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Construction of an electrochemical sensor based on amino-functionalized metal-organic frameworks for differential pulse anodic stripping voltammetric determination of lead

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ABSTRACT

Metal-organic frameworks composite materials have received tremendous attention because of their versatile structures and tunable porosity for various applications. Herein, amino-functionalized metal-organic frameworks ($\text{NH}_2\text{-Cu}_3(\text{BTC})_2$; BTC=benzene-1,3,5-tricarboxylate) was prepared and used as a novel electrode modifier for the determination of trace levels of lead. $\text{NH}_2\text{-Cu}_3(\text{BTC})_2$ shows quite a good capability for the efficient adsorption of lead from aqueous solutions. The parameters affecting the electrochemical process, such as electrolyte solution pH, the amount of $\text{NH}_2\text{-Cu}_3(\text{BTC})_2$ suspension, accumulation potential and accumulation time, were investigated in detail. Under the optimal conditions, the electrochemical sensor exhibited a linear response to the concentration of lead in the range of 1.0×10^{-8} – 5.0×10^{-7} mol L⁻¹ ($R^2=0.9951$) with a detection limit of 5.0×10^{-9} mol L⁻¹. The relative standard deviation of 11 successive scans was 3.10% for 1.0×10^{-8} mol L⁻¹ lead. The method was validated with certified reference material (stream sediment and milk powder) and the analytical results coincided well with the certified values. Furthermore, the method was successfully applied to the determination of target analytes in tap and lake water samples and good recoveries were obtained from different spiked values.

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1. Introduction

Lead is a neurotoxic metallic element that can be absorbed by the body and accumulated in bloods and bones. Excess intake poses an important threat to human health. In particular, it can decrease intelligence and slower neurological and then strongly affects the mental and physical development of children [1,2]. The determination of lead has been carried out with various detection techniques such as electrothermal atomic absorption spectrometry [3], atomic fluorescence spectrometry [4], inductively coupled plasma optical emission spectrometry [5] and electrochemical methods [6,7]. In comparison with other methods, electrochemical methods have attracted greater attention in the last two decades due to their low cost, high sensitivity, easy operation and the ability of analyzing element speciation.

Nowadays, most electrochemical methods are based on the use of modified electrodes, because they exhibit enhanced performance by incorporating the chemistry and physics of the immobilized

species. Among the large variety of chemically modified electrodes, chitosan gold nanocomposite [8], silver nanoparticles [9], bismuth film [10], stannum film [11], stannum/bismuth/poly(p-aminobenzenesulfonic acid) film [12], and bismuth-dispersed xerogel-based composite films [13] have been successfully employed as electrode coatings, providing effective electrochemical gates for the detection of analytes such as lead, zinc, cadmium, tin and mercury. Moreover, the potential of amino group functionalized based electrodes have also been explored as versatile electrode modifiers [14–16].

Metal-organic frameworks (MOFs) are crystalline porous coordination polymers that can be characterized as infinite 1D, 2D, or 3D networks resulting from the combination of metal species and organic linkers. A well-known MOFs is $\text{Cu}_3(\text{BTC})_2$ (BTC=benzene-1,3,5-tricarboxylate), which is formed by paddlewheel secondary building units containing Cu^{2+} dimers coordinatively linked to carboxylic oxygen atoms from organic benzene-1,3,5-tricarboxylate (BTC) ligands [17,18]. Due to large porosity and high surface area, $\text{Cu}_3(\text{BTC})_2$ offers unprecedented opportunities in gas-storage, catalysis, and small molecule sensing. Moreover, development of MOFs based composite for the electrochemical field of interest is becoming increasing. For instance, Copper (II)-based MOFs were used as selective electrocatalysts for the reduction of O_2 and CO_2

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[19,20]. Recent reports suggested that Au-SH-SiO₂ nanoparticles supported on MOF was utilized as a sensor for electrocatalytic oxidation and determination of hydrazine and L-cysteine [21,22].

In this paper, amino-functionalized Cu₃(BTC)₂ composite materials were fabricated as a novel electrode modifier. The electrochemical sensing performance was evaluated for lead sensor, and this new electrode displayed well-defined, sharp and highly reproducible stripping peaks at low concentrations of lead. Various parameters related to the measurement procedure were investigated and optimized to allow the resulting sensors to use in the analysis of real samples.

2. Experimental section

2.1. Apparatus

A CHI660A electrochemical workstation (Chenhua Instrument, Shanghai, China) was used for voltammetric measurements with a three-electrode system. The working electrode was the NH₂-Cu₃(BTC)₂ modified glassy carbon electrode (GCE). The counter electrode was a platinum wire and the reference electrode was an Ag/AgCl electrode. X-ray diffraction (XRD) patterns were recorded on a D8 Advance X-ray diffractometer (Bruker Co., Germany) at room temperature. Field emission scanning electron micrographs (SEM) were obtained with a Hitachi S-4800 microscope (Japan) at an acceleration voltage of 15 kV. Thermogravimetric analysis (TGA) was performed by means of a Pyris 1 TGA (PerkinElmer, America), under N₂ at a scan rate of 10 °C min⁻¹.

2.2. Reagents and materials

A 1.0 × 10⁻² mol L⁻¹ lead stock solution was prepared by dissolving 3.312 g Pb(NO₃)₂ (Jinshan chemicals, Shanghai, China) in 100 mL 1% (v/v) nitric acid. Working standard solutions were obtained by step-wise dilution. Copper (II) nitrate trihydrate (Cu(NO₃)₂ · 3H₂O), 1,3,5-benzene tricarboxylic acid (H₃BTC), *N,N*-dimethylformamide (DMF), 2-amino-1,4-benzenedicarboxylate (ABDC), ethanol and chloroform in this work were at least of analytical reagent grade without further purification and were obtained from Sinopharm Chemical Reagent Co., Ltd. unless otherwise stated. Double de-ionized water (18 MΩ cm) was used throughout the experiments. Reference materials stream sediment and milk powder were purchased from the BHH Biotechnology Co., Ltd. Nitrogen gas (99.999%) was used for purging oxygen in a solution to provide an inert atmosphere.

2.3. MOFs synthesis

NH₂-Cu₃(BTC)₂ was synthesized based on a previous literature after a minor modification [23]: Briefly, copper (II) nitrate trihydrate (12.2 g), H₃BTC (5.8 g), ABDC (1.8 g) were dissolved in a beaker containing DMF (85 mL), de-ionized water (85 mL) and ethanol (85 mL) under magnetic stirring for 30 min, and then heated in a Teflon lined steel autoclave at 85 °C for 24 h. After cooling to ambient temperature, the sky-blue crystals was filtered, washed with DMF and ethanol, and immersed in chloroform, which was decanted and replaced with fresh chloroform two times over three days. The final products were heated at 130 °C for 3 days before use.

2.4. Fabrication of NH₂-Cu₃(BTC)₂ modified electrode

NH₂-Cu₃(BTC)₂ (1 mg) was dispersed in 1 mL DMF and the mixture was agitated in an ultrasonic bath for one hour to achieve a well-dispersed suspension. Prior to use, the bare GCE was polished to a mirror-like surface with 0.05 μm α-Al₂O₃, then rinsed

ultrasonically with water and absolute ethanol and sonicated in de-ionized water. A drop of this dispersion with the volume of 5 μL was coated on the surface of the GCE, and the NH₂-Cu₃(BTC)₂ composite modified electrode was obtained after it was dried in air for approximately 4 h.

2.5. Sensing procedure

In order to get the high sensitivity of detection, anodic stripping voltammetric technique was used and performed in a 10 mL electrochemical cell, if not stated otherwise, containing appropriate amounts of lead and 0.1 mol L⁻¹ of acetate buffer solution (pH=4.5). The preconcentration was carried out at -1.0 V for 300 s under stirring and after a 10 s equilibration period, the voltammogram was recorded by applying a positive-going differential pulse stripping voltammetric potential scan from -1.0 to -0.1 V with a step potential of 10 mV, pulse amplitude of 100 mV and pulse width of 1.0 s. All potentials were referred to the Ag/AgCl reference electrode. The calibration curve was obtained by plotting the peak current versus the lead concentration.

3. Results and discussion

3.1. Characterization studies

The crystal structure and phase purity of the as-synthesized MOFs were characterized by XRD. All the diffraction peaks of the samples can be indexed to those of the highly quality Cu₃(BTC)₂ reported in the literature [18], and no obvious peaks of impurities can be detected in these XRD patterns. As shown in Fig. 1a, the nine major peaks found at 7.78°, 11.73°, 13.34°, 14.72°, 19.16°, 20.28°, 22.31°, 26.11° and 29.44° on the 2θ scale correspond respectively to the (200), (220), (222), (400), (331), (440), (600), (731) and (751) crystal planes. By comparing the XRD of NH₂-Cu₃(BTC)₂ and Cu₃(BTC)₂, we may safely draw the conclusion that the presence of -NH₂ functional group in the MOFs structure has not any effect on the XRD spectrum, indicating that increased amino did not change the metal ions and carboxylic acid organic ligand structure.

Thermogravimetric analysis (TGA) of NH₂-Cu₃(BTC)₂ is presented in Fig. 1b. The sample shows a little weight loss between 23.11 and 121.38 °C, which is ascribed to the removal of H₂O molecules and C₂H₅OH molecules present in the channels and coordinated to the metal centers of the MOF-structure. At temperatures between 121.38 and 288.73 °C, 7.4% of the weight was lost in NH₂-Cu₃(BTC)₂, due to the displacement of the coordinated DMF molecules. All guest molecules can be removed at 288.73 °C. A third large weight change was observed from 289.51 to 596.20 °C. After decomposition at 350 °C, c.a. 35.6% of the starting weight remains, and this residual material could correspond to the formation of copper oxides and metallic copper. Hence, the obtained electrode modifier is stable at the current operating temperature.

The SEM image for the microstructures of the Cu₃(BTC)₂ is presented in Fig. 2, which was obtained as cube-shaped crystals with a smooth surface, demonstrating the good crystallinity of the material. In contrast, the crystal surface texture of NH₂-Cu₃(BTC)₂ was changed dramatically and flocculent substances appeared in the surface. These images were similar to the previous reports [24,25]. This may be caused by impurities or a second phase nucleating on the surface of the crystals. That is, the Cu-BDC started to nucleate on the surface of the crystals when the reaction between BDC and Cu salt to make the Cu-BDC is performed at a lower temperature.

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