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Ultrasensitive and highly stable nonenzymatic glucose sensor by a CuO/graphene-modified screen-printed carbon electrode integrated with flow-injection analysis

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ABSTRACT

We report here a nonenzymatic glucose sensor based on a CuO/graphene-modified screen-printed carbon electrode (CuOG-SPCE) integrated with flow-injection analysis (FIA). The highly active CuOG-SPCE with well-dispersed CuO nanoparticles on graphene surfaces performed excellent electrocatalytic oxidation of glucose. Under optimal FIA conditions, the proposed biosensor can be employed in the quantification of glucose with the linear range from 0.122 μM to 0.5 mM, the desirable sensitivity up to 2367 μA mM^{-1} cm^{-2} and the ultralow detection limit of 34.3 nM (S/N = 3) simultaneously. Good repeatability of 1.92% (n = 30) and less effects of common interfering species including ascorbic acid, uric acid, dopamine, fructose, lactose and sucrose were also demonstrated. The CuO-SPCE with highly sensitive, selective and stable consecutive monitoring (t = 1 h) of glucose is promising for the development of an advanced nonenzymatic glucose sensor device.

1. Introduction

Fast and reliable methods for glucose determination was extensively developed on the use of enzyme based electrode due to its high selectivity [1,2]. However, taking into account of some inevitable drawbacks from intrinsic nature of glucose oxidase [3], the direct electrocatalytic oxidation of glucose without enzyme seems to be promising. Valuable nonenzymatic glucose biosensor was crucial to the sensitivity and the selectivity [4]. In the past few years, various metallic nanomaterials were undertaken to investigate in the promotion of nonenzymatic glucose biosensors [5–9]. In addition, more economical electrocatalysts have been focusing on copper (Cu)-based materials. For instance, Cu [10], cupric oxide (CuO) [11], cuprous oxide (Cu_2O) [12] and CuO/TiO_2 [13] have been evolved from current investigations.

Graphene, which is a two-dimensional monolayer of graphite, has recently received tremendous attention [14–16]. Recently, graphene has been rapidly becoming the attractive electrode material due to their high surface area, excellent electrical conductivity and high stability [17–19]. Graphene-based materials also exhibit a significant potential for biosensor applications [20–23]. Most of the above-mentioned biosensors were based on very smooth glassy carbon electrode (GCE) for glucose detection. Our previous work reported the sensitivity (1065 μA mM^{-1} cm^{-2}) and the detection limit of 1 μM for glucose determination using CuO/graphene-modified GCE [24]. Because of the larger roughness of a screen-printed carbon electrode (SPCE) [25], the SPCE can immobilize and stabilize nanocatalysts. However, there is little information available on the rough SPCE as modifiable base. On the other hand, the flow injection analysis (FIA) technology provides the practical features like the simplicity, low cost and good analytical characteristics [26,27]. Herein, the commercial SPCE incorporated with the FIA system was adopted to achieve the higher detection sensitivity up to 2.4 fold as well as lower detection limit of 34.3 nM compared to our previous work. The electrode composition of CuO/graphene and the SPCE are low-cost, easy to mass produce and simple to fabricate for practical applications. On the other hand, this sensing system is also free from the interference and allows highly sensitive, stable, and feasible continuous glucose monitoring [28,29]. It is believed that the SPCE integrated with FIA can act as a novel platform for the development of next-generation electrochemical glucose sensors.

2. Experimental

2.1. Reagents and electrodes

All reagents were bought from Sigma and used as received. All aqueous solutions were prepared with Millipore de-ionized water (18 MΩ cm^{-1}). Ring-disk screen-printed carbon electrode (RDSPCE) (disk =

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3.14 mm^2 and ring = 7.07 mm^2) was purchased from Zensor R&D (Taichung, Taiwan) [30].

2.2. Preparation of graphene

Graphite powders were used from Alfa (natural, briquetting grade, 10 mesh, 99.9995%) [31]. Graphene oxide powders were prepared following Staudenmaier's method and reduced to graphene powders by annealing at 1050 °C under an argon atmosphere [32,33].

2.3. Preparation of CuO/graphene nanocomposite

Copper nitrate (0.35 g) powders were dissolved in ethylene glycol (50 mL) with the pH value of 12.1. [24] Graphene (0.05 g) powders were added into the reaction solution and then heated to 190 °C for 3 h. The obtained solution was filtered and dried to get the Cu/graphene powders. The resultant Cu/graphene powders were annealed in a tube furnace up to 300 °C to form CuO/graphene powders with the average particle size of around 16 nm. The presence of nanoparticles in the nanocomposite can greatly improve the sensing current due to their catalytic properties [24,31].

2.4. Preparation of modified electrodes

The CuO/graphene powders (6 mg) were mixed with deionized water (3 mL), ethanol (2 mL), and Nafion (60 μL) and then ultrasonically treated to form the inks. [24] Approximately 10 μL of CuO/graphene ink was dropped onto a disk electrode of RDSPCE and dried to form the CuOG-SPCE. For the FIA experiment, approximately 10 μL ink containing Pt nanoparticles was dropped onto ring electrode as the counter electrode.

2.5. Apparatus

Transmission electron microscope (Jeol JEM-1230, 100 kV) and scanning electron microscope (JEOL-7500F) were used to characterize sample morphologies. Electrochemical measurements were performed at a CHI 700D electrochemical workstation (Austin, TX, USA) and portable electrochemical senor interface (Em Stat, Netherlands) with a three-electrode cell assembly. The dynamic amperometric experiments were carried out using portable electrochemical senor interface integrated to an FIA system constructed with a Cole-Parmer microprocessor pump drive (BAS, PM-92E), a Rheodyne model 7125-sample injection valve (20 μL loop) with interconnecting Teflon tube, and a Zensor SF-100 electrochemical cell specifically designed for SPCE.

3. Results and discussion

3.1. Characterization of CuO/graphene and CuOG-SPCE

Fig. 1A displays the typical TEM image of one piece of CuO-decorated graphene (CuO/graphene) sheet. The dark dots are high-density and well-separated CuO nanoparticles. Inset is the corresponding selected area electron diffraction (SAED) pattern of the CuO/graphene. The five major crystalline planes of the ring pattern are (002), $(\bar{1}11)$, (111), (200), and $(\bar{2}02)$ that confirm the existence of CuO phase. A high-

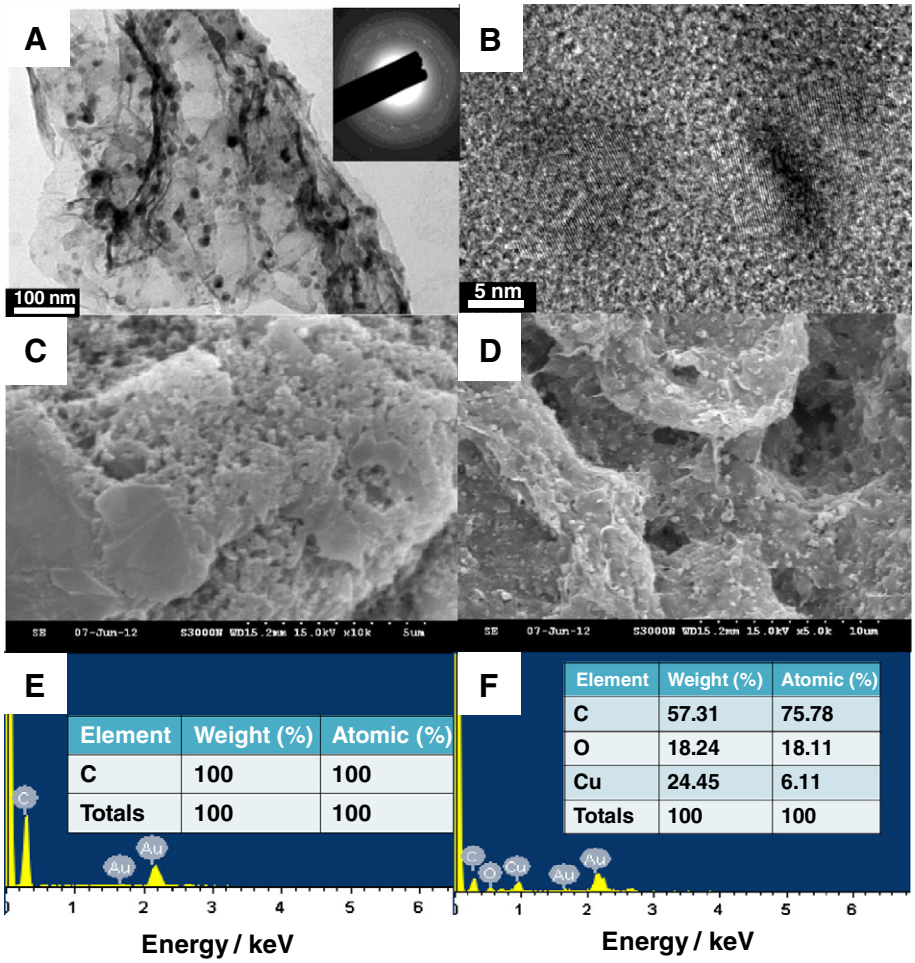

Fig. 1. TEM images of (A) a single sheet of CuO/graphene nanocomposite and (B) CuO nanoparticles. Inset in panel (A) is the corresponding SAED pattern. SEM images of the surfaces of (C) a bare-SPCE and (D) a CuOG-SPCE. Energy dispersive spectroscopy (EDS) spectra of the surfaces of (E) bare SPCE and (F) CuOG-SPCE.