Chapter I


1.1 Introduction to Nanomaterials

Nanomaterials are materials with morphological features smaller than 100 nm in at least one dimension. Materials reduced to the nano scale can show very different properties compared to what they exhibit on a macro scale, enabling unique applications. For instance, opaque substances become transparent (copper); inert materials become catalysts (platinum, gold); stable materials turn combustible (aluminum); solids turn into liquids at room temperature (gold) and insulators become conductors (silicon). Unique aspect of nanotechnology is the vastly increased ratio of surface area to volume, which opens new quantum mechanical effects. Nanoparticles can comprise a range of different morphologies including nano tubes, nano wires, nano fibres, nano dots and a range of spherical or aggregated dendritic forms. Interest in the unique properties associated with materials having structures on a nanometer scale is increasing at an exponential rate.¹ These materials have found application in a wide range of industries including electronics, pharmaceuticals, chemical-mechanical polishing, catalysis, and it is likely that the next few years will see a dramatic increase in the industrial generation and use of nanoparticles.²³ Using a variety of synthesis methods, it is
possible to produce nanostructured materials in the form of thin films, coatings, powders and as bulk materials.

1.2 Nanoporous Materials

A solid material that contains cavities, channels or interstices can be regarded as porous. Porous materials are of great interest in various applications, ranging from catalysis, adsorption, sensing, energy storage and electronics owing to their high surface area, tunable pore size, adjustable framework and surface properties. The specific surface area can reach values of up to several thousand square meters per gram, depending on the material. The behaviour and performance of such materials can be determined by many characteristics such as surface area, porosity and pore size distribution. Physical properties such as density, thermal conductivity and strength are dependent on the pore structure of the solid. Porosity influences the chemical reactivity of solid and the physical interaction of solids with gases and liquids. High surface area porous materials are of great importance especially as catalyst, catalyst supports, thermal insulators, sensors, filters, electrodes and burner materials. The science and technology of porous materials has progressed steadily and is expanding in many new directions with respect to processing methods and applications. Many synthetic pathways have been reported for the synthesis of porous materials, either with a disordered pore system or ordered with various structures, which can meet the demands of the
target application." Porous ceramic materials are synthesized by various methods such as polymer sponge method, foam method, leaching, sintering of particles having a range of sizes, emulsion templating, gel casting, injection moulding, sol-gel process and heat treatment of a ceramic precursor containing carbon rich compound.

**Classification of Pores**

Based on the accessibility of an external fluid, pores can be classified into closed pores and open pores. Closed pores are totally isolated from their neighbours and surface of the particle. They influence macroscopic properties such as bulk density, mechanical strength and thermal conductivity, but are inactive in processes such as fluid flow and adsorption of gases. Pores which have a continuous channel of communications with external surface of the body are called open pores. In Fig. 1.1 region ‘a’ represents the closed pores, and regions such as b, c, d, e and f represent open pores.

![Classification of pores](image)

**Fig. 1.1. Classification of pores**
In the figure ‘b’ and ‘f’ (one end) are described as blind or saccate pores. Based on the pore size, IUPAC classified porous materials into microporous, mesoporous and macroporous as given in the Fig. 1.2.

**Fig. 1.2.** IUPAC classification of pores

### 1.3 Sol-Gel Synthesis of Inorganic Oxides

Sol-gel process is a colloidal route used to synthesize nanomaterials with an intermediate stage including a sol and/or a gel state. Sol is a stable suspension of colloidal particles in a liquid medium and the dimension of the particles in the solid phase is between 1 and 100 nm. Gel is a porous three dimensionally interconnected solid network that expands in a stable fashion throughout the liquid medium.

The chemical reactant, which contains the cation ‘M’ present in the final inorganic sol or gel, is called chemical precursor, whose chemical transformations are complex and involve a competition at the molecular level between the reaction responsible for the formation of open structures and the one leading to dense solid.
The same reactions are responsible for the controlled dispersion of dense colloidal particles in a sol or their agglomeration into a gel. Metal salts and alkoxides are the two main groups of precursors. The general formula of metallic salt is $M_{n}X_{m}$ where ‘$M$’ is the metal; ‘$X$’ is an anionic group. $M(OR)_{n}$ is the general formula of alkoxides. Sol-gel precursors undergo chemical reactions both with water and other species present in the solution. In sol-gel processing, very small colloidal particles are first formed in solution by hydrolysis of organic compounds of metals to the hydrous oxides. These particles are only 3–4 nm in size. These very small particles link together in chains and then 3–D networks that fill the liquid phase as a gel.6 These sol can be casted in any desired shape, with dimensions enlarged to allow for shrinkage during drying and sintering. The precursor sol can be either deposited on a substrate to form a film (e.g. by dip-coating or spin-coating), cast into a suitable container with the desired shape (e.g. to obtain monolithic ceramics, glasses, fibers, membranes, aerogels), or used to synthesize powders (e.g. microspheres, nanospheres). Fig. 1.3 represents sol-gel process and its various products. Advantages of sol-gel process are increased homogeneity, high purity, low processing temperature and high surface area of the gels or powders obtained. The inherent usefulness of this approach is largely due to the ease at which sol-gel derived materials can be prepared, modified, and processed. The mild reaction conditions afford an opportunity to incorporate various molecules such as proteins,
enzymes, dyes, organic, and organometallic reagents into glass composites. Sol-gel derived materials have diverse applications in optics, electronics, energy, space, biosensors, medicine (controlled drug release) and separation (chromatography) technology. Thin films and coatings find application in optics, electronics, protective coatings and porous thin films. Porous gels and membranes find application in filtration, separation, catalysis and chromatography. Furthermore, the average pore size, pore size distribution, surface area, refractive index and polarity of the resultant matrix can also be controlled and tailored via manipulations in the sol-gel processing conditions.

Fig. 1.3. Sol-gel process and its various products
1.4 Sol-Gel Process as Applied to Silica

Silica gels are most often synthesized by hydrolyzing monomeric, tetrafunctional alkoxide precursors employing a mineral acid or base as a catalyst. Most common tetraalkoxysilanes used in the sol-gel process are tetraethoxysilane [TEOS, (SiOC$_2$H$_5$)$_4$] and tetramethoxysilane [TMOS, Si(OCH$_3$)$_4$]. Following reactions are used to describe the sol-gel process of silica.

\[
\begin{align*}
\text{Si-OH} + \text{ROH} & \rightarrow \text{Si-O-RO} \\
\text{Si-OH} + \text{H}_2\text{O} & \rightarrow \text{Si-OH} + \text{ROH} \\
\text{Si-O-H} + \text{Si-OH} & \rightarrow \text{Si-O-Si} + \text{H}_2\text{O}
\end{align*}
\]

The hydrolysis reaction replaces alkoxide groups with hydroxyl groups. Subsequent condensation reactions involving the silanol groups produce siloxane bonds and the by-products, alcohol or water. Under most conditions, condensation commences before hydrolysis is complete. Since water and alkoxysilanes are immiscible, a mutual solvent such as alcohol is normally used as a homogenizing agent. In order to reduce the reactivity of the alkoxide precursor, organic functional groups can be introduced into the siloxane network. This type of alkoxide precursors are known as organoalkoxysilanes. Examples for this type of precursors are methyltrimethoxysilane, trimethylethoxysilane etc. Organically
modified silicates represent hybrid systems in which several precursor types are combined. Schmidt and coworkers developed silicate products with unique properties by combining tetraalkoxysilanes with alkyl substituted and organofunctional alkoxysilanes.\(^8\)

\[
\text{Si(OR)}_4 + R_2 \text{Si(OR)}_2 + Y'R' \text{Si(OC}_2\text{H}_3)_3
\]

R is an alkyl group, R is an alkylene and Y is an organo-functional group such as – \((\text{CH}_2)_3\text{NH}_2\), \((\text{CH}_2)_3\text{NHCO-O-NH}_2\) etc. Unlimited number of chemical and structural modifications is possible in such hybrid systems.\(^9\)

The surface and structural characteristics of the silica gels are affected by various parameters that control the rate of hydrolysis and condensation and these can be summarized into three categories:\(^{10}\)

a) Compositions: Type of starting materials, quantity of water, catalysts and solvents.

b) Reactions (up to gel formation): Rate of mixing, reaction temperature and gelation schemes.

c) Process variables (after gel formation): Type of dehydration, drying temperature and heating.

Mukherjee et al. reported that the molar ratio of \(\text{H}_2\text{O}\) to alkoxides and pH values played a significant role in determining reaction rates.\(^{11}\) Sakka et al. found that the same parameters influence the morphology and composition.\(^{12}\) It has been
reported that the changes in pH values during the sol preparation stage would significantly affect the appearance of sample, porosity, density, viscosity, gelation time, and activation energy.\textsuperscript{13-14} The variations of surface area, pore volume, and pore size distribution were discussed in their studies. Investigations on the effect of different types of catalysts such as HF, HCl, HNO\textsubscript{3}, H\textsubscript{2}SO\textsubscript{4}, HOAc and NH\textsubscript{4}OH during the sol-gel process, which lead to different physical gel structures due to different reaction mechanisms were also studied.\textsuperscript{15,16} Furthermore, Ro et al. found that acidic catalysts were related to the formation of slit-shaped microstructures and cylindrical micropores were obtained by the use of basic catalysts.\textsuperscript{17} Many studies have been carried out on the effect of gelation temperature on the sol-gel process of silica.\textsuperscript{18-19} Increase in the gelation temperature could make the gelation process shorter. Yasumori et al. reported an increase of 50\% in surface area of silica gel by increasing the dehydration temperature.\textsuperscript{20} Lee et al. claimed that increase of drying temperature would cause the pore diameter to become bigger, with a wider distribution.\textsuperscript{21} Acid catalyzed hydrolysis with low H\textsubscript{2}O:TEOS ratio produces weakly branched polymeric sols, where as base catalyzed hydrolysis with large H\textsubscript{2}O:TEOS ratio produces highly condensed particulate sols. Intermediate conditions produce structures intermediate to these extremes.\textsuperscript{16}

Hayashi et al. studied the effect of solvents on the properties such as bulk density, specific surface area, pore size distribution and pore volume of the dried
Depending upon the pH either protonated or deprotonated silanols are involved in the condensation mechanism. Protic solvents hydrogen bond to nucleophilic deprotonated silanols and aprotic solvents hydrogen bond to electrophilic protonated silanols. Hence protic solvents retard base-catalyzed condensation and promote acid catalyzed condensation where as aprotic solvents have the reverse effect. Shukla et al. have studied the effect of ethanol on the morphology, oxide content and density of the TEOS derived gels. Steric factors exert great effect on the hydrolytic stability of alkoxy silanes. Hydrolysis rate is lowered the most by branched-alkoxy hydroxyl or bridging oxygen substitution. The condensation rate of triorganosilanols decreases with increase in the length or branching of the chain of the alkyl radical, or if aromatic groups are present. In the case of tetra functional alkoxides, substituents that increase steric crowding in the transition state will retard condensation. Although inductive effects are important, in the acid catalyzed condensation of dialkyl silanols, steric effects predominate over inductive effects.

1.5 Aging of Gels

Aging is the process of keeping the gels in various solutions for a period of time in order to increase the strength of the gel network so that cracking of gels during drying can be prevented. The chemical reactions that cause gelation continue long after gel point strengthening, stiffening and producing shrinkage of
The composition, structure and properties of gel change during aging. The changes that occur during aging are categorized into three.

1) Polymerization: Increase in connectivity of the gel network by condensation reactions. Schematic representation of polymerization of silica is provided as Fig. 1.4.

2) Coarsening: Process of dissolution and reprecipitation driven by differences in solubility between surfaces with different radii of curvature.

3) Syneresis: Shrinkage of the gel and the resulting expulsion of liquid from the pores.

1.6 Drying of Gels

The microstructure of a xerogel is the consequence of gelation, aging and drying. During drying the gel can initially shrink to accommodate loss of pore fluid maintaining the liquid-vapour interface at the exterior surface of the gel. At the final stage of drying liquid-vapour menisci recede into the gel interior. The magnitude of the capillary pressure, \( P_c \), exerted on the network depends on the surface tension of the liquid, \( \gamma \), the constant angle \( \theta \), and the pore size, \( r \):

\[
P_c = 2 \gamma \cos \theta / r
\]

If the pore size is very small, the capillary pressure will be large. The original gel network collapses due to this pressure. Aging may be used to reduce the extent of collapse of the gel structure during drying.
1.7 Aerogels

Aerogels are a fascinating class of nanoporous materials derived by sol-gel technique which possess sophisticated potentialities for a range of applications. They possess unique properties such as high porosity, large inner surface area, low density, small index of refraction, low sound velocity, low thermal conductivity and low dielectric constant. Aerogels are quite transparent since they scatter light weakly because of the extremely small particle and pore sizes. Important structural properties of aerogels are provided in Table 1.1.
Aerogels find applications as pesticides, in cosmic dust capture, waste water treatment, moulds for casting aluminium metal, aerocapacitors, absorbing media for dessication, heat storage device for automobiles, encapsulation media, hydrogen fuel storage material, ideal dielectric for ultra fast integrated circuits, thermal insulators, fillers, particle detectors, catalysts, gas sensors, light guides, capacitors. Many reviews on aerogel were also published with more focused on the applications of aerogels. Synthesis of aerogel starts with the controlled

<table>
<thead>
<tr>
<th>Property</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk density (g/cc)</td>
<td>0.003-0.500</td>
</tr>
<tr>
<td>Skeletal density (g/cc)</td>
<td>1.700-2.100</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>80-99.8</td>
</tr>
<tr>
<td>Mean pore diameter(nm)</td>
<td>20-150</td>
</tr>
<tr>
<td>Inner surface area (m^2/g)</td>
<td>100-1600</td>
</tr>
<tr>
<td>Refractive index</td>
<td>1.007-1.24</td>
</tr>
<tr>
<td>Thermal conductivity (in air 300)(w/(mk))</td>
<td>0.017-0.021</td>
</tr>
<tr>
<td>Modulus of elasticity (mpa)</td>
<td>0.002-100</td>
</tr>
<tr>
<td>Sound velocity c₁ (m/s)</td>
<td>&lt;20-800</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>1-2 (18-40 GHz)</td>
</tr>
</tbody>
</table>
conversion of a sol into a gel. The growth of clusters or polymer chains from a chemical solution occurs initially and these primary entities cross-link leading to the formation of a coherent network-still embedded in a liquid. The structure of aerogel is characterized by well accessible, cylindrical branched mesopores. Nitrogen adsorption studies, mercury porosimetry, microscopic techniques and scattering techniques (SAXS and SANS) are used to explore the structure of aerogels. Schematic diagram of aerogel structure is presented as Fig. 1.5. When a silica aerogel monolith breaks under force only secondary particle lose contact with one another while primary particle remains undisturbed. So the mesoporous space between these particles would be maintained. The silica aerogels exhibit microstructures consisting of loosely interconnected silica particles which form an open network.

![Fig. 1.5. Structure of aerogel](image)

The first aerogels were made by S. S. Kistler in 1931 from a water glass based recipe. Later Teichner et al. improved this sol-gel process. They
Silica form a coherent network embedded in alcohol. This alcogel was then successfully dried under hypercritical conditions ($T_c=239^\circ\text{C}$, $P_c=81$ bar). Using a two step sol-gel process and CO$_2$ drying, a group at Lawrence Livermore National Laboratory (LLNL) prepared ultra low density aerogels with densities as low as 3 Kg/m$^3$. The potential of the material was only widely recognized in the 1970's when the aerospace industry was looking at the possibility of developing extremely light thermal insulator. Further developments resulted in using aerogel as insulator in pathfinder mission to mars, for insulating the sensitive electronics from harsh temperature of mars. Conventional method of synthesis of aerogel is by a sol-gel process followed by supercritical drying of the wet gel in an autoclave. A schematic diagram which shows the process of synthesis of aerogel is provided as Fig. 1.6. During initial stages of drying, the capillary forces caused by the evaporation of solvents from pores in the gel, create an overall drying stress and local differential stresses owing to non uniform pore size distribution. Silica aerogels are ultra pure gels derived by hydrolysis-condensation reaction of silica alkoxide or salts.
1.7.1 Supercritical Drying

Supercritical drying involves the process of drying a wet gel in an autoclave above the critical temperature and pressure of its solvent. At the critical point of drying there is no longer any distinction between the liquid and vapour phases, and there is no liquid-vapour interface or capillary pressure. The resulting gels called...
Aerogels have about 99% porosity, extremely low densities and a high inner surface area. A schematic representation of supercritical drying is provided in Fig.1.7. At the critical point \([T_c, p_c]\) the density of the liquid and the gas are equal. Supercritical drying can be performed along path A or B. However, this technique is expensive and hazardous, and results in fragile aerogels having low strength. Table 1.2 provides supercritical constants of some solvents.

![Fig. 1.7. Schematic representation of supercritical drying](image)

**1.7.2 Subcritical Drying**

Subcritical drying technique, a less expensive method for the synthesis of aerogel, which involves controlled solvent exchange, aging and surface modification is evolving as a promising technique for the synthesis of aerogel at ambient temperature and pressure.
Table 1.2. Supercritical constants of some solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Tc (°C)</th>
<th>Pc (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>240</td>
<td>7.9</td>
</tr>
<tr>
<td>Ethanol</td>
<td>243</td>
<td>6.3</td>
</tr>
<tr>
<td>Acetone</td>
<td>235</td>
<td>4.7</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>235</td>
<td>4.7</td>
</tr>
<tr>
<td>H₂O</td>
<td>374</td>
<td>22.1</td>
</tr>
<tr>
<td>CO₂</td>
<td>31</td>
<td>7.3</td>
</tr>
</tbody>
</table>

Ambient pressure methods for silica aerogels include surface modification, network strengthening and use of DCCAs. The basic concept of this technique is to improve the strength and stiffness of the gel network and avoid shrinkage or crack during drying.⁴⁶ The extent of shrinkage during drying is governed by the capillary pressure exerted by the pore fluid and the modulus of the solid matrix. Solvent exchange with a low surface tension liquid can reduce the capillary pressure.⁴⁷ Haereid et al. reported that aging of silica gel in a silane solution increase the strength and stiffness of the gel network.⁴⁸ Their study showed that an increase in aging time and pH improve the mechanical strength of the gel network due to dissolution-reprecipitation reactions of silica monomers.⁴⁸ Einarsrud et al. investigated the structural development of silica gels agend in TEOS.⁴⁹ They found that primary particles and cluster size increases when silica is precipitated from the aging solution. Effect of aging time, temperature and concentration of
aging solution on the porosity characteristics of subcritically dried silica aerogels were reported.\textsuperscript{50-51} The investigation showed that best concentration of TEOS in the aging solution and time of aging were 80\% and 48 h respectively. As the temperature of aging increased the bulk density decreased whereas the surface area and pore volume increased. Haerel\textit{t al.} investigated the effect of aging alcogels in water and found a maximum in both modulus and modulus of rupture. This was independent of the aging temperature, but the aging time required to reach the maximum decreased with increasing temperature.\textsuperscript{52} Surface modification with various silylating agents avoid condensation reactions during drying.\textsuperscript{53} Deshpande\textit{et al.} developed a new method for synthesis of aerogel, in which the wet gel is washed with an aprotic solvent, reacted with trimethylchlorosilane (TMCS) and then dried at ambient pressure.\textsuperscript{53} This treatment minimizes shrinkage of the gel by a reduction in the surface tension of the solvent and the contact angle between the solvent and the surface of the silica network. Since neighbouring surface organic groups are chemically inert and detach with little activation energy, the gel is able to re-expand (spring back effect). Rao\textit{et al.} prepared two step processed ambient pressure dried silica aerogel with improved properties in terms of density, volume shrinkage, thermal conductivity, hydrophobicity and optical transmission, at ambient pressure, with TEOS precursor and hexamethyldisilazane (HMDS) as silylating agent.\textsuperscript{54} The best quality silica
aerogels was obtained with the molar ratio of TEOS:HMDS at 1:0.36. They have also studied the effect of silylating agents on properties of silica aerogels prepared by ambient drying and reported that by using the TMOS precursor, TMCS resulted the best quality silica aerogels in terms of monolithicity, visual transparency and lowest density.\textsuperscript{55} Schwertfeger et al. developed a one-step process in which solvent exchange and surface modification were performed simultaneously using a HMDS/TMCS solution.\textsuperscript{56} Kim\textsuperscript{57} and Lee\textsuperscript{58} used a one step solvent exchange/surface modification process using IPA/TMCS/n-Hexane solution. Use of organic additives termed drying control chemical additives (DCCA) to alkoxide solutions is another approach to obtain monolithic aerogel at ambient conditions.\textsuperscript{59} DCCA controls the rate of hydrolysis and condensation reactions, pore size distributions, vapour pressure of pore liquid and hence the drying stresses. If a uniform scale of structure obtains during gelation, it will result in uniform growth of the network during aging. This will improve the strength of the gel and its ability to resist drying stresses.\textsuperscript{60-61} Polyethyleneglycol (PEG) has been used by many researchers as a porogen.\textsuperscript{62-63} They claimed that high concentrations of PEG weaken the solid matrix, whereas small concentrations of PEG strengthen the matrix. Reetz et al. used additives such as polyvinylalcohol and PEG as biocatalyst supports, and found that the lipase activity was significantly enhanced in the presence of these additives.\textsuperscript{64} Rao et al. used glycerol as an additive and achieved
a narrow and uniform distribution of pores. Even though many approaches have been attempted on subcritical drying lot of experimental parameters are still to be optimized for the commercialization of the process.

1.8 Inorganic-Organic Hybrids

Inorganic and organic components mixed at the nanometric scale in virtually any ratio are called inorganic-organic hybrid. The combination of organic and inorganic molecules in different formulations can give rise to a number of hybrid materials whose properties can be tailored, even to mimic nature. Inorganic-organic hybrid materials possess well defined pore structure, highly accessible functional groups and controlled surface reactivity. Inorganic-organic hybrid materials are subject of intense research in the field of contemporary material chemistry as these materials exhibit excellent electrical, magnetic and optical properties. Sol–gel process is very attractive and versatile to prepare inorganic or hybrid films with tunable thickness. Moreover, mild synthetic conditions provided by sol–gel chemistry are advantageous for the incorporation of organic components into the inorganic network, allowing the preparation of a variety of hybrid architectures. Two approaches are widely practiced for the incorporation,

1. Mixing of an organic polymer with a metal alkoxide such as tetraethoxysilane.
2. Introduction of organosilyl group into the organic polymer prior to the sol-gel reaction with metal alkoxide such as tetraethoxysilane.

Usually inorganic-organic hybrids prepared by a sol-gel process show unique mechanical properties such as high ductility, low elastic modulus and high mechanical strength. Typical advantages of organic polymers are flexibility, low density, toughness and formability whereas ceramics have excellent mechanical and optical properties such as hardness, modulus, strength, transparency and high refractive index. If these materials can be combined effectively, a new class of high performance, highly functional inorganic-organic hybrid materials can be prepared. Inorganic-organic hybrids find applications in optoelectronics for protective optical coating, high refractive index films, contact lenses, thin film transistors, light emitting diodes, solar cell, optical waveguide materials and photochromic materials, adsorption, catalysis and high energy fields.

Biocomposites are excellent inorganic-organic hybrid materials produced by natural biomineralisation. Bones, teeth and shells are typical biocomposites, which consists of an organic polymer matrix reinforced by an inorganic deposit. In biocomposites, the inorganic phase is regularly and highly organized in a matrix.

1.9 Silica-Biopolymer Hybrids

The combination of biopolymers with siloxanes under mild chemical conditions has been used for the preparation of silica-biopolymer hybrids in the
form of films for membranes or coatings, or as precursors for the preparation of porous materials. The biopolymer–silica hybrid materials have recently drawn attention owing to their promising properties and compatibility with living matter. These hybrid materials find application in the field of biocompatible materials, bone substituents, cements for bone repair and reconstruction, enzyme and cell immobilization, catalysis and sensors. The presence of functional groups such as amino, amide or carboxyl in some polymers can allow compatibility of the polymeric phase with inorganic matrix at a submicroscopic level through hydrogen bonding with silanol groups. Biocomposite layers of silica and various bone-relevant proteins such as collagen, gelatin and chitosan can be obtained from coating solution containing silica sols mixed with proteins in water/dioxane. The interest in these biopolymers as organic additives in composites of inorganic nano-hybrids is mainly because of its biodegradable, bioadhesive and multifunctional properties. Silica–gelatin biohybrids find application in bone tissue engineering, biocatalysis and controlled drug delivery systems. A number of research articles and reviews are available in literature on the promising properties of silica-chitosan composites. Silica-chitosan composites are also known to act as immobilization matrix for several molecules and complexes. Fuentes et al. synthesized oriented silica-chitosan hybrid films using 3-aminopropyltrimethoxysilane precursor by a sol-gel process. Use of
organically modified silane precursors for the silica component in the hybrids are rare but can impart enhanced properties to the hybrid.

1.9 Gelatin

Gelatin is a protein, which is obtained by breaking the single helix structure of collagen into single stranded molecules. The amino acid composition of gelatin is given in Fig. 1.8. Since it is biodegradable and biocompatible, it is a suitable compound for medical applications. Gelatin is cheap and possesses bioadhesive property. Therefore gelatin-linked inorganic hybrids have applications in biotechnology. In this context, silicate species can be considered as potentially interesting cross-linking agents since they were shown to interact through both electrostatic interactions and hydrogen bonding with some polyaminoacids and proteins.

![Fig. 1.8. Composition of gelatin](image)

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Silica/gelatin composites have been employed for enzyme and cell immobilization. Porous gelatin-siloxane hybrids are finding application as biodegradable scaffolds that act as biocompatible material for bone repair or generation. Physical measurements of the rheological, swelling and thermal properties of the gels and chemical analysis of the number of junctions introduced by chemical cross-linking were used to elucidate the structure of the chemical gelatin networks. The basic structural unit of gelatin is provided in Fig. 1.9.

![Fig. 1.9. A basic structural unit of gelatin molecule](image)

1.10 Chitosan

Chitosan is a copolymer of linked β(1→4), 2-amino2-deoxy-D-glucose and 2-acetamidodeoxy-D-glucan which is mainly used in medical, pharmaceutical, cosmetics and food industries. Chitosan is also used as a flocculent, thickener, film, gas selective membranes, and wound healing promoting agent. Fig. 1.10 shows the structure of chitosan. The presence of amino and hydroxyl functional groups allow these molecules to self assemble into various supramolecular structures and enable them to be used in the synthesis of novel monophasic inorganic materials.

![Fig. 1.10](image)
A number of research articles and reviews are available in literature on silica-chitosan composites which indicate the promising properties of the hybrid. High sorption capacities, stability of metal anions on chitosan and physical and chemical versatility of the biopolymer enable chitosan when incorporated with Pt or Pd to be used in heterogeneous catalysis. Functionalization of these hybrids with organically modified silanes is reported to enhance the properties of these hybrids.
Aerogels are unique among solid materials because of their extremely low densities, large open pores, and a high inner surface area. Hydrolysis and polycondensation of a multifunctional silicon alkoxide is the well known method for the synthesis of silica aerogels. The initially formed gels have a sponge like solid network filled with liquid. Special drying techniques must be applied to exchange the pore liquid with air while maintaining the fragile solid network. Supercritical drying is the most common technique. However the supercritical drying process involves heating and evacuation of highly flammable solvents at high temperature and pressures. In addition supercritically dried aerogels possess very low strength and are fragile. Ambient pressure drying which involves controlled solvent exchange, aging and surface modification is evolving as a promising technique for the synthesis of silica aerogels.

Major problems during the synthesis of aerogels at ambient pressure primarily arise from the large capillary pressure that occurs during drying (a result of the small pore sizes) and low stiffness (a result of the low-density). Tailoring of porosity of aerogels is very much required for different end applications. However information on synthesis conditions to tailor the porosity feature as well as surface modification of silica aerogels is seldom found in the literature. Therefore present work has been designed based on the following:
1) Influence of experimental parameters such as hydrolysis temperature, gelation pH, aging pH and aging solvent on the porosity characteristics is to be investigated in detail. Silica aerogels will be synthesized using organic additives such as PEO, CTAB, PEG and HMTA to control porosity. Effect of concentration of organic templates on the porosity characteristics will be studied.

2) Synthesis of mesoporous materials having regular geometries has been of considerable interest in recent years owing to their great potential in catalysis, adsorption, separation, sensing, medical use, ecology, and nanotechnology. Hence hydrophobic silica microspheres will be synthesized through a sol–emulsion–gel process. Effect of surfactant concentration, aging time, and viscosity of the silica sol on microsphere formation will be investigated.

3) Synthesis of hydrophobic silica-biopolymer hybrid is an area of great interest since it finds application as water repellent coatings in different substrates. Sol-gel process will be used as an effective technique for the synthesis of silica-biopolymer hybrids using gelatin and chitosan as biopolymers. Functionalization of the hybrid will be done using alkylalkoxysilanes such as vinyltrimethoxysilane and methyltrimethoxysilane. These hybrids will be applied as coatings on
different substrates such as glass, leather and textiles. The coatings will be
tested for its transparency, uniformity and hydrophobicity.

The thesis has been designed on the above objectives. The results obtained
have been discussed and correlations have been derived between the experimental
parameters and the properties.