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Electrochemical Sensor for Detection of Ascorbic Acid based on MoS_2-AuNPs Modified Glassy Carbon Electrode

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In this paper, molybdenum disulfide (MoS_2)-gold nanoparticles (AuNPs) composite nanomaterials were prepared by a one-step synthesis method and characterized by scanning electron microscopy (SEM). The electrochemical sensor based on MoS_2-AuNPs/GCE and the electrochemical behavior of ascorbic acid (AA) on the modified electrode was tested by cyclic voltammetry (CV) and Differential Pulse Voltammetry (DPV). The experimental results showed that in phosphate buffer solution, the final modified electrode had the good electrochemical catalytic ability for the oxidation of AA. The reaction of AA on the electrode surface was a surface adsorption control process. The DPV method showed a good linear relationship between the peak current and the concentration in the range of 7.1×10^{-4} ~ 2.77×10^{-3} mol/L. The linear equation was $i_p = 0.6628 + 4.2151c$, the linear regression coefficient R = 0.9925, and the detection limit was $2.1\text{x}10^{-6}$ mol/L (S/N = 3).

Keywords: molybdenum disulfide, gold nanoparticles, AA, CV, DPV

1. INTRODUCTION

AA, a water-soluble vitamin used to maintain normal life activities of the matrix [1], widely exists in drugs, food, and organisms, and is an indispensable substance for life in organisms [2]. And it can't be made by the body itself, which depends on its food and drug intake [3]. Insufficient AA content in the body is likely to cause scurvy, wound ulcers that are not easy to heal, low immunity, and other diseases. Excessive AA content in the body will cause stomach cramps [4]. Common methods for detecting AA content include the fluorescent agent method [5], capillary electrophoresis method [6], redox method [7], high -performance liquid chromatography method [8], and electrochemical method [9]. The electrochemical detection method has the characteristics of a smaller dosage, simple operation, fast analysis speed, and high detection sensitivity [10], so it is more commonly used for testing AA levels [11]. In recent years, the use of electrochemical methods to measure AA has gradually increased.

The structure of MoS_2 nanomaterials is similar to that of graphene-like materials [12] and has the characteristics of the large specific surface areas [13], excellent electrical conductivity, thermal conductivity, and controllable band gap [14]. MoS_2 nanomaterials are widely used in the research of electrode hydrogen storage, electron probe, coating, lubrication, supercapacitor [15], and optical devices.

Metal nanoparticles have the large specific surface areas, good biocompatibility [16], and can significantly improve the electron transfer rate and other properties. AuNPs has been widely used in electrochemical methods due to its simple synthesis and easy surface functionalization [17] and has the ability to improve the rate of electron transfer.

In this study, MoS_2-AuNPs/GCE was prepared by modifying them on the surface of the bare glassy carbon electrode by the drop coating method. The electrochemical behavior of AA on the electrode was detected by the CV method and DPV method. Also, a method for detecting AA was explored, which could be used to determine levels in food and drugs.

2. EXPERIMENTAL

2.1. Chemicals and Apparatus

Scanning electron microscope (S-3000N, Hitachi Japan Limited); CHI660A Electrochemical Workstation (Shanghai Chenhua Instrument Company); Three-electrode system for electrochemical measurement used bare glass carbon electrode (GCE) or modified electrode as a working electrode, saturated calomel electrode (SCE) as the reference electrode, platinum wire electrode as the auxiliary electrode.

Molybdenum disulfide, Polyvinylpyrrolidone, Chloroauric acid, Trisodium citrate, L (+) AA (iSinopharm Chemical Reagent Co., Ltd), other reagents were analytically pure. A mixed solution of NaH_2PO_4 and Na_2HPO_4 was used to prepare a 0.1 mol/L (pH 7.0) phosphate buffer solution (PBS), and the pH was adjusted with H_3PO_4 and NaOH; N_2 was deoxygenated and the experimental water was secondary distilled water. The methods used in this experiment were CV and DPV, among which the parameters used were scan rate, pH ,and AA concentration.

2.2. Preparation of MoS_2 nanosheets

According to the literature report [18], 0.2534 g MoS_2 reagent was weighed and dissolved in 10 mL of water/ethanol (1:1) solvent, so that the concentration reached 25 mg/mL. Then, 0.2013 g PVP (polyvinylpyrrolidone) and 1mL concentrated sulfuric acid were added to the mixed solution, which was reacted in an ice-water bath for 2 hours. The resulting mixture was centrifuged several times. Thus, MoS_2 nanosheets with a large specific surface areas could be prepared.

2.3. Preparation of MoS_2-AuNPs composite nanomaterials

A 100 mL solution of chloroauric acid with a mass fraction of 0.01% was added to the round-bottom flask [19], followed by a 1 mL 0.1 mg/mL mixed homogeneous mixture of MoS_2. The mixed solution was heated and stirred until the solution boils was brought to a boil. After continuous boiling for 2 minutes, 4 mL of trisodium citrate solution with a mass fraction of 1% was added to the boiling solution. After continuing the reaction for 10 minutes, heating was stopped and stirring continued. After the synthetic liquid was naturally cooled to room temperature, it was stored in a refrigerator for characterization and later use [19].

2.4. Preparation of MoS_2-AuNPs/GCE

The bare glassy carbon electrode required in the experiment was polished on the wetted Al_2O_3 powder to the mirror surface, cleaned with secondary distilled water, then the glassy carbon electrode was cleaned with an ultrasonic cleaner in absolute ethanol for about 50 seconds, placed in secondary water for 5 seconds, and finally washed with secondary distilled water. Next, the bare glassy carbon electrode was dried on the surface at room temperature. 10μL of the mixed solution of the ultrasonically dispersed MoS_2-AuNPs composite nanomaterials was absorbed by a microinjector and dropped onto the surface of the bare glassy carbon electrode. Finally, MoS_2-AuNPs/GCE was obtained by air drying at room temperature.

3. RESULT AND DISCUSSION

3.1 SEM characterization of MoS_2-AuNPs composite nanomaterials

The MoS_2 nano and MoS_2-AuNPs composite nanomaterials were characterized by scanning electron microscopy. It can be seen from Figure. 1(A) that the MoS_2 nanomaterials had a large specific surface area, and Figure. 1(B) clearly showed the structure of MoS_2-AuNPs composite materials. AuNPs adsorb on the surface of MoS_2 nanomaterials. This unique structure illustrated that it can be applied electrochemically.

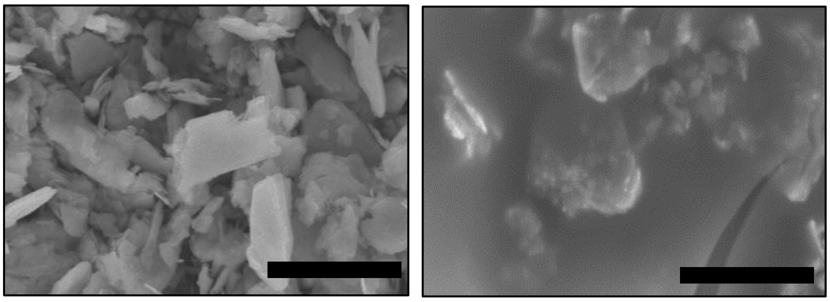

Figure 1. (A) SEM image of MoS_2 , (B) MoS_2-AuNPs. Scale bar: 10 μm.

3.2 Electrochemical behaviors of AA

Figure. 2 was a cyclic voltammogram of AA at a concentration of 0.1 mol/L at different electrodes (a) bare glassy carbon electrode, (b) AuNPs modified electrode, (c) MoS_2 nanomodified electrode, (d) MoS_2-AuNPs/GCE in PBS buffer solution with pH=7.0 at 14 mL. Figure. 2(a) showed that the oxidation peak of AA can hardly be seen in the bare glassy carbon electrode. However, from the curves of Figure. 2 (b) and (c), it was clear that there was a relatively obvious oxidation peak on the glassy carbon electrode modified with AuNPs and MoS_2 nanosheets, respectively, but the position and size of the peak were different. This indicated that the difference of catalytic effect in AA was caused by the different properties of AuNPs and MoS_2 nanosheets. From Figure. 2(d), it can be seen that the oxidation peak effect of AA was better and the oxidation peak potential was negatively shifted, and the peak current effect was strengthened on the MoS_2-AuNPs/GCE. It was indicated that when the composite modified electrode was used, the catalytic effect of the combination of MoS_2 nanometer and AuNPs on AA would reach the best state. This may be due to the ability of MoS_2-AuNPs composite materials to expand the effective contact area on the electrode surface. Thus, the ability of MoS2-AuNPs composite to expand the effective contact area on the electrode surface was studied. This was consistent with the point mentioned in the article "Sensitive and fast analysis of terbutaline sulfate in food using a modified electrode based on a MoS_2-AuNPs nanocomposite." [20]

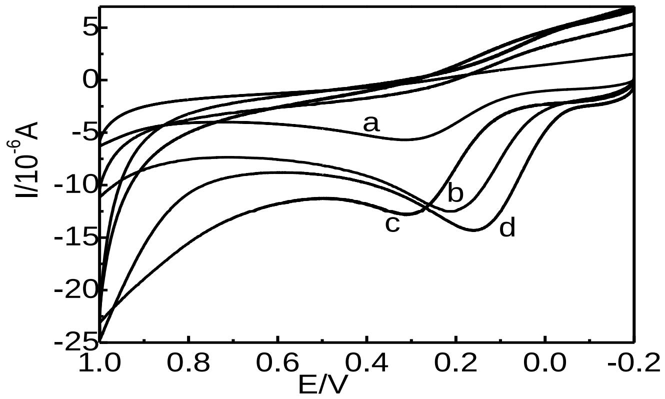

Figure 2. CVs of AA at different electrodes (PBS: pH = 7.0, Scan rate: 0.10V/s, AA concentration: 0.1mol/L) (a-bare glassy carbon electrode, b-AuNPs modified electrode, c-MoS_2 modified electrode, d- MoS_2-AuNPs/GCE)

3.3 Effect of scan rate

CV method was used to examine the effect of changes in scan rate on the electrochemical behavior of AA. The CV curves of the MoS_2-AuNPs/GCE in AA were obtained in the scan rate range of 0.05-0.25 V/s. It can be seen from Figure. 3 that within the scan rate range of 0.05-0.25 V/s, the scan rate increased, and the oxidation peak potential gradually shifted forward. Figure. 3 showed that the scanning rate increased and the oxidation peak current increased in the range of 0.05-0.25 V/s. The oxidation peak current and scan rate showed a good linear relationship within the measured range, this result was similar to that reported by Lin's team.[21] The linear equation between peak current and scan rate was $i_p\,(A) = -1.9318-24.68\ v$, and the correlation coefficient R = 0.9955, indicating that the reaction was a surface adsorption control process.

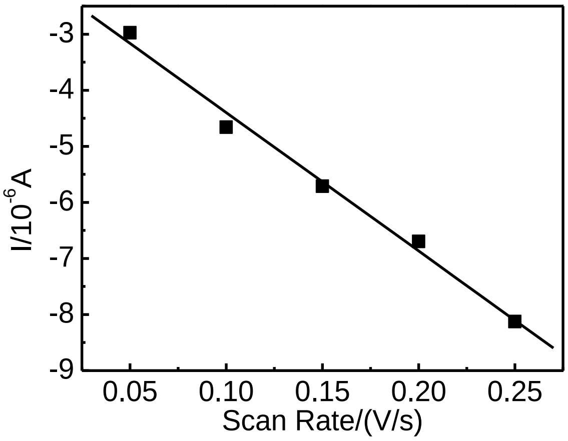

Figure 3. linear relationship between scan rate and peak current

3.4 Choice pH

The pH value of the solution was an important influencing factor in electrochemical detection, so it was necessary to optimize the pH value in the process of electrochemical detection. In this experiment, we studied the effect of solution pH on the electrochemical reaction of AA by the CV method. Figure. 4 showed the relationship between peak current and pH in the pH range of 5.0~8.0. It can be seen from Figure. 4 that the pH value of solution increased and the oxidation peak current increased first and then decreased. And when pH = 7.0, the current of the oxidation peak was largest, which was consistent with the actual pH value of the human body. Therefore, in this experiment, the PBS buffer solution with pH = 7.0 was used as the base solution for the experiment.

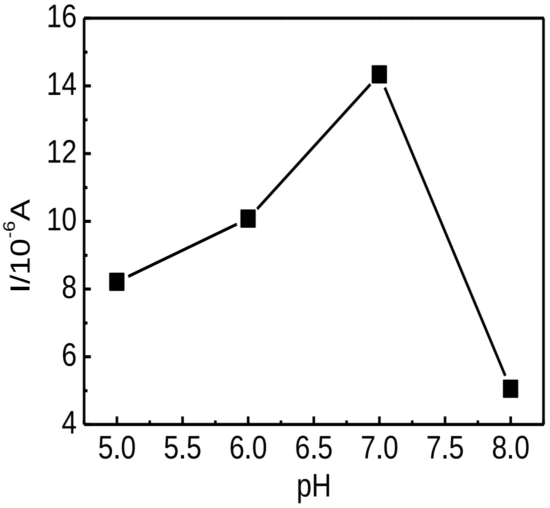

Figure 4. Linear relationship between pH and oxidation peak current

3.5 Working curve and detection limit

In order to better explore the detection limit of the modified electrode for AA, we used the MoS_2-

AuNPs/GCE as the working electrode under the optimal experimental conditions. The relationship between the oxidation peak current of AA and its concentration was determined by the DPV method. Figure. 5 showed the relationship between the oxidation peak current and the concentration of AA in the range of 7.1×10-4-2.77×10-3 mol/L. It can be seen from Figure. 5 that the peak current effect of the oxidation peak was also significantly enhanced with the increase of AA concentration.

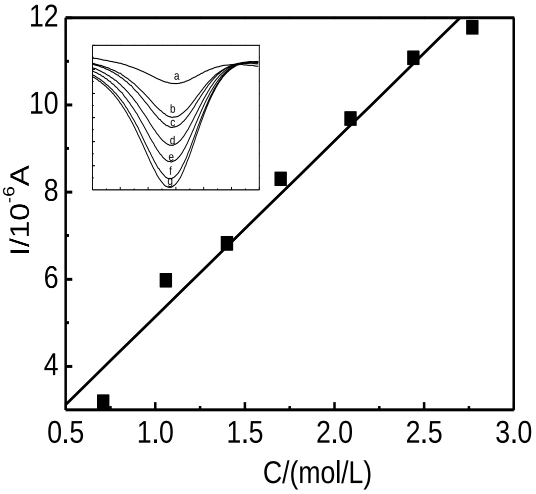

Figure 5. DPVs of AA at different concentrations on MoS_2-AuNPs/GCE, Inset: Relationship between AA and peak current at different concentrations. (PBS:pH=7.0, AA concentrations : a-7.1×10^{-4}mol/L, b-1.06×10^{-3}mol/L, c-1.4×10^{-3}mol/L, d-1.7×10^{-3}mol/L, e-2.09×10^{-3}mol/L, f-2.44×10^{-3}mol/L, g-2.77×10^{-3}mol/L)

The linear regression equation between the oxidation peak current and AA concentration was $i_p = 1.1043 + 4.0339c$, the linear regression coefficient R = 0.9875, and the detection limit of 2.1×10^{-6} mol/L (S/N = 3), showing a good first-order linear relationship. As we can see from the inset of Figure 5 , when the concentration of AA changed, the change of oxidation peak potential of MoS_2-AuNPs/GCE was not obvious, but the change of oxidation peak current was very obvious.The method could also be used to detect the content of AA in vitamin C tablets.

Table 1. Comparison of linear range and detection limit between this paper and published articles

modified electrode	Linear range (μM)	Detection limit (μM)	references
Poly(eriochromeblackT)/GCE	150~1000	10	[22]
CILE	50~7400	20	[23]
AuNPs-β-CD-Gra/GCE	30~2000	10	[24]
MoS_2-AuNPs	710~2770	2.1	This article

3.6 Sample Analysis of Vitamin C Tablets

A piece of vitamin C tablets was ground with a mortar and poured into a beaker. 15 mL solution was prepared by dissolving it with water. The relationship between the concentration of vitamin C tablets and the peak current was determined by the DPV method in PBS buffer solution with pH = 7. The results showed that the content of AA in the tablets was 99.25 mg, and the relative standard deviation (RSD) was 7.5%, which was similar to the content in the instruction.

Table 2. The result of Sample Analysis of Vitamin C Tablets

Sample	AA concentrations（mg）	RSD
Vitamin C	99.25	7.5%

3.7 Stability and reproducibility

Three MoS_2-AuNPs/GCE were prepared as parallel electrodes. The electrode was placed at room temperature for five days and the ascorbic acid of the same concentration was measured. The peak oxidation current was 94.9% of the initial current. The experiment confirmed that the composite electrode had good stability. The relative standard deviation (RSD) of the oxidation peak current of three composite electrodes was 3.4% when ascorbic acid was measured under optimized conditions. The experimental results showed that the composite electrode has good reproducibility.

4. CONCLUSION

In this paper, the electrochemical sensor of AA on MoS_2-AuNPs/GCE was prepared by dropping the coating method. The study showed that the electrode has good electrocatalytic performance and good stability and reproducibility to AA, and can successfully determine AA. This study can provide a method for the detection of AA in the food and drug fields. Therefore, the composite electrode has a good application prospect in the analysis and detection of ascorbic acid.

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