



Electropolymerization of curcumin on glassy carbon electrode and its electrocatalytic application for the voltammetric determination of epinephrine and p-acetoaminophenol



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ABSTRACT

Here in, we report the simultaneous voltammetric determination of epinephrine (EP) and p-acetoaminophenol (AP) on a poly curcumin (1,7 Bis ((4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5 dione), poly CM) modified glassy carbon electrode (GCE) for the first time. The CM was polymerized on to the GCE surface by simple electro polymerization process. A low peak to peak (ΔE_p) separation of 60 mV was observed, indicating fast electron transfer between poly CM and the electrode surface. The electrochemical measurements and surface morphology of the as prepared poly CM film modified electrode were studied using cyclic voltammetry (CV), and field emission scanning electron microscopy (SEM), respectively. Moreover, poly CM modified GCE exhibits enhanced electro catalytic activity toward EP and AP in the linear range of 4.97–230.76 μM and 0.99–230.76 μM and with very low detection limit (LOD) of 0.05 μM and 0.1 μM . The sensitivity is 0.621 and 0.303 $\mu\text{A } \mu\text{M}^{-1} \text{cm}^2$ for EP and AP, respectively. The practical feasibility of the proposed poly CM/GCE was evaluated in adrenaline injection (1 mg mL⁻¹) solutions and paracetamol tablets for the simultaneous determination of EP and AP. We found maximum recovery of 99.2% for adrenaline injection and 97.4% for paracetamol tablets. Finally the modified electrode exhibit excellent repeatability, reproducibility and stability for the selective and simultaneous determination of EP and AP.

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1. Introduction

Curcumin is a bioactive polyphenol component present in the rhizomes of *Curcumin longa*, which is also known as diferuloyl-methane (C₂₁H₂₀O₆). Curcumin has become an intense topic of research due to its interesting biological properties and pharmacological applications such as anti-inflammatory, anti-angiogenic, antioxidant, wound healing and anti-cancer effects [1–4]. The powerful curcumin antioxidant activity, working especially when diverse free radical are produced as a result of physiological process is essentially an electrochemical property, so it has to be investigated from an electrochemical viewpoint in order to characterize its redox behavior and its electrocatalytic role. As a result, investigating the redox process and the catalytic activity of curcumin are of biological importance. Hitherto, there were only few reports on curcumin modified electrodes for various types of electrochemical sensors. So far several reports for the metal incorporated curcumin modified electrodes such as, Ni–curcumin modified glassy carbon electrodes for electrocatalytic oxidation on simple alcohols [5,6],

glucose [7] and some amino acids [8], respectively, based on the redox couple Ni (III)/Ni (II) of Ni (II)–curcumin complex as the catalytic center. To the best of our knowledge, there was no report about the direct electrocatalytic activity of curcumin.

Glassy carbon electrode (GCE) has been made by special type of carbon which was fabricated by pyrolysis of polymer resin [9]. Moreover most of the films were fabricated on GCE and it avenues to the field of electrocatalysis and biosensor applications. Surface treatment of a solid electrode has been used extensively to improve the electrochemical performance of the electrode. Especially, electrochemical pretreatment has been used for cleaning and activating the surface of electrode [10–12]. The surface of the metal and carbon electrodes can be oxidized and various kinds of oxygenous groups, such as phenolic, quinoidal, and carboxyl functionalities, added on the surfaces. The existences of these active groups have been proved by such methods as cyclic voltammetry (CV), differential pulse polarography, scanning probe microscope, scanning electron microscope and X-ray photoelectron spectrum [13–15], respectively.

On the other hand, epinephrine (EP) belongs to the family of catecholamine neurotransmitters, which is widely distributed in the mammalian central nervous system for message transfer process [16]. It is as an important chemical mediator for conveying nerve

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impulse in the mammalian central nervous systems. Furthermore, EP can be used to treat cardiac arrest and bronchodilator for asthma patients [17]. The normal EP concentrations for adults are less than 10 ng/l, hence, abnormal concentration of EP in human body causes to symptoms of several diseases [18]. Hence, a quantitative determination of EP concentration is quite helpful for developing research in disease diagnosis, pharmacological research and life science. Electrochemical methods have been developed to determine epinephrine due to its electroactive nature [19]. In addition, acetoaminophenol (AP) or paracetamol has been widely used as an analgesic drug, relief of moderate pain for headache, backache and for reduction of fevers, respectively [20,21]. So far many analytical techniques have been employed for the detection of acetoaminophenol such as spectrophotometric [22,22], HPLC [23], Flow injection analysis [24] and electrophoresis [25], respectively. Relative to the above methods, we need a simple, highly sensitive and low cost instrument for the detection of acetoaminophenol. Electrochemical methods are found to be convenient, reliable, cheapest and important one for the acetoaminophenol detection [26–28]. However, the oxidation peaks of EP and AP are nearly at the same potentials at the bare electrodes. This results to overlap and fouling during the determination of these compounds. Therefore, fabrication of economically viable electrochemical sensor with simultaneous determination of EP and AP with higher selectivity, stability and sensitivity is still one of the challenging tasks for the electrochemists.

In this paper, we report a highly stable poly curcumin film on the activated GCE for the simultaneous determination of EP and AP. To the best of our knowledge this is the first report to use poly curcumin modified electrode as electrochemical sensor for simultaneous determination of EP and AP. The poly curcumin modified film also offers several distinct advantages including extraordinary stability, high electron transfer rate constant and low detection limit for simultaneous and selective detection for EP and AP. Linear pulse voltammetry (LSV) has been used to evaluate the analytical performance of the sensor in quantification of EP in the presence of AP. Finally, to evaluate the utility of the poly curcumin modified electrode for analytical applications, it also used for the simultaneous voltammetric determination of EP and AP in real samples.

2. Experimental

2.1. Materials and methods

Curcumin (CM) from *curcuma longa* (Turmeric) was purchased from Sigma Aldrich and the required concentration was prepared by using pure ethanol (99%). (–)-Epinephrine, and p-acetoaminophenol were obtained from Sigma Aldrich. Sodium bicarbonate (NaHCO_3) was purchased from Wako Chemicals. All electrochemical studies were performed in phosphate buffer (pH 8) using Na_2HPO_4 and NaH_2PO_4 . The pH was adjusted by using NaOH. All the aqueous solutions were prepared using doubly distilled (DD) water. Pre-purified N_2 gas was purged through the experimental solutions for 15 min prior to electrochemical measurements.

All the electrochemical studies were performed in a CHI 1205A work station. A conventional three electrode system was used for electrochemical measurements. Glassy carbon electrode (GCE) with a working area of 0.079 cm^2 , Ag|AgCl in saturated KCl and Pt wire were used as working, reference and counter electrodes, respectively. The surface morphological studies were carried out using Scanning electron microscopy (Hitachi S-3000H, Japan).

2.2. Preparation of poly CM modified GCE

GCE surface was polished with $0.05\ \mu\text{m}$ of alumina slurry using a Buhler polishing kit. The electrode surface was washed several

times in deionized water and then ultrasonicated for 2 min to remove the adsorbed alumina particles. Then the GCE surface was activated by performing 20 consecutive potential scanning cycles in $0.1\ \text{M NaHCO}_3$ solution in the potential range of -1.0 to $0.55\ \text{V}$ at the scan rate of $100\ \text{mV s}^{-1}$. The activated GCE was washed again with deionized water and transferred into an electrochemical cell containing $50\ \mu\text{M}$ CM in fresh PBS (pH 8) solution. Then 16 consecutive cycles were performed for the electropolymerization process in the potential range of 0.15 – $0.55\ \text{V}$ at the scan rate of $100\ \text{mV s}^{-1}$. Finally the poly CM modified GCE was dried in open air and used for further electrocatalytic studies.

3. Result and discussion

3.1. Electropolymerization of CM on activated GCE and its electrochemical behavior

During electro polymerization of curcumin on bare GCE, no significant peaks were observed, because of its smooth surface and due to the absence of active sites (Fig. 1A bare GCE). However, CM can polymerize on electrochemically activated GCE, mainly due to its high surface roughness and increase in the active sites which lead to enhance in the electron transfer process. Fig. 1A shows the electropolymerization of CM on the activated GCE and Bare GCE. In the first cycle of activated GCE, an anodic peak (a) appears at $0.4\ \text{V}$, which indicates the oxidation of CM leading to the formation of an o-quinone derivative. Upon increasing the number of cycles, the anodic current density significantly decreased while the corresponding anodic peak (a) disappears completely by the end of 16 cycles. In the second cycle, an anodic peak (b) and a cathodic peak (c) appears at $0.14\ \text{V}$ and $0.12\ \text{V}$, respectively that are readily assigned to the quinone/hydroquinone redox couple involving a two electron coupled two proton transfer process [29]. The anodic and cathodic current density increases with increases in the number of cycles, revealing the polymerization of CM on the activated GCE surface. The polymerization process occurred through the nucleophilic reaction of 3,5 dione group and o-quinone group with the functional groups on the activated GCE resulting in the bond formation. The two electron two proton process of poly CM cyclization step was favored by increasing pH [30]. Moreover the pH of the electrolyte solution (pH 8) used for electrocatalytic purpose, which is almost same with pH of the NaHCO_3 solution (pH 8.2).

The cyclic voltammogram response of the activated GCE and poly CM modified GCE in PBS (pH 8) solution is showed in Fig. 1B. In Fig. 1B the activated GCE (peak b) does not exhibit any redox peak in PBS (pH 8) when compared to poly CM modified GCE (peak a). Fig. 1C shows the CVs of activated GCE/CM and bare GCE/CM in PBS containing $100\ \mu\text{M}$ of EP and AP. The activated GCE/CM shows well defined obvious electro catalytic peaks for the simultaneous detection of EP and AP. At the same time the bare GCE/CM electrode shows null response. These results reveals that polymerization process occurred on the activated GCE shows well clear redox peaks with peak to peak separation (ΔE_p) of $60\ \text{mV}$ toward detection of EP and AP. The possible mechanism of electro polymerization reaction (Scheme 1) was reported earlier, shown in below scheme [29].

3.2. EIS, surface morphology and scan rate studies

EIS study has been employed to analyze the detailed electrochemical activities of modified electrode with individual or mixed components. Here the complex impedance can be presented as a sum of the real, $Z'(\omega)$, and imaginary $Z''(\omega)$, components that originate mainly from the resistance and capacitance of the cell. From the shape of an impedance spectrum, the electron-transfer

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