Organofluoro-silica xerogels as high-performance optical oxygen sensors

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Ubiquitous oxygen (O₂) is one of the most important analytes to be assessed in medicine, industry and the environment. Due to a number of advantages, miniaturized optical sol–gel sensors are rapidly replacing older electrochemical sensors. This account provides an overview of fluorinated organically modified silicate (ORMOSIL) xerogels as optical chemical sensors and shows how, together with the dye quenching rate, the subtle structural features of an organofluoro-silica matrix is of fundamental importance in determining the overall sensor performance.

1. Background and introduction

Doped sol–gel silicas are well established platforms for optical sensors due to their high transparency and high sensitivity to external reactants, coupled with unsurpassed versatility and stability.¹ Oxygen, in its turn, is perhaps the single most important analyte in analytical chemistry. O₂ is involved in many chemical and biochemical conversions as either a reactant or a product and its concentration often needs to be measured in medicine, industry and the environment. The search for optical O₂ sensors to replace the conventional electrochemical (Clarke) electrodes has been a major goal of recent chemical research, with studies focusing on polymers² and on sol–gel silicas.³ Optical oxygen sensors are more attractive than conventional amperometric devices because they have a fast response time, do not consume oxygen, are highly stable and do not require frequent calibration. Organically modified silicates (ORMOSILs)⁴ are easily prepared by mild co-condensation of silicon alkoxides functionalized with stable non-hydrolysable organic groups, in the presence of the photoactive species.⁵ The mechanism involves hydrolysis and condensation reactions (eqn (1) and (2) in Scheme 1), and in analytical applications the intermediate gels are generally shaped as thin-films or microfibers:⁶

The overall hydrolytic polycondensation reaction can be written as eqn (3):

\[
\text{Si(OR)}_4 + \text{RSi(OR)}_3 + 7\text{H}_2\text{O} \quad \xrightarrow{\text{condensation}} \quad \text{Si(OH)}_4 + \text{RSi(OH)}_3 + 7\text{ROH} \quad (1)
\]

\[
\text{Si(OH)}_4 + \text{RSi(OH)}_3 \quad \xrightarrow{\text{condensation}} \quad (\text{OH})_2\text{Si–O–SiR(OH)}_2 + \text{H}_2\text{O} \quad (2)
\]

Scheme 1 The sol–gel hydrolytic polycondensation affording ORMOSILs.

The chemical and physical properties of the final doped glasses (porosity, surface area, pore size distribution, shape, hydrophilic–lipophilic balance etc.) can be finely tuned in an immense range by selecting appropriate sol–gel process conditions. The advantages offered by these materials over traditional commercial electrochemical sensors are well rendered by the comparison

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Fiber-optic oxygen sensors | Commercial electrochemical systems
---|---
Based on dynamic equilibrium with surrounding media, O2 is not consumed | Measure the rate of consumption of O2
Responds to pO2 calibration is the same in both gases and liquids | Electrodes can be calibrated for use in gases or liquids, but not both at the same time
Immune to sample matrix, salinity and pH | Affected by the sample matrix; changes in salinity, pH affects sensor readings
Fast response times: <1 s for dissolved O2 and O2 gas | Response times of 60–90 s
Long life (>1 year) | Electrode lifetime <3 months
Frequent calibration unnecessary | Calibration may be required on an hourly basis
Probe temperature range –80 to 80 °C | Temperature range 0 to 45 °C

 ORMOSIL hybrid xerogels are among the best platforms for oxygen sensing thanks to their excellent permeability to oxygen (which enables fast response), high sensitivity (20 ppb) detection limit due to long excited lifetime (5.3 μs), high luminescence quantum yield and O2 quenching efficiency. The sensitivity of the sensor, in fact, depends both on the rate of luminophore quenching by O2, the permeability of the solid matrix to O2, and on the accessibility of the entrapped luminophore. Assuming that the ensemble of luminophore molecules are emitted from largely similar microenvironments, and that the quencher molecules have similar accessibilities to the individual luminophore molecules, one can write the Stern–Volmer relationship (eqn 4).

\[ \frac{I_0}{I} = 1 + K_{SV}[O_2] = 1 + k_q t_0 [O_2] \]  

where \( I_0 \) and \( I \) represent the intensities of luminescence in the absence and presence of O2, respectively, \( K_{SV} \) is the Stern–Volmer quenching constant, \([O_2]\) is the O2 concentration, \( t_0 \) is the excited-state luminescence lifetime in the absence of quencher, and \( k_q \) is the bimolecular rate constant describing the efficiency of the collisional encounters between the luminophore and the quencher.

For the ideal case of a luminophore in an homogeneous microenvironment, a plot of \( I_0/I \) vs. \([O_2]\) will be linear with a slope equal to \( K_{SV} \) and an intercept of unity, allowing a simple single-point calibration of the sensor. On the other hand, a downward-curving Stern–Volmer plot is due to the presence of a multitude of quenching sites within the sensing element, each site with its own Stern–Volmer constant. Sensitivity is measured by the ratio \( I_{N2}/I_{O2} \) where \( I_{N2} \) and \( I_{O2} \) represent the fluorescence intensities in pure nitrogen and pure oxygen environments, respectively (a large ratio pointing to an increase in \( K_{SV} \)).

2 Enhanced performance of fluorinated composites

In general, fluorinated precursors mixed with alkyl-modified silanes form uniform, crack-free xerogel films that can be used to construct O2 sensors that have linear calibration curves, have excellent long-term stability and afford unprecedented sensitivity. Following the first such sensor based on \([Ru(dpp)]^{2+}\) entrapped in an \( n \)-propyl-trimethoxysilane/3,3,3-trifluoropropyltrimethoxysilane (C3-TMOS/TFP-TMOS),10 showing a then unprecedented \( I_{N2}/I_{O2} \) sensitivity of 35 and a response time of less than 5 s, other composite sensors (made of two of the following silanes: tetramethoxysilane (TMOS), \( n \)-propyl-trimethoxysilane (C3-TMOS), 3,3,3-trifluoropropyltrimethoxysilane (TFP-TMOS), phenethyl-trimethoxysilane (PE-TMOS), and pentafluorophenylpropyltrimethoxysilane (PFP-TMOS) were studied in detail (Fig. 2).11

Most recently even more sensitive high performance fiber-optic O2 sensors based on fluorinated xerogels doped with Pt(n) complexes were reported.12 A general result of these studies is that encapsulation of the luminophore within fluorinated silica composites, instead of simple alkyl-modified analogues, enhances the overall performance of the optical sensors.

Representative examples for \([Ru(dpp)]^{2+}\)-based quenchometric sensors are shown in Table 2, where the sensitivity of several fluorinated sensors is reported (with the molar ratio \( F/N \) of fluorinated to non-fluorinated precursors set at 2).
First generation fluorinated sensors were made of [Ru(dpp)3]2+ doped in a TFP-TMOS/C3-TMOS matrix with F/N = 2, and exhibited an I_{N_2}/I_{O_2} of 35/C6 at that time a sensitivity significantly greater than observed with any previous [Ru(dpp)3]2+-based quenchometric sensor, with a fast 5 s response time when switching from a fully deoxygenated environment to a fully oxygenated environment. Furthermore, the Stern–Volmer plot is linear over the full oxygen concentration range (0–100%), indicating that the [Ru(dpp)3]2+ molecules are reporting from a homogeneous microenvironment, since in any case the non-linearity is associated with the luminophore dopant molecules distributed between different sites that exhibit different k_q or s_0 values, as is often the case with many other xerogel-based sensor platforms that exhibit downward curvature and multi-exponential time-resolved intensity decay profiles.

In general, however, entrapment of the Ru-based luminophore in the other xerogels studied in the elegant comparative study mentioned above,\textsuperscript{10} was not homogeneous with the time-resolved intensity decay profiles of the luminescence due to the entrapped [Ru(dpp)3]2+ being well described by the Lehrer model consistent with the [Ru(dpp)3]2+ molecules reporting from two microenvironments within the xerogel matrix, one of which is accessible to, and responsive to, the O_2 quencher molecules, and one in which the luminophore is not accessible to or is non-responsive to the quencher molecules.\textsuperscript{10}

Results in particular showed that while the observed I_{N_2}/I_{O_2} for the TFP-TMOS/C3-TMOS hybrid xerogel with the molar ratio F/N = 1 is the best among [Ru(dpp)3]2+-based O_2-responsive sensor elements, the sensitivity to O_2 could be adjusted by more than 25-fold by controlling the F/N parameter. In detail, the k_q for the TFP-TMOS/C3-TMOS xerogel was the largest among all materials studied reaching a maximum around F/N = 0.5 and dropping by 30–50% as one moves away from the optimal F/N (Fig. 3).

**Table 2** Representative examples of reported I_{N_2}/I_{O_2} for quenchometric oxygen sensors based on dyes immobilized in sol–gel matrixes (adapted with permission from ref. 10; Copyright 2005, ACS Publications)

<table>
<thead>
<tr>
<th>O_2-sensitive dye</th>
<th>Support matrix</th>
<th>Response time</th>
<th>I_{N_2}/I_{O_2}</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(dpp)3]^{2+}</td>
<td>TEOS\textsuperscript{a}</td>
<td>0% O_2 to 100% O_2: 3.5 s; 100% O_2 to 0% O_2: 30 s</td>
<td>12</td>
<td>13</td>
</tr>
<tr>
<td>[Ru(dpp)3]^{2+}</td>
<td>MeTMOS</td>
<td>10 s</td>
<td>3.4</td>
<td>8</td>
</tr>
<tr>
<td>[Ru(dpp)3]^{2+}</td>
<td>C8-TEOS/TEOS</td>
<td>Sensors response times were &lt;5 s</td>
<td>35</td>
<td>10</td>
</tr>
<tr>
<td>PtOEP\textsuperscript{a}</td>
<td>TEOS</td>
<td>60-540 s for the changes for different oxygen concentration</td>
<td>40</td>
<td>14</td>
</tr>
<tr>
<td>PtTFPP\textsuperscript{a}</td>
<td>C8-TEOS/TEOS</td>
<td>0% O_2 to 100% O_2: 0.6 s; 100% O_2 to 0% O_2: 5 s</td>
<td>22</td>
<td>15</td>
</tr>
<tr>
<td>PtOEP\textsuperscript{a}</td>
<td>C8-TEOS</td>
<td>0% O_2 to 100% O_2: 0.7 s; 100% O_2 to 0% O_2: 14 s</td>
<td>47</td>
<td>14</td>
</tr>
<tr>
<td>PtTFPP\textsuperscript{a}</td>
<td>C3-TMOS/TFP-TMOS</td>
<td>0% O_2 to 100% O_2: 3.7 s; 100% O_2 to 0% O_2: 3.7 s</td>
<td>68.7</td>
<td>12</td>
</tr>
<tr>
<td>PtOEP\textsuperscript{a}</td>
<td>C3-TMOS/TFP-TMOS</td>
<td>0% O_2 to 100% O_2: 5.3 s; 100% O_2 to 0% O_2: 5.9 s</td>
<td>82.5</td>
<td>12</td>
</tr>
</tbody>
</table>

\textsuperscript{a}TEOS = tetraethoxysilane. \textsuperscript{b}C8-TEOS = n-octyl-triethoxysilane. \textsuperscript{c}PtOEP = Pt(n) octaethylporphine; PtTFPP = Pt(n) tetrakis pentafluorophenylporphine.
Thus, the reason for the observed sensitivity from these xerogel-based materials arises from $k_q$ and $\tau_0$ both being larger in comparison to the other systems studied; however, the tunability arises exclusively from $k_q$ and not from $\tau_0$.

From a morphological viewpoint, the smoothness and the homogeneity of the composite ORMOSIL films is very high and their crack-free formation proceeded without any added surfactant, due to enhanced hydrophobicity and consequent lower surface tension at the solid/liquid interface during drying of the intermediate alcogel. Under ambient storage conditions, the stability of these hybrid xerogel sensors was constant to within 2% over a six-month period which should be compared to the 5-fold decrease in sensitivity in pure TEOS-based xerogels. Such a stable sensor response over time is due to the increased hydrophobicity of the sol–gel ORMOSIL cages that overcomes the xerogel shrinkage and pore collapse with time, and is a crucial factor in the development of a reliable sensor platform. This outcome, in particular, contrasts with the poor stability of most sensing species immobilized at the surface of organic and inorganic polymers.16

Based on these findings, more recently two innovative phosphorescent Pt porphyrins (Fig. 4) entrapped in the same organofluoro-silica glass TFP-TMOS/C3-TMOS were used to construct the most sensitive optical oxygen sensors known thus far. Produced as optical fibers, such sensors employ either Pt(II) tetraakis pentafluorophenylporphine (PtTFPP) or Pt(II) octaethylporphine (PtOEP). These platinum species have longer lifetimes than Ru(II) dyes, show convenient excitation and emission wavelengths with large Stokes shifts (100–170 nm), and also have a lower luminescence quantum yield. As a result, the optical $O_2$ sensors based on composite fluoro-xerogels doped with PtTFPP or PtOEP luminophores have sensitivities of 68.7 and 82.5, respectively, both yielding linear Stern–Volmer plots (Fig. 5).

Again, the excellent sensitivity of these sensors was attributed to the uniform distribution of the Pt(II) luminophores in the xerogel matrix, and to the improved oxygen diffusivity provided by the fluorinated xerogel. Furthermore, longer excitation and emission wavelengths increase the signal-to-background noise ratio of oxygen sensors, which is particularly useful for in vivo measurements.

The response time of the PtTFPP-doped sensor is 3.7 s when switching from 100% nitrogen to a fully oxygenated environment, and 5.3 s when switching the opposite way (the corresponding response times of the PtOEP-doped sensor are 3.7 and 5.9 s, respectively), Fig. 6. Longer reaction times are, of course, to be expected on changing from 100% nitrogen to atmospheric oxygen concentration.

The approach using organofluoro-alkoxides has a broad applicability and was extended by Chu and Lo to the production of a fiber-optic $CO_2$ sensor.17 The fluorinated platform exhibited a linear response to $CO_2$ concentrations in a wide concentration range (0–30%) whereas in previously reported pyranine-based sensors using alkyl-modified silicon alkoxide, the linear response was limited to 2% $CO_2$.18

Fig. 4 Chemical structures of: (a) PtTFPP and (b) PtOEP complexes.

![Figures](https://example.com/fig4.jpg)

Fig. 5 Stern–Volmer plots for PtTFPP-doped (●) and PtOEP-doped (■) oxygen sensors. (Reprinted with permission from ref. 12. Copyright 2007, Elsevier.)
3 Outlook and conclusions

Fluorinated ORMOSILs doped with sensitizing luminophores provide appropriate sensing films for oxygen sensors thanks to (i) the homogeneous fluorinated microenvironment of the sol–gel cages entrapping the luminophore species, and to (ii) the exceptional diffusivity of the O₂ molecules within the fluorine-modified matrix. As a result, highly sensitive sensors can be obtained with a rapid detection time, linear calibration and stable performance. Pt porphyrins are the best suited sensing species affording the highest O₂ sensitivity and response rapidity of any reported dye-based sensor platform (68.7 and 82.5 sensitivities for the PtTFPP-doped and PtOEP-doped sensors, respectively; and 4–5 s response times). Ruthenium species such as [Ru(dpp)₃]²⁺ also exhibit excellent performance (35 sensitivity and ca. 5 s response times).

Attentive readers may have noted that partial fluorination of the organosilica matrix (FIN = 1 for the [Ru(dpp)₃]²⁺-based sensors) affords the most sensitive sensors. Indeed, a remarkable correlation between the hydrophilic–hydrophobic balance (HHB) of the matrix and reactivity has recently been found to explain the high performance of similarly doped fluorinated xerogels in aerobic catalysis. The HHB depends on the degree of fluorination and on the length of the fluoroalkyl chain linked to the silica network, and reaches a maximum for low F=N values. An insight that will be useful in developing second generation sol–gel entrapped fluorinated silicas for sensing and catalytic applications alike.

The use of a hybrid xerogel support matrix has a number of key advantages compared to previously reported surface-functionalized polymers, including good photostability and high sensitivity to the external environment. Furthermore, the hybrid xerogel matrix provides a simple solution for the production of robust, hydrophobic thin-films with well-defined thickness and excellent gas permeability characteristics for use in planar waveguide fluorescence detection configurations. Considering the ease of miniaturization and fabrication of these sol–gel derived sensors, the introduction of commercial fluorinated sol–gel derived O₂ and CO₂ sensors is only a matter of time.

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References

7 See also at the URL: www.oceanoptics.com.