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Sensitive determination of Amaranth in foods using graphene nanomeshes

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ABSTRACT

In this paper, a new electrochemical sensor used for the determination of Amaranth in foods was reported, where a kind of porous graphene material-graphene nanomeshes (GNM) was employed as electrode modifying materials. The introduction of large pore density to the graphene sheets not only can in favor of more Amaranth molecules adsorbed to the surface of the working electrode through the pores, but also may benefit fast electron diffusion in the electrochemical detection process. So the GNM modified electrode enhanced its electrochemical signal obviously in the determination of Amaranth in foods and exhibited a wider linear response ranging from 5.0×10^{-9} to 1.0×10^{-6} M with a low detection limit of 7.0×10^{-10} M at a signal to noise ratio of 3. This work offers a new route in developing new electrochemical sensors for the determination of colorants additives and other hazard components in foods.

1. Introduction

In order to make the foods more attractive, common beverages, chocolate, cakes, jelly and other foods were added a lot of synthetic colorants [1–4]. However, studies have shown that almost all the synthetic colorants can't provide nutrients to the human body, and excessive in taking even may cause decreased fertility and deformity [4,5]. Amaranth, as a common synthetic azo dye, has been added to the food in large quantities [6–8]. However, it has been confirmed to affect children's mental development and also may cause the appearance of childhood hyperactivity disorder, restlessness and other symptoms [8,9]. Therefore, developing rapid and simple detection means for highly sensitive determination of Amaranth in foods is of great significance. Due to its simple operation process, good sensitivity, quick response, cheap prices and excellent selectivity, electrochemical methods have been widely used for the detection of the Amaranth in foods [8–11]. The electrochemical signal was obtained based on the electroactive hydroxyl group in its structure. As we know, the performance of electrochemical sensors depends on the designing of electrode material [12]. And the key of designing electrode material is synthesis of the materials with high electrical conductivity, large specific surface area and fast electron transfer rate.

Owing to its potential low manufacturing cost, high electrical conductivity and large specific surface area [13–15], graphene has become a very active carbon material in the field of electrochemistry [16–18]. However, the irreversible aggregation and restacking of the graphene sheets limits its applications [19,20]. A lot of dispersing agents such as ionic liquids [21,22], polymer [23], graphene oxides [24] or some other aromatic molecules have been introduced to prevent its agglomeration. However, the limitations lie in the intervention of these dispersing agents has caused graphene's decrease in conductivity [23,25,26].

So, rationally designing the structure of graphene sheets with good properties while retain its excellent conductivity is meaningful [27]. Recently, the graphene nanomeshes have attracted tremendous research interest [28,29]. Its large surface area, high conductivity and porous structure make it a better choice applied to the electrode material.

Here, large scales of graphene nanomeshes (GNM) were prepared via a simple metal etching method [29]. Taking advantage of the unique properties of its high conductivity and porous structure, we successfully applied it to the electrochemical detection of Amaranth in foods. The constructed electrochemical sensor exhibited excellent electrocatalytic activity toward Amaranth. Moreover, the determination of Amaranth in the practical food samples using the presented sensor was also explored with satisfactory results.

2. Experimental

2.1. Chemicals and instrumentation

Graphite oxide (GO) was synthesized using a modified Hummers method as reported before [30]. Nickel (II) acetate and Amaranth were purchased from Aladdin (Shanghai, China). 0.1 M phosphate buffer

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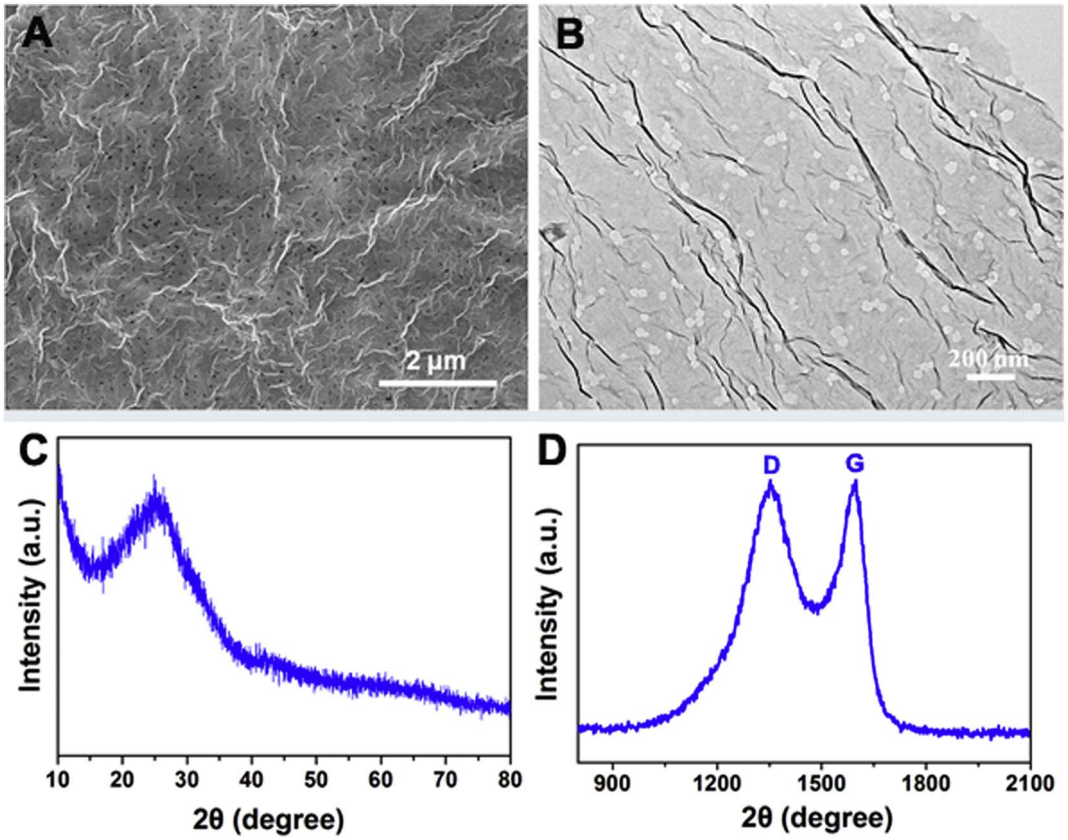

Fig. 1. SEM (A) and TEM (B) images of GNM; XRD patterns (C) and Raman spectra (D) of GNM.

solution (PBS) was prepared using the stock solution of 0.1 M NaH_2PO_4 and 0.1 M Na_2HPO_4, and the pH was adjusted by H_3PO_4 or KOH.

Scanning electron microscopy (SEM) images were obtained on a field emission scanning electron microscopy (S-4800, Hitachi, Japan). Transmission electron microscopy (TEM) measurements were performed on a transmission-electron microscope (Tecnai G2 F20, FEI, USA). Raman spectra analysis was conducted by a reflex Raman spectrometer (inVia, Renishaw, England). Powder X-ray diffraction (XRD) patterns were recorded on an X-ray diffractometer (D8-Advance, Bruker-AXS, Germany). Nitrogen adsorption/desorption measurement were carried out at 77 K in Micromeritics ASAP 2020 M instrument. Electrochemical measurements were carried out on an electrochemical workstation (CHI660D, Shanghai Chenhua Instrument Co., Ltd., China). The working electrode is a bare or a modified glassy carbon electrode (GCE, 3 mm in diameter). A saturated calomel electrode (SCE) and a platinum wire were used as the reference and auxiliary electrode, respectively. Cyclic voltammetry (CV) measurements were performed in 0.5 M KCl solution containing 2.0 mM $[Fe(CN)_6]^{3-}$ and in 0.1 M PBS (pH 7.0) containing 0.2 μM Amaranth at a scan rate of 0.1 V s^{-1}. Square wave voltammetry (SWV) measurements were also performed under the same conditions with potential intervals from 0.4 V to 1.0 V. Chronocoulometry (CC) measurements were also carried out under the same conditions.

2.2. Synthesis of the GNM and RGO

Firstly, an aqueous GO solution (4 mg/mL^{-1}) was prepared by adding 80 mg GO powder into 20 mL deionized water and sonicating for 1 h. Then 30 mL nickel (II) acetate was added into the above GO solution under severe stirring and sonicated for another 20 min. Pay attention to control GO and Ni mass ratio of 10:1. After the precursor solution was freeze-dried by liquid nitrogen for 2 days, the dried powder was then placed in a tube furnace and allowed to proceed for 1 h with the temperature ramped from 20 °C min^{-1} up to 800 °C under a flowing Ar gas. After the furnace was cooled to room temperature under Ar protection, the final product of Ni-Graphene with a blackish color was collected. In order to obtain the GNM, the above Ni-Graphene powder was sequentially treated by diluted hydrochloric acid and washed by water. At last, the resulting powder was dried at 70 °C overnight.

The RGO was prepared as follows: 300 μL of ammonia solution and 20 μL of hydrazine solution were firstly added to 20 mL homogeneous GO dispersion (0.5 mg/mL) in a round bottom flask. After being stirred for a few minutes, the round bottom flask was put in a water bath (60 °C) and lasted for 210 min. The stable black dispersion was obtained and filtered with a nylon membrane (0.22 μm) to obtain the RGO.

2.3. Electrode construction

A proper amount of prepared material was firstly ultrasonically dispersed in distilled water. An optimized volume (10 μL) of the above aqueous dispersion was then drop-cast onto the GCE whose surface has been treated cleanly with a routine process [25].

2.4. Sample preparation

Common fruit drinks and chocolate beans samples were purchased from a local market. The fruit drinks were used directly without treatment. While the sample of chocolate bean was processed by dissolving the outer layer of the lavender chocolate bean into distilled water and then diluted to 50 mL in a volumetric flask. Square wave voltammetry measurements were carried out in PBS (0.1 M, pH 7.0) buffer solutions containing a proper volume of above extract to detect the Amaranth added by the manufacturers in these samples.