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# Flower-like $Fe_2O_3$@$MoS_2$ nanocomposite decorated glassy carbon electrode for the determination of nitrite

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ABSTRACT

A novel ferric oxide/molybdenum sulfide ($Fe_2O_3$@$MoS_2$) modified glassy carbon electrode (GCE) was fabricated by drop casting $Fe_2O_3$@$MoS_2$ and Nafion suspension onto the surface of GCE. Scanning electron microscopy (SEM) image indicates the $Fe_2O_3$@$MoS_2$ has a flower-like nanostructure. Both cyclic voltammetry (CV) and linear sweep voltammetry (LSV) results show the $Fe_2O_3$@$MoS_2$ modified GCE exhibits excellent electrochemical activity in a 0.1 M phosphate buffered saline (PBS) compared to the $Fe_2O_3$ and $MoS_2$ modified GCE. CV results also show the $Fe_2O_3$@$MoS_2$ has excellent electrocatalytic behavior to nitrite in a pH 4.0 PBS. The amperometric response result indicates the $Fe_2O_3$@$MoS_2$ modified GCE can be used to determine nitrite concentration in a wide linear range of 2.0 and 6730 μM with a detection limit of 1.0 μM.



## 1. Introduction

Nitrite, widely used in our daily life as food additive, fertilizing agents and corrosion inhibitor, is recognized as an alarming pollutant to the environment and human health [1]. The excessive ingestion of nitrites via the dietary intake has potential toxic and carcinogenic effects [2]. The World Health Organization (WHO) has reported that the fatal dose of nitrite ingestion is between 8.7 μM and 28.3 μM depending on body weight [3]. Therefore, accurate, rapid, and economical determination of nitrite has attracted much attention. The electrochemical approach is considered to be an environmentally friendly method because no additional chemical loading is required. Besides, the electrochemical techniques are rapid, highly selective and sensitive.

Generally, the electrochemical methods are based on either oxidation or reduction of nitrite at different electrodes. Nanomaterials, including oxides [4,5], graphene [2,6], noble metals [2,6–8] and conducting polymer-based composites [9] have been exploited as active electrocatalysts for nitrite detection. Although the electrochemical determination of nitrite has got the successful development, an electrochemical sensor with better properties, such as easy manufacture, low price, wider operational potential window, renewable surface, and environmentally friendly, is still a challenge.

α-Iron oxide (α-$Fe_2O_3$) nanostructured materials have long been of scientific and technological interest due to their magnetic properties, low toxicity, and biocompatibility in physiological environments [10–12]. It has been used in various fields, such as magnetic resonance imaging (MRI), magnetically assisted drug delivery, anode material, wave adsorption and information storage [12–15]. Recently, $Fe_2O_3$ was tentatively explored as an electrocatalyst and found potential activity toward glucose [16], hydrogen peroxide [17], and reduced nicotinamide cofactors [18]. As we know, 2D or 3D superstructure will provide more surface areas and active reaction sites. Therefore, 2D or 3D structure has been receiving increasing interest [19–21]. Various 3D α-$Fe_2O_3$ structures, such as flower-like [22], chestnut-like [13] and urchin-like [14], have been successfully synthesized via different methods. However, 2D/3D α-$Fe_2O_3$ nanostructured materials based sensors are still challenge.

$MoS_2$, with a 2D layered structure, has attracted much attention in photocatalysis [23], lithium ion batteries [24] and optoelectronic devices [25] due to its excellent electronic and optical properties. Recent researches show that $MoS_2$ is an exciting Hydrogen evolution reaction (HER) catalyst that exhibits promising HER activity in crystalline or amorphous materials and molecular mimics [26–28]. However, to the best of our knowledge no $MoS_2$ composite modified glassy carbon electrodes (GCEs) have yet been reported for nitrite determination. Herein, we fabricated a novel flower-like

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$Fe_2O_3$@$MoS_2$ modified GCE; the $Fe_2O_3$@$MoS_2$ nanocomposite has excellent electrochemical activity in a pH 4.0 PBS and enhanced electrocatalytic performance on nitrite oxidation.

## 2. Experimental

### 2.1. Synthesis of composite material

#### 2.1.1. Synthesis of flower-like $Fe_2O_3$

All the reagents were of analytical grade and used as received without further treatment. $Fe_2O_3$ was prepared via a hydrothermal method as reported previously [21]. To prepare $Fe_2O_3$ catalyst, solutions 1 and 2 were prepared by dissolving 8 mmol $FeSO_4{\cdot}7H_2O$ and 1.6 mmol $NaClO_3$ in 15 mL and 16 mL deionized water, respectively. Next, Solution 2 was added dropwise into Solution 1 under magnetic stir until a primrose yellow transparent solution was obtained (Solution 3). Solution 3 was then transferred into a Teflon-lined autoclave and maintained at 180 °C for 12 h. After cooling to room temperature naturally, the precipitates were collected by powerful magnet, thoroughly washed with ultrapure water and ethanol three times each, and dried in an oven at 60 °C for 10 h.

#### 2.1.2. Synthesis of $MoS_2$ and $Fe_2O_3$@$MoS_2$

In a typical synthesis of $Fe_2O_3$@$MoS_2$, 1 mmol of $Na_2MoO_4{\cdot}2H_2O$ and 5 mmol of thiourea were dissolved in 60 mL of distilled water, and then 0.5 g of the prepared $Fe_2O_3$ were added into the solution. Next, the homogeneous solution was transferred into a 100 mL Teflon-lined autoclave and held at 200 °C for 20 h. After that, the black precipitate was collected by centrifugation, washed three times with distilled water and ethanol, and then dried in an oven at 80 °C for 12 h. As a control experiment, $MoS_2$ nanosheets were prepared under the same conditions without adding $Fe_2O_3$.

### 2.2. Preparation of $Fe_2O_3$, $MoS_2$ and $Fe_2O_3$@$MoS_2$ nanocomposite modified electrode

Prior to modification, a glassy carbon electrode (GCE) was polished with alumina slurry of 0.5 μM on polishing cloth with water and then thoroughly rinsed with water and sonicated in a DI water bath for 10 min before use. For preparation of $Fe_2O_3$, $MoS_2$ and flower-like $Fe_2O_3$@$MoS_2$ modified electrodes, 4 mg samples and 80 μL Nafion (5 wt%) were dispersed in 0.8 mL DI water and 0.2 mL ethanol by ultrasonication for 30 min to obtain a homogeneous suspension (4.0 mg $mL^{-1}$). Then, certain amount of the suspension was dropped onto the surface of GCE and dried at room temperature.

### 2.3. Electrochemical properties

All electrochemical experiments were performed in the electrolytic cell consisted of a glassy carbon (GC) or a modified GC working electrode (3 mm diameter, CHI), a platinum wire counter electrode and a saturated calomel reference electrode (SCE) on a Model CHI 660 E electrochemical workstation. All potentials were referred to a SCE. The pH values of the solutions were determined with a PHS-3 C pH meter.

### 2.4. Characterization

Fourier transform infrared spectroscopy (FT-IR) spectra of the samples were measured on a Cary 610/670 microscope (Varian, US). Scanning electron microscopy (SEM) was examined on a field-emission scanning electron microanalyzer (Hitachi S-4800, Japan). The electron spin resonance (ESR) measurements were carried out using a Bruker A300 spectrometer operated in X-band (9.863 GHz). X-ray photoelectron spectroscopy (XPS) measurements were carried out with an ESCALAB 250 Xi photoelectron spectrometer using Al Kα radiation (Thermo-Fisher Scientific, US).

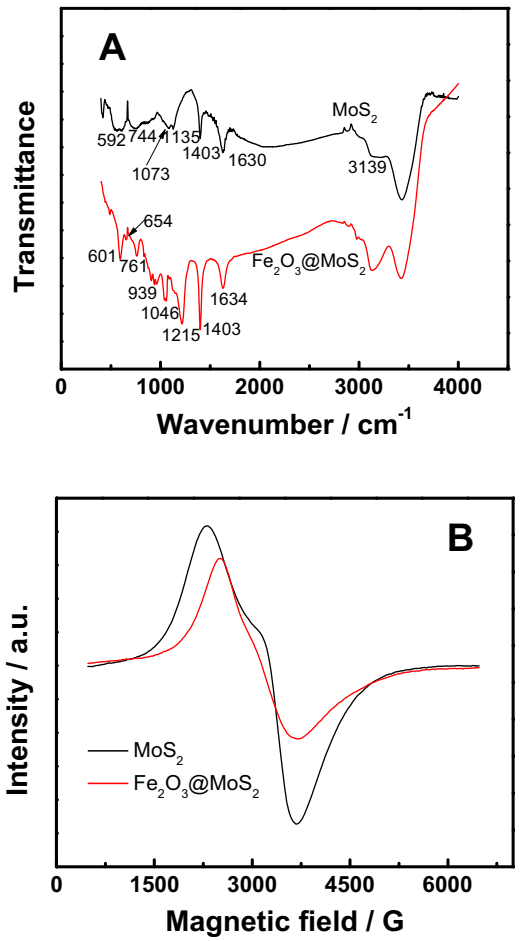


**Fig. 1.** (A) FTIR and (B) ESR spectra of $MoS_2$ and $Fe_2O_3$@$MoS_2$.

## 3. Results and discussion

### 3.1. FT-IR and ESR spectra of $MoS_2$ and $Fe_2O_3$@$MoS_2$

The FT-IR spectra of $MoS_2$ and $Fe_2O_3$@$MoS_2$ composite are shown in Fig. 1A. The peaks appear at about 3139 and 1403 $cm^{-1}$ correspond to the stretching vibration and in-plane bending vibration of O–H, respectively [29]. The bands at about 1630 and 600 $cm^{-1}$ are attributed to the in-plane bending vibration of $OH^-$ group and $\gamma_{as}$ Mo-S vibration, respectively [7,29]. In the spectrum of $Fe_2O_3$@$MoS_2$, new peaks observed at 939, 654 and 601 $cm^{-1}$ are assigned to $\gamma_{as}$ Mo-O vibrations, out of plane bending vibration of $OH^-$ group and stretching vibration of Fe-O, respectively [7,29]. For the ESR measurements, 0.042 g sample was weighed. As can be seen in Fig. 1B, each spectral line consists of a symmetric signal. The value of the peak-to-peak line width $\Delta H_{pp}$ of $MoS_2$ is larger than that of $Fe_2O_3$@$MoS_2$. It was reported that the broadening of $\Delta H_{pp}$ indicated a decrease in the unpaired spin density [9]. Thus, the unpaired spin density of $Fe_2O_3$@$MoS_2$ is higher than that of $MoS_2$. Based on this result, it is expected that the $Fe_2O_3$@$MoS_2$ composite would result in better electrocatalytic performance than that of bare $MoS_2$.