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Low-voltage driven portable paper bipolar electrode-supported electrochemical sensing device

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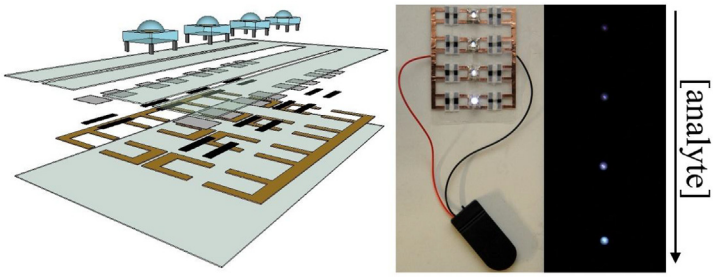
HIGHLIGHTS

- Combination of bipolar electrochemistry, paper devices, and light-emitting diodes.
- Simple fabrication and usage yield stable and accurate sensing to complex samples.
- Low voltage requirement, cheap material and robust structuring enables portability.

GRAPHICAL ABSTRACT



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ABSTRACT

Aiming to overcome the obstacles of power supply requirement and chip usefulness in practice, a low-cost and convenient portable electrochemical sensing device is introduced for the first time, featuring bipolar electrode system, LED read-out, laminated paper-based devices, and low-voltage button cells. The electric circuits of this practical device are constructed on laminating films with copper and conductive carbon tapes, and the reservoirs facilitating chemical reactions are made with chromatography paper. The device is sensitive to electrochemical responses, validated by the demonstrative hydrogen peroxide and enzyme-assisted glucose detection. The business-card-size chip achieves sensitive analyte detection by naked eyes as well as further image processing in both laboratory samples and human serum samples testing, featuring detection limit as low as 1.79 μM and a dynamic range from 10 μM to 10 mM. This new practical design of point-of-care sensing chip entails the properties of facile fabrication, simple usage, high robustness, low power consumption, and accurate sensing showing the attainability of fabricating a useful and portable analytical device.

1. Introduction

Bipolar electrode (BPE) systems use an electric field to polarize an electrode without direct ohmic contacts for Faradic reactions generation at different poles of the electrode [1,2], which can be applied for a wide variety of applications, e.g., microswimmers [3,4], electrokinetic and separation of charged species [5,6], and position-dependent doping of electroactive polymers [7,8]. In addition to conventional BPE designs where single electrodes are exposed to the conductive medium, there are other designs such as dual-channel closed bipolar electrodes and split bipolar electrodes. Differing from conventional BPE operation where electric current flows both in the solution and on the electrode, the conducting medium in a closed BPE system is physically separated by the

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electrode into two half-cells [9]. For split BPE designs, the electrode itself is split into two separate electrodes and connected via an ammeter or voltmeter in order to measure the flowing current or voltage [10]. Conventionally, the electrochemical reactions on the BPE can be reported by transformation into optical signals via electrochemiluminescence (ECL) reporters [9,11–14]. A closed BPE setup for the detection of hydrogen peroxide, ascorbic acid, and glucose using light-emitting diodes (LEDs) was introduced by Wang et al. without the use of luminescent reagents [15]. Due to design simplicity and operation convenience, the BPE system is highly attractive for integration with various portable devices for lab-on-a-chip setups. However, for practical applications, reducing the use of less-economical material and production methods, e.g., indium tin oxide or gold as electrodes or ECL reagents [2,9,15], and adopting unbulky device design are inevitable.

Paper-based devices have emerged as a promising choice for miniature analytical platforms due to easy fabrication, high biocompatibility, low cost, and widespread availability [16]. Supporting substrate, e.g., filter paper, is first divided into fluidic channels and sensing areas via means of hydrophobic treatment or simple shaping processes [16]. These devices have been used in many applications, such as colorimetric enzymatic assays [17,18], electrochemical process [19], immunoassays [20,21], etc. The combination of paper-based devices with the BPE system has recently been proposed, providing advantages of design simplicity and economical fabrication [22–24]. Despite its versatility, conventional paper-based devices encounter prevailing problems such as insufficient physical or chemical protection against environmental interference. To overcome this, various solutions have been proposed, such as enclosing the paper substrate inside layers of printed wax [25] or polymer laminating films [26,27]. Among different solutions, the use of polymer lamination not only provides protection to the device and reagent, but also increases device durability by strengthening substrate mechanical property [27,28]. Due to these merits, laminated paper-based devices hold deep potential to serve as analytical tools for developing regions, point-of-care purposes, and *in situ* operations.

In this study, a laminated device, integrating the BPE system with paper-based substrates into a new class of electrochemical sensor, is fabricated. This design incorporates LEDs as the signal reporter into a split BPE setup to replace measuring equipment such as ammeters or voltmeters, allowing straightforward analyte detection with naked eyes. The laminated platform design provides paper substrates with chemical and physical protection, vastly increasing device robustness and mechanical strength. Due to the exceptionally high Faraday efficiency and low voltage requirement of closed BPE systems and LED's high sensitivity, the potential change triggered by redox reactions in paper reactors is reflected as alteration in LED brightness, and quantitative analysis can be achieved with subsequent camera/cell phone image processing. This business-card-size portable sensing chip provides convenient and prompt electrochemical responses, and due to the low voltage requirement of LED, its feasibility can be further advanced by the integration of button cells. The use of bulky external power supply is therefore avoided and the device performance is found to be identical. To demonstrate the feasibility of this design, redox reactions of hydrogen peroxide and glucose in presence of glucose oxidase are used to power four-pin LEDs. Detection limits and dynamic ranges are calculated from the obtained LED luminescence intensity. The substantial reduction in fabrication cost and complexity have greatly benefited practical device design and moved the portable electrochemical sensor to the next generation.

2. Experimental

2.1. Chemicals and materials

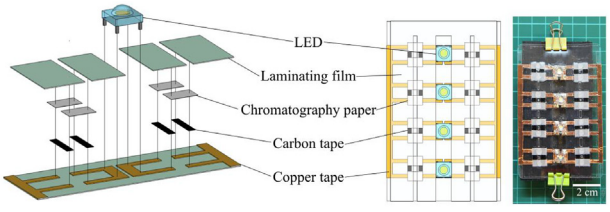
Hydrogen peroxide (H_2O_2), D-glucose, glucose oxidase (GOx), sodium phosphate dibasic, sodium phosphate monobasic, maltose, lactose, and D-fructose were purchased from Sigma-Aldrich (St. Louis, MO, USA). Copper foil tapes and conductive carbon tapes were purchased from Pentad Scientific Corporation (Hsinchu, Taiwan). LED, soldering equipment, and laminating films were purchased from Chung-Yi Opto Technology (Taipei, Taiwan), Taiyo Electric (Hiroshima, Japan), and Simbalion (Taipei, Taiwan), respectively. The conductive silver pen was purchased from Chemtronics (Kennesaw, GA, USA). Human serum samples were provided by Rainbow Biotechnology (Taipei, Taiwan). The external power supply equipment (Keysight E3631A) was obtained from Keysight Technologies (Santa Rosa, CA, USA). Ultrapure water (>18.2 MΩ·cm) generated from ELGA PURELAB classic system (Taipei, Taiwan) was used throughout the experiments.

2.2. Device fabrication

The device design and assembly of this approach is demonstrated in Scheme 1. Copper foil tape, carbon conductive tape (2 mm × 12 mm), and chromatography paper (5 mm × 10 mm) were first shaped as needed independently. Copper foil tape and carbon conductive tape were utilized for electric circuit connection, and the paper pieces acted as reagent reservoirs for electrochemical reactions. These pieces were arranged into circuits on the bottom thermoplastic laminating film layer in the order of copper foil tape, carbon conductive tape, and chromatography paper, while hole outlets (1 mm × 5 mm) were cut on the top laminating film layer for later analyte introduction. The device was then laminated by a TCC-6000 laminating machine (Yung Hong Enterprises, Kaohsiung, Taiwan) at 130 °C with a rolling speed of 150 cm/min. After lamination assembly, four-pin LED were soldered onto the circuits and the device was ready for analyte detection.

2.3. Electrochemical sensor operation

After introducing analyte and buffer solution into appropriate chromatography paper reservoirs, the device circuit was connected to a DC power supply via the side copper tapes. A camera was used to record the LED brightness change after 30 s of reaction under ambient environment (room temperature and pressure, in dark). The photographs were taken with an EOS 60D single lens reflex camera collocated with a Canon EFS17-55 mm f/2.8 lens (Tokyo, Japan).



Scheme 1. (Left) Assembly drawing of one reaction set. (Right) Top view of the laminated paper-based bipolar electrochemical sensing device containing four parallel reaction sets connected with the conductive circuit. The photo at the far right depicts an actual device fabricated accordingly.