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A facile one-pot strategy for the electrochemical synthesis of poly(3,4-ethylenedioxythiophene)/Zirconia nanocomposite as an effective sensing platform for vitamins B_2, B_6 and C

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ABSTRACT

Conducting polymers have been studied extensively due to their intriguing electronic and redox properties. To improve and extend their functions, the fabrication of multi-functionalized conducting polymer nanocomposites has attracted a great deal of attention. Herein, for the first time, a simple one-step electrodeposition method was developed for the synthesis of poly(3,4-ethylene-dioxythiophene)/Zirconia nanoparticles (PEDOT/ZrO_2NPs) composite film on a glassy carbon electrode (GCE). Data from scanning electron microscopy, energy dispersive spectrum, FTIR and UV/vis spectra, and various electrochemical techniques demonstrated that PEDOT/ZrO_2NPs nanocomposite was successfully synthesized. The obtained PEDOT/ZrO_2NPs nanocomposite film showed large specific area, high conductivity, rapid redox properties and had encapsulated structures, which make it an excellent sensing platform for sensitive determination of vitamin B_2 (VB_2), vitamin B_6 (VB_6) and vitamin C (VC). Electrochemical results obviously reveal that the catalytic peak currents of vitamins obtained at PEDOT/ZrO_2NPs/GCE are much higher than those at PEDOT/GCE, ZrO_2NPs/GCE and bare GCE. Using differential pulse voltammetry, detection limits of 0.012 μM, 0.20 μM and 0.45 μM were obtained for VB_2, VB_6 and VC, respectively at PEDOT/ZrO_2NPs/GCE. Furthermore, the modified electrode exhibited good reproducibility and long-term stability, as well as high selectivity. The facile and easy electrochemical approach used for the preparation of PEDOT/ZrO_2NPs nanocomposite may open up new horizons in developing of cost effective electrochemical sensors.

1. Introduction

Poly(3,4-ethylenedioxythiophene), an electrically conducting conjugated polymer combines some very interesting properties including transparent thin films, high conductivity, large band gap width, superior biocompatability, excellent stability or optical transparency in its conducting state, as well as an environment-friendly features [1–3]. These unique characteristics make PEDOT a desirable material in a variety of applications, including solar cells [4], organic light emitting devices [5] and electrochemical sensors [6]. Recently, the developments in nano-structured conducting polymers and polymer nanocomposites have large impact on electro-catalysis research and sensing applications [7]. Thus considerable attention has been paid on the synthesis of PEDOT/organic–inorganic nanomaterials that exhibit unique properties of both individual components in a synergistic manner. Especially, PEDOT/metal oxide nanomaterials are important in understanding the structure–activity relationships. Driven by these attractive properties, a number of researches in this field have been committed to the combination of PEDOT with metal oxide nanomaterials, including ZnO nanowires [8], MnO_2 [9], and TiO_2 nanoparticles [10]. Among the metal oxide nanomaterials, ZrO_2NPs have gained considerable attention as alternative electrode materials due to their thermal stability, chemical inertness, and lack of toxicity [11,12]. More conveniently, metallic oxide of ZrO_2 film could be prepared by electroreduction of $ZrOCl_2$ at bare or functionalized gold electrode surface [13,14]. For these aforementioned reasons, the combination of ZrO_2NPs and PEDOT could increase the mechanical properties of polymer and enhance the electrical characteristics by facilitating the charge-transfer processes between the two components when used as electrodes for constructing of efficient electrochemical sensors.

Water-soluble vitamins, VB_2, VB_6 and VC are essential constituents of food required for normal growth, self maintenance and functioning of human and animal bodies. As biologically and pharmaceutically important organic compounds, they are widely used as food additives or antioxidants for pharmaceutical purpose [15]. For example, VB_2 is a primary component of flavoenzymes

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in the human body and catalyzes a variety of biochemical reactions, involving carbohydrate and protein or fat metabolism. It can promotion skin, nails, and hair's normal growth, and eliminate the mouth, lips, tongue inflammation, also can promote vision, reduce eye fatigue [16]. VB_6 plays a vital role in the activities of many enzymes and always coexists with VB_2. It is a compound essential for the synthesis and metabolism of amino acid [17]. Furthermore, VB_6 is also important for the maintenance of a healthy skin and normal function of the nervous and immune systems. As we know, VC is an enzymatic cofactor for the synthesis of biologically important molecules, such as collagen, carnithine, catecholamine, myelin, neuroendocrine peptides and acts as a free radical scavenger in biological systems by hydrogen atom transfer [18]. It is a significant vitamin in the human diet. As a consequence, the simultaneous determination of VB_2, VB_6 and VC is an important topic in clinic medicine.

In the recent years, numerous analytical methods have been used to determine these vitamins, such as HPLC [19], chemiluminescence [20], spectroelectrochemical techniques [21], UV/vis [22], fluorescence [23], and capillary electrophoresis [24]. However, these methods suffer from high costs, extensive pre-treatment steps, long analysis times, and low sensitivity. These disadvantages limit the application of such methods primarily to laboratory settings and prohibit their use for rapid analysis under field conditions. In this case, bioelectrochemists and electroanalytical chemists have shown great interest in this area and various modified electrodes have been constructed to overcome these difficulties for the simultaneous determination of vitamins. For instance, Gu et al. established an electrochemical method for the vitamins B_2, B_6 and C detection based on the electrochemically pretreated glassy carbon electrode [15]. Revin and John fabricated 3-amino-5-mercapto-1,2,4-triazole (p-AMTa) film modified electrode to quantify vitamins B_2, B_9 and C by DPV technique [16]. Wu et al. constructed a novel sensor for the determination of vitamin B_6 in the presence of vitamins B_1 and B_2 using ruthenium tris(2,2′)bipyridyl $(Ru(bpy)_3^{3+}$ modified electrode [25]. Very recently, our group synthesized electroactive species doped PEDOT films by electropolymerization and used as electrochemical sensors for vitamins B_2, B_6 and C with acceptable sensitivity [26].

It is well known that one-step electrochemical method shows some clear advantages [17,27]. First, it is very simple, green and fast; without any toxic reductive agents being used, therefore, it will not result in contamination of the resultant products. Second, adjusting the exterior electrochemical parameters and the required reaction conditions are mild. Third, the resultant nanocomposites are especially suitable for electrochemical applications due to their direct deposition onto conducting substrate. Inspired by this, in the present study, we report a facile one-step electrochemical approach to the synthesis of high quality PEDOT/ZrO_2NPs nanocomposite utilized as an efficient electrode material for simultaneous determination of VB_2, VB_6 and VC (as shown in Scheme 1). Such nanocomposite combines the advantages of PEDOT (high conductivity and stability) together with ZrO_2NPs (good electrochemical activity) and exhibits good electrochemical performance and good electrocatalytic activity towards the redox reaction of VB_2, VB_6 and VC. As the outstanding performance, the sensor was successfully evaluated to detect the contents of VB_2, VB_6 and VC in honey samples.

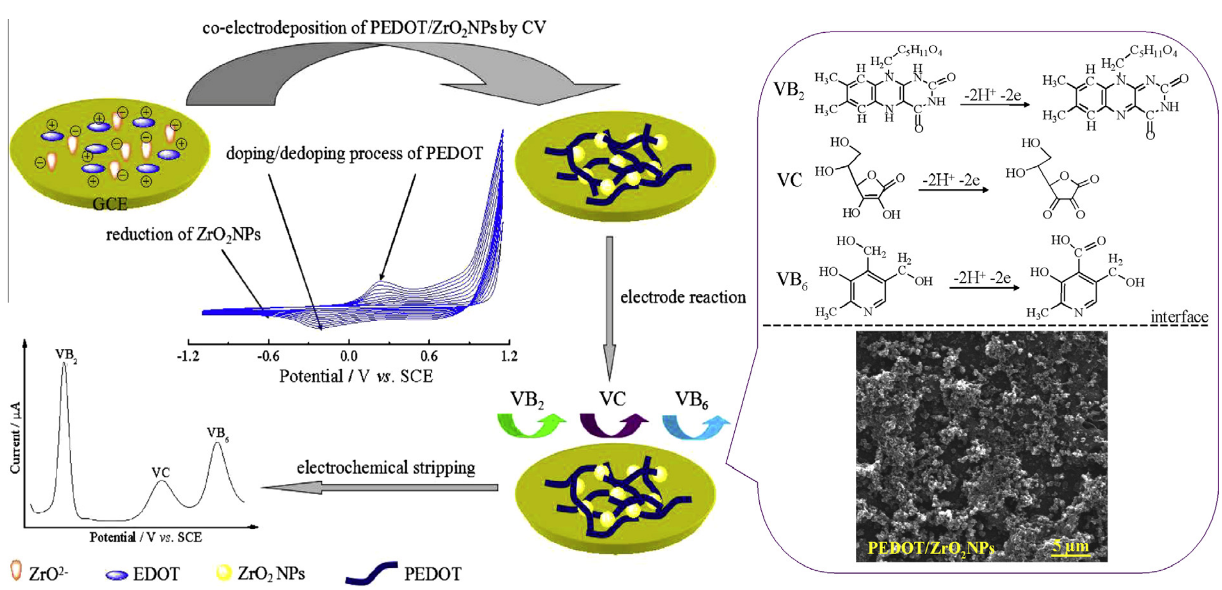
2. Experimental

2.1. Chemicals and reagents

3,4-Ethylenedioxythiophene (EDOT) was purchased from Sigma–Aldrich (USA). Zirconium oxychloride ($ZrOCl_2$), potassium chloride (KCl), potassium hexacyanoferrate ($K_3[Fe(CN)_6]$), Potassiun ferrocyanide ($K_4[Fe(CN)_6]$), disodium hydrogen phosphate dodecahydrate (Na_2HPO_4), and sodium dihydrogen phosphate dehydrate (NaH_2PO_4) were obtained from Sinopharm chemical reagent Co. Ltd. VB_2, VB_6 and VC were purchased from Bio Basic Inc. 0.05 M VB_2, 0.1 M VB_6 and 0.1 M VC stock solutions were prepared with redistilled water. All other reagents were of analytical grade, and redistilled water was used throughout the experiments.

2.2. Apparatus

Scanning electron microscopy (SEM) analysis was performed using a JSM-5600LV microscope (JEOL Ltd., Japan). The FTIR spectra were recorded on a Nexus 670 FTIR spectrophotometer (Nicolet Instruments) using a KBr disk at a resolution of 4 cm^{-1}. The UV/vis spectra were obtained using a Perkin-Elmer Lambda 900 ultraviolet–visible-near-infrared spectrophotometer (Germany). All



Scheme 1. Schematic illustration for the electrochemical synthesis of PEDOT/ZrO_2NPs by a facile one-step strategy and oxidation mechanism of VB_2, VB_6 and VC at PEDOT/ZrO_2NPs film.