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Ni-Co-S/PPy core-shell nanohybrid on nickel foam as a non-enzymatic electrochemical glucose sensor

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ABSTRACT

A nickel-cobalt-sulfide nanosheet (Ni-Co-S NS)/polypyrrole nanowire (PPy NW) core/shell-structured composites on nickel foam (NF) was synthesized by facile electrodeposition processes for electrochemical non-enzymatic glucose sensor. PPy NWs grew on the NF substrate by a potentiostatic deposition method, and then the PPy NWs were further served as skeletons for electrodeposition Ni-Co-S nanosheets. The ternary Ni-Co-S NSs as the shell and PPy NWs as the core on the flexible NF constructed the 3D micro/nano structure. The as-prepared Ni-Co-S/PPy/NF electrode was characterized by scanning electron microscopy (SEM) and energy-dispersive X-ray spectrometer (EDS). The electrochemical sensor was used for the detection of glucose by chronoamperometry. The introduction of the interconnected Ni-Co-S NSs can provide accessible pathways for electrolyte and have high sensitivity to glucose. Compared with the NF and PPy/NF electrodes, the Ni-Co-S/PPy/NF micro/nano-hybrid electrode exhibited higher catalytic activity towards electro-oxidation of glucose. The developed Ni-Co-S/PPy/NF electrode showed two linear electrochemical responses to glucose in the range from 2 μM to 140 μM with a correlation coefficient of R^2 = 0.937 and 0.14 mM to 2 mM with a correlation coefficient R^2 = 0.978, and the detection limit is 0.82 μM. Furthermore, the prepared biosensor demonstrated high selectivity to glucose in the presence of uric acid, ascorbic acid and D-fructose.

1. Introduction

Glucose is an important small biological molecule for life processes and its practical application in various fields such as biotechnology, food industry, clinical diagnostics, etc [1,2]. There are many methods for detecting glucose such as high performance liquid chromatography, fluorescent spectrometer, biosensor, gas chromatography and electrochemical sensors [3–6]. Among these methods, electrochemical sensors are paid more attention by research workers due to several advantages, such as simplicity, prominent sensitivity, high selectivity and ease of operation [7,8]. Electrochemical glucose sensors are mainly divided into two categories: glucose oxidase based enzymatic sensors and electrochemical non-enzymatic glucose sensors. Recently, electrochemical non-enzymatic glucose sensors have received considerable attention which overcomes disadvantages of enzymatic biosensors, such as poor reproducibility, high-cost enzymes and insufficient long-term stability [9,10].

Various nanostructured materials contained metal (Au, Ni, Cu) [11–13], metal alloy (Ni-Co) [14] and metal oxide (Co_3O_4, NiO) [15,16] are widely applied to fabricate non-enzymatic electrochemical glucose sensors due to their low-cost, environmentally friendly and excellent electrochemical properties. Because of the large specific surface areas and excellent catalytic activities, nickel oxide and cobalt oxide nanostructures are particularly used in the detection of glucose. For example, Chen et al. [16] prepared a porous NiO modified glassy carbon electrode (GCE) used for electrochemical determination of glucose. Zhang et al. [15] reported a Co_3O_4 hollow nanododecahedra modified electrode for electrochemical glucose sensing, and an electrochemical glucose sensor was fabricated by Wang et al. [17] using a hollow nanospheres $NiCo_2O_4$/rGO composites. However, the nickel oxides and cobalt oxides have either poor electrical conductivity or poor electrochemical stability, which limit the applications [18,19]. To overcome the limitation, metal sulfides including cobalt sulfides, nickel sulfides, copper sulfides, and especially ternary nickel cobalt sulfides have been identified to be a suitable electrochemical material of electrode widely used in supercapacitor, hydrogen evolution and electrochemical sensor, which have higher conductivities, better stability and more electrochemically active sites than that of the corresponding metal oxides [20,21]. Huo et al. [22] synthesized the 3D Ni_3S_2 nanosheet arrays grown on Ni foam applied to a high-performance supercapacitor and non-enzymatic glucose sensor by a facile one-step hydrothermal approach, which manifested as-prepared Ni_3S_2 nanosheet

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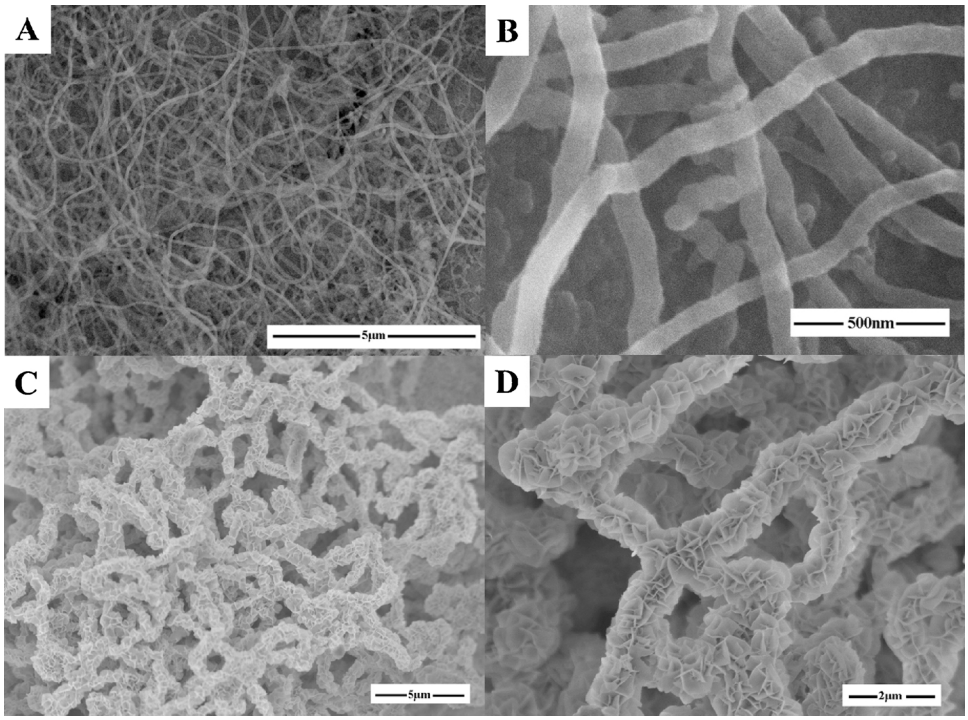

Fig 1. SEM images of the PPy/NF (A) and (B), the Ni-Co-S/PPy/NF (C) and (D) electrode.

arrays are endowed with fast electron transport and excellent structural stability. Peng et al. [23] fabricated highly active, stable cobalt sulfide/reduced graphene oxide/carbon nanotube (CoS_2/RGO−CNT) nanocomposites as flexible electrodes for hydrogen evolution, which have high HER activity and high catalytic stability. Li et al. [24] reported Ni-Co sulfide nanosheets with both ultrathin thickness and nanoscale pores for supercapacitors, which have high specific capacitance and excellent rate capability. Due to the synergistic effect of two metallic sulfide materials, the Ni-Co-S nano-materials have better catalytic activities and anti-interference ability for the preparation of the electrochemical non-enzymatic sensor [25,26].

Herein, we report an electrochemical non-enzymatic glucose sensor based on ternary Ni-Co-S NS/PPy NW core-shell structure on the NF. The nanohybrid composed of the PPy NW core which constructed a three dimensional (3D) micro/nano structure on the NF substrate and the Ni-Co-S NS shell grown on the PPy NW which acted as the electro-oxidation catalyst to glucose. Electrochemical performances demonstrated that the Ni-Co-S/PPy/NF electrode showed a remarkable electrocatalytic activity to glucose, and wide linear responses with a low limit of detection resulting from the synergistic effects of Ni-Co-S, PPy and NF. Interference studies of uric acid (UA), ascorbic acid (AA) and D-fructose were measured, and the results showed that the Ni-Co-S/PPy/NF electrode had a high selectivity for the electrochemical detection of glucose.

2. Experimental

2.1. Reagents and apparatus

Sodium carbonate (Na_2CO_3), cobalt chloride hexahydrate ($CoCl_2{\cdot}6H_2O$), nickel chloride hexahydrate ($NiCl_2{\cdot}6H2O$), thiourea ($CS(NH_2)_2$), sodium hydroxide (NaOH), glucose, uric acid (UA), ascorbic acid (AA) and D-fructose were purchased from Sinopharm Chemical Reagent Co. Ltd. Pyrrole (Py, 98%) and sodium p-toluenesulfonate were purchased from Aladdin (Shanghai, China). Ni foam (99.8%, 1.0 mm in thickness) was purchased from Taiyuan city Yingze district power battery sales and cut into small pieces with dimensions of 4 × 1 cm.

The morphology and energy-dispersive X-ray spectrometer (EDS) of the NF, the PPy/NF and the Ni-Co-S/PPy/NF were performed using scanning electron microscopy (SEM, HITACHI-S8000). Chronoamperometry (CA) and cyclic voltammetry (CV) were performed by a CHI650E electrochemical workstation (Chenhua, Shanghai, China) with a conventional three-electrode cell that the modified electrode as a working electrode, a Pt plate as a counter electrode and a saturated calomel electrode (SCE) served as a reference electrode.

2.2. Preparation of the PPy/NF electrode

Nickel foam substrate was washed by ultrasonication in ethyl alcohol, 3 M HCl solution and deionized water for 10 min, respectively. The PPy NWs were electrochemically deposited onto the NF with a conventional electrochemical three electrode cell at room temperature. The electrolyte solution contained 0.15 M pyrrole, 0.1 M sodium p-toluenesulfonate and 0.1 M Na_2CO_3. In order to obtain the PPy NWs, the potentiostatic deposition was carried out at a potential of 1.2 V for 1000 s. After electrochemical polymerization, a uniform black film covered the surface of the NF, and then the PPy NW coated NF (PPy/NF) electrode was washed by deionized water.

2.3. Synthesis of the Ni-Co-S/PPy/NF electrode

The Ni-Co-S NS were prepared by one-step electrochemical deposition in a three electrode cell using the PPy/NF electrode as the working electrode [25,26]. The Ni-Co-S NSs were electrochemical synthesized in an aqueous electrolyte contained 10 mM $CoCl_2$, 5 mM $NiCl_2$ and 0.75 M thiourea using cyclic voltammetry at a scan rate of 5 mV/s for 15 cycles in the range of −1.2 V to 0.2 V (vs. SCE). Subsequently, the Ni-Co-S/PPy/NF electrode was rinsed with deionized water several times and dried at 60 °C for 10 h in an air dry oven.

3. Results and discussion

The SEM images of the PPy NWs on the surface of the NF substrate are showed in Fig. 1A and B. According to the figures, the skeleton of the NF was fully covered by the continuous and homogeneous PPy NWs