Synthesis and characterization of highly hydrophobic, oil-absorbing aerogels for oil spill applications; A Review

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Abstract. The review report reflects on the potential of highly hydrophobic silica aerogel as a viable material for oil absorption application in the clean-up of oil spills on oceans. The review presents the conventional clean-up technologies, silica aerogel synthesis and coatings by sol-gel method and simulation techniques to predict the maximization of efficiency as well as mechanical characteristics for practical applications.

1. Introduction
Water pollution is a bane to the aquatic animals, plants, human, and climate and severely changes the ecosystem. Pollution due to spillage of oils especially heavy oils affects several aquatic animals function like respiration, feeding, and thermo-regulation [1]. At an equivalent time, the whole ecosystem can change due to the present chemical components and elements of the spilled oil that are noxious to the environment. The main sources of pollution are produced from the disposal of chemical substances originating from medical, chaotic agricultural fertilizers, industrial and household waste. Industrial oily wastewater and organic solvents have become a serious environmental and ecological problem, due to increasing industrial wastewater production and frequent oil spill accidents [2]. When an oil spill occurs, many elements of the environment are affected, depending on the immensity of the spill and its location. The environmental and economic demands emphasize the development of feasible methods to fabricate materials which can remove oil from water effectively [3, 4].

2. Standard current mechanical methods of oil spill clean up
Oil spills are harmful due to the hydrophobic nature of oil. It is a very thick liquid that is extremely hard to wash off any surface and less dense than water. It takes an energy consuming method for separation of water and oil with some conventional methods being skimming, combustion, gravity separation, filtration, centrifugation, flotation, coagulation, and electric field, dispersals, burning [5], or bioremediation are employed [5,6,7].

It is often difficult to choose the appropriate method for cleaning up oil spill and is usually situation dependent. Standard current methods aren’t able to solve spillages today because common absorbents tend to suffer from environmental incompatibility, low separation selectivity and low absorption capacity [6]. Each method should be weighed individually and comparatively, to determine the most efficient and effective way to manage an environmental disaster such as oil spill [7]. Besides high absorbent capabilities, porous aerogels are light weight
and hydrophobic, they can float on water and repel water, and thus ease separation from cleaned water [6].

3. Aerogels

‘Aerogel’ isn’t a selected mineral or material with a group chemical formula, rather, the term is employed to encompass all materials with a selected geometrical structure. This structure is an extremely porous, solid foam, with high connectivity between branched structures of a few nanometres across’ [8]. Within the aerogel structure, little is solid, with up to 99.8% of the structure consisting of air. This unique composition gives aerogel it’s often dubbed as the ‘frozen smoke’. Though aerogel is technically foam, it can take various different shapes and forms. The majority of aerogel is composed of silica, but carbon, iron oxide, organic polymers, semiconductor nanostructures; gold, copper and even plant cellulose can also form aerogel.

Silica aerogels have unusual properties of extremely high porosity (>98%) with a three-dimensional network of silica particles, low densities (~ 3 kg/m$^3$), high specific surface areas (~ $10^6$ m$^2$/kg), high dielectric strength, and low thermal conductivity (~0.02 W/(m K), less than air), low mean free path of diffusion and low refractive index (1.003-1.05). These properties have made aerogels novel and intriguing materials for various scientific, technological and industrial applications in matrices for nuclear wastes [9], inertial confinement fusion [10], light weight thermal and acoustic insulation [11, 12], oil spill clean-up systems [13,15], underwater pressure sensitive devices [14], aeronautical/aerospace and coatings [16-19].

3.1. History of aerogels

The first report on the preparation of silica aerogels was published by Samuel Stephens Kistler [20], as a result of a bet with Charles Learned over it could take place of the liquid in jellies with gas without causing shrinkage. Aerogels are carried out by supercritical drying. Because of very tedious and time consuming procedures, there was no follow up interest in the field of aerogels till around mid-1960s.

In 1966 John B. Peri reported work on aerogels using silica alkoxide precursor [21]. The first aerogels were produced from silica gels. Silica aerogels is the most extensively studied and used type of aerogel.

In 1968 Prof. S.J. Teichner and his team succeeded in developing silica aerogels using tetramethoxysilane and base catalyst NH$_4$OH within half a day [22]. Since then various groups started working on silica aerogels for different scientific and technical applications, especially for Cerenkov radiation detectors (for the capture of micrometeorites and cosmic dust) and thermal insulation systems.

In 1983 the Arlon Hunt and the Microstructured Material Group found that the toxic compound TMOS (tetramethyorthosilicate) could be replaced with TEOS (tetraethyorthosilicate), a much safer reagent. This did not change the quality of the aerogels produced.

At the University of New Mexico, lead by C. Jeff Brinker and Doug Smith, and other researchers of different institutions had become successful at eliminating the supercritical drying method used in production of aerogels by chemically modifying the surface of the gel before drying [12]. This work causes the founding of nanopore to commercialize lower-cost aerogels.

F. Schwertfeger et al. organically modified silica aerogels were prepared by NH$_4$OH-catalyzed hydrolysis and condensation of RSi(OMe)$_3$ (R is methyl, methacryloxypropyl, glycidoxypropyl) mixtures, followed by supercritical drying with methanol or CO$_2$. This work lead to the founding lower-cost aerogels [23].

In recent days using MTMS (methyltrimethoxysilane) or VTMS (vinyltrimethoxysilane) precursor, different flexible organic-inorganic hybrid aerogels were made. Rao et al. using supercritical drying produced flexible (reversible compression of up to 60%) as well as bendable superhydrophobic and low density gels [14]. Xu et al. produced these gels using ambient drying choosing the right condition [24].
4. Synthesis Method

4.1. Sol-gel process for preparation of silica aerogels

Hydrophobicity of silica aerogel could be determined by surface treatments and other condition during the preparation. The sol-gel process can be divided into different steps, such as the formation of a colloidal solution, gelation, aging, and drying. In order to prepare silica aerogel, there are three main steps firstly, wet gel forming by using sol-gel process, Then the solvent exchange step by removing of entrapped solvents from the wet gel which is considered the important step in the production of aerogels. Finally drying step under different conditions such as ambient drying, supercritical drying, and freezing drying.

4.1.1. Wet gel forming by using sol-gel process

The most common technique used for producing silica gels is the alkoxide gelation. This technique involves the reaction of a silicon alkoxide with water in a solvent such as ethanol or acetone, usually in the presence of basic catalyst [12]. In this technique every ingredient has its own function.

\[
\text{Alcosol} \equiv \text{Precursor} + \text{Solvent} + \text{Catalysts}
\]

\[
\begin{align*}
\text{TEOS} & \equiv & \text{EtOH/MeOH} & \text{Acid and Base} \\
\text{Hydrolysis:} & \text{The reaction of a metal alkoxide (M-OR) with water, forming a metal hydroxide (M-OH)} & [25].
\end{align*}
\]

For example [26]:

\[
\text{Si(OC}_2\text{H}_5\text{)}_4 + 4\text{H}_2\text{O} \xrightarrow{\text{C}_2\text{H}_5\text{O}_4} \text{Si(OH)}_4 + 4\text{C}_2\text{H}_5\text{OH}
\]

4.1.2. Solvent exchange using sol-gel process

Condensation: A condensation reaction course when two metal hydroxides (M-OH + HO-M) combine to give a metal oxide species (M-O-M). The reaction forms one water molecule. [25]

For example: Modification to convert hydrophilic property of the aerogel into hydrophobic was through with five percent hexamethyldisilazane (HMDZ) in hexane for twenty-four hour and lastly the unprocessed HMDZ was removed by washing the gel with hexane for 24 h[26].

In the second step, the condensation of these hydrolyzed species. The solvent exchange was carried out with hexane for twenty-four hour. Surface chemical

\[
\begin{align*}
\text{Si (OH)}_4 + \text{Si (OH)}_4 & \xrightarrow{\text{NH}_2\text{OH}} =\text{Si-O-Si=} + 4\text{H}_2\text{O} \quad \text{(2)} \\
\text{Si(OH)}_4 + \text{Si(OC}_2\text{H}_5\text{)}_4 & \xrightarrow{\text{NH}_2\text{OH}} =\text{Si-O-Si=} + 4\text{C}_2\text{H}_5\text{OH} \quad \text{(3)}
\end{align*}
\]

Silylation: A solution of various reactants that are undergoing hydrolysis and condensation reactions. The molecular weight of the oxide species produced continuously increased. As these species grow, they may begin to link together in a three dimensional network [25].

The surface chemical modification process with Hexamethyldisilazane (HMDZ) in hexane was administered. The non-polar groups of the HMDZ provides for the surface chemical modification of the gel through the –Si–(CH₃) by the replacement of hydrogen from Si–OH group by Si–R groups, where R = methyl groups [26].

4.1.3. Solvent exchange using sol-gel process

Usually three typical drying methods, ambient pressure drying, supercritical drying and freeze-drying were used to dry the wet gel.

4.1.3.1. Freeze drying process
Freeze drying may be a third generation drying technology, which has four definite stages: freezing, vacuum, sublimation and condensing. Because of absence of air preventing oxidative deterioration, there is no possibility of structural damage from heat to the final product [27]. There are some barriers related with freeze drying, [28] such as the slow rate of sublimation, requirement of solvent exchange and, most important, due to crystallization the increase of the solvent volume. Freeze drying is approximately four to eight times costlier than air drying therefore the method is mostly used for smaller scale applications producing costlier products.

4.1.3.2. Supercritical drying process
Supercritical drying process leads to the presence of supercritical fluid mixtures in the gel pores without remnants of any liquid phase. This drying procedure thus avoids the presence of any intermediate vapour–liquid transition and surface tensions in the gel pores, preventing the gel structure from the pore collapse phenomenon (i.e., changes in the macroscopic level) during solvent elimination. Supercritical drying requires specialized equipment, and presents significant safety hazards due to its high-pressure operations.

![Fig 1: Schematic representation of supercritical drying auto-clave [29].](image)

4.1.3.3. Ambient-pressure drying process
Most commonly used drying method in aerogel production is ambient-pressure drying (APD). The drying is administered at ambient pressure preferably using reduced or elevated pressures. APD is used to obtain silica aerogel with lower linear shrinkage, homogeneous microstructure, high mechanical property and low cost. This method has received considerable attention from industry cause of cheap and safe drying process for large-scale production of aerogels. [26].

4.2. Sol-gel process for preparation of silica aerogels
A type of window glazing coating with the silica aerogel film, which is more transparent than a bulk aerogel, also can provide many applications in the field of advanced transparent super insulation materials. An ambient drying process has been developed in order to synthesize window glazing coated with silica aerogel films. The aerogel film might be manufactured by this process of wet gel films obtained via a dip/spin coating of the silica sol on a glass slide. Before drying, the isopropanol solvent in wet gels was exchanged with n-heptane to minimize the drying shrinkage. The transmittance of window glazing was over 90%; the thickness, refractive index, and porosity of silica films were 0.16–10 µm, 1.08– 1.09, and 80–84% respectively. The predicted optimal thermal conductivity (0.2 W/(m K)) of the window glazing would be obtained at the aerogel thickness of 100 µm (0.016 W/(m K)) [33].
A new pseudo one-dimensional architecture for Dye-Sensitized Solar Cells (DSSC) photoanodes was prepared using templates of low density, high surface area, mesoporous aerogel thin films. ZnO was conformally deposited with a controlled variable thickness on the aerogel templates by Atomic Layer Deposition (ALD). The electrodes integrated into DSSCs exhibited good light harvesting efficiency and outstanding power efficiencies compared with other ZnO based DSSCs. A main limitation to the overall efficiency was observed to be mass transport. The excellent initial performance reported herein, the convenience of fabrication, and therefore the flexibility of design make ALD coated aerogel template photoanodes a promising candidate to maneuver beyond nanoparticle electrodes in DSSCs [34].

ALD is right for applying precise and conformal coatings over nanoporous materials. They have used ALD to coat two nanoporous solids: anodic alumina oxide (AAO) and silica aerogels. AAO possesses hexagonally ordered pores with diameters $d \sim 40$ nm and pore length $L \sim 70$ microns. The AAO membranes were coated by ALD to fabricate catalytic membranes that demonstrate remarkable selectivity in the oxidative dehydrogenation of cyclohexane. Additional AAO membranes coated with ALD Pd films show capability as hydrogen sensors. Silica aerogels have rock bottom density and highest area of any solid material. These materials give out as an excellent substance to fabricate novel catalytic materials and gas sensors by ALD [35].

A novel process for coating of aerogels with polymeric materials using spouted bed technology. Firstly, spherical silica aerogel particles with a high surface area up to 1100 $m^2/g$ and particles diameter ranging from 200 µm to few millimetres were produced. Then, the aerogel particles were loaded with a model drug by adsorption from supercritical CO$_2$ phase. The loaded aerogel particles were coated with different polymeric materials in a slit-shaped spouted fluidized bed with two horizontal gas inlets and adjustable gas supply. The corresponding polymers were sprayed as an aqueous suspension or as melts. The process conditions for coating were optimized accordingly. The physical, mechanical, structural and release properties of the resulting formulations were evaluated. This technology allows to provide a specific release mechanism of pharmaceuticals from aerogels and to broaden aerogel applications in pharmaceutical technology [36].

Aerogels are solids with high porosity (<100 nm) and hence possess extremely low density (~0.003 g/cm$^3$) and very low conductivity (~10 W/(m K)). In recent years, aerogels have attracted more and more attention due to their surprising properties and their existing and potential applications in wide range of technological areas. Thermal insulation properties of aerogels will be helpful in building envelope. The improvements of thermal insulation systems have future prospects of large savings in primary energy consumption. It can be concluded that aerogels have great potential in a wide range of applications as energy efficient insulation, windows, acoustics, and so forth [37].

The coated mesh (spraying a hybrid acrylic polymer on stainless steel mesh), with a static water contact angle of 153° and a sliding angle of 4.5°, was applied to separate a series of oil–water mixtures and non-polar liquids with separation efficiency of nearly 99%. The coated mesh still kept separation efficiency at approximately 99%, indicating good mechanical stability even after 25 separation cycles for n-hexane/water mixture. After 20 abrasion cycles, the water contact angle of the mesh remained 145° [15].

A porosity of 98.1% was achieved with the technique to produce novel magnetic poly (styrene-divinylbenzene) (Poly (St-DVB)) monoliths with highly open porous structure and lipophilicity of high internal phase emulsions (HIPEs). The porous monolith was hydrophobic with a water contact angle of 142° and absorbed oils from water selectively with an oil intake capacity of approximately 23 times its own mass. Incorporation of carbonyl iron powders (CIPs) enabled magnetism allowing the oil-soaked composite to be readily collected by a magnet. The composite saturated with oils could be regenerated by simple centrifugation, and the tests showed that the oil intake capacities were not impaired after 10 absorption/regeneration cycles [16].
### 4.3. Computational modelling

The synthesis of silica aerogels provided great impulsion for characterizing and optimizing their molecular structures, it can be a challenge in understanding their structure-property-functional relationship at several hierarchies of length scales. The molecular dynamic modelling and simulations have been developed to tackle these challenges. Development of new molecular dynamic force fields, generating aerogels percolated backbones and compelling algorithms for characterizing their structural, mechanical and thermal properties results in understanding of silica aerogels [39].

![Fig 2: Various porous backbone of silica aerogels generated through (a–c) negative pressure rupturing, (d) expanding, heating, and quenching scheme](image)

A mathematical heat transfer model for a silica aerogel-based thermal insulation coating was developed. The model can estimate the thermal conductivity of a two-component coating with potential binder intrusion into the nanoporous aerogel structure. The latter is modelled using a so called core–shell structure representation. For model validation, data from several previous experimental investigations with silica aerogels in various binder matrices were used. A parametric study demonstrates that the model can be used, qualitatively, on the thermal conductivity of an insulation coating. The model can be used as an optimization algorithm if relevant data is available for service life exposure conditions and raw material costs. [40].

In architectural surface coating film, a mathematical model was developed to describe the thermal behaviour of the aerogel SiO$_2$ material. These types of materials allow temperature conservation within a panel. Porous material properties, microstructure, boundary conditions, etc were the considered conditions for modelling. From the study of the material’s micrometry, an image processing algorithm implemented using MATLAB was constructed with regular grids of 6192. This research contributes towards the thermal analysis of special insulating materials as alternatives of applications in the construction industry [41].

### 5. Characterization

#### 5.1. Elasticity (Young’s Modulus)

The best monolithic aerogel samples, those with the fewest chips or cracks, were selected for mechanical uniaxial compression testing [30]. Silica aerogels are subjected to small levels of uniaxial...
loading; the resulting stress–strain curves are initially linear. Then, as the loading level increases, they become concave with increasing slope.

\[
\text{Young’s Modulus} = \frac{\text{Stress}}{\text{Strain}} = \frac{mgL}{\pi r^2 \Delta L} = \text{slope of stress vs. strain graph}
\]

where \( L \) is the original length of the aerogel, \( \Delta L \) is the change in length after the application of the load and \( r \) is the radius of the aerogel sample under study, \( m \) is the mass placed on the aerogel sample, \( g \) is the acceleration due to gravity (9.8 m/s\(^2\)) [14].

![Figure 3](image-url)

Fig 3: Three states of the elastic superhydrophobic silica aerogel sample: a without stress, b with applied stress, and c after releasing the applied stress [13]. The numbers are in metre. The best monolithic aerogel samples, those with the fewest chips or cracks, were selected for mechanical uniaxial compression testing [30].

5.2. Bulk density
The bulk densities (\( \rho_b \)) of the prepared aerogels were calculated as function of the gel mass-to-volume ratio [24].

\[
\text{Bulk density (} \rho_b \text{)} = \frac{\text{Mass}}{\text{Volume}}
\]

Mass will be measured with microbalance. Volume will be measured by filling aerogel granules in measuring cylinder of known volume.

5.3 Porosity (Skeletal density)
The skeletal density was tested by helium pycnometry, and the porosities [37] were calculated as

\[
\% \text{ Porosity} = [1 - \frac{\rho_b}{\rho_s}] \times 100; \\
\text{where } \rho_b : \text{bulk density}, \rho_s : \text{skeletal density } \sim 1.9 \text{ g/cm}^3
\]

The absorption capacity of the silica aerogels for several organic solvents and oils was also measured. Aerogels were placed inside the organic liquids for about 10 min then isolated for weight measurements. To avoid evaporation of absorbed organic liquids, weight measurements were performed immediately after absorption [31].

5.4 Contact angle
For contact angle measurement, a droplet of water was placed on the surface of hydrophobic aerogel using micro-syringe. The contact angle is evaluated using photographic method recommended by Rao and coworkers [29-31], from measurements of the drop height \( h \), and contact width \( b \). The contact angle for the silica aerogels was measured before exposing the samples to humid environment and after exposing the samples to humidity [32].
Fig 4: Illustration of direct measurement technique on a TMOS based aerogels [25].

Contact angle (θ) = 2 \tan^{-1} \left[ \frac{2h}{b} \right]

Where, b: base contact length and h: height of the water droplet.

5.5 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopic studies tell the approximate information on surface modification from hydrophilic to hydrophobic based on observed changes in the peak intensity for the absorption peak at 1630 cm\(^{-1}\) and 2950 cm\(^{-1}\) associated with Si-OH and C-H bonding, respectively [32].

In case of hydrophilic silica aerogel, the absorption peak observed at about 3400 cm\(^{-1}\) assigned to free or absorbed water and is amid the peak noticed at 1630 cm\(^{-1}\) is that the characteristic peak for the Si-OH bond, liable for hydrophilic nature of the silica aerogels. The peak intensity for the absorption peaks at 2950 cm\(^{-1}\) like C–H bonding is found to be increased for hydrophobic and further for super hydrophobic aerogels. The peak intensity at 3400 cm\(^{-1}\) and 1630 cm\(^{-1}\) is found to be decreased as compared thereto of noted for hydrophilic silica.

Fig 5: FTIR spectra of silica aerogels: (a) Hydrophilic (b) Hydrophobic and (c) Superhydrophobic [32]

6. Discussion

Silica aerogels have broad potential as an oil absorption capacity. The elastic highly hydrophobic aerogels were prepared using two different methods.

1. methyltrimethoxysilane (MTMs) precursor by two-step sol-gel process followed by supercritical drying /ambient drying.
2. sodium silicate precursor followed by supercritical drying /ambient drying.

To obtain aerogels of high contact angle with high elasticity with low Young’s Modulus, various sol-gel processing parameters are to be optimized. The response surface methodology (RSM) is a widely used mathematical and statistical method for modelling and analyzing a process in which the response of interest is affected by various variables [50] and the objective of this method is to optimize the response [51]. These methods are exclusively used to examine the "surface," or the relationship
between the response and the factors affecting the response. RSM is empirical statistical modelling technique used for multiple regression analysis by quantitative data obtained from experiments. RSM is used to determine the optimum input variables for the extraction of oil/organic compounds [52].

To evaluate the effect of operating parameters on the extraction of oil/organic compounds, few independent variables will be selected. For example independent variables are volume ratio of precursor and ambient temperature in °C. It can be expressed as the dependent variable $Y$ (i.e. contact angle) is a function of $X_1$ and $X_2$.

$$Y = f(X_1) + f(X_2) + e$$

Where $Y$ is the response (dependent variable i.e. contact angle), $X_1$ and $X_2$ are independent variables and $e$ is the experimental error [42].

We expected that silica aerogel can be used for oil-spill cleanup. Besides, we establish the relationship between surface energy and water/oil contact angle to understand the mechanisms that occur during the oil/water separation process.

![Flow chart to optimize contact angle for novel superhydrophobic aerogel preparation.](image)

**Fig 6:** Flow chart to optimize contact angle for novel superhydrophobic aerogel preparation.

In this review, a systematic literature survey has been carried out to analyse the state of the art of the synthesis and characterization of hydrophobic to superhydrophobic silica-based aerogels, with an aim of acquiring possible route maps to synthesize superhydrophic and mechanically durable aerogel for oil spill application in high seas. In Fig. 6, we have outlaid such a proposed route map, where we aim to synthesize Silica Aerogels using the conventional sol-gel chemical route with the help of RSM determined chemical stoichiometry, following physical treatments based on the parameters obtained from Molecular Dynamics simulations to maximize surface oil-absorbing characteristics for the various stoichiometries and minimize experimental effort. Quantum mechanical atomistic-scale models are to be used to select and design the material for enhanced mechanical strength and explore a stable hybrid material using carbon-silicon oxide compound to optimize the hydrophobic oil-absorbing character of silica aerogel with mechanical strength of carbon-based polymers.

**7. Conclusion**

A novel material for oil absorption from oil/water mixtures can be prepared from hydrophobic silica aerogels using a preparation method that is relatively simple, economic, and environment friendly. A wide variety of synthesis routes have been developed for the production of silica aerogels. For the industrial production of silylated, hydrophobic silica aerogel materials, the precursors and processes
can be selected primarily on the basis of process simplicity, energy consumption and raw material cost as all synthesis routes can carry excellent materials on the laboratory scale. The synthesized silica aerogels of this work show large specific surface area, excellent water repellence and high selective absorption of non-polar liquids and oils in combination with superior absorption recyclability. Moreover, the superhydrophobic silica aerogel shows high oil-absorbing efficiency. It has many advantages such as low cost, biodegradable, and simple preparation procedure, thus it has promising potential to be used in the field of oil-water separation in daily life and could be directly applied to the water treatment industry.

Computational modellings predict that the purpose of thermal distribution across the pores of the material for a range of new materials is to shed light on the choice of aerogels with the highest efficiency. For optimization of extraction conditions one of the most important method is that the predicted values in the model should be verified experimentally. Response Surface Methodology (RSM) has many advantages when compared to classical methods. It needs fewer experiments to study the effects of all the factors and the optimum combination of all the variables can be revealed. The interaction (the behaviour of one factor may be dependent on the level of another factor) between factors can be determined. It also requires less time and effort. With all of these advantages, it will be used in surface area maximization during synthesis in future [42, 43].

The future of this unique material will be determined by sophisticated RSM and algorithms that may allow predicting enhancement of not only the atomistic and macroscopic hydrophobic properties but also the mechanical characteristics for sustainable application-grade material. A MATLAB model shall be used for a detailed experimental investigation for surface area maximization during synthesis. A combined modelling-synthesis-characterization technique will be greatly beneficial to design aerogels capable of enhanced absorption of non-polar liquids and oils in combination with superior absorption recyclability.

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