



# Ni-doped molybdenum disulfide nanoparticles anchored on reduced graphene oxide as novel electroactive material for a non-enzymatic glucose sensor



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## ARTICLE INFO

### Article history:

Received 16 August 2016  
Received in revised form  
15 December 2016  
Accepted 23 December 2016  
Available online 29 December 2016

### Keywords:

Ni-MoS<sub>2</sub>/rGO composites  
Deposition-precipitation  
Diffusion coefficient  
Catalytic rate constants  
Non-enzymatic glucose sensor

## ABSTRACT

In the present paper, Ni-doped molybdenum disulfide nanoparticles/reduced graphene oxide (Ni-MoS<sub>2</sub>/rGO) composites have been synthesized with a facile, effective and simple strategy by using a deposition-precipitation method and followed calcining under N<sub>2</sub> flow. The as-prepared composites were characterized via X-ray diffraction (XRD), Raman spectrum, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and electrochemical methods. The results reveal that the Ni-MoS<sub>2</sub>/rGO composite could own highly exposed catalytic sites, favorable conductivity, and excellent electron transport rates due to the large specific surface area and electrical conduction efficiency of rGO, as supporter. It is precisely because of these advantages that result in the excellent electrocatalytic oxidation performance of the Ni-MoS<sub>2</sub>/rGO composite to glucose. Subsequently, electrochemical measurements indicate that the optimized Ni-MoS<sub>2</sub>/rGO catalyst processed a rapid response time within 2 s, wide linear range of 0.005–8.2 mM, good reproducibility and ideal stability. In addition, the results of kinetic studies show that this modified electrode possesses large diffusion coefficient ( $D = 1.83 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$ ) and catalytic rate constants ( $K_{cat} = 6.26 \times 10^5 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ). Above all, the Ni-MoS<sub>2</sub>/rGO composites appear to be a promising catalyst for non-enzymatic glucose sensor.

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## 1. Introduction

Graphene, as an important part of these advanced carbon nano-materials, is a single-atom thick, two-dimensional (2D) sheet of carbon atoms arranged in a hexagonal network isolated from its 3D parent material, graphite [1]. The unique properties of graphene, such as outstanding surface area, high thermal conductivity, fast electron mobility, and strong chemical durability [2,3], have been well documented. Owing to its amazing performances and potential applications, graphene is attested to one of the hottest researched 2D layered nano-material today. The enormous success of graphene have led researchers to explore a whole new range of isostructural analogs of graphene, for instance, hexagonal boron nitrides (BN) and 2D transition metal dichalcogenides (TMDCs) [4]. Compared with other types of TMDC materials, molybdenum disulfide (MoS<sub>2</sub>), which is comprised of three atom layers

with strong molecular intralayer bonds (coordination bonds), but weak interlayer bonds (van der Waals interactions), has aroused great attention by reason of its appreciable band gap with exotic properties [4–6]. In the past few years, graphene and MoS<sub>2</sub> have individually been applied widely to sensors [7,8], energy storage [9,10], hydrogen generation [11], and hydrodesulphurization [12]. However, an inevitable problem is the restacking property of MoS<sub>2</sub> when it is used individually, as this nature lead to the activity and application of MoS<sub>2</sub> being restricted. Graphene, as a new kind of catalyst support material, can be used to combine with MoS<sub>2</sub> to improve the catalytic properties of individual material effectively. As a new material, the hybrids of graphene and MoS<sub>2</sub> attract growing interests of many research groups currently.

Recent works have demonstrated that MoS<sub>2</sub>-graphene and its related composites is a promising electrocatalyst that has shown excellent electrocatalytic activity for small biological molecules. Feng et al. have recently used Au nanoparticles/poly (diallyldimethylammonium chloride)-graphene-MoS<sub>2</sub> nanomaterial prepared via hydrothermal method for electrochemical detection of eugenol [13]. Huang et al. have synthesized the layered MoS<sub>2</sub>-graphene composites and Au nanoparticles/MoS<sub>2</sub>-

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polyaniline nanocomposites to be as an electrochemical sensor of ascorbic acid, dopamine and hydrazine [4,14]. However, the electrochemical detection objects and catalytic properties of this kind of composites are still limited by its nature and need to be developed. It is well-known that the electrochemical catalytic properties of MoS<sub>2</sub> catalysts can be effectively promoted by the introduction of a foreign metal element, such as Fe, Co and Ni, in the MoS<sub>2</sub> lattice, which affords the opportunity to engineer the electronic and surface structures [15,16]. Among these metals, the doping of Ni atom is widely used to develop new catalytic objects or improve the electrochemical catalytic performance. For instance, D. Wang et al. prepared Ni-doping MoS<sub>2</sub> nanoparticles by a simple hydrothermal method as highly effective hydrogen evolution reaction catalysts [17]. Ni nanoparticle-MoS<sub>2</sub> nanosheet hybrid was successfully synthesized by J. Huang et al. via chemical reduction method, and this material can be utilized for the non-enzymatic determination of glucose [18], but its narrow linear range limit should be improved for the detection of various samples.

In the recent decades, glucose sensor has received increasing attention because of its importance role for fast measurement of glucose in the areas of clinical diagnostics, food industry and biotechnology [19–21]. Commercialized glucose biosensors are based on the glucose oxidase for glucose detection. Although enzyme-based sensors normally show high sensitivity and selectivity, these sensors are easy to be influenced by external environment, such as temperature, pH, and ambient humidity [22,23]. Non-enzymatic glucose sensors based on direct electrochemical oxidation of glucose will be an alternative technique to avoid these drawbacks, as well as have a bright future and prospect of potential commercial application.

Herein, we utilized a simple and scalable strategy to fabricate the Ni-doped molybdenum disulfide nanoparticles/reduced graphene oxide (Ni-MoS<sub>2</sub>/rGO) with different proportions of Mo and Ni by the calcining of the corresponding precursors under N<sub>2</sub> flow. A sequence of characterization methods were employed to analyze compositions, structures and morphologies of the nanocomposites. Based on the Ni-MoS<sub>2</sub>/rGO composites, a non-enzymatic glucose sensor was established and the detection performances of this glucose sensor have also been tested using cyclic voltammetry and amperometric method. The results showed that this material displayed an excellent electrocatalytic activity because of the improved conductivity as well as electron transport rates due to rGO and the highly exposed catalytic sites. Moreover, the Ni-MoS<sub>2</sub>/rGO composite also showed large diffusion coefficient ( $D = 1.83 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$ ) and catalytic rate constants ( $K_{cat} = 6.26 \times 10^5 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ).

## 2. Experimental

### 2.1. Chemicals and reagents

Glucose, (NH<sub>4</sub>)<sub>2</sub>MoS<sub>4</sub>, Ni(CH<sub>3</sub>COO)<sub>2</sub>, CH<sub>3</sub>COOH, NaOH, NaCl and Nafion (NF) solution (5 wt%) were obtained from Sigma-Aldrich, while ascorbic acid (AA), uric acid (UA), dopamine (DA), acetaminophenol (AP), V<sub>B</sub>, sucrose and maltose were purchased from Beijing Dingguo Biotechnology Co. Ltd. All reagents were at least of analytical grade and used as received without any treatment. All of aqueous solutions were prepared using deionized water.

### 2.2. Instruments

X-ray diffraction (XRD) patterns were obtained on an X-ray D/max-2200 vpc (Rigaku Corporation, Japan). Raman spectroscopy patterns were obtained by using a confocal microprobe Raman system (HR800, Jobin Yvon). X-ray photoelectron spectroscopy (XPS)

was measured using an ESCA LAB 250 spectrometer (Thermo Electron Corp) with a monochromatic Al K $\alpha$  source ( $h\nu$  1486.6 eV). The morphologies of our composites were researched by using scanning electron microscopy (SEM, XL-30 ESEM, Philips Company) and transmission electron microscopy (TEM, JEM-2100F, Japan).

The electrochemical experiments were performed on a GHI 830B electrochemical analyser (CH Instruments, Shanghai Chenhua Instrument Corporation, China) and a PARATAT 2273 electrochemical workstation (AMETEK Instruments, USA) using a traditional three-electrode configuration: Ag/AgCl (in saturated KCl solution) as the reference electrode, a platinum wire as the counter electrode, and the composite modified glassy carbon electrode (GCE) as the working electrode. The electrolyte was NaOH aqueous solution and all experiments were carried out at room temperature.

### 2.3. Synthesis of Ni-MoS<sub>2</sub>/rGO composites

According to Hummers and Offeman method [24], graphene oxide (GO) was synthesized from natural graphite powder. Typically, 0.1 g of powder GO were added into the mixture of 10 mL of CH<sub>3</sub>COOH and 20 mL of deionized water under stirring at 65 °C. The precursor of Ni-Mo compounds-carbon was prepared by dropwise adding 20 mL (0.0192 M) aqueous of (NH<sub>4</sub>)<sub>2</sub>MoS<sub>4</sub> and 10 mL aqueous of Ni(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O with the molar ratios of Mo to Ni (1:0, 5:1, 3:1, 1:1 and 1:3) into the above solution under stirring for 2 h. The suspension was separated by centrifugation, washed with deionized water and dried in the oven at 80 °C in air overnight. The precursor was collected and calcined for 4 h at 600 °C under N<sub>2</sub> atmosphere to obtain composites which were denoted as MoS<sub>2</sub>/rGO, Ni-MoS<sub>2</sub>-1/rGO, Ni-MoS<sub>2</sub>-2/rGO, Ni-MoS<sub>2</sub>-3/rGO and Ni-MoS<sub>2</sub>-4/rGO, respectively. The overall preparation procedure of Ni-MoS<sub>2</sub>/rGO composites was schematically shown in Scheme 1.

### 2.4. Preparation of the modified electrodes

Prior to modification, the GCE was polished to mirror smooth against alumina slurries, which were prepared with 1, 0.3 and 0.05  $\mu\text{m}$  alumina powder, respectively. Then rinsed with ethanol and deionized water in an ultrasonic bath and dried in air. Catalyst suspension was prepared by mixing 3 mg of the catalysts into 1 mL of Nafion solution (0.5 wt%). Ni-MoS<sub>2</sub>-3/rGO composite modified GCE was obtained by casting 10  $\mu\text{L}$  of the catalysts suspension on the electrode surface and dried in air at laboratory temperature. All modified electrodes used in the experiments were prepared with the same method.

## 3. Results and discussion

### 3.1. Characterization of the Ni-MoS<sub>2</sub>/rGO sample

The typical XRD pattern of the GO (a), MoS<sub>2</sub>/rGO (b) and Ni-MoS<sub>2</sub>-3/rGO (c) samples are shown in Fig. 1A. The diffraction peak of XRD at around 10.4° (a) is assigned to a layered structure with a basal spacing of 0.85 nm. In comparison, the newly-appeared diffraction peaks are observed for MoS<sub>2</sub>/rGO (b) and Ni-MoS<sub>2</sub>-3/rGO (c). To be emphasized, a broad peak can be observed at around 25.8° (b and c), which is the (002) plane of rGO. Beyond that, the characteristic peak of GO at 2 $\theta$  of 10.4° (a) disappeared, indicating that GO has been reduced successfully to rGO after the synthesis process. As can be seen, the diffraction peaks of MoS<sub>2</sub>/rGO (b) and Ni-MoS<sub>2</sub>-3/rGO (c) at 2 $\theta$  of 14°, 33°, 40°, 50° and 58°, which can be assigned to the (002), (100), (103), (105) and (110) planes, conform to the characteristic diffraction peaks of MoS<sub>2</sub> (JCPDS card No. 37-1492). Most often, nickel may exist in three distinct forms, including nickel situated in the carbon lattice, nickel in NiS<sub>2</sub> or Ni<sub>3</sub>S<sub>2</sub> [25,26] and nickel located in the NiMoS phase [16]. The resulting

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