In situ synthesis of graphene-encapsulated gold nanoparticle hybrid electrodes for non-enzymatic glucose sensing

CrossMark

Tran Duy Thanh [a], Jayaraman Balamurugan [a], Jun Yeon Hwang [b], Nam Hoon Kim [a], Joong Hee Lee [a, c, *]

[a] Advanced Materials Institute of BIN Convergence Technology (BK21 Plus Global) & Dept. of BIN Convergence Technology, Chonbuk National University, Jeonju, Jeonbuk, 561-756, Republic of Korea
[b] Institute of Advanced Composite Materials, Korea Institute of Science and Technology, Eunha-ri San 101, Bongdong-eup, Wanju-gun, Jeonbuk, 565-905, Republic of Korea
[c] Carbon Composite Research Centre, Department of Polymer & Nanoscience and Technology, Chonbuk National University Jeonju, Jeonbuk, 561-756, Republic of Korea

ARTICLE INFO

ABSTRACT

A novel route for in-situ synthesis of high-quality gold nanoparticles-encapsulated few layered graphene (AuNP-FLG) nanohybrids has been established. The AuNP-FLG nanohybrids were successfully synthesized by chemical vapor deposition technique and used as an electrocatalyst for high sensitive non-enzymatic glucose sensors. The amperometric response of the AuNP-FLG based electrode achieved an excellent electrocatalytic activity towards glucose oxidation with a wide linear detection range of 6 μM–28.5 mM, low detection limit of 1 μM and a sensitivity of 0.195 μA mM^{-1} cm^{-2} at operating potential of 0.0 V. Furthermore, the electrode also showed long-term stability (retention of 95.4% after two week) with negligible interference from ascorbic acid, 4-acetamidophenol and uric acid. The results implied that AuNP-FLG could be a promising electrode material in the development of non-enzymatic glucose sensors.

1. Introduction

Glucose plays an important role in the diagnosis of diabetes mellitus [1], which is a very common disease and one of the leading causes of death and disability in the world [2]. The worldwide increase in diabetes mellitus is of great concern and has led to the development of excellent sensitive, selective and reliable analytical sensors to monitor glucose. Electrochemical glucose sensors are generally classified into two categories, enzymatic and non-enzymatic. The strategy for the fabrication of glucose oxidase (GO_x)-based biosensors is based on the direct electrochemistry of GO_x [3]. However, the drawback of these enzyme-based glucose sensors is their lack of long-term stability because of the intrinsic nature of the enzymes (although GO_x is quite stable compared with other enzymes). Also, enzymes such as GO_x are expensive, and their activity can be easily affected by temperature, the pH of the solution, and humidity. To address these issues, many attempts have been made to detect glucose without using enzymes. Most of these non-enzymatic electrochemical glucose sensors rely on a current response to the direct electrochemical oxidation of glucose at the electrode surface. Early research in this area has focused on the use of noble metals, such as Pt and Au [4,5].

In this context, the activity of these electrodes quickly deteriorates at a fast rate due to the accumulation of chemisorbed intermediates that block the electrode surface. Moreover, these electrodes often suffer from some interference because of the electrochemical oxidation of certain electrochemically active species under physiological conditions [6]. All these drawbacks along with their high production cost, limit their use at a commercial scale. The rapid development of nanotechnology and the identification of numerous nanostructured materials have paved the way for development of improved non-enzymatic glucose biosensors [7–10]. It is important to note that carbon-based nanomaterials have recently attracted a great deal of attention in the area of biosensors. However, graphene, a single-layer sp^2 carbon, has been considered as a potential material for this application [11–13].

Graphene, the foundation of all carbon nanostructures, has

become a rising star in various fields due to its excellent properties, such as large specific surface area, high mechanical properties, extraordinary electrical and thermal conductivities, biocompatibility and so on [14]. Furthermore, it exhibits a wide electrochemical potential window, which is comparable to that of graphite, glassy carbon, and even boron-doped diamond electrodes [15]. These exceptional characteristics make graphene a promising material for applications in electrocatalysis with enhanced electron transfer rates [16–19]. Among various graphene based materials, reduced graphene oxide (rGO) has been studied in great detail [18–20]. But the aggregation of rGO layers caused by $\pi-\pi$ stacking interactions, a large number of defects on a planar structure and the presence of oxygen functional groups on rGO impede the efficient electron transfer rate and severely affect the performance. It has been found that graphene synthesized by chemical vapor deposition (CVD) is suitable due to having fewer planar defects, which improve the electron transport properties and electrocatalytic activity [21,22].

In general, nobel metal nanoparticles have the ability to change graphene electronic structure leading to important synergistic effects that improve the analytical selectivity and sensitivity. In comparison to other noble metals, gold nanoparticles (AuNPs) have been widely used as electrocatalysts in various applications due to their unique chemical and physical properties, good biocompatibility, chemical stability and antifouling ability [23,24]. Therefore, it is anticipated that the combination of AuNPs and CVD-grown graphene could produce enhanced electrochemical performance in sensing. However, the strength of the attachment between AuNPs and graphene significantly affects the electrocatalytic activity of nanohybrids. It was reported that the interactions of AuNPs with pristine, defect-free graphene is very weak due to the inert nature of covalently bonded sp^2 carbon atoms on the basal plane of graphene [25–27]. However, Ding et al. reported that the strong interactions between graphene and AuNPs occurred due to the in-plane defects of graphene, including non-hexagonal rings and vacancies [26]. Therefore, it is necessary to develop a suitable approach to enhance the interactions between AuNPs and CVD-grown graphene.

In this report, a new type of AuNPs and FLG nanohybrids through CVD technique, which was used as a novel sensing electrode material has been developed for electrochemical detection of glucose effectively. The major advantage of this nanohybrid is highly improved interactions between AuNPs and FLG sheets through formation of AuNP-encapsulated FLG structures with suitable amount of in-plane defects on FLG nanosheets. Furthermore, the nanohybrid based non-enzymatic glucose sensors are made without using any polymer binders. Compared to the previous reports, these sensors offer higher electrocatalytic active performance with wide linear detection range, low detection limit, good reproducibility and excellent electrochemical stability towards electrooxidation of glucose.

2. Experimental

2.1. Reagents and solutions

Glucose, hydrogen tetrachloroaurate (HAuCl$_4$·3H$_2$O), potassium hexacyanoferrate(II) trihydrate (K$_4$[Fe(CN)$_6$])·3H$_2$O, sodium hydroxide (NaOH), ascorbic acid (AA), uric acid (UA), ammonium persulfate ((NH$_4$)$_2$S$_2$O$_8$), polymethylmethacrylate (PMMA), sodium monohydrogen phosphate (Na$_2$HPO$_4$), and sodium dihydrogen phosphate (Na$_2$HPO$_4$) were purchased from Sigma Aldrich Chemicals Co. (USA). Indium doped tin-oxide (ITO) conducting glass was purchased from HS technologies and cut into small pieces (1 cm × 2 cm) to serve as a working electrode. An uncoated copper substrate with a 25 μm thickness purchased from Alfa Aesar Co. (USA), was used as the substrate to synthesize graphene. Argon, hydrogen and methane gases were used as carrier, reducing and carbon source gas, respectively. Ultra-pure water, filtered using an EYELA Still Ace SA-2100E1 (Tokyo Rikakikai Co., Japan), was used throughout the experiments.

2.2. Synthesis of AuNP-FLG nanohybrids

In order to synthesize AuNP-FLG nanohybrids using a gas mixture of methane (CH$_4$), hydrogen (H$_2$) and argon (Ar) by the atmospheric pressure CVD (APCVD) method, 25 μm thick Cu foils were used as substrates. In a typical procedure, 1 mM HAuCl$_4$ solution was electrolessly deposited on the Cu substrate with different deposition time (1, 3 and 5 min). The AuNP deposited Cu foil was placed in the center of a horizontal quartz tube mounted inside a high-temperature furnace, and was then heated at 1000 °C under the flow of Ar (900 sccm), H$_2$ (50 sccm) and CH$_4$ (2 sccm) for 30 min to synthesize graphene nanosheets. After completion of the reaction, the sample was quickly cooled down under the same flow rates of Ar, H$_2$, and CH$_4$. The PMMA supporting transfer process was chosen for easy handling and preventing from folding or tearing of the grapheme [28] (Fig. 1). Before etching the Cu substrate, PMMA solution is coated on the synthesized graphene. The Cu substrate was etched away by (NH$_4$)$_2$S$_2$O$_8$ solution (5 wt.%) for several hours Then the PMMA coated graphene was cleaned with deionized water and transferred onto the SiO$_2$ substrate in a reverse direction. The SiO$_2$ substrate was removed in the water bath to leave the PMMA coated graphene-AuNPs. Finally, PMMA was removed by acetone. Graphene was then carefully transferred on to indium doped tinoxide (ITO) conducting substrate, dried at 60 °C for 2 h and followed by heat treated at 400 °C for 60 min in an Ar/H$_2$ atmosphere to remove impurities. The obtained nanohybrids were designated as AuNP-FLG-1, AuNP-FLG-3 and AuNP-FLG-5, consistent with deposition time 1, 3 and 5 min, respectively. Bare FLG was also synthesized by an identical procedure without involving HAuCl$_4$·3H$_2$O. The AuNP-FLG nanohybrid synthesis procedure is schematically illustrated in Fig. 1.

2.3. Fabrication of working electrodes

ITO conducting glass substrates were ultrasonicated thoroughly in acetone, ethanol, and double distilled water for 10 min each to remove organic pollutants and other contaminants. AuNP-FLG nanohybrids (1 cm × 1 cm) were carefully transferred onto the ITO conducting substrates, and allowed to dry at 60 °C for 2 h followed by annealing at 400 °C for 60 min in an Ar/H$_2$ atmosphere.

2.4. Material characterization

Field-emission scanning electron microscopy (FE-SEM) images and energy dispersive X-ray analysis (EDAX) were carried out on a JSM-6701F (JEOL, Japan). The ImageJ software (National Institutes of Health, USA) was used to calculate particle size of AuNPs based on FE-SEM images of AuNP-FLG nanohybrids. Transmission electron microscopy (TEM) measurements were carried out on an H-7650 (Hitachi Ltd., Japan) microscope at 120 kV in Jeonju center of KBSI. Raman spectroscopy analysis was performed by a Nanofinder 30 (Tokyo Instruments Co., Japan). The XPS characteristics of the samples were analyzed using Theta Probe (Thermo Fisher Scientific Inc., USA).

2.5. Electrochemical characterization

A three-electrode system was used to evaluate the