



Phosphomolybdic acid functionalized graphene loading copper nanoparticles modified electrodes for non-enzymatic electrochemical sensing of glucose



Jiaoyan Xu ^a, Xiyue Cao ^a, Jianfei Xia ^{a,*}, Shida Gong ^a, Zonghua Wang ^{a,**}, Lin Lu ^{a,b}

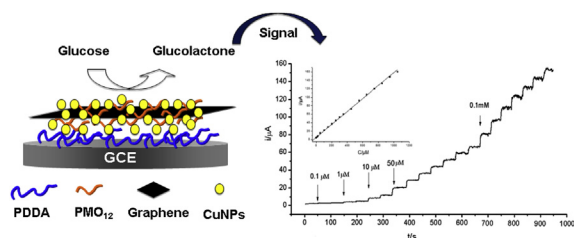
^a College of Chemistry and Chemical Engineering, Shandong Sino-Japanese Center for Collaborative Research of Carbon Nanomaterials, Collaborative Innovation Center for Marine Biomass Fiber Materials and Textiles, Laboratory of Fiber Materials and Modern Textile, The Growing Base for State Key Laboratory, Qingdao University, Qingdao 266071, PR China

^b Zibo Normal College, Zibo, Shandong 255100, PR China

HIGHLIGHTS

- Cu/PMo₁₂-GR/GCE as a non-enzymatic glucose electrochemical sensor.
- PMo₁₂ is efficient for the uniform growth of Cu-NPs and electron transport.
- The sensor exhibits good sensitivity and specificity towards glucose.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 12 May 2016

Received in revised form

15 June 2016

Accepted 16 June 2016

Available online 22 June 2016

Keywords:

Phosphomolybdic acid

Graphene

Copper nanoparticles

Non-enzymatic glucose sensing

Amperometric detection

ABSTRACT

A sensitive non-enzymatic glucose electrochemical biosensor (Cu/PMo₁₂-GR/GCE) was developed based on the combination of copper nanoparticles (CuNPs) and phosphomolybdic acid functionalized graphene (PMo₁₂-GR). PMo₁₂-GR films were modified on the surface of glassy carbon electrode (GCE) through electrostatic self-assembly with the aid of poly diallyl dimethyl ammonium chloride (PDDA). Then CuNPs were successfully decorated onto the PMo₁₂-GR modified GCE through electrodeposition. The morphology of Cu/PMo₁₂-GR/GCE was characterized by scanning electron microscope (SEM). Cyclic voltammetry (CV) and chronoamperometry were used to investigate the electrochemical performances of the biosensor. The results indicated that the modified electrode displayed a synergistic effect of PMo₁₂-GR sheets and CuNPs towards the electro-oxidation of glucose in the alkaline solution. At the optimal detection potential of 0.50 V, the response towards glucose presented a linear response ranging from 0.10 μM to 1.0 mM with a detection limit of $3.0 \times 10^{-2} \mu\text{M}$ (S/N = 3). In addition, Cu/PMo₁₂-GR/GCE possessed a high selectivity, good reproducibility, excellent stability and acceptable recovery, which indicating the potential application in clinical field.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

The electrochemical approach for glucose detection has attracted significant attention for its simplicity, high reliability, sensitivity, selectivity and low cost. Since the first enzyme electrode was reported in 1962 [1], most researches on glucose sensing have

* Corresponding author.

** Corresponding author.

E-mail addresses: xiajianfei@126.com (J. Xia), wangzonghua@qdu.edu.cn (Z. Wang).

involved the use of glucose oxidase. Although these biosensors express a highly sensitive performance, the lack of stability originating from the intrinsic nature of the enzymes has limited their applications. The activity of these enzymes can be easily affected by temperature, pH, humidity, toxic chemicals and so on. Considering these drawbacks, non-enzymatic electrochemical sensors have become a highly desirable project for glucose detection [2]. The majority of these nonenzymatic electrochemical glucose sensors rely on the current response of glucose oxidation directly at solid electrode surface. However, the traditional electrodes have poor analytical performance due to their slow electrode kinetics and high over-potential. And the electrocatalytic surfaces of the electrodes are always blocked by the accumulation of chemisorbed intermediates, which resulted in a lose of electrocatalytic activity. In addition, the electrodes often suffer from the influence coming from some electroactive species during electrochemical detection of glucose under physiological conditions.

In recent years, a variety of nanomaterials [3,4], especially the carbon-based nanocomposites [5–8], have been introduced to the fabrication of non-enzymatic electrochemical glucose sensors due to their desirable chemical, physical and electronic properties, which can enhance the sensing performance. Among these materials, graphene-based nanocomposites [9–11] have aroused extensive interest and become attractive choices for glucose non-enzymatic sensing. The reason is that graphene-based nanocomposites could provide large electrochemically active surface areas and enhance the electron transfer between electrode and glucose effectively, leading to a more rapid and sensitive current response. Up to now, various metal-graphene and metal oxide-graphene nanocomposites have been reported for the fabrication of non-enzymatic glucose sensor, including of Pd nanoparticles-graphene oxide [12], Ag nanoparticles-graphene [13], Fe₃O₄-graphene [14], MnO₂-graphene [15], Co₃O₄-graphene [16], SnO₂-graphene [17], copper oxide-graphene [18,19], ZrO₂-graphene [20] and so on. And the performance of the graphene-based non-enzymatic glucose biosensor relies not only on the properties of the individual components, such as the electron transport ability of the substrates and the catalytic activities of metal or metal oxide nanoparticles, but also on the effective structural integration and electrical communication of the components. Therefore, it is important to develop methods to improve the intimate contact between the components.

The addition of intermedium is an important strategy to improve electrical communication. Using this strategy, many multi-component glucose biosensors have been reported, such as Pd nanoparticles/naftion/graphene [21], Ni/querctin/graphene [22], polyvinylpyrrolidone/graphene/nickel nanoparticles/chitosan [23] and so on [24]. But, many additions like naftion and chitosan are mainly not chosen as electron intermedium but as stabilizer. Because they are not active materials for glucose sensing, they may degrade the sensitivity of glucose detection. Polyoxometalates anions (POMs), a type of well-known polynuclear metal-oxo cluster compounds represented by Keggin-type phosphomolybdate (PMo₁₂) [25], can be introduced to fabricate metal nanoparticles/graphene-based glucose biosensor as intermedium. One of the most important properties of PMo₁₂ is the potential for reversible multi-electron redox reactions, which makes it to be an attractive candidate for electrocatalysis and electroanalysis [26,27]. We have reported a novel phosphomolybdic acid/graphene composite modified electrode for determination of folic acid [28]. The synergistic effect of phosphomolybdic acid and graphene improved the analytical performances of the electrode. Additionally, PMo₁₂ can also act as a dispersant and stabilizer to prevented the hydrophobic graphene from agglomerating [29]. Therefore, PMo₁₂ is suitable to fabricate graphene-based glucose electrochemical sensor as active

materials. In order to immobilize PMo₁₂ on electrode surface effectively and maintain its beneficial properties, a variety of methods have been used, including of Langmuir-Blodgett (LB) technique [30], electrodeposition [31] and so on [32–34]. In this research, electrostatic self-assembly is used with the assistance of Poly(diallyldimethylammonium chloride) (PDDA), a positively charged polyelectrolyte [35]. And the PDDA can enhance the conductivity further [36,37], which is beneficial for the performance improvement of the electrocatalyst.

Herein, we report a novel non-enzymatic glucose electrochemical sensor based on cooper nanoparticles (CuNPs) and graphene (GR). To make intimate contact between CuNPs and GR, which can improve analytical performance of the sensor, PMo₁₂ is introduced to the modified electrode through electrostatic self-assembly with the assistance of PDDA. With the synergistic effect of PMo₁₂, GR sheets and CuNPs, this proposed glucose sensor exhibits excellent electrocatalytic activity towards the glucose with a fast amperometric response, low detection limit and wider linear range. It is capable to assay the glucose in human serum samples contained other coexisting interferences.

2. Experimental

2.1. Chemicals and materials

Glucose was purchased from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China). Keggin-type phosphomolybdic acid H₇PMo₁₂O₄₂·xH₂O (denoted briefly as PMo₁₂) was ordered from Tianjin Regent Co., Ltd. (Tianjin, China). Graphite was provided by Qingdao Fujin Graphite Co., Ltd. (Qingdao, China). Dopamine (DA) was purchased from Sigma-Aldrich (St. Louis, MO, USA). Ascorbic acid (AA) was obtained from Shanghai Reagent Factory (Shanghai China). Uric acid (UA) was purchased from Sinogharm Chemical Reagent. PDDA was ordered from Sigma-Aldrich (St. Louis, MO, USA). CuSO₄, NaOH and other reagents were of analytical grade.

2.2. Apparatus

Scanning electron microscopy (SEM) and transmission electron microscope (TEM) images were obtained by JEOL JSM-7001F and JEOL JEM-2100, respectively. Cyclic voltammetry (CV) and amperometric measurements were performed using a CHI-660C electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd., China) with a conventional three-electrode cell. A glassy carbon electrode (GCE) was used as bare electrode, and the modified GCE (Cu/PMo₁₂-GR/GCE) was used as the working electrode. A platinum wire was used as the auxiliary electrode. All the potentials quoted here were referred to a saturated calomel electrode (SCE) as the reference.

2.3. Preparation of the Cu/PMo₁₂-GR/GCE

GR was prepared according to our previously reported method [38]. 10 mg GR was fully dispersed in 10 mL of PMo₁₂ solution by ultrasonication for 30 min. Then the PMo₁₂ functionalized GR (PMo₁₂-GR) was obtained.

A GCE was first sequentially polished with 0.3 μm and 0.05 μm alumina powders. Then the GCE was ultrasonically cleaned in ethanol and double-distilled water respectively followed by drying at room temperature before use. The as-prepared GCE was soaked in PDDA (10 wt%) for 15 min, and then took it out to dry by air. After that, a PDDA/GCE was obtained. Then we put the PDDA/GCE in the suspension liquid of PMo₁₂-GR for 15 min, and then took it out and dried it in room temperature. Repeated the same process, we could

Download English Version:

<https://daneshyari.com/en/article/1162727>

Download Persian Version:

<https://daneshyari.com/article/1162727>

[Daneshyari.com](https://daneshyari.com)