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Fabrication of gold nanoparticles/L-cysteine functionalized graphene oxide nanocomposites and application for nitrite detection

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ABSTRACT

In this paper, the gold nanoparticles/L-cysteine functionalized graphene oxide (AuNPs/GO-SH) nanocomposites was synthetized with a simple approach for nitrite determination. The prepared nanocomposites were characterized by scanning electron microscopy, transmission electron microscopy, X-ray diffraction and Raman spectroscopy, etc. A pair of well-defined redox peaks was founded for AuNPs/GO-SH hybrids with a formal potential of 0.90 V in 0.1 M phosphate buffered solution by cyclic voltammetry. Under optimal conditions, the sensor could detect nitrite as low as 0.25 μM with a wide linear response range from 5 to 1000 μM, high sensitivity and excellent selectivity. The superior results of nitrite determination in pickled radish showed a promising application for determination of nitrite in food.

1. Introduction

Intensive use of nitrite as fertilizing agent in agriculture and food additive caused a serious nitrite pollution of water and industrial sites [1]. It was found in water due to chloramination which may give rise to the formation of nitrite within the water distribution system, and it has a great effect on people's health [2]. The allowable maximum value of nitrite in water is 2.17 $\mu M\,L^{-1}$ [3]. Because of the potential toxicity to human health, it's important to develop a simple, rapid and accurate method for nitrite determination. At present, there are many methods for determination of nitrite, such as spectrophotometry [4,5], ion chromatography [6], colorimetry [7,8], chemiluminescence [9], capillary electrophoresis [10,11], fluorescence spectroscopy [12] and coincidence [13]. However, they are largely limited by the limitation of expensive or complex operations. In comparison, electrochemical analysis is extensively used for the advantages of simple instrument, low cost, quick analysis and high sensitivity.

Graphene oxide (GO), a two-dimensional nanomaterial, has attracted tremendous attention recently because of its extraordinary properties. The unique nanostructure and properties hold great promise for potential applications in extensive technological territories, such as nanoelectronics [14], supercapacitors [15], batteries [16], and sensors [17,18]. Due to the less stability of GO, the chemical modifying become essential to improve its stability and introduce special functionalities. At present, there are many hybridization materials such as graphene polymer nanocomposites [19,20], graphene metal nanoparticles [21], graphene metal oxide [22,23] have been reported. However, the more attentions were payed to produce a synergistic effect and multiple functions of graphene hybrid materials rather than GO modified in electrochemical system. Generally, GO is used for the application of electrochemical sensors, but GO modified by mercapto (GO-SH) was less used. GO-SH can make nanoparticles loaded better, which enhances the efficiency of electron transfer between materials and electrode.

There are some effective methods to improve the properties of the substrate material, such as chemical, magnetics, electrochemistry. According to reports, chemical doping for carbon nanomaterials is the preferred method. Many nanomaterials were used to fabricate functional GO nanocomposites, such as Au, Pd, Ag, Pt, Fe, Co, SiO_2, TiO_2 and so on [24–32]. Zhang and coworkers constructed a sensor based on reduced graphene oxide hollow microspheres which was encapsulated with gold nanoparticles

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(AuNPs) by spray drying. This prepared sensor, typically operated at a working potential of 0.82 V (vs. SCE), has a linear response nitrate concentration in the range of 5.0 μM to 2.6 mM, and a detection limit as low as 0.5 μM [33]. Li and his team synthesized a functional Ag-Fe_3O_4-GO magnetic nanocomposite and prepared a novel nitrite sensor. The two linear ranges of this sensor were: one from 0.5 to 720 μM with the sensitivity of 1996 μA mM^{-1} cm^{-2}; the other from 0.72 to 8.15 mM with the sensitivity of 426 μA mM^{-1} cm^{-2}. Besides, the sensing system exhibited a detection limit of 0.17 μM [34].

In this work, an AuNPs/GO-SH nanocomposite was prepared to modify the glassy carbon electrode (GCE) for the electrochemical determination of nitrite in high sensitivity and wide concentration range. Furthermore, scanning electron microscopy (SEM) and other methods were used to characterized the structure of the prepared AuNPs/GO-SH, and cyclic voltammetry (CV) was used to evaluate the electrochemical behavior of the modified electrode. The prepared sensor was used for application in determination of nitrite in pickled radish because of outstanding performance with a low detection limit, a wide linear range and high sensitivity.

2. Experimental

2.1. Chemicals and materials

Graphite powder was purchased from Qingdao Chenglong Graphite Technology Company (Qingdao, China). $KMnO_4$, $NaNO_3$, H_2SO_4, 3-ammonia propyl-3-ethoxy silane, L-cysteine, N, N′-dicyclohexylcarbodiimide, $K_3Fe(CN)_6$, $K_4Fe(CN)_6$, KCl, glucose, uric acid (UA), ascorbic acid (AA), dopamine (DA) and $NaNO_2$ were purchased from Sinopharm Chemical Reagent Co, Ltd (Beijing, China). All reagents were analytical grade and used as received. Nanopure deionized and distilled water (18.25 MΩ cm^{-1}) was used in all of the experiments.

2.2. Apparatus

CV and Electrochemical impedance spectroscopy (EIS) were performed on a CHI660C electrochemical system (Chenhua Instruments, Shanghai, China) equipped with a personal computer for data storage and processing. The measuring unit was a conventional three-electrode system, with a GCE as the working electrode (Diameter: 3 mm, Chenhua Instruments, Shanghai, China), an Ag/AgCl/KCl (saturated) electrode as the reference, and a platinum wire as the counter electrode. SEM was performed on an S-4800 electron microscope (Hitachi, Ltd., Japan). SEM (S-4800) and transmission electron microscopy (TEM, JEOL 2010F, 200 kV) were used to study the morphology and microstructure of prepared compound. The UV-visible absorption spectra (UV-Vis) was performed on a Thermo Nano Drop 2000C (Thermo, America) and Raman spectroscopy was performed on a Thermo DXR Microscope (Thermo, America). All of the experiments were conducted at room temperature.

2.3. Preparation of GO

GO was prepared by applying the improved Hummers method [35]. H_2SO_4 (23 mL, 98%) was cooled in ice bath and graphite (0.5 g) with $NaNO_3$ (0.5 g) was added under vigorous stirring. After the graphite was completely dispersed, $KMnO_4$ (3 g) was added gradually under stirring at below 10 °C. Subsequently, the ice bath was removed and stirred for 1 h at 35 °C, and then suffered to ultrasonic for 20 min. Next, double-distilled water (40 mL) was added to the mixture and maintained at 90 °C for 30 min H_2O_2 (100 mL 5%) was added at 60 °C to eliminate the excess MnO_4^-. Finally, the mixture after filtered was washed by 5% HCl for removing metal ions and doubly distilled water for adjusting the pH to 7.0. The final production was obtained after drying at 80 °C.

2.4. Preparation of the GO-SH

The suspension of GO (0.2 g) in anhydrous ethanol (30 mL) was sonicated for 1 h. Then 3-ammonia propyl-3-ethoxy silane (2 mL) was added and refluxed at 70 °C for 8 h. The obtained product was purified by anhydrous ethanol and dried for 10 h. Moreover, the suspension of resulted powder (0.2 g) in N, N-Dimethylformamide (DMF) (50 mL) was sonicated for 15 min and Dicyclohexylcarbodiimide (DCC) (0.1 g) with L-cysteine (0.1 g) was added to the suspension and refluxed at 70 °C for 24 h. The obtained product was purified by anhydrous ethanol and dried for 10 h again.

2.5. Preparation of AuNPs/GO-SH hybrids

AuNPs/GO-SH was synthesized by the reduction of $HAuCl_4$ on the GO-SH surface with ethylene glycol (EG) as the reducing agent. 0.02 g GO-SH was suspended in 21 mL DMF with aiding of ultrasonication for 30 min then, a mixture of EG (40 mL) and $HAuCl_4$ (14 mL, 0.01 M) was added to the suspension with magnetically stirring for 30 min and refluxed at 80 °C for 10 h. The prepared composite was washed using anhydrous ethanol and dried at 70 °C.

2.6. Preparation of AuNPs/GO-SH/GCE

First, the GCE was polished to a mirror-like surface using 0.3 μm and 0.05 μm γ-alumina slurries and washed with water and ethanol in an ultrasonic bath before drying in air for use. The AuNPs/GO-SH (5 μL) solution was dripped onto the clean surface of the GCE to form the AuNPs/GO-SH/GCE which was rinsed with water for the physical removal of the adsorbed species before use. The sensing strategy for nitrite is illustrated in Scheme 1. CV and EIS techniques were employed to characterize the various modified electrodes in 0.1 M acetate buffer solution. In all of the electrochemical experiments, the soaking time before measurement was 2 s.

2.7. Preparation of real sample

The preparation of real sample included three steps. First of all, take a certain amount of pickle, flushed with ultrapure water surface impurities, and then use the juicer fully squeezed into juice, Ultrasonic 30 min, every 5 min shaking, 75 °C water bath for 5 min, then through the 0.45 μm filter membrane filtration, Finally, take a certain amount of filtrate to detection. The pictures of steps were shown in Fig. S6.

3. Results and discussion

3.1. Characterization of AuNPs/GO-SH

The surface morphologies of GO, GO-SH and AuNPs/GO-SH were investigated using SEM and TEM. As Fig. S1a and Fig. S1b showed that GO and GO-SH displayed a typical crumpled and wrinkled structure which provided a large rough surface as frame for further chemical modification. Compared with Fig. S1b, we can observe that the AuNPs presenting on the surface of the GO-SH sheets exhibits a spherical structure (Fig. 1a). Moreover, the TEM image of AuNPs/GO-SH (Fig. 1b) showing a uniform dispersion further proved that AuNPs decorated on the surface of GO-SH.

To further investigate, powder X-ray diffraction (XRD), UV-Vis, Raman spectroscopy, and the Fourier transform infrared spectroscopy (FT-IR) were used to improve the characterizations of GO, GO-