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Electrocatalytic determination of chloramphenicol based on molybdenum disulfide nanosheets and self-doped polyaniline



Ruirui Yang, Jinlong Zhao, Meijing Chen, Tao Yang*, Shizhong Luo, Kui Jiao

State Key Laboratory Base of Eco-chemical Engineering, College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, China

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ABSTRACT

In this paper, a novel molybdenum disulfide (MoS_2) intercalated by self-doped polyaniline (SPAN) via ultrasonic exfoliating method was prepared to show outstanding conductivity and synergistic electrocatalytic activity using chloramphenicol (CAP) as a case. In the ultrasonic process, due to the strong π - π^* stacking interaction and electrostatic repulsion, the negatively charged SPAN served as an intercalator to result in few-layers MoS_2 nanosheets, which were exfoliated from bulk MoS_2 . This nanocomposite was characterized by scanning electron microscopy, transmission electron microscopy and differential pulse voltammetry. The obtained nanocomposite owns large conjugated structure and rich negative charge, which can improve the adsorption of conjugate structured CAP with the detection range from 0.1 to $1000 \mu\text{mol L}^{-1}$. The results also showed that the electrocatalytic responses were further affected by the mass ratio of SPAN- MoS_2 and the ultrasonication time. Our electrocatalytic platform could be further applied in the adsorption and detection of other positively charged biomolecules or aromatic molecules.

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1. Introduction

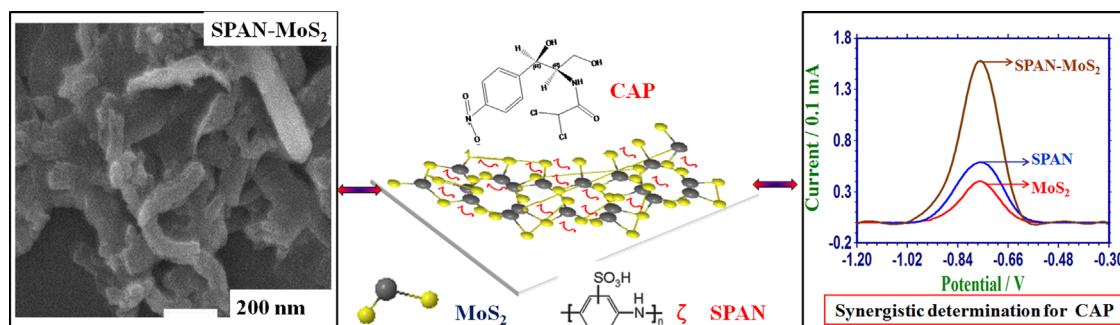
Molybdenum disulfide (MoS_2) nanosheet is a two-dimensional layered material similar to graphene [1]. Owing to its inherent properties, which overcome the shortcomings of the zero band gap of graphene [2,3], it has attracted extensive attention in electrochemical field. For example, the individual MoS_2 modified electrode has been employed for the reduction of H_2O_2 with a low detection limit of 2.5 nmol L^{-1} [4]. Moreover, the electrochemical reduced MoS_2 has been widely used for the determination of dopamine (DA) and ascorbic acid (AA) [5]. Besides, MoS_2 has been integrated with other functional materials, such as polyaniline (PANI), to construct novel nanocomposites showing obviously synergistic effect. MoS_2/PANI nanowires could greatly improve Li^+ -storage properties owing to the hierarchical structure of MoS_2/PANI . The optimal ratio of mixture (MoS_2 66.7%: PANI 33.1%) exhibited an excellent charge capacity [6]. Huang et al. prepared PANI/ MoS_2 nanocomposite with a larger contact surface area, which provided a direct and fast electron path and presented synergistic effect for improving electrochemical performance [7]. Additionally, this PANI/ MoS_2 nanocomposite could be further integrated with gold nanoparticles (AuNPs) to show a synergistic electrocatalytic oxidation to DA in the linear range from 1 to $500 \mu\text{mol L}^{-1}$ with the low detection limit of $0.1 \mu\text{mol L}^{-1}$ ($S/N=3$) [8].

Chloramphenicol (CAP) is a broad-spectrum antibiotic [9]. So far, the methods for determination of CAP mainly include high performance liquid chromatography method [10–12], chemiluminescence method [13], gas chromatography-mass spectrometry [14], surface plasmon resonance biosensor [15], and so on. However, these methods usually required expensive equipments and time-consuming extraction. In contrast, electrochemical method offers the advantages of low cost, simplicity, and relatively short analysis time, which was widely applied for the determination of CAP [16–18]. For example, Xiao et al. investigated the sensitive voltammetric determination of CAP based on single-wall carbon nanotube-gold nanoparticle-ionic liquid composite film modified glassy carbon electrodes [19]. Molecularily imprinted polymer also showed very high CAP recognition ability via differential pulse voltammetry (DPV) [20]. More recently, nitrogen-doped graphene nanosheets (N-G) decorated with AuNPs (Au/N-G) has been used for the electrochemical detection of CAP via the synergistic effect of two nanomaterials [21]. However, MoS_2 nanosheets have not been developed for the electrocatalytic detection of CAP so far.

As a confirmed effective preparation method of two-dimensional nanosheets, liquid exfoliation has been widely adopted with the help of some surfactants and polymers through ultrasonication [1,22,23]. Herein, for the first time, self-doped polyaniline (SPAN) was intercalated into bulk MoS_2 through a simple and low-cost method via ultrasonication to realize liquid exfoliation of bulk MoS_2 . The nanocomposite owns the benzene ring structure and the negative charge, which endow it could easily adsorb some conjugate structured or positively charged biomolecules or molecules [24], here,

* Corresponding author. Tel.: +86 532 84022858; fax: +86 532 84023927.

E-mail address: taoyang@qust.edu.cn (T. Yang).



Scheme 1. MoS₂ nanosheets enhanced by SPAN for synergistic determination of CAP.

CAP as a case. To our best knowledge, MoS₂ was first adopted for the electrochemical determination of CAP, which showed outstanding conductivity and synergistic electrocatalytic activity (Scheme 1).

2. Experimental

2.1. Apparatus and reagents

Electrochemical measurements were carried out with a CHI 660C (Shanghai CH Instrument Company, China). A platinum wire was used as 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. The ultrasonic process was carried out by KQ-500B sonifier (500 W, Kunshan ultrasonic instruments Co., Ltd.), and the pH values were measured via a model PHS-25 digital acidometer (Shanghai Leici Factory, China). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) measurements were carried out on a JSM-6700F scanning electron microscope (Japan Electron Company) and JEM 2100 transmission electron microscope, respectively.

Bulk molybdenum disulfide (MoS₂, ≥ 99.0%, Tianjin BASF Chemical Co., Ltd.). Aniline (Tianjin Da Mao Chemical Factory). *m*-Aminobenzenesulfonic acid (ABSA, purity > 98.0%, Fluka, USA). Cetyltrimethyl ammonium bromide (CTAB, Tianjin Bodi Chemical Co., Ltd.). Chloramphenicol (C₁₁H₁₂N₂Cl₂O₅, Shanghai Bioengineering Co., Ltd., China). The chloramphenicol (CAP) reserving solution was prepared by dissolving it into a certain amount of ethanol solution. All the other chemicals were analytical grade and all aqueous solutions were prepared with Aquapro ultrapure water (resistivity: 18 MΩ, Aquaplast AWL-1002-P, Ever Young Enterprises Development Co., Ltd., China).

2.2. The fabrication of CPE and the modified electrodes

The CPE was fabricated by mixing graphite powder with solid paraffin at a ratio of 3/1 (w/w) in a mortar. Then it was heated at 72 °C, agitated and grounded using pestle for 5–6 times. Following, the homogeneous paste was packed firmly into one end of a glass tube (the diameter was about 4 mm), simultaneously inserting a copper wire to the paste in the inner hole of the tube as electrical contact [25,26]. SPAN was synthesized according to Ref. [27]. Detailed process is described as follows: First, a certain quality of aniline, ABSA, and CTAB were dissolved in 40 mL, 0.15 mol L⁻¹ HCl, then 20 mL, 0.06 mol L⁻¹ ammonium persulfate solution (APS) was added. In succession, it was put in refrigerator at 5 °C for 24 h. Finally, a puce flocculent precipitate was obtained and filtered, and then dried in the air naturally. Thus, SPAN was obtained. Later, 0.01 g SPAN and 0.01 g MoS₂ were mixed, dispersed in ultrapure water, followed by ultrasonication for a certain time, and then a

homogenous mixture of SPAN–MoS₂ was formed. For comparison, the MoS₂ nanosheets were obtained by mixing with ultrapure water with a concentration of 1.0 g L⁻¹ just without SPAN existing, and then ultrasonicated for a given time to form the dispersion solution. Changing the mass ratio between SPAN and MoS₂ or the ultrasonication time, a series of SPAN–MoS₂ hybrid materials can be acquired. 20 μL of the mixed liquor was dripped on the bare CPE surface and dried in the air naturally. The obtained electrode was named as SPAN–MoS₂/CPE. Similarly, MoS₂/CPE and SPAN/CPE were prepared. A refresh electrode surface was rapidly generated through extruding a small plug of the paste with a stainless steel rod and then polishing the obtained surface on a white paper [25] ready for next-step modification.

2.3. Electrochemical measurements

Cyclic voltammetry (CV) measurements were carried out in 1.0 mmol L⁻¹ [Fe(CN)₆]^{3-/4-} (1:1) containing 0.1 mol L⁻¹ KCl with the potential scanning range from 0.6 V to –0.3 V at a scan rate of 0.1 V s⁻¹.

DPV: The pulse amplitude, pulse width, and pulse period were set as 0.05 V, 0.06 s, and 0.2 s. Scan range from –0.3 V to –1.2 V. Unless especially noted, all the supporting electrolyte all experiments were PBS (pH 7.0) containing a certain amount of CAP.

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

3. Result and discussion

3.1. Characterization of the SPAN–MoS₂ hybrid

The representative SEM and TEM images of MoS₂, SPAN, and SPAN–MoS₂ are displayed in Fig. 1. The SEM image of MoS₂ (Fig. 1A) displays an obviously layered structure, which can be further proved by the typical TEM image, showing multilayer nanosheets (Fig. 1B). From Fig. 1C, the SPAN nanofibers are interconnected together to form almost uniform netlike nanostructures with 65–85 nm in diameter. The TEM image of SPAN (Fig. 1D) further clearly displays the net-like nanostructure of SPAN nanofibers. Compared with the sole MoS₂ (Fig. 1A and B) or SPAN (Fig. 1C and D), fibrous and layered structure can be simultaneously observed for SPAN–MoS₂ in Fig. 1E, showing that the fibrous SPAN has successfully integrated with the layered MoS₂. Moreover, the intercalation of SPAN and MoS₂ can also be confirmed by the TEM image (Fig. 1F), where the SPAN nanofibers are coated by transparent MoS₂. In the process of intercalation, MoS₂ can serve as backbone to maintain the nanowired network structure. The π–π* interaction between SPAN and MoS₂ promotes the intercalation without damage their original properties.

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