



Fabrication of Vertically aligned Copper Nanotubes as a Novel Electrode for Enzymatic Biofuel Cells



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ABSTRACT

Herein, Laccase catalysed oxygen reduction reaction on polyaniline coated copper nanotube bio-cathode was studied. The copper nanotubes were grown in anodic aluminium oxide template on which conductive polymer polyaniline was electrodeposited. Laccase was covalently immobilized using a linker molecule glutaraldehyde. The effective wiring of enzyme with bio-cathode was confirmed by linear sweep voltammetry, chronoamperometry and open circuit potential measurement. All electro analysis was performed in conventional three electrode system using platinum wire counter electrode and Ag/AgCl reference electrode. The bio-cathode in air saturated phosphate buffer showed maximum OCP and current of 0.59 V and 140.12 μAcm^{-2} respectively. Moreover, electrochemical impedance analysis confirmed decrease in charge transfer resistance with the immobilization of enzyme on CuNTs/polyaniline electrode. The bio-cathode showed reproducibility and stability over the period of examination.

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1. Introduction

Fuel cell is an efficient energy conversion device that transforms chemical energy directly into electrical energy. It consists of two electrodes. The fuel is catalytically oxidized at the anode and the oxidant is reduced at the cathode. The simultaneous redox reaction at the electrodes generates electricity [1,2]. Enzymatic biofuel cells (EBFCs) harnesses energy from oxidation of organic compounds using purified enzymes as catalyst [3]. High conversion efficiency (<80%) and operation under normal condition (room temperature and neutral pH) are the major advantages of EBFCs. Moreover, high specificity and selectivity of enzymes eliminate the requirement of membrane to separate electrodes [4,5]. The EBFCs have been envisioned as power source for portable electronic devices, wireless network, medical implants, and self-powered biosensors. It has been successfully examined both *in-vivo* and *in-vitro* conditions. The most commonly studied anodic and cathodic

enzyme for implantable devices are glucose oxidase and laccase respectively [6,7]. But the low power output results from insufficient electron transfer, sluggish kinetics and high internal resistance are the main obstacle in commercialization [8].

Oxygen is the preferred electron acceptor because of high redox potential (400 mV to 800 mV) and limitless availability. But high over potential and slow kinetics at neutral pH makes oxygen reduction energetically expensive [9]. Laccase, bilirubin oxidase and tyrosinase are the extensively examined for electro-catalytic oxygen reduction. Laccase belong to the multicopper oxidases family which utilize four copper ions to catalyse oxygen reduction reaction [10]. Electrical communication between electrode and enzyme occurs via mediated electron transfer or direct electron transfer (DET) [11]. In mediated electron transfer, redox active molecules are used to shuttle electrons from redox centre of enzyme to the electrode [12]. By using DET between enzymes and the electrode, biofuel cells can operate close to the thermodynamic redox potential of the enzyme and, thereby, maximizing the OCP. Despite the substantial efforts to establish direct communication between enzyme and electrode, it still remains a challenging issue because the active site is buried in deep pocket [11,13].

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The one dimensional nanomaterials have the capability to establish direct electrical communication with redox centre of enzymes and improve performance of bio-electrodes in terms of electro active surface, porosity and electron transfer rate [14,15]. In recent years, a wide range of conducting nanotubes and nanowires (metallic and polymeric) received a high interest due to their good conductivity and increased surface area. Besides multi walled carbon nanotube, copper nanotubes have potential application in current collectors for Li-ion batteries. Among conductive polymers, polyaniline (PANI) has attracted the highest interest due to its ease of synthesis, low cost, unique redox tune ability and good environmental stability. It has promising applications in various fields, such as corrosion protection, sensors, and actuators because of excellent electrical conductivity, high chemical and electrochemical stability makes it a favourable choice for fabrication of bio-electrode. Templates with nanosized pores (anodic aluminium oxide and polycarbonate membrane) are used to grow nanostructures arrays for fuel cell and battery electrodes [16,17].

Herein, the possibilities of using polyaniline coated copper nanotubes (CuNTs) array as a potential bio-cathode for EBFCs has been explored. The major advantages of CuNTs are easy to fabricate, high electronic conductivity, comparatively cheap and provide large surface area for enzyme immobilization. The bio-cathode was fabricated by immobilization of laccase on polyaniline coated CuNTs array. This could open a new pathway for other metal nanotubes to find a place in EBFCs.

2. Material and Methods

2.1. Materials

Laccase crude from *Trametes Versicolor* (24 units/mg), disodium phosphate (Na_2HPO_4), mono sodium phosphate (NaH_2PO_4), dimethyl formamide ($\text{HCON}(\text{CH}_3)_2$), sodium chloride (NaCl), and sodium hydroxide (NaOH) were purchased from Sigma Aldrich, India. Anodic Aluminium Oxide (AAO) templates were purchased from Whatman Inc. Aniline ($\text{C}_6\text{H}_5\text{NH}_2$), copper sulphate (CuSO_4), sulphuric acid (H_2SO_4), nitric acid (HNO_3), poly ethylene glycol ($\text{H}(\text{OCH}_2\text{CH}_2)_n\text{-OH}$), oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) and glutraldehyde ($\text{CH}_2(\text{CH}_2\text{CHO})_2\text{O}$) were purchased from Merck, India. Ultrapure water with resistivity of $18.2\text{ M}\Omega$ was used for all the experiments. The supporting electrolyte, phosphate buffer (0.1 M, pH 5.0), used for electro analysis of bio-cathode was prepared by dissolving required salts in deionized water. The aniline polymerization was performed by cyclic voltammetry using 0.1 M aniline dissolved in oxalic acid. The glutraldehyde solution (2.5%, pH 5.0) was prepared in 0.1 M phosphate buffer.

2.2. Equipment

The electro analysis was performed at room temperature in a small glass tube with capacity 15 ml containing 10 ml of buffer solution. The electro-catalytic activity of bio-cathode was examined by linear sweep voltammetry, chronoamperometry, and electrochemical impedance spectroscopy on a potentiostat/galvanostat (CHI 660E). A platinum wire (Diameter –0.5 mm, Length –2 cm) counter electrode and Ag/AgCl reference electrode (1.0 M KCl) was used in all electrochemical testing. The aniline polymerization was performed on the same instrument using oxalic acid (0.3 M) as supporting electrolyte containing aniline (0.1 M). The impedance analysis was performed at open circuit potential in frequency ranging 100 KHz–0.1 Hz with an overlaid potential of 5 mV. The morphology of CuNTs was examined using a Field Emission Scanning Electron Microscopy (FESEM, JMS-6700F).

2.3. Preparation of 3D Electrodes

The polycrystalline CuNTs array was grown by electro-deposition within the pores of commercially available AAO membrane ($60\ \mu\text{m}$ thick and 10^9 pores cm^{-2}). The pore diameter was 200 nm. A seed layer of silver was deposited on AAO template by thermal evaporation that provides electrical contact for deposition of copper. The electro-deposition of copper in the AAO template was performed using a potentiostat in conventional two electrode system. It was carried out in acidic copper sulphate solution (CuSO_4 0.24 M, H_2SO_4 1 M), in which additives (poly ethylene glycol 900 ppm, NaCl 150 ppm) was added to control the pore diameter of nanotubes [18]. The spacing between template and counter electrode was 45 mm and total volume of the solution was 100 ml. The electro-deposition was carried out at a current 40 mA using a standard potentiostat. The AAO template was subsequently etched with 6 M NaOH solution to get free standing CuNTs. The trace of remaining NaOH was removed by gently rinsing with deionized water and then the samples were dried in vacuum at 60°C [19]. The length of copper nanotube was determined by strength of current and deposition time whereas thickness is determined by pore size of template [20].

2.4. Electro-deposition of Poly-aniline on Copper Nanotubes (CuNTs)

A layer of polyaniline was electro polymerized on CuNTs. It provides amine group for enzyme immobilization and also protects electrode from corrosion. The electro-polymerization was carried out using cyclic voltammetry in potential range -0.20 V to 0.60 V (vs Ag/AgCl) at the scanning rate of 50 mVs^{-1} (Fig. 1). Prior to aniline deposition, the working and counter electrode was cleaned by sonication in acetone and deionized water and dried in hot air oven at 50°C . The polymerization was performed in a 50 ml glass cell containing 0.1 M aniline and 0.3 M oxalic acid. The resulting electrode was washed three-four times with deionized water to remove excess of unbound aniline and subsequently dried in hot air oven.

2.5. Immobilization of Enzymes on the Poly-Aniline coated CuNTs Electrodes

The immobilization of enzyme on electrode by covalent bonding not only improves its stability but also solves the problem of washing out in continuous flow of electrolyte. Enzyme

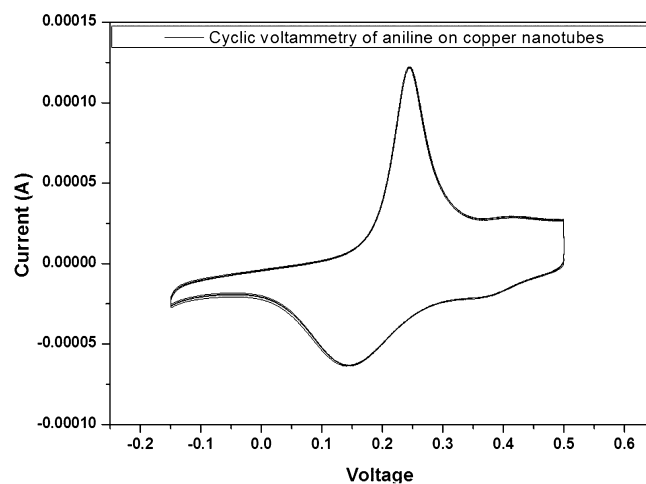


Fig. 1. Cyclic voltammetry of electro polymerization of conductive polymer polyaniline on CuNTs electrode in the potential range of -0.2 V to 0.6 V at the scan rate of 50 mVs^{-1} .

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