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Effect of carbon nanofiber surface functional groups on oxygen reduction in alkaline solution

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HIGHLIGHTS

- Different surface functional groups were successfully imported onto CNF surface.
- CNF–ON exhibited the highest ORR activity, followed by CNF–OX, CNF–CO and CNF–OH.
- CNF–ON could catalyze ORR through the $4e^-$ pathway.

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ABSTRACT

Carbon nanofibers (CNFs) with different content of surface functional groups which are carboxyl groups (CNF–OX), carbonyl groups (CNF–CO) and hydroxyl groups (CNF–OH) and nitrogen-containing groups (CNF–ON) are synthesized, and their electrocatalytic activities toward oxygen reduction reaction (ORR) in alkaline solution are investigated. The result of X-ray photoelectron spectroscopy (XPS) characterization indicates that a higher concentration of carboxyl groups, carbonyl groups and hydroxyl groups are imported onto the CNF–OX, CNF–CO and CNF–OH, respectively. Cyclic voltammetry shows that both the oxygen- and nitrogen-containing groups can improve the electrocatalytic activity of CNFs for ORR. The CNF–ON/GC electrode, which has nitrogen-containing groups, exhibits the highest current density of ORR. Rotating disk electrode (RDE) characterization shows that the oxygen reduction on CNF–ON/GC electrode proceeds almost entirely through the four-electron reduction pathway, the CNF–OX/GC, CNF–CO/GC and CNF–OH/GC electrodes proceed a two-electron reduction pathway at low potentials (−0.2 V to −0.6 V) followed by a gradual four-electron reduction pathway at more negative potentials, while the untreated carbon nanofiber (CNF–P/GC) electrode proceeds predominantly by a two-electron reduction pathway within the whole range of potential studied.

1. Introduction

Recently, intensive attention has been paid to CNFs due to their outstanding structural, mechanical, and extraordinary electrical properties [1,2]. CNFs can be utilized for a variety of promising applications, such as, structural and functional composites, and they are also widely used as catalyst support in fuel cells because of their low cost, long cycle life and high electrical conductivity [3]. Studies have shown that metal nanoparticles supported on CNFs provide much improvement in catalytic activity [4,5]. Platelet CNF (p-CNF) has a stronger interaction with Pd nanoparticles and the electrocatalyst supported on p-CNF exhibits a higher electrochemical surface area and more positive onset reduction potential of oxygen reduction reaction than that supported on activated carbon [6].

CNFs are also considered to be promising candidates for the ORR catalysts in alkaline fuel cells due to their high surface area, high chemical and thermal stability and high electrical conductivity [7,8]. Before being used as catalysts, the CNFs are usually oxidized to introduce oxygen-containing surface groups to increase the active sites. Many studies have shown that the oxygen-containing surface groups formed on CNF are closely related to the oxidation methods, while air oxidation and acid oxidation are the frequently used methods [9]. Air oxidation treatment preferentially forms hydroxyl and carbonyl groups, while acid treatment forms carboxylic acid

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groups on the surface of CNF [10,11]. Intensive efforts have been devoted on the N-doped carbon materials due to their high electrocatalytic activity and low overpotential. Several methods can be employed to synthesize N-doped carbon nanotubes, such as, arc-discharge [12], laser ablation [13], modified chemical vapor deposition (CVD) methods [14,15] and high temperature pyrolysis [16].

The ORR plays a significant role in controlling the performance of the cathode in a fuel cell, and efficient ORR electrocatalysts are essential for the practical applications of the fuel cells [17,18]. The reduction of oxygen at carbon based electrodes has been extensively studied [19,20]. The ORR proceeds through either a four-electron pathway producing water as the end product, or a two-electron pathway producing hydrogen peroxide as the intermediate [21,22]. The electrocatalytic activity towards ORR is not only depended on the microstructure, such as the edge plane and the basal plane of the CNFs [23], but also significantly determined by the surface functional groups, such as oxygen-containing groups [24] and nitrogen-containing groups [25]. Xu et al. [26] examined the reduction of oxygen on several carbon surfaces and found the oxygen-containing groups could improve the proton transfer rate. Qu et al. [25] synthesized a nitrogen-doped graphene (N-graphene) by chemical vapor deposition using NH_3 as the nitrogen source, and found the N-graphene electrode could act as a metal-free ORR catalyst via a four-electron pathway in alkaline fuel cells. However, it remains unclear that which type of functional groups plays the major role towards ORR.

In this paper, we studied the relationship between the types of surface functional groups and their electrocatalytic activity towards ORR in alkaline solution. Different treating methods were used to introduce the oxygen-containing surface groups onto CNFs, and the properties of surface functional groups on the modified CNFs were studied by XPS. The effects of different types of surface functional groups on the catalytic activity toward ORR were evaluated by cyclic voltammetry (CV) experiment. Rotating disk electrode technology was applied to investigate the ORR mechanism on CNF catalysts.

2. Experimental

2.1. Surface modifications of carbon nanofibers

The acid-treated CNF was achieved by sonochemical treatment [2,27]. Typically, the surface treatment process was as follows: 2.0 g of fishbone CNFs (f-CNFs, 95% purity from Shenzhen Nanotech Port Co., Ltd) were sonochemically treated in a mixed acid solution containing concentrated HNO_3 (188 mL), concentrated H_2SO_4 (160 mL) and ultrapure water (12 mL, 18.2 MΩ cm) in an ultrasonic bath for 2 h at 60 °C. After the surface treatment, the CNFs were filtered and thoroughly washed with ultrapure water before being dried overnight at 120 °C. The acid-treated CNF was denoted as CNF–OX and the untreated CNF was denoted as CNF–P.

The air-treated CNF was achieved through air oxidation performed in a temperature programmed tube furnace [28]. Specifically, 2.0 g of f-CNFs were placed in the tube furnace and heated from 25 °C to 600 °C at a rate of 5 °C min^{-1} under air atmosphere. After the temperature was maintained for 2 h, the furnace was cooled to room temperature slowly. The remaining CNFs were washed with ultrapure water, and then dried at 120 °C overnight. The air-oxidized CNF was denoted as CNF–CO.

Partial conversion of the acidic groups, carboxylic acid groups in particular, on the CNF–OX surface to hydroxyl groups was performed according to the procedure described by Jos van Dillen et al. [29,30]. 0.20 g of lithium aluminum hydride ($LiAlH_4$) was dissolved in 25 ml of fresh anhydrous tetrahydrofuran (THF), while 0.5 g of CNF–OX was dispersed in 50 ml of fresh anhydrous THF. The $LiAlH_4$ suspension was carefully added to the CNF–OX suspension under the nitrogen flow and stirred for 20 h. After the reaction, the mixture was filtrated and washed with anhydrous THF, 0.1 M HCl solution and ultrapure water in series till the filtrate was neutral. The sample was dried at 120 °C overnight and denoted as CNF–OH.

The electrocatalytic activity could be improved by doping the nitrogen atoms into the carbon network according to many reports [25,31]. In this paper, the melamine was used as the nitrogen source to synthesize N-doped CNF (CNF–ON) as reported by Sheng et al. [32]. Briefly, 0.5 g of CNF–OX and 2.5 g of melamine were mixed together by grinding, forming a uniform gray mixture. The mixture in a crucible with a lid was then placed into a corundum tube with nitrogen flow and heated to 700 °C at a rate of 5 °C min^{-1}, and then held for 1 h at 700 °C. The possible doping is that the melamine which was adsorbed on the CNF surface at low temperature, condensed and formed carbon nitride after increasing the temperature, and then the carbon nitride decomposed and doped into graphene layers [32]. The N-doped CNF was denoted as CNF–ON.

2.2. Characterization of carbon catalyst

The textural properties of the modified CNFs were obtained from N_2 adsorption–desorption isotherms (ASAP 2010, Micromeritics, USA) at −196 °C after out-gassing the samples at 190 °C. Specific surface areas were calculated with the Brunauer–Emmett–Teller equation, and the pore volumes and pore size distributions were calculated using the Barrett–Joyner–Halenda (BJH) method. Raman spectroscopy was employed to characterize the functionalized CNFs using a Renishaw InVia Reflex Raman spectrometer with an Ar-ion laser beam at an exciting radiation wavelength of 514.5 nm.

The X-ray photoelectron spectroscopy characterization of CNF was performed using a Kratos AXIS Ultra DLD spectrometer equipped with monochromatic Al Kα radiation at a power of 45 W. To exclude any effects on the values of binding energies due to charging of the sample during the XPS analysis, the data we got were corrected by a linear shift such that the peak maximum of the C1s binding energy of adventitious carbon corresponded to 284.8 eV.

2.3. Electrochemical measurements

Electrochemical measurements were carried out on a PGSTAT 30 electrochemical workstation (Eco Chemie B.V. the Netherlands) and a rotating disk electrode (pine instruments). All experiments were conducted in a three electrode system at 20 ± 1 °C. The working electrode was prepared as follows. A suspension of CNF ink was prepared by ultrasonically dispersing 0.6 mg of CNFs in 90 μl of ethanol and 10 μl of Nafion (5 wt.%) solution for 20 min, and a total of 5 μl of the above solution was carefully pipetted onto a glassy carbon (GC) electrode with 5 mm in diameter, followed by solvent evaporation at room temperature in ambient air for 30 min. An Ag/AgCl (10 wt.% KCl) electrode and a Pt wire were used as the reference and the counter electrodes, respectively. 0.1 M KOH aqueous solution was used as the electrolyte.

3. Results and discussion

3.1. BET and Raman characterizations of CNFs

Table 1 shows the typical textural properties of different treated-CNFs obtained from N_2 adsorption–desorption at cryogenic temperature. The BET surface area is increased after oxidation treatment, which may be due to the more surface groups or an