

1. PREPARATION OF THIN FILMS VIA SO-GEL PROCESS

SPECIAL TOPICS IN NANOTECHNOLOGY SCIENCE

MASARYK UNIVERSITY

Ing. Mgr. Barbora Holubová, Ph.D.

barbora.holubova@tul.cz

Institute for Nanomaterial, Advanced Technologies and Innovation

Technical University of Liberec

2. ORIGINS AND IMPACT

The origin of sol-gel chemistry was the observation in the 19th century that an alkoxide prepared from SiCl_4 started to form a gel when exposed to air. This was later found to be driven by atmospheric moisture causing first hydrolysis of the silicon alkoxide and then condensation. These processes have since been widely studied and can be carefully tuned, for example through acid or base catalysis, to form gels with very different structures.

Initially, the sol-gel process referred to hydrolysis and condensation processes. The term 'sol-gel' is now used for a diverse range of chemistries. The synthesis of solid materials such as metal oxides from solution-state precursors. These can include metal alkoxides that crosslink to form metal-oxane gels, but also metal ion-chelate complexes or organic polymer gels containing metal species.

Today, the potential sol-gel process is reflected by the fact that many of its products are entering a variety of markets.

Mater. Horiz., 2016, 3, 91–112
Chem. Soc. Rev., 2011, 40, 696–753

3. ORIGINS AND IMPACT

Sol-gel dip coatings are mentioned in the patent literature for the first time in 1939, and many reports of single oxide coatings followed, till the sixties. Around 1970 the sol-gel synthesis of defined multicomponent oxides was reported and from this point on there followed an avalanche of publications.

First commercial products from Schott company on the market in 1953:

- TiO_2 coatings (containing Pd) for sun-shielding (cermet),
- $-\text{SiO}_2/\text{TiO}_2\text{-TiO}_2\text{-SiO}_2$ triple antireflecting coating,
- $\text{TiO}_2\text{-SiO}_2\text{-TiO}_2$ triple for rear-view mirrors.

DISLICH, H., P.HINZ.. *J of Non-Crystalline Solids*. 1982, 48(1), 11-16
BRINKER, C. J.y, G W. SCHERER. Boston: Academic Press, c1990. ISBN 9780121349707



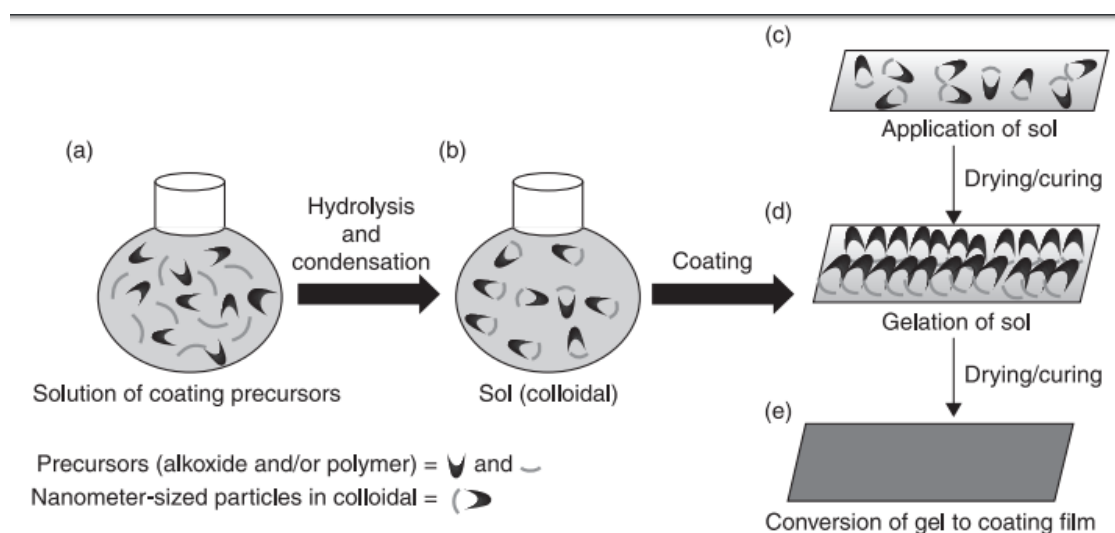
4. PRINCIPLES of sol-gel processing

5. PRINCIPLES of sol-gel processing

During the sol-gel processing, a "sol" (a colloidal solution) gradually transforms towards a "gel" system containing both a liquid phase and solid phase with morphologies ranging from discrete particles to continuous polymer networks. It is driven by a row of hydrolysis and condensation reactions till the resulting network is fully condensed (interlinked).

Aside from precursor preparation, the sol-gel process can be summarized in the following key steps:

- (i) Synthesis of the 'sol' from hydrolysis and partial condensation of alkoxides.
- (ii) Formation of the gel via polycondensation to form metal-oxo-metal or metal-hydroxy-metal bonds.
- (iii) Syneresis or 'aging' where condensation continues within the gel network, often shrinking it and resulting in expulsion of solvent.
- (iv) Drying the gel either to form a dense 'xerogel' via collapse of the porous network or an aerogel for example through supercritical drying.
- (v) Removal of surface M-OH groups through calcination at high temperature up to 800 °C (if required).



12.2 Various stages of sol-gel coating preparation and application to substrate: preparation of solution of coating precursors (a), formation of sol through hydrolysis of precursors followed by progressive condensation reactions (b), application of sol on the metal substrate (c), gelation of sol on substrate which results in the formation of a three-dimensional network throughout the liquid medium (d) and conversion of gel into solid coating film after drying/curing (e).

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Corrosion Protection and Control Using Nanomaterials, 2012, 304-329

6. PRINCIPLES of sol-gel processing

The sol can be either deposited on a substrate to form a film (e.g., by dip-coating or spin coating), cast into a suitable container with the desired shape to obtain monolithic ceramics, glasses, fibers, membranes, aerogels, or used to synthesize powders. The stadium of gel is then necessary to obtain either powders (through conventional drying process) or monoliths (typically though “supercritical” drying).

The rheology of the colloidal hybrid dispersions can be easily adjusted, hybrid materials can be processed through many methodologies used for organic polymers among them: film deposition methods, fiber extrusion, fiber pulling, electrospinning, electrochemical deposition, (soft)lithography based techniques (dip-pen, X-Ray. . .), TPA, aerosol or spray, ink-jet printing.

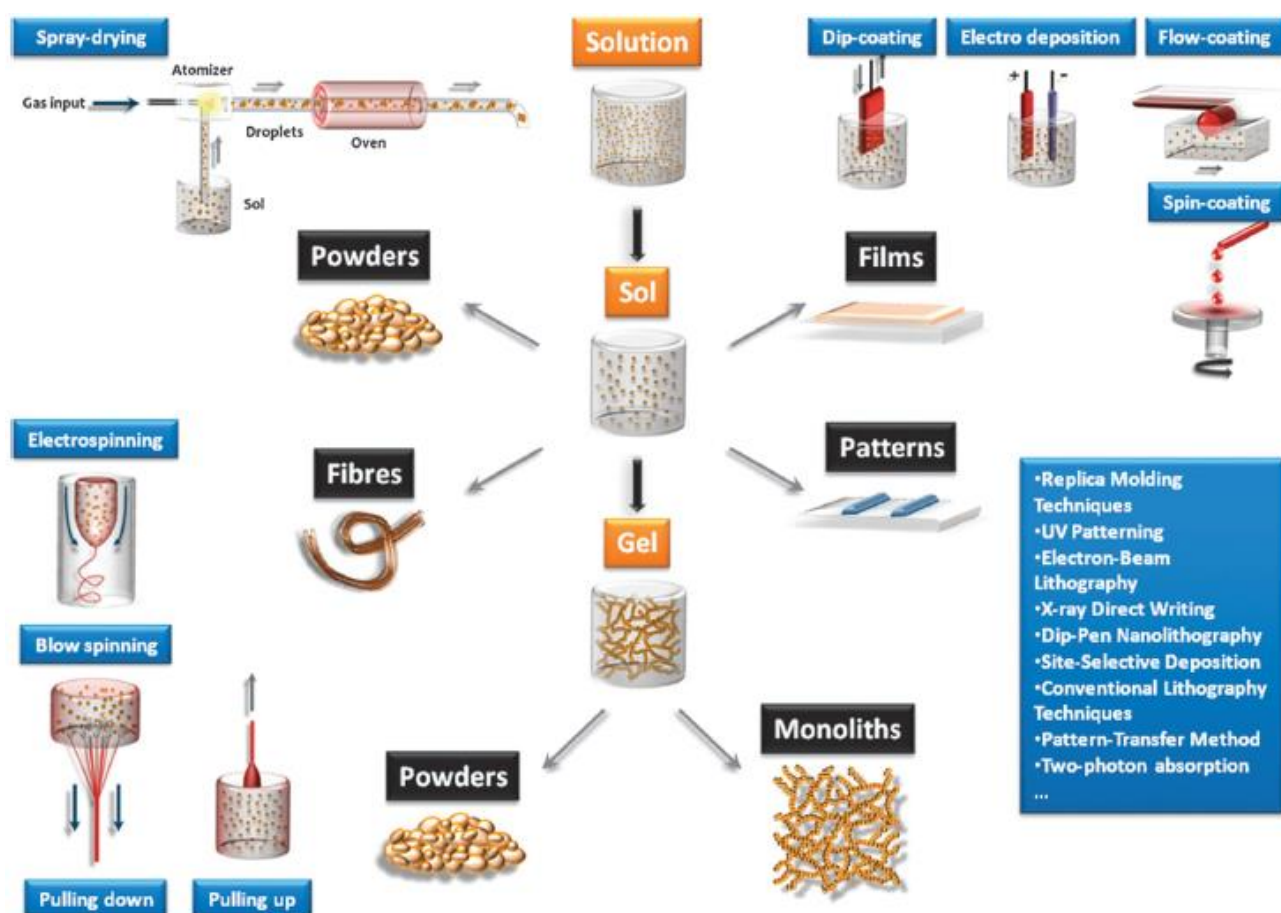


Fig. 4 Processing routes to materials using sol-gel methods.

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Chem. Soc. Rev., 2011, 40, 696–753

7. PRINCIPLES of sol-gel processing – PRECURSORS

Sol-gel chemistry originated with the hydrolysis and condensation of metal alkoxides, although it can also occur between hydrated metal species. Most of the examples of alkoxide-based sol-gel chemistry involves early transition group metals (e.g. Ti, Zr) or early p-block elements (e.g. Al, Si), however there are many

other examples of elemental alkoxides. Metal alkoxides can be prepared in a number of ways depending on the nature of the metal. As with the original synthesis, metal chlorides can be reacted with alcohols. Highly reducing metals, i.e. alkali metals and lanthanides, can react directly with alcohols to produce the corresponding alkoxide and hydrogen.

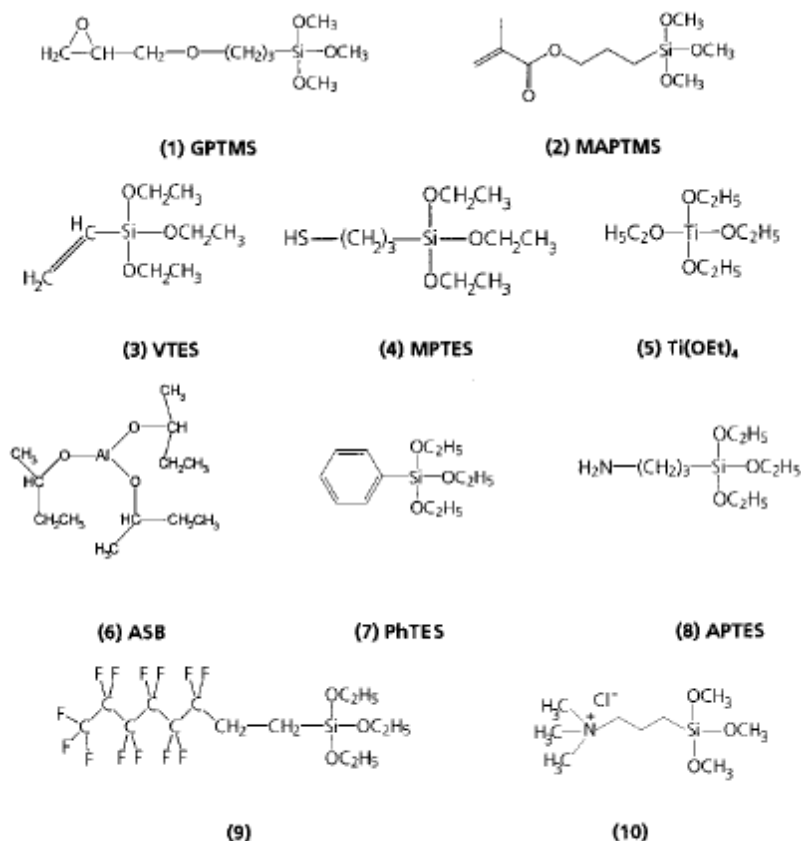


Figure 2. Organo(alkoxy)silanes and metal alkoxides serving as precursors for sol–gel-derived (hybrid) materials.

Mater. Horiz., 2016, 3, 91–112
 Chem. Mater., Vol. 13, No. 10, 2001

8. PRINCIPLES of sol-gel processing – CHEMICAL MECHANISM

The key to mastering sol–gel chemistry of alkoxides requires understanding of the central hydrolysis and condensation reactions. These are strongly affected by process parameters such as the nature of the R-group (e.g. inductive effects), the ratio of water to alkoxide and the presence and concentration of catalysts.

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9. PRINCIPLES of sol-gel processing – CHEMICAL MECHANISM

Hydrolysis results in the replacement of an alkoxy group with a hydroxyl with a pentacoordinate transition state in both the acid (Scheme 1) and base (Scheme 2) catalysed systems. Depending on the conditions and the Si/H₂O ratio, more than one alkoxy group may be hydrolysed (eqn (1)). The rate of each hydrolysis step depends on the stability of the transition state which in turn depends on the relative electron withdrawing

or donating power of $-OH$ versus $-OR$ groups. **The result is that successive hydrolysis steps get progressively slower under acidic conditions and faster under basic conditions.**

Condensation follows a similar pattern, being catalysed by either acid (Scheme 3) or base (Scheme 4) and resulting in the formation of siloxane bonds (or metaloxane bonds for other metals). The progression of condensation depends on the degree of hydrolysis that has already occurred as a silanol group is required on at least one silicon centre. If hydrolysis is complete before the first condensation step occurs, the resulting product $(OH)_3Si-O-Si(OH)_3$ has 6 sites for subsequent condensation steps. **This is observed in basic conditions, where hydrolysis steps get progressively faster.**

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10. INFLUENCE of key parameters – CATALYSIS

Under the basic conditions, multiple condensation steps result in small, highly branched agglomerates in the 'sol' which eventually crosslink to form a colloidal gel. This is beneficial primarily for the preparation of powders.

In acidic conditions, where the first hydrolysis step is typically the fastest, condensation begins before hydrolysis is complete. Condensation often occurs on terminal silanols, resulting in chain like structures in the sol and network-like gels. This is beneficial primarily for the preparation of fibres and coatings.

The condensation reaction is followed by an inorganic polymerization process with SiO_2 nanoparticles formation. This process is strongly pH dependent. Thus, acidic conditions lead to dense microporous (pore size < 2 nm) networks and in alkaline conditions mesoporous (2 nm $<$ pore size < 50 nm) gels are obtained.

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Bulletin of the Transilvania University of Braşov, Series I, Vol. 4 (53) No. 1 - 2011

11. Influence of key parameters – CATALYST

Hydrolysis is most rapid and complete when catalysts are employed. Although mineral acids or ammonia are most generally used in sol-gel processing, other known catalysts are acetic acid, KOH, amines, KF, HF, titanium alkoxides, and vanadium alkoxides and oxides. Many authors report that mineral acids are more effective catalysts than equivalent amounts of base. By varying the catalyst, numerous effects on gelation time, porosity, density, and volume shrinkage on drying process can be obtained.

Also, the use of the catalyst can favour either the hydrolysis or the condensation. The rate of silicon alkoxides hydrolysis exhibits a minimum at $pH = 7$ and increases exponentially at both lower and higher pH . That is in contrast with the rate of condensation, which exhibits a minimum at $pH = 2$ and a maximum around $pH = 7$. Under acidic conditions, the condensation of TEOS, with $R = 4$, was minimized at $pH = 2$ and maximized at intermediate pH values for various types of acid.

SCHUBERT, U., N. HÜSING. Weinheim: Wiley-VCH, c2012

Journal of Non-Crystalline Solids 100 (1988) 31-50

Bulletin of the Transilvania University of Braşov, Series I, Vol. 4 (53) No. 1 - 2011



12. INFLUNCE of key parameters – WATER : SILANE MOLAR RATIO

Water itself is important and alkoxide : water ratio can be tuned to limit hydrolysis. The quantity of water in the sol-gel solution strongly influences the hydrolysis and condensation kinetics. At fixed silane concentration, an increase in water content leads to a corresponding increase in hydrolysis and condensation rate.

For obtaining SiO₂ films, R = 2 is insufficient for complete hydrolysis and higher R-values are required. Under low R-value, a matrix with a more open structure is produced due to incomplete hydrolysis and, consequently, less cross linking in the sol-gel material.

E.g.: For TEOS thin coatings, there is a very large ratio interval - when other conditions are modified, layers are formed at R = 1 – 25 (i.e., hydrolysis reactions run sufficiently with sufficient polycondensation).

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13. INFLUENCE of key parameters – STERIC AND INDUCTIVE EFFECT OF SILANE PRECURSORS

Many different silicon alkoxides exist and the inductive and steric effects of the R group can impact on hydrolysis rates.

Higher alkyls networks such as Si(OHex)₄ leads on un-reacted or not completely reacted monomers which remain in the system and evaporate during drying and heating. Branching and increasing of the chain length of precursor substituent decreases the hydrolysis rate.

The consistent acceleration and retardation of hydrolysis with increasing x under acidic and basic conditions, respectively, suggests that the hydrolysis mechanism is subject to inductive effects and (based on the consistent trends) is apparently unaffected by the extent of alkyl substitution. Because increased stability of the transition state will increase the reaction rate, the inductive effects are evidence for positively and negatively charged transition states or intermediate under acidic and basic conditions, respectively. This line of reasoning leads to the hypothesis that under acidic conditions, the hydrolysis rate decreases with each subsequent hydrolysis step, whereas under basic conditions, the increased electron withdrawing capabilities of OH (and OSi) compared to OR may establish a condition in which each subsequent hydrolysis step occurs more quickly as hydrolysis and condensation proceed.

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14. INFLUENCE of key parameters – SOLVENT

Two important characteristics of solvents are:

- (1) polarity, which largely determines the solvating ability for polar or non-polar species,
- (2) the availability of labile protons: This determines whether anions or cations are solvated more strongly and whether or not the solvent can participate in dissociative reactions such as alcoholysis of hydrolysis.



Because hydrolysis is both hydroxyl and hydronium ion catalyzed, solvent molecules which hydrogen bond to hydroxyl ions or hydronium ions reduce the catalytic activity under basic and acidic conditions, respectively. Therefore, aprotic solvents, which do not hydrogen bond to hydroxyl ions, have the effect of making hydroxyl ions more nucleophilic, whereas protic solvents make hydronium ions more electrophilic.

BRINKER, C. J.y, G W. SCHERER. Boston: Academic Press, c1990. ISBN 9780121349707

15. STRUCTURAL EVOLUTION

During the sol-gel process, the number of oligomeric/polymeric products increase and the products recombine. The viscosity increases until the system gels (the liquid is trapped in the gel and interconnected continuous network emerges).

The gel is a flexible medium - adjacent groups touch and condense, making the gel even more viscous. These movements displace the remaining liquid, which may result in collapse of gel network.

BRINKER, C. J.y, G W. SCHERER. Boston: Academic Press, c1990. ISBN 9780121349707

16. AGING AND DRYING

Another important feature of sol-gel processing is converting the solvent-filled gel into a dry solid. Simple evaporation of solvent from a silica gel is possible, but the movement of solvent through the gel subjects it to considerable capillary forces resulting in collapse of the network. This can be countered to some extent by aging the gel for a long time prior to drying but some densification is unavoidable due to expulsion of the sol from within the gel body (syneresis).

Heating at relatively high temperatures (100-500 °C) is carried out to accelerate this phase, removes the organic species and leads to formation of covalent Si-O-Si bonds. Many of these Si-O-Si bonds are not stable at temperature below 450 °C and typically, temperatures higher than 1000 °C are needed to achieve bonding energy close to bulk fracture energy.

The products of the uncontrolled drying (**called xerogels**) often have a high surface area due to the large number of small pores but without addition of structure-directing agents this porosity is generally disordered. If a larger pore volume is required, gels can be dried under supercritical conditions to produce **aerogels** with up to 98% air (or other gas) by volume.

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17. THIN FILMS via sol-gel process

18. THIN FILMS via sol-gel process

In terms of fibres and thin films from alkoxide precursors, the most important factor is tuning the water : alkoxide : solvent ratio and type of catalyst.

The resulting sol can then be variously deposited (spin/dip coated, back up rolled etc.) onto a surface to produce metal oxide thin films.

A consistent trend is apparent:

- 1) acid-catalyzed hydrolysis with low H_2O/Si ratios produces weakly branched "polymeric" networks, whereas
- 2) base-catalyzed hydrolysis with large H_2O/Si ratios produces highly branched "colloidal" particles.

FOR THIN FILMS: the first option is optimal!

Typical sol-gel strategy for thin films involves:

- Acid catalysis
- Low to large H_2O/Si ratios (as already stated $R = 1 - 25$)
- Greater volume of solvent
- Mild to high temperature aging depending on the organosilane content
- Dip coating

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19. THIN FILMS via sol-gel process - APPLICATIONS

Coatings are still by far the most widespread application of sol-gel chemistry since films and coatings development dates back several decades. The main reasons for this are dual.

First, the easiness and quickness to prepare a “product” starting from a solution, a sol or a gel is something very rewarding for the scientist. After the solution preparation from precursors using different hybrid routes, one has the ability to easily create a material leading to applications, to verify and to discover properties, just implementing various available deposition processes as described above, right away.

Second, cost also explains the numerous applications of sol-gel coatings. Indeed, thin film deposition, membrane casting, and coating encapsulation require a quite small amount of solution to protect, to decorate, and to confer new functional properties on a substrate, even a large-sized one. The required solution volume is small and liquid-deposition devices or machines are much cheaper than physical-based deposition methods (PVD, laser ablation, ALD. . .). Liquid-based techniques are therefore a very easy and economical way to process and produce multi-functional coatings exhibiting protective, decorative or smart properties.

Chem. Soc. Rev., 2011, 40, 696–753



20.-23. THIN FILMS via sol-gel process – BIOMATERIALS

The intimate mixing at a molecular or nanoscopic level of organic or biologic components (molecules, oligomers, polymers) with inorganic components need mild processing and chemical conditions (low temperatures, and pressure, adequate solvents). These conditions are found in bottom up approaches such as those associated with sol-gel chemistry.

Chem. Soc. Rev., 2011, 40, 696–753

Examples of interesting and recent research in sol-gel thin film coatings:

Protein array consisting of sol-gel bioactive platform for detection of *E. coli* O157:H7

W. Lee et al. / Biosensors and Bioelectronics 20 (2005) 2292–2299

In the current study, the protein array based on the sol-gel-derived surface was fabricated for detection of *E. coli* O157:H7. In order to immobilize the antibody on the solid surface, sol-gel-derived material was prepared and coated to slide glass based on dip-coating method. And then, antibody was immobilized to the porous surface of sol-gel-derived layer via physical adsorption. It is anticipated that the technique involving the preparation of sol-gel derived bioactive platform can be applied to the protein chip based detection such as diagnosis, biochemical research, and so on.

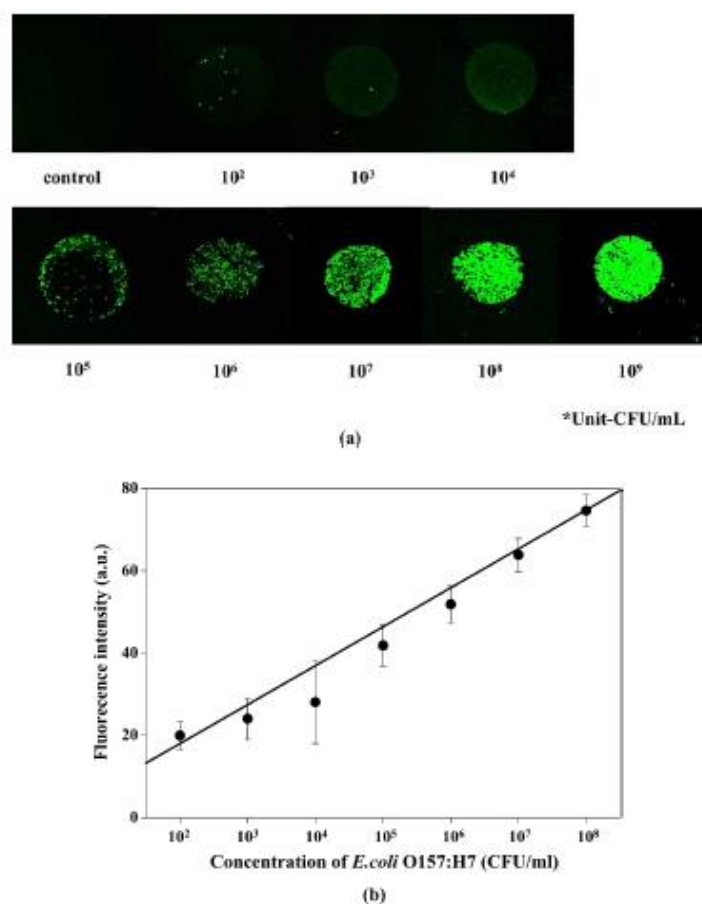


Fig. 6. Detection of *E. coli* O157:H7 by means of protein array fabricated on the sol-gel bioactive platform: (a) fluorescence micrographs of protein array which was arranged in the order of concentration, (b) change of fluorescence intensity with respect to *E. coli* O157:H7 concentration.

Fabrication and characterization of porous biomedical Vitallium alloy with 58S bioglass coating prepared by sol-gel method

Haftbaradaran-Esfahani, App Surf Sci, 506 (2020) 144959

Cobalt-based alloys are used as medical implants due to their excellent mechanical properties and suitable biocompatibility. However, its application in the body is restricted due to mechanical mismatch and bio neutrality. This study aimed to fabricate a porous Vitallium alloy and apply 58S bioglass coating on this substrate to improve its mechanical and bioactivity behavior.

24.-28. THIN FILMS via sol-gel process - PROTECTION

Sol-gel coatings providing significant improvements to existing products, as new or substitute articles, bringing extended functionalities to substrates, reducing production costs or increasing product lifetimes.

SMART coatings: antidust, antiscratch, self-cleaning, antireflective, anticorrosion, antifogging, antirain etc.

Chem. Soc. Rev., 2011, 40, 696–753

Adv. Funct. Mater. 2018, 1704158

Sol-gel based hybrid silane coatings for enhanced corrosion protection of copper in aqueous sodium chloride

J. Balaji et al. / Journal of Molecular Liquids 302 (2020) 112551

It is important to protect the Cu surface in corrosive NaCl/sea water environment due to its valuable use in many industries specifically power stations, cooling towers and shipbuilding.

Various concentrations of p-aminothiophenol doped 3-glycidoxypropyltrimethoxysilane based sol-gel matrices (PATP-GPTMS) are prepared through hydrolysis and condensation reactions.

All the results exposed that, the PATP-GPTMS/Cu coating enhanced the corrosion protection of Cu in aqueous 3.5% NaCl medium.

Preparation of hybrid nanocomposite coatings via sol-gel method for hydrophobic and self-cleaning properties

O. Kesmez / Journal of Molecular Structure 1205 (2020) 127572

Hybrid organic-inorganic, hydrophobic and photocatalytic nanocomposite coatings that include Ce doped TiO₂ nanoparticles (c-TiO₂ NPs) were developed with the sol-gel process.

Tetraethyl orthosilicate and 3-(glycidyloxypropyl)trimethoxysilane were used for hybrid polymer network.

Photocatalytic hybrid nanocomposite films are highly transparent and do not have color changes noticeable with the naked eye and that also exhibit oleophobic properties.

The long term protection of the 14th century “Last Judgment Mosaic” situated above the gates of the St Vitus cathedral in Prague castle.

The selected coating for treatment of the entire 13 m x 10 m mosaic is a multilayer system composed of a hybrid organic-inorganic functional layer made from organo alkoxysilanes and oxide nanoparticles, placed between the multicolored glass substrate and a fluoropolymer coating. This coating combination is a transparent efficient anti-corrosion barrier, much better than all tested organic polymers.

J. Mater. Chem., 2005, 15, 3559–3592



29.-31. THIN FILMS via sol-gel process - ENERGY

Energy applications for sol-gel derived materials are more recent than smart coating applications. Hybrids and composites today mainly address fuel cells, Li-batteries and photovoltaic devices. In fuel cells, O–I materials are widespread in the protonic-based low temperature cell class (PEMFC) as membranes, active layers, or bipolar plates.

Chem. Soc. Rev., 2011, 40, 696–753

Suppression of Ag migration by low-temperature sol-gel zinc oxide in the Ag nanowires transparent electrode-based flexible perovskite solar cells

J. Kang et al., Organic Electronics 82 (2020) 105714

large-area flexible transparent Ag NWs networks electrode were fabricated through spray coating, and composite electrode combining Ag NWs and low-temperature sol-gel ZnO layer was developed for use in flexible perovskite solar cells. The modification of Ag NWs electrode by sol-gel ZnO film layer caused the slight influence on the transmittance and sheet resistance of the electrode, but significantly improved the mechanical properties. The reduced surface roughness and effective surface protection of sol-gel ZnO caused significant improvement in the device performance. Meanwhile, ZnO interface layer acted as a protecting film which can dramatically restrain the diffusion of Ag, improving the continuous illumination stability. This work provided a route to improve the performance and stability of flexible perovskite solar cells based on the printed Ag NWs electrode.

32.-34. THIN FILMS via sol-gel process – OPTO-ELECTRONICS

Redistribution layers in dielectrics and optical layers for chip size packaging, semiconducting matrices in display technology, in sensing systems as well as in LED manufacturing are also based on the classical silicones and siloxanes. As the chemical reactive functionality of the silica backbone, one will find epoxy, all kinds of alkenyl and styrene groups, whereas methyl and phenyl are used to improve dielectric and thermal properties. For better thin film processing and adaptation to costs, such materials were blended with certain polymers. In addition, particular metal oxide nanoparticles have been used as fillers to alter the rheology, permittivity and thermal stability and finally to adapt to processing. Depending on the field of application, they are tuned towards dielectric properties. For optical ones, they high light stability and a certain refractive index. These specifications determine the chosen chemical composition: class-II hybrids, like ORMOCERs are in focus in addition to functionalised silicones.

Chem. Soc. Rev., 2011, 40, 696–753

Highly sensitive NO₂ sensors based on organic field effect transistors with Al₂O₃/PMMA bilayer dielectrics by sol-spin coating

Q. Xie, et al., Organic Electronics 74 (2019) 69–76

In summary, we fabricated the OFET NO₂ gas sensors by using Al₂O₃/PMMA bilayer dielectrics, and reported the sensing property of devices under different Al₂O₃-sol concentrations. The sensors based on Al₂O₃/PMMA bilayer dielectrics exhibit high sensitivity and responsivity, low limit of detection, low baseline drift and short response/ recovery time at room temperature. The nice reproducibility and obviously strong stability show promising practical application potential. Moreover, from surface morphology and charge transport analyses, we demonstrated that the combination of an ordered semiconductor layer and efficient charge transport ability should be an access to achieve high-performance organic sensors for toxic and



harmful gases. The OFET sensors based on Al₂O₃/PMMA bilayer dielectrics propose an effective solution to the formation and modulation of OFET gas sensor with high sensing properties as well as potential for flexible and portable sensors of simple preparation, low cost and energy consumption.

35. THIN FILMS via sol-gel process – DECORATIVE

Colored glass bottles are usually produced from glass melts containing transition metal ions like iron, chromium, cobalt and others, according to a desired color. When differently colored bottles are mixed in the re-melting process for recycling, desired colors are very hard to be obtained. If the colored bottles could be produced by using organic colorants coated on bottle surface that are decomposed and burned out in a molten furnace, a great advantage for the new recycling system would be recognized.

J Sol-Gel Sci Technol (2013) 65:4–11

36. SOL GEL PROCESS - CONCLUSIONS

Sol-gel chemistry offers some particular advantages, centred on the ability to produce a solid-state material from a chemically homogeneous precursor. By trapping the “randomness of the solution state” and thereby ensuring atomic level mixing of reagents, one should be able to produce complex inorganic materials such as ternary and quaternary oxides at lower processing temperatures and shorter synthesis times. Furthermore, sol-gel chemistry should enable greater control over particle morphology and size. In reality, producing a homogeneous precursor at room temperature does not ensure homogeneity throughout a reaction and many sol-gel routes have therefore been designed to combat or control phase segregation during synthesis. Neither is it always necessary to ensure complete ‘randomness’ in the precursor. In fact, some of the most interesting advances in the sol-gel field in recent years have come from gels that have some degree of ordering and structure.

Mater. Horiz., 2016, 3, 91–112

SOL-GEL PROCESS – MAJOR ADVANTAGES

- “ Eco-friendliness
- “ Possibility to tailor properties at nano-scale
- “ Multi-functionality
- “ Good mechanical properties due to inorganic network
- “ Flexibility of coating and compatibility with organic additives due to organic moiety
- “ Possibility of thick coatings due to independently polymerizable organic groups
- “ Suitability for deposition on different substrate materials: metals, ceramic tiles, glass, plastics, wood, textile...
- “ Low temperature, ultraviolet UV or NIR curability
- “ Amenability for deposition on large areas with robotic automation
- “ Scalability of sol synthesis and coating deposition

Mater. Horiz., 2016, 3, 91–112

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Chem. Mater. 2001, 13, 3422-3435

J Sol-Gel Sci Technol (2013) 65:4–11

Adv. Funct. Mater. 2018, 1704158



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