



A novel voltammetric sensor for ascorbic acid based on molecularly imprinted poly(*o*-phenylenediamine-*co*-*o*-aminophenol)



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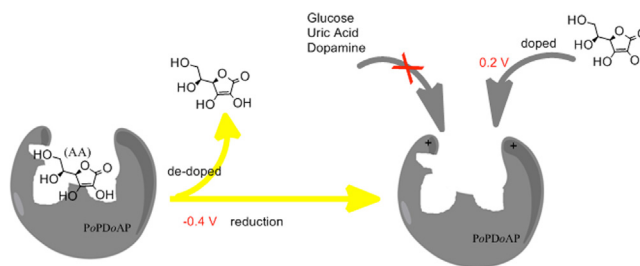
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HIGHLIGHTS

- A molecularly imprinted copolymer, PoPD_oAP, was prepared as a new AA sensor.
- The copolymer sensor exhibited a high sensitivity and selectivity toward AA.
- The performance of the AA sensor was improved due to the broadened usable pH range.

GRAPHICAL ABSTRACT



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ABSTRACT

A molecularly imprinted copolymer, poly(*o*-phenylenediamine-*co*-*o*-aminophenol) (PoPD_oAP), was prepared as a new ascorbic acid (AA) sensor. The copolymer was synthesized by incorporation of AA as template molecules during the electrochemical copolymerization of *o*-phenylenediamine and *o*-aminophenol, and complementary sites were formed after the copolymer was electrochemically reduced in ammonium aqueous solution. The molecularly imprinted copolymer sensor exhibited a high sensitivity and selectivity toward AA. Differential pulse voltammograms (DPVs) showed a linear concentration range of AA from 0.1 to 10 mM, and the detection limit was calculated to be 36.4 μM. Compared to conventional polyaniline-based AA sensors, the analytical performance of the imprinted copolymer sensor was improved due to the broadened usable pH range of PoPD_oAP (from pH 1.0 to pH 8.0). The sensor also exhibited a good reproducibility and stability. And it has been successfully applied in the determination of AA in real samples, including vitamin C tablet and orange juices, with satisfactory results.

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1. Introduction

Ascorbic acid (AA) is distributed widely in fruits and vegetables, which plays important roles in human metabolism as a free radical scavenger [1]. AA can also be used in the treatment of radical induced diseases such as cancer and Parkinson's disease [2]. Thus, the development of a simple and reliable method for the

determination of AA with high sensitivity and selectivity is of great importance. Among the methods reported for the determination of AA, electrochemical method is considered to be a hot topic of interest because of its simplicity, low cost and easy miniaturization [3–9].

The past two decades have seen a considerable development of molecular imprinting technique as a useful approach for the recognition and isolation of target molecules [10–12]. The general principle of molecular imprinting lies in the polymerization of monomers in the presence of a template (the imprinted molecule) [13]. Recently, molecular imprinting based on conducting polymers has attracted more and more attention [14–17], since

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conducting polymers possess unique electrical, thermal, and mechanical properties [18].

Polyaniline (PAn) is one of the most promising conducting polymers due to its high conductivity, good redox reversibility and stability, and swift color change with applied potential [19–21]. However, the pH dependence of PAn is quite small, i.e., PAn has low conductivity and electrochemical activity at $\text{pH} > 4.0$ [20], which limits its practical applications. Since the electrochemical determination of AA is usually performed under weakly acidic or neutral conditions (5.0–7.0) [3–9], the determining results of AA by the PAn-based sensors are not satisfactory due to the limited pH dependence of PAn [3,8,9].

Recently, aniline-based copolymers have been synthesized and applied as new molecularly imprinted polymers (MIPs) [21,22], since this type of copolymer not only retains the properties of PAn but also possesses new properties brought from the other monomer. It is noteworthy that the incorporation of aminophenol into PAn-based copolymer will broaden the usable pH region of the copolymer, since hydroxy functional groups on phenyl ring can be oxidized and reduced reversibly [23–27]. For example, poly(aniline-*co-p*-aminophenol) was synthesized and used to construct an electrochemical sensor for determining H_2O_2 at pH 5.0 [28]. Mu [29] synthesized poly(aniline-*co-o*-aminophenol) and investigated the electrocatalytic activity of this copolymer toward the reduction of As (V) at pH 6.0. More recently, poly(aniline-*co-m*-aminophenol) was synthesized by chemical oxidation of aniline and *m*-aminophenol, and the resulting copolymer was used for the recognition of glutamic acid enantiomer in our group [21].

Herein, a novel voltammetric sensor for the determination of AA was proposed based on the molecularly imprinted poly(*o*-phenylenediamine-*co-o*-aminophenol) (PoPDoAP). The imprinted copolymer shows a high sensitivity and selectivity for sensing of AA, which may be due to the broad usable pH range (from pH 1.0 to pH 8.0) of the copolymer discussed in our previous research [30]. As far as we are aware, this is the first report on the determination of AA by molecularly imprinted conducting copolymer based AA sensor, and its successful applications to the determination of AA in commercially available vitamin C tablet and orange juices have been demonstrated in this work.

2. Experimental

2.1. Reagents and apparatus

o-Phenylenediamine (*o*-PD) and *o*-aminophenol (*o*-AP) were purchased from Aladdin Chemistry Co., Ltd. (Shanghai, China). AA, uric acid (UA), dopamine hydrochloride (DA) and D-glucose were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All other reagents were of analytical reagent grade and used without further purification. All solutions were prepared by doubly distilled water.

Differential pulse voltammetry was carried out on a CHI 660D electrochemical workstation (CH Instruments, Chenhua Co., Shanghai, China). Impedance analysis was conducted with a model VersaSTAT 3 electrochemical system (Princeton Applied Research, USA). Frequency sweeps extended from 10^5 to 0.01 Hz in a 0.1 M HCl solution containing $10 \text{ mM } \text{K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$ redox probe, and it was operated at the open circuit potential (0.3 V) using a sine wave potential of 5 mV. A conventional three-electrode system was used for the electrochemical measurements, which comprised of a platinum foil as the counter electrode, a saturated calomel electrode (SCE) as the reference electrode and an imprinted copolymer, imprinted PoPDoAP, as the working electrode. Fourier transform infrared (FTIR) spectra of the copolymer before and after the extraction of AA templates were recorded on a FTIR-8400S spectrometer (Shimadzu, Japan).

2.2. Preparation of imprinted and non-imprinted PoPDoAP electrode

The preparation of molecularly imprinted PoPDoAP is quite similar with that of PoPDoAP [30] except the addition of AA as template molecules. Firstly, electrodeposition of PoPDoAP film on a glassy carbon electrode (GCE) was carried out by cyclic voltammetry in 100 mL solution of water and alcohol (v/v 3:2) containing 0.02 M *o*-PD, 0.04 M *o*-AP and 0.01 M AA, and the pH was adjusted to 5.5 with 0.1 M HCl. Pt foil and SCE were used as the counter electrode and reference electrode, respectively. The cycling potential range was between -0.2 and 1.2 V with a scan rate of 100 mV s^{-1} . The electrodeposition was finished after 20 cycles. After that, the three-electrode system was transferred into a 1% ammonium aqueous solution, and a negative potential of -0.4 V was applied on the PoPDoAP electrode for 1000 s for the extraction of AA templates and formation of complementary sites.

A control electrode, non-imprinted PoPDoAP (NIP PoPDoAP), was prepared in every case under the same experimental conditions but without adding AA during the electrodeposition of PoPDoAP.

2.3. Enrichment and determination of AA

The AA-imprinted PoPDoAP was immersed in 0.02 M phosphate buffer saline (PBS) containing 0.01 M AA, and the pH was adjusted to 5.5 with 0.1 M NaOH. A positive potential of 0.2 V was applied to the imprinted copolymer for 1000 s for the enrichment of AA. Then, differential pulse voltammetric experiments were performed for the determination of AA enriched in the imprinted copolymer film. Increment potential of 0.002 V, pulse width of 0.05 s, pulse period of 0.2 s, and sample width of 0.0167 s were selected. Owing to the recognition sites generated in the imprinted copolymer, AA can be detected sensitively and selectively. A schematic representation of imprinting, extraction and enrichment of AA by the copolymer electrode is shown in Scheme 1.

3. Results and discussion

3.1. Selection of reactive monomers

Since most conducting polymers synthesized by electrochemical oxidation are in the oxidation state with positive charge on their backbone, it is easy for anions to be incorporated into the polymer films during the polymerization process. The acidity coefficients of AA are 4.2 ($\text{p}K_{a,1}$) and 11.3 ($\text{p}K_{a,2}$), it is obvious that the pH value of the polymerization solution containing AA templates should be above 4.2 to make AA exist in its anionic form. However, traditional PAn-typed conducting polymers have small activity at $\text{pH} > 4.0$, which limits their application as AA sensors. Copolymers obtained from the copolymerization of aminophenol and aniline or its derivatives have opened up a new avenue. The useful pH region of these copolymers is widely broadened, even to pH 11.0, due to the introduction of $-\text{OH}$ groups which can be oxidized and reduced reversibly [20,21,28,29]. Therefore, *o*-PD and *o*-AP were selected as the reactive monomers for electrodeposition, and the resulting copolymer can be a good candidate for the determination of AA under a weakly acidic condition (pH 5.5).

3.2. Proof of AA incorporation

Since AA is in its anionic form at pH 5.5, it can be easily incorporated into the positively charged PoPDoAP during the polymerization process. Fig. 1 shows the differential pulse voltammograms (DPVs) of PoPDoAP doped with AA templates and NIP PoPDoAP in 0.02 M PBS (pH 5.5). As can be seen, at the copolymer

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