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Oxygen and relative humidity monitoring with films tailored for enhanced photoluminescence

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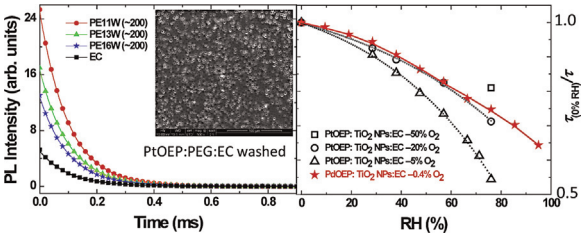
HIGHLIGHTS

- Novel porous dye-doped polyethyleneglycol:ethyl cellulose (PEG:EC) films with PEG washed off.
- ×4.7 increase in the photoluminescence (PL) in O_2 monitoring.
- PL enhancement due to voids/material refraction index contrast.
- <10% differentiation in relative humidity (RH) monitoring with nanoparticle-doped EC.
- RH monitoring, unattained with EC without nanoparticles.

GRAPHICAL ABSTRACT



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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 O_2-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 ~8000) led to ~4.4× enhancement in the PL (in comparison to PS films). Lower M_w ~200 PEG with a PEG:EC ratio of 1:1 led to a PL enhancement of ~4.7×. 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 O_2 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 O_2 concentration. Surprisingly, this RH sensitivity

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vanishes by adding PEG to EC, including by washing PEG off. In contrast, doping EC with TiO_2 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.

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:

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

where I_0 and τ_0 are the unquenched values [2,5,9,10]. The detection sensitivity S is often defined as the ratio τ_0/τ (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*-butylaminothionyl-phosphazene). 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× [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 films have attracted wide, general interest because of their promising use in optics, photonics, electronics, and biotechnology [20–23]. The microporous structures are often achieved by lithography [24] or phase separation methodologies [25–29]. In this work, enhanced PL was realized by doping or by creating voids in blended polyethylene glycol (PEG):polystyrene (PS):dye and PEG:ethyl cellulose (EC):dye sensing films. Different PEG:PS or PEG:EC ratios, film drying rates and thicknesses, as well as different molecular weights (M_w) of PEG were tested. A stronger scattering effect was observed when the PEG was washed off by water, which did not affect the other film constituents. PL signal enhancements of up to ~4.4-fold were observed for porous PtOEP:PS and up to ~4.7-fold for porous PtOEP:EC sensing films. The method is easy to realize and does not limit the enhancement to 3-fold when employing UV excitation, as was the case with TiO_2 NPs in PS [13]. The PL enhancement increases the S/N ratio and therefore the reliability of monitoring high [O_2]. Light scattering in the sensing films explains the PL enhancement in the presence of voids (the larger PL enhancement was obtained when PEG was washed off, creating voids) and nanoparticles.

The relative humidity (RH) effect on τ for the different O_2 sensing films is also presented. The TiO_2 NP-doped EC matrix showed the largest RH effect with an increase of 70% in τ for PtOEP:EC at 3–7% oxygen and 50% for PdOEP:EC at 0.2–1% oxygen. While blending PEG with EC led to the disappearance of the RH effect, doping EC with TiO_2 NPs enabled RH monitoring with better than 10% resolution due to the advantage of significant PL enhancement. This <10% differentiation in the RH was unattained with the undoped dye:EC films. Hence, O_2 and RH could be monitored at certain O_2 concentrations using two sensing films, one of which is RH 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 ~10,000), PS (M_w ~280,000), PEG (M_w ~200, ~400, ~1,000, and ~8,000), EC (water insoluble with 48% ethoxyl groups), LiF, bathophenanthroline (BPhen) and *tris*-(8-hydroxyquinoline) aluminum (Alq_3) were purchased from Sigma–Aldrich. MoO_3 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 TiO_2 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 ~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 1:60–1:120. The PtOEP or PdOEP concentration was kept at 1 mg mL^{-1}. 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 μL on 18 × 18 mm^2 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 μm; the thickness of the 1:60 EC films was ~11–13 μm; the thickness of the 1:120 EC films was ~19–24 μm. 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 h and then drying it in flowing air for another 1 h, 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