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Oxygen, relative humidity, and interlayer related issues in organic electronics

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Oxygen, relative humidity, and interlayer related issues in organic electronics

by

Weipan Cui

A dissertation submitted to the graduate faculty in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Major: Condensed Matter Physics

Program of Study Committee:
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2014

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Chapter 1 Introduction to OLEDs, OPVs and Photoluminescence (PL)-based O₂ Sensor

1.1 Theory of π Conjugated Materials

SP hybridization

The carbon atom (1s²2s²2pₓ2pᵧ) displays sp hybridization by mixing 2s and 2p atomic orbitals in sp, sp² and sp³ hybrids. For example, sp² hybridization (1s²2sp²2sp²2sp²2p), which often occurs in the double bond, is realized by mixing one 2s orbital with two of the three 2p orbitals and hence a total of three sp² orbitals and one p orbital are formed, as shown in the Fig. 1-1(a). The bond formed between two sp² orbitals is a σ bond, and hence, three σ covalent bonds with 120° angles are formed in a molecular plane. The bond formed by 2p–2p overlapping is a π bond, which is perpendicular to the molecular plane, as indicated in Fig. 1-1(b). A σ bond exists, as an example, in C-C and C-H bonds of organic molecules; it is the strongest covalent bond. A π bond is formed by overlapping of the two lobes of the atomic p orbitals, as in the C=C double bond; it is weaker than the σ bond [1].

![Diagram of sp² hybridization and σ and π bonds](image)

**Fig. 1-1** (a) sp² hybridization and (b) σ and π bonds
HOMO and LUMO

Conjugated organic aromatic molecules contain alternating single and double carbon bonds. The electronic properties of such molecules are largely determined by the \( \pi \) electrons due to their weaker bonding. Such delocalized \( \pi \) electrons extend over several adjacent atoms. The highest occupied molecular orbital (HOMO) in conjugated organic molecules corresponds to the valence band in inorganic systems. The lowest unoccupied molecular orbital (LUMO) corresponds to the conduction band. As shown in Fig.1-2, the difference between the HOMO and LUMO is the band gap, which determines the light absorption onset and emission wavelengths, together with selection rules for optical transitions [2].

Fig.1-2 Schematic diagram for molecular orbitals
**Exciton and charge transport**

Absorption of a photon by a semiconductor creates an electron in the conduction band and a hole in the valence band. The bonding of the electron and hole by the Coulomb force forms an exciton with its energy slightly less than the unbound electron and hole. The exciton is an electrically neutral quasiparticle and its energy is determined by the dielectric constant of the material. For materials with a large dielectric constant, a Wannier exciton is formed with the typical binding energy on the order of 0.01 eV. For materials with a low dielectric constant, such as conjugated aromatic molecules, a Frenkel exciton is formed with atypical binding energy of 0.1 to 1 eV. The exciton recombines to emit a photon or phonon, or to an electron and a hole [3].

Efficient charge transport requires the charges to be able to move within the molecules without being trapped or scattered. Charge carrier mobilities are influenced by many factors, such as molecular packing, disorder, impurities, temperature, electric field, charge-carrier density, molecular weight, and pressure [4]. In disordered systems like organic materials, the charge transport is by site-to-site hopping rather than band-like transport. The mobility in OLEDs is given by Eq.(1.1) [5]:

\[ \mu = \mu_0 e^{\frac{-\Delta}{kT}} e^{\beta \sqrt{E}} \]  

(1.1)

Where \( \mu_0 \) is the zero-field factor, \( \Delta \) is the activation energy, \( E \) is the electric field, and \( \beta \) is a field-dependent coefficient.

**Energy transfer**

Energy transfer is the interaction between an excited energy level and another lower energy level without photon emission from the higher-energy state. As examples, energy transfer is often observed between suitable donor and acceptor molecules, or in host-guest systems in OLEDs. Two kinds of energy transfer are dominant, Forster resonance energy transfer (FRET)
and Dexter energy transfer (DET). FRET is the process where the energy released from the excited energy level of a donor or host material excites an energy level of an acceptor or guest material through Coulombic interaction (nonradiative dipole–dipole coupling). Its efficiency is inversely proportional to the sixth power of the distance between the donor and acceptor, and it occurs within 10 nm in nanoseconds [6]. DET is the process where the donor and acceptor exchange energy due to the overlap of their wave-functions. Its rate reduces exponentially with the distance, with a typical distance of 1.5-2 nm. FRET occurs only between singlet states, while the DET takes place both in singlet-singlet and triplet-triplet systems, as shown in the Fig.1-3. DET is also a quenching process indicated by the decrease of the fluorescence intensity of a given substance.

**Fig.1-3** Forster resonance energy transfer and Dexter energy transfer [7]

**Fluorescence and Phosphorescence**

Electron in the excited state can be realized by light absorption or electrical injection to the LUMO or conduction band. As indicated in Fig. 1-4 and Eq. (1.2), a molecule in the excited
singlet ($S_1$) state can undergo several processes: (1) non-radiative relaxation, where the excitation energy is dissipated as heat, (2) fluorescent emission by transiting the electron to the ground state, (3) conversion to a triplet state by intersystem crossing and then phosphorescent emission, or through interaction with a second molecule through fluorescence quenching.

\[
\begin{align*}
\text{Excitation: } & S_0 \xrightarrow{\text{Excited}} S_1 \\
\text{Fluorescence (emission): } & S_1 \rightarrow S_0 + h\nu_{em} + \text{heat}
\end{align*}
\]  

(1.2)

\[
\text{Singlet: } |S, S_z\rangle = |0, 0\rangle = \frac{1}{\sqrt{2}}[\uparrow \downarrow - \downarrow \uparrow]
\]

\[
\text{Triplet: } |S, S_z\rangle = \begin{cases} 
|1, -1\rangle = \downarrow \downarrow \\
|1, 0\rangle = \frac{1}{\sqrt{2}}[\uparrow \downarrow + \downarrow \uparrow] \\
|1, 1\rangle = \uparrow \uparrow
\end{cases}
\]  

(1.3)

Fig.1-4 Jablonski diagram for light emission [8]

Two electrons, with opposite spins due to the Pauli exclusion principle, can occupy each energy level. According to the electron spin configurations (scheme 1.3), one singlet ($S=0$) and three triplet ($S=1$) states result in the statistically 25% singlet excitons (SEs) and 75% triplet
excitons (TEs) that are formed upon charge injection in OLEDs. Fluorescence and phosphorescence are obtained from the corresponding transitions of the SEs and TEs to the ground state.

1.2 Organic Light Emitting Diodes (OLEDs)

Introduction

OLED is a diode in which the emissive organic layer emits electroluminescent (EL) light in response to an electric current. It has found application in solid state lighting and displays, for example, phones, computer monitors and TV screens, luminescent window glass, and interactive light switching. OLED displays can use either passive-matrix OLEDs (PMOLED) or active-matrix OLEDs (AMOLED); the latter requires a thin-film transistor backplane to switch each individual pixel on or off, but allows for higher resolution and larger display sizes.

OLEDs can be divided into two main groups based on their materials: those based on small molecules and those based on polymers. They can also be divided in terms of device architecture as bottom emitting or top emitting diodes. Compared with inorganic LEDs, OLEDs have the advantages of (1) potentially lower future cost, by using suitable fabrication methods, such as inkjet printing and roll-to-roll vapor deposition, (2) light weight and flexibility, by using flexible plastic substrates, (3) wider viewing angles approaching 90° from the normal and improved brightness, and (4) better power efficiency and fast response time (< 0.01 ms), in addition to other attributes, such high EL efficiency and low driving voltage, ease of fabrication, and environmental friendly. Currently, OLEDs still have issues with short lifetime and low efficiency in the blue, color balance, and damage by oxygen and water [9].
**OLEDs’ structure**

The structure of OLEDs evolved from a single organic layer to multi-layers sandwiched between two electrodes. OLEDs’ architecture includes a substrate, anode, hole injection layer (HIL), hole transport layer (HTL), emissive layer (EML), hole blocking layer (HBL), electron transport layer (ETL), electron injection layer (EIL) and cathode [10], as indicated in the Fig. 1-5. The substrate is a transparent plastic or glass, or a metal foil with high heat conductivity. The anode is often the transparent or semi-transparent electrode on the substrate, whose function is to inject holes into organic layers. It requires a high work function (~4.7 - 4.9eV) and low roughness. Glass or plastic substrate coated with ITO or with a conducting and transparent polymer (high conductivity Poly(3,4-ethylendioxythiophene) polystyrene sulfonate (PEDOT:PSS)) are typical choices [11]. To lower the barrier for hole injection from the anode, the HIL requires a material with high mobility, high glass transition temperature, and good electron blocking. The HTL transports holes and should block electrons from reaching the anode to prevent charge recombination. Charge recombination occurs in the EML; it leads to emission of light. It requires high efficiency for recombination, long lifetime, and good color purity.
Different wavelengths are realized by choosing materials with the right energy gap (see Fig. 1-2). The ETL requires good electron transport and hole blocking. The cathode is typically a metal with low-to-medium work function (~2.9 - 4.8eV), whose function is to inject electrons into organic layer. LiF or CsF with Al (-4.2eV) or Ag (-4.8eV) are common cathodes. In top emitting devices, the cathode is semi-transparent. Additional layers (antireflection layer or microlens) are usually used to help extract light that is wave-guided in the glass or ITO/organic layers, which increases the OLEDs’ efficiency.

The EL band of standard OLEDs is broad due largely to the EML disorder. Microcavity OLEDs, with e.g., a metallic cathode and a semitransparent metal anode, exhibit narrower bands with the emission wavelength determined by the cavity length [12]. A thin Ag layer (~25– 40nm) is often the choice for emission in the visible and Al (~15– 20nm) for the UV.

**OLEDs’ principle of operation**

OLED’s operation includes carriers injection, carriers transport, and exciton recombination. As shown in the Fig. 1-6 (a), when a forward voltage is applied to the OLED, electrons are injected from the cathode to the LUMO of the adjacent ETL and the holes from the anode to the HOMO of the HTL. Since often the work function of the cathode is lower than the LUMO of the ETL and the work function of the anode is higher than the HOMO of HTL, injection barriers exist for both electron and hole injection, (see Fig. 1-6). However, the charge carriers can pass the triangle potential barriers under the applied voltage by quantum tunneling.

Organic layers are amorphous with Van der Walls interaction, which is weaker than chemical bonds in inorganic semiconductors. Carriers are generally trapped in localized states and hop between different potential wells with phonon-assisted and field-assisted energy. The mobility of organic materials is typically ~10^-6 ~ 10^-3 cm²/(Vs), which is several orders of magnitude lower
than that of inorganic materials, whose mobility is typically larger than $10^2 \text{cm}^2/(\text{Vs})$. The low mobility leads to accumulation of charges in the bulk organic layers, which screens the applied voltage and results in the charge redistribution. This explains the ohmic behavior at low voltage and injection-limited behavior at high voltage.

**Fig.1-6** (a) and (b) Principle of OLED operation

Due to the lower electric dielectric constant ($\sim 3 - 5$) of the organic materials, Frenkel excitons are usually formed in the organic layers with binding energy of $\sim 0.3-1$ ev and a binding radius of $\sim 1$ nm. The excitons recombine in the recombination zone (EML) by emitting light when electrons at the excited state relax to the ground state.

The maximum internal quantum efficiency (IQE) of a fluorescent OLED is limited to 25% according to the SE spin statistics. However, emission induced by intermolecular interactions occurs under high exciton density through triplet-triplet annihilation (TTA). More than 25% fluorescence efficiency is obtained due to production of one SE by two TEs. However, it is still low compared to the phosphorescence from TEs. Spin-orbit coupling due to heavy metal core leads to intermolecular system crossing (ISC) between singlet and triplet states. By using these heavy metal-containing phosphorescent materials, TEs can decay radiatively, hence improving the IQE of the device [13]. Up to $\sim 63\%$ efficiency was attained for phosphorescent OLEDs [14].
**OLEDs’ characterization**

In characterizing OLEDs various measurements are typically performed. Such measurements include emission spectra, lifetime, and current-voltage-luminance (J-V-L) relations, based on which the efficiency is calculated. Emission spectra are measured in terms of peak emission and bandwidth (color purity). The efficiency can be expressed in two ways: luminance efficiency in Cd/A units and power efficiency in lm/W, which is the basis for comparison of the different OLEDs. Luminance efficiency describes the total brightness in a certain direction at a certain current density, while power efficiency describes the total light flux in the front direction under a certain electric power. The external quantum efficiency (EQE) is the ratio of the number of emitted photons toward the front and the number of injected electrons. Furthermore, the luminescent quantum yield $\Phi_n$ is another factor to consider, which is largely dependent on the material itself. $\Phi_n$ in films is usually smaller than that in solutions due to “concentration quenching” or “self quenching”, and guest-host systems are widely used to get more efficient emission. OLED’s lifetime refers to the long-term ability to operate at a lower input power at a given luminance. It indicates the speed of degradation and it is an important factor for real world applications.

**1.3 Organic Photovoltaics (OPVs)**

**Introduction**

Organic photovoltaics is a branch of organic electronics, where organic solar cells (OSCs), producing electricity from sunlight by the photovoltaic effect, are researched and developed. It deals with semi-conductive organic materials for light absorption, charge transport, and charge collection. As with OLEDs, OSCs are divided into small molecule solar cells and polymer solar cells. They are also divided into bi-layer or bulk hetero-junction OSCs, based on their
architecture. Similar to OLEDs, OSCs have the advantage of potential low cost, lightweight, flexible design, and ease of fabrication, while disadvantages include lower efficiency in comparison to some of the inorganic cells and particularly, short lifetime. The optical absorption coefficient of organic molecules is high, so a large amount of light can be absorbed by a small amount of materials. For efficient OSCs, control of the morphology and interfaces is very important.

**OSCs’ structure**

As shown in the Fig. 1-7, the architecture of OSCs includes a substrate, a transparent electrode, active layers and a counter electrode. Additional interfacial layers are often introduced between the electrode and the active layer for better device performance. The frequently used substrate is glass due to its low cost and good barrier against oxygen and water. Another choice of substrate material is plastic due to its flexibility and light weight. The latter is especially suitable for the solution-based OSCs using low temperature and roll to roll deposition [15]. The transparency, thermal stability, and oxygen and water permeability, however, remain issues [16,17]. Indium tin oxide(ITO) is a common electrode material and is commercially available, including ITO-coated glass. ITO has over 85% transparency in the visible and its conductivity is 3000~6000S/cm [18].
The work function of ITO is in the range of -3.7 to -5.1eV, depending on surface treatment, such as solvent cleaning and UV ozone treatment, which increases the work-function [19,20]. Other transparent electrodes include transparent conducting oxide (TCO) such as Al doped ZnO, fluorine-doped tin oxide (FTO) [21-23], carbon nanotubes [23], and PEDOT:PSS [25,26].

The active layers are usually composed of two materials, a donor (D) and an acceptor (A). The D and A have different HOMO (ionization energy) and LUMO (electron affinity) levels, so that electrostatic forces are generated at the interface between layers of these materials, which enables excitons dissociation into electrons and holes. The performance of the device is influenced by the carrier mobility, exciton diffusion length, film morphology, frontier energy level alignment, band gap, and absorption coefficient. The encapsulated device lifetime is determined by its ambient stability, thermal stability, and robustness of the various interfaces. Thus, in choosing materials for the active layers electrical, optical, and stability attributes should be considered. Typical small-molecule donor materials include phthalocyanines (for instance, CuPc [27,28], PbPc [29], SnPc [30], ClAlPc [31] and TiOPc [32], and ZnPc [33], while acceptor materials are perylene diimides and fullerenes [34-36] (for instance C_{60}, C_{70} and [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM)). Deposition of the back electrode is the final step in device fabrication and it is followed by deposition of an encapsulation layer to prevent diffusion of O_2 and moisture. In choosing the electrode materials the following should be considered: (1) the built-in electric field, whose function is to help separate the charges; it is determined by the difference in the work function of the two electrodes. Since the work function of the ITO electrode is -4.7eV, a lower work function for another electrode is needed, such as Al (~4.2eV), Ag (~4.7eV) and Ca (~2.9eV), (2) the alignment of the work function with the energy level of the active layer, and (3) The contact should be Ohmic for effective charge collection[37].
Interfacial layers are used to prevent charge leakage into the electrodes and exciton quenching at the organic/electrode interface. A thin PEDOT:PSS layer (~40nm) is usually deposited on top of the ITO anode. This layer planarizes the ITO to prevent surface spikes, increases the work function up to ~5.1eV to form an ohmic contact with the donor layer, creates a more uniform surface conductivity to help charge collection, and blocks the electrons to increase the open circuit voltage ($V_{oc}$). PEDOT:PSS, however, is highly acidic, which etches the ITO and results in indium ions diffusion into the active layers. Interfacial modification at the cathode requires materials with hole blocking and good electron transport properties [38-42]. A thin LiF layer (~1nm) often precedes the Al cathode, protecting the active layer from hot Al atoms and slightly alters the Al work function [43]. Another purpose of an interfacial layer is to introduce an optical spacer to maximize possible light absorption, for instance a TiO$_2$ layer preceding the Al layer serves for this purpose [44].

**OPVs’ principle**

Figure 1-8 demonstrates the principle of the OPV. As seen, 5 major processes occur upon light absorption [45-47]: (1) exciton generation (2) exciton diffusion; the excitons generated in the active film diffuse to the D/A interface, generating a charge transfer (CT) state (3) exciton
dissociation; i.e., charge separation due to the potential drop at the interface; some excitons may undergo geminate recombination to create a phonon or a photon. (4) Charge drift; the free carriers move to the electrodes due to the potential difference between the two electrodes, and (5) charge collection at the electrodes.

**Fig.1-9** solar spectrum [48]

Fig.1-9 shows the solar spectrum, indicating that materials with high absorption in the visible and IR regions are suitable OPV materials. The average solar radiation power density is 100 mW/cm$^2$. The donor and the acceptor materials are categorized first by their energy levels (HOMO and LUMO) and then by their electron or hole mobility. Bi-layer or bulk hetero-junction (BHJ) structures are chosen to achieve more efficient exciton dissociation. BHJ is advantageous in comparison to bi-layer design as exciton dissociation is improved due to increased D/A interface area. The disadvantage, however, is in regard to worse charge drift and charge collection due to potentially discontinuous D and A domains from the bulk toward the electrodes. For solution-based OSCs, an additional step of slow drying (~0.5-1 hr) under a petri-dish is sometimes needed for the phase separation [36]. Baking is also performed to crystallize
the organic material to obtain higher carrier mobility. Since electric or magnetic fields also enhance the dissociation, electric or magnetic nano-particles are sometimes introduced in the active layer [49].

**OSC characterization**

Several attributes, described next, are used in characterizing OSCs. The photovoltaic power conversion efficiency (PCE) is calculated by Eq. (1.4)

\[
\eta = \frac{I_{\text{max}} \times V_{\text{max}}}{P_{\text{in}}} = \frac{I_{\text{sc}} \times V_{\text{oc}} \times FF}{P_{\text{in}}}
\]

(1.4)

where \(I_{\text{sc}}\) (unit: A) is the short circuit current density under zero bias, \(V_{\text{oc}}\) (unit: v) is the open circuit voltage under zero current, and FF (fill factor) is the ratio of the maximum electrical power to the \(I_{\text{sc}} \times V_{\text{oc}}\) product, as indicated in the Fig. 1-10.

Another attribute that describes the performance of the OSC is the quantum efficiency; the external quantum efficiency (EQE) is defined as the ratio of the number of charge carriers collected by the solar cell to the number of photons and the internal quantum efficiency (IQE) is defined as the ratio of the number of charge carriers collected by the solar cell to the number of photons absorbed by the cell.

![I-V curves of solar cells](image)

**Fig.1-10** I-V curves of solar cells
Measuring the dark current, flowing through photosensitive cells when no photons are entering the device, which is referred to as reverse bias leakage current in non-optical devices and the capacity-voltage or capacity-frequency relations, which indicate the charge distribution in the device and hence trapping sub band-gap states are also informative device features.

1.4 Fabrication Methods

Standard cleaning

The substrate used for OLEDs and OPVS is usually ITO-coated glass. It requires a standard cleaning before device fabrication. The cleaning steps include use of a surfactant (to remove oil), water (to remove the surfactant), 2-propanol (to remove water), acetone (to remove some residual organic chemicals), and 2-propanol (to remove acetone). Next, the substrate is fast dried by blowing gas and then UV-ozone or O₂ plasma treated to further remove surface carbonaceous contamination. Solvent cleaning lowers the ITO work function due to C contamination and UV ozone or oxygen plasma raise the work function by removing these contaminations and affecting the oxygen vacancy concentration on the surface [50-52]. Also, UV ozone and oxygen plasma result in a more hydrophilic surface suitable for the following PEDOT:PSS layer. The substrate is transferred to a nitrogen or argon-filled glovebox with the minimal O₂ (< 20 ppm) and moisture (<0.1 ppm) levels.

Thermal evaporation

One common approach of device fabrication is vacuum thermal evaporation, where a source material is placed in a crucible or boat, which is heated by an electric filament. A pool of melted metal forms in the boat cavity and evaporates into a cloud above the source, as shown in the Fig. 1-11. Thermal evaporation enables fabrication of multilayers with controlled thickness. It enables generating relatively easily a pattern of the device using masks. Several parameters can
be systematically varied in a single deposition, which greatly enhances optimization of various parameters. Also, the existing evaporation equipment in industry can easily be utilized for the production of OLEDs and OSCs.

In thermal evaporation, the purity of the film depends on the quality of the vacuum and purity of the source material. Acceptable vacuum ($<10^{-6}$ Torr) and high purity material are preferred. High deposition rates may minimize the relative rate of gaseous impurity inclusion and obtain good film purity. The evaporation rate for organic materials is $\sim$1-2 Å/s, for Ag or Au it is $\sim$1-2 Å/s, and $\sim$4-5 Å/s for Al. Limited by the wire filaments, thick films are hard to realize and some metals with a high melting point are hard to be deposited. The disadvantage of the thermal evaporation is that it requires a complex vacuum system. Furthermore, material waste is an issue, which increases cost.

![Thermal evaporation](image)

**Fig.1-11** thermal evaporation [53]

**Spin coating**

Spin coating is also a common method for device fabrication. Since polymers cannot be deposited by thermal evaporation due to decomposition of the material under heat, solution based methods are the only ways for these materials. The material is first dissolved in the solvent (water or an organic solvent), and then the solution is cast on the substrate, which is located on a spin coater. Thin organic films are obtained by spinning the substrate at a certain speed. Solution
concentration, spin rate, and spin duration determine the films’ thickness and affect the morphology. The solvents are another factor to be considered due to their different evaporation rate. For OSCs’ fabrication, two or more materials are mixed and D/A phase separation is required upon film formation. A low evaporation rate solvent (e.g., 1,2-Dichlorobenzene (DCB)) is preferred and an additional step of drying under a semi-sealed container is sometimes needed [36]. The baking step removes the residual solvent and can affect the films’ morphology and other attributes such as charge transport and recombination.

Spin coating is easily conducted and excludes the need for a vacuum system. Doping is easily achieved without the need for more complex co-evaporation. An issue related to spin coating is the fabrication of multilayers due to dissolution of a preceding layer by the solvent used for the following layer. Hence solvent orthogonality is required. Furthermore, lack of combinatorial and patterning methods hinder the application in displays. Large panels can be realized by roll-to-roll deposition or inkjet printing.

**Degradation and encapsulation**

There are two major types of degradation in OLEDs: (1) intrinsic degradation, which refers to the decrease in the luminance during device operation. It could be categorized into several reasons---for example, morphological instability of the hole transport layer due to crystallization and increase in the surface roughness [54,55], the penetration of indium from the ITO into the organic layer, resulting in PL (photoluminescence) quenching [56], and an accumulation of trapped positive charges at the HTL/EML interface resulting in a decrease in PL[57]. (2) Degradation due to external factors—for example, a direct contact between the anode and the cathode leading to sudden loss of the PL [58], thermal induced degradation at temperatures above the glass transition temperature leading to catastrophic failure [59], dark spot degradation
as a result of the formation and growth of non-emissive defects [60,61], oxidation of the metal
cathode or delamination of the metal due to oxygen and water [62,63].

The degradation of OSCs is similar to that of OLEDs and it can also be divided in two main
categories [64, 65]: intrinsic degradation and extrinsic degradation. One difference from OLEDs
is the photo-bleaching and photo-oxidation of the $\pi$-conjugated material, since OSCs are
operating under high intensity of light.

Encapsulation provides control over dark-spot degradation and delamination of the electrode
by blocking oxygen and water. A typical encapsulation technique is using a glass lid with a seal
of UV-cured epoxy resin between the glass substrate and the lid. Diffusion of water and oxygen
through the epoxy seal has to be considered in this case. Moreover, this technique has some
problems with flexible devices due to the rigidity of the encapsulation material. A flexible
encapsulation method has been developed, which is based on barrier coated flexible lids and thin
film coatings directly in contact with the device surface [66,67].

The material for device encapsulation should meet the requirements of high dielectric
breakdown, high volume resistivity, proper refractive index matching with other layers, low
water vapor transmission rate (WVTR) and oxygen transmission rate, and high glass transition
temperature (Tg). For instance, the requirement of the diffusion rate for OLEDs or OPVs is to
have a WVTR under $10^{-6}$ g/m$^2$/day [68]. Since oxygen and water will interact with the organic
material under UV illumination, it is also needed to consider light transmission, hydrolysis, and
UV absorption degradation.

Inorganic and organic materials can be used for encapsulation [69-72]. Though inorganic
materials are commonly used due to a good combination of all these requirements, organic
materials have an advantage of flexibility in the synthesis, such as ease to change the molecular
weight, energy levels, band-gap, and solubility [73]. Organic materials can also be disposable and have relatively lower negative effect on the surroundings [74]. In term of structure, encapsulation could be one single thin film or multilayered with multilayer encapsulation preferred.

1.5 Optical Oxygen Sensors

Of all oxygen detection techniques, optical method based on photoluminescence (PL) are sensitive and suitable for various applications in areas such as environmental, medical, chemical, and agricultural [10,75] in both liquid and gas phase in possible. Despite significant advances, R&D is ongoing to obtain better, more reliable monitors for specific applications. New oxygen sensitive materials, new matrix materials which the oxygen sensitive material is embedded), new sensing films’ structures, and structural integration of oxygen sensors are still among intensive research topics. Furthermore, durable and reliable oxygen sensors, namely sensors suitable for detecting O₂ under various conditions (pH, relative humidity, or temperature) are also needed [76,77].

Principle of operation

When an atom or molecule is electronically excited through the absorption of a photon, the excited electron will return to the ground state by radiative and non-radiative decay. If a quenching agent (Q) is present, it will provide another channel for decay. As shown in Eq. (1.5),

\[
\begin{align*}
A^* & \xrightarrow{k_r} A + h\nu \\
A^* & \xrightarrow{k_{nr}} A \\
A^* + [Q] & \xrightarrow{k_q} A
\end{align*}
\]

(1.5)

The decay rate is given by Eq. (1.6)
\[
\begin{align*}
\frac{d[A^*]}{dt} &= -(k_r + k_{nr} + k_q [Q])[A^*] \\
[A^*] &= [A^*]_0 e^{-(k_r + k_{nr} + k_q [Q])t}
\end{align*}
\] (1.6)

Here \(k_r\) and \(k_{nr}\) are the radiative and non-radiative decay constants and \(k_q\) is the bimolecular quenching constant (unit: 1/s). \(\tau_0 = \frac{1}{k_r + k_{nr}}\) is the PL decay time in absence of the quencher (also called intrinsic decay time) and \(\tau = \frac{1}{k_r + k_{nr} + k_q [Q]}\) is the PL decay time in presence of the quencher, which is dependent on its concentration [Q]. The ratios \(\tau_0/\tau\) and \(I_0/I\) (the corresponding PL intensities ratio) are shown in Eq. (1.7), where \(K_{SV}\) is the Stern-Volmer (SV) constant and plots of \(\tau_0/\tau\) or \(I_0/I\ vs [Q]\) are the (ideally linear) SV relations.

\[
\frac{I_0}{I} = \frac{\tau_0}{\tau} = \frac{k_r + k_{nr} + k_q [Q]}{k_r + k_{nr}} = 1 + k_q \tau_0 [Q] = 1 + K_{SV} [Q] = 1 + K_{SV} [O_2]
\] (1.7)

Oxygen is a suitable quencher of phosphorescent dyes such as platinum octaethylporphine PtOEP (\(\tau_0 \sim 100\ \mu s\ [78]\)) and the Pd analog PdOEP (\(\tau_0 \sim 1\ \text{ms}\ [10]\)) due to its unique triplet ground state. Such dyes embedded in a polymeric matrix constitute the sensing films.

Though \(O_2\) detection can be made through both \(I\) and \(\tau\) modes. The latter is advantageous since it is independent of changes in the excitation light intensity, background light, or minor changes in the sensing film. Pulse operation is used in the \(\tau\) mode, which also enhances the lifetime of OLEDs due to reduction of heat dissipation during operation, and that of the sensing films due to reduced photo-bleaching under constant light exposure (especially UV light).

**Integrated all-organic oxygen sensors**

The advantage of using OLEDs and OPDs in sensors is their potential ease of integration, which results in compact, field-deployable, and potentially inexpensive monitors. By combining
the OLED and OPD and using the time domain monitoring it may be possible to eliminate lenses and optical filters for compact devices. An a-Si:H-based photo detector can also be integrated since it can be deposited at low temperature [79], however, its response time was found to be too slow for monitoring in the advantageous time domain. The OPD has the advantage of tunable absorption spectra using the proper organic materials, as is the case with OLEDs’ emission. The OLED/sensing film/OPD integration can be in front detection or back detection geometries, as shown in the Fig 1-12. The back detection prevents direct illumination of the PD by the excitation light and hence enhances the signal to noise (S/N) ratio.

![Schematic of O2 sensors](image)

**Fig.1-12** Schematic of O₂ sensors (a) back detection and (b) front detection geometries [10]

The disadvantage of the integrated all-organic sensor is the relatively shorter operational lifetime of the OPD and of the OLED, if operated at high intensities. This issue however, is not as critical as in other OLED and OSC applications, as sensing films are often less stable and disposable. Also, OPDs lack internal gain and hence their sensitivity is lower than that of photomultiplier tubes (PMTs) or avalanche PDs. The latter, however, require high voltages for their operation. As a result of the lower detection sensitivity of OPDs, at high [O₂] the intensity of PL is relatively low. Additionally, the broad band OLED spectrum can significantly increase the noise when operating the sensor in the intensity mode even when using optical filters,
gratings, or polarizers. There are several methods to minimize these problems: (1) narrowing the full-width half-maximum (FWHM) of the excitation band by using micro-cavity OLEDs [80], (2) operating the OLED in the pulse mode [81], and (3) increasing the outcoupling of OLEDs’ light directly into the sensing film. Developing efficient sensing films is an on-going research endeavor. As shown, in this work we developed sensing films with voids or embedded nanoparticles to enhance the PL and lower the background signal [82]. We also designed sensing films that monitor the relative humidity via their response to [O₂] [83].

1.6 Dissertation Organization

This dissertation is comprised of 6 chapters. Chapter 1 is a general introduction to organic semiconductors, OLEDs, OSCs and PL-based oxygen sensors. Chapter 2 describes the detection of oxygen in the OLED’s active layer to determine the effects of the fabrication environment on device performance. Chapter 3 describes approaches to enhance the PL in O₂ sensors by designing porous sensing films. This chapter describes also simultaneous monitoring of O₂ and relative humidity. Chapter 4 describes the modification of interfacial layers in small molecule organic solar cell, using alkali fluoride interlayers. Chapter 5 describes modification of an interfacial layer in a polymer solar cell and addresses also all organic oxygen sensors, where OLEDs and OPDs are integrated with the sensing film. Chapter 6 is a summary of the thesis.

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Chapter 2: Luminescence Decay Times of PdOEP:PVK OLEDs Fabricated in Controlled O₂ and H₂O Environments

modified from Weipan Cui, Rui Liu, Alex Smith, Joseph Shinar, and Ruth Shinar

Proceedings of SPIE 2011

Abstract

Residual levels of O₂ in OLEDs and their relation to device performance were evaluated by measuring (1) the photoluminescence (PL) decay time (following pulsed UV LED excitation) of the O₂ sensing dye Pd octaethylporphyrin (PdOEP) doped in the active OLED layer poly(N-vinylcarbazole) (PVK) and (2) the electroluminescence (EL) decay time (following a bias pulse) of glass/ITO/PEDOT:PSS/6 wt.% PdOEP:PVK/CsF/Al OLEDs. The active layer was prepared under various conditions of exposure to controlled O₂ levels and relative humidity. PdOEP was used successfully for monitoring exposure of PdOEP:PVK to low levels of oxygen and shortened device PL decay times often indicated device deterioration. The PL decay time at various applied voltages and the EL decay time at various current densities were monitored to evaluate degradation processes related to oxygen and other bimolecular quenching phenomena.

2.1 Introduction

As is well known, water and to a lesser extent O₂ result in degradation of OLEDs [1-4]. Studies showed that the growth rate of dark spots at defect sites due to water is faster by three orders of magnitude in comparison to pure O₂ [2]. Water causes delamination of the metal electrode and oxygen oxidizes it at the interface with the organic layer [2]. In the case of degradation due to dark spots, it was shown that one can peel off the cathode from a degraded OLED and redeposit a fresh cathode on the existing organic surface with the resulting device still functioning [2,3].
Encapsulation is obviously an effective way to prevent the diffusion of water and oxygen following device fabrication, which greatly increases the operational lifetime of OLEDs. Fabrication of the organic layers must often be conducted in oxygen- and moisture-free environments to avoid their introduction into the devices. Indeed, device stability is greatly enhanced when fabricated under ultra-high vacuum [5].

In this work we studied the effect of oxygen and water on the OLEDs’ active layer. We monitored the photoluminescence (PL) decay times ($\tau_{\text{PL}}$) following exposure of the structures glass/ITO/PEDOT:PSS/6 wt.% PdOEP:PVK (termed ‘films’) to various O$_2$ levels, [O$_2$]. Additionally, in such structures, the active layer was prepared in environments containing controlled levels of gas-phase oxygen and water vapor. The [O$_2$] (associated with the residual O$_2$ level in the OLEDs’ active layer) was monitored also in similarly-prepared complete devices, i.e., where a CsF/Al cathode was deposited on the ‘films’, by monitoring $\tau_{\text{PL}}$. The electroluminescence (EL) decay time ($\tau_{\text{EL}}$) following a bias pulse in such devices was also monitored.

PL-based oxygen sensors have been studied extensively [6-11]. Such sensors are often based on a polymeric matrix doped with an oxygen-sensitive dye (sensing film) whose PL intensity ($I$) and $\tau_{\text{PL}}$ (following an excitation pulse) decrease with increasing [O$_2$]. Pt octaethylporphyrin (PtOEP) and Pd octaethylporphyrin (PdOEP) are common oxygen-sensitive dyes. Monitoring $\tau_{\text{PL}}$ is advantageous over monitoring $I$ since $\tau_{\text{PL}}$ is independent of moderate changes in the sensing film, light source intensity, and background light. Optical filters are not always needed when operating in the $\tau$ mode, resulting in more compact devices. The unquenched $\tau_{\text{PL}}$ of PdOEP is $\sim$1 ms [10], which makes it suitable for monitoring trace [O$_2$]. Ideally (and in particular at low [O$_2$]), the relation between $I_0/I$ or $\tau_0/\tau_{\text{PL}}$ and [O$_2$] follows the Stem-Volmer (SV) equation (2.1)
\[ \frac{I_0}{I} = \tau_0/\tau_{PL} = 1 + K_{SV}[O_2], \]  

(2.1)

where \( I_0 \) and \( \tau_0 \) are the unquenched values.

We successfully used a PdOEP-doped PVK active layer to monitor \( \tau_{PL} \) and hence assess residual \( O_2 \) in the OLEDs as well as \( O_2 \) in-diffusion following device fabrication. We note that \([O_2]\) is the gas-phase exposure value and not the actual oxygen concentration within the organic layer. However, the monitored \( \tau_{PL} \) for the complete devices, fabricated under various conditions, corresponded to an \([O_2]\) significantly lower than the actual exposure level of the ‘films’ during fabrication, before thermal evaporation of the cathode. As discussed later, this situation indicates that only low \( O_2 \) levels remained trapped within the OLED active layer. The \( \tau_{PL} \) and \( \tau_{EL} \) of the devices at various photoexcitation intensities and current densities, respectively, were also monitored. Results show that deposition of the active layer in the presence of 21% dry oxygen resulted in minimal \( O_2 \) trapping, as \( \tau_{PL} \) was similar to the unquenched value. This observation indicates that \( O_2 \) has either reacted with the organic material (i.e., it was consumed) and/or was pumped out prior to the thermal evaporation of the cathode in low vacuum (~10\(^{-5}\) Torr).

Exposure to 100% dry oxygen leads to a somewhat lower \( \tau_{PL} \), but significantly lower \( \tau_{EL} \). The \( \tau_{PL} \) was independent of the intensity of the excitation source, which indicates that its reduction is largely due to oxygen and less to triplet-triplet annihilation (TTA). Exposure of the active layer to \( O_2 \) in a moist environment is more destructive, with a shorter device \( \tau_{PL} \) often associated with increased degradation.

2.2 Experimental Procedure

Material

The 15 ohms/square ITO-coated glass substrates were obtained from Colorado Concept Coatings. PVK and CsF were obtained from Sigma-Aldrich, PEDOT:PSS from Clevios, PdOEP
from Frontier Scientific, and chlorobenzene from Fisher Scientific. Al was obtained from Alfa Aesar.

**OLED fabrication**

The ITO-coated glass was cleaned sequentially with surfactant, deionized water, acetone, and 2-propanol, and dry-blown with nitrogen gas after the cleaning process. It was then treated for 5 min in a UV-ozone oven. PEDOT:PSS was spin coated at 1000 rpm for 180 s, then baked at 160°C for 30 min in air and for 30 min in a glovebox. 6 wt.% PdOEP:PVK solution (9 mg/mL in chlorobenzene) was spin coated at 1000 rpm for 1 min and then baked at 60°C for 30 min in the glovebox. 1 nm CsF and 100 nm Al were deposited on the active layer to complete the devices.

**PL and EL decay times**

The PL decay curves of ‘films’ and devices were obtained with a Hamamatsu R6060 photomultiplier tube (PMT) operated at -980 V. A 1 ms 50 Hz UV-LED excitation pulse, driven by an Avtech AV-1011B pulse generator, was used for PL excitation. The excitation wavelength peaked at 395 nm and it was suitable only for PdOEP (and not PVK) excitation. The OLED EL decay curves were similarly monitored, with the OLED directly driven by the pulse generator at different applied voltages. Both $\tau_{PL}$ and $\tau_{EL}$ were extracted from the decay curves using a single exponential fit. The gas-phase [O$_2$] was controlled via mixing with Ar at different flow rates using mass-flow controllers. The total flow rate was kept constant at 200 sccm. To evaluate device performance, the current vs voltage was measured using a Keithley 2000 multimeter and a programmable Kepco power supply DPS-40-2M.
2.3 Results and Discussion

‘Film’ PL decay times

Fig. 2-1 shows the decay curves following exposure to different \([O_2]\)

![Decay Curves](image)

**Fig. 2-1.** PL decay curves for PdOEP:PVK films at 0-1% gas-phase oxygen.

**Table 2-1.** PL decay times for different gas-phase \([O_2]\).

<table>
<thead>
<tr>
<th>([O_2]) (%)</th>
<th>0</th>
<th>0.17</th>
<th>0.33</th>
<th>0.50</th>
<th>0.67</th>
<th>0.83</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>τPL (μs)</strong></td>
<td>1090-20</td>
<td>704±18</td>
<td>575±18</td>
<td>457±15</td>
<td>405±15</td>
<td>363±12</td>
<td>331±10</td>
</tr>
</tbody>
</table>

![SV Relation](image)

**Fig. 2-2** The SV relation between \(τ_0/τ_{PL}\) and the gas-phase concentration of \(O_2\).
The decay curves are exponential, and, as expected, $\tau_{PL}$ decreased with increasing $[O_2]$. The $\tau_{PL}$ values are summarized in Table 2-1. At 0% $[O_2]$ (i.e., Ar atmosphere) $\tau_0 \sim 1090$ μs. Fig. 2-2 shows the SV relation between $\tau_0/\tau_{PL}$ and gas-phase $[O_2]$. This linear relation served as a calibration line for evaluating $[O_2]$ for ‘films’ and devices prepared under various conditions.

As seen from Table 2-1 and Figs. 2-1 and 2-2, the PdOEP:PVK film is suitable for monitoring low-level $[O_2]$.

Fig. 2-3 shows the change of the PL decay time over 60 min of Ar blowing for three active layers that were differently-treated for 18 h in the dark. These three treatments included keeping the film (i) in the glovebox, where the oxygen level was < 10 ppm, (ii) under dry air (21% O$_2$) conditions, and (iii) under 100% dry, pure O$_2$. Initially, shortened $\tau_{PL}$ values were observed following exposure to air and 100% O$_2$, with $\tau_{PL}$ for the latter case shorter, as expected. However, by 1 h Ar blowing the trapped O$_2$ is gradually removed.

The lower $\tau_{PL}$ following 1 h of Ar blowing for the active layers exposed to air indicates residual O$_2$. As shown below in Table 3, pumping is more effective in eliminating that O$_2$. We note that moisture has no effect on $\tau_{PL}$ for a given $[O_2]$, as shown in Table 2-2 for 0.5% $[O_2]$ and a relative humidity of 15, 60, and 95%.

**Table 2-2.** The effect of humidity on the films’ PL decay time.

<table>
<thead>
<tr>
<th>Relative Humidity</th>
<th>15%</th>
<th>60%</th>
<th>95%</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau_{PL}$ (0.5% O$_2$)</td>
<td>471±15</td>
<td>462±15</td>
<td>481±15</td>
</tr>
</tbody>
</table>
Fig. 2-3 The change of $\tau_{PL}$ for differently-treated active layers (for 18 h in the dark) during 1 h of Ar blowing.

**Device PL decay times**

Table 2-3 shows the $\tau_{PL}$ values obtained for devices and the estimated $[O_2]$ based on the calibration line of Fig. 2-2. The values of $\tau_{EL}$ at 0.01 mA/cm$^2$ are also shown.

**Table 2-3** Device $\tau_{PL}$ and estimated $[O_2]$ for devices fabricated following different active layer treatments. Shown are the conditions under which the active layer was kept for 18 h in the dark. The $[O_2]$ in treatments 4 & 5 was 21%. **The error in the measured decay times is ± 20 µs.**

<table>
<thead>
<tr>
<th>Exposure conditions</th>
<th>Vacuum</th>
<th>Glovebox</th>
<th>100% Dry $O_2$</th>
<th>Dry air</th>
<th>Humid air</th>
</tr>
</thead>
<tbody>
<tr>
<td>Device $\tau_{PL}$ (µs)</td>
<td>980</td>
<td>913</td>
<td>896</td>
<td>945</td>
<td>469</td>
</tr>
<tr>
<td>Calculated $[O_2]$ (%)</td>
<td>0%</td>
<td>0.03%</td>
<td>0.04%</td>
<td>0.02%</td>
<td>0.48%</td>
</tr>
<tr>
<td>$\tau_{EL}$ at 0.01 mA/cm$^2$ (µs)</td>
<td>816</td>
<td>797</td>
<td>302</td>
<td>766</td>
<td>142</td>
</tr>
</tbody>
</table>

As seen, at 0% $[O_2]$ $\tau_{PL}$ is 980 µs; this value was obtained also following prolong pumping prior to cathode deposition. It is shorter than the value obtained for ‘films’ (1090 µs), which may be due to PL quenching by the cathode and not to the presence of $O_2$. The calculated values of
[O$_2$] in Table 2-3 show little difference for the exposure environments of vacuum (1), glovebox (2), 100% dry O$_2$ (3), and dry air (4). The long $\tau_{PL}$ values for these four cases (896-980 µs) indicate that residual O$_2$ in the films was largely removed by 15 min of pumping prior to cathode deposition. By comparison to Fig. 2-3, pumping is more efficient than Ar blowing for O$_2$ removal.

**Fig. 2-4** PL decay times and maximal (DC) intensity of the PL (inset) at different voltages applied to the UV-LED excitation source, for a device exposed to 100% dry O$_2$ (treatment 3), which was then kept in air in the dark for ~80 days.

Exposure to humid air, however, results in a much shorter device $\tau_{PL}$ (469 µs) in comparison to the values for other exposure conditions (896-980 µs). This shorter device $\tau_{PL}$ is not due to bimolecular quenching (mostly triplet-triplet annihilation, TTA) [12], as indicated in Fig. 2-4, which shows that the device $\tau_{PL}$ is independent of the voltage (up to ~4.2 V) applied to the UV LED (i.e., the excitation intensity). The absence of significant TTA is due to a relatively low triplet density resulting from excitation by the low-power UV LED rather than a laser. This differs from TTA occurring during charge injection in these devices (see Fig. 2-5). Also, since moisture itself has no effect on the ‘film’ $\tau_{PL}$ (see Table 2-2), the shorter device $\tau_{PL}$ for the humid
air exposure condition is possibly due to residual trapped O\textsubscript{2} and/or introduction of nonradiative decay channels for PdOEP.

Fig. 2-4 also indicates that the CsF/Al cathode appears to serve as a barrier for O\textsubscript{2}, slowing its in-diffusion. The device $\tau_{\text{PL}}$ changed, but only from \(~900\) to \(~800\) $\mu$s following \(~80\) days in air. Additionally, exposure of the active layers (the ‘films’ without the CsF/Al cathode) for 18 h to light under ambient conditions degrades the PdOEP, so that no PL was observed. However, exposure of the devices to light under the same conditions results in only a small decrease in the PL intensity. This behavior indicates that the cathode protects the active layer from O\textsubscript{2} in-diffusion, which otherwise photo-oxidizes the PdOEP.

AFM images (not shown) showed no structural differences between the differently treated active layers; in all cases the root mean square roughness was \(~0.6\) nm.

**Device EL decay times**

Fig. 2-5 shows $\tau_{\text{EL}}$ versus current density for differently-treated active layers.

![Graph showing EL decay time vs current density](image)

**Fig.2-5** $\tau_{\text{EL}}$ versus current density for differently treated active layers for 18 h in the dark prior to cathode deposition.
As expected, O\textsubscript{2} and moisture degrade the devices, resulting in shorter $\tau_{\text{EL}}$, as shown also in Table 2-3. The $\tau_{\text{EL}}$ at 0.01 mA/cm\textsuperscript{2} is $\sim$300 $\mu$s for devices in which the PdOEP:PVK was exposed to 100% O\textsubscript{2} and $\sim$140 $\mu$s when exposed to humid air. The observed shortening of $\tau_{\text{EL}}$ with increasing current density is due largely to bimolecular quenching processes [13].

Exposure of the active layer to 100% dry O\textsubscript{2} results in a long $\tau_{\text{PL}}$ ($\sim$900 $\mu$s), but short $\tau_{\text{EL}}$ ($\sim$300 $\mu$s). This behavior may indicate that O\textsubscript{2} is consumed as it reacts with PdOEP:PVK [14]. This consumption of O\textsubscript{2} reduces the gas molecules' concentration in the active layer (resulting in a long $\tau_{\text{PL}}$), but it degrades the device. Hence, while short $\tau_{\text{PL}}$ of devices often indicated degradation, long $\tau_{\text{PL}}$ does not necessarily indicate a non-degraded device.

2.4 Conclusions

We showed that Pd octaethylporphyrin (PdOEP) can be used for evaluating the effect of oxygen in poly(N-vinylcarbazole) (PVK)-based organic light emitting diodes (OLEDs). By monitoring photoluminescence (PL) decay time $\tau_{\text{PL}}$ of films and devices and electroluminescence (EL) decay time $\tau_{\text{EL}}$ of OLEDs it was possible to gain information regarding degradation processes in OLEDs whose active layer was prepared under various conditions. While shortening of $\tau_{\text{PL}}$ often indicated a degraded device, long $\tau_{\text{PL}}$ was not always indicative of non-degraded devices. For example, preparation of the OLED active layer in the presence of 100% dry O\textsubscript{2} had a small effect on the device $\tau_{\text{PL}}$, but $\tau_{\text{EL}}$ shortened significantly and the device performance degraded. The long $\tau_{\text{PL}}$ is likely a result of O\textsubscript{2} consumption following its reaction with the organic materials and pumping prior to cathode deposition, which largely removes the quenching gas molecules. The lack of dependence of the device $\tau_{\text{PL}}$ in this case on the voltage applied to the ultraviolet light emitting diode (UV-LED) excitation source, which results in increased PL intensity, indicates that the degradation is induced by O\textsubscript{2} and less by triplet-triplet annihilation
(TTA). Moisture that degrades the OLEDs indicates increased O\textsubscript{2} trapping and/or introduction of additional nonradiative decay channels for PdOEP, shortening $\tau_{\text{PL}}$. The $\tau_{\text{EL}}$ is also shortened significantly in this case. TTA is evident from the shortening of $\tau_{\text{EL}}$ with increased OLED applied voltage for active layers kept in the glovebox or exposed to dry air. This shortening, however, is significantly weaker for active layers kept under vacuum.

Acknowledgements

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Chapter 3. Oxygen and Relative Humidity Monitoring with Films Tailored for Enhanced Photoluminescence

Modified from Weipan Cui, Rui Liu, Eeshita Manna, Joong-Mok Park, Fadzai Fungura, Joseph Shinar, and Ruth Shinar, Analytica Chimica Acta, in press

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 $\sim$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 $\sim$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 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.

3.1 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 O₂ concentration [1-9]. Ideally, the relation between [O₂] and I and τ is given by the Stern–Volmer (SV) equation:

\[
\frac{I_0}{I} = \frac{\tau_0}{\tau} = 1 + K_{SV}[O_2] \tag{3.1}
\]

Where \(I_0\) and \(\tau_0\) 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 [O₂]. 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 O₂ 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 TiO₂ 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 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 is washed off, creating voids) and nanoparticles.
The relative humidity (RH) effect on $\tau$ for the different O$_2$ sensing films is also presented. The TiO$_2$ NPs-doped EC matrix showed the largest RH effect with an increase of 70% in $\tau$ 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.

3.2 Experimental Procedure

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.

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 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 \( \mu \)L on 18x18 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 \( \mu \)m; the thickness of the 1:60 EC films was \~11 to 13 \( \mu \)m; the thickness of the 1:120 EC films was \~19-24 \( \mu \)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.

**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) (49nm)/tris-(8-hydroxyquinoline)aluminum (Alq\(_3\)) (56nm)/LiF(1nm)/Al(100nm), and Al(15nm)/MoO\(_x\) (7nm)/4, 4'-cyclohexylidenebis [N, N-bis (4-methylphenyl) benzenamine (TAPC)(10nm)/ 4, 4'-N, N'-dicarbazole-biphenyl (CBP)(25nm)/bathophenanthroline(BPhen)(25nm)/LiF(1nm)/Al(100nm), respectively. The excitation sources were driven with 1 ms or 100
\( \mu s \) 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 \([O_2]\) were obtained with a Hamamatsu R6060 photomultiplier tube (PMT) in the back-detection geometry [32] using a 600nm long-pass filter. For gas-phase \(O_2\) sensing, high purity Ar and \(O_2\) were mixed using mass flow controllers to generate different \(O_2\) concentrations at a constant flow rate of 200sccm (for PtOEP) or 500sccm (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 \(O_2\) 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.

3.3 Results and Discussion

(1) PL enhancement with porous films

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 \(O_2\) sensing as removal of the PVP by water results in unstable films due to partial leaching of the \(O_2\) 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.

Fig. 3-1. 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 $M_w$~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 $M_w$~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.
Images and optical properties of porous sensing films

Figure 3-1 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 μL 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 $M_w \approx 8000$.

![Images](image.png)

**Fig. 3-2.** 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.

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. 3-1(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 ~1µm using PEG with $M_w \sim 8000$ to ~4 µm using PEG of $M_w \sim 200$ (see examples in Fig. 3-2 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 3-3 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.3-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. 3-1(a) and 3-11(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. 3-1).

**PL enhancement with PEG:PS porous films**

Figure 3-4 (a) 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

![Graph](image)

**Fig. 3-4.** (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 ($M_w$~1000):PS ($M_w$~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 $M_w$~8000).
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., $PL_{\text{porous film}}/PL_{\text{reference uniform film}}$) 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 10× for PtOEP:PS doped with TiO$_2$ NPs using green OLED excitation, however, the enhancement was limited to ~3× 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 ~4× 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 ~4× 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 10× PL enhancement for the PEG:PS 1:4 (PEG $M_w \sim 8000$) film and 13× for the PEG:EC 1:1 (PEG $M_w \sim 200$) 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 3-4(b) compares the SV lines for a PS film and a PEG:PS1:4(W) (PEG Mw ~8000) film. As seen, the SV relations are linear over the whole range (0-100%), with the decay times $\tau$ 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.3-S2(a) of the Supplementary Data for 0 to 10% [O$_2$] using a PS film and a PEG:PS1:6 (PEG Mw ~8000) film excited by a green LED.

**PL enhancement with PEG:EC porous films**

As seen in Fig. 3-1(d), EC-only films are uniform, but porous structures are obtained in blended PEG:EC films, as was also reported earlier for such films indifferent applications [47].
Fig. 3-5. (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 $M_w \sim 200$).

For PS, the largest PL enhancement was obtained using PEG($M_w \sim 8000$) in PEG:PS1:4 (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 3-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 ($M_w$
~200 to ~1000) beyond the PEG:EC1:1 ratio results in non-usable, disintegrated sensing films following washing.

Fig. 3-5 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 µs pulses of green light. The maximum PL enhancement is 4.7×. 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 ~22µm. The results, however, for ~10 and ~20 µm thick films (PtOEP:EC 1:60 and 1:120, respectively) are similar as shown in Fig. 3-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. 3-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. 3-5(b).

However, as shown in the example of Fig. 3-6, the data analysis is more reliable using the blend film at high [O$_2$].

![PL decay curves](image)

**Fig. 3-6.** PL decay curves obtained under the same conditions for PtOEP-doped EC and PE11W at 100% O$_2$
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. 3-S4 of the Supplementary Data, which shows the relative PL enhancement vs temperature.

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 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.

(2) Effect of Relative Humidity (RH) on O₂ sensing

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].

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 TiO$_2$; it was enhanced to ~4.5x for 2 mg/mL TiO$_2$, saturating at this concentration. We note that $\tau$ values at various [O$_2$] were not affected by the titania concentration up to 6 mg/mL, unlike the situation with TiO$_2$NP-doped PS [13]. This behavior may be due to the higher permeability of EC to O$_2$.

**Fig. 3-7.** SV relations under dry (0% RH) and wet (95% RH) conditions for (a) PtOEP:TiO$_2$ NPs:EC film and (b) PdOEP:TiO$_2$ NPs:EC film.
The RH effect is shown in the SV relations of Fig. 3-7 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 3-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 [O₂]. The difference increases sharply, to nearly 70%, from 0 to 3% [O₂], remains largely unchanged from 3 to 7% [O₂], and then decreases gradually with increasing [O₂], to practically no RH effect at 100% [O₂]. 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 [O₂] range. The normalized difference in τ for PdOEP:TiO₂ NPs:EC sensing films is ~50% for 0.2 – 1% [O₂].

**RH calibration curves**

The PtOEP:EC and PdOEP:EC sensing films clearly show different τ values at 0% and 95% RH at a given [O₂], 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% [O₂] (Fig. 3-S4) and ~50% for PdOEP:TiO₂ NPs:EC at 0.2 – 1% [O₂].

Figures 3-8(a) and (b) show τ vs RH at 5% and 0.4% [O₂] using PtOEP and PdOEP dyes, respectively; the lower [O₂] for PdOEP is due to the strong quenching of PdOEP’s PL even at very low [O₂]. τ increases strongly with increasing RH, indicating that O₂ diffusion into the sensing film and/or dye accessibility are strongly hindered. Fig.3-8(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,
Fig. 3-8. (a) \( \tau \) vs RH at 5\% \( \text{O}_2 \) for PtOEP:Tio\(_2\) NPs:EC (1:2:60); (b) \( \tau \) vs RH at 0.4\% \( \text{O}_2 \) for PdOEP:Tio\(_2\) NPs:EC (1:2:60); (c) \( \tau_{\% \text{RH}}/\tau \) vs RH for 50\%, 20\% and 5\% \( \text{O}_2 \) for PtOEP:Tio\(_2\) NPs:EC (1:2:60) and 0.4\% \( \text{O}_2 \) for PdOEP:Tio\(_2\) NPs:EC (1:2:60).
indicating the trend in \( \tau \) 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 \([O_2]\).

### 3.4 Conclusions

An increase in the photoluminescence (PL) of luminescent oxygen sensors (Pt octaethylporphyrin (PtOEP)- or Pd octaethylporphyrin (PdOEP) -doped in modified polystyrene (PS) and ethyl cellulose (EC)) is obtained by creating porous or nano particle (NP)-doped sensing films. The porous structures are realized by blending PS or EC with polyethylene glycol (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 PEGdecorated 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 ultraviolet (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\(^\circ\)C for PS films and 120\(^\circ\)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 signal-to-noise (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 photomultiplier tubes (PMTs) and avalanche photodiodes, which also require high voltage. Though the detection sensitivity is reduced, the enhanced PL provides better reliability in the measurements, and the results consequently present a significant step toward the integration of compact components in oxygen monitors.

The relative humidity (RH) can also be monitored with some of the PtOEP- and PdOEP-based oxygen sensing films, but not with PS or even PEG:EC films. In contrast, PtOEP (PdOEP):TiO₂ NPs:EC films show a similar RH effect as PtOEP (PdOEP):EC with the advantage of enhanced PL intensity due to light scattering by the particles, which enables significantly better resolution of the RH level. The RH dependence of τ depends strongly on [O₂]. The normalized difference in τ values at 95% and 0% RH is ~70% at 5% O₂ using PtOEP-based sensing films and ~50% at 0.2-1% O₂ using PdOEP-based films. The PL enhancement enables differentiating RH changes of <10%, which is unattained with PtOEP:EC devoid of the NPs. This differentiation, though [O₂]-dependent, enables assessing [O₂] and RH using two films, i.e., a RH insensitive film for determining the actual [O₂] and another film that is RH sensitive.

**Supplementary Data**

![Fig. 3-S1. Reflection (R) and transmission (T) for PS50, PP14, and PP14W devoid of the dye](image-url)
**Fig. 3-S2.** PL intensity at different [O$_2$] for (a) PtOEP-doped PS and PP16W (PEG $M_w$~8000) and (b) PdOEP-doped EC and PE11W (PEG $M_w$~200)\textsuperscript{a}

\textsuperscript{a}The measurements were performed at constant excitation intensity and PMT bias. Due to the limited linear region of the PMT, the PL intensity could not be measured at higher [O$_2$] under those conditions.

**Fig. 3-S3.** PL intensity for various EC based films indicating minor thickness and PEG:EC ratio effects.
Fig. 3-S4. Relative PL intensity in the absence of O₂ vs temperature (a) for PS and PP14W (PEG $M_w$~8000) and (b) for EC and PE11W (PEG $M_w$~200). Both plots are normalized to the PL intensity at room temperature of PS (a) or EC (b).

Fig. 3-S5. The normalized % difference in $\tau$ values at 0 and 95% RH for different [O₂] (normalized to the former): $100 \times (\tau_{95\%RH}/\tau_{0\%RH})$; the sensing film is PtOEP:TiO₂ NPs:EC (1:2:60 wt. ratio).
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.

References

Chapter 4. Thin Air-plasma-treated Alkali Fluoride Layers for Improved Hole Extraction in Copper phthalocyanine/C_{70}-based Solar Cells


Abstract

Alkali fluorides, mostly LiF and CsF, are well-known to improve electron injection/extraction in organic light-emitting diodes (OLEDs) and organic solar cells (OSC). They are also utilized, though to a lesser extent, for hole injection in OLEDs. Here we demonstrate a new role for such fluorides in enhancing OSCs’ hole extraction. We show that an ultrathin air-plasma treated alkali fluoride layer between the indium tin oxide (ITO) anode and the active layer in copper phthalocyanine CuPc/C_{70}-based OSCs increases the short circuit current by up to ~17% for cells with LiF and ~7% for cells with NaF or CsF. The effects of the fluoride layer thickness and treatment duration were evaluated, as were OSCs with oxidized and plasma-treated Li and UV-ozone treated LiF. Measurements included current voltage, absorption, external quantum efficiency (EQE), atomic force microscopy, and x-ray photoelectron spectroscopy, which showed the presence of alkali atoms F and O at the treated ITO/fluoride surface. The EQE of optimized devices with LiF increased at wavelengths >560 nm, exceeding the absorption increase. Overall, the results indicate that the improved performance is due largely to enhanced hole extraction, possibly related to improved energy-level alignment at the fluorinated ITO/CuPc interface, reduced OSC series resistance, and in the case of LiF, improved absorption.

4.1 Introduction

Organic solar cells (OSC) are promising to become a low-cost and environmentally friendly alternative for inorganic solar cells (SC) [1,2]. They can be deposited on flexible substrates such
as plastic and are potentially printable [3,4]. Small molecule OSCs have the advantage of simple layer-by-layer deposition, which is a problem with polymer SCs due to the difficulty of finding orthogonal solvents suitable for the different layers [5,6]. As is well known, one of the outstanding challenges of OSCs is to enhance extraction of photogenerated charge carriers. As cell performance depends greatly on the interfaces between the various layers [7–9], it is essential to minimize the energy barrier between the electrodes and the organic layers to achieve a nearly ohmic contact. Different interfacial layers between the electrodes and the organic layers have been used to improve charge collection and reduce surface recombination. For example, poly(3,4-ethylenedioxy thiophene): poly(styrenesulfonate) (PEDOT:PSS) [10], MoO$_3$ [11], V$_2$O$_5$ [12], and NiO$_x$ [13] were used for efficient hole collection in OSCs. LiF [14], CsF [15], Cs$_2$CO$_3$ [16], and TiO$_x$ [9,17] interlayers deposited between the organic layers and the cathode were found to assist in electron collection, increasing the power conversion efficiency (PCE) [9,10].

In organic light emitting diodes (OLEDs), LiF and CsF have been widely used to enhance electron injection at the metal cathode [18–21]. It was reported that they either dope the preceding organic layer [22,23], form dipole layers at the interface [24], or, in some cases, react with the preceding organic layer [25]. It was also reported that LiF/Al yields a lower work function electrode [19,26,27]. A recent electron paramagnetic resonance study of OLEDs showed that the doping effect by Li was strongly dependent on the organic material adjacent to the LiF [28]. Similar behavior was found in OSCs [29]. While it is well established that in typical OLEDs LiF serves as an efficient electron injection layer, studies on ITO/LiF demonstrated improved hole injection in OLEDs as well [30]. This improvement was attributed to an increased ITO/LiF work function to $\text{WF} \sim 5.2$ eV with 1 nm LiF, from $\text{WF} \sim 4.8$ eV of the ITO [31]. The WF further increased with LiF film thickness to 5.6 eV for 5 nm LiF on ITO. NaF
(on ITO) was also reported to assist in hole injection in OLEDs following UV-ozone treatment, also as a result of an increased $\psi_f$ to $\sim5.1$ eV [32]. The formation of Na—O bonds was proposed to be responsible for this increased $\psi_f$. Recently, an increase in the work function of chlorinated ITO was reported [33,34]. This increase was associated with a layer of surface In—Cl dipoles [33]. Hence, alkali fluorides, like oxides, are also likely to increase the composite ITO work function for better alignment with the highest occupied molecular orbital (HOMO) of the adjacent organic active layer, copper phthalocyanine (CuPc) in this study.

This work shows for the first time enhanced hole extraction in OSCs induced by ultrathin air plasma treated alkali fluoride layers deposited on the ITO anodes. The structure of the devices was ITO/LiF, NaF or CsF 1 nm/CuPc 15 nm/C$_{70}$ (30 or 27 nm)/Bphen (3.5 nm)/Al (120 nm). (Bphen is 4,7-diphenyl-1,10-phenanthroline; the thin Bphen layer acts as an exciton- blocking layer.) [35] We demonstrate that LiF, and to a lesser extent NaF and CsF, enhance hole collection following air-plasma treatment. We investigated the effect of the duration of the air-plasma treatment, including the effect of the layers on the subsequent growth of the CuPc and C$_{70}$ layers. In addition to control experiments of OSCs with ITO (without the LiF interlayer) that was air-plasma treated for various durations, reference measurements with UV-ozone-treated LiF and differently-treated Li layers on the ITO were also performed. As expected, these measurements exclude the effect of Li diffusion into the active layer in enhancing device performance, and prove that pristine Li—O bonds do not improve the short circuit current $J_{SC}$ to the same degree as the air-plasma treated LiF layer. J-V characteristics, x-ray photoelectron spectroscopy (XPS), absorption, and external quantum efficiency (EQE) spectra, as well as atomic force microscopy (AFM) were employed to elucidate the observed OSC performance enhancement. The treated fluorides are believed to reduce the energy barrier for hole extraction,
which leads to a higher JSC and PCE. Importantly, the plasma treatment of the alkali fluorides was essential for improving the ohmic contact, lowering the high series resistance RS observed in devices with the as-deposited fluorides.

4.2 Experimental Procedure

As mentioned, devices studied were of the structure ITO/LiF, NaF or CsF x nm/CuPc (15 nm)/C₇₀ (30 or 27 nm)/Bphen (3.5 nm)/Al (120 nm). These thicknesses of CuPc, C₇₀, and Bphen layers were found to be optimal. The active area of all cells was 0.11 cm². The ITO-coated glass substrates were purchased from Colorado Concept Coatings. Prior to cell fabrication, they were cleaned sequentially with surfactant, deionized water, acetone, and isopropanol, and blown dry with nitrogen. In all cases (including in control experiments, i.e., experiments in the absence of the fluorides) the ITO was air-plasma treated for 20 min; changing the duration had only a minor effect on such reference cell performance. The alkali fluoride layers were deposited on the ITO by thermal vacuum (∼10⁻⁶ mbar) evaporation inside a glovebox and then air-plasma treated. Next, the organic layers were thermally evaporated. The effect of the interfacial layers was studied systematically. The thickness of the fluoride layers varied from 0 to 4 nm, by a 1 nm step. Air-plasma treatment (Harrick PDC-32G Plasma Cleaner/sterilizer; 18 W) was performed on these layers for durations of 0, 10, 20, and 30 min. The deposition rate of CuPc and C₇₀ was ∼0.1 nm/s, and of Bphen ∼0.15 nm/s. CuPc (dye content 97%), Bphen (≥99%), LiF (99.995%), NaF (99.99%), and CsF (99.9%) were all purchased from Sigma-Aldrich. C₆₀, C₇₀ (>99%) was purchased from Nano-C. All materials were used without further purification. The effects of treating LiF in a UV ozone oven or replacing LiF by a 1 nm Li layer were also studied. Three different treatments of the latter were tested: 1. an untreated thin Li layer on which CuPc was deposited without breaking the vacuum; 2. an air-oxidized Li layer, and 3. an air oxidized layer
that was subsequently air-plasma treated for 20 min. J – V characteristics of the OSCs were obtained using a 100 mW/cm² ELH bulb for illumination. The EQE was measured at 0 V. Absorption spectra were taken with an Ocean Optics spectrometer. XPS data were obtained using a Physical Electronics 5500 multi-technique system, and AFM images were acquired with a Digital Instruments system. We note that all the experiments were performed multiple times to ensure the validity of the conclusions and the comparisons are to optimized control OSCs without the fluoride layers.

4.3 Results and Discussion

1 Optimization of the device.

The structure of the small molecular solar cells is ITO/CuPc/C₇₀(C₆₀)/BPhen/Al. Optimization for the thickness of these layers are performed according to their exciton diffusion lengths. Table 4-1(a), 4-1(b) and 4-1(c) shows the 13~19nm CuPc, 25nm~30nm C₆₀(C₇₀) and 3.5nm BPhen is best for the device. The optimized thickness for CuPc and C₆₀ is less than the diffusion length for those two materials (CuPc ~ 20nm and C₆₀ ~ 40nm) because no further purification is conducted before those two materials are used.

<table>
<thead>
<tr>
<th>Thickness (CuPc)</th>
<th>Vₒc (V)</th>
<th>Jₒc (mA/cm²)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13nm</td>
<td>0.44</td>
<td>5.1</td>
<td>55.4</td>
<td>1.23</td>
</tr>
<tr>
<td>15nm</td>
<td>0.44</td>
<td>5.14</td>
<td>54.8</td>
<td>1.24</td>
</tr>
<tr>
<td>19nm</td>
<td>0.45</td>
<td>5.01</td>
<td>55.2</td>
<td>1.24</td>
</tr>
</tbody>
</table>

* The error for Vₒc is ±0.005V; the error for Jₒc is ±0.1 mA/cm²; The error for FF is ±0.5%; The PCE error is within 5%, The error of Vₒc, Jₒc and FF and PCE is the same for the table 4-1, table 4-2, table 4-3(b), table 4-4, table 4-5.
The optimization of the device is based on the C₆₀ because it is cheaper than C₇₀, similar results are obtained for C₇₀.
Table 4-1 (b) Optimized thickness for C₆₀, Here CuPc and BPhen are fixed at the thickness of 15 nm and 3nm. (see page 71 for errors)

<table>
<thead>
<tr>
<th>Thickness (C₆₀)</th>
<th>$V_{oc}$ (v)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20nm</td>
<td>0.46</td>
<td>3.92</td>
<td>60</td>
<td>1.08</td>
</tr>
<tr>
<td>25nm</td>
<td>0.46</td>
<td>4.47</td>
<td>59</td>
<td>1.22</td>
</tr>
<tr>
<td>30nm</td>
<td>0.45</td>
<td>4.75</td>
<td>58.5</td>
<td>1.25</td>
</tr>
<tr>
<td>35nm</td>
<td>0.44</td>
<td>4.6</td>
<td>58.8</td>
<td>1.19</td>
</tr>
</tbody>
</table>

Table 4-1 (c) Optimized thickness for BPhen, Here CuPc and C₆₀ are fixed at the thickness of 15nm and 27.5 nm. (see page 71 for errors)

<table>
<thead>
<tr>
<th>Thickness (BPhen)</th>
<th>$V_{oc}$ (v)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3nm</td>
<td>0.44</td>
<td>4.36</td>
<td>56.5</td>
<td>1.08</td>
</tr>
<tr>
<td>3.5nm</td>
<td>0.43</td>
<td>5.07</td>
<td>55.6</td>
<td>1.21</td>
</tr>
<tr>
<td>4nm</td>
<td>0.44</td>
<td>4.61</td>
<td>55.</td>
<td>1.11</td>
</tr>
</tbody>
</table>

Fig. 4-1 the diagram of the energy level of the device
$V_{oc}$ is always kept constant since it is only determined by the difference of the LUMO of acceptor C$_{60}$ and HOMO of the donor CuPc. $I_{sc}$ is related to the exciton generation and diffusion, and carrier transportation. The low current from the thinner film is due to low light absorption, and the low current from the thicker film is due to low carrier mobility.

2 Alkali fluoride as an interface layer.

As indicated in the Fig. 4-1, there is an energy gap between the ITO and CuPc, which may be a barrier for charge collection. An interfacial layer need to be introduced to pin the energy level and help extraction of the hole at the CuPc layer. Plasma induced thin LiF layer on the ITO can increase the performance of the OLED due to energy level pinning. We notice that plasma induced thin alkali fluoride can also improve the performance of the small molecular based OPVs. LiF was proven that there is 17% enhancement in the efficiency, which is done by Teng Xiao, as shown in the Fig. 4-2. The NaF, KF, RbF and CsF materials and the plasma effect are done below.

![Fig. 4-2 J-V characteristic of LiF modified small molecule OPVs (done by Teng Xiao)](image)

(1) Plasma effect.

CsF and LiF are two common materials for the interfacial layer at the cathode for OLEDs. The interfacial layer at the anode is tested for OPVs. The thin CsF layer (1~2nm) was deposited
at the top of the ITO and then treated in four modes: (1) in the air-plasma; (2) left the in the glovebox; (3) left the in the air; (4) baking 120°C at air. The time duration for all of three treatment is about 20-30 min before the fabrication of the device. As seen in the Table 4-2, bad device performance is obtained whether the CsF layer was left in the air or the glovebox (Argon), or baking at the high temperature. The large series resistance (10^3~10^4 ohms) for those cases indicates that even 1nm thin CsF layer is almost an insulated layer. The extraction is totally blocked because work function of CsF may not be suitable for a hole collection. Air-plasma treated thin CsF layer included device shows a better performance than the reference one, a device without an extra CsF layer. The series resistance decreases and the short circuit current increase about 9%, which may indicate better hole extraction.

Table 4-2 the effect of the thin CsF layer in different conditions (see page 71 for errors)

<table>
<thead>
<tr>
<th>Thickness</th>
<th>$V_{oc}$ (v)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CsF (0nm)</td>
<td>0.44</td>
<td>5.86</td>
<td>54.7</td>
<td>1.4</td>
</tr>
<tr>
<td>CsF (1nm) Air-plasma</td>
<td>0.44</td>
<td>6.37</td>
<td>54.7</td>
<td>1.54</td>
</tr>
<tr>
<td>CsF (1nm) Air</td>
<td>0.22</td>
<td>1.21</td>
<td>13.1</td>
<td>0.04</td>
</tr>
<tr>
<td>CsF (1nm) Argon</td>
<td>0.27</td>
<td>0.64</td>
<td>18.2</td>
<td>0.03</td>
</tr>
<tr>
<td>CsF (1nm) 120°C air</td>
<td>0.1</td>
<td>0.09</td>
<td>18</td>
<td>0.001</td>
</tr>
</tbody>
</table>

(2) Different level and time of Plasma

Different levels of the plasma were checked for the CsF layer. The plasma has three levels: low, median and high, and their powers are listed in the Table 4-3 (a). As seen in the Table 4-3 (b), only median level air-plasma treatment has the higher efficiency than the reference. Both high and low level of air-plasma results in even worse performance. It was believed that air
<table>
<thead>
<tr>
<th>Input power</th>
<th>100W</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low</td>
<td>680V DC</td>
</tr>
<tr>
<td>Medium</td>
<td>700V DC</td>
</tr>
<tr>
<td>High</td>
<td>720V DC</td>
</tr>
</tbody>
</table>

Table 4-3 (a) Level of the plasma (power)

Table 4-3 (b) Effect of the different level of the air plasma. (see page 71 for errors)

<table>
<thead>
<tr>
<th>Plasma level</th>
<th>V&lt;sub&gt;oc&lt;/sub&gt; (v)</th>
<th>J&lt;sub&gt;sc&lt;/sub&gt; (mA/cm&lt;sup&gt;2&lt;/sup&gt;)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference</td>
<td>0.48</td>
<td>4.76</td>
<td>46.9</td>
<td>1.06</td>
</tr>
<tr>
<td>High</td>
<td>0.48</td>
<td>4.42</td>
<td>46</td>
<td>0.99</td>
</tr>
<tr>
<td>medium</td>
<td>0.48</td>
<td>4.98</td>
<td>49.3</td>
<td>1.18</td>
</tr>
<tr>
<td>low</td>
<td>0.47</td>
<td>4.53</td>
<td>41.6</td>
<td>0.89</td>
</tr>
</tbody>
</table>

plasma etching leads to the partially reaction of CsF with O<sub>2</sub>, and in result the presence of the Cs<sub>2</sub>O at the ITO surface, as we will discuss it later. The proper Cs<sub>2</sub>O may alter the working function for the ITO, which may better match the HOMO of the CuPc layer. The lower efficiency from low and high level air-plasma may be due to the less and more Cs<sub>2</sub>O and thus unbalanced energy level pinning. This is further proven by the different etching time for medium air-plasma. The results shown that 20 min is best for the device, with less than 1-2min or more than 1hr treatment leads to totally failure of the device.

(3) Thickness of the CsF layer

Different thickness of the CsF layer (media level air plasma treatment for 20 min) are also tested. From the Table 4-4, 1-2 nm CsF gives the best efficiency; 3nm CsF has already led to the bad efficiency; 4nm CsF leads to totally failure of the device. This may be due to the fact that
that the thick CsF (≥4nm) layer cannot be totally oxidized by the air plasma because the protective Cs$_2$O layer formed on the surface prevent the further oxidization of the CsF by O$_2$. The remain CsF underneath is still an insulated layer and a blocking barrier for hole collection, and thus leads to low current.

**Table 4-4** Effect of the different CsF layer (media level plasma for 20min) (see page 71 for errors)

<table>
<thead>
<tr>
<th>Thickness (CsF)</th>
<th>$V_{oc}$ (v)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.44</td>
<td>6.04</td>
<td>56.6</td>
<td>1.5</td>
</tr>
<tr>
<td>1nm</td>
<td>0.45</td>
<td>6.26</td>
<td>55</td>
<td>1.57</td>
</tr>
<tr>
<td>2nm</td>
<td>0.44</td>
<td>6.31</td>
<td>56.9</td>
<td>1.6</td>
</tr>
<tr>
<td>3nm</td>
<td>0.41</td>
<td>5.84</td>
<td>45</td>
<td>1.08</td>
</tr>
<tr>
<td>4nm</td>
<td>0.37</td>
<td>1.85</td>
<td>11</td>
<td>0.07</td>
</tr>
</tbody>
</table>

(4) Other alkali fluorides interface layer

The other three alkali fluoride materials (NaF, KF and RbF) with different thickness are tested and the results are shown in the Table 4-5(a), 4-5(b) and 4-5(c). With air plasma etching, 2~3nm NaF leads to an enhancement in the efficiency; 1~2 nm KF or RbF layer results in little decrease in the efficiency thought the devices are not insulated. Possible explanation may be that the energy levels from air plasma treated KF or RbF layer do not match the HOMO of the CuPc, but the other three alkali chlorides (LiF, NaF and CsF) do. The reason of the phenomenon is still unknown, possibly relating the combination of the alkali metal with O$_2$. 
Table 4-5 (a) Effect of the NaF layer (medium plasma for 20min) (see page 71 for error)

<table>
<thead>
<tr>
<th>Thickness (NaF)</th>
<th>V&lt;sub&gt;oc&lt;/sub&gt; (v)</th>
<th>J&lt;sub&gt;sc&lt;/sub&gt; (mA/cm&lt;sup&gt;2&lt;/sup&gt;)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.47</td>
<td>5.69</td>
<td>50.3</td>
<td>1.36</td>
</tr>
<tr>
<td>1nm</td>
<td>0.45</td>
<td>6.11</td>
<td>53</td>
<td>1.46</td>
</tr>
<tr>
<td>2nm</td>
<td>0.46</td>
<td>6.19</td>
<td>58.1</td>
<td>1.66</td>
</tr>
<tr>
<td>3nm</td>
<td>0.48</td>
<td>6.21</td>
<td>57.5</td>
<td>1.72</td>
</tr>
<tr>
<td>4nm</td>
<td>0.42</td>
<td>1.74</td>
<td>20.5</td>
<td>0.15</td>
</tr>
</tbody>
</table>

Table 4-5 (b) Effect of the KF layer (medium plasma for 20min) (see page 71 for error)

<table>
<thead>
<tr>
<th>Thickness (KF)</th>
<th>V&lt;sub&gt;oc&lt;/sub&gt; (v)</th>
<th>J&lt;sub&gt;sc&lt;/sub&gt; (mA/cm&lt;sup&gt;2&lt;/sup&gt;)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.45</td>
<td>5.92</td>
<td>58</td>
<td>1.54</td>
</tr>
<tr>
<td>1nm</td>
<td>0.46</td>
<td>5.75</td>
<td>55.2</td>
<td>1.45</td>
</tr>
<tr>
<td>2nm</td>
<td>0.46</td>
<td>5.56</td>
<td>55.1</td>
<td>1.42</td>
</tr>
<tr>
<td>3nm</td>
<td>0.26</td>
<td>0.48</td>
<td>19.7</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Table 4-5 (c) Effect of the RbF layer (medium plasma for 20min) (see page 71 for error)

<table>
<thead>
<tr>
<th>Thickness (RbF)</th>
<th>V&lt;sub&gt;oc&lt;/sub&gt; (v)</th>
<th>J&lt;sub&gt;sc&lt;/sub&gt; (mA/cm&lt;sup&gt;2&lt;/sup&gt;)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.45</td>
<td>5.94</td>
<td>57.9</td>
<td>1.54</td>
</tr>
<tr>
<td>1nm</td>
<td>0.45</td>
<td>5.91</td>
<td>56.5</td>
<td>1.5</td>
</tr>
<tr>
<td>2nm</td>
<td>0.44</td>
<td>5.93</td>
<td>54.8</td>
<td>1.44</td>
</tr>
<tr>
<td>3nm</td>
<td>0.45</td>
<td>5.67</td>
<td>55.7</td>
<td>1.42</td>
</tr>
<tr>
<td>4nm</td>
<td>0.4</td>
<td>1.65</td>
<td>13.2</td>
<td>0.09</td>
</tr>
</tbody>
</table>
3 Absorption and quantum efficiency

Absorption and QE measurement were taken with and without CsF and NaF layer, as shown in the Fig. 4-3. The absorption curves show only small difference in the absorption in visible wavelength. QE measurements show there is obvious enhancement in the wavelength 400-550nm. The results indicate that the enhancement in the efficiency from the thin CsF or NaF layer is not due to the change of the absorption but electronic properties of the device, which in known as the hole extraction.

![Absorption and QE measurement](image)

**Fig. 4-3** (a)Absorption of the active layer and (b) quantum efficiency of the device

4 XPS

XPS data from table 6-1 and 6-2 show the percentage of the atom components versus the time duration of the air plasma CsF and NaF layers on ITO. With the increasing air plasma time,

<table>
<thead>
<tr>
<th>Table 4-6(a) CsF (20nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plasma time</td>
</tr>
<tr>
<td>-------------</td>
</tr>
<tr>
<td>30 min</td>
</tr>
<tr>
<td>10 min</td>
</tr>
<tr>
<td>0 min</td>
</tr>
</tbody>
</table>
### Table 4-6(b) NaF (30nm)

<table>
<thead>
<tr>
<th>Plasma time</th>
<th>C 1s</th>
<th>O 1s</th>
<th>F 1s</th>
<th>Na 1s</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 min</td>
<td>13.81</td>
<td>16.62</td>
<td>28.71</td>
<td>40.86</td>
</tr>
<tr>
<td>10 min</td>
<td>8.39</td>
<td>6.40</td>
<td>37.47</td>
<td>47.74</td>
</tr>
<tr>
<td>0 min</td>
<td>4.12</td>
<td>0.85</td>
<td>42.32</td>
<td>52.71</td>
</tr>
</tbody>
</table>

**Fig. 4-4** XPS spectrum for air plasma for NaF layers with different etching time

The relative concentration of the O increase while the concentration of F decrease. For NaF, the concentration of O(1s) increases from only 0.85% before air plasma, to 6.4% after 10 min air-plasma and 16.62% after 30 min air-plasma. F component decreases from 42% to 29%. The component Na is almost unchanged. The change of the percentage of the O component indicates the existence of the Na oxides (Na$_2$O) in the air plasma NaF layer. The shift of the binding energy also indicate the presence of the Na oxides. As shown in the Fig. 4-4, the large binding energy indicates that Na is like to bind with O, which is probable Na$_2$O. It was also shown by other group that the energy level of air-plasma thin NaF layer is about -5.2eV, which is very better than ITO (-4.8eV) for the alignment of the energy level of CuPc (HOMO -5.2eV). This better energy level alignment explains lower series resistance and the higher short circuit current.
in the device with the air plasma NaF layer. For the air-plasma CsF layer, we also observed the increase of the O component with 10-30 min air-plasma etching (from 19% to 28%). The initial high percentage of the O component is from ITO, since 20nm CsF is not thick enough to block the ITO by XPS measurement.

5 AFM images

Fig.4-5 shows the AFM image for the CuPc layers, which are on the top of the 4 different surface: 1. ITO surface as reference; 2. plasma treated 1nm CsF surface; 3. 1nm CsF surface; and 4. plasma treated 4nm CsF surface (CsF is on the top of ITO). For the first two cases, the CuPc surface is smooth and RMS is about 4.2nm and 3.6nm, respectively. The devices fabricated on those two surface have normal device performance, and low RMS surface seems to have a better efficiency. Further AFM images for the Bphen layer (ITO/(CsF 1nm)/CuPc/C_{70}/BPhen), on those two surface also show the smooth surface, and the low RMS is observed for the air plasma treated CsF case. For the last two cases, the small dot in the last two AFM image (c) and (d) indicates the uneven surface, and RMS for both cases are 5.4nm and 9.1nm, respectively. It may be due to an aggregation of the CsF on the surface of ITO, and in turns further aggregation of CuPc afterwards. The devices based on those two surface have a failure in the performance. The CsF layer is like to have an effect on the surface of organic layer afterwards. Air plasma may
remove the thin CsF (1-2nm) surface contact property, leading to the better interfacial layer for the hole extraction.

4.4 Conclusions

We have shown that a thin 1 nm layer of LiF on the indium tin oxide (ITO) anode in copper phthalocyanine / fullerene-70 (CuPc/C_{70}) -based organic solar cells (OSCs) enhances short circuit current density (J_{SC}) and power conversion efficiency (PCE) by up to \sim 17\% following air-plasma treatment due mainly to improved hole extraction. Similar behavior with a 6\% to 7\% enhancement was observed for plasma-treated NaF and CsF. These observations may be related to improved energetics and hence a nearly ohmic contact. Formation of alkali-O bonds, based on X-ray photoelectron spectroscopy (XPS) analyses, is also believed to contribute to the enhanced hole extraction. The best enhancement was observed for a 1 nm LiF layer air-plasma treated for 20 min. ultraviolet (UV)–ozone treatment of such layers had a smaller effect. The light absorption and the external quantum efficiency (EQE) of the devices with treated alkali fluoride layers further support hole extraction from CuPc to the anode as one mechanism responsible for the observed enhanced performance. Light absorption increased for structures with LiF but was largely unchanged for NaF or CsF. The results consequently demonstrate the viability of air-plasma-treated thin fluoride layers, and in particular LiF, as interfacial layers between the ITO anode and the donor layer in small molecule CuPc/C_{70}-based OSCs.

Acknowledgments

This work was partially supported by the Iowa Power Fund. Ames Laboratory is operated by Iowa State University for the US Department of Energy (USDOE) under Contract No. DE-AC 02-07CH11358. TX, MC, RL, and JWA were supported by Office of Basic Energy Sciences, Division of Materials Science and Engineering, USDOE.
Reference

[34] Z. Q. Xu et al., Appl. Phys. Lett. 98(2011), 253303
Chapter 5 Improving Polythiophene: Fullerene-based Organic Solar Cells and Integrating the OPDs in the O₂ Sensing Measurement


Abstract

Improved organic solar cells with an indium tin oxide (ITO) electrode, an interlayer of Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS), an active layer poly(3-hexylthiophene-2,5-diyl): [6,6]-phenyl-C₆₀-butyric acid methyl ester (P3HT:PCBM) and a Ca/Al electrode (ITO/PEDOT:PSS/P3HT:PCBM/Ca/Al) were obtained via simple treatments of the PEDOT:PSS layer. The treatments included (i) diluting PEDOT:PSS with deionized water or ethylene glycol (EG) prior to spin coating on the ITO, (ii) spin-coating EG over the PEDOT:PSS layer, and, for comparison (iii) adding gold nano-particles to the PEDOT:PSS layer. The optimal spin coating rate and duration for the PEDOT:PSS in each of the treatments and for EG were obtained. The second treatment resulted in the best performance with a power conversion efficiency of 4.7% and fill factor of 71%; the corresponding values for the devices with the untreated PEDOT:PSS were 3.9% and ~68%. To evaluate the origin of the observed improvements several parameters were monitored. These included the conductivity of the PEDOT:PSS layer, the external quantum efficiency of the devices, and their I-V curves, which indicated an increase of ~16% in the short-circuit current. Other measured characteristics included the thickness of the PEDOT:PSS layer and its transmittance, as well as the absorption spectra of ITO/PEDOT:PSS/P3HT:PCBM, its morphology (using atomic force microscopy and SEM imaging), and surface chemical composition (using Auger and x-ray photoelectron spectroscopy). The results indicate that in addition to the enhanced PEDOT:PSS conductivity
that improves charge extraction, the morphology of the active layer is possibly also responsible for the observed improvements, by enhancing the absorbance of the PEDOT:PSS/P3HT:PCBM structure via scattering effects, and hence the short-circuit current.

Key issues in using organic light emitting diodes (OLEDs) as excitation sources in structurally integrated photoluminescence (PL)-based sensors are the low forward light outcoupling, the OLEDs’ broad electroluminescence (EL) bands, and the long-lived remnant EL that follows an EL pulse. The outcoupling issue limits the detection sensitivity (S) as only ~20% of the light generated within standard OLEDs can be forward outcoupled and used for sensor probe excitation. The EL broad band interferes with the analyte-sensitive PL, leading to a background that reduces S and dynamic range. In particular, these issues hinder designing compact sensors, potentially miniaturizable, that are devoid of optical filters and couplers. We address these shortcomings by introducing easy-to-employ multiple approaches for outcoupling improvement, PL enhancement, and background EL reduction leading to novel, compact all-organic device architectures demonstrated for simultaneous monitoring of oxygen and pH. The sensor comprises simply-fabricated, directionally-emitting, narrower-band, multicolor microcavity OLED excitation and small molecule- and polymer-based organic photodetectors (OPDs) with a more selective spectral response. Additionally, S and PL intensity for oxygen are enhanced by using polystyrene (PS):polyethylene glycol (PEG) blends as the sensing film matrix. By utilizing higher molecular weight PS, the ratio \( \tau_0/\tau_{100} \) (PL decay time \( \tau \) at 0% O\(_2\)/ \( \tau \) at 100% O\(_2\)) that is often used to express S increases 1.9 to 20.7\( \times \) relative to the lower molecular weight PS, where this ratio is 11.0. This increase reduces to 1.7\( \times \) when the PEG is added (\( \tau_0/\tau_{100} = 18.2 \)), but the latter results in an increase 2.7\( \times \) in the PL intensity. The sensor’s response time is <10 s in all cases. The microporous structure of these blended films, with PEG decorating PS pores,
serves a dual purpose. It results in light scattering that reduces the EL that is waveguided in the substrate of the OLEDs and consequently enhances light outcoupling from the OLEDs by \(~60\%\), and it increases the PL directed toward the OPD. The multiple functional structures of multicolor microcavity OLED pixels/microporous scattering films/OPDs enable generation of enhanced individually addressable sensor arrays, devoid of interfering issues, for \(O_2\) and pH as well as for other analytes and biochemical parameters.

5.1 Introduction

The development of organic solar cells is a fast-growing field as such devices have the advantage of being flexible, simple to fabricate, and potentially low cost [1–4]. Solar cells with a poly(3-hexylthiophene):[6,6]-phenyl-C\(_{60}\)-butyric acid methyl ester (P3HT:PCBM) active layer have been studied extensively with reports of typical power conversion efficiency (PCE) of \(~3\%\) to \(~5\%\) and fill factors (FF) of \(~50\%\) to \(~70\%\) [4–11]. The PCE and FF depend on the starting materials, fabrication conditions and treatments at various stages of device fabrication. As an example, a PCE of 4.4% was obtained by varying the annealing conditions of the active layer [7,8]. The PCE was improved to 5.3% by replacing the PEDOT:PSS layer with NiO\(_2\) [9]. A PCE of 5% was obtained for a single cell with TiO\(_x\) as an optical spacer, and a two-unit tandem structure with 6.5% PCE was obtained by applying the TiO\(_x\) layer as an electron transport and collecting layer for the first unit and as a stable foundation to fabricate the second unit [10–12]. To obtain a good short-circuit current (ISC), the active layer needs to have strong absorption of the solar spectrum, efficient exciton diffusion, good charge transfer, and sufficient charge extraction at the electrodes [13]. To achieve a high open-circuit voltage (\(V_{OC}\)), the offset between the highest occupied molecular orbital (HOMO) of the donor material and the lowest unoccupied molecular orbital (LUMO) of the acceptor material should be high, and ohmic contacts between
the electrodes and the organics are required [13–16]. To get a high FF, the series resistance of the device should be low and the shunt resistance should be high. The polymer/electrode interfaces and the active layer properties play an important role in determining these parameters [17–19].

It is well known that the conductivity of PEDOT:PSS films is enhanced by over 100-fold by addition of organic materials, such as dimethyl sulfoxide (DMSO), N,N-dimethylformamide, tetrahydrofuran, sorbitol (with baking), glycerol, or ethylene glycol (EG) to the aqueous PEDOT:PSS solution [20–30]. Depending on the additive, the enhancement was related to the dielectric constant of the additive and to retention of some of the solvents used in the film [26], to reorientation of PEDOT chains with heat treatment [29], and to washing away of PSS [27]. For diethylene glycol addition, it was suggested that the particle size of the PEDOT:PSS reduces as the insulating, inter-particle excess PSS layer becomes very thin [28]. It was also shown that not only dilution of the PEDOT:PSS solution with EG enhances the conductivity, but also immersing the untreated PEDOT:PSS in EG solution for a few minutes [21]. It was reported that EG affects the solubility of the PEDOT:PSS film in water, suggesting, together with other measurements, that EG affects the conformation of the polymer chains with the surface becoming more hydrophobic. The conformational change of the PEDOT chains was attributed to the interaction between the dipole of one of the polar groups (only additives with two or more polar groups were found to enhance conductivity) of the organic additive and the dipoles or positive charges on the PEDOT [21]. It was also reported that the size of the PEDOT:PSS particles was increased by adding DMSO [23]. The increased conductivity was linked to the increased particles’ size, due to reduced particle boundaries. Hence, there are still different fundamental explanations for the enhanced PEDOT:PSS conductivity upon addition of polar solvents.
Additives to PEDOT:PSS that enhance performance of solar cells were also evaluated. In addition to the effect of DMSO [23], for example, the substitution of ITO by PEDOT: PSS and PEDOT:PSS doped with glycerol or sorbitol was studied [22]. Glycerol and the surfactant ethylene glycol butyl ether at specific concentrations were also mixed with PEDOT:PSS for improved ink-printed solar cells [24]. The authors suggested that these additives may also affect the morphology of the ink-jet printed PEDOT:PSS, with a strong ionic interaction between the glycerol and the PEDOT, including with the addition of low-levels of the surfactant to enhance the conductivity. Improved device performance was attributed to surface morphology and enhanced conductivity that increase charge collection [24]. As every step in the fabrication of the solar cells affects device performance, this paper describes a systematic study of the effect of treatments of the PEDOT:PSS layer on the performance of the common P3HT:PCBM-based solar cells. Morphology variations of P3HT:PCBM were observed, with increased roughness, when PEDOT:PSS was treated in different ways. The treatments included (i) dilution of the as-received PEDOT:PSS solution with deionized (DI) water or (ii) with EG, and (iii) spin coating EG over the PEDOT:PSS layer. Among the various treatments that included optimization of the dilution and spin coating rate and duration, treatment (iii), namely the EG-treated PEDOT:PSS layer (following the fabrication of the latter from the original aqueous solution) exhibited the largest change in the P3HT:PCBM morphology, which is probably responsible for the observed largest improvement in the, $I_{SC}$, FF, and PCE. Importantly, small aggregates of PCBM, whose size depended on the anneal period of the EG-treated PEDOT: PSS layer, were observed at the surface of the active layer. These aggregates at the active layer/cathode interface may improve charge extraction and light absorption, and hence $I_{SC}$, FF, and PCE. Importantly, the conductivity of PEDOT:PSS exhibited a relatively minor contribution to the enhanced performance.
The all-organic PL-based sensing platform comprises OLED pixels, organic photodetectors (OPDs) and thin sensing elements, all fabricated on inexpensive common substrates such as glass or plastic. In integrated structures, the OLEDs and sensing films were often fabricated on two back-to-back attached glass slides [31-33]. Several recent studies evaluated the properties of OLED-based sensors and demonstrated their feasibility for monitoring (bio)chemical analytes such as oxygen, carbon dioxide, glucose, lactate, pH, and algal [32, 34-40].

As is well known, the detection of O₂ using optical sensors is based on monitoring O₂-induced changes in the PL intensity (I) or decay time τ of an oxygen sensitive dye, such as platinum octaethylporphyrin (PtOEP), embedded in a polymeric matrix, such as polystyrene (PS). Analysis is based on the Stern–Volmer (SV) equation [31,41,42]. where I₀ and τ₀ are the unquenched values, K_SV is the SV constant, and [O₂] is the O₂ concentration. Based on the change of the PL intensity, an easily detectable colorimetric oxygen sensor can also be achieved via the incorporation of two or more oxygen sensitive lumophores [43]. The pH monitoring is based on the change in the fluorescence of the pH-sensitive dye fluorescein that exhibits multiple pH dependent ionic equilibria. As only the monoanion and dianion are fluorescent with different quantum yields, the PL varies with the solution pH [44]. A dual sensing platform demonstrating the utility of the multicolor microcavity OLED array in an all-organic structure with multi-function films was designed for monitoring O₂ and pH by evaluating changes in both the PL intensity and decay time. These analytes are key in, e.g., agricultural, environmental and biological processes monitoring [45-47], and therefore a practical and compact device is very desirable.
5.2 Experimental Procedure

Materials

P3HT (P#200) was obtained from Rieke Metals and PCBM from nano-C; both materials were used without further purification. A solution of a 1:1 weight ratio of P3HT:PCBM in 1,2-dichlorobenzene, with a concentration of 30 mg/mL was used. The P3HT solution was filtered using a 0.22 lm Millex PTFE Filter before it was mixed with PCBM. The mixture was then stirred for 24 h before spin-coating. PEDOT:PSS was a CleviosTM P VP AI 4083 obtained from H.C. Starck. The PEDOT:PSS ratio was 1:6 by weight and the solid content 1.3–1.7%. EG was obtained from Fisher Scientific.

PtOEP and N,N-diphenyl-N,N-bis(1-naphthylphenyl)-1,1-biphenyl-4,4-diamine (NPB) were obtained from H.W. Sands. PEG, PS, tris(8-hydroxyquinolinato) Al (Alq3), LiF, copper phthalocyanine (CuPc), and C70 were purchased from Sigma–Aldrich. MoO3 was purchased from Strem Chemicals. HCl and toluene were obtained from Fisher Scientific and fluorescein from Invitrogen.

Procedures

The PEDOT:PSS layers (40 nm thick) were baked for ~1 h at 120°C under ambient conditions; they were then transferred into an argon-filled dual-sided MBraun glovebox. The oxygen level in the glovebox was ~30 ppm and that of water <0.1 ppm. Three different treatments of the PEDOT:PSS were evaluated in an attempt to improve the device performance. These treatments were: (i), diluting PEDOT:PSS with DI water (ii) mixing PEDOT:PSS with EG, and (iii) spin-coating EG following fabrication of the PEDOT: PSS layer. Each treatment was optimized by varying the spin-coating speed and duration as well as the dilution ratio as detailed above. The P3HT:PCBM solution was spin-coated on top of the PEDOT:PSS layer at the
optimized 600 rpm rate for 60s, and immediately placed under a petri dish for 2 h before baking at 110°C for 12 min. The Ca (25 nm)/Al (100 nm) were deposited on the P3HT:PCBM layer by low vacuum (10^6 mbar) thermal evaporation. The active layers in all devices were fabricated under the same experimental conditions.

The O₂ sensing films were prepared by drop-casting 200 L of toluene solution on the back of the 1 × 1 in. 2 OLED substrates with 1 mg/mL PtOEP embedded in three different matrices: 40 mg/mL lower $M_w$ PS ($M_w$ ~45,000), 40 mg/mL higher $M_w$ PS ($M_w$ ~280,000) and 40:10 mg/mL higher Mw PS ($M_w$ ~280,000): PEG (number averaged molecular weight $M_n$ = 1000 ± 50), denoted as samples L40, H40, and H40G10, respectively. The resulting films on the encapsulated OLED devices were allowed to dry in the dark at ambient temperature for at least 12 h. The concentration of the fluorescein (chosen following fluorescence monitoring at various dilutions to exclude concentration quenching) was 6 M in pH 10 buffer. μC-OLED were thermally evaporated on the glass substrates in a vacuum chamber (background pressure ~10⁻⁶ Torr) located in the Ar-filled glovebox with structures as 40 nm Ag/3 nm MoO₃/42 nm NPB/56 nm Alq3/1 nm LiF/100 nm Al for the blue μC-OLED and 40 nm Ag/7 nm MoO₃/49 nm NPB/61 nm Alq3/1 nm LiF/100 nm Al for the green μC-OLED. The evaporation rate of organic layers was ~1 Å/s. 3 × 3 mm² individually addressable μC-OLED pixels were fabricated with 3 mm gap between them. The encapsulating cover glasses were glued using Torr Seal epoxy to prevent water and O₂ exposure of the pixels. Various levels of O₂ were generated by flowing O₂/Ar mixtures controlled by the mass flow controllers while maintaining a constant total flow rate. The pH was controlled by stepwise adding 30 L of diluted HCl into a 2 mL testing reservoir. The PL data was monitored and analyzed in the time or intensity domain. We used statistical analysis and fast Fourier Transform (FFT) filtering. We note that each value of $\tau$ is based on averaging
1200 decay curves and the error for a single sample is <3% at high O\textsubscript{2} levels, where it is the highest.

**Measurements**

The thickness of PEDOT:PSS layers was estimated with an AFM by using a sharp blade to generate ~9 lm wide cuts in the layer. In all cases a thickness of ~40 nm resulted in devices with the best performance, regardless of the treatment. I–V curves were obtained using a 100 mW/cm\textsuperscript{2} ELH bulb. The EQE was measured at 0 V. AFM measurements were performed using a Digital Instruments system. SEM and Auger were measured with JEOL JAMP 7830F.

An Ar-filled glovebox was used for OLED fabrication. For the time-resolved signal analysis, the OLEDs were driven with a 100 μs electrical pulse generated by an Avtech AV-1011B pulse-generator. The PL was monitored with either a Hamamatsu R6060 photomultiplier tube (PMT) or OPDs. The gas-phase O\textsubscript{2} concentration was obtained using Tylan FC-280 mass flow controllers.

**5.3 Results and Discussion**

(1) **Optimization of the device**

**PEDOT:PSS layer**

Indium tin oxide (ITO) (typically 90% In\textsubscript{2}O\textsubscript{3}, 10% SnO\textsubscript{2} by weight) is one of the most widely used transparent conducting oxides because of its two chief properties: its electrical conductivity and optical transparency, as well as the ease with which it can be deposited as a thin film. A PEDOT:PSS layer on the surface of the ITO has several advantages: smooth of the ITO surface; better spread of the organic solvent on the top of the PEDOT:PSS layer and thus better uniform active layer was obtained; better alignment of the work function of the ITO and HOMO of the P3HT layer. Proper thickness of the PEDOT:PSS layers are required since thin layer leads
to uneven surface and thick layer leads to the low conductivity of the interface layer and thus bad device. Experience shows that 40nm PEDOT:PSS is the best for the device. Baking at 120°C for about 1 hour is necessary to get rid of the water since water is harmful for the organic device.

**Active layer**

The thickness of the active layer is crucial to the performance of the device. Thicker layers have good absorption of the solar light, but the dramatically worse electronic properties. The diffusion length of the exciton at P3HT is about 20nm and PCBM less than 40nm. For a full dissociation of the exciton at the donor-acceptor interface, the total thickness of the active layer is limited to 60nm at most for the bi-layer structure. The hetero-junction structure is introduced, which the thickness of the active layer can extend to 100-200nm at the cost of relative low drop in the electronic properties.

During the fabrication, the thickness of the active layer is determined by two factors: the concentration of the solution and spin rate and time of the spin-coating. Here 400rpm and 600rpm using the 30mg/ml P3HT:PCBM with the ratio 1 to 1 leads to the equally good performance of the device, due to the better light absorption for the thicker film from 400rpm spin-rating and the better electronic properties for thinner film from 600rpm.

The phase separation is an important step to have a hetero-junction structure in the active layer. Due to different solvent evaporation and different solubility for the P3HT and PCBM materials, P3HT and PCBM domains are formed. During this process, P3HT tends to sink and PCBM tends to go up. The rate of the solvent evaporation determines the degree of the phase separation. Fast dry speed leads to no separation of the two materials and slow dry speed leads to a total separation of the two material. No or little hetero-junction is formed for both cases. The
optimization of dry time is about 30 min ~ 60 min to obtain a comparable good interface for solar cells.

Temperature annealing is another step for a good device. A certain degree of the crystallization at the temperature higher than glass transition makes the electron and hole mobility increase by up to 1~2 order. The baking temperature and baking time are two factors in controlling annealing. The results show that pre-annealing is better than post-annealing, and the temperature is about 110°C for 12min for the 600 rpm, while 160C to 110C for 400 rpm.

**Cathode layer**

Ag, Al and Au are common metals for cathodes. Due to their high work function (-4.2eV, -4.2eV, -4.8eV), ohmic contact is barely formed at the interface between acceptor material (PCMB) and these metals. Low work function Ca (-2.9eV) is introduced in this case to have less barrier for hole extraction at the organic/inorganic interface. The high electrical resistivity and reactivity of Ca limit the thickness of this layer 20~25nm and require additional 100nm Al protective layer. The results show that the total efficiency increase from 2% to 3.7% with Ca.

**(2) Modify the interface layer**

Usually, the spin rate for PEDOT:PSS is about 3000-5000 rpm. The thicker PEDOT:PSS layer from low spin rate leads to worse device, since the conductivity of the PEDOT:PSS is much lower than the ITO or Metal. Thinner layer from high spin rate increase the efficiency but at the risk of the uneven and un-continuous surface. We use the device with regular PEDOT:PSS layer as reference cells, and its efficiency is 3.7%

From the Table 5-1, for DI water diluted PEDOT:PSS, the dilution of 70% DI with 30% PEDOT:PSS at the spin rate of 500rpm is the best condition. Au nano-particle doped PEDOT:PSS increase the efficiency, most of them are from the short circuit current. There is a
slight increase in the Voc and FF. DI water diluted PEDOT:PSS also leads to the increase of the efficiency. EG treated PEDOT:PSS have the highest enhancement in the efficiency, which is about 27% enhancement in efficiency (done by Teng Xiao). All these results are also shown in the Fig. 5-1 as J-V curves.

Table 5-1 Device characteristics of solar cells prepared with different treatments of the PEDOT:PSS layer. The EG was spin coated over the PEDOT:PSS layer at various rates for 60 s. The error for open circuit (Voc) is ±0.005V; short circuit current density (Jsc) ±0.2mA/cm²; fill factor (FF) ±0.5; power conversion efficiency (PCE) within 5%.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Voc (V)</th>
<th>Jsc (mA/cm²)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EG 2000 rpm</td>
<td>0.57</td>
<td>11.5</td>
<td>71.3</td>
<td>4.70</td>
</tr>
<tr>
<td>70% DI</td>
<td>0.57</td>
<td>11.2</td>
<td>69.5</td>
<td>4.44</td>
</tr>
<tr>
<td>Au nano-particles</td>
<td>0.56</td>
<td>10.8</td>
<td>70.9</td>
<td>4.28</td>
</tr>
<tr>
<td>Untreated PEDOT:PSS</td>
<td>0.55</td>
<td>9.94</td>
<td>67.6</td>
<td>3.70</td>
</tr>
</tbody>
</table>

**Fig. 5-1** I-V Curves for P3HT:PCBM-based solar cells, with the PEDOT:PSS layer treated with Au nanoparticles and DI water, each added to the PEDOT:PSS solution, and with EG that was spin-coated on the untreated PEDOT:PSS layer (see text for the details). The I-V curve for the cell with the untreated PEDOT:PSS layer is also shown for comparison.
Fig. 5-2. External quantum efficiency vs wavelength for devices with optimized untreated PEDOT:PSS (squares), optimized DI water dilution (circles), optimized Au concentration (triangles), and optimized EG treatment (inverted triangles). See text for details.

Fig. 5-3 The transmission of an untreated PEDOT:PSS film (black line), PEDOT:PSS film with Au nano-particles (green), PEDOT:PSS film prepared from a 5 fold dilution (red), and PEDOT:PSS film with post-fabrication EG treatment (blue).

QE measurement also show that there is enhancement in the wavelength from 450nm-600nm, as indicated in the Fig. 5-2. To further show why the different treated PEDOT:PSS results in the enhancement in the short circuit current. The transmissions of the different treated PEDOT:PSS are measured, and as shown in the Fig. 5-3 the treated PEDOT:PSS has better transmission than the regular PEDOT:PSS except Au nano-particles., which may be due to the absorption of the
light (short wavelength) by the small nano-particles. However, possible plasmonic effect from Au nano-particles may enhance the absorption of the light in the active layers, which may make up the loss in the transmission. The different size of the Au nano-particle are tried, and 20nm is the best one according the aggregation of the small nano-particles and roughness of the PEDOT:PSS surface, we also tried Ag nano-particles with the size of 40 and 50nm. since the thickness of the PEDOT:PSS is limited to 40-50nm, the larger size of the nano-particles may make the surface uneven and leads to uneven electric field across the active layer and short circuit between the anode and cathode. The smaller size may be not good for the plasmonic effect and leads to little enhancement in the electric field across the active layers.

![Absorption spectra](image)

**Fig. 5-4** The absorption spectra of the active layer on the PEDOT:PSS layer, with untreated PEDOT:PSS film (black line), PEDOT:PSS film with Au nano-particles (green), PEDOT:PSS film prepared from DI water diluted solution (red), and PEDOT:PSS film with post-fabrication EG treatment (blue)

The measurement of absorption of light in the active layers indicates that the stronger absorption of the light from the wavelength from 450nm-600nm, including the Au nano-particles
doped PEDOT:PSS layer, as shown in the Fig. 5-4. The enhancement in the absorption is only a few percent, the most enhancement in the short circuit current is from the hole extraction.

![Image](https://via.placeholder.com/150)

**Fig. 5-5** Morphology of PEDOT:PSS films using AFM: left top: Au:PEDOT:PSS; right top: 3.3-fold DI water diluted PEDOT:PSS; Left bottom: EG treated PEDOT:PSS following the fabrication of the latter; right bottom: untreated surface. The scale for the image is 10µm

To exclude the effect of the PEDOT:PSS thickness on the absorption, the film thicknesses were measured by making fine cuts (~9 µm wide) on them with a sharp blade, and using scanning AFM (scan size: 20 µm) across the cuts to measure the films’ thickness. The AFM results showed that the typical thickness of the optimized PEDOT:PSS layers of both treated and untreated samples are around 40 nm. The roughness of the PEDOT:PSS layer increased slightly following treatment and a more condensed packing of particles (Fig. 5-5) was observed.

Specifically, the particles appeared smaller for the DI water and EG treated samples, in particular for the latter. The untreated surface showed larger particles in accordance to previous reports suggesting the removal of excess inter-particle PSS.
Fig. 5-6 AFM images of the morphology of P3HT:PCBM films (full scale 20 µm) following different PEDOT:PSS treatments. Top left: Au:PEDOT:PSS/P3HT:PCBM; Top right: 3.3 fold DI water diluted PEDOT:PSS/P3HT:PCBM; Bottom left: EG-treated PEDOT:PSS/P3HT:PCBM; Bottom right: untreated PEDOT:PSS / P3HT:PCBM; The scale for the image is 10µm

Fig. 5-7 SEM image of a P3HT:PCBM film on top of EG-treated PEDOT:PSS at different scales of 4 µm (top left), 10 µm (top right), 20 µm (bottom left) and 100 µm (bottom right)

Morphology variations in the P3HT:PCBM layers (Figs. 7 and 8) were also observed using AFM and SEM imaging. As seen, small bumps, ~1 µm wide, are distributed over the surface area of the P3HT:PCBM layer spin-coated on the EG-treated PEDOT:PSS layer; This probably
indicates increased aggregated PCBM level and result in an improved FF, since more of the acceptor PCBM molecules contact the metal cathode, and hence more efficient charge extraction.

(3) All organic O\(_2\) and PH sensor

All organic O\(_2\) sensor

Fig. 5-8(a)–(c) demonstrate the evolution of the OLED-based O\(_2\) sensor from the original set-up shown in (a), where two glass slides were attached back-to-back and a long-pass filter was placed in front of the PD. Due to light absorption by the Al electrode and waveguided modes within the ITO and organic layers and within the glass substrate, only \(\sim 20\%\) of the light generated within the OLED is forward outcoupled and hence usable for excitation [48]. In Fig. 9(b) the regular OLED is replaced by a \(\mu\)C OLED [49]. The concentrated narrow emission from the \(\mu\)C device (full width at half maximum FWHM \(\sim 27\) nm) reduces the fraction of scattered background EL and provides more efficient excitation as reported earlier [33]. The figure also shows the more compact design where the sensing element is fabricated by dropcasting (i.e., applying a drop of) toluene solution containing 1:40 mg/mL PtOEP:PS directly on the back of the OLED’s substrate and allowing the solution to dry on the substrate. The index matching of the PS film \((n \approx 1.6)\) disrupts the total internal reflection at the glass/air interface, which enhances the intensity of the excitation light that reaches the PtOEP dye.

To generate a more compact structure the optical filter was removed and a small molecule CuPc/C\(_{70}\) (CuPc is the copper phthalocyanine donor and C\(_{70}\) is the fullerene acceptor)-based OPD with the structure ITO/1 nm air-plasma-treated LiF/15 nm CuPc/30 nm C\(_{70}/3.5\) nm 4,7-diphenyl-1,10-phenanthroline (BPhen)/120 nm Al was used to achieve a compact all organic-based O\(_2\) sensor. Although polymer photovoltaic devices are usually more efficient than the
Fig. 5-8 Evolution of the back-detection organic-based O₂ sensor: (a) Original set-up. (b) Sensing film with more permeable higher Mw PS matrix directly drop cast on the back of the OLED substrate excited by a µC OLED with a significantly narrower emission band at the absorption band of PtOEP. (c) Modified scattering matrix of blended PS:PEG. (d) Images comparing the macroscopic morphology of L40, H40 and H40G10 matrices. The top image shows the neat films dropcast on 18 × 18 mm² glass substrates. The bottom image shows the smoother L40 film and the rougher higher H40 film with 100 nm Al layer deposited on the dried films. (e) SEM image of the higher Mw PS:PEG film with a 4:1 weight ratio.

Fig. 5-9 (a) External quantum efficiencies of CuPc/C₇₀ (black squares) and P3HT:PCBM (red circles)-based OPDs. The device structures are ITO/1 nm air-plasma-treated LiF/15 nm CuPc/30 nm C₇₀/3.5 nm BPhen/120 nm Al and ITO/PEDOT:PSS/P3HT:PCBM/Ca/Al. The EL of the µC OLED (dashed green line) and PL of the PtOEP: H40G10 sensing film (solid red line). (b) The sensing signal excited by the µC OLED detected by CuPc/C₇₀ OPD at various O₂ concentrations.
small-molecular ones, the choice of the OPD relies on more than just device efficiency. Fig. 5-9(a) compares the optimized external quantum efficiency (EQE) of two conventional OPDs, i.e., those based on P3HT:PCBM [50,51] or CuPc/C70. The former has a higher power conversion efficiency (PCE) and was used in sensing applications previously [32]. However, in order to further enhance the signal to noise ratio, it is preferable to use an OPD that collects more photons at the longer PL wavelength and is much less responsive to the green region of the EL, when PL intensities rather than \( \tau \) values are monitored.

The EQE spectra of the OPDs, the \( \mu \)C green EL, and the PtOEP PL bands are shown in Fig. 5-9(a). As seen, the CuPc/C70 OPDs are better suited for PtOEP-based \( \text{O}_2 \) sensing. The optimized device with a thin air-plasma-treated LiF layer for better hole extraction exhibits a PCE of \( \sim 2\% \), as reported earlier [52]. The photocurrents measured with this OPD for changing \( \text{O}_2 \) concentration are shown in Fig. 5-9(b). As clearly seen, the organic-based \( \text{O}_2 \) sensor successfully performs with a fast response of \(< 10 \text{ s}\), including the Ar/\( \text{O}_2 \) mixing and transport time.

**Dual sensing platform for dissolved \( \text{O}_2 \) and pH**

In an earlier study we demonstrated multicolor sky-blue to red \( \mu \)C OLED arrays fabricated in a simple method [49]. We applied a similar method to the dual sensing platform for dissolved \( \text{O}_2 \) (DO) and pH monitoring. This compact dual platform is promising since these two parameters are of great importance in cultivation and bioprocess monitoring [45,46]. Fig. 5-10(a) is the schematic of the setup. The PtOEP:H40G10 film was directly dropcast on the back of the OLED substrate and the fluorescein was dissolved initially in a pH 10 buffer solution. By adding diluted hydrochloric acid (HCl) and controlling the \( \text{O}_2/\text{Ar} \) gas mixture that flows into the solution, it was possible to control the DO and pH levels. Pixels of \( 3 \times 3 \text{ mm}^2 \) blue and green \( \mu \)C OLEDs (device structure: 40 nm Ag/3 nm MoO3/42 nm \( \alpha \)-NPB/56 nm Alq3/1 nm LiF/100 nm Al for the
blue μC OLED and 40 nm Ag/7 nm MoO₃/49 nm α-NPB/61 nm Alq₃/1 nm LiF/100 nm Al for the green μC OLED) with normal direction peak emissions at ~490 nm (FWHM = 23 nm) and ~540 nm (FWHM = 27 nm), respectively, as shown in Fig. 5-10(b), were fabricated on a common substrate. Those emissions bands are suitable for fluorescein absorption, and as mentioned earlier, for PtOEP absorption, respectively. The separation between the pixels was 3 mm; the PD was positioned between the two pixels. As mentioned, the PL signals obtained with the green OLED (meant to excite only the O₂-sensitive PtOEP) varied slightly with pH as well. One way to overcome this issue and actually realize simultaneous monitoring of the DO and pH is to analyze the time resolved PL and background signals. All the results are shown in the Fig. 5-10(c) and Fig. 5-10(d). As demonstrated in Fig. 5-11(a), at the turn-off edge of the green μC OLED bias pulse, the luminescent decay signal is comprised of three parts: the decaying OLED excitation background, the fluorescence decay of fluorescein, and the phosphorescence decay of PtOEP, which is much slower than the first two. Hence, a typical decay signal first exhibits a sharp decrease caused by the drop of the OLED EL and the fluorescein’s luminescence. The following long decay results from PtOEP’s response to different O₂ concentrations. The amplitude difference between the on-pulse signal intensity and the start of the PtOEP phosphorescent decay relates to the pH value + a constant OLED background. Hence, the change in this difference is indicative of the pH. That is, the DO and pH can be simultaneously analyzed with the τ and I modes, respectively. In order to prove the validity of such an analysis, we compared the time-resolved decay signals at four extreme conditions: (i) 0% O₂, pH ~ 10, (ii) 100% O₂, pH~10, (iii) 0% O₂, pH~4 and (iv) 100%O₂, pH~4. The transient signals of these four conditions are shown at the top left part of Fig. 5-11(b). By following the downward arrow to compare signals with the same O₂ concentrations, it is found that for exposure to both 0% and
100% gas-phase $O_2$, the on-pulse amplitudes are higher for pH $\sim$10 and lower for pH $\sim$4 with the same PL decay times at the $\mu$s range. By following the arrow to the right to compare signals at the same pH, as seen, the difference of the transient decays between 0% and 100% $O_2$ is obvious. With the contributions of the PtOEP PL subtracted, the fast-decaying amplitudes are unchanged at a constant pH.

![Diagram](image)

Fig. 5-10 (a) Schematics of the dual sensing platform for $O_2$ and pH. The OLED pixels are $3 \times 3$ mm$^2$ and the gap between them is 3 mm. (b) The normal direction EL spectra of the blue and green $\mu$C OLEDs. (c) The signal intensity detected by the P3HT:PCBM OPD at different $O_2$ and pH levels with the blue $\mu$C OLED. (d) The signal intensity detected by the CuPc/C$_{70}$ OPD at different $O_2$ and pH levels with the green $\mu$C OLED.
Fig. 5-11 (a) The components of the monitored signal following the OLED pulse: the phosphorescence decay of PtOEP, the fluorescence decay of fluorescein and the OLED background. (b) Luminescent signals obtained by using the green μC OLED at (i) 0% O<sub>2</sub>, pH ~10, (ii) 100% O<sub>2</sub>, pH~10, (iii) 0% O<sub>2</sub>, pH~4, (iv) 100% O<sub>2</sub>, pH~4

5.4 Conclusions

Various treatments of the poly(3,4-ethylenedioxythiophene):poly (styrenesulfonate) (PEDOT:PSS) layer in indium tin oxide (ITO) / PEDOT:PSS / poly(3-hexylthiophene-2,5-diyl): [6,6]-phenyl-C<sub>60</sub>-butyric acid methyl ester (P3HT:PCBM) / Ca/Al solar cells resulted in improved overall device performance. In particular, the use of a PEDOT: PSS film with spin coated Ethylene glycol (EG) on it post-fabrication resulted in an increase in the P3HT:PCBM absorption, and hence, an increase of ~16% in short circuit current (I<sub>SC</sub>) and a 27% increase in power conversion efficiency (PCE), from 3.7% in the cell with the untreated PEDOT:PSS to 4.7% in the former. The fill factor (FF) increased to 71–72% (from ~68% in the untreated cell).

Dilution of PEDOT:PSS with deionized (DI) water, and not only with organic solvents, also improved device performance. Based on the above results, it appears that the improved devices result mostly from an increased surface roughness of the P3HT:PCBM associated with the treatment and consequently graininess of the PEDOT:PSS layers. The increased roughness
generates a better contact with the metal electrode, which, possibly, together with the observed PCBM aggregates near the cathode improves charge extraction. The improved PEDOT:PSS transmission and PEDOT:PSS/P3HT:PCBM absorption, together with the improved PEDOT:PSS conductivity in some of the cases, improved the \(I_{sc}\) and the overall cell performance. This improvement is possibly also due to improved light scattering by the rougher surfaces that results in enhanced absorption in the active layer. The results do not indicate that a change in the thickness of the PEDOT:PSS films is a major contributor to the observed improvements, as optimized spin-coating conditions were employed in each case (untreated and treated PEDOT:PSS) and the optimized thicknesses of the different layers were comparable. Similarly, changes in the PEDOT:PSS conductivity did not correlate with the improved performance. The simple routes that led to the significantly increased PCE are expected to be applicable to other organic-based solar cells.

we have successfully constructed an all-organic electronic-based novel sensing platform architecture for simultaneously monitoring \(O_2\) and pH. This was achieved by applying multiple methods to improve the sensor performance and analyze the obtained data. For oxygen detection, Pt octaethylporphyrin (PtOEP) embedded in higher molecular weight (Mw) polystyrene: polyethylene glycol (PS:PEG) matrix was directly cast on the back of the OLED substrate for higher \(O_2\) permeability and stronger OLED electroluminescence (EL). Importantly, \(\tau_0/\tau_{100}\) consequently improved from \(~11\) to \(~21\). PEG was blended with PS to form scattering microstructures that enhance the detectable signal intensity \(~2.7\) fold. For better signal to noise ratio, green micro-cavity (\(\muC\)) OLEDs, with spectrally narrowed and concentrated EL, together with a copper phthalocyanine/fullerene-70 (CuPc/C\(_{70}\)) -based organic photo detector (OPD), whose spectral response is better suited to the PtOEP photoluminescence (PL), were utilized. For
the dual monitoring of dissolved oxygen (DO) and pH, two μC OLED excitation sources were fabricated combinatorially with the normal direction peak emission wavelengths designed for the O₂-sensitive PtOEP and the pH-sensitive fluorescein. In this way, one could extract a 2-D data table for monitoring these two important analytes. Furthermore, from the transient decay signals following the OLED pulses, one could resolve the signals related to DO and pH by employing both the τ and I detection modes. Hence, the two analytes could be monitored simultaneously.

The combination of the PtOEP:PS:PEG sensing film coupled with the multicolor microcavity OLEDs and the appropriate OPD and the possibility to combine time- and intensity-domain analyses pave the way for realizing a more simple and cost-effective all organic electronic O₂ and pH monitors, which can be expanded to detect other (bio)chemical analytes.

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Reference

Chapter 6 Summary

Photoluminescence (PL)-based optical O$_2$ sensors have applications in agricultural, medical and industrial areas. Currently, compact optical O$_2$ sensors are of the most interest due to their relatively small physical size and potentially low cost. Also, durable detection of O$_2$ with relative humidity (RH) is a promising topic since both of these parameters often need to be monitored in areas such as organic devices or food packaging. All organic electronics is one way to have compact sensors since these organic devices can be fabricated into one substrate, with the added advantages of being flexible and lightweight. The main issue is that low PL signals from optical O$_2$ sensing films make it difficult to have reliable O$_2$ detection with regular low-sensitivity organic photo-detectors (OPDs). In this thesis, modification of optical O$_2$ sensing films to obtain a higher PL, and modification of an interlayer in OPDs to obtain higher sensitivity, were performed to produce all organic optical O$_2$ sensors. Resolution of small change in RH was achieved through higher PL signals from modified sensing films, enabling simultaneous monitoring of RH and O$_2$. Furthermore, the effect of O$_2$ and RH on the organic devices (organic light emitting diodes (OLEDs) and organic photovoltaics (OPVs)) is analyzed by monitoring O$_2$ sensor signals to better understand O$_2$- and RH-induced degradation during the fabrication process.

After a brief introduction to organic devices and optical O$_2$ sensors in Chapter 1, Chapter 2 shows the application of the optical O$_2$ sensors in OLEDs and it is concluded that it can also be applied in OPV devices. The film composed of the oxygen-sensitive dye Pd octaethylporphyrin (PdOEP) doped in poly(N-vinylcarbazole) (PVK), not only as an active layer for OLEDs but also as sensing films for O$_2$ monitoring, is used to obtain information on the degradation of OLEDs when these films are exposed to different fabrication environments. The devices’
electroluminescence (EL) and PL indicate the OLED’s performance, and the latter also shows trapping of O$_2$ molecules in the active layers of the OLED. The results show that water and high level O$_2$ lead to relatively inferior devices; water may help trap O$_2$ molecules in the OLED’s active layer; reaction of O$_2$ with organic material PdOEP may occur in the presence of light. Furthermore, the study provides information about the fabrication environment for OLED and OPV devices, as well as a method for the diffusion of O$_2$ through the thin films.

Chapter 3 presents the modification of the sensing films to achieve high PL signals for reliable O$_2$ detection. A relatively low PL signal from the regular optical O$_2$ sensing films makes integration difficult, especially when photo detectors (PD) with no internal gain are used. Higher PL may be obtained through more O$_2$-sensing dyes or more excitation light. However, considering the self-quenching of dye at high concentration and the short lifetime for OLEDs at high brightness, modification of the sensing films is a preferred way to obtain a high PL signal. This modification is realized by creating porous voids in the sensing films. Light scattering from the voids increases the optical path of the excitation light and hence more absorption of the light by the dye. Scattering of PL from the dye gives the PD more opportunity to access to the resulting PL signal, which initially was partially blocked by OLEDs in back detection mode. Optimization of the porous structure, including the size of the voids and average distance between them, results in up to ~4.5 times PL enhancement. The PL enhancement, especially when ultraviolet (UV) light is used as the excitation source, is more promising since the dye PdOEP/ Pt octaethylporphyrin (PtOEP) is 5 ~ 6 times more sensitive to UV than to green light.

PL enhancement by doping TiO$_2$ nano particles (NPs) in the sensing films enables resolution of small changes in RH at certain O$_2$ levels (for PtOEP, this [O$_2$] is 1~10%, and for PdOEP it is 0.2~1%). This <10% RH resolution makes it possible to realize O$_2$ and RH detection, where one
RH insensitive O₂ sensing film determines the O₂ level and another RH sensitive sensing film determines the RH level.

More sensitive OPDs are another step toward reliable O₂ monitoring. Modifications of these OPD devices are presented in Chapter 4 and 5. The treated interlayer improves the contact between the electrode and the organic layer, whose hole or electron extraction will be enhanced due to the reduced barrier. thin LiF, NaF or CsF air-plasma-treated layer on the indium tin oxide (ITO) was shown to be an efficient interlayer for small molecule-based OPDs (up to ~17% enhancement) and Ethylene glycol (EG) treated poly(3,4-ethylenedioxythiophene):poly (styrenesulfonate) (PEDOT:PSS) layer for polymer based (up to ~27%). The enhancement in the short circuit current makes both modified devices suitable for better photo detection.

Based on these modifications of the sensing films and OPDs, an all organic optical O₂ sensor was realized, which was composed of excitation source OLEDs, porous sensing films and OPDs. This optical O₂ sensor fabricated with all organic components represents a significant step toward real integration.