

Regular Article

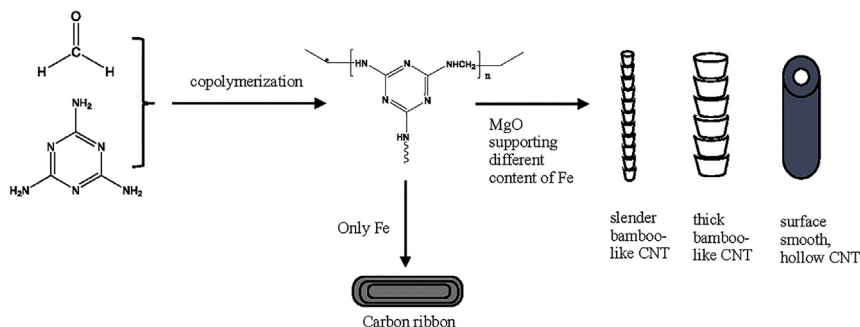
Nitrogen-doped carbon nanotubes based on melamine-formaldehyde resin as highly efficient catalyst for oxygen reduction reaction



Xin Zhang, Ying Huang*, Xuefang Chen, Qiao Gao, Weichao Zhang

MOE Key Laboratory of Material Physics and Chemistry under Extraordinary Conditions, Shaanxi Engineering Laboratory for Graphene New Carbon Materials and Applications, School of Natural and Applied Sciences, Northwestern Polytechnical University, Xi'an 710072, PR China

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 29 June 2017

Revised 20 August 2017

Accepted 29 August 2017

Available online 1 September 2017

Keywords:

Oxygen reduction reaction

Nitrogen-doped carbon nanotube

MgO supporting Fe

ABSTRACT

The preparation of highly efficient and cheap electrocatalysts toward oxygen reduction reaction is significant for many electrochemical cells. Here we facilely synthesized nitrogen doped carbon nanotube by pyrolyzing melamine formaldehyde resin and Fe loading on MgO. There were mainly three morphologies observed, slender bamboo-like CNT, thick bamboo-like CNT, surface smooth, hollow CNT. The content of Fe loading on MgO had little influence on morphologies of CNT, however, when no MgO as support, only carbon ribbon obtained. The MgO as support was also significant for the formation of CNT. The samples with CNT formed represented better catalytic activity than control samples with no-CNT obtained, the morphology of CNT was beneficial for catalytic process. The sample C₁-CNT with lowest content of Fe on support represented best catalytic activity which was competitive with 20% Pt/C in half-wave potential. The C₁-CNT also showed outstanding stability and improved selectivity towards ORR, making it a promising alternative to Pt in application of fuel cells and metal-air batteries.

© 2017 Elsevier Inc. All rights reserved.

1. Introduction

Design and preparation of nano-materials with high efficiency in catalyzing oxygen reduction reaction (ORR) is a key process in developing highly efficient fuel cells and lithium air batteries [1,2]. However, the kinetic sluggish ORR at the cathode results in

the use of precious platinum with scarcity in nature, which prohibits the wide commercialization of these green energy convert devices [3–5]. Therefore, the great efforts have been made to develop highly efficient and cheap no-precious metal catalysts [6–9].

In this regard, carbon nano-materials, such as graphene [10–14], carbon nanohorn [15], carbon nanofiber [16], carbon nanotube [17] and mesoporous carbon [18–20], have been important candidates to develop that kind of electrocatalysts due

* Corresponding author.

E-mail address: yinhg@nwpu.edu.cn (Y. Huang).

to their excellent electronic conductivity, huge specific surface area. Especially, when the heteroatoms (N, S, P and B) are doped into the carbonaceous skeleton, the ORR performance can be greatly enhanced by effectively modulating the chemisorption energy of O_2 , catalytic sites, and the reaction mechanism [21]. Among these dopants, N-doped carbon nanotube (NCNT) has attracted much more attention since 2009, Gong and co-workers prepared vertically aligned NCNT arrays by pyrolyzing of iron(II) phthalocyanine, which presented excellent electrocatalytic performance [22]. Following this breakthrough study, plenty of research has been conducted about NCNT. Rao et al. searched the active site of NCNT and ascribed the electrocatalytic activity to pyridinic-type nitrogen sites [23]. The similar work was further done by Guo et al. in 2016 [24], they found the ORR active sites in N-doped carbon materials are carbon atoms with Lewis basicity next to pyridinic N.

Regarding to the preparation of NCNT, chemical vapor deposition (CVD) has been adopted in many reports with metal particles as catalysts and acetonitrile [25], imidazole [26], aniline and pyridine [27], and etc. as C and N precursors. The other way of fabricating NCNT is pyrolyzing C, N precursors with metal salt. Yang et al. pyrolyzed P123, melamine, and $Fe(NO_3)_3$ at 800 °C in N_2 and prepared bamboo-like Carbon nanotube/ Fe_3C nanoparticle hybrids, which exhibited good ORR activity both in alkaline and acidic media [17]. A more interesting work was represented by Meng et al. in 2017, they used MOF crystals acting as a single precursor for both nanocatalysts and carbon sources, through a low-temperature pyrolysis process. MOF transformed into oriented CNT-assembled architectures that had a large specific surface area, suitable pore size distribution, robust frameworks, resulting in excellent electrochemical performance [28]. Generally, the synthesis method and precursors have a significant impact on the morphology and performance of NCNT.

Here, we synthesized nitrogen-doped carbon nanotubes by decomposition of melamine formaldehyde resin under high temperature. The resin could one step transformed into nitrogen contained CNT and formed active center under the catalyzing of Fe loading on MgO. There were mainly three morphologies observed. The content of Fe loading on MgO had little influence on morphology of CNT. However, when only Fe as catalysts, only carbon ribbon obtained. The MgO as support was significant for the formation of CNT. Compared with samples that had no-CNT obtained, the CNT synthesized from MF resin represented better catalytic activity, the morphology of CNT was beneficial to improve catalytic activity.

2. Experimental

2.1. Synthesis of electrocatalysts

Iron nitrate, Melamine, formaldehyde solution, magnesium oxide and sodium hydroxide came from Sinopharm Chemical Reagent Co. Ltd., China as an analytical reagent grade and were used without further purification. Commercial multi-wall carbon nanotube purchased from Chengdu Organic Chemicals Co. Ltd., Deionized water was used in all experiments. the method partly referred to related articles [29,30].

2.1.1. Synthesis of Fe@MgO catalysts

0.5 g ferric nitrate was dissolved in 100 ml alcohol and then 5 g MgO was mixed. Then heating the slurry to evaporate alcohol under vigorous stirring. The Fe@MgO catalysts with different content of Fe were prepared under same procedure by adding 2.5 g, 5 g ferric nitrate. They were named with C_1 , C_2 , C_3 , respectively.

2.1.2. Synthesis of MF resin

Melamine and formaldehyde copolymerize to get the MF resin. Typically, 12 g melamine was dissolved in the solution of 30 ml deionized water and 24 ml formaldehyde under vigorous stirring, then adjusting the pH of mixture to 8–9. The solution was heated to 80 °C for about 30 min in a water bath until the solution became clear and colorless. After cooling down to 40 °C, 10 ml acetic acid was added to initiate the condensation reaction. The solution was stirred overnight and the product was collected by filtration. Finally, the powder resin was dried at 80 °C.

2.1.3. Synthesis of nitrogen doped CNT

In a typical preparation, 0.75 g above Fe@MgO catalysts was ground with 3 g MF resin powder in a mortar to uniformly mix. The mixture was put into a furnace to suffer a heat treatment under 200 °C for 3 h with a heating rate of 1 °C/min, then pyrolyzed at 900 °C for 1 h in Ar atmosphere with a ramp rate of 5 °C/min. The obtained sample was put into 0.5 M H_2SO_4 at 80 °C for 3 h to remove undue metal and unstable components, then filtered and washed with deionized water. Then secondly annealing sample under the same procedure as previous pyrolysis procedure. According to the use of Fe@MgO catalysts, the final products were labeled as C_1 -CNT, C_2 -CNT, C_3 -CNT, respectively.

Out of comparison, the samples of only Fe, only MgO, no Fe@MgO catalysts were prepared under same procedure as control samples. Typical, 0.068 g ferric nitrate (the similar proportion of Fe with C_1 -CNT) was dissolved in 100 ml ethanol and 3 g MF resin was added, then evaporating the ethanol and getting the powder, they suffered the same pyrolysis procedure and acid treatment as above. The final product was labeled as “Fe-resin”. In addition, 0.75 g MgO was mixed with 3 g MF, then suffered same procedure to get the “MgO-resin”. Pure MF resin was used to get the sample “resin”.

2.2. Physical characterization

The morphology of the samples was observed using a scanning electron microscope (SEM, HITACHI S-4800) and transmission electron microscopy (TEM, JEOL JEM 2010). Raman spectra were got from a Raman spectrometer (Renishaw WIRE3.4) using a 532 nm laser. XRD patterns were obtained using an X-ray diffractometer (Rigaku D/Max 2500 V/PC) equipped with a $Cu K\alpha$ source operating at 36 kV and 200 mA. The surface characterization of the synthesized samples was analyzed by using X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD) with carbon 1s at 284.6 eV as a reference to conduct a charge correction.

2.3. Electrochemical characterization

ORR activity of catalysts was evaluated using a rotating disk electrode system (ALS, RRDE-3A) in 0.1 M KOH electrolyte. The test was performed using Gamry Electrochemical Station (reference 600) in a conventional three-electrode system, including a platinum wire as the counter electrode, an Ag/AgCl electrode as a reference electrode, glassy carbon (GC, 3 mm in diameter) as work electrode and was polished before use.

The catalyst ink was prepared by dispersing 5 mg catalyst in mixture of 1 ml ethanol and 5 wt% Nafion solution (50 μ L) with sonication for 1 h. The catalyst ink (9 μ L) was pipetted on the surface of GC whose active electrode area is 0.0707 cm^2 , then dried in air to get a catalyst load of 0.606 mg/cm^2 . For comparison, the commercial Pt/C (20 wt%, Johnson Matthey) electrode was also made to get a load of 48.5 μ g Pt/ cm^2 .

In the Cyclic voltammetry (CV) and Linear sweep voltammetry (LSV) tests, 30 min gas purging was necessary before tests began. CV test was conducted at 0.2 V to -1 V with a scan rate of

Download English Version:

<https://daneshyari.com/en/article/4984325>

Download Persian Version:

<https://daneshyari.com/article/4984325>

[Daneshyari.com](https://daneshyari.com)