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Electrochemical determination of ascorbic acid in fruits on a vanadium oxide polypropylene carbonate modified electrode

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Abstract

A novel vanadium oxide polypropylene carbonate modified glassy carbon electrode was developed and used for the measurement of ascorbic acid (AA). The electrode was prepared by casting a mixture of vanadium tri(isopropoxide) oxide ($VO(OC_3H_7)_3$) and poly(propylene carbonate) (PPC) onto the surface of a glassy carbon electrode. The electrochemical behavior of the $VO(OC_3H_7)_3$–PPC film modified glassy carbon electrode was investigated by cyclic voltammetry and amperometry. This modified electrode exhibited electrocatalytic response to the oxidation of ascorbic acid. Compared with a bare glassy carbon electrode, the modified electrode exhibits a 220 mV shift of the oxidation potential of ascorbic acid in the cathodic direction and a marked enhancement of the current response. The response current revealed a good linear relationship with the concentration of ascorbic acid in the range of 4×10^{-8} and 1×10^{-4} mol L^{-1} and the detection limit of 1.5×10^{-8} mol L^{-1} ($S/N = 3$) in the pH 8.06 Britton–Robinson solution. Quantitative recovery of the ascorbic acid in synthetic samples has been obtained and the interferences from different species have been studied. The method has been successfully applied to the determination of ascorbic acid in fruits. The concentrations of ascorbic acid measured by this method are in good agreement with the literature value. It is much promising for the modified films to be used as an electrochemical sensor for the detection of ascorbic acid.

Keywords: Vanadium tri(isoproxide) oxide; Poly(propylene carbonate); Ascorbic acid; Electrocatalysis; Organically modified electrode

1. Introduction

Ascorbic acid (AA) is a powerful antioxidant naturally present in many foods, especially fruits and vegetables, and plays an important role in the prevention of infectious diseases. Apart from its vitamin activity, ascorbic acid is frequently used in the food industry as an antioxidant to prevent undesirable changes in color, taste and odour. Because of its biological and technological importance, it is of great interest in the food field to have rapid and sensitive methods for its routine and reliable determination.

The direct electrochemical oxidation of ascorbic acid is possible but requires high overpotentials, the equilibrium potential of the couple is −0.185 V versus saturated calomel electrode (SCE) [1], but oxidation at bare glassy carbon or platinum electrodes requires potentials of +0.4 and +0.6 V versus SCE, respectively. These high overpotentials result in electrode fouling, poor reproducibility, low selectivity and poor sensitivity and thus this technique is rarely employed analytically. The poor reproducibility of direct electrochemical oxidation of ascorbic acid has led to interest in the use of mediators and modified electrodes to catalyze the electrochemical oxidation of ascorbic acid. For example, electrode surfaces modified with immobilized quinone groups [2], adsorbed 7,7,8,8-tetracyanoquinodimethane (TCNQ) [3], electropolymerized films of poly(pyrrole) [4,5] or "self-doped" poly(aniline) [6,7] and polymer film modified electrodes [8–11] have all been studied.

Polymer film modified electrodes can be differentiated from other modification methods such as adsorption and covalent bonding because they commonly involve multilayer adsorption, which can increase the concentration of the eletrocatalyst resulting in obvious analytical signals. To-

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gether with its ease of preparation, good stability and reproducibility, the polymer film modified electrode is particularly advantageous for electroanalytical research [12]. Many researches were put on the polymer matrix, such as poly(ethylene oxide) (PEO) [13], poly(vinyl chloride) (PVC) [14], poly(methyl methacrylate) (PMMA) [15], polyacrylonitrile (PAN) [16], poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) [17–19] and so on.

Poly(propylene carbonate) (PPC) is a new kind of hydroxyl terminated aliphatic polycarbonate composed of carbon dioxide and propylene epoxide [20] that can be used as adhesives, solid electrolytes, photoresists, barrier materials, flexibilizers and plasticizers [21,22]. In the past studies, we found that V_2O_5 had high electrocatalytic activity for ascorbic acid, but it is slight resolvable in water. So it is difficult to modify uniformly on the electrode or the count of modified electrode is less. Thus, we selected the other vanadium species (vanadium tri(isoproxide) oxide ($VO(OC_3H_7)_3$)) as electrocatalyst. Because PPC and $VO(OC_3H_7)_3$ are analogous, they can possess miscibility; $VO(OC_3H_7)_3$ would be held well in PPC modified film.

In this paper, we present the fabrication of vanadium tri(isopropoxide) oxide and poly(propylene carbonate) film modified glassy carbon electrode. Its electrochemistry behavior is studied in details. The modified electrode not only exhibits high electrocatalytic activity for ascorbic acid but also shows remarkable stability, which is important for practical applications.

2. Experimental

2.1. Reagents

Poly(propylene carbonate) (Ave. $M_n \sim 50{,}000$ (GPC)) were obtained from Aldrich Chemical Company Inc. Ascorbic acid, lithium perchlorate ($LiClO_4$), vanadium pentoxide (V_2O_5) and tetrahydrofuran (THF) were obtained from Shanghai and used without further purification. Britton–Robinson (B–R) buffers were obtained by titrating a mixed acid solution (0.04 mol L^{-1} boric acid, 0.04 mol L^{-1} phosphoric acid and 0.04 mol L^{-1} acetic acid) with 0.2 mol L^{-1} NaOH to the required pH. Pure water was used throughout, obtained by means of Millipore Q water purification set. All other chemicals were of analytical grade.

2.2. Measurements

Electrochemical experiments were performed with a CHI 630A electrochemical analyzer (CH instruments, USA) in a conventional three-electrode cell. The working electrodes (WE) were modified or unmodified glassy carbon electrodes (GCEs Model CHI 104). Platinum electrode was used as the counter electrode (CE) and a saturated calomel electrode (SCE) as the reference electrode (RE). All potentials were measured and reported versus SCE. All experiments were carried out at room temperature. The buffer and sample solutions were purged with purified nitrogen for at least 15 min to remove oxygen prior to experiments.

Infrared spectrum of the sample was recorded with Perkin-Elmer Spectrum One FTIR spectrophotometer in the 400–4000 cm^{-1} region using a sample on the KBr plate.

2.3. Preparation of the film

GCEs (diameter 3 mm) were polished before each experiment with 1, 0.3 and 0.05 μm alumina powder, respectively, rinsed thoroughly with doubly distilled water between each polishing step, then washed successively with 1:1 nitric acid, acetone and doubly distilled water in ultrasonic bath and dried in air.

Preparation of $VO(OC_3H_7)_3$–PPC film is described as follows. First 16 g of vanadium pentoxide (V_2O_5) in 40 mL of isopropanol was refluxed with 2 mL of sulfuric acid (98%) for 7 h at 80–90 °C, cooled, centrifuged and extracted with THF. Then extraction was dried at room temperature to remove THF, and the yellow vanadium tri(isopropoxide) oxide was obtained. In this reaction, sulfuric acid plays as a catalyst. Organically modified PPC sol was prepared by mixing PPC with $LiClO_4$ ($LiClO_4$ enhance the conductance of the film) in THF for 24 h at room temperature. PPC sol was freshly prepared before use. Finally, $VO(OC_3H_7)_3$ was then mixed with PPC sol; 2 μL of above sol was dropped onto the surface of a GCE and allowed to dry at room temperature for 48 h. The $VO(OC_3H_7)_3$–PPC film modified GCE was obtained.

3. Results and discussion

3.1. Surface morphology and spectral characteristics of the $VO(OC_3H_7)_3$–PPC film

A typical surface morphology of the $VO(OC_3H_7)_3$–PPC film is shown in Fig. 1. It was found that the film surface was very uniform.

In Fig. 2, typical FT-IR spectral patterns are shown for $VO(OC_3H_7)_3$–PPC, $VO(OC_3H_7)_3$, PPC and V_2O_5. The characteristic bands of $VO(OC_3H_7)_3$ and PPC V_2O_5 can be observed in Fig. 2b and c, respectively. The spectrum of $VO(OC_3H_7)_3$–PPC composite (Fig. 2a) is similar with $VO(OC_3H_7)_3$ (Fig. 2b). It was also observed from the spectra that there was a slight change in the band positions of Fig. 2b, suggesting a weak interaction between the $VO(OC_3H_7)_3$ and PPC. Besides, it is possible to note that the bands at $VO(OC_3H_7)_3$–PPC are narrower than those for the $VO(OC_3H_7)_3$. This effect can be attributed to coulombic interactions between the two organic polymeric chains, although we are not able to discern the contribution of each one and more works are underway to further investigation of this point. Fig. 2d shows the spectra of V_2O_5. From Fig. 2b and d, it can be seen the difference of main bands between