



# Fabrication of polyaniline/graphene oxide composite for graphite felt electrode modification and its performance in the bioelectrochemical system



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## ABSTRACT

In order to overcome the unsatisfactory stability of polyaniline (PANI) modified graphite felt (GF) electrode, graphene oxide (GO) was introduced into PANi/GO composite for GF modification in this study. PANi/GO composite was fabricated via a convenient and low-cost electropolymerization method. Scanning electron microscope, Raman spectrum and Fourier transform infrared spectrum demonstrated that PANi/GO composite was successfully coated onto the GF surface. The electrochemical activity, pH dependence and stability of the PANi/GO modified GF electrode were significantly improved after modification, as was indicated by cyclic voltammetry and chronoamperometric tests. The application of PANi/GO modified GF electrode in a bioelectrochemical system (BES) confirmed its superior electrogenesis performance, in terms of much higher maximum power density achieved. The improved biocompatibility, electrochemical activity and stability suggested that PANi/GO modified GF electrode had a promising potential in the BES application for the wastewater treatment.

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## 1. Introduction

Bioelectrochemical system (BES), known as a novel and renewable biotechnology for wastewater treatment, has drawn much attention in the past decades. However, the low power density of BES hinders its practical applications [1]. In order to increase power generation, BES architecture, solution chemistry and electrode materials have been elaborated [2]. Significant improvements in terms of power generation could be realized through the modification of the electrode materials [3]. Generally, carbonaceous materials, such as graphite felt (GF), have been extensively used as electrodes in BES, due to their low cost, large specific surface area, good electrical conductivity, high mechanical strength and limited corrosion sensitivity [4]. Nevertheless, the hydrophobic surface of GF is not beneficial for bacterial attachment and biofilm formation [5]. In addition, limited electrochemical activity needs to be improved for higher energy efficiency. In general, efforts in terms of GF modification have been made to improve the electrochemical properties of GF electrode for its application in BES.

Polyaniline (PANI), known as a famous conducting polymer, has been widely employed as active electrode modifier due to its low

fabrication cost, excellent electrochemical activity, good biocompatibility and unique acid–base doping/dedoping property [6]. For instance, Li et al. [7] reported that PANi could be suitable for both abiotic cathode and biocathode in BES, with greatly enhanced power densities. In addition, Ghasemi et al. [8] reported that microorganism adhesion on the electrode was significantly increased after the modification of the electrode by PANi. However, the conductivity and electrochemical activity of PANi are strongly suppressed by high pH value, especially when pH above 6 [9]. Nevertheless, the neutral to slightly alkaline condition is required for the development and maintenance of the microorganism community on the BES bioanode or biocathode. Previous literatures suggested that introducing pH functional groups or excellent conductive dopants into PANi chain could be an available way to improve the electrochemical activity of PANi in electrode modification [9,10]. What's more, the poor cycle life of PANi also limited its real application [11]. Doping support materials with outstanding electrical, chemical, and mechanical properties into PANi fibers should be a promising way to improve the stability of PANi.

Currently, graphene (GE) and graphene-base materials have drawn much attention in electrode and supercapacitor applications due to their impressive mechanical and electrochemical properties [12–14]. Importantly, graphene oxide (GO), as the most familiar graphene-base material, can be made in large quantities

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with less cost than GE or carbon nanotubes (CNTs) via chemical method [15]. Unlike GE, the nano-scale GO is covered by hydrophilic oxygen functional groups [16]. As a result, it can be easily dispersed in aqueous solution, which may be beneficial for interaction with a particular polymer, such as PANi. Meanwhile, GO exhibited favorable biocompatibility due to its unique structure properties, exactly meeting the requirement of BES bioanode or biocathode [17]. However, GO nanosheets suffer from the problem that they are difficult to deposit onto a substrate as uniform film [18]. In addition, its practical application as electrode material or electrode modifier alone is limited due to its unsatisfactory conductivity.

Considering the unique properties of PANi and GO, it can be inferred that PANi/GO composite materials without the drawback of single material but with both high electrochemical performance and good stability could be obtained by developing their synergistic composite materials. Recently, PANi and GO composite has been synthesized successfully through chemical methods and applied as supercapacitor materials [11]. The electrical conductivity, specific capacitance and stability of the composite were higher than each individual component, indicating a synergistic effect between PANi and GO. Herein GO not only serves as the electrochemical and mechanical support material, but also provides a large surface for the well-dispersed deposition of nanoscale PANi particles [19]. Considering the coverage of hydrophilic oxygen functional groups on the GO surface, it can be assumed that the pH dependence of the PANi/GO composite could be simultaneously improved. Therefore, the performance of BES electrode could be possibly improved by using PANi/GO composite as electrode modifier. An attempt has been made by Lv et al. [20] to prepare polypyrrole (PPy) and GO hybrid materials for BES electrode modification. Combination of PANi and GE for bioanode modification has also been reported [21]. Significant improvements have been observed in these studies, suggesting that the combination of polymers and graphene-base materials could exactly meet the requirements of the BES electrode modification. However, to the best of our knowledge, the modification of GF electrode based on the fabrication of PANi/GO composite via an electrochemical method has not been reported in the previous studies. Moreover, the performance of the PANi/GO modified GF electrode in terms of stability and catalytic activity could be improved via a synergistic effect between PANi and GO. In addition, the systematic investigations in terms of morphology, structure, biocompatibility, electrochemical activity and electrochemical stability are still absent and the mechanisms involved are not fully understood.

In the present study, the PANi/GO modified GF electrode with high electrochemical activity was firstly prepared via a convenient and low-cost electrochemical method. This rapid-hybrid polymerization was quite simple without the need of vast apparatus or the assistance of cooling or heating. Characterization of the modified electrodes with contact angle, scanning electron microscopy (SEM), Raman spectrum, Fourier transform infrared spectrum (FT-IR) and cyclic voltammetry (CV) was conducted. Furthermore, the pH dependence and stability of the modified electrode were evaluated. The power performances of BES using different anode materials (i.e., blank GF electrode, PANi modified GF electrode, and PANi/GO modified GF electrode) were also compared.

## 2. Materials and methods

### 2.1. Electrode modification

Polyacrylonitrile-based graphite felts (Chemshine Carbon CO., China) were cut into pieces of  $\varnothing$  75 mm  $\times$  3 mm (projected surface area 44 cm<sup>2</sup>) before modification. Then all the graphite felts were thoroughly cleaned in a hot H<sub>2</sub>O<sub>2</sub> (10%, 90 °C) solution for 1 h in

order to remove impurities, followed by rinsing with deionized water for 30 min and drying in oven at 70 °C for 5 h. 300 mesh natural graphite powders (Sinopharm Chemical Reagent Co., China) were oxidized to graphite oxide using Hummers method [22]. The as-prepared graphite oxide was added into deionized water with a concentration of 1.5 mg mL<sup>-1</sup>. Then the mixture was treated by ultrasonic for 80 min to obtain a homogeneous GO suspension. Aniline distilled under reduced pressure and 37% HCl were then added into this GO suspension at concentrations of 0.05 M and 1.0 M, respectively. At last, a facile one-step electrodeposition method was adopted for GF modification, i.e., GF was soaked into the electrolyte described as above and was applied with a constant potential of 0.9 V for 30 min. The prepared GF was dried in oven at 70 °C for 12 h and marked as GF + PANi/GO. For comparisons, the electrode modification with PANi alone was also conducted likewise. PANi modified GF electrode (marked as GF + PANi) was prepared by electropolymerization of 0.05 M aniline in the presence of 1.0 M HCl, with an identical total charge density passed. The GF treated as the above process in the absence of PANi and GO was marked as GF.

### 2.2. Characterization of the modified electrode

The hydrophobicity of electrode before and after modification was analyzed with Milli-Q water by contact angle tester (KRUSS, DSA30, Germany). The surface microstructure of the modified electrodes was characterized by SEM (JEOL, JSM-6380, Japan) at an accelerating voltage of 30 kV. The nitrogen absorption measurement was carried out by using a Brunauer–Emmett–Teller (BET) apparatus (Micromeritics, ASAP 2020, USA) at liquid nitrogen temperature (−196 °C). Before BET analysis, the GF and modified GF electrodes were cut into pieces. Raman spectrum was recorded from 200 to 2000 cm<sup>-1</sup> with an integrated confocal Raman Microscopy System (LabRAM Aramis, HORIBA Jobin Yvon, France) using a 532 nm laser beam. FT-IR spectrum was obtained with a FT-IR spectrometer (Thermo Scientific, Nicolet iS10, USA). All electrochemical characterizations were conducted with a potentiostat (Bio-Logic Science Instruments, VMP3, France) and performed in a standard three-electrode system, where the modified electrode (20 mm  $\times$  10 mm) served as the working electrodes, a Pt electrode and Ag/AgCl electrode (assumed + 0.197 V vs. SHE) as counter electrode and reference electrode, respectively. The electrochemical activity of the modified electrodes was studied by cyclic voltammetry (CV) measurements at a scan rate of 5 mV s<sup>-1</sup> with the range of −0.2 to 0.8 V in 1.0 M H<sub>2</sub>SO<sub>4</sub> solutions. To evaluate the influence of pH on the electrochemical activity of the modified electrodes, the following CV tests were carried out in the solutions of 0.3 M Na<sub>2</sub>SO<sub>4</sub> with different pH values, i.e., 2.0, 4.0, 6.0 and 8.0. Before the formal test, the electrodes were soaked in the aforementioned solutions for 1 h and pretreated for three cycles in the corresponding solution. Then the forth cycle was come into use in this work. During the test, the electrolyte solution was stirred by a magnetic stirrer in order to prevent a significant change of pH around the electrode. Chronoamperometric (CA) experiments were conducted to explore the stability of modified electrodes.

### 2.3. BES reactor set-up and operation

Three two-chamber BES reactors consisting of two cylindrical compartments with equal dimensions ( $\varnothing$  80 mm  $\times$  50 mm) were operated simultaneously in parallel. Cation exchange membranes (Membrane International, Ultrex CMI-7000, USA) were settled to separate the two compartments. The effective empty volume for each compartment was 250 mL. The modified (or unmodified) graphite felts were used as the anodes and bare graphite felts were used as the cathodes, with dimensions of  $\varnothing$  75 mm  $\times$  3 mm. Ti

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