Electrochimica Acta 220 (2016) 545–553

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Preparation of spinel nickel-cobalt oxide nanowrinkles/reduced graphene oxide hybrid for nonenzymatic glucose detection at physiological level

Guangran Ma, Min Yang, Chenyi Li, Haiyan Tan, Liang Deng, Shi Xie, Fugang Xu*, Li Wang*, Yonghai Song*

Key Laboratory of Functional Small Organic Molecule, Ministry of Education, College of Chemistry and Chemical Engineering, Jiangxi Normal University, 99 Ziyang Road, Nanchang 330022, China

ARTICLE INFO

Article history:
Received 10 August 2016
Received in revised form 23 October 2016
Accepted 24 October 2016
Available online 24 October 2016

Keywords:
spinel nanocrystal
nickel cobalt oxide
glucose
electrochemical sensor
electrocatalysis

ABSTRACT

Nickel-cobalt oxide nanowrinkles with spinel-type crystal structure supported on reduced graphene oxide ($NiCo_2O_4$ NWs-rGO) was prepared to develop a sensitive and stable nonenzymatic glucose sensor. The $NiCo_2O_4$ NWs-rGO hybrid were prepared by a facile one-pot hydrothermal reaction, and sequential calcination in air. The morphology, composition and crystal structure of the $NiCo_2O_4$ NWs-rGO hybrid were characterized by scanning electron microscope, transmission electron microscope, selected area electron diffraction, and energy-dispersive spectroscopy. The electrochemical behavior of the hybrid and its catalytic activity towards glucose oxidation were investigated by several electrochemical methods. Compared with single component NiO or Co_3O_4, spinel type $NiCo_2O_4$ NWs displayed higher catalysis towards glucose oxidation. Further integration of $NiCo_2O_4$ with graphene could reduce the overpotential and enhance the catalytic current due to the improved conductivity and dispersity of $NiCo_2O_4$. The $NiCo_2O_4$ NWs-rGO based glucose sensor showed a wide linear range of 0.005-8.6 mM, a low detection limit of 2 μM (S/N = 3), and an improved stability. A satisfactory recovery was also obtained for glucose detection in human serum at physiological level. Our results indicate rationally combine spinel type mixed metal oxide with graphene is a good alternative to fabricate advanced metal oxide based electrochemical sensors.

1. Introduction

Electroactive nanocrystals of metal oxide have received considerable attentions in nonenzymatic electrochemical sensors and devices due to their easy preparation, high stability, low cost, high abundance and comparable catalysis with some noble metal materials [1,2]. However, most metal oxide has low conductivity, which seriously degrades the performance of electrochemical sensors [1,2]. Therefore, an effective approach to enhance the conductivity of metal oxide nanocrystals while maintain or even elevate their electrocatalytic activity is in great demand for developing advanced electrochemical sensors with low cost and high performance.

Up to now, combining metal oxide with conducting materials is one of the most efficient and widely reported approach to enhance the performance of metal oxide based sensors [2–6]. Among various conducting materials, graphene has received considerable attention at present due to its large surface area, high conductivity and easy preparation [7]. Until now, many graphene-metal oxide hybrid or composites, such as Fe_3O_4-rGO [8,9], Co_3O_4-rGO [10], CuO-rGO [11], Cu_2O-rGO [12,13], NiO-rGO [14,15] hybrids have been fabricated and applied in electrochemical sensors. These hybrids usually display much higher activity than that of corresponding single metal oxide component. However, two dimensional graphene or its hybrid with ordinary metal oxide nanoparticles tends to aggregate on electrode surface, and thus decreases the active surface area, and limits the further improvement of sensing performance.

Besides integrating metal oxide with conducting materials, tailing the structure of metal oxide material itself is also an effective way to improve its conductivity, electrochemical activity and other properties. Recently, mixed transition metal oxides with

* Corresponding authors. Tel.: +86 791 88120861; fax: +86 791 88120861.
E-mail addresses: fgxu@jxnu.edu.cn (F. Xu), lwang@jxnu.edu.cn (L. Wang), yhsong@jxnu.edu.cn (Y. Song).

http://dx.doi.org/10.1016/j.electacta.2016.10.163
0013-4686/

a spinel structure have attracted an upsurge of interest in many electrochemical applications [16]. The ternary nickel cobaltite $NiCo_2O_4$, as one typical example is widely studied due to its low cost, easy preparation [17], and much higher electrical conductivity and electrochemical activity than that of NiO or CoO [18] due to coexistence of active Ni and Co species [19]. These properties make spinel type $NiCo_2O_4$ an attractive electrochemical energy material with promising applications in lithium battery and supercapacitors [16–19]. However, the applications of $NiCo_2O_4$ in electrochemical sensors are rarely reported. Recently, $NiCo_2O_4$ was explored to achieve the non-enzymatic detection of glucose [20,21] and H_2O_2 [22], but these sensors suffer from poor catalysis and narrow linearly responsive range [20]. For example, the up limit of linear range of $NiCo_2O_4$ based glucose sensor is 65 μM [20] or 4.7 mM [21], which does not fully cover the physiological level of 4–7 mM glucose in human blood [23]. Besides, low active surface area, poor dispersity and complex preparation of these $NiCo_2O_4$ based nanomaterials also hinder the practical application of these sensors.

In this paper, a new hybrid composed of spinel type $NiCo_2O_4$ nanowrinkles grown on reduced graphene oxide ($NiCo_2O_4$ NWs-rGO) was prepared and its applications in catalytic oxidation and amperometric detection of glucose were investigated in detail. The advantages of the $NiCo_2O_4$ NWs-rGO based sensor include: (1) The hybrid material could be prepared by a facile and easy accessible one-pot hydrothermal reaction combined with subsequent calcination at low cost and high yield. (2) The $NiCo_2O_4$ NWs-rGO displays large surface area, good conductivity and thus much enhanced catalysis towards glucose oxidation than that of NiO, Co_3O_4 or $NiCo_2O_4$; (3) Most importantly, $NiCo_2O_4$ NWs-rGO with high stability and wide linear response range (up limit extended to 8.56 mM) could be used to directly detect glucose at physiological level without tedious dilution treatment. The $NiCo_2O_4$ NWs-rGO based sensor also shows a satisfactory recovery for glucose detection in human serum.

2. Experimental

2.1. Materials and reagents

Nickel nitrate ($Ni(NO_3)_2·6H_2O$), cobalt nitrate ($Co(NO_3)_2·6H_2O$), sodium hydroxide (NaOH), hexamethylenetetramine (HMT), potassium permanganate ($KMnO_4$) trisodium citrate ($Na_3Cit·2H_2O$), and glucose were purchased from Shanghai Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Uric acid (UA), ascorbic acid (AA), H_2O_2 solution (30 wt %), phosphate acid (H_3PO_4) and graphite (325 mesh) were supplied by aladdin (Shanghai, China). All chemicals used were analytical grade. Ultrapure water ($\geq$18.2 MΩ·cm) was used for preparation of buffer and standard solutions.

2.2. Preparation of $NiCo_2O_4$ NWs-rGO hybrid

Graphene oxide (GO) was first synthesized based on a modified Hummer's method [24]. For the synthesis of $NiCo_2O_4$ NWs-rGO hybrid, 5 mg GO was dispersed in 20 mL H_2O by ultrasonication for 30 min. Then 0.116 g $Ni(NO_3)_2·6H_2O$, 0.232 g $Co(NO_3)_2·6H_2O$, 0.28 g HMT and 0.0588 g $Na_3Cit·2H_2O$ were added into the above solution. The mixture was sonicated for another 5 min, and then refluxed with rigorous stirring in an oil bath at 90 °C for 6 h. After that the black precipitate was harvested by centrifugation and washed with DI water and ethanol for several times. Finally, the obtained product was freeze-dried overnight and further annealed at 300 °C for 3 h in air with a heating rate of 1 °C min^{-1} to obtain the final product $NiCo_2O_4$ NWs-rGO.

In order to demonstrate the advantages of $NiCo_2O_4$ NWs-rGO hybrid, other nanomaterials including single component NiO or Co_3O_4, and unsupported spinel $NiCo_2O_4$ were also prepared by a similar approach, except that graphene oxide or certain metal salt was not added in corresponding synthesis.

2.3. Preparation of modified electrode

To fabricate modified electrode, 0.5 mg $NiCo_2O_4$ NWs-rGO was dispersed into 1 ml H_2O to form a suspension, then 5 μL of the suspension was coated on the polished glassy carbon electrode (GCE) and dried in air. Finally, 5 μL nafion solution (0.05%) was coated on it to get the $NiCo_2O_4$ NWs-rGO modified GCE referred as $NiCo_2O_4$ NWs-rGO/GCE. Other material modified GCE was shorten as NiO/GCE, Co_3O_4/GCE, or $NiCo_2O_4$/GCE, respectively.

2.4. Characterization

The morphologies of the products were observed by a scanning electron microscope S-3400N (Hitachi, Japan) or transmission microscope JEM 2100 (JEOL, Japan). Electrochemical experiments were performed on a CHI 760D electrochemical workstation (CH Instrument, Shanghai) using a three electrode system with platinum wire as counter electrode, Hg/Hg_2Cl_2 (KCl saturated) electrode as reference electrode and $NiCo_2O_4$-rGO/GCE or other material modified GCE as working electrode. Freshly prepared sodium hydroxide solution (0.1 M) was used as the supporting electrolyte. Electro-chemical impedance spectroscopy (EIS) was performed with the same three-electrode configuration in an electrolyte solution of 0.1 M KCl containing 1 mM $[Fe(CN)_6]^{4-/3-}$, in a frequency range from 0.1 Hz to 1 MHz with an amplitude of 5 mV. All electrochemical studies were performed under ambient conditions.

2.5. Real sample analysis

The human serum was from local hospital. These samples were treated by trichloroacetic acid before used for analysis [25]. Briefly, the serum of human blood was separated by centrifugation. Then, 150.0 μL trichloroacetic acid (TCA) was added to the 5 mL serum sample in order to denature the proteins. Subsequently, the samples were centrifuged at 5000.0 rpm for 10.0 min. An amount of 1.9 mL of the supernatant was mixed with 0.1 mL NaOH (2.0 M) to produce the serum sample for electrochemical analysis.

3. Results and discussion

3.1. Preparation and characterization of $NiCo_2O_4$ NWs-rGO hybrid

Spinel type mixed valence of transition metal oxide have been widely used in electrochemical capacitors and lithium battery [16–19]. Here, the hybrid of spinel type $NiCo_2O_4$ with rGO was prepared to explore its electrochemical sensing performance. Fig. 1a,b shows the SEM images of the $NiCo_2O_4$ NWs-rGO hybrid. The low magnified image shows lots of sheet-like products piled on the substrate (Fig. 1a). Highly magnified image indicates that the surfaces of these sheets are flocky with many wrinkles and heave ridges decorated on the surface (Fig. 1b). The size of these sheets ranges from several hundred nanometers to more than one micrometer, which is similar to the size distribution of GO, implying that growth of $NiCo_2O_4$ may be guided by GO as template. In the absence of GO, $NiCo_2O_4$ micro-nanostructures with nanowrinkles decorated on surface were also observed. However, these $NiCo_2O_4$ wrinkles are connected with each other to form a large aggregate (Fig. 1c,d). The size of wrinkles is larger than that on the $NiCo_2O_4$ NWs-rGO hybrid (Fig. 1d). Compared with $NiCo_2O_4$, $NiCo_2O_4$ NWs-rGO displays improved dispersity as these $NiCo_2O_4$ wrinkles are grown on GO sheet as template. The improved