ARTICLE IN PRESS

INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2017) 1–10

Available online at www.sciencedirect.com

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Facile synthesis of efficient core-shell structured iron-based carbon catalyst for oxygen reduction reaction

Guang-Lan Li [a,*], Cai-Di Liu [a], Li-Fang Yuan [a], Qiu-Mei Wu [b], Wen-Wen Chen [a], Guang-Chun Cheng [a], Bei-Bei Yang [a], Ce Hao [a]

[a] State Key Laboratory of Fine Chemicals, Dalian University of Technology, Panjin, 124221, Liaoning, China

[b] State Key Laboratory of Powder Metallurgy, Central South University, Changsha, 410083, Hunan, China

ARTICLE INFO

Article history:
Received 4 September 2017
Received in revised form
27 October 2017
Accepted 9 November 2017
Available online xxx

Keywords:
Core-shell structure
Two-step anneal
Mesoporous catalyst
Oxygen reduction reaction

ABSTRACT

Controlled synthesis of efficient core-shell non-precious metal catalysts for oxygen reduction reaction (ORR) is undoubtedly crucial but challenging for the extensive application of fuel cells and metal-air batteries. Herein, we prepared a core-shell structured Fe/FeC_x nanoparticles and porous carbon composited catalyst (Fe/FeC_x@NC) via a facile two-step heat treatment strategy. The Fe/FeC_x@NC-$800_{-0.5}$ prepared with secondary anneal at 800 °C for 0.5 h exhibits superior ORR performance to the commercial Pt/C in terms of comparable onset potential, higher half-wave potential, and outstanding long-term durability in alkaline media. Through combining the physical and electrochemical characterizations of Fe/FeC_x@NC-T_{-t} with different anneal temperature and precursors, the outstanding ORR performance of Fe/FeC_x@NC-$800_{-0.5}$ is caused by the synergistic effect between Fe/FeC_x core and enriched pyridinic N- and graphitic N-doped carbon shell as well as porous carbon with large specific surface area. The structure-activity relationship of core-shell structured Fe–N–C catalysts for ORR provides directions for the development of advanced nonprecious metals catalysts.

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Introduction

Rational design and construction of advanced materials with superior catalytic performances for oxygen reduction reaction (ORR) are particularly important to develop highly efficient energy conversion and storage devices, such as fuel cells and metal-air batteries [1,2]. The prohibitive cost and scarcity of Pt-based catalysts have stimulated vast exploration of alternative nonprecious metal catalysts (NPMCs) [3–7]. Among the NPMCs, iron-based nitrogen doped carbon (Fe–N–C) catalysts are often regarded as the potential candidates because of their acceptable cost, outstanding activity, remarkable stability, and free from immune to the methanol-crossover effect [3,8–10]. Tremendous efforts have been focused on the research of advanced Fe–N–C catalysts, however, to meet the requirements for real application of fuel cells and metal-air batteries, their performances need to be further improved [2].

To achieve this, the Fe–N–C catalysts with different kinds of active sites and/or structures have been researched [11–14]. Among these materials, core-shell structured Fe–N–C

* *Corresponding author.*
E-mail address: guanglanli@dlut.edu.cn (G.-L. Li).

https://doi.org/10.1016/j.ijhydene.2017.11.072

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Please cite this article in press as: Li G-L, et al., Facile synthesis of efficient core-shell structured iron-based carbon catalyst for oxygen reduction reaction, International Journal of Hydrogen Energy (2017), https://doi.org/10.1016/j.ijhydene.2017.11.072

catalysts with the iron species confined in the carbon shell may be paid more attention [15–18] due to that the unique electronic interaction between metal species core and carbon shell [19], and the modifiable carbon shells, such as the specific surface area (SSA), pore volume, and the electrical conductivity may modify the active sites density and mass transport property and thus influence the ORR activity [20–22]. For instance, Bao and co-workers demonstrated that iron nanoparticles encapsulated within carbon layers alone could greatly increase the ORR properties of surrounding carbon layers through changing the charge-density which distributes on the outer N-doped carbon (NC) layers [19]. Xing and Li et al. synthesized a catalyst for ORR in the form of hollow spheres, which is composed of uniform Fe_3C nanoparticles embedded in the graphitic layers. Compared with the catalysts without Fe_3C or nitrogen doping, the obtained catalyst shows apparently higher ORR activity [23]. Through etching the catalysts by hot acids and ball milling to destroy the carbon shell, it was demonstrated that the high ORR performance should be ascribed to the synergetic effects between the Fe_3C core and graphitic N-doped carbon shell, and the protection of carbon shell as well [23].

Differently from iron or FeC_3 core alone, many researchers also devoted to explore Fe/FeC_x composite as the core. For instance, Feng et al. reported an iron-based hybrid with core-shell structure (Fe/Fe_3C) encapsulated by N-doped carbon nanotubes synthesized with a hard-templating method, which also exhibited appealing ORR activity [24]. More importantly, although many researches about the core-shell structured materials with iron-based composite core and NC shell have been reported, the controllable synthesis of core-shell structure with desired mesoporous and high SSA by a simple strategy is still a great technological challenge.

Herein, we fabricated a mesoporous core-shell structured catalyst with Fe/FeC_x core and NC shell via a facile two-step annealing strategy using glucose, aniline and $FeCl_3$ as precursors, and SiO_2 nanospheres as template which is conducive to increase the limited specific surface area and expose more active sites. The low cost precursors and facile preparation method promote the large-scale production. The optimized Fe/FeC_x@NC-$800_{-0.5}$ catalyst exhibits comparable catalytic activity for the ORR to that of commercial Pt/C. The secondary anneal time, temperature, and precursors were modified to verify the effect of active site and texture on the ORR performance. These studies may shed light on the origin of prominent ORR performance for core-shell structured Fe–N–C catalysts, and open paths for rationally developing superior ORR performance catalysts.

Experiment

Chemicals and reagents

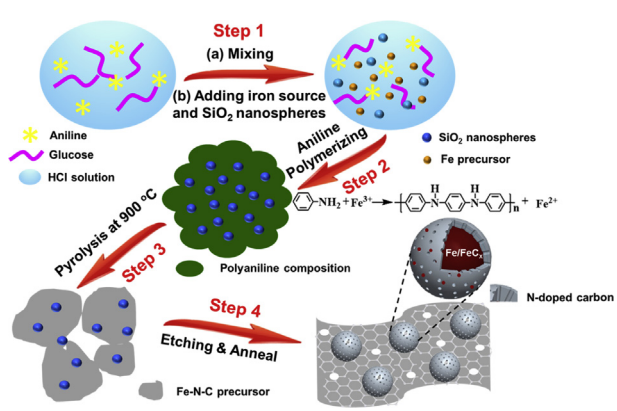
D-Glucose, NaOH (≥96%), and concentrated hydrochloric acid (≥37%) were obtained from Kermel. $FeCl_3 \cdot 6H_2O$ (≥99.0%) and aniline (99.5%) were purchased from DAMAO. SiO_2 (50 nm, 40 wt% in aqueous solution) was purchased from Haiyi Scientific & Trading Co., Ltd. Nafion (5 wt%) was obtained from Sigma Aldrich. All chemicals were used as received without any purification.

Synthesis of Fe/FeC_x@NC-T_{-t} catalysts

The preparation procedure for Fe/FeC_x@NC-T_{-t} (T = 700, 800, 900 °C; t = 0.5, 1, 2 h) catalysts is illustrated in Scheme 1. Take the typical procedure of Fe/FeC_x@NC-$800_{-0.5}$ as an example: first, 1.8216 g of glucose and 0.6 mL of aniline (carbon and nitrogen precursor) were ultrasonically dissolved into 20 mL of 0.5 M HCl solution. Then 7.5 g of SiO_2 template was added under stirring to form homogeneous mixture. After that, 25 mL of 1.2 M $FeCl_3$ solution (iron precursor) was dropwise added into the above mixture under vigorous stirring in ice-water bath (<15 °C) and kept for 16 h. The obtained mixture was then dried at 100 °C overnight and then pyrolized at 900 °C for 1 h with a heating rate of 5 °C min^{-1} in N_2. To remove SiO_2 template, the above pyrolized product was etched in 2.0 M NaOH solution at 80 °C for 12 h. After thoroughly washed with water, filtrated and dried in vacuum at 80 °C for 8 h, Fe–N–C was obtained. The Fe–N–C sample was finally pyrolized at 800 °C for another 0.5 h under flowing N_2 at a rate of 3 °C min^{-1} and Fe/FeC_x@NC-$800_{-0.5}$ catalyst was afforded. Fe/FeC_x@NC-$700_{-0.5}$, Fe/FeC_x@NC-$900_{-0.5}$, Fe/FeC_x@NC-800_{-1} and Fe/FeC_x@NC-800_{-2} catalysts were also prepared with the same method as those for Fe/FeC_x@NC-$800_{-0.5}$ except for prepared at different temperatures and time for the second heat treatment. To better understand the catalytic performance and reveal the active sites in Fe/FeC_x@NC-$800_{-0.5}$ catalyst, Fe-N-$800_{-0.5}$, N-C-$800_{-0.5}$, and Fe-C-$800_{-0.5}$ were also prepared for comparison using aniline (0.6 mL) and 1.2 M $FeCl_3$ (25 mL), glucose (1.8216 g) and aniline (0.6 mL), and glucose (1.8216 g) and 1.2 M $FeCl_3$ (25 mL) as precursors respectively under the same synthesis conditions as those for Fe/FeC_x@NC-$800_{-0.5}$, i.e., first pyrolized at 900 °C for 1 h, then etched with NaOH solution for 12 h and finally pyrolized at 800 °C for 0.5 h.

Characterization

Transmission electron microscopy (TEM) was recorded on JEOL JEM-2000EX microscope at 120 kV. High resolution transmission electron microscopy (HRTEM) was carried out on



Scheme 1 – Schematic illustration of construction process for Fe/FeC_x@NC-T_{-t} (T = 700, 800, 900 °C; t = 0.5, 1, 2 h) catalysts.

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