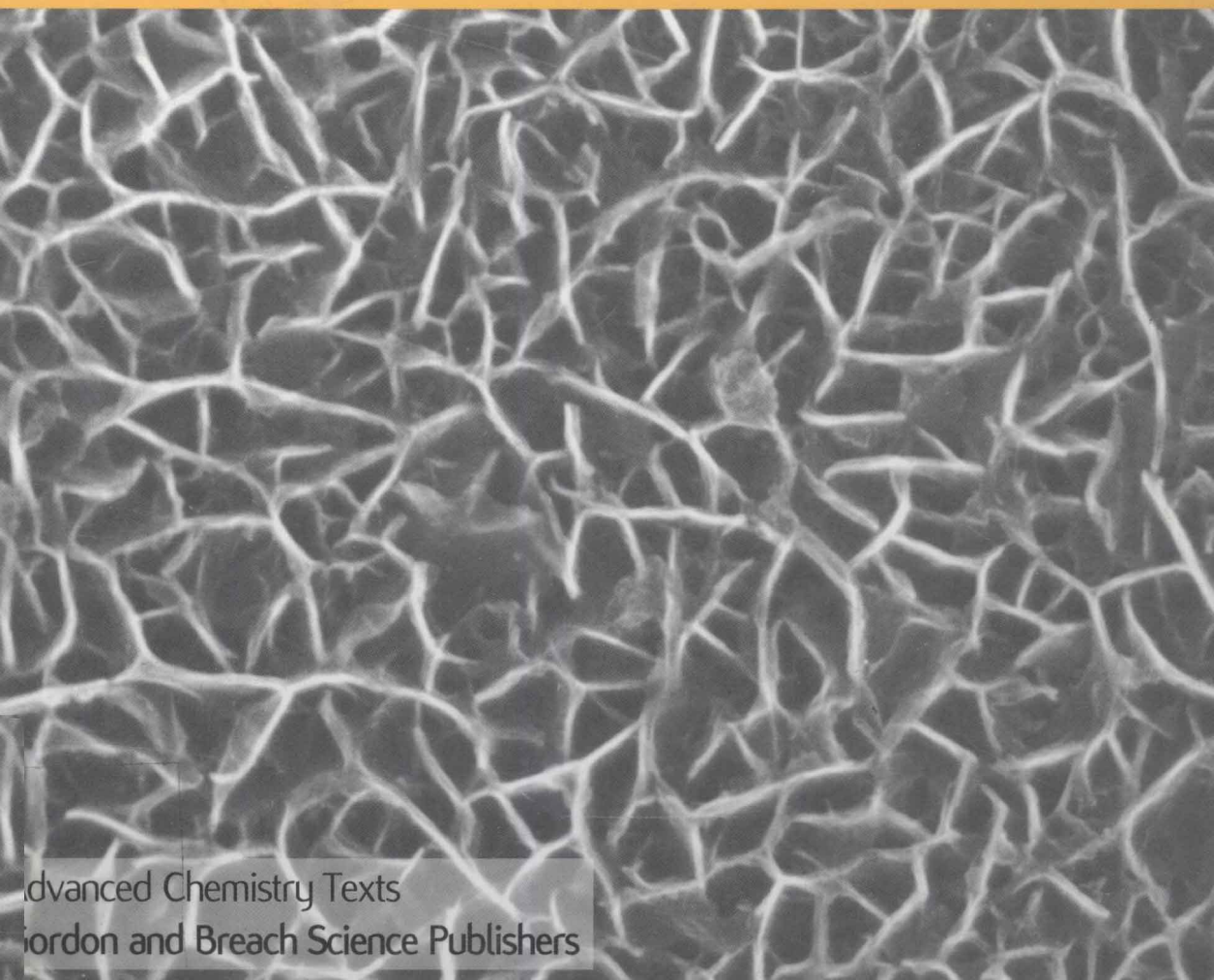


Sol-Gel Materials Chemistry and Applications

John D. Wright and Nico A.J.M. Sommerdijk



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Sol-Gel Materials

Chemistry and Applications

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Sol-Gel Materials

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Preface

Sol-gel processing methods were first used historically for decorative and constructional materials. In the last century many new applications were developed, initially largely empirically but later on a more scientific basis as new characterisation techniques became available. Today sol-gel methods are reaching their full potential, enabling the preparation of new generations of advanced materials not easily accessible by other methods yet using mild, low-energy conditions. It is therefore appropriate that the topic should increasingly be included in advanced undergraduate, MSc and taught PhD courses in the areas of chemistry, physics and materials science. There is currently no concise introductory text which covers all the major areas of the subject. The aim of our book is to fill this evident gap in the market and to facilitate the development of new courses. It has been written to guide those who wish to join the growing ranks of sol-gel scientists, by providing an accessible introduction to the development, mechanisms, chemistry, characterisation methods and applications of the technique. It provides the reader with an extensive yet concise grounding in the theory of each area of the subject, as well as detailing the real and potential applications and the future prospects of sol-gel chemistry.

The task of summarising such a vast and growing multi-disciplinary field into a volume of this size and price has proved demanding, yet we believe we have gone a long way towards achieving our aim of bridging the gap between an accessible textbook and a useful research resource. The basic ideas are described clearly for the newcomer, while their development to current research level is exemplified with numerous references. The references cited, while including many illustrative original papers as well as key reviews, are intended to facilitate further exploration of the literature rather than serving as a comprehensive bibliography. We apologise to authors of many excellent papers whose work could not be included: omissions are inevitable but not deliberate.

Where possible, key fundamental ideas and other important sections of the text have been identified by shading the relevant sections. In some parts of the text, notably the chapters covering characterisation and applications, where it has been difficult to identify some sections as more important than others, little use has been made of the shading. In these areas, the absence of shaded areas should not be taken as an indication that the material is of lesser significance.

We acknowledge a considerable debt to the international sol-gel community for assisting our own development in this area. In particular the conference series of International Workshops on Glasses and Ceramics from Gels has provided personal contacts and broad perspectives. In several countries the community has set up national sol-gel groups which provide valuable support and stimulus, especially for new workers in the field. The classic text *Sol-gel Science: The Physics and Chemistry*

of Sol-gel Processing by C.J. Brinker and G.W. Scherer (Academic Press: London 1990) remains an essential background reference, although the present work is designed to appeal to a different audience as explained above, and is more concise as well as including many new developments that have occurred in the decade between the two works.

Finally, we thank the publishers for their forbearance and support, and the advisers who commented in a helpful and constructive way on our manuscript.

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INTRODUCTION

Sol-gel materials encompass a wide range of inorganic and organic/inorganic composite materials which share a common preparation strategy. They are prepared via sol-gel processing involving the generation of colloidal suspensions ("sols") which are subsequently converted to viscous gels and thence to solid materials.¹ This controlled method has many advantages, which led to its historical use before the underlying scientific principles were understood. In recent years increased understanding of these principles has led to a great increase of interest in the method, and to its application in the production of a wide variety of advanced materials. To appreciate these developments it is first necessary to consider some general features of the process.

1.1 COLLOID STABILITY

A sol is a dispersion of colloidal particles² suspended in Brownian motion within a fluid matrix. Colloids are suspensions of particles of linear dimensions between 1 nm (10\AA) and 1 μm (10^4\AA). The formation of uniform suspensions of colloidal particles can be understood by calculation of the sedimentation rates assuming that the particles are spherical so that Stokes' Law may be applied. Equating gravitational and frictional forces:

$$\begin{aligned}\text{Sedimentation rate } dx/dt &= [(4\pi r^3/3)(\rho' - \rho)g]/6\pi r\eta \\ &= [2r^2(\rho' - \rho)g]/9\eta\end{aligned}\quad (1.1)$$

where η = viscosity of surrounding medium

ρ = density of surrounding medium

ρ' = density of colloid particle material

r = radius of colloid particle.

For a material of density 2 g/ml in water, the calculated sedimentation rates are:

Radius	Sedimentation rate
10^{-9}m	$2 \times 10^{-12} \text{ m/s}$ (8nm/h)
10^{-8}m	$2 \times 10^{-10} \text{ m/s}$
10^{-7}m	$2 \times 10^{-8} \text{ m/s}$
10^{-6}m	$2 \times 10^{-6} \text{ m/s}$ (8mm/h)

At normal temperatures thermal motion and convection currents are sufficient to counteract any tendency for sedimentation to occur at such low rates, and uniform suspensions are observed so long as the colloid particles remain stable.

The stability of colloidal particles is determined by their resistance to aggregation, and can be remarkably high. Thus gold sols are still in existence at the Royal Institution in London which were prepared there by Michael Faraday some 150 years ago. Clearly, if all sols displayed such stability the sol-gel method would not be useful for preparing solid materials.

At first sight the stability of small colloid particles is surprising, since surface tension leads to very high pressure differences across surfaces with small radii of curvature. For a particle of radius r , density ρ and relative molar mass M , with surface tension γ , the pressure difference across the curved surface, p_r , compared to that across a flat surface, p_o , is given by the Kelvin equation:

$$RT \ln (p_r/p_o) = 2\gamma M/\rho r \quad (1.2)$$

This has been verified experimentally, and predicts the following ratios:

r/m	p_r/p_o
10^{-7}	1.01
10^{-8}	1.1
10^{-9}	3.0

Thus small particles should tend to dissolve while larger particles should grow, as observed in Ostwald ripening of precipitates. Furthermore, attempts to generate colloidal particles by grinding solid materials frequently fail because the particles re-join under the mechanical stresses or because of attractive forces between particles, unless precautions are taken to prevent this (e.g. by grinding in presence of a surface active material, for example grind sulphur and glucose and disperse in water.) In stable sols, this is prevented because in practice colloidal particles tend to acquire surface charge by ionisation or by adsorption of ions or polar molecules from solution. The charged surface layer in turn attracts a second more diffuse layer of ions of opposite charge in the surrounding solution. The van der Waals attractive forces which potentially lead to aggregation fall off as r^{-6} . However the electrostatic repulsions between the like-charged ions of the diffuse layers around neighbouring charged colloid particles vary as r^{-1} . Thus, unless the thickness of the diffuse layer can be reduced substantially, the repulsions dominate the van der Waals attractions and the particles are stable against aggregation. Increasing the ionic strength of the solution, and in particular increasing the charge on the counter-ion, is the main way in which the diffuse layer thickness can be reduced.

For example, colloidal material in freshwater rivers is frequently precipitated at the saline limit where the river meets the seawater, leading to the formation of typical

estuary features. Similarly, Al^{3+} is often used to coagulate colloidal impurities in water treatment plants. In this case, physical entrapment of the colloid particles in gelatinous $\text{Al}(\text{OH})_3$ at high pH is a contributing factor in addition to the ionic charge effect. Conversely, if salt water floods agricultural soil, the surface Ca^{2+} ions which stabilise soil colloid particles are replaced by Na^+ which is less strongly held and easily washed off, leading to the coagulation of the soil colloid structure and formation of hard intractable masses. Treatment with gypsum (calcium sulphate) restores the original surface charge leading to eventual recovery of the soil structure.

1.2 CONTROL OF PARTICLE NUCLEATION

These environmental examples show that it is often possible to *control the physical aggregation of colloidal particles*. However, the degree of control possible in sol-gel synthesis of materials also includes:

- a) *the ability to determine the sizes of the initial colloid particles,*
- b) *the ways in which chemical links are formed between different colloid particles, and*
- c) *the subsequent development, drying and densification of the resulting aggregates.*

Control of the sizes of initial colloid particles depends on the fact that precipitation involves 2 steps: nucleation and growth. To obtain colloids, the nucleation rate should be much faster than the growth rate. Nucleation depends on the degree of supersaturation which can be achieved before precipitation, which is determined by solubility. Thus nucleation rates will be highest for substances with very low solubility. The growth rate of particles formed by the initial nucleation depends on:

- i) the amount of material available,
- ii) the diffusion rate of material from solution to growing particle (limited by viscosity),
- iii) the ease of orientation and incorporation of the molecules from solution into the solid lattice and
- iv) the growth-inhibiting effects of impurities and other species adsorbed onto the particle surfaces.

Thus, for sparingly soluble materials the nucleation rate is very high while the amount of material available for growth of the nuclei is very small, so small particles are obtained (e.g. ferric chloride treated with boiling water gives a ferric oxide colloid — and as expected from the above discussion of colloid stability, the largest particles are obtained when the pH is close to the isoelectric point at which the net charge on the hydrolysed species is zero.^{3,4}

1.3 THE SILICON ALKOXIDE SOL-GEL PROCESS

Control of the ways in which chemical links are formed between different colloid particles, and the subsequent development, drying and densification of the resulting

aggregates will be illustrated in detail in chapters 2 and 3 by reference to silica produced by the sol-gel route starting with hydrolysis of silicon alkoxides. The stages in this process occur slowly enough to allow detailed study by a variety of methods such as NMR and infra-red spectroscopy. For other alkoxides, such as metal alkoxides which are much more reactive, the same series of steps, although occurring in principle, may not all be significant since some occur so rapidly that they are not amenable to either study or control. These steps are as follows:

Hydrolysis:	$\text{Si(OR)}_4 + n\text{H}_2\text{O} \longrightarrow \text{Si(OR)}_{4-n}(\text{OH})_n + n\text{ROH}$
Condensation:	$\text{X}_3\text{SiOH} + \text{HOSiX}'_3 \longrightarrow \text{X}_3\text{Si-O-SiX}'_3 + \text{H}_2\text{O}$ or $\text{X}_3\text{SiOR} + \text{HOSiX}'_3 \longrightarrow \text{X}_3\text{Si-O-SiX}'_3 + \text{ROH}$
Gelation:	Formation of a "spanning cluster" across the vessel, giving a network which entraps the remaining solution, with high viscosity.
Ageing:	A range of processes, including formation of further cross-links, associated shrinkage of the gel as covalent links replace non-bonded contacts, Ostwald ripening and structural evolution with changes in pore sizes and pore wall strengths.
Drying:	The loss of water, alcohol and other volatile components, first as syneresis (expulsion of the liquid as the gel shrinks), then as evaporation of liquid from within the pore structure with associated development of capillary stress which frequently leads to cracking. This may also include supercritical drying, in which capillary stress is avoided by the use of supercritical fluids (e.g. CO_2) in conditions where there are no liquid/vapour interfaces.
Densification:	Thermal treatment leading to collapse of the open structure and formation of a dense ceramic.

1.4 ADVANTAGES OF SOL-GEL SYNTHESIS

From the above introduction, a number of reasons for the particular value of and interest in sol-gel synthesised materials become apparent:

1. The temperatures required for all stages apart from densification are low, frequently close to room temperature. Thus thermal degradation of both the material itself and any entrapped species is minimised, and high purity and stoichiometry can be achieved.
2. Precursors such as metal alkoxides and mixed alkyl/alkoxides are frequently volatile and easily purified to very high levels (e.g. by distillation or sublimation) using techniques developed for the microelectronics industry. This further contributes to high-purity products.

3. Since organometallic precursors involving different metals are frequently miscible, homogeneous controlled doping is easy to achieve.
4. The chemical conditions are mild. Hydrolysis and condensation are catalysed by acids and bases, but extreme pH conditions may easily be avoided, especially by the use of “two step” methods in which acid catalysed hydrolysis is followed by rapid neutralisation or buffering. In this way pH sensitive organic species (e.g. dyes) and even biological species including enzymes and whole cells may be entrapped and still retain their functions.
5. Highly porous materials and nanocrystalline materials may be prepared in this way.
6. By appropriate chemical modification of the precursors, control may be achieved over the rates of hydrolysis and condensation, and over colloid particle size and the pore size, porosity and pore wall chemistry of the final material.
7. Using functionalised precursors, covalent attachment of organic and biological species to porous silicate glass structures is possible.
8. By controlling the ageing and drying conditions, further pore size and mechanical strength control may be achieved.
9. By using organometallic precursors containing polymerisable organic ligands, materials may be produced which contain both inorganic and organic polymer networks.
10. Entrapped organic species may serve as templates for creation of pores with controlled size and shape. Subsequent removal of these species (for example by heat or strong acid treatment) leaves “molecular footprints” with potential as catalytic sites.
11. Since liquid precursors are used it is possible to cast ceramic materials in a range of complex shapes and to produce thin films or fibres as well as monoliths, without the need for machining or melting.
12. The optical quality of the materials is often good, leading to applications for optical components.
13. The low temperature of sol-gel processes is generally below the crystallisation temperature for oxide materials, and this allows the production of unusual amorphous materials.

1.5 LIMITATIONS OF SOL-GEL SYNTHESIS

Despite all these advantages, sol-gel materials are not without limitations. The precursors are often expensive and sensitive to moisture, limiting large scale production plants to specialised applications such as optical coatings. The process is also time-consuming, particularly where careful ageing and drying are required. Although this need not be a limiting factor where long continuous production runs are envisaged, it does mean that the total volume of material in the processing line is inevitably significantly higher than in faster processes. Finally the problems of dimensional change on densification, and of shrinkage and stress cracking on drying, although not insuperable, do require careful attention. These significant limitations emphasise the need to optimise sol-gel materials to exploit their advantages to the

maximum in applications where they can provide properties not attainable by other methods.

1.6 OVERALL STRUCTURE OF THIS BOOK

The ways in which these advantages may be realised will be made clear in subsequent chapters of this book. Chapters 2 and 3 explore the reaction mechanisms and opportunity for chemical control in silica sol-gel materials, while chapter 4 develops these themes for metal oxide gels. Chapter 5 covers the methods which are available for characterisation of sol-gel materials. Chapters 6 and 7 describe the applications of silica and organically modified silica ("ormosil") sol-gels, and metal oxide sol-gels, respectively. Finally in chapter 8 we consider future prospects for sol-gel materials, with reference to developments in their chemistry, characterisation methods and applications.

1.7 THE HISTORICAL DEVELOPMENT OF SOL-GEL PROCESSING

To end this chapter we return to its first paragraph, where we pointed out that because of the advantages of sol-gel methods they were put to practical use long before any scientific understanding had been developed. A brief survey of the history of sol-gel technology⁵ not only recognises the intuitive skills of earlier generations, but also serves to emphasise that despite its present high-technology niche it has its roots in constructional, decorative and artistic functions, albeit with the common objective of achieving effects in materials which could not have been achieved by other available methods of the time.

1.7.1 Origins

The earliest use of colloids to prepare functional materials is seen in the cave paintings at Lascaux in France, dating back 17,000 years. The pigments used were based on iron oxide, carbon and clays, ground into fine powders, graded by sedimentation and dispersed in water using natural oils as surface active stabilisers. It is interesting that this decorative use of a technology closely related to much more recent ceramic decoration methods substantially pre-dates the use of ceramics in construction or other more practical applications.

The next major development was the use of firing techniques in addition to simple grinding to alter the chemistry of the mineral precursors. Some 8000 years ago, early examples of the use of plaster and brick occurred. Genesis 11 v.3 describes bricks produced using "thorough burning" and held together with bitumen for the building of the tower of Babel. Neolithic sites often contain polished plaster floors. At Yiftah El in Israel a 180m² example would have needed over 2 tons of lime, which would have required over 10 tons of wood to fire the kiln.⁶ In these examples we see the beginnings of the sol-gel ideas, in that fine powdered or colloidal material in suspension was moulded and then dried and densified by chemical action or by firing at high temperature.

Next, glazing methods were developed to seal the surfaces of porous clay vessels.⁷ In China by 2000BC silicate glazes with high calcium content fired at high temperatures were in use. In Mesopotamia by the second century the glazing chemistry