Journal of Sol-Gel Science and Technology (2022) 102:478–481
https://doi.org/10.1007/s10971-021-05640-9

INVITED PAPER: FUNDAMENTALS OF SOL–GEL AND HYBRID MATERIALS PROCESSING

Birth of the sol–gel method: early history

Sumio Sakka[1]

Received: 15 July 2021 / Accepted: 6 September 2021 / Published online: 11 October 2021

Abstract

Congratulations on "United Nations International Year of Glass 2022." I would like to acknowledge the efforts made by the International Commission on Glass with the Community of Glass Associations and the Glass Art Society to promote the status of glass. I am very much pleased to contribute an article on the birth of the sol–gel method and its growth in early times for a Special Issue of Journal of Sol–Gel Science and Technology, which is published to celebrate the Year of Glass. At present, the sol–gel method is employed not only for manufacturing optical glass fibers for communication, but also for processing a wide range of functional, high technology materials, such as photonic, electronic, micromechanical, chemical, and bionic materials. The sol–gel method typically involves the following steps: (1) starting from a solution containing pure precursors, (2) conversion of the solution to a sol and then to a gel by hydrolysis and polycondensation, (3) forming into desired shapes such as bulk, film, and fiber during gelation of the sol, and (4) thermal treatment of the gel into a solid material at low temperatures. It should be noted, however, that there are many variants. For instance, the method of fabrication of a solid material by heating the shaped compact of gel powders prepared from a solution or sol is also called the "sol–gel method." In this case, "starting from a solution" is important.

Keywords Glass · Sol–gel · Coating films · Organic–inorganic hybrids · Microcomposites · History

1 Helmut Dislich: father of the sol–gel method

In 1971, Dislich of the Schott glass company in Germany published a paper [1] entitled "New routes to multicomponent oxide glasses." The paper showed that gel crumbs derived from homogeneous solution consisting of alkoxides of sodium, boron, aluminum, and silicon produced transparent sodium aluminoborosilicate glass plates of rectangular shape with the dimension of about 4 cm × 1.5 cm × 2 mm on hot pressing at surprisingly low temperatures as low as 630 °C. The glass seemed to be of Pyrex type. It is well known that Pyrex-type glass needs very high temperatures higher than 1500 °C for fabrication by conventional glass making technique, that is, melt-quenching technique.

✉ Sumio Sakka
sakkasum89@gmail.com

[1] Kyoto University, Kyoto, Japan

Dislich's paper amazed me very much. I felt a kind of shock, seeing the fact that glass is formed at very low temperatures around its glass transition temperature. Then I recalled the words of Professor I. Sawai, who was the leader of the glass laboratory at Kyoto University when I joined the laboratory as faculty member in 1953. He told me that if one fabricates glass at room temperature, he will be given Nobel Prize.

2 Research works on glass just after 1971: sol–gel preparation of glass

2.1 Activities of glass scientists

Many glass scientists were highly interested in Dislich's work and started the research on the low temperature sol–gel preparation of glass. I was lucky to be able to take up the new "sol–gel method" research theme with my colleague Dr K. Kamiya, who was an Associate Professor at that time, in the newly established Laboratory of Mie University in 1972. We carried out a study [2] on sol–gel glass formation in the TiO_2-SiO_2 system without the use of hot pressing. Given amounts of titanium isopropoxide $Ti(OC_3H_7)_4$ and tetraethoxysilane $Si(OC_2H_5)_4$ were mixed, reacted at 80 °C in a sealed flask for 3 h and then kept open in air for hydrolysis by air humidity. The solution became viscous gradually and gelled into a transparent mass with many fissures in a week or so. When a gelled mass of composition $3TiO_2 \cdot 7SiO_2$, for instance, was heated to 500 and 700 °C, it was broken into small transparent pieces of several millimeters in size. IR spectra showed that these small pieces were binary glasses with little amounts of non-bridging oxygen. Thus, we had obtained TiO_2-SiO_2 glasses without melting and hot-pressing. With these results, we joined the International Congress on Glass held in Kyoto in 1974. Our communication was the only study focused on the sol–gel method presented during the Congress. Our paper attracted the attention of many attendees and they gave us their comments. Half of them commented that it is very much interesting. The other half told us that the starting alkoxide compounds are too expensive to be decomposed into glass.

The above-mentioned study gave us an idea that we might obtain shaped bulk glasses from alkoxide solutions without hot pressing [3], if we carefully selected the composition of the starting solution consisting of alcohol as solvent, water for hydrolysis, acid for catalysis and metal alkoxides, the condition of hydrolysis and polycondensation, and the condition of drying of the gel mass.

Also, we had an image on the features of sol–gel formation of glass as follows:

(1) Start from a solution.
(2) Shaping (making form) during the sol-to-gel transition.
(3) Heating of the gel up to relatively low elevated temperatures.

Many groups of glass scientists must have started to study the sol–gel method. Actually, most of them made considerable efforts in preparing bulk silica glass [4–6] by this approach. The reason for this is that in the 1970s, the preparation of bulk silica glass as preform for optical fiber drawing was a key technology for the realization of optical telecommunication.

2.2 Preparation of optical fibers: chemical vapor deposition versus sol–gel method

Optical fibers based on silica glass for optical communication are drawn from optical fiber preforms of cylindrical shape. Since about 1970, most of the preforms have been prepared [7] by "chemical vapor deposition." In this method of fabricating the preform, gases, such as $SiCl_4$ and $GeCl_4$, are blown out from a burner, mixed in space, oxidized by heating with an oxy-hydrogen torch, and deposited as SiO_2:GeO_2 soot (gel glass powder compact), and then sintered to a SiO_2:GeO_2 preform. This processing seems to be a variant of the sol–gel method, for it starts from liquid and the bulk shape is formed during hydrolysis and condensation reactions. It should be assumed, however, that this method was invented independent from Dislich's paper [1].

It can be added that many years later the typical sol–gel method was applied to prepare a part of the optical fiber preform [8, 9]. Moreover, around 2000, a complete preform of 25 kg in weight was prepared by typical sol–gel method and commercialized [10].

2.3 Preparation of coating films by the sol–gel method

Besides bulk silica glass, a number of papers dealing with the sol–gel preparation of coating films were published.

In 1976, Fukushima et al. [11] published a paper on the preparation of $BaTiO_3$ films on substrate by the sol–gel method. Yoldas and Partlow [12] made beta-alumina films from a mixture of aluminum alkoxide and sodium alkoxide by the dipping method in 1980. The deposited films were heated up to 1300 °C to precipitate fine beta-alumina crystals. It is noted that this temperature is much lower than the temperature of 1700 °C, required for the conventional method of sintering oxide powder compacts. In 1980, Ogiwara and Kinugawa [13] published a paper on the preparation of transparent In_2O_3 conducting films on glass substrates. Indium acetylacetonate was deposited on the substrate and then decomposed into oxide by heating. These works of preparing coating films on glass or other substrates indicate that the sol–gel method is suited for the preparation of coating films, and in other words, coating films will be one of the important fabrication targets of the sol–gel method, as is noted later.

3 International Workshop on Glasses and Glass Ceramics from Gels in 1981

In October 1981, an international meeting focusing on the sol–gel method, called the International Workshop on Glasses and Glass Ceramics from Gels [14], was held in Padova, Italy, in October 8–9. This meeting was proposed by Prof. V. Gottardi of the University of Padova, in order to promote the sol–gel method for glass formation. According to Gottardi, Chairman of the Organizing Committee, the meeting had 18 scientific communications and 80 participants from 10 countries.

Among the authors delivering presentations, we found the names of active and famous glass scientists: C. J. Brinker, P. F. James, L.C. Klein, J.D. Mackenzie, E.R.

Plumer, H. Rawson, S. Sakka, H. Scholze, M. Yamane, and J. Zarzycki. Naturally, their presentations were centered around "glass," that is, they talked about comparisons between glasses from melts and from gels, kinetics of glass formation from solutions, gel-to-glass transformations, sol–gel transformations, and so on. These subjects were scientifically quite interesting. Although I greatly enjoyed this meeting, these subjects alone do not give us detailed perspectives for the future of the sol–gel method.

In contrast to this, 4 out of 18 communications concerned functional coatings or films prepared by sol–gel processing for practical applications, such as anti-reflective films and conducting films, single layer antireflection films, oxidation resisting films on porous silicon, and sol–gel-derived vitreous supports for Pd catalysts. It should be noted that these studies on application-oriented sol–gel derived materials were carried out by younger researchers: P. Hinz [15], S. P. Mukherjee [16], J. Schlichtung [17], M. Guglielmi, G. Carturan [18], and so on. It was considered that these studies would promote the sol–gel method, expanding the area covered by such solution-based approaches. However, the older glass scientists, including myself, could not think of this at that time, and it took them some years to turn their minds to new materials prepared by the research theme sol–gel method.

The participants of the International Workshop returned home, feeling that a new paradigm of research was opened and promising to meet together in the Second Workshop held 2 years later.

4 Second International Workshop on Glasses and Glass Ceramics from Gels, 1983: invention of organic–inorganic hybrids

The Second Sol–Gel Workshop was held in July 1–2, 1983 in Wuerzburg, Germany. Twenty-seven research papers [19] were presented and 109 participants attended the Workshop. The papers published in this Workshop represented the research results during the 2 years since the first Workshop and are summarized below.

It is natural that 11 papers out of 27 were devoted to the basic research on the sol–gel process, such as hydrolysis and condensation of alkoxysilanes, sol–gel transition, gel to glass transition, homogeneity of gels, and gel-derived glasses and structural development during the gel to glass transition. Six papers dealt with the preparation of glasses by the sol–gel method.

Special attention should be paid to four papers on the preparation of coating films of silica on microscope glass slide [20], IR-reflecting ITO coatings on float glass [21], and Fe, Cr, and Co oxide films on float glass [22]. These papers on coating films informed us that the sol–gel method was suitable for the preparation of coating films on semiconductor and glass substrates. Coating processes based on the sol–gel method are simple, compared to the conventional coating methods, where the oxide materials are sintered, pulverized into fine powder, and then formed into suspensions.

The most innovative material prepared by the sol–gel method was brought about by the last presentation. Helmut Schmidt from the Institut fuer Silicatforschung, Wuerzburg talked about sol–gel prepared contact lenses, which consisted of an organic–inorganic hybrid material [23]. This material was synthesized by hydrolysis-polycondensation reactions involving epoxysilane, methacryroxysilane, and titanium alkoxide. In this hybrid, the inorganic parts (–Ti–O–Si–O– or –Si–O–Si–O–) are bonded to the organic part (–Si–$(CH_2)_3$–O–CO–CH(CH_2) CH_2–) by covalent bonding. Such hybrid materials have the features of both inorganic and organic substances. The most important point is that only the sol–gel method can produce organic–inorganic hybrid materials. After the presentation, Professor Mackenzie asked a question to Schmidt, "Are you wearing contact lenses made of the new material that you invented?" This question well expresses how the attendants were surprised at Schmidt' talk.

5 Progress of the sol–gel method after the Second Sol–Gel Workshop: invention of organic–inorganic microcomposites

In 1984, 1 year after the Second Sol–Gel Workshop where Schmidt presented the study on the organic–inorganic hybrid, Avnir et al. [24] published a paper reporting on the preparation of microcomposites, which consist of silica gel films containing fluorescent molecules of rhodamine 6G. A coating solution consisting of ethanol, tetramethoxysilane, hydrochloric acid, triton-x-100, and rhodamine 6G was deposited on a glass plate and heated for 4~7 h at 110 °C. Every rhodamine 6G molecule was fixed in the gel without coagulation so that its fluorescent property would not be lost. It was assumed that the functional organic molecules can be replaced by more durable pigments, and the silica matrix can be replaced by other oxides such as Al_2O_3 and TiO_2. It must be stressed that such microcomposites can be prepared only by the sol–gel method.

Here, I finish writing about the "Birth of the sol–gel method: early history" by pointing out that the three significant inventions based on the sol–gel method, that is, (1) formation of films on substrates by the sol–gel method, (2) organic–inorganic hybrid materials, and (3) organic–inorganic microcomposites were made in earlier times from 1971 to 1984. Moreover, these inventions established the foundations for promoting the sol–gel method as an indispensable advanced processing technology for the fabrication of functional materials needed in wide range of areas, including electronics, photonics, micromechanics, and biomedical technology.

6 Concluding remarks

In this article I looked back at the birth and early history of the sol–gel method. This method was initiated and developed by glass researchers during the 1970s and early 1980s, and later it was highly promoted as a processing technology for almost all kinds of materials. I would like to add, however, that the sol–gel method raised the value of glass very much. Photocatalyst coating films produce self-cleaning glass, contributing to solving environmental problem. Glass sheets supporting sol–gel-prepared dye-sensitized solar cells may provide us with sustainable clean energy. Antireflection coating, antifogging coating, UV-absorbing coating, etc. promote the performance of window glasses and glass substrates as well as optical glasses.

Compliance with ethical standards

Conflict of interest The author declares no competing interests.

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