

# Sol-Gel Materials Chemistry and Applications

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

Advanced Chemistry Texts



# Sol-Gel Materials Chemistry and Applications

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# Sol-Gel Materials Chemistry and Applications

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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.

# 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.<sup>1</sup> 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 particles<sup>2</sup> suspended in Brownian motion within a fluid matrix. Colloids are suspensions of particles of linear dimensions between 1 nm (10Å) and 1 µm (10<sup>4</sup>Å). 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  $\eta$  = viscosity of surrounding medium  
 $\rho$  = density of surrounding medium  
 $\rho'$  = 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 <sup>-9</sup> m	2 × 10 <sup>-12</sup> m/s (8nm/h)
10 <sup>-8</sup> m	2 × 10 <sup>-10</sup> m/s
10 <sup>-7</sup> m	2 × 10 <sup>-8</sup> m/s
10 <sup>-6</sup> m	2 × 10 <sup>-6</sup> 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  $\rho$  and relative molar mass  $M$ , with surface tension  $\gamma$ , 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,  $\text{Al}^{3+}$  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  $\text{Ca}^{2+}$  ions which stabilise soil colloid particles are replaced by  $\text{Na}^+$  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.<sup>3,4</sup>

## 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