Ordered-standing nickel hydroxide microchannel arrays: Synthesis and application for highly sensitive non-enzymatic glucose sensors

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Abstract

A non-enzymatic glucose sensor is constructed by using nickel hydroxide (Ni(OH)₂) modified silicon microchannel plates (MCP) as the sensing materials. The 3D ordered Si MCP is fabricated by electrochemical etching and the Ni(OH)₂ coating are prepared by electroless plating. The nanocomposite electrode exhibits good catalytic activity toward oxidation of glucose in 0.1 M KOH. This non-enzymatic glucose sensor boasts a fast amperometric response time of less than 5 s, sensitivity of 0.25 mA mM⁻¹ cm², and detection limit of 3.5 μM at a signal-to-noise ratio of 3. The sensor shows superior stability, anti-interference capability, and selectivity. The good analytical capability, low cost, and compatibility with silicon technology make the Ni(OH)₂/Si MCP electrode promising in amperometric non-enzymatic glucose detection.

1. Introduction

The development of novel glucose sensors with high sensitivity, reliability, fast response, and good selectivity is crucial to diagnosis and treatment of diabetes mellitus, clinical biochemistry, waste water treatment, and the food industry [1–3]. Since Clark and Lyons utilized glucose oxidase to produce the first enzymatic electrode in 1962 [4], it has attracted extensive attention. Conventional glucose sensors involve the use of glucose oxidase (GOD) which catalyzes oxidation of glucose in the presence of O₂ to produce hydrogen peroxide. The signal transduction is based on oxidation of the hydrogen peroxide. Although this type of biosensors displays very high sensitivity and selectivity to glucose, the complicated immobilization procedures, thermal and chemical instability, and high cost of enzymes have hindered progress. Nevertheless, many types of enzymatic glucose sensors have aroused interest and been applied to direct electrochemical oxidation of glucose [5]. Some noble metals (Pt, Au, Ag, etc.), alloys (Pt–Pb, Pt–Au, Ni–Pd, etc.), metal oxides (RuO₂, CoO, MnO₂, etc.), carbon nanotubes, and graphene have been used in the fabrication of non-enzymatic glucose sensors [3,6–8]. In particular, nickel-based nanomaterials exhibit remarkable activity owning the presence of the Ni(OH)₂/NiOOH redox couple formed in an alkaline medium [9–10]. Compared to the other materials, Ni is relatively economic. As known that nano/microstructured materials exhibit enhanced electrochemical performance and many types of Ni-based materials have been fabricated with various structures such as nanoparticles [11–12], nanoflake arrays [13], and so on.

The use of Ni-based nanomaterials requires a supporting substrate. An ideal support should have the following properties: (1) high surface area for catalyst loading; (2) excellent conductivity and convenient routes for electron transfer; (3) compatibility with silicon technology to enable device miniaturization. Silicon microstructures such as Si microchannel plates (MCP) possess unique properties including ordered structure, biocompatibility, multifunctionality, and compatibility with microelectronics technology [14]. These advantages make Si MCPs promising in electrochemical sensors. In this work, a non-enzymatic glucose sensor based on Ni(OH)₂/Si MCP electrodes is fabricated and the performance is studied systematically.

2. Experimental details

2.1. Materials and reagents

The wafer used to fabricate the Si MCPs was single-side polished, p-type silicon with a resistivity of 2–9 Ω cm, and a thickness...
of 525 μm. Hydrofluoric acid, dimethylformamide, ammonium fluoride, sodium hydroxide, ethanol, and all other reagents were of analytical reagent grade and used without purification. The specific resistivity (18 MΩ) of de-ionized water was used and all the experiments were carried out at room temperature in a clean environment.

2.2. Preparation of silicon microchannel plates

The silicon microchannel plates were fabricated according to Ref. [15] using a chemical etching procedure. The silicon wafers were cleaned by a standard RCA process, rinsed with de-ionized water several times, and dried with nitrogen. Silicon oxide as the masking layer was formed by thermal oxidation, and lithography and wet etching were utilized to define the electrochemically etched locations. The masking pattern was made of 5 × 5 μm squares with a spacing of 6 μm between the centers of each neighboring square. Before electrochemical etching of the silicon substrate, an aqueous tetramethylammonium hydroxide (TMAH) was used to produce pits on the surface. High aspect ratio Si MCPs were fabricated by electrochemical etching using a solution of hydrofluoric acid and dimethylformamide at the optimal current density (10 mA cm⁻²), etching bias (15 V), and temperature (20 °C). A cooling system was used to prevent temperature increase caused by illumination. The etching current density was stabilized by a program based on LabVIEW. The composition of the etchant and etching time were adjusted to control the lengths of the Si MCPs. The fabrication process of the Si MCP and schematic drawing of the etching system are depicted in Fig. 1.

2.3. Preparation of nickel oxide-modified silicon microchannel plates (NiO/Si MCP)

Electroless plating was conducted because the channels in the silicon MCP could be coated with metal uniformly and the thickness of the metal film could be easily controlled by the bath composition and temperature [16]. For uniform fabrication of the electrode for glucose sensing, the separated Si MCPs was segmented into small chips with a rectangular shape by laser cutting. The chips were cleaned using the standard RCA process. The samples were dried at 30 °C with nitrogen and weighed on an ultra-microbalance with a precision of ±0.001 mg (Mettler Toledo, Switzerland). They were put into a buffer solution (TritonX-100) for 30 s to decrease the inner stress and enhance wetting prior to immersion in the plating bath for 20 min. Afterwards, they were taken out and rinsed with water. Plating was carried out at 70 °C in a solution prepared by mixing nickel sulfate (NiSO₄), ammonium sulfate ((NH₄)₂SO₄), ammonium fluoride (NH₄F), sodium citrate (C₆H₅Na₃O₇), in sodium lauryl sulfate (CH₃(CH₂)₁₀CH₂OSO₃Na) in deionized water. NiSO₄ was used as the metal source and C₆H₅Na₃O₇ as the complexing agent. During deposition, the pH was adjusted to pH 8.0 by addition of ammonia. Afterwards, the nanocomposite was annealed at 500 °C for 300 s in a rapid thermal annealing (RTA) system. Copper wires were connected to the silver

![Fig. 1. (a) Fabrication process of the Si MCP and (b) schematic drawing of the etching system.](image-url)
2.4. Apparatus and measurement procedures

The morphology of the silicon (Ni(OH)₂)/Si MCP was characterized by scanning electron microscopy (SEM, JSM-6360LA). The crystalline structure of the (Ni(OH)₂)/Si MCP nanostructure was determined by X-ray diffraction (XRD) using Cu Kα radiation (Rigaku, RINT2000, Japan). A vertical goniometer (Model RINT2000) was used and the continuous scanning mode (2°/h) with an interval of 0.02° and scanning rate of 10°/min was adopted. The electrochemical experiments were performed on a three-electrode cell controlled by an electrochemical workstation (LK3200A, Lanlike, China). The electrochemical catalytic property of the electrodes towards glucose oxidation was investigated by cyclic voltammetry (CV) in 0.1 M KOH solution at a scanning rate of 5 mV s⁻¹. All of the potentials were referenced to the 3 M KCl saturated Ag/AgCl electrode (home-made) and the measurements were performed at room temperature.

3. Results and discussion

3.1. Formation of the Ni(OH)₂/Si MCP electrode

Several studies have been devoted to the investigation of the electrochemical behavior of nickel electrodes in an alkaline solution and it has been shown that anodic oxidation of the nickel electrode in an alkaline solution involves the NiO/Ni(OH)₂ and Ni(OH)₂/NiOOH redox reactions [17,18]. Hence, the nickel hydroxide coating is produced on the sidewall of the Si MCP by cyclic voltammetry (CV). The Ni(OH)₂/Si MCP electrode is prepared in an aqueous solution of 0.1 M KOH at a scan rate of 50 mV s⁻¹ for 100 cycles. The nickel modified Si MCP serves as the working electrode, a platinum wire forms the counter electrode, and Ag/AgCl serves as the reference electrode. The CV curves in Fig. 2 shows a pair of well-defined cathodic (−0.1 V) and anodic (0.69 V) peaks corresponding to the Ni²⁺/Ni³⁺ couple. In the second potential cycling, the redox peak is nearly constant after several cycles and the current increases gradually. This process can be summarized as follows:

\[
\text{Ni}^{2+} + 2\text{OH}^- \rightarrow \text{Ni(OH)}_2
\]

The amount of Ni(OH)₂ spontaneously formed due to the interaction with H₂O or OH⁻ is still limited so that the redox peaks shift in the CV. Raising the potential leads to the conversion of more NiO to Ni(OH)₂. Therefore, sufficient redox couples of Ni(OH)₂ and NiO-OH are produced and a pair of redox peak appears since the hydroxyl groups on the surface of the metal oxide are extremely sensitive to oxidation:

\[
\text{Ni(OH)}_2 + \text{OH}^- \rightarrow \text{NiOOH} + \text{H}_2\text{O} + \text{e}^-
\]

3.2. Characterization of the Ni(OH)₂/Si MCP electrode

Fig. 3a depicts the top-view and cross-sectional SEM images of the electrochemically etched Si MCP with a high aspect ratio. The surface has a regular square morphology with all the channels aligned. The etched microchannel depth reaches approximately 200 μm and the square holes are about 5 μm in length. The use
of a structure with such a large vertical surface area to load the sensing materials is expected to increase the sensitivity of the sensor while maintaining the original small substrate footprint. After electroless nickel plating, nickel nano-grains several to hundreds of nanometers in size exist on the inner walls as the current collector layer of the sensor, as shown in Fig. 3b. The surface of the nickel layer is not smooth and so it can provide more surface area to form nickel hydroxide. The morphology of the Ni(OH)₂ film on the side-wall surface is depicted in Fig. 3c. Fig. 3d is the magnified picture of Fig. 3c. The morphology of the Ni(OH)₂ film with the nano-flake morphology on the channels is not the same possibly due to the asymmetry of ion concentration deep inside the microchannels. The nano-flakes are intertwined to produce a nano-porous Ni(OH)₂ film with a large surface area and short diffusion distance and excellent electrochemical performance is expected.

The XRD pattern of Ni(OH)₂/Si MCP is shown in Fig. 4. The Si signal from the MCPs is masked by other signals. The Ni(OH)₂/Si MCP shows very little changed compared to the Ni/Si MCP the small peaks at 2θ = 12° correspond to the α-Ni(OH)₂ phase. It is caused by the unstable α-Ni(OH)₂ under the alkaline conditions [19].

3.3. Voltammetric behavior of glucose on the Ni(OH)₂/Si MCP electrode

The electrocatalytic behavior of the Ni(OH)₂/Si MCP electrode towards oxidation of glucose is investigated by cyclic voltammetry in the potential range from −0.4 V to 0.8 V. The CVs of the Ni(OH)₂/Si MCP electrode in 0.1 M KOH in the absence (solid line) and presence (dashed line) of glucose at a scanning rate of 5 mV s⁻¹ are presented in Fig. 5a. In the alkaline electrolyte medium, the Ni(OH)₂/Si MCP electrode shows a pair of well-defined redox peaks attributed to the Ni(II)/Ni(III) couple. After addition of 5 mM glucose, the intensity of the oxidation peak increases sharply, indicating that the Ni(OH)₂/Si MCP can catalyze oxidation of glucose in KOH. Oxidation of glucose by the Ni(OH)₂/Si MCP electrode proceeds as Ni(III) + glucose → Ni(II) + gluconolactone as an irreversible process [20]. Catalytic conversion of Ni(III) to Ni(II), which is before electrochemical reduction, can enrich Ni(II) in the electrolyte thus boosting the anodic reactions.

The influence of the scanning rate on the cyclic voltammogram response of the Ni(OH)₂/Si MCP electrode is evaluated and the results are displayed in Fig. 5b. The Ni(OH)₂/Si MCP electrode redox peak current rises with scanning rates and both the anodic and cathodic peak currents show a linear response to the scanning rates (Fig. 5c) suggesting a surface controlled process with correlation coefficients is 0.988 [21].
The stability of the electrode is investigated by the amperometric response in 1 mM glucose solution. The measurement is performed every 2 days and the sensor was stored at 60°C in an electric oven when not in use. The current response only decreases by 6% after 2 weeks thus showing good stability. The selectivity of the Ni(OH)₂/Si MCP electrode is not affected significantly by AA and UA under the experimental conditions.

4. Conclusion

A Ni(OH)₂/Si MCP electrode prepared by electrochemical etching and electroless plating is applied to glucose sensing. The Ni(OH)₂/Si MCP film consists of crystals with different morphologies on the inner walls of the microchannels. The Ni(OH)₂/Si MCP electrode delivers excellent electrochemical performance in glucose oxidation including a fast response time of less than 5 s, low detection limit of 3.5 μM, linear detection of glucose in the concentration range between 0 and 8 mM, and high sensitivity of 0.25 mA mM⁻¹ cm⁻². The good performance arises from the high valence nickel species and large surface-to-volume ratio of the Si MCP. The Ni(OH)₂/Si MCP electrode has good stability and selectivity albeit in the presence of common interfering species. Boasting compatibility with microelectronics technology, fast response, high sensitivity, as well as long-term stability, the sensor has immense potential in pharmaceutical and clinical detection of glucose.

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