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Diameter effect of electrospun carbon fiber support for the catalysis of Pt nanoparticles in glucose oxidation

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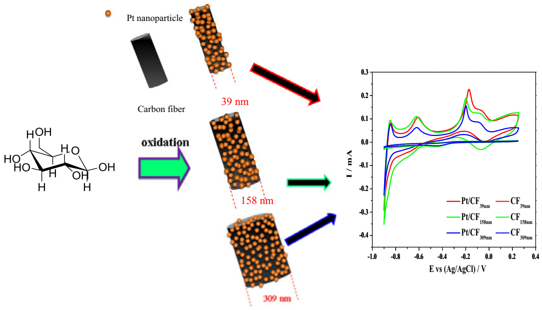
HIGHLIGHTS

- Electrospun CFs are successfully used as Pt catalyst support for glucose oxidation.
- CF_{39nm} with a high curvature allows for more Pt atoms to be on the surface.
- The order of $Pt/CF_{39nm} > Pt/CF_{158nm} > Pt/CF_{309nm}$ for j_0 is obtained.
- Pt/CF_{39nm} provide highest real surface area and maximum power for glucose oxidation.

GRAPHICAL ABSTRACT



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ABSTRACT

Electrospun carbon fibers (CFs) with diameters of 39 nm (CF_{39nm}), 158 nm (CF_{158nm}), and 309 nm (CF_{309nm}) were used as Pt-catalyst supports for a glucose oxidation reaction. Based on experimentally balanced comparisons using electrochemical methods, CF_{39nm} with higher curvature and smaller diameter had a greater number of Pt atoms on the surface. Compared with the CF_{158nm} and CF_{309nm} systems, CF_{39nm} has a higher electrochemically real surface area and greater catalytic activity on glucose oxidation. The Tafel analyses demonstrated that the exchange current density from an early rest potential (−0.81 V) for the CF_{39nm} system was 9.08×10^{-3} mA cm^{-2}, greater than 8.41×10^{-3} mA cm^{-2} for CF_{158nm}-supported Pt nanoparticles and 7.39×10^{-3} mA cm^{-2} for CF_{309nm}-supported Pt nanoparticles. In addition, as data supporting the catalytic characterization for glucose oxidation, all of the CF-supported Pt nanoparticles showed remarkable tolerance to foreign substances in the application of a non-enzymatic glucose sensor, where CF_{39nm}-supported Pt nanoparticles (Pt/CF_{39nm}) showed a higher sensitivity (2.03 μA mM^{-1} cm^{-2}), detection limit (33 μM), and linear range (0.3–17 mM). The high recovery by serum sample analyses further confirmed the potential of Pt/CF_{39nm} as a glucose sensor. The promising results showed the feasibility of these electrospun CFs being applied for both glucose fuel cells and non-enzymatic glucose sensors.

Abbreviations: AA, ascorbic acid; PEMFCs, polymer electrolyte membrane fuel cells; CF, carbon fiber; CF_{39nm}, carbon fibers of 39 nm diameter; CF_{158nm}, carbon fibers of 158 nm diameter; CF_{309nm}, carbon fibers of 309 nm diameter; CV, cyclic voltammetry; DGFC, direct glucose fuel cell; DMF, *N*,*N*-dimethylformamide; GCE, glassy carbon electrode; HRTEM, high-resolution transmission electron microscopy; IFC, implantable fuel cell; IPA, isopropyl alcohol; LOD, limit of detection; PAN, polyacrylonitrile; Pt/CF_{39nm}, CF_{39nm}-supported Pt nanoparticles; Pt/CF_{158nm}, CF_{158nm}-supported Pt nanoparticles; Pt/CF_{309nm}, CF_{309nm}-supported Pt nanoparticles; Pt/CFs, carbon nanofiber-supported Pt nanoparticles; SDS, sodium *n*-dodecyl sulfate; SEM, scanning electron microscope; TGA, thermogravimetric analyzer; UA, uric acid; XPS, X-ray photoelectron spectroscopy; XRD, X-ray diffraction spectroscopy.

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1. Introduction

Utilizing expensive Pt-based nanocatalysts is an important issue for electrocatalytic devices, such as polymer electrolyte membrane fuel cells (PEMFCs) [1,2]. To increase the utilization of Pt-based catalysts, carbon nanomaterials used as supports for the catalysts are necessary. It has been reported that the performance of the catalyst in a PEMFC is dependent on the morphology of the carbon support [3–5]. Interestingly, the utilization of Pt-catalysts can be improved to 69.1% if carbon fiber (CF) is employed, compared with 35.2% in the carbon powder system [1]. The CF as support can provide good conductivity and high surface areas with good connection between the catalytic nanoparticles in the reaction layer, resulting in enhanced Pt-utilization. Sung and co-workers successfully demonstrated that the exchange current density (j_0) could be increased to 2.2 mA cm^{-2} using Pt/carbon powder mixed with calcined Pt/CF to increase the electrochemical surface area [2]. Liu and co-workers further showed a high-efficiency electrode of bimetallic Pt–Au/CF for the oxidation of formic acid [6]. While the use of CFs as a catalyst support is gaining interest, further research seems to be necessary to obtain more insights into the comparison of CFs of different diameters.

Most recently, the electrocatalytic glucose oxidation reaction has been of particular interest, which can be simultaneously applied for the elemental reaction in a direct glucose fuel cell (DGFC) [7–9], implantable fuel cell (IFC) [10,11], and glucose sensor [12–14]. For DGFC [7] and IFC [10], Pt is an active catalyst and is often employed as the anode to catalyze glucose oxidation. As for a glucose sensor, Pt nanoparticles also can be used for a non-enzymatic glucose sensor [15], which has greater thermal and chemical stability than an enzymatic sensor [16]. Herein, the CFs of 39 nm (CF_{39nm}), 158 nm (CF_{158nm}), and 309 nm diameter (CF_{309nm}), were prepared by electrospinning 3, 5, and 7 wt% polyacrylonitrile (PAN), respectively, dissolved in a *N*,*N*-dimethylformamide (DMF) solution, and applied as carbon supports for the catalysis of the glucose oxidation reaction by Pt nanoparticles. Spinning from PAN solution is the industrial process used to fabricate carbon fibers; however, the diameter of the carbon fibers obtained is of the order of tens of micrometers. Vapor-grown carbon fibers, using metal as a catalyst and carbon-containing gas as a precursor, can be used to prepare graphitic carbon fibers, but the fibers are short and the cost is high [17,18]. In recent years, a highly developed technique, called electrospinning, has gained substantial attention for the synthesis of carbon nanofibers [19–21]. Electrospinning is a convenient and low-cost process for generating polymer nanofibers. The diameter of the electrospun fibers ranges from less than 100 nm to several micrometers; therefore, they are feasible as high-performance filters, tissue scaffolds, and electrode materials [22]. Precursor nanofibers, which are prepared using electrospinning followed by heat treatment at 800–2800 °C in N_2 atmosphere, produce carbon nanofibers. The electrospun carbon nanofibers possess a straight, continuous, and interconnected structure that enhances the electron-conductive pathway, and the small diameter increases the specific surface area. The aim of this research was to compare fairly and discuss the support effect of CFs with a diameter of less than 100 nm, electrospun from PAN, for the glucose oxidation properties, activity, and kinetics. In addition, the prepared CF-supported Pt nanoparticles (Pt/CFs) can also be successfully applied as a non-enzymatic glucose sensor.

2. Experimental

2.1. Synthesis of electrospun carbon fibers with 39 nm, 158 nm, and 309 nm diameters and material analysis

To prepare CF_{39nm}, 150,000-g/mol PAN was dissolved in DMF (99.8%) to prepare a 3-wt% solution. The solution underwent vigorous stirring for 24 h at room temperature to form a homogeneous solution. A conventional single-nozzle electrospinning process was carried out at room temperature in air to prepare the nanofibers. The as-prepared polymer solution was placed in a 10-mL glass syringe with a 16G stainless-steel needle. The syringe was transferred to an electrospinning device, which consisted of a power supply (You-Shang Technical Corp.), a syringe pump (KDS 100, KD Scientific), and a flat metal collector. During electrospinning, various parameters were manipulated to obtain nanofibers without defects such as beads or a high surface roughness. The flow rate, applied voltage, and collecting distance were set at 0.7–1.0 mL h^{-1}, 15–17 kV, and 15–18 cm, respectively. The resulting membranes containing nanofibers were dried in air to remove the residual solvent. The CF membranes were then stabilized in a tube furnace at 250 °C for 6 h in air, and then carbonized at 1300 °C for 1 h in Ar. The heating rates for the stabilization and carbonization processes were fixed at 5 °C min^{-1} and 2 °C min^{-1}, respectively. The carbon powders containing CF_{39nm} for use as catalyst supports were ground from the membranes after heat treatment. The carbon powders CF_{158nm} and CF_{309nm} were prepared based on the same method, using 7- and 10-wt% PAN/DMF solutions, respectively. The morphologies and chemical bonds on the surface of the CFs were characterized using a scanning electron microscope (SEM; JEOL, JSM-6700F) and X-ray photoelectron spectroscopy (XPS, AXIS Ultra DLD, Kratos Analytical), respectively.

2.2. Synthesis of carbon-nanofiber-supported Pt nanocatalyst and material analysis

The nanofiber-supported Pt nanoparticles, in which CF_{39nm}, CF_{158nm}, and CF_{309nm} were used as supports and named Pt/CF_{39nm}, Pt/CF_{158nm}, and Pt/CF_{309nm}, respectively, were synthesized by self-regulated reduction with sodium *n*-dodecyl sulfate (SDS) [23]. For Pt/CF_{39nm}, 10 mg of powdered 39-nm nanofibers, and ~0.0673 mmol of $H_2PtCl_6{\cdot}6H_2O$ were reduced using 1-dodecanol that had been released from 100 mL of a 0.1 M SDS solution refluxed for about 19 h. The Pt/CF_{158nm} and Pt/CF_{309nm} composites were obtained by the same method using CF_{158nm} and CF_{309nm}, respectively. Before the material and electrochemical analyses, the different Pt/CF powders were redispersed in ethanol and the obtained solutions were precipitated to remove free SDS and other impurities using centrifugation at 4000 rpm. The morphologies, dispersities, and crystalline structures of the prepared Pt/CFs were examined using high-resolution transmission electron microscopy (HRTEM; JEOL, JEM-2100) and X-ray diffraction spectroscopy (XRD; Bruker D8; Cu anode; 1.54184 Å). The element identification of Pt/CF powders was characterized using a XPS instrument (AXIS Ultra DLD, Kratos Analytical). To estimate precisely the weight percentages of active Pt catalysts in samples of Pt/CF_{39nm}, Pt/CF_{158nm}, and Pt/CF_{309nm}, thermal decomposition analyses of nanocubes and nanoparticles were carried out using a thermogravimetric analyzer (TGA; DT-Q600).