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Simultaneous detection of Cd(II) and Pb(II) by differential pulse anodic stripping voltammetry at a nitrogen-doped microporous carbon/Nafion/bismuth-film electrode

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ABSTRACT

Recently, metal-organic frameworks (MOFs) and their carbon derivates have been demonstrated as new electrode modifying materials for electrochemical sensing. In this work, the first example of the detection of heavy metal ions with a MOF-derived sensing platform was presented. The platform was based on a glassy carbon electrode (GCE) modified by Nafion-bismuth/nitrogen doped microporous carbon (NMC) composite, in which the NMC was derived from a zeolitic imidazolate framework-8 (ZIF-8). The good dispersibility, large specific surface area (941 $m^2 g^{-1}$), high nitrogen content (25.0 at.%) and good electrical conductivity of the NMC materials, as well as the synergistic effects of Nafion and bismuth-film contributed to the enhanced signals of the electrode during the differential pulse anodic stripping voltammetry (DPASV) measurements for simultaneous detection of trace Cd(II) and Pb(II) in aqueous solution. The calibration curves for Cd(II) covered two linear ranges varying from 2 to 10 $\mu g L^{-1}$ and 10 to 100 $\mu g L^{-1}$. As for Pb(II), the linear calibration curves ranged from 0.5 to 10 $\mu g L^{-1}$ and 10 to 100 $\mu g L^{-1}$. The detection limits were estimated to be 1.5 $\mu g L^{-1}$ (S/N = 3) for Cd(II) and 0.05 $\mu g L^{-1}$ (S/N = 3) for Pb(II), which were 2 times and 200 times lower than the guideline values of drinking water given by the World Health Organization (WHO), for Cd(II) and Pb(II), respectively. In addition, the good reproducibility and stability of the modified electrode offered a promising perspective for the detection of trace metal ions in practice. Compared with other porous carbon modified electrodes that obtained by either drop-casting or screen-printing method, the proposed Nafion/Bi/NMC/GCE showed a much lower detection limit for Pb(II) and a lower or comparable detection limit for Cd(II). Moreover, the obtaining of uniformly ordered N-doped carbon polyhedron could shed light on the preparation of other heteroatom-doped electrode modifying materials for the detection of heavy metal ions.

1. Introduction

Heavy metal ions are known to pose acute or chronic risks to ecosystem at very low concentrations because of their high toxicities, high stabilities and propagated accumulation through food chains.[1] As two major heavy metal pollutants, cadmium and lead are normally generated from industry and continuously present in soil, drinking water and aquatic environments.[2,3] Therefore, the detection of these two metal ions at trace level is of great concern. A variety of analytical methods are commonly used for Cd(II) and Pb(II) analysis, including atomic absorption spectroscopy (AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES), and inductively coupled plasma mass spectrometry (ICP-MS), *etc.*[4,5] Although reliable results with high sensitivities can be obtained by these spectroscopic methods, the disadvantages such as costs of these instruments and complex operation procedures may limit their applications.[6,7] Sensitive, low cost and simple analytical methods that can be applied for on-site monitoring are still required.

Compared to spectroscopic techniques, the electrochemical technique, especially anodic stripping voltammetry (ASV) has been considered as a promising method for the detection of heavy metal ions because of the advantages of low cost, high

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sensitivity and good portability.[6,8] Differential pulse anodic stripping voltammetry (DPASV), as one kind of ASV method, has been applied for the detection of trace heavy metal ions because of its remarkably high sensitivity.[9] DPASV measurement usually includes a preconcentration step of the analyte and an electrochemical stripping step of the accumulated analyte on the surface of the working electrode.[6,10] A proper selection of the working electrode is an important prerequisite for sensitive electrochemical detection.

With the combination of nanomaterials and DPASV analytical technique, a few modified electrodes towards the detection of heavy metal ions have been fabricated, including carbon nanotube (CNT) modified electrode, graphene composite electrode, mesoporous MgO modified glassy carbon electrode, porous Co_3O_4 microsheets electrode, nanostructured magnesium silicate electrode, *etc*.[3,11–16] To achieve better performance with these electrodes, sophisticated modification processes are required to get CNT or graphene material with good dispersity and stability.[3,6,15,17] The chemical stabilities and the electrical conductivities of the metal oxides or silicate based materials also need to be improved. Therefore, the preparation of functionalized carbon materials with simple routes are still of great interests.[18]

Lately, porous carbon materials, especially heteroatoms (e.g., N, B, and S) doped carbons with ordered structures, have been considered as good candidates for electrode modification materials because of their superior performance in electrochemical capacitors and electrochemical sensing, owing to their high area to volume ratios, low resistances and large voltage windows, *etc*.[19–22] Among numerous dopants, nitrogen is an excellent element for the chemical doping of carbon because of its high compatibility with the carbon matrix.[23] It has been reported that nitrogen-doped carbon (NC) can be developed by either a post-treatment of carbon or an in-situ pyrolysis of nitrogen-containing precursor.[24] The in-situ pyrolysis is more favorable since the post-treatment methods may result in NC with low stability, low nitrogen content (< 10 at.%) and non-uniformly functionalized surface, as pointed out by Shen and Fan.[21] So far, some nitrogen-containing polymers, such as polyvinylpyrrolidone, polyacrylonitrile, polypyrrole, melamine have been used for the preparation of nitrogen-functionalized mesoporous carbon.[19,25–27] However, the reports on the preparation of highly ordered porous carbons with high nitrogen contents are still quite rare.

Metal-organic frameworks (MOFs) have been recently used as new sacrificial templates or precursors for the preparation of highly ordered porous carbon materials.[20,22,28–32] For example, Xu's group demonstrated firstly the carbonization of furfuryl alcohol (FA) inside micropores by using a MOF-5 as the sacrificial template.[28] The surface areas of the obtained porous carbons could be larger than 3000 $m^2 g^{-1}$ with their modified synthesis procedures.[31] Yang *et al.* synthesized a MOF-derived carbon with high porosity that enabled exceptional H_2 storage capacities at both 77 K (1 bar) and 298 K (100 bar), surpassing all the known physisorptive materials.[32] Gai *et al.* recently prepared a nitrogen doped porous nanopolyhedra (N-PCNPs) by using ZIF-8 as precursor.[20] They demonstrated that such N-PCNPs could be successfully used as electrode modifying materials for simultaneous electrochemical detection of ascorbic acid, dopamine and uric acid in aqueous solution.[20]

Herein, we present a simple way to prepare a nitrogen doped microporous carbon (NMC) by using a nanosized MOF as the precursor through direct carbonization at a relatively low temperature, and the first application of NMC on the modification of electrode for heavy metal ion detection. The intrinsic highly ordered and porous structure of the carbon-based materials, the high affinity to metal ions and the strong electron donor nature of the nitrogen atoms, which are known to contribute to the electrochemical activity of the NMC material,[24,33] were proved to be able to improve the sensitivity of heavy metal ion detection.

In this work, a zeolitic imidazolate framework-8 (ZIF-8) with methylimidazole linkers as nitrogen source was used.[29,34] The direct carbonization resulted in NMC nanoparticles with maintained highly ordered porous structure that inherited from the original ZIF-8 and small particle size as 40 nm. The obtained NMC showed good dispersity and durability to acids or alkalis. The NMC was characterized by nitrogen adsorption measurement, scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS), and used as electrode modifying material for the detection of trace Cd(II) and Pb(II) via DPASV technique. The adding of the NMC and the incorporating of bismuth film led to well defined stripping signals of the modified electrode.

This new sensing platform showed potential to be a sensitive, selective and repeatable electrochemical sensor for simultaneous determination of trace Cd(II) and Pb(II). It may also provide insights into the preparation of sensing platforms for electrochemical quantification of other heavy metal ions.

2. Experimental

2.1. Chemicals and Apparatus

All chemicals were of analytical grade and used as received. Nafion (5 wt.% in low aliphatic alcohols, Sigma) was diluted with N,N-Dimethylformamide (DMF, Tianjin OuBoKai Chemical Industry) to get a 0.3 wt.% Nafion-DMF solution. Deionized water ($\geq$18.2 MΩ) was used for the preparation of aqueous solutions. A 0.1 mol L^{-1} acetate buffer (HAc–NaAc) was prepared by mixing appropriate amounts of CH_3COOH (Tianjin ZhiYuan Chemical Reagent) and CH_3COONa (Tianjin BaiShi Chemical Industry) and used for the preparation of supporting electrolyte. Stock solutions of Bi(III), Cd(II) and Pb(II) with concentration of 1,000 mg L^{-1} were prepared with $Bi(NO_3)_3{\bullet}5H_2O$ (Aladdin), $Cd(NO_3)_2{\bullet}4H_2O$ (Sigma) and $Pb(NO_3)_2$ (Tianjin Guangfu Fine Chemical Research Institute), respectively. Bi(III), Cd(II) and Pb(II) standards with different concentrations were obtained by diluting the stock solutions in the supporting electrolytes.

DPASV was performed in a conventional three-electrode cell with a CHI660E electrochemical workstation (CH Instruments, Shanghai, China). A nitrogen doped microporous carbon modified glassy carbon electrode (GCE, 3 mm in diameter, Gaoss Union Technology Co., Wuhan, China) was served as the working electrode. A Ag/AgCl (Saturated. KCl) electrode (Gaoss Union Technology Co., Wuhan, China) and a platinum wire (CH Instruments, Shanghai, China) were used as the reference and counter electrode, respectively. A vacuum tube furnace (GSL-1500X, Kejing technology, Hefei, China) was used for the carbonization of ZIF-8. X-ray powder diffraction (XRD) was carried out with an X-ray diffractometer (D8, Bruker Germany). A scanning electron microscope (German Zeiss, Germany) was used to characterize the morphology of the materials. X-ray photoelectron spectra were recorded with an Al Ka X-ray source (Escalab 250, Thermo Fisher Scientific, USA). Nitrogen adsorption-desorption isotherms and Brunauer-Emmett-Teller (BET) surface areas of the materials were determined with an Autosorb-IQ-MP gas sorption analyzer (USA).

2.2. Preparation of ZIF-8 and NMC

ZIF-8 was synthesized according to the previously reported method.[35] 1.032 g $Zn(NO_3)_2{\bullet}5H_2O$ (Tianjin HongYan Chemical Reagent) was dissolved in 80 mL methanol (Tianjin BaiShi Chemical Industry) to form solution A. 1.052 g 2-methylimidazole (Sigma)