



Electrochemical determination of luteolin in peanut hulls using graphene and hydroxyapatite nanocomposite modified electrode



Pengfei Pang, Yanpei Liu, Yanli Zhang*, Yuntao Gao, Qiufen Hu

Key Laboratory of Chemistry in Ethnic Medicinal Resources, State Ethnic Affairs Commission and Ministry of Education, Yunnan University of Nationalities, Kunming 650031, PR China

ARTICLE INFO

Article history:

Received 12 October 2013

Received in revised form

23 December 2013

Accepted 29 December 2013

Available online 5 January 2014

Keywords:

Luteolin

Peanut hulls

Graphene nanosheets

Hydroxyapatite

Glass carbon electrode

ABSTRACT

A simple and sensitive electrochemical method was developed for the determination of luteolin based on the graphene nanosheets (GNs) and hydroxyapatite (HA) nanocomposite modified glassy carbon electrode (GCE). The electrochemical behaviors of luteolin indicate that GNs and HA modified GCE (GNs/HA/GCE) can greatly enhance the electrocatalytic activity in the redox process of luteolin. It leads to a considerable improvement of the redox peak current for luteolin and allows the development of a sensitive voltammetric sensor for the determination of luteolin. A series of experimental parameters including the pH of supporting electrolyte, scanning rates, accumulation amount of GNs and HA were optimized. The results showed that the oxidative peak currents increased linearly with the concentration of luteolin in the range of 2.0×10^{-8} to 1.0×10^{-5} M, with a detection limit of 1.0×10^{-8} M ($S/N=3$). The analytical performance of this sensor has been evaluated for detection of luteolin in peanut hulls as a real sample with satisfactory results.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

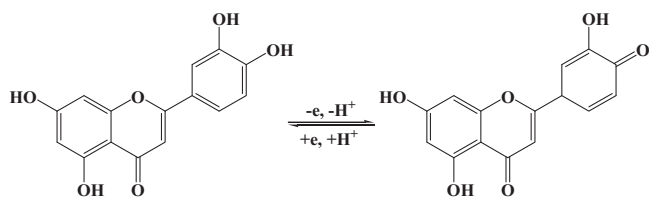
Flavonoids, plant polyphenolic compounds abundant in fruits and vegetables, exhibit a wide variety of biochemical and pharmacological effects, including antioxidant free-radical scavenging, anti-inflammatory, anti-carcinogenic and other beneficial properties [1,2]. The flavonoid luteolin (3',4',5,7-tetrahydroxyflavone, Scheme 1), abundant in celery, green pepper, parsley, perilla leaf and chamomile tea, is of particular interest for biological activity. Recent studies have shown that this compound has several types of biological effects including anti-inflammatory, anti-bacterial and anti-oxidant, as well as displaying anti-proliferative activity against cancer cells [3,4]. Therefore, investigating the redox process and electrocatalytic capability of luteolin is of great importance. Great deal of methods has been reported for the determination of luteolin in flavonoids, including high-performance liquid chromatography (HPLC) [5,6], capillary electrophoresis [7,8], spectrophotometry [9]. Most of these methods have their own shortcomings, such as time-consuming, low sensitivity and complicate experimental process. Luteolin is electroactive compound which has the catechol group on the B ring (3',4'-dihydroxyl), so the development of an electrochemical method for luteolin determination is an attractive alternative due to its sensitivity, rapid response, simplicity of operation and

cost-effectiveness, as well as the minimal sample pretreatment involved.

Graphene, a single layer of carbon atoms bonded together in a hexagonal lattice, has stimulated a vast amount of research in recent years [10–14] due to its unique characteristic such as high surface area, remarkable electrical conductivity, high Young's modulus and thermal conductivity. This two-dimensional material is distinctly different from carbon nanotubes (CNTs) and fullerenes [15,16], and exhibits unique properties which have fascinated the scientific community. The subtle electronic properties of graphene suggest that it has the ability to promote electron transfer when used as the electrode material, which provides a new way of designing novel electrochemical sensors and biosensors [17–19]. It has been reported that graphene nanosheets electrodes were successfully applied to study and determine some biological and organic molecules, including enzyme [20], DNA [21], small biomolecules [22], heavy metal ions [23], gas [24] etc. On the other hand, one possible route to harnessing these properties for application would be to incorporate graphene sheets in a composite material [25,26]. The manufacturing of such composites requires not only that graphene sheets be produced on a sufficient scale but that they also be incorporated, and homogeneously distributed, into various matrices. The scaled-up and reliable production of graphene offers a wide range of possibilities to synthesize graphene-based nanocomposites for various applications such as the Li-ion batteries [27], supercapacitors [28], fuel cells [29,30], photovoltaic devices [31], photocatalysis [32], as well as capacitive deionization [33].

* Corresponding author. Tel.: +86 871 65910017.

E-mail address: yanli.zhang@yahoo.com (Y. Zhang).



Scheme 1. The chemical structure and oxidation mechanism of luteolin.

In recent years, significant research effort has been made in developing non-silica-based inorganic hybrid nanomaterials for their potential applications in biology, electronics and information technology [34,35]. Hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH})$, HA), a bio-ceramic analogous to the mineral component of bone with great biocompatibility and particular multi-adsorbing sites, has attracted a lot of attention because of its extensive applications such as bone cement, tooth paste additive, adsorbents, protein separation and immunosensor [36–41]. Nanostructured HA particles with a higher surface area would be more desirable for their use in many fields. However, the conductivity of HA crystals is too low for the material to be considered a candidate for use in electrochemical devices [42,43]. One approach to improve the conductivity of HA is to dope the crystals with ions or nanoparticles [37,44]. For example, gold–hydroxyapatite nanocomposite has been reported as electrochemical immunosensor for the detection of antigen due to its large surface area [45].

In this work, graphene nanosheets (GNs) and hydroxyapatite (HA) nanocomposite modified glassy carbon electrode (GCE) has been fabricated to study the electrochemical behavior of luteolin in detail. Under the optimum conditions, differential pulse voltammetry (DPV) was developed for the direct determination of luteolin, and a detection limit of 1.0×10^{-8} M was achieved by this method. With such a GNs–HA composite modified electrode, luteolin in water extracts from peanut hulls was successfully detected.

2. Experimental

2.1. Reagents and apparatus

Luteolin was purchased from Shanghai Yuanye biological technological Co., Ltd. and used without further purification. Graphite, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{HPO}_4$ and ammonia were purchased from Sinopharm Chemical Reagent Co., Ltd. All other reagents were of analytical grade and were used as received. The standard stock solution (2×10^{-3} mol L⁻¹) of luteolin was stored at 4 °C darkly before use. Britton–Robinson (B–R) buffer solution with various pH values was used as supporting electrolytes. Double distilled water was used through all experiments.

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements were carried out on a CHI660D electrochemical workstation (CHI Instrument Company, Shanghai). A standard three electrode cell was used for all electrochemical experiments with bare or GNs/HA modified GCE ($d = 3$ mm) as working electrode, a platinum (Pt) wire as an auxiliary electrode and an Ag/AgCl as a reference electrode, respectively. All experiments were performed at room temperature.

Scanning electron microscopy (SEM) was obtained on a NoVa Nano SEM 430 Ultra-high resolution Field Emission Scanning Electron Microscope (FEI Company, Netherlands).

2.2. Synthesis of graphene and hydroxyapatite

Graphene was synthesized from purified natural graphite by the modified Hummers method [46,47,25,48]. In a typical synthesis, 2.5 g graphite was slowly added into a stirred concentrated

H_2SO_4 (60.0 mL) cooling in an ice–water bath. The mixture of 1.25 g KNO_3 and 7.5 g KMnO_4 were added slowly to the suspension more than 30 min under 5 °C and maintained 2 h. Then the ice bath was removed and the suspension was maintained at 35 °C for 1 h until the suspension become pasty and gray in color. After this, 120 mL H_2O were slowly added into the mixture and the temperature increased 95 °C and maintained for 30 min. The suspension was then diluted with 350 mL warm water and treated with 100 mL 6% H_2O_2 to reduce the residual permanganate and manganese dioxide. The suspension was filtered and washed with 1 M HCl to the filter cake without SO_4^{2-} . The filter cake was dried in the vacuum at 50 °C over night.

After these procedures, the prepared graphite oxide (GO) was reduced to graphene according to the reported method [25,48]. The GO (150 mg) was dispersed in 100 mL H_2O at flask for ultrasonication to a homogeneous dispersion. 3 mL hydrazine solution was added in the flask and the solution turn black. The suspension was slowly heated to 95 °C to reflux 24 h and filtered. The filter cake was washed with 5×100 mL deionized water and 5×100 mL methyl alcohol and dried to storage.

The hydroxyapatite was synthesized by wet chemical method. Briefly, 150 mL of 0.5 M $\text{Ca}(\text{NO}_3)_2$ solution was added into 20 mL of 0.5 M $(\text{NH}_4)_2\text{HPO}_4$ solution under stirring at 37 °C until well mixed. After that, the pH values of the mixtures were adjusted to 10 using ammonia water. Then 70 mL of 0.5 M $(\text{NH}_4)_2\text{HPO}_4$ solution was added gradually dropwise into mixed solution under vigorous agitation, during which the pH values were monitored and maintained to be 10 by titration of diluted ammonia water. Afterwards, the mixtures were further stirred for 2 h and aged for 24 h at 37 °C. The resulting liquid crystalline mixture was centrifuged, washed, and finally dried at 90 °C in an oven.

2.3. Electrode preparation

The as-synthesized graphene (10 mg) was dissolved in 100 mL deionized water to ultrasonic agitation until forming a homogeneous black suspension. A glassy carbon electrode (GCE, diameter of 3 mm) was successively polished with 0.3 and 0.05 μm $\alpha\text{-Al}_2\text{O}_3$ slurry on an abrasive cloth and thoroughly cleaned with ethanol and distilled water under ultrasonication. After being dried with high-purity nitrogen gas, 5 μL of 0.1 mg mL⁻¹ graphene solution was first dropped onto the pretreated GCE and dried under an infrared heat lamp to yield the graphene-modified GCE (GNs/GCE). Then, the electrode was rinsed with distilled water. The immobilization of hydroxyapatite was accomplished by dropping 5 μL of 0.1 mg mL⁻¹ hydroxyapatite solution on GNs/GCE. The obtained GNs/HA/GCE was dried at room temperature and used for subsequent electrochemical analysis.

2.4. Sample preparation

Peanuts were purchased from a local market (Kunming, China) and divided into hulls and edible parts. The peanut hulls were dried under room temperature and finely ground using a blender. The milled peanut hulls (50 mg) were extracted with 100 mL of ethanol at room temperature for 2 h. The sample was filtered with sand core funnel (10 μm) and distilled in a rotary evaporation and diluted to 100 mL with ethanol in a calibrated flask.

2.5. Measurements

The standard solution or sample solution of luteolin was added into 0.1 M B–R buffer solution (pH = 5.0). For the accumulation of luteolin on GNs/HA/GCE, the electrode was placed in B–R buffer solution containing luteolin. The CV was recorded from 0 to 0.6 V at a scan rate of 0.1 V s⁻¹. The DPV was performed from 0 to

Download English Version:

<https://daneshyari.com/en/article/742895>

Download Persian Version:

<https://daneshyari.com/article/742895>

[Daneshyari.com](https://daneshyari.com)