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Electrocatalytic oxidation of morin on electrodeposited Ir-PEDOT nanograins

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ABSTRACT

Nanoclusters of Ir were electrochemically deposited on carbon fiber paper (CFP) substrate modified with poly (3,4-ethylenedioxythiophene) (PEDOT), a conducting polymer between the potential range 0.0 V and 0.6 V at 0.05 V/s scan rate. The electrocatalytic activity of Ir–PEDOT/CFP electrode towards oxidation of morin, a flavonoid was significantly greater than that of PEDOT/CFP and bare CFP electrodes. Factors affecting the anodic peak of morin namely, effect of pH, scan rate and number of cycles were optimized. The electrochemical route involved adsorption controlled and irreversible processes. Under optimal conditions, the linear dynamic range for the determination of morin was found to be 0.12 nM–2.80 nM. The significantly low detection limit (42.18 pM) demonstrates the ultrasensitivity of the proposed method. The reliability of the method was evaluated for the quantification of morin present in mulberry leaves, guava leaves and grape wine.

1. Introduction

Flavonoids are a class of polyphenols, which naturally occur as antioxidants in plants, fruits and flowers. Morin (2-(2,4-dihydroxyphenyl)-3,5,7-trihydroxy-4H-chromen-4-one) is one of the most common flavonols belonging to Moraceae family, present in mulberry leaves, grapes, figs and some of the ayurvedic healing herbs. Morin possesses excellent pharmacological effects such as antioxidant, antimicrobial and anti-inflammatory properties (Middleton, Kandaswami, & Theoharis, 2000; Elangovan, Sekar, & Govindasamy, 1994). Morin has a resorcinol moiety in ring A (the hydroxyl groups at C5 and C7), a catechol moiety in ring C (hydroxyl groups at C2′ and C4′) and a hydroxyl group at C3, a keto group at C4 and a C2═C3 double bond in ring B (Fig. 1). Hydroxyl groups at positions 3 and 4′ present in morin are electrochemically oxidisable and forms corresponding quinones. However, a m-quinone cannot be formed from the 5, 7 dihydroxy groups present in ring A. Another important structural feature of morin is C2═C3 double bond is in conjugation with C═O at position 4 which enhances the electron delocalization from ring B (Jacob, Hagai, & Soliman, 2011).

Several traditional analytical methods have been reported in the literature for determination of flavonols, such as gas chromatography (Kostic, Mitic, & Mitelic, 2004), spectrofluorometry and HPLC (Pavun et al., 2009), UV–vis absorption spectrophotometry (Proestos, Boziaris, Nychas, & Komaitis, 2006) and electrochemical analysis (Wu, Guan, & Ye, 2007; Masek, Zaborski, & Chrzescijansaka, 2011). Among these, the electrochemical analysis has gained considerable importance because of less-expensive, low power consuming and distinct approaches towards the method development, which enhances sensitivity and selectivity towards the analyte.

Literature survey reveals that very few reports exist for the use of modified electrodes in the electrochemical determination of morin (Bagheri, Hajian, Rezaei, & Shirzadmehr, 2016; Ferreira, Greco, Delarmelina, & Weber, 2015; Masek et al., 2011; Temerk, Ibrahim, & Kotb, 2011; Ziyatdinova, Ziganshina, & Budnikov, 2014; Wang, Xu, Zhao, & Hu, 2007). Recently, a novel molecularly imprinted electrochemical sensor based on Pd nanoparticles-porous graphene carbon nanotubes (CNTs)/glassy carbon electrode (GCE) has been reported for an analogue of morin named quercetin (Yang, Xu, Ye, Zhao, & Zeng, 2017). The disadvantage of this method was the tedious electrode preparation process. Sasikumar et al. (2017) used vanadium pentoxide nanoflakes film modified GCE for the detection of morin. This method was found to be less sensitive and selective. Varghese, Chitravathi, and Munichandraiah (2016) have effectively utilized the hydrogen bonding property offered by the polymer host matrix for the determination of morin. But the method could not illustrate electron transfer kinetics due to low conductivity of the polymer.

When metal nanoparticles such as Pt, Pd, Ru, Au, etc. are uniformly

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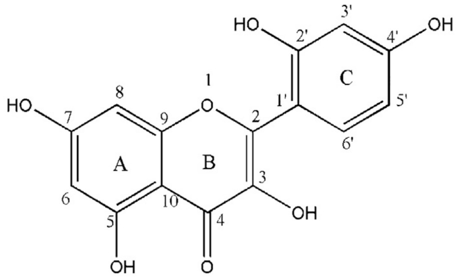

Fig. 1. Structure of morin.

dispersed and immobilized on a supporting host matrix, a thin film of conducting polymer (CP) display stronger adsorbability, greater catalytic activity and roughening of conductive sensing interface (Kishore, Viswanathan, & Varadarajan, 2008; Rahmani, Hajian, Afkhami, & Bagheri, 2018; Bagheri, Afkhami, Khoshsafar, Hajian, & Shahriyari, 2016). CPs such as polyaniline (PANI), polypyrrole (PPy), polythiophene (PTh) and poly(3,4-ethylenedioxythiophene) (PEDOT) are good supporting host materials (Li et al., 2007; Otomo, Nishida, Takahashi, & Nagamoto, 2008; Patra, Barai, & Munichandraiah, 2008). They offer good electronic conductivity, appropriate chemical inertness, significant interaction with metal nanoparticles and excellent adhesion to the electrode (Rahmani, Bagheri, Behbahani, Hajian, & Afkhami, 2018; Molaei, Bagheri, Asgharinezhad, Ebrahimzadeh, & Shamsipur, 2017). Some of the reports available in the literature are dispersion of Pd nanofibers on PANI films (Pandey and Lakshminarayanan, 2009), Pd nanoparticles dispersed on PPy functionalized graphene (Zhao, Zhan, Tian, Nie, & Ning, 2011), dispersion of Pt particles on PANI, PPy and poly-(2-hydroxy-3-aminophenazine) (Joice, Varghese, Sudhakar, Ganesh, & Selvaraj, 2018) for electrocatalytic oxidation of various analytes. Ir was found to be highly stable and exhibits high metallic conductivity when compared to Ru. Ir and IrO_x can be considered as excellent catalysts over other metal nanoparticle based catalysts due to their strong affinity towards OH or O species. Irshad and Munichandraiah, 2015 have already demonstrated the electrocatalytic efficiency of Ir in electrochemical reactions. The high electrocatalytic efficiency of Ir towards oxidation of organic molecules are yet to be explored extensively. In the present investigation, Ir nanograins were dispersed on PEDOT host matrix which is electrochemically deposited on CFP electrode. The presence of PEDOT host matrix facilitates the uniform distribution of Ir nanograins. The developed electrode has been successfully applied for the quantification of morin in mulberry leaves, guava leaves and grape wine.

2. Experimental

2.1. Reagents and materials

Morin, iridium chloride and 3,4-ethylenedioxythiophene (EDOT) were procured from Sigma Aldrich-Merck (> 99%). Potassium ferricyanide, dipotassium hydrogen phosphate, monopotassium phosphate and Sodium dodecylsulphate (SDS) (Analytical grade) were procured from SD Fine-Chem Pvt Ltd., India. Double distilled water was used in preparing the aqueous solutions. A Toray carbon fiber paper (CFP) (0.2 mm) was employed as the substrate in the electrodeposition of PEDOT and Ir. 1 cm^2 (geometrical area) of a portion of CFP having length 2 cm and breadth 0.7 cm was exposed to the electrolyte. The remaining part of CFP was covered with a PTFE tape and a copper wire was connected to this using silver conducting ink to establish electrical contact. 0.01 M EDOT, 0.01 M SDS and 0.1 M H_2SO_4 was used to deposit PEDOT electrochemically (Patra and Munichandraiah, 2009). Ir was dispersed in PEDOT coating on CFP using 0.002 M $IrCl_3$ and 0.1 M H_2SO_4 voltammetrically. Electrochemical impedance spectroscopy (EIS) measurements were performed in 5 mM potassium ferricyanide solution containing 0.1 M KCl. A 50 mL glass cell with ground glass joints was used to place the working electrode (bare CFP electrode or PEDOT modified CFP electrode for the deposition of PEDOT and Ir respectively), counter electrode (Pt foil electrode) and reference electrode (saturated calomel electrode – SCE). The electrochemical measurements were carried out at room temperature in the range 22 ± 1 °C in an air-conditioned room.

2.2. Instrumentation

Potentiostatic deposition of PEDOT and Ir, EIS measurements were performed using Electrochemical analyser, CH 180 (CH Instruments, Inc. USA) and Differential voltammetric technique was performed on CHI609 electrochemical analyser (CH Instruments, Inc. USA). Field emission Scanning electron microscopic images with Energy dispersive X-ray spectroscopy (EDS) were recorded using Zeiss Gemini company Scanning electron microscope (SEM) model Ultra 55. Rigaku SmartLab X-ray diffractometer using Cu Kα radiation ($\lambda = 1.5406$ Å) was used to obtain Powder X-ray diffraction (XRD) patterns. LabRAM HR FT-Raman module was used for FT-Raman analysis. Thermo Nicolet, Avatar 370 was used to record FT-IR spectra.

2.3. Preparation of PEDOT/CFP and Ir-PEDOT/CFP

EDOT monomer was subjected to electrochemical oxidation in an acidic electrolyte to produce PEDOT as a coating on the anode. In the present work, SDS has been used as a surfactant in order to improve the adherence between the substrate and PEDOT. The electrochemical deposition of PEDOT on CFP electrode has been described in detail in ESM SI 1. Ir-PEDOT/CFP electrode was prepared by depositing Ir in 0.002 M $IrCl_3$ + 0.1 M H_2SO_4 voltammetrically in the range 0.0–1.6 V vs SCE at a scan rate of 0.05 V/s (25 cycles). Ir was deposited on PEDOT modified CFP and on bare CFP electrodes for comparative studies. Fig. S1(A) and (B) represents the cyclic voltammograms of CFP in EDOT containing electrolyte and PEDOT/CFP in $IrCl_3$ containing electrolyte respectively.

2.4. General procedure for the determination of morin using Ir-PEDOT/CFP electrode

A glass cell containing 20 mL PBS (pH 7.0) and morin solution (15×10^{-10} M) was used in the electrochemical determination of morin by cyclic voltammetry between the potential 0.0 V and 0.6 V at 0.05 V/s scan rate. The quantitative determination of morin was carried out by DPV technique in the potential range 0.0–0.6 V with 0.05 V (pulse amplitude), pulse width of 0.06 s and pulse period of 0.5 s. The anodic peak currents of the analyte were measured at 1.90 V vs SCE and a calibration graph was constructed for quantitative analysis of morin.

2.5. Preparation of mulberry leaves, guava leaves and grape wine samples

Morus nigra L. (Raw mulberry leaves) and *Psidium guajava* (Raw Guava leaves) were cleaned and dried in a hot air oven for 2 h at 80 °C. About 20 g of the dried and powdered leaves were weighed, treated with aqueous ethanol (1:1, 50 mL) and filtered. The filtrate was rinsed with hexane and the aqueous layer was separated using ethyl acetate. This was dried and the residue was dissolved in ethyl alcohol and made upto the mark in a 20 mL volumetric flask. After suitable dilution, an aliquot of sample solution (20 μL) was used for the analysis of morin using the optimized procedure. Standard addition method was used to establish the reproducibility of the proposed method (Grajek, Wawro, & Kokocha, 2015; Pongsak and Parichat, 2010).

Homemade grape wine (100 mL) was filtered with 0.50 μm filter and centrifuged at 4000 rpm for 5 min. An aliquot of the solution was used for the analysis of morin using the proposed procedure (Yola, Gupta, Eren, Sen, & Atar, 2014).