

HIGH-SENSITIVITY LOW-COST ON-CHIP CHEMILUMINESCENCE DETECTION BASED ON INTEGRATED ORGANIC PHOTODIODES

Introduction

Chemiluminescence (CL) offers a simple but sensitive means of monitoring low level analyte concentrations. CL is particularly attractive for portable microfluidic assays, because the CL reaction acts as an internal light source, thereby lowering instrumentation and power requirements while providing a low signal background.

Traditionally CL assays have been monitored using expensive and non-portable externally mounted photomultiplier tubes (PMTs) and microscope based collection optics. More recently the use of silicon photodiodes has been reported on silicon microchips, which are still relatively high-cost and thus unsuitable for disposable devices [1]. Here we overcome this bottleneck by using solution processable organic photodiodes in combination with molded poly(dimethylsiloxane) (PDMS) based microfluidic chips, thereby providing a sensitive, low-cost, rapid prototyping and compact route towards disposable diagnostic devices.

Microfluidic Chip Fabrication

- Standard soft lithography technique
- SU-8 negative photoresist used to make the mold
- PDMS (Dow Corning Sylgard 184 Kit, monomer and hardener mixed in ratio of 10:1 by weight) is poured onto the SU-8 master
- PDMS is cured at 65°C for 3 hours and carefully peeled off the master
- To form an enclosed channel, the structured PDMS layer is placed in conformal contact with the glass side of the polymer photodetector.

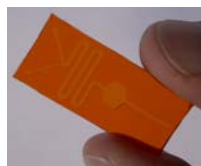


Figure 1 Microfluidic Chip

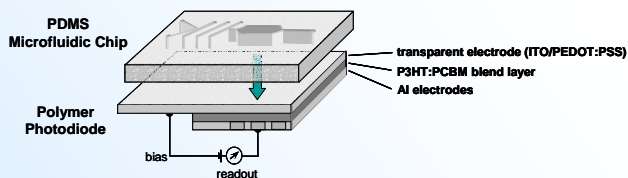


Figure 2 Schematic of the PDMS microfluidic chip with integrated low-cost polymer photodetector for on-chip CL based bioassay detection. The absence of a light source and the low power requirements of the polymer photodiode detector enable battery operation.

Polymer Photodetector

Polymer photodetectors were made from a blend of regioregular poly(3-hexylthiophene) [P3HT] and 1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6)-C61 [PCBM].

Fabrication:

- Blend spin coated over ITO-coated glass substrate on which a PEDOT:PSS injection layer had been previously deposited
- Deposition of an aluminum cathode through a shadow mask
- Device encapsulated in N₂ atmosphere by securing a metal can (fitted with a dessicant patch) to the device side of the glass substrate with a UV-cured adhesive

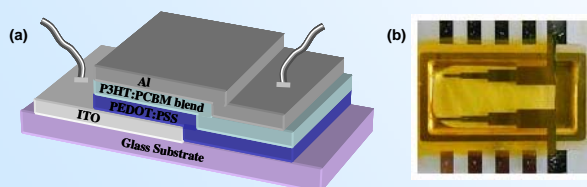


Figure 3 Polymer photodetector (a) Schematic structure (b) Encapsulated device.

Characterization:

- Photoresponse from 350 nm to 670 nm (shown in Figure 4)
- External Quantum Efficiency of ~60% at 510nm
- Rise time of 1µs

Chemiluminescence Detection

To test the suitability of our integrated detectors for point-of-care testing we performed a peroxyoxalate CL based bioassay on-chip. Hydrogen peroxide (H₂O₂) was selected as the model compound for CL based quantitation because it is produced by a number of enzymes in the presence of specific analytes such as alcohol, glucose, and cholesterol.

The CL reagents used were bis(2-carbopentyloxy-3,5,6-trichlorophenyl) oxalate (CPPO), dimethylaminopyridine (DMAP) catalyst and 9,10-diphenylanthracene dye (cyalume green).

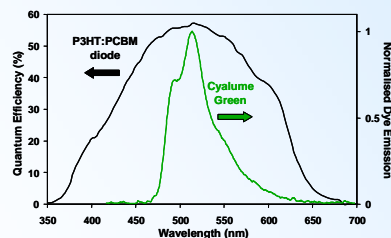


Figure 4 Quantum efficiency spectrum of P3HT:PCBM photodiode and normalised emission spectrum of the employed green CL dye. The emission spectrum of the green dye is well matched to the spectral response of the photodiode, enabling high-sensitivity detection.

Figure 4 depicts the CL emission overlap with the spectral responsivity of the polymer detector. CL emission occurs via energy transfer from an excited state intermediate to the dye molecule (indirect CL). The CL reagent/dye/catalyst and the H₂O₂ test solution are pumped into the two inlets of a Y-type microfluidic chip and the CL reaction is initiated at the Y-junction where diffusion mixing starts as seen in Figure 5.

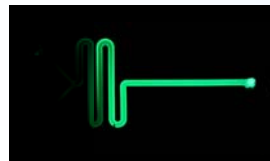


Figure 5 On-chip chemiluminescence initiated by diffusion mixing in a Y-type microfluidic chip. The reagents are pumped in through the two inlets on the left and waste collected at the outlet on the right.

To measure the detection limit of the detector, the photoresponse was measured for varying H₂O₂ concentrations. Data seen in Figure 6 shows a detection limit of <10µM.

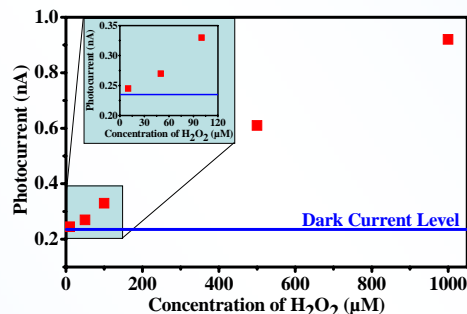


Figure 6 Photocurrent response as a function of hydrogen peroxide concentration. Response shows linear behavior as expected.

Conclusion

While the presented results already demonstrate a 100-fold sensitivity gain compared to previous work with organic small molecule photodiodes [2], we anticipate a further 100 to 1000-fold improvement in the limit-of-detection by optimisation of the chemiluminescence assay, reduction of the background signal by light-proofing, and improvements to the photodiode fabrication protocol.

References:

- [1] A.M. Jorgensen, K.B. Mogensen, J.P. Kutter, O. Geschke; Sens. Actuator B-Chem 2003, 90, 15-21.
- [2] O. Hofmann, P. Miller, P. Sullivan, T. S. Jones, J.C. deMello, D.D.C. Bradley, A.J. deMello; Sens. Actuator B-Chem 2005, 106, 878-884.