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Short communication

Comparison of performances of bioanodes modified with graphene oxide and graphene–platinum hybrid nanoparticles

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ABSTRACT

The performances of graphene oxide (GO) and graphene–platinum hybrid nanoparticles (Gr-Pt hybrid NPs) were compared for biofuel cell (BFC) systems. This is the first study that constitutes these nanomaterials in BFC systems. For this purpose, fabricated bioanodes were combined with laccase modified biocathode in a single cell membraneless BFC. Power and current densities of these systems were calculated as 2.40 μW cm^{-2} and 211.90 μA cm^{-2} for GO based BFC and 4.88 μW cm^{-2} and 246.82 μA cm^{-2}, for Gr-Pt hybrid NPs based BFC. As a result, a pioneer study which demonstrates the effective performances of combination of graphene with Pt was conducted.

1. Introduction

Since its discovery in 2004, graphene and graphene based nanomaterials have been extensively used in electrochemical systems due to excellent conductivity, electrocatalytic activity, high thermal conductivity, excellent mechanical flexibility and good biocompatibility [1–11]. The reason of electrocatalytic activity of this material is explained by the presence of oxygen containing groups on graphene surface which is believed to enhance the electron transfer rate [5,12].

On the other hand, hybrid nanoparticles (NPs) can be defined as the combination of at least two materials in terms of structural form. In electroanalytical applications, combination of these structures may sometimes enhance the electron transfer rate hence provides more suitable environment in terms of immobilization process [7,13,14]. Xu et al. used ethylene glycol (EG) and suitable metallic reagents to prepare graphene–metal NPs [15]. They demonstrated that, the water–EG mixture containing graphene oxide (GO) sheets was much more stable without metallic salts, and no obvious structural changes were observed on individual GO sheets in that medium. On the other hand, when metal particles like platinum (Pt) was added onto GO sheets, the stable system was broken and Pt can be easily reduced in the water–EG solution to form metallic Pt NPs. Then these resulting metallic NPs play a pivotal role in catalytic reduction of GO with EG. Additionally, these NPs attach onto the graphene sheets through van der Waals interactions and prevent the aggregation and restacking of the reduced GO during the reduction process. As a result, graphene-metallic particle composites were formed. Following this procedure, we manage to demonstrate that combination of graphene with Pt shows better electrocatalytic activity compared to GO in electrochemical genosensors [7]. After the observation of this effect, we decided to prepare a biofuel cell (BFC) by fabricating two different bioanodes with the usage of GO and graphene–platinum hybrid NPs (Gr–Pt hybrid NPs) and compared their outcomes in terms of current and power density values. So the present work constitutes the first usage of these graphene based nanomaterials in BFC systems. For the fabrication of bioanodes, proper amounts of GO or Gr–Pt hybrid NPs were incorporated into composite glassy carbon paste electrode (GCPE) which contained glucose oxidase (GOx) enzyme. For biocathode, laccase (Lac) included GCPE was prepared. Then these two electrodes were combined in a single cell, and a membraneless BFC was obtained.

2. Experimental

2.1. Chemical reagents

Glassy carbon micro powder (GC, %99.95, 2–12 μm), graphite powder, mineral oil, Lac, GOx, p-benzoquinone (BQ), potassium dihydrogen phosphate (KH_2PO_4), sodium hydroxide (NaOH), sodium nitrate

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($NaNO_3$), hydrogen peroxide (H_2O_2), EG and chloroplatinic acid hexahydrate (H_2PtCl_6) were purchased from Sigma-Aldrich. D+ Glucose monohydrate and sulfuric acid (H_2SO_4, 95–97%) were obtained from Merck. Ultrapure water was used in all solutions. All chemicals were of analytical grade and were used without further purification.

2.2. Instrumentation

Current-voltage measurements of BFC were conducted with Autoranging Mini Multimeter (MN16A). pH measurements were made with Thermo Electron Corporation. IKA® RH basic 2 hotplate was used to synthesize the graphene based NPs.

2.3. Fabrication of GO NPs and Gr–Pt hybrid NPs

GO was prepared by modifying the Hummers–Offeman method [16]. Briefly, 1 g of graphite powder was added into 23 mL 98% H_2SO_4 solution and stirred at room temperature for 24 h. After that, 100 mg of $NaNO_3$ was added in to the mixture and stirred for 30 min. Then, 46 mL water was added into the above mixture for a period of 25 min. Finally, 140 mL of water and 10 mL of 30% H_2O_2 were added into the mixture. The GO in the resulting mixture was removed by centrifugation.

Gr–Pt hybrid NPs were synthesized from GO powder. For this purpose, 10 mg portion of GO powder was dispersed in 10 mL of water by sonication for 1 h [15,17,18]. Then 20 mL of EG and 0.5 mL of 0.01 M H_2PtCl_6 were added to the solution and stirred for 30 min. After that, the mixture was put in an oil bath and heated at 100 °C for 6 h with magnetic stirring. The Gr–Pt hybrid NPs were centrifuged in order to be separated from the EG solution and washed with deionized water five times.

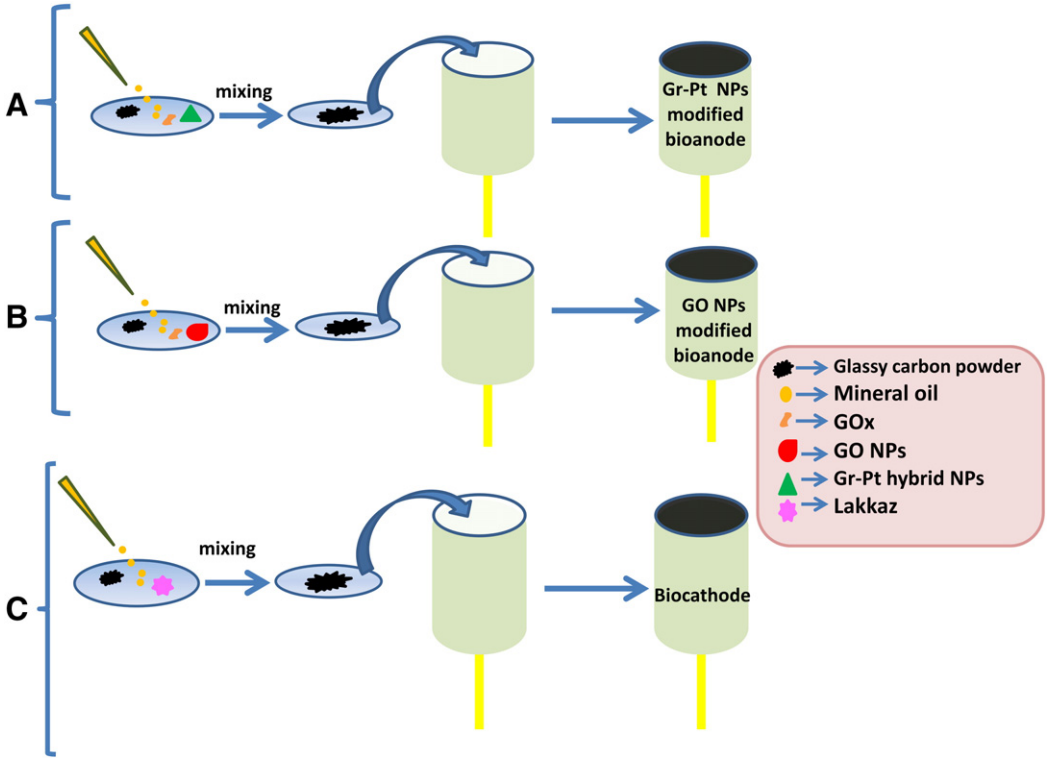
The resulting products were dried in a vacuum oven at 60 °C 1 for 12 h [15]. Finally, the prepared Gr–Pt hybrid NPs and GO were dispersed to 10 mg mL^{-1} in water by ultrasonication and stored at 4 °C when not used [7].

2.4. Electrode preparation

In this study, plane, GO and Gr–Pt hybrid NPs modified bioanodes were prepared and combined with biocathode. For the preparation of plane bioanode; GCPE was prepared by hand mixing of GC micro powder, GOx enzyme and mineral oil in the mass ratio of 66:14:20. For graphene based bioanodes, 6 μL of GO NPs or Gr–Pt hybrid NPs (10 mg/mL dispersed in ultrapure water) was incorporated to GCPE and GOx enzyme [7]. On the other hand, biocathode electrode was prepared by hand mixing of GC micro powder, Lac enzyme and mineral oil in 66:14:20 mass ratio where all the resulting pastes were then packed firmly into Teflon rod's electrode cavity as shown in Scheme 1. Finally electrode surfaces were polished by using a weighing paper. Then, GCPE/GOx|Glucose,BQ,O_2|Lac/GCPE; GCPE/GO/GOx|Glucose,BQ,O_2|Lac/GCPE and GCPE/Gr–Pt/GOx|Glucose,BQ,O_2|Lac/GCPE BFC systems were obtained.

2.5. Biofuel cell measurements

The GCPE/GOx|Glucose,BQ, GCPE/GO/GOx|Glucose,BQ or GCPE/Gr–Pt/GOx|Glucose,BQ bioanode and GCPE/Lac|O_2 biocathode were utilized in a membraneless single cell BFC and current-voltage measurements were measured by a multimeter. Bioanode half cell reaction based on oxidation of glucose to gluconolactone where BQ was used as mediator. At the biocathode, Lac enzyme reduced O_2 molecule to H_2O. Current (I) values of the BFC were measured while different resistances (R) (from 1 Ω to 10 MΩ) were inserted to the circuit in order to calculate cell voltage (V_{cell}) (Vcell = I × R) and power (P) (P = Vcell × I). The current density (i) (i = I/A) and power density (W = P/A) values were obtained by dividing current and power values by surface area of the electrode (A = 0.126 cm^2).



Scheme 1. Preparation of A) bioanode with Gr–Pt hybrid NPs, B) bioanode with GO NPs and C) biocathode.