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Highly sensitive and selective electrochemical sensor based on porous Co_3O_4 nanoflowers for voltammetric determination of glucose

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Highly sensitive and selective electrochemical sensor based on porous Co_3O_4 nanoflowers for voltammetric determination of glucose

Jingting Hu

State Grid Jilin Electric Power Research Institute, Changchun 130021, China
414933604@qq.com

Abstract. Porous Co_3O_4 nanoflowers (denoted as Co_3O_4 NFs) was synthesized by hydrothermal method. The morphology and composition of the Co_3O_4 NFs were characterized by SEM, TEM and XRD, respectively. Accordingly, the Co_3O_4 NFs was used as electrocatalysts for the detection of glucose. The Co_3O_4 NFs electrode showed extremely high sensitivity and a low detection limit for the electrocatalytic oxidation for glucose. The interference study was also implemented with interferents, and the proposed Co_3O_4 NFs electrode demonstrated excellent selectivity toward UA, fructose and NaCl. This glucose sensor can also detect the glucose concentration in human serum, indicating Co_3O_4 NFs can be commercialized as non-enzymatic glucose sensor in the future.

1. Introduction

World Diabetes Day is in November 14th. Diabetes is harmful to health. When glucose concentration is more than 7 mM and other relevant clinical symptoms appear, the patient can be diagnosed with diabetes. [1-3] As a result, the rapid, accurate approaches for the detection of glucose are of significance in chemical and biological sensors. Glucose has been analyzed with enzyme sensors routinely owing to their good selectivity and high sensitivity. There exist some drawbacks for enzyme sensors inevitably, such as poor stability, time-consuming operating procedures, the need for expensive reagents and the presence of serious matrix effects. [4-5] To some extent, the pH, humidity and temperature also have effects on stability of the enzyme. [6-9] Consequently, it has become particularly important to look for proper enzymeless electrode materials as glucose sensors.

Noble metal based nanomaterials have been used to fabricate decorated electrode for electrocatalyzing glucose. However, noble metal suffers from some disadvantages such as high price and low abundance. [9-15] Transition metals oxides have been attracted enormous attentions and utilized extensively in many fields such as highly sensitive optoelectronic, gas and biosensors. [16-18] In the past decades, Cu_xO-, MnO_2- NiO_x-based nanomaterials have been designed and constructed enzyme-free glucose sensors. [19-29] Cobalt oxide nanocomposites have attracted great interests because of their potential application in supercapacitors, heterogeneous catalysts and lithium batteries. [30-35] Given that their enhanced electrocatalytic behavior and good chemical stability, Co_3O_4 can also be selected as an excellent potential candidate for the active electrodes materials. The electrochemical performance of Co_3O_4 may be regulated such as particle size, surface morphology and adhesion capacity to conductive substrates. It is worth noting that porous structure is beneficial to ion diffusion and mass diffusion. Therefore, it is urgent to optimize the structures for improving the electrocatalytic performance.

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In this work, mesoporous Co_3O_4 nanoflowers (denoted as Co_3O_4 NFs) was obtained by hydrothermal method. And it was used as electrocatalyst for the detection of glucose. The Co_3O_4 NFs showed extremely high sensitivity and excellent selectivity for the electrocatalytic oxidation for glucose compared with other previously reported sensors. The interference study was carried out with ascorbic acid, uric acid and dopamine. The proposed Co_3O_4 NFs electrode showed excellent selectivity. This glucose sensor can also detect the glucose concentration in human serum, which indicated Co_3O_4 NFs can be commercialized as non-enzymatic glucose sensor in the future.

2. Materials and methods

2.1. Preparation of the Co_3O_4 NFs electrode

Co_3O_4 NFs on Ni-foam were prepared by a hydrothermal reaction. Nickel foam was cut into 0.5 cm × 0.5 cm slices in size and corroded with 6 M HCl for 2 h to remove the skin oxide layers. Then, 1 ml 0.8 mM of $CoCl_2$•$6H_2O$ and 1 ml 0.4 mM of $CO(NH_2)_2$ were transferred into a Teflon-lined stainless autoclave. Aftererwards, the pretreated Ni foam was immersed into the mixed solution and maintained 95 ºC for 8 h. The precursor of $Co(OH)_{1.10}Cl_{0.2}(CO_3)_{0.35}$•$1.74H_2O$ was formed on the Ni foam. The precursor-modified Ni-foam was rinsed with distilled water and ethanol three times in sequence, followed by drying at 60 ºC for 1 h. The precursor was annealed in air at 400 ºC for 1 h with the heating rate of 2 ºC/min to obtain dark-colored Co_3O_4 NFs.

3. Results and discussion

3.1. Electrocatalytic Oxidation of glucose at Co_3O_4 NFs Electrode.

The cyclic voltammetry curves of the bare Ni foam and the Co3O4 NFs based non-enzymatic electrode was recorded in the presence of 1 mM glucose with a potential range from 0 to +0.7 V in 0.1 M NaOH solution at scan rate of 50 mV/s. As shown in Fig. 1(a), the background current for Co_3O_4 NFs was higher than that of bare Ni foam, which could be assigned to the inclusion of the Co_3O_4 nanoflowers supported on the Ni faom.

Fig. 1b depicted the CVs of the Co3O4 NFs in 0.1 M NaOH solution in the absence and presence of glucose. Upon adding 1.5 mM glucose, a remarkable change was seen from the CV curves. A obvious increase of the oxidation peak at 0.45 V was observed associated with the formation of CoO_2, which resulted from the oxidation of glucose to gluconolactone catalyzed by the conversion of CoO_2 to CoOOH. The possible reaction mechanism at Co3O4 NFs electrode in NaOH solution was proposed as follows.

Co_3O_4 + OH- + H_2O → 3CoOOH + e- (1)

CoOOH + OH → $2CoO_2$ + H_2O + e- (2)

$2CoO_2 + C_6H_{12}O_6 \rightarrow 2CoOOH + C_6H_{10}O_6$ (3)

Fig. 1c and d showed the CVs of the Co_3O_4 NFs in 0.1M NaOH solution in the presence of 0.5 mM glucose at different scan rates in the range from 10 mV s-1 to 80 mV s-1. The redox peak currents are linear with the square root of the scan rate, revealing a diffusion-controlled electrochemical process.

In order to obtain a better current response, constant potential chronoamperometry was implemented by varying the potential around the anodic peak potential. Therefore, 0.45 V was chosen as the optimum applied working potential for subsequent amperometric measurement. This optimum potential was apparently lower than the oxidation potential in previous reports. The relatively low potential for glucose detection was closely bound up high conductivity of the conductive substrates and the porous structure of Co_3O_4 nanoflowers, which can facilitate the charge and mass transfer involved in glucose oxidation in this system. To some degree, the required energy for the reaction could be reduced and the reaction dynamics could be accelerated, which was reflected in the reduced oxidation potential.

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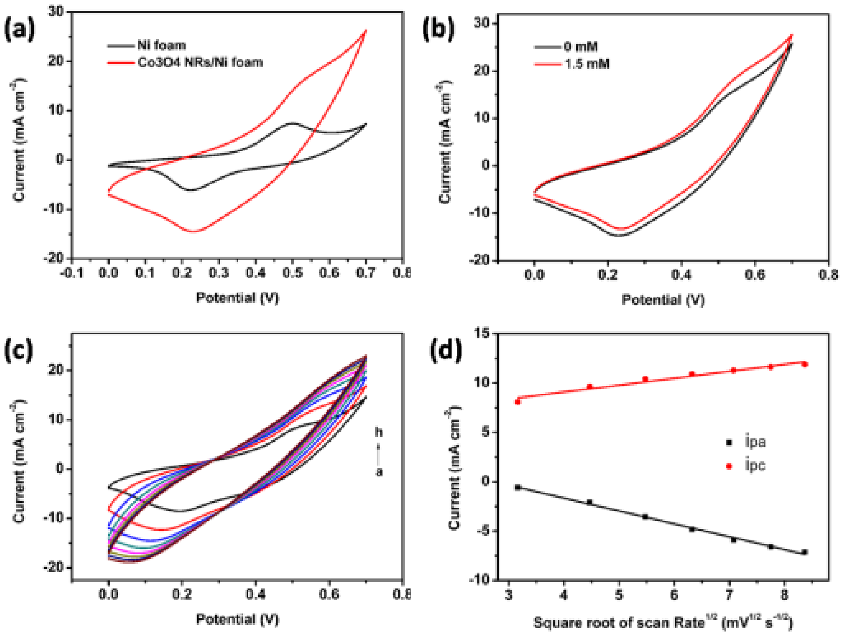

Fig. 1 (a) Cyclic voltammograms of the Ni-foam and the Co3O4 NFs electrode in the presence of 1.0 mM glucose. Scan rate: 50 mV s-1. (b) Cyclic voltammograms of the Co_3O_4 NFs/Ni-foam electrode in the absence of glucose and in the presence of 1.5 mM glucose. (c) Cyclic voltammograms of the Co_3O_4 NFs/Ni-foam in 0.1 M N2-saturated NaOH at different scan rates (from the top to bottom: 10-80 mV s-1). (d) Plots of peak currents as a function of the square root of the scan rate.

3.2. Long-term stability of the sensor

The long-term stability of Co_3O_4 NFs electrode was also investigated to evaluate the performance of the sensor. The Co_3O_4 NFs electrode was not in use and stored at 298 K. 99.3% of the initial current response Co_3O_4 NFs were remained two weeks later, implying the good stability of the as-prepared sensor.

3.3. Real sample analysis

The resulting sensor demonstrated extremely high sensitivity and selectivity toward the determination of glucose. To evaluate the application prospect, the proposed Co_3O_4 NFs sensing system was applied to the determination of glucose in human blood serum. 10 µL of serum sample was added to 4 mL of 0.1 M NaOH solution, and the current response was recorded 0.45 V vs. SCE. Recovery testing was carried out to demonstrate the validity of the proposed method. The obtained recoveries of the proposed method ranged from 98.13% to 102.05%. For comparison, the concentrations of glucose in these samples were also detected by a spectrophotometric method. The results tested by both methods showed a good agreement. These results indicated the proposed Co_3O_4 NFs had an excellent accuracy for glucose sensing, and could be applied to the determination of glucose in human serum samples.

4.Conclusions

In conclusion, Co_3O_4 nanoflowers on Ni foam were synthesized by hydrotheraml method. The porous structure of Co_3O_4 nanoflowers can facilitate to excellent catalytic performance for glucose oxidation such as extremely high sensitivity and a low detection limit. In addition, the sensor also showed excellent stability and good selectivity to glucose detection.

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