



Synthesis and characterization of graphene-cobalt phthalocyanines and graphene-iron phthalocyanine composites and their enzymatic fuel cell application



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ARTICLE INFO

Article history:

Received 11 February 2014
Accepted 5 September 2014
Available online 26 September 2014

Keywords:

Graphene
Cobalt phthalocyanine
Iron phthalocyanine
Glucose
Oxygen reduction reaction
Enzymatic fuel cell

ABSTRACT

We prepared graphene (GR)-cobalt phthalocyanine (CoPc) and GR-iron phthalocyanine (FePc) composites by simple and facile chemical reduction method for enzymatic fuel cell (EFC) applications. The successful formation of the composites was confirmed by scanning electron microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDX), X-ray diffraction and electrochemical methods. The as-prepared composites were used for the construction of glucose/O₂ EFC. The anode of the EFC was prepared by immobilizing glucose oxidase (GOx) at the GR-CoPc composite modified glassy carbon electrode (GCE). GCE/GR-CoPc/GOx exhibited excellent electrocatalytic ability towards oxidation of glucose. In addition, the modified electrode showed appreciable stability, repeatability and reproducibility. GR-FePc composite exhibited superior electrocatalytic ability towards oxygen reduction reaction (ORR). A membraneless glucose/O₂ EFC has been fabricated employing GCE/GR-CoPc/GOx and GCE/GR-FePc as anode and cathode respectively. The fabricated EFC offered a maximum power density of 23 μW cm⁻² which is comparable with the previously reported EFCs and it exhibited appreciable stability and repeatability. From this study, we infer that GR based MPcs have great potential for the fabrication of EFCs.

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1. Introduction

Metal phthalocyanines (MPcs) are two dimensional (2D) organic macrocyclic molecular catalysts (MN₄) with metal atoms at the center [1,2]. MPcs have unique physicochemical properties, outstanding electronic and optical properties and structurally analogs to porphyrins [3,4]. Owing to the rich redox chemistry, MPcs are widely used as mediators or electrode modifiers for the immobilization of enzymes such as glucose oxidase (GOx) and are used for biosensor and energy device applications [5]. However, one major issue of physically adsorbed MPcs on electrode surface is their poor stability and usually peel off from the electrode surface [5]. In addition, MPcs have low electrical conductivity, which reduces the electronic transfer rate at the electrode surface resulting in poor electrochemical activity. Therefore, MPcs require suitable support to harvest their excellent electrochemical properties [6]. Conducting

polymers such as polypyrrole, polythiophene or polyaniline are utilized as active supporting materials through electrochemical copolymerization at the electrode surface [7–10]. Due to their large surface area, excellent electronic and mechanical properties, carbon nanotubes (CNTs) are proved to be a versatile support to stabilize MPcs [11,12]. Graphene (GR), a single layer of graphite is one of the most investigated nanomaterials of carbon in recent times attributed to its excellent electronic and electrocatalytic properties [13,14]. All over the past years, GR is proved to be an excellent supporting mat to stabilize various electrocatalysts such as metal nanoparticles [15], metal oxides [16,17] and polymers [18]. Recently, a handful of reports are commenced to utilize GR as supporting mat to stabilize MPcs through layer by layer [19], self-assembly [20] and adsorption/intercalation methods [21]. Herein, we are describing a simple and elegant chemical reduction method to stabilize MPcs (cobalt phthalocyanine (CoPc) and iron phthalocyanine (FePc)) on GR sheets. The formation of the GR-MPcs nanocomposites was characterized by various methods and the nanocomposites were utilized for the fabrication of enzymatic fuel cell applications.

World population has reached 7.2 billion by 2014, while the world population is estimated to be 10.5 billion by 2050. By 2050,

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one-third of the world's energy need to come from solar, wind, fuel cells and other renewable resources [22,23]. Climate change, population growth, and fossil fuel depletion mean that renewable energy devices will need to play a superior role in the future than they do today [24]. Enzymatic fuel cells (EFCs) are one of the promising future alternative sources of renewable energy, in which enzymes acts as biocatalysts to extract energy from renewable fuels such as carbohydrates (glucose, sucrose and fructose) and alcohol (ethanol, methanol, glycerol) [25,26]. EFCs are associated with important advantages such as manufacturability, simplicity, portability and specificity of enzymes [27,28]. Unlike conventional fuel cells which are usually require expensive metals as catalysts, EFCs require comparatively cheaper enzymes as catalysts [29]. The main shortcomings of the EFCs are low power output, poor stability and short enzyme lifetimes. Glucose/O₂ enzymatic fuel cells are the most studied EFCs in last 50 years in which glucose is bio-catalytically oxidized to gluconolactone by glucose oxidase (GOx) at the anode, while oxygen is reduced to water at the cathode [30,31]. The preparation of suitable matrix with good electrical conductivity, stability, and antifouling property to immobilize GOx at the electrode surface is one of the most important tasks in the fabrication of Glucose/O₂ EFCs [32]. The major limitations in immobilizing GOx are poor electrical communication between the active site of the GOx and the electrode surface and enzyme leaching. Different approaches are reported for the immobilization of GOx to improve the electron transfer between GOx and electrodes that include carbon nanotubes [33], metal oxides [34], metal nanoparticles [35], graphene [36], conducting polymers [37] and sol-gel matrix [38]. More specifically, the use of carbon nanomaterials based modified electrodes are widespread owing to their low background noise, large potential window, low cost and easy preparation protocols [39,40]. Herein, we prepared GR supported CoPc nanocomposite and explored it as an ideal matrix for the immobilization of GOx. Electrochemical studies revealed that GR-CoPc is a suitable matrix to attain direct electron transfer between GOx and electrode surface. The GR-CoPc composite modified electrode possesses high surface area, good electrical conductivity and offer high stability. Moreover, MPcs are the best alternative to precious platinum metal catalysts for the oxygen reduction reaction (ORR) [41,42]. Also, we prepared GR-FePc nanocomposite by simple chemical reduction approach and the composite exhibited superior ORR ability and therefore we employed it as cathode for the construction of EFC.

The main aim of the present work is to connect the excellent physicochemical properties of GR with rich redox chemistry of MPcs through simple and facile chemical method and explore their application towards fabrication of EFC. The chemical reduction synthesis of MPcs and electrode preparation method involve simple and easily adoptable procedures. We have used graphene oxide (GO), an oxygenated derivative of graphene as precursor for the preparation of GR-CoPc and GR-FePc composites due to its significant advantages such as low cost and simple production from graphite, easy processing in aqueous dispersion and available sites for functionalization [43,44]. To the best of our knowledge, this is the first report employing GR based MPcs for the EFC application. We believe that our report will bring considerable interest in the preparation of GR based MPcs towards the development of highly efficient EFCs.

2. Experimental

2.1. Materials

Graphite (powder, <20 μm), cobalt (II) phthalocyanines (β-form, Dye content 97%), iron (II) phthalocyanines (Dye content ~90%), glucose oxidase (GOx, type x-s from *Aspergillus Niger*), D-

(+)-glucose (≥99.5%) and hydrazine monohydrate were purchased from sigma-Aldrich and used as received. All the other reagents were purchased from sigma-Aldrich and used without further purification. The supporting electrolyte used for the electrochemical studies was 0.05 M Phosphate buffer solution (PBS), prepared using NaH₂PO₄ and Na₂HPO₄, while the pH was adjusted to get the desired pH using either H₂SO₄ or NaOH. Prior to each experiment, the electrolyte solutions were deoxygenated with pre-purified N₂ for 15 min unless otherwise specified. Glucose stock solution was prepared in PBS (pH 7) and kept aside for one day to attain mutarotation.

2.2. Instrumentation

The electrochemical measurements (Cyclic voltammetry and linear sweep voltammetry) were carried out using CHI 611A electrochemical work station (CH Instruments, Inc. (U.S.A)) supplied by Anatech Company Ltd., Taiwan. Electrochemical studies were performed in a conventional three electrode cell using BAS GCE as a working electrode (area 0.071 cm²), Ag/AgCl (saturated KCl) as a reference electrode and Pt wire as a counter electrode. Ag/Ag⁺ (AgNO₃) filled with acetonitrile containing 0.1 M tetrabutylammonium perchlorate (TBAP) has been used as the reference electrode for reactions involving non-aqueous solvents. Scanning electron microscopy (SEM) studies were performed using Hitachi S-3000H scanning electron microscope (SEMTECH Solutions, USA). Energy-dispersive X-ray (EDX) spectra were recorded using HORIBA EMAX X-ACT, Sensor + 24 V = 16 W, resolutions at 5.9 keV (Horiba Productx-act horiba, SN: 55267). Electrochemical impedance spectroscopy (EIS) studies were carried out using EIM6ex ZAHNER (Kroanch, Germany). EIS experiments were performed in PBS (pH 7) containing 5 mM Fe(CN)₆^{3-/4-} with applied AC voltage 5 mV and frequency from 0.1 Hz to 100 kHz. UV-Visible absorption spectroscopic measurements were carried out using Hitachi U-3300 spectrophotometer (EquipNet, Inc., USA). Powder X-ray diffraction (XRD) studies were carried out using XPERT-PRO (PANalytical B.V., The Netherlands) diffractometer (Cu Kα radiation, $k = 1.54 \text{ \AA}$). Rotating disc electrode (area = 0.284 cm²) experiments were carried out with analytical rotator AFMSRX (PINE instruments, USA).

2.3. Methods

2.3.1. Fabrication of anode

GR-CoPc composite was prepared by simple chemical reduction approach. Briefly, graphite oxide was prepared from graphite by modified Hummers method [45] and exfoliated to graphene oxide (GO) via ultrasonic agitation followed by centrifugation at 3000 RPM for 30 min 10 ml CoPc dispersion (0.01 M in DMF) was added to GO dispersion (0.5 mg mL⁻¹) and the resulting mixture was stirred for 1 h. Hydrazine monohydrate (0.5 ml) was added to the mixture and refluxed at 155 °C for 12 h. After completion of the reaction, the product was cooled and filtered. GR-CoPc composite was washed with copious amount of water and ethanol and dried. Finally, it was redispersed in DMF (1 mg mL⁻¹) and used for the preparation of modified electrodes. GCE surface was polished with 0.05 μm alumina slurry using a Buehler polishing kit, then washed with water, ultrasonicated for 4 min and dried. And then, 5 μL of GR-CoPc composite was drop cast onto the GCE surface and dried at ambient conditions. Afterwards, 7 μL of GOx (10 mg mL⁻¹) was drop cast onto the GR-CoPc modified GCE and dried at room temperature. Then the resulting modified electrode, GCE/GR-CoPc/GOx was gently washed with water to remove loosely adsorbed GOx and used for the electrochemical experiments. For comparison, GR, CoPc and GR-CoPc modified GCEs were also prepared accordingly.

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