Electrochimica Acta 78 (2012) 200–204

Contents lists available at SciVerse ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Controlled electrochemical behavior of indium tin oxide electrode modified with Pd nanoparticles via electrospinning followed by calcination toward nitrite ions

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ARTICLE INFO

Article history:
Received 11 January 2012
Received in revised form 5 April 2012
Accepted 27 May 2012
Available online 17 June 2012

Keywords:
Electrospinning
Pd nanoparticles
Modified electrode
Nitrite
Electroanalysis

ABSTRACT

Palladium nanoparticles (PdNPs) modified indium tin oxide (ITO) electrode was fabricated via electrospinning followed by calcination. The results of scanning electron microscopy (SEM) images and X-ray photoelectron spectroscopy (XPS) indicated the PdNPs were immobilized on the ITO electrode surface successfully. The electrochemical behavior of the modified electrodes could be adjusted easily by changing the collected time of electrospinning. The prepared electrodes exhibited high sensitivity, good reproducibility and stability toward NO_2^-. The current responses were linear with NO_2^- concentrations in a wide range with low detection limit. The proposed method can be successfully applied to the determination of NO_2^- in real water samples.

1. Introduction

Nanostructured materials often show exotic electronic, optical, and magnetic properties, taking great promise for a wide spectrum of applications. Morphology-controlled synthesis of nanostructures attracts great interests in material chemistry because the physical and chemical properties are strongly dependent on the preparation procedure, size, and shape [1–4]. Nanofibers and nanowires with their huge surface area to volume ratio have the potential to significantly improve current technology and find application in many areas such as nanocatalysis, tissue scaffolds, protective clothing, filtration and nano-electronics [5,6]. Although there are other methods of fabricating nanofibers, few, if any, can match electrospinning in terms of its versatility, flexibility and ease of fiber production [7]. Not only polymer materials but also inorganic materials could be fabricated into fibers by electrospinning. For instance, continuous copper nanofiber networks were fabricated by a low-cost and scalable electrospinning process. The Cu nanofiber networks show superior performance when compared to the Cu thin films [8]. Recently, the study of chemically modified electrode by electrospinning method becomes a very active field. For example, different noble metals and carbon fiber nanocomposite modified electrodes were prepared [9,10]. However, a very high temperature (1100 °C) is needed, and the preparation process must be protected with reduction and/or inert gas for such a kind of nanocomposite.

Nitrite is ubiquitous within environmental, food and physiological systems. It is an important indicator of water pollution. The European Community recommends that the level of nitrite should never exceed 0.1 mg L^{-1} (~2.2 μM) in drinking water (Council Directive 80/778/EEC). Nitrite is a carcinogenic and teratogenic to human beings as their level in the blood exceeds the safety standard [11]. Therefore, it is very important to determine the content level of nitrite ion for the environment and the public health. Several analytical techniques have been proposed for the determination of nitrite ion, such as high performance liquid chromatography [12], spectrophotometry [13], flow injection analysis [14], ion chromatography [15], and so on. In addition, the electrochemical methods have aroused widespread interests in recent years which are characterized by their low cost, easy operation and high sensitivity [16–20].

In this work, an electrochemical nitrite sensor was proposed based on electrospun of mixture solution of palladium(II) acetate and polyvinylpyrrolidone (PVP) on indium tin oxide (ITO) electrode. The electrospun electrodes were annealed at 500 °C for 2 h in air. The production at the electrospun electrode surface was not nanofibers but nanoparticles (NPs). The modified electrodes exhibited attractive performances for nitrite detection, such as high sensitivity, good reproducibility and stability. Moreover, the proposed sensor was also used to determine nitrite in real samples with satisfactory results. The results indicate that the electrospun

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http://dx.doi.org/10.1016/j.electacta.2012.05.149

noble metal salt with suitable polymer is a promising method for novel chemically modified electrodes.

2. Experimental

2.1. Chemicals

All chemicals were analytical grade, or better, and were used as received. Palladium(II) acetate (98%) and PVP (M_W = 1,300,000) were purchased from Alfa Aesar. Sodium nitrite was purchased from Alfa Aesar. Phosphate buffer solutions (PBS) were prepared with 0.2 M NaH_2PO_4 and 0.2 M Na_2HPO_4. Absolute ethanol is of analytical grade from Beijing Chemical Reagent Company. ITO conductive glass was purchased from Shenzhen CSG Display Devices Co., Ltd. (Shenzhen, China). Ultrapure water from Water Purifier (Sichuan Water Purifier Co. Ltd., China) was used in all the experiments.

2.2. Apparatus

The electrochemical experiments were performed using a CHI832C electrochemical workstation (CH Instruments, Inc., Shanghai). The experiments were carried out using a conventional three-electrode with an ITO electrode as the working electrode, a platinum coil as the auxiliary electrode, and an Ag/AgCl (saturated KCl) electrode as the reference electrode. The O-ring with 4.4 mm inner diameter was used to seal the ITO electrode for all electrochemical experiments (geometry area is ca. 0.152 cm^2). Pt microelectrode with diameter of 25 μm was used as working electrode for comparison. All the measurements were carried out at room temperature. The scanning electron microscopy (SEM) images and energy dispersive X-ray (EDX) data were obtained from an XL30 ESEM FEG SEM (Philips, Netherlands). To get clear SEM images, a thin gold film was sprayed on the sample before the characterization. X-ray photoelectron spectroscopy (XPS) measurement was conducted with an ESCALAB-MKII spectrometer (VG Co., UK) with an Al K_α X-ray radiation as the X-ray source for excitation and a chamber pressure of 3.5×10^{-7} Pa.

2.3. Preparation of the Pd NPs modified ITO (PdNPs/ITO) electrode

At first, 0.010 g $Pd(CH_3CO_2)_2$ was mixed with 1.0 g PVP and 9.0 mL absolute ethanol, the mixture was magnetically stirred at room temperature for 12 h and used as electrospinning precursor. The mass ratio of Pd is only 0.06% in the solution. A plastic syringe was filled with the precursor and pumped by a syringe pump (KDS 100, KD-Scientific, USA) at a rate of 1.0 mL h^{-1}. The metallic needle of the syringe was linked to a High Voltage DC Power Supply (Tianjin Dongwen, China) positioned at 150 mm from a grounded ITO electrode (50 mm × 10 mm rectangle). The ITO slide was pretreated to ensure its cleanness. The electrospinning was carried out with an applied voltage of 12 kV, a temperature of 25 °C, a relative humidity of 45–70%, and collected time of 15 or 30 s. After left in air for 6 h, the electrospun modified electrodes were calcined at 500 °C for 2 h in air with a heating rate of 1 °C 4 min^{-1} to completely remove the organics. Pd NPs modified ITO (PdNPs/ITO) electrodes were obtained after cooling to room temperature.

2.4. Measurement procedure

The electrochemical properties of the modified electrode were studied by cyclic voltammetry (CV) in 0.2 M pH 7.2 PBS. Differential pulse voltammogram (DPV) was recorded by applying a positive-going potential scan from 0.6 to 1.0 V (with a step increment of

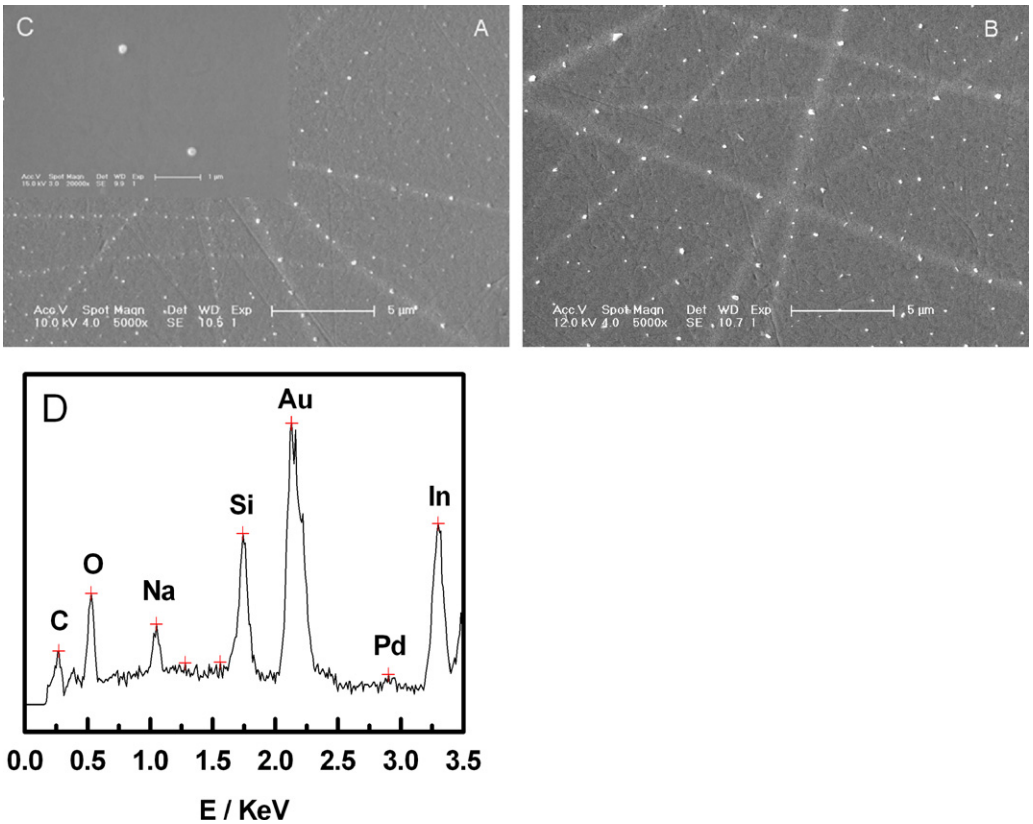

Fig. 1. SEM images of the PdNPs/ITO electrode with different collected time of (A) 15 s and (B) 30 s. The scale bar is 5 μm. The inset (C) is enlarged image of (A), and the scale bar is 1 μm. (D) Corresponding EDX data of (B).