



A novel nonenzymatic hydrogen peroxide sensor based on electrospun nitrogen-doped carbon nanoparticles-embedded carbon nanofibers film



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ABSTRACT

A novel nonenzymatic electrochemical sensor for the detection of hydrogen peroxide (H₂O₂) was developed based on free-standing nitrogen-doped carbon nanoparticles-embedded carbon nanofibers (NCNPFs) film, which were prepared by the carbonization of electrospun polypyrrole nanoparticles/polyacrylonitrile (PPy NPs/PAN) composite nanofibers. A series of NCNPFs-*x* samples with different mass concentration of PPy NPs to PAN (wt.%) were prepared. When the PPy NPs precursor is 12 wt.%, large amount of resulting NCNPs are embedded uniformly in NCNFs substrate without obvious aggregation. The as-obtained NCNPFs-12 wt.% has smaller diameter, higher content of pyrrolic-N and more defective sites, which result in high electrocatalytic activity for H₂O₂ reduction. The NCNPFs-12 wt.%-based H₂O₂ sensor shows a fast amperometric response within 2 s, and a wide linear range of 5.0×10^{-6} to 2.7×10^{-2} M with a high sensitivity of $383.9 \mu\text{A} \mu\text{M}^{-1} \text{cm}^{-2}$. In addition, this nonenzymatic sensor displays good selectivity, high reproducibility and long-term stability. Because of the remarkable analytical performances, the NCNPFs-12 wt.%-based electrochemical sensor shows potential applications for the detection of H₂O₂ in human serum and disinfectant samples with satisfactory results.

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1. Introduction

Hydrogen peroxide (H₂O₂) has widespread applications in the fields of food, pharmaceutical, environmental protection, chemical synthesis [1–3], and so on. Besides, as a common reactive oxygen species (ROS), H₂O₂ plays critical roles in various physiological processes, and may be involved in many pathological conditions including diabetes, neurodegeneration, Alzheimer's disease, and cancer [4,5]. Therefore, it is necessary to explore a rapid, sensitive and accurate method for the detection of H₂O₂. Numerous measurement methods, such as spectrophotometry [6], chemiluminescence [7], fluorescence [8], colorimetry [9], and electrochemical methods [10–13], have been developed for the determination of H₂O₂. Among these techniques, electrochemical sensors have attracted much more attention because of their rapid response, high sensitivity, good selectivity, and low cost [14,15]. Traditionally, enzymes, such as horseradish peroxidase

(HRP) [16], cytochrome c (Cyt c) [17], and myoglobin (Mb) [18], were often used for the construction of electrochemical H₂O₂ sensors. However, the enzyme-based sensors would suffer from complex fabrication procedures, environmental instability, and low reproducibility [19–21], which limited their application. To overcome these problems, it is highly desirable to develop nonenzymatic electrochemical H₂O₂ sensors.

In recent years, noble metal (Pt, Au, Ag) materials have been widely used in the construction of electrochemical H₂O₂ sensors [22–24]. Ju and Chen [25] prepared nitrogen-doped graphene quantum dots supported Au nanoparticles (Au NPs-N-GODs) for the amperometric detection of H₂O₂ with a linear range of 0.25–13327 μM and a detection limit of 0.12 μM. Although these noble metal-based sensors have avoided most disadvantages of enzyme-based sensors, the high cost of metal precursors and surface fouling still limit their practical applications [3]. Accordingly, designing non-precious metals or metal-free materials with remarkable analytical performances for the sensing of H₂O₂ becomes an urgent assignment. Recently, nitrogen-doped carbon nanomaterials have received increasing interest in electrochemical sensors [26,27]. Incorporation of nitrogen atoms into

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carbon materials can yield a large number of defective sites and improve the electron-donor ability, leading to the enhanced electrocatalytic activity of bulk carbon materials [28,29]. Zhang et al. [30] reported that 2D ordered mesoporous carbon nitride (OMCN) showed improved electrocatalytic activity for the reduction of H_2O_2 , and that the proposed H_2O_2 sensor displayed a linear range of 4–12400 μM with a detection limit of 1.52 μM . Xu et al. [31] developed a H_2O_2 sensor based on nitrogen-doped carbon nanotubes (NCNTs), which also had excellent analytical performances with a linear range of 1.76–139 μM and detection limit of 0.37 μM . Nevertheless, electrospun nitrogen-doped carbon nanofibers (NCNFs) have rarely been studied in the electrochemical detection of H_2O_2 in spite of their excellent properties, including free-standing structure and excellent electrocatalytic activity [32].

In this work, we prepared a novel nitrogen-doped carbon nanofibers material, denoted as nitrogen-doped carbon nanoparticles-embedded carbon nanofibers (NCNPFs) film. NCNPFs were simply prepared by the carbonization of electrospun polypyrrole nanoparticles/polyacrylonitrile (PPy NPs/PAN) composite nanofibers. The effect of the mass concentration of PPy NPs to PAN (wt.%) on the morphology, structure and electrocatalytic activity of the resulting composite material was demonstrated. Compared with other samples, NCNPFs obtained with 12 wt.% PPy NPs precursor (NCNPFs-12 wt.%) had the highest electrocatalytic activity for H_2O_2 reduction, and thus was applied to the electrochemical detection of H_2O_2 . The NCNPFs-12 wt.%-based H_2O_2 sensor showed excellent analytical performances with promising application in the determination of H_2O_2 in human serum and disinfectant samples.

2. Experimental

2.1. Materials

PAN (average $M_w=150,000$), ascorbic acid (AA, $\geq 99\%$), dopamine hydrochloride (DA, 98.5%), uric acid (UA, $\geq 99\%$) and Nafion (5 wt.%) were purchased from Sigma–Aldrich. N,N-Dimethyl-formamide (DMF, $\geq 99.5\%$) and H_2O_2 (30 wt.%) were purchased from Beijing Chemical Reagent Co., China. Pyrrole (99%) was purchased from Aladdin. Human serum samples were obtained from healthy volunteers.

2.2. Preparation of NCNPFs-x

PPy NPs used in this work were firstly prepared according to the previous report [33]. NCNPFs-x were prepared by the carbonization of PPy NPs/PAN composite nanofibers, which were obtained via electrospinning a DMF solution containing 10 wt.% PAN and the desired amount of PPy NPs. The NCNPFs-x samples are referred to as NCNPFs-6 wt.%, NCNPFs-12 wt.% and NCNPFs-18 wt.%, where 6 wt.%, 12 wt.% and 18 wt.% represent the different mass concentration of PPy NPs precursor to PAN. The thermal treatment of the electrospun composite nanofibers was similar to our previous work [34]. Briefly, the PPy NPs/PAN nanofibers were firstly stabilized at 280 °C for 60 min, and then were carbonized at 900 °C for 60 min. The heating rate for the stabilization and carbonization procedure was 5 °C/min and 10 °C/min, respectively. The whole thermal treatment process was conducted in an enclosed device composed of two porcelain boats and in the atmosphere of N_2 . For comparison, pure NCNFs were prepared via the same process, and CNFs were also prepared according to the above process, except that they were treated in one porcelain boat and stabilized in air.

2.3. Fabrication of electrochemical H_2O_2 sensor

Prior to the construction of the sensor, the glassy carbon electrode (GCE) with a diameter of 3 mm was polished carefully with alumina slurry, followed by rinsing with ethanol and double-distilled water. The CNFs, NCNFs and NCNPFs-x films were tailored to a disk shape with a diameter of 3 mm and directly attached to the surface of the pretreated GCE. Then, the modified electrodes were glued by 1.0 μL of Nafion solution (0.5 wt.%) and left to dry at room temperature. The modified electrodes were marked as CNFs/GCE, NCNFs/GCE and NCNPFs-x/GCE, respectively.

2.4. Electrochemical measurement

All the electrochemical measurements were performed by using a three-electrode system on a CHI 832C electrochemical workstation (Chenhua Instrument, China). The modified electrodes obtained above were used as the working electrodes. A platinum plate and Ag/AgCl (saturated KCl) were used as the counter and reference electrode, respectively. All the experiments were carried out in phosphate buffer solution (PBS) (0.1 M, pH 7.4) at room temperature. Before measurement, all the solutions used were bubbled with high purity nitrogen for 30 min, and then the nitrogen atmosphere was maintained throughout the measurement.

2.5. Characterization

Transmission electron microscope (TEM) experiments were performed on a TECNAI F20 field-emission transmission electron microscope operated at 200 kV. X-ray photoelectron spectra (XPS) were recorded from an ESCALAB-MKII X-ray photoelectron spectrometer with an excitation source of Al $K\alpha$ radiation. Raman spectra were recorded from a Renishaw RM-1000 with a laser excitation of 514.5 nm.

3. Results and discussion

3.1. Preparation and characterization of NCNPFs-x

The NCNPFs-x samples were prepared by the thermal treatment of PPy NPs/PAN composite nanofibers obtained by electrospinning the mixture of PPy NPs and PAN. The mass concentration of PPy NPs to PAN (wt.%) has a significant effect on the final morphology and structure of NCNPFs-x. Fig. 1 shows the TEM images of pure NCNFs (A), NCNPFs-6 wt.% (B), NCNPFs-12 wt.% (C) and NCNPFs-18 wt.% (D). Compared with pure NCNFs, when the PPy NPs precursor was 6 wt.%, we can see that only a few nitrogen-doped carbon nanoparticles (NCNPs) were embedded in NCNFs substrate, and the diameter of NCNPFs-6 wt.% (174 ± 19 nm) was similar to that of pure NCNFs (180 ± 12 nm). Accompanied with PPy NPs increased to 12 wt.%, the density of NCNPs attached on the surface of NCNFs increased, and the composite diameter decreased to 140 ± 22 nm. Besides, NCNPs are embedded uniformly without obvious aggregation. However, with much higher PPy NPs precursor concentration (18 wt.%), many NCNPs aggregated on the surfaces of NCNFs with larger diameter (202 ± 23 nm). It is worth to note that all the prepared samples exhibit a self-supporting membrane structure with high flexibility, which could be easily tailored to the designed shape for electrode modification.

The introduction of N in NCNFs and NCNPFs-x was characterized by N1s XPS. The high-resolution N1s spectra (Fig. 2) can be deconvoluted into three main peaks with the binding energy of 398.1, 400.6 and 401.2 eV, corresponding to pyridinic-N, pyrrolic-N and graphitic-N, respectively [35]. The content of pyrrolic-N for NCNFs (Fig. 2A), NCNPFs-6 wt.% (Fig. 2B), NCNPFs-12 wt.% (Fig. 2C) and NCNPFs-18 wt.% (Fig. 2D) is calculated to be 37.6%, 39.8%, 48.0%

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