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Thin-film organic photodiodes as integrated detectors for microscale chemiluminescence assays

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Abstract

We report the use of thin-film organic photodiodes as integrated optical detectors for microscale chemiluminescence. The copper phthalocyanine–fullerene (CuPc–C_{60}) small molecule photodiodes have an external quantum efficiency of ~30% at 600–700 nm, an active area of 2 mm × 8 mm and a total thickness of ~2 mm. Simple detector fabrication, based on layer-by-layer vacuum deposition, allows facile integration with planar chip-based systems. To demonstrate the efficacy of the approach, CuPc–C_{60} photodiodes were used to monitor a peroxyoxalate based chemiluminescence reaction (PO-CL) within a poly(dimethylsiloxane) (PDMS) microfluidic device. Optimum results were obtained for applied reagent flow rates of 25 μL/min, yielding a CL signal of 8.8 nA within 11 min. Reproducibility was excellent with typical relative standard deviations (R.S.D.) below 1.5%. Preliminary quantitation of hydrogen peroxide yielded a detection limit of ~1 mM and linearity over at least three decades. With improved sensitivity and when combined with enzymatic assays the described integrated devices could find many applications in *point-of-care* diagnostics.

Keywords: Organic photodiode; Microchip; Chemiluminescence; Microfluidic

1. Introduction

Chemiluminescence (CL) is a common detection method for liquid phase analysis [1]. CL reactions typically involve the formation of a metastable reaction intermediate or product in an electronically excited state. Subsequent light emission can result directly from the excited compound returning to the ground state (direct CL) or via an energy transfer process to a suitable fluorophore (indirect CL) [2]. While luminol or lucigenin based direct CL has found widespread analytical applications, indirect peroxyoxalate CL (PO-CL) based methods are surprisingly limited. This is in part due to the low solubility and CL efficiency of oxalate esters in aqueous media. However, the addition of surfactants or microemulsions can overcome these limitations [3]. In organic solvents, PO-CL based methods yield high CL quantum efficiencies [4] and can be used in conjunction with a wide range of fluorophores [5]. To minimize interference from quenching or enhancing compounds and increase selectivity, CL is often used for post-separation detection [6–8] or coupled with specific enzymatic reactions [9]. Since the CL reaction acts as an internal light source, instrumental requirements are low. The minimal background signal also results in very low detection limits. All these characteristics make CL amenable for high sensitivity multi-analyte detection in microfluidic systems [10,11]. The small dimensions typically encountered in microfluidic devices enhance diffusion based reagent mixing while the reaction rate and CL

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output can be conveniently controlled via the applied flow rate [12].

In previous reports of CL detection within microfluidic environments the CL signal was detected and quantified using externally mounted photomultiplier tubes (PMTs) [8,12]. However, recently, Jorgensen et al. have reported the use of integrated silicon photodiodes for monitoring CL reactions within microfluidic systems [13]. Although, the authors demonstrate an elegant and efficient fluidic system for integrated CL detection, fabrication of the silicon photodiodes involved a series of complex doping, deposition and patterning steps. An alternative approach is to use solution-processable semiconducting polymers or vacuum deposited small molecule organic semiconductors, which offer simpler routes to device fabrication and tunable optical properties. These characteristics have been extensively demonstrated for thin-film polymer light emitting diodes (pLEDs) which are now entering the market place for simple display applications [14–16]. Interestingly such devices, which comprise one or more layer of organic semiconducting material sandwiched between two electrodes, not only emit light under electrical excitation but can also generate a measurable current under illumination [17]. The photovoltaic effect in organic photodiodes is based on the formation of electron–hole pairs (excitons) and subsequent dissociation and charge collection at the electrodes. While photo-induced charge generation is enhanced by large interfaces between electron donor and acceptor materials, good connectivity to the collection electrodes must also be ensured. Photodiodes based on interpenetrating networks formed from phase-segregated polymers [18] have demonstrated quantum efficiencies >80% under zero bias [19]. Comparable efficiencies, bandwidths and faster response times of $\sim 1\,\mu s$ can be obtained by using small molecule organic materials [20]. With alternating multilayers of copper phthalocyanine (CuPc) and 3,4,9,10-perylenetetracarboxylic bis-benzimidazole (PTCBI), quantum efficiencies up to 80% have been reported under reverse bias [21]. As an alternative acceptor material with longer exciton diffusion length, the fullerene C_{60} has been successfully used in bilayer [22] and blend heterojunction devices [23] for solar cell applications, yielding high power conversion efficiencies.

The work presented herein is aimed at extending the application of organic photodiodes from solar cells to optical detectors in microfluidic systems. We report the successful integration of CuPc–C_{60} small molecule photodiodes with polydimethylsiloxane (PDMS) microfluidic devices for the monitoring of PO-CL reactions. 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. alcohol, glucose, cholesterol) [24]. Integrated portable detection systems for hydrogen peroxide could thus find widespread applications in *point-of-care* diagnostics.

2. Experimental

2.1. Microfluidic set-up

CL microfluidic devices were fabricated in-house from poly(dimethylsiloxane) (PDMS). Using a Sylgard 184 Silicone Elastomer kit (Dow Corning, Coventry, UK), monomer and hardener were mixed at a ratio of 10:1 (w/w), degassed for 30 min and then poured into a flat molding dish. After curing at 95 °C for 1 h the 840 μm thick PDMS layer was pealed off and attached to a chromium coated glass plate (Nanofilm, Westlake Village, CA, USA). Structuring of the PDMS was performed by cutting the channels with a scalpel blade. The layout of the CL microdevices is shown schematically in Fig. 1. The device comprises two inlets, a straight mixing channel and an outlet. For quantitation experiments a microfluidic layer with a third inlet was also used. All inlets are 1000 μm wide, 840 μm deep and 1 cm long. The main channel is 1000 μm wide, 840 μm deep and 8 cm long. Channels were sealed by placing a 3 mm thick PDMS slab in conformal contact with the structured PDMS layer. Fluidic access holes at the channel ends were punched with a blunt 394 μm ID, 711 μm OD syringe needle (BD, Oxford, UK). Capillaries were inserted through the access holes to serve as fluidic reservoirs (150 μm ID, 367 μm OD, Composite Metal Services, Hallow, UK). For flow generation a PHD 2000 syringe pump (Harvard Apparatus, Edenbridge, UK) with two 1 mL Bee Stinger gastight syringes (BAS, West Lafayette, IN, USA) was employed. The syringes were connected to 1.6 mm ID high-pressure fingertights (VWR, Poole, UK) via 762 μm ID PEEK tubing (Supelco, Bellefonte, PA, USA). The outlet of the fingertights comprised 356 μm ID Teflon tubing (Anachem, Luton, UK) which could be connected to the capillary reservoirs of the CL microdevices.

2.2. Organic photodiode fabrication

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 [23]. In short, the devices were fabricated on 1 mm thick indium-tin-oxide (ITO) coated glass substrates (CRL Opto, Hayes, UK) after initial cleaning by ultrasonication with acetone and methanol for 20 min each. The organic layers were grown by vacuum deposition in a Spectros system with a base pressure of about 8×10^{-8} mbar (Kurt J. Lesker Company, Hastings, UK). The organic materials used in the devices were 97% grade CuPc (Sigma-Aldrich, Gillingham, UK), twice purified by thermal gradient sublimation prior to deposition, and 99.5% C_{60} (MER Corp., Tucson, AZ, USA), used as received. For the photodiodes employed in the flow optimization experiments 58 nm thick layers comprising 60% (w/w) CuPc and 40% (w/w) C_{60} were deposited. The mixed layers were grown by co-deposition from independent organic evaporation sources, with the deposition rates monitored by a series