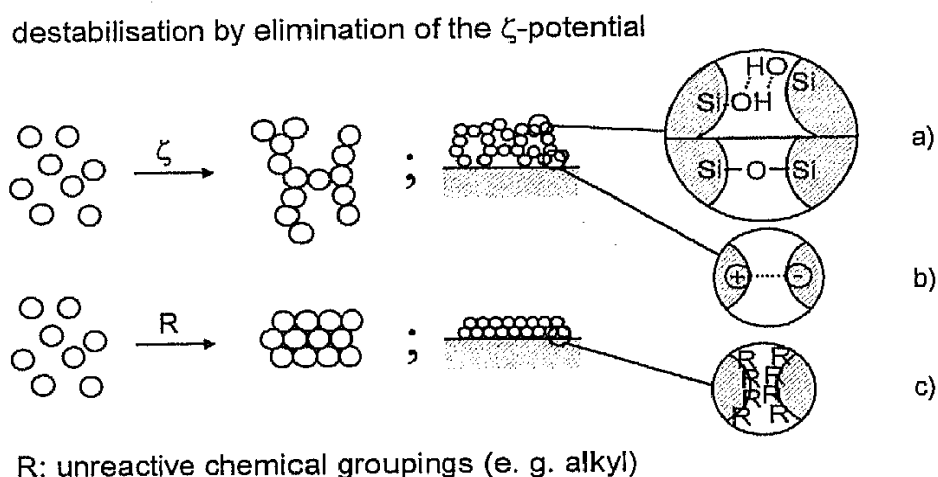


Fig. 1: Models for small particle interactions and destabilization processes of reactive and non-reactive surfaces; a: hydrogen bonds; b: dipole interactions; c: van der Waal's forces.

rather uncontrolled, and irregularly structured gels or precipitates are formed. As a consequence, in gels the green density is rather low ($\leq 20\%$ by volume). If the surface of the small particles, however, is covered by unreactive groupings, only weak van der Waal's forces are active and it should be possible to obtain more regularly packed solids. Typical interaction mechanisms are hydrogen bonds (in solution), dipole-dipole interactions, hydrophobic interactions, van der Waal's forces or even the formation of chemical bonds.

In oxidic systems, which, in general, are covered by hydroxyls, particle aggregation very often is accompanied by neck formation and aggregates are formed which cannot be redispersed (hard agglomerates). If further processing to monoliths or thick films is required, these agglomerated systems are difficult to be shaped defect-free, and defect structures leading to problems in densification and defect-containing microstructures are produced (pin hole formation, pore formation, stress formation).

For these reasons, it is very important to develop solutions for the control of the surface reactivity of small particles, which is not only interesting for the control of the particle-to-particle interaction but also to generate desired surface reactivities for example for further reactions or to generate desired charges for ξ -potential tailoring, e.g. polymerisation, polycondensation.

The aim of this paper is to show principle synthesis routes for particles with tailored surface reactivities and to give examples for the preparation of powders and colloids and examples for processing them to materials already in or close to application.

2. General considerations and results

Appropriate surface modification cannot only be of interest in the case of the control of the particle surface reactivity, but also to be used as a means for controlling the growth reaction by itself. In the growing system, after nucleation has taken place, the growth reaction is determined by the decrease of the free energy. In equations (1) and (2), the nucleation frequency is expressed as a function of the free energy of nucleation, the free energy of diffusion and the surface free energy σ [4, 5].

$$I = A \cdot e^{-\frac{(\Delta G_n + \Delta G_D)}{kT}} \quad (1)$$

$$A = 2 n_v \cdot v^{1/3} \frac{kT}{h} \sqrt{\frac{\sigma}{kT}} \quad (2)$$

ΔG_n : free energy of nucleation

ΔG_D : free energy of diffusion

n_v : number of species able to nucleate

v : volume of a single species

σ : surface free energy

If the volume v changes are small and the diffusion rate is high compared to the nucleation step, nucleation and growth are mainly dependent on the surface free energy σ , which depends on the surface area of the growing particles. This leads to the concept of introducing agents interfering with the nucleation process and interfering with the growing surface.

In fig. 2, free energy dependence of a nucleating and growing system is schematically shown as a function of the particle radius. After exceeding the critical nucleation radius, the free energy starts to decrease, and the system grows. If strongly bonded components are added to the surface an energy barrier can be introduced which leads to a stop of the growth process.

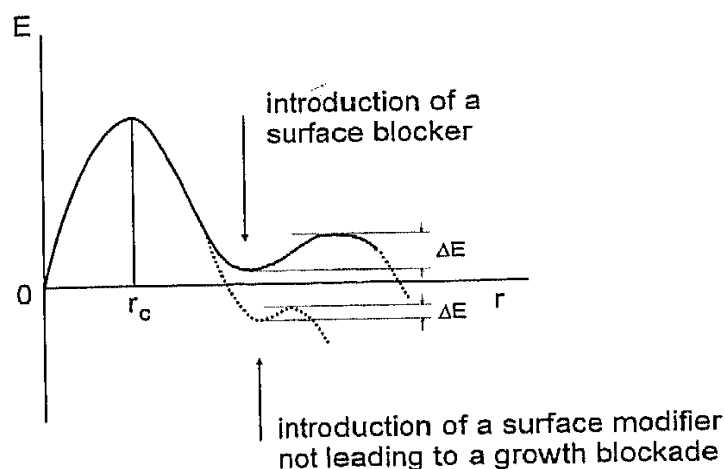


Fig. 2: Model of the growth reaction as a function of the surface free energy and the effect of surface additives; r_c : critical radius for nucleation.

This model suggests the possibility to control growth and particle size by use of appropriate surface additives during a growth or precipitation process. In order to carry out surface modification, the bonds between the modifying molecule and the surface are of importance. Furthermore, by appropriate choice of this modifying molecules, e.g. by using bi- or multifunctional molecules, the surface properties of particles can be varied either with respect to its surface charge or its surface reactivity. In this paper, it is demonstrated how the described principles can be used for the synthesis of a nano-scale particulate system and its processing to materials like ceramics and inorganic-organic composites.

3. Synthesis of Small Particles with Narrow Size Distributions

From the principles pointed out in the introduction, a concept of small particle synthesis has been developed. In this concept, several assumptions are incorporated. Firstly, it is

assumed that bonds with sufficient strength can be built up to a growing particle's surface.

Secondly, it is assumed that each component adsorbed on the particle's surface requires a specific area and that an optimum coverage exists leading to a minimum of the surface free energy. This then leads to the conclusion that for components not interrupting the growth process but bond to the surface with sufficient strength, the particle size is controlled by the concentration of these "ligands" in the system. The schematics for this model is shown in fig. 3.

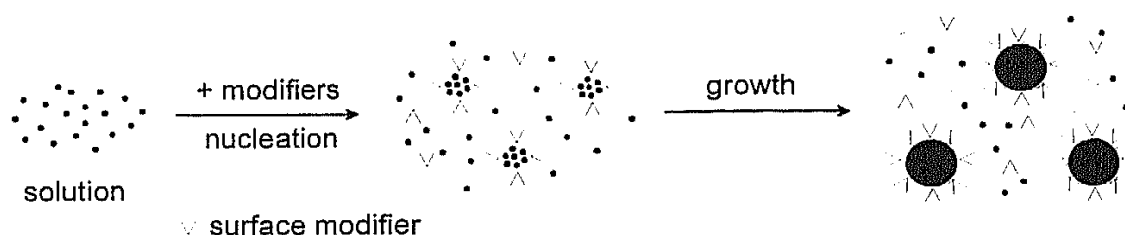


Fig. 3: General principles for the synthesis of small particulate systems by control of the surface reactivity.

For demonstrating the bond strength, investigations have been carried out with hydrolysed alkoxides after complexation. In sol-gel reactions, alkoxides are interesting starting compounds since they are soluble in a variety of solvents, e.g. alcohols, in which acids or bases also can be dissolved in order to adjust appropriate pH. Reactive alkoxides can form complexes with a variety of components like carboxylic acids (carboxylate complex formation [6], β -diketones [6 - 8], or even etheralcohols [9]. Examples are titanium alkoxides, zirconium alkoxides or aluminum alkoxides. The question arises whether this complex forming ability can be transferred from the ionic state in solution to ions incorporated in nano-scale particles. In principle, surface ions in a crystalline lattice are in a very unsaturated state, and for these reasons it should be possible to coordinate these unsaturated entities by saturating ligands. In fig. 4, an example is given, resulting from a reaction of $\text{Al}(\text{OR})_3$ and a β -diketone (ethyl aceto acetate) by hydrolysis and condensation. The particle size as determined by photon correlation spectroscopy after hydrolysis is about 2 nm ($\pm 10\%$) and was identified as boehmite.

As one can see from the shift of the carbonyl frequencies, there is no difference between the non-hydrolysed and hydrolysed complexed form, leading to the conclusion that the β -diketone complex is still intact on the nanoparticles.

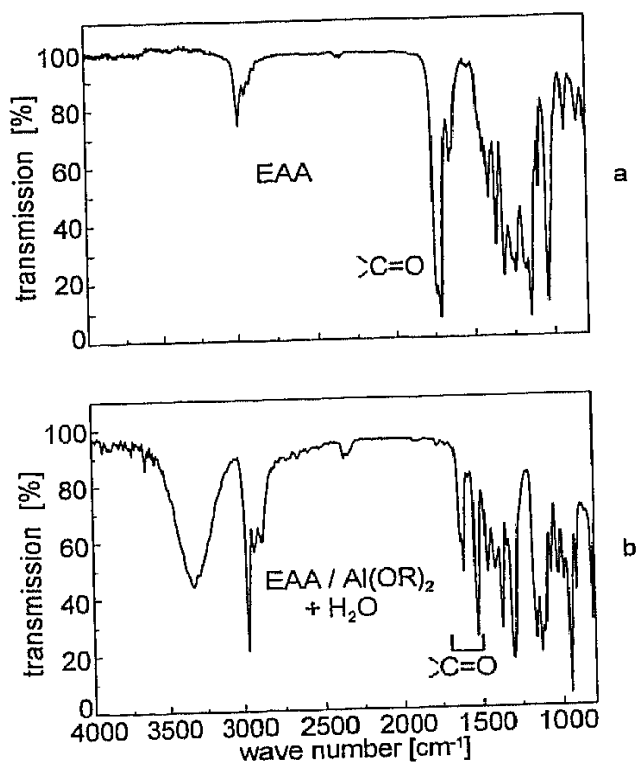


Fig. 4: IR spectra of ethylaceto acetate (a), after complexing with Al(i-prop)₃ (b) and after subsequent hydrolysis (b).

In order to find out how far the ligand concentration can be used for tailoring the particle size in a wider range, experiments with Zr alkoxides and two different types of ligands have been carried out. In fig. 5, two examples are given with a nucleating and growing system in presence of β -diketones or alkoxylic acids. The particle size was determined as a function of the ligand concentration. A $y = 1/x$ relation should be expected if the ligand concentration is the size controlling parameter.

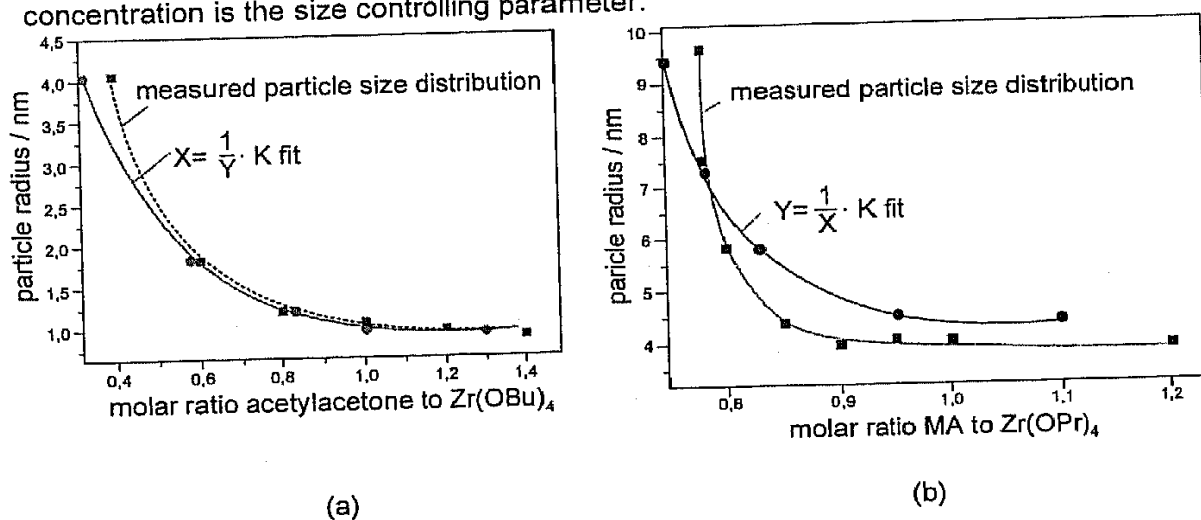


Fig. 5: Zr alkoxides reacted with acetyl acetone (a) and methacrylic acid (MA) (b) and subsequently hydrolysed by addition of H₂O; dependence of particle size on the ratio alkoxide: complex former as determined by photon correlation spectroscopy (after [10]).

The figures show the fitting of the experimental curve with a calculated curve and as one can see in the case of the β -diketones, where a strong bond can be assumed, the theoretical curve fits very well to the experimental curve. In the case of a carboxylic acid, where an adsorption - desorption equilibrium has to be taken into consideration, the fit is not quite as well. Summarising it is to say that assuming a surface free energy driven model, particle size follows a rather simple function, depending on the ligand concentration, but anyway calibration curves for different systems should be possible. For the synthesis of metal colloids, the described approach is depending on the presence of components having sufficient affinity to the metal surface as well as being able to stabilize the metal ion. In the case of Au and Ag, amines were found to be able to play this ambivalent role. For this reason, the soluble metal salts (e.g. nitrates or chlorides) were reacted with γ -aminopropyl triethoxysilanes or γ -aminoethyl aminopropyl triethoxysilane (DIAMO) to form amino complexes followed by a photochemical reduction, the details of which were published elsewhere [11], and the particle sizes were determined as a function of the complex former ratio. In fig. 6, curves are shown.

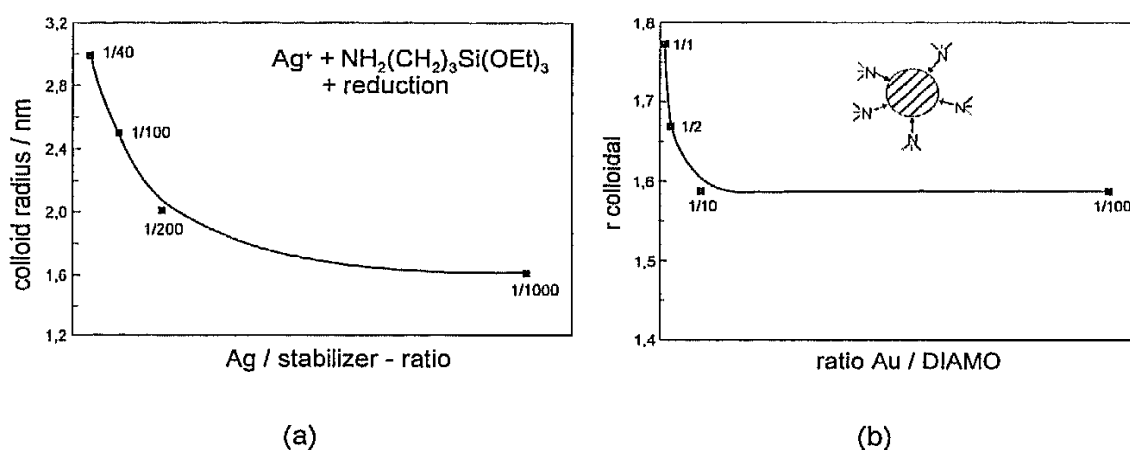


Fig. 6: Dependence of particle size of metal colloids obtained from complexed metal salts in MeOH by photochemical reaction. a: Ag/ γ -aminopropyl triethoxysilane; b: Au/DIAMO [12].

In this case, rather high concentrations of complex formers had to be used in order to obtain these curves. This is explained by a relatively unfavorable adsorption-desorption equilibrium of the amines on the colloid surface. Silanes have been used in order to generate a "second" reactivity and to use these precursors for further sol-gel processing. The particle size distributions obtained by these methods have been determined by TEM and are relatively narrow within a range of ± 1.5 nm deviation from the average.

The results show that the described principle can be employed for ceramic as well as for metal particles. The use of bifunctional ligands (e.g. organofunctional silanes or functionalized acids) is of special interest since they allow to add special reactivities to

the particles. In the following, some composite developments are described, using two different preparation routes, the preparation of particles within and separately from the matrix system.

4. Nanocomposite Development

4.1. In-situ grown ZrO_2 containing systems

Based on the considerations shown above, several materials developments have been carried out. Beside the fact, that the results have been used for the preparation of pure ceramic nano scale systems [13], the synthesis of composites with nanoparticles is of interest for various reasons, for example, for the preparation of transparent composites, if particle sizes are used below the Rayleigh scattering limit.

Two routes have been developed for the composite synthesis, the so-called in-situ route, that means the generation of nanoparticles within a reactive system which later on can be reacted to the composite matrix or the separate preparation route where nanoparticles are prepared outside of the matrix systems and then modified to obtain an appropriate surface to be introduced into the matrix system.

In the first example, the in-situ synthesis of a zirconia nanoparticle containing system is described. The basic principle of the in situ route is shown in fig. 7. Little experimental details are shown elsewhere [14, 15]. As matrix former, γ -methacryloxypropyl triethoxy-silane (MPTS) was used in order to form an inorganic-organic composite matrix by combination of polymerization and polycondensation of silanol groupings.

Methacrylic acid was used as complex former, since the double bond of MA should be able to react with other monomeric acrylates, and various types of polymerization reactions should be accessible (e.g. radical polymerization, thermally or photochemically initiated), and photoresist properties for micropatterning should be possible.

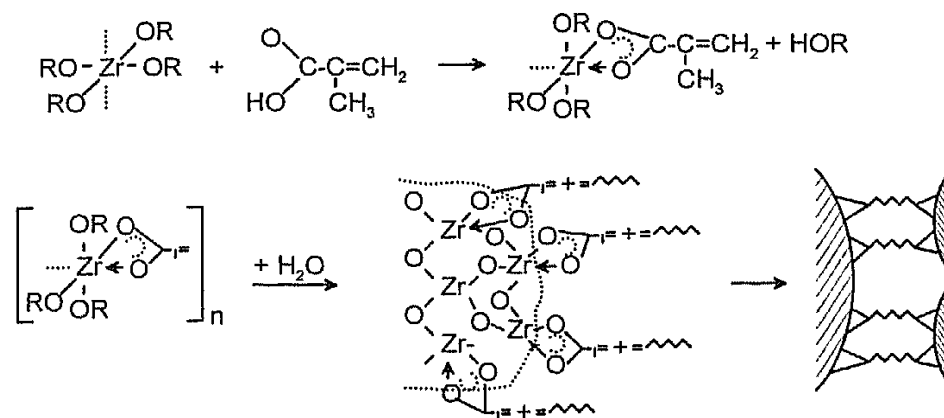


Fig. 7: Model of the ZrO₂ nanoparticle containing in situ grown composite; $\backslash\backslash$: methacrylate type of monomers.

In order to obtain sufficient transparency, the particle size has been established at about 2 nm by appropriate choice of the Zr:MA ratio. The material was synthesized by complexing zirconium alkoxides by methacrylic acid [16], hydrolysing the system with an understoichiometric concentration of water and mixing it with a prehydrolysed methacryloxy group containing silane. After polymerizing the system at temperatures of around 100 °C with a photoinitiator, a clear transparent composite was obtained. In order to follow the reaction, the carbonyl frequency of the methacrylic acid was monitored by IR spectroscopy and by electron scattering measurements the crystallinity of the system was investigated. In fig. 8, the IR spectrum of the carbonyl frequencies of the system and the electron diffraction patterns are shown [17].

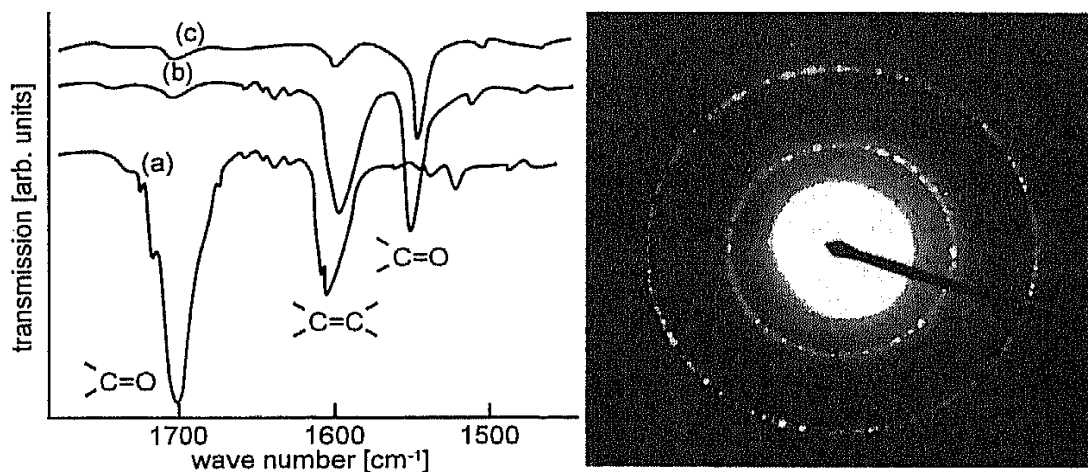


Fig. 8: IR spectrum of the carbonyl frequency (a: methacrylic acid; b: zirconia alkoxide complex with methacrylic acid, hydrolyzed and mixed with a methacryloxy group containing silane; c: polymerized film after 2 weeks of water exposure.); electron diffraction pattern: after photocuring and heat treatment at 120 °C. The pattern can be attributed to a mainly monoclinic phase.

Fig. 8 shows that a crystalline phase is formed at extremely low temperatures through the in-situ growth process.

ZrO₂ also could be detected in HTEM investigations [18]. Films prepared from this system are highly transparent and have been used for patterning processes, for waveguides diffractive gratings and micro-lens arrays [19]. Moreover, and this seems to be of importance, in the polymerized system the bonds between the zirconia particles and the methacrylic acid are still present.

This finding leads to the question about the mobility of the particles in the polymerizing system during a photopolymerization process. As already shown elsewhere [19], it could be shown that this type of system could be polymerized to high degrees of conversion including the double bonds of the MA bond to ZrO₂. For generating a "driving force" for a difference of double bonds, a gradient electromagnetic field has been established, obtained by the interference of two laser beams (two-wave mixing process). As it is already well known from the photopolymerization state of the art with photo masks or two wave mixed laser beams with polymers, partial polymerization can be introduced into films and diffractive grating patterns are obtained due to the polymerization shrinkage in the photopolymerized areas. However, if the full area is irradiated after the first step the pattern disappears due to the polymerization of the rest of the volume. The question arises whether in the multicomponent system with components having a higher refractive index (in this case the zirconia) a diffusion process of zirconia particles can be initiated to establish permanent refractive index changes. In order to prove this hypothesis, the two-wave mixing irradiation process has been used. After the partial polymerization, the film was fully irradiated by a UV lamp and completely polymerized. Micro Raman and analysis showed that in the areas polymerized in the first step in the two wave mixing process show an increased concentration of zirconia compared to the areas irradiated in the second step only. The basic process is shown in figure 9 and the Raman patterns in fig. 10 which show a higher concentration of ZrO₂ within the firstly irradiated

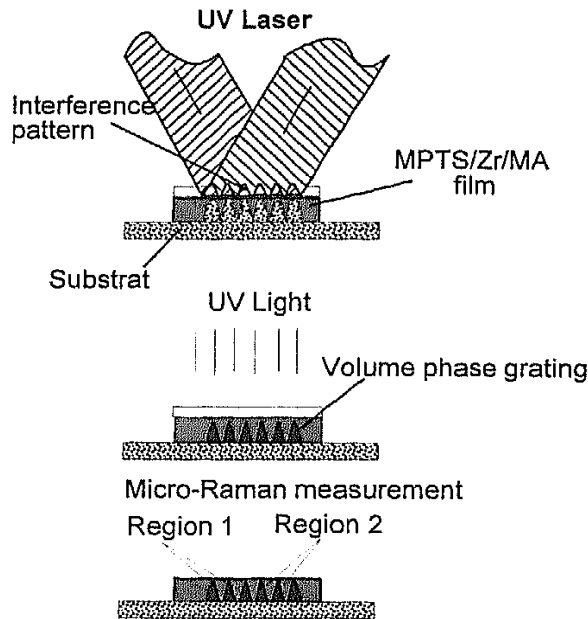


Fig. 9: Schematics of the two-wave mixing process for the fabrication of a volume diffraction pattern based on the composition ZrO_2 :MA:methacryloxy propyl trimethoxy silane (MPTS) = 1:1:1 (after [15]); region 1: irradiated, region 2: non-irradiated zone.

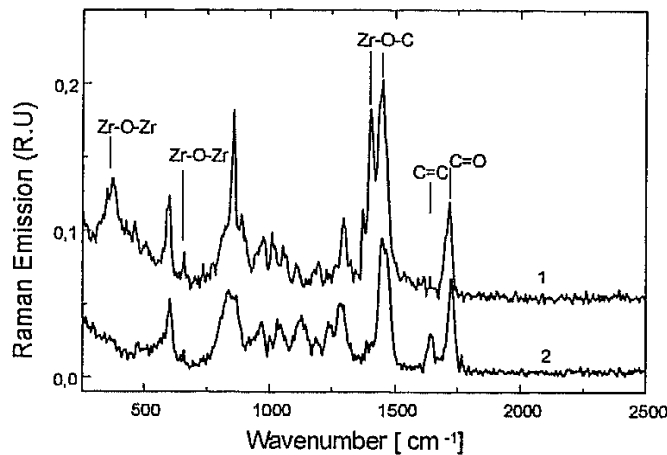


Fig. 10: Micro Raman spectra of region 1 and 2.

ions and which confirms the hypothesis that during the first irradiation step zirconia particles diffuse into the polymerizing areas, driven by a chemical potential gradient. The differences in refractive indices to be obtained by this route have been determined and reach from 0.001 to 0.03, depending on ZrO_2 contents [18]. In the second polymerization step the concentration gradients are completely immobilized, so that a stable system is shown. In fig. 11, the diffractive grating produced by this process is shown. This process has also been used for the development of micro Fresnel lenses by a different two wave mixing process [19].

The investigations have shown that it is possible to generate in-situ nanocomposites which can be photopolymerized and, moreover, that through gradient electromagnetic fields a diffusion of zirconia particles can be introduced. The diffusivity of the zirconia particles is linked to the methacrylic acid groups bonded to the surface which move into

areas with lower content of double bonds due to the consumption of them by the polymerization step.

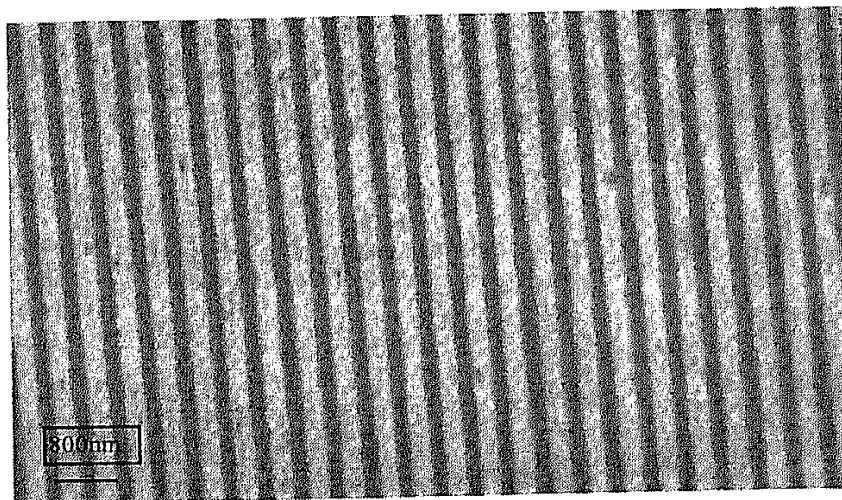


Fig: 11: Diffractive grating after full irradiation.

4.2 Fe Oxide Containing Nanocomposites

It is well known that FeO_x nanoparticles can be produced by precipitation from $\text{Fe}^{2+}/\text{Fe}^{3+}$ containing aqueous solutions [20], but they form agglomerates. These agglomerates can build up strong aggregates, caused by condensation reactions of the OH-groups at the surface of the nanoparticles. If isolated nanoparticles should be prepared, it is necessary to destroy the agglomerates and to stabilize the individual particles [21 - 24]. For this reason, thermal ultrasonic energy has been used to destroy the agglomerates, but the lifetime of the individual particles is only very short due to a rapid reagglomeration rate.

To prevent the immediate reagglomeration, a new approach has been developed, based on the ultrasonic energy deagglomeration of iron oxide particles in the presence of reactive surface modifiers. In order to establish an appropriate surface reactivity, bifunctional compounds have been used, where one of the functional groups was supposed to interact with the iron oxide surface and the other to stabilize the particles by building up a surface potential and to generate desired surface reactivity. For this reason, γ -aminopropyl triethoxy silane was used. The schematics of the reaction is shown in fig. 12. The amino silane is hydrolysed in the aqueous solution, leading to an adsorption of the $=\text{SiOH}$ groupings on the $=\text{FeOH}$ group containing particles as soon as they are separated. The amino grouping of the silane is building up a ξ potential preventing re-agglomeration. The isoelectric point of the suspension is shifted from pH 6 (uncoated Fe oxide system) to pH 9 (after coating), showing clearly the effect of the coating process.

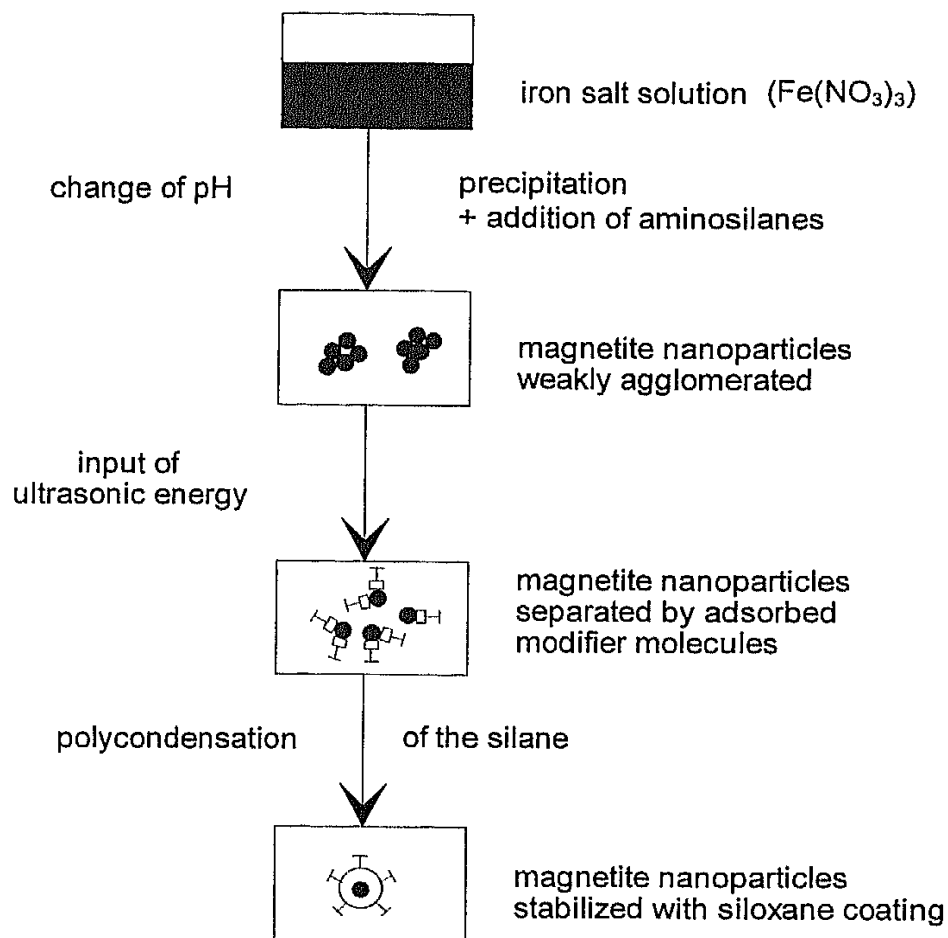


Fig.12: Reaction scheme for the synthesis of modified magnetite.

The process has to take place over 48 hrs of elevated temperature ($70 - 90\text{ }^\circ\text{C}$) to be completed. After this time, the coating is irreversible. This is interpreted by a subsequent polycondensation of $\equiv\text{Si-OH} + \text{HO-Si}\equiv \rightarrow \equiv\text{Si-O-Si}\equiv$ of the silanes adsorbed or bonded to the Fe oxide particles surface.

The effect of the ultrasonic treatment with and without the addition of γ -aminopropyl triethoxysilane is shown in fig. 13. The particle size distribution was determined by photon correlation spectroscopy and by ultracentrifugation.

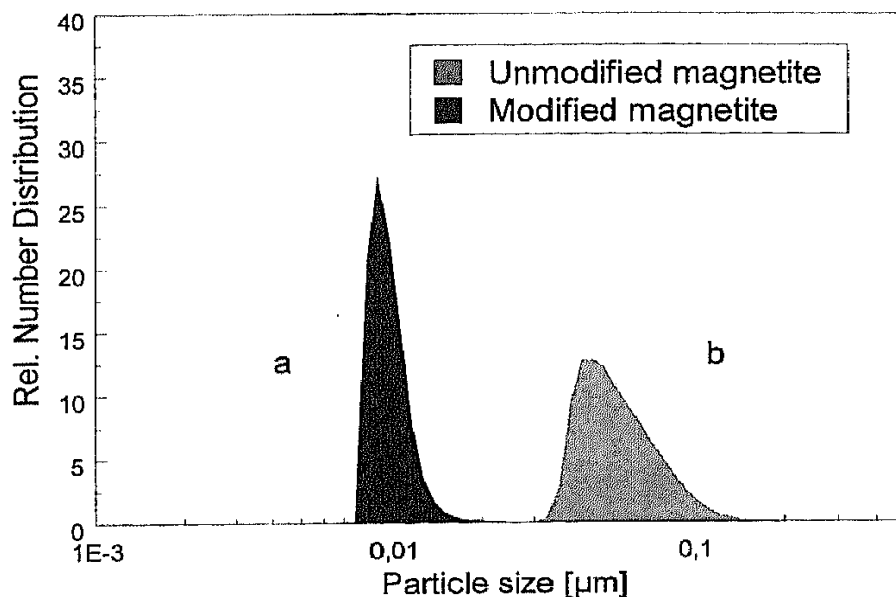


Fig. 13: Particle size distribution of precipitated Fe oxide particles, a: in presence of aminosilanes, b: without aminosilanes.

One clearly can see the effect of the surface modifier on particle size and distribution.

The aqueous suspension can be transformed into dry powders by removal of the water and completely redispersed. In order to synthesize polymer-ceramic nanocomposites, the powder was dispersed in ethanol and a commercially available diepoxide (Degacure K 126) was dissolved in the suspension. Thin films of about 1 - 2 μm were prepared by dip coating of microscopic slides and cured by UV light using a photo initiator (Degacure K 385). The solid films were investigated by HRTEM [25]. In fig. 14 the process is depicted, and fig. 15 shows the HRTEM image of the resulting nanocomposite.

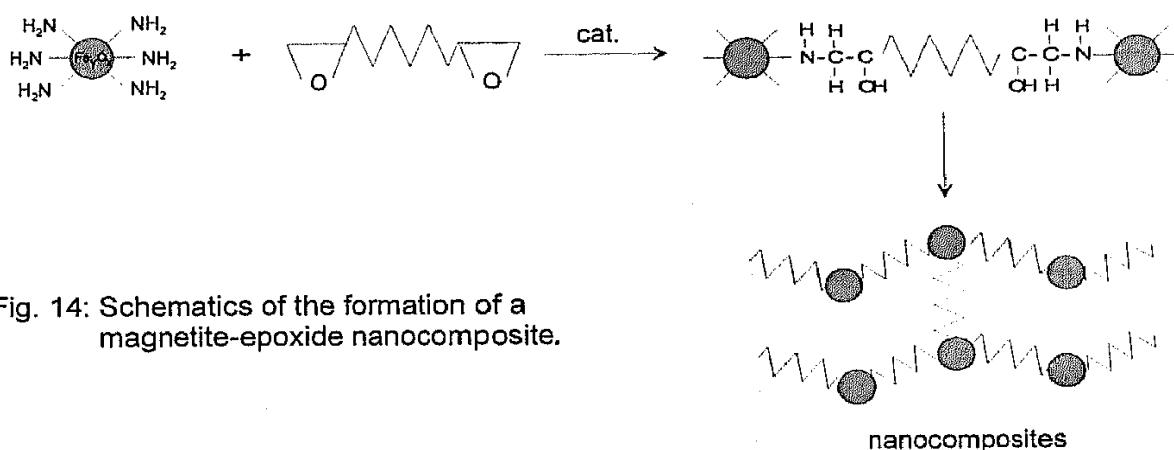


Fig. 14: Schematics of the formation of a magnetite-epoxide nanocomposite.

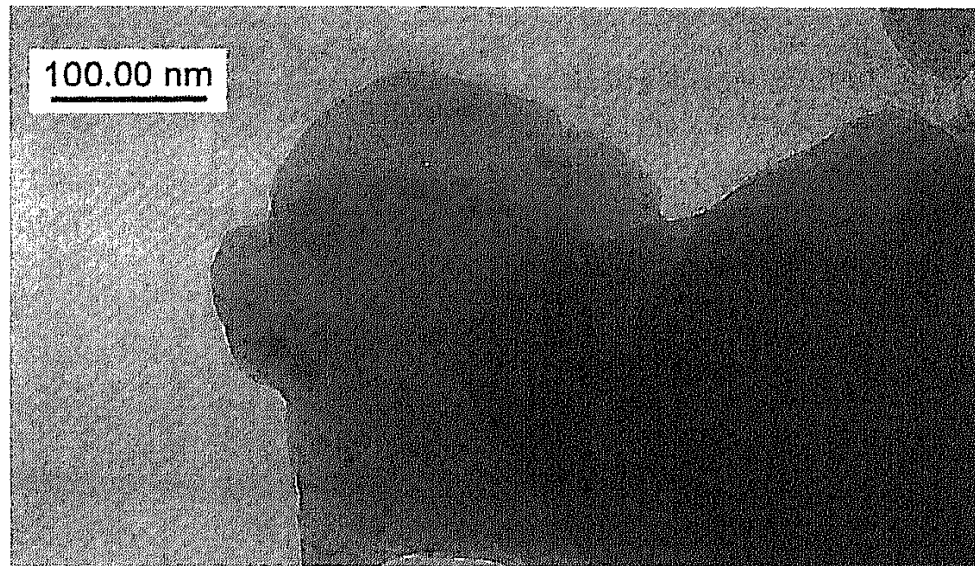
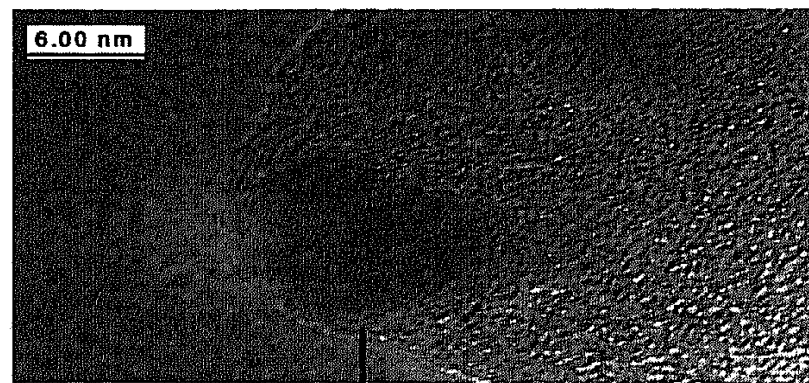


Fig. 15: HRTEM micrograph of a magnetite-epoxide nanocomposite.

The micrograph clearly shows the completely deagglomerated magnetite particles within the epoxide matrix. The films are superparamagnetic with magnetisation limits close to bulk magnetite and do not show any hysteresis. The question whether magnetite or maghemite is the dominating phase could not be clearly answered, neither by Moessbauer spectroscopy nor by HRTEM. In fig. 16 the HRTEM micrograph of a Fe oxide nanoparticle within the nanocomposite is shown. The lattice parameters within the possible preciseness fit to maghemite as well as to magnetite.



Processed image of the Fe oxide nanocrystallite.

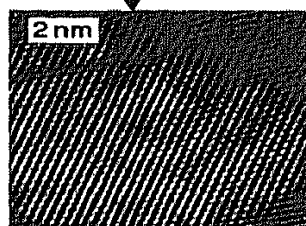


Fig. 16: HRTEM micrograph of Fe oxide nanoparticles in the composite film.

The films show a superparamagnetic behavior without any hysteresis at room temperature and a saturation magnetisation of about 80 % of a bulk magnetite phase (calculated on the iron oxide content as basis). The results show that the so-called separate preparation route, that means the preparation of nanoparticles separately from the matrix system using surface modifiers can be used to fabricate nanocomposites similar to those prepared by the in situ route. Using this approach, it was possible to synthesize completely deagglomerated amino group modified magnetite particles in the range between 6 and 20 nm by varying the processing parameters (concentration and pH). Investigations on chemical stability showed that the amino groups are surprisingly stably bonded to the surface (stable between pH 3 and 11). Amino groups are important since they easily can be reacted with biological molecules, organic monomers or sol-gel precursors to be incorporated into various types of matrices.

4.3 Metal Colloid Containing Systems

As shown in chapter 2 metal colloids can be formed using the surface reactivity control approach, too. It is well known that noble metal colloids show quantum size effects leading to non-linear optical properties (high third-order susceptibilities) based on the plasmon resonance of hot electrons. The question arises how far these effects can be influenced by the surface properties of these colloids, since the χ^3 value is strongly affected by the so-called local electric field factor f [11] ($\chi^3 \sim f^4$), and f depends strongly on the dielectric function of the surrounding media. To investigate this question, two different types of nanocomposites have been prepared. The general preparation route is shown in fig. 17. For this reason, amino group containing silanes and alternatively SH-group containing silanes have been used for the stabilisation of the colloids during and after the photochemical reduction step [11]. In this case, the $-NH_2$ and $-SH$ groupings are supposed to act as bonding agents to the particle surface or as complex formers. In fig. 18 the HRTEM micrograph of a Au particle after reduction is shown.

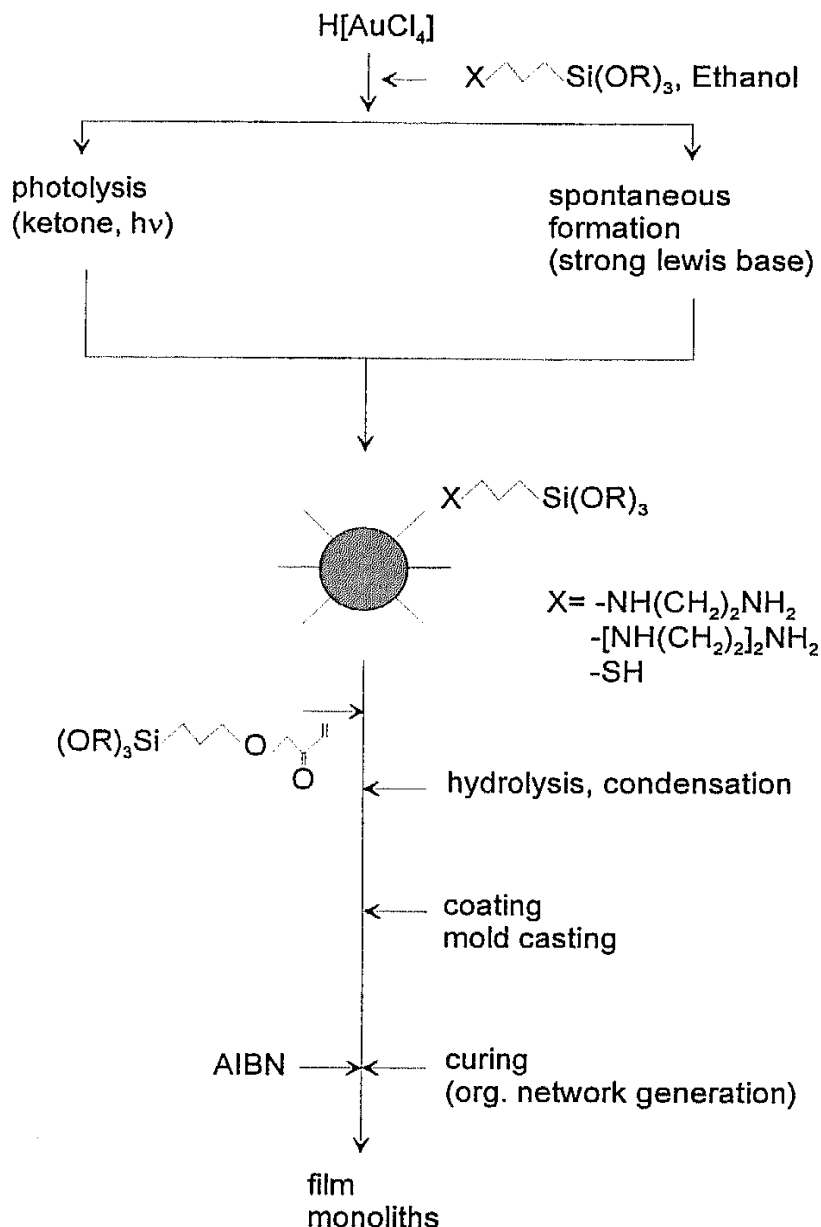


Fig. 17: Preparation scheme of Au containing nanocomposites; AIBN: azobis isobutyronitrile.

Twin formation is typical. The average size depends on the complex former concentration and was chosen to be about 7 - 9 nm. In combination with methacryloxy group containing silanes a polymerization/polycondensation process was carried out on films of about 3 μm in thickness obtained by dip coating of microscopic slides. These films have been photocured by adding AIBN as photoinitiator. In fig. 19 a Au particle in a composite matrix prepared from amino grouping covered Au particles and a methacryloxy silane, located at the film surface is shown. One can recognize an interface structure different from the bulk structure. In this case, the particle size is around 12 nm.

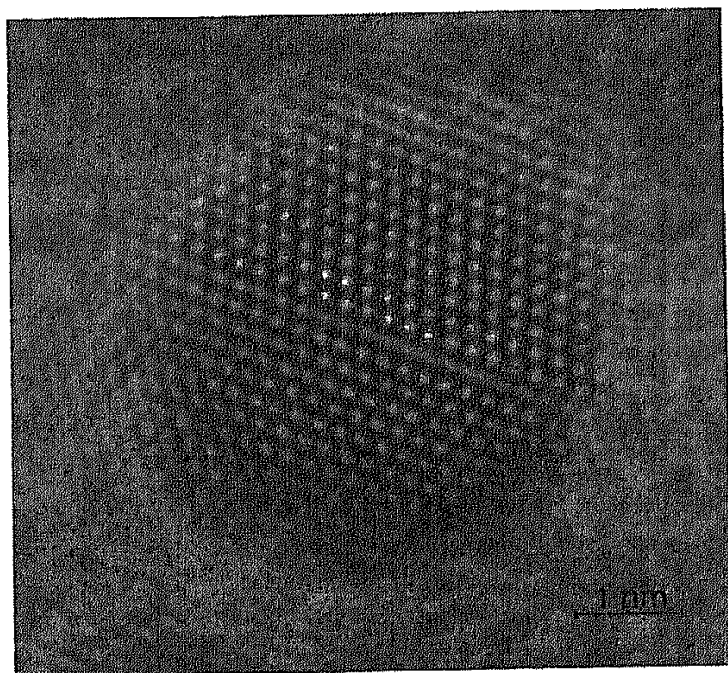


Fig. 18: Au colloid prepared by amino group control.

The non-linear properties have been determined by a four-wave mixing process, generating a self-induced diffractive grating. The χ^3 value then can be calculated from the diffraction efficiency [11].

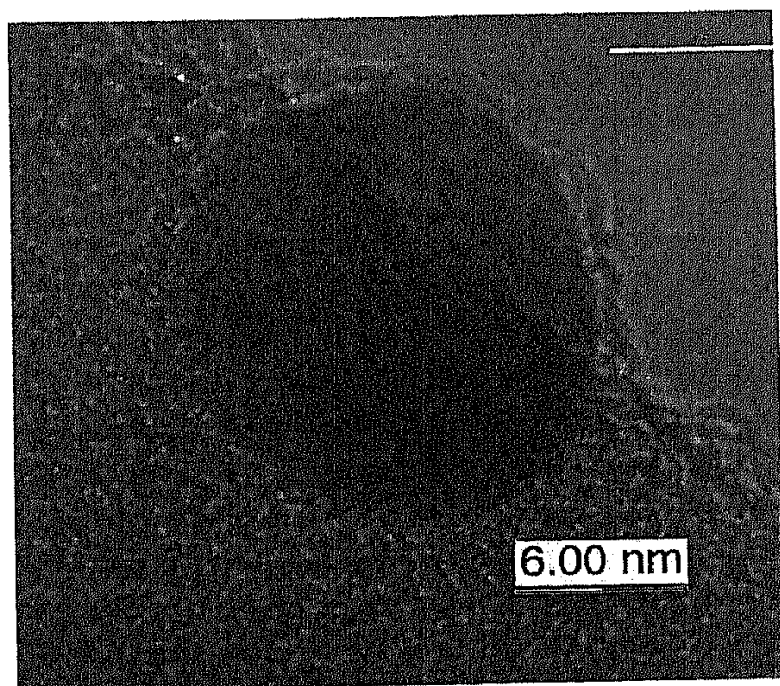


Fig. 19: Au particle in a composite matrix after polymerization of the methacrylic groupings.

Au colloid in Ormocer coating (amino silane ligand)

In table 1 the results of the χ^3 measurements of various composites and after firing them are shown.

Table 1: χ^3 values of Au particles of about 10 nm in different matrices; χ_m^3 = value calculated for the pure metal.

Matrix	Ligand	$\chi_m^{(3)}$ [esu]
Composite	NH ₂ -	2.0 10 ⁻⁶
	SH-	9.0 10 ⁻⁷
SiO ₂ *	NH ₂ -	7.0 10 ⁻⁷
	SH-	<1 10 ⁻⁷

*after burning out the organics

The results show that very high χ^3 values were obtained in the amino ligand case. For SH ligands, the values are distinctly lower. If the organics are burnt out, the χ^3 values drop sharply. In the case of NH₂, the drop is far lower than in the case of SH. Whereas the amino groups are burnt out completely, leaving back a pure SiO₂ matrix, SH leads to sulfate formation entrapped in the system. The SO₄²⁻ ion as a ligand seems to interfere in an undesired way with respect to high χ^3 values.

The results show that the interface generated in Au colloid systems affects the χ^3 value strongly and is able to influence it by two orders of magnitude. In the described system, electron donating ligands seem to be able to increase the χ^3 value substantially.

5. Conclusion

The described investigations have shown that the synthesis and processing of new materials by chemistry opens interesting perspectives with respect to composite materials. The most interesting part is the possibility of the surface chemistry of the nucleating and growing particulate systems as well as the control of their further reactivity. Control of surface thermodynamics was used for the synthesis of nanoparticles with controlled sizes, and a simple model has been developed for the correlation between particle size and surface modifier concentration in cases of strong surface-to-modifier interaction. Using bifunctional ligands, it is possible to generate highly reactive nanoparticles within a reactive matrix and to fabricate in situ composites.

The results show that various types of nanocomposites can be obtained using sol-gel processing.

6. Acknowledgements

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