Sensors and Actuators B 208 (2015) 421–428

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

Novel graphene-gold nanohybrid with excellent electrocatalytic performance for the electrochemical detection of glucose

Li Ruiyi[a], Zhang Juanjuan[a], Wang Zhouping[b], Li Zaijun[a,c,*], Liu Junkang[a], Gu Zhiguo[a], Wang Guangli[a]

[a] School of Chemical and Material Engineering, Jiangnan University, Wuxi, China
[b] School of Food Science and Technology, Jiangnan University, Wuxi, China
[c] Key Laboratory of Food Colloids and Biotechnology, Ministry of Education, Wuxi 214122, China

ARTICLE INFO

Article history:
Received 20 September 2014
Received in revised form 28 October 2014
Accepted 2 November 2014
Available online 14 November 2014

Keywords:
Graphene
Gold nanoparticles
Nanohybrid
Electrochemical detection
Sensor
Glucose

ABSTRACT

Graphene-gold nanohybrids have become a hot research topic in material science, because the hybridization can be an effective strategy to enhance the functionality of materials and the integration of nanomaterials on graphene nanosheets potentially paves a new way to improve their electronic, chemical and electrochemical properties. The study reported a novel graphene-gold nanohybrid with excellent electrocatalytic performance for electrochemical detection of glucose. First, the monodisperse gold nanoparticles (GNs) were prepared via the citrate reduction associated with pH-shifting. The resulting GNs give an average particle size of 6 nm and narrow size distribution. Then, one part of the GN solution was mixed with the graphite oxide solution, which followed by the ascorbic acid reduction and unidirectional freeze-drying to prepare graphene aerogel@GNs (GA@GNs). The formed GA@GNs offers a well-defined three-dimensional and orientated porous structure. In addition, the most of GNs in the aerogel was embedded in the intertwined graphene sheets. Finally, another part of the GN solution was sucked into the GA@GNs to obtain GA@GNs/GNs. It was subjected to freeze-drying and thermal annealing in air at 180 °C to remove the citrate modified on the surface of GNs. Because their active sites were well exposed outside, the adsorbed GNs are of high catalytic activity. The study shows that the as-prepared GA@GNs/GNs gives high electrical conductivity (15.4 S m^{-1}), specific surface area (291.6 m^2 g^{-1}) and apparent heterogeneous electron transfer rate constant (14.8 ± 0.12 cm s^{-1}). The sensor based on the GA@GNs/GNs displays ultrasensitive electrochemical response to glucose, owing to largely enhanced electron transfer, mass transport and catalytic activity. Its peak current linearly increases with the increase of glucose in the range from 0.01 to 16 mM with the detection limit of 0.004 mM ($S/N = 3$). The analytical method presents the advantage of sensitivity, repeatability and stability compared with present glucose sensors. It has been successfully applied in the detection of glucose in serum samples with the spiked recovery of 95.7–104.2%. The study also provides a promising approach for building on various graphene-metal nanohybrids with excellent electrochemical performance for sensing, catalysis and energy storage/conversion devices.

1. Introduction

Graphene has unusual electronic properties as a result of its Dirac points, positions in its single-sheet honeycomb lattice of carbon atoms at which the energy bands of electrons from adjacent atoms link up. These allow electrons in the bands to speed across the material that like cars changing roads at major intersections instead of getting stuck on one jammed road. The research confirms that the electrons in graphene move so fast that they seem to have no mass, and are, in effect, moving at the speed of light [1]. Up to now, graphene become ideal electrochemical materials in sensing [2], electrocatalysis [3], supercapacitor [4] and lithium-ion battery [5]. However, graphene does not provide a specific catalyst to a particular oxidation/reduction process, it is difficult to solely use as the catalyst for chemical sensors and electrocatalysis. Fortunately, the problem can be resolved by the introduction of gold nanoparticles (GNs). There have been attempts to apply gold as a catalyst in the form of nanoparticles. In the recent years, GNs have been well-fabricated in different sizes and their unique

---

[*] Corresponding author at: School of Chemical and Material Engineering, Jiangnan University, Wuxi, China. Tel.: +86 13912371144.
E-mail address: zaijunli@263.net (L. Zaijun).

http://dx.doi.org/10.1016/j.snb.2014.11.004
0925-4005/

properties were investigated from various approaches [6]. The resulting GNs have different physical, chemical, and electrical properties from bulk gold because of the quantum confinement effect in small size and the large fractions of surface atom [7]. It was also found that the GNs have excellent catalytic activities [8]. Graphene-gold nanohybrid has become a hot research topic in material science, because the hybridization can be an effective strategy to enhance the functionality of materials, and the integration of nanomaterials on graphene nanosheets potentially paves a new way to enhance their electronic, chemical and electrochemical properties [9].

Main methods for the synthesis of graphene-gold nanohybrid are the chemical reduction [10], self-assembly [11] and electrochemical reduction [12]. The chemical reduction method is to mix graphene or graphene oxide with chloroauric acid, then add a strong reducing agent such as sodium borohydride and hydrazine hydrate into the mixed solution to simultaneously reduce graphene oxide and chloroauric acid. They precipitated from aqueous solution to obtain graphene-gold nanohybrid. The method has the advantages of simple operation. But it needs to use large amounts of toxic chemicals, which will bring harmful to operator health and the environment. To avoid the use of highly toxic chemicals and improve dispersivity of the hybrids, many environmentally friendly reducing agents were developed for fabrication of graphene-gold nanohybrid [13]. For example, Su and co-workers reported a facile one-pot green synthesis of large-scale and semitransparent graphene-gold hybrid membrane, in which glucose was used for reducing graphene oxide and chloroauric acid in one liquid system synchronously. The graphene-gold hybrid membrane was finally fabricated at a liquid-air interface by a self-assembly process. The nanohybrid has been successfully applied in fabricating an electrochemical biosensor of hydrogen peroxide [14]. Different from the chemical reduction method, the self-assembly method uses the pre-prepared graphene and GNs to fabricate graphene-gold nanohybrids. Often, the self-assembly method includes the modification of graphene and the self-assembly of GNs on modified graphene sheets [15]. First, one functional reagent was modified on the surface of graphene sheets. Then, GNs were self-assembled on surface of the modified graphene through their interaction. The chemical functionalization of graphene offers the means of modifying its already existing fascinating electronic properties. It can also result in the formation of covalent and ionic bonds as well as non-covalent van der Waals interactions. This would improve the immobilizations of GNs on the graphene sheets. For example, Wang and co-workers proposed a new covalent method to prepare nanohybrids of thionin pre-modified graphene and GNs [16]. In the strategy, thionin was used as bridging molecule between GN and graphene oxide. GNs were tightly anchored on the modified graphene through the formation of amide bonds between COOH groups on the GN surface and NH_2 groups on the thionin modified graphene. The surface modification of GNs with peptide CALNN provides the stability of obtained nanohybrids in the physiological environment, because of electrostatic repulsion and space hindrance between graphene sheets. Moreover, they also investigated bio-application properties of the nanohybrid. After coated by poly-L-lysine, the nanohybrids can be a promising candidate for photothermal therapy. Due to simple, fast, and green nature, the electrochemical reduction of GO is attractive for synthesis of graphene-gold nanohybrid. Usually, GNs were added to GO aqueous solution. The mixture is then reduced at a negative potential to yield a graphene-gold nanohybrid. More important is the electrochemical method can be directly applied to fabricate graphene-gold nanohybrid on the electrode surface. But graphene sheets are not separated by GNs since they are mostly located on the surface of graphene film [17]. To overcome the problem, Sun and co-workers reported a new strategy to prepare graphene-gold nanohybrid film by cyclic voltammetry [12]. The graphene layers were spaced by the layer of GNs. As a result, the conductivity and surface area of graphene-gold nanohybrid were remarkably enhanced. However, these methods cannot avoid obvious agglomeration and precipitation of GO nanosheets in the electrolyte due to the redox reaction between chloroauric acid and GO. In previous work, we developed a green and controllable strategy to fabricate well-dispersed graphene-gold nanohybrid film as sensing materials for the detection of hydroquinone and resorcinol [18]. The technique allows single-layer graphene nanosheet and GNs were alternately electrodeposited on surface of the glassy carbon electrode. The resulting graphene-gold nanohybrid film provides excellent dispersity and electrocatalytic activity. Despite these great progresses, the fabrication of graphene-gold nanohybrid with ideal electron transfer, mass transport and catalytic activity is still facing great challenges.

The study focused on the fabrication of a novel graphene-gold nanohybrid with excellent electrocatalytic performance and its application for the electrochemical detection of glucose. The unique structure largely improves the mass transport, electron transfer and electrocatalytic activity. The sensor based on the nanohybrid provides the advantage of sensitivity, repeatability and stability when compared with present glucose sensors.

2. Experimental

2.1. Materials and reagents

Chlorauric acid, citric acid, ascorbic acid and glucose were purchased from Sigma-Aldrich Chemical Company (Mainland, China). Graphite oxide (GO) was prepared from natural graphite by Hummers' method [19]. Phosphate-buffered saline (PBS, pH 7.0, Na_2HPO_4-KH_2PO_4-NaCl-KCl, 0.01 M) was prepared in the laboratory. The chitosan solution was prepared by dissolving 5.0 g of chitosan in 100 ml of 1.0% (v/v) acetic acid. All other reagents employed were of analytical reagent grade or with highest quality and were purchased from Shanghai Chemical Company (Shanghai, China). Ultra pure water (18.2 MΩ cm) purified from a Milli-Q purification system was used throughout the experiment.

2.2. Preparation of the monodisperse GNs

The monodisperse GNs were prepared using a reported method [20]. In a typical procedure, a 2.0 ml of citric acid aqueous solution (0.175 M) is quickly added into 50 ml of boiling chlorauric acid aqueous solution (0.5 mM) that is stirred and refluxed. After waiting a period of 10 s, a 0.15 ml of the sodium hydroxide solution (1.0 M) is instantly introduced into the reacting solution to shift the pH from acidic to neutral. The solution was refluxed at 100 °C for 1 h, then cooled to ambient temperature, and finally filtered using a cellulose acetate membrane with the bore diameter of 0.26 to obtain the monodisperse GN solution.

2.3. Synthesis of the GA@GNs/GNs

A100 mg of GO was dispersed in 25 ml of the pre-prepared GN solution by the ultrasonication to form a homogeneous dispersion. Then, added 200 mg of ascorbic acid into the mixed solution in cylindrical glass vial, which was then placed in boiling water bath for 20 min. Next, the vial was immersed in a liquid nitrogen bath to freeze for 0.25 h. After being thawed at room temperature, the vial was again placed in boiling water bath to further reduce GO sheets for 6 h. The resulting hydrogel was sequentially subjected to dialysis in water to remove soluble species and then dried by freezing drying. Finally, the obtained GA@GNs was immersed in