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Flexible sensor for dopamine detection fabricated by the direct growth of α-Fe_2O_3 nanoparticles on carbon cloth

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ABSTRACT

Porous α-Fe_2O_3 nanoparticles are directly grown on acid treated carbon cloth (ACC) using a simple hydrothermal method (denoted as ACC-α-Fe_2O_3) for employment as a flexible and wearable electrochemical electrode. The catalytic activity of ACC-α-Fe_2O_3 allowing the detection of dopamine (DA) is systematically investigated. The results showed that the ACC-α-Fe_2O_3 electrode exhibits impressive electrochemical sensitivity, stability and selectivity for the detection of DA. The detection limit determined with the amperometric method appears to be around 50 nM with a linear range of 0.074–113 μM. The impressive DA sensing ability of the as prepared ACC-α-Fe_2O_3 electrode is due to the good electrochemical behavior and high electroactive surface area (19.96 cm^2) of α-Fe_2O_3 nanoparticles anchored on the highly conductive ACC. It is worth noting that such remarkable sensing properties can be maintained even when the electrode is in a folded configuration.

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1. Introduction

Over the past few decades, numerous biosensors for various target materials such as DNA, glucose, amino acids, protein and other substances have been developed [1–4]. In recent years, demand for the development of inexpensive smart biosensors with high sensitivity and selectivity has increased due to their potential contribution to modern medical treatment which would strengthen our ability to detect diseases in the initial stages. Dopamine (DA), made by amino acids, is one of the excitatory neurotransmitters released by the brain. An excess or deficiency of DA has effects in both humans and animals. Abnormal amounts of DA in the human body causes disorders such as uncoordinated movement, reduces pleasurable feelings, and can cause addiction or memory loss[5]. Since DA plays such a significant role in the human system, tremendous efforts have been made over the past few years to detect DA levels with high sensitivity and selectivity by using spectrometry, high-performance liquid chromatography, electrochemistry and other analytical techniques [6–8]. Among these techniques, electrochemistry has proven to be most suitable for the direct monitoring of DA, on account of its excellent characteristics of high sensitivity, prompt response and low detection limit [9]. However, in practical applications it is still a challenge to develop a flexible electrochemical DA sensor with good sensitivity and stability, which can serve as a smart wearable biosensor device.

Conventionally, glassy carbon electrodes (GCE) [10] or screen printed carbon electrodes (SPCE) [11,12] have been utilized as electrochemical biosensors for the detection of DA. However, there are limitations to these types of electrodes, such as low or high overpotential, poor electron transfer ability, low sensitivity and poor selectivity [13–16]. In order to overcome these problems, it is necessary to modify the bare electrode with metal or semiconducting materials. Modified GCEs for the electrochemical detection of biomolecules are usually fabricated using electrocatalysts comprised of an individual or a combination of carbon nanomaterials, metal oxides, metal sulfides, noble metals or metal alloy nanoparticles that have been coated as a thin film on the GCE [5,17]. Although modified GCEs offer an improvement compared to a bare electrode, they still suffer from limitations such as high cost, fragility, repeated requirements for cleaning and polishing, all of which make it challenging to develop low cost electrodes with the desired shape which is a prerequisite for commercialization.

In recent years, there has been growing interest in the development of wearable biosensors, which would open up a revolutionary opportunity to monitor patients even in remote areas which is cru-

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cial for the development of modern healthcare [16]. Carbon cloth (CC) is one of the most attractive materials for flexible electrochemical sensing applications due to its good electrical conductivity, large specific surface area, high capacitance, chemical and thermal stability and, most importantly, ease of wearability due to its flexible nature [18–22].

On the other hand, among the semiconductor nanomaterials, α-Fe_2O_3 has been investigated extensively for electrochemical sensing, catalysis, solar cell and energy conversion applications due to its abundance, low cost, high stability in aqueous solutions ($pH > 3$) and environmental benignity [23–25]. For example, α-Fe_2O_3 possesses a narrow band gap of about 2.0–2.2 eV, absorbs light up to 600 nm and collects a maximum of 40% of the solar spectrum energy, which makes it a good potential candidate for photocatalytic application [26,27]. It also exhibits high oxygen ion mobility on the surface of the particles and thus shows remarkable catalytic behavior in redox reactions for gas sensing applications [28–30].

A hybrid of carbon nanostructures and semiconductor nanomaterials have been shown to be ideally suited for biosensor applications, producing good conductivity [31,32], good catalytic behavior [33], biocompatibility [34], ease of functionalized [35,36] and large active surface areas [37]. By combining the advantages of α-Fe_2O_3 nanoparticles and CC in the present work, we fabricate a hybrid structure, by directly growing the α-Fe_2O_3 nanoparticles on the surface of functionalized CC using the hydrothermal method. The prepared acidic carbon cloth (ACC)-α-Fe_2O_3 electrode is then utilized for the determination of DA.

We compare the catalytic activity of the ACC, GCE-α-Fe_2O_3, and ACC-α-Fe_2O_3 electrodes for the detection of DA in 0.01 M PBS. Our results show that the ACC-α-Fe_2O_3 electrode exhibits superior electrocatalytic activity towards the oxidation of DA than the ACC and GCE-α-Fe_2O_3 electrodes. In addition, such excellent behavior can be retained even when the ACC-α-Fe_2O_3 electrode is kept in a folded configuration.

2. Experiments

2.1. Materials and methods

All of the chemicals and reagents were used as received without further purification. The iron(III) nitrate nanohydrate (99.99%), dopamine hydrochloride, ascorbic acid (AA), uric acid (UA) and phosphate buffer saline (PBS) were purchased from Sigma-Aldrich. Commercial grade ethanol was used for the purification of α-Fe_2O_3 nanoparticles and double distilled water prepared in our lab.

The surface morphology of ACC-α-Fe_2O_3 was analyzed by field-emission scanning electron microscopy (FE-SEM, JSM-6500) with an energy dispersive x-ray (EDX) spectrometer 101 (FESEM): JOEL6400. The crystal structure and chemical composition of the prepared α-Fe_2O_3 were characterized by X-ray diffraction (Bruker, D8 PHASER with an X Flash) and Raman spectrometry (Horiba Jobin UV 800, Raman spectrometer with an excitation of 630 nm). The electrochemical sensing measurements were carried out using a potentiostat (17040E cell test system, Solarton analytical). Electrochemical studies were performed in a conventional three-electrode cell using GCE and ACC-α-Fe_2O_3 as the working electrode, saturated Ag/AgCl as the reference electrode and Pt wire as a counter electrode. Before starting the electrochemical experiments, the electrolyte was de-aerated using nitrogen.

2.2. Surface modification of CC

Prior to the hydrothermal process, the CC surface was pretreated in a mixture of concentrated HNO_3 and H_2SO_4 (3:1) at 80 °C for 2 h then washed with distilled water and ethanol and dried in a vacuum oven at 60 °C for 12 h.

2.3. Growth of α-Fe_2O_3 nanoparticles on ACC

Iron(III) nitrate nonahydrate (4 g) was dissolved in 80 mL of deionized water and this solution was stirred at 25 °C for 1 h. The pH of the solution was maintained at 1.5 by either adding water or a sodium hydroxide aqueous solution to the ferric solution. Subsequently, the above solution was poured into the Teflon-lined stainless steel autoclave and a 2 × 2 cm piece of CC fastened to a Teflon holder was placed in the solution. The reaction mixture in the Teflon-lined stainless steel autoclave was transferred into a muffle furnace and hydrothermally treated at 200 °C for 20 h. The product was then naturally cooled down to room temperature. The red colored α-Fe_2O_3 film grown on the bottom side of the CC (ACC-α-Fe_2O_3) was carefully taken out of the Teflon-lined stainless steel autoclave. The ACC-α-Fe_2O_3 cloth was washed with water and ethanol and dried in a vacuum oven at 60 °C for 12 h. A schematic representation of the procedure for the direct growth of α-Fe_2O_3 nanoparticles on ACC is shown in Fig. 1. A similar procedure was used for the synthesis α-Fe_2O_3 nanoparticles but without using CC. The α-Fe_2O_3 nanoparticles were separated from the solution by centrifugation at 6000 RPM for 20 min followed by washing three times in both water and ethanol.

2.4. Fabrication of the ACC-α-Fe_2O_3 electrode

A piece of aluminum wire 5 cm in length was connected to the ACC and ACC-α-Fe_2O_3 electrodes with silver contacts followed by the application of an epoxy coating that completely covered the top of the ACC-α-Fe_2O_3 electrode in order to block water diffusion, as shown in Fig. 1. The α-Fe_2O_3 modified GCE electrode (GCE-α-Fe_2O_3) was fabricated by manually polishing the GCE with a 0.25 μm alumina slurry, then cleaning it with water and drying it in N_2. Then, 10 μL of 1 mg/mL α-Fe_2O_3/water dispersion was drop cast onto the GCE followed by drying at 50 °C to ensure complete evaporation of the water. Thereafter, the ACC-α-Fe_2O_3 or α-Fe_2O_3 modified GCE was transferred to an electrochemical cell containing 4 mL of 0.01 M PBS (pH 7). The geometric surface area of ACC-α-Fe_2O_3 and GCE-α-Fe_2O_3 electrodes is around 1 cm^2 and 0.079 cm^2, respectively.

3. Results and discussion

3.1. Characterization of ACC-α-Fe_2O_3

The direct growth of porous α-Fe_2O_3 nanoparticles on the CC was successfully carried out using the hydrothermal method. The crystal structure of ACC-α-Fe_2O_3 and ACC is confirmed by the X-ray diffraction (XRD) results shown in Fig. 2. The XRD profile of the ACC shows two broad shoulders at 24.9° and 42.7°, which correspond to the (002) and (100) phases of hexagonal graphitic carbon. The ACC-α-Fe_2O_3 shows major sharp peaks at around 24.1°, 33.1°, 35.6°, 40.8°, 49.4°, 54.0° and 57.5°, which correspond to the characteristic diffraction planes indexed at (012), (104), (110), (113), (024), (116) and (018) for the crystal phase of α-Fe_2O_3. All of these diffraction peaks are closely match the hematite phase (α-Fe_2O_3) of the reference profile: JCPDS Number 33-0664. There are no other characteristic peaks revealing the existence of crystalline phases, thus confirming the formation of pure α-Fe_2O_3 on ACC.

To further confirm the formation of α-Fe_2O_3 on ACC, the Raman spectra of pristine ACC and ACC-α-Fe_2O_3 were examined, as shown in Fig. 3. The Raman spectra of ACC-α-Fe_2O_3 show the characteristic peaks located at 225, 245, 291, 410, 428, 495, 611, 658 and 1315 cm^{-1}. The typical characteristic α-Fe_2O_3 (hematite) A_{1g} mode

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