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Electrochemical detection of pyridoxal using a sonoelectrochemical prepared highly-oxidized carbon nanosheets modified electrode

Su Yao[a], Gongke Li[b], Yanqing Liu[a,*], Shoulian Wei[a], Hongwu Wang[a,*], Xiqing Huang[a], Zetao Luo[a]

[a] School of Food & Pharmaceutical Engineering, Zhaoqing University, Zhaoqing, 526061, China
[b] School of Chemistry, Sun Yat-sen University, Guangzhou, 510275, China

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ABSTRACT

In this paper, highly-oxidized carbon nanosheets (hCNSs) was prepared with a very simple and low cost sonoelectrochemical method. Compared with the electrochemical method without ultrasonic irradiation, the hCNSs which obtained with ultrasonic irradiation exhibited different ratio of oxygen-containing groups and better electrocatalytic property. The electrochemical behaviour and the electrooxidation mechanism of pyridoxal on the hCNSs modified electrode were investigated in detail. Compare to it on the glassy carbon electrode, the peak current of pyridoxal on the hCNSs modified electrode showed 64-folds enhancement. So a sensitive differential pulse voltammetry method based on the hCNSs modified electrode was proposed for the determination of pyridoxal. Its linear range was 2×10^{-8}–1×10^{-6} mol L^{-1} and the detection limit was 5.4×10^{-9} mol L^{-1}. The method has been applied to the analysis of pyridoxal in the urine and plasma sample.

1. Introduction

Due to its large surface area, high conductivity, excellent stability, and low cost, carbon nanosheets (CNSs) has been used in various fields including lithium-ion battery [1,2], sodium-ion battery [3], supercapacitor [4], electrocatalysis [5], water treatment [6], surface-enhanced Raman scattering [7] and electrochemical sensor [8,9]. Therefore, many routes have been reported to get CNSs, such as chemical vapor deposition [10], carbonization reaction [11], solvothermal reaction [12], sonochemical synthesis [13], microwave synthesis [14], arc discharge [15] and chemical blowing [16].

Graphite was also used to prepare CNSs as a carbon source with chemical oxidation or electrochemical oxidation process [17,18]. The weak van der Waals bond between the graphite layers was further weakened in the oxidation process. On the other hand, the oxygen-containing groups such as hydroxyl, carboxyl, epoxy group and ketonic group on the graphite surface increased the hydrophily of the graphite. Therefore, the oxidized graphite layers such as graphene oxide and CNSs could be easily exfoliated from the graphite surface. The exfoliation process could be enhanced with some efficient methods such as ultrasonic treatment and ionic liquid intercalation. For example, in the traditional chemical oxidation preparation method of graphene oxide, the graphene oxide was exfoliated from the graphite oxide by ultrasonic treatment [19]. In the electrochemical oxidation, the oxidation degree of graphite anode was always deeper than it in the chemical oxidation. Therefore, the oxidized graphite layers could spontaneously exfoliate from the graphite surface. While ionic liquid intercalation [20] was added in the electrochemical oxidation process, the spontaneous exfoliation of the graphite layers should be further enhanced, then the morphology and properties of the electrolytic product should be observably promoted.

In our previous work, a flowing electrolytic method had been used to get carbon nanoparticles and CNSs [21]. But an expensive plunger pump and a specialized electrolytic cell were necessary in this preparation method. In this paper, a more convenient and low-cost ultrasonic electrolytic method was proposed to prepare highly-oxidized CNSs (hCNSs). The ultrasonic power had promoted the electrolytic efficiency and exfoliation efficiency, and high-quality hCNSs were generated in the ultrasonic electrolysis process.

As a kind of vitamin B6, pyridoxal plays an important role in the metabolism [22]. The lack of pyridoxal would lead to various kinds of inflammation [23], neurologic symptoms [24] and anemia [25]. Therefore, it is necessary to build a sensitive and accurate determination method of pyridoxal. High performance liquid chromatography [26], spectrophotometry [27], chemiluminiscence [28] and electrochemical methods [29,30] had been reported for the detection of pyridoxal. The hCNSs modified electrode showed excellent electrocatalytic property for the electrooxidation of pyridoxal, so a sensitive differential

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* Corresponding authors.
E-mail addresses: yqliucn@hotmail.com (Y. Liu), hwwangcn@hotmail.com (H. Wang).

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pulse voltammetry (DPV) method was proposed in this study. The electrochemical behavior and the electrooxidation mechanism of pyridoxal had been investigated in detail. Eventually, the method was successfully applied to the determination of pyridoxal in spiked urine and plasma samples.

2. Materials and methods

2.1. Regents and apparatus

The spectrum pure graphite rods were purchased from Leqing graphite industry, Leqing, China. Pyridoxal hydrochloride and all the other chemicals were of analytical grade and purchased from Aladdin, Shanghai, China. Acetate buffer solution (ABS, 0.2 mol L^{-1}, pH = 5.0) and the phosphate buffer solution (PBS, 0.2 mol L^{-1}, pH = 7.0) were prepared with double-distilled water. The stock solution of 5×10^{-3} mol L^{-1} pyridoxal was prepared by directly dissolving pyridoxal hydrochloride in double-distilled water and stored in a refrigerator at 4 °C.

The electrolytic voltage was supplied from a Zhaoxin KXN-645D DC power source. The ultrasonic power was provided from a Kexi KX-1613T ultrasonic cleaner was used to provide the ultrasonic irradiation. A JEM-2010HR transmission electron microscope (TEM) was used to investigate the morphology of the electrolytic product. An Escalab 250 X-ray photoelectron spectrometer were used to investigate the surface groups of the electrolytic products. The X-ray photoelectron spectrometer was equipped with the Mono Al Kα X-ray radiation as the source for excitation at a pressure of less than 2×10^{-9} mbar in the chamber.

The electrochemical experiments were performed with a CHI-1222B Electrochemical Analyzer (Chenhua, Shanghai, China) with a three electrode system which consist of a glassy carbon electrode (GCE, $\varphi = 3$ mm) as the working electrode, a titanium rod as the inert counter electrode and a saturated calomel electrode (SCE) as the reference. The electrolyte solution was 20 mL 0.2 mol L^{-1} ABS (pH = 5.0) unless otherwise noted. The acetic acid and sodium acetate in the ABS were play the role of the supporting electrolyte. The parameters of DPVs were as follows: the increased E and amplitude were 0.01 and 0.05 V; the pulse width, sampling width and pulse period were 0.05, 0.0167 and 0.2 s; the quiet time was 2 s and the sensitivity was 1×10^{-5}A.

2.2. Sonoelectrochemical preparation of hCNSs

The scheme of the ultrasonic electrolytic device was shown in Fig. 1. A 50 mL beaker which contained 40 mL 2×10^{-4} mol L^{-1} PBS was used as the electrolytic cell. Two spectrum pure graphite rods were used as the anode and cathode. The anode and cathode were fixed in the beaker with a simple home-made Teflon holder, and the gap between the anode and cathode was 2 mm. The electrolytic potential was 60 V, the ultrasonic power was 80 W, and the electrolytic time was 3 h. After the electrolysis, the PBS became brown color. The brown PBS which containing the electrolytic product was collected and then subjected to 20 min of centrifugation at 4000 r.p.m. to remove large graphite particles.

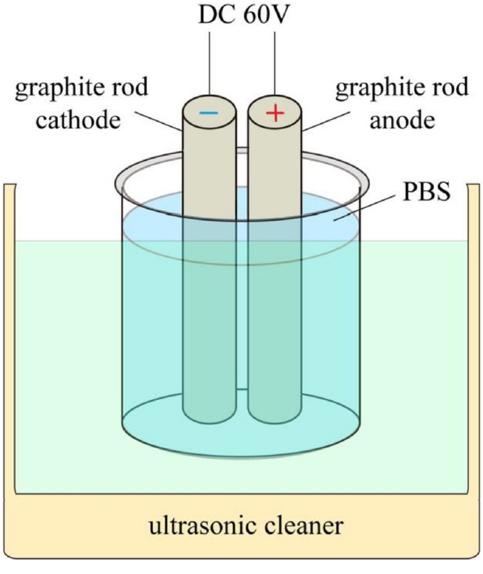

Fig. 1. Scheme of the ultrasonic electrolytic device.

2.3. Preparation of hCNSs modified electrode

The bare GCE was polished with 0.05 μm gamma alumina powder and rinsed ultrasonically with redistilled water. The hCNSs modified electrode was prepared by casting 6 μL hCNSs dispersion on the GCE surface and dried under an infrared lamp. After the modification, the hCNSs modified electrode was scanned with DPV from 0.4 V to 1.0 V for 10 times. This procedure made the modified electrode clean and stable in the DPV measurement.

2.4. Sample preparation

The urine and plasma sample was taken from a healthy female volunteer. An appropriate amount of standard pyridoxal solution was added into the urine and plasma as the spiked samples. The spiked urine and plasma samples were diluted (1:20) with ABS and directly analyzed.

3. Result and discussion

3.1. Characterization of electrolytic product

During the sonoelectrochemical preparation, the anodic graphite rod became thinner while it was oxidized. The oxidized graphite layers as the electrolytic product was exfoliated from the graphite surface. Two kinds of electrolytic products which prepared with and without ultrasonic irradiation were collected and observed with TEM. As shown in Fig. 2A and B, the TEM images exhibited that the morphologies of the two kinds of products were both wrinkled CNSs, whose typical scale was about 1–3 μm.

Even the two kinds of products had similar morphologies, their XPS data showed an obvious difference of their surface groups. As shown in Fig. 2C, the C1 s region of CNSs' XPSs consisted of three peaks located at 284.5, 286.7, and 288.7 eV, corresponding to the C—C, C—O—C and —COOH bond. Comparing to the CNSs which prepared without ultrasonic irradiation, the CNSs which prepared with ultrasonic irradiation showed a lower peak height at 286.7 eV. It meant that the CNSs which prepared with ultrasonic irradiation have fewer epoxy groups. According to the calculation of the peak area, the CNSs which prepared with ultrasonic irradiation have about 18.2% epoxy groups and 10.8% carboxyl, while the CNSs which prepared without ultrasonic irradiation have about 22.0% epoxy groups and 10.5% carboxyl (Atomic %). Therefore, the two kinds of electrolytic product were all highly-oxidized CNSs (hCNSs), which with the different content of their epoxy groups. The ultrasonic irradiation allowed the graphite layers at a lower oxidation degree exfoliated from the graphite surface, so the CNSs which prepared with ultrasonic irradiation have fewer epoxy groups.

3.2. Electrochemical behavior of pyridoxal on hCNSs modified electrode

In order to evaluate the electrocatalytic property of hCNSs, the electrochemical behavior of pyridoxal on hCNSs modified electrode was investigated by CV and DPV. As shown in Fig. 3A, pyridoxal exhibited an irreversible oxidative peak at the potentials of 0.92 V on both GCE and the hCNSs modified electrode. As shown in Fig. 3B, when the concentrations of pyridoxal was 1×10^{-6} mol L^{-1}, the oxidative peak