



Direct electrocatalytic and simultaneous determination of purine and pyrimidine DNA bases using novel mesoporous carbon fibers as electrocatalyst



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ABSTRACT

Novel mesoporous carbon fibers (MCFs) were fabricated through a self-templating strategy and solution growth process. MCF modified glassy carbon electrode (MCF/GCE) was proposed for the direct electrocatalytic and simultaneous determination of four DNA bases (guanine (G), adenine (A), thymine (T) and cytosine (C)) using differential pulse voltammetry (DPV) measurement. The MCF/GCE exhibits satisfactory electrocatalytic activity by significantly enhancing the oxidation peak currents and lowering the oxidation potentials toward the four bases when compared with those on GCE. Especially, MCF greatly accelerates the electron transfer of pyrimidine base, which have high oxidation potentials and slow electron transfer kinetics. Moreover, MCF/GCE realizes the simultaneous determination of four DNA bases with low detection limits, high sensitivity and wide linear range. More important, the proposed electrode was successfully applied in the direct detection of bases in herring sperm DNA sample with satisfactory results. Besides, the MCF/GCE shows good long-term stability and reproducibility. These superior performances of MCF/GCE toward purine and pyrimidine DNA bases provide a good possibility for applying the MCF/GCE in our further DNA biosensor research.

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1. Introduction

Deoxyribonucleic acid (DNA) carries heritage information and instructs the biological synthesis of proteins and enzymes through the process of replication and transcription of genetic information. DNA is a block copolymer with four types of deoxyribonucleotide monomers differentiated by their bases [1,2]. Guanine (G) and adenine (A) (purines), thymine (T) and cytosine (C) (pyrimidines) are the four bases in DNA and their sequence in the double-stranded structure contains the information for the self-replicating of DNA. The abnormal change of the base in organism suggests the deficiency and mutation of the immunity system and may indicate the presence of various diseases. Their concentration levels are considered as important parameter for diagnosis of cancers, AIDS, disease progress and therapy responses [3,4]. Therefore, the analysis of these bases has great significance to bioscience and clinical diagnosis. Many methods have been developed for the detection and quantification of DNA bases, such as high-performance liquid chromatography (HPLC) [5], capillary electrophoresis (CE) [6],

laser-induced fluorescence detection [7] and mass spectrometry (MS) [8]. Compared to above methods, electrochemical method is rapid, convenient and low-cost for sample analysis. Therefore, electrochemical techniques have become an important tool to investigate the direct electrochemistry of DNA bases. The electrocatalytic oxidation of purine bases with different modified electrodes has been reported [9–11], however, the electrochemical detection of pyrimidine bases is rarely reported because of their high oxidation potentials and slow electron transfer kinetics [12]. Therefore, simultaneous electrochemical detection of purine and pyrimidine bases is of great difficulty. In order to overcome these limitations, novel electrode materials with a wide potential window and a high electrocatalytic activity are required.

As electrode materials, many advanced nanostructured carbon materials such as multi-walled carbon nanotubes (MWCNTs) [13], graphene (GR) [14] and ordered mesoporous carbon (OMC) [15] have attracted widespread attention, owing to their superior electrocatalytic performance. Besides the carbon nano-materials mentioned above, carbon nanofiber (CNF) is another excellent material with high electrocatalytic capability. Despite the excellent capability of CNF, it is difficult to precisely manipulate the pore texture and morphology, which can greatly affect the electrocatalytic performance of CNF. In order to overcome this problem,

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recently, Li et al. [16] reported a novel and simple self-templating method for the preparation of mesoporous carbon fibers (MCFs). This kind of MCF features a 1D nanostructure with a 3D interconnected mesoporous network and a large surface area, which play an important role in improving the electrocatalytic activity. Be that as it may, few studies on the electrocatalytic property and analytical applications of this kind of MCF have been reported.

Based on what is mentioned above, for the first time, we present the direct electrocatalytic and simultaneous detection of four DNA bases using the prepared MCF as a high-performance electrocatalyst. MCF shows remarkable electrocatalytic activity toward purine and pyrimidine DNA bases and it may be a promising material for further fabricating sensitive DNA biosensor.

2. Experimental

2.1. Reagents and apparatus

The G, A, T, C and herring sperm DNA were obtained from Sigma–aldrich (MO, USA). Sodium hydroxide (NaOH), phosphoric acid (H_3PO_4), sodium hydrogen phosphate (Na_2HPO_4), sodium dihydrogen phosphate (NaH_2PO_4), ethanol, hydrochloric acid (HCl), anhydrous zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2$), potassium ferricyanide ($\text{K}_3\text{Fe}(\text{CN})_6$), ethylene glycol (EG) and N,N-dimethylformamide (DMF) were purchased from Aladdin Industrial Corporation (Shanghai, China). The Ag/AgCl electrode, Pt wire, glassy carbon electrode (GCE, diameter: 3 mm), polishing pad and alumina slurry were supplied from Chenhua Instrument (Shanghai, China). Double-distilled water was used throughout the whole experiment. The 0.1 M phosphate buffer solution (PBS, pH 7.4) prepared from Na_2HPO_4 , NaH_2PO_4 and H_3PO_4 was employed as supporting electrolyte.

Electrochemical detection was performed on a CHI 760E electrochemistry workstation (Chenhua Instrument, China) with a conventional three-electrode system. The working electrode was the MCF modified glassy carbon electrode (MCF/GCE); an Ag/AgCl electrode and a piece of Pt wire were served as reference and counter electrode, respectively.

The transmission electron microscopy (TEM) images were recorded on a JEM-2100F transmission electron microscope (JEOL, Japan) operating at 200 kV. Scanning electron microscopy (SEM) images were determined with a Philips XL-30 ESEM operating at 3.0 kV. Nitrogen adsorption–desorption experiment was performed on an ASAP 2020 (Micromeritics, USA), first, the samples were dried at 350 °C for more than 5 h, and then experimental procedure was set on ASAP 2020 instrument, then the nitrogen adsorption–desorption measurement was carried out at a liquid nitrogen temperature of -196 °C. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface area. Through treating nitrogen adsorption–desorption isotherm ($P/P_0 = 0.05–0.25$) with BET equation: $\frac{P/P_0}{V(1-P/P_0)} = \frac{1}{V_m C} + \frac{C-1}{C} \frac{P/P_0}{V_m}$, the V_m was obtained to calculate the specific surface area (S) of the analyte ($S \text{ (m}^2/\text{g)} = 4.354 * V_m$). (In BET equation, V is the volume adsorbed at pressure P and absolute temperature T ; P_0 is the vapor pressure of the gas at temperature T ; V_m is the volume of gas adsorbed when the adsorbent surface is covered with a unimolecular layer and is termed the monolayer. The constant C is mathematically related to the heat of adsorption. If the function $(P/P_0)/V(1 - P/P_0)$ is plotted against P/P_0 , a straight line should result, the slope and intercept of which give the values of V_m and C , respectively. Then the V_m was obtained to calculate the specific surface area of the analyte [17].). X-ray photoelectron spectra (XPS) were collected using an ESCALAB-MKII 250 photoelectron spectrometer (VG Co.) with Al-Ka X-ray radiation as the X-ray source for excitation.

2.2. Catalyst and electrode preparation

MCF was synthesized according to the method reported by Li et al. [16]. In a typical synthesis, 2.0 g anhydrous zinc acetate (structural constructor and the porogen) was mixed with 45 mL ethylene glycol (carbon precursor, $n_{\text{Zn}(\text{CH}_3\text{COO})_2} : n_{\text{EG}} = 1:73.83$) and then stirred at 150 °C for 90 min in a N_2 saturated flask. The slurry (zinc glycolate) was collected by centrifugation, oven-dried and calcination at 600 °C for 2 h in N_2 . After calcination, all the obtained composites (zinc oxide/carbon) were added into 2.0 M aqueous hydrochloric acid solution (20 mL) with stirring overnight to remove zinc oxide, then mixed the product with water, centrifugation for several times (washing process) and then dried in oven. The dried product was named as mesoporous carbon fiber (MCF).

MCF modified bare glassy carbon electrode (MCF/GCE) system was prepared using the drop coating method as follows. Before modification, the GCE was polished with 1.0, 0.3 and 0.05 μM alumina slurry in sequence on a polishing cloth and then rinsed with double-distilled water between each polishing step. Then 1 mg MCF was added into 1 mL DMF, sonication and agitation to obtain a suspension. Finally, 5 μL of MCF suspension (1 mg mL^{-1}) was casted on the well-polished GCE surface and then dried the solvent under an infrared lamp. Therefore, the MCF modified glassy carbon electrode was fabricated and named as MCF/GCE.

2.3. DNA sample preparation

The herring sperm DNA was hydrolyzed as follows for quantification of G and A. 3 mg of herring sperm DNA was digested with 1 mL of HCl (1.0 M) in a sealed glassy tube (10 mL). After heating in a boiling water bath for 60 min, the pH of the solution was adjusted to 7.0 with 1.0 mL NaOH (1.0 M). Finally, the solution was diluted to 10 mL using 0.1 M PBS (pH 7.4).

3. Results and discussion

3.1. Characterization of MCF

The electrocatalytic activity of carbon nano-materials greatly depends on their morphology and microstructure. In this paper, SEM and TEM were employed to gain insight into the morphology of MCF. Fig. 1A–C shows the typical SEM images of the as-prepared MCF at different magnifications. As can be clearly seen, the MCF shows typical fibrous morphology and these fibers are entangled together without any by-products. The diameter size distribution of MCF (Fig. 1F) indicates that the mean diameter of MCF ($N = 100$) is 154.19 nm. Fig. 1D and E shows the TEM images of a single MCF, the MCF exhibits a well-designed 1D nanostructure and a rough surface, which can significantly facilitate the electron transfer. Actually, a single fiber is composed of several mesopores (insert of Fig. 1E), which are attributed to the removal of ZnO crystals dispersed on the surface and embedded in the carbon matrix. These small mesopores can increase the effective electrode surface area, which is beneficial for electrocatalysis.

Fig. 2A presents the nitrogen adsorption–desorption isotherm of the prepared MCF. According to the IUPAC classification, it exhibits a typical IV type isotherm with a hysteresis loop that corresponds to capillary condensation taking place in mesopores. The surface area of MCF is up to $887.64 \text{ m}^2 \text{ g}^{-1}$ obtained by BET method. In addition, Fig. 2B shows the pore-size distribution of MCF, which indicates a quite narrow pore size distribution centered at about 3.9 nm. The high surface area and the existence of numbers of mesopores make MCF a promising electrode material for electrocatalysis application.

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