

Modification of Glass Surfaces by Multifunctional Chemical Coatings

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1. Introduction

Glass is a very important material for a variety of reasons [1]. It is characterized by a high transparency in the visible range, which is caused by phase dimensions far below the Rayleigh scattering limit. Beside decorative applications, the main function of glass was the hermetic separation of two spaces, for example, in architectural glazing, in-door and out-door, in containers to keep the content hermetically separated from the environment. Another important field were optical glasses to be used in optical instruments and components. More recently, ultra-pure glasses based on SiO_2 have been developed for low-loss long-distance transmissions in the area of information technologies.

In connection with the demands for special functions (e.g. reflective or antireflective), coatings on glass have gained more and more importance. For this reason, passive coatings have been developed to provide more or less selective transmission or reflection. This has become important for optical systems, optical filters as well as for architectural glazings in order to decrease or enhance energy transmission in a desired way. In the future, this will become of more and more importance for automotive glazing, too. With a few exceptions, these coatings are deposited on glasses by gas phase techniques (magnetron sputtering, PVD, CVD).

Wet chemical processes are only employed to some extent on plate glass (e.g. Schott, Calorex[®], Amiran[®]), optical filters, mirrors or reflectors in lamps. In the field of passive optical coatings, there is a sort of competition between gas phase deposition and wet techniques. Due to the more advanced developments in gas phase techniques, at present they are superior to those based on chemical techniques. On the other hand, the potential of chemical material synthesis for coatings on glass is only at its infancy and not yet exploited so far.

One of the most interesting aspects of the chemical synthesis is its potential to produce highly sophisticated chemical structures in order to provide multifunctional or smart properties and to transport these structures onto the glass surface without destroying them. Especially inorganic chemistry in connection with the sol-gel process is a very interesting means to realize this goal. In addition to this, the sol-gel process allows the incorporation of organics or the growth of nano-scale particles within these composites, leading to highly transparent, multifunctional or smart systems. For this reason, different synthesis routes have been developed and a variety of possibilities are existing [2 - 4]. The objective of this paper is to summarize recent developments for the synthesis and application of sol-gel-derived coatings on glass and to point out their usefulness for new glass applications.

2. Principles for Chemical Synthesis

The sol-gel process describes a method using molecular or colloidal inorganic precursors in solution to build up inorganic networks [5]. Additionally, these networks can be modified by organic components due to the low reaction temperatures to be used. Fig. 1 shows the principles of the gel formation. Depending on

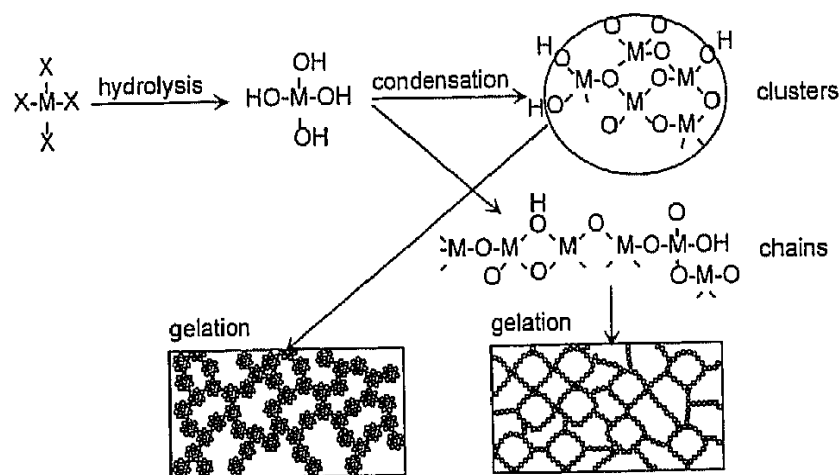


Fig. 1: Schematics of the formation of gel structures.

the reaction conditions and precursors, different gel structures can be obtained, which corresponds to a more

colloidal type of gel or polymer type structures of gel [6]. It is of importance to realize that the basic difference between sol formation and precipitation is only the result of small particles stabilization. Whilst in precipitation processes the growth of particles, for example by a crystallization process, is not hindered, in sol-gel processes, due to the presence of ions adsorbed on the particle surface, an electric charge is built up which then prevents further growth and agglomeration. In this

case, so-called electrostatically stabilized sols are formed to be gelled by shifting the surface charge to zero (point-of-zero charge). This can be realized by solvent evaporation or pH change. Electric charge stabilization in sols which, in general, have particle sizes in the lower nano range, only allows low solid contents, which is due to the range of the electric repulsion forces. In the gelation step, an aggregation takes place with an irregular arrangement of the gel particles causing low "green densities" of the gel, as indicated in fig. 1. This is one of the major processing obstacles in sols, restricting the applications mainly to their films. Bulk processing requires complicated and long-term processes [6, 7].

There are several possibilities to overcome these problems. One of the routes is to reduce the particle-to-particle interaction by using small organic molecules bonded to the surface of the colloidal particles instead of electric charges. Small molecules have to be used in this case since organic polymers used as additives in the ceramic processing, would lead to an intolerable volume fraction of organic materials in these systems. For this reason, tailored chemical bonds have to be developed for the surface modification. In this case, one can expect a higher package density of the colloidal systems, resulting in higher coating thicknesses or even bulk materials. The concept is shown in fig. 2. Another concept is to reduce the network

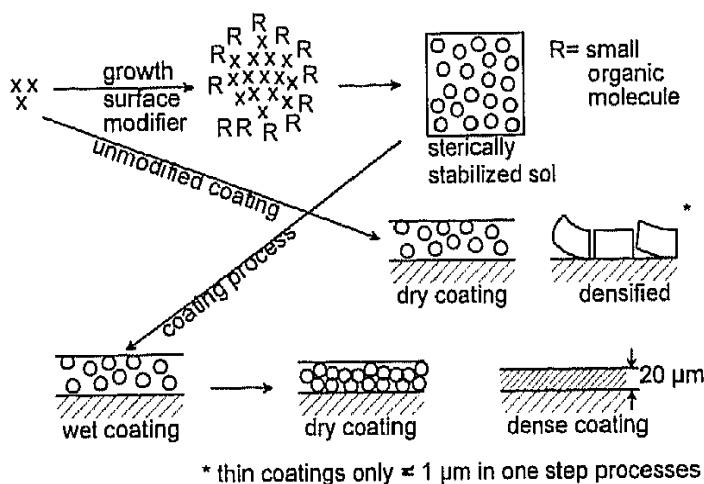


Fig. 2: Concept of the controlled sol-gel processing to higher packing densities for thick films by surface-modified colloids [after 8].

connectivity by substituting metal oxygen bonds by organic groupings not able to undergo a condensation reaction. This principle has been used for introducing new functions into sol-gel materials and to generate inorganic-organic hybrid materials as well as for obtaining high solid content systems, as shown in fig. 2 [9 - 11]. The combination of the colloidal route with the organically modified route leads to a new type of material, the so-called nanocomposites. These nanocomposite materials are of interest since

inorganic solid-state properties can be introduced into the materials which, at the same time, can stay highly transparent if the particle size is below the Rayleigh scattering limit. Rayleigh scattering depends strongly on the particle size (by the power of 3) and the difference of the refractive index between the matrix and the particle. Roughly spoken, if the particle size diameter is below about 1/20 of the wavelength to be used, the Rayleigh scattering can be neglected in many cases. In principle a variety of materials like metals, semiconductors, glasses and ceramics can be used to be introduced into these matrices, creating interesting functions [12]. Due to the high transparency of these systems, they are interesting candidates as coatings on glasses. The synthesis of this material is based on sol-gel chemistry, colloidal chemistry, organic and polymerization chemistry. In fig. 3 the general synthesis principle is given, showing the variability of the route. The colloids

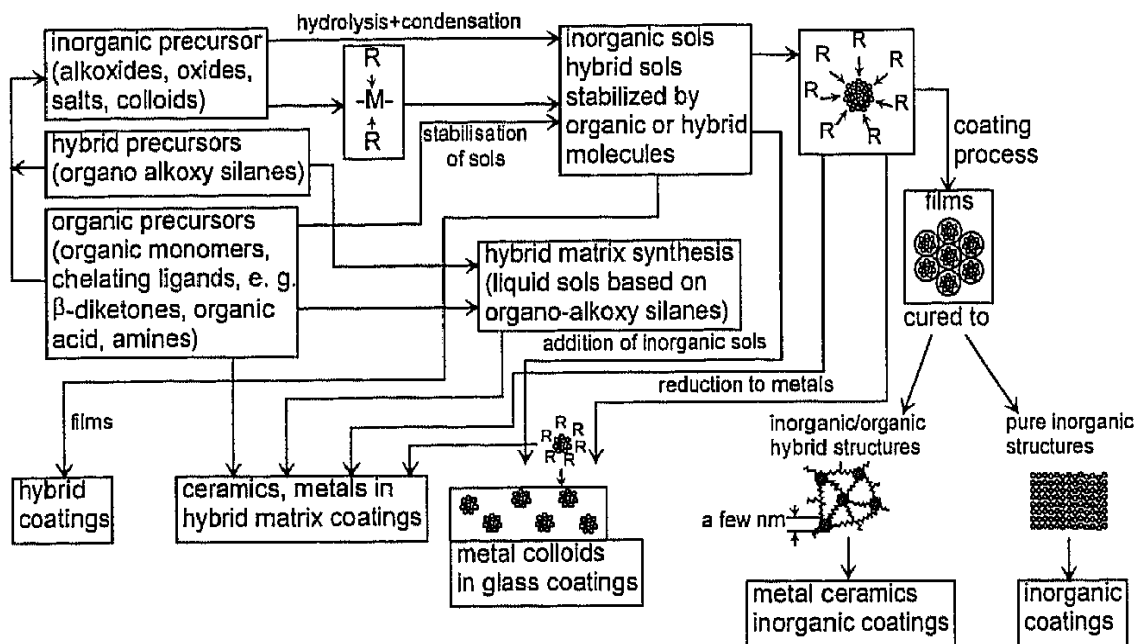


Fig. 3: General synthesis routes for the preparation of inorganic-organic nano-composites.

can be prepared within the reaction mixture or outside of the matrix system and added to this system later. The colloids have been prepared by the use of well-known sol-gel routes in the case of oxides [5] e.g. for zirconia, alumina, titania or silica from alkoxides, stabilized by various surface modifiers like β -diketones, organic acids or ether alcohols [13 - 15]. For semiconductors like cadmium sulfide or metals, especially noble metals or copper, precipitation or reduction mechanisms in solution have been developed using amines as complex formers and stabilizers

[16, 17]. Ligand stabilization during reduction leads to a perfect avoiding of agglomeration. If amino silanes are used, the silanes can be further reacted to fix the colloid into a sol-gel matrix. In the following, some examples for material development using this approach will be shown.

3. Material Development

3.1 SiO₂-Based Coatings

3.1.1 Micropatternable SiO₂ Films

SiO₂ films based on sol-gel techniques are one of the best investigated areas in sol-gel chemistry [5]. This is due to the fact that hydrolysis and condensation of tetraethyl orthosilicate can be tailored in a wide range, and investigations can be carried out rather easily. As a result one can say that it seems to be very easy to make thin films by SiO₂, but as soon as one wants to obtain thicker coatings, the poor relaxation behavior and a relatively low solid content prevent the formation of thicker films. Thus, for example, for obtaining 10 μm thick coatings, 30 or more dip coating steps would be necessary with intermediate drying and firing. As shown elsewhere [8], it is possible to prepare sol-gel precursors having silica contents above 50 wt.-% based on colloidal silica, commercially available from Bayer company or Nissan company as starting materials. This can be obtained by reacting the sols with methyl trimethoxy silane, which leads to a partially deactivation of the surface hydrolysis through a condensation process with methyl groups. The modified sols can be applied as coatings up to 30 μm in thickness. The resulting films can be pregrooved due to their softness, showing high aspect ratios (fig. 4). As shown elsewhere [8], films made by these systems can be densified to almost fully dense SiO₂ with indices of refraction close to 1.46 and temperatures between 500 and 700 °C. This is far away from the T_g of SiO₂, pointing out that viscous flow cannot be taken into consideration as a sintering mechanism. Due to the lack of viscous flow, the pregrooved patterns remain unchanged during the densification step. In fig. 4 the pattern obtained by embossing is shown before and after firing.

As one can see, the shape of the patterns did not change. It is of special interest that the sharp edges still are present after densification. With this system, it is possible to generate purely inorganic micropatterns for a variety of purposes (e.g. microlens arrays, gratings).

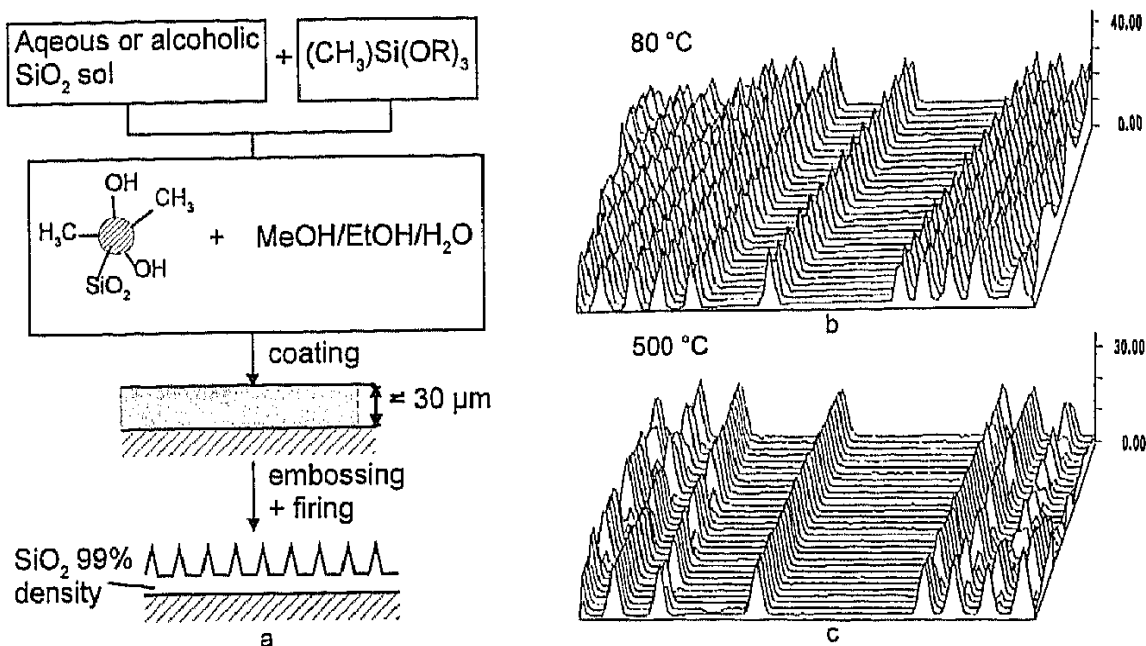


Fig. 4: Reaction scheme for SiO_2 thick film fabrication (a) and profilometer plot of an unfired (b) and a fired profile (c); ordinate scale: μm .

3.1.2 Effect on Thermal Stability of SiO_2 Coatings on Glass Fibers

Another important property of this system is its very high softening point, which is due to the composition (pure SiO_2). If glass fibers are coated with the system, their temperature stability can be increased substantially. For example, it is possible to increase the long-term temperature stability of glass fiber fabrics from $500 - 600^\circ\text{C}$ to 1050°C . In fig. 5, strips of glass rovings are heat treated by a gas burner. As one can see, the uncoated strip melts away within seconds. Further experiments have

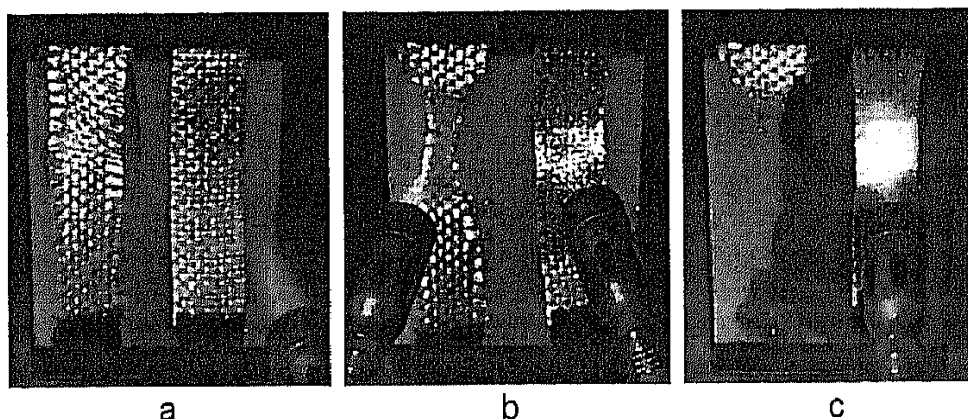


Fig. 5: Effect of a nano sol coating on glass fiber fabrics; (a) coated (left) and uncoated (right) fabric, not temperature-treated; (b) uncoated and coated fabric during heating; (c) after 2 minutes heating.

shown that it is also possible by simple dip coating to improve the temperature stability of parts made from glass fibers substantially.

3.1.3 Metal Colloids in SiO₂ Organically Modified Coatings

If this type of matrix system is modified by an epoxy functional silane (for example, glycidyoxypropyl trimethoxy silane), it can easily be mixed with metal amino complexes if the amines have additional alkoxy silane groupings (γ -aminopropyl triethoxy silane). Hydrolysis and condensation of this type of systems then lead to transparent films, too. Platinum, palladium, gold and copper have already been used [16, 18 - 19]. The results of these investigations show that the reduction of the metal complexes to metals can take place at rather low temperatures (between 150 and 300 °C). At these temperatures a thermal reduction takes place, followed by a nucleation and diffusion process of the reduced species to form metal colloids. As shown in [16, 18 - 19], the reduction and colloidal growth process can be influenced strongly by the type of ligands used for stabilization of the metal precursor. Using these techniques, inorganic-organic composite coatings with thicknesses of 100 nm up to 20 μm can be fabricated on glass and turned into inorganic-organic composite systems by thermal treatment with desired colours (e.g. yellow for silver, red to blue for gold, green for copper and brown to black for palladium). Due to the high coefficient of extinctions (up to 10^{-5}), even with very thin coatings very intensive colours can be obtained. For example, with palladium, coatings with thicknesses of 200 μm can be obtained with optical densities up to 3. Thin coatings also can be fired to pure inorganic coatings maintaining their optical properties. Thus, it is possible to obtain tinted silicate glasses in a very simple way. Of course, all of these systems can be micropatterned or, if organic with polymerizable ligands are incorporated and used in photolithographic processes for obtaining microstructures.

3.1.4 Low Surface Free Energy Coatings

Furthermore, the previously described systems can be used for introducing other functions. If in systems based on SiO₂ colloids alkoxy silanes with perfluorinated side chains are introduced and specific synthesis processes are used, as shown in fig. 6, homogeneous liquid sols can be obtained suitable for coating techniques.

These systems do not show any loss of adhesion if the perfluorinated silane content does not exceed 2 - 3 mole-%. With higher contents, the adhesion is decreasing. However, even with perfluorinated silane contents of about 1.2 to 2 %, the

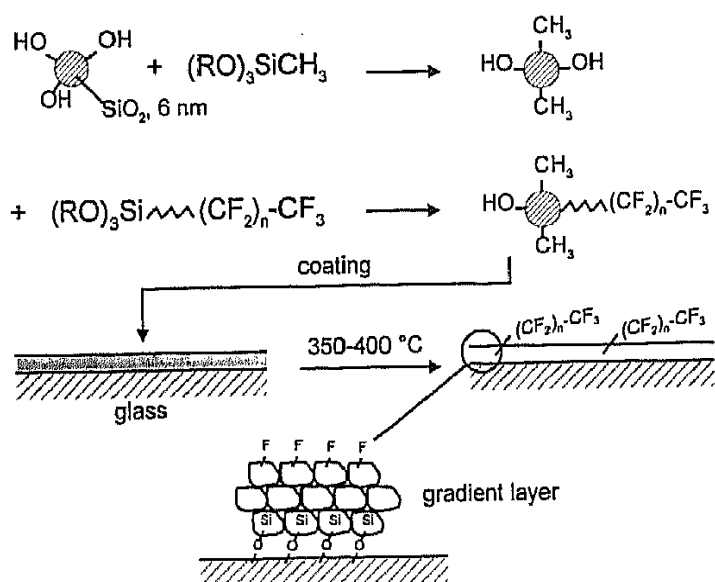


Fig. 6: Principles of the formation of high temperature fluorinated coatings on glass [after 20].

contact angle against water and against oleophilic solvents is at its maximum. The calculated number for the surface free energy is around 18 mJ/m², which is below the value of polytetrafluorethylene (20 mJ/m²).

This is due to a self-aligning effect driven by the interface and surface thermodynamics (fig. 6). These systems can be used for coating glass surfaces and fired at temperatures between 350 and 400 °C. After firing the surface of the coatings is glass-like with hardness and abrasion resistance very close to that of glass. The low surface free energy value is still present, leading to anti-soiling behavior of the glass surface.

Summarizing, it is to say that the use of specific colloidal techniques based on tailored surface chemistry to control the particle-to-particle interaction leads to a variety of coatings on glass including micropatterning techniques, increase of temperature resistance, special optical or chemical and physical properties.

3.2 Multifunctional and Intelligent Coatings

Semiconducting or proton-conducting coatings on glass have been of interest for a long time, and as shown by [21], tungsten oxide films can be prepared from aqueous sols. Tungsten oxide films are of interest due to their reducibility to form very intensively coloured bronzes, as basic investigations have shown [21, 22]. This process is reversible and can be induced by the migration of protons and cations into the tungsten oxide film as far as this film has sufficient porosity.

However, in order to obtain photochromic behavior on glasses, a complete redox system has to be developed, consisting of a transparent electrode on the glass surface. In this case, thin indium oxide layers commercially available can be used. The basic principle of this system is shown in fig. 7. On both sides of the two glass

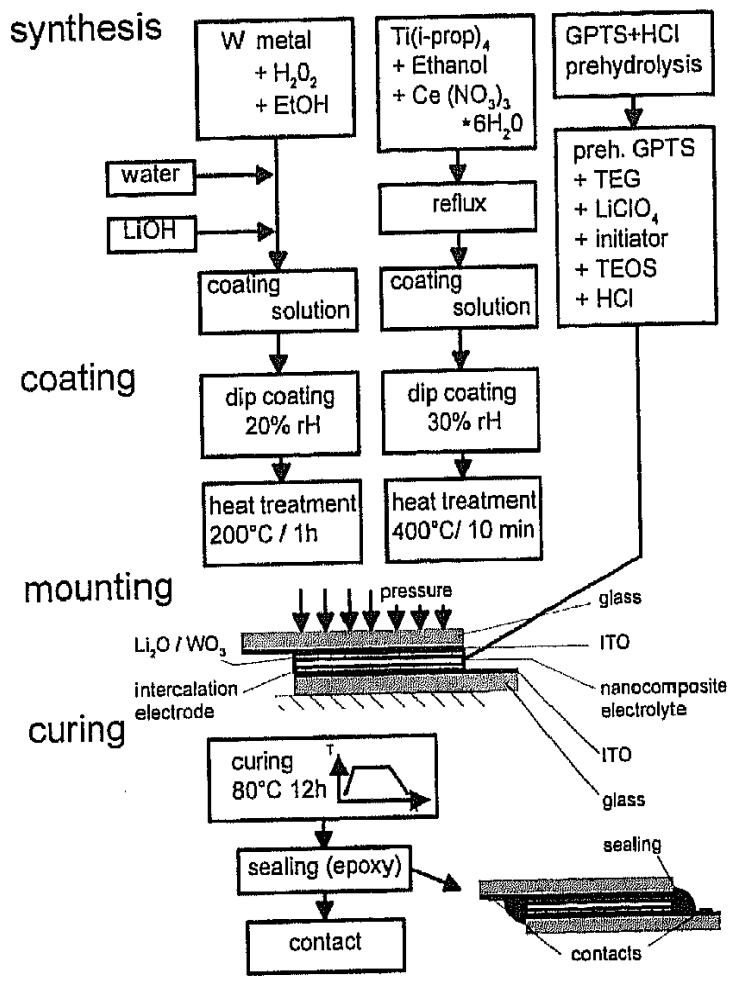


Fig. 7: Flow diagram of the fabrication of an electrochromic system.

substrates covered with conductive transparent electrodes, two redox electrodes have been deposited [22], WO_3 as photochromic and CeO_2/TiO_2 as intercalation electrode. As shown elsewhere [23], it was possible to develop an electrolyte system based on an SiO_2 ormoecer nanocomposite, which is able to provide ionic conductivities in the range of 10^{-4} to 10^{-6} Siemens. The tungsten electrode was improved substantially using alkali

ion-containing WO_3 (e.g. lithium tungstenate). In this process, sols of lithium tungstenate have been developed [24], which allow to stabilize the electrochromic layer thermally at temperatures up to $220\text{ }^\circ\text{C}$ without losing reactivity. Based on these investigations, electrochromic devices had been developed showing no fatigue after 100,000 cycles. The performance is shown in fig. 8. With exception of the transparent ITO-electrodes, the whole system is based on sol-gel materials. The switching time is about 5 seconds for bleaching and 10 seconds for darkening.

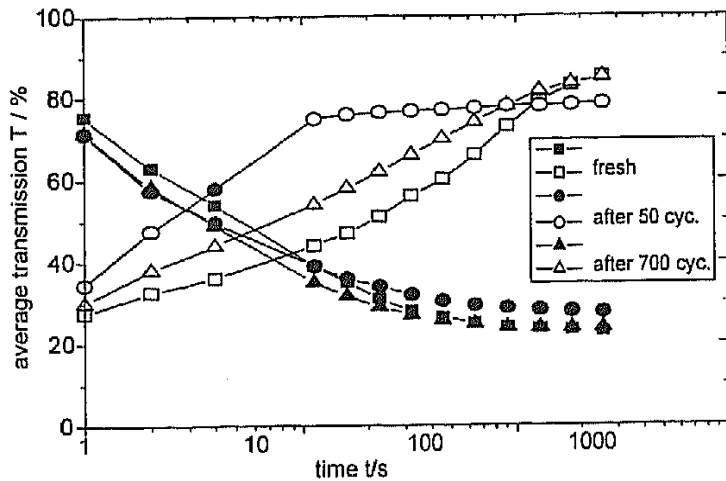


Fig. 8: Darkening and bleaching of sol-gel-derived new electrochromic systems (350 - 700 nm).

Another example for an intelligent behavior has been developed on the basis of a controlled release system for providing permanent wettability on glass surfaces. As it is

well known, the hydrophilic nature of glass surfaces disappears rather fast under atmospheric conditions due to the adsorption of all kinds of contaminants. For this behavior, the SiOH groups on the glass surface are responsible [25]. As shown in [26], it is possible to synthesize inorganic-organic sol-gel materials based on an SiO₂/TiO₂ backbone the hydrophilic groupings of which are glycol groupings bonded to the silicon atom. These materials show contact angles in the range of 15 - 20° against water, however, they are rather hydrophilic. However, the hydrophilic properties also in this case can be decreased by the deposition of contaminants.

In order to overcome these problems in this type of materials, a controlled release system has been developed where specific tensides are incorporated into the films. The details of the development have been described elsewhere [27]. The schematics of the mechanism is given in fig. 9. The effectiveness of the detergents can be

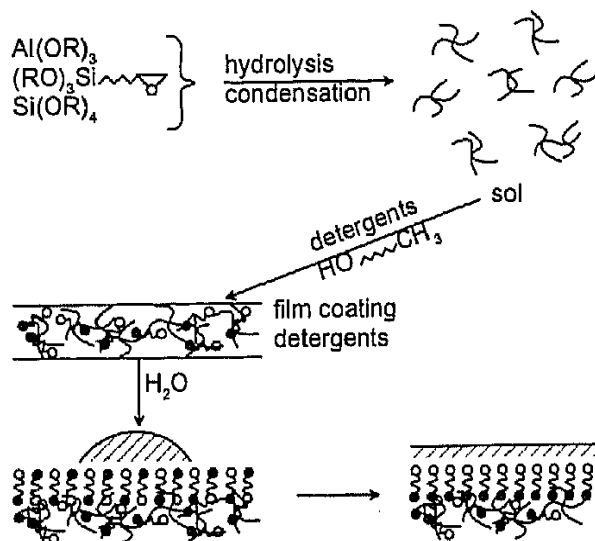


Fig. 9: Principles of the effect of detergents incorporated into an inorganic-organic composite matrix [after 27].

tailored by the intrinsic hydrophilicity or hydrophobicity of the matrix. This can be obtained by controlled ring opening reaction of the epoxide, whereas the unopened epoxide was polymerized by methyl imidazol as catalyst to a polyethylene oxide

chain. With this system, contact angles of 0° can be obtained (complete spreading of water).

4. Conclusion

The few examples show that by chemical synthesis a variety of coatings for multifunctional glass surfaces can be developed. For practical use, appropriate coating techniques have to be developed, too. The whole field, however, is at its infancy.

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