Integrated Sensing Platform Based on Quantum Dot Light Emitting Diodes

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Abstract

Integrated sensing platform based on quantum dot light emitting diodes (QLEDs) is proposed. The use of QLEDs as excitation source can improve the power efficiency by 57% and above. The narrow emission band of QLED eliminates the excitation and emission overlap therefore increase the validity and accuracy of sensing. High brightness of QLED lowers down the operation voltage. Ease and flexibility of fabrication make it convenient for integration and miniaturization.

Keywords

QLED, PL based sensor, Integration.

1. Objective and Background

Photoluminescence (PL) – based chemical and biological sensors have been widely investigated for potential medical, environmental, and industrial applications [1-4]. Based on monitoring the analyte-induced photoluminescence change, such sensors typically consist of a luminescent sensing component whose PL is dependent on analyte concentrations, a light source to excite the PL, a photodetector to measure the PL, and the electronics to process signal [2]. Selection of each component, especially the light source, would influence the final size of the whole system, thus interfering the cost and possibility of integration. Traditional light sources (such as lasers, lamps, and inorganic light-emitting diodes (LEDs)) are either bulky and/or costly. They cannot be integrated with the other components due to size, geometrical, or operational constraints, or require intricate integration procedures for their incorporation in a structurally integrated, compact device.

Organic light emitting diodes (OLEDs) are attractive excitation sources to help alleviate these problems for PL based sensors because of their small size (nm to mm pixels), low voltage, low cost, ease of fabrication via thermal evaporation or solution processing on simple substrates such as glass and plastics, and therefore their compatibility with microfluidic chemical and biological systems and great potential for multi-analyte analysis with highly integrated micro-sized pixel arrays [4-8]. However, several issues emerge as the study and application of OLED based PL sensing expand. The intrinsic limitations of OLEDs (including low brightness, broad emission spectra and long radiative lifetime) can be reasoned out after we fully understand the working mechanism of OLED based PL sensor. The OLED based sensor usually works in two modes: PL intensity I -based detection mode or PL radiative lifetime τ -based detection mode, using the Stern-Volmer (SV) equation:

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

where I_0 and τ_0 are the unquenched values and K_{SV} is a temperature dependent constant. Sensor of I based detection mode is simple to fabricate and easy to operate, however susceptible to change in the excitation source intensity caused by decay, dye leaching etc. The τ -based detection mode is more stable and consistent since it won't be affected by changes in the sensing film, excitation source, or background light. Therefore there is no need for reference sensor of sensor calibration compared with I -based detection mode. Though it requires complicated transient PL setup and OLED working in pulsed mode.

As a PL based sensor, the ability to differentiate the emission light of sensing component from the excitation light from OLED is important. So ideally the excitation spectrum and PL emission spectrum should be well separated. In practice, the broad electroluminescence (EL) band of OLED usually overlap significantly with the PL emission spectrum and a bandpass filter is thus necessary between the OLED and sensing film, which results in considerable light waste, decreases the power efficiency of such a sensor, and increases the working voltage to reach the desired brightness. Without bandpass filter, the not fully blocked EL tail mixed in detection would affect the accuracy of detection result. Furthermore, in τ -based detection mode, OLED works in pulse mode and the EL radiative lifetime needs to be much shorter than sensing film's PL radiative lifetime, rendering exclusive PL decay time detection. Hence fluorescent OLEDs are preferred over phosphorescent OLED because of their short radiative lifetime, while on the other hand the former's brightness is not as good as the latter's [1, 2].

Considering the limitations of OLED-based PL sensor, here we propose the use of our high brightness Quantum Dot LED (QLED) instead of OLED to solve these issues in both working modes. The QLED keeps all the advantages of OLED as excitation source in PL based sensor: ease of fabrication and integration, small size, and low cost. With similar structure to OLED, QLED could have wavelength tuned EL emission peaks simply by using quantum dots of different sizes in active layer. Further, the EL spectrum of QLED is much narrower than OLED. These features are much favorable since we can shift the EL peak to get a better fit of the sensing material's absorption peak, while in

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the meantime avoid overlap with PL emission spectrum, even for small Stokes shift material. Moreover, quantum dot emitters have pretty short radiative lifetime, namely several to tens of ns, which is negligible compared with the PL decay time of the luminescent sensing material. This could generate more accurate measured results for τ-based detection mode. Finally, QLED has high power and efficiency, which in all make it a profound replacement of OLED as excitation source in PL-based integrated sensing platform.

Similar as the OLED based PL sensor [3], the device working lifetime for long-term usage is of less importance in QLED based PL sensor, since the sensing probes often come out with a shorter lifetime. Regarding the easy fabrication and low cost of QLED, it is promising for disposable sensors.

2. System and Results

The schematic structure of a compact back detection QLED-based PL sensor is shown in Fig. 1(a), similar to an OLED-based sensor. The QLED and sensing film are fabricated on two sides of the substrate while the photodetector (PD) is on the back of QLED, which enables the in-situ detection of analyte sample. Like OLED sensor, there are no needs for optical fibers, lens or mirrors in such a compact structure, and its thickness is determined mostly by the substrate [4], since the QLED and PD are thin film devices of only hundreds of nanometers thick. Light mixture of photoluminescence of sensing film and EL of QLED will go through the interval area between adjacent metal electrodes, and go into a long pass filter, leaving the PL signal alone detected by photodetector. Unlike OLED-based sensor (Fig. 1(b)), the QLED based sensor does not need the band-pass filter to eliminate the EL overlapping with PL emission, because of the narrow band of QLED EL emission. This makes the fabrication much easier, while the long pass filter can cover the whole area of PD, without need for patterned filter film.

Our hybrid inverted QLED is fabricated on the indium tin oxide (ITO) coated glass with the structure of ITO/ZnO nanoparticles/Cs_2CO_3/CdSe-ZnS-CdZnS core-shell-shell QDs/ 2,2',7,7'-tetrakis[N-naphthalenyl(phenyl)-amino]-9,9-spirobifluorene (spiro-2NPB)/LG101 hole injection layer/Al anode. The ITO/ZnO/Cs_2CO_3/ QDs layers are solution processed using spin coating, and afterwards the organic layers and anode Al are evaporated in vacuum. The detail of synthesis of QDs and fabrication process are previously published in [4]. Such a simple fabrication procedure facilitates the integration of the sensor, even for micro-array multianalyte detection sensor. By controlling the quantum dot size and compositions we can tune the peak wavelength of the QDs emission. Ultra-high brightness of 165,000 Cd/m^2 can be achieved by our red QLED device at current density of 1000 mA/cm^2 with a driving voltage as low as 5.8 V, which is double peak brightness of state-of-the-art OLED devices with only around half of their driving voltages. Our green QDs can obtain FWHM of 38nm (Fig. 2 green line) and PL quantum yield above 95%, while the green QLED device fabrication and improvement are still in progress. With such a high brightness and low working voltage QLED, and higher than OLED energy efficiency in sensing as proved below, we can expect the QLED-based PL sensor to be much more efficient than OLED-based sensor.

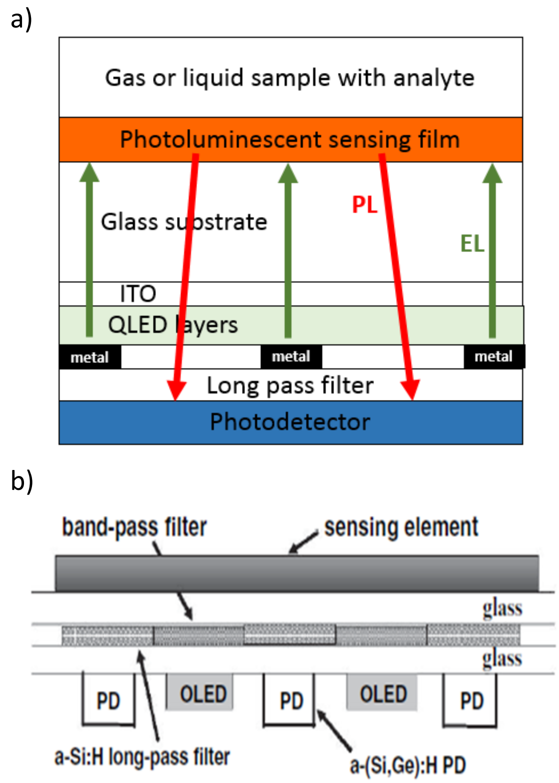

Figure. 1 a) The schematic structure of a compact back detection QLED based PL sensor. b) Envisioned compact back detection OLED based PL sensor array. Reprinted from Ref. [5]. Copy right @ 2008 Springer.

To illustrate the improvement in power utilization of QLED-based sensor due to narrow and wavelength-fit emission peak, here we compare spectra of OLED, doped OLED from Ref. [3], and green QDs. Take PtOEP:PS film used in OLED-based oxygen sensor as an example, and assume its PL power conversion yield keeps the same for absorption of photons of different energy. The spectra of different excitation sources are normalized by their integration irradiance energy, and respective absorption is calculated according to the absorption of PtOEP:PS film. As a result, benefitted by narrow band and 532nm peak emission (close to sensing film's ~535nm absorption peak), absorption can be increased by 57% over original OLED by green QD, compared to 11% by doped OLED. Because of the narrow absorption peak of PtOEP:PS film, the improvement could be higher if narrower emission peak is obtained. In fact, if the published green QLED with a full width half maximum (FWHM) of 29 nm [6] can be tuned to 534 nm peak emission, then the improvement would increase to 63%. It should be mentioned that here we calculate the absorption of OLED spectrum without using bandpass filter, which will further lower the efficiency for traditional OLEDs. This on the other hand proves higher absorption efficiency improvement by QLED.

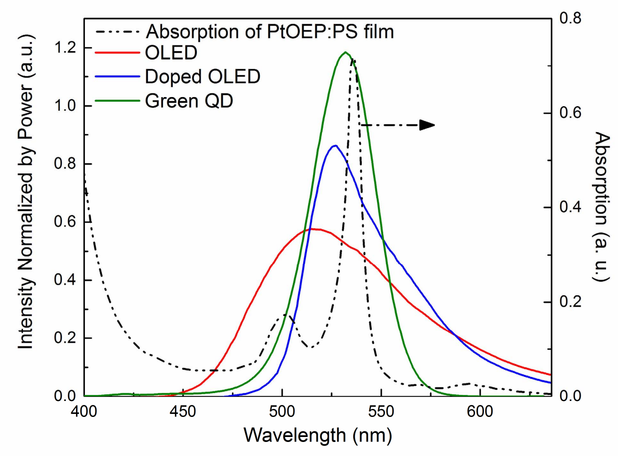

Figure. 2 Spectra of OLED, doped OLED [3] and green QDs; and absorption of PtOEP:PS sensing film [3].

Table. 1 Calculated power absorption proportion and corresponding improvement compared with OLED spectra.

	Power absorbed (a. u.)	Improvement
OLED	0.154	0
Doped OLED	0.171	11%
Green QDs (38 nm)	0.242	57%
Green QDs (29 nm)	0.250	63%

It is also seen from the spectra that even with the use of a 600-nm long pass filter, the long wavelength EL emission from OLED is still mixed in the measured signal which can induce distortion especially when oxygen level is high. For the green QD emission, this problem is eliminated. If τ-based detection mode is used, we can even expect to get rid of the long pass filter, since the typical QD decay time ~15 ns [7] is far less than the PL decay time of sensing element, thus separating the EL excitation and PL emission decay into different time range. This is an absolute advantage over OLED excitation source, which has at least ~100ns decay time [8].

3. Conclusion

We propose the use of QLED instead of OLED as the excitation source in compact PL-based sensor to overcome OLED's issues of low brightness, high operation voltage, broad emission spectra, and long radiative lifetime. Being solution processable thin film devices, the fabrication of QLED is similar to OLED or even easier. Simple procedure and different choices of substrate make it easy to make integrated and miniature sized and even flexible sensing platform. Moreover, QLED-based sensing system can be further simplified by removing unnecessary components. The need for patterned filter is avoided, since the bandpass filter for excitation light is not necessary. In τ-based detection mode the long pass filter is also possibly removable, considering the negligible QLED EL decay time. With the use of QLED as EL excitation source, the problem of EL PL mixing at long wavelength region is eliminated; and by tuning the peak wavelength to better fit the absorption of sensing film, the energy efficiency can be improved by over 57%, even up to 63% with narrower QD emission band. In addition, the high brightness of QLED allows for lower operation voltage. In summary, QLED-based integrated sensing platform enjoys the advantages of ease of fabrication, simplicity of integration, low cost, high efficiency, low operation voltage, and being signal-noise free and thus is highly promising for future portable medical, environmental, or industrial sensing applications.

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