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Electrodeposition of poly(3,4-ethylenedioxythiophene)/reduced graphene oxide/manganese dioxide for simultaneous detection of uric acid, dopamine and ascorbic acid

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ABSTRACT

A simple and sensitive sensor of poly(3,4-ethylenedioxythiophene)/reduced graphene oxide/manganese dioxide modified glassy carbon electrode (PrGO/MnO_2) was fabricated via cyclic voltammetry (CV) for simultaneous detection of uric acid (UA), dopamine (DA) and ascorbic acid (AA). The PrGO/MnO_2 composite film possessed excellent electrocatalytic rate and high selectivity towards the oxidation of UA, DA and AA in 0.1 M PBS (pH 6.0). The peak potential separation (ΔE_p) of AA-DA, AA-UA and DA-UA were 166, 312 and 146 mV, respectively. The detection limits of 1.00, 0.02 and 0.05 μM with a linear response of 1–800, 0.03–45 and 0.3–80 μM were obtained for AA, DA and UA, respectively. This sensor also showed an excellent stability (reproducibility and repeatability).

1. Introduction

Uric acid (UA) presents in the human body as a primary final product of purine metabolism and high levels of UA found in urine and human serum will lead to gout, hypertension and kidney injury [1,2]. Dopamine (DA) plays a significant role in the mammalian central nervous system which serves as an important neurotransmitter that helps to maintain hormonal balance as well as emotion control [3]. Low level of DA causes neurological disorders, such as Schizophrenia and Parkinson's disease [4] and high levels of DA will cause to hyperactive and insomnia syndrome [5]. Ascorbic acid (AA) presents naturally as an antioxidant in citrus fruits such as orange, grapes and lemon. An antioxidant is used for the prevention of the risk of having a common cold, infertility and cancers [6]. In addition, it can be used to cure for hepatic and scurvy disease [7]. Detection of UA, AA and DA simultaneously is highly important as these three compounds coexist in human living systems. Their presence in the human body must be controlled in order to keep alarm their abnormal concentration levels which may cause certain diseases. These three compounds have similar electrochemical properties which complicate the identification of their oxidation potential that often overlapped and foul the electrodes [8,9]. Thus, the interest towards the development of electrochemical-based sensors for simultaneous detection of these three compounds has increased significantly.

Electrodes modified with reduced graphene oxide (rGO) film [10], copolymer film [11], nanofibers [12], carbon nanotube [13] and chitosan [14] have been employed for detection of UA, DA and AA simultaneously. The rGO has excellent properties in the application for simultaneous detection of UA, DA and AA because of its excellent conductivity, high carrier mobility, high electron transfer rate and electrocatalytic activity [15,16]. In addition, rGO has been used to stabilize the noble metals such as alloys, Pd, Au, Pt and Ag where it acts as an effective support matrix [17–19]. Furthermore, those composites which combining the rGO and noble metals have been applied for simultaneous detection of UA, DA and AA by electrochemically [19,20]. However, the modification of electrode using composite containing rGO and metal nanomaterials has some limitations such as high-cost low selectivity and sensitivity [19]. To overcome these problems, the rGO-based electrodes could be modified with other materials such as conducting polymer or/and metal oxides in order to fabricate electrochemical sensors with great sensitivity, low-cost and high selectivity for the simultaneous detection of UA, DA and AA. Among the variety of conducting polymers, poly (3,4-ethylenedioxythiophene) (PEDOT) has a low band gap polymer with high electrical stability and good conductivity. EDOT as a monomer of PEDOT has a small steric interaction between the repeating units in its polymer and has strong electron donating ability [21,22]. PEDOT has been widely applied in biomolecules sensors such as PEDOT/S-β-CD [23] and MWCNT/PEDOT [24]

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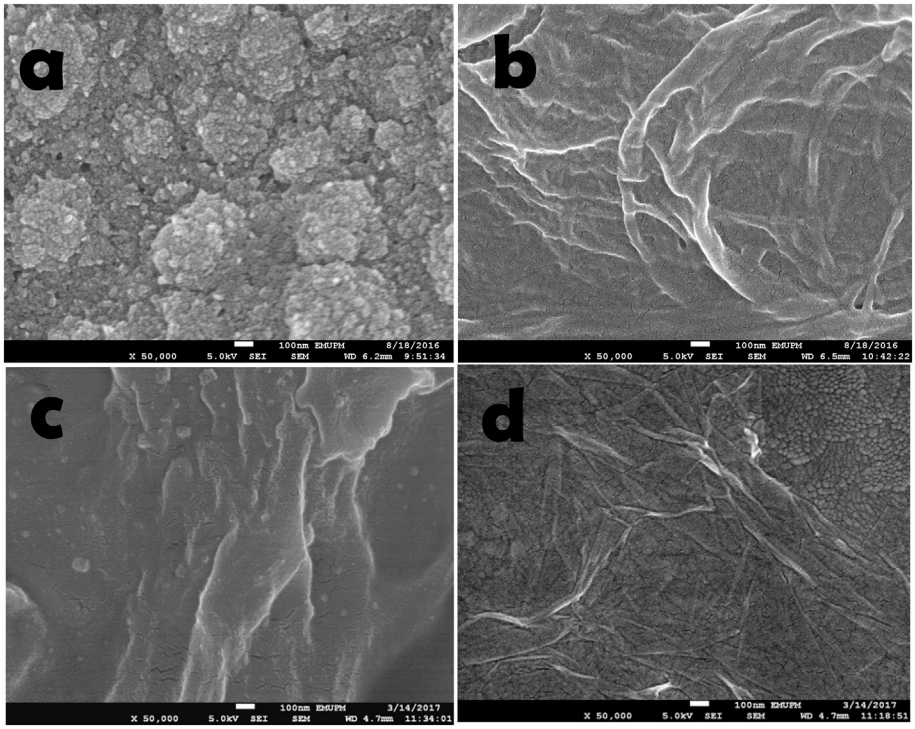

Fig. 1. FESEM images of (a) PEDOT, (b) rGO, (c) PrGO and (d) PrGO/MnO_2 films.

composites for the detection of catecholamine and H_2O_2. While, PEDOT [25], PEDOT/Pd [26] and PEDOT/Au [27] were used for simultaneous detection of UA, DA and AA. Zhang et al. [28] have reported that PEDOT/GO prepared via liquid-liquid interfacial polymerization could detect rutin with good linear dependence.

Metal oxide electrodes have shown some advantages in electrochemical sensor analysis due to exhibit unique performance in electronic, optical, magnetic and catalytic aspects [29]. There have been much research works focused on metal oxide-graphene based composite for the sensor application such as graphene/CuO, graphene/TiO_2, graphene/Fe_3O_4 and graphene/SnO_2 that have high detection in bio and chemical sensors [30]. Bao et al. [31] discovered that manganese dioxide (MnO_2) possesses some advantages such as low-cost, high specific capacitance and non-toxicity compared to nickel, ruthenium, cobalt and vanadium. MnO_2 is also well-known and commonly used for catalysis and electrochemical sensor applications as reported by Rodrigues et al. [32] and Nijjer et al. [33]. Šljukić and Compton [34] have investigated that modified electrodes containing MnO_2 are useful for the detection of nitrite ions, H_2O_2 and ascorbic acid. Therefore, it is crucial to develop alternative modified electrodes containing PEDOT, rGO and MnO_2 in order to obtain an environmental friendly sensor, low-cost, high sensitivity and high-performance for simultaneous detection of UA, DA and AA in practical applications.

In our previous work [35], an electrochemical sensor of PEDOT and rGO modified electrode (PrGO) was fabricated for detection of UA. This fabricated PrGO electrode demonstrated a good detection limit towards UA with a value of 0.19 µM in the range of 1–300 µM of UA. The combination of PEDOT and rGO matrix produced excellent biosensor platform which have large surface area, high electron transfer, high conductivity and good electrochemical activity [36,37] towards detection of UA. However, its electrocatalytic activity towards AA and DA was poor and it was not capable of detecting UA, DA and AA simultaneously.

In this work, PrGO/MnO_2 electrode was fabricated as an electrochemical sensor in which the PEDOT and rGO were deposited electrochemically on the surface of glassy carbon electrode (GCE). MnO_2 was then electrodeposited on top of the PrGO composite. The as-prepared PrGO/MnO_2 electrode was used for simultaneous detection of UA, DA and AA. In comparison to PrGO and bare GCE, PrGO/MnO_2 electrode has shown high electron transfer rate and good peak potential separation in the determination of UA, DA and AA.

2. Experimental

2.1. Reagents

Graphene oxide (GO) and potassium permanganate ($KMnO_4$) were obtained from Graphenea and R&M chemicals, respectively. 3,4–ethylenedioxythiophene (EDOT), UA, DA and AA were purchased from Sigma-Aldrich. Potassium chloride (KCl) and sulfuric acid (H_2SO_4) were purchased from Fisher. Potassium ferricynanide ($K_3Fe(CN)_6$), potassium ferrocyanide ($K_4Fe(CN)_6$), potassium di-hydrogen phosphate (KH_2PO_4) and di-potassium hydrogen phosphate (K_2HPO_4) were purchased from Merck. Phosphate buffer solution (PBS) was prepared by mixing an appropriate quantity of a standard stock solution of 0.1 M KH_2PO_4 and 0.1 M K_2HPO_4. Deionized water from Millipore (Milli-Q, 18.2 MΩ·cm) was used to prepare all aqueous solutions.

2.2. Preparation of PrGO modified electrode

The glassy carbon electrode (GCE) was cleaned with alumina slurry (0.5 µm) and it was sonicated in nitric acid (HNO_3): distilled water (1:1) followed by deionized water for 10 min. The PrGO composite was deposited electrochemically onto the GCE in a solution containing 0.01 mg/ml GO and 0.01 M EDOT by using CV technique between 1.2 V and −1.5 V with a scan rate of 0.1 V/s for 3 cycles. MnO_2 was then electrodeposited onto PrGO composite in the potential range of 0.2 to −0.6 V in a solution containing 0.01 M $KMnO_4$ and 1 M H_2SO_4 with a scan rate of 0.01 V/s for 3 cycles.

2.3. Instrumentation

All electrochemical measurements were carried out using a three-electrode system consisting of the counter electrode (Pt wire), reference