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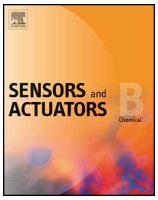

Molybdenum nitride/nitrogen-doped multi-walled carbon nanotubes hybrid nanocomposites as novel electrochemical sensor for detection L-cysteine

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ABSTRACT

In this work, we reported a novel, facile and effective strategy by using hydrothermal reaction and following high-temperature pyrolysis under the ammonia flow to fabricate the molybdenum nitride nanosheets/N-doped multi-walled carbon nanotubes (MoN/N-MWNTs) hybrid nanocomposite. MoN/N-MWNTs nanocomposite was characterized via X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and electrochemical methods. This nanocomposite exhibits excellent electrocatalytic oxidation of L-cysteine (L-CySH). An amperometric L-CySH sensor was constructed based on the MoN/N-MWNTs modified glassy carbon electrode. The as-prepared MoN/N-MWNTs nanocomposite has favourable conductivity, large surface area due to the MWNTs as supporter and highly exposed active sites of MoN. Moreover, the influence of different loading amounts of MoN was researched. The optimized MoN/N-MWNTs catalyst showed a wide detection range that was composed by two line segments (5 μM– 0.79 mM and 0.79 mM–12.60 mM), a sensitivity of 198.59 nA μM^{-1} cm^{-2} in the low concentration range, a rapidly response within 1.5 s as well as good reproducibility and stability.

1. Introduction

L-CySH, a sulfur-containing amino acid, which is one of approximately twenty amino acids commonly found in natural proteins, plays a crucial role in biological systems [1]. For example, it could be applied to a potential radiation protector and its deficiency has a concerned with manifestation, such as skin lesions, slowed growth, liver damage and cancer [2–5]. Additionally, the couple of L-cystine/L-cysteine is generally used as a model for the role of the disulfide bond and thiol group in proteins in a variety of biological media [1]. Therefore, under many circumstances, it's the most significant aspect to achieve fast and real-time for detecting L-CySH [6]. Some analysis methods, such as spectroscopic method [7] and liquid chromatography [8,9], have been employed to detect L-CySH, however they are usually complex, time-consuming and high cost. Compared to these approaches, electrochemical method has more significant advantages, such as easily automated, low cost, high sensitivity and possible being readily integrated with other techniques for multi-analysis [10,11].

Recently, transition metal compounds, such as transition metal nitrides (TMNs), transition metal sulfides, and transition metal oxides, have been employed in electrochemical detection of biological molecules. Yang et al. synthesized thin-layered MoS_2/PANI nanocomposite via ultrasonic exfoliation of bulk MoS_2 and in situ polymerization of aniline for Chloramphenicol detection [12]. Bai et al. researched the catalytic mechanism of L-CySH at an easy-prepared chitosan and β-MnO_2 nanowires modified glassy carbon electrode [13]. Among these transition metal compounds, TMNs, for example MoN, TiN, NbN and so on, have an advantage in terms of physical properties, such as hardness, wear resistance, and superconductivity [14], but this kind of catalysts cannot provide high surface area and small particle size, resulting in low current density. In order to overcome this disadvantage, the introductions of carbon materials, which own excellent electrical performance and high surface area, have been regarded as an ideal way.

Over the past decades, several carbon-based materials, including fullerene [15], ordered mesoporous carbon (OMC) [6,16], carbon nanofibers [17], and carbon nanotubes (CNTs) [18], have been employed for electrochemical oxidation and detection of L-CySH. Among these above materials, CNTs, which consist of two

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distinct classes of nanotubes, single-wall nanotubes (SWNTs) and multi-wall nanotubes (MWNTs), have obtained a lot of attention due to their unique structural characteristics, large surface area, high electrical conductivity, high mechanical and chemical stability [19,20]. Although several electrochemical methods based on CNTs with improved response have been reported [18,21–23], the detection properties for the electrochemical oxidation of L-CySH, such as detection range and sensitivity, are still full of challenge. To invest the CNTs with desired detection properties, several strategies have been developed [24]. Among these methods, introduction of the nitrogen (N) heteroatom in CNTs can adjust the valence orbital energy levels of the adjacent carbon atoms and have been proven to be an efficient method to yield a large amount of defective sites [25–27]. Xu et al. prepared nitrogen-doped carbon nanotubes as a novel electrochemical sensor, showing excellent electrocatalytic activity towards the oxidation of hydrogen peroxide [24]. Therefore, a strategy of combination of MoN with N-doping MWNTs can be regarded as one of the most ideal methods to improve the electrocatalytic performance for L-CySH.

In this paper, we propose a facile strategy to fabricate MoN/N-MWNTs nanocomposites with different loading amounts of MoN nanosheets by the high-temperature calcining of the corresponding Mo-compounds-carbon precursors under ammonia flow. A series of methods were employed to confirm the characterizations of MoN/N-MWNTs. The electrochemical oxidation of L-CySH was investigated using cyclic voltammetry and amperometric method at the MoN/N-MWNTs modified electrodes. The conductivity and surface area of MoN/N-MWNTs nanocomposite have been effectively improved by introduction of MWNTs, and more active sites are exposed. The optimal nanocomposite shows good detection performance toward L-CySH and could potentially be used as a new platform for electroanalysis of L-CySH.

2. Experimental

2.1. Chemicals and reagents

Hexaammonium heptamolybdate tetrahydrate [$(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$] and thiourea were purchased from Sinopharm Chemical Reagent Co. A series of amino acid of L-cysteine (L-CySH), L-glutamic (L-Glu), L-valine (L-Val), L-isoleucine (L-Ile), L-phenylalanine (L-Phe), L-tyrosine (L-Tyr) and glucose were all obtained from Beijing Dingguo Biotechnology Co. Ltd. Carboxylic group functionalized multi-walled carbon nanotubes (MWNTs-COOH) and Nafion (NF) solution were purchased from Aldrich. The electrolyte was 0.1 M phosphate buffer solution (PBS, pH 7.0) and an aqueous solution containing different concentrations of L-CySH were freshly prepared every day. All other reagents were at least of analytical grade and used without any treatment. All aqueous solutions are confected with double distilled water.

2.2. Instruments

The morphological characterizations were obtained with scanning electron microscopy (SEM) using a Philips XL-30 ESEM. X-ray diffraction (XRD) patterns were obtained on an X-ray D/max-2200vpc (Rigaku Corporation, Japan) instrument. X-ray photoelectron spectroscopy (XPS) was measured using an ESCALAB 250 spectrometer (Thermo Elestron corp) with Al Kα radition (1486.6 eV) as the excitation source.

All the electrochemical experiments were performed with a CHI 830 B electrochemical Analyzer (CH Instruments, Shanghai Chenhua Instruments, USA) and a PARSTAT 2273 (AMETEK instruments) electrochemical workstation in a conventional three-electrode. The modified glass carbon electrode (GCE 3 mm diameter) was used as the working electrode. An SCE electrode served as a reference electrode, and a platinum electrode was applied as the counter electrode.

2.3. Synthesis of MoN/N-MWNTs composites

The nanocomposites were prepared as previously reported [28,29]. Typically, 30 mg of powdery MWNTs-COOH were added into 35 mL of uniform mixed aqueous solution containing $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ and thiourea with the mole ratio of 1:2. After 30 min of ultrasonication, the resulting homogeneous solution was transferred to a Teflon-lined autoclave and hydrothermally treated at 210 °C for 24 h. The suspension was separated by centrifugation and washed with double-distilled water, followed dried in the oven at 70 °C in air overnight. The composite was collected and calcined for 3 h at 900 °C under ammonia flow. The obtained products were respectively named as MoN/N-MWNTs-1, MoN/N-MWNTs-2 and MoN/N-MWNTs-3 corresponding to the different amounts (0.05, 0.1 and 0.2 mmol) of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$. For comparison, the MWNTs-COOH was also calcined under the same condition. The overall preparation procedure of MoN/N-MWNTs nanocomposite was schematically shown in Scheme 1.

2.4. Preparation of the modified electrodes

Before the modified, GCE was polished with 1, 0.3 and 0.05 μm alumina powder, respectively. Then cleaned with ethanol and double-distilled water in an ultrasonic bath and dried with high-purity nitrogen steam. MoN/N-MWNTs-1 nanocomposite modified GCE was obtained by casting 5 μL of the suspension (3 mg mL^{-1} in 0.5 wt% NF) on the electrode surface and dried in air at laboratory temperature. For comparison, the MoN/N-MWNTs-2/NF/GCE, MoN/N-MWNTs-3/NF/GCE and other modified electrodes were also prepared with the same method.

3. Results and discussion

3.1. Characterization of MoN/N-MWNTs

Structural features of the resultant samples were characterized by XRD patterns. Fig. 1A displays XRD of MWNTs (a) and MoN/N-MWNTs-1 nanocomposite (b). The diffraction peaks of XRD at 2θ of 26.1° and 42.9° (a) are assigned to (002) and (101) planes of the hexagonal graphite structures of MWNTs, respectively [30]. In comparison, after doping of N atoms (b), the newly-appeared diffraction peaks are observed, apart from two characteristic peaks of MWNTs. To be emphasized, the sharp peak at 2θ of 26.1° shift to a broad peak of typical amorphous carbon. The XRD of samples containing different loading amounts of MoN are shown in Fig. 1B. The diffraction peaks of MoN/N-MWNTs-1 (a), MoN/N-MWNTs-2 (b) and MoN/N-MWNTs-3 (c) almost conform to the standard XRD pattern of MoN (JCPDS card No.25-1367), and meanwhile, the results are matched with earlier report [31]. The most obvious difference between the three nanocomposites is that there are some new diffraction peaks appeared for MoN/N-MWNTs-2 (b) and MoN/N-MWNTs-3 (c). It needs to be stressed that those peaks of impurity belong to Mo_2C, which is likely that a small amount of molybdenum atoms are bond to carbon with the increasing of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ in the process of synthesis.

XPS measurements were further employed to analyze the elemental composition of MoN/N-MWNTs. It is seen in Fig. 2A that the XPS spectra of the (a) MoN/N-MWNTs-1, (b) MoN/N-MWNTs-2 and (c) MoN/N-MWNTs-3, show the presence of molybdenum, nitrogen, carbon and oxygen atoms. The peaks of molybdenum and nitrogen atoms have an increasing trend as the growth of the amount of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$. The XPS binding energies of Mo3d