



A novel phosphomolybdic acid–polypyrrole/graphene composite modified electrode for sensitive determination of folic acid



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ABSTRACT

A novel phosphomolybdic acid–polypyrrole/graphene composite modified glassy carbon electrode has been fabricated for the sensitive determination of folic acid based on the inhibitory activity of folic acid towards the redox behavior of Keggin-type phosphomolybdic acid. The redox behavior of the modified glassy carbon electrode is investigated by cyclic voltammetry and the electrochemical behavior of folic acid is studied by differential pulse voltammetry. From this study, it is found that on the modified electrode the redox process of phosphomolybdic acid is surface-controlled, which can form a much stronger complex with folic acid than H^+ in 0.01 M H_2SO_4 . The reduced peak current of phosphomolybdic acid has a good linear relationship with FA concentration in the range from 1.0×10^{-9} to 2.0×10^{-7} M, and the detection limit of FA is calculated to be 3.3×10^{-11} M.

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1. Introduction

Folic acid (FA), a widely distributed water-soluble vitamin, is an electroactive component that is of considerable biological importance in the haematopoietic system. FA is also a kind of coenzyme that controls the generation of ferrohaeme [1,2]. The deficiency of FA can lead to a series of diseases, such as gigantocytic anemia, mental devolution, heart attack and stroke [3,4]. It has also been reported that low folate status is notably associated with congenital malformations of the spine, skull and brain for women who is planning or capable of pregnancy [5]. Therefore, the development of sensitive techniques for the determination of FA has attracted considerable attention. So far, many methods have been proposed for the determination of FA, such as high-performance liquid chromatography (HPLC) [6], spectrophotometry [7], fluorescence [8] and so on. However, most of these techniques suffer from the disadvantages of complexity, time-consuming and expensive instruments. Alternatively, electrochemical method has become a powerful technique for the determination of FA due to its advantages of simplicity, excellent reproducibility, good stability, low cost and high sensitivity [9,10]. Nevertheless, direct electrochemical reduction of FA usually requires a relatively high reduction poten-

tial on common electrodes with a slow kinetics. In order to overcome these problems, many efforts have been made to develop novel materials for the modification of electrode [9,11,12,13,14]. For example, Yang and co-workers constructed a voltammetric sensor for FA detection by using ordered mesoporous carbon modified glass carbon electrode (GCE) [11]. Wei et al. studied the voltammetric behavior of FA on a multi-walled carbon nanotube modified gold electrode [12]. Kalimuthu demonstrated the selective determination of folic acid (FA) in the presence of important physiological interferents by using electropolymerized film of 5-amino-2-mercapto-1,3,4-thiadiazole modified GCE and the detection limit was found to be 2.3×10^{-10} M [9]. Although these methods had low detection limits, their cost were so high that a new method with low cost and fairly low detection limit was urgently needed.

Graphene (GR) [15,16] is a two-dimensional material, which exhibits high electrical conductivity, combining with mechanical strength and chemical inertness. Thus, GR has become a promising material for potential applications in many areas, including sample preparation [17,18], electrochemical sensors [19–22], electrocatalyst [23] and drug carriers [24].

Polyoxometalates anions (POMs), a type of well-known polynuclear metal-oxo cluster compounds represented by Keggin-type phosphomolybdate (PMo_{12}), have attracted increasing interests in the fields of catalysis, biology and medicine due to their unique

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chemical, structural, and electronic properties [25–27]. One of the most important properties of PMo_{12} is its potential for reversible multi-electron redox reactions, which makes it suitable for the fabrication of electrochemical sensors [27]. So far, a variety of methods have been developed to immobilize PMo_{12} on electrode surface effectively and maintain or enhance its beneficial properties, including electrodeposition [28,29], layer-by-layer assembly [30,31], Langmuir–Blodgett (LB) technique [32], chemical adsorption [33] and entrapment into polymers matrixes [34]. The most promising modified electrode is prepared by entrapping POMs into conducting polymer films, which may not only avoid the interferences of large molecules that can pass through the matrix and react at the electrode surface, but also accelerate the kinetics of some electrochemical reactions [35]. As an oxidized polymer [36] with high conductivity, polypyrrole (PPy) has been of great interest in its potential applications in the area of biosensors [37,38]. The composites PMo_{12} -PPy could be synthesized by electrochemical polymerization on the electrode. PPy can not only stabilize the structure of POMs but also enhance their catalytic activity. To the best of our knowledge, there have been few reports on the fabrication of PMo_{12} -PPy/GR modified electrode.

Herein, a novel PMo_{12} -PPy/GR modified GCE was developed to construct an electrochemical sensor for the determination of FA. GR played important roles in not only providing high surface area and activity for electrochemical polymerization of the composites PMo_{12} -PPy, but also improving the electric contacts between the composites and biomolecules.

2. Materials and methods

2.1. Apparatus and materials

Folic acid (FA) was purchased from Shanghai Science and Technology Development Co., Ltd. (Shanghai, China). Pyrrole (Py) was obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Keggin-type phosphomolybdic acid $\text{H}_7\text{PMo}_{12}\text{O}_{42}\cdot x\text{H}_2\text{O}$ (denoted briefly as PMo_{12}) was ordered from Tianjin Regent Co., Ltd. (Tianjin, China). Graphite was provided by Qingdao Fujin Graphite Co., Ltd. (Qingdao, China). All chemicals were of analytical grade. Cyclic and differential pulse voltammetry experiments were performed on a CHI-660C electrochemical workstation (Chenhua Instrument Co., Ltd., Shanghai, China) with a conventional three-electrode cell. A glassy carbon electrode (GCE) was used as bare electrode, and the modified GCE was used as the working electrode. A platinum wire was used as the auxiliary electrode. All the potentials quoted here were referred to a saturated calomel electrode (SCE) as the reference. Transmission electron microscopy (TEM) was carried out on JEOL JEM-2100 (Japan) at 90 kV. Scanning electron microscopy (SEM) images were obtained by JSM-7001F (Japan).

FA standard solution at the concentration of 1.0×10^{-4} M was prepared by dissolving 4.4 mg FA in 20 mL of 0.1 M NaOH, followed by diluting to 100 mL with doubly distilled water. Buffer solutions consisted of 0.50 M H_2SO_4 and Na_2SO_4 . All solutions were prepared by doubly distilled water.

2.2. Preparation of the PMo_{12} -PPy/GR/GCE

A GCE was carefully polished with 0.3 μm and 0.05 μm alumina powders, respectively. Then the GCE was ultrasonically cleaned in ethanol and double-distilled water, followed by drying at room temperature before use. GR was prepared according to our previously reported method [20]. A 1 mg GR was fully dispersed in 1 mL of double-distilled water by ultrasonication for 30 min. A 6 μL of the resulting GR solution was dropped on the pre-polished

GCE and allowed to dry under an IR lamp to obtain the GR-modified electrode (GR/GCE). The GR/GCE was cycled between -0.1 and $+0.8$ V at 100 mV/s for eight cycles in 0.5 M H_2SO_4 containing 6.0×10^{-2} M pyrrole and 5.0×10^{-3} M PMo_{12} to obtain the modified electrode donated as PMo_{12} -PPy/GR/GCE.

3. Results and discussion

3.1. Characterization of the PMo_{12} -PPy/GR

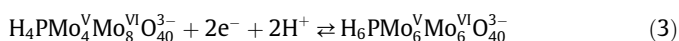
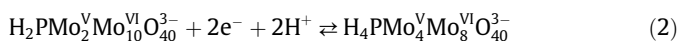
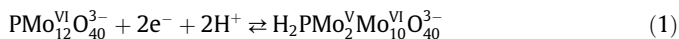
As shown in Fig. 1a, the TEM image of the GR exhibits a wrinkle-like thin sheet, which is the feature structure of GR. The morphology and structure of PMo_{12} -PPy and PMo_{12} -PPy/GR were characterized by SEM. From Fig. 1b, the PMo_{12} -PPy with an average size of ~ 50 nm is unevenly deposit on the glassy electrode. However, the SEM of PMo_{12} -PPy/GR shows that tiny particles of PMo_{12} -PPy were uniformly deposited on GR modified electrode with a porous three-dimensional structure. This should be attributed to the effect of GR, which can provide high surface area, a rough surface scaffold and the three-dimensional structure. The distinct structure is beneficial for the transmission of biomolecules in further electrochemistry reaction.

3.2. Electrochemical behaviors of the modified electrode

Fig. 2 shows the representative cyclic voltammograms of GR/GCE in 0.5 M H_2SO_4 containing Py and PMo_{12} with electropolymerization scanning from $+0.8$ to -0.2 V (vs. SCE) for eight cycles. It is observed that there are three pairs of prominent peaks in the voltammogram of PMo_{12} , denoting the intrinsic electrochemical property of PMo_{12} [39]. In addition, the peak current increased gradually with successive cycles, indicating that PMo_{12} was effectively doped in PPy matrix and the PMo_{12} -PPy film was formed on the surface of GR/GCE. However, as the increase of the film thickness, the obstruction of ions increased and the electrons shuttling decreased in the thick film. In addition, when the polymerization number was greater than 8 cycles, the as-made film became so thick that it was easy to fall off, which largely limited its electrochemical stability. In order to obtain a high quality PMo_{12} -PPy film and prevent the film from dropping from the electrode, 8 cycles was chosen in our experiment.

As shown in Fig. 3(a), when the scan rate changed, the cathodic peak currents were almost the same as the corresponding anodic peak currents, while the peaks changed gradually. When scan rates were lower than 100 mV/s, the peak currents were proportional to the scan rates (Fig. 3(b)), which indicates that the redox process of PMo_{12} is surface-controlled.

As shown in Fig. 4(a), three reversible pairs of redox peaks were observed for PMo_{12} -PPy/GR/GCE. On the PMo_{12} -PPy/GR/GCE, the peak-to-peak separation between the corresponding anodic and cathodic peaks ($\Delta E_p = E_{pa} - E_{pc}$) of PMo_{12} for the peaks I-i, II-ii, III-iii were 90, 88, 91 mV, respectively. Three redox peaks corresponded to three successive two-electron processes, respectively.



The redox process of PMo_{12} is accompanied by inserting and exploding proton. Thus, the electrochemical behavior of PMo_{12} is greatly affected by pH of the supporting electrolyte. As shown in Fig. 4, when pH was in the range from 0.3 to 2.7, the peak currents of the three waves gradually decreased. When pH was higher than 2.0, PMo_{12} anion was unstable and the redox peaks gradually

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