Fluorinated ORMOSIL for Oxygen Sensor

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ABSTRACT

Sensors persist to make significant impact in daily life. There has been a strong demand for producing highly sensitive, selective, responsive, and cost effective sensors. As a result, research emphasis is on developing new sensing materials and technologies. In this context, the use of nanomaterials for the construction of sensor devices constitutes one of the most exciting approaches. In this respect ormosils which can be used to form ultra-fine and uniform film are very desirable. These films of single and multiple component compositions can be produced on a nanoscale particle size for sensor applications.

We have developed composite xerogel thin films and studied their analytical figures of merit as quenchometric sensors for gaseous O_2. Lumniphores proposed to be used are Pt(II) octaethylporphine (PtOEP) and Pt(II) meso-tetra(N-methyl-4-pyridyl)porphyrin tetrachloride (PtTMP). The various silane precursors to be used for the preparation of doped xerogel are pentafluorophenylpropyltrimethoxysilane (PFTMOS)/ n-octyltrimethoxysilane (C_8TMOS)/ n-propyltrimethoxysilane(C_3TMOS). The results show that PtOEP doped composites form uniform, crack-free xerogel films that can be used to construct high sensitivity O_2 sensors that have linear calibration curves and excellent long-term stability which indicates the homogeneous environment of the luminophore in these cases. The O_2 sensing profile is fully reversible over entire O_2 range from 0-100%. For PtOEP-doped PFTMOS/C_8TMOS/ C_3TMOS, while keeping C_8TMOS and C_3TMOS at the same molar ratio, sensitivity (I_{N2}/I_{O2}) decreases with increased PFTMOS% from 20 to 30%, which is due to the decreased bimolecular quenching constant. However, very less sensitivity was observed for PtTMP-doped PFTMOS/C_8TMOS/ C_3TMOS as compared to PtOEP-doped PFTMOS/C_8TMOS/ C_3TMOS composites.

Keywords: Sensors, ormosils, oxygen sensing

1. INTRODUCTION

Sensors and sensing technology play a crucial role in the process of information gathering. The need for high throughput label-free multiplexed sensors for chemical and biological sensing has increased in the last decade in the newer application areas, viz., healthcare genetics, diagnostics, and drug discovery; environmental and industrial monitoring; quality control, etc. Chemical sensors are defined as the analytical devices that convert the chemical potential energy of targeted analyte into a proportionate measurable signal. In most of the chemical sensors, although sensitivity has increased significantly in recent years, however, not much improvement has been seen in terms of their selectivity. The selectivity of a chemical sensor is limited by the properties of the sensor materials that are used in a specific technology.

There is not a single sensing class or technology that can effectively detect everything of interest in every possible environment. Rather, selecting the optimum sensing approach from a group of materials or technologies [1-4] may be the best method to address the sensing needs. In this respect ormosils which can be used to form ultra-fine and uniform film are very desirable. This process also allows us to create solid-state platforms for the chemical sensors that are optically transparent which are both chemically and thermally stable. The unique characteristics of the sol-gel derived materials are: optical transparency, effective dopant entrapment, nanoporous structure for small molecules, free diffusion, tailed physicochemical properties, and mechanical stability. Given these, sol-gel methods are “ideal” for chemical sensor applications.

Sol-gel processed xerogels can be used for sensor applications by introducing a reporter/ recognition element (fluorophore, dye, protein) during the appropriate step in the sol-gel process[5] or by creating molecularly imprinted materials [6,7]. When introduced in the sol-gel processing solution, the indicator can become entrapped within the xerogel matrix. The xerogel matrix will form around the recognition element without, in many cases, altering the physical or chemical structure. This simple protocol contributes to the attractiveness of sol-gel processed xerogels as sensor platforms. There have been a significant number of luminescence-based O_2 sensors reported in the literature based on sol-gel-derived materials doped with nationally and internationally [8-15]. The common features of these sol-gel-derived O_2 sensors are that the Stern-Volmer plots (I_0/I *vs.* [Q]) are nonlinear, the sensor response is not stable over the long term, or both. Hence, the development of sol-gel-derived materials doped with luminophores with stable sensor response is desirable.

Doping of ormosil with a suitable material improves the property of immobilization matrix considerably. Fluorine [16- 19] is the most electronegative element in the periodic table and has the smallest atomic radius (0.64 Å) after hydrogen and helium. The F-C bond is the strongest single bond (450 Kcal mol^{-1}). Accordingly, the unique chemical and physical properties of fluorinated materials are rising [16-19], such as: (i) enhanced hydrophobicity and lipophobicity, (ii) high

ISBN: 978-93-83083-79-4

thermal and oxidative stability, (iii) weak intermolecular interactions, (iv) low surface energy and surface tension, (v) low refractive index, (vi) exceptional chemical and biological inertness, and (vii) high gas-dissolving capacity. Research indicates that certain fluorinated xerogel platform exhibit high permeability to O_2 [17, 20], and fluorocarbon-in-water emulsions are being developed for *in vivo* oxygen transport to function as blood substitutes [18, 21]. Among various lumniphores, metalloporphyrin complexes [20, 22] exhibit long luminescent lifetimes [22] and high quantum yields [23].

2. RESULTS AND DISCUSSION

2.1 Methodology for ormosil preparation

Different ratios of silane precursors like pentafluorophenylpropyltrimethoxysilane (PFTMOS)/ *n*-octyltrimethoxysilane (C_8TMOS)/ trimethoxypropyylsilane (C_3TMOS) were taken. Various combinations of different precursors were tried to optimize the condition for preparation of xerogel thin films. Among all the combinations tried only two conditions were found to be suitable for preparation of stable films. One was with precursors PFTMOS, C_8TMOS and C_3TMOS mixed together (6.5 mmol in total) by varying PFTMOS% from 0 to 30% while keeping C_8TMOS% and C_3TMOS % the same.

In detail, 0, 0.169, 0.338, 0.507 ml of PFTMOS, 0.838, 0.755, 0.671, 0.587 ml of C_8TMOS, and 0.479, 0.431, 0.383, 0.335 ml of C_3TMOS were mixed in a glass vial, respectively along the sequence. To the mixture, 1.25 ml of EtOH (22 mmol) and 0.4 ml of 0.1 N HCl (containing 22 mmol H_2O and 0.04 mmol HCl) were then added. The capped mixtures were sonicated for 2 h at room temperature. The other film was keeping the concentration of all precursors same but adding only 0.25 mL of ethanol and 1 mL of water. These optimized materials were spin-casted onto glass surface to create a thin layer xerogel.

2.2 Characterization and application of prepared ormosils:

A series of luminophores Pt(II) octaethylporphine (PtOEP) and Pt(II) meso-tetra(N-methyl-4-pyridyl)porphyrin tetrachloride (PtTMP) were doped in the optimized xerogels. Spin-casted composite ORMOSILs (organically modified silicates) xerogel films sequestered with luminophore Pt(II) octaethylporphine (PtOEP) and Pt(II) meso-tetra(N-methyl-4-pyridyl)porphyrin tetrachloride (PtTMP) were prepared. Scanning electron microscopy and steady-state luminescence measurements were used to investigate the structure of these films, their analytical figures of merit, and determine the underlying reasons for their observed performance.

ISBN: 978-93-83083-79-4

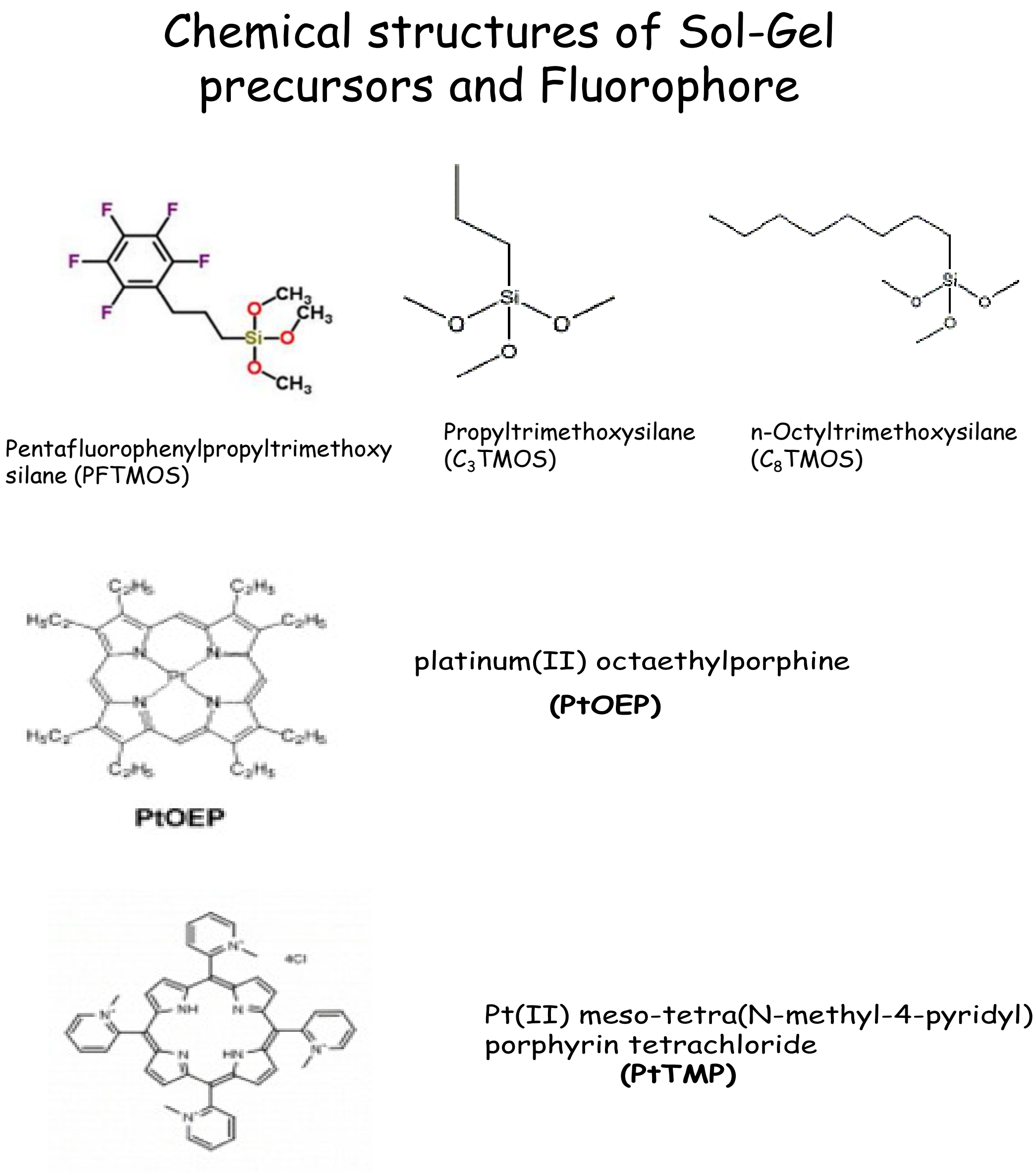

Fig. 1 Structures of various ormosil precursors and fluorophores used for ormosil formation

The choice of the alkoxysilane is the first parameter to be considered in order to successfully prepare an Ormosil. Silanes (precursors of the Ormosil) are a form of silica, which is a polar adsorbent that adsorbs polar solutes tightly. Additionally, they form siloxane, after hydrolysis followed by condensation having highly complicated porous structure and stable chemical properties. N- octyltrimethoxysilane is an alkoxysilane which is highly hydrophobic in nature which is hydrolyzed to produce hydroxyl groups in the presence of water, which is followed by polycondensation of the hydroxyl groups at ambient temperature. Similarly the groups of propyltrimethoxysilane are also hydrolyzed. Siloxane is formed in the condensation and polycondensation reactions of various precursors. Pentafluorophenylpropyltrimethoxysilane precursor improves the property of prepared ormosils. Fluorinated ormosils had improved hydrophobicity and lipophobicity, low surface energy and surface tension, low refractive index, exceptional chemical and biological inertness, and high gas-dissolving capacity. These fluorinated xerogel platforms exhibited high permeability to O_2. The fluorinated ormosils were successfully used for encapsulating lumniphores PtOEP and PtTMP. The SEM results show that PtOEP doped composites form uniform, crack-free xerogel films. Further, these films can be used to construct high sensitivity O_2 sensors that have linear calibration curves and excellent long-term stability which indicates the homogeneous environment of the luminophore in these cases. The O_2 sensing profile is fully reversible over entire O_2 range from 0-100%. For PtOEP-doped PFTMOS/C_8TMOS/ C_3TMOS, while keeping C_8TMOS and C_3TMOS at the same molar ratio, sensitivity (I_{N2}/I_{O2}) decreases with increased PFTMOS% from 0 to 30%, which is due to the decreased bimolecular quenching constant. However, very less sensitivity was observed for PtTMP-doped PFTMOS/C_8TMOS/ C_3TMOS as compared to PtOEP-doped PFTMOS/C_8TMOS/ C_3TMOS composites.

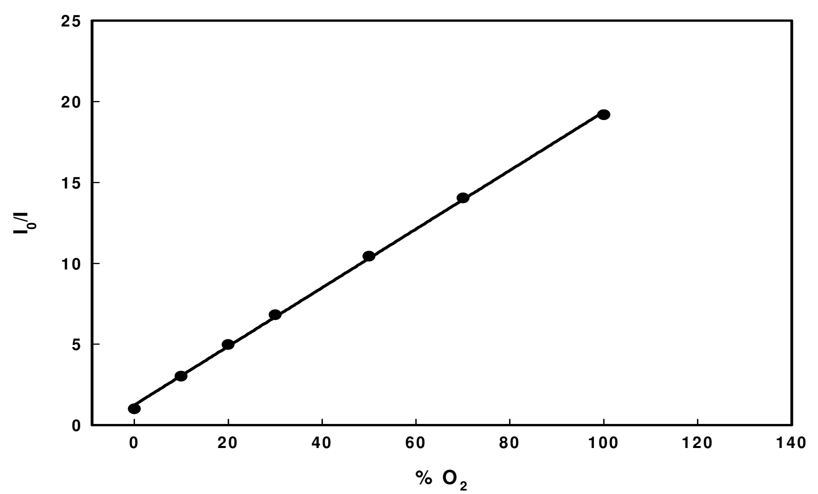

Fig. 2 Stern-Volmer plot of PtOEP-doped PFTMOS/C_8TMOS/ C_3TMOS O_2 responsive film on glass slide

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3. CONCLUSION

Sol-gel derived materials with different physical or physiochemical properties, such as pore size, shape and surface area or polarity, refractive index, and density can be easily formed depending on the precursors used and sol-gel processing conditions. Spin-casted composite ORMOSILs of PFTMOS/C_8TMOS/C_3TMOS with suitable luminophores i.e. PtOEP-doped can be used to prepare oxygen sensors with improved sensor response times, sensitivities and recovery rates because of their relatively short path lengths for diffusion, optical transparency and thermal stability. The selectivity of a chemical sensor which is limited by the properties of the sensor materials that are used in a specific technology can be easily improved by constructing these suitable materials .

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ISBN: 978-93-83083-79-4