Journal of Colloid and Interface Science 535 (2019) 436–443

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

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

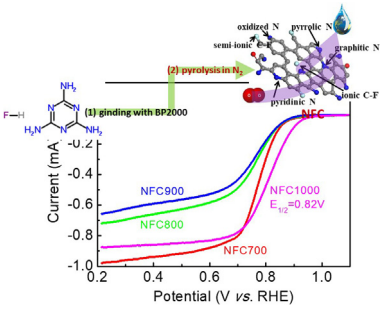
Regular Article

Oxygen reduction reaction with efficient, metal-free nitrogen, fluoride-codoped carbon electrocatalysts derived from melamine hydrogen fluoride salt

Hui-Juan Zhang [a,b,c], Sunwu Yao [a], Jing Geng [a], Zi-Feng Ma [d], Junhe Yang [a,b]

[a] School of Materials Science and Engineering, University of Shanghai for Science and Technology, Shanghai, China
[b] Shanghai Innovation Institute for Materials, Shanghai, China
[c] State Key Laboratory Breeding Base of Coal Science and Technology Co-founded by Shanxi Province and the Ministry of Science and Technology, Taiyuan University of Technology, Shanxi, China
[d] Department of Chemical Engineering, Shanghai Jiaotong University, Shanghai, China

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 31 July 2018
Revised 26 September 2018
Accepted 27 September 2018
Available online 9 October 2018

Keywords:
Electrocatalysts
Oxygen reduction reaction
Metal-free
N, F-codoped carbon
Melamine hydrogen fluoride salt

ABSTRACT

In this study, we successfully demonstrate an efficient, metal-free nitrogen, fluoride-codoped carbon (NFC) oxygen reduction reaction (ORR) electrocatalyst, which is produced by directly pyrolyzing melamine hydrogen fluoride salt (using as a single N and F precursor for the first time) mixed with carbon black BP2000 in a N_2 atmosphere. The ORR electrocatalytic performances are evaluated by rotating ring disk electrode experiments in 0.1 M KOH. The NFC electrocatalyst prepared at the optimized temperature of 1000 °C (NFC1000) demonstrates a high ORR electrocatalytic activity with a peak potential of 0.82 V (*vs.* RHE), half-wave potential of 0.82 V (*vs.* RHE), predominant direct 4-electron reaction pathway, and good durability and methanol tolerance. Transmission electron microscopy equipped with mapping, X-ray diffraction and X-ray photoelectron spectroscopy results indicate that NFC1000 possesses an amorphous carbon structure with a homogenous codoped distribution of N and F at 2.25 at% and 1.52 at%, respectively. N_2 adsorption-desorption analysis reveals that the as-prepared NFC1000 has a high surface area of 1169 $m^2 g^{-1}$. This study provides a feasible approach to synthesize low-cost and highly efficient metal-free heteroatom-doped carbon-based electrocatalysts.

E-mail addresses: hjzhang@usst.edu.cn (H.-J. Zhang), jhyang@usst.edu.cn (J. Yang)

https://doi.org/10.1016/j.jcis.2018.09.097
0021-9797/

1. Introduction

The oxygen reduction reaction (ORR), a kinetically sluggish reaction at the cathode, is significantly important to fuel cells and metal-air batteries [1–3]. Currently, metal-free heteroatom (N, B, S, P or F)-doped carbon materials, especially N-doped carbon, have been widely reported because they not only have excellent ORR electrocatalytic performance, stability and methanol tolerance but also low cost and environmentally friendly properties [4–7]. For example, Qiao's group designed and synthesized a series of nonmetal-element-doped graphene materials, and their ORR performances were comparable to that of the state-of-the-art Pt catalyst [4]. Zhao and coworkers prepared N-doped activated carbon using low-cost coal liquefaction residues, and this material had a large specific surface area of 3130 $m^2 g^{-1}$ and better stability than that of commercial Pt/C catalysts [6]. Li and his collaborators reported an N-doped graphitic carbon material from the pyrolysis of deep-eutectic solvents, and the material displayed an efficient ORR performance with an onset potential of 0.97 V and half potential of 0.84 V [7]. Based on theoretical calculations and experimental studies, researchers believe that the different electronegativities of heteroatoms (B = 2.04, N = 3.04, S = 2.58 and P = 2.19) compared to that of C (2.55) can induce a charge redistribution in adjacent C atoms to generate net positive or negative charges, greatly promoting O_2 adsorption and its subsequent reduction [8–10].

Furthermore, compared to single doping, codoping of carbon materials with N and other metal-free heteroatoms leads to a higher ORR electrocatalytic performance due to synergistic effects [11–13]. For example, Huang and colleagues compared the ORR electrocatalytic performance of N-doped CNTs (N-CNTs), B-doped CNTs (B-CNTs) and NB-codoped CNTs (NB-CNTs) and concluded the following order: NB-CNTs > B-CNTs > N-CNTs [11]. Li's group prepared a N, S-codoped ketjen black electrocatalyst with a high ORR activity, long-term stability and good methanol tolerance [12]. In addition, Li and his coworkers reported CNTs single-, double- and triple-doped with B, N and S and found synergetic effects with the double- and triple-doped CNTs [13].

In the periodic table of elements, F has the highest electronegativity (3.98) and can polarize adjacent C atoms to a greater extent. However, to the best of our knowledge, only a few studies on N, F-codoped carbon materials as ORR electrocatalysts have been reported thus far [10,14–23]. For instance, Sahu and coworkers demonstrated that a H_2/O_2 polymer electrolyte fuel cell produced a peak power density of 165 mW cm^{-2} at a load current density of 850 mA cm^{-2} based on a N, F-codoped graphite nanofiber (N-F/GNF) cathode electrocatalyst [10]. Additionally, Li and collaborators illustrated that the ORR electrocatalytic performance of N, F dual-doped mesoporous graphene (NF-MG) was very similar to that of Pt/C electrocatalysts because of the synergistic effect of N and F [16]. Moreover, Wang and collaborators demonstrated that the synergistic effect of F and N sharply polarizes adjacent C atoms and facilitates the formation of defect-induced active sites [20]. These electrocatalysts are usually synthesized using ammonium fluoride (NH_4F) as the N and F single precursor [10,16,18–23], but the disadvantageous facile decomposition of NH_4F (with a low melting point of 98 °C) causes a low content of F doping. Consequently, it is necessary to exploit a new synthetic method for N, F-codoped carbon electrocatalysts.

Herein, a facile and novel synthesis strategy is employed to synchronously dope N and F into carbon black as an efficient electrocatalyst (NFC) for the ORR by using melamine hydrogen fluoride salt (MF) as the single N and F precursor. Compared to the properties of NH_4F, MF not only possesses a higher content of N but also has a higher decomposition temperature in the pyrolysis process. Physical characterizations are carried out by transmission electron microscopy equipped with mapping (TEM-mapping), N_2 adsorption-desorption, X-ray diffraction (XRD), Raman and X-ray photoelectron spectroscopy (XPS). Electrochemical measurements are conducted by cyclic voltammetry (CV) and rotating ring disk electrode (RRDE) measurements in alkaline solution. Since melamine is a kind of alkali, it can react with most acids, such as boric acid, sulfuric acid, and phosphoric acid, so the preparation method can be extended to other metal-free heteroatom-doped carbon-based electrocatalysts.

2. Experimental

2.1. Preparation of NFC electrocatalysts

Scheme 1 simply illustrates the synthesis procedure of the NFC electrocatalyst, in which melamine hydrogen fluoride salt (MF) was used as the single N and F precursor for the first time. Compared to the commonly used NH_4F precursor, MF not only possesses a higher content of nitrogen but also has a higher melting point in the pyrolysis procedure. MF generated from an acid and base neutralization reaction can prevent F loss at low temperature and induce highly efficient doping of F and N in carbon. The synthesis process is described in detail as follows.

(1) As shown in Fig. 1a, the MF precursor was synthesized using a typical acid and base neutralization reaction. First, melamine (2.52 g) was completely dissolved in deionized water (225 mL) under vigorous stirring at 80 °C. Second, hydrofluoric acid (3.02 g) was added dropwise into the solution. Finally, after stirring for 2 h, the solution was dried in an oven at 80 °C to form melamine hydrogen fluoride salt (MF) as a single N and F precursor.

(2) A mixture of 0.2 g carbon black (Black Pearls 2000, BP2000) and 0.2 g of the as-prepared MF were ground in an agate mortar. Then, this mixing powder was transferred into a quartz boat, placed in a furnace, and pyrolyzed in a N_2 atmosphere at a certain temperature for 90 min with a heating rate of 5 °C min^{-1} (Fig. 1b). In this case, a series of NFC electrocatalysts were synthesized at 700 °C, 800 °C, 900 °C and 1000 °C, and correspondingly denoted as NFC700, NFC800, NFC900, and NFC1000, respectively.

2.2. Physical characterizations

Morphology measurements were recorded on a transmission electron microscope (TEM, FEI, Tecnai). X-ray diffraction (XRD) was conducted on a Bruker D8-Advance (Germany) instrument using a Cu Kα radiation (λ=0.154 nm) at 40 kV and 40 mA. N_2 adsorption-desorption isotherm analysis was carried out on an ASAP 2020-Physisorption Analyzer (Micromeritics, USA). Raman analysis operated at a laser wavelength of 532 nm was recorded on a LabRAM HR Evolution spectrometer. XPS was performed on a PERKIN ELMZR PHI 3056 spectrometer using Al Kα monochromated radiation.

2.3. Electrochemical tests

The working electrode was prepared according to the following method: First, 5 mg NFC electrocatalyst powder was dispersed ultrasonically in 950 μL ethanol and 50 μL DuPont Nafion perfluorinated resin solution (5 wt%). Next, 20 μL of this ink was transferred onto a glassy carbon electrode for air drying. All electrochemical measurements were evaluated at a potential scan rate of 5 mV s^{-1} in 0.1 M KOH solution by using a platinum mesh