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A flexible and disposable battery powered by bacteria using eyeliner coated paper electrodes

Ramya Veerubhotla[a], Debabrata Das[a,*], Debabrata Pradhan[b,*]

[a] Department of Biotechnology, Indian Institute of Technology, Kharagpur, West Bengal 721302, India
[b] Materials Science Centre, Indian Institute of Technology, Kharagpur, West Bengal 721302, India

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ABSTRACT

Herein, an environment friendly paper-based biobattery is demonstrated that yields a power of 12.5 W/m^3. Whatman filter papers were used not only as support for electrode fabrication but also as separator of the biobattery. To provide electrical conductivity to the paper-based cathode and anode, commercially available eyeliner containing carbon nanoparticles and Fe_3O_4 was directly employed as conductive ink without any binder. With an instant start-up, the as-fabricated biocompatible electrodes could hold bacteria in an active form at the anode allowing chemical oxidation of organic fuel producing current. The facile process delineated here can be employed for the tailored electrode fabrication of various flexible energy harnessing devices.

1. Introduction

Considering the energy and environmental crisis looming over future generations, it becomes imminent to explore every possible ways to generate energy through cleaner and greener processes. One approach to address the above issue is to employ biofuel cells or microbial fuel cells (MFCs) to generate energy from the wastewater or similar other organic fuels (Zhou and Dong, 2011; Zhou, 2015a; Wang et al., 2015). Electrodes, being an indispensible component, have a profound impact on the efficacy and functionality of the fuel cell device. The basic requirements of an electrode are electrically conducting behaviour and stability in the electrolyte. Thus, carbon-based materials have so far been recognized as the most attractive electrode materials in the electrochemical devices (Huang and Wang, 2014; Zhou and Guo, 2015b). In recent years, carbon nanotubes (CNTs) and graphene have been used as electrodes of fuel cells to further improve the performance (Xie et al., 2011; Yuan and He, 2015). These carbon-based materials are generally coated on a suitable support such as carbon paper, carbon cloth, graphite, glass etc. to function as electrode. More recently, paper has emerged as an inexpensive, convenient, and flexible platform causing a paradigm shift in the development of next generation energy conversion and storage devices such as fuel cells (Zhang et al., 2012; Arun et al., 2014; Esquivel et al., 2014), batteries (Chen et al., 2014; Nyström et al., 2009), and supercapacitors (Wang et al., 2014; Hu et al., 2012; Yuan et al., 2012). The unique properties of the paper include (i) variable porosity enabling high surface area, (ii) light weight, user-friendly, compactness, and biodegradability, (iii) ease of generating tunable electrodes with desired electrical and surface properties, and (iv) automatic passive pumping of fluid into the reaction sites by capillary action (Sharifi et al., 2015). This makes paper a promising inexpensive matrix to fabricate portable energy generation and storage devices (Nguyen et al., 2014).

Paper-based electrodes are conventionally fabricated by methods such as screen printing (Metters et al., 2014; Shitanda et al., 2015; Li et al., 2015), inkjet printing (Kwon et al., 2013; Hu et al., 2010), spin coating (Mostafalu and Sonkusale, 2014), and oxidative chemical vapour deposition (Barr et al., 2011). Paper comprises of cellulosic fibers and is non-conductive in nature. Thus, paper is being made conductive by depositing conductive inks prepared using CNTs or silver that are expensive (Hu et al., 2009). In this study, we demonstrate for the first time, a cost-effective approach to prepare paper-based electrodes, by using commercially available eyeliner as a conductive ink. Our findings suggest that simple conformal coating of eyeliner can make the surface of the paper conductive due to the inherent amorphous carbon present in the eyeliner. This also eliminates the need for tedious electrode fabrication methods thus lowering of the overall production costs (Hu et al., 2009). The rationale behind the use of eyeliner coated paper electrodes is that (1) both paper and eyeliner are readily available low-cost materials, (2) electrode preparation does not require any additional chemicals, binders, intermediate modification steps or tedious deposition methods, and (3) it is possible to control the loading and distribution of eyeliner. Conductive patterns and tracks can be deposited on paper or textiles for flexible and wearable electronics by using eyeliner in lieu of conductive inks.

* Corresponding authors.
E-mail addresses: ddas.iitkgp@gmail.com (D. Das), deb@matsc.iitkgp.etnet.in (D. Pradhan).

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Tuning the electrical and surface properties by nanoparticles addition can further broaden the scope of this invention paving its way to the development of application-oriented tailored paper electrodes. Here, we show that biofuel cells can be powered by bacteria using these eyeliner coated electrodes.

MFCs exploit the bacterial metabolism for the production of bioelectricity using biodegradable organic matter. MFC is environment friendly when air-cathode (cathode using air for oxygen reduction) is employed as it yields water as the only by-product. Interfacing the paper-based air-cathode into the MFCs extends their application to portable power sources that are renewable and self-sustainable. One of the major drawbacks of the paper-based biobattery is the evaporation of electrolyte making the system unsustainable for longer duration. Although such configuration is suitable for instant power generation in resource limited settings, uninterrupted electricity generation is a challenging task unless suitable arrangements are made. In addition, some amount of oxygen always diffuses into the anode through the pores of paper matrix, which in turn decreases the performance of electrogenic bacteria. The concept of such a paper-based microbial battery was introduced by Fraiwan et al. using carbon cloth electrodes, sodium polystyrene sulfonate infiltrated paper as proton exchange membrane, and ferricyanide as catholyte (Fraiwan et al., 2013). Following this, Lee and Choi fabricated a bacteria powered battery with screen painted carbon electrodes as anode and a nickel-sprayed paper-based cathode coated with activated carbon catalyst using binder (Lee and Choi, 2015). Here, we demonstrate the simplest paper-based MFC device where both cathode and anode were the eyeliner coated paper (no binder was used) along with a virgin Whatman filter paper as separator. Unlike the earlier studies, no other type of carbon support was employed in the present work for fabricating the MFC device. Owing to the porous nature of eyeliner coated film obtained, an enhanced adhesion of bacteria resulted in a superior power generation capability. The as-fabricated devices were found to generate instant power from microlitres of electrolyte without the most commonly used expensive Nafion membrane (Fraiwan et al., 2013).

2. Materials and methods

2.1. Electrode preparation

A conductive ink was prepared by diluting the commercially available eyeliner (LAKMÉ INSTA-LINER) with an equal volume of water. Dilution not only reduces the viscosity of the eyeliner but also aids in homogenous spreading of the ink materials. This eyeliner ink was painted on a Whatman 1 filter paper with an ordinary paint brush without prior treatment or addition of any binder or chemical. The inherent wicking capability of the paper resulted in quick absorption of eyeliner ink into it. The eyeliner coated paper was dried at room temperature producing a thin and freestanding electrode.

2.2. Device fabrication

Fig. 1a shows the schematic illustration of the MFC device assembled by stacking a wax paper, anode, and a separator followed by cathode. Fig. 1b and c show the photographs of eyeliner coated paper-based cathode and anode, respectively. The cathode and anode were prepared by painting the eyeliner ink on the Whatman 1 filter paper in an area of 4 cm×4 cm and 2 cm×2 cm, respectively. A higher cathode surface area was selectively adopted to maximize the power generation in the device owing to the major role played by the cathode. An aluminium foil was used as current collector at anode. The anode and cathode were connected by a 10 kΩ resistor during the current measurements. Fig. 1d shows different components of the device and the final assembled MFC device is shown in Fig. 1e.

2.3. Characterization

The surface morphology and energy dispersive X-ray (EDX) analysis of the eyeliner and carbon black coated electrode were examined by a field emission scanning electron microscopy (FE-SEM) [Zeiss Supra 40 FE-SEM] equipped with an Oxford EDAX detector. The microstructure of eyeliner was studied with a Tecnai G2 (FEI) transmission electron microscope (TEM) operated at 200 kV. The crystallographic phase of the coated electrodes were characterized by X-ray powder diffraction (XRD) with a Rigaku Ultima III diffractometer using Cu $K\alpha_1$ irradiation at a power of 40 kV×40 mA. Raman measurements were carried out with a Horiba Jobin Yvon T64000 Raman spectrometer using argon-krypton mixed ion gas laser as excitation source.

2.4. Microbial strain, media and MFC operation

The present biofuel cell was operated with *Shewanella putrefaciens* (ATCC BAA1097™) as the biocatalyst. Prior to inoculation, the culture was grown in autoclaved Luria-Bertani (LB) media (HiMedia Labs, India) for 36 h at 37 °C. LB was a nutrient rich media consisting of 10 g tryptone, 5 g yeast extract, and 10 g NaCl per litre dissolved in distilled water. Four devices were fabricated to study the performance and 400 µL of bacterial culture was injected to the anode of each device using an insulin syringe (1 mL) for each experimental run. It is to be noted that the volume of paper-based anode and cathode were estimated to be 72 µL and 288 µL, respectively. Thus 400 µL of media

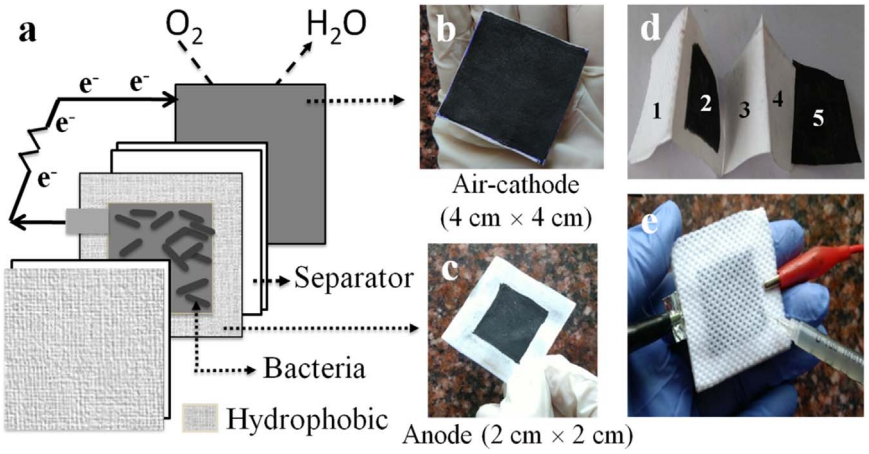

Fig. 1. (a) Schematic of the bacteria powered biofuel cell. Digital photographs of (b) air-cathode and (c) anode prepared by coating eyeliner on the filter paper. (d) Different components of the paper-based device (1. Hydrophobic layer; 2. Anode; 3 and 4. Whatman 1 filter paper as separator; 5. Air-cathode) (e) Digital photograph of the final device.