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MOF-derived Fe_2O_3 nanoparticle embedded in porous carbon as electrode materials for two enzyme-based biosensors

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ABSTRACT

MOF-derived nanomaterials in porous carbon possess excellent conductivity and distinctive microstructure, which could improve the analysis performance of biosensors by loading large amounts of enzymes and accelerating electron transfer. In this research, Fe_2O_3@C was derived from annealing of Fe-1,3,5-benzenentricarboxylate, and then its composition and morphology were confirmed by scanning electron microscopy (SEM), X-ray diffraction (XRD) and energy dispersive spectroscopy (EDS). Moreover, two biosensors based on Fe_2O_3@C and ionic liquid (IL)/nafion (NF) for sensing analysis of H_2O_2 and paraoxon were investigated by immobilizing myohemoglobin (Mb) and acetylcholinesterase (AChE) on carbon paste electrodes (CPE), respectively. Electrochemical studies demonstrated that as-prepared biosensors exhibited excellent electrochemical performance towards H_2O_2 and paraoxon with the detection limit as low as 1.7×10^{-7} M and 1.2×10^{-14} M, respectively. Especially present NF/AChE/NF-Fe_2O_3@C/CPE enhanced sensitivity for the determination of paraoxon. The results indicated that Fe_2O_3@C was a promising electrode material in the development of multifarious biosensors fabrication with sensitive detection of target molecules other than H_2O_2 and paraoxon.

1. Introduction

In the past few decades, enzyme-based biosensors have attracted considerable interest because of their high sensitivity, low cost, and inherent miniaturization [1,2]. However, there are still some problems largely limiting the fabrication of enzyme-based biosensors such as direct electron transfer difficulties, transfer instability, denaturation during the immobilization of enzyme on electrode substrate. Therefore, the key considerations for immobilizing enzymes are how to retain its bioactivity and accelerate electron transfer [3,4]. In order to solve these problems, it is necessary to develop the excellent support matrix that provide better environment for loading the enzyme efficiently and maintaining the enzymatic bioactivity.

Metal-organic frameworks (MOFs), inspired by their high surface area, porosities, and abundant carbon-containing linkers, have been demonstrated to be the sacrificial templates for fabricating porous metal oxides or carbon nanostructures via thermal decomposition under controlled atmosphere [5–7]. More significantly, the porosity and long-range ordering of MOFs can impart their MOF-derived hollow structures some unique features and MOF-derived nanoparticle embedded in porous carbon has excellent conductivity and stability [8–11]. In addition, as an environment-friendly n-type semiconductor oxide, Fe_2O_3 is drawing intense interest not only for its unique properties but also for its applications in many fields such as lithium-ion batteries, sensors, anticorrosive agents and pigments [12]. Especially, porous carbons Fe_2O_3 nanomaterials are playing a critical role in electrochemical, in terms of improved electrochemical properties of the transducers and better conjugation with biological compounds [13–16].

Currently, many papers have focused on the synthesis and application of porous carbon Fe_2O_3. For example, Chen et al. [17] designed a novel hybrid nanostructure by coating Fe_2O_3 nanoparticles with multi-walled carbon nanotubes to enhance the lithium storage capability of Fe_2O_3. Besides, using MnO_2 nanorods as templates, Lou et al. [18] also fabricated carbon-coated α-Fe_2O_3 nanorods through a template-engaged redox etching method. However, the synthesis of porous carbon Fe_2O_3 usually involves tedious and complicated steps, expensive sacrificial templates, or time-consuming solvothermal reactions in autoclaves. If Fe_2O_3 could be uniformly embedded into a conductive porous carbon matrix by a facile and scalable synthesis strategy, it would be one of the most effective approaches toward high-performance electrode

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materials, which can be employed as building blocks for the assembly of nanostructured surfaces for the construction of reliable and robust electrochemical biosensors.

H_2O_2 and paraoxon were considered target molecules for enzyme-based biosensors development [19]. On one hand, H_2O_2 is a reactive oxygen species that affects cellular mechanisms and induces oxidative damage [20]. In recent years, heme proteins electrodes based on various materials have attracted great interest for the detection of H_2O_2, including transition metal oxides [21], conducting polymers [22], MOFs [23] and graphene [1] etc. Nevertheless, it has still some deficiencies such as enzymes or proteins denaturation, low reproducibility, and stability. On the other hand, paraoxon, as one kind of the most commonly applied pesticides in agriculture, is harmful to the health of human beings. Because of rapid response, simple operation, high sensitivity, AChE-based biosensors have emerged as a promising technique for the detection of paraoxon [24,25]. Even though AChE biosensors have shown satisfactory results for pesticides analysis [26–28], it is essential to search for new materials with good electronic conductivity for the effective immobilization of AChE. To the best of our knowledge, there are few reports on a multiplex assay purpose by the immobilization of AChE and Mb, respectively.

Herein, we developed an in-situ synthesis strategy to fabricate Fe_2O_3 nanoparticles embedded in porous carbon matrix (Fe_2O_3@C) with internal void space by annealing of room-temperature preformed Fe-based MOFs which consist of Fe^{2+} ions and oxygen-containing trimesic acid linkers (Fe-BTC). Moreover, two biosensors based on Fe_2O_3@C and ionic liquid (IL)/nafion (NF) for sensing analysis of H_2O_2 and paraoxon were investigated by immobilizing myohemoglobin (Mb) and acetylcholinesterase (AChE) on carbon paste electrodes (CPE), respectively.

2. Experimental section

The chemicals, apparatus, electrochemical measurements and measurement procedure are described in detail in Supporting Information.

2.1. Synthesis of Fe_2O_3@C

The typical synthetic experiments of Fe_2O_3@C were as shown in Fig. 1A. Solution A: $FeSO_4{\cdot}7H_2O$, (278 mg) was dissolved in a methanolic solution (25 mL) under agitated stirring to give a transparent solution. Solution B: trimesic acid (H_3BTC, 630 mg) and PVP (K-30, 0.3 g) were also dissolved in a methanolic solution (25 mL) under agitated stirring to give a transparent solution. Solution A was added into solution B under vigorous stirring at room temperature. The resulting solution was incubated at room temperature without any interruption for 24 h. The resulting precipitation (Fe-BTC) was centrifuged and washed with several times with methanol and finally dried under oven at 60 °C. Fe_2O_3@C was successfully obtained by thermal decomposition of Fe-BTC precursors in N_2 at 570 °C for 2 h.

2.2. Preparation of the modified electrodes

The preparation of CPE was described previously [29], the detail was described in Supporting Information.

The preparation procedure of modified electrode as follows: Firstly, 5 mg Fe_2O_3@C sample and 10 μL of IL were dispersed into 1 mL 0.1 M pH 7.0 PBS under sonication. Then, 10 μL above suspension was casted onto the surface of a freshly polished CPE to obtain Fe_2O_3@C/IL/CPE, which was dried at room temperature. At last, the Mb/Fe_2O_3@C/IL/CPE was prepared by casting 5 μL of Mb solution (5 mg mL^{-1}) onto the Fe_2O_3@C/IL/CPE, respectively. The Mb-based electrodes were evaporated at 4 °C in a refrigerator to form a stable film.

The preparation procedure of AChE modified electrode as follows: Firstly, 3 mg of Fe_2O_3@C powders and 200 μL 0.5% (Wt/V) NF solution were dispersed into 800 μL 0.1 M pH 7.0 PBS under sonication for 30 min to obtain homogeneous suspension of NF-Fe_2O_3@C. Then 6 μL of suspension above was cast onto the surface of a freshly polished CPE to obtain NF-Fe_2O_3@C/CPE, which was dried at room temperature to form a stable film. Furthermore, AChE/NF-Fe_2O_3@C/CPE was prepared by casting 8 μL of AChE solution (0.2 mg mL^{-1}) onto NF-Fe_2O_3@C/CPE. The AChE/NF-Fe_2O_3@C/CPE modified electrode was dried at 4 °C in a refrigerator. Finally, the AChE/NF-Fe_2O_3@C/CPE modified electrode was coated with 5 μL of 0.5% (Wt/V) NF as the protective membrane to obtain NF/AChE/NF-Fe_2O_3@C/CPE and stored in 0.1 M pH 7.0 PBS at 4 °C in a refrigerator. The 0.5% (Wt/V) NF solution was prepared by diluting 5% (Wt/V) of NF with 0.1 M pH 7.0 PBS.

2.3. Detection of paraoxon

The detection of paraoxon is described in detail in Supporting Information.

3. Results and discussion

3.1. Characterization of Fe_2O_3@C

FT-IR spectra of synthesized Fe-BTC and H_3BTC were shown in Fig. 1A. In the FTIR spectra, it is observed that the characteristic bands of (1650 cm^{-1}) of the carboxylic groups shifted to 1740 cm^{-1}, which proved that the iron ions were coordinated with the carboxylate ligands to form successfully the MOFs [30].

Fig. 1B-I shows a typical SEM image of Fe_2O_3@C, and Fig. 1B-II is its larger image (40,000×). As can be seen, the Fe_2O_3@C were composed with lots of bulk. Furthermore, many particles varied in size dispersed around the sheet-like Fe_2O_3@C, and interconnected with each other to form many cavities. The cavity could provide largely exposed surface area, conducive to the enzyme or proteins adsorption through the whole modified electrode.

Fig. 1B-III exhibits the XRD patterns of the prepared materials. The peaks at 33.12°, 35.62°, 43.48°, 49.42°, 57.5°, 62.38° and 63.96° correspond to the (104), (110), (024), (018), (214) and (300) planes of Fe_2O_3, respectively. The peak at 24° corresponds to the (002) plane of C. Element analyses from EDS (Fig. 1B-IV) methods verify the presence of C, O and Fe, and O and Fe atomic ratio is about 3:2. Therefore, the as-prepared material is Fe_2O_3@C. As shown in Fig. S2, the XPS survey spectrum shows typical characteristic peaks of Fe_2O_3 at 711 and 725 eV, referring to the $Fe2p_{3/2}$ and $Fe2p_{1/2}$ respectively, which implying that the characteristic peaks of Fe_2O_3 [31,32].

3.2. Electrochemical behaviors of Mb modified electrodes

3.2.1. Optimization parameters of the biosensor performance

The enzyme amount and volume of IL/Fe_2O_3@C were importance constituents of the biosensor. As shown in Fig. S3, the influence of enzyme amount and volume of IL/Fe_2O_3@C in the electrode on the performance of biosensor was studied. It was found in Fig. S3A that the increase of volume of IL/Fe_2O_3@C could significantly improve the amperometric response of Mb. The reason might be that the IL/Fe_2O_3@C could provide better environment for efficiently loading the Mb and accelerate electron transfer. However, when the volume of IL/Fe_2O_3@C was more than 10 μL, the thickness of the film increased, which would increase the distance between Mb and underlying electrode and block the electron transfer, resulting in a decrease of the amperometric response. From Fig. S3B, it