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Electrospun zirconia-embedded carbon nanofibre for high-sensitive determination of methyl parathion

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ABSTRACT

Carbon nanofibers embedded with ultrafine zirconia nanoparticles (ZrO_2-CNFs) are fabricated via a new methodology. Polyvinylpyrrolidone (PVP) and polymethylmethacrylate (PMMA) binary polymers containing zirconium *n*-butoxide are first dissolved in dimethylformamide, and the resulting solution is electrospun and heat-treated. The tetragonal zirconia nanoparticles formed, with a size of 5 ± 2 nm in diameter, are uniformly distributed in the carbon nanofibres. Using Nafion as an additive, ZrO_2-CNFs are drop-cast onto the glassy carbon electrode (ZrO_2-CNF/GCE) and the modified electrode is then applied to detect methyl parathion (MP) using differential pulse voltammetry. Two linear relationships are found at the concentration ranges of 1×10^{-9}–2×10^{-8} g/L and 2×10^{-8}–2×10^{-7} g/L, with a detection limit of 3.4×10^{-10} g/L (S/N > 3). The electrospun-based ZrO_2-CNF is a very promising coating material for electrochemical sensing of organophosphorus compounds.

1. Introduction

Organophosphorus compounds (OP) are highly neurotoxic substances, and reckless use of OP pesticides results in their residues existing in various environmental matrices. For instance, OP pollution in natural aquatic systems has been a threat to human health [1]. Therefore, there is an urgent need to develop effective methods for accurate measurement of OP in water.

Zirconia (ZrO_2) is an environmentally benign and stable compound. It has been used for OP adsorption [2] and selective determination of organophosphorus agents [3–5] due to its strong affinity to phosphorus groups [6]. Currently, ZrO_2 nanomaterials have been produced by various methods including electrochemical deposition [4], hydrothermal [7] and calcination [8]. However, it is difficult to synthesize ultrafine ZrO_2, due to inevitable particle agglomeration during heat treatment. Also, the poor conductivity of ZrO_2 limits its electrochemical applications [9]. Carbon nanofiber (CNF), as a conductive matrix for loading metal or metal oxides nanoparticles, can not only reduce particle–particle aggregation in the preparation or usage process, but also improve the conductivity.

Electrospun CNF has attracted much attention in electrochemical sensing [10,11] and energy storage [12] applications, due to its excellent conductivity, large surface area and aspect ratio. Usually, ZrO_2-CNFs are prepared by adding the pre-synthesized ZrO_2 particles into a polymer matrix [13] or by hot-pressing a mixture of ZrO_2 and CNF [14]. The pre-synthesized ZrO_2 is poorly distributed in the matrix and severe agglomeration occurs upon heating.

In this paper, a simple method for the fabrication of ZrO_2-CNFs by electrospinning polyvinylpyrrolidone (PVP) and polymethylmethacrylate (PMMA) binary polymers containing zirconium tetrabutyl precursor is proposed, without the need of pre-synthesizing ZrO_2 particles. Adding PMMA to the precursor not only improves the spinnability of the fibre, but also increases the specific surface area of it, due to full decomposition of PMMA during heat treatment [15]. This is the first report about fabrication of ultrafine ZrO_2 nanoparticles modified CNF, and the modified electrode has a great potential for OP analysis. It is a highly sensitive sensor because of its large amount of active sites, highly porous structure and good conductivity.

2. Experimentals

2.1. Materials

Zirconium n-butoxide (ZrB, 80% in 1-Butanol), PVP (MW-1300 kDa), PMMA (MW = 120 kDa) and Nafion solution (5%) were purchased from Sigma and used as received. Methyl parathion (MP,

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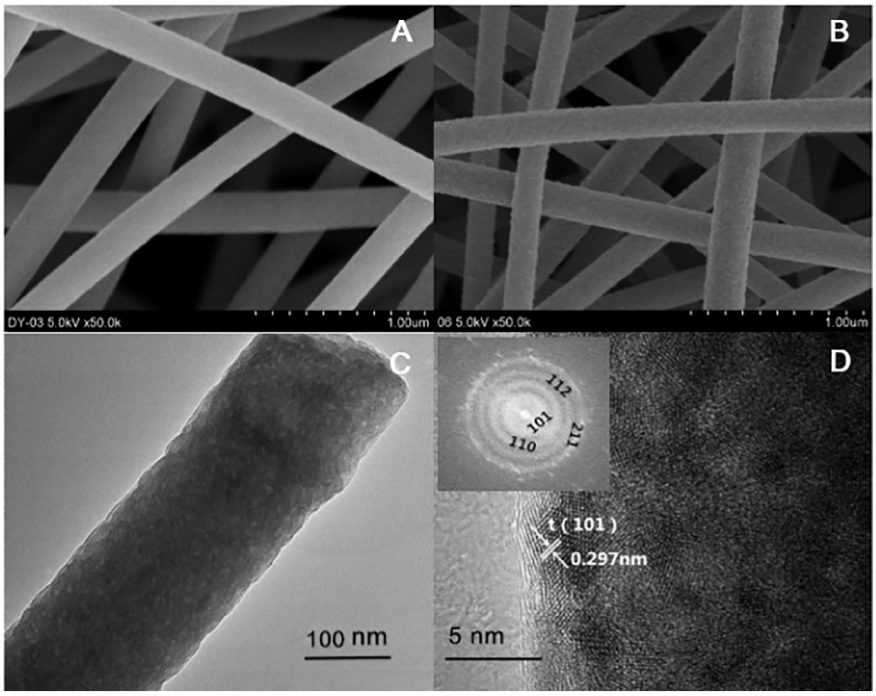

Fig. 1. FE-SEM images of the ZrB-PVP-PMMA fibres (A) and ZrO_2-CNF (B). TEM images of ZrO_2-CNF at low magnification (C) and high magnification (D). The inset in (D) corresponds to the electron diffraction pattern.

1 g/L in methanol) and all other reagents were from Sinopharm. Ultrapure water (Thermo) was used throughout these experiments.

2.2. Fabrication of ZrO_2-CNF

In a typical procedure, 1.0 g PVP and 0.8 g PMMA were dissolved into 8 mL *N*,*N*-dimethylformamide (DMF) with vigorous stirring to form a homogeneous PVP-PMMA solution. 1.0 g ZrB was dissolved into 1 mL glacial acetic acid, and then added to the above solution (mass ratio of PVP to ZrB = 1:1). The mixture was magnetically stirred for 2 h, and immediately transferred into a syringe before electrospinning. A 25 gauge stainless steel needle on the syringe was connected to a high-voltage generator. Electrospinning was conducted in air under a voltage of 12 kV, a solution feeding rate of 1.5 mL/h and a distance between the needle and the collector of 15 cm. The electrospun fibres were then collected on an Al foil. The as-spun ZrB-PVP-PMMA composite fibres were left in air overnight to allow complete hydrolysis of ZrB. Subsequently, these nanofibers were first stabilized at 150 °C for 20 h, and then pre-oxidized at 320 °C for 1.5 h at a rate of 2 °C/min in an ambient environment. This was done to increase the rigidity of polymer chains in the presence of PMMA, preventing fibres from breaking during heat treatment. Finally the pre-oxidized fibres were carbonized at 800 °C for 1 h at a rate of 5 °C/min under nitrogen flow to produce the desired ZrO_2-CNFs. The CNF without Zr precursor was also prepared as a control (mass ratio of PVP to ZrB = 1:0). A series of ZrO_2-CNF samples was fabricated using the various electrospinning solutions with the ratio of PVP and ZrB of 1:0.5, 1:1.5 and 1:2.0, respectively.

2.3. Preparation of ZrO_2-CNF modified GCE (ZrO_2-CNF/GCE)

A glassy carbon electrode (GCE, 3 mm diameter) was polished with 1.0, 0.3 and 0.05 μm Al_2O_3 slurry, respectively, and then sonicated in water and ethanol successively for 2 min each. The cleaned electrode was dried by nitrogen immediately before use. The drop-cast solution was prepared by sonicating a mixture of ZrO_2-CNF (0.1 g/L) and Nafion solution (0.01% w/w) in ethanol for 10 min. 8 μL of ZrO_2-CNF-Nafion suspension was then drop-cast onto a GCE surface to obtain a ZrO_2-CNF/GCE.

2.4. Characterization

Morphology of the nanofibres was studied by scanning electron microscopy (SEM, Hitachi, S-4800) and transmission electron microscopy (TEM, JEOL. JEM-2100F). The component and crystalline structure of nanofibers were characterized by Fourier transform infrared spectroscopy (FTIR, Nicolet 6700), X-ray photo spectroscopy (XPS, AXIS Ultra DLD) and X-ray diffraction (XRD, D/max-2550VB + /PC).

2.5. Electrochemical measurements

Electrochemical experiments were carried out with a μ-AUTOLAB-III electrochemical workstation in a conventional three-electrode system with a ZrO_2-CNF/GCE working electrode, a Pt wire auxiliary electrode and a Ag/AgCl reference electrode (3 M KCl).

For MP measurement, differential pulse voltammetry (DPV) was applied in a deoxygenated acetate buffer (0.1 M, pH = 5) solution. The ZrO_2-CNF/GCE was preconcentrated at − 1.0 V in the MP-containing acetate buffer for 6 min in order to adsorb and get the reduced MP onto the electrode surface. The DPV curve was recorded from − 0.6 V to 0.6 V with a potential step of 4 mV, an amplitude of 25 mV, and a scanning rate of 10 mV/s. After each measurement, the electrode was rinsed with ethanol to remove MP before reuse.

3. Result and discussion

3.1. Characterization of ZrO_2-CNF

The ZrB-PVP-PMMA pristine fibres are first fabricated via electrospinning the PVP-PMMA blend polymer containing ZrB, and the ZrO_2-CNFs formed are obtained after carbonization of the pristine fibre. Fig. 1A and B shows SEM images of the pristine ZrB-PVP-PMMA fibres and ZrO_2-CNFs, respectively. The pristine fibres are uniformly distributed with a very smooth surface, and the average diameter of the