Oxygen and Relative Humidity Monitoring with Films Tailored for Enhanced Photoluminescence

Weipan Cui,¹ Rui Liu,¹ Eeshita Manna,¹ Joong-Mok Park,¹ Fadzai Fungura¹,

Joseph Shinar,^{1*} and Ruth Shinar^{2*}

¹*Ames Laboratory – USDOE and Physics & Astronomy Department*

²*Microelectronics Research Center and Electrical and Computer Engineering Department*

Iowa State University, Ames, IA 50011

Abstract

Approaches to generate porous or doped sensing films, which significantly enhance the photoluminescence (PL) of oxygen optical sensors, and thus improve the signal-to-noise (S/N) ratio, are presented. Tailored films, which enable monitoring the relative humidity (RH) as well, are also presented. Effective porous structures, in which the O₂-sensitive dye Pt octaethylporphyrin (PtOEP) or the Pd analog PdOEP was embedded, were realized by first generating blend films of polyethylene glycol (PEG) with polystyrene (PS) or with ethyl cellulose (EC), and then immersing the dried films in water to remove the water-soluble PEG. This approach creates pores (voids) in the sensing films. The dielectric contrast between the films' constituents and the voids increases photon scattering, which in turn increases the optical path of the excitation light within the film, and hence light absorption by the dye, and its PL. Optimized sensing films with a PEG:PS ratio of 1:4 (PEG's molecular weight $M_w \sim 8000$) led to $\sim 4.4\times$ enhancement in the PL (in comparison to PS films). Lower $M_w \sim 200$ PEG with a PEG:EC ratio of 1:1 led to a PL enhancement of $\sim 4.7\times$. Film-dependent PL enhancements were observed at all oxygen concentrations. The strong PL enhancement enables (i) using lower dye (luminophore) concentrations, (ii) reducing power consumption and enhancing the sensor's

operational lifetime when using organic light emitting diodes (OLEDs) as excitation sources, (iii) improving performance when using compact photodetectors with no internal gain, and (iv) reliably extending the dynamic range.

The effect of RH on O₂ sensing is also presented. Dye:EC films are sensitive to the RH, as shown by the change of the dye's PL decay time with RH at a given O₂ concentration. Surprisingly, this RH sensitivity vanishes by adding PEG to EC, including by washing PEG off. In contrast, doping EC with TiO₂ nanoparticles maintains the RH effect with the advantage of significant PL enhancement. This enhancement enables differentiation of <10% changes in the RH, which is unattained with the dye:EC sensing films. The results are discussed in terms of the composition, thickness, and microstructure, whether porous or nanoparticle doped, of the composite films.

Key Words: O₂ sensor, porous sensing films, photoluminescence enhancement, light scattering, relative humidity effect

*Corresponding authors: rshinar@iastate.edu (RS); jshinar@iastate.edu (JS)

Acknowledgements: We thank Geyuan Liu for assistance in transmission measurements. Ames Laboratory is operated by Iowa State University for the US Department of Energy (USDOE) under Contract No. DE-AC 02-07CH11358. RL, EM, JMP, and FF were supported by Basic Energy Sciences, Division of Materials Science and Engineering, USDOE.

1. Introduction

Photoluminescence (PL)-based oxygen sensors often utilize the oxygen sensitive dyes platinum octaethylporphyrin (PtOEP), or the palladium analog PdOEP, embedded in a polymeric matrix, whose PL intensity I and decay time τ depend on the O_2 concentration $[O_2]$ [1-9]. Ideally, the relation between $[O_2]$ and I and τ is given by the Stern–Volmer (SV) equation:

$$I_0/I = \tau_0/\tau = 1 + K_{SV}[O_2] \quad (1)$$

Where I_0 and τ_0 are the unquenched values [2,5,9,10]. The detection sensitivity S is often defined as the ratio $\tau_0/\tau(100\% O_2)$ or $I_0/I(100\% O_2)$ [5]. Various approaches were developed to enhance S and the PL intensity, as low PL signals limit the oxygen dynamic range and reliability of monitoring high $[O_2]$. These approaches include modifications of the sensing films. For example, an increase in the PL intensity was observed when silica nanoparticles (NPs) were doped into PtOEP:PDMS or PtOEP:C4PATP [11,12], where PDMS is polydimethylsiloxane and C4PATP is poly(*n*-butylaminothionylphosphazene). However, adsorption of O_2 on the surface of the silica NPs resulted in complex oxygen transport and PL quenching mechanism. In another example, Zhou et al. [13] showed that adding high dielectric constant TiO_2 NPs to PtOEP:PS results in scattering that increases the optical path of the excitation light in the sensing film and therefore the dye's light absorption and PL. However, TiO_2 has a strong absorption in the UV (where the O_2 -sensitive dyes strongly absorb), which renders it less suitable for use with UV excitation, with a lower PL signal enhancement of $3\times$ [13]. Hence, improvement of sensing films is still desired to produce stronger PL signals, especially at high $[O_2]$ where the PL is massively quenched, and for compact sensors, where photodetectors (PDs) with no internal gain, such as Si-photodiodes or thin film-based inorganic and organic PDs, are used in structurally integrated sensors [14-19].

In this work doped or porous films were used to enhance the PL. Microporous polymeric thin

1
2
3
4 films have attracted wide, general interest because of their promising use in optics, photonics,
5
6 electronics, and biotechnology [20-23]. The microporous structures are often achieved by
7
8 lithography [24] or phase separation methodologies [25-29]. In this work, enhanced PL was
9
10 realized by doping or by creating voids in blended polyethylene glycol (PEG):polystyrene
11
12 (PS):dye and PEG:ethyl cellulose (EC):dye sensing films. Different PEG:PS or PEG:EC ratios,
13
14 film drying rates and thicknesses, as well as different molecular weights (M_w) of PEG were
15
16 tested. A stronger scattering effect was observed when the PEG was washed off by water, which
17
18 did not affect the other film constituents. PL signal enhancements of up to ~4.4-fold were
19
20 observed for porous PtOEP:PS and up to ~4.7-fold for porous PtOEP:EC sensing films. The
21
22 method is easy to realize and does not limit the enhancement to 3-fold when employing UV
23
24 excitation, as was the case with TiO₂ NPs in PS [13]. The PL enhancement increases the S/N
25
26 ratio and therefore the reliability of monitoring high [O₂]. Light scattering in the sensing films
27
28 explains the PL enhancement in the presence of voids (the larger PL enhancement was obtained
29
30 when PEG is washed off, creating voids) and nanoparticles.

31
32
33 The relative humidity (RH) effect on τ for the different O₂ sensing films is also presented.
34
35 The TiO₂ NP-doped EC matrix showed the largest RH effect with an increase of 70% in τ for
36
37 PtOEP:EC at 3-7% oxygen and 50% for PdOEP:EC at 0.2-1% oxygen. While blending PEG with
38
39 EC led to the disappearance of the RH effect, doping EC with TiO₂ NPs enabled RH monitoring
40
41 with better than 10% resolution due to the advantage of significant PL enhancement. This <10%
42
43 differentiation in the RH was unattained with the undoped dye:EC films. Hence, O₂ and RH
44
45 could be monitored at certain O₂ concentrations using two sensing films, one of which is RH
46
47 insensitive.

2. Experimental Procedure

2.1. Materials

PtOEP, PdOEP and *N,N'*-bis(naphthalen-1-yl)-*N,N'*-bis (phenyl)benzidine (NPB) were obtained from H. W. Sands. Polyvinylpyrrolidone (PVP) ($M_w \sim 10,000$), PS ($M_w \sim 280,000$), PEG ($M_w \sim 200, \sim 400, \sim 1,000$, and $\sim 8,000$), EC (water insoluble with 48% ethoxyl groups), LiF, bathophenanthroline (BPhen) and tris-(8-hydroxyquinoline) aluminum (Alq₃) were purchased from Sigma-Aldrich. MoO₃ was purchased from Strem Chemicals. 4, 4'-cyclohexylidenebis [N, N-bis (4-methylphenyl) benzenamine] (TAPC) and 4, 4'-N, N'-dicarbazole-biphenyl (CBP) were purchased from Luminescence Technology Corporation. Toluene was obtained from Fisher Scientific and TiO₂ NPs with a 360 nm average diameter from Dupont.

2.2. Methods

Following measurements on a wide array of dye:matrix ratios, dye:PS ($M_w \sim 288,000$) reference films were prepared from toluene solutions containing dye:PS mass ratios of 1:40 – 1:60. Dye:EC reference films were similarly prepared from toluene solutions containing dye:EC mass ratios of 1:60 to 1:120. The PtOEP or PdOEP concentration was kept at 1 mg/mL. Different amounts of PEG (4 -12 mg with 40 mg PS or 10-60 mg with 60 mg EC in 1 mL toluene) with different M_w were added to the PS or EC. Films were obtained by drop-casting 80 μ L on 18x18 mm² glass substrates, which were cleaned using a standard cleaning procedure and UV-ozone treatment [29,30]. The thickness of the 1:40 PS films was 7-8 μ m; the thickness of the 1:60 EC films was ~ 11 to 13 μ m; the thickness of the 1:120 EC films was ~ 19 -24 μ m. The measured variations in the film thickness may be partially related to the surface roughness. The results

described below focus mostly on dye:PEG:PS films obtained from solutions with a 1:10:40 ratio and dye:PEG:EC films from solutions of a 1:60:60 ratio.

Different solvent evaporation procedures were conducted by first leaving the film in the hood for a fast dry of 1-2 min or placing the film under a petri dish for a slower 30 min drying process. The films were then dried in a hood for additional ~20 h. PEG was washed off by immersing the dried film in water for 1 hour and then drying it in flowing air for another 1 hour, which resulted in peeled off EC-based films with reproducible performance. The EC, like PS, was unaffected by the water treatment. Dye leaching was not observed with reproducible results to within ~5% in repeated measurements over 6 months.

2.3. Instruments

Green ($\lambda_{em} = 525$ nm) and UV ($\lambda_{em} = 395$ nm) (inorganic) LEDs, or green and UV microcavity OLEDs were used as excitation sources [32,33]. The structures of the green and UV microcavity OLEDs were Ag (25nm)/MoO_x (5nm)/*N,N'*-bis(naphthalen-1-yl)-*N,N'*-bis (phenyl)benzidine (NPB) (49 nm)/tris-(8-hydroxyquinoline) aluminum (Alq₃) (56 nm)/LiF (1 nm)/Al (100 nm), and Al (15 nm)/MoO_x (7 nm)/4, 4'-cyclohexylidenebis [N, N-bis (4-methylphenyl) benzenamine] (TAPC) (10 nm)/ 4, 4'-N, N'-dicarbazole-biphenyl (CBP) (25 nm)/bathophenanthroline (BPhen) (25nm)/LiF (1 nm)/Al (100 nm), respectively. The excitation sources were driven with 1 ms or 100 μ s electrical pulses (for exciting PdOEP or PtOEP, respectively) generated by an Avtech AV-1011B pulse-generator at a repetition rate of 50 Hz. The PL signals at different [O₂] were obtained with a Hamamatsu R6060 photomultiplier tube (PMT) in the back-detection geometry [32] using a 600 nm long-pass filter. For gas-phase O₂ sensing, high purity Ar and O₂ were mixed using mass flow controllers to generate different O₂ concentrations at a constant flow rate

of 200 sccm (for PtOEP) or 500 sccm (for PdOEP); no flow rate dependence was observed. Various RH values were generated by bubbling Ar through water at room temperature and mixing with dry O₂ or Ar at the desired ratio. The resulting RH values were verified using a RH meter (Taylor digital humidiguide). Images of the porous films were obtained by either a camera, an optical microscope (Olympus Vanox), or a scanning electron microscope (SEM). The transmission and reflection spectra were measured using a tungsten lamp fiber-coupled to an Ocean Optics spectrometer equipped with an integrating sphere.

3. Results and discussion

3.1. PL enhancement with porous films

3.1.1. Material selection

PS and EC are common materials used as dye matrices for monitoring oxygen in different ranges [4,7-10, 34-37]. Blend films of these materials to produce porous microstructures were explored for various other applications [20,21,38,39]. Repeated experiments we conducted using water-soluble PVP in blends indicated that this material cannot be used for O₂ sensing as removal of the PVP by water results in unstable films due to partial leaching of the O₂ sensing dye. PEG:PS blend films are also porous even before the PEG is washed off [40-42]. Unlike the PVP:PS, PEG:PS films performed reproducibly with no indication of loss of PtOEP or PdOEP following removal of the PEG by immersing the film in water. Enhanced PL was observed with the dye:PEG:PS porous sensing films. Furthermore, PEG is advantageous being nontoxic and biocompatible [43], and blending it with high M_w PS or EC at the concentrations of interest results in solutions that are less viscous and hence more amenable to forming sensing films.

3.1.2. Images and optical properties of porous sensing films

Figure 1 shows photographs and SEM images of various films: (a) and (b) are photographs of films without the dye: (a) PS50 (where the number indicates PS mass in mg in 1 mL toluene), PEG:PS (10:40), and PEG:PS (10:40) following immersion of the film in water (denoted PEG:PS(W)) and (b) EC120 (where the number indicates EC mass in mg in 1 mL toluene), PEG:EC (60:60) and PEG:EC (60:60)(W). The ratio numbers indicate mass ratio in 1 mL toluene and W stands for washed; in all cases 80 μ L were used for film preparation. As seen, the PS50 and EC120 films are transparent. With added PEG, the films become less transparent, and more so when the PEG is washed out. The SEM images also indicate differences, as shown in (c) and (d) for dye-doped films. The PtOEP:PS and PtOEP:EC films are uniform. Voids are seen in dye-doped PEG:PS and PEG:EC films on the surface and in the bulk [40]. When the films are immersed in water, the PEG, which initially decorates pores formed in the PS [40,41], is removed, but as discussed later, likely not completely for the PEG with $M_w \sim 8000$.

Multi-component films undergo phase separation due to differences in their relative solubility in a specific solvent and different solvent evaporation rates in the different domains of the drying film [39,44,45]. Phase separation indeed explains pore formation in the PEG:PS and PEG:EC films [40,41]. The size of the voids in both PEG:PS and PEG:EC was affected by the M_w of PEG, with lower M_w values producing larger voids. This behavior was reported previously for PEG:PS:toluene (PEG M_w 200-1000) [40]. As seen in Fig. 1(c), for PEG:PS films, but only when using the PEG with $M_w = 8000$, washing off PEG leads to the merging of small voids into larger pores; the nature of this behavior is not clear. Optical microscopic imaging of the different pre-washed PS and EC films with different PEG M_w values showed that the voids' sizes increase from $\sim 1 \mu\text{m}$ using PEG with $M_w \sim 8000$ to $\sim 4 \mu\text{m}$ using PEG of $M_w \sim 200$ (see examples in Fig. 2

for pre-washed PtOEP:PEG:EC films). The average distance between voids varied with different PEG:PS or PEG:EC ratios, typically decreasing with increasing PEG fraction.

Figure 3 shows the transmission and reflection spectra of as-prepared and washed PEG:EC 1:1 (PE11 or PE11W) films (without the dye); The corresponding data for PEG:PS 1:4, denoted in the figure as PP14 and PP14W, is shown in Fig. S1 in the Supplementary Data. These films provided the optimal PL. The transmission of the washed PEG:EC films, where the PEG was largely removed by immersing the film in water, is ~40%; that of the thinner similarly treated PEG:PS film is ~75%; this difference is demonstrated also in Figs. 1(a) and 1(b). This behavior is due to the thicker PEG:EG films and related increased scattering. It is likely also associated with increased scattering related to the morphology of the films, with the PEG:EC films having smaller voids with a higher density in comparison to PEG:PS (see Fig.1).

3.1.3. PL enhancement with PEG:PS porous films

Figure 4a compares the PL decay curves for the PdOEP-doped PS and PEG:PS films, including films dried at different rates before and following their immersion in water. As seen, fast drying results in larger PL intensities, with the PL intensity of the slow dried film, reproducibly, even weaker than that of the reference uniform PS film. This situation is likely due to coalescing of voids during the slow drying, and hence the formation of larger PS and PEG regions and disappearance of the finer microstructure. Similar results were reported for a slow-dried hydrophilic poly(2-vinylpyridine) in PS [25,29]. As seen, the strongest PL signals were obtained for a PEG:PS film following its immersion in water. Similar results were obtained for the PtOEP-doped PEG:PS sensing films.

The PL intensity enhancement, using green and UV LEDs, for PtOEP-doped PEG (different M_w s):PS($M_w \sim 280,000$) films relative to the PL intensity of a PS only film (i.e., PL_{porous}

film/ $PL_{\text{reference uniform film}}$) ranged from 2.7 to 4.4. PEG:PS 1:4(W) typically exhibited the largest enhancements. Using the green LED, the enhancements were 4.0x, 3.8x, and 4.4x for M_w 400, 1000, and 8000, respectively. With the UV LED the corresponding enhancements were 3.0x, 4.0x, and 3.6x. Different PL enhancements are likely associated with the PEG:PS ratio and film pore size and separation. However, there is no trend in the PL enhancement for different M_w PEG except that the enhancement was consistently lower for the lowest $M_w = 200$ (2.5x and 2.7x).

Zhou et al. reported an enhancement of up to 10x for PtOEP:PS doped with TiO_2 NPs using green OLED excitation, however, the enhancement was limited to ~3x when using a UV lamp for excitation due to absorption by the TiO_2 NPs at shorter wavelengths. The enhancement was ascribed to light scattering due to the large difference in the refractive indices of PS, $n \sim 1.58$ and TiO_2 , $n \sim 2.8$ [13]. The porous sensing film of this study leads to a higher ~4x enhancement with UV LED excitation. Since light absorption by PtOEP and PdOEP is ~4-5 times stronger at 385-395 nm in comparison to 525-535 nm [46], this ~4x PL enhancement is significant and useful.

We tested also OLED-excited sensors, fabricating the porous sensing films on the back of microcavity UV OLEDs. We observed a 10x PL enhancement for the PEG:PS 1:4 (PEG M_w ~8000) film and 13x for the PEG:EC 1:1 (PEG M_w ~200) film. The larger PL enhancement when using OLEDs is due to stronger brightness of LEDs and therefore increased dye absorption/saturation.

PL enhancement for PEG:PS ratios smaller than 1:9 was always weaker than for the above-mentioned ratios, while films with higher PEG:PS ratios were often destroyed when immersed in water. The PL enhancement using the green excitation source was often larger than that using the UV source, which is expected due to the weaker dye absorption in the green.

Figure 4(b) compares the SV lines for a PS film and a PEG:PS 1:4(W) (PEG M_w ~8000) film.

As seen, the SV relations are linear over the whole range (0-100%), with the decay times τ extracted using single exponential fittings. For reliable analysis using the PS film at high $[O_2]$, the intensity of the excitation source and voltage on the PMT had to be increased. Hence, the PL enhancement at high $[O_2]$ is particularly important because it improves the S/N ratio and thus extends the reliable detection range, which is often limited due to low S/N. As seen, a lower sensitivity S , i.e., the slope of the SV line, was observed for the PEG:PS film that showed enhanced PL intensity. This behavior alludes to reduced O_2 diffusion within the film, as is the case also for NP-doped films [12,13,42]. Nevertheless, the measurement reliability at high $[O_2]$ was higher with the blend film without the need to increase the voltages applied to the (O)LED and PMT. This behavior is demonstrated for a PEG:EC film in the following section. The PL enhancement is largely independent of $[O_2]$ as shown in Fig. S2(a) of the Supplementary Data for 0 to 10% $[O_2]$ using a PS film and a PEG:PS 1:6 (PEG $M_w \sim 8000$) film excited by a green LED.

3.1.4. PL enhancement with PEG:EC porous films

As seen in Fig. 1(d), EC-only films are uniform, but porous structures are obtained in blended PEG:EC films, as was also reported earlier for such films in different applications [47]. For PS, the largest PL enhancement was obtained using PEG ($M_w \sim 8000$) in PEG:PS 1:4 (W) sensing films excited by the green LED. For EC, lower M_w PEG ($M_w \sim 200$) was the best for PEG:EC 1:1 (W) films (see Table S1 in Supplementary Data). A higher PEG M_w results in unusable solutions due to higher viscosity. Unlike the case with PEG:PS, we did not observe strong merging of smaller voids following the removal of PEG for PEG:EC. In contrast, the voids' borders became sharper following PEG removal. Increasing the concentration of PEG ($M_w \sim 200$ to ~ 1000)

beyond the PEG:EC 1:1 ratio results in non-usable, disintegrated sensing films following washing.

Fig. 5 shows the PL intensity vs time for PtOEP:PEG:EC (PEG M_w ~200) films with different PEG:EC ratios at 0% O_2 excited by 100 μ s pulses of green light. The maximum PL enhancement is 4.7 $\times$. Unlike the PEG:PS, the PEG:EC films' drying rate has little effect on the films' performance. The thickness of the films varied from ~10 to ~22 μ m. The results, however, for ~10 and ~20 μ m thick films (PtOEP:EC 1:60 and 1:120, respectively) are similar as shown in Fig. S3 in Supplementary Data. As is the case for PEG:PS films, the optimal PL intensity enhancement for PEG:EC 1:1 is largely independent of $[O_2]$ (Fig. S2(b) in Supplementary Data). Also similar to the PEG:PS films, a lower S ~27 compared with S ~40 with the EC only film was obtained for PEG:EC films, as shown in the non-linear SV plots of Fig. 5(b). However, as shown in the example of Fig. 6, the data analysis is more reliable using the blend film at high $[O_2]$.

3.1.5. Stability of the porous structures

The stability of the porous structures was monitored through repeated absorption/emission spectra and PL enhancement measurements, including at temperatures up to 100°C for PS-based films and 120°C for EC-based films. The absorption and emission spectra of PtOEP and PdOEP were unchanged with and without PEG addition, which also implies, interestingly, that the dye was not incorporated into the PEG-rich domains. The PL enhancement of the porous structures was maintained for at least 6 months (data not shown) when the films were kept in the dark under ambient conditions. The porous structures exhibited enhanced PL also at higher temperatures, as shown in Fig. S4 of the Supplementary Data, which shows the relative PL enhancement vs temperature.

3.1.6. PL enhancement process

Zhou et al. described the schematic and function of dye-doped uniform sensing films and of dye- and titania NP-doped porous films [13,42]. In explaining the PL enhancement two processes related to the porosity and refractive index contrast in the films (the refractive index of PS is $n = 1.58$, of PEG $n = 1.45$, and of the voids $n = 1$) were considered: 1. The enhanced absorption of the excitation light by the dye due to multiple reflections of that light by the NPs in the film, which increases its optical length. 2. The potentially enhanced PL that reaches the PD (also due to scattering by the NPs) in the back-detection geometry, in which the OLED pixels partially block the PL.

The higher PL enhancement following the removal of the PEG in PEG:PS films (see Section 3.1.3) may be due to the increased/optimized size of the voids and increased refractive index contrast. The generally somewhat lower PL enhancement with UV excitation is likely due to the wavelength-dependent absorption coefficient of the dye. A large absorption coefficient of the dye, in general, leads to a reduced PL enhancement due to absorption saturation. Hence, when using green excitation of PEG:PS films the enhancement is expected to be larger than when using UV excitation (as the absorption is ~4-5 times stronger at the shorter wavelengths). Loss due to waveguiding is neglected, as in general, such a loss in thin drop-cast films is small due to a non-uniform film thickness and surface.

3.2. Effect of Relative Humidity (RH) on O₂ sensing

3.2.1. Effect of matrix

In monitoring [O₂], the effect of other environmental parameters such as the RH has to be considered. Typically, hydrophobic films that are insensitive to humidity are preferred [35,48-50].

The effect of RH on O₂ sensing was therefore tested using the various films described above. As expected, there was no effect when using the hydrophobic PS matrix. The blended PVP:PS films showed an initial RH effect, however, as mentioned, these films were unstable with observable dye leaching. PS:EC blend films (ratios 1:9 – 9:1) showed a RH effect, but it was significantly smaller than the RH effect on O₂ sensing using the EC-only film. The RH effect on EC films was reported previously; the effect was assigned to changing of the oxygen permeability in the matrix [35].

3.2.2. Effect of doping EC with TiO₂ NPs

The effect of RH using PEG:EC films with PtOEP or PdOEP was tested. However, surprisingly, no RH effect was observed for such films. The vanishing of RH effect due to the PEG is not clear, but may be due to absorption of the humidity by PEG. If this scenario is indeed valid, the results allude to remnant PEG in the washed films of this study.

TiO₂ NP-doped PtOEP:EC sensing films exhibited the advantage of a significantly increased PL intensity, which enabled much better resolution of the RH in comparison to EC only films. The PL was enhanced by ~3x for 0.5 mg/mL TiO₂; it was enhanced to ~4.5x for 2 mg/mL TiO₂, saturating at this concentration. We note that τ values at various [O₂] were not affected by the titania concentration up to 6 mg/mL, unlike the situation with TiO₂ NP-doped PS [13]. This behavior may be due to the higher permeability of EC to O₂.

The RH effect is shown in the SV relations of Fig. 7 for PtOEP and PdOEP. The plots are linear only over a limited [O₂] range, as was also seen previously, particularly for PdOEP-based sensors [6].

Figure S5 of the Supplementary Data shows the % difference in τ values for PtOEP at 0 and

95% RH, normalized to the former, as a function of $[O_2]$. The difference increases sharply, to nearly 70%, from 0 to 3% $[O_2]$, remains largely unchanged from 3 to 7% $[O_2]$, and then decreases gradually with increasing $[O_2]$, to practically no RH effect at 100% $[O_2]$. This behavior is possibly due to the fact that humidity can hinder oxygen permeation into the EC matrix [35], which is pronounced mostly at the lower $[O_2]$ range. The normalized difference in τ for PdOEP:TiO₂ NPs:EC sensing films is ~50% for 0.2 – 1% $[O_2]$.

3.2.3. RH calibration curves

The PtOEP:EC and PdOEP:EC sensing films clearly show different τ values at 0% and 95% RH at a given $[O_2]$, however, different RH levels in the 0 to 95% range cannot be differentiated due to small PL differences in these films. In contrast, PtOEP:TiO₂ NPs:EC and PdOEP:TiO₂ NPs:EC sensing films, which exhibit enhanced PL, enable such finer differentiation. As mentioned, the normalized difference in τ is ~70% for PtOEP:TiO₂ NPs:EC at 4 – 7% $[O_2]$ (Fig. S4) and ~50% for PdOEP:TiO₂ NPs:EC at 0.2 – 1% $[O_2]$.

Figures 8(a) and 8(b) show τ vs RH at 5% and 0.4% $[O_2]$ using PtOEP and PdOEP dyes, respectively; the lower $[O_2]$ for PdOEP is due to the strong quenching of PdOEP's PL even at very low $[O_2]$. τ increases strongly with increasing RH, indicating that O₂ diffusion into the sensing film and/or dye accessibility are strongly hindered. Fig. 8(c) shows also the ratio of τ at 0% RH to τ at different RH values vs RH for the PdOEP film exposed to 0.4% O₂ and the PtOEP film exposed to 5% and 20% O₂. A point at 75% RH for the PtOEP film at 50% O₂ is also shown, indicating the trend in τ variation with RH for different $[O_2]$. Hence, the current results suggest that monitoring $[O_2]$, with a suitable RH sensitive film, enables determination of the RH using a second, reference film, which is insensitive to the RH for obtaining the actual $[O_2]$.

Conclusions

An increase in the PL of luminescent oxygen sensors (PtOEP- or PdOEP-doped in modified PS and EC) is obtained by creating porous or NP-doped sensing films. The porous structures are realized by blending PS or EC with PEG and the common dyes PdOEP or PtOEP in toluene. During film formation and solvent evaporation the PEG-rich phase separates from the PS- or EC-rich phases, creating surface and bulk PEG-decorated voids. The PL enhancement is due to internal scattering of the light by these voids, which leads to increased absorption by the dye. Stronger scattering is observed when the PEG is (likely incompletely) removed following immersion of the films in water. The removal of PEG increases slightly the voids' size in EC and more so in PS, with the washed PEG:EC film exhibiting a significantly stronger reflection. The contrast between the refractive indices of PS or EC and the generated voids intensifies the scattering and consequently the PL intensity.

Using UV excitation, a maximal $\sim 4\times$ PL enhancement is achieved for PEG:PS and PEG:EC sensing films. A $\sim 4.5\times$ enhancement is observed for both films using green light excitation. The porous structures are stable and can be kept in air in the dark for at least six months with minimal change in performance. Moreover, the voids in the films remain largely intact at temperatures up to 100°C for PS films and 120°C for EC films. Such PL enhancement of 4-4.5 fold, especially at high $[O_2]$, extends the reliable oxygen dynamic range, which is often limited by low S/N ratio when using uniform sensing films. The PL enhancement enables the use of lower dye concentrations and lower voltages applied to the excitation sources. It also enables using photodetectors with no internal gain, such as Si-photodiodes and organic photodetectors rather than bulky and/or expensive PMTs and avalanche photodiodes, which also require high voltage. Though the detection sensitivity is reduced, the enhanced PL provides better reliability in the

1
2
3
4 measurements, and the results consequently present a significant step toward the integration of
5
6 compact components in oxygen monitors.
7

8
9 The RH can also be monitored with some of the PtOEP- and PdOEP-based oxygen sensing
10
11 films, but not with PS or even PEG:EC films. In contrast, PtOEP (PdOEP):TiO₂ NPs:EC films
12
13 show a similar RH effect as PtOEP (PdOEP):EC with the advantage of enhanced PL intensity
14
15 due to light scattering by the particles, which enables significantly better resolution of the RH
16
17 level. The RH dependence of τ depends strongly on [O₂]. The normalized difference in τ values
18
19 at 95% and 0% RH is ~70% at 5% O₂ using PtOEP-based sensing films and ~50% at 0.2-1% O₂
20
21 using PdOEP-based films. The PL enhancement enables differentiating RH changes of <10%,
22
23 which is unattained with PtOEP:EC devoid of the NPs. This differentiation, though [O₂]-
24
25 dependent, enables assessing [O₂] and RH using two films, i.e., a RH insensitive film for
26
27 determining the actual [O₂] and another film that is RH sensitive.
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

References

- [1] D. B. Papkovsky, New oxygen sensors and their application to biosensing, *Sens. Actuators B* 29 (1995) 213.
- [2] S.-K. Lee, I. Okura, Optical sensor for oxygen using a Porphyrin-doped Sol–Gel glass, *Analyst* 122 (1997) 81.
- [3] A. Mills, A. Lepre, Controlling the response characteristics of luminescent Porphyrin plastic film sensors for oxygen, *Anal. Chem.* 69 (1997) 4653.
- [4] P. Douglas, K. Eaton, Response characteristics of thin film oxygen sensors, Pt and Pd octaethylporphyrins in polymer films, *Sens. Actuators B* 82 (2002) 200.
- [5] Y. Amao, Probes and polymers for optical sensing of oxygen, *Microchim. Acta* 143 (2003) 1.
- [6] J. Shinar, R. Shinar, Organic light-emitting devices (OLEDs) and OLED-based chemical and biological sensors: an overview, *J. Phys. D: Appl. Phys.* 41 (2008) 133001.
- [7] Y. Cai, A. Smith, J. Shinar, R. Shinar, Data analysis and aging in phosphorescent oxygen-based sensors, *Sens. Actuators B* 146 (2010) 14.
- [8] M. Quaranta, S.M. Borisov, I. Klimant, Indicators for optical oxygen sensors, *Bioanal Rev.* 4 (2012) 115.
- [9] X.-d. Wang, O.S. Wolfbeis, Optical methods for sensing and imaging oxygen: materials, spectroscopies and applications, *Chem. Soc. Rev.* 43 (2014) 3666.
- [10] R. Shinar, Z. Zhou, B. Choudhury, J. Shinar, Structurally integrated organic light emitting device-based sensors for gas phase and dissolved oxygen, *Anal. Chim. Acta* 568 (2006) 190.
- [11] X. Lu, I. Manners, M.A. Winnik, Polymer/Silica composite films as luminescent oxygen sensors, *Macromolecules* 34 (2001) 1917.
- [12] X. Lu, M.A. Winnik, Luminescence quenching in polymer/filler nanocomposite films used in oxygen sensors, *Chem. Mater.* 13 (2001) 3449.
- [13] Z. Zhou, R. Shinar, A.J. Allison, J. Shinar, Enhanced photoluminescence of oxygen sensing films through doping with high dielectric constant particles, *Adv. Funct. Mater.* 17 (2007) 3530.
- [14] R. Shinar, D. Ghosh, B. Choudhury, M. Noack, V.L. Dalal, J. Shinar, Luminescence-based oxygen sensor structurally integrated with an organic light-emitting device excitation source and an amorphous Si-based photodetector, *J. Non Cryst. Solids* 352 (2006) 1995.

- [15] D. Ghosh, R. Shinar, V. Dalal, Z. Zhou, J. Shinar, Amorphous and nanocrystalline p-i-n Si and Si₃Ge photodetectors for structurally integrated O₂ sensors, *J. Non Cryst. Solids* 354 (2008) 2606.
- [16] Y. Cai, R. Shinar, Z. Zhou, J. Shinar, Multianalyte sensor array based on an organic light emitting diode platform, *Sens. Actuators B* 134 (2008) 727.
- [17] K.S. Nalwa, Y. Cai, A.L. Thoeming, J. Shinar, R. Shinar, S. Chaudhary, Polythiophene-fullerene based photodetectors: tuning of spectral response and application in photoluminescence based (Bio) chemical sensors, *Adv. Mater.* 22 (2010) 4157.
- [18] I.M.P.D. Vargas-Sansalvador, C. Fay, M.D. Fernandez-Ramos, D. Diamond, F. Benito-Lopez, L.F. Capitán-Vallvey, LED-LED portable oxygen gas sensor, *Anal. Bioanal. Chem.* 404 (2012) 2851.
- [19] B. Lamprecht, A. Tschepp, M. Cajlakovic, M. Sagmeister, V. Ribitsch, S. Köstler, Luminescence lifetime-based capillary oxygen sensor utilizing monolithically integrated organic photodiodes, *Analyst* 138 (2013) 5875.
- [20] H. Sirringhaus, N. Tessler, R. H. Friend, Integrated optoelectronic devices based on conjugated polymers, *Science* 280 (1998) 1741.
- [21] S. Watheim, E. Schaffer, J. Mlynek, U. Steiner, Nanophase-separated polymer films as high-performance antireflection coatings, *Science* 283 (1999) 520.
- [22] E. W. H. Jager, E. Smela, O. Inganäs, Microfabricating conjugated polymer actuators, *Science* 290 (2000) 1540.
- [23] X. Li, J. Gao, L. Xue, Y. Han, Porous polymer films with gradient-refractive-index structure for broadband and omnidirectional antireflection coatings, *Adv. Funct. Mater.* 20 (2010) 259.
- [24] E. Ostuni, C. S. Chen, D. E. Ingber, G. M. Whitesides, Selective deposition of proteins and cells in arrays of microwells, *Langmuir* 17 (2001) 2828.
- [25] M. Boltau, S. Walheim, J. Mlynek, G. Krausch, U. Steiner, Surface-induced structure formation of polymer blends on patterned substrates, *Nature* 391 (1998) 877.
- [26] Z. Mitov, E. Kumacheva, Convection-induced patterns in phase-separating polymeric fluids, *Phys. Rev. Lett.* 81(1998) 3427.
- [27] U.H.F. Bunz, Breath Figures as a Dynamic Templating method for polymers and nanomaterials, *Adv. Mater.* 18 (2006) 973.
- [28] J.-K. Kim, K. Taki, S. Nagamine, M. Ohshima, Periodic porous stripe patterning in a polymer blend film induced by phase separation during spin-casting, *Langmuir* 24 (2008) 8898.

- [29] L. Xue, J. Zhang, Y. Han, Phase separation induced ordered patterns in thin polymer blend films, *Prog. Polym. Sci.* 37 (2012) 564.
- [30] J.-M. Park, Z. Gan, W.Y. Leung, R. Liu, Z. Ye, K. Constant, J. Shinar, R. Shinar, K.-M. Ho, Soft holographic interference lithography microlens for enhanced organic light emitting diode light extraction, *Opt. Express* 19 (2011) 786.
- [31] M. Cai, Z. Ye, T. Xiao, R. Liu, Y. Chen, R.W. Mayer, R. Biswas, K.-M. Ho, R. Shinar, J. Shinar, Extremely efficient indium–tin-oxide-free green phosphorescent organic light-emitting diodes, *Adv. Mater.* 24 (2012) 4337.
- [32] R. Liu, Y. Cai, J.-M. Park, K.-M. Ho, J. Shinar, R. Shinar, Organic light-emitting diode sensing platform: challenges and solutions, *Adv. Funct. Mater.* 21 (2011) 4744.
- [33] R. Liu, C. Xu, R. Biswas, J. Shinar, R. Shinar, MoO₃ as combined hole injection layer and tapered spacer in combinatorial multicolor microcavity organic light emitting diodes, *Appl. Phys. Lett.* 99 (2011) 093305.
- [34] S. Draxler, M.E. Lippitsch, I. Klimant, M. Kraus, O.S. Wolfbeis, Effects of polymer matrices on the time-resolved luminescence of a ruthenium complex quenched by oxygen, *J. Phys. Chem.* 99 (1995) 3162.
- [35] K. Eaton, P. Douglas, Effect of humidity on the response characteristics of luminescent PtOEP thin film optical oxygen sensors, *Sens. Actuators B* 82 (2002) 94.
- [36] V.A. Hughes, P. Douglas, Effect of lumophore and plasticiser concentration on the heterogeneity of oxygen quenching in thin film oxygen sensors, *J. Fluoresc.* 16 (2006) 403.
- [37] S.R. Ricketts, P. Douglas, A simple colorimetric luminescent oxygen sensor using a green LED with Pt octaethylporphyrin in ethyl cellulose as the oxygen-responsive element, *Sens. Actuators B* 135 (2008) 46.
- [38] P.T. Tanev, M. Chlbwe, T.J. Plnnavala, Titanium-containing mesoporous molecular sieves for catalytic oxidation of aromatic compounds, *Nature* 368 (1994) 321.
- [39] C.J. Brabec, S. Gowrisanker, J.J.M. Halls, D. Laird, S. Jia, S.P. Williams, Polymer–fullerene bulk-heterojunction solar cells, *Adv. Mater.* 22 (2010) 3839.
- [40] J.-K. Kim, K. Taki, M. Ohshima, Preparation of a unique microporous structure via two step phase separation in the course of drying a ternary polymer solution, *Langmuir* 23 (2007) 12397.
- [41] R. Liu, Z. Ye, J.-M. Park, M. Cai, Y. Chen, K.-M. Ho, R. Shinar, J. Shinar, Microporous phase-separated films of polymer blends for enhanced outcoupling of light from OLEDs, *Opt. Express* 19 (2011) 1272.
- [42] R. Liu, T. Xiao, W. Cui, J. Shinar, R. Shinar, Multiple approaches for enhancing all-organic

electronics photoluminescent sensors: Simultaneous oxygen and pH monitoring , Anal. Chim. Acta 778 (2013) 70.

[43] Y. Li, R. Liu, Y. Huang, Synthesis and phase transition of cellulose-graft-Poly(ethylene glycol) copolymers, J. Appl. Polym. Sci. 110 (2008) 1797.

[44] S.Sakurai, C. Furukawa, A. Okutsu, A. Miyoshi, S. Nomura, Control of mesh pattern of surface corrugation via rate of solvent evaporation in solution casting of polymer film in the presence of convection, Polymer 43 (2002) 3359.

[45] L. Cui, H. Wang, Y. Ding, Y. Han, Tunable ordered droplets induced by convection in phase-separating P2VP/PS blend film, Polymer 45 (2004) 8139.

[46] J. Kalinowski, W. Stampor, J. Szmytkowski, M. Cocchi, D. Virgili, V. Fattori, P.D. Marco, Photophysics of an electrophosphorescent platinum II porphyrin in solid films, J. Chem. Phys. 122 (2005) 154710.

[47] D. Solpan, M. Şahan, The Separation of Cu^{2+} and Ni^{2+} from Fe^{3+} Ions by complexation with alginic acid and using a suitable membrane, Sep. Sci. Technol. 33 (1998) 909.

[48] H. He, R.J. Fraatz, M.J.P. Leiner, M.M. Rehn, J.K. Tusa, Selection of silicone polymer matrix for optical gas sensing, Sens. Actuators B 29 (1995) 246.

[49] Y. Xiong, Z. Ye, J. Xu, Y. Zhu, C. Chen, Y. Guan, An integrated micro-volume fiber-optic sensor for oxygen determination in exhaled breath based on iridium(III) complexes immobilized in fluorinated xerogels, Analyst, 138 (2013) 1819.

[50] C. Toncelli, O.V. Arzhakov, A. Dolgova, A.L. Volynskii, J.P. Kerry, D.B. Papkovsky, Phosphorescent oxygen sensors produced by spot-crazing of polyphenylenesulfide films, J. Mater. Chem. C (2014). DOI: 10.1039/C4TC01390E.

(a) PS50 PP14 PP14W

(b) EC120 PE11 PE11W

(c) PtOEP:PS PtOEP:PEG:PS PtOEP:PEG:PS(W)

(d) PtOEP:EC PtOEP:PEG:EC PtOEP:PEG:EC(W)

Fig. 1. Left to right: (a) photographs of films of PS, 1:4 PEG:PS, and 1:4 PEG:PS following immersion in water (denoted PP14W); PEG's $M_w \sim 8000$. (b) photographs of EC; 1:1 PEG:EC, and 1:1 PEG:EC washed (PE11W) films; PEG's M_w is 200. (c) SEM images of: 1:40 PtOEP:PS, 1:10:40 PtOEP:PEG:PS, and 1:10:40 PtOEP:PEG:PS(W); PEG's $M_w \sim 8000$ (d) SEM images of: 1:60 PtOEP:EC, 1:60:60 PtOEP:PEG:EC, and 1:60:60 PtOEP:PEG:EC(W); PEG's M_w is 200.

Fig. 2. Microscope images of pre-washed 1:60:60 PtOEP:PEG:EC films with varying M_w of PEG. Left to right: 200, 400, 1000, and 8000.

Fig. 3. Reflection (R) and transmission (T) for EC120, PE11, and PE11W films devoid of the dye.

Fig. 4. (a) Comparison of the PL decay curves at 0% O_2 of PdOEP-doped films: PS, the fast and slow dried unwashed 1:4 PEG:PS (PP14), and the fast-dried washed (PP14W); PEG($M_w \sim 1000$):PS($M_w \sim 280,000$). The decay times for the four curves are all ~ 1.45 ms. Similar trends were obtained for PtOEP. (b) SV relations for PtOEP-doped PS and PP14W (PEG $M_w \sim 8000$).

Fig. 5. (a) PL intensity decay of PtOEP-doped PEG:EC(PEG $M_w \sim 200$) at different PEG:EC ratios, following immersion in water, excited by a 100 μs green LED pulse at 0% O_2 . (b) SV plots for EC and PE11W (PEG $M_w \sim 200$).

Fig. 6. PL decay curves obtained under the same conditions for PtOEP-doped EC and PE11W at 100% O₂.

Fig. 7. SV relations under dry (0% RH) and wet (95% RH) conditions for (a) PtOEP:TiO₂ NPs:EC film and (b) PdOEP:TiO₂ NPs:EC film.

Fig. 8. (a) τ vs RH at 5% O₂ for PtOEP:TiO₂ NPs:EC(1:2:60); (b) τ vs RH at 0.4% O₂ for PdOEP:TiO₂ NPs:EC(1:2:60); (c) $\tau_{0\%RH}/\tau$ vs RH for 50%, 20% and 5% O₂ for PtOEP:TiO₂ NPs:EC (1:2:60) and 0.4% O₂ for PdOEP:TiO₂ NPs:EC(1:2:60).