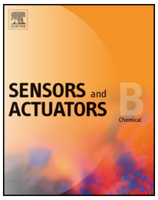
Sensors and Actuators B 265 (2018) 435–442

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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



Design and fabrication of Ag-CuO nanoparticles on reduced graphene oxide for nonenzymatic detection of glucose

Da Xu[a], Chengling Zhu[a], Xin Meng[a], Zhixin Chen[b], Yao Li[a], Di Zhang[a], Shenmin Zhu[a,*]

[a] State Key Laboratory of Metal Matrix Composites, Shanghai Jiao Tong University, Shanghai 200240, PR China
[b] School of Mechanical, Materials & Mechatronics Engineering, University of Wollongong, Wollongong, NSW 2522, Australia

ARTICLE INFO

Article history:
Received 12 December 2017
Received in revised form 13 March 2018
Accepted 14 March 2018
Available online 14 March 2018

Keywords:
Graphene
Silver
CuO
Non-enzymatic sensor
Glucose

ABSTRACT

In this study, a nano Ag-CuO/rGO (reduced graphene oxide) composite was designed and constructed as a novel nonenzymatic glucose sensor. The composite was fabricated through a one-step synthesis process. In the process, Ag-CuO with an average particle size of 10 nm formed and dispersed homogeneously on the surface of rGO sheets. When used for nonenzymatic glucose sensing, the resultant Ag-CuO/rGO composite showed a high sensitivity of 214.37 μA mM^{-1} cm^{-2} and an extremely wide linear response from 0.01 to 28 mM with a 0.76 μM detection limit (S/N = 3) at +0.6 V. The excellent sensing properties of the composite are probably due to the synergistic effect of the combination of Ag, CuO nanoparticles and rGO. The electron transfer is improved by the addition of Ag nanoparticles, and the composite electrode possesses larger surface area due to the rGO. The Ag-CuO/rGO composite doe not only show the good catalytic activity, excellent selectivity but also outstanding long term stability, good reproducibility, which makes it a novel type of composite for nonenzymatic glucose sensing.

© 2018 Elsevier B.V. All rights reserved.

1. Introduction

As a common disease, diabetic mellitus is a huge threat to human health. Rapid and accurate detection of blood glucose in a clinical diagnosis is of great significance [1]. There are many types of blood glucose sensors: electrical, electrochemical, optical, mechanical and others [2] according to the detection mechanism. Among them, electrochemical sensors have received extensive attentions due to their low cost, simple fabrication, reproducible and good sensing performance. Generally, electrochemical glucose sensors can be divided into enzyme-based sensors and non-enzyme sensors. Although they have a high sensitivity and selectivity, the stability and durability of the enzyme-based sensors are vulnerable to environmental factors during a detection process [3]. A non-enzyme sensor works on direct electro-oxidations without the use of enzymes and is a promising substitute, owing to its low cost, high stability, fast response and excellent sensitivity [4].

Various nanomaterials have been used to fabricate non-enzymatic sensors for glucose detection, including metals (Au, Ag, Pt, etc.), metal oxides (CuO, Co_3O_4, NiO, etc.), alloys (PtAu, PtCu, etc.) and various carbons (porous carbon, carbon nanotubes, graphene, etc.). Nanostructured metal oxides are potential materials for non-enzymatic glucose sensing, because of their good chemical stability, catalytic activity, controllable size and biological compatibility [5]. In particular, some metal oxides of multiple- valence, such as CuO, NiO, and Co_3O_4 can be used as efficient non-enzymatic glucose sensors. They can react with glucose directly without the use of enzymes. As a p-type semiconductor, CuO is attractive for its good sensing performance, good stability and high electrochemical activity [6]. However, the high charge transfer resistance of CuO-based electrodes limits their potential sensing properties. To reduce the charge transfer resistance, nano-carbon materials (e.g., carbon nanotubes, mesoporous carbons, and graphene) are introduced as a support for CuO nanoparticles (CuO NPs) based sensor. Kim et al. [4] reported that an electrochemical glucose sensor consisting of CuO–SWCNT composite films showed a linear response from 0.05 to 1800 μM and a good sensitivity of 1610 μA mM^{-1} cm^{-2}. Similarly, CuO nanoparticles prepared on a mesoporous carbons (MCs) matrix shown a linear concentration response from 0.4 μM to 7.3 mM and a good sensitivity of 1154.1 μA mM^{-1} cm^{-2} for nonenzymatic glucose sensing [7].

The 2D nanomaterials, sensitive to external stimulus, are promising for electrochemical applications [8,9]. As a new member of 2D carbon materials, graphene attracts tremendous attentions for non-enzymatic sensing because of its outstanding conductivity, low noise level, large surface area, excellent stability and

---

* Corresponding author.
E-mail address: smzhu@sjtu.edu.cn (S. Zhu).

https://doi.org/10.1016/j.snb.2018.03.086
0925-4005/© 2018 Elsevier B.V. All rights reserved.

wide electrochemical window [10]. Sun et al. [11] reported that CuO/graphene composites have a linear response from 1 μM to 8 mM and the sensitivity of 1065 μA mM^{-1} cm^{-2} for nonenzymatic glucose sensing. Graphene as a matrix is deemed to increase the conductivity between the electrode and the active material, in this case CuO. However, the interaction between the analyte and the active material is another limiting factor to the sensing properties. Fortunately, the limitation can be solved by incorporating noble metal nanoparticles with active metal oxides [12,13]. Among these noble metals, Ag is particularly attractive because of its relatively low cost, good conductivity and chemical stability. It was suggested that the anchoring of Ag nanoparticles onto a CuO containing electrode would improve the electron transfer not only between the electrode and the active CuO, but also between the analyte molecules in aqueous solution and the CuO. [12]. The design and preparation of Ag-CuO/graphene ternary composite electrode would be promising in the nonenzymatic sensing of glucose.

In this study, we constructed a novel composite electrode as a nonenzymatic glucose sensor. The composite sensor consists of Ag-CuO NPs on rGO sheets (Ag-CuO/rGO) and its performance of glucose sensing was then investigated. The Ag-CuO/rGO was fabricated by calcination after the first hydrothermal process. The effect of the content of Ag NPs on the sensing properties was studied. By taking advantages of the large surface area of reduced graphene oxide and high electronic conductivity of Ag NPs, the obtained composite modified glassy carbon electrode (Ag-CuO/rGO/GCE) exhibited an excellent performance with a high sensitivity of 214.37 μA mM^{-1} cm^{-2} and a very wide liner response from 0.01 to 28 mM.

2. Material and methods

2.1. Reagents

Graphite powders (325 mash) were supplied by XFNANO Materials Tech Inc. Uric acid (UA), dopamine hydrochloride (DA), ascorbic acid (AA) and Nafion (5 wt%) were supplied by Sigma-Aldrich. $Cu(NO_3)_2$, $AgNO_3$, ammonia, NaOH and others were all obtained from Sinopharm Chemical Reagent Co., Ltd.

2.2. Apparatus

Characterizations were conducted on scanning electron microscopy (SEM, JEOL JSM-6360LV, 15 kV), transmission electron microscopy (TEM, JEOL 2010 TEM, 200 kV) and raman spectra (RM, Renishaw in Via Raman microscope), powder X-ray diffraction (XRD, Rigaku D/max2550VL/PC system), and X-ray photoelectron spectroscopy (XPS, Perkin-Elmer PHI-5400 spectrometer) with Mg Kα radiation. All electrochemical measurements were performed in a three-electrode system on CHI-660E electrochemical workstation, with a modified glassy carbon electrode (GCE, diameter of 3 mm) as a working, Ag/AgCl electrode as reference and platinum wire as auxiliary electrode, respectively. The cyclic voltammetry (CV) is carried out at a range of −0.3 V to 1.0 V in 0.1 M NaOH with different glucose concentration. Chronoamperometry (I–t) is conducted in 0.1 M NaOH upon consecutive addition of glucose every 50 s at 0.6 V (vs Ag/AgCl) and electrochemical impedance spectroscopy (EIS) in 0.1 M KCl with 5 mM $K_3[Fe(CN)_6]$/ $K_4[Fe(CN)_6]$.

2.3. Fabrication of CuO/GO and Ag-CuO/GO composite

Graphene oxide (GO) was prepared via modified Hummers method as our previous work [14]. Nanocomposites with an optimum Ag NPs content (the molar ratio of Ag/Cu is 1/50) of Ag-CuO/GO were synthesized. First, 40.0 mg GO was dispersed into 40 mL H_2O under ultrasonication for 1 h to obtain a homogeneous solution. Next, 1 mL of $Cu(NO_3)_2$ (1 M) solution and 0.2 mL of $AgNO_3$ (0.1 M) were added into GO solution. After stirring for 1 h, ammonia (1 M) solution was used to adjust the pH of the mixed suspension to 10, stirring for 1 h again. The mixed suspension was then sealed into a 100 mL Teflon container and heated at 130 °C for 6 h. The obtained dispersion was then centrifuged, and washed with ultra-pure water several times followed by freeze drying. For comparisons, CuO/GO composite and Ag-CuO/GO composites containing different Ag NPs contents (the molar ratio of Ag/Cu is 0, 1/200, 1/100, 1/20 and1/10) were synthesized using the same method.

2.4. Fabrication of Ag-CuO/rGO composite

A hydrothermal method followed by an annealing process was used to the fabrication of Ag-CuO/rGO composite. The hydrothermal conditions are the same as above-mentioned, only add 1 mL of ascorbic acid (1 M) solution to the mixture before pH adjustment. After freeze drying, the product was annealed at 300 °C for 4 h in air. The composite thus prepared was assigned as Ag-CuO/rGO.

2.5. Fabrication of Ag-CuO/rGO/GCE

First of all, alumina powders with different size (1.0 μm, 0.3 μm and 0.05 μm) were applied to polish the GCE. Next, the GCE was cleaned with water and absolute ethanol for several times under ultrasonication, and dried in air. Then 10 μL 2 mg mL^{-1} ethanol suspension of Ag-CuO/rGO was transferred onto the GCE. After drying, 5 μL of Nafion (0.5 wt%) was then dropped onto the modified GCE and dried in air again to get Ag-CuO/rGO/GCE. Nafion is generally used as an electrode modifier agent [15], which can be used for the fixation of electrode materials. It could increase the selectivity and stability of the sensor for glucose due to the good selective permeability [16]. In the same procedure, CuO/GO/GCE and Ag-CuO/GO/GCE were prepared for comparisons.

3. Results and discussion

3.1. Fabrication and characterization of Ag-CuO/rGO composites

The fabrication process of the Ag-CuO/rGO composite is described in Scheme 1. Firstly, $Cu(NO_3)_2$ and $AgNO_3$ were mixed with GO solution, during which Cu^{2+} and Ag^+ were adsorbed onto GO sheets through their interactions with oxygen-containing groups. Subsequent addition of ammonia resulted in the formation of $[Cu(NH_3)_4]^{2+}$ and $[Ag(NH_3)_2]^+$ [17] in situ on the surface of the GO sheets. In the subsequent hydrothermal reaction, GO was reduced as rGO by the environmentally friendly reductant of ascorbic acid, so did the reductions of $[Ag(NH_3)_2]^+$ and $[Cu(NH_3)_4]^{2+}$to metal Ag and Cu (the XRD pattern of intermediate Ag-Cu/rGO is presented in Fig. S1). Finally, the Cu turned into CuO through a calcination process and Ag-CuO nanoparticles formed on the surface of the rGO (Ag-CuO/rGO).

The morphologies of the Ag-CuO/rGO and Ag-CuO/GO composites were examined firstly by SEM. The Ag-CuO in Ag-CuO/GO has a plate-like structure. The length and width of this structure are measured as ~800 nm and ~400 nm, respectively (Fig. 1A). The predominant feature in Ag-CuO/rGO is the wrinkled rGO as shown in Fig. 1B. And the Ag-CuO is much finer and only visible at a much higher magnification as shown in Fig. 1C that shows many small Ag-CuO particles uniformly distributed on the rGO sheets. The homogenous distribution of Ag, Cu, C and O is further evidenced by the EDS mapping images of Ag–CuO/rGO in Fig. S2. TEM was further used to characterize the Ag-CuO/rGO composite. Fig. 1D and

Download English Version:

https://daneshyari.com/en/article/7140033

Download Persian Version:

https://daneshyari.com/article/7140033

Daneshyari.com