Electrochimica Acta 251 (2017) 71–80

Contents lists available at ScienceDirect

Electrochimica Acta

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

Research Paper

An electrochemical sensor based on metal-organic framework-derived porous carbon with high degree of graphitization for electroanalysis of various substances

Jiaoyan Xu, Jianfei Xia*, Feifei Zhang, Zonghua Wang*

College of Chemistry and Chemical Engineering, Shandong Sino-Japanese Center for Collaborative Research of Carbon Nanomaterials, Collaborative Innovation Center for Marine Biomass Fiber Materials and Textiles, Laboratory of Fiber Materials and Modern Textile, the Growing Base for State Key Laboratory, Qingdao University, Qingdao 266071, PR China

ARTICLE INFO

Article history:
Received 16 June 2017
Received in revised form 17 August 2017
Accepted 17 August 2017
Available online 24 August 2017

Keywords:
Metal-organic frameworks
Carbonization
Electroanalysis
Graphitization
N-doped

ABSTRACT

A MOF-derived porous carbon with high specific surface area and robust structure was successfully synthesized by carbonizing zeolitic imidazolate framework (ZIF-8). With the investigation of the carbonization temperature and the preparation process, the synthesized ligand-derived carbon matrix (Z-1000) displayed a high electrical conductivity and electrochemical activity owing to the spatially ordered porous structure, high graphitization and doped nitrogen. In order to test the electrochemical properties of this material, a range of substances were detected by Z-1000 modified electrodes (Z-1000/GCE) and satisfactory results were obtained. In optimized conditions, the linear responses of the Z-1000/GCE for uric acid (UA) and catechol (CT) were obtained from 0.001 mM to 0.3 mM with detection limit of 1.4×10^{-8} M and 2.78×10^{-7} M, respectively. And a linear range for hydroquinone (HQ) was in the region of 0.001 mM–0.2 mM with detection limits of 2.15×10^{-7} M. These unique physical and chemical properties made it hold great promise in the development of multifunctional sensor. Meanwhile, the low cost and facile preparation of MOF-derived carbon made it become a potential candidate for electroanalysis.

1. Introduction

Over the last few decades, carbon materials have been widely used in various fields including energy [1], environment [2] and so on [3]. Due to their special properties and extensively applications [4,5], carbon materials have been regarded as the most potential and common catalysts [6]. Among all existing carbon materials, porous carbon materials have attracted tremendous attention and research interest owing to their large specific surface area, adjustable pore structure and low cost [7]. For electrochemical application, the highly ordered pore structure and graphitization degree of porous carbons are considered to be of great significance [8,9]. To prepare porous carbon with ordered pore structure, two main strategies have been developed: 1) template-directed deposition [10,11] such as chemical vapor deposition, and 2) pyrolysis of appropriate carbon precursors which can be obtained via controlled self-assembly [12–15]. Although template-directed deposition has been developed into a mature method for synthesis of ordered porous carbons, complicated procedures and the use of special rigid nano-casting molds which cause the high cost and time-consuming limit its application in large-scale industrial production. Therefore, pyrolysis of carbonaceous material seems to be a feasible approach to fabricate an ordered porous structure. However, it is a challenge to find a carbon precursor the frame of which would not collapse during the process of carbonation.

Metal-organic frameworks (MOFs) are a class of crystalline porous materials constructed by alternatively connecting the metal ions or small metallic clusters with organic ligands [6]. Recently, owing to their diversified morphologies, tunable pore structure and large surface, MOFs have turned out to be ideal precursors and templates to form ordered porous carbon via pyrolysis. Up to now, increasing numbers of MOFs have been reported to be chosen as precursors and templates for fabricating ordered porous carbon such as MOF-5 [16], ZIF-8 [1] and BMZIFs [17,18]. Among these MOFs, ZIF-8 [19] with a high carbon content and stable property is considered to be an excellent candidate for synthesizing porous carbon directly upon carbonization [20]. In particular, the high mechanical strength and thermal stability play

* Corresponding authors. fax: +86 532 85950873; Tel: +86 532 85950873.
E-mail addresses: xiajianfei@126.com (J. Xia), wangzonghua@qdu.edu.cn (Z. Wang).

http://dx.doi.org/10.1016/j.electacta.2017.08.114
0013-4686/

a crucial role in forming carbon material with highly ordered holes and robust structure. In addition, ZIF-8 derived porous carbons possess C-N active sites with electrocatalytic activity because of the appropriate nitrogen content in organic ligands. There are a growing number of reports on the synthesis and application of ZIF-8 derived porous carbon [21–23]. However, most of researches on ZIF-8 derived porous carbon have focused on the field of energy. There are few reports on the electrochemical sensing application.

According to the literature, the pyrolysis temperature is an important condition for the electronic conductivity and electrocatalytic activity of porous carbon [24]. But in the only two reports related to ZIF-8 derived porous carbon based electrochemical sensor [25,26], they have not investigated the electrochemical performances of porous carbons under different pyrolysis temperatures. Moreover, the porous carbons have been prepared through direct pyrolysis under a flow of nitrogen gas at high temperature with a heating rate of 5 °C min^{-1}. They have not removed the free water and bound water before the pyrolysis at high temperature. And the water may influence the graphitization of ZIF-8, which can influence the electronic conductivity.

Herein, we present a facile and low cost method to synthesize ordered porous carbon with robust 3D structure. A Zn-based zeolitic imidazolate framework, ZIF-8, was synthesized through one-pot process and used as the precursor. After that, the ordered porous dodecahedrons were obtained by removing free water, bound water and completely pyrolyzing ZIF-8 at high temperature under the protection of argon atmosphere (Scheme 1). Besides, the effects of pyrolysis temperature on the materials properties were also investigate. ZIF-8 was pyrolyzed under different temperatures (from 600 °C – 1000 °C) in argon atmosphere and the obtained materials were indexed with temperature. Due to the high N content of organic ligand, the carbon material (Z-1000) with uniform N-doped was obtained under 1000 °C. The uniform N-doped could greatly improve the electrochemical performance of the obtained carbon material. Furthermore, Z-1000 could integrate the advantages of 3D ordered porous material and graphene. The synergistic effects of graphene structure and porous structure could promote electron transfer and help to sieve molecular, which lead to the improved selectivity of the detection platform. Then the Z-1000 was used to modify a glassy carbon electrode and used as an electrochemical detection platform. The modified electrode (Z-1000/GCE) showed high electrocatalytic activity toward the electrochemical oxidation of uric acid (UA), catechol (CT) and hydroquinone (HQ). Furthermore, the Z-1000/GCE presented excellent sensitivity, selectivity, stability, good repeatability and satisfying recoveries in real samples for the electrochemical detection of UA, CT and HQ.

2. Experimental

2.1. Chemicals and materials

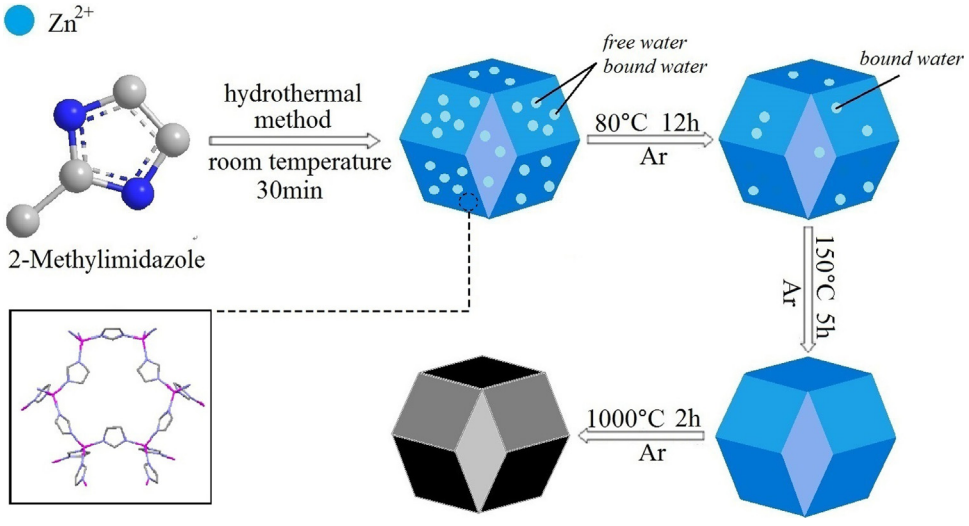
Zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$, 99%) and 2-methylimidazole ($C_4H_6N_2$, 98%) were purchased from Aladdin Reagent Co. Ltd. (Shanghai, China). Uric acid ($C_5H_4N_4O_3$, AR), hydroquinone ($C_6H_6O_2$, AR) and catechol ($C_6H_6O_2$, AR) were ordered from Tianjin Regent Co., Ltd. (Tianjin, China). Methanol (CH_3OH, ≥99.5%) was obtained from Shanghai Reagent Factory (Shanghai, China). Nafion solution (5%, DuPont) was diluted into 0.5 wt %. Na_2HPO_4, NaH_2PO_4 and other reagents were of analytical grade. The water used in this experiment was deionized water.

2.2. Apparatus

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images were obtained by JEOL JSM-7001F and JEOL JEM-1200, respectively. Powder X-ray diffraction (PXRD) data was obtained by Rigaku Ultima IV diffractometer. The X-ray photoelectron spectra (XPS) were obtained by using an X-ray photoelectron spectroscope (K-Alpha, Thermo Fisher Scientific ESCALAB250Xi, USA) with an Al Kα X-ray source (1486.6 eV). The Raman spectra were recorded on HOKIBA HR evolution at an excitation wavelength of 532 nm at room temperature. The surface area measurements were performed with N2 adsorption/desorption isotherms at liquid nitrogen temperature (77 K) using automatic volumetric adsorption equipment (Belsorp-max). A traditional three-electrode cell performed by CHI-660C electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd., China) was employed for cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements. The Z-1000/GCE was used as the working electrode and a platinum wire was worked as the auxiliary electrode. All the potentials quoted here were referred to an Ag/AgCl electrode as the reference.

2.3. Synthesis of the ZIF-8

The synthesis of the ZIF-8 was performed by one-pot reaction reported in the previous lecture [27]. 22.70 g 2-methylimidazole



Scheme 1. The preparation of ZIF-8 crystals and the synthesis process of Z-1000.