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A novel 3-D fabrication of platinum nanoparticles decorated micro carbon pillars electrode for high sensitivity detection of hydrogen peroxide

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ABSTRACT

We report a novel fabrication technology for microscale carbon pillars (MCP) decorated with platinum/carbon nanoparticles (Pt/C NPs) for hydrogen peroxide (H_2O_2) detection. The fabrication process involves three sequential steps: spray-coating of Pt/C nanoparticles, polydimethylsiloxane (PDMS) soft molding, and high temperature carbonization of polyacrylonitrile (PAN), which has great potential for large scale and high throughput manufacturing. The amperometric response of MCP based H_2O_2 sensor exhibits superior electrochemical activity and charge transfer ability with a sensitivity of 1280–1750 $\mu AmM^{-1}\,cm^{-2}$ and a linear dynamic range (LDR) to 7000 μM. Most importantly, the developed fabrication method can be used for a wide variety of functional nanomaterials for different applications such as electrochemical analysis, sustainable energy and biosensing.

1. Introduction

Today's analytical chemistry calls for complex instrumentation and considerable support, including special laboratory facilities and highly skilled personnel. However, chemical and biological sensing devices that are robust, portable and easy to use will lead to more innovative strategies for analytical instrumentation. In addition, they have other advantages such as requiring fewer reagents to operate and yielding reliable information continuously [1]. For instance, amperometric biosensors, usually formed by biologically surface-modified voltammetric electrodes, are gaining increasing importance owing to their high reliability, robustness and high sensitivity [2]. The early actual electrochemical sensors were based on the chemical modification of carbon paste. Complex functional groups such as silver ion were introduced to the carbon surface for the measurement of concentration of silver [3]. Another modification method was developed by Yao and Musha who dissolved anthraquinone (AQ) in the pasting liquid for immobilization of electroactive species [4]. These days most of electrochemical sensors were fabricated on glassy carbon electrode. Different materials, such as, anthraquinone [5], ordered mesoporous carbon modification [6], and nickel hexacyanoferrate/chitosan/carbon nanotubes (NiHCF/CS/CNTs) nanocomposite films [7], were immobilized on the surface of glassy carbon electrodes to improve their electrochemical response.

Nanostructured materials are becoming the focus of electrochemical sensor research. For instance, thionin nanowires [8] and CuO-MWCNTs [9] have been reported to improve hydrogen peroxide sensitivity of sensors. The performance of electrochemical sensor can be future improved by the use of so called hybrid nanostructures. He et al. built Ag nanoparticle 3D catalyst on a graphite substrate using $Na_2Ti_3O_7$ nanowire as 3D frames for loading Ag nanoparticles [10]. Fe_3O_4–Ag hybrid submicrosphere was synthesized and developed as hydrogen peroxide sensor by Liu et al. [11]. Gold nanoparticles were attached on ordered mesoporous carbon (OMC) as hydrogen peroxide sensors [12]. A synthetic method to incorporate copper sulfide nanoparticles inside the mesopores of OMC is also reported for hydrogen peroxide sensor development [13].

However, random hybrid nanostructures hardly provide repeatable performance. There is no report for organized hybrid micro and nanoscale structures on the working electrode surface to further enhance sensor performance and repeatability. It is easy to understand that a 3-D organized microscale structure embedded with nanostructures such as catalyst metal nanoparticles can take advantage of both unique catalytic properties of metal NPs and high surface area provided by the microstructures, to achieve high performance and repeatable electrochemical sensing.

In this paper, a novel method to fabricate platinum/carbon-nanoparticles-decorated micro carbon pillars (Pt/C NPs MCP)

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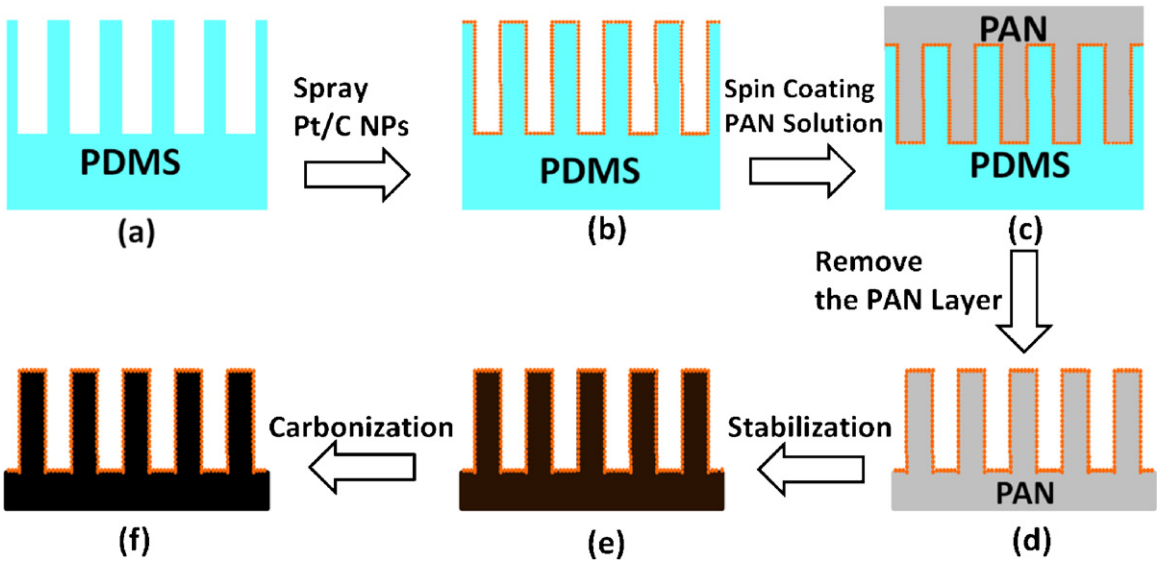

Fig. 1. Schematic of the fabrication process of Pt/C nanoparticles decorated micro carbon pillars.

electrodes is presented. The Pt/C NPs MCP sensor demonstrates superior properties well suitable for electrochemical sensing including low density, low electrical resistance, high resistance to chemical attack and impermeability to gases and liquid [14]. In addition, the surface to volume ratio of Pt/C NPs MCP is much larger than the traditional glassy carbon electrode thanks to high density micro pillar structure. Another critical feature of Pt/C NPs MCP electrode is its superhydrophilic property after thermal treatment, which can effectively prevent the gas bubbles from generating on electrode during hydrogen dioxide detection. In the first section, the process, materials and key parameters for Pt/C NPs MCP fabrication are introduced and discussed. Then the stabilization of polyacrylonitrile (PAN) material is described and analyzed using Fourier Transform Infrared Spectroscopy (FTIR) technique. In the meantime, the cyclic voltammetry (CV) measurement was conducted to characterize the charge transfer and electrochemical activity of developed Pt/C NPs MCP structure. At last, serious of experiments were performed to evaluate the performance of Pt/C NP MCP based hydrogen peroxide sensor.

2. Experimental

2.1. Materials and instruments

Polyacrylonitrile (PAN) with molecule weight of 150,000 and N,N-dimethylformamide (DMF) were ordered from Sigma–Aldrich. The assay of DMF is greater than 99.8%. The polydimethylsiloxane (PDMS) for mold fabrication of soft molding was purchased from Dow Corning Corp. The Pt nanoparticles (2.9 nm) and carbon black nanoparticle (50 nm) were ordered from Alfa Aesar.

Bruker Tensor 27 was used for the FTIR measurement for PAN samples after stabilization. The morphology of Pt/C NPs MCP was studied using a field emission scanning electron microscope (JEOL-SEM, JSM-7401F). Cyclic voltammetry (CV), and amperometric measurements were conducted using a VersaSTAT 3 potentiostat (Princeton Applied Research, TN). A Pt wire (99.9%, Alfa Aesar) and Ag/AgCl electrode (BASi) were used as counter and reference electrodes in the measurement, respectively.

2.2. Pt/C NPs MCP fabrication

The complete fabrication process is illustrated in Fig. 1 and consists of four steps: (1) PDMS mold fabrication; (2) preparation of molding material; (3) spray-coating of Pt/C ink and molding process; and (4) stabilization and carbonization of PAN pillars. These steps are described in detail below.

2.2.1. PDMS mold fabrication

PDMS was chosen as the mold material for molding of micro pillar arrays for two reasons: (1) PDMS has a lower surface energy than other substrates such as silicon and quartz, which can ease the mold removal after molding; (2) PDMS based molding method is well suited for low cost, large scale and high throughput nanomanufacturing. The PDMS was prepared by mixing the PDMS base and curing agent at a 10:1 ratio for 5 min in a glass container. A vacuum oven was used to remove the bubbles generated from mixing. A silicon substrate fabricated by deep reactive ion etching (DRIE) process to form micro pillar arrays was used as mothermold. Then the PDMS was evenly poured onto the surface of silicon substrate prior to being cured in a pressurized, heat-treated vacuum chamber for 60 min at 75 °C. After the PDMS film was peeled off from the silicon substrate, the micro holes arrays were formed on the PDMS mold and the PDMS mold is ready for spray coating process.

2.2.2. Preparation of molding material

The PAN (Sigma–Aldrich, molecular weight: 150,000) was dissolved in DMF solvent with a weight ratio of 2:8 and stirred at 80 °C for 4 h. The dissolving time depends on the PAN concentration and amount. The higher concentration, the longer dissolving time is required. After a successful mixing, the PAN solution is clear and transparent. Commercially available Pt/C nanopowders were dispersed in DI water with a concentration of 5% to produce "Pt/C ink". An ultra-sonication of 5–10 min for "Pt/C ink" is required before the spraying process.

2.2.3. Spray-coating of Pt/C ink and molding process

The ultrasonic "Pt/C ink" was uniformly sprayed on the surface of PDMS mold using an air brush system (average droplet size: 6 μm) at room temperature (20 °C). During the spray process, the tiny Pt/C droplets were formed at the nozzle exit of the air brush system under pressured air. The distance between the mold surface and the nozzle exit was optimized to obtain the smallest droplets for a rapid solvent evaporation. After each coating, the cotton Q-tip with ink was used to repaint the mold surface to limit coffee stain effects [15].