CrossMark

A novel and sensitive hexadecyltrimethylammoniumbromide functionalized Fe decorated MWCNTs modified carbon paste electrode for the selective determination of Quercetin

Veera Erady [a], Ronald J. Mascarenhas [a,b,*], Ashis K. Satpati [c], Simon Detriche [d], Zineb Mekhalif [d], Joseph Delhalle [d], A Dhason [e]

[a] Research and Development Centre, Bharathiar University, Coimbatore 641 014, Tamilnadu, India
[b] Electrochemistry Research Group, Department of Chemistry, St. Joseph's College, Autonomous, Lalbagh Road, Bangalore 560 027, Karnataka, India
[c] Analytical Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 094, Maharashtra, India
[d] Laboratoire de Chimie et d'Electrochimie des Surface, University of Namur, 61 Rue de Bruxelles, B–5000 Namur, Belgium
[e] Soft Condensed Matter, Raman Research Institute, Sadashivanagar, Bangalore 560 080, Karnataka, India

ARTICLE INFO

ABSTRACT

The fabrication of differential pulse voltametry (DPV) sensor for the effective detection of Quercetin (QR) was achieved by modifying carbon paste electrode (CPE) with Iron decorated multi walled carbon nano tubes (Fe-MWCNTs) followed by drop casting of hexadecyltrimethylammonium bromide onto the surface for optimal results. Cyclic voltammetry and DPV techniques were used for qualitative and quantitative analysis of QR (Quercetin) respectively. The sensor revealed impressive electro-catalytic behavior towards oxidation of QR with almost 6.4 times increase in current compared to bare carbon paste electrode CPE and also decrease in the energetics. Under optimum conditions, a wide linear dynamic range of 0.06 to 3000 μM, with a lower limit of detection, 1.20 nM with S/N = 3 was observed. Absence of peak for the interfering molecules such as Folic acid and Ascorbic acid makes it a unique sensor with significant analytical advantage. The quantification of QR at this sensor was not affected by the presence of 1000 fold Uric Acid implying that the sensor is capable of specifically identifying QR in a mixture of interfering molecules. In this paper, we demonstrate that with minimal use of modifiers and simple procedures of fabrication, the fabricated sensor exhibits excellent stability, reproducibility and swift responses. Application of the developed electrode was demonstrated by detecting QR in wine and coconut water samples with satisfactory recoveries.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Quercetin (QR) is classified as a polyhydroxyphenol. Fruits and vegetables are essentially composed of these nonvolatile polyphenolic compounds and their derivatives [1–4]. QR can prevent hay fever, heart diseases, allergies, cold and coughs. It shows well documented antiviral, anti-inflammatory, and anti cancer activities and is seen as a cure for Alzheimer's [5–10]. Since plants and herbs rich in polyphenols have beneficial properties [11–13], it is important to develop a superior sensor for accurate quantification of QR.

Common methods employed to determine QR are chromatography, chronocoulometry, HPLC, controlled potential coulometry, UV–Vis spectroscopy, emission and absorption spectroscopy, mass spectroscopy and microcalorimetric determination [14–21]. These methods suffer

from specificity and sensitivity. They require sample pretreatment and expertise in handling the equipment and the process is time consuming and expensive. Being electro-active, QR can also be determined electrochemically. Electrochemical determinations have advantages over other techniques such as wide linear dynamic range, low power requirements, efficient and swift responses towards electron transfer. However, determination of QR by this method faces certain issues such as loss of repeatability caused by the accumulation of QR on the surface of the electrode resulting in the need for regeneration of the electrode surface after every experiment [22]. Different types of sensors have been prepared for this purpose using various types of modifications [23–35].

Since the discovery of carbon nanotubes (CNTs) in the year 1991 by Iijima, exhaustive experimental and theoretical research work on these materials have opened up a plethora of tantalizing novel applications in electronics, chemistry as well as material sciences to name a few. There are two main types of carbon nanotubes characterized by their structure. The SWCNTs (singlewalled carbon nanotubes) which are single graphene sheet of a few nanometer in diameter and several microns

in length and MWCNTs (multiwalled carbon nanotubes) are multiple coaxial tubes of graphite sheets ranging from two to fifty in number forming the tubes [36]. The CNTs are suitable for further modifications. This leads to further development of better and more suitable sensors as per the need of the researcher. Apart from these properties, CNTs have many desirable features, such as ability for excellent electron transfer when used as modifiers in electrochemical reactions, high stability and retention of activity for prospective biosensors. Thus, the construction of efficient sensors using nanotubes is very promising in the field of biotechnology, pharmaceutical industry and environmental research. The use of carbon paste electrode (CPE) with innovative modifications has already been reported in literature. Fabrication of MWCNTs sensor and its comparison with CPE based on its selectivity and sensitivity has been reported [37]. A highly effective and selective sensor, ionic-liquid/Schiff base/MWCNTs/nanosilica [38] for nano level detection of lead (II) in hazardous wastes is reported. A facile electrochemical sensor using a high performance magnetite/carbon nanotube paste is used to detect haloperidol in pharmaceutical and biological samples [39]. A carbon paste electrode modified with molecularly imprinted carbon nanotubes [40] is used for the determination of levofloxacin. Many modifications based on CNTs for facile determination of molecules are reported in literature [41–50]. A worthy mention would be the development of poly (Solid Red A) modified carbon nano tube paste electrode and its application for simultaneous determination of epinephrine, uric acid and ascorbic acid [51]. CPE with novel modifications equips us with a wider variety of sensors to detect biologically and environmentally important molecules. Electrochemical sensors are far more superior when compared to its counterparts such as mass, optical and thermal sensors due to its experimental simplicity, sensitivity and cost effectiveness. They have reached the commercial stage where they are used for wide range of important applications in the fields of pharmaceuticals, inorganic and organic pollutants, drugs, food stuffs, enzymes, environmental research and genetic materials to name a few [52–75].

One such modification of the electrochemical sensor has been suggested in our work. Iron nanoparticles decorated MWCNTs, (Fe-MWCNTs) using (hexadecyltrimethylammonium bromide) CTAB as a surfactant have, so far, not been used as a sensor to simultaneously detect QR in the presence of interfering molecules. Our aim was to develop a highly sensitive and selective differential pulse voltammetric (DPV) sensor to determine QR at physiological pH with improved detection limit free from the effect of interfering molecules. Reports suggest the use of difficult procedures at non-physiological pH for the determination of QR. Here, we demonstrate the use of casting CTAB over Fe-MWCNTs using carbon paste as the base material for the sensor. The electro-catalytic behavior was examined by Cyclic Voltammetry (CV) and DPV. The control experiments were done using bare CPE, modified CPE with Fe-MWCNTs, (Fe-MWCNTs/CPE) and modified CPE with CTAB and Fe-MWCNT, (CTAB @Fe-MWCNTs/CPE). The results revealed an impressive electrocatalytic activity towards the oxidation of QR at CTAB @ Fe-MWCNTs/CPE. The modified electrode was then applied for the determination of QR, individually and in the combined presence of Uric acid (UA), Ascorbic acid (AA) and Folic acid (FA). A unique observation was that the sensor, CTAB @Fe-MWCNTs/CPE, did not detect AA and FA at physiological pH but gave a peak for UA and two prominent well resolved peaks for QR. The peak potential for UA appeared at a much higher potential. We have succeeded in developing a modified electrode which exhibits unusual sensitivity and selectivity to detect QR in real samples such as coconut water and wine.

2. Experimental

2.1. Reagents and materials

Quercetin hydrogen chloride (SRL, India), dimethyl sulfoxide (DMSO), KH_2PO_4, NaOH, CTAB, H_3PO_4, KCl (procured from Merck, India) were of analytical grade and used without further purification.
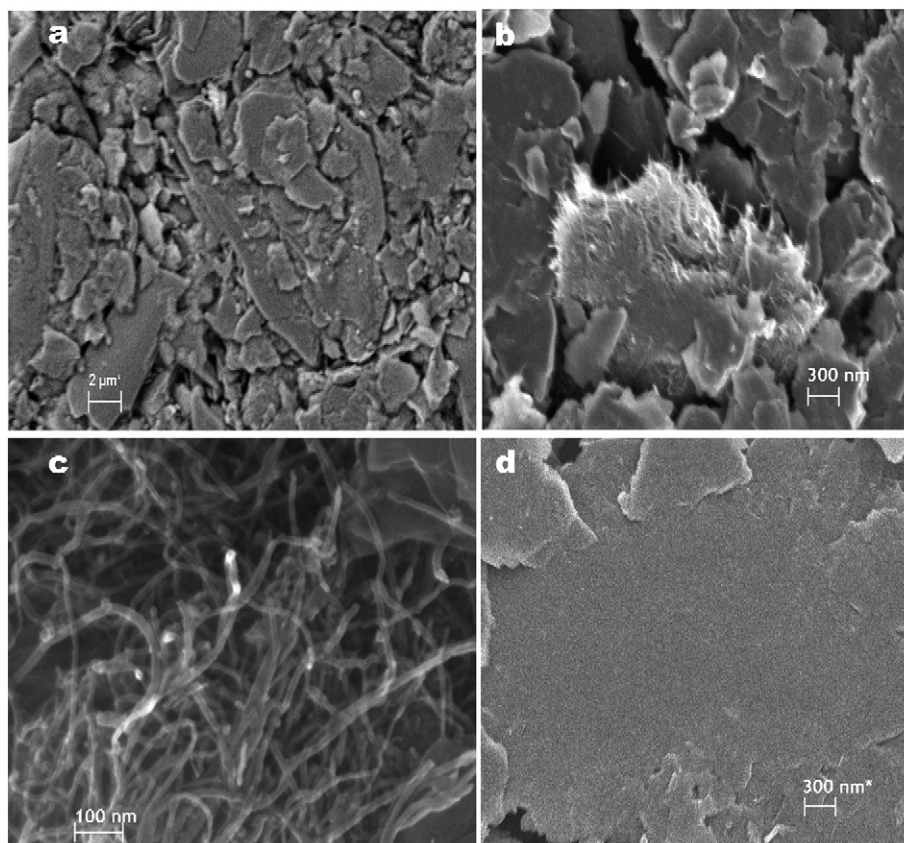

Fig. 1. Fe-SEM images of (a) CPE, (b) Fe-MWCNTs/CPE, (c) CTAB/CPE and (d) CTAB @Fe-MWCNTs/CPE.