The electrochemical performance of Self-doped polyaniline-Molybdenum disulfide nanocomposite for vitamin B2 determination

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Abstract: In this work, the self-doped polyaniline-molybdenum disulfide (SPAN-MoS2) nanocomposite with outstanding conductivity and synergistic electrochemical activity was prepared by the ultrasonic exfoliating method. In the ultrasonic process, the negatively charged SPAN served as an intercalator to result in few-layers MoS2 nanosheets exfoliated from bulk MoS2. The obtained SPAN-MoS2 nanocomposite owns large conjugated structure and rich negative charge because of the strong π-π* stacking interaction and electrostatic repulsion, which can enhance the adsorption of some conjugate structured and positively charged biomolecules, such as vitamin B2 (VB2). The results also displayed that the electrochemical responses were further affected by the mass ratio and the ultrasonication time.

Keywords: Self-doped polyaniline; Molybdenum disulfide; vitamin B2; Synergistic effect.

Introduction

Today, we attach great importance to environmental protection, emphasizing green materials, creating green furniture industries, the most important is the use of environmentally friendly materials. At the meantime, extensive attentions have been focused on some 2D nanomaterials¹, so the low-cost and environmentally friendly method was applied to prepare a kind of material for determination, which including the transition metal dichalogenides (e.g., MoS2, etc.) due to their 2D layer structure analogous to graphene. What is different from graphene is that MoS2 overcomes the shortcomings of the zero band gap of graphene. Owing to its inherent properties, it has attracted extensive attention in the electrochemical field. For example, the individual MoS2 modified electrode has been employed for the reduction of H2O2 with a low detection limit of 2.5 nmol/L.² And the electrochemical reduced MoS2 has been widely used for the determination of dopamine (DA) and ascorbic acid (AA). Besides, MoS2 has been integrated with other functional materials, such as polyaniline (PANI), self-doped polyaniline³,⁴ to construct novel nanocomposites for showing the synergistic effect to improve redox behaviors. MoS2/PANI nanowires can greatly improve Li⁺-storage properties owing to the hierarchical structure of MoS2/PANI and the PANI-hybrid structures have been investigated by Schmidt et al. and the optimal admixture (MoS2 66.7 %; PANI 33.1 %) exhibited a high charge capacity⁵. Wang et al. prepared PANI/MoS2 nanocomposite with a large contact surface area⁵, which could be further integrated with gold nanoparticles (AuNPs) for serving as a synergetic electrocatalyst to DA⁶.

As a kind of drug, in the process of production of vitamin B2, there will be resulting in environmental pollution more or less. To reduce the impact on the environment as much as possible, it is necessary to detect the amount of residue of VB2. And so far, many methods are supplied for VB2 determination. TLC-scanning determination, spectrophotometric method, high performance liquid chromatography, fluorescence spectroscopy are the traditional methods. But the special environment of detection and the more tedious process are required, such as treating with physical or chemical ways, which can limit the development of other methods. Peidong Xu et al. prepared a sensitive vitamin B2 electrochemical sensor based on molecularly

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imprinted nonconducting polymer of o-aminophenol by potentiosstat polymerization in the presence of vitamin B2 (VB2) on a glassy carbon electrode, the sensor exhibited good sensitivity, selectivity, and reproducibility to VB2 with the detection limit 2.3851 nmol/L. A self-assembled monolayer of l-cysteine was used for the determination of vitamin B29. Wenying Zhong et al. apply fluorescence resonance energy transfer quenching for determination of vitamin B210. However, the process is fussy and produces higher energy consumption. Meanwhile, more highlights are focused on the simultaneous determination of various vitamin B. The three-dimensional fluorescence spectra was used as the method to analysis VB1, VB2, and VB6 in B-vitamins complex tablets.11 The artificial neural networks and partial least squares regression were applied to UV spectral data for quantitative determination of thiamin hydrochloride (VB1), riboflavin phosphate (VB2), pyridoxine hydrochloride (VB6) and nicotinamide (VPP) in pharmaceutical samples12. A fast, versatile, cheap, and environmentally safe analytical method for quantifying VB2, VB3, VB6 and VB7 in Corn steep liquor (CSL) was developed13. The electrochemically synthesized electroactive species-doped PEDOT films with nanostructure were applied as electrochemical sensors for simultaneous determination of VB2, VB6 and VC14. Application of renewable silver amalgams annular band electrode to the voltammetric determination of vitamins C, B1, and B215. As a justified effective preparation method of two-dimensional nanosheets, liquid exfoliation has been widely adopted with the help of some surfactants and polymers through ultrasonication16-18.

Herein, SPAN was integrated with MoS2 to construct a specific structured and negatively charged nanocomposite through a simple and low-cost method by ultrasonication accompanying intercalation. The SPAN-MoS2 nanocomposite owning the special benzene ring structure and the negative charge endow it could easily be attached by some conjugate structured or positively charged biomolecules or aromatic molecules19. In this paper, SPAN-MoS2 nanocomposite was prepared, owning the conjugated benzene ring structure and positive charge and showing outstanding conductivity and synergistic electrocatalytic activity of constructed platform, for efficient detection of VB2.

Experimental section

The preparation of SPAN-MoS2 nanocomposite

0.01 g SPAN and 0.01 g MoS2 were mixed, and dispersed in ultrapure water, followed by ultrasonication for a certain time, and then a homogenous mixture of SPAN-MoS2 was formed. Changing the mass ratio between SPAN and MoS2 or the ultrasonication time, a series of SPAN-MoS2 hybrid materials were obtained. The ultrasonic process was carried out by KQ-50E signifier (Kunshan ultrasonic instruments Co., Ltd.), and the resulted composite was characterized through scanning electron microscopy (SEM) (JSM-6700F machine, JEOL, Tokyo, Japan) and transmission electron microscopy (TEM) micrographs (JEM 2100 transmission electron microscopy). SPAN was synthesized according to the ref20. Bulk molybdenum disulfide (MoS2, analytical pure) was provided from BASF Chemical Co, Ltd. (Tianjin, China).

The fabrication of the modified electrode

20 μL of the above mixture of SPAN-MoS2 was dropped on the bare carbon paste electrode (CPE), surface and dried in the air naturally. The CPE was prepared by the method reported by Yang21. The obtained electrode was named as SPAN-MoS2/CPE. Similarly, MoS2/CPE and SPAN/CPE were prepared. The next, we optimized a series of the condition and using the modified electrode for highly sensitive detection of vitamin B2.

Electrochemical measurements

The electrochemical measurements were carried out by Cyclic voltammetry (CV) and Differential pulse voltammetry (DPV), with a CHI 832 (Shanghai CH Instrument Company, China). A platinum wire was used as the auxiliary electrode, a saturated calomel electrode (SCE) was used as the reference electrode, and a carbon paste electrode (CPE) or modified electrode was used as the working electrode. All the supporting electrolyte in all experiments were B-R (pH 4.0) containing a certain amount of VB2.

In this process, the reported result for every electrode was the mean value of three parallel measurements.

Results and discussion

Characterization of the SPAN-MoS2 hybrid

The morphology and structure of nanocomposites are characterized by SEM and TEM, as shown in the Fig.1. The representative SEM and TEM images of MoS2, SPAN, and SPAN-MoS2 display an obviously layered structure. MoS2 flat layer could be observed in Fig.1A and 1B. Fig.1C and 1D reveal the net-like nanostructure of SPAN with the diameter of 70-90 nm and length of several micrometers. The fibrous and layered structure can be simultaneously observed for SPAN-MoS2 in Fig.1E, F, which demonstrated that the fibrous SPAN has successfully intercalated with the layered MoS2. This unique structure of the nanocomposites provides the continuous and multiple passageways for highly effective electron conduction and created a higher specific surface.
Figure 1. SEM images of the MoS₂ (A), SPAN (C), SPAN-MoS₂ (E) and TEM images of the MoS₂ (B), SPAN (D), SPAN-MoS₂ (F)

Electrochemical reduction behavior of VB₂

The electrochemical behaviors of 1.0×10⁻³ mol/L VB₂ at different modified electrodes were investigated in B-R (pH 4.0), which are shown in Fig. 2A. Compared with MoS₂/CPE (curve a) and SPAN/CPE (curve b), SPAN-MoS₂/CPE (curve c) displays a highest reduction peak current. This implied that SPAN-MoS₂ could promote the electron exchange between the electrode surface and the VB₂, which is ascribed to the special benzene ring structure and the negative charge of SPAN-MoS₂ could easily absorb some conjugate structured or positively charged VB₂ and show the synergistic effect. Furthermore, the mass ratio of the mixture can affect the electrochemical behavior of VB₂. Fig. 2B shows the reduction peak current of VB₂ being influenced by the hybrid materials with the different mass ratio from 1:1 to 1:5. From the results, we can discover that the current response of VB₂ at SPAN-MoS₂ (1:3)/CPE (curve c) is higher than the other modified electrodes. Therefore, the mass ratio of 1:3 was selected as the optimum for the subsequent experiments. In addition, the ultrasonication time and pH was optimized in Fig. S1. When the hybrids being ultrasonicated for 4 h and the pH is 4.0, it shows the best performance.
Detection of VB2 with different concentrations

Based on the optimum results above, the response of VB2 with different concentrations was detected. Fig. 3A shows the determination of a series of concentrations of VB2 with the range of 1~100 μmol/L. When the concentrations of VB2 increased, the peaks current increased (Fig. 3A). The relationship of DPVs and concentrations of 1~100 μmol/L are shown in Fig. 3A. The linear relationships between the reduction peak current values (Ip) and the concentrations of VB2 are displayed. In the concentrations range (1~100 μmol/L), the linear equation is Ip = 0.319C+2.348, (R²=0.9828) (Fig. 3B). The limit of detection (S/N = 3) is 3.5×10−7 mol/L.

![Figure 3](image)

**Figure 3.** (A) Representative DPVs for the determination of VB2 in B-Rat SPAN-MoS2 (1:3)/CPE with VB2 concentrations ranging from 1~100 µmol/L (B) Calibration plots of the reduced peak current versus different concentrations of VB2

Stability and reproducibility of the modified electrode

The most important factor on the practical application of the sensor is the stability and reproducibility. To confirm the long-term stability of the electrochemical sensor, the modified electrode was put off 15 days at room temperature. During the period, the modified electrode was used to test the same concentration of VB2. The analytical result did not show an obvious decline (relative standard deviation (RSD) ≤ 5%), which demonstrates that the electrodes had good stability. The reproducibility of the modified electrode was estimated by 1.0×10⁻³ mol/L VB2 with ten modified electrodes made by the same method, and the RSD was found to be 3.62% for reduction peak current of VB2. This indicated satisfying reproducibility of the fabrication protocol.

Conclusion

In summary, a simple and low-cost technique was applied to prepare SPAN-MoS2 nanocomposites in the paper. Through ultrasonication of the mixed dispersion of bulk MoS2 with SPAN co-existing, the negatively charged SPAN ceaselessly diffused and intercalated into the MoS2 layers to form a homogenous and three-dimensional interconnected structure. Compared with the sole MoS2 or SPAN, SPAN-MoS2 interface with the mass ratio of 1:3 (SPAN/MoS2) and ultrasonication time of 4h have the highest peak currents, displaying remarkable synergistic effect for the reduction of VB2. The developed sensing platform displays acceptable reproducibility, long-term stability, high sensitivity, and low detection limit, which shows a broad prospect for further application in biosensor and medicine fields.

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