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

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ABSTRACT

We report the use of novel low-cost disposable organic photodiodes for high-sensitivity detection of on-chip chemiluminescence assays. By planar integration of the photodiode, spatial matching of the pixel size to the microchannel dimensions and by chemically tuning the detector responsivity to the luminescence emission we have achieved sensitivities equivalent to PMT based detection. This bodes well for the applicability of our disposable detection systems to point-of-care diagnostic testing.

Keywords: integrated detection, organic photodiodes, chemiluminescence, disposable diagnostics

1. 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 by 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.

2. RESULTS

We report polymer photodetectors made from a blend of regioregular poly(3-hexylthiophene) [P3HT] and 1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6)-C_{61} [PCBM]. The blend was spin coated over an ITO-coated glass substrate on which a PEDOT:PSS injection layer had been previously deposited. Deposition of an aluminum cathode through a shadow mask completed the diode structure. The detector has a

photoresponse from 350 nm to 670 nm, with an external efficiency of ~60% at 510nm and a rise time of 1µs [2].

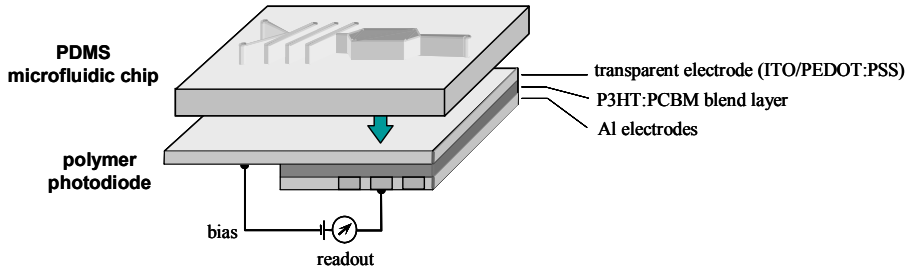

Figure 1: Schematic of the PDMS microfluidic chip with integrated low-cost polymer photodetector for on-chip CL based bioassay detection. The absence of a lightsource and the low power requirements of the polymer photodiode detector enable battery operation.

The microfluidic chip fabrication was based on standard soft lithography. standard photolithography used on negative SU-8 photoresist to make mold. PDMS (Dow Corning Sylgard 184), monomer and hardener mixed in a ratio of 10:1 (w/w), is poured onto the SU-8 master and cured at 65ºC for 3 hours. Cured PDMS is then 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.

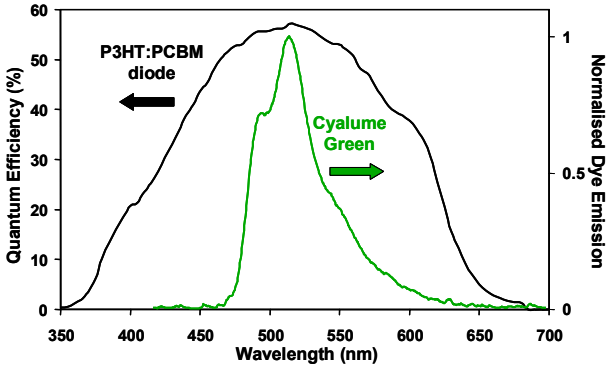

Figure 2: Quantum efficiency spectrum of P3HT:PCBM photodiode and normalised emission spectrum of the employed green CL dye. The emission spectrum of the green dye is well matched to the spectral response of the photodiode, enabling high-sensitivity detection.

To test the suitability of our integrated detectors for point-of-care testing we performed a peroxyoxalate CL based bioassay on-chip. Hydrogen peroxide 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). The CL reaction was initiated by pumping the CL reagent/dye/catalyst and the hydrogen peroxide test solution into a Y-type micromixer. CL emission results from energy transfer from an excited state intermediate to the dye molecule (indirect CL). Figure 2 depicts the CL emission overlap with the spectral responsivity of the polymer detector.

The photodiode response was measured for varying hydrogen peroxide concentrations and then compared to results obtained with a microscope mounted high-sensitivity PMT. Figure 3 illustrates that the polymer detector and the high-sensitivity PMT have a comparable response with a hydrogen peroxide detection limit <10 μM.

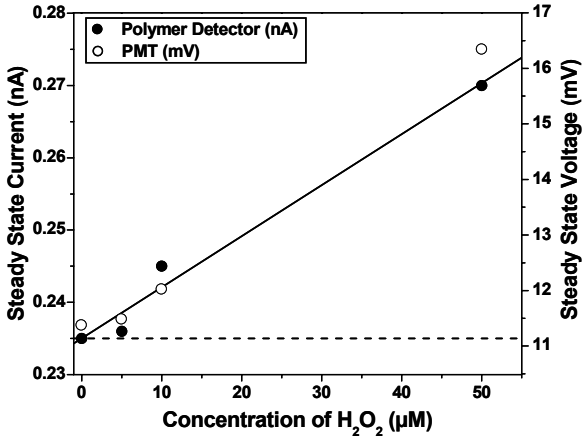

Figure 3: CL signal as a function of hydrogen peroxide concentration for polymer detector (●) and high-sensitivity PMT (○). The dashed line corresponds to the photodiode dark current. Note that for both detectors, a detection limit <10 μM is obtained under non-optimised CL conditions.

3. CONCLUSION

While the presented results already demonstrate a 100-fold sensitivity gain compared to previous work with organic small molecule photodiodes [3], 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

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