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Biosensors and Bioelectronics

journal homepage: www.elsevier.com/locate/bios

Short communication

Enzymatic fuel cells based on electrodeposited graphite oxide/cobalt hydroxide/chitosan composite–enzyme electrode

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ARTICLE INFO

Article history:

Received 16 July 2012

Received in revised form

5 October 2012

Accepted 5 October 2012

Available online 18 October 2012

Keywords:

Enzymatic fuel cell

Electrodeposition

Graphite oxidation

Cobalt hydroxide

Glucose oxidase

Laccase

ABSTRACT

Enzymatic fuel cells (EFCs) use redox enzymes with high electron transfer rates that lead to high power density from bioavailable substrates. However, EFCs are limited by the difficult electrical wiring of the enzymes to the electrode. Therefore, deposition of Co(OH)₂ onto graphite oxide (GO) was improved for efficient wiring of the enzymes. The GO/Co(OH)₂/chitosan composites were electrodeposited for immobilization of glucose oxidase (GOD) or laccase on an Au electrode, respectively. The electrical properties of the bioelectrode according to cyclic voltammetry were improved using GO/Co(OH)₂/chitosan composites. The anode and cathode system was composed of GOD and laccase as biocatalysts and glucose/oxygen as substrates under ambient conditions (pH 7.0 and 25 °C). The EFC using GO/Co(OH)₂/chitosan composites with a mediator delivered a high power density of up to 517 ± 3.3 μW/cm² at 0.46 V and open circuit voltage of 0.60 V. These results provide a promising direction for further development and application of EFCs.

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1. Introduction

Fuel cells are devices that convert chemical energy into electrical energy. However considerable interest has developed towards the development of an enzymatic biofuel cell (EFC) as they can be employed as an *in vivo* power source for many applications (Barton et al., 2004; Davis and Higson, 2007; Minteer et al., 2007). An EFC performs enzymatic catalysis, namely activity at near-room temperature and neutral pH and selectivity (Barton et al., 2004). However, an EFC has a short lifetime, low current density, and poor power density, which are related to enzyme stability, electron transfer rate, enzyme loading, and inefficient electron conduction (Kim et al., 2006; Minteer et al., 2007). To improve electron transfer in the electrode, one of the most widely studied EFCs is the mediator, which typically uses electron transferring agents that participate in redox reactions with the enzyme and help in the rapid transfer of electrons to and from the electrode. It is evident that when nanostructures of conductive materials are used, the large surface area of these nanomaterials can increase enzyme loading and facilitate reaction kinetics; thus, improving EFC power density.

Graphene is an excellent carbon material for energy-conversion/storage systems because of its high specific surface area, good chemical stability, and excellent electrical and thermal conductivity (Kim et al., 2011; Pham et al., 2012). Graphite oxide (GO), one of the most important derivatives of graphene, is characterized by its special surface properties and layered structure (Stankovich et al., 2006; Seredych and Bandosz, 2007). Specifically, due to the oxygen-containing functional groups (hydroxyl, carboxyl, and epoxy groups) on carbon nanosheets (CNS), GO can be oxidized under appropriate conditions to form two-dimensional CNS (Paci et al., 2007). These GO sheets possess large surface areas and, thus, may be potential support materials to load nanocrystals. GO with oxygenated functional groups can act as a nucleation center to anchor active materials, such as metal hydroxide, onto the surface. Thus, it should be reasonably feasible to synthesize well-dispersed GO based composites (Wang et al., 2011).

Cobalt hydroxide (Co(OH)₂) materials are attractive due to their layered structure with large interlayer spacing and their well-defined electrochemical redox activity (Zhou et al., 2009). A great deal of interest has been centered on utilizing Co(OH)₂ material in alkaline batteries, fuel cells, and supercapacitors (Cao et al., 2004; Ramesh and Kamath, 2008; Wang et al., 2010). Considering the high specific area of GO, which can serve as an excellent building block for nanocomposites (Jin et al., 2007; Li et al., 2009a), and the fact that GO is a promising electrode

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material, consistently providing good electrochemical performance in strong electrolytes (Stoller et al., 2008), the combination of Co(OH)₂ and GO may produce synergistic results and provide a system with enhanced electrochemical properties (He et al., 2010).

Chitosan is a linear hydrophilic polysaccharide derived by deacetylation of the natural biopolymer chitin. It has large numbers of reactive amine groups that play an important role in ion sorption and dissolubility (Jiang et al., 2006). Due to its attractive biocompatibility, biodegradability, nontoxicity, high mechanical strength, and cheapness, chitosan has been extensively used as an immobilization matrix (Wang et al., 2009a; Song et al., 2010). In view of its relatively poor electrical conductivity, chitosan is usually combined with GO, redox mediators, and metal nanoparticles (Liu et al., 2005; Li et al., 2008; Kaushik et al., 2008; Wang et al., 2009; Song et al., 2010). Moreover, electrodeposition is a popular electrode modification technique that has been widely used to fabricate sensors and fuel cells. This technique exhibits good stability, reproducibility, and a short response time (Chen et al., 2002; Yang et al., 2010a). Electrodeposition is universally used to deposit alloys and high quality semiconductors (Chandrasekara and Pushpavanam, 2008).

In this study, a novel bioelectrode technique that employs GO/Co(OH)₂/chitosan composites was applied for an EFC. The GO/Co(OH)₂ composites with a mediator were synthesized and the anodic and cathodic bioelectrodes were fabricated on the Au electrode using the electrodeposition technique. The electrical properties of a basic EFC based on a GOD and laccase system were investigated. The main objective of this study was to evaluate the possibility of developing an EFC using GO/Co(OH)₂/chitosan composites with a mediator by electrodeposition of organic-inorganic hybrid systems and immobilization of enzymes.

2. Material and methods

2.1. Materials

Cobalt chloride hexahydrate (CoCl₂·6H₂O, Riedel-de Haën, Seelze, Germany), graphite (powder, < 20 μm), ammonia water (NH₄OH, 28%), *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDC), *N*-hydroxysuccinimide (NHS), chitosan (medium MW, deacetylation 75–85%), nitric acid (fuming, > 90%), D-glucose, and sulfuric acid (≥ 95%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). TAE buffer (25 ×) was purchased from Bio Basic Inc (Markham Ontario, CAN). Hydrogen peroxide solution (≥ 34.5%) was purchased from Samchun Pure Chemical (Kangnam-Gu, South Korea). GOD (enzyme activity > 100 U/mg, Bio Basic Inc.) from *Aspergillus niger* and laccase (enzyme activity ≥ 0.5 U/mg, Sigma-Aldrich) from *Trametes versicolor* were used as the anode and cathode biocatalysts, respectively.

2.2. Preparation and electrodeposition of GO/Co(OH)₂/chitosan composites with mediator

GO was synthesized from graphite powder by a modified Brodie method (Steurer et al., 2009), in which pre-oxidation of graphite was followed by oxidation. Graphite (4 g) was mixed with 34 g of NaClO₃. Then, the mixture was slowly added to 100 ml of HNO₃ under stirring at room temperature for 24 h. After cooling, the GO was settled in 2000 ml water, the supernatant was decanted, and the remaining product was centrifuged and washed with deionized water. The washing process was repeated until the pH of the solution was neutral. After drying under vacuum in an oven at 110 °C, GO was obtained as a gray powder.

The GO/Co(OH)₂ composites were prepared by the method of Wang et al. (2011). The typical route was as follows. GO (0.1 g) was dispersed in 100 ml deionized water and ultrasonicated for 1 h. CoCl₂·6H₂O (2 M) was dissolved in 10 ml of deionized water. The above CoCl₂·6H₂O solution was dropwise added into the GO suspension with vigorous stirring for 24 h. Subsequently, the NH₄OH solution was dropwise added into the above solution with continuous stirring until the pH was 9. After aging for 12 h, the resulting products were separated by centrifugation and washed with deionized water and ethanol several times, and then dried at 60 °C in a vacuum oven for 2 h.

The surface of each electrode was polished to a mirror-like finish with 0.3 μm Al₂O₃ powder, followed by 0.05 μm Al₂O₃ powder. The polished electrode was immersed in Piraha solution (a solution of 30% H₂O₂ and concentrated H₂SO₄ mixed at a volume ratio of 1:3), after which it was rinsed ultrasonically with water and absolute ethanol for 3 min.

The chitosan solution was prepared by dissolving 0.1 g of chitosan solid in 100 ml of 25 × TAE buffer and 3% acetic acid solution. The undissolved chitosan was filtered with nylon mesh. After the GO/Co(OH)₂ composites were synthesized using the procedure described above, 3 g of GO/Co(OH)₂ composites were dispersed in the chitosan solution. The adsorption of GO/Co(OH)₂/chitosan composites to the electrode was accomplished using a power supply at 50 V for 2 min. The electrodes were washed three times with deionized water and stored in 0.1 M phosphate buffer solution at 4 °C.

2.3. Preparation of bioelectrodes

GOD (for the anode) or laccase (for the cathode) was immobilized onto the electrode modified with GO/Co(OH)₂/chitosan composites in 0.1 M phosphate buffer solution (pH 7.0) containing 0.1–4 mg/ml of GOD or laccase, respectively, and a subsequent incubation for approximately 8 h at 4 °C in 0.12 M EDC and 0.14 M NHS. The enzyme modified GO/Co(OH)₂/chitosan composites were prepared by covalent coupling of the chitosan to the amine-monolayer using the EDC/NHS coupling agent (Lee et al., 2009). The bioelectrodes were washed three times with 0.1 M phosphate buffer solution and deionized water and stored in 0.05 M phosphate buffer solution at 4 °C, respectively.

2.4. Preparation of an EFC using the anode and cathode

The electrolyte solution was composed of a 0.05 M phosphate buffer (pH 7.0) containing 0.1 M of D-glucose and O₂ (bubbling with highly purified oxygen (99.995%) for 30 min) as substrates (Lee et al., 2011). The modified electrodes were connected to analyze the EFC power curves. Glucose was oxidized to gluconic acid by GOD immobilized on the GO/Co(OH)₂/chitosan with a mediator at the GOD/GO/Co(OH)₂/chitosan anode. O₂ was reduced to water by the bioelectrocatalysis of laccase immobilized on the GO/Co(OH)₂/chitosan with a mediator at the laccase/GO/Co(OH)₂/chitosan cathode. The surface area of the cathode and the anode was adjusted to 0.0314 cm² disc electrodes (gold, 1 mm radius), and the total electrolysis solution volume in the vessel was 3 ml.

2.5. Characterization and electrochemical measurements

The synthesized products were characterized structurally and morphologically using X-ray photoelectron spectroscopy (XPS, ESCA 2,000, VG Microtech Ltd., Sussex, England). The surface properties and composition of the composite were investigated by Fourier transform infrared (FT-IR, Spectrum GX1, Perkin Elmer Ltd., Waltham, MA, USA) spectroscopy (in KBr pellets, in the range

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