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Bimetallic $Fe_{15}Pt_{85}$ nanoparticles as an effective anodic electrocatalyst for non-enzymatic glucose/oxygen biofuel cell

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ABSTRACT

The present work describes an abiotic energy harvesting strategy from electrocatalytic glucose oxidation based on bimetallic FePt nanoparticles (NPs) with a unique onset oxidation potential of −0.63 V *vs.* Ag/AgCl and a maximum current density of 3.7 mA cm^{-2} at the physiological-like condition (pH 7.4). At first, the effect of Fe proportion and particle size on the electrocatalytic activity is investigated and it is found that the small size of $Fe_{15}Pt_{85}$ have the highest activity toward glucose oxidation. For the proposed abiotic system the cathode material is constructed from nitrogen doped graphene decorated with Pt NPs. The anode material is prepared via a simple one-step co-precipitation method and the cathode material was synthesized through a one-pot electrochemical synthesis route. The morphology, crystal structure and chemical composition of prepared nanostructure materials are characterized by various techniques. Based on the polarization profile and power density plot the designed glucose biofuel cell has an open-circuit potential of 0.64 V and provides a maximum power density of 95 μW cm^{-2} at a cell voltage of 0.44 V. Such abiotic glucose fuel cells have a great promise to be optimized, miniaturized to power bioimplantable devices without utilizing any complex system.

1. Introduction

The producing electricity from biomasses as the clean and renewable energy sources has attracted enormous research attention in the past few decades [1]. Amongst the various kinds of biomasses glucose (GL, $C_6H_{12}O_6$), as a most viable source in body tissues and environments, possess a theoretical high energy density of 4430 $Whkg^{-1}$ (based on a thermodynamic calculation) for total oxidation to CO_2 and H_2O with 24 electron transfers [2]. Utilizing the GL/O_2 biofuel cell (BFC) is an important strategy to obtain clean electrical energy that could replace the lithium batteries in the future. Generally, based on the catalysts that are being used to enable the electrode reactions, there are three main types of GL BFC available [3], enzymatic, microbial, and abiotic (non-enzymatic). Although the enzymatic and microbial GL/O_2 BFCs have shown excellent selectivity and offer higher power densities compared to the abiotic counterparts. But, their requirement for the multifaceted conditions and their short lifetime have limited the long-term implantable applications of the GL/O_2 BFCs [3,4]. Furthermore, costly and prolong process of enzyme purification as well as the frequent need to add mediators are drawbacks of enzymatic electrodes. Therefore, interests in abiotic catalysts as a long-term stable alternative have recently been renewed.

Platinum and carbon supported platinum catalysts (Pt/C) have shown strong activity, long-term stability and biocompatibility for catalytic applications. However, these materials suffer from many limitations such as prohibitive cost, slow oxidation kinetics of fuels and deactivation due to the formation of unidentified intermediates during the fuel oxidation [5]. To overcome these obstacles, three major strategies have been used namely (a) decreasing the Pt content in the catalyst through alloying Pt with other inexpensive metals such as Fe, Ni, and Cu; (b) developing other non-Pt noble metal NPs or non-noble metal catalysts; and (c) designing carbon nanostructures as catalyst supports to enhance the catalytic activity [6,7]. These catalysts have mainly been performed at high temperature (> 100 °C) condition and at the acidic or basic solutions [8,9] where, the operating conditions that are greatly different from physiological environments. In the

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past few years glucose BFCs that can be operated at the natural-like condition have been developed based on either various types of noble metal nanostructures or different carbon structures supported Pt [10–14]. Among the various types of Pt-based bimetallic structures, FePt NPs have been very attractive due to its biocompatibility, outstanding magnetic properties [15–17], catalytic performances for oxygen reduction [18], as well as oxidation of formic acid and methanol [19–21]. However, to the best of our knowledge, there have been no revisions on GL electrooxidation catalyzed by FePt NPs.

The physical, chemical and structural properties of supporting materials are factors that impact the distribution and stabilization of the catalyst materials as well as the diffusion kinetics of reactants and products [7]. Among various carbon-based materials, graphene (Gr) appears to be a good candidate as catalyst support due to its superior electrical conductivity, excellent mechanical flexibility, chemical stability, remarkable thermal conductivity, high surface-to-volume ratio and monolayer thickness [22–24]. The electronic properties and as a consequence, electrocatalytic behaviour of Gr can be modulated via doping with heteroatoms, particularly nitrogen, which can significantly enhance electronic and optical properties of Gr due to the π-delocalization [25]. In addition, the experimental evidences and quantum mechanical calculations have indicated that substitution of nitrogen atoms in the carbon frameworks of electrodes; especially in the form of pyridinic and graphitic nitrogen significantly enhances their electrocatalytic activities for oxygen reduction reaction (ORR) [26]. A number of methods have been reported for preparation of Gr and N-Gr decorated with Pt NPs for fuel cell applications [27–30]. Those methods are usually costly, convoluted and involve several steps such as Gr synthesis, N-doping process, Pt synthesis and decorating process. Yet, there are challenges for implementing efficient methods to synthesis heteroatom-doped-Gr and decorating them with metal NPs and bimetallic FePt NPs with high electrocatalytic activities in natural-like environment. Thus, development of novel facile methods to synthesis N-Gr decorated with Pt NPs and FePt is highly desirable and commercially and technologically important.

Here, for the first time we demonstrate a non-enzymatic GL BFC in the neutral solution. FePt NPs was prepared through a simple one-step co-precipitation method and microemulsion processing and was used as anode material. The electrocatalytic ability and durability of prepared composite toward ORR and oxidation of glucose are examined and compared with a commercial Pt/C (10% Pt). The morphology and crystallographic structures of the synthesized FePt NPs were characterized with X-ray diffraction (XRD), Scanning electron microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDX) as well as Transmission and scanning transmission electron microscopy (TEM/STEM). N-doped graphene decorated with Pt NPs (Pt/N-Gr) is used as cathode material and prepare through a direct one-pot electrosynthesis as described in our previous work [31].

2. Experimental section

2.1. Materials and instruments

H_2PtCl_4, $FeCl_2.xH_2O$, oleic acid, hydrazine hydrate (%85) and platinum on activated carbon with 10% of Pt loading (Pt/C 10%) were purchased from Merck. Triton X-114 was obtained from ACROS. The graphite rod, graphite powder, acetonitrile, lithium perchlorate, phosphate buffer salts, sulfuric acid solution, potassium hydroxide were purchased from Merck. The phosphate buffer saline (PBS) solution electrolyte was prepared from commercial resources which were obtained from Merck. The platinum wire, which was used as counter electrode and mass source for production of platinum NPs, was purchased from Metrohm. The electrochemical synthesis of Pt/N-Gr and all electrochemical studies including cyclic voltammetry, linear sweep voltammetry with rotating electrode and amperometry were carried out using a μAUTOLAB modular electrochemical system (ECO Chemie, Ultrecht, The Netherlands) equipped with a PGSTAT type III module driven by GPES software in conjunction with a conventional three-electrode system (an Ag/AgCl/3 M KCl and platinum wire as reference and counter electrode, respectively) and a personal computer for data acquisition and processing. The glassy carbon (GC) electrodes with diameter of 2 mm were used as electrochemical platform for catalyst support. The modified GCs with Pt/N-Gr and Pt/C, 5 μL of dispersed solution of the desired materials (5 mg ml^{-1} in ethanol) was cast on the electrode surface and dried at room temperature. In order to activate the prepared electrodes, they were cycled in 0.5 M H_2SO_4 from 0.0 to 1.2 V for 20 times, internally. To achieve nitrogen or oxygen saturated solutions, the electrolyte solution was purged by nitrogen or oxygen gas for 5 min before each experiment. Cyclic voltammograms was recorded by scan rate of 0.02 Vs^{-1} and all experiments were done at room temperature ($\sim$298 K).

2.2. Structural characterization

SEM images and EDX were obtained with a MIRA3 TESCAN HV: 20.0 KV. XPS was performed using an Omicron Nanotechnology equipped with an EA 125 Energy Analyzer and a DAR 400 X-Ray source. TEM/STEM images were achieved using a FEI Tecnai Osiris Scanning Transmission Electron Microscope (200 KV). XRD was performed using a Bruker D8 Advance differactometer equipped with a copper source and a General Area Detector Diffraction System (GADDS).

2.3. Synthesis of FePt nanoparticles

Bimetallic FePt NPs were synthesized using co-precipitation method and microemulsion processing, which was described elsewhere [32], with major modifications (Fig. 1A). Aqueous metal salts of Pt and Fe (in minimum amount of water) were mixed with a nonionic surfactant (Triton X-114, $C_{30}H_{54}O_9$) in n-hexane to obtain microemulsions involved of aqueous nanodroplets. The metal salts in the microemulsion were reduced to FePt NPs using hydrazine. In a typical synthesis, 0.022 mole Triton X-114 was added to 10 mL n-hexane and dissolved by agitating the mixture for 10 min at 30 °C. In a separate glass 0.002-0.045 mmol of $FeCl_3$ and 0.01 mmol of K_2PtCl_4 to obtain $Fe_{15}Pt_{85}$, $Fe_{30}Pt_{70}$, $Fe_{50}Pt_{50}$ and $Fe_{85}Pt_{15}$ were dissolved in 0.5 mL of deionized water (to adjust the particle-size of FePt alloy, the amount of water was varied from 0.4 to 1.3 mL). The two microemulsions were mixed with each other and sonicated for 30 min. After that, 1.5 mL of n-butanol was used as a co-surfactant to improve particle shape. Upon adding 0.15 mL hydrazine to the magnetically stirred microemulsion, maintained at 30 °C, the initially transparent yellow solution turned into a dark dispersion. After 45 min, 0.35 mmol oleic acid was added to the microemulsion and aged for 10 min. The NPs were separated from the solution using an external magnetic field or centrifugation followed by washing with ethanol for three times. The NPs were re-dispersed in ethanol for further applications.

2.4. Synthesis of Pt/N-Gr nanostructure

Pt/N-Gr was synthesized through the method described in our previous work [31]. In brief, to produce the Pt/N-Gr nanohybride, potential cycling is performed over a potential window of $\pm$3.0 V at scan rate of 0.3 Vs^{-1} in the pure acetonitrile containing 0.5 M $LiClO_4$ as a supporting electrolyte. A graphite rod (with diameter of