Hydrogen bubble dynamic template fabrication of nanoporous Cu film supported by graphene nanaosheets: A highly sensitive sensor for detection of nitrite

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ABSTRACT

High surface area nanoporous Cu film (NPCF) has been successfully synthesized using a hydrogen bubble dynamic template on the graphene nanosheets (GNs) modified glassy carbon electrode (GCE). The effect of different synthesis conditions such as applied potential and deposition time on the NPCF morphology was investigated. The structure and constituent of the NPCF-GNs/GCE were characterized by scanning electron microscopy (SEM), energy-dispersive x-ray (EDX), X-ray diffraction (XRD), electrochemical impedance spectroscopy (EIS) and electrochemical methods. The study on electrocatalytic performance of the NPCF-GNs/GCE demonstrated that this electrode has excellent catalytic activity toward nitrite oxidation. The quantitative measurement of nitrite by amperometric method showed a wide concentration range (0.1–100 $\mu mol\,L^{-1}$) with a detection limit and a sensitivity of $8.87 \times 10^{-8}\,mol\,L^{-1}$ and $3.1\,AL/mol\,cm^2$, respectively. The excellent electrochemical response and high sensitivity of the proposed electrode were attributed to the 3D structure of NPCF and the synergic effect of NPCF and GNs. Furthermore, this electrode showed some other advantages including good repeatability, high reproducibility, long-term stability and anti-interference performance toward nitrite sensing. The applicability of the proposed electrode was proved by successful determination of nitrite in real samples (tap water, river water and sausage samples).

1. Introduction

Catalyst materials have a main role in industrial processes; catalysis is increase in the rate of a chemical reaction due to the participation of an additional substance which called a catalyst. In most cases, reactions occur faster with a catalyst because they require less activation energy. Since catalysts are not consumed in the catalyzed reactions, they can continue to act repeatedly. Although in most of cases, only tiny amount of catalyst is required.

Electrocatalytic reactions have a main importance in electrochemistry and they play an essential role in appearing various technologies related to environmental pollution and food safety [1–3]. High surface area and size-dependent catalytic properties are key characteristics which act as driving forces in improving catalysts efficiency. Nanostructure materials exhibit improved catalytic performance compared to their conventional counterparts. So, nanostructure materials have attracted a great deal of attention which may be utilized in electrocatalysis [4–6].

Nanoporous materials have been reported as excellent materials for using in electrode modification. Because, they have a three dimensional pore structure, high surface to volume ratio and excellent electrical conductivity that increase the reaction rates. Furthermore, nanoporous materials can be have a significant effect on the kinetics of reactions, which is usually contributed to the high activity of the nanostructures and enormous amount of their active sites [7–9].

Various methods have been used for the synthesis of nanoporous materials. The most common approach is the template-directed synthesis method. Generally, the template-based method is composed several steps including: creation of a porous template, pores filling and template removal. In this method removing the template needs to difficult procedures [10,11]. Recently, a gas bubble dynamic template has been developed as a new green and favorable template. This method is very easy and efficient for preparation of a nanoporous structure with a uniform pore size. This method includes hydrogen bubbles accompanying a metal deposition process. In this process, H^+ ions are reduced to H_2 molecules and then they conglomerated into bubbles. The prepared bubbles act as a dynamic template for direct electrochemical deposition of metals. At the same time, the metal particles deposit between the hydrogen bubbles and form the 3D nanoporous structure on the substrate. This method is preferred to the

other methods; because it is very simple, low cost and removing the unwanted template materials after deposition is not necessary [12–14].

Carbon nanostructures have been extensively utilized in electrochemistry due to the small residual current, wide potential window, excellent chemical stability and easy renewable surface. Graphene nanosheets (a two-dimensional carbon material) were recognized as a promising material for depositing the metal nanostructures due to their unique physical and chemical properties. In recent years, nanometal/graphene composite materials have received increasing attention owing to their improved electrochemical properties [15,16].

Nitrite has been extensively used as food additive, fertilizing agent and corrosion inhibitor. Because of more usage of nitrite in agriculture and industry, wastewaters have high amount of nitrite that is caused increasing contamination of water sources. Nitrite is a carcinogenic agent in the human body since; this ion can bind irreversibly with hemoglobin and produces methemoglobin which reduces oxygen transport capability of blood. Furthermore, nitrite can be easily converted to influential carcinogenic N-nitrosamines in the stomach [17,18]. Therefore, accurate determination of nitrite has a practical importance in public health and environmental safety. Also, the levels of nitrite can be considered as indicators of environmental pollution and food control. Numerous methods have been developed for nitrite monitoring based on spectroscopy, chemiluminescence, ion chromatography and capillary electrophoresis. All the mentioned techniques require complicated and expensive instrumentations. While, the electrochemical techniques are the powerful methods for measurements due to some advantages such as rapid response and simple operation [19,20].

In this paper, we reported the fabrication, characterization and analytical performance of a nitrite sensor based on the nanoporous Cu film supported by graphene nanosheets modified glassy carbon electrode. The nanoporous Cu film was synthesized by a very simple one-step electrochemical approach and used for the sensitive detection of nitrite. The characterization and performance of the newly fabricated nitrite sensor were studied using SEM, EDX, XRD, EIS and cyclic voltammetry (CV) methods, and the results were discussed.

2. Experimental

2.1. Reagents and chemicals

Copper sulfate ($CuSO_4$) and sulfuric acid (H_2SO_4) were purchased from Merck (Germany). Graphene nanosheets (Carbon content 99.5 wt %, diameter 1–20 μm, thickness 5–15 nm) were purchased from Xiamen Knano Graphit Technology Co. (China). All other chemicals were of pure analytical grade and they were used as received. Stock standard solutions were prepared by dissolving reagents in distilled water. All solutions were maintained at 4 °C in the dark. Aliquots from the stock solution were used for preparation of working solutions.

2.2. Instrumentation

Electrochemical measurements were done using potentiostat & galvanostat Autolab PGSTAT30 (Eco Chemie B.V., The Netherlands) with a conventional three electrode cell. A glassy carbon electrode (diameter, 2 mm) was used as the working electrode. A platinum wire and a saturated calomel electrode (SCE) were used as the auxiliary and the reference electrodes, respectively. All electrodes were purchased from Azar electrode Co. (Iran).

The structural morphology and elemental quantitative analysis of electrode surfaces were studied by scanning electron microscope (MIRA3 TESCAN, made in the Czech Republic) equipped with an energy dispersive spectrometer. The XRD patterns of all electrode surfaces were recorded on an X-ray diffractometer (D500S) using Cu Ka (k = 1.54 Å) radiation source (30–40 kV and 40–50 MA) in the range of 2θ = 35–850. All electrochemical experiments were performed

at room temperature.

2.3. Preparation of working electrode

The GCE was polished with alumina/water slurry and sonicated in ethanol and distilled water for 5 min. After that, 3 μL of dimethylformamide (DMF) suspension containing 5 mg/mL GNs was dropped on top of the electrode surface and dried in air to obtain the GNs/GCE.

Fabrication of nanoporous Cu film on the surface of GNs/GCE was carried out by potentiostatic technique. The electrodeposition was performed in $0.5 \, mol \, L^{-1}$ or $0.1 \, mol \, L^{-1}$ H_2SO_4 containing $10 \, mmol \, L^{-1}$ $CuSO_4$ by applying constant potential to working electrode.

2.4. Preparation of real samples

The water samples obtained from a local river and tap water were used without any pretreatment. The sausage samples were purchased from a local market. The extraction of nitrite ions from sausage samples was performed as follows.

Each sausage sample was grinded and a portion of puree (2.0 g) was mixed with borax saturated solution (20.0 mL) and the mixture was boiled for 30 min. In order to protein precipitation, 5.0 mL of $ZnSO_4$ 30% solution was added and heated in water bath at 60 °C for 10 min. After removing the upper oil layer, the remaining liquid was centrifuged and the separated supernatant was diluted to 100 mL. The prepared sample was stored at 4 °C for electrochemical determinations.

Spectrophotometric method was used as a standard method for determination of nitrite in real samples [21]. In this method, nitrite was determined through formation of a reddish purple azo dye produced at pH 2.0–2.5 by coupling diazotized sulfanilamide with N-(1-naphthyl)-ethylenediamine dihydrochloride (NED dihydrochloride). Photometric measurements can be made if a 5-cm light path and a green color filter were used. The color system obeys Beer's law up to 180 μg N/L with a 1-cm light path at 543 nm. Higher NO_2^- concentrations can be determined by diluting a sample.

3. Results and discussion

3.1. Morphological characterization of NPCF-GNs/GCE

SEM is a powerful technique to reveal the morphological characteristics of the synthesized structures. Thus, SEM technique was applied to explore the morphology of the nanostructures on the surface of the modified electrode.

Fig. 1a presents the image of the bare GCE surface after cleaning process. As can be seen, the GCE substrate is completely smooth and featureless. Whereas, the GNs/GCE (Fig. 1b) shows a typical wrinkled sheet structure of graphene; providing a large rough surface as a scaffold for loading metal nanostructures.

Electrodeposition of copper was investigated in H_2SO_4 solution with various concentrations (0.1 and $0.5 \, mol \, L^{-1}$) containing $10 \, mmol \, L^{-1}$ $CuSO_4$. The synthesized copper film in these solutions was different due to the absence or presence of hydrogen bubbles. Hydrogen bubbles can be formed in $0.5 \, mol \, L^{-1}$ H_2SO_4 solution due to high concentration of H^+ ions in this solution; while there is no enough H^+ ions in $0.1 \, mol \, L^{-1}$ H_2SO_4 solution to form hydrogen bubbles.

Fig. 1c shows the image of Cu film fabricated in $0.1 \, mol \, L^{-1}$ H_2SO_4 solution containing $10 \, mmol \, L^{-1}$ $CuSO_4$ and in the absence of hydrogen bubbles. It can be seen, the electrode surface is totally covered by a typical non-porous Cu film. In contrast, the Cu film fabricated in $0.5 \, mol \, L^{-1}$ H_2SO_4 solution containing $10 \, mmol \, L^{-1}$ $CuSO_4$ and in the presence of hydrogen bubbles shows a uniform porous network texture (Fig. 1d).

Scheme 1 illustrates the steps involved in preparation of a porous Cu film and shows that hydrogen bubbles have a sacrificial template