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Sol Gel Process: An Overview to Synthesize Nanomaterial's

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ABSTRACT

This paper review for the effective approach to the synthesis of nanomaterials, design and preparation of nanoparticles with high functionality i.e., to fabricate nanomaterials which have the suitable properties for applications. The fabrication of nanomaterials of tailored properties involve the control of size, shape, structure, composition and purity of their constituents.Sol gel chemistry is a versatile tool that can be used to produce organic and inorganic hybrid materials that have properties that can be difficult to obtain from only inorganic and organic synthetic approaches.The solgel process is a wetchemical technique (also known as chemical solution deposition) widely used recently in the fields of materials science and ceramic engineering.Even small quantities of dopants, such as organic dyes and rare earth elements, can be introduced in the sol and end up uniformly dispersed in the final product. A solgel process offers several advantages over other methods, better homogeneity, controlled stoichiometry, high- purity, phase-pure powders at a lower temperature and flexibility of forming dense monoliths, thin films or nanoparticles**.** The purpose of this paper is to better understand the chemistry involved during the preparation of nanomaterials by sol gel method, in order to have a good control and fine properties of the final material.

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INTRODUCTION

Materials having structures and sizes that fall within the range of 1 to 100 nm are referred to as nanomaterials. Nanomaterials are associated with a diversity of uses within the medical field, for instance, nanoparticles in drug-delivery systems, in regenerative medicine and in biomaterials science and diagnostic systems.[1,2]

Fundamental to the success of materials science and technology is the availability of high-quality materials exhibiting specific tailor-made properties together with an appropriate shape and microstructure. Solution based methods especially water based methods offer numerous advantages. Cheap and easy to handle precursors, low cost, simple equipments, low energy input and the eco-friendly nature are few of them. Moreover they allow the easy tailoring of synthesis parameters throughout the whole process, which may be exploited to achieve a more precise control of composition, shape and size of the resulting material. Since the synthesis route determines the properties of the material, the preparation method chosen is very important when designing materials for specific applications. And therefore sol gel routes for the synthesis of nanostructures are a valuable alternative to conventional processing and gas phase synthesis, with known commercial applications. Through this process, homogeneous inorganic oxide materials with desirable properties of hardness, optical transparency, chemical durability, tailored porosity, and thermal resistance, can be produced at room temperatures, as opposed to the much higher melting temperatures required in the production of conventional inorganic glasses. [3-5]

Sol-gel related methods have been successfully extended to the synthesis of selected carbides, nitrides, and sulfides. Sulfides have received the most attention among these materials because of their catalytic[6-11], electronic-[12,13] and optical[14-15] properties. Other potential applications include optical materials in IR windows, solar cells, lasers, phosphors, and light emitting diodes[14-16]. Sol-gel routes are attractive, as they provide a solution based approach to many simple and complex materials[17-20]. The reaction outcome can often be influenced by careful control of several reaction variables.

I. SOL-GEL TECHNIQUE

Sol gel technology, due to its simplicity and low cost, has gained much notoriety in the glass and ceramics field. The sol gel process produces a variety of inorganic networks from precursors such as silicon alkoxides, titanium alkoxides and other monomer precursors, based on the hydrolysis and condensation of metal or non metalalkoxides. Futhermore, sol gel processing can produce interconnecting inorganic and organic networks. Such methods are used primarily for the fabricationof materials (typically metal oxides) starting from a colloidal solution (*sol*) that acts as the precursor for an integrated network (*gel*) of either discrete particles or network polymers. Typical precursors are metalalkoxides and metal salts (such as chlorides, nitrates and acetates), which undergo various forms of hydrolysis and polycondensation reactions [21].This can be accomplished in any number of ways. The simplest method is to allow time for sedimentation to occur, and then pour off the remaining liquid. Centrifugation can also be used to accelerate the process of phase separation. Removal of the remaining liquid (solvent) phase requires a drying process, which is typically accompanied by a significant amount of shrinkage and densification. The rate at which the solvent can be removed is ultimately determined by the distribution of porosity in the gel. The ultimate microstructure of the final component will clearly be strongly influenced by changes imposed upon the structural template during this phase of processing.

The sol is made of solid particles of a diameter of few hundreds nanometers suspended in a liquid phase. Then the solid particle condensed in a new phase (gel) in which a solid macro molecules is immersed in a liquid phase (solvent).

This process occurs in liquid solution of organometallic precursors which by means of hydrolysis and condensation reactions, leads to the formation of a new phase.

M-O-R + H_2O → M-O-H + R-OH (hydrolysis)

M-OH + HO-M → M-O-M + H_2O (water condensation)

R- O-H + HO-M → M-O-R + H_2O (alcohol condensation)

A thio sol-gel process in which metal salt/complex act as the metal source reacts with H_2S for thiolysis reaction similar to H_2O for hydrolysis reaction in the conventional sol-gel process, as follows:

M - OR + H_2O → M-OH + R-OH

M - OR + H_2S → M-SH + R-OH

The development and the current status of the solution-Sol-Gel or the Sol-Gel (SG) process for preparation of different ceramic materials in various (i.e., bulk, powder, wire, thin film, aerogel, etc.) forms and shapes have been outlined. In view of the much greater attention having been paid to oxide-ceramics, the chemistry of the main precursors being employed for them, i.e., metal alkoxides, is briefly described followed by an indication of the efforts being made to elucidate (by the latest physico-chemical techniques) the mechanism of the different steps involved, e.g. mixing of solutions; conversion from solution to sol and then to gel and finally sintering the gel to the desired ceramic material, in the Sol-Gel Procedure. A brief account is also presented of the efforts being made to extend the applications of the technique to new demands such as those of super-conducting materials.

The much lower temperature(s) of operation involved in the process facilitate the applications of the SG technique to the Organically Modified Ceramics (Ormocers) and other materials suitable for applications in areas like non-linear optics and bio-systems. The SG technique is now being rapidly extended to many other types of materials such as nitrides and sulphides. Finally, an attempt has been made to peep into the future potential of the fastly developing SG processes[22].

General preparation of sol gel[23-26]:

In sol gel process initially a stable colloidal solution called sol is formed. The sol is a liquid suspension of solid particles ranging in size from 1 nm to 1 micron. It can be obtained by hydrolysis and partial condensation of precursors such as an inorganic salt or a metal alkoxide. The further condensation of sol particles into a three dimensional network produces a gel material. The gel is a diphasic material in which the solids encapsulate the solvent. The molecular weight of the oxide species produced continuously increases. The materials are referred to aqua sol or aqua gels when water is used as a solvent and aquosol or alcogel when alcohol is used. The encapsulated liquid can be removed from a gel by either evaporative drying or with supercritical drying /extraction. The resulting solid products are known as xerogel and aerogel respectively. When gels are dried by evaporation, the dried product is called xerogel. When the gels are dried by supercritical drying, the dried gel is called aerogels. The aerogel retains high porosity and has very high pore volume.

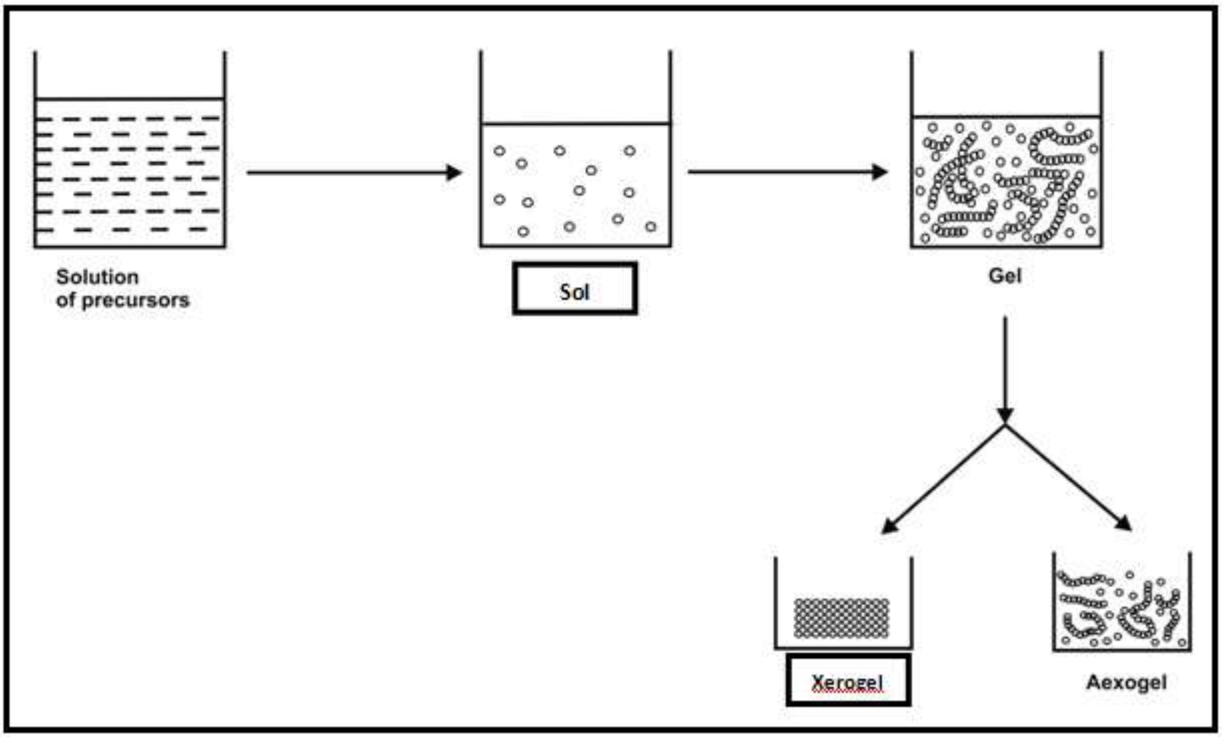

Fig1. General scheme of preparation by sol-gel method

The sol gel method is distinguished from other routes of material preparation from solutions or melts such as precipitation and crystallization by two main characteristics:

1. Formation of clear colloidal solution due to primary condensation of dissolved molecular precursors.
2. These colloidal particles merge during subsequent gelation stage into polymeric chain by chemical bonding between local reactive groups at their surface.

Both stages are controlled by condensation chemistry that can include as a first step, hydrolysis of hydrated metal ions or metal alkoxides molecules. The condensation chemistry in this case is based on olation/oxolation reactions between hydroxylated species. Olation is a condensation process in which a hydroxyl bridge "–OH--" bridge is formed between two metal centers.

The oxolation is a condensation reaction in which an oxo bridge "-O-" is formed between two metal centers.Activation and polycondensation: Metal alkoxides are used as precursors in sol-gel operation. Metal alkoxides are most extensively used as these are commercially available in high purity and their solution chemistry is well documented. For preparation of alumina and zirconia aluminiumpropoxide and zirconium propoxide are used respectively as precursors.

The metal alkoxides are hydrolysed in alcohol solution containing a controlled amount of water. The sol gel chemistry can be represented by following two reactions:

$$\text{Hydrolysis:} \quad \text{-M-OR} + H_2O \longrightarrow \text{-MOH} + \text{ROH}$$

$$\text{Condensation:} \quad \text{-M-OH} + \text{XO-M-} \longrightarrow \text{-M-O-M-} + \text{XOH}$$

Where M= metal ; X = H or R (alkyl group)

This is a very simplified representation without giving details of the intermediate or end products. However this gives an idea of formation of three dimensional gel network coming from the condensation of partially hydrolyzed species.

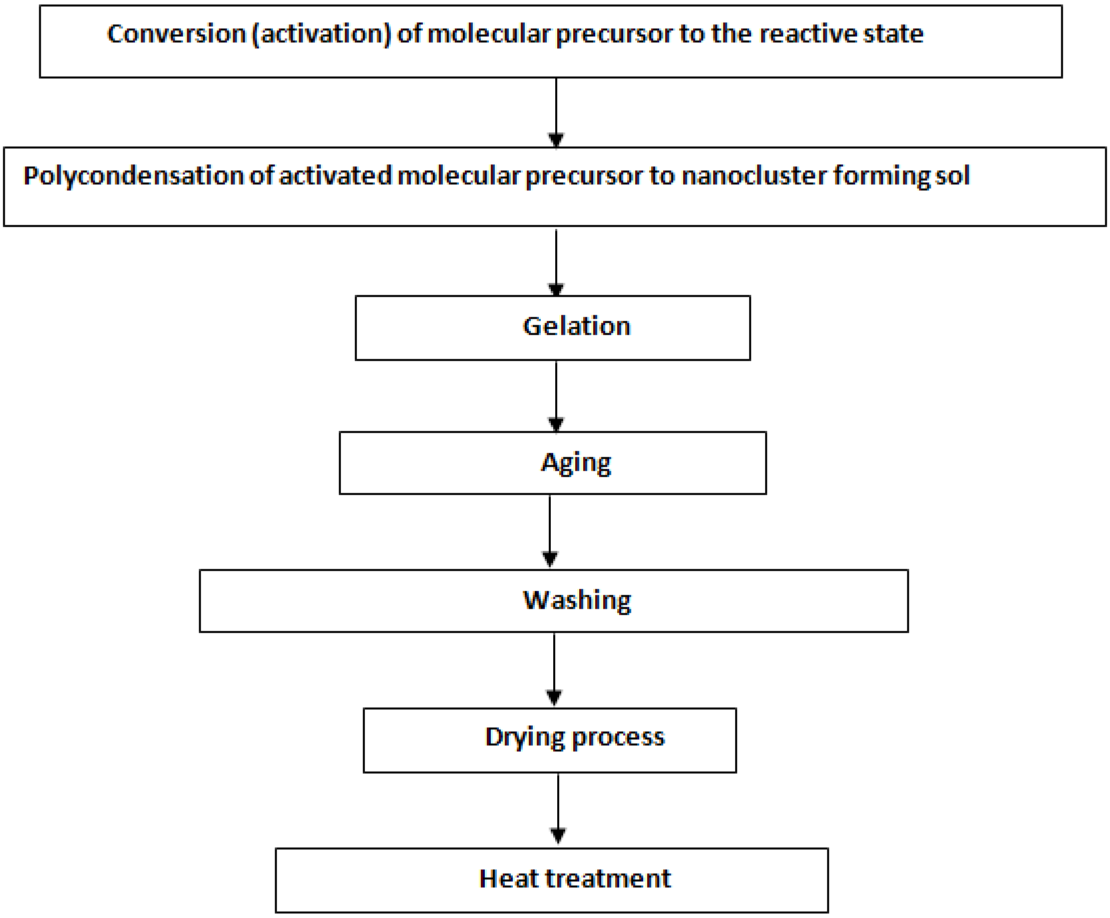

Fig 2. Steps in sol gel processing

Parameters affecting any of the two reactions will affect the properties of the final product. Two of the main parameters that affect are (1) amount and rate of water addition and (2) pH of the solution. The amount of water added is expressed in terms of hydrolysis ratio 'h' and defined as

$$h = \frac{\text{moles of water}}{\text{moles of metal alkoxide M(OR)}_m}$$

After a period of time the sol experiences a transition from liquid solution to a cross-linked gel state where it can support an elastic stress. This period of time is known as gel time or gelation time, and during this time the viscosity of the solution undergoes a rapid increase corresponding to the transition from a viscous fluid to an elastic gel. At the end of gelation there is a continuous phase containing a structure that reflects formation and branching of particles under specific growth conditions. The formation of a network results in entrapping of the solution. The gel structure is determined by the ionic character of the M-O bond and the relationship between the hydrolysis and condensation rate.

Aging: After visible formation of gel, processing proceeds to the aging step where the structure and the properties of the formed network continue to change up to the point that yields the target density. It represents the time between the formation of the gel and the removal of solvent. As long as the pore liquid remains in the matrix, a gel is not static and can undergo many transformations. This step includes four processes: polycondensation, syneresis, coarsening, and phase transformation.

Polycondensation between surface functional groups continues to occur after the gel point. This process is actually desirable as it leads to a more cross-linked network that is mechanically stronger and consequently easier to handle. However, extensive condensation can lead to shrinking of the gel to such an extent that the solvent is actually expelled in a phenomenon called syneresis. Parameters that affect this process include temperature, time, and pH of the pore liquid. However, studies of these effects are still very qualitative.

A typical preparation of zirconia aerogel in which zirconium propoxide is used as precursor. The sol prepared from precursor solution is aged for 2h and then supercritically dried. In this example calcination is done in two steps.

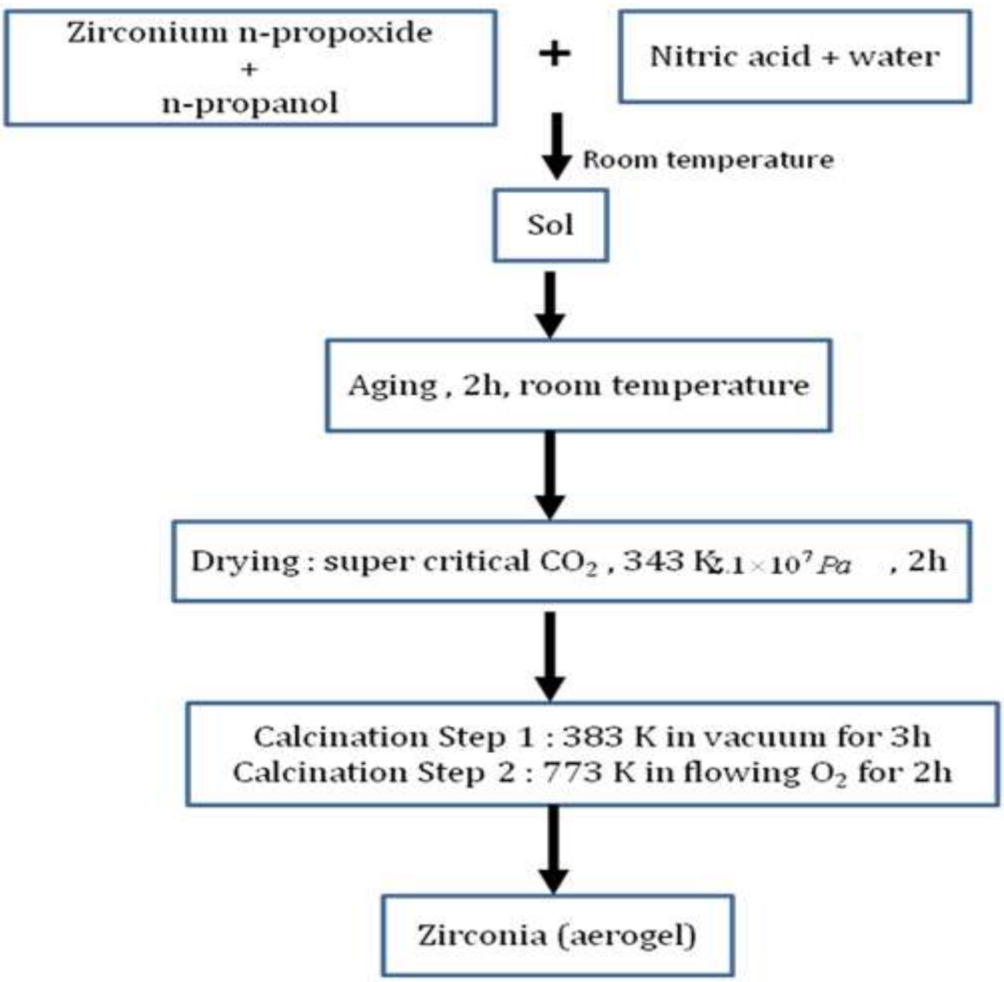

Fig 3. Sol-gel parameters in preparation of zirconia aerogels

II. APPLICATION OF SOL GEL TECHNIQUES

Sol- gel technology has shown its merits in the preparation of multi-component oxides and thin films: high purity, stoichiometry and chemical homogeneity, microstructure control, atomic scale mixing, large compositional flexibility and low temperature viscous sintering. The sol-gel approach is a cheap and low-temperature technique that allows for the fine control of the product's chemical composition. It can be used in ceramics processing and manufacturing as an investment casting material, or as a means of producing very thin films of metal oxides for various purposes. Sol-gel derived materials have diverse applications in optics, electronics, energy, space, (bio)sensors, medicine (e.g., controlled drug release), reactive material and separation (e.g.,chromatography) technology[27-29] .Metal sulfides are used as catalysts for hydrodesulfurization in the petroleum industry, as lubricants, and as electrodes in lithium batteries[30-32].Another advantage of sol-gel methods is the wide range of accessible shapes, which include fine powders, fibers, thin films, xerogels, aerogels, and monoliths[33].

The specific use of sol gel produced materials is derived from the various materials shapes generated in the gel state, i.e., monoliths, films, fibres and mono-sized nano powders. Many specific applications include optics, protective and porous films, optical coatings and so on.

III. SCOPE OF PRESENT INVESTIGATION

A careful survey of the literature suggest that it is possible to synthesize complexes of various metals with nitrogen, sulfur and oxygen donor ligands which might serve as precursor of their sulfides, oxides and nitrides by sol gel route and formation of desired nanoparticles.These derived materials have diverse applications in optics and electronics.

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