



Conjugated polymer-mediated synthesis of nitrogen-doped carbon nanoribbons for oxygen reduction reaction



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ABSTRACT

Nitrogen doped carbon materials, as the most promising non-metal electrocatalyst for oxygen reduction reaction (ORR), have attracted great attention because of their catalytic activities approaching to that of commercial Pt/C, good ethanol tolerance, low price and chemical stability. Here, we demonstrate the conjugated polymer-mediated synthesis of a series of nitrogen doped carbon nanoribbons (NDCNRs) through direct carbonization of polyaniline-polypyrrole (PANI-PPy) nanofibers with different monomer ratios. It is important to point out that ammonium fluoride (NH₄F) applied in the carbonization process benefits for the production of more defect sites, higher surface area as well as electrochemically active surface area, and the morphology conversion from nanofibers into nanoribbons, though F element doping is not detected in the F-NDCNRs. With optimized monomer ratio (aniline:pyrrole = 1:3), the as-obtained F-NDCNRs(1:3), with higher content of graphitic-N, graphitic-N/pyridinic-N ratio and defect density, provide admirable ORR catalytic performance with an onset potential of 0.976 V vs RHE and a half-wave potential of 0.864 V vs RHE. This study provides new insights into the synthesis of efficient metal-free nitrogen doping carbon materials for ORR applications.

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1. Introduction

Increasing demand for large-scale fuel cells has led to plenty of effort in developing cost-effective and durable non-precious-metal (NPM) or non-metal catalysts. Particularly, low-cost NPM materials have been intensively investigated in order to replace the commercial Pt/C catalysts for oxygen reduction reaction (ORR), which is the key reaction for many renewable energy devices such as fuel cells and metal-air batteries [1]. Among many others, carbon materials have been regarded as the most promising alternatives, and it is well known that doping some types of heteroatoms into the carbon frameworks gives rise to notable enhancement in

electrochemical performance, enabling faster transfer rate of proton and electron at the electrode/electrolyte interface during the ORR. Although a series of heteroatoms such as phosphorus [2–4], boron [5,6], and sulfur [7–9] have been proved to be able to enhance the ORR activity, nitrogen-doped carbon materials, with excellent long-term durability and improved catalytic activity due to the high electronic conductivity and electronegativity of N atoms [10–12], are still regarded as the highest potential alternatives to high-cost Pt-based catalysts.

Conjugated polymers (CPs), containing N or S heteroatoms such as polypyrrole (PPy), polyaniline (PANI), and polythiophene (PT), are widely studied in various applications due to their unique conductivity and optical features [13–15]. With their structural advantages, controlled carbonization of conjugated polymers with particular morphology has emerged as an efficient way to prepare nitrogen-doped carbon materials in recent years [16,17], as such CPs have both the carbon source and heteroatom source for the functional carbon materials [18–22]. Preparation of heteroatom-doped carbon materials through the CP-mediated pathway is also

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facile and easy in terms of methodology, as compared to arc-discharge of carbon electrodes in a nitrogen-containing gas atmosphere [23], magnetron sputtering of a graphite in a nitrogen atmosphere [24], and exposure of graphite to nitrogen plasma [25]. For N-doped carbon materials, the debate about effective constituent focuses on the pyridinic N (N bonded to two carbon atoms) and graphitic N (N bonded to three carbon atoms, also called substituted N or quaternary N) [1,10,26–28]. It is difficult to determine which type of nitrogen creates the active sites during the catalysis process by comparing samples subjected to treatment or pyrolysis at different temperatures, as the size of the π -conjugated system is also dependent on the annealing temperature. In addition, the catalytic performance is also associated with the morphology and the graphitization degree of the evaluated carbon materials. Therefore, a novel and effective experimental design for heteroatom-doped carbon materials with controlled active sites remains urgent and challenging.

Herein, we demonstrate the synthesis of a series of one-dimensional (1D) metal-free nitrogen doped carbon nanoribbons (NDCNRs) via carbonization of polyaniline-polypyrrole (PANI-PPy) copolymer nanofibers with various monomer (aniline:pyrrole) ratios. The surface area, electrochemically active surface area, nitrogen species and defect content can be tuned by the monomer (aniline:pyrrole) ratios and assistance of NH_4F during the carbonization process. The optimized NDCNRs exhibit a comparable ORR activity to commercial Pt/C catalyst. This work implies that the conjugated polymer-mediated synthesis technique can be promising in preparing metal-free nitrogen doping carbon materials for energy applications.

2. Experimental

2.1. Materials

Aniline and pyrrole (National Medicine Group Chemical Reagent co., LTD) were distilled in reduced pressure and stored at low temperature under the protection of nitrogen. Hydrochloric acid (HCl, 12 M aqueous solution), cetyl trimethyl ammonium chloride (CTAC), ammonium persulfate (APS) and ammonium fluoride (NH_4F) were all AR grade (National Medicine Group Chemical Reagent co., LTD) and used as received without further purification. Pt/C (20%) was purchased from Alfa Aesar.

2.2. Synthesis of polyaniline-polypyrrole (PANI-PPy) nanofibers

The synthesis of PANI-PPy nanofibers was carried out through a micellar templated method as previously reported [29]. In a typical procedure, 0.1 mol mixture of aniline and pyrrole with definite molar ratios (9:1,3:1,1:1,1:3,1:9) was dissolved in 50 mL 0.1 M HCl aqueous solution containing CTAC of 12 times critical micelle concentration (cmc) as the surfactant. After 5 min magnetic stirring, the mixture was maintained in an ice-water bath for 30 min. Then 5 mL APS aqueous solution pre-cooled in the ice-water bath was poured into the above uniform solution to initiate the polymerization reaction. The molar ratio of the monomer to APS was kept equal. After 24 h reaction in the ice-water bath, the PANI-PPy copolymer was centrifuged and washed repeatedly with deionized water and ethyl alcohol until the filtrate became colorless. Then the precipitate was dried in a vacuum drier at 80 °C for 12 h.

2.3. Synthesis of nitrogen-doped carbon nanoribbons (NDCNRs)

The PANI-PPy copolymers were dispersed in 0.1 M NH_4F aqueous solution under magnetic stirring for 30 min. The obtained dispersed system was centrifuged and dried at 80 °C for overnight.

Then, the samples were heated to 900 °C at a speed of 5 °C min^{-1} according to our previous work on converting poly(*o*-methylaniline) into carbon materials [22], and maintained for 2 h under N_2 protection to complete the carbonization process. After cooling down, N-doped carbon nanoribbons with the pre-treatment of NH_4F are obtained and named as F-NDCNRs(x), where x (= 9:1, 3:1, 1:1, 1:3, 1:9) represents the molar ratio of aniline to pyrrole. By contrast, NDCNRs(x) without NH_4F treatment were also fabricated.

2.4. Characterization

X-ray diffraction (XRD) data were collected on a Rigaku D/MAXRC X-ray diffractometer using Cu K_α radiation source (45.0 kV, 50.0 mA). Scanning electron microscopic (SEM) images were obtained on a Quanta 200S (FEI). Transmission electron microscopic (TEM) images were acquired on JEM-2100 transmission electron microscope. The Raman spectra were collected on a Renishaw in Via micro Raman spectroscopy system using a 532 nm laser. Nitrogen adsorption/desorption isotherms were collected on a QUADRASORB SI-KR/MP (Quantachrome, USA). X-ray photoelectron spectroscopy (XPS) was performed using a PHI 5400 ESCA System with an Al $\text{K}\alpha$ radiation as the X-ray source.

2.5. Electrochemical measurements

Electrochemical performance tests were carried out using a rotating disk electrode (RDE) with a three-electrode system on a CHI660D electrochemical station at room temperature. The reference and counter electrodes were saturated calomel electrode (SCE) and platinum wire, respectively. The as-prepared catalysts were adequately dispersed in 5% Nafion ethanol-water solution to form a 5 mg mL^{-1} suspension for measurement. Then 7.5 μL of above uniform suspension were dropcasted on a glassy-carbon disk electrode with a diameter of 5 mm as the working electrode. For ORR electrocatalysis, cyclic voltammograms (CV) were carried out and recorded between -0.8 and 0.2 V vs SCE at a scan rate of 50 mV s^{-1} in O_2 (or N_2)-saturated 0.1 M KOH electrolyte. Subsequently the linear sweep voltammograms (LSVs) were obtained in the O_2 -saturated 0.1 M KOH electrolyte at the scan rate of 50 mV s^{-1} with varying rotating speeds ranging from 225 to 2500 rpm. To investigate the tolerance to methanol crossover, methanol was added into the electrolyte to obtain a 3 M methanol solution during a whole LSV test. All of the potentials were referenced to reversible hydrogen electrode (RHE).

3. Results and discussion

Conjugated polymer-mediated synthesis of nitrogen-doped carbon nanoribbons can be depicted in Fig. 1a. The micellar templated strategy for the fabrication of conjugated copolymer nanofibers has been reported previously [29,30]. Here, the PANI-PPy copolymer nanofibers were synthesized using CTAC as the micellar template at a concentration of 12 cmc, where the resultant micelles of anionic surfactant hold the rod-like shape [29]. After the protonated aniline and pyrrole molecules were well adsorbed on rod-like CTAC micelles, APS was put into the emulsion to initiate the oxidative polymerization and fabricate PANI-PPy nanofibers. It could be seen that all PANI-PPy nanofibers with different molar ratios of aniline (An) and pyrrole (Py) displayed uniform and curled 1D structures with diameters varying from ~ 15 nm to ~ 30 nm, as revealed by the transmission electron microscopy (TEM) images (Fig. 1b and Fig. S1) and scanning electron microscopy (SEM) images (Fig. S2). Subsequent annealing of PANI-PPy nanofibers at 900 °C under N_2 gas protection results in the formation of carbon nanoribbons (Fig. 1c and Fig. S3). Breaking the nanofibers into

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