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INORGANIC-ORGANIC SOL-GEL PROCESSING FOR GLASSES AND NANO COMPOSITES

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1. Introduction

The sol-gel process describes a method for the synthesis of non-metallic inorganic materials by a chemical route. The formation of an inorganic network is based on a condensation process from reactive precursors. As precursors a variety of "inorganic" monomers or "oligomers" can be used. These are alkoxides, soluble salts, oxides, hydroxides or even colloids. During the condensation step, the formation of a three-dimensional network takes place. The structure of this network depends mainly on the structure of the cross-linking species and in multicomponent systems on their homogeneity, that means, distribution of the different components. These structures of the salts depend mainly on the reaction conditions and composition, that means, on the thermodynamics of the reacting system, and a considerable number of parameters can be used for the reactions. Based on this variability, the structures of the gels can be varied in a wide range, too. Whereas the SiO_2 system has been investigated by numerous authors very thoroughly, the state of the art in other systems is comparably low. Especially the influence of sol structures on gel structures, gel properties and downstream properties of materials is rather rudimentary. The difference between a simple precipitation process based on the above mentioned reaction mechanisms in the sol gel process is the fact that sols can be stabilized and used for further processing like monolithic gel formation, coatings or fiber drawings. But in order to stabilize these sols, the interaction or reactivity between the sol components has to be taken into consideration.

A very simple way of sol stabilization is the electric charge stabilization or the ξ potential. This rather simple way can be carried out by choosing the appropriate pH value which, depending on the different systems, creates electric charges on the surface of the particles and generates repulsing forces in order to avoid precipitation. As a rule, during the sol-gel synthesis, from most compositions particular systems are obtained, that means, the growth reactions generate small, mainly spherical particles, if no crystallization appears, which then aggregate and gelate, if no stabilization is applied. Exceptions can be observed in SiO_2 systems where, depending on the pH value, the cross-linking reaction of silanole group containing monomers is not isotropic and chain formation can be observed [1]. These chains then may undergo a cross-linking reaction forming all types of polymerized networks.

Another exception are systems derived from alkoxides which are reacted with complex formers like β -diketones or carboxylic acids, blocking reactive sides of the alkoxides for further condensation and thus leading to an anisotropic polymeric molecule growth, enabling the formation of chains [2 - 4].

It is of high interest to control sol properties with respect to further processing of materials. For example, for the fabrication of monolithic ceramics from these sols, high solid contents after gelation are necessary in order to end up with high green densities. For effective further processing, these densities should be above 60 % by volume. Conventional gels normally show much lower solid contents, forbidding ceramic processes due to the large sintering shrinkage. Only in the case of silica, attempts have been made to produce preforms for fibre drawings by gelation or to fabricate monoliths from SiO_2 gels [5]. Another important factor is the formation of the coatings from sols, and again high shrinkage rates are one of the major drawbacks for the formation of thick layers. As demonstrated by an excessive literature review from Brinker and Scherer [6], there seems to be a 'magic' thickness in the range of one μm which cannot be exceeded by sol-gel coatings and, as demonstrated by Lange [7], the reason is the insufficient relaxation capability of inorganic gels not high enough to dissipate stresses occurring during drying and sintering of gel layers and thus leading to energy dissipation by crack formation. This is a second reason for investigating the behavior of sol particles which in most cases are in the range from several to 100 nm. Control of relaxation behavior would enable new processing types. Another interesting feature of the small particle is the large surface, forming a large interface either to the solvent or to the atmosphere. As shown from nanocrystalline metals [8], the units near the surface are completely different from the bulk material, exhibiting extremely interesting properties, and it is of interest to control or to vary these interfaces because the overall effect to be expected may be very high due to the very large surface. In this paper, some basic ideas about the treatment of colloidal particles surfaces in sol-gel processing are given, and some examples of material development will show the effect of this surface treatment.

2. General Consideration

As already mentioned above, sols have to be stabilized if gelation or precipitation shall be avoided. In fig. 1, some possibilities of stabilization of particles are shown.

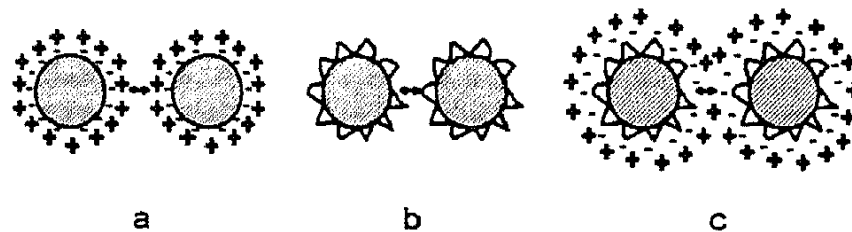


Fig. 1: a: electrostatic stabilization; b: steric stabilization by polymer adsorption; c: steric and electrostatic stabilization by polyelectrolyte adsorption.

These types of stabilization are well known and used in ceramic processing for technical production. In these processes, the particle sizes, however, are in the range of some μm , but, as a rule, not below 500 - 100 nm. In these cases, the

spacer volume (range of the electric field used for the repulsion or adsorbed organic polymers volume) does not play an important role. Going to very small particles, e. g. in most of the sols ranging from some to 20 or 50 nm, the spacing volume becomes more and more important, and especially with particles in the lower nano range, the spacing mechanisms shown in fig. 1 lead to extremely low solid contents thus leading to difficulties with respect to high solid content processing. For these reasons, the conception of a short range repulsing mechanism has to be taken into consideration, and the use of short or small molecules selectively binding to the particle surface without generating long range repulsion by electric fields has to be developed. In addition to this, the interaction between these types of molecules and the particle surface can provide an additional means to tailor the particle properties, especially if these properties can be influenced by electron donating accepting molecules. This might be of interest, especially in semiconducting systems, e. g. semiconductor quantum dots. Furthermore, it can be of interest to use molecules for the surface covering having additional chemical reactivities to be used for further processing.

3. Conceptions for a Colloid Stabilization

In fig. 2, a survey over different types of surface stabilization is shown schematically [9 - 15].

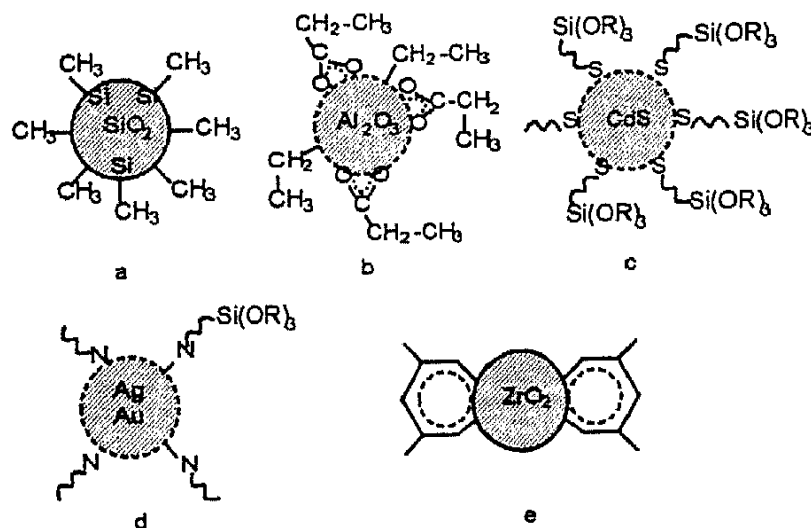


Fig. 2: Examples for stabilization of colloids by small molecule interaction.
a: methylsilane-modified SiO_2 ; b: propionic acid-modified boehmite; c: sulfide-modified CdS ; d: amine-modified noble metals; e: β -diketonate-modified ZrO_2 .

As one can see from fig. 2, there exists a variety of possibilities of reacting particle surfaces with selectively reacting small molecules. It is not quite clear how far these molecules can contribute to generating well defined particle size or particle size distribution. But as shown from theoretical works from Strehlow [16], there is a reasonable chance for using this type of molecules not only for

covering the surface, but to decrease the surface free energy to stabilize these particles. As shown by Rinn [17], the variation of the concentration of surface reacting ligands as the only parameter can be used for tailoring the diameter of monosized particles. For the interpretation of these surprising findings, the model of surface free energy minimum can be used. In this model, one assumes that for minimizing the surface free energy, a certain coverage per surface unit by the absorbed ligand leads to the energy minimum, and for these reasons, for each ligand concentration a special particle size results.

3.1 Reduction of Particle-to-Particle Interaction

The reduction of particle-to-particle interaction is extremely important if small particle containing systems should be processed to monoliths or to coatings, especially if thicker coatings are required. Therefore, it seems to be suitable to use inert groups to shield the surfaces, and for SiO_2 , the use of a methyl group seems to be an appropriate means. For an irreversible binding of methyl groups to SiO_2 particles, the reaction with methyl silanes can be used. The schematics of the reaction is shown in fig. 3a. In the case of alumina, e. g. for boehmite sols, small molecular weight carboxylic acids have been used, as schematically shown in fig. 3b. In fig. 3c, the infrared spectrum of coated boehmite particles ranging between 15 and 40 nm is shown and compared to propionic acid, and as one can see, the "salt" formation in the particulate system clearly can be observed.

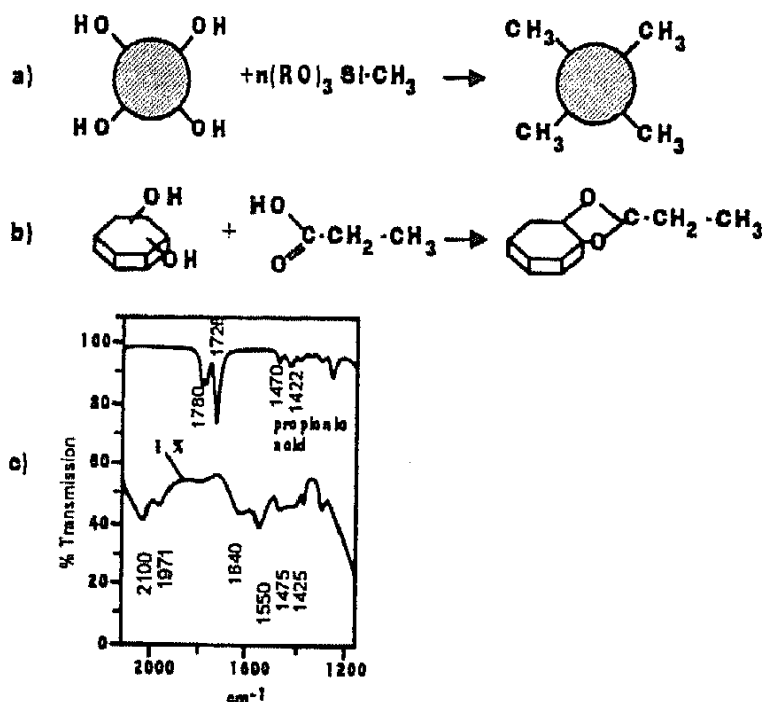


Fig. 3: a: Formation of CH_3 group surface-modified SiO_2 sols by reaction with allyl alkoxy silanes; b: formation of surface-covered boehmite; c: IR spectra of free and adsorbed propionic acid [18].

3.2 Metal Colloid Formation

The formation of metal colloids, e. g. from noble metal compounds, is very well established and used, e. g. for the colouring of lead crystal glasses. In this case, gold colloids are used for gold tuby glass. In order to receive the intensive colours, colloids have to be grown to appropriate particle sizes. Similar processes are used for obtaining yellow to brown colours on glasses from silver colloids. Colloids of this type can be obtained in solution and in the case of gold, the particles aggregate to larger units. Addition of appropriate ligands have been used for stabilizing these colloids. If these ligands are bifunctional and contain hydrolysable silane groupings (e. g. aminopropyl triethoxysilane), the system can be used for further sol-gel processing and the novel type of sol-gel precursor containing metal colloids can be prepared. The schematics of this process is shown in fig. 4 [10].

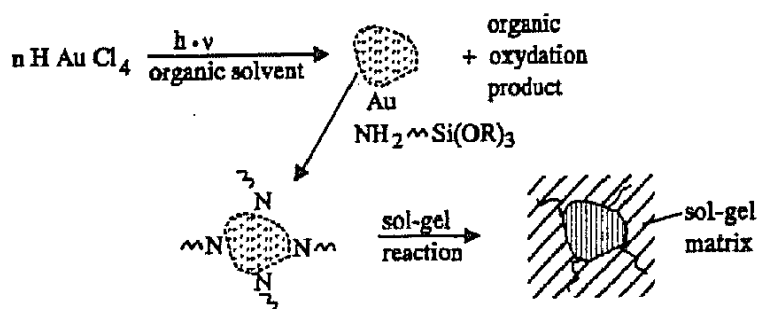
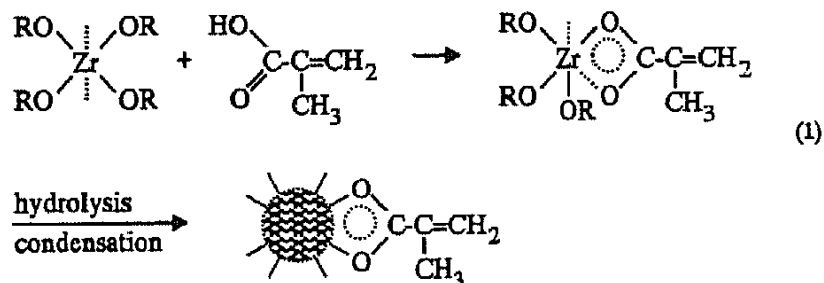


Fig. 4: Draft of the formation of the particle containing sol-gel materials.

3.3 Active Ligand Stabilization

A means of silane stabilization already can be considered as an active ligand. However, this principle can be extended to a variety of reactivities, and organic reactions are of special interest since ligands to be used in organic processing, for example, polymerization, lead to the interesting potential of using this type of components, for example, for photocuring processes or photolithography. This conception has been used by Sanchez [19] and by Krug [20]. Whereas Sanchez used β -diketones containing allyl groups for polymerization, Krug was using methacrylic acids to stabilize zirconia particles and to use them in inorganic-organic sol-gel processes containing other polymerizable methacrylates. The schematics of this type of stabilization is shown in eq. 1.



All the stabilization processes shown above are based on the fact of modifying colloidal particles by special ligands to stabilize them and to generate desired novel chemical reactivity in order to process them to materials without uncontrolled gelation.

4. Material Development Examples

4.1 Thick SiO₂ Layers

In order to develop thick SiO₂ layers, the conception of interaction reduction was used. In this process, the surface covering of colloidal particles by methyl groups could be achieved by using methyl group silane containing sols for coating colloidal SiO₂ particles [11]. The process is based on a biphasic emulsion process in which commercially available SiO₂ sols are coated with the methyl group silane system.

Whereas the sol (with particle sizes of about 7 nm) precipitates if concentrated to solid contents of 10 - 20 wt.-% as a maximum, the modified sol (particle sized in diameter about 8 nm determined by photon correlation spectroscopy) can be concentrated up to 50 wt.-% showing no precipitation and, what is rather surprising, having low viscosities in the ranges below 100 mPa·s to be used for coating processes. These sols are completely clear and do not show any light scattering, proving that no aggregates above the light scattering limit of about 20 nm are formed and showing the perfectness of the coating method for these sols. These sols can be used for coating, and coatings up to 10 μm after densification can be achieved in a one-step dip coating process. After densification at 500 °C, densities up to about 98.8 % of the theoretical density measured by reflective index measurement are obtained.

4.2 Silver or Silver Halide Containing Systems

Silver colloid and silver halide containing systems have been prepared by using silver nitrate as a starting compound and photoreducing it in the presence of amino silanes. The spectra of the silver colloids show the typical absorption of silver colloids in the range of some nm as known from literature. In these systems, the silver can be incorporated into sol-gel derived glass matrices to form silver colloid containing systems. Treatment with HCl leads to silver halide and photochromic layers. In fig. 5, the formation of silver by UV light in the transparent silver halide layers and the temperature bleaching of this process is shown in the X-ray pattern [21].

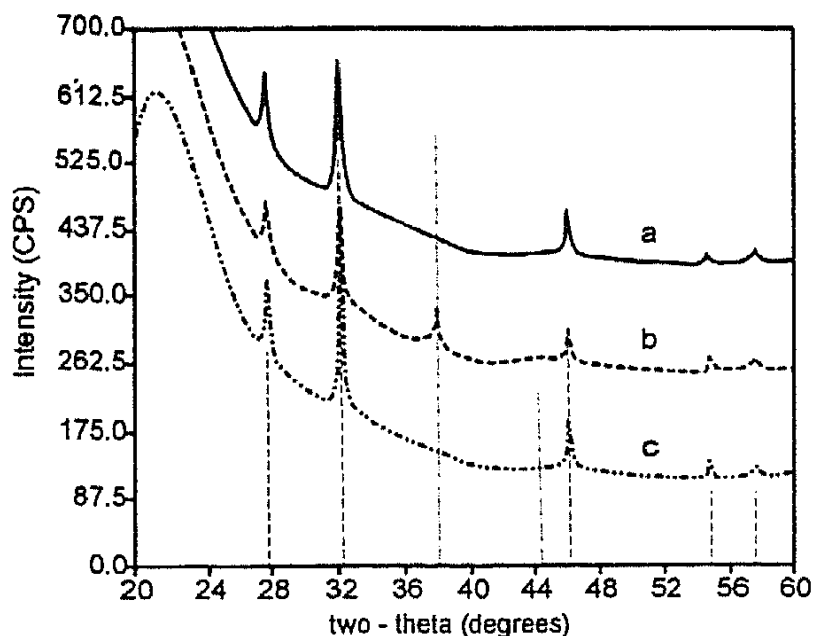


Fig. 5: X-ray patterns of silver halide in transparent sol-gel layers. a: before, b: after irradiation; c: after bleaching.

As one can see, the UV light leads to the formation of crystalline silver particles.

It is remarkable that in two μm thick layers darkening up to 85 % can be reached. The calculated coefficient of extinction of this process is almost two orders of magnitude higher as known from silver halide containing photochromic inorganic glasses derived from melting processes.

4.3 Nonlinear-Optical Gold Containing Systems

In a similar way as shown in the case of silver, gold colloid containing systems can be obtained by using γ -aminopropyl triethoxysilane or diaminosilane. In the case of the use of the diaminosilane, spontaneous reduction of the used gold precursors (AuCl_4) takes place which is attributed to the strong particle-to-ligand interaction, leading to a low surface free energy. The reduction is thermodynamically driven and an oxidation of hydrocarbons in the solvent system takes place [22]. Again, this stabilized gold colloids can be used for being incorporated into glass or ORMOCER matrices by cocondensation of the silanes with the sol-gel precursors.

4.4 Zirconia Methacrylate Systems

As shown elsewhere [23], zirconia alkoxides can be reacted with methacrylic acid up to the ratio of zirconia to methacrylic acid (MA) 1:2. These complexes are rather stable against hydrolysis [12], but depending on the complex ratio, they can be hydrolyzed and condensed to clusters without destroying the methacrylic acid-to-zirconia bonds. The cluster size can be established between 2 and 40 nm. This can be used to introduce rather high zirconia contents into inorga-

nic-organic sol-gel matrices without aggregation, that means, the particles can be homogeneously distributed in the matrix, and if they are kept below 20 nm, no light scattering losses are observed. The methacrylic group can be used for photocuring, and if laser light is used, laser photolithography can be applied. As already shown [12, 13], the process can be used for a variety of micropatterning processes like embossing or laser lithography, holographic grating fabrication or mask aligner techniques. Planar waveguides and channel waveguides showing very low optical losses have been prepared by this system. The proper choice of the zirconia content allows the establishment of desired refractive indices and buffer layers, waveguides and claddings can be prepared from one and the same type of material.

5. Conclusions

As one can see from the conception and from the examples, the control of small particle surfaces can be used as an interesting means for the preparation of novel sol-gel precursors to be used in a variety of processes for the fabrication of coatings (inorganic, inorganic-organic), active optical materials and interesting processing techniques.

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