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Synthesis of hierarchical $Ni(OH)_2$ hollow nanorod via chemical bath deposition and its glucose sensing performance

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ABSTRACT

Hierarchical $Ni(OH)_2$ hollow nanorods were deposited on zinc oxide (ZnO) nanorods by using a chemical bath deposition. The ZnO template was electrodeposited on ITO-glass and removed using an alkaline solution, and then, the hierarchical structure of the hollow $Ni(OH)_2$ consisted of nanoflakes was obtained. The morphology of the $Ni(OH)_2$ was confirmed via scanning electron microscopy and transmission electron microscopy, and its composition was determined via X-ray diffraction and X-ray photoelectron spectroscopy. The $Ni(OH)_2$ hollow nanorods exhibited a hierarchical structure with a large specific surface area and a high level of electrocatalytic activity for glucose oxidation in an alkaline condition. The $Ni(OH)_2$ hollow nanorod arrays had a wide detection range from 2 to 3862 μM, with a detection limit of 0.6 μM (s/n = 3). Furthermore, the modified electrode could detect glucose at a temperature as high as 75 °C with a sensitivity of 2904.9 $\mu A\,mM^{-1}\,cm^{-2}$. The glucose sensor showed excellent selectivity in the presence of several interfering electroactive species, and it can therefore be used to detect glucose in human serum samples.

1. Introduction

Fast and accurate glucose detection is a fundamental issue because glucose is not only a key nutrient for biological metabolism, but it is also an essential compound for medical, biotechnological, nutritional, and environmental applications [1,2]. The electrochemical method to determine the presence of glucose by using a glucose oxidase modified electrode has attracted a considerable amount of attention due to its simplicity, accuracy, and rapid analytical process when compared to other techniques. Despite the fact that commercial enzyme-based glucose sensors are mass-produced and possess excellent sensitivity and selectivity, the intrinsic instability of the enzyme can lead to a decrease in catalytic activity over time, limiting the applicability of such sensors [3,4]. For example, glucose oxidase starts to irreversibly inactivate at 50 °C, and when the temperature reaches 60 °C, only 20% of the initial activity remains [5]. To address such issues, nonenzymatic electrochemical sensors have been extensively studied as alternatives for glucose sensing, and these have been developed to be cost effective and to possess high sensitivity, rapid response time, and long-term stability. Nonenzymatic electrochemical sensors have been prepared using nanostructured materials, such as noble metals [6], transition-metal oxides or hydroxides [7,8], conducting polymers [9], or carbon-based nanomaterials [10,11]. These nanomaterials provide a large surface-to-volume ratio and improve the catalytic activity for glucose sensing.

Nickel hydroxide [$Ni(OH)_2$] is one of the most important transition-metal hydroxides, and it is widely used in supercapacitors, batteries, and sensors [12–14]. $Ni(OH)_2$-based electrodes exhibit remarkable activity for glucose sensing due to the redox couple of $Ni(OH)_2$/NiOOH for which NiOOH can be easily reduced by glucose. A number of approaches, including hydrothermal synthesis [15], electrodeposition [16], and chemical precipitation [17] have been developed to synthesize $Ni(OH)_2$ nanostructures with different morphologies, including nanoparticles, nanoflakes, and nanosheets.

In recent years, hollow nanostructures have been prepared through various synthetic means, and these are widely used in a number of fields including optoelectronics, catalysis, drug delivery, energy storage systems, and biosensors due to their high specific surface area, easy permeability, short diffusion pathways for electrons and ions, low cost, and improved reactivity [18]. Hollow NiO spheres fabricated through hydrothermal synthesis have been shown to possess improved response time and sensitivity toward glucose oxidation [19]. Hollow Cu_2O nanotubes were synthesized and used to detect hydrogen peroxide and glucose [20]. Although

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the hollow structures have a high surface area when compared to those of nanoparticles or nanosheets, the small pore volume and very thick shell are the main reasons for low sensitivity during glucose sensing. None of the hollow structures mentioned above are suitable to prepare electrochemical sensors because it is difficult to attach a hollow structure onto the electrode substrate without developing a large contact resistance. It is considered that a hollow nanostructure with a high pore volume may be deposited directly on any electrode substrate to improve the sensing performance by inducing a fast electron-transfer rate and a high electrical conductivity [21].

Herein, we present a novel nonenzymatic glucose sensor constructed using hollow $Ni(OH)_2$ nanorod arrays assembled from nanoflake walls and deposited on ZnO as a template via chemical bath deposition. The hollow nanorods exhibit a high pore volume, with pore sizes of ~500 nm in length and 450 nm in width, and the shell is as thin as ~75 nm. The hierarchical nanostructure of the proposed sensor provides a high surface area as well as easy permeability for diffusion and electron transfer of glucose. Thus, the hollow $Ni(OH)_2$ nanorod arrays exhibit an improved sensing performance with a broad detection range and excellent sensitivity. In addition, the proposed sensor can function and maintain its sensitivity even at temperatures beyond 50 °C, at which enzymatic sensors generally cannot function.

2. Experimental

2.1. Chemicals and apparatus

Zinc chloride ($ZnCl_2$), sodium nitrite ($NaNO_3$), nickel sulfate hexahydrate ($NiSO_4{\cdot}6H_2O$), glucose, ascorbic acid (AA), uric acid (UA), dopamine (DA), and L-aspartic acid (L-AA, ≥98% purity) were purchased from Sigma–Aldrich (USA). Aqueous ammonia (~25–30%) and potassium persulfate (≥95%) were supplied by Duksan (Republic of Korea). A NaOH solution (0.1 M) was obtained from Samchun (Republic of Korea). All chemicals were of analytical grade and were used as received. Indium tin oxide (ITO) coated-glass ($R_s \sim 10\ \Omega$) was purchased from Daekyong Ltd. (Korea).

The surface morphologies of the modified electrodes were investigated via scanning electron microscopy (SEM, JEOL JSM-7000F, Japan). The hollow nanorod structures of the synthesized $Ni(OH)_2$ were investigated via transmission electron microscopy (TEM, JEM-ARM200F, Japan) combined with energy dispersive X-ray spectroscopy (EDX) to determine the metal distribution. The elemental analysis was carried out via X-ray photoelectron spectroscopy (XPS) with a VG Scientific ESCA 2000 spectrometer equipped with an Al-K^{α} X-ray source operating at a power of 170 W (13 mA and 13 kV). The X-ray diffraction (XRD) patterns were collected using a Bruker D8 Advance diffractometer (Germany) equipped with a Cu K_α source (λ = 1.54056 Å). All electrochemical measurements were performed using a VSP potentiostat (Princeton Applied Research, USA) at room temperature. A conventional three-electrode system consisted of the modified ITO electrode, a platinum plate, and Ag/AgCl (saturated KCl solution) as the working, counter, and reference electrodes, respectively. Unless otherwise mentioned, all experiments were carried out at room temperature.

2.2. Electrodeposition of ZnO nanorod arrays

Before deposition, the ITO electrode (working area: 1 cm × 1 cm) was cleaned through ultrasonication in ethanol, acetone, and DI water. A constant current of $-0.25\ mA\ cm^{-2}$ was applied on the ITO electrode in an aqueous solution containing 0.5 mM $ZnCl_2$ and 0.1 M $NaNO_3$ until the charge reached $2\ C\ cm^{-2}$. An oil bath was used to maintain the temperature of the system at 80 °C. The ZnO nanorod (ZnO NR)-modified electrode was washed with water and was then dried overnight at 50 °C.

2.3. Preparation of hollow $Ni(OH)_2$ nanorod arrays (HR)

The $Ni(OH)_2$ nanoflakes were subjected to chemical bath deposition as described in the literature [22] with ZnO NR as the template for the $Ni(OH)_2$ growth. Briefly, the ZnO NR-modified electrodes were placed vertically in a freshly prepared solution of 2 mL of aqueous ammonia (25–28%) + 8 mL of 1 M nickel sulfate + 6 mL of 0.25 M potassium persulfate and were held at 25 °C for 15 min. The electrodes were then rinsed with a large amount of water and were dried overnight in an oven. The modified electrode was labeled c-$Ni(OH)_2$@ZnO NR. For comparison, an e-$Ni(OH)_2$/ZnO NR electrode was fabricated through electrodeposition in 0.1 M $Ni(NO_3)_2$ + 0.1 M KNO_3 aqueous solution with an applied potential of −1.0 V for 3 min. Finally, the ZnO template was removed by dipping the samples in 6 M NaOH solution for 1 h at room temperature. The hollow-type electrodes were dried at 60 °C for 24 h and were labeled as c-$Ni(OH)_2$ HR (prepared by a chemical bath deposition) and e-$Ni(OH)_2$ HR (prepared by electrodeposition). The fabrication of the electrodes is illustrated in Fig. S1 in the Supporting Information.

3. Results and discussion

Various methods can be used to easily acquire and etch 1-dimensional ZnO nanorods in both acidic and basic solution to produce a hollow tubular structure. Nickel based electrodes are usually considered to be the most sensitive materials for use in nonenzymatic sensors [23], and among these, $Ni(OH)_2$-modified electrodes are the most suitable and promising candidates since they offer greater stability, direct production, and reduced cost when compared to other Ni-based materials [24]. In this study, various modified hollow $Ni(OH)_2$ electrodes were successfully prepared with a ZnO template by following the methods described in the literature. The electrochemical properties and the sensing performances were then characterized.

3.1. Characterization of the proposed c-$Ni(OH)_2$ HR electrode

The different surface morphologies of the modified electrodes are shown in Fig. 1. The ZnO nanorods were fabricated on ITO electrode through electrodeposition in the presence of nitrate. As shown in Fig. 1A, the ZnO nanorods were vertically aligned onto the ITO electrode with an average diameter and length of 163 ± 32 nm and 1.15 ± 0.06 μm, respectively. After the chemical bath deposition of $Ni(OH)_2$, the ZnO NR was uniformly wrapped with $Ni(OH)_2$ nanoflakes, and the morphologies of the array were retained (Fig. 1B). The c-$Ni(OH)_2$@ZnO NR had an average diameter of 464 ± 50 nm. As shown in Fig. 1C, the removal of the ZnO template had no significant effect on the morphology of c-$Ni(OH)_2$ HR. In the case of the electrodeposition of $Ni(OH)_2$, the surface of the rod was very smooth, and the ends of the rod were observed to have partially opened after the ZnO had been removed (Fig. 1D). EDX analysis was performed to confirm the removal of ZnO by measuring the contents of each element in the proposed electrodes. Before dissolving the ZnO nanorods, there were obvious energy peaks for zinc, and the atomic content was ~70% (Fig. 1E). However, as shown in Fig. 1F, the energy peak for zinc decreased after the alkali treatment, and only 8% of the zinc atoms were retained, indicating that most of the ZnO had been dissolved in the NaOH solution.

The hierarchical structure of the as-prepared electrodes was observed in further detail via TEM, as shown in Fig. 2. The