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The electro-synthesized imprinted PEDOT film as a simple voltammetric sensor for highly sensitive and selective detection of vitamin K_3 in poultry drug samples

Zhouxiang Zhang[a,b], Jingkun Xu[a,*], Yangping Wen[b,*], Jie Zhang[a,b], Wanchuan Ding[a,b]

[a] School of Pharmacy, Jiangxi Science and Technology Normal University, Nanchang 330013, PR China
[b] Key Laboratory of Agricultural and Applied Chemistry, Jiangxi Agricultural University, Nanchang330045, PR China

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ABSTRACT

Poly(3,4-ethylenedioxythiophene) (PEDOT) as a potential molecularly imprinted polymer (MIP) for the promising application in different fields is being closely concerned, but the denseness and smoothness in the morphology and structure of PEDOT hinder the application of the imprinted PEDOT film. In this paper, a simple voltammetric sensor with high sensitivity and selectivity based on the imprinted PEDOT film with imprinted sites as a recognition element for the trace analysis of vitamin K_3 (VK_3) in poultry drug samples was developed by the one-step electro-polymerization of commercially-available monomer 3,4-ethylenedioxythiophene in the presence of the template molecule VK_3. The imprinted PEDOT/GCE could efficiently discriminate VK_3 from its structural analogs, and the imprinted PEDOT sensor displayed good linearity with VK_3 concentrations in the wide range of 0.009 to 35 μM with a low limit of detection 0.00031 μM under the optimal conditions. The proposed method was successfully applied for the selective determination of VK_3 in poultry drug samples. All results indicated that the proposed imprinted electrode will provide a promising mimetic sensing platform for the determination of VK_3 in animal feedstuffs, livestock products and veterinary drugs.

1. Introduction

Vitamin K_3 (VK_3), an artificial menadione sodium bisulfate, is an effective clinical drug in medicine, which can be used to cure various diseases owing to VK_3 deficiency. Recently, VK_3 also added improperly or illegally into feedstuffs to promote livestock and poultry growth and prevent disease in livestock and poultry. However, it is toxic in excessive dosage or when abused. Consequently, it is crucial to monitor VK_3 levels in animal feedstuffs, livestock products and veterinary drugs. Diversified techniques such as UV detection [1], HPLC [2,3], fluorescence detection [4,5], flow injection analysis [6] for the measurement of VK_3 are widely used in the analysis of practical samples [7].

The above-mentioned methods have various shortcomings including complicated operation, troublesome and time-consuming pretreatment, low-level efficient and high cost. As an alternative, electrochemical technique is a powerful analytical tool because of its advantages of facile operation, sensitive and time saving. To our knowledge, polarographic methods for VK_3 determination were reported by the electrochemistry (electrochemical behaviors and properties) of VK_3 [8–10]. Unfortunately, current signals have not increased linearly with concentrations, and sensitivity, linear range, and the selectivity of these methods were very bad. Even worse, mercury related electrodes limited their applications in medical and biological fields due to their toxicity. Interestingly, electrochemical sensors based on chemically modified electrodes for the VK_3 determination have been received attention due to high sensitivity and wide linear range [11–16]. For example, electrochemical behaviors of VK_3 on rotating disk electrode based on glassy carbon electrode (GCE) were reported by Alonso et al. [11]. Subsequently, Vire et al. reported the VK_3 determination using the square-wave adsorptive stripping voltammetry [13], Liu et al. also detected the VK_3 using the as-fabricated interdigitated array microelectrodes (Pt-IDA and Au-IDA) [15], and we previously fabricated an electrochemical sensor based on PEDOT:PSS-CMC-Pd@rGO for the VK_3 detection in feedstuff and animal blood samples [16]. But, the selectivity and practicability of these sensors for VK_3 determination still needed to be further improved owing to the poor anti-interferent ability in complex samples containing structural analogs.

Molecular imprinted polymers (MIPs), with creating specific cavities in synthetic polymer matrices with memory for template molecules, are one of the most potential materials in the area of artificial molecular recognition systems, which have been increasingly attracted more and more attention over the last few decades [17,18]. MIPs were

* Corresponding authors.
E-mail addresses: xujingkun@jxstnu.edu.cn (J. Xu), wenyangping1980@gmail.com (Y. Wen).

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obtained by polymerizing corresponding functional monomer in the presence of template molecules. After template molecules were removed, there were many sites in polymers that they were complementary to template molecules in shape and size. Due to their low cost, stable mechanical properties, unparalleled features of structure predictability, specific recognition and extensive applications, MIPs had developed a wide range of applications in diversified fields including capillary electrochromatography, liquid chromatography, solid phase extraction and electrochemical sensor [19–23], and there were many methods to fabricate MIPs such as spin-coating, layer-by-layer self-assembly, electro-polymerization and more [24–27]. In comparison with other preparative methods of MIPs, MIPs via the electro-polymerization had superior performance in regard to the adherence to the surface of transducer as well as simplicity and speed of production. What's more, the electro-polymerization had many advantages such as easily control of film thickness and morphology, high reproducibility, the possibility of polymer preparation and operation in aqueous solution [28].

Conducting polymers (CPs), which had many superior properties such as good mechanical stability, simple preparation, possibility of miniaturization, their interesting electrical and electrochemical properties, had attracted extensive attentions in the fabrication of efficient chemo/biosensors [29–33]. CPs as molecular recognition units in chemo/biosensors is a wide public concern over research area [34–36]. Among CPs, poly(3,4-ethylenedioxythiophene) (PEDOT), has been received many attentions and broadly studied because it exhibited very interesting properties including high electrical conductivity, low band gap, superior environment stability and good biocompatability than most other CPs [37–40]. Owing to these properties, PEDOT has rapidly become the subject of considerable interest for the preparation of efficient chemo/biosensors. In our previous work, PEDOT and its derivatives have been fabricated as efficient chemo/biosensors for the practical application in agricultural environment, products, and food [41–43]. However, environmental factors such as temperature and pH seriously influenced the performance of electrochemical biosensors, while the selectivity affected the practical application of electrochemical chemosensors. Thus, it is very necessary for us to explore electrochemical mimetic sensors based on PEDOT and its derivatives.

Imprinted sensors as one of excellent mimetic sensors, they combine the merit of both biosensors and chemosensors. However, there were little reports on imprinted PEDOT sensors [44–49]. Ho group reported amperometric sensor based on imprinted PEDOT films for the detection of morphine using precipitation polymerization, electrochemical polymerization, and microfluidic system [44–46]. Unfortunately, the denseness and smoothness in morphology and structure of PEDOT film hinder the development of imprinted sensors, which is very unfavorable for the removal of template molecules, the enlargement of specific surface areas, the enhancement of sensing performance like sensitivity and others [47], different methods have been employing to solve problems mentioned-above. Subsequently, poly(3,4-ethylenedioxythiophene-co-thiophene-acetic acid) copolymer for sensing atrazine [48], PEDOT as substrate electrode for modification of imprinted TiO_2 and its application in detecting nicotine [49], imprinted particles that were entrapped into PEDOT films for determining diphenylamine was reported [50]. Although we successfully prepared PEDOT derivatives as the mimetic material for sensing carbendazim [51], PEDOT remain a potential mimetic material for the application of sensors owing to its unique advantages. To date, PEDOT as promising MIPs is being closely concerned, a variety of physical and chemical methods were utilized for the potential application in different fields of imprinted PEDOT films [52].

In this paper, we fabricated a simple VK_3 voltammetric sensor based on the electro-synthesized molecularly imprinted PEDOT film with imprinted sites, and morphology, parameters, performance, and practicability of the imprinted PEDOT electrode were discussed.

2. Experimental

2.1. Reagents

Tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) and acetonitrile (ACN) were purchased from Beijing lark technology Co., Ltd. 3,4-Ethylenedioxythiophene (EDOT) was bought from Sigma-Aldrich. Disodium hydrogen phosphate dodecahydrate ($Na_2HPO_4{\cdot}12H_2O$) and sodium dihydrogen phosphate dehydrate ($NaH_2PO_4{\cdot}2H_2O$) were obtained from the Sinopharm Chemical Reagent Co., Ltd. 0.1 M Phosphate buffer solutions (PBS) containing various pH values were obtained from stock solutions of $NaH_2PO_4{\cdot}2H_2O$ and $Na_2HPO_4{\cdot}12H_2O$. Vitamin K_3 (VK_3), vitamin K_1 (VK_1), 2,3-Dichloro-1,4-naphthoquine (DINA) and 2-Amino-3-Chloro-1,4-naphthoquine (ACNA) were all purchased from Beijing lark technology Co., Ltd. 0.05 M VK_3 stock solution was obtained in ethanol and kept in dark at 4 °C. The poultry drug "vitamin K_3 soluble powder" which could stanch and diminish inflammation was purchased from local factory. All other reagents were analytical grade and used without further purification.

2.2. Apparatus

Voltammetric experiments were carried out using CHI660B electrochemical workstation (Shanghai Chenhua Instrument Company, China) with a three-electrode system in a conventional electrochemical cell at room temperature. The PEDOT-MIP/GCE was used as the working electrode, an Ag/AgCl was served as the reference electrode with a platinum wire as the counter electrode. The pH of PBS was measured with a pH meter CT-6023. The scanning electron microscopy (SEM) was performed with JSM 6701F. The atmosphere of experiments was made by passing N_2 over the solution during experiments.

2.3. Preparation of imprinted modified electrode

Before modification, GCE was polished by chamois leather containing 0.05 μm alumina slurry until a mirror surface was achieved. Subsequently, the GCE was ultrasonically cleaned in doubly-distilled deionized water, absolute ethanol, and doubly-distilled deionized water each for 5 min, respectively. As shown in Scheme 1, the PEDOT imprinted electrode was fabricated using a three-step process. 0.02 M EDOT and 0.015 M VK_3 were dissolved in ACN containing 0.2 M Bu_4NBF_4. After that, EDOT with template molecule VK_3 was deposited on the GCE surface using cyclic voltammetry in potential range from 0 to 1.4 V during 20 cycles [53]. The template molecule was removed by immersing the imprinted electrode into elution solution with slightly stirring. Thus, PEDOT-MIP/GCE was attained. Moreover, PEDOT-NIP/GCE was obtained under same conditions without template molecule.

3. Results and discussion

3.1. Characterization of imprinted electrode

Different modified electrodes could be prepared by the electrochemical polymerization of functional monomers. Similarly, molecularly imprinted electrodes could be obtained by the electrochemical polymerization of functional monomers in the presence of template molecules, and template molecules could interact with functional monomers via hydrogen bonds [34]. Thus, −OH groups of VK_3 might interact with C−O groups of EDOT prior to the pre-polymerization, and PEDOT-MIP/GCE could be formed by method mentioned-above.

The surface morphology of PEDOT-NIP/GCE (A), PEDOT-MIP/GCE without removing VK_3 (B) and PEDOT-MIP/GCE with removing VK_3 (C) was presented in Fig. 1. There were many apparent cavity structures in PEDOT-MIP/GCE, which provided a large surface area for the adsorption of target species [55]. However, all SEM images revealed that PEDOT-NIP/GCE (A), PEDOT-MIP/GCE without removing VK_3 (B) and