Fe/N/C carbon nanotubes with high nitrogen content as effective non-precious catalyst for oxygen reduction reaction in alkaline medium

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ABSTRACT

The non-precious metal catalysts usually have low nitrogen content, resulting in poor oxygen reduction reaction (ORR) performance. Herein we demonstrated a strategy to synthesize the Fe/N/C carbon nanotubes (Fe—N—BCNTs) with high nitrogen content. The strategy included pyrolysis of ferric chloride and dicyandiamide, polymerization of pyrrole onto intermediate product's surface, and following by calcination in N_2 atmosphere. Electrochemical test results show that the catalyst exhibits highly efficient ORR activity with an onset potential of 0.995 V (*vs* reversible hydrogen electrode) in 0.1 M KOH solution, 30 mV more positive than that of 20 wt. % Pt/C catalyst. The excellent ORR performances could be attributed to the more nitrogen functional groups in Fe—N—BCNTs-PPy-800 catalyst, which is revealed by Raman and XPS. Moreover, the prepared catalyst exhibits better methanol tolerance and higher stability in comparison to commercial Pt/C catalyst.

Introduction

Fuel cells have attracted tremendous attention during the last decades because it is considered as a clean and efficient power source to replace the traditional energy [1,2]. The cathode oxygen reduction reaction (ORR) is a crucial step that determines the performance of fuel cells [3], and Pt-based materials are known as the most commonly used catalysts for ORR [4—6]. However, Pt-based catalysts suffer many drawbacks, such as their high cost, limited resource, intolerance to methanol oxidation and poor durability, which hinder the large-scale applications of fuel cells [7—11]. To overcome the above shortcomings, a range of non-precious metal

catalysts (NPMCs) have been developed to replace Pt-based materials in the past few decades. Among these, transition-metal-coordinating nitrogen-doped carbon catalysts (M−N−C) have gained more and more attention due to their superior catalytic activity and stability [12−15].

In 1964, Jasinski et al. firstly reported the ORR catalytic activity of macrocyclic N$_4$-complexes combined with transition metals [16], and later Yeager et al. showed the macrocyclic structure was not essential to the ORR activity [17]. Since then, many M−N−C based catalysts have been developed, while iron and cobalt become the most widely used transition metals owing to their high natural abundance [18]. Usually, M−N−C based catalysts are synthesized through pyrolysis of precursors containing transition metal, nitrogen, and carbon [1,19,20]. For example, Liang et al. respectively prepared iron−nitrogen-doped carbon and cobalt−nitrogen-doped carbon from polyaniline−Fe complex and vitamin B12, which used ordered mesoporous silica SBA-15, silica nanoparticles and montmorillonite as templates for forming mesoporous structures [21]. Recently, Wei et al. fabricated high-performance Fe$_3$C/Fe−N−C catalysts for the ORR by using tissue, commercial filter paper, or cotton as carbon source, dicyandiamide as nitrogen source, and iron-tannin framework as iron source [22]. Many studies used melamine or dicyandiamide as nitrogen source to synthesize metal−nitrogen−carbon catalysts [22−25]. However, nitrogen contents of these catalysts are very low due to volatilization of melamine or dicyandiamide in the process of pyrolysis [23]. Pyrrole is a heterocyclic aromatic organic compound whose nitrogen content is 20.9%. As polymer of pyrrole, polypyrrole has many merits, such as nonvolatility and good stability. Therefore, polypyrrole on surface of these catalysts could not only protect the catalysts, but also increase the number of "N" active sites.

Herein, we have developed a strategy to prepare Fe/N/C carbon nanotubes (denoted as Fe−N−BCNTs) with high nitrogen content, including pyrolysis of ferric chloride and dicyandiamide (DCD), polymerization of pyrrole onto intermediate product's surface, and following by calcination in N$_2$ atmosphere. TEM, SEM, XRD, Raman and XPS were conducted to study the morphology and structure of the prepared catalysts. Compared with 20 wt. % Pt/C catalyst, the as-synthesized Fe−N−BCNTs catalysts exhibit excellent ORR activity, higher stability and better methanol tolerance in alkaline media.

Experimental section

Synthesis of Fe−N−BCNTs

Fe−N−BCNTs were synthesized by a direct pyrolysis of dicyandiamide and ferric chloride. In a typical synthesis, 5.0 g dicyandiamide and 2.5 g ferric chloride hexahydrate (FeCl$_3$·6H$_2$O) were dispersed into deionized water (300 mL) via vigorous stirring. Then, the mixture was dried at 110 °C for 10 h. The dried samples were respectively transferred to a tube furnace and annealed at a preset temperature from 700 to 900 °C for 1 h in nitrogen atmosphere. Subsequently, the residuum was dissolved in 2 M HCl solution for 24 h to remove the exposed iron species, followed by being washed with deionized water and dried at 80 °C for 10 h. These obtained samples were denoted as Fe−N−BCNTs-X (X indicates the pyrolysis temperature, 700−900 °C).

Synthesis of Fe−N−BCNTs-PPy

1.5 g Fe−N−BCNTs-800 and 2.5 g anhydrous ferric chloride were dispersed into acetonitrile (100 mL) via vigorous stirring. Subsequently, 0.5 mL pyrrole was added dropwise to the above mixed solution under continuous stirring at room temperature. After constant stirring of 12 h for complete polymerization, the product was separated by filtration and being washed with ethanol and water. The obtained hybrid were denoted as Fe−N−BCNTs-PPy.

Synthesis of Fe−N−BCNTs-PPy-800

The obtained Fe−N−BCNTs-PPy and 1.0 g ferric chloride hexahydrate were then mixed in deionized water (300 mL) through vigorous stirring and dried at 110 °C overnight. The dried mixture was subjected to pyrolysis at 800 °C for 1 h under flowing N$_2$ atmosphere. After that, the pyrolyzed product was preleached in 2 M HCl solution for 24 h, followed by being washed with deionized water and dried at 80 °C for 10 h. The obtained powdered sample was denoted as Fe−N−BCNTs-PPy-800. The synthesis procedure of Fe−N−BCNTs-PPy-800 was illustrated in Fig. 1.

Physical characterization

The Fe−N−BCNTs morphologies were investigated using scanning electron microscopy (SEM, LEO1530VP) and transmission electron microscopy (TEM, JEM-2010). X-ray diffraction (XRD) patterns were recorded on an X-ray diffractometer (D/max-IIIA, Japan). Raman spectra were tested by using an Aramis LabRam spectrometer. X-ray photoelectron spectroscopy (XPS) was recorded on an ESCALAB 250Xi. An ASAP 2010 Micromeritics analyzer was used to measure the nitrogen adsorption and desorption isotherms.

Electrochemical measurements

The electrochemical performances of the prepared catalyst were characterized by cyclic voltammetry (CV) and linear sweeping voltammetry (LSV) using an electrochemical workstation Zennium (Zahner) at room temperature (25 °C). A saturated calomel reference electrode (SCE) and a platinum wire were used as the reference and counter electrodes, respectively. The working electrode was a rotating ring-disk electrode (platinum ring, 7.5 mm o.d. and 6.5 mm i.d.; glassy carbon disk, 5.0 mm in diameter, RRDE). The thin-film electrode was prepared as follows. 8.0 mg of the catalyst was dispersed in 2.0 mL of Nafion/ethanol (0.50 wt. % Nafion) by sonication for 160 min. After that, 5 μL of the mixture was dropped onto the glassy carbon disk through a pipet, yielding the catalyst loading of 0.10 mg cm^{-2}. By comparison, the ORR activity for the commercial 20 wt. % Pt/C catalyst (HiSPEC3000, Johnson Matthey) was also measured.