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Electrooxidation of morin on glassy carbon electrode modified by carboxylated single-walled carbon nanotubes and surfactants

Guzel Ziyatdinova*, Endzhe Ziganshina, Herman Budnikov

Analytical Chemistry Department, A.M. Butlerov Institute of Chemistry, Kazan Federal University, Kremlyevskaya, 18, Kazan, 420008, Russian Federation

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ABSTRACT

Voltammetric characteristics of morin on glassy carbon electrode (GCE) modified by carboxylated single-walled carbon nanotubes (SWNT-COOH) and surfactants in phosphate buffer have been found. Cationic cetylpyridium bromide (CPB), nonionic Triton X100 and anionic sodium dodecylsulfate surfactants under different concentrations have been tested as modifier of SWNT-COOH/GCE. The form of CVs and oxidation potentials are not changed significantly in the presence of all type surfactants on the electrode surface that confirms negligible influence of surfactant on electron transfer rate. Morin oxidation currents are increased on surfactant-modified electrodes. The best characteristics are observed on CPB (1 μM)/SWNT-COOH/GCE when 1.8-fold increase of oxidation currents has been observed in comparison with SWNT-COOH/GCE. Mechanism of morin oxidation on CPB/SWNT-COOH/GCE is suggested on the basis of relationship between oxidation potential and pH of supporting electrolyte. Electrooxidation is adsorption-controlled irreversible two-step process with participation of one electron and one proton on each step. The linear dynamic ranges of morin determination under conditions of differential pulse voltammetry are 0.1-100 and 100-750 μM with the limits of detection and quantification 28.9 and 96.0 nM of morin, respectively. The developed approach applied for morin quantification in mulberry leaves using preliminary extraction with ethanol.

1. Introduction

Morin (3,2′,4′,5,7-pentahydroxyflavone) is one of the natural flavonoids that is presented in plants, fruits, flowers and plant derived materials [1,2]. It belongs to flavonol subclass and consists of two aromatic rings (A and B in Scheme 1) which are linked by an oxygen-containing heterocycle (ring C).

Morin possesses various biological and biochemical effects including anti-inflammatory, antineoplastic, cardioprotective activities [3–5] and chemopreventive effect against oral carcinogenesis *in vitro* and *in vivo* [6]. Moreover, it shows antioxidant properties that realized via different mechanisms: scavenging of reactive oxygen species, inhibition of the enzymes participating in reactive oxygen species production, chelation of low valent metal ions such as Fe^{2+} or Cu^{2+} and regeneration of membrane bound antioxidants such as α-tocopherol [7–10].

Antioxidant properties of morin are caused by ability to electron transfer that allows to use electrochemical methods for their investigation. Electrochemical measurements leading to the determination of physicochemical parameters for antioxidants (e.g., redox potential, number of electrons transferred, electrode reaction rate constant, etc), are relevant also for understanding the reaction mechanisms. On the other hand, the electroanalytical techniques have advantages over other analytical methods, such as rapid response, higher sensitivity and low detection limits, as well the possibility to improve the selectivity by using suitable electrode conditions.

Therefore, a number of electrochemical methods using bare glassy carbon (GCE) [11,12], platinum [13,14] and hanging mercury dropping [15] electrodes as well as various modified electrodes based on graphene oxide/silver nanoparticles [16], poly(tetrafluroethylene)-deoxyribonucleate acid film-modified GCE [17], polyvinylpyrrolidone-doped carbon paste electrode [18], multi-walled carbon nanotubes-paraffin oil paste electrode [19] and nujol-graphite or diphenylether-graphite paste electrodes [20] have been developed for morin determination. Application of chemically modified electrodes increases the sensitivity and selectivity of quantification. Different types of

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* Corresponding author. Analytical Chemistry Department A.M. Butlerov Institute of Chemistry Kazan Federal University Kremlyevskaya, 18 Kazan Russia 420008 Tel.: +7 843 2337736; fax: +7 843 2387901.

E-mail address: Ziyatdinovag@mail.ru (G. Ziyatdinova).

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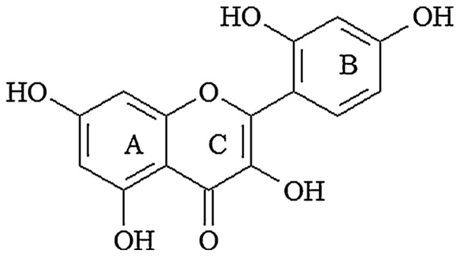

Scheme 1. Structure of morin.

voltammetry have been applied for the evaluation of morin-DNA interactions [17,21] that clarifies the pharmacokinetics of morin.

Surfactants are used in electroanalytical chemistry as substances improving the electrochemical characteristics of biologically active substances [22–25]. Two important properties of surfactants are advantageously used in electroanalysis namely adsorption at the interface and self-aggregation into organized structures [26]. Therefore, surfactants are able to modify and control the properties of electrode surfaces leading to changes in reaction rates and pathways. Combination of surfactants with carbon nanomaterials as electrode surface modifier is another opportunity to affect on electrochemical processes and not investigated enough.

The present work is focused on electrochemical behavior of morin on GCE modified with carboxylated single-walled carbon nanotubes (SWNT-COOH) and surfactants being investigated for the first time and development of differential pulse voltammetric procedure for its quantification.

2. Experimental

2.1. Reagents

Morin hydrate (85% purity) was purchased from Sigma (Germany). Its 0.02 M stock solution was prepared daily dissolving a definite amount of the substance in 5.0 mL of ethanol (rectificate). More dilute solutions (model solutions) were prepared before measurements in 10.0 mL volumetric flasks by dilution of the stock solution with supporting electrolyte (0.1 M phosphate buffer (PB)). The ethanol portion was reduced to 5%.

Carboxylic acid functionalized single-walled carbon nanotubes (SWNT-COOH) with OD 4-5 nm and length 500-1500 nm (90% purity) were obtained from Sigma-Aldrich (Germany).

Surfactants Triton X100 from Sigma (Germany), sodium dodecyl sulfate (SDS) from Panreac (Spain) and cetylpyridinium bromide (CPB) from Aldrich (Germany) were used. Their stock solutions (0.1 M) were prepared by dissolving a definite amount of the appropriate substance in 10.0 mL of water. More dilute solutions were prepared by exact dilution of the stock solution.

All other chemicals were of analytical reagent grade purity and used as received. Double distilled water was used for the measurements. The experiments were carried out at laboratory temperature (25 °C). All solutions were kept in glass vessels at +4 °C.

2.2. Apparatus

Voltammetric measurements were performed on potentiostat/galvanostat μAutolab type III with the software GPES, version 4.9.005 (Eco Chemie B.V., Netherlands). The electrochemical cell consisted of working GCE (SWNT-COOH/GCE or surfactant/SWNT-COOH/GCE) with 3.14 mm^2 geometric surface area, silver-silver chloride saturated KCl reference electrode and counter electrode (platinum wire).

Scanning electron microscopy (SEM) of the electrode surfaces was performed using tabletop scanning electron microscope TM-1000 (Hitachi, Japan).

“Expert-001” pH meter (Econix-Expert Ltd., Russia) equipped with the glass electrode was used for pH measurements.

2.3. Preparation of the modified electrodes

The GCE was carefully polished with alumina (0.05 μm) on polishing cloth. Then, it was rinsed with acetone and double distilled water before use. Homogeneous suspension of SWNT-COOH with final concentration of 0.5 mg mL^{-1} was got by ultrasonic dispersion for 10 min in double distilled water. Electrodes modification was performed by coverage of the GCE with 4 μL SWNT-COOH suspension without any electrochemical precondition of the electrode surface and evaporation to dryness.

Surfactant/SWNT-COOH/GCE was prepared in the same way as SWNT-COOH/GCE with additional drop casting of 2 μL surfactant solution of corresponding concentration in the range of 1-10000 μM.

2.4. Procedures

2.4.1. Scanning electron microscopy (SEM)

SEM images of the electrode surfaces were performed at room temperature in ambient conditions. The 4 μL of SWNT-COOH suspension were dropped on the GCE surface and allowed to evaporate to dryness. Then SEM-image of the surface was scanned at accelerating voltage of 15 kV and emission current 35.7 mA. The same procedure was applied for Surfactant/SWNT-COOH/GCE.

2.4.2. Cyclic voltammetry

10.0 ml of supporting electrolyte containing 5% ethanol or morin model solution were added in electrochemical cell and cyclic voltammograms were recorded at potential range from 0.1 to 1.0 V and scan rate of 100 mV s^{-1}.

2.4.3. Differential pulse voltammetry (DPV)

10.0 ml of supporting electrolyte containing 5% ethanol or morin model solution were added in electrochemical cell and anodic DP voltammograms were registered within the potential range from 0 to 1.0 V using the pulse amplitude of 50 mV, pulse width 50 ms and scan rate 10 mV s^{-1}.

2.4.4. Sample preparation and morin quantification

Raw mulberry leaves (*Morus nigra* L.) were used. Preliminary extraction of morin with ethanol was applied. A representative portion of the milled leaves (0.1 g) was accurately weighted and quantitatively transferred into separating funnel. Then, 2 mL of ethanol were added and shaked for 15 min. The extract was collected and used for further measurements.

The standard addition method was employed for the quantification of the morin. 0.25 mL of the extract was transferred into the cell with 9.75 mL of the supporting electrolyte. The additions of morin stock solution were 2.5-7.5 μM. DP voltammograms in the range of 0-1 V at scan rate 10 mV s^{-1} were recorded. Morin content was recalculated per 1 g of raw leaves.

2.4.5. Statistical analysis

All measurements were performed 5 times. Statistical evaluation was performed at significance level of 5% by SPSS for Windows software (SPSS Inc., USA). All data were expressed as the $X \pm \Delta X$ where X was the average value and ΔX was the confidence interval.

Regression analysis was performed using OriginPro 8.0 (OriginLab, USA) software.