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Preparation of nickel oxide and carbon nanosheet array and its application in glucose sensing

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ABSTRACT

Nickel oxide and carbon (NiO/C) nanosheet array was fabricated on Ti foil for the first time by calcining the precursor, which was synthesized through the hydrothermal reaction of nickel acetate, urea and glucose. The slow release of OH^- by the hydrolysis of urea aided in the direct nucleation and adhesion of precursor seeds on Ti substrate. The presence of carbon ensured a large specific surface area and good conductivity of the final NiO/C composite. The prepared NiO/C nanosheet array exhibited higher catalytic oxidation activity of glucose compared with the pure NiO nanosheet at a detection limit of 2 μM, linear range up to 2.6 mM ($R^2=0.99961$), and sensitivity of 582.6 $\mu A m M^{-1} cm^{-2}$. With good analytical performance, simple preparation and low cost, this composite is promising for nonenzymatic glucose sensing.

1. Introduction

Glucose determination has attracted considerable interest in biotechnology, clinical diagnostics and the food industry [1]. A number of studies have focused on developing electrochemical glucose sensors over the past few decades [2] and enzymatic glucose biosensors with good selectivity and sensitivity have been successfully developed [3,4]. However, these biosensors lack long-term stability [5]. Thus, different nonenzymatic glucose sensors should be explored [6–10].

Nonenzymatic electro-oxidation of glucose using Ni-based material has been extensively studied, since Fleishman and his co-workers [11] demonstrated that organic compounds could be partially oxidized at a nickel anode in alkaline solution. Glucose sensors based on Ni metallic nanomaterials exhibited high catalytic oxidation activity over glucose [12–14]. However, Ni metallic nanomaterials are unstable and easily oxidized in air and solution. Therefore, considerable efforts have been focused on the use of nickel oxide to modify the electrodes. Cheng et al. [15] devised NiO nanoparticles modified carbon paste electrode. Liu et al. [16] prepared Ni/NiO nanoparticle-loaded carbon nanofiber paste electrode. These proposed electrodes exhibited long-term stability towards the glucose determination. However, a common problem that occurred when using NiO to modify electrodes is the poor charge transport.

Carbon materials have received considerable attention because of their unique properties, such as excellent conductivity, high surface area-to-volume ratio, and good physicochemical stability [17]. Carbon nanotubes, diamond like carbon and graphene have been used to improve the conductivity of composite in the glucose determination [18–20]. However, the preparation of these carbon materials is not simple and economy. Considering this point, partially graphitized carbon would be a good substitute. An important example was demonstrated by Huang et al. [21]. The electronic conductivity of NiO/C composite was improved after the incorporation of partially graphitized carbon. The prepared composite exhibited much better performance as lithium-ion battery electrode material than pure NiO. However, to our knowledge, using NiO and partially graphitized carbon composite for nonenzymatic glucose sensing has never been discussed before. Stimulated by this result, NiO and partially graphitized carbon composite nanosheet array was synthesized in our laboratory.

In this article, NiO/C nanosheet array was successfully fabricated on Ti substrate using a two-step method. The slow release of OH^- by the hydrolysis of urea was assumed to explain the nucleation and adhesion of precursor seeds on Ti substrate. The fabrication process was simple and cheap. Furthermore, the presence of partially graphitized carbon ensured a large specific surface area and good conductivity of the final NiO/C composite. As a result, the NiO/C nanosheet array exhibited shorter response time, lower detection limit and higher sensitivity towards the

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detection of glucose compared with pure NiO nanosheet. With good analytical performance, simple preparation and low cost, this NiO/C composite is promising for nonenzymatic glucose sensing.

2. Experimental

2.1. Reagents

All chemicals, including nickel acetate, urea, glucose, and sodium hydroxide (NaOH), were obtained from Sinopharm Chemical Reagent Company and used as received without further purification. All aqueous solutions were prepared in distilled water. The titanium foil was 99% pure.

2.2. Apparatus

Products were characterized by scanning electron microscopy (SEM; JSM-6700 F, 5.0 kV), powder X-ray diffraction (XRD; Bruker D-8 Avance, Cu $K\alpha$ radiation, 1.5418 Å), Raman spectroscopy (Confocal Raman Microspectroscopy, RM-1000, 514.5 nm), transmission electron microscopy (TEM; JEM-2010FEF, 200 kV), and Nitrogen adsorption–desorption measurements (Micromeritics Tristar 3000 analyzer).

All electrochemical experiments including electrochemical impedance spectroscopy (EIS) were carried out using a CHI 660C Electrochemical Work Station (CH Instrument Company of Shanghai, China). A conventional three-electrode system was adopted with NiO/C nanosheet array modified Ti foil as the working electrode, Pt wire as counter electrode, and saturated calomel electrode (SCE) as the reference electrode. All potential values were referred to the SCE.

2.3. Fabrication of NiO/C or pure NiO nanosheet array on Ti foil

NiO/C nanosheet array was prepared on Ti substrate by first dissolving nickel acetate, urea and glucose in 60 ml distilled water to achieve 0.05, 0.25 and 0.01 M, respectively. Ti foils were placed vertically in the solution. The mixing solution was transferred into a 100 ml Teflon-lined stainless steel autoclave and kept at 120 °C for 10 h. The substrate was then washed, dried at 60 °C and further annealed in N_2 gas at 500 °C for 2 h. A uniform NiO/C nanosheet array film was then formed on Ti foil. Carbon in the NiO/C composite was incorporated by the hydrothermal reaction of glucose in the first mixing solution. The glucose used here could be replaced by sucrose or cellulose.

To understand the role of carbon in final composite, pure NiO nanosheet array was prepared on Ti substrate for contrast. NiO nanosheet array was prepared by first dissolving nickel acetate and urea in 60 ml distilled water to achieve 0.05 and 0.25 M, respectively. Ti foils were placed in the solution as substrate. The solution was kept at 120 °C for 10 h. Then Ti foils were washed, dried at 60 °C and further annealed in N_2 gas at 500 °C for 2 h. Pure NiO nanosheet array film was then uniformly formed on Ti foil.

2.4. Electrochemical experiments

The electrochemical behavior of the prepared electrode was investigated by cyclic voltammetry (CV). NiO/C nanosheet array modified Ti foil (NiO/C–Ti) and pure NiO nanosheet array modified Ti foil (NiO–Ti) were evaluated as the working electrode. Amperometric curves were recorded after adding the glucose solution to the electrolyte.

3. Results and discussion

3.1. Preparation and morphology of NiO/C nanosheet array grown directly on Ti substrate

NiO/C nanosheet array film was fabricated on Ti substrate in two steps, as shown in Fig. 1. According to recent report, the polymerization and dehydration of the hydroxyl group in glucose molecules under hydrothermal condition could result in a complicated mixture of organic compounds [22]. The organic compounds were transformed into partially graphitized carbon under anneal treatment in protective gas [23]. In the hydrothermal process, both urea and glucose played important roles. The hydrolysis of urea provided a source of anions during the formation of the precursor $Ni_2(OH)_2(CO_3)$ [24]. The polymerization and dehydration of glucose under hydrothermal treatment generated a mixture of organic compounds. The organic compounds uniformly coated on the precursor $Ni_2(OH)_2(CO_3)$. During the next anneal in N_2 gas, the precursor decomposed into NiO [25]. The organic compounds were transformed into a carbon shell coating on the NiO nanosheets. Different kinds of metal oxide and carbon composites were prepared using similar method [26–28]. The possible precipitation reactions were as follows:

$$CO(NH_2)_2+H_2O\rightarrow NH_4^+ + OH^- + CO_3^{2-} \quad (1)$$

$$Ni^{2+}+OH^- + CO_3^{2-}\rightarrow Ni_2(OH)_2(CO_3)\downarrow \quad (2)$$

$$Ni_2(OH)_2(CO_3)\rightarrow NiO+H_2O+CO_2 \quad (3)$$

The typical morphology of the prepared NiO/C nanosheet array is illustrated in Fig. 2(A–C), as observed by SEM. The prepared NiO/C composite is uniformly distributed on Ti foil on a large-scale. The film consists of interconnected nanosheets with 90–120 nm thickness and lateral sizes of 600–900 nm. These nanosheets have rough surfaces. They are decorated with small sphere particles with a diameter of 60–90 nm.

The direct growth of NiO/C nanosheet array on Ti foil was ascribed to urea. The slow release of OH^- by the hydrolysis of urea aided in the nucleation and adhesion of precursor seeds on Ti substrate. To confirm this point, pure NiO nanosheet array was prepared without the additive of glucose in the first reaction solution.

The typical morphology of pure NiO nanosheet array is illustrated in Fig. 2(D and E). The structure is similar to that of NiO/C nanosheet array. However, the pure NiO nanosheets have smooth surfaces. No other materials, such as small sphere particles, are observed. These nanosheets are aligned vertically to the Ti foil, enabling robust mechanical adhesion and electrical contact of every nanosheet to the substrate. This result implies that glucose has no relationship with the direct growth of nanosheet array on Ti substrate.

In other two contrast experiments, urea was replaced by ammonia or sodium hydroxide. Nothing was obtained on Ti substrate, as observed from Fig. 2(F) and its inset. This result confirmed that urea played an important role in the direct growth

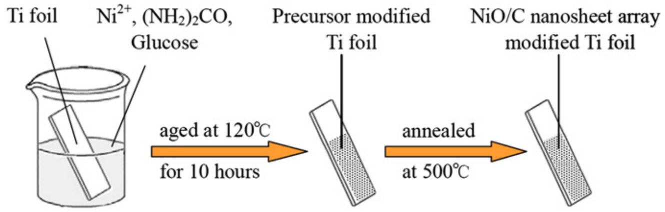

Fig. 1. Fabrication processes of the NiO/C nanosheet array film grown directly on Ti foil.