Electrochimica Acta 213 (2016) 273–282

Contents lists available at ScienceDirect

Electrochimica Acta

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

From chicken feather to nitrogen and sulfur co-doped large surface bio-carbon flocs: an efficient electrocatalyst for oxygen reduction reaction

Yajun Fang, Hongjuan Wang, Hao Yu, Feng Peng*

School of Chemistry and Chemical Engineering, Key Laboratory of Fuel Cell Technology of Guangdong Province, South China University of Technology, Guangzhou, 510640, China

ARTICLE INFO

Article history:
Received 3 March 2016
Received in revised form 18 July 2016
Accepted 21 July 2016
Available online xxx

Keywords:
fuel cells
oxygen reduction reaction
bio-carbon catalyst
nonmetal co-doped carbon flocs
nitrogen species
porous structure

ABSTRACT

Nitrogen and sulfur co-doped bio-carbon flocs (NSC) with large BET surface areas and porous structures are obtained via pyrolysis of zinc-based metal-organic coordination polymer (MOCP-Zn) that is synthesized through a hydrothermal reaction between zinc salt and polypeptides derived from chicken feather. The as-prepared carbon flocs exhibit a superior performance towards oxygen reduction reaction (ORR) both in alkaline and acid media. Especially, the as-prepared NSC-3.5 can be comparative to Pt/C, exhibiting a promising application in the acidic environment of the proton exchange membrane fuel cell. It is proven that the enhanced ORR activities can be attributed to the high content of pyridinic- and graphitic-type nitrogen and large surface areas with abundant porous structures. Moreover, the growth mechanism of nitrogen and sulfur co-doped bio-carbon materials from chicken feather *via* coordination reaction and biomineralization process is investigated. This study develops a new method to prepare nonmetal-doped bio-carbon materials from waste biomass with enhanced electrocatalytic performances for ORR.

1. Introduction

The activity of electrocatalyst for oxygen reduction reaction significantly affects the performance of fuel cells and metal-air batteries [1]. To date, the most common and efficient electrocatalysts for ORR are platinum-based catalysts. However, the high cost and scarcity of platinum have hindered the large-scale commercial application of fuel cells [2]. Many efforts have therefore been devoted to develop Pt-free electrocatalysts in fuel cells. In recent decade, metal-free heteroatom-doped carbon materials (e.g. N, B, P, S), especially nitrogen-doped carbons, were demonstrated to be efficient metal-free ORR catalysts due to their excellent durability and good tolerance to methanol and carbon monoxide compared with commercial Pt/C catalyst. Many studies have demonstrated that most of carbon-based catalysts only exhibit moderate activity in alkaline condition [3–8]. However, presently, the grail in oxygen reduction on metal-free electrocatalysts is not in alkaline medium, but in acid medium, because of the acidic environment of the proton exchange membrane fuel cell. Therefore, it is still imperative and attractive to develop novel carbon-based catalysts with improved performance for ORR in acidic medium.

In this regard, the synthesis of carbon materials doped with dual or multi heteroatoms have been confirmed to be an efficient strategy [9–11]. It is because that the synergistic effect between the co-doping heteroatoms could notably enhance the ORR properties of carbon materials [12,13]. Another attractive method is to enhance the specific surface area of the carbon materials. With an appropriate porous structure, mesoporous carbons exhibit enhanced ORR performance due to the benefited electron transport, mass transfer and more reactive active sites exposure [14–16].

Metal-organic coordination polymer (MOCP), a kind of inorganic-organic hybrid compound, is constructed from transition metal irons and coordinated ligands to form an infinite arrays with one-, two- or three dimensional structures [17–19]. Owing to its self-sacrificial nature, inherent porous structures and high carbon content, MOCP is capable as a sacrificial template for casting highly porous carbon materials via direct carbonization without the extra addition of carbon source and pore-forming agent [19,20].

Chicken feather is the main waste residue or by-product of chicken consumption. The main component of chicken feather is keratin that could be easily degraded into polypeptides or

* Corresponding author. Tel.: +86 20 87114916; fax: +86 20 87114916.
E-mail address: cefpeng@scut.edu.cn (F. Peng).

http://dx.doi.org/10.1016/j.electacta.2016.07.121
0013-4686/

compound amino acids containing a large amount of nitrogen and sulfur. Meanwhile, the rich functional groups of amino acids have a strong ability for coordination with metal ions [21,22].

Stimulated by the aforementioned ideas, we proposed an environmental-friendly synthetic route for nitrogen and sulfur co-doped bio-carbon flocs (NSC) from chicken feather. In this work, MOCP-Zn backbones constructed with Zn^{2+} as connectors and polypeptides derived from chicken feather as linkers were successfully formed via a mild hydrothermal process. After the calcination of MOCP-Zn, nitrogen and sulfur co-doped porous carbon flocs with high surface areas were obtained. Compared with Pt/C catalyst, the as-prepared NSC exhibits enhanced ORR activity in alkaline medium and also show a considerable ORR performance in acid medium. Furthermore, the growth mechanism of NSC was investigated.

2. Experimental Section

2.1. Sample preparation

Degradation of chicken feather into polypeptides: chicken feather was thoroughly washed by acetone and dried at 110 °C. The cleaned feather was cut into debris and placed in a 100 mL Teflon autoclave, and then mixed with aqueous ammonia (the weight ratio of the chicken feather and aqueous ammonia is 1:15). After a hydrothermal reaction at 150 °C for 3 h under alkaline condition, chicken feather was degraded into polypeptides. Subsequently, ammonia solution containing polypeptides was dried in oven at 110 °C and milled into powder to obtain polypeptides that was used as the sole source of carbon, nitrogen and sulfur in the following experiment.

Synthesis of Zn-based coordination polymers (MOCP-Zn): the mixture of $Zn(NO_3)_2{\cdot}6H_2O$ (3.486 g, 5 mmol), the as prepared polypeptides powder (2.5 g), and CH_3OH (60 mL) was placed in a beaker with stirring under environmental condition for 30 min. The initial pH value of the mixture was 4.15. 1 M HNO_3 solution was slowly added into the mixture to adjust the pH value of the mixture (pH = 3.5, 2.5 or 1.0). After stirring for 6 h, the turbid liquid was placed in a 100 mL Teflon autoclave and heated at 180 °C for 15 h. After filtering and washing with distilled water, dark-brown powder precursor containing Zn-based coordination polymer (MOCP-Zn) was obtained and it was denoted as P-x (x indicates pH value, 1.0, 2.5, 3.5, 4.15).

Preparation of N, S co-doped bio-carbon flocs: the obtained precursors (P-1.0, 2.5, 3.5, and 4.15) were carbonized directly in an argon atmosphere at 800 °C for 2 h. The black powder was impregnated in 2 M HCl solution for 12 h to eliminate Zn, and then washed and dried to obtain the N, S co-doped bio-carbon flocs, being separately labeled as NSC-1.0, NSC-2.5, NSC-3.5 and NSC-4.15 from corresponding P-x precursors.

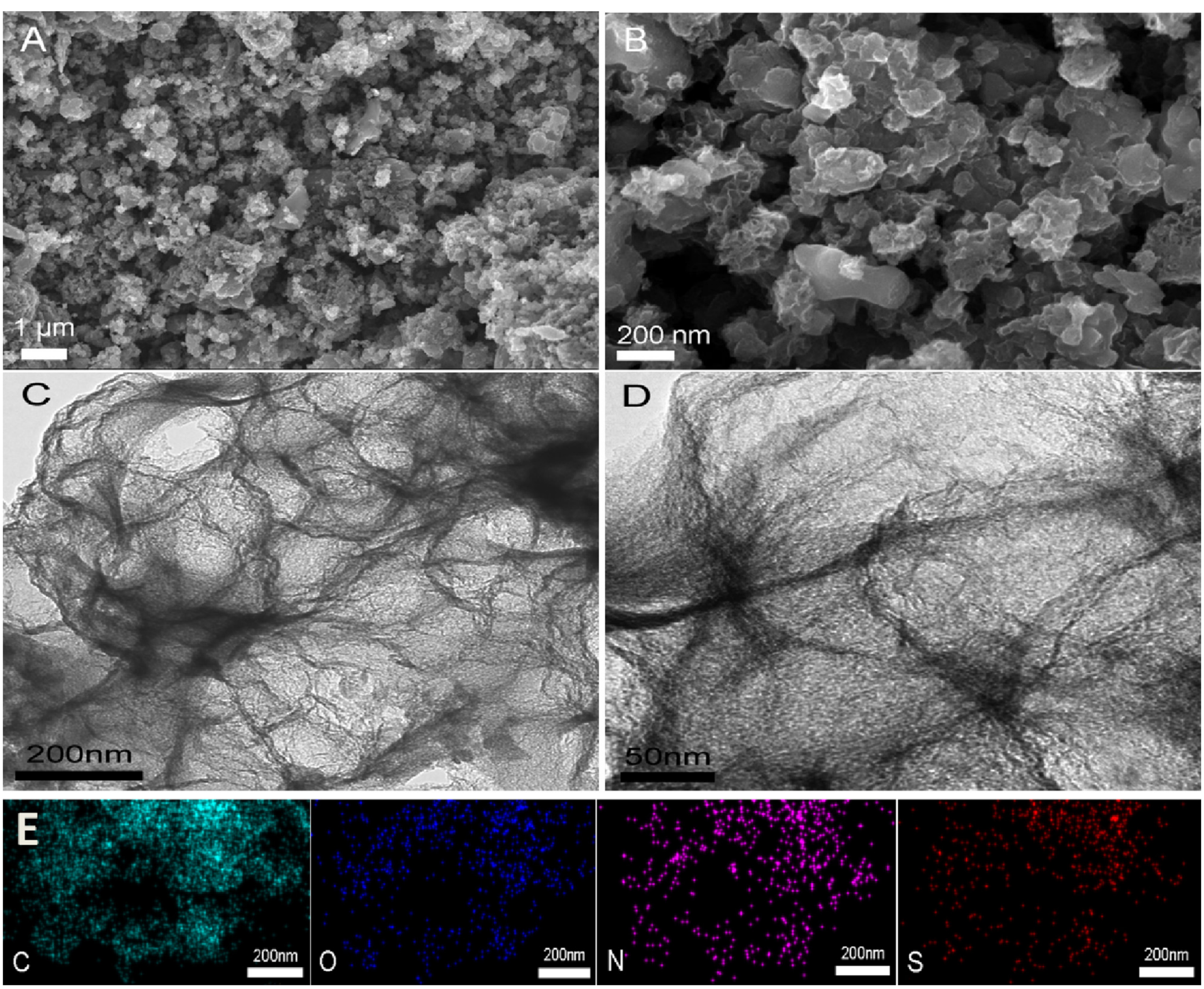

Fig. 1. SEM (A and B) and TEM (C and D) images of NSC-3.5 and the elemental mappings (E) of C, O, N and S.