Chinese Chemical Letters 27 (2016) 231–234

Contents lists available at ScienceDirect

Chinese Chemical Letters

journal homepage: www.elsevier.com/locate/cclet

Original article

Thin-layered MoS_2/polyaniline nanocomposite for highly sensitive electrochemical detection of chloramphenicol

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ARTICLE INFO

Article history:
Received 7 May 2015
Received in revised form 19 June 2015
Accepted 19 August 2015
Available online 28 September 2015

Keywords:
MoS_2
Polyaniline
Electrochemical detection
Chloramphenicol

ABSTRACT

In this study, we synthesized molybdenum disulfide/polyaniline (MoS_2/PANI) nanocomposite *via in situ* polymerization of aniline in the presence of thin-layered MoS_2. The as-prepared MoS_2/PANI nanocomposite obtained an improved electrochemical performance due to the physisorption interaction between aromatic aniline and the basal plane of MoS_2. Furthermore, we constructed a new kind of electrochemical sensor based on MoS_2/PANI nanocomposite for the detection of chloramphenicol, which showed an excellent performance. The sensor has a high sensitivity and wide detection range from 1×10^{-7} mol/L to 1×10^{-4} mol/L, with a low detection limit of 6.9×10^{-8} mol/L.

1. Introduction

Chloramphenicol (CAP), as a broad-spectrum antibiotic, has a strong bactericidal power and therapeutic efficacy [1]. However, it has serious toxic side effects on hematopoietic system such as aplastic anemia [2]. In addition, long-term intake of a trace of CAP can cause the imbalance of body's normal flora. To build highly sensitive detection of CAP therefore has important significance. So far, many methods have been used for the determination of CAP, such as gas chromatography–mass spectrometry [3,4], high performance liquid chromatography [5], capillary zone electrophoresis [6], chemiluminescence [7], electrochemical sensor [8] *etc*. Among these methods, electrochemical sensor possesses the advantages of low cost, rapid analysis speed and high sensitivity.

As an outstanding conducting polymer with excellent electrochemical properties, biocompatibility and chemical stability, polyaniline (PANI) has been a promising material in sensing fields [9]. Moreover, in order to improve the performances and applications of PANI-based sensors, PANI was often combined with other functional materials. For example, Yang *et al.* prepared an ERGNO/PANI-based DNA sensor which showed a wide linear range and low detection limit due to the synergistic effect of ERGNO and PANI [10].

MoS_2 is a type of layered transition metal sulfide that constructed of three atom layers stacked by weak van der Waals forces and possesses an analogous structure to graphene [11]. It is commonly used as a solid lubricant as well as catalysts for hydrodesulfurization reaction and hydrogen evolution reaction [12,13]. In recent years, due to its layered structure, MoS_2 has attracted great attention in the fields of electrochemistry and electronics. Integrating MoS_2 with other functional materials, can bring improved properties due to their synergistic effect. For example, MoS_2/graphene composites exhibited more excellent electrochemical performances than MoS_2 or graphene in lithium ion battery [14]. Although MoS_2/PANI have been synthesized and used in lithium ion batteries [15,16], the application of MoS_2/PANI nanocomposite in electrochemical sensing has been reported scarcely.

In this work, the thin-layered MoS_2/PANI nanocomposite was synthesized *via* the combination of ultrasonic exfoliation of bulk MoS_2 and *in situ* polymerization of aniline. The as-prepared MoS_2/PANI nanocomposite exhibited excellent conductivity and large electroactive surface area. Furthermore, we developed a new sensitive electrochemical sensor based on this nanocomposite for the detection of CAP. Due to the special 3D structure of MoS_2/PANI nanocomposite easily absorbing the conjugated CAP and the excellent electrochemical performance, the sensor achieved the highly sensitive detection of CAP with a wide detection range and low detection limit.

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http://dx.doi.org/10.1016/j.cclet.2015.09.018

2. Experimental

2.1. Apparatus and reagents

Electrochemical measurements were performed on a CHI 760D electrochemical workstation (Shanghai CH Instrument Company, China) with a three-electrode system. A saturated calomel electrode and a platinum wire were used as reference electrode and counter electrode respectively, and a bare carbon paste electrode (CPE) or modified CPE was used as working electrode. The ultrasonic process was performed with a KQ-500B sonifier. The morphology of as-prepared composite was characterized by JSM-6700F scanning electron microscopy (SEM), JEM-2100 transmission electron microscopy (TEM). X-ray diffraction (XRD) measurement was investigated on a Rigaku D/Max-2550 diffractometer with Cu Kα radiation.

Bulk MoS_2, aniline, ammonium persulfate and CAP were respectively purchased from BASF Chemical Co., Ltd. (Tianjin, China), Tianjin Damao Chemical Factory, Tianjin Guangcheng Chemical Co., Ltd. and Shanghai Bioengineering Co., Ltd. The CAP stock solution was prepared with ethanol and then diluted to the given concentration using 0.3 mol/L phosphate buffer solution (PBS). All other reagents were of analytical grade, commercially available and used as received. Aqueous solutions were made with ultrapure water.

2.2. Preparation of MoS_2/PANI nanocomposite

A certain amount of MoS_2 was dispersed in 80 mL of 1 mol/L $HClO_4$ aqueous solution and sonicated for 4 h to get thin-layered MoS_2 dispersion. Then 0.465 g of aniline and 10 mL of ethanol were added. Afterward, the obtained mixture was stirred and put in refrigerator at −10 °C. At the same time, 0.76 g of ammonium persulfate was dissolved in 10 mL of 1 mol/L $HClO_4$ aqueous solution, and then the resulting solution was put in refrigerator at −10 °C as well. 20 min later, the two dispersions were mixed, and the obtained mixture reacted at −10 °C for 18 h. Finally, a precipitate was collected by filtration and washed with ultrapure water until the filtrate became clear, then naturally dried at room temperature. The resulting lump solid was grounded at room temperature to give a black powder. The MoS_2/PANI nanocomposite was obtained.

In addition, pure PANI was prepared using similar method but in absence of MoS_2.

2.3. Fabrication of the modified electrodes

The carbon paste electrode (CPE) was prepared by Yang *et al.*'s report [17]. 0.5 g/L MoS_2/PANI made with ultrapure water was sonicated for 1 h, 20 μL of which was dripped onto the tip of CPE and naturally dried in the air at room temperature. The obtained electrode was denoted as MoS_2/PANI/CPE. Similarly, PANI/CPE was prepared. And 0.5 g/L thin-layered MoS_2 suspension was obtained from dispersing bulk MoS_2 in DMF and then sonicating it for 4 h. Then MoS_2/CPE was obtained in the same way.

2.4. Electrochemical measurements

Differential pulse voltammetry (DPV) measurements were carried out in 0.3 mol/L PBS supporting electrolyte. The scan

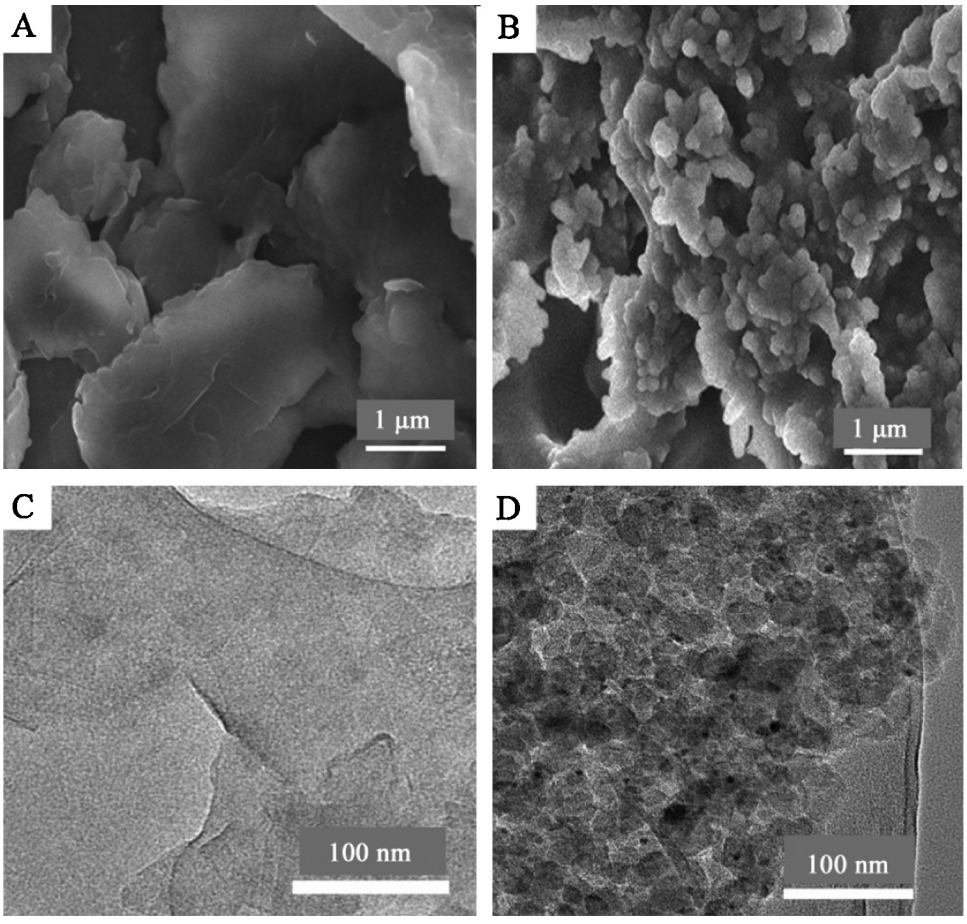

Fig. 1. SEM images of (A) MoS_2 and (B) MoS_2/PANI and TEM images of (C) MoS_2 and (D) MoS_2/PANI.