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Hierarchical flower-like NiO hollow microspheres for non-enzymatic glucose sensors

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ABSTRACT

Hierarchical flower-like NiO hollow microspheres were controllably prepared by a facile hydrothermal method using carbon spheres as the template. Their structure and properties for non-enzymatic glucose sensors were investigated. The results showed that the hierarchical flower-like NiO hollow microspheres are composed of the interconnecting porous NiO nanoplates and each nanoplate is assembled by NiO nanoparticles with the length of about 12.5 nm and the width of about 10 nm. Furthermore, the hierarchical flower-like NiO hollow microspheres obtained at different temperatures were analyzed with the electro-catalytic activity toward the oxidation of glucose in alkaline solution, and the glucose sensor with hierarchical flower-like NiO hollow microspheres obtained at 550 °C exhibits the best performance with the linear range of 5 μM–364 μM and sensitivity of 288.87 mA mM^{-1} cm^{-2}. The sensor is also used for detection of glucose with a relative concentration ranging from 2.96 mM to 7.46 mM and sensitivity of 37.82 mA mM^{-1} cm^{-2}. More importantly, long-term stability and favorable anti-interference were obtained as a result of the hierarchical hollow structure.

1. Introduction

Development of glucose sensors is of great importance in various fields, including environmental monitoring, clinical diagnostics and food industry [1–3]. Compared with other methods, the electrochemical technique is a promising tool for the construction of simple and low-cost sensors due to its high sensitivity, good selectivity and ease of operation [4–6]. Generally, electrochemical sensors for glucose determination are classified into two major types: enzymatic and non-enzymatic modified sensors. Owing to its high selectivity and fast response to enzyme reaction, glucose oxidase (GOD) is always used in enzymatic modified sensors, in which glucose reacts with oxygen to produce glucolactone with the catalyzing assistance of GOD [7–9]. However, the activity of enzymatic glucose sensors is extremely sensitive to environmental conditions and highly dependent on the enzyme immobilization techniques which result in poor stability, high cost and complex fixed technique [10–12].

To solve this problem, considerable interest has been paid on non-enzymatic glucose sensors. Recently, many transition metals and transition metal oxides are used as non-enzymatic sensor materials to determine glucose based on their excellent electrochemical activity [13–15]. Among them Ni-based nanomaterials exhibited remarkably catalytic oxidation activity over glucose as a result of the catalytic effect originating from the formation of the redox couple of Ni(II)/Ni(III) on the electrode surface in alkaline medium [16–17].

It is well known that the nano-/microstructure materials exhibit special properties compared to the relatively bulky materials, which may enhance the electrochemical performance. Some non-enzymatic glucose sensors have been successfully developed by using NiO-based materials with various structures, such as nanofibers [18–19], nanoparticles [4,20–21], and nanoflake arrays [22]. In addition, hollow-sphere structured NiO materials have also been intensively investigated due to their novel interior geometry and surface functionality [23–25], but the organic matters are induced as the morphology oriented agent to acquire the hollow structure. This procedure pollutes the final products and imposes restrictions on the sensing property to some degree, although they comparatively made progress in their work.

Inspired by the previous works, hierarchical flower-like NiO hollow microspheres were synthesized with carbon spheres as the template via a facial hydrothermal method. We further discussed the influence of different temperatures in the formation of the special structure and explained the mechanism. The constructed NiO hollow microspheres with the hierarchical flower-like structure have the best electrochemical property in our series of glucose sensors, and are especially outstanding on sensitivity compared with the other non-enzymatic glucose sensors [13–14,16–17] due to the special morphology and structure.

2. Experimental part

2.1. Chemicals and apparatus

Nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$), sodium hydroxide (NaOH), urea, ascorbic acid, L-leucine, NaCl, L-lysine, L-proline, sucrose

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and glucose were purchased from Aldrich (Milwaukee, WI, USA). All reagents were of analytical grade and used as received without further purification, and all solutions were prepared with deionized water.

The morphology of as-prepared materials was observed by scanning electron microscopy (SEM) on S-4700, operated at an accelerating voltage of 15 kV. Transmission electron microscopy (TEM) measurement was carried out with H-008. The chemical compositions of the prepared NiO/C microspheres were determined by energy dispersive X-ray (EDX). Powder X-ray diffraction (XRD) datum was recorded on DX-2600 with Cu Kα radiation ($\lambda = 0.15406$ nm) to get the crystallographic characteristics of the samples. Thermogravimetric analysis (TGA) was carried out on a TGA/DSC LF 1600 system at a rate of 10°C min^{-1} from 50 °C to 700 °C in nitrogen. Electrochemical measurements were performed with a CHI630D analyzer (Shanghai Chenhua Instrument Co. China).

2.2. The preparation of different NiO hollow microspheres

2.2.1. Synthesis of carbon spheres

Sucrose (13.861 g) was dissolved in distilled water (135 ml), and stirred with a magnetic stirrer to give a clear solution in a beaker. Then the solution was transferred into Teflon autoclaves, sealed and maintained at 180 °C for 10 h. The precipitate was collected by centrifugation and washed with distilled water and ethanol several times after it cooled to room temperature naturally. At last, it was dried at 80 °C for 6 h, and the dark-brown block product was obtained.

2.2.2. Synthesis of $Ni(OH)_2$/C precursors

Carbon spheres (0.144 g) and $NiCl_2 \cdot 6H_2O$ (0.0952 g) were dispersed in 80 ml distilled water by ultrasonicating for 0.5 h and stirring for 0.5 h to ensure that Ni^{2+} ions can be sufficiently adsorbed on the surface of carbon balls. Then urea (0.5 g) was added and remained being stirred for 0.5 h. After that, the solution was transferred into a Teflon autoclave and kept at 90 °C for 8 h. The obtained suspension was cooled to room temperature and centrifuged to obtain the $Ni(OH)_2$/C precursor. The as-obtained product was washed several times with distilled water, and dried at 80 °C.

2.2.3. Synthesis of different NiO hollow microspheres

The $Ni(OH)_2$/C precursor was put into the sequencing tube furnace and heated to 550 °C with air drummed into at the rate of 7 °C per minute, and kept at 550 °C for 2 h. Then the furnace was gradually cooled to room temperature. By adjusting the final temperature, the NiO-HMs at 350 °C/450 °C/650 °C are separately obtained.

2.3. Electrochemical testing

The working electrode was prepared as follows: The NiO-HM samples (5 mg) were dissolved in a mixture of 20 μl Nafion and 5 ml absolute ethanol. A suspension was obtained under ultrasonic agitation for a few minutes. Then 20 μl of the mixture was dropped onto the cleaned GCE and dried at 50 °C in oven. All experiments were conducted using a three-electrode electrochemical system with a GCE based working electrode, an Ag/AgCl reference electrode and a platinum slice counter

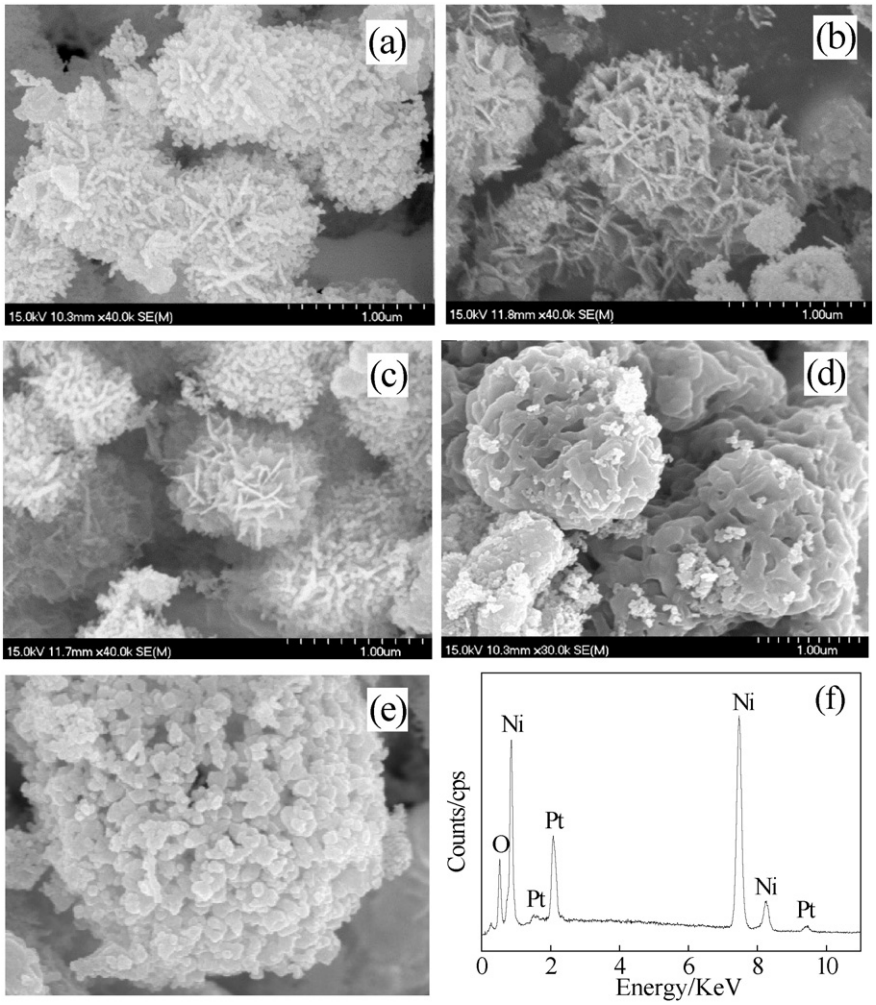

Fig. 1. (a)–(d) SEM imagines of the NiO hollow microspheres at 350 °C/450 °C/550 °C/650 °C; (e) the partial photo; and (f) EDX pattern of NiO-HMs-550.