INTEGRATED OPTICAL DETECTION FOR MICROFLUIDIC SYSTEMS USING THIN-FILM POLYMER LIGHT EMITTING DIODES AND ORGANIC PHOTODIODES

Oliver Hofmann[1], Paul Miller[2], John C. deMello[2], Donal D.C. Bradley[3] & Andrew J. deMello[2]
[1]Molecular Vision Ltd., 90 Fetter Lane, London EC4A 1JP, United Kingdom
[2]Department of Chemistry & [3]Department of Physics, Imperial College London, South Kensington, London SW7 2AZ, United Kingdom

Abstract

In this paper the development of lightsources and detectors for integrated microchip based optical detection is reported. A polyfluorene based pLED with peak emission at 488 nm was successfully employed as a lightsource for microchip electrophoresis. With a pLED drive voltage of 5.5 V, separations of fluorecein and 5-carboxyfluorescein could be detected at concentrations down to 1 μM. In separate experiments, thin-film organic photodiodes were employed as integrated detectors for microscale chemiluminescence. The copper phthalocyanine-fullerene (CuPc-C_{60}) small molecule photodiodes have an external quantum efficiency of ~30% at 550 to 650 nm. The photodiodes were used to monitor a peroxyoxalate based chemiluminescence reaction (PO-CL) within a poly(dimethylsiloxane) (PDMS) microfluidic device. Preliminary PO-CL based quantitation of hydrogen peroxide yielded a detection limit of 1 mM.

Keywords: polymer LEDs, organic photodiodes, chemiluminescence, integrated detection

1. Introduction

Polymer light emitting diodes (pLED) comprise one or more layers of conjugated polymer sandwiched between two electrodes and emit light under electrical excitation. The emission colour can be controlled by changing the chemical structure of the semiconducting polymer. Owing to the simple layer-by-layer deposition procedures for the polymer components the pLEDs can be readily integrated with microfluidic systems. To demonstrate the efficacy of the approach, the polyfluorene diode is used as an excitation source for the detection of fluorescent dyes separated on-chip by electrophoresis. Similar in structure to pLEDs, organic photodiodes generate a measurable current under illumination. Photodiodes based on small molecule blends have demonstrated efficiencies up to 80% (electrons out/photons in). We report the successful integration of CuPc-C_{60} heterojunction photodiodes with polydimethylsiloxane (PDMS) microfluidic devices for the monitoring of PO-CL reactions. PO-CL reactions involve the formation of a metastable reaction intermediate and light emission is based on an energy transfer process to a suitable fluorophore. For quantitation, hydrogen peroxide was selected as a model compound because it is produced by a number of enzymes when in contact with specific analytes and dissolved oxygen (e.g. glucose, cholesterol).

2. Experimental

Fabrication of the polyfluorene pLEDs on an indium tin oxide (ITO) coated glass substrate was based on spin coating of the active layer and thermal evaporation of the electrodes. Details of the fabrication are described elsewhere [1]. CE microdevices were manufactured in-house and comprised a 50-μm-wide and 40-μm-deep microchannel network etched into a planar glass substrate. Injection and separation of fluorescein and 5-carboxyfluorescein was performed under applied electric fields up to 3000 V. Detection was based on an oil immersion objective and a silicon avalanche photodiode (SPCM-AQR-141, EG&G Canada).

The fabrication of the CuPc-C_{60} heterojunction organic photodiodes and the effect of composition and architecture on device performance is described in detail elsewhere [2]. The mixed CuPc / C_{60} layers were grown on ITO coated glass substrates by co-deposition from independent

organic evaporation sources. For the devices employed in the current studies 58 nm thick layers comprising 60 w/w-% CuPc and 40 w/w-% C_{60} were deposited. This was followed by deposition of bathocuproine (BCP). Al electrodes were deposited by evaporation through a shadow mask yielding three detection strips with an active area of 2 mm x 8 mm each. For characterisation of the organic photodiodes a PO-CL reaction was performed on chip. Microfluidic devices for PO-CL were made from PDMS and structured by cutting out the channels with a scalpel blade. The layout of the CL microdevices is shown schematically in Figure 1. PO-CL reagents were extracted from Cyalume lightsticks (American Cyanamid Company). The active components are Bis (2-carbopentyloxy-3,5,6-trichlorophenyl) oxalate (CPPO), 9,10-diphenylantracence dye (both reagent A) and hydrogen peroxide (reagent B). For quantitation experiments with hydrogen peroxide, 5 mM 4-Dimethylaminopyridine (DMAP) was used as a catalyst to increase CL-intensity.

3. Results and discussion

For proof-of-concept a thin-film pLED based on polyfluorene with an emission maximum at 488 nm and an active area of 40 um x 1000 um was used as an excitation source for fluorescence detection in microchip-based electrophoresis. Fluorescein and 5-carboxyfluorescein could be detected at concentrations as low as 1 μM with a mass detection limit of 50 femtomoles. This is similar to detection limits obtained with a mercury lamp excitation source. The drive voltage required to generate sufficient emission from the pLED was only 3.7 V.

In separate experiments novel organic photodiodes were tested as microchip based detectors (Figure 1). PO-CL reagents A and B were hydrodynamically pumped through microchip inlets 1 and 2, respectively. Flow rates were optimised between 5 and 200 μL/min, yielding chemi-luminescence signals from 1.4 to 6.3 nA with highest signals observed for 25 μl/min (Figure 2). For higher flow rates the short residence time resulted in incomplete mixing of the reagents and reduced chemiluminescence signals. For the optimised 25 μL/min flow conditions, reproducibility of the CL signal was determined by repeating experiments three times on the same microchip. RSD values for the steady-state signal after ~11 minutes, were typically below 1.5%. This reproducibility is clearly sufficient for quantitative analysis and demonstrates the potential of both microchip based PO-CL and integrated detection with CuPc-C_{60} photodiodes. As a model compound, hydrogen peroxide was quantified using the PO-CL / organic photodiode approach. Preliminary experiments suggest a detection limit of ~1 mM (signal-to-noise ~10). While this is sufficient for the monitoring of most fermentation processes [3], significant sensitivity gains are expected through device optimisation. Experiments are ongoing to apply the PO-CL reaction to the detection of commonly used fluorescence labels.

4. Conclusions & outlook

Combining the thin-film pLEDs and organic photodiodes should yield powerful integrated detection systems for a wide range of applications. The tunable optical properties, simple fabrication, small size and low cost of the described detection components have obvious benefits for portable *in-the-field* and *point-of-care* devices. Over the next five years we envisage organic semiconductor based optical detection arrays becoming a key component of multi-analyte microfluidic systems for the *point-of-care* market.

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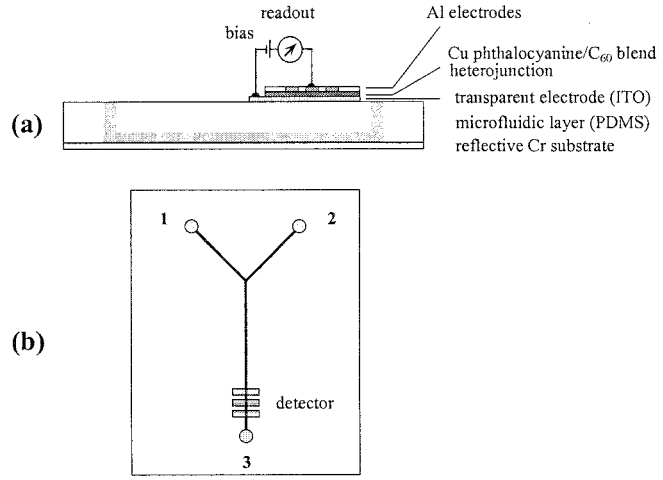

Figure 1. (a) Side view of organic photodiode integrated with planar PDMS microchip. (b) Layout of PDMS microchip comprising two inlets (1,2), mixing channel and outlet (3). Mixing channel is 1000-µm-wide, 800-µm-deep and 7-cm-long. The detector is positioned below the mixing channel (active area: three strips of 8 mm x 2 mm). Only one detector strip was used for the current studies.

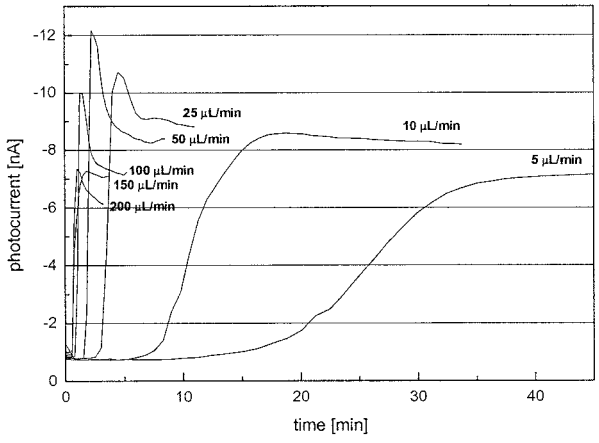

Figure 2. Monitoring of chemiluminescence reaction with organic photodiode on PDMS microchip. PO-CL reagents A and B were applied to inlets 1 and 2, respectively. Flow rate was varied to optimise mixing and chemiluminescence signal intensity.