

# SYNTHESIS AND PROCESSING OF NANO SCALED CERAMIC POWDERS AND COMPOSITE COATINGS USING SOL-GEL AND RELATED TECHNIQUES

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## 1. Introduction

Nanoscaled particles are of interest from various reasons for different types of materials, since many material properties change dramatically when dimensions are reduced to the nanometer scale. An impressive example is the significant decrease of the sintering temperature of ceramic powders [1], allowing new ceramic coatings and cofiring techniques, the preparation of new types of ceramic membranes, [2,3,4] and the increase of mechanical strength of ceramic bodies, caused by the decreased size of defects. The decrease of processing temperatures is also used for the preparation of high purity  $\text{SiO}_2$  glasses from dispersed Aerosil powders [5] particulate silica gels or by the combined alkoxide-particulate method [6,7]. In the case of polycrystalline nano phased metals and metal alloys, where the material properties are determined by grain boundary phases, some interesting physical phenomena as plastic behaviour or extremely high coefficients of diffusion have been reported [8] in the last years. Composites with nano sized metallic or semiconductor (e. g. metal halides) particles in glasses have been developed for photochromics [9,10] or are applied since ancient times for glass staining. In these metal colloid composites the optical properties base on a plasmon resonance effect in combination with quantum size effects [11] and therefore depend on the colloid size and concentration and are strongly influenced by the geometric shape of the nano particles [12,13,14]. Recently sol-gel synthesis routes are investigated for the synthesis of noble metal colloid containing organic-inorganic layers [15,16] or glass like coatings [17] since they offer interesting non linear optical properties ( $\chi^3$ -ef-

fects). Since investigations of stabilized metal colloids in alcoholic solutions [18,19] have shown that the particle size distribution has a strong impact on the non linear optical properties, the main goal for the synthesis and processing is to control the size of the quantum dots in the case of metal colloids as well as for semiconductor quantum dots, that have been intensively investigated in the last years (metal chalcogenides) [18,19,20,21,22].

Although nano scaled particles offer a lot of interesting material properties their preparation and processing cause some serious problems. It is obvious that the control of the particle size and the size distribution is a very important task for materials with strongly size dependent properties. This also includes the prevention of agglomeration. In many cases agglomeration is caused by van der Waals forces that increase with  $d^n$ , where  $d$  is the mean interpartical distance, and therefore reach very large values if  $d$  decreases down to the nm range. Another obstacle for the preparation of nano scaled particles are sufficient quantities. Gas phase condensation reactions suffer from relatively low yields and cause trouble with the control of the particle size distribution and with agglomeration effects. Routes from the liquid phase in principle easily allow a preparation on a large scale, but stabilization mechanisms are necessary in order to limit the particle growth and to prevent agglomeration. The further processing of nano scaled particles to compact materials (e.g. sintered ceramic bodies) also requires surface deactivation for the prevention of particle agglomeration during densification but this automatically decreases the package density of the material.

The objective of this paper is to show the usefulness of precipitation and growth reactions in solutions for the synthesis and the processing of nano scaled systems e.g. ceramics and quantum dot containing glass like materials.

## 2. Results and discussion

### 2.1. General

The formation of solid particles from a liquid solution starts with a nucleation and growth process, that can be described with equation (1) by the Gibbs-function  $G$  as

$$G = 4\pi\sigma r^2 - \frac{4}{3}\pi\gamma r^3 \quad \text{with} \quad (1)$$

$r$  = particle radius

$\sigma$  = specific surface free energy

$\gamma$  = specific binding energy

The first term ( $4\pi\sigma r^2$ ) describes the energy required to increase the particle surface and the second term ( $-\frac{4}{3}\pi\gamma r^3$ ) is equal for the binding energy, that is set free since  $r$  increases (see fig. 1).

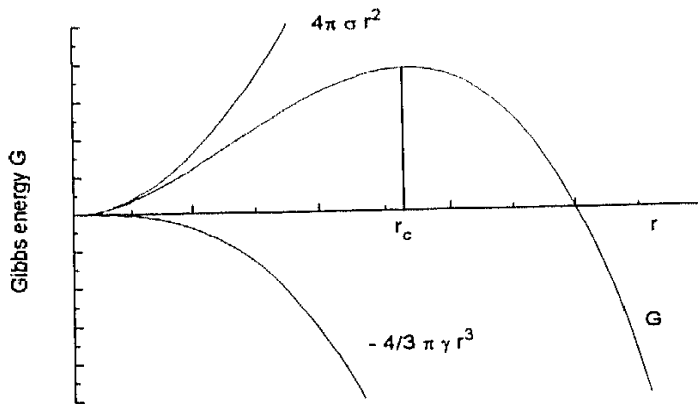


Fig.1. Gibbs free energy as function of particle radius

The nucleation process requires energy ( $\Delta G > 0$ ) and after the critical nucleus radius has overcome particles growth spontaneously ( $\Delta G < 0$ ), controlled by the diffusion of „monomers“ and particles. This process can be stopped by agglomeration effects, that may be diffusion controlled (Smoluchowsky equation) or reaction

controlled [23], leading to more or less compact clusters of agglomerated colloidal particles with a finite cluster size in the  $\mu\text{m}$  region with a relatively narrow size distribution. Especially for the preparation of nano sized semiconductor and metal particles in aqueous or alcoholic solutions the stabilization by capping techniques (ligating, coordinating) using electrostatic effects (micelle capping) or organic molecules (phenylates, alkyls) [24] is a very effective way to prevent agglomeration by covering the surface of the nano particle. The thermodynamics and kinetics of this process are not completely understood yet, but it seems plausible that the blocking of the surface hinders or interrupts the growth of the particle. Using complex forming ligands this can be done in two possible ways as shown in fig. 2:

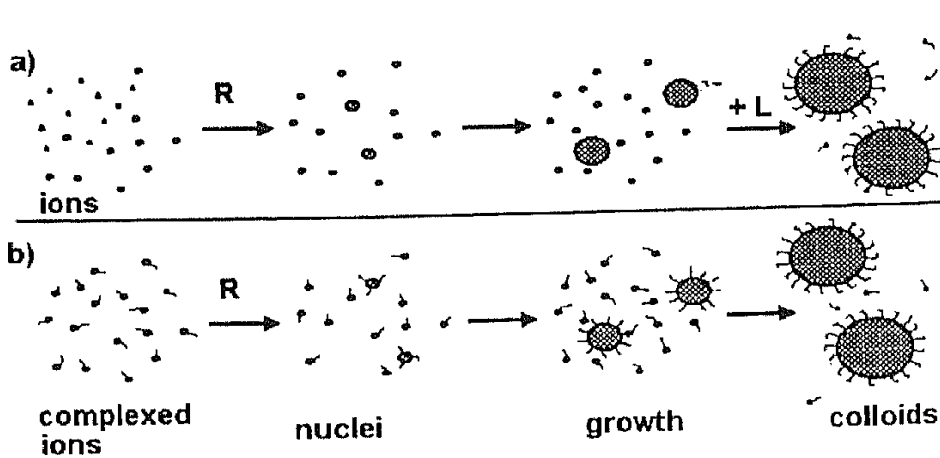


Fig. 2. scheme of nucleation and particle growth from ions in solutions (R = initiation reaction step for producing active species, e.g. hydrolysis in sol-gel reactions or reduction for metal colloid formation, L = addition of a surface modifying ligand.

In fig 2a) the complexing agent L is added to the solution after nucleation has taken place and the growth process has been started. In fig 2b) nucleation is initiated after the ions have been complexed. In route a) after the initiation reaction the growth process takes place immediately after the nucleation step, but the growth process cannot be controlled in its early stage and can only be stopped by adding the stabilizer L, so that the colloidal size distribution should be broad. In route b) a stabilization effect of the ligand L can occur, leading to a reduced nucleation frequency and growth rate. However, as shown in [16, 17] in the case of Au complexes, the opposite effect can be obtained too, if the specific interfacial free energy of the ligand to the reduced species ( $\text{Au}^0$ ) is higher than the complex formation energy: In this case, ligand addition to the ionic species leads to spontaneous reduction of  $\text{Au}^{3+}$  to  $\text{Au}^0$ . In both cases the average colloid size can be controlled by variation of the stabilizer concentration. The binding mechanism between colloid and stabilizer may be due to acid-bases reactions (Pearson theory [25]), Brönstedt and Lewis type, donor / acceptor functions, electrostatic or Van der Waals forces but for all cases it has to be postulated, that through the ligand to surface interactions a minimum of the Gibbs-function is realized.

The concept of the interfacial free energy minimum controlled synthesis can also be used for the fabrication of nano sized ceramic powders by the microemulsion technique [26]. Fig. 3 shows the principle of a water-in-oil emulsion (w/o emulsion).

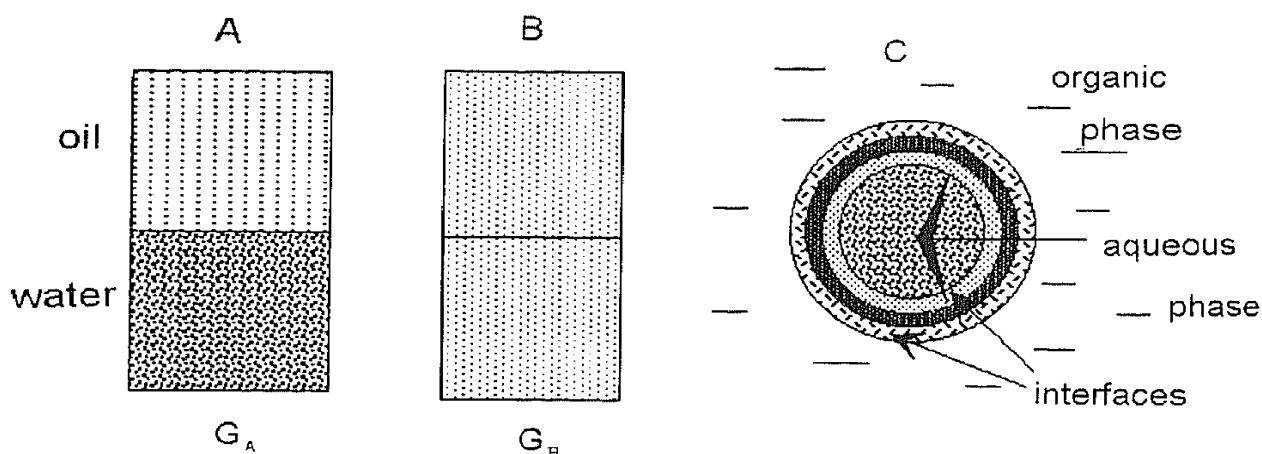


Fig. 3. Principle of w/o microemulsion technique (A = 2 phasic system, B = microemulsion, C = single droplet with tailored interfaces by a combination of bipolar systems (e.g. short chain tensides, after [28]),  $G_A$ ,  $G_B$  = Gibbs free energy of the two phasic system and the microemulsion resp.

Starting from a two phasic system (A) the water phase is dispersed as fine droplets in the water immiscible oil phase by an input of mechanical energy (B). By interfacial

active components, the interfacial tension between the two phases can be decreased and a thermodynamical instable system ( $G_A$ ) can be changed to a stable one ( $G_B$ ). The droplet size now can be controlled by the tenside concentration and a thermodynamically stable microemulsion is obtained. The thermodynamical stability of a microemulsion ( $\mu e$ ) is required for the generation of nanosized particles by a precipitation step in the water phase droplets (C), since stable conditions during this process are necessary for reproducible results. Therefore the Gibbs free energy of the microemulsion  $G_B$  has to become lower than that of the two phasic system  $G_A$ , as expressed by equation (2):

$$\Delta G = G_B - G_A < 0 \quad (2).$$

$G_B$  and  $G_A$  may be written as

$$G_A = G(w) + G(o) + G_A(w/o) \quad (3) \text{ and}$$

$$G_B = G(w) + G(o) + G_B(w/o) + G_{mix} \quad (4),$$

where

$G(w)$  = Gibbs free energy of the water phase

$G(o)$  = Gibbs free energy of the oil phase

$G_A(w/o)$  = surface free energy of the 2 phasic system

$G_B(w/o)$  = surface free energy of the microemulsion

$G_{mix}$  = Gibbs free mixing energy,

assuming that the Gibbs free energy of the two phases ( $G(w)$  and  $G(o)$ ) does not differ from the 2 phasic system and the microemulsion. With eq. (3) and (4) equation (2) becomes

$$\Delta G = G_{mix} + \sigma \Delta A \quad (5),$$

where  $\sigma \Delta A$  describes the difference of the surface free energies  $G_B(w/o)$  and  $G_A(w/o)$ , since

$\sigma$  = surface tension

$\Delta A$  = difference of the area of interfaces in case B and A

The Gibbs free mixing energy  $G_{mix}$  (see equation (5)) is equal to  $-T \Delta S$ , since  $\Delta H_{mix} = 0$ . Thus  $\Delta G$  can be expressed by eq. (6) as:

$$\Delta G = \sigma \Delta A - T \Delta S \quad (6),$$

becoming  $< 0$ , if  $\sigma$  is decreased sufficiently by the emulsifyer.

Especially nonionic surfactants with HLB values of about only 10 (HLB = hydrophilic-lipophilic-balance [27]) are suitable for the preparation of stable w/o microemulsions even at room temperature [28].

The yield of microemulsions can be increased by increasing the water phase content, but this is limited by the inversion point, where a water in oil emulsion converts into a oil in water emulsion.

A similar synthesis route starts from a homogeneous solution of the appropriate precursor (e. g. metal alkoxides or salts) and a surface modifying agent in alcohol or water. By changing the pH value a precipitaton reaction is induced. The surface modifying agent covers the surface of the so formed particles (agglomerates) and thus limits the growth of the precipitates to an average size depending on the surface modifier to precursor ratio. After elimination of the solvent the resulting powder can be dried and calcinated.

## 2.2. Synthesis

The principles of the microemulsion technique have been proven by the synthesis of oxides ( $\text{Fe}_x\text{O}_y$ ,  $\text{ZrO}_2$ ,  $\text{TiO}_2$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{CuCr}_2\text{O}_4/\text{CuFe}_2\text{O}_4$ ) [28, 29 , 30 , 31 ] and titanates (barium titanate, PZT) [32 ]

The preparation of oxide particles by interface controlled precipitation reaction from homogeneous solutions has successfully been demonstrated for  $5\text{-Y}_2\text{O}_3/\text{ZrO}_2$  [33 ] using different oxide to surface modifier ratios.

The principle of growth controlling by bifunctional ligands (compare fig. 2) has successfully been applied for the synthesis of non agglomerated nanosized metal colloids in alcoholic solutions and sols for the synthesis of Ormocer materials as described for Au [16, 17], Ag [17,34 ] and Pd [35 ] using different types of aminio silanes as stabilizers and different reduction mechanisms (generation of organic radicals by UV irradiation, chemical reduction). The metallic character of these colloids has been proven by UV-VIS spectroscopy, since metallic colloids show absorbances of light due to their plasmon resonance. Since measured and calculated [36 ] absorbance spectra were in good agreement, the colloid size could be determined from the spectroscopic data [14,37 ], indicating that the colloid size can be controlled in the range between 1 and 50 nm by the stabilizer concentration.

The same principle has been applied for the generation of nanosized CdS particles (semiconductor quantumdots) [38 , 39 , 40 ] in ethanolic solution and Ormocer sols.

In this case the variation of particle size can also be detected by UV-VIS spectroscopy, since the band gap increases with decreasing particle radius leading to a significant blue shift in absorbance and emission spectra [41].

The surface energy control by coordinative ligands can be also be used for the preparation of oxide nano particles in sol-gel materials. An interesting example is the preparation of nano sized  $ZrO_2$ -particles by complexing Zr alkoxides with methacrylic acid (MAS) [42]. As indicated by photon correlation spectroscopy spherical shaped, highly stable  $ZrO_2$  clusters are obtained and the mean particle sizes can be tailored in the between 2 and 10 nm by variation of the ratio of Zr : MAS between 1 : 1.8 and 1 : 0.8.

### 2.3. Processing

The chemical synthesis of nanosized particles offers a great variety of materials engineering by different types of processing techniques that shall be demonstrated here by some examples. The preparation of  $5-Y_2O_3/ZrO_2$  particles by an interface controlled precipitation technique [33] leads to ceramic powders with adjustable sintering temperatures as shown in fig 4.

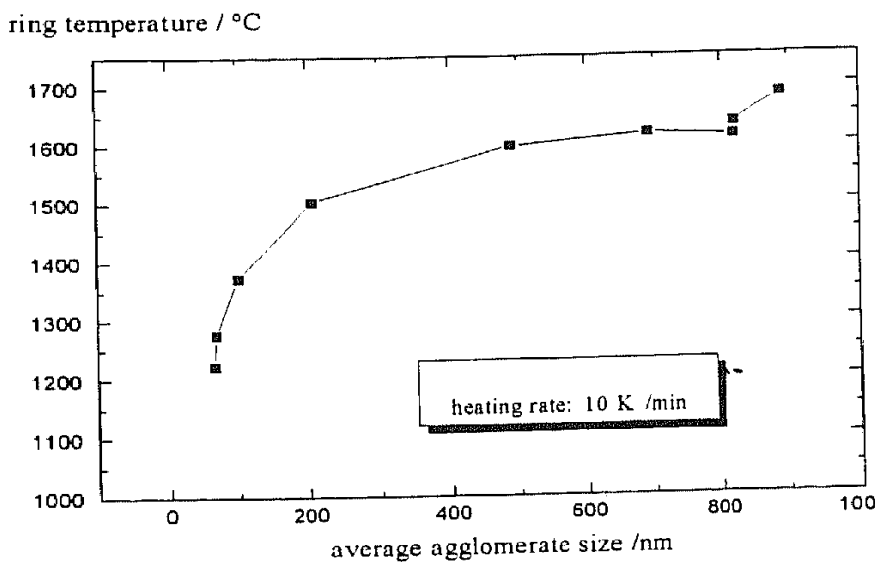


Fig.4. Sintering temperature of  $5-Y_2O_3/ZrO_2$  powders for different agglomerate sizes, synthesized by an interface controlled precipitation technique using different amounts of surface modifier, dry pressed samples with 48-55 % green density, sintered density >95 % (after [33])

It shows that based on a nano particle processing, the agglomerate size can be decreased down to 60 nm, leading to a substantial reduction of the sintering temperature. As expected the sintering temperature tremendously decreases with decreasing agglomerate size from 1700 °C down to 1200 °C for an average particle

size of 100 nm. The obtained density of the sintered bodies was over 95 % of its theoretical value.

In this case the deagglomeration during the processing step could be obtained completely due to a dry pressing processing. For this reasons, the densification shoes a two step function (according to fig. 5).

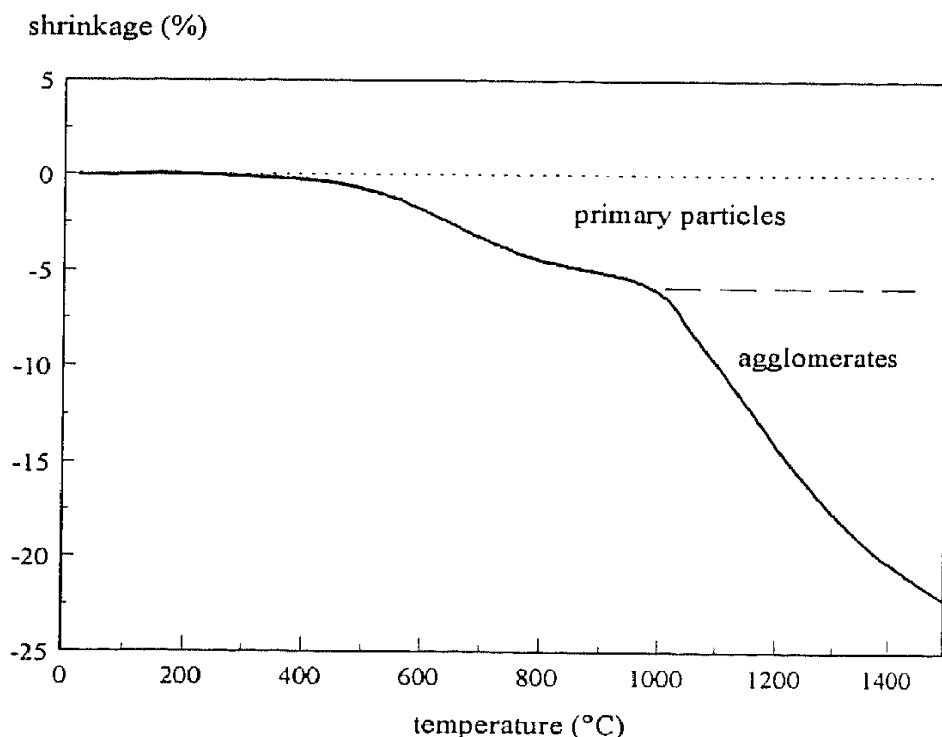


Fig.5. Sintering behaviour of 5-Y-ZrO<sub>2</sub>, particle size 15 nm, agglomerate size > 1 μm, heating rate 10 K/min after [33]

## 2. 4. Nano composites

The preparation of nano sized ZrO<sub>2</sub>-particles by complexing Zr alkoxides with methacrylic acid (MA) [42, 43 ] in organic-inorganic composites opens up interesting possibilities for optical applications, since these materials are suitable for fine patterning techniques as lithography, holography, embossing or direct laser writing through photopolymerization of the double bonds [44 ]. Their refractive index  $n_e$  can be matched by the incorporation of nano sized ZrO<sub>2</sub>-particles. Fig. 6 shows an example for the combination of laser writing with the formation of buffer and cladding layers using the same basic system with different ZrO<sub>2</sub> contents to tailor  $n_e$  for the fabrication of optical waveguides.



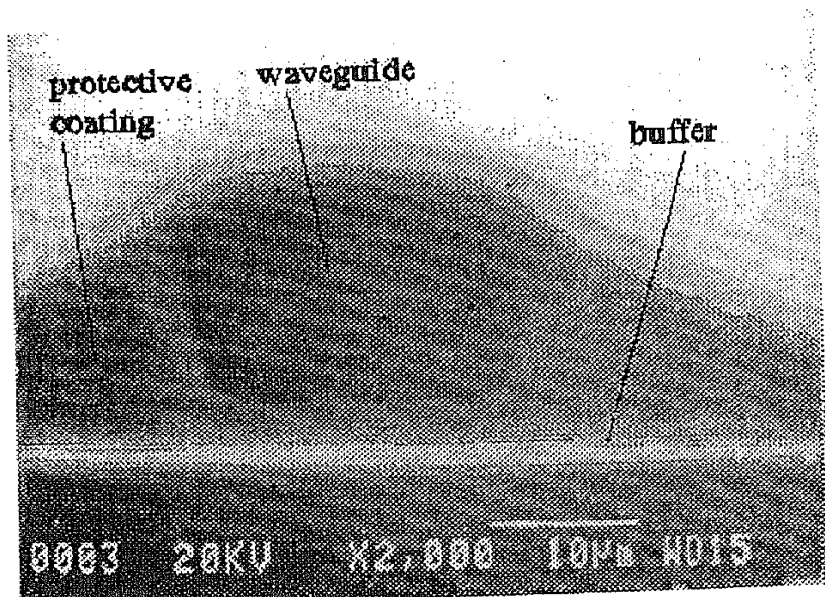


Fig. 6. SEM-micrograph of a sandwich buffer/strip waveguide/protective coating of organic-inorganic composites composed of  $ZrO_2/MA/(RO_3)Si(CH_2)_2 - O - CO - C(CH_3) = CH_2$  containing nano sized  $ZrO_2$ -particles for refractive index matching [42]

In a first step, the substrate is coated with a buffer layer to be independent on the index of refraction of the substrate material and to minimize surface scattering by substrate roughness. This film is polymerized by UV curing. In a second step, a second film with a higher  $n_e$  is prepared and polymerized by laser writing. After removing the unpolymersed film the desired patterns are ob-

tained. Finally, the patterns are covered by the cladding film having a lower index of refraction than the strips.

## 2.5. Composites with metal particles

Nano sized metal particles stabilized by bifunctional ligands can be processed to coloured films by coupling the colloids to a desired matrix using the chemical reactivity of the „second“ function of a stabilizing ligand. By introducing the stabilized colloids into an appropriate sol, common coating techniques can be applied and, if ligands with polymerizable double bonds are used, curing processes like UV curing can be used. Thermal densification, depending on the sol-gel matrix material is also possible.

Since metal colloids have relatively large molar coefficients of extinction (in the range of  $10^5$  l/mole·cm) high optical densities can be obtained even in coatings of about 1  $\mu m$  in thickness. Fig. 7 shows an example for Pd colloids embedded in an  $SiO_2$  coating on glass, densified at different temperatures in different atmospheres ( $N_2$ , Ar and  $N_2/H_2$ ) [35].

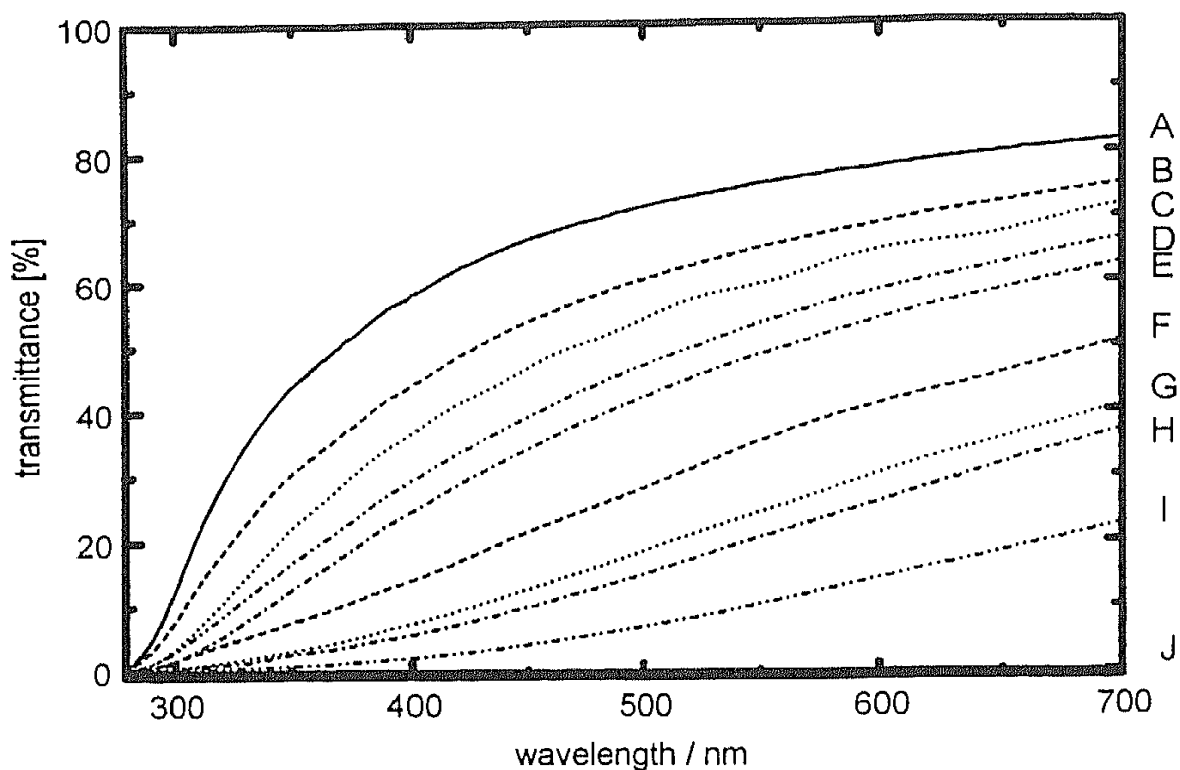


Fig. 7. Transmittance spectra of Pd colloid containing SiO<sub>2</sub> coatings (3 μm thickness, Pd concentration 2 wt%, densified at different temperatures in different gas atmospheres (Ar, N<sub>2</sub>, H<sub>2</sub>+N<sub>2</sub>): A = 250 °C in Ar; B = 300 °C in H<sub>2</sub>+N<sub>2</sub>; C = 300 °C in N<sub>2</sub>; D = 300 °C in Ar; E = 400 °C in H<sub>2</sub>+N<sub>2</sub>; F = 400 °C in N<sub>2</sub>; G = 400 °C in Ar; H = 500 °C in H<sub>2</sub>+N<sub>2</sub>; I = 500 °C in N<sub>2</sub>; J = 500 °C in Ar [35]

For the preparation of the coatings complexed Pd ions (constant Pd:stabilizer ratio of 1 :6) were introduced to the sol and the colloid formation was obtained during the thermal densification of the sol-gel matrix. As concluded from WAXS measurements the densification in inert or reducing gas atmosphere is necessary in order to prevent the formation of PdO nano particles at elevated temperatures.

The Pd to stabilizer ratio has a strong influence on the colloid size and the size distribution. This is illustrated by the following fig. 8, showing the particle size distribution of Pd colloids in an SiO<sub>2</sub> matrix (xerogel powder) after thermal densification at 500 °C in N<sub>2</sub> atmosphere [35], determined by TEM investigations.

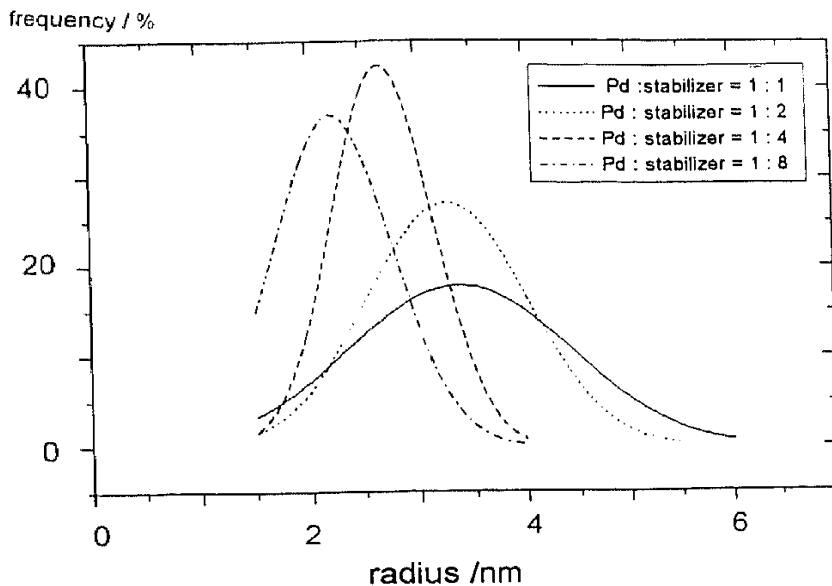


Fig. 8. Size distribution (Gauss fit) of Pd colloids in a  $\text{SiO}_2$  xerogel matrix after thermal densification at 500 °C in  $\text{N}_2$  atmosphere for different Pd : stabilizer ratios in the sol [35].

It is evident that the mean particle size decreases and the size distribution gets narrower with increasing stabilizer content. The stabilizer concentration also influences the temperature onset for the colloid formation during the thermal densification of the matrix. For a Pd : stabilizer ratio of 1 : 1 colloid formation occurs at room temperature for a ratio of 1 : 8 the onset is

shifted to 200 °C, as determined from WAXS investigations [35].

## 2.6. Semiconductor particles

The mechanisms for the stabilization of nano sized particles in sol-gel matrices by functionalized silanes can also be used for the preparation of composites containing semiconductor quantumdots, as shown in the case of CdS-particles in organic-inorganic coatings and monoliths, using thiosilane as stabilizer [41]. It has been shown that by variation of the thiosilane concentration and the concentration of the sulphur source (HMDS) in the sol the CdS particle size can be controlled in the range between 1 and 5 nm in diameter with a narrow size distribution. As an example fig 9 shows a TEM micrograph and the size distribution of CdS particles in an Ormocer monolith (synthesized from GPTS/TEOS) using thiosilane as stabilizer with an Cd:thiosilane ratio of 1 : 100 and an equimolar amount of HMDS as sulphur source.

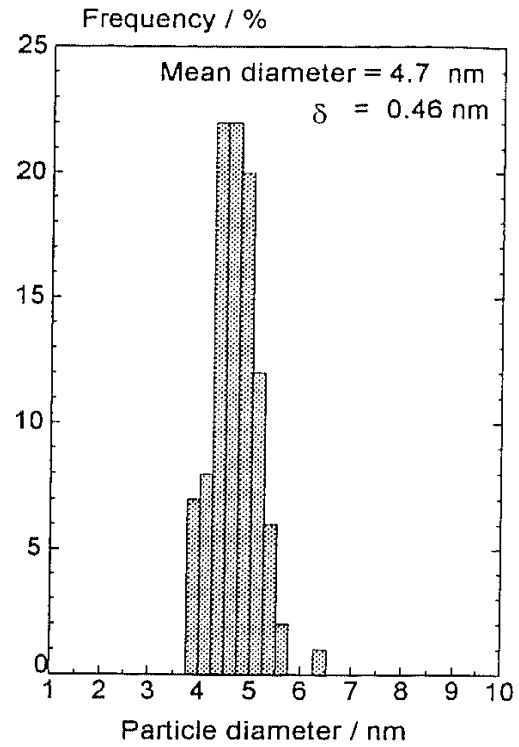
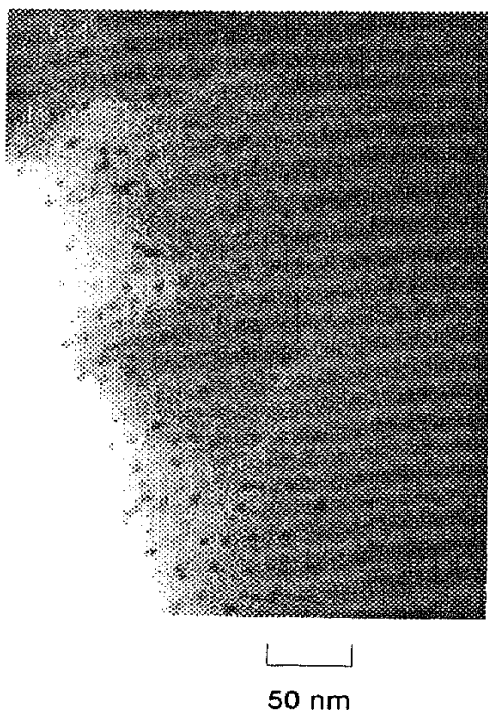


Fig 9. TEM micrograph and size distribution of CdS particles in an inorganic organic monolith synthesized from GPTS/TEOS using thiosilane as stabilizer with an Cd:thiosilane ratio of 1 : 100 and an equimolar amount of HMDS as sulphur source for a Cd : stabilizer ratio of 1 : 100 , monolith preparation by sol casting and solvent evaporation at 80 °C for 76 h after [41]

From fig. 9 a particle size of  $(4.70 + 0.46)$  nm in diameter is presented. Applying these techniques, the influence of particle size, ligand type (donor/acceptor) and matrix properties on the optical properties will be investigated. Since the Bohr radius of CdS is of about 2.8 nm from particle sizes  $> 10$  nm in diameter and a narrow size distribution maximum  $\chi^3$ -effects [45 ] should be expected.

### 3. Conclusion

It has been shown that the principle of the minimization of the Gibbs free energy of nano sized particles by using interfacially active substances (ligands, emulsifiers) leads to thermodynamically stable systems for the preparation of nano sized ceramic powders or oxide, metal or semiconductor particle containing sol-gel derived composites. By this way the nucleation and growth as well as the agglomeration of nano sized phases can be controlled rather easily and distinguished contamination

of the phase boundaries is obtained. Therefore these chemical synthesis routes seem to be suitable for the production of nanophased materials with adapted material properties on a relatively large scale.

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