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Fabrication and application of a novel plant hormone sensor for the determination of methyl jasmonate based on self-assembling of phosphotungstic acid–graphene oxide nanohybrid on graphite electrode

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ABSTRACT

A novel methyl jasmonate (MeJA) sensor based on phosphotungstic acid/graphene oxide (PTA/GO) nanohybrid was developed by layer-by-layer assembling on a pre-anodized graphite electrode. Owing to the synergistic effect of the good conductivity, high surface area of GO and the solid super-acidity of PTA, the MeJA electrochemical sensor exhibited excellent electrocatalytic activity for the oxidation of alkylene group in MeJA, displaying as a wide linear response from 5.0×10^{-7} to 8.0×10^{-5} M and a low detection limit of 2.0×10^{-7} M in 0.1 M $HClO_4$ solution.

1. Introduction

Graphene, a one-atom-thick planar sheet of sp^2-bonded carbon atoms, has attracted intense interest recently. This material is fascinating in its exceptional electronic, thermal, and mechanical properties with the promise of a range of applications [1]. The oxide of graphene (GO), usually exfoliated from graphite oxide by a mild ultrasonic treatment and bearing lots of electroactive oxygen-containing functional groups and disorder on the basal planes and edges of graphene [2–4], has been proved to possess overwhelming physical/chemical properties applications in a variety of fields, e.g., material sciences [5] and electronic devices [6]. The unique properties of large surface area, excellent conductivity, good chemical stability and easy fabrication, also make GO the star material in the fields of sensors and electrocatalysis [7–9], which often exhibits electroanalytical performance as excellent as or better than carbon nanotubes [10]. Considering the strong tendency of monolayeric graphene sheet to agglomerate into multilayeric graphite [11], a variety of substances like ionic liquid [12], chitosan [13] and alkylamine [14] are intercalated into the interlayers of GO, providing a simple but effective approach to the further functionalization of GO.

The catalytic redox activity of heteropoly acids (HPAs) has attracted much attention, due to their special molecular structures and some very useful properties, including the high stability of most of their redox states and the possibility to tune their redox potentials by changing the heteroions and/or the addenda ions [15]. These properties make HPA attractive as redox catalysts for electrochemical processes of a variety of poor electroactive species, e.g., NADH [16] and alcohols [17].

Methyl jasmonate (MeJA) is a natural plant hormone, which plays an important role in plant growth and development, fruit ripening and responses to environmental stresses [18]. Therefore, the determination of MeJA in plants extracts has attracted increasing interests. Some analytical methods for MeJA, such as gas chromatography with mass spectrometry detector [19–21], reverse-phase capillary liquid chromatography interfaced with an electrospray tandem mass spectrometer [22], and reverse-phase liquid chromatography–gas chromatography with flame ionization detector [23,24] have been established. Although these techniques are either sensitive or selective for the determination of MeJA, they usually suffered from some disadvantages (e.g., complex instrument and being time consuming) and were unsuitable for in situ analysis. Recently, we firstly reported two electrochemical sensors

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for the rapid determination of MeJA with high sensitivity and low cost, but both sensors are constructed from expensive glassy carbon electrodes and operated at relatively large oxidation overpotentials [25,26].

In this work, a novel sensor based on the highly active phosphotungstic acid/graphene oxide (PTA/GO) nanohybrid catalyst for the electrochemical oxidation of MeJA was described. The MeJA sensor, prepared by layer-by-layer assembling of GO and PTA on a pre-anodized low-cost graphite electrode, possessed high electrocatalytic activity for the oxidation of alkylene group in MeJA, with a significantly reduced oxidation overpotential (for about 300 mV) and an apparently improved detection limit compared with our previous works [25,26]. Mechanism for electrocatalytic oxidation of MeJA was researched by cyclic voltammetry, differential pulse voltammetry and chronocoulometry. This work not only developed a novel sensing system for the sensitive determination of MeJA, but also proposed an effective catalyst for the electrochemical detection of alkylene group-based organic substances, which may greatly expand the research area of plant hormone MeJA.

2. Experimental

2.1. Reagents

MeJA, methyl dihydrojasmonate (DH-MeJA), jasmone (JA) and abscisic acid (ABA) were purchased from Sigma–Aldrich. Multi-walled carbon nanotube (MWNT) was bought from Nanotimes Co., Chengdu, China. Graphite (specpure), 1,2-ethylenediamine (1,2-$NH_2(CH_2)_2NH_2$), 1,6-diaminohexane (1,6-$NH_2(CH_2)_6NH_2$), dodecylamine ($CH_3(CH_2)_{11}NH_2$), PTA, phosphomolybdic acid (PMA), silicotungstic acid (STA), chloroauric acid ($AuCl_4{\cdot}4H_2O$), cinnamaldehyde, and other chemicals were purchased from the Sinopharm Group Chemical Reagent Co., Ltd., China with analytical grade purity. The solution of MeJA was prepared with methanol and stored at 4 °C in darkness. The water used was re-distilled.

2.2. Apparatus

Electrochemical measurements were carried out on a CHI 660A electrochemical workstation (Chenhua Instruments, China) in a three electrode system using a MeJA sensor working electrode, a saturated calomel reference electrode (SCE) and a platinum wire counter electrode.

Field emission scanning electron microscopy (FESEM) images were obtained on Sirion 200 field scanning electron microscope (FEI, Holland). Fourier transform infrared spectroscopy (FTIR) spectra were measured with EQUINOX 55 (Bruker, Germany). X-ray diffraction (XRD) data were collected by D8 ADVANCE X-ray powder diffractometer (AXS, Bruker). Elemental analysis (EA) was performed at Vario Micro cube Organic Elemental Analyzer (Elementar, Germany).

High performance liquid chromatographic (HPLC) detection was carried out according to the report [22] with an Agilent 1100, coupled with a mass spectrometry detector. Separation was achieved on a capillary C18 reverse-phase column (4.6 mm i.d. × 50 mm length). The sample injection volume was 10 μL. The gradient mobile phases were aqueous 1% hydrochloric acid/5 mM ammonium acetate (solvent A) and 1% hydrochloric acid/5 mM ammonium acetate in methanol (solvent B). The HPLC was run at a flow rate of 15 μL/min. Elution started at 0% B and increased linearly to 38% B over 20 min. The mass range (m/z) scanned was 45–600 amu.

2.3. Synthesis of GO and alkylamine intercalated GO

GO was synthesized according to a modified Hummer's method [27]. Thereafter, 1,2-$NH_2(CH_2)_2NH_2$, 1,6-$NH_2(CH_2)_6NH_2$ or $CH_3(CH_2)_{11}NH_2$ was intercalated into GO [14] and was denoted as C_2N_2–GO, C_6N_2–GO and C_{12}N–GO, respectively, followed by dispersing in water with ultrasonication.

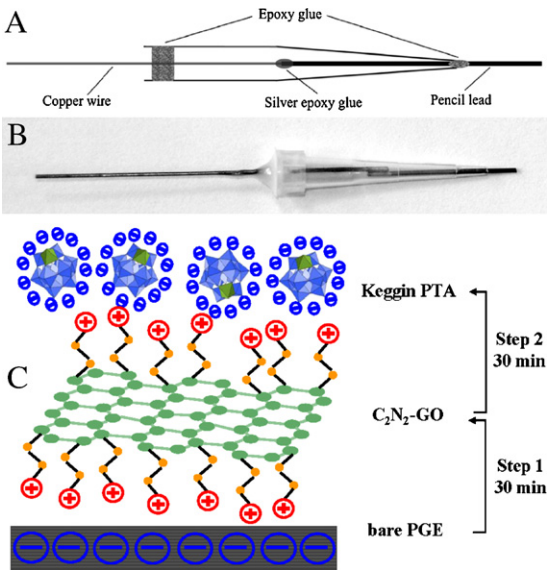

Fig. 1. (A) Structural model of GE. (B) Photo of GE. (C) Schematic representation of the procedure for fabricating PTA/C_2N_2–GO nanohybrid modified AGE. Step 1: assembling of positively charged C_2N_2–GO on negatively charged AGE; step 2: assembling of negatively charged PTA on C_2N_2–GO coated AGE.

2.4. Preparation of the MeJA sensor

Graphite electrode (GE) was home-made from the pencil leads (diameter 0.7 mm, HB, comprising about 81 wt% graphite and 19 wt% clay, which were purchased from a local market) according to our previous work [28]. The structural model and photo of GE were shown in Fig. 1A and B, respectively.

A GE was anodized at +1.8 V for 240 s in 0.1 M $HClO_4$ and then successively scanned between 1.2 and 1.8 V until stable cyclic voltammograms were obtained. The prepared anodized graphite electrode (AGE) was rinsed by water for further use.

The self-assembly process was carried out according to Fig. 1C. Briefly, a negatively charged AGE was immersed into 2 mg mL^{-1} positively charged amine-GO (step 1), and then was dipped in 20 mM PTA aqueous solution with plenty negative charges (step 2), each was for 30 min. After ilka self-assembly treatment, the electrode was thoroughly rinsed with water and dried in air to obtain PTA/GO nanohybrid modified AGE (denoted as PTA/GO/AGE or MeJA sensor).

2.5. Extraction of MeJA from the spikelets of wheat

The wheat spikelets samples were obtained from Jiangxi Agricultural University China. They were frozen in liquid nitrogen from the moment they were picked up and had been lyophilized. A portion of 1.0 g of spikelet samples was then ground to fine powder in mortar using a pestle, collected in a vessel, and mixed with 35 mL of methanol for over night extraction in a refrigerator. The supernatant was collected after centrifugation at 12,000 rpm for 20 min.

2.6. Analytical procedure

5.0 mL of 0.1 M $HClO_4$ solution was added to the cell containing a specific amount of MeJA. Unless stated otherwise, differential pulse voltammetry (DPV) began at 0.9 V with a 240-s accumulation time. All experiments were conducted at room temperature.