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A novel nitrogen-doped graphene fiber microelectrode with ultrahigh sensitivity for the detection of dopamine

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ABSTRACT

A novel nitrogen doped graphene fiber (NGF) was fabricated via a simple and facile wet-spinning strategy followed by annealing at high temperature, which can be applied as a remarkable electrode material. The NGF microelectrode shows good sensitivity and selectivity for the detection of dopamine with a wide linear response in the range of 0.1 μM to 80 μM, with the detection limit of 30 nM and an ultrahigh sensitivity of 22.08 μA μM^{-1} cm^{-2}. Such high performance enables the NGF to be a prominent material in the branch of electrochemical analysis.

1. Introduction

Microelectrodes are considered to be a kind of electrode with microscopic dimensions [1,2]. Compared to conventional macroelectrodes, microelectrodes have a number of advantages, such as enhanced mass transport, reduced IR drop and high current density [3,4]. Besides, the tiny size also broadens the application to micro and high-resistance systems [5,6]. Fibers with well-defined structures have been widely fabricated as cylindrical microelectrodes, which involves only a single dimension of diffusion. For example, carbon fiber is a commonly used microelectrode material due to its low cost and good biological compatibility [7–9]. However, the low response current and poor electrocatalysis of carbon fiber microelectrodes seriously limit their application in detection [10].

Chemically reduced graphene produced from the graphene oxide (GO) precursor has been widely applied in the field of the electroanalysis because of the inherent defects and residual oxygenated functional groups, which can act as the active sites. In addition, for further improving the electrocatalytic property of graphene electrodes, nitrogen doping has been considered to be a facile and effective approach. The doped N atom has a comparable atomic size and contains five valence electrons for bonding with carbon atoms [11], which can change the intrinsic electronic structure and act as the active site. The nitrogen doped graphene shows excellent electrocatalytic activity, thus improving the device performance in various applications such as sensors, fuel cells and electronic devices [12–14]. These advantages enable nitrogen doped graphene to be a prominent electrode material in in vitro or in vivo detection.

In this paper, we report a facile and straightforward method for the fabrication of nitrogen-doped graphene fiber (NGF) via a wet-spinning strategy followed by thermal annealing. As an electrode material, the NGF possesses enhanced electrocatalytic activity compared with that of graphene fiber (GF). For detection of dopamine (DA), the NGF microelectrode (NGFM) exhibited an ultrahigh sensitivity of 22.08 μA μM^{-1}-cm^{-2} and a low detection limit of 30 nM with the linear range of 0.1 μM to 80 μM.

2. Experimental

2.1. Synthesis of N-doped graphene fiber

GO was synthesized from natural graphite powder according to the modified Hummers method [15]. For the fabrication of NGF, the graphene oxide/polypyrrole fiber (GPF) was firstly prepared as the precursor via a wet-spinning strategy, as reported in our previous work [16]. Then, the NGF was obtained by annealing GPF at 1000 °C for 3 h under Ar/H_2 atmosphere. The NGFs with different diameters were fabricated by using needles with different sizes of spinnerets as 0.05 mm, 0.25 mm, 0.5 mm and 1.2 mm. Except for special statement, the size of the spinneret was 0.05 mm. For comparison, graphene fiber (GF) was fabricated by a wet-spinning strategy, which was reported by Gao's group [17] and then annealing at 1000 °C for 3 h under Ar/H_2 atmosphere.

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2.2. Fabrication of N-doped graphene fiber microelectrode

NGF was glued with silver print conductive paint onto a copper wire. The fiber-copper wire was inserted through a glass capillary with suitable length of fiber and copper wire outside. Both ends of the capillary tip were sealed with epoxy resin. The exposed NGF was cut to be 2.0 mm in length as the cylindrical microelectrode for use and the exposed copper wire was connected with the electrochemical workstation.

2.3. Characterization and measurements

The morphology of the NGF sample was observed by scanning electron microscope (SEM, JSM-7500F). Raman spectra were recorded by using a RM 2000 microscopic confocal Raman spectrometer (Renishaw PLC, England) fitted with 633 nm and 532 nm laser. X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCALab220i–XL electron spectrometer from VG Scientific using 300 W AlKα radiation.

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were measured by a three-electrode electrochemical cell system on a CHI 660D electrochemical workstation (CH instruments, China), where the NGFM sample acted as the working electrode, an Ag/AgCl (KCl, 0.1 M) electrode as the reference electrode, and a Pt wire (0.5 mm diameter) as the counter electrode. All of the solutions were de-oxygenated by bubbling nitrogen gas for 15 min before measurements and maintained under nitrogen atmosphere during the measurements.

3. Results and discussion

As shown in Fig. 1A, the continuous production of GPF was very fast and efficient via a direct wet-spinning strategy. The NGF was fabricated by annealing the as-prepared GPF under Ar/H_2 atmosphere. Upon the thermal treatment, the polypyrrole will decompose and provide nitrogen source for in situ doping when the GO was reduced to graphene. SEM shows rough surface with plentiful wrinkles sheet-like morphologies for GF (Fig. 1B) and NGF (Fig. 1C) with the same diameter of 15 μm. The crumpled regions could lead to a highly accessible surface for the diffusion of the electrolyte, which is favorable for the electrochemical application. Besides, the diameter of the NGF can be easily controlled in the range of 15–70 μm by tuning the precursor GPF via changing the size of spinneret of the needles. It can be clearly seen that the morphologies of these fibers are similar, demonstrating the universality of our method for fabricating NGF with different diameters. Fig. 1C–F display the NGFs fabricated by using different needles with the sizes of spinnerets as 0.05 mm (C), 0.25 mm (D), 0.5 mm (E) and 1.2 mm (F). As a consequence, the formed NGFs have different diameters of 15 ± 3 μm (Fig. 1C), 30 ± 3 μm (Fig. 1D), 50 ± 3 μm (Fig. 1E), 70 ± 3 μm (Fig. 1F), respectively.

Fig. 2A shows the Raman spectra of GPF, GF and NGF. As can be seen, the spectrum of GPF displays a series of peaks at ca. 980 and 1091 cm^{-1}, which is consistent with the peaks of the polymerized polypyrrole [18, 19], indicating the successful polymerization of pyrrole along graphene sheets. The peaks centered at 1350 and 1596 cm^{-1} are corresponding to the D and G bands of carbon materials, respectively [20]. As expected, no peak of polypyrrole was obtained for NGF. Furthermore, NGF has an I_D/I_G ratio of ca. 1.17, which is higher than that of GF (ca. 1.02). This indicates that the doped nitrogen atoms induced defects into the graphene surface [21,22].

X-ray photoelectron spectroscopy (XPS) was used to analyze the surface composition and nitrogen bonding configurations in NGF. As shown in Fig. 2B, the NGF has a predominant graphitic C 1s peak at around 285.3 eV, a weak O 1s peak at around 532.4 eV, and a N 1s peak located at around 400.6 eV. The prominent N 1s peak observed confirms the successful nitrogen doping into the graphene sheets (2.3% N/C atomic ratio). The N 1s peak spectrum of the NGF (Fig. 2C) can be resolved into three constituents: pyridinic-N (~398.3 eV), pyrrolic-N (~400.9 eV) and graphitic-N (~402.9 eV), suggesting N atoms have been incorporated into the graphene frameworks and transformed into three nitrogen-doped structures in the graphene layers [23,24].

The electrochemical characterization of the GFM and NGFM was carried out upon CV technique. According to Fig. 3A, sigmoid-shaped voltammograms were achieved on both GFM (black line) and NGFM (red line) in the solution of 0.5 M KCl containing 5.0 mM $K_3Fe(CN)_6$, revealing the spherical diffusion on the microelectrodes. The diffusion limit current of NGFM was 1.0 μA, which was about two times that of GFM (0.48 μA). The high current density and sensitivity response of NGFM can be attributed to the N-doping effect [25]. The influence of the diameter was illustrated in Fig. 3B. With the increase of the fiber diameter, the shape of CV remains sigmoid, corresponding to the spherical diffusion to the microelectrode. As we know, the spherical diffusion

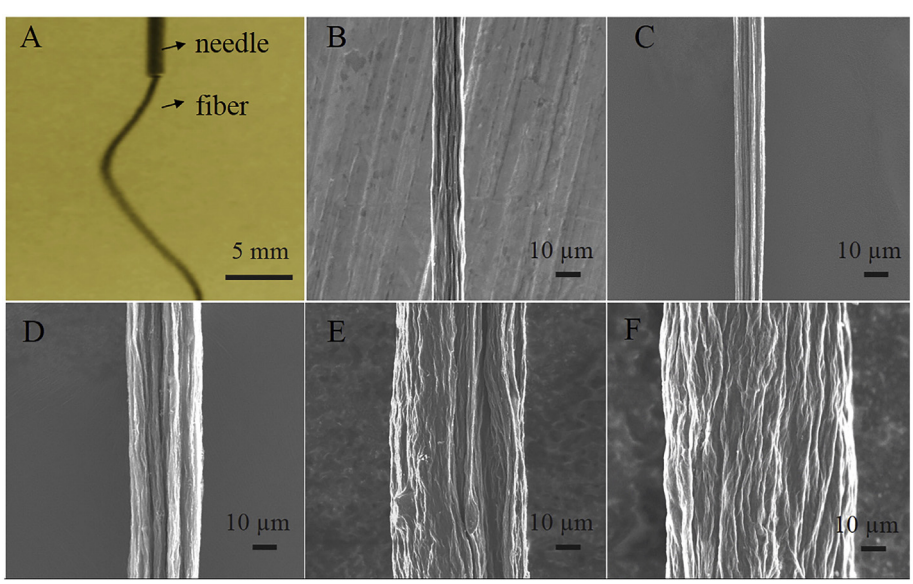

Fig. 1. (A) A photo of the continuous production of GPF. SEM images of (B) GF and (C) NGF. (C–F) SEM images of the NGFs derived from spinnerets with sizes of 0.05 mm (C), 0.25 mm (D), 0.5 mm (E) and 1.2 mm (F).