Lithium-doped NiO nanofibers for non-enzymatic glucose sensing

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A B S T R A C T

Lithium-doped NiO nanofibers were synthesized using electrospinning followed by calcinations. The morphology, crystal structure, and electrochemical activities of these nanofibers were characterized, respectively, with scanning electron microscopy (SEM), transmission electron microscope (TEM), X-ray diffraction (XRD), and electrochemical techniques. Electrocatalytic oxidation of glucose was found on these nanofibers in 0.1 M NaOH. The catalytic oxidation current was linear with the concentration of glucose in the range of 0.5 to 278 μM. The detection limit was calculated to be 0.1 μM. Lithium-doped NiO nanofiber is thus a potential electrode material for the construction of non-enzymatic glucose sensor.

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1. Introduction

Quantitative determination of glucose is of great importance to diabetic patients and thus the development of various glucose biosensors has been studied extensively during past decades [1–3]. Among these biosensors, enzyme (e.g., glucose oxidase and glucose dehydrogenase)-based biosensor is the biggest player. Due to the intrinsic features of protein, the disadvantages of enzyme-based biosensors are however quite obvious, including poor stability, less possibility of being used in a severe environment, and high cost [1–3].

To overcome these shortcomings, the fabrication of non-enzymatic glucose sensors has been suggested and tried [2,4–6]. For example, various nanostructures from noble metal (e.g., Pt, Au, Ag, etc.) [4–10], metal alloys (e.g., Pt-Pb, Pt-Ru, Pt-Au, etc.) [4–6,11–13], and metal oxide (e.g., CuO, NiO, Co_3O_4, etc.) [14–18] as well as carbon nanostructures (e.g., tubes, wires, particles, dots, etc.) [19–23] have been frequently utilized as the electrode material for such a purpose. In comparison to enzyme-based glucose biosensors, non-enzymatic glucose sensors have shown the features of good stability, simplicity and reproducibility, although their sensing performance (e.g., sensitivity, linear range, detection limit, etc.) varied with the electrode materials applied [4–6].This is because the properties (e.g., nature, morphology, size, shape, etc.) of these electrode materials synthesized with approaches [4–6,24,25] (e.g., thermal decomposition, polymer matrix template synthesis, sol-gel, dry-etching, and electrospinning) are different, resulting in varied electrochemical activities and electrocatalytic ability towards glucose.

Electrospinning is one of the perfect methods to get the controlled synthesis of these nanostructures with more uniform characteristics and higher reproducibly as well as lower cost [26–32]. These long and continuous nanofibers produced using such a process have the diameters of several micrometers down to a few nanometers, leading to high specific surface areas. During an electrospinning process, the nanofibers can be doped with either metal oxides or metal ions (e.g., Cr, Co, Mn, Fe, Pd, Li, etc.) [26–29], leading to enhanced conductivities, faster electron transfer processes, and/or higher electrocatalytic abilities. For example, lithium-doped NiO (Li-NiO) nanofibers have shown increased conductivity due to the substitution of Li^+ ions to Ni^{2+} [33]. These nanofibers are therefore widely used for drug delivery [29,30], energy conversion and storage [31,32], and sensor development [25–28].

In our lab, we applied electrospinning, followed by calcinations, to produce Li-NiO nanofibers. It is known that bulk NiO, an intrinsic p-type semiconductor [34,35], is actually a good electrocatalyst for glucose oxidation in alkaline media. Surprisingly, there is no report focusing on the utilization of Li-NiO nanofibers for non-enzymatic glucose sensing application. Herein, the first part of this communication summarizes the characterization results of as-prepared Li-NiO

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nanofibers using SEM, TEM, XRD, and electrochemical techniques. The application of Li-NiO nanofibers for non-enzymatic glucose sensing is then detailed, including linear working range, detection limit, etc.

2. Experimental

Polyvinyl pyrrolidone (PVP, molecular weight = 1,300,000), nickel nitrate hexahydrate [$Ni(NO_3)_2 \cdot 6H_2O$], lithium nitrate ($LiNO_3$), D-glucose, dimethylformamide (DMF), ethanol, and sodium hydroxide were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). The Nafion stock solution (0.1 wt%) (Sigma-Aldrich, USA) was prepared using isopropanol.

The synthesis of Li-NiO nanofibers is described as following. First, 0.8 g PVP was dissolved at room temperature in the mixture of ethanol (5.3 mL) and DMF (3.5 mL). The quantities 0.4 g $Ni(NO_3)_2 \cdot 6H_2O$ and 0.02 g $LiNO_3$ were then added into the mixture. After magnetically stirring for 12 h, the mixture was loaded into the syringes for electrospinning. The electrospun conditions were as follows: a needle with an inner diameter of 0.5 mm, a flow rate of 0.5 mL h^{-1}, a gap distance of 11 cm, an applied voltage of 15 kV, and a collector of the aluminum foil. NiO nanofibers were synthesized using a similar procedure but without the addition of $LiNO_3$. The nanofiber precursor was then calcined in air at 500 °C for 3 h to remove the polymer matrix. The treated nanofibers suspension was then prepared by suspending 5 mg nanofibers in 1.0 mL H_2O.

The characterization of the nanofibers was conducted with SEM (JEOL, JSM-5510LV), TEM (JREOL, JEM-2100), XRD (Germany), and a CHI 760E electrochemical workstation (Shanghai Chenhua Company, Shanghai, China). The XRD is equipped with a Bruker D8 diffractometer, a Cu Ka radiation (40 kV, 40 mA), and a Ni filter. For electrochemical measurements, a conventional three-electrode system was used. A platinum foil was the auxiliary electrode, and a saturated calomel electrode (SCE) was the reference electrode. The working electrode was either a bare glass carbon electrode (GCE, 3 mm in diameter) or GCE modified with Li-NiO or NiO nanofibers. These modified electrodes were fabricated via direct casting of 5 μL 5 mg mL^{-1} nanofiber suspension onto the clean surface of GCE. After drying in air with an infrared lamp, an aliquot of 5 μL 0.1 wt% Nafion solution was casted to avoid the leakage of nanofibers from the electrode surface.
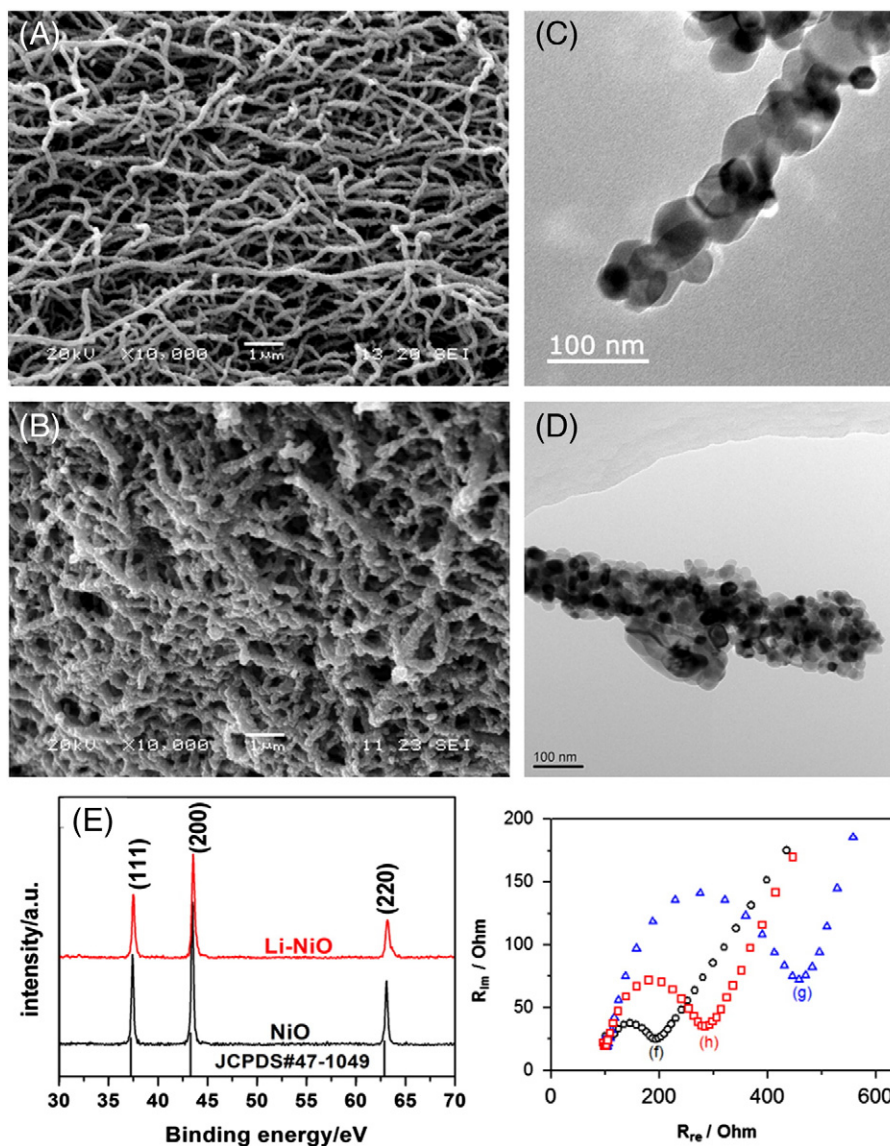

Fig. 1. SEM (a, b) and TEM (c, d) images of NiO (a, c) and Li-NiO (b, d) nanofibers; (e) XRD patterns of NiO and Li-NiO nanofibers; Nyquist plots of a GCE (f), NiO/GCE (g), and Li-NiO/GCE (h) in 5.0 mM Fe[(CN)$_6$]$^{3-/4-}$ + 0.1 M KCl.