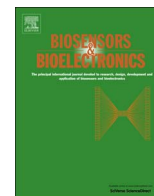




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Electrocatalytic determination of nitrite based on straw cellulose/molybdenum sulfide nanocomposite

Honggui Wang^a, Fangfang Wen^a, Yajie Chen^a, Ting Sun^a, Yao Meng^a, Ya Zhang^{a,b,*}^a Jiangsu Key Laboratory of Environmental Material and Engineering, School of Environmental Science and Engineering, Yangzhou University, Yangzhou, Jiangsu 225127, PR China^b School of Chemistry and Chemical engineering, Yangzhou University, Yangzhou, Jiangsu 225009, PR China

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ABSTRACT

Cellulose is the most abundant, renewable, biodegradable natural polymer resource on earth, which can be a good substrate for catalysis. In this work, straw cellulose has been oxidized through 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)-mediated oxidation, and then a TEMPO oxidized straw cellulose/molybdenum sulfide (TOSC-MoS₂) composite has been synthesized via a hydrothermal method. Fourier transform infrared spectroscopy (FT-IR) and X-ray diffraction (XRD) analysis confirm that TOSC and MoS₂ have successfully composited. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images show the TOSC as a carbon nanotube-like structure and edged MoS₂ grows on the TOSC substrate. The TOSC-MoS₂ modified glassy carbon electrode (GCE) is used as a simple and non-enzymatic electrochemical sensor. Cyclic Voltammetry (CV) result shows TOSC-MoS₂ has excellent electrocatalytic activity for the oxidation of nitrite. The amperometric response result indicates the TOSC-MoS₂ modified GCE can be used to determine nitrite concentration in wide linear ranges of 6.0–3140 and 3140–4200 μM with a detection limit of 2.0 μM. The proposed sensor has good anti-interference property. Real sample analysis and the electrocatalytic mechanism have also been presented.

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1. Introduction

Intensive use of nitrite as fertilizing agents in agriculture and food additive in some industrial sectors causes a severe nitrite pollution of water sources and industrial sites (Brylev et al., 2007). It has been reported that excessive ingestion of nitrites via the dietary intake has potential toxic and carcinogenic effects (Wang et al., 2015). Nitrite is recognized as an alarming pollutant to the environment and human health (Zhang et al., 2016). Therefore, simple, rapid and sensitive determination of nitrite in environmental samples is important.

Many analytical techniques have been developed to determine nitrite, such as chromatography (Jobgen et al., 2007; Ferreira and Silva, 2008), capillary electrophoresis (Miyado et al., 2007), chemiluminescence (Liu, et al., 2014) and electrochemistry (Menart et al., 2015; Wang et al., 2015; Zhang et al., 2016). Among the techniques mentioned above, the electrochemical approach is considered to be an environmentally friendly method, because no additional chemical loading is required. Nitrite determination has

been previously achieved by enzymatic biosensors, which are usually based on the immobilization and electrical wiring of nitrite reductase (NiR) (Almeida et al., 2007). However, the major obstacles of the NiR-based nitrite biosensors are the poor stability of the enzyme and the difficulty in establishing an electrical communication with the immobilized reductase. Therefore, there is demand for the development of more reliable and efficient non-enzymatic sensors for sensitive analysis of nitrite.

Recent advances have revealed that molybdenum sulfide has excellent catalytic activity if prepared properly and would be promising and inexpensive alternatives to Pt for the electrochemical applications (Hwang et al., 2011; Lopez-Sanchez et al., 2013; Voiry et al., 2013; Zhou et al., 2014). However, bulk MoS₂ also possesses disadvantages, such as lower activity than noble metal catalysts and their high resistance to sulfur poisoning productivities (Shen et al., 2014; Zhu et al., 2014). It has been reported that edges in the MoS₂ are highly energetic and considered as active sites in catalysis (Kiran et al., 2014). The way to solve this problem is to synthesize MoS₂-based composite with more edges.

To fabricate catalysts, supporting materials are important because active part can disperse well on them and then results in better catalytic performance. Various carbon-based supporting materials have been reported to construct catalysts, such as graphene (oxide), carbon nanotubes and carbon black (Akter et al.,

* Corresponding author at: Jiangsu Key Laboratory of Environmental Material and Engineering, School of Environmental Science and Engineering, Yangzhou University, Yangzhou, Jiangsu 225127, PR China.

E-mail address: zhangya@yzu.edu.cn (Y. Zhang).

2016; Zhang et al., 2014). Cellulose is a semi-crystalline polysaccharide, formed as fibers with width ranging from 5 to 20 μm and length in the range of 0.5 up to several millimetres (Kalia et al., 2014), which can be found in nature almost exclusively in plant cell walls (wood, cotton, bamboo, straw etc.) (Iwamoto et al., 2007). It is found that cellulose can convert to carbon nanotube-like structure under proper TEMPO-mediated oxidation (Koga et al., 2010; Saito et al., 2007). To date, many nanocellulose-based catalysts have been reported. For example, Li and coworkers have reported a novel regenerated cellulose (RC)/TiO₂/ZnO nanocomposite, which has been prepared via electrospinning technology and sol-gel process followed by hydrothermal method (Li et al., 2014). CdS nanoparticle functionalized natural cotton cellulose (CC) electrospun nanofibers have been synthesized via combining the electrospinning technique and the chemical bath deposition method (H. Liu et al., 2015; Q.Y. Liu et al., 2015).

In the present work, a simple and non-enzymatic electrochemical sensor has been fabricated by a modified straw cellulose/molybdenum sulfide. The natural obtained straw cellulose is oxidized through a TEMPO-mediated oxidation. Then the TEMPO oxidized straw cellulose is dispersed in the solution containing Na₂MoO₄·2H₂O and thioacetamide. The resulting TOSC-MoS₂ composite was obtained by a hydrothermal method. SEM and TEM images display edged MoS₂ grows on the TOSC substrate. The TOSC-MoS₂ modified glassy carbon electrode (GCE) shows excellent electrocatalytic activity for the oxidation of nitrite, which could be used as an effective sensor for the assessment of nitrite.

2. Experimental

2.1. Reagents

Native cellulose (straw pulp) was provided by Yongfeng Yu life paper (Yangzhou) Co., Ltd. (Yangzhou, China). 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO), Na₂MoO₄·2H₂O, NaBr, NaClO, HCl, NaOH, K₂HPO₄, KH₂PO₄, thioacetamide and other chemicals were purchased from Sinopharm Chemical Reagent Company. All the reagents were of analytical grade and used as received without further treatment. All solutions were prepared with DI water.

2.2. Preparation of modified electrode

2.2.1. TEMPO-mediated oxidation of straw cellulose (SC)

Straw cellulose was prepared via TEMPO-mediated oxidation according to the literature (Saito et al., 2007). Briefly, 10 g native cellulose (straw slurry) was suspended in 1000 mL DI water containing 0.16 g TEMPO and 1 g sodium bromide (NaBr). 0.1 M HCl was added into sodium hypochlorite (NaClO, 5 wt%), adjusting pH to be 10. Then a certain amount of the NaClO solution, corresponding 5 mmol/g of the straw cellulose was added to the slurry. The mixture was violently stirred at room temperature and the pH was maintained to be 10 by adding 0.5 M NaOH. After two hours, the oxidized cellulose was washed thoroughly with water on filter papers set in a filter flask. The wet cellulose was dried at a temperature of 60 °C in the oven.

2.2.2. Preparation of TOSC-MoS₂

In a typical synthesis of TOSC-MoS₂, 1 mmol of Na₂MoO₄·2H₂O, 5 mmol of thioacetamide and certain amount of TOSC were dissolved in 60 mL of distilled water. Next, the homogeneous solution was transferred into a 100 mL Teflon-lined autoclave and held at 180 °C for 20 h. After that, the black precipitate was collected by filtration, washed three times with distilled water and ethanol, and then dried in an oven at 80 °C for 12 h. As a

control experiment, MoS₂ was prepared under the same conditions without adding TOSC.

2.2.3. Preparation of modified electrode

Prior to modification, a 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 the modified electrodes, 4 mg TOSC-MoS₂ 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. All electrochemical experiments were performed in a 0.1 M phosphate buffer solution (PBS, which was prepared using 0.1 M phosphoric acid, K₂HPO₄ and KH₂PO₄) unless otherwise noted.

2.3. Apparatus and measurements

All electrochemical experiments were performed in the electrolytic cell containing a 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 FT-IR spectra of the samples were measured on a Cary 610/670 microscope (Varian, US). The XRD patterns were obtained by a Bruker D8 advance X-ray diffractometer using monochromatic Cu K α radiation ($\lambda=1.5406 \text{ \AA}$) with an accelerating voltage of 40 kV and current of 40 mA. Scanning electron microscopy was examined on a field-emission scanning electron microanalyzer (Hitachi S-4800, Japan). TEM (Transmission electron microscopy) was recorded on a Tecnai G2 F30 S-TWIN transmission electron microscope. The pH values of the solutions were determined with a PHS-3C pH meter.

3. Results and discussions

3.1. Electrode modification

The electrode modification and electrocatalytic mechanism are expressed in Fig. 1. Firstly, the straw pulp was modified using a TEMPO method (2.2.1); then TOSC-MoS₂ was synthesized by a hydrothermal method (2.2.2); the obtained TOSC-MoS₂ was drop-casted onto the surface of clean GCE (2.2.3); finally, the TOSC-MoS₂ modified GCE was used to determine nitrite in a PBS. The electrocatalytic mechanism will be discussed in Section 3.3 based on the results of electrochemical tests.

3.2. Characterization

The TOSC-MoS₂ composite is confirmed by FT-IR spectra (Fig. S1). Bending vibrations of the OH⁻ groups are observed at 1591 cm⁻¹ and 1404 cm⁻¹. The band at 1404 cm⁻¹ corresponds to the out-plane bending vibration whereas the band at 1591 cm⁻¹ is due to the in-plane bending vibration of OH⁻ (Ahmad et al., 2009). The weak peaks at 613 cm⁻¹ at both MoS₂ and TOSC-MoS₂ composite are assigned to γ_{as} Mo-S vibration (H. Liu et al., 2015; Q.Y. Liu et al., 2015). The peaks at 2914, 1018 and 896 cm⁻¹ are attributed to the C-H stretching, the C-O-C pyranose ring skeletal vibration and the C₁-H deformation vibrations, respectively (Yang et al., 2015). It is clearly seen that the TOSC-MoS₂ composite exhibits both characteristic bands of MoS₂ at 1591, 1404, 613 cm⁻¹ and TOSC at 2914, 1018, 896 cm⁻¹, revealing a hybrid structure. The XRD patterns of MoS₂, TOSC and TOSC-MoS₂ composite are shown in Fig. S2. The diffraction peaks at $2\theta=14.4^\circ$, 33° and 56.6° ,

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