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Acetylene black paste electrode modified with graphene as the voltammetric sensor for selective determination of tryptophan in the presence of high concentrations of tyrosine

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ABSTRACT

A reliable sensor was fabricated by modifying an acetylene black paste electrode with graphene (denoted as GR/ABPE) for sensitive and selective determination of tryptophan (Trp). Due to the high sorption ability, large surface area and numerous active sites, the GR/ABPE showed a strong enhancement effect on the oxidation of Trp, and greatly increased the peak current. The parameters affecting the Trp determination were investigated. In 1.0 M H_2SO_4 the voltammetric responses of Trp and tyrosine (Tyr) were well separated into two distinct peaks with peak potential difference (ΔE_{pa}) of 115 mV. Under the optimized conditions, in the presence of 0.1 mM Tyr, the oxidation peak current of Trp was proportional to its concentration in the range between 0.1 μM and 0.1 mM, with the limit of detection of 60 nM (S/N = 3). The GR/ABPE was applied to the direct detection of Trp in pharmaceutical and biological samples with satisfactory results. This work provides a simple and easy approach to selective detection of Trp in the presence of Tyr.

1. Introduction

Tryptophan (Trp) is an essential amino acid with diverse physiological roles, functioning both independently or via incorporation into the structure of larger molecules or polymers, such as proteins. It is a precursor for biologically important molecules, such as the neurotransmitter serotonin and the neurohormone melatonin. Besides, it is a vital constituent of proteins and indispensable in human nutrition for establishing and maintaining a positive nitrogen balance [1]. Since the presence of Trp in vegetables is scarce, Trp is sometimes added to dietary and feed products as a food fortifier and to pharmaceutical formulations in order to correct possible dietary deficiencies. Nevertheless, when it is improperly metabolized, it creates a waste product in the brain that is toxic, causing hallucinations and delusions [2]. Therefore, simple, sensitive and low-cost determination of Trp is of great significance to people's health.

At present, many methods have been established to detect Trp, such as high performance liquid chromatography (HPLC) [3,4], spectrophotometric procedures [5–7] and electrochemical methods [8–16]. The chromatographic methods are often tedious and time-consuming, and require a complicated instrument and a skilled operator, which make them less convenient in practice. The spectrophotometric methods involve laborious and slow procedures with the modification of Trp by numerous reagents. In contrast, the electrochemical methods have attracted more attentions with the advantages of low cost, easy to prepare, fast response, high sensitivity, and real-time detection in situ condition. Some chemically modified electrodes have been reported for the determination of Trp [8–15], and comparative analytical figures of merit for different electrodes are summarized in Table 1. Although these sensors can offer high sensitivity and low detection limit, they suffer from a main drawback, which is moderate selectivity. According to these studies, the oxidation peak potential for another electroactive amino acid, tyrosine (Tyr), is very close to that of Trp, and the voltammetric responses of Trp and Tyr exhibit severe overlapping, which makes their practical applications limited. In order to eliminate the interference of Tyr, Ozcan and Sahin adopted a different approach for the determination of Trp based on the electrochemical reduction of oxidation product of Trp formed in situ on graphite electrode [16]. Trp often coexists with tyrosine (Tyr) in food processing, pharmaceutical formulations and biological fluids. Accordingly, to determine Trp in the presence of Tyr selectively based on its electroactivity is of great challenge.

Graphene (GR), a "rising star" nanostructured carbon material, has attracted great attention for both fundamental science and applied research [17]. GR is a two-dimensional sheet of carbon atoms bonded by sp^2 hybrid orbitals. This structural characteristic is the reason for the extraordinary properties of GR, which include a very large surface area, high electrical conductivity, and exceptional thermal and mechanical properties [18]. Because of its novel properties, GR has received considerable interest for potential applications in many fields such as composite materials, supercapacitors and electrochemical sensors [19–21]. On the other hand, acetylene black (AB),

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Table 1
Comparison of the efficiency of some modified electrodes in the electrochemical determination of tryptophan.

Technique	Electrode	Linear range (μM)	Detection limit (μM)	Reference
CV [a]	PGA/CNTPE [c]	0.05–100	0.01	[8]
DPV [b]	BuCh/GCE[d]	2–60	0.6	[9]
DPV	nanoAu-MWCNTs/GCE[e]	5–100	3	[10]
Amperometry	CeHCF/MWNT/GCE[f]	0.2–100	0.02	[11]
Amperometry	CNF/CPE[g]	0.1–119	0.1	[12]
DPV	MWNTs/GCE[h]	0.25–100	0.027	[13]
DPV	β-CD-MNPs/GCE[i]	0.8–300	0.5	[14]
DPV	Au-NPs/GCE[j]	0.09–50	0.08	[15]
DPV	ETPGE[k]	0.5–50	0.05	[16]
Derivative voltammetry	GR/ABPE	0.1–100	0.06	This work

[a] Cyclic voltammetry.
[b] Differential pulse voltammetry.
[c] Poly-glutamic acid modified carbon nanotube-doped carbon paste electrode.
[d] Butyrylcholine modified glassy carbon electrode.
[e] Gold nanoparticles decorated multiwalled carbon nanotube modified glassy carbon electrode.
[f] Hexacyanoferrate incorporated multi-walled carbon nanotubes modified glassy carbon electrode.
[g] Electrospun carbon nanofibers modified carbon paste electrode.
[h] Multi-walled carbon nanotube modified glassy carbon electrode.
[i] β-Cyclodextrin/Fe_3O_4 hybrid magnetic nano-composite modified glassy carbon electrode.
[j] Gold nanoparticles modified glassy carbon electrode.
[k] Electrochemically treated pencil graphite electrode.

a special kind of carbon black, another carbon nanomaterial, is made by the controlled combustion of acetylene in air under pressure. On account of its porous structure and many fascinating properties such as excellent electric conductivity, large specific surface area and strong adsorptive ability, AB has attracted more and more attention of scientists and has been widely used in electrochemistry and electroanalysis [22–24]. However, the fabrication of electrochemical sensors by combining the advantages of GR and AB for analytical application has not been reported in any literatures.

In the present work, we describe the preparation of an acetylene black paste electrode modified with graphene (denoted as GR/ABPE) and investigate its performance for the selective determination of Trp. In general GR can be large-scale synthesized by chemical reduction of graphene oxide (GO) with different kinds of reducing agents such as hydrazine hydrate and sodium borohydride [25,26]. In this laborious procedure, the excessive amounts of reducing agents employed may contaminate the resulting materials [27]. Furthermore, GR is hydrophobic and tends to form irreversible agglomerates due to van der Waals interactions and strong π–π stacking [28], which limit its further application. Recently electrochemical reduction of GO to produce GR has been proposed with different electrochemical techniques such as cyclic voltammetry [29] or controlled potential method [30], which is simple, time-saving, and nontoxic with green nature than the chemical reduction method. In this paper, GR/ABPE was obtained by potentiostatic reduction of exfoliated graphene oxide sheets on the surface of an acetylene black paste electrode. Due to the synergetic effects of conductive GR and AB, the direct electron transfer between Trp and electrode surface can be efficiently achieved. Additionally, the signals for Trp and Tyr at the GR/ABPE are well separated with the peak potential difference (ΔE_{pa}) of 115 mV in 1.0 M H_2SO_4. As far as we know, the contents undertaken here have not been reported so far. Based on this, a sensitive, selective, rapid and convenient analytical method was developed for Trp detection.

2. Experimental

2.1. Chemicals and solutions

L-Tryptophan and L-tyrosine were purchased from Sinopharm Chemical Reagent Co. Ltd., China. Acetylene black (AB, purity > 99.99%) was supplied by STREM Chemicals, USA. All other chemicals were of analytical reagent grade from Shanghai Chemical Reagent Co. Ltd., China and used without further purification. All solutions were prepared with doubly distilled water. All experiments were carried out at room temperature.

2.2. Apparatus

Cyclic voltammetry (CV) was measured on CHI 660D electrochemical workstation (Chenhua Instrument Co. Ltd., Shanghai, China) controlled by a microcomputer with CHI660 software. A model JP-303E polarographic analyzer (Chengdu Instrument Factory, Chengdu, China) was used to give second-order derivative linear sweep voltammograms for quantitative analysis. A conventional three-electrode system was used throughout, where a GR/ABPE (1 mm inner diameter) served as the working electrode, a Pt wire as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. All potentials reported were versus the SCE. A digital pHs-3c Model pH meter (Shanghai Leichi Instrument Factory, Shanghai, China) was used for the preparation for buffer solutions in electrochemical experiments.

2.3. Preparation of GO

Natural graphite powder is oxidized to graphite oxide using a modified Hummers method [31]. To begin, 0.5 g of graphite, 0.5 g of $NaNO_3$, and 23 mL of H_2SO_4 were stirred together in an ice bath. 3 g of $KMnO_4$ was slowly added to the mixture. Next, the mixture was transferred to a 35 °C water bath and stirred for about 2 h, forming a thick paste. 40 mL of water was then slowly added, the reaction solution was stirred for 30 min while the temperature was raised to 95 °C. 100 mL of water was then added, followed by the slow addition of 3 mL of H_2O_2 (30%), which turned the color of the solution from dark brown to yellow. The resulting suspension was filtered, washed with 1 M HCl and twice with deionized water, and vacuum-dried at 50 °C for 24 h to obtain graphite oxide. The graphite oxide was then dispersed in deionized water (0.5 mg mL^{-1}) and exfoliated to GO by ultrasonication for 2 h. It was then centrifuged at 6000 rpm for 30 min to remove the excess, unoxidized graphite and unexfoliated graphite oxide.

2.4. Fabrication of GR/ABPE

Acetylene black paste electrode (ABPE) was fabricated by mixing 3.0 g of acetylene black powder and 0.5 g of solid paraffin thoroughly