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Electrochemical synthesis of gold nanoparticles decorated flower-like graphene for high sensitivity detection of nitrite

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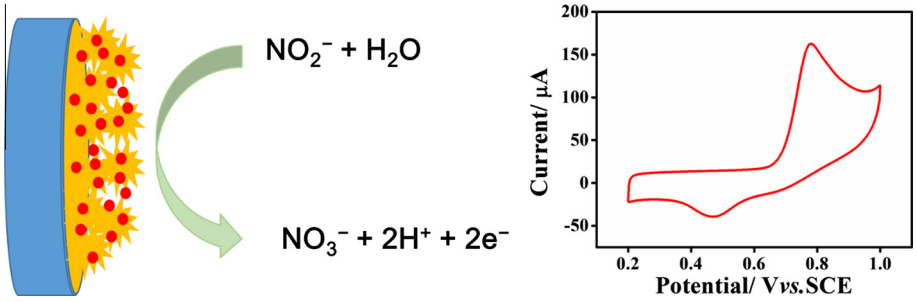
GRAPHICAL ABSTRACT

The spherical Au nanoparticles/3D flower-like graphene was prepared by a facile and low-cost electrochemical method and used for sensitive determination of nitrite.



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ABSTRACT

In this paper, the spherical Au nanoparticles and 3D flower-like structure graphene were successively deposited on glassy carbon electrode (GCE) (Au/f-GE/GCE) via a facile and two-step electrodeposition method for the detection of nitrite ions ($NaNO_2$). The morphology and composition elements were confirmed by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) and X-ray diffraction measurements (XRD). Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were used to evaluate the electrochemical behaviors of $NaNO_2$ on the as-prepared electrode. Compared to f-GE/GCE and Au/GCE, Au/f-GE/GCE showed a sharp and obvious oxidation peak at 0.78 V. The oxidation peak current of $NaNO_2$ was linearly proportional to its concentration in the range from 0.125 to 20375.98 μM, with a detection limit of 0.01 μM (at S/N = 3). Furthermore, the experiment results also showed that the as-prepared electrode exhibited excellent reproducibility and long-term stability, as well as good recovery when applied to the determination of $NaNO_2$ in pickled pork samples.

1. Introduction

Nitrite ion (NO_2^-), an inorganic compound, has been widely exploited in our daily life as an additive in foods and a corrosion inhibitor, and recognized as an alarming pollutant to the environment and human health [1,2]. An excessive level of nitrite

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in the body of human, not only can lead to the irreversible oxidation of hemoglobin to methemoglobin, but also can react with dietary components to form a nitrosamine, resulting in cancer and hypertension [3–5]. The World Health Organization has reported that the fatal dose of nitrite ingestion is between 8.7 μM and 28.3 μM [6,7]. As a consequence, it is necessary to develop reliable methods for the detection and monitoring of nitrite. Up to now, many techniques have been developed to determine NO_2^- levels, such as spectrophotometry [8,9], chemiluminescence [10,11], high-performance liquid chromatography [12] and electrochemical methods [13–16]. Among them, the electrochemical methods are proven to be powerful tools due to its fast procedure, low cost, low detection limit and high accuracy. Unfortunately, the electrochemical oxidation of nitrite at the traditional electrodes suffers large overpotentials and the electrodes tend to be poisoned by the products generated during the electrochemical process.

To resolve these problems, one strategy is to use various noble metal nanostructures in the construction of the working electrode to enhance the sensitivity for the detection of nitrite due to their excellent catalysis, unique dimensions and high effective surface area [17–19]. In particular, Au nanoparticles have been extensively explored for the determination of nitrite because of its excellent conductivity, unique structure, well electrocatalytic ability and biocompatibility. For instance, Jiang et al. used coupled graphene and Au nanoparticles to fabricate the electrochemical biosensor for detecting nitrite [20]. Li and his co-workers prepared the sensor of gold nanoparticles (AuNPs) and sulfonated graphene, which displayed electrocatalytic activity in the detection of nitrite [21]. It is worth noting that the Au based electrodes could be modified with some other supporting materials, such as transition metal oxides, conducting polymer and graphene, to achieve great selectivity and sensitivity for the detection of the nitrite [20–25].

On another front, as a potentially excellent electrode supporting material in electrochemical application such as supercapacitors, electrocatalysis and sensors, graphene (GE) has been attracted particular attentions owing to its peculiar properties including large specific surface area, unique electronic properties, excellent physicochemical properties, high chemical and thermal stability [26–28]. However, such surface expansion is still inherently limited by the two-dimensional (2D) nature of the planar electrodes. Some attempts have been made to construct three-dimensional (3D) electrodes. Dong et al. synthesized 3D graphene/Cobalt oxide electrode for high-performance supercapacitor and non-enzymatic glucose detection by the chemical vapor deposition [29]. Yue et al. have developed a supercapacitor with the 3D flower-like graphene by the electrochemical method [30]. Therefore, fabricating a novel sensor modified with Au nanoparticles (AuNPs) and 3D flower-like graphene for detecting nitrite should be elaborately considered and designed.

Herein, a facile and efficient electrochemical approach was been used to prepare 3D flower-like graphene (f-GE). And then the AuNPs were reduced on the graphene surface to form Au/f-GE by potentiostatic deposition. With large specific surface area, highly conductive pathways, and well-defined flowers structure, this new 3D Au/f-GE electrode architecture holds a great promise for electrochemical sensing nitrite. This work might exploit the opportunities for developing novel 3D electrochemical sensors with excellent sensitivity and reproducibility.

2. Experimental

2.1. Materials and reagents

Graphite powder, disodium hydrogen phosphate (Na_2HPO_4), sodium dihydrogen phosphate (NaH_2PO_4), cupric sulphate anhydrous ($CuSO_4$), chloroauric acid ($HAuCl_4$), glucose, potassium chloride (KCl) and disodium chloride (NaCl) were purchased from Sinopharm Chemicals Reagent Co., Ltd. Ascorbic acid (AA), uric acid (UA) and dopamine (DA) were obtained from Acros Organics. All chemicals were of analytical reagent grade and used as received. 0.1 M phosphate buffer solution (PBS) with pH 7.0 prepared from NaH_2PO_4 and Na_2HPO_4 was chosen for the electrolyte solution in the present experiments. Double distilled water was used throughout the experimental process.

2.2. Apparatus

Scanning electron microscopy (SEM) (S-4700, Hitachi High Technologies Corporation, Japan) was used to characterize the morphologies and the energy-dispersive X-ray analyzer (EDX) of the obtained materials. X-ray diffraction (XRD) measurements were carried out to analyze the sample structure using an X'Pert PRO multiple crystals (powder) X-ray diffractometer (PANalytical Company, Holland). All the electrochemical experiments were performed in a conventional three-electrode system at room temperature using a CHI 760E potentiostat/galvanostat (CH Instrumental Co. Ltd, China). The glassy carbon electrodes (GCEs, 3 mm diameter) modified by the as-prepared nanocomposites were used as working electrodes, a Pt wire and saturated calomel electrode (SCE) as the counter electrode and reference electrode, respectively. All of the measurements were carried out at room temperature.

2.3. Preparation of 3D Au/f-GE/GCE

Prior to use, the bare GCEs were firstly polished with alumina powder (0.3 and 0.05 μm) to obtain mirror-like surfaces, and then sonicated with absolute ethanol and double water for about 5 min, respectively. Subsequently, the GCEs were rinsed thoroughly with double water and dried for the following experiment use.

Graphene oxide (GO) solution was prepared by the modified Hummers' method [31]. The fabrication of f-GE/GCE was as follows: Firstly, 10 μL GO ink (0.5 mg mL^{-1}) was sprayed onto the GCE followed by electrochemical reduction to reduced graphene oxide (GE) in a Na-PBS (0.1 M, pH = 4.1) solution at a constant potential of −0.9 V. Secondly, copper nanoparticles were deposited thereon in 5.0 mM $CuSO_4$ solution at a constant potential of −0.4 V with a charge of 1.0×10^{-2} C to form the Cu/GE. And then, another 10 μL GO ink was added on the above obtained surface that was the same as the above strategy to fabricate a sandwich construction of GE/Cu/GE. Finally, the Cu particles were electrolyzed at a constant potential of 0.1 V in the Na-PBS (0.1 M, pH = 4.1) solution for 1000 s and simultaneously flower-like graphene formed from the surface of the underlying GE layer on the electrode. Here, the Cu nanoparticles were used as the template, when a potential higher than the oxidation potential of Cu, an oxidation reaction ($Cu \rightarrow Cu^{2+} + 2e^-$) occurred on the copper particles. As the reaction progressed, the GE sheets which were coated on the copper particles would transform and turned to stand up from the surface of the substrate. The rose GE sheets interconnected with each other, and as a result, the 3D flower-like GE structures were formed. The Au/f-GE/GCE was synthesized by the obtained immersed into a 3.0 mM $HAuCl_4$/0.5 M H_3PO_4 solution at a constant potential of −0.2 V with a charge of 5.0×10^{-3} C. The amount of Au was calculated to be about 3.4 μg according to the integrated charge of Au electro-deposition (assuming a 100% current efficiency). The overall synthetic procedure for f-GE was illustrated in Scheme 1. For comparison, f-GE/GCE and Au/GCE were also fabricated by the similar method.