



Review Paper

Sol-Gel Derived Nanomaterials and Its Applications: A Review

Amit Kumar¹, Nishtha Yadav², Monica Bhatt³, Neeraj K Mishra³, Pratibha Chaudhary⁴ and Rajeev Singh^{3*}

¹Department of Polymer Science, Bhaskaracharya College of Applied Sciences, University of Delhi, New Delhi, 110075, INDIA

²Department of Chemistry, Amity University, Noida, Uttar Pradesh 201313, INDIA

³Material/ Organometallics Laboratory, Department of Chemistry, ARSD College, University of Delhi-110021, INDIA

⁴Maitreyi College, University of Delhi, Bapudham Complex, Chanakyapuri, New Delhi, 110021, INDIA

Available online at: www.isca.in, www.isca.me

Received 3rd November 2015, revised 23rd November 2015, accepted 15th December 2015

Abstract

Sol gel technique has come across as a convenient route to synthesize nanoparticles using various precursors. Starting from the earlier work on the silica material and now covering precursor like metal-oxides and organic-inorganic hybrids, this method has proved to be flexible, economical and less complex as compared to conventional routes for nanoparticle synthesis at relatively low temperatures. This process has been extensively used in the field of ceramics, glass and thin-film-coatings. This review, sol-gel technique has been studied explaining its origin, processing, applications and advantages. Sol-gel derived materials have a wide range of uses. This review is a study about sol gel derived materials, the process and its applications.

Keywords: Sol-Gel, nanomaterials, applications.

Introduction

Sol-gel is a methodology of producing small particles in material chemistry. It is mostly used for the synthesis of metal oxides. The initial step of this process is converting monomers or the starting material into a sol, i.e., a colloidal solution which is the precursor for the further formation of a gel. This gel is made up of discrete particles or polymers. Most commonly used precursors are chlorides or metal alkoxides. These precursors are hydrolysed and polycondensed for the formation of colloids. Sol-gel process is preferred due to its economical feasibility and the low-temperature process which gives us control over the composition of the product achieved. Small amounts of dopants like rare earth elements and organic dyes can be used in the sol which homogeneously disseminates in the product formed finally. The synthesized product is used as an investment casting material in the processing and manufacture of ceramics. Thin metal oxide films can also be produced using this for further uses. Materials synthesized from Sol-gel technique have a wide area of applications in energy, space, optics, sensors, electronics, reactive material and separation technology (e.g., chromatography), medicine (e.g., controlled drug release).

Steps Involved In Sol-Gel

Sol or colloidal solution is a solution where distribution of particles of the size $\sim 0.1-1 \mu\text{m}$ takes place in a liquid in which the only suspending force is the Brownian motion. A gel is formed when solid and liquid phases are dispersed in each other. In this process, initially, colloidal particles are dispersed in a liquid forming a sol. Deposition of this sol can produce thin coating on any substrate by the means of spraying, spinning or

coating. The particles in the sol are left to polymerize by removing the stabilizing components and further produce a complex network gel. The remaining organic and inorganic components pyrolyze in the end by heat treatments to form amorphous or crystalline coatings²⁻⁵. Sol-gel comprises of two major reactions: alcoholic group hydrolysis and its condensation.

Precursor sol which is obtained can be given a desired shape using appropriate casting container. It can also be deposited on a substrate to form a film by dip coating or spin coating or used to synthesize microsphere or nanosphere powders.

Steps involved in sol-gel process

Mixing: In this part of this method, a colloidal solution is formed via mechanical mixing of colloidal particles in water as a solvent at a precipitation preventing pH. The metal alkoxide precursor $\text{M}(\text{OR})_4$ reacts with water and undergoes hydrolysis and polycondensation reactions, the formation of a colloidal dispersion of extremely small particles (1–2 nm) takes place that finally converts into a 3-D network of the corresponding inorganic oxide.

Casting: Sol has a low viscosity which makes it easier for it to cast into a mold or shape. A suitable mold must be chosen in order to avoid the sticking of the gel to the casting container.

Gelation: As process takes place, three-dimensional networks start forming from colloidal particles and condensed silica. The size of the particles and the gelation process decides the properties of the gel. In the gelation process, there is a

subsequent increase in the viscosity and this will result in the shape of casting container. Over the time, with controlled change in viscosity, fibers are spun together while the gelation

occurs. Gelation results into agglomeration with colloidal particle which is due to interactions among the components which can be electrical in nature².

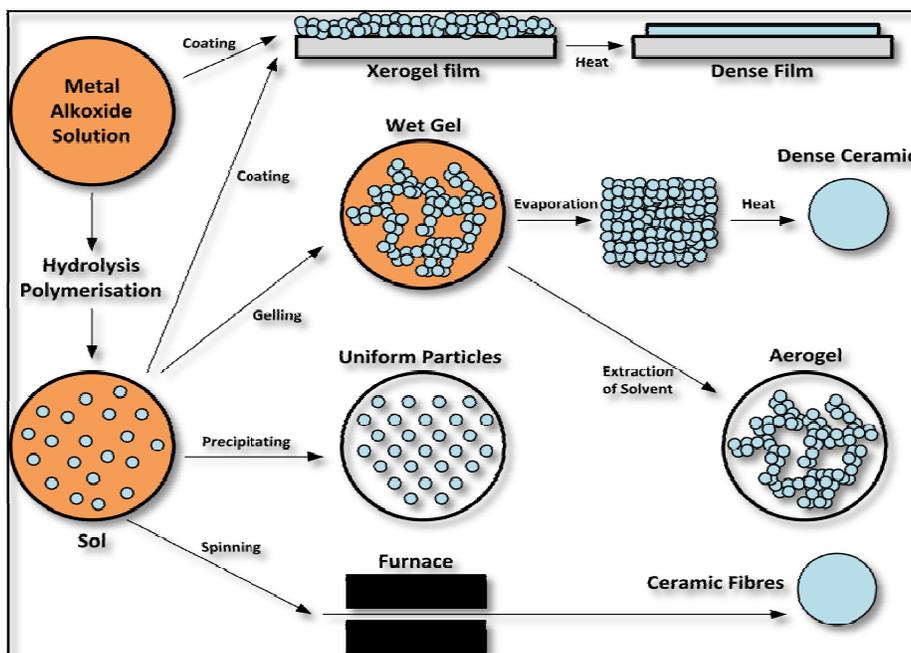
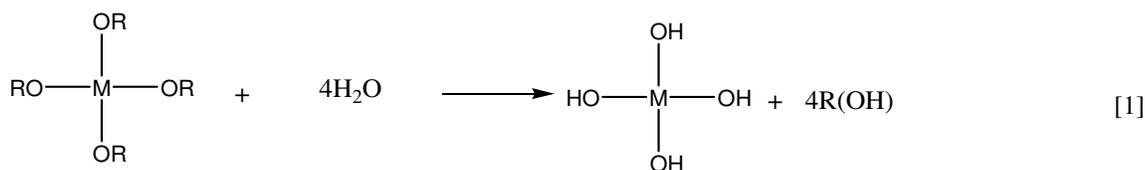


Figure-1
 Scheme of sol-gel technique¹

Hydrolysis



Polymerization

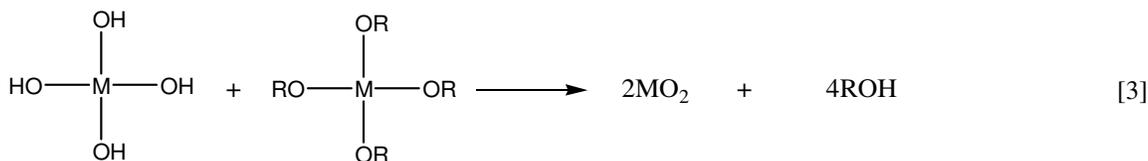
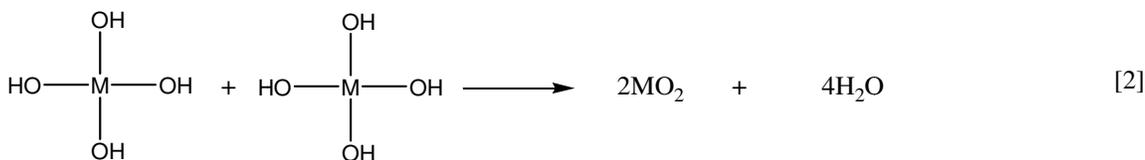


Figure-2
 Hydrolysis and polymerization while mixing step in sol gel process

Aging: This part of sol-gel process is also called Syneresis. It includes the maintenance of the cast object for a period which can vary from hours to days. During the aging process, polycondensation continues along with solution it is immersed in and the gel-network will reprecipitate. This process will increase the thickness of interparticle necks and decrease the porosity. Hence, the potency of the gel increases with this and produces a product which is resistive to cracking while drying.

Drying: In the drying process, excess of solvent is removed from the complex network. During drying, a large capillary stresses can develop when the pores are small. These stresses cause the gels to crack instantly and can only be stopped if the drying process is controlled by decreasing the liquid surface. This can be done by elimination of very small pores or addition of surfactants, by hypercritical evaporation, which can stop the solid and liquid portions to interact. The aerogel becomes of low density after drying. It gains a very good thermal insulation when it is placed between the glass plates and is finally evacuated.

Densification: The gel produced is heated at elevated temperatures which will cause densification of the gel. This will also eliminate the pores in the gel and makes the density approximately around fused quartz or silica. The temperature of densification depends on the pore dimension, pore connectivity and its surface area³.

Historical Background

Sols and gels are among many naturally occurring matters not only in biological system where they consist of the blood, serum, eye vitrea but also in clay and silica gels in materials science⁴. In 1861, Graham found the colloidal material science⁷ although Faraday made the oldest sol from gold colloidal particles in a laboratory in 1853⁵. Ebelmen, in 1846, made the first stable silica gel ever. The following century, a tremendously huge variety of oxides, complex mixed oxide and some non-oxides compositions were produced by sol-gel

technology. Silicates were the most studied among all other compositions⁸. Various feild of sciences has contributed to lay the background of the sol-gel technology. The later domains consists the formation of sol particles, stabilization of sol, coagulation and precipitation and its gelation process. It also includes the recent coordination chemistry advancement to prepare novel precursors with which even further elaborate sol-gel products can be prepared. La Mer introduced a logical explanation for the controlled formation of colloidal particles by proper growth from solutions of appropriate starting materials⁹.

Information provided by La Mer was successfully applied for growth of homogeneously sized particles by Matijevic¹⁰. The electrostatic interactions between the colloidal particles will control the coagulation or stabilization of sol. Further studies of this aspect of colloids was done by Derjaguin, Verwey, Landau and Overbeek in a theory currently compiled under the tag of D.L.V.O theory representing the scientist's initials¹¹. This theory was awarded with Nobel Prize in Physics. It is also possible to control the coagulation by grafting various organic polymers on colloidal particles. In this case, interactions between the grafted polymers and the solvent are critical. The steric theory that unifies the underlying science is derived from a theory on the behaviour of polymer solutions, by Flory and by Huggins¹¹. The former scientist was granted the Nobel Prize in chemistry. Next, Flory and Stockmayer established a precise definition of the gelation phenomenon, for polymer solutions undergoing growth by condensation reactions. The gel point was defined as the critical value of the extent of condensation reactions, where for the first time a 3D continuous network was formed. This network was only limited by the size of the container, but the critical value was itself independent of the size of the container. The theory of Flory and Stockmayer was found to correspond with Hammersley's possible percolation models. Mandelbrot¹² in fractal geometry showed the gel complex network architecture after the gelation. Other mathematical techniques termed diffusion limited aggregation (DLA) were developed for dense colloidal particles.

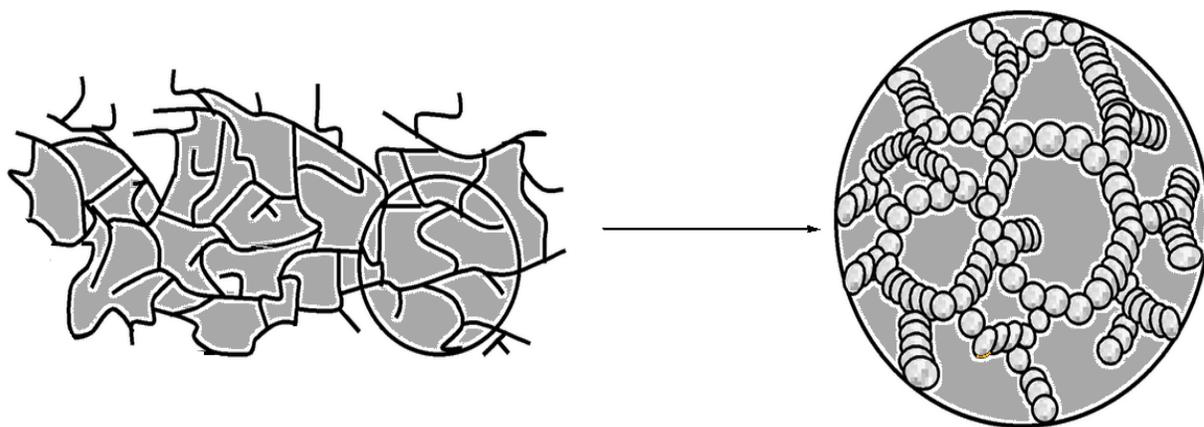


Figure-3
Gelation to form Cross linked 3-D network⁶

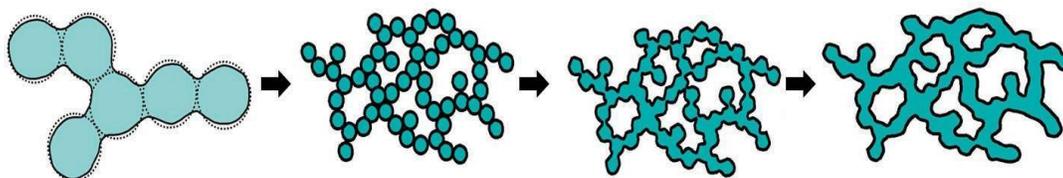


Figure-4
Aging process⁶

Advancement and improvement in sol-gel technique: Gel drying is a vital process for significant applications of the sol-gel technique. Kistler¹³ studied the supercritical drying for the first time which led to the production of aerogels with an exceptionally high pore volume of up to 99.8%. The discovery of miscellar materials took place by doping of sols with chemical additives. Chemical synthesis in co-ordination chemistry has led to the recent developments in the sol-gel¹⁴. One of major issue is to produce materials with different surface functions such as inducing hydrophobic nature. Besides this, grafting, chemical immobilization via chemical compounds like molecular catalysts, enzymes, or other bio-molecules is required. Inorganic-organic hybrid materials with interesting properties can be developed by organic molecules capable of polymeric gelation.

Advantages of Sol Gel: Improved adhesion between substrate and the top coat. Due to the gel state, materials can be molded into complex geometries. High-purity products are obtained due to the ceramic oxides precursors which are dissolved in appropriate solvent for the sol-gel transformation. It is a low temperature using process (200-600°C). It is a simple, economic and effective method to produce high quality coatings.

Disadvantages of Sol Gel

Due to some limitations, the sol-gel technique cannot achieve its full industrial potential. Some of them are having high permeability, low wear-resistance, weak bonding, and hard porosity control. For a crack-free property, 0.5 μm is the maximum coating thickness limit. Thick coatings might turn out a failure during the thermal process. Presently, sol-gel technology suffers a drawback due to the thermal mismatch and its surface-dependence. Clearly, lack of scientific understanding of this complex reaction is one of the major drawbacks of this technique¹⁵. One of the drawbacks of sol-gel method is its expensive raw materials, drying and sintering and its time-taking process¹⁶⁻²⁰.

Applications of Sol-Gel

Ceramics: Ceramics is a word derived from Greek term *Keramos* which means potter's clay. A ceramic material is a non-metallic, inorganic, material and is generally crystalline. It is one of the most important non-metals and we should know the tools and techniques for high quality good cost effective processing of ceramic material. In recent works, different types

of ceramics have been used like alumina and silicon carbide. All the ceramics have low density and are ductile. They have high corrosion resistance, hardness and wear resistance. In the sol-gel methodology for making concentrated colloidal suspensions (sols) of a hydrous oxide, oxide ceramics or hydrous hydroxide precursor are dehydrated to form gels which then yield an oxide upon calcinations. Previously, all the work has been done with glass forming systems (specifically silica and alumina) but now the work on sol-gel is being done with a broader range including metal alkoxides²¹. Current work involves producing bulk monolithic parts, fibres, powders and composites²². This route is comparatively simple and is done under mild conditions. Simplification of the bulk sintered metal oxide ceramics can be done along with broadening of the variety of materials that can be produced, specially mixed-oxide ceramics^{23,24}. The time taken in the processing of the sol-gel technique if slow drying of the gel is necessary. The solvents required are potentially dangerous, there is a need for controlled atmospheres during raw material preparation and handling and the raw materials used are expensive²⁵. The preparation of ceramic precursor powders by a sol-gel process has to be done in a liquid phase, hence, the pickup of impurities and production of dust is minimal²⁶. Also the use of alkoxides when they are carefully purified, decrease the chances of ionic impurities and then produces organic products which can be easily volatilized. All of these are those critical considerations which should be taken care of when working with toxic materials or with highly pure technical ceramic.

Preparation of multicomponent materials is also facilitated by sol-gel reactions; the mixing of sols can provide a high degree of homogeneity which is important in making electronic ceramics. Although some complexing might to occur in solution, order to obtain particles which are homogeneous on the microscopic scale, the reaction rates of the mixed alkoxides must be similar. Recently, work has been done on producing bulk ceramics by sintering gels directly as monolithic shapes. The availability of the highly pure and homogeneous has motivated the same. A large amount of shrinkage occurs due to the amount of liquid used in the process. Sol-gel processes for the direct production of ceramics appear to be most attractive as a method of preparing films, but even when films are prepared, one can encounter poor lubrication to the substrate and crazing. The film thickness, the relative thermal expansion coefficients of film and substrate, and the chemical homogeneity of the dried, unsintered film are important.

Applications of sol gel derived ceramics: The use of ceramic parts in gas turbine engines has many advantages over conventional parts, such as higher operating temperatures, improved fuel efficiency, reduced weight and greater thrust-to-weight ratio. Using ceramic materials also decreases the dependence on strategic materials. Ceramics are inherently less dense than metallic alloys while they retain their strength at higher temperatures. Because of their bonding, most monolithic ceramics are brittle and lack fracture toughness. In ceramic engine parts, these characteristics have led to catastrophic failure due to point contact stresses. Recently developed fiber-reinforced ceramic matrix composites offer the promise of overcoming these problems. The fracture toughness for these composites is significantly higher than for monolithic materials. Further applications are:

Sol gel derived Ceramic-Carbon Composite Electrodes: CCEs have numerous properties viz, rigidity, porosity, having a renewable external surface and chemically modifiable. Ceramic-Carbon electrodes are relatively stable to the carbon paste electrodes. As compared to the organic and monolithic composite carbon electrodes, these are more agreeable towards chemical modification²⁷.

Sol gel derived ceramic membrane: In order to improve the gas separation performance, sol-gel modification of mesoporous alumina is a technique that has proven to be successful. A fine microporous top layer is formed which results in activated transport and molecular sieve-like separation²⁸.

Sol-Gel-Derived Ceramic-Carbon Nanotube Nanocomposite Electrodes: Fabrication of nanocomposite electrodes made of sol-gel-derived ceramic-carbon nanotube can be done in a silicate gel matrix by doping multiwalled carbon nanotubes (MWNTs). An elaborate study has been done on the electrochemical behavior and potential electrochemical applications of the ceramic-carbon nanotube nanocomposite electrodes (CCNNEs)³⁰.

Thin Film Coating

Extremely thin layers of materials such as TiO₂, SiO₂, MgF₂, gold, aluminium which can be applied to the surface of a substrate like metal, crystals, glass or ceramics, to effect a change in its optical properties come under the category of thin-film coatings. These coatings can produce several effects like

reflection, refraction, conductivity and anti-reflection. This modification can be carried out by the number of coating layers, expert calibration of material selection considering the thicknesses of each respective thin film layer which is relative to the incidental wavelengths of light. Many hi-tech devices are entirely dependent on thin-film coatings, e.g. flat panel TV screens and solar cells, spectacle lenses, smart phones, etc. Plastic substrates when applied with these coatings produce products with light weight and better performance than conventional materials. When we replace glass with plastic, the costing is cut by half. The non-coated plastic substrates cannot bear exposure to environmental conditions like UV radiations, rain, varied temperatures which may cause wear and tear like abrasion damage, chipping, scuffing, etc. Thin film formation can be done by centrifugal or gravitational draining followed by drying. Sol-gel technique is deeply related to chemistry due to the presence of colloidal suspensions. In 1846, Ebelmen³¹ observed the hydrolysis and polycondensation of tetraethylorthosilicate (TEOS) which is better known as tetraethoxysilane after which it was applied and opened a new technology. The first patent of sol-gel was published in 1939 comprising of optical properties of the prepared SiO₂ and TiO₂ for. In 1955, the potential of sol-gel in the fabrication of high-purity glasses -using methods not possible with traditional ceramic-processing techniques- was recognized³² which resulted in production of homogeneous multicomponent glasses. Sol-gel technique was used for the synthesis of coatings for glass surfaces reported in 1965 by Schroeder³³. Although they were mainly interested in single-oxide optical coatings of SiO₂ and TiO₂, mixed-oxides coatings were also produced. During the late 1980s and 1990's, sol-gel technology also found uses in a variety of technology fields, such as biomedical applications. Numerous amount of literature work is available which cover the ceramic oxide system applications derived from the sol-gel route³⁴.

In 1989, sol-gel technology for powder and coating purposes was introduced in Australia by collective efforts of groups of scientists from University of Technology, Sydney, University of NSW, ANSTO, Monash University, DSTO and Silicon Technologies Pty Ltd (later Sustainable Technologies Pty Ltd) which were supported by ARC, ERDC and GIRD grants which gave rise to a large number of publications which covered a range of ceramics from titanates, ceramic superconductors, single and mixed oxides and calcium phosphate³⁵.

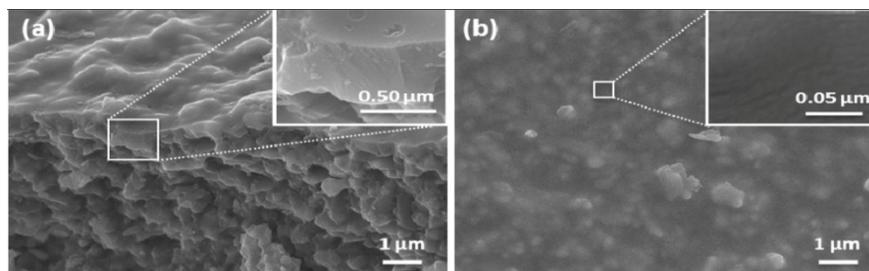


Figure-5

Sol-gel derived synthesized silica membrane and the underlying alumina substrate in a) Cross-section and b) top surface²⁹

Marikkannan M et al prepared metastable orthorhombic SnO₂ coating (figure-6) via sol-gel route which initiated the idea that the method of fabricating tin oxide is promising and in order to determine the viability of these films for various TCO applications further work is needed to analyze the electrical properties of the films³⁶.

Applications of sol gel derived thin films coatings: Electronic Films: Bulk materials generally are observed to have constant physical properties irrespective of their dimension. A material develops significant changes when it reaches nanoscale size. With the change in the surface area to volume ratio, As the surface area to volume ratio changes, different properties tend to appear such as localized surface Plasmon resonance in some noble nanoparticles, quantum confinement in semiconductor particles(Q-dots), superparamagnetism in metal oxide material and some nanocomposites and electrocatalytic properties. Memory devices, optoelectronic devices, and biosensors have been applied with all these new properties³⁷⁻³⁸.

Porous Films: Porous films have a wide variety of uses because of their large surface area. Some of these areas are solar cells

and surface reactions. For the areas involving large surface reactions, porous TiO₂ thin films with large surface areas are favourable³⁹.

Nanoparticle

Nanoparticle remains the most significant part in the creation of any nanostructure. Metallic nanoparticles have distinctive physical and chemical properties from mass metals (e.g., lower liquefying focuses, high specific surface ranges, optical properties, mechanical qualities and specific charges), properties that may demonstrate appealing in different modern applications⁴⁰. Different routes can be taken to prepare Nano hybrids namely sol gel, solvothermal, microwave, coprecipitation and aqueous techniques. Preparation of nano materials may be arranged into chemical and physical systems of substance. The physical methods are taking into account subpart of mass metals like mechanical smashing or pounding of mass metal, curve release between metal terminals, and so forth. Metal nanoparticles subsequently created are typically huge in size and have wide size distribution.

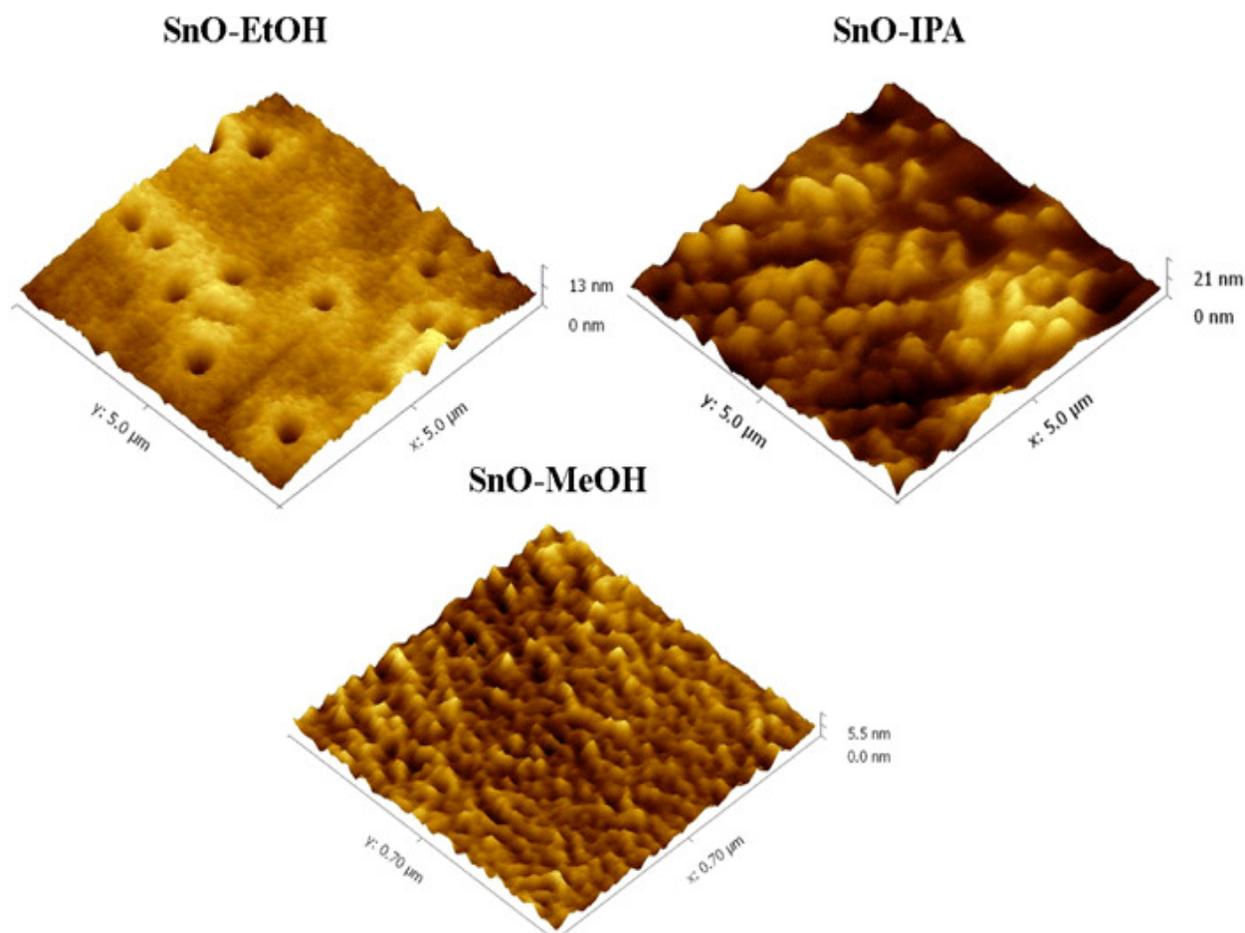


Figure-6
AFM images showing the morphology of sol gel derived Sn-O thin films

A few physical strategies have been accounted for the amalgamation of nanosized particles. These incorporate vapour build-up techniques, shower pyrolysis, mechanical misshaping, thermochemical disintegration of metal-natural antecedents in fire reactor, and other airborne procedures given name after the vitality sources connected to give the high temperature amid gas particle change⁴¹. Alteration of physiochemical properties can be done by varying their size i.e. particles change the color, by decreasing the size, semiconducting materials exhibit metallic properties and non magnetic particles become magnetic⁴². Sol-gel route to synthesize nanoparticles relatively needs less expensive instruments. In this method, particles are built up by molecule-by-molecule addition in the molecular synthesis. A controlled nucleation and particle growth is required during the process of nanoparticle as the particles easily form agglomerates and clumps. This technique is based on soft chemical processes chemistry at low temperature and pressure) which is why it has risen its interest in the nanosciences. In addition to that, it produces particles with constant composition, high purity, no toxicity and reproducibility. Also, their use is permitted in materials in contact with food and in pharmaceutical applications⁴³.

Nanohybrid

Hybrid as per material science means a material composing different materials together which were conventionally called composites. Other than the solvent, organic molecules can be added to the sol and become physically entrapped upon gelation in the cavities formed in the network. The reaction takes place under the standard conditions of the sol-gel process, namely pH of the system and the aqueous conditions. Hence, the hydrolysis of the organic groups becomes intolerable, but can be partially neglected if buffer solution is used which is necessary due to the entrapment of the biological molecules in the gel. Phase separation or leaching occurs due to the differences in polarity which is due to the unstable materials obtained in physical entrapment. Organic moieties like trialkoxysilanes can be chemically modified to overcome such problem. The unnecessary further linkages and co-condensation is the main cause of physical entrapment. Chemical linkage between the inorganic and organic components is the preferential route. Sometimes, it is necessary to perform a controlled phase separation between sol-gel particles and the entrapped molecules.

Starting materials with stable Si-C bonds are used for co-condensation reactions with tetraalkoxysilanes besides the entrapment of organic systems. Smaller species may also be formed in the organo trialkoxysilane based sol-gel process. Generally, organic moieties have a huge effect on the properties of the final hybrid product. The network density is reduced as the degree of condensation of a hybrid material prepared by trialkoxysilanes is generally smaller than in the case of tetraalkoxy silanes. Also, the functional group incorporates changes the properties of the final material⁴⁴. Bioactive hybrids

are applicable in bioreactors and biosensors in the field of biotechnology. They have high activity of enzymes, anti-bodies to perform certain specific reaction which is unlikely to happen via general chemical routes. Immobilization of active biospecies takes place in order save them from denaturation and for reuse. This bio-immobilization can be done via natural and synthetic polymers (polysaccharides, polyacrylamides, alginates, etc.) through entrapment. Inorganic materials such as sol-gel processed glasses and ceramics offer significant advantages over organic polymers. They exhibit better thermal, chemical stability and mechanical strength. Moreover they don't swell in most solvents preventing the leaching of entrapped biomolecules. A new kind of hybrid biosensor is developed based on change in enthalpy during the enzymatic oxidation of glucose recorded as a thermometric peak by a sensitive thermistor which has been recently described in order to detect glucose in fruit juice, Coca Cola and human blood serum. Hybrid sol-gel immunosensors have been developed for the analysis of pesticides⁴⁵.

Conclusion

Sol-gel technique intends to desirably control the dimensions of a material on a nanometer scale of from the initial stages of processing. Chemical processing, controlled high purity, and better homogeneity can be used to enhance the property of materials. This lower temperature processing technique is a major advantage over the conventional techniques of the nanoparticle synthesis. Other advantages of this process include net shape casting, film coating and fiber pulling.

Acknowledgement

The work has been supported by University Grant Commission, New Delhi, India, Major Research Project F. No 42-286/2013 (SR).

References

1. <http://www.spectraresearch.com/news.html>, (2015)
2. Verwey E.J.W. and Overbeek J.T.G., H. Kruyt, ed., Colloid Science, 1, Elsevier, Amsterdam, The Netherlands, (1948)
3. Hench L.L. and West J.K., *Chem. Rev.*, **90**, 33-72 (1990)
4. W. Ford, *Ceramics Drying*, Pergamon, New York, 1986
7. H. Dislich, *J. Non-Cryst. Solids*, **57**, 371, (1983)
5. H. Dislich, *J. Non-Cryst. Solids*, **57**, 371 (1983)
6. <http://homepages.rpi.edu/~plawsky/Research/Processing.html>, (2015)
7. Graham, T. Liquid diffusion applied to analysis. *Philos. Trans. R. Soc. Jpn*, **29**, 902 (1970)
8. Robinson, Arthur L, A chemical route to advanced ceramic, *Science*, **233**, 25-27 (1986)

9. Huang, Y., and Pemberton, J.E., Colloids and Surfaces A: Physicochem, *Eng. Aspects*, **360**, 175–183 (2010)
10. Matijevic E., Butterworth Heinemann, London, 39-59 (1994)
11. A.C Pierre, *Sol Gel Technology*, (2000)
12. Adv Polym Sci., 242: 29–89 Vladimir Aseyev, Heikki Tenhu, and Françoise M. Winnik, (2011)
13. Kistler S S, Coherent expanded aerogels, *J Phys Chem*, **36**, 52-64 (1932)
14. Sol-gel synthesis of solids by J. Livage, Encyclopedia of Inorganic Chemistry, R. Bruce King, John Wiley edition, New York, 3836-3851 (1994)
15. Mackenzie J.D., *Journal of Non-Crystalline Solids*, **100**, 162-168 (1988)
16. Deng Z, Wang J, Wei J, Shen J, Zhou B and Chen L, *J Sol Gel Sci Technol*, **19**, 677-680 (2000)
17. Venkateswara Rao A, Bhagat S.D, Hirashima H and Pajonk GM, *J Colloid Interface Sci*, **300**, 279-285 (2006)
18. El Rassy H, Buisson P, Bouali B, Perrard A, Pierre AC, *Langmuir*, **19**, 358-363 (2003)
19. Harrels JH, Ebina T, Tsubo N and Stucky G, *J Non-Cryst Solids*, **298**, 241-251 (2002)
20. Allie C, Pirard R, Lechloux AJ, Pirard JP, *J Non-Cryst Solids*, **246**, 216-228 (1999)
21. Budd, K. U, S. K. Dey, and D. A, *Material Research Society Symposium Proceedings*, **73**, 711-716 (1986)
22. Woodhead J.L, *Science of Ceramics*, **4**, 105-112 (1968)
23. Wymer R.G. and Coobs J.H., *Proceedings of the British Ceramic Society*, (7), 61-79 (1967)
24. Zarzycki J.A, Wright F. and Dupuy J., Martinus Nijhoff Publishers, Dordrecht, Netherlands. eds., Glass current issues, 203-223 (1985)
25. MacKenzie J.D, jji Larry L. Hench and Donald R, Ulrich, eds. Ultrastructure processing of ceramics, glasses, and composites. John Wiley and Sons, Inc., New York, New York, 15-26 (1984)
26. Tsionsky M., Gun G., Giezer V. and Lev O., *Anal. Chem.*, **66**, 1747-1753 (1994)
27. Fletcher J.M. and Hardy C.J., Application of sol-gel processes to industrial oxides, *Chemistry and Industry* (2), 48-51 (1968)
28. de Lange R.S.A., Keizer K. and Burggraaf A.J., *Journal of Membrane Science*, **104**, 81-100 (1995)
29. Elma M., Yacao C., D. Costa J.C. and Wang D.K., *Membranes*, **3(3)**, 136-150 (2013)
30. Gong K., Zhang M., Yan Y., Lei Su, Mao L., Xiong S. and Chen Y., *Anal. Chem.*, **76**, 6500-6505 (2004)
31. Ebelmen, *Ann. Chim. Phys. Ser.*, **57**, 319-355 (1846)
32. Roy D.M. and Roy R., *Am. Mineral*, **39**, 957-975 (1955)
33. Schroeder H., *Paint Varnish Prod.*, **55**, 31-46 (1965)
34. Chai C., Ben-Nissan B., Pyke S. and Evans L., *Mater. Manuf. Process*, **10**, 205–216 (1995)
35. Choi A.H. and Ben Nissan B., *Journal of crystalline Australian Ceramic Society*, **50**, 121-136 (2014)
36. Marikkannan M., Vishnukanthan V., Vijayshankar A., Mayandi J. and Pearce J.M., *Aip Advances*, **5**, 027122 (2015)
37. Benlarbi M., Farre C., Chaix C., Lawrence M.F., Blum L.J., Lysenko V. and Marquette C.A., *Synthetic Metals*, 2675–2680 (2010)
38. Sumio Sakka and Toshinobu Yuko, chemistry, spectroscopy and application of sol-gel glasses, ed R. Reisfeld, spring-verla, Berlin, 89 (1992)
39. Alan P.B., Use of sol-gels in the application of ceramic oxide thin films, (1987)
40. Horikoshi S. and Serpone N., microwaves in nanoparticles synthesis, wiley, (2013)
41. Tavakoli A., Sohrabi M. and Kargar A., 7 Institute of Chemistry, Slovak Academy of Sciences DOI: 10.2478/s11696-007-0014-7, (2007)
42. Gajewicz A., Puzyn T., Rasulev B., Leszczynska D. and Leszczynski J., nanoscience and nanotechnology-Asia, **1** (2011)
43. Lin H.P. and Chung Yang M., *Chem. Res.*, **35**, 927 (2002)
44. Schubert U., Hüsing N. and Lorenz A., *Chem. Mater.*, **7**, 2010–2027 (1995)
45. Livage J., Carodin T. and Roux C., Functional hybrid material, ed. P.Gomez-Romero, and C. Sanchez, Functional Hybrid Materials, Wiley-VCH, Weinheim, (2004)