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Electrochemical behavior of folic acid in neutral solution on the modified glassy carbon electrode: Platinum nanoparticles doped multi-walled carbon nanotubes with Nafion as adhesive

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ABSTRACT

Platinum nanoparticles (PtNPs) were used in combination with multi-walled carbon nanotubes (MWCNTs) with Nafion as the adhesives for fabricating sensitivity-enhanced electrochemical folic acid (FA) sensor. The modifier, PtNPs doped MWCNTs (PtNPs/MWCNTs), was characterized by transmission electron microscopy (TEM) and electrochemical method, it also showed an excellent character for electrocatalytic oxidization of FA. In addition, the experimental parameters such as pH values, the concentration of PtNPs/MWCNTs and the scan rate were optimized. Due to the fine characteristics of PtNPs/MWCNTs, a good linear relationship between the anodic peak current and FA concentration in the range 2.0×10^{-7}–1.0×10^{-4} M was observed. The detection limit of 5.01×10^{-8} M was achieved with the linear correlation coefficient $R = 0.9948$. The relative standard derivation was 1.9% for 5×10^{-6} M FA in 11 repeated determinations. This modified electrode showed excellent sensitivity and stability for the determination of FA.

1. Introduction

Folic acid (FA, *N*-[*p*-{[(2-amino-4-hydroxy-6-pteridinyl)methyl] amino}benzoyl]-l-glutamic acid, shown in Scheme 1) is a water-soluble B-vitamin that occurs naturally in a wide variety of foods, such as broccoli, cabbage, cauliflower, fruit and nuts. A deficiency of FA in the diet is closely linked to the presence of neural tube defects in newborns and to an increased risk of megaloblastic anemia, cancer, Alzheimer's disease, cardiovascular disease and some psychiatric disorders [1–3]. Therefore, the determination of FA in the pharmaceutical, clinical and food samples has drawn significant attention and a reliable and sensitive detection method is highly expected. At present, various techniques have been employed for quantification of FA, viz. chromatography [4–6], spectrophotometry [7–9], thermogravimetry [10,11] chemiluminescence [12,13], enzyme-linked ligand sorbent assay [14,15]. However, these techniques are complex, time-consuming and expensive in the way of instruments using [16].

Electrochemical methods have also been applied to the detection of FA. In addition, due to its advantages of simplicity, rapid response, excellent reproducibility, high stability, low cost and low detection limit, enormous interest has been attracted [17–19]. 1950–1960s of the last century, William et al. [20] first reported the purification of crude products and polarographic determination of leucovorin, as well determined the position of the formyl pyridine ring. DC and AC polarographic method was being used for the first time for the examination of the polarographic behavior, electrolysis conditions, catalytic reduction and pK values of FA [21,22]. The electrochemical reaction and adsorption behavior of FA had been studied at mercury electrode by using adsorptive stripping voltammetry. In the result, FA was detectable at 1×10^{-11} M through 10 min accumulation [23]. Le Gall and van den Berg [24] used cathodic stripping voltammetry to determine FA with a hanging mercury drop electrode, the voltammetric response was linear to the FA concentration from 9.0×10^{-11} to 5.0×10^{-7} M. Although the detection limit of the polarography is quite low, their application in the direct determination of FA is limited due to the poor reproducibility. Chemically modified electrodes have received high attention in the development of electrochemical sensors and biosensors. Modification on the electrode surface can accelerate the electronic transmission process of the redox mediator, in order to achieve electrocatalytic reactions, thereby enhancing the detective sensitivity and improving the reproducibility. Various inorganic and organic materials have been used to fabricate modified electrodes in the detection of FA, which can enhance the transfer rate of the electron and reduce the over potential for the detection of substrates including single-walled carbon

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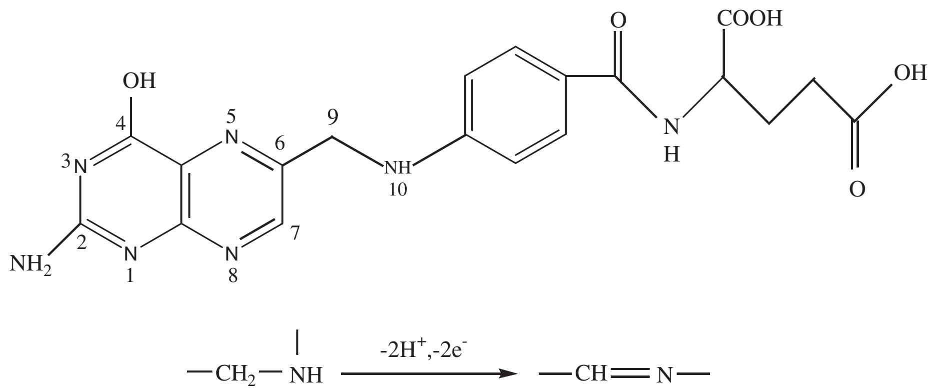

Scheme 1. Structure of folic acid (FA) and oxidation of folic acid at C9–N10, which is reported to mimic biological oxidation.

nanotubes ionic liquid [25–27], TiO_2 nanoparticles [28], 2,2′-[1,2-ethanediylbis-(nitriloeth ylidyne)]-bis-hydroquinone double-walled carbon nanotubes [29], mercury meniscus [30], molybdenum (VI) complex carbon nanotubes [31], multiwall carbon nanotubes [32], Single-wall carbon nanotube film [17], Lead film [33] and Ferrocenedicarboxylic acid modified multiwall carbon nanotubes [34]. As mentioned in the above, the modified electrodes exhibit high sensitivity of FA determination. However their preparation and construction are often rather complicated and the prices of modifying substances are usually higher. The stabilities and reproducibilities of such modified electrodes are relatively low.

The application of nano-carbon materials in various fields of science and technology has been extensively developed due to their unique properties. Since discovery in 1991, carbon nanotubes (CNTs) have been one of the most actively studied materials due to their exclusive structure and extraordinary physical properties, such as large ratio of surface area to mass, high electrical conductivity and remarkable mechanical strength. There has been growing interest in using CNTs in fabricating biological devices owing to their ability to promote the transfer rate of electron in biomolecules [35]. Besides CNTs, metal nanoparticles have also received much attention recently. Various examples of the electrochemical applications are the modification of electrodes with redox active nanomaterials in order to develope electrochemical sensors [36]. Pt nanoparticles (PtNPs) are the most widely utilized nano-metal materials owing to their excellent physical and catalytic properties. PtNPs are always used for the modification of electrode [37]. Nanostructured Pt-based highly sensitive platform had shown an excellent characteristic for enzyme-free amperometric sensing of H_2O_2 [38]. Wang and coworkers reported on the ultrafine platinum particle-modified carbon fiber microelectrode for the detection of hydrazine [39]. Birkin et al. demonstrated that platinum nanoparticles could be used for constructing electrochemical sensors with remarkably improved sensitivity toward H_2O_2 with single-wall carbon nanotubes [40]. In addition, Ikariyama et al. pressed the emphasis on the usefulness of platinum particles being the modified material for micro-enzyme sensors [41]. Accordingly, it displayed extraordinary performance with high sensitivity and fast responsiveness. Considering the excellent electrocatalytic characteristics of both MWCNTs and PtNPs, PtNPs/MWCNTs nanocomposites would be an ideal electrode material for amperometric FA sensors. Promising results with these structures have been announced in relevant applicational fields, such as direct methanol fuel cells [42,43] and glucose biosensors [44] and H_2O_2 sensors [45,46]. However, up to date, there is no published study regarding the use of PtNPs/MWCNTs being an electrode of an amperometric FA sensor.

In previous reports, the determination of FA has been investigated fully, both for analytical purposes and for fundamental mechanistic interest. Generally accepted that the electrode process of folic acid can be expressed as: the reductive process consists of three distinct steps in acidic media and one reductive step in alkaline media [47]. Only one oxidized step in anodic way of polarization was observed in acidic medium as well as in alkaline media. Most of the previous studies are conducted in strong acidic solution or strong alkaline solution. Though the detection limit is low [17,25–34], the application in the detection of real samples is limited. As is well known, FA works primarily in the brain and nervous system and is necessary for the synthesis of DNA. Determination of FA is often required in the pharmaceutical, clinical and food samples. Meanwhile, FA is easily to be oxidized in alkaline solution and the thermal instability exists when FA in acidic solution. Therefore, neutral solution is proposed in the electrochemical detection of FA. It is the aim of the present work to specify the kinetic parameters of FA on the surface of PtNPs/MWCNTs modified glassy carbon electrode in neutral Phosphate-Buffered solution (PBS). We also evaluated the anodic performance of PtNPs/MWCNTs modified electrode in quantification of FA. The results showed that the proposed method is sensitive in the determination of FA. The detection limit, linear dynamic range, and sensitivity to FA with PtNPs/MWCNTs electrode is comparable to, and even better than, those recently developed modified electrode which determined in acidic or alkaline conditions.

2. Experimental

2.1. Chemicals

All chemicals used were of analytical reagent grade and purchased from Sigma unless otherwise stated. Doubly distilled water was used throughout. A 1×10^{-2} M folic acid standard solution was prepared by dissolving 0.221 g folic acid in 10 mL of 0.5 M NaOH and completing the volume to 50 mL with doubly distilled water. This solution was kept in a refrigerator and protected from light. Working standards were daily prepared by diluting the stock solution with doubly distilled water. 0.1 M PBS with different pH values, Nafion-perfluorinated ion-exchange resin (5 wt.%), $H_2PtCl_6{\cdot}6H_2O$ were used. MWCNTs (with a diameter of about 25–40 nm and length of around 1–10 μm) with carboxylic groups were obtained from Shenzhen Nanotech Co., Ltd. (Shenzhen, China). FA tablets were obtained from Peking University Pharmaceutical Co., Ltd. (Beijin, China) and used without further purification.

2.2. Apparatus

Electrochemical measurements were performed on a CHI 660d Electrochemical workstation (Shanghai Chenhua Instrument Corporation, China). The three-electrode system consisted of a glassy