

REVIEW PAPER

## Sol-gel Technology for Sensor Applications

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### ABSTRACT

Sol-gel processes refer to the transition of predefined compositions of inorganic alkoxides precursors from liquid sol phase to solid gel phase. The phenomenon of sol-gel was known to mankind for more than 150 years. It is because of concerted efforts of researchers from multidisciplinary fields, sol-gel science transformed to technology. Several products are already commercially available for applications in optical coatings, nanocomposites, and public healthcare. Potential applications in the areas of biosensors and environmental monitoring are expected. Newer applications with nanotechnology appear too exciting. An attempt has been made to address important applications of sol-gel technology, particularly in sensing techniques from the defence perspective.

**Keywords:** Sol-gel technology, nanomaterials, healthcare, sensors, defence applications

### 1. INTRODUCTION

The term sol-gel was first coined in the late 1800s. It generally refers to a low-temperature method using inorganic precursors that can produce ceramics and glasses with better purity and homogeneity than through high temperature conventional processes<sup>1</sup>. Two most attractive features of the sol-gel process are that it can produce compositions that cannot be created with conventional methods, and that the mixing level of the solution is retained in the final product, often up to the molecular scale.

Sol-gel method has been successfully used to manufacture a variety of products, viz., bulk glasses<sup>2</sup>, optical fibers<sup>3</sup>, special coatings, ultra-pure powders, and multifunctional materials. Figure 1 shows different types of materials made from sol-gels. Sol-gel-processed transparent porous matrix offers the possibility of doping various organic and inorganic molecules<sup>5-8</sup>. Sol-gel process has been used to

fabricate materials which can be used as new laser materials, nanocomposites, biomimetic systems, and so on. Because of potential in fabrication of a wide variety of new materials, understanding of sol-gel processes has become the centre of interdisciplinary research, viz., physics, chemistry, biology, biotechnology, biochemistry, electronics, and related engineering branches. Sol-gel materials have a wide range of applications, from environmental monitoring, biosensors for healthcare, to nanotechnology for sensing clinically-important analytes.

### 2. BASICS OF SOL-GEL PROCESS

The sol-gel process is a versatile technique which involves the transition of a predefined composition from liquid sol (mostly colloidal) phase into a solid gel phase<sup>9</sup>. Sol-gel processing involves the hydrolysis of a metal alkoxide followed by condensation and polymerisation reactions, leading to the sol-gel state.

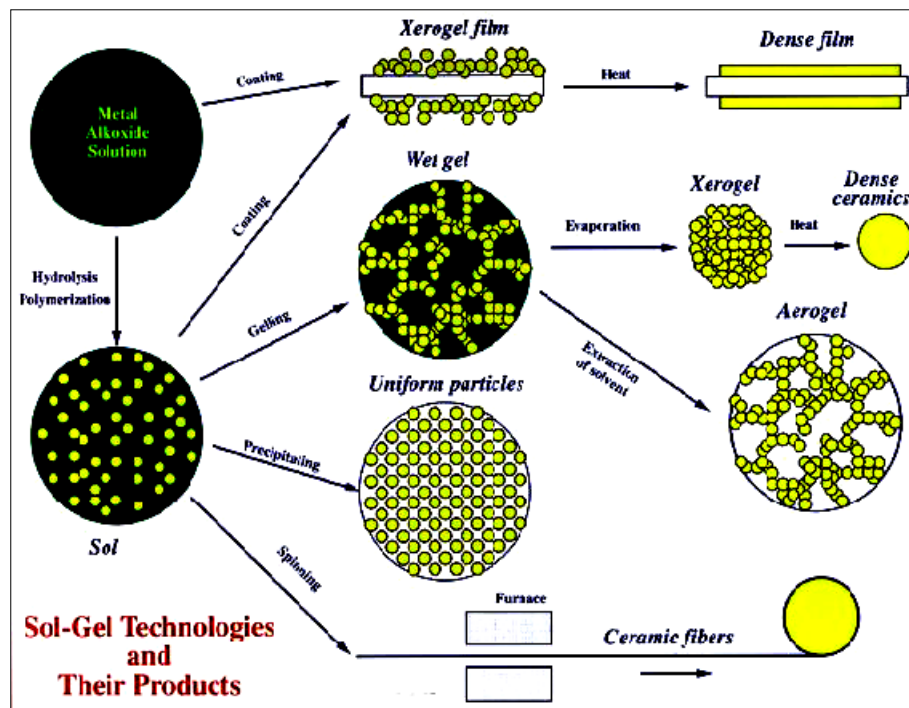
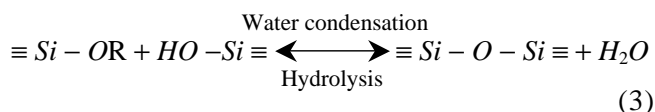
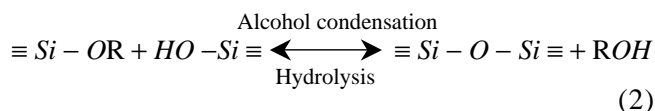
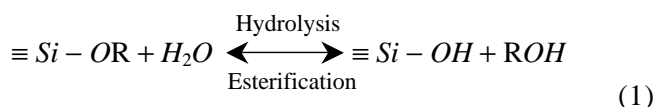


Figure 1. Different types of materials prepared from sol-gels.

These general reactions are shown below:



Metal alkoxides are most popular because these react readily with water. The most widely used metal alkoxides are the alkoxy silanes, such as tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS). However, other alkoxides such as aluminates, titanates, and borates often mixed with TEOS<sup>10</sup> are also commonly used in the sol-gel process. This process is complicated because of several interrelated processes in the sol-gel transitions, leading to the formation of network of interconnected pores within the resultant glasses. Understanding of sol-gel science has formed contents of several review articles in journals and books<sup>1,10</sup>.

At the functional group level, these three reactions are generally used to describe the sol-gel process, viz., hydrolysis, alcohol condensation, and water condensation. However, the characteristics and properties of a particular sol-gel inorganic network are related to a number of factors that affect the rate of hydrolysis and condensation reactions, such as water to precursor molar ratio ( $R$ ), type of solvent, nature of catalyst and its concentration,  $pH$ , temperature, time, aging conditions, and drying. Thus, by controlling these factors, it is possible to vary the structure and properties of the sol-gel-derived inorganic network over a wide range.

The hydrolysis reaction [Eqn (1)] through the addition of water, replaces alkoxy groups ( $OR$ ) with hydroxyl groups ( $OH$ ). Subsequent condensation reactions [Eqns (2) and (3)] involving the silanol groups ( $Si-OH$ ) produce siloxane bonds ( $Si-O-Si$ ) plus the by-products water or alcohol. In most of the conditions, condensation commences before hydrolysis is complete. However, conditions such as  $pH$ ,  $H_2O/Si$  molar ratio ( $R$ ) and catalyst can force completion of hydrolysis before condensation begins. Additionally, because water and alkoxides are immiscible, a mutual solvent, such as an alcohol,

is utilised. In the presence of this homogenising agent, viz. alcohol, hydrolysis is facilitated due to the miscibility of the alkoxide and water. As the number of siloxane bonds increases, the individual molecules are bridged and jointly aggregate in the sol. When the sol particles aggregate or inter-knit into a network, gel is formed. Upon drying, trapped volatiles (water and alcohol, etc) are driven off and the network shrinks and further condensation occurs. The addition of solvents and certain reaction conditions may promote esterification and depolymerisation reactions according to the reverse of Eqns (1), (2), and (3)<sup>1,11-15</sup>. The strength of the wet gel increases with aging, which reduces the chance of cracking during drying.

The use of organically-modified silanes (ORMOSILS) for developing new sol-gel-derived materials has increased rapidly in recent years. These materials are organic-inorganic hybrid materials, which combine the properties of an inorganic glass and an organic polymer. This can be a novel way to prepare high optical quality nanocomposite materials with desirable properties<sup>16</sup>.

### 3. ADVANTAGES OF SOL-GEL TECHNOLOGY

Sol-gel-derived materials are inherently inhomogeneous. Such heterogeneity results from the variations in pore size, shape, surface area, thickness uniformity, particularly in case of films, surface characteristics, and local solvent composition, leading to the formation of a wide range of distinct physical and chemical environment in the molecular scale dimensions. The synthetic (preparative), aging, and drying conditions used for sol-gel processing determine the average physico-chemical properties of the final material. These spatially varying properties influence the mechanical, optical, and other material characteristics. Better understanding of compositions, *vis a vis*, internal properties of these materials will thus provide a better way to control homogeneity.

A variety of methods have been used to characterise the sol-gel materials. These include, nuclear magnetic resonance (NMR), infrared (IR), Raman, fluorescence spectroscopy, cryogenic gas adsorption analysis, thermogravimetry, viscometry, small angle x-ray

scattering (SAXS) and small angle neutron scattering (SANS)<sup>17</sup>. Recently, advanced microscopic techniques, viz., atomic force microscopy (AFM) and scanning electron microscopy (SEM) were found to be useful to characterise the sol-gel materials<sup>18-21</sup>. Imaging ellipsometry is extremely useful in determining the thickness and refractive indices of from sol-gel derived thin films<sup>22</sup>. These techniques are capable to extract detailed information about local physical and chemical environments, interfacial structure, gel rigidity, single molecule diffusivity, and material inhomogeneity. Therefore, the characterisation of the individual microscale environment is an important area of research in sol-gel science. This is one of the areas of interest in sol-gel research<sup>23-28</sup>.

The advantages of sol-gel materials outscore all these limitations. Major advantages of sol-gel materials are:

- Compatible with many organic or inorganic reagents
- Chemically, photochemically, and thermally stable as compared to organic polymer
- Optically transparent, and thus suitable for various spectroscopic-based analytical measurements
- Cast as monoliths, coated as thin films on slides and fibre and ground into powder
- Controllable surface area, average pore size and its distribution, and fractal dimensions which can be miniaturised to micron and even sub-micron (nano) sizes
- Allow control of conductivity through the choice of the metal or metal alkoxide
- Enhance the stability of the encapsulated molecules by virtue of the rigidity of the cage, and most importantly, prevent leaching of proteins due to the effective caging<sup>9,29</sup>

### 4. AREAS OF RESEARCH

Due to the numerous favorable properties of sol-gel method, this technology has several applications in different branches of science and engineering. The field of bioorganically-doped sol-gel matrices

has exhibited its diversity and potential applications in many frontiers of modern materials science including optical materials, biocatalysts, electrochemistry, immunochemistry, chemical sensors, and biosensors<sup>30</sup>.

To date, sol-gel processing has largely been used to develop advanced optical coatings, solid-state lasers, lasing materials, and electrooptic materials<sup>10,31,32</sup>. Sol-gel-derived metal chalcogenides (*CdS*, *ZnS*, *CdTe*), titanium oxides and other nanocrystalline semiconductor-doped xerogels are also used as promising sensing materials because of their photocatalytic activity and good optical characteristics<sup>32</sup>. Sol-gel processing has also been used to form stable chromatographic stationary phase<sup>33</sup>. Colloidal silica powders synthesised by sol-gel method are extensively used commercially as catalytic supports, for modifying surface properties of synthetic films, increasing the hardness, durability, and integrity of coatings<sup>34</sup>.

In biosensor applications, sol-gel can act as optical transducer material for monitoring the chemical and/or biochemical reactions initiated by sensing molecules entrapped in the porous glasses and the chemical environment outside the matrix. In biosensor research, designing the nature and composition of material, has been one of the limitations. Biosensors have enormous applications in clinical diagnosis, food and drink analysis, pollution control and monitoring, and in military applications. Following are the few selective areas of general interest:

#### 4.1 Sol-gel Glasses, Optical Fibres, and Nanocomposite Materials

Depending upon the precursor molecule and molar ratio (*R*), the sol is transformed to gel at room temperature, and after systematic heat-treatment procedures, various types of glasses and composite materials are designed and fabricated<sup>16</sup>. Sol-gel-derived fabrication of fibre, using either hand or spinning apparatus, has been demonstrated by several research groups. Fibres up to 1 m length were drawn<sup>35</sup>. These fibres were studied for *pH* sensing and as laser dye when appropriately doped by fluorescent molecules, viz., fluorescein and rhodamine-6G<sup>36,37</sup>. Nanoparticles of semiconductors or metals

have been widely investigated for applications in nonlinear optics<sup>38</sup>. Fusion of sol-gel and nano technologies can thus open various new applications. Mesoporous silica films with an excellent heat-insulating property and the relatively low dielectric value play important role in electronic and magnetic devices<sup>39</sup>, those with pore sizes of 5 nm to 50 nm are also of interest for applications in photonics, optoelectronics, lightweight structural material, thermal insulation, and optical coating<sup>38-41</sup>.

The special network structure can be used in sound detection<sup>40</sup>. Porous silica films are also used as adsorbents, scaffolds for composite material synthesis, in separation technology<sup>42</sup>, and molecular and biological engineering<sup>43</sup>. Currently used silica films with high refractive indices can thereby be replaced by porous silica films so that more light can reach the active surface because of the lower scattering losses and the efficiency of the solar cell is thus increased. In view of this, nano-and mesoporous silica films with uniform pore dia 50-300 nm have attracted attention in their fabrication and efforts have been made in this area<sup>44-46</sup>. Low-dielectric constant films are in demand to reduce capacitance between interconnects and improve the switching speed in ultra large-scale integrated circuits. Porous dielectric films formed by sol-gel technology are also becoming important for future microelectronic technology<sup>47</sup>.

#### 4.2 Nanoporous Carbon Xerogels and Aerogels as Hydrogen-storage Materials

One of challenges for the hydrogen fuel economy is to find a reasonably cheap, safe, compact, and reversible hydrogen-storage media. Highly nanoporous carbon materials have potential applications. Nanoporous carbon materials can be designed by subcritical or supercritical drying of gels using the sol-gel techniques. Supercritical drying is the final and most important process in making aerogels. In this process, the liquid within the gel is removed, leaving only the linked silica network. This can be performed by venting the ethanol above its critical point (high temperature—very dangerous) or by prior solvent exchange with *CO*<sub>2</sub> followed by supercritical venting (lower temperature—less dangerous). This process

is performed only in an autoclave specially designed for this purpose. Carbon xerogels or aerogels would result depending on whether the drying was carried out in the subcritical or supercritical states. These materials will be subjected to surface activation steps and the resulting materials will be tested for their hydrogen-storage capacities. High specific surface area ( $> 2000 \text{ m}^2/\text{g}$ ) and nanoporous nature (pore size  $\sim 1\text{--}50 \text{ nm}$ ) of these materials could provide the desired hydrogen-storage capacity. These materials will find applications in renewable energy programmes.

## 5. APPLICATION OF SOL-GEL TECHNOLOGY FOR DEFENCE

The strength of defence of a nation is determined not only by the modern state-of-the-art inventories but also on the capability of the nations to continuously develop better variants of these items. However, the role of men behind the machine remains always as the most critical factor for functional forces. Sensor systems play key roles in both men and machine fronts. The following sections are therefore divided into two parts to address both the issues where sol-gel technology appears to be useful in a variety of ways.

### 5.1 Sensors for Healthcare

Sol-gel technology can be used in development of biosensors for medical applications. Biosensors can be put as a system for detecting and monitoring physiological changes in Armed Forces personnel during battlefield operations, monitoring drinking water, toxic gases in the environment, and protection from UV light in high altitude areas. Recently, biotechnology applications have been extensively studied, where biomolecules (such as proteins, enzymes, antibodies, etc) are incorporated into sol-gel matrices. Applications include monitoring of biochemical processes, environmental testing, food processing, and drug delivery for use in pharmaceutical or agricultural industries. Other biomedical applications include coatings for metal implants and bone-grafting materials. Cosmetic applications include sunscreen lotions and makeup that incorporate UV radiation absorbers.

### 5.2 Sol-gel Entrapped Reagents for Optical Sensing of Water Pollutant

Transition metal ions can have profound biological effects on animals and the environment, even at extremely low concentrations, often  $< 1 \text{ mg/l}$ . Therefore, it is important to detect and monitor levels of transition metals, even in low concentrations, to assess the health risks and for environment monitoring. Cadmium (*Cd*), a major pollutant in some areas, is an example of a transition metal that can be selectively detected using fluorescence-based sensors. Anthryl tetra acid (ATA) has recently been reported to be a selective  $\text{Cd}^{+2}$  sensor. The Environment Protection Agency (EPA) Standard for maximum permissible  $\text{Cd}^{+2}$  concentration in drinking water is  $0.005 \text{ mg/l}$ . Long-term exposure of *Cd* above this level can potentially cause kidney malfunctions. Trace quantities of *Cu*, although essential for health, but excess amount ( $1.3 \text{ mg/l}$ ) has adverse effects on health. It causes gastrointestinal problems and kidney damage in case of long-term exposure. Recently, a selective pyrene-based sensor for  $\text{Cu}^{+2}$  has been developed. Lead (*Pb*) is also one of the major serious environmental and health hazards. Lead toxicity affects kidneys and reproductive systems. The FDA limit for *Pb* in drinking water is  $0.015 \text{ mg/l}$ . Recently, a sensor for  $\text{Pb}^{+2}$  ions in the acetonitrile solutions has been reported.

Organic reagents, that change colour upon interaction with metal ions, are also reported to be entrapped in porous silica sol-gel matrices for the detection of various metal ions. Zusman<sup>50</sup>, *et al.* developed the sensors for various metal ions such as  $\text{Fe}^{+3}$ ,  $\text{Al}^{+3}$ ,  $\text{Co}^{+3}$ ,  $\text{Ni}^{+2}$ ,  $\text{Cu}^{+2}$ , and  $\text{Pb}^{+2}$  as well as changes in pH by monitoring the characteristic colour changes in the doped monolithic xerogel glass blocks. The response times were of the order of seconds and sensitivities were  $< 10^{-7} \text{ mol/l}$ .

Further development resulted disposable tube detectors based on doped sol-gel glasses for water analysis<sup>51,52</sup>. When a solution was sampled through a tube detector, a specific metal ion was complexed by the organic reagent, forming a coloured section of the glass bed. The length of the coloured section was related to the concentrations of the metal ions.

A cyanide sensor has also been developed by encapsulating iron (III) porphyrin in a sol-gel-derived titanium carboxylate thin film<sup>53</sup>. A sensor for oxalate determination using oxalate oxidase encapsulated in sol-gel glass is also reported<sup>54</sup>. Plaschke<sup>55</sup>, *et al.* immobilised porphyrin derivatives covalently bound to dextran in sol-gel-derived thin films to develop stable mercury sensors. The stability of the mercury sensor was found to be more than 6 weeks. Flora and Brennan<sup>56</sup>, reported the development of fluorometric detection of  $Ca^{+2}$  based on an induced change in the conformation of cod III parvalbumin entrapped within a sol-gel processed glass. Many of these experimentally demonstrated sensors could be useful for Armed Forces for detecting and monitoring the pollutants in drinking water at unfamiliar locations like army bases in battlefield and during management of natural calamities.

### 5.3 Sol-gel UV-Pearls

With the increasing public knowledge that ultraviolet rays from the sun is the primary cause of skin aging, wrinkles, and skin cancer, people use sunscreens more often; in higher concentrations, and in daily-wear cosmetic preparations. A direct consequence of the increasing use of sunscreen molecules is that an increased amount of these molecules may penetrate into the body through the epidermis. Moreover, when UV light is absorbed by the sunscreen molecules, photodegradation products, including free radicals, may be formed and may interact with body tissues. Sol-gel techniques are available to develop/produce inert glass microparticles that can hold high concentration of sunscreen molecules within a thin shell of inert sol-gel glass. An Israeli firm has already manufactured under the product name "UV-pearls". This is considered to be a safe UV filter. Product of this type will be of importance for civilian and Armed Forces at high altitudes.

### 5.4 Sensors for Detection/Monitoring of Gases

Detection and monitoring of gases at low levels are often routine activities in laboratories and industries. Environmental monitoring of toxic gases has become important due to increasing levels of pollutants as well as in the event of intentional accidents. In

general, environmental monitoring system will require rugged systems. Sol-gel materials are environment-friendly and stable at high temperatures and humidity. Sol-gel methods have been used in the detection of nitrogen monoxide (*NO*) using cobalt tetrakis (5-sulfothienyl) porphyrin-doped silica glass prepared by the sol-gel method<sup>57</sup>. Blyth<sup>58</sup>, *et al.* demonstrated the feasibility of *NO* and *CO* sensing based on biomolecules such as myoglobin, cytochrome c and haemoglobin. The utility of various entrapped hemoproteins in sol-gel was also demonstrated for *CO*, *NO* and  $O_2$  sensing<sup>54,59,60</sup>. Oxygen permeability of sol-gel coatings has been investigated by the selective oxygen quenching of phosphorescent probes (such as platinum octaethylporphine) doped in sol-gel glasses<sup>61</sup>. It was also demonstrated that a series of sol-gel glass coatings with different degrees of oxygen permeability could be prepared by the sol-gel process using different compositions of precursors and different functional groups (methyl, phenyl, octyl, propyl, etc). Therefore, fibre-optic oxygen sensors based on these sol-gel coatings can have a tunable optimum oxygen sensitivity range<sup>61</sup>. Samuel<sup>62</sup>, *et al.* in an effort to solve reagent-leaching problem, found that polymerisation of TMOS at high acidity and low-water content resulted in non-leachable yet reactive sol-gel as demonstrated with oxygen sensing by fluorescence of entrapped pyrene. McCraith<sup>63,64</sup>, *et al.* developed oxygen sensor based on sol-gel glass doped with a ruthenium complex  $Ru^{II}$ -tris (2,2'-bipyridine) or  $R^{II}$ -tris (4, 7-diphenyl-1, 10-phenanthroline).

#### 5.4.1 Chlorine Sensors

The history of chemical warfare traces back to a single man, Fritz Haber, who developed poison gases for Germany during the world war I. Haber was a world-famous chemist, who had developed a crucial process for extracting nitrates from the atmosphere. This process was used to manufacture fertiliser, and later to make explosives. He initially focused on chlorine gas ( $Cl_2$ ), a highly reactive chemical used in the dye industry. Using the sol-gel technology, it looks feasible to make sensors for  $Cl_2$  gas. The weight (or swelling) of silicate matrices prepared using sol-gel method varies with chlorine content<sup>65</sup> like  $CaCl_2$ . The enhanced swelling of

these silicate matrices in high ionic strength can be explained by the development of significant osmotic pressure in the sol-gels. The movement of these ions along with their respective hydration spheres results in the swelling of the sol-gels. This effect creates a critical osmotic pressure within the framework that leads to swelling of the gel. Thus, sol-gel technology has potential to develop gas sensors, both toxic and non-toxic.

## 6. DEVELOPMENT OF NEW SOL-GEL LASER MATERIALS

Laser are important in defence for more than a single purpose. Sensing applications often require new laser materials depending upon the applications envisaged. Sol-gel, being highly stable towards temperature and maintains its optical properties, thus is an obvious choice for researchers in developing laser materials. Sol-gel-processed materials have been used in the area of solid-state lasers<sup>66,67</sup>. The sol-gel method also provides a convenient route to prepare luminescent glass optical fibres doped with rare earth ions<sup>68,69</sup>, waveguides<sup>70,71</sup>, and lasers<sup>72</sup>. The sol-gel technique has also been used to fabricate nonlinear, optically active composites for applications in optical telecommunications<sup>73</sup>. Organically modified sol-gel-processed materials exhibit excellent nonlinear optical properties.

In optical fibre, electromagnetic radiation is guided by appropriate channels with high and low refractive indices. Neodymium ions are important in active medium for laser. Co-doping with aluminium significantly increases the solubility and avoids clustering of the laser-active neodymium (*Nd*) ions in the sol-gel-derived materials, that are later used to draw the fibres. Various combination with different co-doping elements and appropriate thermal treatments offer the possibility to optimise the fluorescence lifetime and the energy transfer between the various doping ions (which is an essential parameter for efficient laser emission). This in turn reduces the losses caused by absorption in the host materials. Erbium (*Er*)-doped sol-gel microlaser has tremendous applications in various analytical techniques<sup>74</sup>. This type of laser is efficient and can be implanted/coupled with many sensing devices using the optoelectronics.

## 7. DEVELOPMENT OF SENSING DEVICES FOR MANAGEMENT OF BIOTERRORISM

Sol-gel process can be used in developing advanced materials for biomimetic sensors for countermeasures against chemical and biological warfare agents. Design of nanoporous materials for biomimetic sensors is an important development in the management of bioterrorism. This was basically motivated by the mechanisms found in biological systems, for example, designing of electronic nose, based on natural sense of smell. An important application of these sensors is in detecting biological/chemical warfare agents such as anthrax, sarin, and mustard gas in the battlefield or in the environment. Generally, these sensors are expected to reproduce or surpass the human senses. In this pursuit, the critical parameters for designing the sensors are the detection time, concentration levels, and specificity of detecting agent/molecule. The choice of sensor material and its design are important steps that limit these parameters.

Usually the sensor materials used are thin films of polymer or polymer-carbonblack composite. The sensing mechanism is usually based on swelling of sensing materials by the analyte, which in turn depends upon the diffusion and adsorption characteristics of the materials. The diffusion depends upon the micro structure and nanostructure of the polymer film and the adsorption depends upon the nature and extent of interaction between the polymer and the analyte. Thus, an intelligent design of sensor materials would entail optimising the micro/nanostructures and interaction effects of the polymer film. Sol-gel techniques are widely used to design nanoporous polymers, in designing materials with porosity and pore sizes between 0-80 per cent and 1-50 nm, respectively. Polyurethane/polyurea, phenol-formaldehyde and epoxy-amine chemistries might be used to design nanoporous materials for sensing applications. The nanoporous morphology of these materials would be optimised by controlling the reaction, solvation, and phase-separation characteristics of the system. Subsequently, the pore activity of these materials can be modified using chemical grafting techniques based on sulfonation and esterification (amino acids) reactions. Such grafting techniques impart hydrophilicity and bioactivity. In

effect, functional nanoporous materials would be designed for sensing applications using sol-gel and subsequent chemical grafting techniques.

## 8. DEVELOPMENT OF RADIATION-SENSITIVE MATERIALS

Detection and monitoring of ionising radiation in the environment due to accidental nuclear emergencies and/or in occupational exposure are of great importance for defence personnel and radiation workers in hospitals and nuclear industries. The importance of radiation monitoring has become all the more important after the 9/11 terrorist attack in USA in 2001. Although various nuclear instruments are available for monitoring radiation in the environment, these are not only expensive but also require technical support for both maintenance and operation. Moreover, it is known that nuclear environment is hazardous also for instruments for routine operation. Another serious concern is when the temperature rises during nuclear explosions, several types of monitoring equipment start malfunctioning. However, it will not be practical to install available equipment in quick succession at several places in the events of nuclear emergencies, or even monitoring of radiation levels at different geographical locations. Because of these reasons, suitable radiation monitoring techniques need to be developed.

Sol-gel process is emerging as a potential technology for the development of radiation dosimeters for several types of applications. Recently, few research groups have demonstrated the usefulness of sol-gel-doped rare earth materials in radiation dosimetry. Luminescence properties of rare earth element,  $Eu^{3+}$  doped in sol-gel were found to be dramatically increased with ionising radiation. The dose-response<sup>77</sup> appeared to be linear up to 400 Gy. In 2001, Ferreria<sup>78</sup>, *et al.* reported a sol-gel-based new manufacturing process for thermoluminescent dosimeters.

An interesting application of sol-gel combining with optical fibre has been reported as a medical radiation sensor for use in radiation therapy of cancer<sup>79,80</sup>. Few commonly known porphyrin-type molecules, viz., phthalocyanines in sol-gel matrix have demonstrated radiation sensitivity up to  $10^6$  Gy. Some fluorescent molecules also tend to have dose-dependent radiation sensitivity.

There have been few reports on the possible use of optical fibres coated with rare earth elements again using sol-gel method for applications in radiation dosimetry in nuclear installations. Radiation hardness is another common phenomenon in optical fibre where the attenuation of visible light in certain wavelength range increases with the absorbed radiation dose<sup>81</sup>. In all these studies, mostly  $\gamma$  radiation has been used for irradiation of sol-gel glassy matrix containing various probing molecules/elements and detection of the absorbed radiation dose has been carried out using either absorption or luminescence measurements. Both, absorption and fluorescence-based measuring methods are simple and can be translated into portable readout device. Development of sol-gel-based radiation-sensitive materials is an important research area of our interest.

## 9. PROSPECTS OF SOL-GEL INITIATIVES

Though sol-gel process was known as early as 1800s, but in the last two decades due to concerted multidisciplinary efforts, sol-gel applications have increased manifold despite various limitations. Many of the above-cited examples like optical materials for lasers, sensors for gas and water pollutants, biomimetics, nanocomposites, and radiation-sensitive materials are relevant for a variety of applications in defence. It is important to focus on such an area with multidisciplinary approach. The present research activities in the area of sol-gel started a couple of years ago<sup>83</sup>. The focus was to understand the characteristics of sol-gel materials as a function of different compositions<sup>23-28</sup>. Knowledge has been gained on the physico-chemical properties of these materials for developing applications in biosensors. Research is also in progress to develop radiation-sensitive materials using sol-gel technology<sup>82</sup>. It is important to further research activities to develop sol-gel materials for sensing applications.

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