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A highly-sensitive VB_2 electrochemical sensor based on one-step co-electrodeposited molecularly imprinted WS_2-PEDOT film supported on graphene oxide-SWCNTs nanocomposite

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ABSTRACT

A highly-sensitive electrochemical sensor based on single walled carbon nanotubes (SWCNTs) nanocomposite electro-catalyst supported molecularly imprinted poly(3,4-ethylenedioxythiophene) (PEDOT) film modified with two-dimensional layered tungsten sulfide (WS_2) nanosheet for the detection of vitamin B_2 (VB_2) was successfully developed. Molecularly imprinted WS_2-PEDOT film was prepared by the electrochemical *co*-polymerization of functional monomer 3,4-ethylenedioxythiophene in the presence of template molecule VB_2 and WS_2 nanosheet. SWCNTs nanocomposite modified electrode was obtained by drop-coating SWCNTs dispersion containing graphene oxide (GO) onto GCE surface. WS_2 was used for improving the denseness and smoothness in the morphology and structure of PEDOT. GO was employed for enhancing the electro-catalytic capacity of SWCNTs and the interaction with template molecule via functional groups. The imprinted sensor was characterized, and its performance and parameters were investigated and optimized using linear sweep voltammetry. Under optimized conditions, the prepared imprinted sensor displayed a good linear response to VB_2 in wide concentration ranges from 0.002 to 0.9 μM with a low detection limit of 0.7 nM, and successfully applied to electrochemically detect VB_2 in drug samples with good reproducibility, repeatability and storage stability. The new design for the facile fabrication of mimic electrode will open up a new horizon in the development of highly-sensitive biomimic/imprinted sensors.

1. Introduction

Vitamin B_2 (VB_2), also called riboflavin, is one of water soluble vitamins, which is widely present in food and pharmaceutical products. It has significant roles in our human body. But VB_2 cannot be synthesized through human body and need acquire from eggs, meats, liver, cheeses and tea, etc. Its insufficient will cause orogenital syndrome, eye lesions, skin disorders, and so on. Thus, it is imperative to develop a rapid, selective and high sensitive method for detecting trace amounts of VB_2 in foods and pharmaceuticals. Several researches were reported for the VB_2 determination in different matrices based on various analytical techniques, including high performance liquid chromatography, fluorescence, capillary electrophoresis and chemiluminescence. The electrochemical sensing techniques have attained extensive applications in pharmaceutical, biological, environmental and food analysis because of its high sensitivity, fast response, easy preparation, low cost and online detection [1, 2]. Therefore, electrochemical techniques for sensing VB_2 have been studied by many groups [3–9]. For example, Sá et al. fabricated bismuth-film electrode for voltammetric studies on VB_2 [4], Nezamzadeh-Ejhieh et al. reported the voltammetric determination of VB_2 using zeolite-modified carbon paste electrodes [5], and Mehmeti et al. voltammetrically detect VB_2 by manganese dioxide-modified carbon paste electrode [6]. We previously reported PEDOT electrochemical sensor that exhibited excellent performance for sensing VB_2 [8], but their selectivity was still needed to improve.

Molecularly imprinting technique has evoked increasing interest as a highly-effective way for improving the selectivity of electrochemical sensors and overcome the effect of environmental factors (e.g. organic solvents, acids, bases, and metal ions) toward biological activity and the lifetime of electrochemical biosensors [10, 11]. Molecular imprinted polymers (MIPs) has many advantages such as high affinity recognition sites for template molecules in comparison with non-molecularly imprinted polymers (NIPs), low cost, easy preparation and long lifetime relative to biomacromolecule like enzymes and antibody. Recently, molecularly imprinted electrochemical sensors, which combine with advantages of electrochemical techniques with MIPs, are a wide public

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concern over research areas [12, 13]. Nevertheless, it is known that the traditional molecularly imprinted electrochemical sensors only have the efficient recognition ability of immunosensors and are hard to possess the efficient catalytic ability of enzyme sensors Hence, it was imperative to design a novel imprinted sensor holding the excellent performance of enzyme sensors.

Conducting polymers (CPs) as MIPs have been paid very close attention toward the fabrication of highly-sensitive sensors owing to its good mechanical stability, high electrical conductivity, easy functionalization, good simple preparation and possibility of miniaturization [14–17]. Poly(3,4-ethylenedioxythiophene) (PEDOT), one of the most outstanding CPs, have been widely used for the fabrication of efficient bio/chemo-sensors [18–21]. We also successfully fabricated a simple molecularly imprinted electrochemical sensor based on the electro-synthesized imprinted PEDOT (MIPs-PEDOT) film in organic system for the voltammertric detection of vitamin K_3 detection, which exhibits high sensitivity and selectivity [22]. Nevertheless, we also found that the electrochemical sensor based on electro-synthesized PEDOT film in aqueous system easily form the homogeneous dense, compact structure and smooth morphology, which hinder the application of the MIPs-PEDOT film [23–25], the introduction of different materials could improve the structure and morphology of PEDOT film [8, 18–22, 25]. Moreover, many groups have built different composites served as electrode substrate to straightly improve properties of imprinted film based on CPs [26–30]. Especially nanomaterials incorporated MIPs exhibited extended lifetime up to several years, storage at adequate temperatures and are reusable with 200 times cheaper cost, Meanwhile, imprinted nanomaterials also improved the rebinding property, lowered mass transfer resistance and better accessibility of template toward the recognition site due to the small size and large surface area/volume ratio [31]. Furthermore, nanomaterials with enzyme-like characteristics (nanozymes) as next-generation new artificial enzymes are exploring to mimic different kinds of enzymes for the development of novel imprinted sensors [32, 33].

Carbon nanotubes (CNTs) as excellent electrocatalysts have attracted considerable attentions in electrochemical sensor due to extraordinary electrocatalytic activity and large surface area [34–37]. However, there is a water processibility about pure CNTs when it is used as electrode materials. CNTs are easy to precipitate because of van der Waals forces and π-π interactions, which result in some difficulties for electrode modification [38–42]. Graphene oxide (GO) with many oxygen-containing groups such as hydroxyl groups, carboxyl groups and epoxy groups, possesses large surface area and high electrocatalytic activity, which can effectively improve the water dispersibility and electrocatalytic ability of other modified materials and be beneficial to interact with other analytes [40–43]. More importantly, CNTs and GO are the most popular and wide use of carbon nanomaterials in the field of sensing due to unique characteristic properties. Hence, GO/CNTs nanocomposites possessing both of their advantages, have been extensively employed in the construction of electrochemical sensors, which exhibit excellent electrochemical sensing ability [40–42].

Tungsten sulfide (WS_2), a new two-dimensional (2D) layered graphene analogues, is an excellent graphene-like electronic nanomaterial beyond graphene due to lower defect density, higher carrier lifetime, faster hole mobility and direct bandgap [44–46]. Nowadays, WS_2 consisting of the metal W atom layers surrounded with a sandwich structure between two sulfur atom layers, has attracted fascinating attention for sensing and biosensing [47], In this work, WS_2 nanosheet was selected to improve the morphology structure and properties of the MIPs-PEDOT film, GO was employed for enhancing the electro-catalytic capacity of single-walled CNTs (SWCNTs) and the interaction with template molecule via functional groups. Then SWCNTs-GO modified GCE as electrode substrate was obtained by drop-coating SWCNTs dispersion containing GO, MIPs-PEDOT film was prepared on the surface of SWCNTs-GO modified glassy carbon electrode (GCE) by the electrochemical polymerization of functional monomer 3,4-ethylenedioxythiophene in the presence of template molecule VB_2 and WS_2 nanosheets. The imprinted sensor was characterized by linear sweep voltammetry (LSV), scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDS), and the anti-interference, reproducibility, repeatability and storage stability of the imprinted sensor had also been explored.

2. Experimental

2.1. Reagents

3,4-Ethylenedioxythiophene (EDOT) was bought from Sigma-Aldrich. WS_2 bulk powder, D-(+)-glucose, boric acid, phosphoric acid were purchased from Aladdin Chemistry co., Ltd. GO and ultra-high purity of SWCNTs dispersion (0.16 wt%) were purchased from Naijing Xianfeng Nanomaterials Technology co., Ltd. n-Butyllithium (1.6 M in hexanes), vitamin C (VC), vitamin B_1 (VB_1) and vitamin B_1 (VB_{12}) were attained from J&K Chemical Ltd. Hexane, uric acid (UA) and 4-acetaminophen were purchased from Shanghai Vita Chemical reagent co., Ltd. Lithium perchlorate ($LiClO_4$) was purchased from Xiya Reagent co., Ltd. Sodium hydroxide (NaOH) was bought from Beijing North Fine Chemicals co., Ltd. VB_2, vitamin B_3 (VB_3) and vitamin B_6 (VB_6) were purchased from Shanghai Blue Technology Development co., Ltd.

2.2. Apparatus

The electrochemical experiments were carried out using CHI660E electrochemical workstation (Shanghai Chenhua Instrument Company, China) with a three-electrode system in a conventional electrochemical cell at room temperature. The WS_2-MIPs/GO-SWCNTs/GCE was used as the working electrode, and saturated calomel electrode (SCE) was served as the reference electrode with a platinum sheet as the counter electrode. The pH of the buffer solution was measured with a portable pH meter CT-6023 pH. The supersonic treatment was conducted in GT-2120QTS 400 W (Guangzhou GT Ultrasonic co., Ltd). The SEM was performed with Hitachi S4800 (Japan). The chemical composition of the prepared nanocomposite was measured by EDS performed in SEM with EDAX Genesis (America).

2.3. Synthesis of GO-SWCNTs nanocomposite

4 milligrams GO was weighed and dissolved in 4 ml deionized water with ultrasonic 30 min. Then, 4 ml SWCNTs dispersion was added into 1 mg/ml GO dispersion and stirred 1 h. Finally, GO-SWCNTs nanocomposite was obtained after homogenous mixing.

2.4. Preparation of WS_2 nanosheets

The WS_2 nanosheets were prepared by lithium intercalation technique, including two steps, Li intercalation and exfoliation procedures, which is similar with the previous reports [48, 49]. In brief, 0.5 g of natural WS_2 bulk powder was added to 20 ml hexane containing 5 ml butyl lithium under N_2 atmosphere, the mixture was then heated up to 80 °C for 48 h. The resulting mixture was centrifuged to remove excess lithium and organic residues. Then, the intercalated WS_2 was immediately transferred into 250 ml deionized water following by sonication in a sonic bath for 1 h. After that, the dispersion was centrifuged 30 min, and the 2 mg/ml WS_2 supernatant was carefully collected for further use.

2.5. The fabrication processes of sensing electrode

Prior to the modification, the GCE was carefully polished with a leather containing 0.05 μm alumina slurry, and then ultrasonically cleaned in deionized water, ethanol absolute and deionized water each for 5 min, respectively. The fabrication processes of the WS_2-MIPs/GO-