



Engineering multi-stage nickel oxide rod-on-sheet nanoarrays on Ni foam: A superior catalytic electrode for ultrahigh-performance electrochemical sensing of glucos

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ABSTRACT

Hierarchical nanoarray is an appealing architecture for molecular recognition on account of its larger surface area and easier accessibility for target molecules compared with single-stage nanoarray and traditional nanoparticle. Herein, we demonstrate that surface-engineering of multi-stage nickel oxide rod-on-sheet nanoarrays on Ni foam (NiO NS@NR/Ni foam) exhibits ultra-high catalytic activity toward electro-oxidation of glucose. When used for nonenzymatic sensing of glucose, this NiO NS@NR/Ni foam electrode shows a wide response range of 0.75–3837 μM , a low determination limit of 0.75 μM , a high sensitivity of 2739.5 $\mu\text{A mM}^{-1} \text{cm}^{-2}$, and a fast response time of less than 4 s. This proposed sensor also demonstrates high selectivity, good long-term stability and practicability in real human serum samples for glucose detection.

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1. Introduction

Glucose, as an important necessity existing in human blood to provide energy for our daily activities, however could bring diabetes mellitus when the amount of it exceeds some value [1]. At present, commercial glucose sensing devices are still bio-recognition elements-integrated electrochemical biosensors wherein glucose oxidase (GOD) assists the electrochemical oxidation toward glucose [2]. Although these sensing devices possess high sensitivity and selectivity, they inevitably suffer from high cost and inherent fragility of natural enzymes, as well as complex and tedious enzyme immobilization procedures [3]. Non-enzymatic electrochemical glucose sensors based on nanomaterials-induced direct electrocatalytic oxidation, due to their high sensitivity, good reproducibility and low-cost of electrode materials, are thus much expected to replace GOD-based biosensors for glucose sensing [4,5]. Till now, noble metals (like Au, Pt, and Pd) and their metal alloys (like Pt-Au, Pt-Pd, and Pt-Ru) still possess the highest catalytic activities for non-enzymatic glucose electro-oxidation

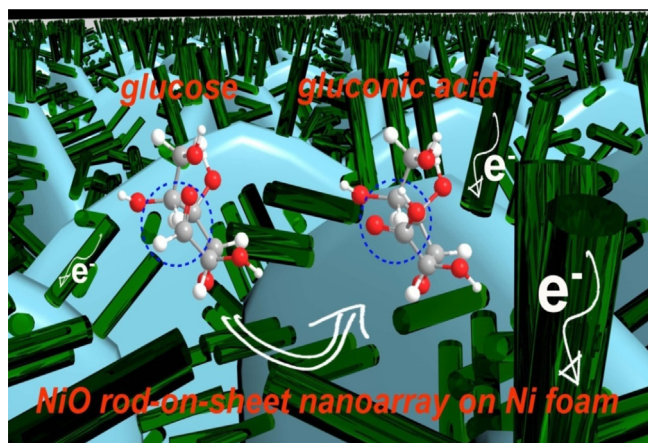
[6–11], but the high cost of such catalysts limits their commercial applications. Therefore, much effort has been devoted in recent years to develop earth-abundant inorganic or organic catalysts-based non-enzymatic sensing devices for glucose detection, wherein the electrode materials include transition-metal oxides/hydroxides/sulfides/phosphides/nitrides and carbon materials [5,12–24].

Ni-based compounds like NiO [25], Ni(OH)₂ [26], Ni₃S₂ [27], NiS [28], and Ni₂P [29], that have been received intensive attention and thus extensively investigated in other electrochemical fields like water electrolysis, supercapacitors, and lithium ion batteries, have been also demonstrated their considerable potential in non-enzymatic electrochemical sensing of glucose on account of the electro-oxidation behaviors resulting from the redox couple of Ni³⁺/Ni²⁺ in alkaline medium. Among them, NiO-based catalytic materials are the most-reported electrode materials in glucose sensing. Traditionally, such catalysts have to be immobilized on electrode surfaces using Nafion, which however may increase the series resistance, block the active sites, and thus bring decreased catalytic performance [13]. By comparison, direct growth of NiO nanoarray on current collectors like Ni foam or carbon cloth ensures strong mechanical adhesion, effective electronic contact between catalytic material and current collector, easy diffusion of electrolytes and much exposure of more catalytic active sites [13,30,31].

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Scheme 1. Schematic diagram of the electrocatalytic oxidation of NiO NS@NR/Ni foam toward glucose in base.

However, the inherent low-conductivity and relative-low surface area of nanoarrayed NiO catalysts also impede the further enhancement of their glucose sensing performances. Based on these issues, several strategies have been proposed in recent years: I) Integrating NiO with other catalytic materials like Au [32], CuO [33], and CNTs [34] to build hybrid nanoarrays with much larger surface area or enhanced conductivity. II) Fabricating high-surface-area NiO nanoarrays like vertical and open-cell nanosheet, nanoflake or nanowire architectures with more exposed active sites [13,31–33]. III) Direct topotactic conversion of NiO into nanoporous Ni₃S₂ [15] and Ni₂P [20] nanoarrays with much enhanced conductivity and larger surface area. All these schemes could much improve the glucose sensing performance of NiO itself.

Except these, in view of hierarchical nanoarray has larger surface area and easier accessibility for target molecules compared with single-stage nanoarray [35–37], developing multi-stage NiO nanoarrays with larger surface area and more active sites are highly required for improving the glucose electro-oxidation performance. Besides, note that, different from other substrates like metal plates, meshes and cloths, metal foams like Ni and Cu foams could perform well both as electrocatalysts and support materials due to the inherent catalytic activities of Ni and Cu elements toward varieties of electrocatalytic reactions [37,38]. Thus, assembling catalytic materials onto metal foams will improve the electrocatalytic performances of corresponding electrodes by synergistic effects. Herein, we propose a novel facile strategy of surface-engineering of multi-stage NiO rod-on-sheet nanoarrays on Ni foam (NiO NS@NR/Ni foam) and demonstrate it could behave as a superior 3D catalytic electrode for high-performance glucose oxidation (Scheme 1). When integrated in a sensing platform for glucose detection, this NiO NS@NR/Ni foam shows superior sensing performance with a wide response range of 0.75–3837 μM , a fast response time of less than 4 s, a low determination limit (LOD) of 0.75 μM , and a high sensitivity of 2739.5 $\mu\text{A mM}^{-1} \text{cm}^{-2}$, as well as high selectivity, reproducibility, and practicability in real human serum samples.

2. Experimental

2.1. Chemical reagents

Nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), glucose, sodium hydroxide (NaOH) powder, sodium chloride (NaCl), urea, hydrochloric acid (HCl), ascorbic acid (AA), fructose (Fru), and other chemicals were obtained from Sinopharm Chemical Reagent Co. Ltd. L-Cysteine (L-Cys) and lactose (Lac) were purchased from Sigma-Aldrich. All

chemicals were analytical grade and used without any further purification. Deionized (DI) water was used throughout all experiments.

2.2. Apparatus

The electrochemical measurements were carried out on a CHI 600E electrochemical workstation with a three-electrode system: a NiO NS@NR/Ni foam electrode as the working electrode, an Ag/AgCl (3 M KCl) electrode as the reference electrode, and a Pt electrode as the counter electrode. The area of working electrode is 0.25 cm^2 in all experiments. Powder X-ray diffraction (XRD) patterns were obtained using a powder diffractometer (Bruker D8 Advanced Diffractometer System) with a Cu $K\alpha$ (1.5418 Å) source. The structure and composition of NiO NS@NR/Ni foam were characterized by field-emission scanning electron microscopy (SEM: Hitachi S-4800 Hitachi Co., Japan). Transmission electron microscopy (TEM) photographs were examined by a Philips Tecnai F20 (Oregon) or Carlzeiss EM912 Ω EF-TEM (Germany).

2.3. Preparation of NiO NS@NR/Ni foam electrode

In a typical procedure, a piece of Ni foam (approximately 2 $\text{cm} \times 3 \text{cm}$) was treated with the mixture solution of hydrochloric acid and DI water (1:3) in a beaker for 5 min, in order to remove the organics and oxide layer on the surface. Then, the Ni foam was thoroughly washed in DI water for 3 min. After that, 4 mmol $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 20 mmol urea and 40 mmol NH_4F were dissolved in 40 mL DI water by magnetic stirring. The resulting homogeneous solution and Ni foam were then transferred into a 50 mL Teflon-lined stainless steel autoclave and maintained at 120 °C for 9 h. After that, the sample was taken out, cleaned by DI water and dried at 60 °C in an oven. Finally, the as-prepared product was calcined at 300 °C for 2 h in an argon atmosphere in a tube furnace.

3. Results and discussion

3.1. Morphological and structural characteristics of the proposed NiO NS@NR/Ni foam

Fig. 1A shows the XRD pattern of NiO scratched down from Ni foam in the diffraction angle range of 30–80°. The positions and relative intensities of all diffraction peaks are well matched with the standard diffraction pattern of NiO (JCPDS No. 47-1049), indicating high crystallinity and high purity of NiO itself. The low-magnification SEM image (Fig. 1B) suggests that the skeleton of Ni foam is fully covered with dense NiO nanostructure up to about 3.92 μm in thickness (inset in Fig. 1B). A closer view of such structure (Fig. 1C) reveals that it is actually a multi-stage rod-on-sheet architecture with the total thickness of about 70 nm and the diameter of these nanorods to be 17–30 nm. The EDX spectrum of NiO NS@NR/Ni foam confirms the co-presence of Ni and O elements and corresponding elemental mapping images demonstrate the uniform distribution of these elements on the foam skeleton (Fig. 1D). The rod-on-sheet nanoarray structure of NiO could be also supported by the TEM result, as shown in Fig. 1E. Corresponding high-resolution TEM image shows a lattice fringe with an interplanar distance of 0.242 nm, which is indexed to the (200) plane of NiO (Fig. 1F). All these results could well support the successful fabrication of multi-stage NiO rod-on-sheet nanoarrays on Ni foam.

3.2. Electrochemical behavior of the NiO NS@NR/Ni foam toward glucose

The electrocatalytic performance of this NiO NS@NR/Ni foam toward glucose is evaluated by the cyclic voltammetry (CV) method

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