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One-step solvent exfoliation of graphite to produce a highly-sensitive electrochemical sensor for tartrazine

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ABSTRACT

Exfoliated graphite was facilely prepared through one-step liquid exfoliation of graphite powder in N-methyl-2-pyrrolidone. The resulting exfoliated graphite was redispersed into N,N-dimethylformamide, and then used to modify the surface of glassy carbon electrode (GCE) *via* solvent evaporation. The electrochemical behaviors of tartrazine were studied, and a sensitive oxidation peak was observed. Interestingly, the oxidation peak current of tartrazine was greatly improved on the surface of exfoliated graphite-modified GCE. The considerable peak current enlargement indicates that the exfoliated graphite exhibits remarkable signal enhancement effects toward tartrazine oxidation. The influences of pH value, amount of exfoliated graphite, accumulation potential and time were examined on the oxidation signal of tartrazine. As a result, a sensitive and rapid electrochemical method was developed for the detection of tartrazine. The linear range was from 5 µg/L to 0.2 mg L^{-1}, and the detection limit was 1.5 µg/L (2.8 nM). This new sensor was used in soft drink samples, and the detected results consisted with the values that obtained by high-performance liquid chromatography.

1. Introduction

Graphene, a novel two-dimensional monolayer of carbon atoms, has obtained increasing attention since its discovery [1,2]. Due to extraordinary chemical and physical properties such as large surface area, high catalytic activity, and strong accumulation ability, graphene has been widely used to modify electrode surface to improving the detection sensitivity. For example, the response signals of dopamine [3], guanine/adenine [4], ractopamine/clenbuterol [5], nitrite [6], hydroquinone/catechol [7], sunset yellow [8,9], and pyrosine [10], were reported to be significantly increased by graphene. Among these studies, graphene was predominantly obtained by chemical oxidation of graphite using strong oxidizing reagents such as concentrated sulfuric acid, KMnO$_4$, P$_2$O$_5$, K$_2$S$_2$O$_8$, *etc.* However, chemical oxidation based strategies have some intrinsic drawbacks, such as consumption of a large amount of strong oxidizing reagents, complicated and rigorous treatments, and potential destruction of intrinsic structure of graphite.

The monitoring of synthetic dyes in foods is quite important because of their potential harmfulness to human beings. Tartrazine is a synthetic azo colorant that commonly used in the food industry. In order to guarantee the food safety, the presence and content of tartrazine must be controlled, and development of rapid, simple and sensitive analytical method for tartrazine is quite important. From the chemical structure that shown in Fig. 1, we clearly found that tartrazine contains azo group, which is electrochemical active and can be reduced on electrode surface, especially on mercury electrode surface. Thus, adsorptive stripping voltammetry using hanging mercury drop electrode was developed for the detection of tartrazine [11]. However, the used mercury electrode is toxic, leading to environmental pollution and adverse health effects. In addition, tartrazine is also electrochemically detected based on the direct oxidation of phenolic hydroxyl group, and it is proven that the oxidation of phenolic hydroxyl group transfers one electron and one proton [12]. Thus, various non-mercury electrodes were also developed for the electrochemical detection of tartrazine

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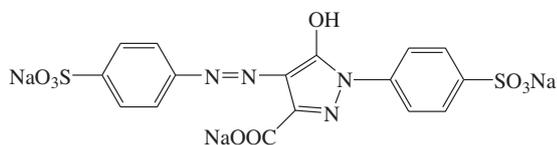E-mail address: kbwu@hust.edu.cn (K. Wu).

Fig. 1. Chemical structure of tartrazine ($M = 534.35\,\mathrm{g\,mol^{-1}}$).

utilizing the oxidation signals. For example, graphene composite film-modified electrodes [12,13], carbon nanotube-modified electrodes [14–16], gold nanoparticles-modified electrodes [17,18], and an acetylene black nanoparticle-modified electrode [19], have been reported.

Solvent exfoliation was proven to be a effective, mild and convenient approach to prepare graphene [20,21]. N-methyl-2-pyrrolidone (NMP) is an inexpensive organic solvent with low toxicity, and has been successfully used to exfoliate graphite to yield graphene nanosheets [22]. Herein, exfoliated graphite was easily obtained through one-step ultrasonic exfoliation of graphite powder in NMP. After that, the exfoliated graphite samples were dispersed into N,N-dimethylformamide (DMF), forming a stable suspension. By solvent evaporation, an exfoliated graphite film-modified glassy carbon electrode (GCE) was achieved. Compared with the unmodified GCE, the exfoliated graphite-modified GCE greatly enhanced the oxidation signals of tartrazine, exhibiting remarkable surface enhancement effects. Apparently, the prepared exfoliated graphite is more active for the oxidation of tartrazine, and significantly increases the detection sensitivity of tartrazine.

2. Experimental

2.1. Reagents

All chemicals were of analytical grade and used directly. Tartrazine (Sigma) was dissolved into ultrapure water to prepare standard solutions, and stored at 4 °C. Graphite powder (spectral pure), NMP and DMF were purchased from Sinopharm Chemical Reagent Company (Shanghai, China). Ultrapure water (18.2 MΩ) was obtained from a Milli-Q water purification system and used throughout.

2.2. Instruments

Electrochemical measurements were performed on a CHI 830D electrochemical workstation (Chenhua Instrument, Shanghai, China) with a conventional three-electrode system. The working electrode was an exfoliated graphite-modified GCE, the reference electrode was a saturated calomel reference electrode (SCE), and the auxiliary electrode was a platinum wire. Scanning electron microscopy (SEM) was performed with a Nova NanoSEM450 microscope (FEI Company, Netherlands).

2.3. Preparation of exfoliated graphite-modified GCE

Firstly, exfoliated graphite was obtained *via* ultrasonic exfoliation of graphite powder in NMP solvent. In a typical preparation, 5.0 g graphite powder was added into 500.0 mL NMP, and then sonicated in a KQ-100B ultrasonicator (frequency: 40 kHz, powder: 100 W; Kunshan Ultrasonic Instrument Co., Ltd, China) for 48 h. After that, the resulting suspension was centrifuged, washed with ultrapure water and ethanol several times, and finally dried in vacuum at 60 °C for 5 h.

Secondly, 10.0 mg of exfoliated graphite was exactly weighed, and then added into 10.0 mL of DMF. After 30-min ultrasonic
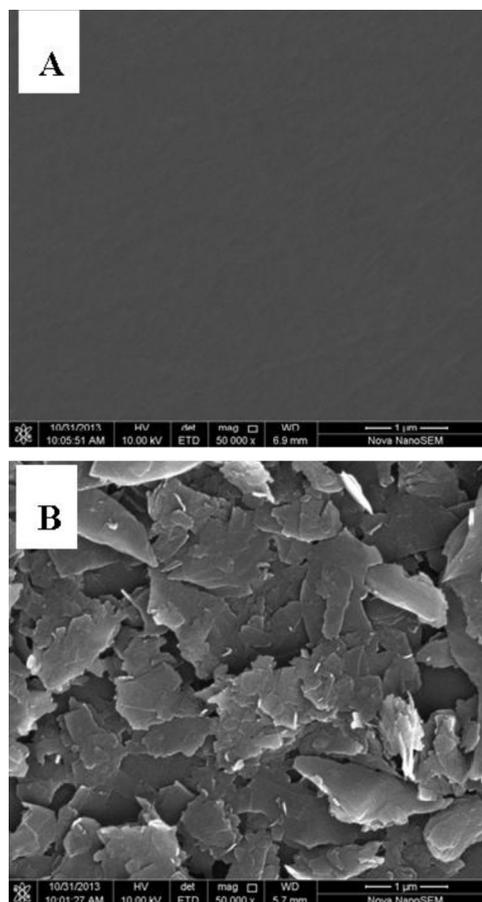

Fig. 2. SEM images of GCE (A) and exfoliated graphite-modified GCE (B).

treatment, a stable and brown suspension with concentration of 1 mg mL^{-1} was achieved.

Finally, GCE with diameter of 3 mm was polished with 0.05 μm alumina slurry, and sonicated in ultrapure water to give a clean surface. After being dried, 5.0 μL of exfoliated graphite suspension was coated on GCE surface, and then dried under an infrared lamp in air.

2.4. Analytical procedure

Unless otherwise stated, 0.1 M acetate buffer with pH of 4.6 was used as supporting electrolyte for tartrazine detection. After 3-min accumulation at 0.6 V, the differential pulse voltammograms were recorded from 0.6 to 1.2 V, and the oxidation peak current at 0.97 V was measured for tartrazine. The pulse amplitude was 50 mV, the pulse width was 40 ms and the scan rate was 40 mV s^{-1}.

3. Results and discussion

3.1. Morphology characterization

The surface morphologies of GCE and exfoliated graphite-modified GCE were characterized using SEM. As seen in Fig. 2A, the surface of unmodified GCE was very smooth and featureless. After modification with exfoliated graphite, it was found that the GCE surface was coated by tabular nanosheets (Fig. 2B). From the comparison, it was apparent that the surface roughness of exfoliated graphite-modified GCE increased obviously, and three-dimensional structure was more abundant.