Graphene Oxide Doped Poly(hydroxymethylated-3,4-ethylenedioxythiophene): Enhanced Sensitivity for Electrochemical Determination of Rutin and Ascorbic Acid*

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Abstract A novel graphene oxide doped poly(hydroxymethylated-3,4-ethylenedioxythiophene) (PEDOT-MeOH/GO) composite film was synthesized and utilized as an efficient electrode material for simultaneous detection of rutin and ascorbic acid (AA). PEDOT-MeOH/GO films were synthesized on glassy carbon electrode (GCE) by a facile one-step electrochemical approach and were characterized by scanning electron microscopy, UV-Vis spectroscopy, FTIR spectra and electrochemical methods. Then the PEDOT-MeOH/GO/GCE was applied successfully in the simultaneous detection of rutin and AA. The results showed that the oxidation peak currents of rutin and AA obtained at the PEDOT-MeOH/GO/GCE were much higher than those at the traditional conducting polymer PEDOT/GO/GCE, PEDOT-MeOH/GCE, PEDOT/GCE and bare GCE. Under optimized conditions, the linear ranges for rutin and AA are 20 nmol/L to 10 µmol/L and 8 µmol/L to 1 mmol/L, respectively. The detection limit is 6 nmol/L for rutin and 2 µmol/L for AA (S/N = 3), which are lower than those of the reported electrochemical sensors.

Keywords: Conducting polymer; Graphene oxide; Nanocomposites; Simultaneous determination; Electrochemical sensor.

INTRODUCTION

Conducting polymer composites have attracted much attention for a variety of applications because of their many features including low weight, low cost, corrosion resistance, and ease of processing and shaping[1,2]. To date, the combination of conducting polymer with carbon materials, such as fullerenes and carbon nanotubes has been widely studied because of their outstanding properties, such as electrochemical, thermal and mechanical properties[3,4]. However, different from the mentioned carbon materials, graphene oxide (GO) has created a new field of carbon-filled nanocomposites in recent years. GO, the oxidation form of graphene, bears two-dimensional plane and lots of functional groups, such as carboxyl, hydroxyl and epoxide, rendering it hydrophilic and dispersible in aqueous solutions[5, 6]. This property, along with its abundance of negatively charged carboxyl groups, makes it an excellent dopant for the electropolymerization of polymer-based nanocomposites[7].

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Poly(3,4-ethylenedioxythiophene) (PEDOT), one of the conducting polymers among the various families, has been studied extensively because it combines a low oxidation potential and moderate bandgap with good stability in the oxidized state, high conductivity and highly transparent in thin, oxidized films\cite{8,9}. In comparison with other conducting polymers, PEDOT was found to be much more stable and able to retain its conductivity even after storage at high temperatures. Combining the advantageous features of PEDOT and GO, Si et al. reported a facile electrodeposition method to fabricate the GO doped PEDOT (PEDOT/GO) film for the simultaneous determination of hydroquinone (HQ) and catechol (CT) as an electrochemical sensor\cite{10}. The modified electrode showed enhanced electron transfer properties and good electrocatalytic activity to the redox reactions of HQ and CT. Liu et al. prepared PEDOT/GO nanocomposites via interface polymerization of EDOT in the presence of GO\cite{11}. It is found that such PEDOT/GO nanocomposites exhibit good catalytic activity toward the oxidation of nitrite and can be used as a sensor for detection of nitrite.

Although PEDOT-based nanocomposites have so many advantages, the poor water solubility of 3,4-ethylenedioxythiophene (EDOT) is a major disadvantage, which limits their further application in biosensors. Recent studies show that the poor aqueous solubility of EDOT can be improved by addition of an appropriate pendant side group onto the backbone\cite{12}. EDOT-MeOH is one of the derivatives of EDOT, which exhibits higher solubility in water than EDOT\cite{13}. Moreover, the resulting PEDOT-MeOH film was proven to display better biocompatibility\cite{14,15}, higher conductivity\cite{16} and better electrochemical properties\cite{17−19}. To date, however, little work has been reported on the synthesis of PEDOT-MeOH/GO composites via a direct electrodeposition approach and the study of their electrochemical performances.

Rutin (3’,4’,5,7-tetrahydroxyflavone-3-β-D-rutinoside), as a kind of the most abundant bioactive flavonoid called as vitamin p, is widely present in multivitamin preparations and more than 70 herbal remedies. As a natural flavone derivative, rutin has a wide range of physiological activities including anti-inflammatory, hemostat, antibacterial, anti-tumor and anti-oxidant\cite{20−22}. Based on these properties, rutin is always used clinically as the therapeutic medicine\cite{23}. Ascorbic acid (AA), known as vitamin C, is a powerful water-soluble antioxidant. It plays a key role in protecting living cells against oxidative injury and has been used clinically for the treatment and prevention of scurvy, common cold, mental illness, cancer and AIDS\cite{24}. As to the efficacy, some works have claimed better results from the use of rutin in combination with AA than from rutin alone in pharmaceutical preparations. Furthermore, rutin and AA often present together in fruits, vegetables, teas and Chinese herbs\cite{25}. Therefore, developing a simple, sensitive and accurate analytical method for the simultaneous determination of rutin and AA is of great significance.

Up to now, a number of techniques such as spectrophotometry\cite{26}, capillary electrophoresis\cite{27−29}, high-performance liquid chromatography\cite{30} and electrochemical methods\cite{25,31}, were employed for the determination of rutin and AA. Among these methods, electrochemical method is simple and sensitive. However, the sensitivity and selectivity of electrochemical method usually depends on the electrode material.

Herein, we for the first time report a facile one-step electrochemical approach to the synthesis of high quality PEDOT-MeOH/GO film on a glassy carbon electrode (GCE) by using GO and EDOT-MeOH as the starting materials. It is found that the PEDOT-MeOH/GO/GCE exhibited good electrochemical performance and good electrocatalytic activity to the redox reactions of rutin and AA. Thus, the prepared PEDOT-MeOH/GO/GCE film was used for the simultaneous determination of rutin and AA as an electrochemical sensor. The proposed method possesses several advantages such as wide linear range, excellent repeatability and long-term stability, low cost, environmentally friendliness and simplicity.

**EXPERIMENTAL**

**Reagents**

Rutin and ascorbic acid were purchased from Aladdin and Bio Basic Inc, respectively. EDOT was purchased from Aldrich. EDOT-MeOH was synthesized by our research group. GO was purchased from Nanjing XFNANO Materials Tech Co., Ltd. Rutin and ascorbic acid stock solutions (0.01 mol/L) prepared with absolute