Facile preparation of three-dimensional NiO nanosheets array on carbon sphere and its high-performance nonenzymatic glucose detection

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Abstract. An ultrathin NiO nanosheets array loaded on carbon spheres were prepared by coprecipitation method and calcination approach. The as prepared NiO nanosheets contain high surface specific area due to their cross-sectional NiO three-dimensional structure which leads to more susceptible contacting between nanosheets and electrolyte. As the results, the reversible redox reaction should be accelerated. Moreover, NiO nanosheets array@carbon sphere (NiO@C) nanocompounds were mixed with Nafion solution and loaded onto glassy carbon electrodes (GCEs) to form a high performance non-enzymatic electrochemical glucose sensor. Cyclic voltammetric (CV) and Amperometric studies indicated NiO@C nanocompounds demonstrated excellent electrocatalytic activities for glucose detection.

1. Introduction

Electrochemical method for glucose analysis and detection in is of great practical significance and crucial demand in the sphere of biological engineering, ecosystem conservation, clinical diagnoses, food industry and agricultural production [1, 2]. Enzymatic biosensor has been constructed which is a typical device for detecting biological materials due to its great electrochemical activity and highly selectivity. However, enzymes containing glucose oxidase (GOD) are not only very expensive, but also very easy to inactivate under some special conditions such as high temperature or different pH, which results in difficulty in getting the analysis of the real samples [3].

Nanostructured metal and metal oxides, including NiAl-LDH [4], NiCo2O4 [5], Ni (OH)2 [6], have been widely used as non-enzymatic catalysts in the field of glucose biosensing due to their low price and high electrochemical activity. In a variety of nanomaterials, nickel-carbon nanocomposites with unique structures are particularly regarded because the composites have excellent electrical conductivity as well as more electrocatalytic active sites [7-9].

Herein, a three-dimensional array of NiO nanosheets were loaded on carbon spheres by coprecipitation method and subsequent calcination approach. Carbon sphere was in-situ growth from the glucose precursor and used as a conductive substrate on which the electrochemically active NiO nanosheets were uniformly loaded. Because the as prepared NiO@C nanomaterial has a large specific surface area, more electrochemically active sites can be in sufficient contact with the glucose in the electrolyte. In addition, due to its great conductivity, the reversible electrochemical reaction was totally...
facilitated [10]. Therefore, this unique nanostructured NiO@C nanocompounds were suitable to be chosen as electrocatalysts for glucose detection, and the nonenzymatic biosensors which constructed with this NiO@C have high sensitivity and excellent selectivity.

2. Experiment

2.1. Preparation of NiO@C Nanocomposite

5.8158 g nickel nitrate hexahydrate, 3.7513 g aluminum nitrate nonahydrate, 3.6 g of urea and 0.7206 g glucose were mixed and dissolved into 200 mL deionized water. Then the mixture was placed in a 110 °C oil bath and stirred vigorously for 9 h. After the completion of stirring, the mixture was quickly transferred to a Teflon-lined autoclave which then placed in a 100 °C oven for 15 h. Subsequently, the products were washed three time in NaOH and deionized water, and calcinated in N\textsubscript{2} at 1000 °C for 2 h. Finally, the products of NiO@C nanocomposites were obtained.

2.2. Fabrication of NiO@C Electrodes

10 mg/mL NiO@C nanocompounds were mixed with 1% Nafion solution. GCEs which diameter is 3 mm were polished with Al\textsubscript{2}O\textsubscript{3} slurry (0.15 μm) and then cleaned with isopropanol and ultrapure water in an ultrasonic cleaner. In the end, 6 μL of the NiO@C solution was added dropwise onto the cleaned GCE surface and dried under the infrared lamp.

3. Results and Discussion

The morphology of as-synthesized NiO@C nanocompounds were measured by SEM. Figure 1 indicates the SEM images of NiO@C nanocompounds. Rich NiO nanosheets had a rough and interconnected structure and were uniformly loaded on spherical carbon, which show large specific surface area and rich active sites of NiO@C. It can be seen from the figure 1b that the thickness of the NiO nanosheets is just about 10 nm, which are also highly conducive to electron transfer [7].

![Figure 1](image-url)

Figure 1. SEM images of NiO@C nanocompounds under different magnification: (a) 20 μm, (b) 2 μm.

The phase structures of as-prepared NiO@C nanocompounds was further investigated shough XRD measurement. Figure 2 indicated XRD pattern of NiO@C nanocompounds, and a series of characteristic peaks were observed at 2θ values of 37.2, 43.3, 62.8 and 75.4, which can be indexed to (101), (012), (110) and (113) plane reflections of cubic structure of NiO (JCPDS no. 44-1159) phase [8].

The electrochemical performance of as-prepared NiO@C nanocomposites was tested in 0.1 M KOH solution. It could be seen from Figure 3a that the CV diagram of NiO@C nanocompounds without glucose had a pair of reversible redox peaks [9], which could be assigned to the valence transition between Ni (II) and Ni (III) species in the KOH electrolyte. In addition, Figure 3a also showed CV curve of as-synthesized NiO@C nanocompounds in 0.1 M KOH solution containing 1 mM glucose. The
Faraday current representing glucose oxidation was significantly increased, and the whole processes can be explained by the following reaction formula [10]:

$$\text{Ni(II)} + \text{OH}^- \rightarrow \text{Ni(III)} + \text{e}^-$$
$$\text{Ni(III)} + \text{Glucose} \rightarrow \text{Ni(II)} + \text{Glucolactone}$$

Figure 2. XRD pattern of the NiO@C nanocomposite.

Figure 3. (a) CV diagram of the as-synthesized NiO@C nanocompounds and the nanocompounds in 0.1M KOH solution without (blakc line) and with 1 mM glucose (red line) at the scan rate of 50 mV s$^{-1}$. (b) Amperometric sensing of glucose by the successive addition of glucose for the as-snythesized nanocompounds at 0.59 V in 0.1 M KOH.

Glucose detecting was measured by chronoamperometry in 0.1 M KOH solution, and Figure 3b showed the amperometric curve of subsequent successive addition of glucose. For the NiO@C nanocompounds, the oxidative currents increased rapidly as glucose continued to increase, and the steady-state current could be reached 92% within 10 s. As a result, it can be seen that NiO@C nanocompounds has excellent catalytic performance for glucose and is very suitable for constructing glucose electrochemical biosensors.
4. Conclusion
A coprecipitation method and calcination approach were used for constructing a 3D NiO@C nanocompounds, which ultrathin NiO nanosheets array uniformly loaded on carbon spheres. This excellent structure provides more electrochemical reactive sites and is more conducive to contact with glucose substrates, which favors fast reversible faradic redox reactions. Therefore, the as-synthesized NiO@C nanocompounds can be applied for an excellent glucose biosensor with high electrochemical activity and sensitivity. The combination of NiO, and C makes the NiO@C nanocompounds a very promising electrocatalyst for constructing biomolecules' biosensors in practical applications.

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