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Nickel oxide hollow microsphere for non-enzyme glucose detection

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ABSTRACT

A facile strategy has been developed to fabricate nickel oxide hollow microspheres (NiO-HMSs) through a solvothermal method by using a mixed solvent of ethanol and water with the assistance of sodium dodecyl sulfate (SDS). Various techniques, including transmission electron microscopy (TEM), scanning electron microscopy (SEM), and powder X-ray diffraction (XRD), were used to characterize the morphology and the structure of as-prepared samples. It was confirmed that the products possess a hollow microsphere structure that is constructed by interconnecting porous nanoplate framework. Electrochemical studies indicate that the NiO-HMS exhibits excellent stability and high catalytic activity for electrocatalytic oxidation of glucose in alkaline solutions, which enables the NiO-HMS to be used in enzyme-free amperometric sensors for glucose determination. It was demonstrated that the NiO-HMS-based glucose biosensor offers a variety of merits, such as a wide linear response window for glucose concentrations of 1.67 μM–6.87 mM, short response time (3 s), a lower detection limit of 0.53 μM ($S/N=3$), high sensitivity ($\sim$2.39 mA mM^{-1} cm^{-2}) as well as good stability and repeatability.

1. Introduction

Development of glucose sensors is of great importance in a variety of fields, including medical applications of blood glucose testing, environmental monitoring, pharmaceutical analysis, and process control in food and textile industries. In the past decades, tremendous effort has been devoted to exploring reliable glucose sensor technique aiming to realize in vitro or in vivo glucose measurements and to achieve rapid response, high sensitivity, excellent selectivity, and low cost. A few potential glucose sensing approaches have been developed for measuring glucose concentrations based on fluorescent, optical, acoustic, transdermal, surface plasmon resonance, electro-chemiluminescence, and electrochemical signals (Chen et al., 2013; Heller and Feldman, 2008; Ronkainen et al., 2010; Scognamiglio, 2013; Wang, 2008). Among these techniques, the electrochemical sensor has been recognized as one of the most convenient and promising approaches due to its numerous merits, such as simplicity, high sensitivity, low production cost, attractive lower detection limit, and compatibility for miniaturization (Chen et al., 2013; Wang et al., 2007, 2008; Heller and Feldman, 2008). Electrochemical detection of glucose is usually based on the glucose oxidase (GOD) enzymatic reaction, in which glucose reacts with oxygen to produce gluconolactone and hydrogen peroxide (H_2O_2) with the catalyzing assistance of GOD. Therefore, the glucose level can be indirectly measured through electrochemical determination of the consumption of dissolved oxygen or the production of H_2O_2. The drawback of this approach is that the activity of GOD is extremely sensitive to the environmental conditions (e.g., temperature, pH, etc.) and highly dependent on the enzyme immobilization techniques, leading to insufficient long-term stability and unsatisfactory reproducibility (Sasso et al., 1990; Liu et al., 2007; Li et al., 2010a; Wilson and Turner, 1992). To address these issues, enormous effort has been devoted to exploring non-enzyme glucose biosensors in recent years. It is therefore highly desirable to develop efficient electrocatalysts for electrochemical reaction of glucose (Jiang and Zhang, 2010; Park et al., 2006).

Recent advancements in this field have suggested that a variety of transition metals and transition metal oxides (e.g., Au, Pd, Pt, Cu, Ni, CuO, NiO, CoO, MnO_2, etc.,) could work as electrocatalysts for glucose oxidation reactions in alkaline electrolytes, which makes it possible for non-enzymatic determination of glucose (Cao et al., 2013; Chen et al., 2013, 2008; Jiang and Zhang, 2010; Kang et al., 2007; Li et al., 2010a, 2010b; Liu et al., 2009; Moussy et al., 1994; Rong et al., 2007; Salimi and Roushani, 2005; Song et al., 2005; Wang, 2008; Wang et al., 2008; Yang et al., 2010; Zhai et al., 2013; Zhu et al., 2013). Ni-based materials have been extensively investigated as electrode materials for constructing non-enzyme biosensors because they can function as efficient catalysts for the

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electrocatalytic oxidation of glucose resulting from the redox couple of Ni^{3+}/Ni^{2+} in the alkaline medium (Danaee et al., 2012, 2008; Ding et al., 2011b; Jiang and Zhang, 2010; Liu et al., 2009; Lu et al., 2009; Luo et al., 2013; Tian et al., 2013). So far, most Ni-based non-enzymatic glucose sensors are constructed by modifying substrates with nickel-based nanoparticles, nickel/carbon hybrids, or porous nickel nanomaterials. Hollow structures should deserve more attention for design and fabrication of biosensors with improved performance. However, it still remains a great challenge to fabricate NiO hollow structures especially without the assistance of hard templates (Lou et al., 2008). Furthermore, there are few reports on Ni-based hollow structures for glucose biosensor applications, despite the fact that the hollow structure and corresponding properties, such as well-defined interior voids, high specific surface area, low density, and structural stability, may bring about various advantages such as high sensitivity, good stability, and low detection limit.

We herein demonstrate a non-enzymatic electrochemical sensor for glucose determination based on NiO nanoplate-constructing hollow microsphere (NiO-HMS)-modified electrodes. Such a porous hollow microsphere structure offers a suitable structure and a large surface area, facilitating electrolyte or ion transport at the solid/liquid interface and allowing the active materials to easily access glucose molecules. It was demonstrated that the NiO-HMSs are constructed by an interconnecting nanoplate framework and show desirable performance with excellent repeatability and long-term stability for non-enzymatic biosensor applications.

2. Experimental

2.1. Materials and synthesis

All chemicals were used as received from Sigma-Aldrich without treatment. NiO-HMSs were synthesized using a solvothermal method. In a typical experiment, 0.1 g of sodium dodecyl sulfate (SDS) was dissolved in 30 ml ethanol and 30 ml water at room temperature. 5.0 mM urea and 5.0 mM nickel chloride ($NiCl_2$) were then added into the solution with vigorous agitation. The mixed solution was then transferred to a 100 ml Teflon-lined stainless steel autoclave and heated at 160 °C for 10 h. After completely cooling down, the products were filtered and then washed for three times with distilled water and absolute alcohol, respectively. The green powders after drying were calcined at 500 °C for 2 h to convert to NiO. Bulk NiO was prepared by stoichiometrically mixing $NiCl_2$ with KOH, followed by annealing the green precipitate at 500 °C for 2 h.

2.2. Characterization

The structure and the morphology of the samples were characterized using a LEO 1530 scanning electron microscope (SEM) and a Hitachi model H-800 transmission electron microscope (TEM). Power X-ray diffraction (XRD) was conducted on a Scintag XDS 2000 X-Ray Diffractometer. Specific surface areas, pore volume and pore size distributions were tested at 77 K through Brunauer–Emmett–Teller (BET) nitrogen adsorption-desorption (Shimadzu, Micromeritics, ASAP 2010 Instrument).

2.3. Electrochemical testing

The modified electrode was prepared as follows: the glass-carbon electrode (GCE) was polished with alumina slurry, and then ultrasonically cleaned alternately in ethanol and double-distilled water. The NiO-HMSs (5 mg) were dissolved in a mixture of 0.05 mL Nafion and 0.45 mL distilled water. A suspension was obtained under ultrasonic agitation for a few minutes. Then 6 μL of the mixture was dropped onto the cleaned GCE and allowed to dry at room temperature. All electrochemical measurements were carried out on a Model CHI 760D Electrochemical Workstation (CH Instruments, USA) using a conventional three-electrode system fitted

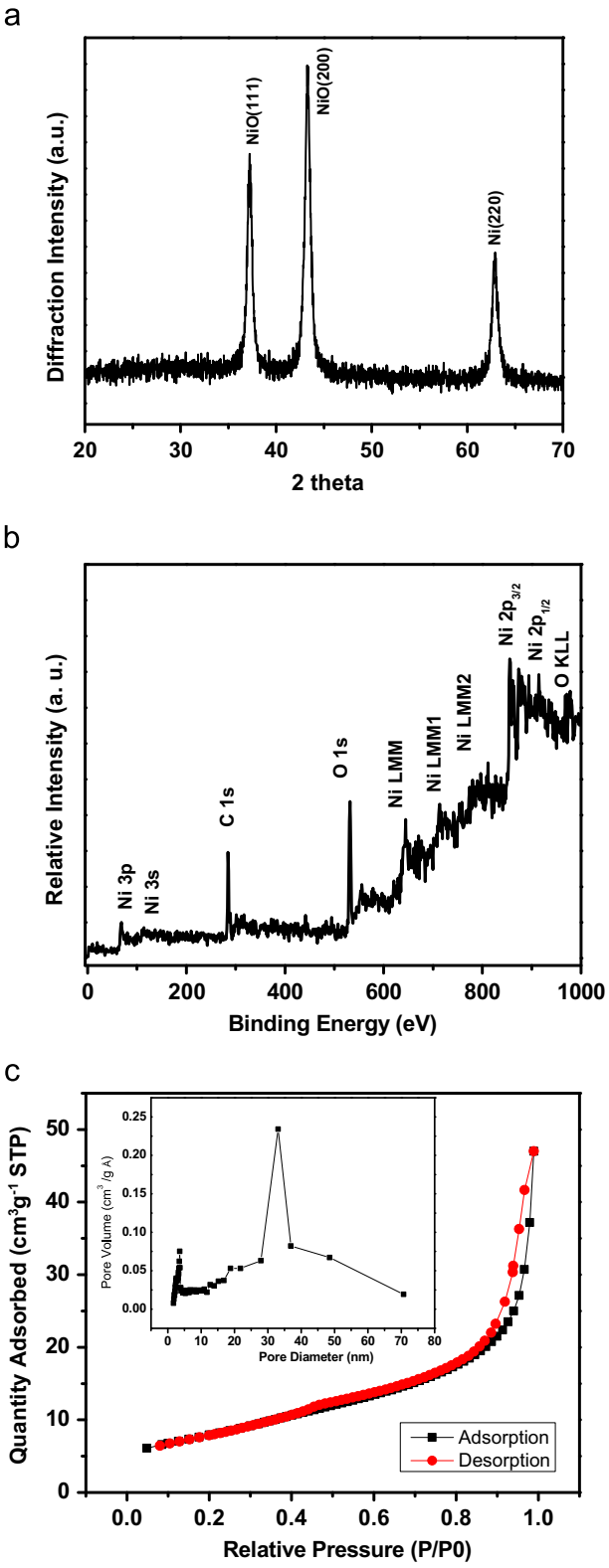

Fig. 1. (a) XRD pattern, (b) XPS spectrum, and (c) Nitrogen adsorption/desorption isotherms of the NiO-HMS.