

Sol-gel nanocomposites as functional optical materials

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ABSTRACT

Small particle processing opens a variety of interesting aspects for optical applications. For the utilization, the sol-gel process offers a variety of routes, like colloid synthesis, incorporation into sol-gel derived matrices and in combination with photopolymerizable components patterning processes based on photolithography. In this paper, a summary over a new conception of colloid stabilization and colloid processing by multifunctional ligands and further processing routes for optical applications is given.

1. INTRODUCTION

Organic modification of sol-gel materials provides some interesting aspects for the sol-gel processing as well as for final properties. As far as processing is concerned, it is possible to produce thick layers without cracking^{1,2}. This can be attributed to the increased relaxation of these materials, caused by various mechanisms. Another important aspect for processing is the introduction of reactive organic groupings to create photoresist behavior, which allows patterning mechanisms as photolithography, laser writing or photocuring assisted embossing. In order to achieve the desired properties, the structure has to be controlled very thoroughly, especially with respect to phase separation between the organic and the inorganic phase. Chemistry is an important tool to control the reaction parameters and to synthesize multifunctional materials. It can be used in various ways for optical material synthesis by sol-gel methods: to synthesize organic-inorganic matrix materials³, to synthesize or stabilize semiconductor quantum dots⁴⁻⁶ and to incorporate them into organic matrices, to vary the refractive index⁷, or to incorporate active organic molecules⁸. This paper summarizes some important aspects of chemical synthesis of our recent work in the field of preparation of inorganic-organic composite materials for optical purposes.

2. CHEMICAL PRINCIPLES

The control of the phase size is of importance for avoiding heterogeneities causing increased light scattering. If alkoxides from Zr, Ti or Al have to be used, sol synthesis leads to colloids which have to be kept on a nano level. As shown in⁹⁻¹¹, this can be carried out by complexation of the alkoxides, blocking active sites for condensation. It can also be carried out by chemically reacting the surface with inert groups. In fig. 1 (next page), a flow chart of the different ways for surface controlling is given.

The basic idea was to control growth and aggregation by surface control of the growing (or already grown) particles in order to avoid aggregation and to keep the size on a nano level. In addition to this, by proper choice of the ligands, a surface reactivity could be established, allowing a variety of reactions, such as polymerization or hydrolysis and condensation.

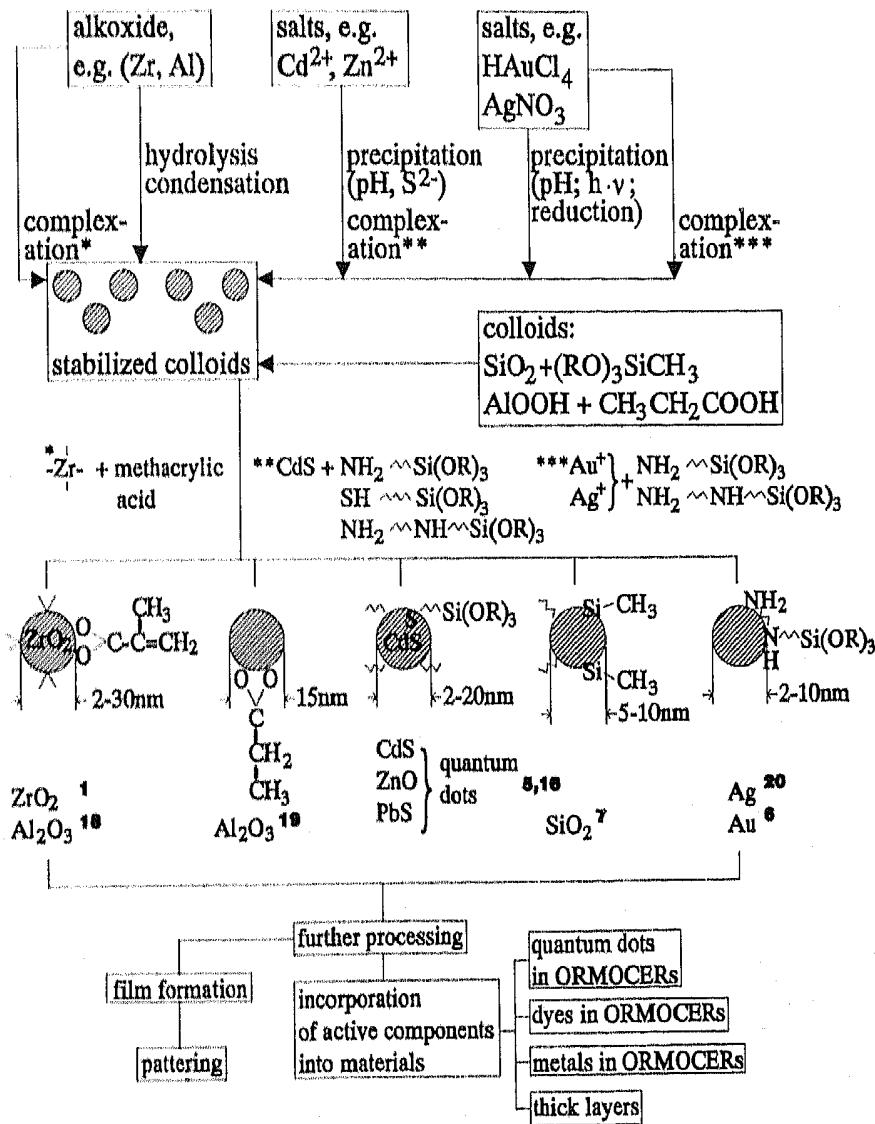
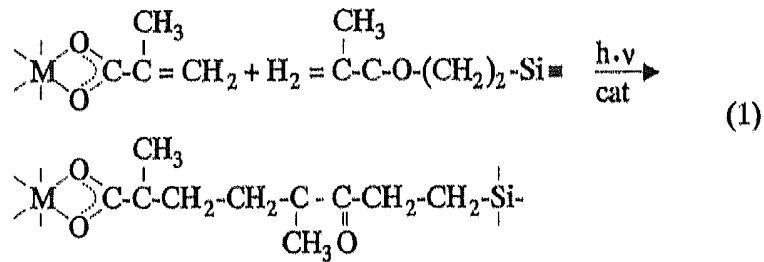


Fig. 1: Flow chart of the preparation and stabilization of nanosized colloids and of further processing.

3. PHOTOCHEMISTRY

The complexation of alkoxides with methacrylic acid allows the incorporation of polymerizable ligands to a variety of inorganic sol-gel precursors like Al alkoxides, Zr alkoxides or lanthanide element alkoxides. In the case of Zr, even with excess water¹ the acid-to-Zr bond is not destroyed at room temperature. The formation of precipitates depends strongly on the Zr:MA ratio¹, and in alcoholic solutions precipitation with excess water occurs if r exceeds 1:0.8. Below this ratio, the particle size of the colloidal system can be adjusted between 2 and 6 nm by varying r , as shown in¹. In the presence of silanes of the type $\text{RSi}(\text{OR})_3$, as shown by NMR investigations^{12,13} the Zr-MA complex acts catalytically on hydrolysis and condensation of the silanes. Weak signals in ²⁹Si-NMR have been found which can be interpreted by the formation of Zr-O-Si bonds, but this needs further proofs. If R is a photopolymerizable group, e. g. $\equiv\text{Si}-(\text{CH}_2)_2\text{OCOC}(\text{CH}_3)=\text{CH}_2$, it can be crosslinked to the MA-alkoxide complex (eq. (1)).



Materials based on these systems have been optimized especially for passive waveguides and as model materials for patterning. Films made from these materials can be obtained up to 20 μm in thickness and show optical losses of less than 0.1 dB/cm. They can be photopolymerized by laser beams (laser writing), by UV light using masks (photolithography) or during an embossing process, or gratings can be obtained by generating an energy modulated beam by two wave mixing. It is of interest that the volume shrinkage is in the range of only some volume-% from the dried to the cured film. Near net shaping is possible. The refractive index can be adapted between 1.39 up to 1.57, depending on composition, as schematically shown in fig. 2^{1, 14}.

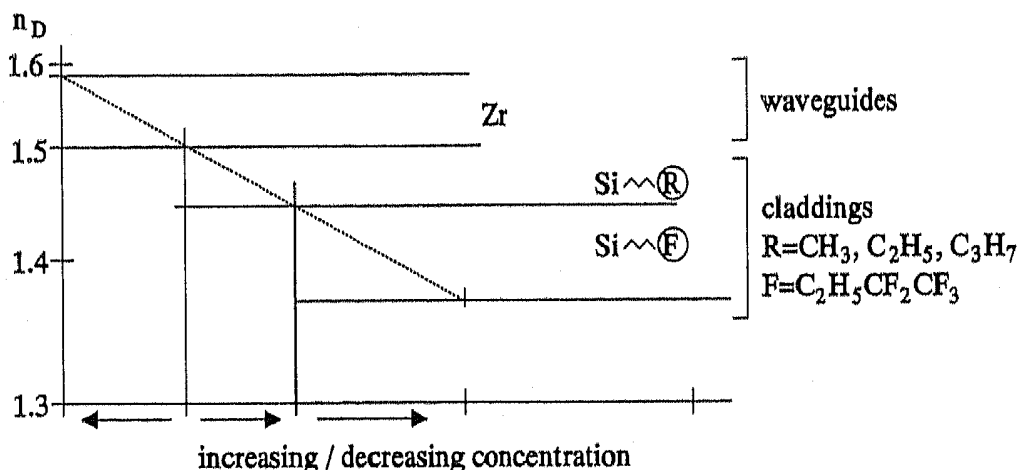


Fig. 2: Adjustment of refractive indices with Zr of functional silane containing composites (after 1, 14). Arrows indicate increasing contents of the effective components; experimental details are given in 1, 14.

The refractive index variation can easily be used for guiding systems together with polymerizing components such as methacryloxy silanes; all of them can be patterned by the methods indicated above. The uncured systems can be purified by vacuum and heat treatment from "impurities" responsible for high DK values like H₂O or OH groups. These intermediates, depending on the organic group content are still soluble in organic solvents and can be used for coatings. Due to their low content of H₂O and OH, they show breakthrough voltages of > 15 V/ μm which is sufficient for poling experiments. First experiments of the incorporation of organic dyes, e. g. Disperse Red ($\chi^2 \approx 0,22 \text{ pm/V}$), shows the stability of the χ^2 value over more than 50 days, which is substantially longer than in PMMA as matrix¹⁵. These findings will be systematically optimized in the future work. During the poling, the curing of the Disperse Red containing film is carried out by photopolymerization as described in eq. (1).

The investigations show that these types of systems can be processed very easily and the matrix properties can be adapted to a variety of needs.

4. ACTIVE COLLOIDS

The incorporation of colloidal particles as described in the previous chapter, comprises passive particles only. As active particles, semiconductor colloids (quantum dots) or metal colloids are of interest. Preparation and properties of semiconductor quantum dots (SQD) are described in 4. But colloids in solutions are restricted in handling and application. Spanhel and coworkers in our institute have shown how to stabilize SQDs by bifunctional ligands in order to incorporate them into sol-gel processing and the techniques described above. In fig. 3, a flow chart over the possibilities of processing is shown.

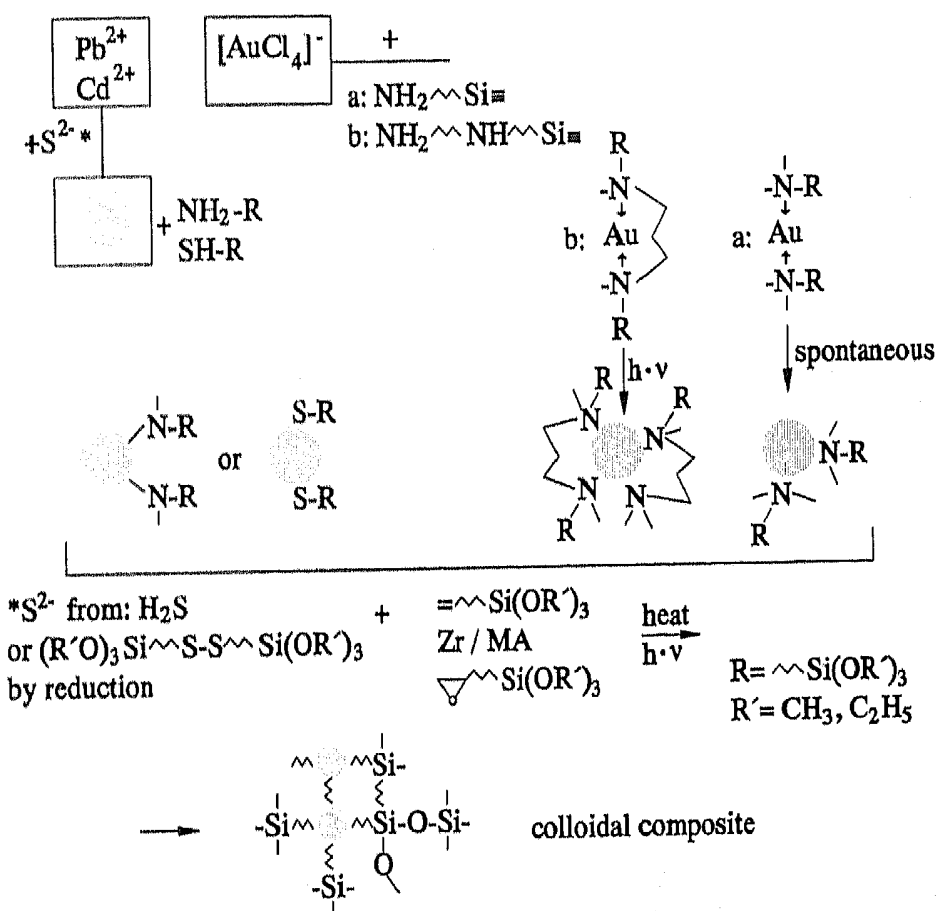


Fig. 3: Flow chart of the formation of active composites (after 5, 6, 16).

The process can be applied onto a variety of metals and SQDs and includes perfect stabilization of the colloids with high "sol-gel" reactivity. In fig. 4 (next page), some optical spectra of QD and Au containing composites are shown. First χ^3 experiments by picosecond self diffraction measurement show χ^3 values in the range of 10^{-9} esu on CdS/PbS SQDs¹⁶.

The spectra show cut off wavelengths to be attributed to quantum effects (CdS), influence of the ligands on the band gap energy and typical absorption of metal colloids. Incorporation into ORMOCER matrices do not change the spectra, indicating the shielding effect on the ligands. The size of the colloids ranges from some to 20 nm, proved by TEM investigations, in accordance with the optical spectra. χ^3 measurements by self diffraction experiments show values around 10^{-9} esu for CdS/PbS systems.

The incorporation of the colloids into sol-gel matrices can be performed by a variety of techniques. Inorganic as well as organic matrices can be used. Photoinitiated colloid growth in the case of gold can

be combined with the curing process and of films by photopolymerization and thus, colloid growth and film curing can be carried out in a one-step reaction⁶.

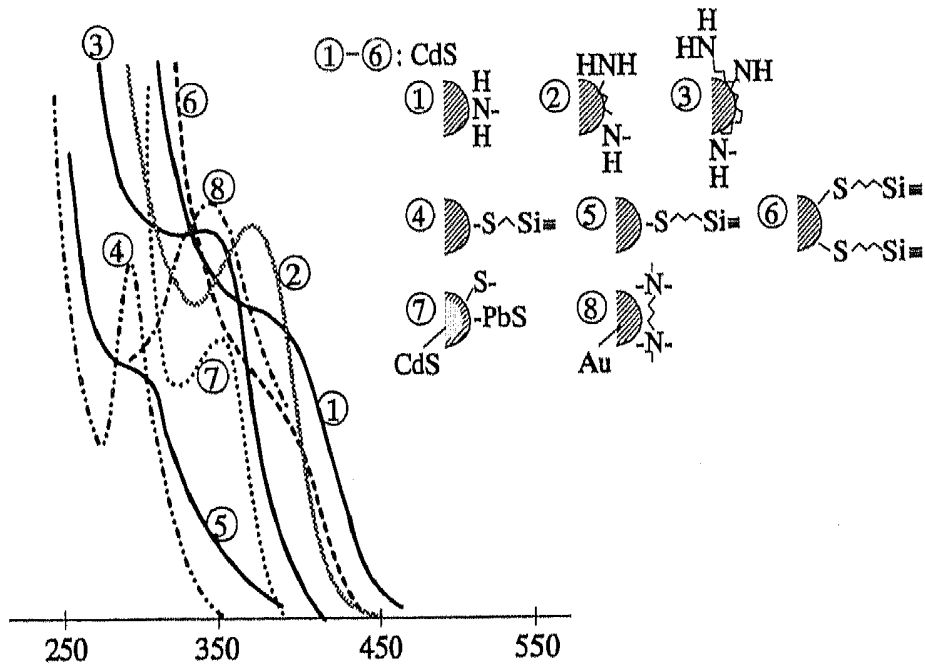


Fig. 4: Optical spectra of SQD and metal colloids; no difference in the optical spectra between solutions and solid composites can be detected.

5. FILM PROCESSING

As shown above, the control of surface chemistry of colloids leads to a variety of interesting processing properties. These principles can also be used for SiO₂ film processing combined with additives. Reacting of SiO₂ colloids with methyl group containing silanes leads to sols to be used for a one-step dip coating process for thicker layers¹⁷. The system does not show any cracking up to cured film thicknesses of 8 μm. ZrO₂ or TiO₂ can be incorporated into these systems in order to vary the index of refraction. Optical losses measured in planar waveguides (cured at 500 °C) show losses of less than 1 dB/cm. In fig. 5, the schematics of the particle coating is shown. It is believed that the reduced particle interaction (due to the CH₃ groups) leads to an increased relaxation during drying and, as a consequence, cracks can be avoided. The CH₃ groups are burnt out between 400 and 500 °C. SiO₂ layers after 500 °C do not show any detectable porosity.

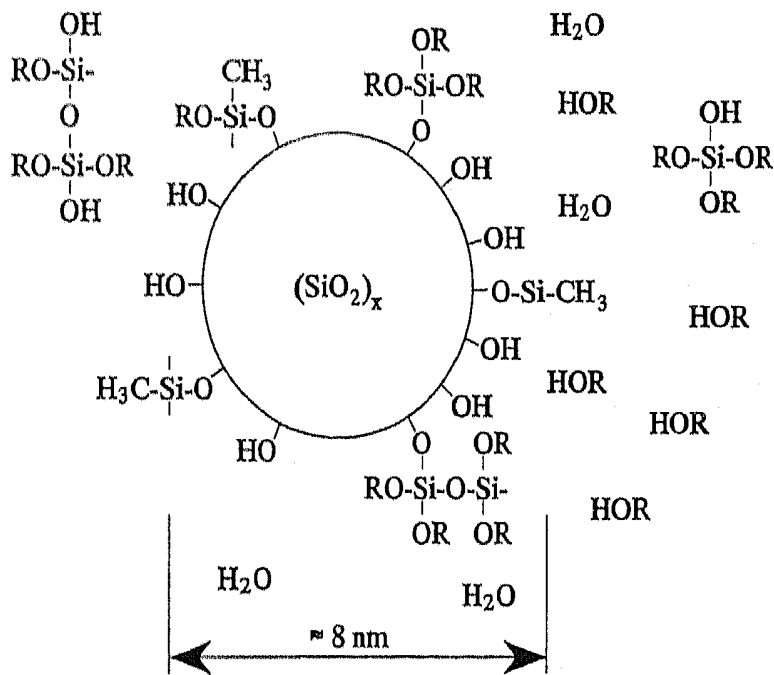


Fig. 5: Model of CH₃ modified SiO₂ colloids.

6. CONCLUSION

The principle of colloid stabilization by functional or multifunctional ligands can be used for the preparation of nanocomposites with tailored properties with respect to processing of final material properties. Thus, it is possible to keep the colloid size on a nano level, suitable for optical applications. The principle can be used for a variety of compositions, e. g. SQDs, metal colloids or oxidic particles.

7. REFERENCES

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