Applied Surface Science 463 (2019) 386–394

Contents lists available at ScienceDirect

Applied Surface Science

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

Full Length Article

Doped porous carbon nanostructures with N—Co—O catalytic active sites for efficient electrocatalytic oxygen reduction reaction

Cheng Chen[a,c], Meirong Liu[a], Huizhen Rao[a], Yuqing Liu[a], Shen Lin[a,*], Jian-Ke Sun[c], Jie Zhang[b,c,*]

[a] College of Chemistry & Materials Science, Fujian Normal University, Fuzhou, Fujian 350007, PR China
[b] MOE Key Laboratory of Cluster Science, School of Chemistry and Chemical Engineering, Beijing Institute of Technology, Beijing 100081, PR China
[c] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, CAS, Fuzhou, Fujian 350002, PR China

ARTICLE INFO

Keywords:
Porous carbon nanostructures
Metal-organic framework
N—Co—O catalytic active sites
Electrocatalyst
ORR

ABSTRACT

A cobalt metal-organic framework constructed by 4-(4-pyridyl)-benzoic acid was used as the precursor to afford a series of Co nanoparticles embedded and N/O-doped porous carbon materials **CoNOC-T_c-t** (where T_c represents the carbonization temperature and t represents the carbonization time), which possess high surface area, hierarchically micro-, meso- and macropores, and high graphitization as well as the uniformly enchased N—Co—O catalytic active sites derived from pyridine nitrogen atom and chelating carboxylate coordinated octahedral cobalt (II) center. These **CoNOC-T_c-t** porous carbon nanostructures have demonstrated prominent catalytic activities toward oxygen reduction reaction (ORR) in alkaline medium. Compared with commercial Pt/C catalyst, the **CoNOC-800-1** (annealed at 800 °C for 1 h) exhibits excellent selectivity *via* an efficient four-electron-dominant ORR process, as well as the superior durability and methanol tolerance, making it a cost-effective Pt-free ORR electrocatalyst. More importantly, the novelly designed N—Co—O catalytic active sites are proposed and well demonstrated by experiments, which provides a promising approach to develop heteroatom-doped carbon-based electrocatalytic materials.

1. Introduction

Metal-organic frameworks (MOFs) are a new class of highly customizable porous crystalline materials constructed by metal ions/clusters and organic linkers. In the past few years, MOFs have emerged as promising candidates for the synthesis of heteroatom doped (B, N, O, P or S, etc.) porous carbon materials due to their plentiful heteroatom-containing organic ligands and readily self-sacrificial through direct pyrolysis [1–5]. A number of typical MOFs, such as MOF-5 [6], Al-PCP [7], ZIF-67 [8] and ZIF-8 [9] have been demonstrated as promising self-sacrificial templates to afford high-efficiency nanoporous carbon materials. And, they have been developed for various applications, especially for oxygen reduction reaction (ORR) [1,10–21], an important reaction for fuel cells that with the purpose of avoid or minimize the use of precious metals such as platinum family metal [22–27].

The investigations of employ cobalt-contained MOFs as precursors for preparing non-platinum catalysts have been aroused since the ORR activity on cobalt phthalocyanine was discovered [28]. The cobalt-based MOF-derived carbon materials possess some important advantages [10]. The graphitized carbon, which is usually carbonized via catalysis over transition metals, would enhance electrical conductivity. In addition, such carbon materials can afford high surface area and hierarchical pores to guarantee the free diffusion of electrolyte and dissolved oxygen to the catalytic active sites. Moreover, the pivotal heteroatoms such as N and Co-based valid active sites can be homogeneously distributed in the carbon materials for promoting electrocatalysis [29–30]. Until now, there are some high-performance cobalt-based MOF-derived nanoporous carbon materials have been developed for ORR. Such as the CNCo-20 and the phosphorus doped P-CNCo-20 derived from bimetallic MOFs that are designed by the Jiang and coworkers [31]. And Lu et al. have developed a series of Co-MOF-derived dual metal and nitrogen co-doped carbon (M/CoNC) catalysts that are able to deliver prominent ORR activities, even comparable to commercial Pt/C catalyst [32]. Guo and Zou groups have well-designed Co@Co_3O_4@C–CM that shows almost identical activity but superior stability and methanol tolerance for the ORR relative to the commercial Pt/C in alkaline medium [21]. Qiu et al. reported hybrid nanocages with double-shells that outer shells consisted of Co-N-doped graphitic carbon and inner shells consisted of N-doped micro-porous carbon by templating against core-shell metal-organic frameworks exhibiting

---

* Corresponding authors at: MOE Key Laboratory of Cluster Science, School of Chemistry and Chemical Engineering, Beijing Institute of Technology, Beijing 100081, PR China (J. Zhang). College of Chemistry & Materials Science, Fujian Normal University, Fuzhou, Fujian 350007, PR China (S. Lin).
E-mail addresses: shenlin@fjnu.edu.cn (S. Lin), zhangjie68@bit.edu.cn (J. Zhang).

https://doi.org/10.1016/j.apsusc.2018.08.183
Received 26 June 2018; Received in revised form 4 August 2018; Accepted 21 August 2018

superior bifunctional catalytic properties [33]. Gu and co-workers reported a novel approach for fabrication of Co-N_x-embedded 1D mesoporous carbon nanofibers with graphitic carbon-encased Co nanoparticles originated from ZIF-8/ZIF-67, which is explored as an efficient bifunctional electrocatalyst for both ORR and OER [34]. Wang and Lou groups used ZIF-67 particles as the single precursor, and synthesized N-doped carbon nanotube frameworks (NCNTFs), which exhibited remarkable electrocatalytic activity and stability, and even outperform a commercial Pt/C electrocatalyst as a bifunctional electrocatalyst [8]. More importantly, previous research focused on transition metal–N complex on carbon matrixes (such as Co(Fe)–N) [29–37], and the pyridinic-N and graphitic-N have been well demonstrated to be the major catalytic active sites for ORR [38–40]. But, the effect of doped oxygen was seldom discussed [41], let alone the mechanism of catalytic process on metal–O catalytic active site. Since the oxygen is unavoidably existed in the MOF-derived carbon materials, an insight into structure–property relationships of O-doped catalysts and direct instruction for the O species and their function will promote further developments of high-performance MOF-derived carbon catalysts.

In this paper, we have used a 4-fold-interpenetrated pseudodiamond metal-organic framework **Co-MOF**, which possesses a 1D square-sectioned channel (with a window size of 6.8 Å × 6.8 Å) constructed by the 4-(4-pyridyl)-benzoic acid ligands and cobalt, as the precursor to prepare the target porous carbon nanostructures [42]. The purposes of employing such oxygen and nitrogen co-coordinated **Co-MOF** as template lie on two aspects. For one thing, each cobalt (II) center adopts a distorted octahedral geometry by coordinating to two pyridine nitrogen atoms and two chelating carboxylate groups of 4-(4-pyridyl)-benzoic acid (Fig. S1-S2, ESI), this coordination center can produce unique N—Co—O catalytic active site after calcination. The second, oxygen-enriched MOF is beneficial for creating desired pores with hierarchical pore sizes due to the releasing of large amount gaseous products (such as CO_2 and water vapour) as pore-forming agent during the carbonization process [43].

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.apsusc.2018.08.183.

2. Experimental section

2.1. Materials and instruments

All chemicals were obtained from commercial sources and were of analytically pure grade unless otherwise noted. The morphology and structure of **CoNOC-800-1** was characterized by using scanning electron microscopy (SEM) on a JEOL JSM 6700F microscope and transmission electron microscopy (TEM) on a JSM 2100F electron microscope. The X-ray photoelectron spectroscopy (XPS) analyses were carried out on a Thermo Scientific ESCALAB 250XI, and the binding energies were calibrated based on the C 1s peak at 284.8 eV. Powder X-ray diffraction (PXRD) patterns were recorded on a MiniFlex600 diffractometer with Cu Kα ($\lambda = 1.5406$ Å) at a scan speed of 2° $\min^{-1}$. Raman spectra were recorded on a Labram HR Evolution spectrometer made by Horiba Jobin Yvon Corporation, using an argon ion laser with an excitation wavelength of 532 nm. Pore characteristics of the materials were assessed from nitrogen sorption isotherms measured at 77 K on a Micromeritics ASAP2020. Elemental analysis of C, N and O was performed on a Vario EL III CHNOS elemental analyzer.

2.2. Synthesis and characterization of crystal materials

A mixture of $Co(NO_3)_2 \cdot 6H_2O$ (0.5 mmol) and 4-(4-pyridyl)-benzoic acid (1.0 mmol) were dissolved in the *N,N*-dimethylformamide solution (6 mL) in a Teflon vessel of the hydrothermal bomb and stirred for 30 min. The vessel was sealed, placed in an oven and heated at 110 °C for 2 days, and then allowed to cool slowly to room temperature within 2 days. The claret-red crystals of **Co-MOF** were collected and washed with dried DMF. Yield: 70% (based on Co). Powder XRD pattern of as-synthesized sample agrees well with the simulated **Co-MOF** (Fig. S1, ESI).

2.3. Synthesis and characterization of porous carbon materials **CoNOC-T_c-*t***

The **Co-MOF** crystals (1.0 g) were transferred into an alumina boat and heated to the target temperature (700–1000 °C) at a heating rate of 5 °C·min^{-1} and carbonized for 1 h under flowing argon atmosphere, then cooled to room temperature procedurally to obtain porous carbon materials **CoNOC-700-1**, **CoNOC-800-1**, **CoNOC-900-1** and **CoNOC-1000-1**. The **CoNOC-800-3** was synthesized in the same procedure except for prolonged carbonization time for 3 h. Then the coarse products underwent a pickling process with 3 M H_2SO_4 aqueous at 100 °C for 24 h in order to etch the inactive Co nanoparticles, and washed thoroughly with lots of deionized water to yield **CoNOC-T_c-*t*** catalysts. Finally, these products were activated in vacuum at 100 °C for two hours prior to use. Elemental analysis calculated for C, N and O contents were listed in the Table S1.

2.4. Electrochemical measurement

Electrochemical measurements were carried out in a conventional three-electrode system on the CHI 660C and CHI 760 electrochemical stations (Shanghai Chenhua, China). A rotating disk electrode (RDE) with a glassy carbon (GC) disk of 5 mm in diameter and a rotating ring-disk electrode (PINE AFE6R2GCPT) with a Pt ring (5.61 mm inner diameter and 8.5 mm outer diameter) and a GC disk of 5.5 mm diameter were used as the substrate for the working electrode. Ag/AgCl (filled with 3 M KNO_3 solution) and a Pt wire were used as reference and counter electrode, respectively. All measured potentials in this study were converted to the reversible hydrogen electrode (RHE), according to the equation: $E_{RHE} = E_{Ag/AgCl} + 0.207 + 0.059pH$ [44]. The catalyst inks were obtained by sonicating the catalyst (4 mg) in 990 μL ethanol containing 10 μL of Nafion solution (5 wt%) and was drop-coated onto a previously polished and cleaned glassy carbon electrode surface to afford an uniform thin film with a constant loading of 0.160 mg·cm^{-2} (the loading of Pt/C was 0.160 mg·cm^{-2}) in all cases. The electrode was dried at room temperature in air without any heating process and was used as the working electrode for all further electrochemical tests. Then the N_2/O_2 flow was bubbled into the cell for about 30 min to achieve either an oxygen-free or oxygen-rich electrolyte. The cyclic voltammetry (CV) tests were measured in N_2 and O_2-saturated 0.1 M KOH solution with a scan rate of 10 mV·s^{-1}. RDE/RRDE polarization curves were acquired in O_2-saturated 0.1 M KOH solution at different rotation rates with a sweep rate of 5 mV·s^{-1}.

The number (n) of electrons transferred in ORR process can be determined by the Koutecky-Levich equation:

$$\frac{1}{J} = \frac{1}{JL} + \frac{1}{JK} = \frac{1}{B\omega^{\frac{1}{2}}} + \frac{1}{JK}$$

$$B = 0.62nFC_0D_0^{\frac{2}{3}}V^{-\frac{1}{6}}$$

Here, J, J_K and J_L represent the measured, kinetic and diffusion limiting current density, respectively. ω is the angular velocity of the disk; n is the overall number of electrons transferred; F is the Faraday constant (96485C·mol^{-1}); C_0 is the bulk concentration of O_2 in the 0.1 M KOH electrolyte (1.2×10^{-6} mol·cm^{-3}); D_0 is the diffusion coefficient of O_2 in 0.1 M KOH electrolyte (1.9×10^{-5} cm^2·s^{-1}); V is the kinematic viscosity of the electrolyte (0.01 cm^2·s^{-1}).

The hydrogen peroxide yield (H_2O_2 %) and the electron transfer number (n) were calculated with the following equations: