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Egg derived nitrogen-self-doped carbon/carbon nanotube hybrids as noble-metal-free catalysts for oxygen reduction

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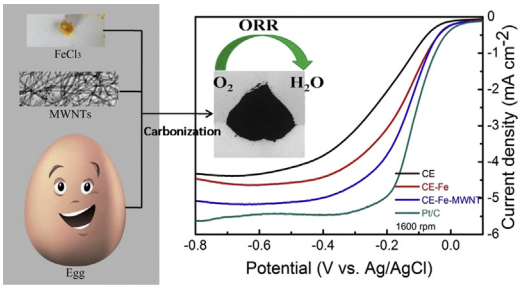
HIGHLIGHTS

- Novel non-noble metal catalysts for ORR are obtained using eggs as N and C sources.
- The catalyst shows a catalytic activity comparable to Pt/C in alkaline media.
- The catalyst has superior stability and fuel tolerance than Pt/C in alkaline media.
- It provides a promising alternative to noble metal catalysts by using eggs.

GRAPHICAL ABSTRACT



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ABSTRACT

Currently, the development of nitrogen (N) doped carbon based non-precious metal ORR catalysts has become one of the most attractive topics in low temperature fuel cells. Here, we demonstrate a green synthesis route of N-self-doped carbon materials by using eggs as N sources combining with iron sources and multi-walled carbon nanotubes (CE–Fe–MWNT). After carbonized, such hybrid materials possess an outstanding electrocatalytic activity towards ORR comparable to the commercial Pt/C catalyst in alkaline media, and both superior stability and fuel (methanol and CO) tolerance than the commercial Pt/C catalyst, which provide a promising alternative to noble metal catalysts by using abundant natural biological resources.

1. Introduction

Pt-based catalysts represent a state of the art in the electrocatalysis of oxygen reduction reaction (ORR) for low temperature fuel cells (LTFCs) which can convert chemical energy directly into electricity without combustion processes and with high energy conversion efficiencies [1]. However, Pt is both expensive and scarce, greatly limiting its widespread implementation in LTFCs. Besides, Pt-based catalyst still suffers from serious intermediate tolerance, such as carbon monoxide (CO) poisoning and methanol crossover as well as poor stability in an electrochemical environment [2–6]. Consequently, considerable research efforts have been devoted to developing a high performance noble-metal-free catalyst (NMFC) with earth-abundant elements.

Carbon is a very common element, which widely exists in the Earth. The heteroatom doped carbon materials not only exhibit high catalytic activity and long-term stability, but also excellent CO and methanol poisoning resistances [1,7–9]. Hitherto, investigating heteroatom doped carbon catalysts for ORR becomes one of the hottest topics in LTFCs. As reported, the carbon based catalysts have been achieved by doping various heteroatoms (such as N, B, P, S, Fe or Co) [3,7,10–13]. Among them, transition metal N-doped carbon

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materials have exhibited the best catalytic performance for ORR [7,10,14]. However, such N-containing compounds are either expensive or harmful to human health, because most of N sources always derive from expensive organic monomers containing nitrogen element or ammonia [15–17]. Therefore, the long-term development of N-doped carbon electrocatalysts with non-toxic and cheaper N sources is highly desirable.

Eggs are natural and widely available biological materials with abundant heteroatoms (C, H, O, N, et al.). It can take place of conventional N-containing organic compounds or ammonia to develop the N-doped carbon catalyst, meeting the requirements for nontoxic and inexpensive properties. In this paper, the egg is employed as a N source mixing with the transition metal iron and multi-walled carbon nanotubes (MWNTs). After cooked, dried and carbonized at high temperatures and followed post-treatments (PTs) including ball milling, acid leaching and the second heat treatment (as shown in Fig. 1), the CE–Fe–MWNT hybrid material is obtained. Here the highly graphitized MWNTs provide a robust matrix for hosting the active sites due to its superior electrical conductivity and excellent mechanical and chemical stability. The electrochemical characterization shows that this hybrid material possesses an outstanding electrocatalytic ORR activity in alkaline media, and both superior stability and fuel (methanol and CO) tolerance compared to the commercial Pt/C catalyst. This work shows a good example for taking advantage of the abundant resources provided by natural biological materials as a promising alternative for costly Pt-based catalysts.

2. Experimental section

2.1. Materials

Eggs were purchased from local super market. The multi-walled carbon nanotubes (MWNTs, with ca. 80 nm in diameter and ca. 110 $m^2 g^{-1}$ in surface area) were treated in an aqueous HCl solution for 24 h to remove the potential metal impurities. Ferric chloride ($FeCl_3 \cdot 6H_2O$) and potassium hydroxide (KOH) were purchased from Sinopharm Chemical Reagent, and Nafion solution (5 wt %) was obtained from Sigma–Aldrich. All the chemicals were used as delivered without further treatment. Ultra pure water was obtained from a Lab. ultra pure water filter system with a resistivity $\geq$18 MΩ cm^{-1}. Rotating disk electrodes of glassy carbon (RDE, 5 mm in diameter) were purchased from Tianjin Aida Hengsheng Tech. Co., China.

2.2. Material syntheses

Eggs were diluted with an equal amount of water. And then 0.1 mol L^{-1} $FeCl_3$ mixing with MWNT solution was added dropwise to the above suspension and kept stirring for 2 h (Fe: MWNT: egg = 0.1: 0.2: 10, wt. %). The mixture was cooked in a water bath (100 °C, 2 h), and then dried in an air-circulating oven at 80 °C to obtain the precursor. The precursor was carbonized at 900 °C in an inert atmosphere. Temperature settings were as follows: the precursor was performed at 200 °C for 0.5 h at a heating rate of 2 °C min^{-1} in an inert atmosphere, subsequently it was performed at 900 °C for 2 h at a heating rate of 5 °C min^{-1} in an inert atmosphere, and then the sample was cooled under the same atmosphere from 900 °C to 60 °C. After that, the black carbon was transferred into a milling tank and grinded on a planetary ball mill (Nanjing Chishun Science & Technology Co., Ltd. PM) for 4 h at 250 rpm. The resulting black carbon powder was pre-leached in 0.5 M H_2SO_4 at 80 °C for 8 h to remove unstable and inactive species from the catalyst, followed by thoroughly washed in de-ionized water and absolute ethyl alcohol, and then dried at 80 °C under vacuum. Finally, the product was heat-treated again at 900 °C for 2 h at a heating rate of 5 °C min^{-1} in nitrogen atmosphere to obtain the CE–Fe–MWNT catalyst. The specific synthesis process of CE–Fe–MWNT catalyst is shown in Fig. 1.

2.3. Physical and chemical characterizations

The morphology and structure of the samples were further analyzed using JSM-7100F field emission scanning electron microscope (FESEM) and JEM-2100F high-resolution transmission electron microscopy (TEM). Nitrogen adsorption–desorption isotherms were recorded at 78 K with a Micromeritics ASAP 2020 Brunauer Emmett Teller (BET) analyzer. The electronic structure of surfaces for the catalyst was performed using VG-Multi-lab2000 X-ray photoelectron spectroscopy (XPS). Accurate iron content of these catalysts was performed using inductively coupled plasma-atomic emission spectrometry (ICP-AES). Raman spectroscopy

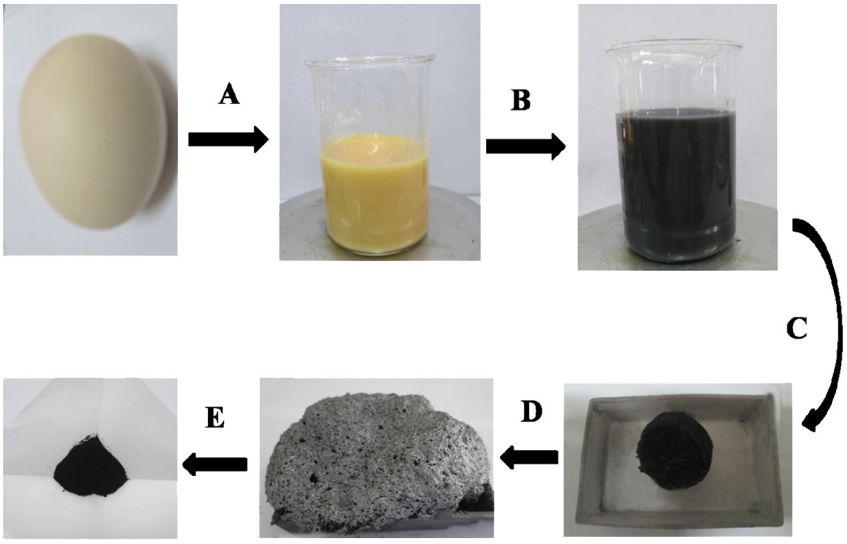

Fig. 1. Schematic of the synthesis process of CE–Fe–MWNT catalyst. (A) Cracking the egg and mixing with water. (B) Adding $FeCl_3$ mixing with MWNT solution. (C) Cooking and drying it. (D) The precursor was carbonized in an inert atmosphere. (E) The post-treatment including ball milling, acid leaching and the second heat treatment.