Optical oxygen sensing materials based on a novel dirhenium(I) complex assembled in mesoporous silica

Yanhong Liu, Bin Li, Yan Cong, Liming Zhang, Di Fan, Linfang Shi

A new dirhenium(I) complex \(\text{fac-}[\text{Re(CO)}_3(4,7\text{-dinonadecyl-1,10-phenanthro -line})_2(4,4\text{-bipyridyl})]\) (trifluoromethanesulfonate)\(_2\) (denoted as D-Re(I)) is assembled in MCM-41 and SBA-15 type mesoporous silica support. The emission peaks of D-Re(I) in D-Re(I)/MCM-41 and D-Re(I)/SBA-15 are observed at 522 and 517 nm, respectively. Their long excited lifetimes, which are of the order of microseconds, indicate the presence of phosphorescence emission arising from the metal to ligand charge-transfer (MLCT) transition. The luminescence intensities of D-Re(I)/MCM-41 and D-Re(I)/SBA-15 decrease remarkably with increase in the oxygen concentration, meaning that they can be used as optical oxygen sensing materials based on luminescence quenching. The ratios \(k_q/k_{0}\) of D-Re(I)/MCM-41 and D-Re(I)/SBA-15 are estimated to be 5.6 and 20.1, respectively. The obtained Stern–Volmer oxygen quenching plots of the mesoporous sensing materials could be fitted well to the two-site Demas model and Lehrer model.

1. Introduction

Determination of oxygen concentration has long been the focus in many areas ranging from atmospheric control to river pollution monitoring. In the past decade, optical oxygen sensors based on the decrease of luminescent intensity or excited-state lifetime of the sensing material as a function of oxygen concentration have become more and more attractive compared with conventional amperometric devices owing to the advantage of quick response time, no consumption of oxygen, high sensitivity and high resolution as well as continuous determination of oxygen concentrations in remote, hazardous, or in vivo environments [1–3]. In most cases, the sensing material is composed of an indicator dye dispersed within oxygen permeable support, such as polymers, sol–gel derived silica-based materials, and Langmuir–Blodgett monolayer films [4–6]. Recently, the mesoporous silica material is expected to be an effective support for the preparation of oxygen sensors with excellent performances. Owing to its three-dimensional porous structure, oxygen could diffuse within highly ordered and nearly parallel channels, which is necessary for higher sensitivity and shorter response time [7,8]. Mesoporous silica based composites represented one of the best permeable supports, such as polymers, sol–gel derived silica-based materials, and Langmuir–Blodgett monolayer films [4–6]. Recently, the mesoporous silica material is expected to be an effective support for the preparation of oxygen sensors with excellent performances. Owing to its three-dimensional porous structure, oxygen could diffuse within highly ordered and nearly parallel channels, which is necessary for higher sensitivity and shorter response time [7,8]. Mesoporous silica based composites represented one of the best permeable supports, such as polymers, sol–gel derived silica-based materials, and Langmuir–Blodgett monolayer films [4–6]. Recently, the mesoporous silica material is expected to be an effective support for the preparation of oxygen sensors with excellent performances.
2. Experimental section

2.1. Reagents and measurement

4,4′-dimethyl-2,2′-bipyridine (99%, Aldrich), 1-iodoocadecane (95%, Aldrich), 4,4′-bipyridine (98%, Aldrich), Re(CO)₅Cl (98%, Strem), 2,2′-bipyridine (99%, Lancaster), silver trifluoromethanesulfonate (99%, Aldrich) were used as received. All other solvents for synthesis were of analytical grade and were used without further purification. ¹H NMR spectra were recorded on a Bruker AC 400 spectrometer. CHN elemental analysis was performed on a 240 Perkin-Elmer analyzer. Small-angle X-ray diffraction (SAXRD) patterns were recorded with a Rigaku-Dmax 2500 diffractometer using Cu Kα (λ = 1.5405 nm) radiation at 0.02° (2θ) scanning step. The IR absorption spectra were measured in the region of 400–4500 cm⁻¹ by a Fourier transform infrared (FTIR) spectrophotometer (Model Perkin-Elmer 580B) with a resolution of ±4 cm⁻¹. The Re(I) ion content was analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES) measurement with a TJA-POEMS spectrometer. The D-Re(I)/MCM-41 and D-Re(I)/SBA-15 composites were dissolved in the mixture of hydrofluoric acid and nitric acid for ICP measurement. The oxygen sensing properties of the D-Re(I)/MCM-41 and D-Re(I)/SBA-15 composites were investigated using a Hitachi-4500 fluorescence spectrophotometer equipped with a xenon lamp (150 W) operating in the range of 200–900 nm. For the Stern–Volmer plots measurements, oxygen and nitrogen were mixed at different concentrations via gas-flow controllers and flowed directly into the gas chamber sealed with a close fitting sub-seal rubber lid equipped with two (in and out) tubes. 1 min is usually allowed between changes in the N₂/O₂ concentrations to ensure that a new equilibrium point had been established. Equilibrium was evident when the luminescence intensity remained constant (±2%). The sensing response curves were obtained using the same instruments. All measurements were performed at ambient temperature.

2.2. Synthesis of the D-Re(I) complex

Fig. 1 shows the molecular structure of D-Re(I). The ligand 4,7-dinonylacety1-1,10-phenanthroline (d19-phen) was obtained according to the literature [21]. The D-Re(I) was synthesized by modification of reported literatures [22–24]: 0.3 mmol Re(CO)₅Cl and 0.3 mmol d19-phen were dissolved in 16 mL benzene and refluxed for 2 h under N₂ flow and fac-Cr(Re(CO)₅)(d19-phen) was obtained by evaporating the solvent and subsequent recrystallization from dichloromethane/hexane. Then 0.2 mmol fac-Cr(Re(CO)₅)(d19-phen) and 0.3 mmol silver trifluoromethanesulfonate (AgOTf) were mixed and refluxed in acetonitrile for 8 h in the dark under N₂ from which a white residue with a clear yellow solution was obtained. After filtration, the filtrate was evaporated to give a bright yellow solid fac-[(CH₃CN)Re(CO)₅(d19-phen)]OTf (Re(I)). Finally, 0.1 mmol Re(I) and 0.05 mmol bridging ligand 4,4′-bipyridyl were refluxed in benzene for 24 h under N₂. The resulting solution was evaporated to give a bright yellow residue, which was purified by column chromatography (silica-gel using ethyl acetate/n-hexane (1:1, v/v) as the eluent). The desired di-rhenium(I) complex was finally obtained: Yield: 32%. ¹H NMR (300 MHz, CDCl₃, relative to Me₄Si): δ d19-phen: 3.31 (m, 4H, –CH₂–), 3.19 (m, 4H, –CH₂–), 1.82 (m, 8H, –CH₂–), 1.49 (m, 8H, –CH₂–), 1.26 (m, 120H, –(CH₂)₁₅–), 0.88 (t, 12H, J = 6.6 Hz, –CH₃), 9.36 (d, 4H, J = 5.5 Hz, H at 2.9-position), 8.17 (s, 4H, H at 5.6-position), 7.88 (d, 4H, J = 5.4 Hz, H at 3.8-position), 4.4′-bipyridyl: 8.28 (d, 4H, J = 6.7 Hz, ortho to N), 6.68 (d, 4H, J = 6.8 Hz, meta to N). Anal. Calcd. for C₁₁₈H₇₈N₆O₁₂F₆S₂Re₂: C, 58.80; H, 7.55; N, 3.21.

2.3. Preparation of MCM-41 and SBA-15 mesoporous silica with the physically incorporated D-Re(I) complex (denoted as D-Re(I)/MCM-41 and D-Re(I)/SBA-15)

MCM-41 and SBA-15 were synthesized according to the literatures [25,26]. The templates were removed from the mesoporous silicas by calcination at a rate of 1 °C/min and remained at 550 °C for 6 h. The luminophor D-Re(I) complex was incorporated into mesoporous molecular sieves to obtain the assembled composite materials by the following procedure: 100 mg of the mesoporous host was added into the 10 mL dichloromethane solution of D-Re(I) complexes (1 mg), and the mixture was stirred under ambient conditions for 24 h. The resulted suspension was filtered which gave a pale yellow powder. The powder was washed repeatedly with dichloromethane until the solution was colorless under ultraviolet illumination and then dried in air. Finally, the physically encapsulated oxygen sensor materials D-Re(I)/MCM-41 and D-Re(I)/SBA-15 were obtained as pale yellow powders. Before the Stern–Volmer plots measurements, the D-Re(I)/MCM-41 and D-Re(I)/SBA-15 composites were fully ground for about 20 min to get good enough powder that can be pressed firmly into the sample holder. This grinding process is essential for the oxygen sensing measurement to withstand the high rate gas flow.

3. Results and discussion

The SAXRD patterns of MCM-41 and D-Re(I)/MCM-41 samples, as illustrated in Fig. 2(a), both consist of a strong (1 0 0) reflection at the low angle region ranging from 1° to 2.4° (2θ) and three other reflections (1 0 1, 2 0 0, 2 1 0) located at the higher angle range, being typical of two-dimensional hexagonal structure (P6/mmm). The presence of these four diffraction peaks indicates that two samples have MCM-41 type...
architecture with long range order [12]. Very similar SAXRD results have also been obtained in the SBA-15 systems, as shown in Fig. 2(b). The diffraction pattern in the SBA-15 systems shows three peaks which can be indexed to a hexagonal array of mesopores as for MCM-41: reflections due to the diffraction planes (1 0 0), (1 1 0), and (2 0 0) are observed. The close d_{100} spacing values of all of these samples indicate that their framework hexagonal ordering has been preserved after the incorporation of D-Re(I) into the mesoporous silica materials.

Fig. 3a shows the FTIR spectra of the D-Re(I) dichloromethane solution, D-Re(I)/MCM-41 and D-Re(I)/SBA-15. The peaks located at 2029, 1992, and 1919 cm$^{-1}$ could be ascribed to the vibration of the three carbonyl ligands in a perturbed C$_3v$ environment [32]. The emission spectra of D-Re(I)/MCM-41 and D-Re(I)/SBA-15 red shift by approximately 8 and 3 nm, respectively. Such red shifts are probably due to the formation of the J-aggregates, which would lead to bathochromic shift in transition energy after assembly within the mesoporous silica support [32].

Fig. 4 shows the room temperature spectral response of D-Re(I)/MCM-41 and D-Re(I)/SBA-15 under different oxygen concentrations. It is found that the relative emission intensity decreases markedly as the oxygen volume fraction increased and the emission peak does not shift or change in shape. The luminescent intensities of D-Re(I)/MCM-41 and D-Re(I)/SBA-15 decreased by 82.6% and 95.2%, respectively, upon changing from pure nitrogen to pure oxygen conditions, which are promising as sensing probes due to very high degrees of quenching.

Performance of optical sensors based on the luminescence quenching is examined by the Stern–Volmer equation. For well behaved oxygen sensing materials in which the luminophor was dispersed uniformly within homogeneous media, the intensity I and lifetime $\tau$ of the luminophor fit the linear Stern–Volmer equation [27]

$$I_0/I = 1 + K_{SV}pO_2 = 1 + K_q\tau_0pO_2$$

where $pO_2$ is the partial pressure of oxygen at 1 atmosphere pressure, $\tau_0$ and $\tau$ are lifetimes, $I_0$ and $I$ are intensities. The subscript 0 denotes the value in the absence of quencher. $K_{SV}$ is the Stern–Volmer constant. $K_q$ is the bimolecular quenching constant. A plot of $I_0/I$ versus oxygen concentration should give a linear relationship with a slope of $K_{SV}$, and an intercept of 1 on the y-axis. The lifetime decay of luminophore in homogeneous media can be described by a single exponential equation [28]

$$I(t) = I_0 \exp(-t/\tau)$$
where $I(t)$ is the luminescence intensity at time $t$, and $e$ is the pre-

Fig. 5 presents the intensity-based Stern–Volmer plots for D-Re(1)/MCM-41 and D-Re(1)/SBA-15. As shown in Fig. 5, the Stern–Volmer oxygen quenching plots of D-Re(1)/MCM-41 and D-Re(1)/SBA-15 appear to deviate from linearity especially at low O$_2$ concentration. The downward curvature plots necessitate a more complex model than a single species quenched bimolecularly.

When quenching takes place in a solid support, the nonlinear Stern–Volmer equation is often the case, in which Demas two-site model could have excellent ability to fit the experiment data. In this model, the straight-line intensity Stern–Volmer equation [28] then becomes

$$\frac{I_0}{I} = 1 + \frac{K_{SV1} [O_2]}{f_{01}} + \frac{K_{SV2} [O_2]}{f_{02} (1 - f_{01})}$$

where $f_{01}$ and $(1 - f_{01})$ values are the fraction of each of the two sites contributing to the unquenched intensity, and $K_{SVi}$ values are the associated Stern–Volmer quenching constants for the two sites, one of which is easy to be quenched but the other is not. At low oxygen concentration, easily accessible luminescence molecules are quenched more effectively, whereas the quenching responses at high oxygen concentrations are increasingly dominated by the less accessible domains. Meanwhile, when $K_{SV2} = 0$, the Demas model collapses to the Lehrer model [29,30], which is also able to fit the experiment data reasonably. The equation is shown below.

$$\frac{I_0}{I} = \frac{1}{f_{01} (1 + K_{SV1} [O_2]) + (1 - f_{01})}$$

It is worth noting that either Demas two-site model or Lehrer model can be used to fit the intensity-quenching curves of all of these samples. Table 1 lists the intensity-based Stern–Volmer oxygen quenching fitting parameters: the quenching constants, $K_{SV1}$, $K_{SV2}$ and the fractional contributions of the two-site components. It can be seen that Demas two-site model is more effective at fitting intensity data. The origin of the nonlinearity is a result of the luminophor molecules existing in two sites within the mesoporous silica materials in which one site is more heavily quenched than the other.

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Gas</th>
<th>$x_1$</th>
<th>$\tau_1$ (µs)</th>
<th>$x_2$</th>
<th>$\tau_2$ (µs)</th>
<th>$\langle \tau_m \rangle$ (µs)</th>
<th>$r^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-Re(1)/MCM-41</td>
<td>N$_2$</td>
<td>0.16</td>
<td>2.45</td>
<td>0.06</td>
<td>7.93</td>
<td>3.94</td>
<td>0.9990</td>
</tr>
<tr>
<td>D-Re(1)/SBA-15</td>
<td>N$_2$</td>
<td>0.10</td>
<td>4.26</td>
<td>0.09</td>
<td>12.16</td>
<td>8.00</td>
<td>0.9989</td>
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</table>

In these Lehrer and Demas two-site models mentioned above, there are two excited-state lifetime components for the luminescence species, and the excited lifetime decay analysis may be described by [13]

$$I(t) = x_1 \exp(-t/\tau_1) + x_2 \exp(-t/\tau_2)$$

where $I(t)$ represents the fluorescence intensity at time $t$, the subscripts 1 and 2 denote the assigned lifetime components, and $x_i$ denotes the pre-exponential factors. The intensity-weighted mean lifetime $\langle \tau_m \rangle$ can be calculated with the expression: [28]

$$\langle \tau_m \rangle = \sum_{i=1}^{2} x_i \tau_i / \sum_{i=1}^{2} x_i$$

The unquenched lifetimes of the different mesoporous oxygen sensing materials under N$_2$ atmosphere are measured as shown in Table 2. Both of the data are found to be well-fit by the double exponential Eq. (6), which further confirms that the Re(1) ions occupy the microscopic scale heterogeneous local environment in the mesoporous silica materials MCM-41 and SBA-15. The result of the excited-state decay profile is consistent with the Stern–Volmer plot.

The oxygen-quenching sensitivities $I_{01}/I_{100}$ ($I_{100}$ is the luminescence intensity under 100% oxygen) of D-Re(1)/MCM-41 and D-Re(1)/SBA-15 are estimated to be 5.6 and 20.1, respectively. It is well known that a sensor with $I_{01}/I_{100}$ more than 3.0 is a suitable oxygen sensing device, so D-Re(1)/MCM-41 and D-Re(1)/SBA-15 could be used to develop oxygen sensing materials. The high sensitivity may be ascribed to the large x-dimine ligand d19-phen in the D-Re(1) complex. In previous work, Sacksteder et al. [18] reported the plausible quenching mechanism, that quenching is based on the collision of oxygen and the x-dimine ligand L. Because a large L would result in fewer binding sites to accommodate binding pocket, the larger the x-dimine ligand L, the larger fraction of molecules would be easily quenched. Additionally, D-Re(1)/SBA-15 demonstrated higher sensitivity in comparison to D-Re(1)/MCM-41. This phenomenon can be explained as following, though the detailed mechanism is still unclear. According to Eq. (1), the main differences in the sensitivity are the unquenched photoluminescence mean lifetime $\langle \tau_0 \rangle$ (as shown in Table 2) and the bimolecular quenching constant $K_B$. Because of the nonexponential decay of the samples, the mean lifetime $\langle \tau_0 \rangle$ was considered here. The lifetimes of the dye in solution, MCM-41 and SBA-15 are 4.53, 3.94 and 8.00 µs, respectively. It is well known that the movement of the probe molecules in solution is relatively free. However, when the molecules are dispersed in the pores of SBA-15, the rigid inorganic walls largely restrict their vibration, resulting in the decrease of the non-radiative transitions caused by vibration; hence, the increase of the lifetime. The shorter lifetime of D-Re(1)/MCM-41 may be due to the -OH quenching effect.

Table 2

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Fig. 5. Stern–Volmer plots of D-Re(1)/MCM-41 (the empty one) and D-Re(1)/SBA-15 (the solid one). The solid lines represent the best fit using the Demas two-site model.
which plays an important role in the silica based oxygen sensing materials [12,23]. Compared with D-Re(I)/SBA-15, the smaller pore in MCM-41 gives a shorter distance between the –OH group and the probe molecules and thus a higher quenching probability. To test whether lifetime \( \langle t_0 \rangle \) can be the only scaling parameter, \( \langle \langle I_0 / I \rangle \rangle = 1 \) vs \( \langle \langle t_0 \rangle \rangle \) is plotted against oxygen concentration [31], as shown in Fig. 6. It can be seen that this renormalization of the data brings the plots closer together, but the difference still exists. Meanwhile, it is well known that the pore diameter of SBA-15 is larger than MCM-41. And the enhanced sensitivity may be partly due to a more rapid diffusion of oxygen in SBA-15 than that in MCM-41.

Besides sensitivity, short response time is also important for oxygen sensors. Fig. 7 shows the typical dynamic response of the samples on exposure to pure N2 and O2 atmosphere varied periodically. From this time dependent measurement, the 95% response time \( t_r \) and 95% recovery time \( t_a \) in an alternating atmosphere of pure N2 and O2 can be calculated. Generally, the values are defined as the time taken for a sample to attain 95% of its total emission intensity change when the gas is changed from pure N2 to pure O2 \( (t_\uparrow) \) and from pure O2 to pure N2 \( (t_\downarrow) \), respectively. The \( t_r \) values of D-Re(I)/MCM-41 and D-Re(I)/SBA-15 are about 19 and 7 s and the \( t_a \) values are estimated to be 41 and 43 s, respectively. This result shows that the response time is shorter than the recovery time distinctly and this obvious difference can be explained by the stronger adsorption of oxygen than that of nitrogen on the silica surface [13]. It is well known that the reproducibility of oxygen sensing materials under irradiation is one of the key analytical characters of merit for practical applications, which allows monitoring of an increasing and decreasing PO2 continuously. As shown in Fig. 7, stable and reproducible signals upon repeated exposure to oxygen/nitrogen cycles were also obtained for both of the D-Re(I)/MCM-41 and D-Re(I)/SBA-15.

4. Conclusion

In this work, a new dirhenium(I) complex D-Re(I) was synthesized and assembled in mesoporous silica materials MCM-41 and SBA-15, which were investigated in view of the application in optical oxygen sensors. The quenching sensitivities of D-Re(I)/MCM-41 and D-Re(I)/SBA-15 are estimated to be 5.6 and 20.1, respectively. The high sensitivity may be ascribed to the large \( \pi \)-donor and \( \pi \)-acceptor interactions, which allows monitoring of an increasing and decreasing PO2 continuously. As shown in Fig. 7, stable and reproducible signals upon repeated exposure to oxygen/nitrogen cycles were also obtained for both of the D-Re(I)/MCM-41 and D-Re(I)/SBA-15. The signal reproducibility plus relatively high sensitivity make D-Re(I)/SBA-15 a promising potential oxygen sensor.

Acknowledgments

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References