



Short communication

The effect of edge carbon of carbon nanotubes on the electrocatalytic performance of oxygen reduction reaction



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ABSTRACT

The oxygen reduction reaction (ORR) has been investigated on fish-bone carbon nanotubes (F-CNTs) and parallel carbon nanotubes (P-CNTs). The results showed that the F-CNTs exhibited much higher activity than P-CNTs, which originated from the higher fraction of edge carbon atoms. The dependence of ORR peak potential on the fraction of edge carbon atoms was determined quantitatively for the first time. The density functional theory calculations clearly unveiled the mechanism of edge carbon atoms facilitating the ORR performance.

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1. Introduction

The traditional Pt-based catalysts for ORR hinder the large-scale application of fuel cells because of their limited natural resources, high price, instability and easy poisoning [1]. Therefore, great efforts have been made to design and synthesize non-precious metal ORR electrocatalysts [2,3]. Among all these non-precious metal ORR catalyst, sp^2 carbon materials are considered to be one of the most potential ORR catalysts due to their abundant free-flowing π electrons, good conductivity and easy doping properties [3–5]. However, the pure sp^2 carbon materials commonly show poor catalytic activity for ORR. In recent years, many reports demonstrated that the electrochemical properties of carbon catalysts could be improved remarkably by doping different elements, such as nitrogen [3], boron [5] and sulfur [6]. Besides doping, another way to improve the electrocatalytic performance of carbon material is adjusting the microstructure of carbon, especially the content of edge carbon atoms. Many reports have demonstrated that edge carbon atoms indeed influenced the electrochemistry property [7–9]. Compton et al. also reported that the edge-plane-like defect sites of carbon materials significantly improved the catalytic activity, electron transfer and chemical reactivity [10,11]. Recently, Dai et al. [7] attributed the high ORR electrocatalytic activity and durability of N-doped carbon nanotube–graphene complex to not only the nitrogen doping but also the dominant of its abundant edges and defect sites. However, the effect of edge carbon on facilitating the ORR performance has not been explicitly demonstrated and the catalytic mechanism is still unclear.

To this end, we designed a series of CNTs with different fractions of edge carbon atoms and compared their ORR catalytic activities. The dependence of ORR peak potential on the fraction of edge carbon atoms was determined quantitatively. Moreover, the mechanism of edge carbon atoms improving ORR performance was elucidated by the density functional theory (DFT) calculations.

2. Experimental

P-CNTs were kindly supplied by Tsinghua University and F-CNTs were purchased from Shenzhen Nanotech Port Co. Ltd. To remove residual metal catalyst, CNTs were stirred in concentrated HCl for 6 h and then washed with deionized water to pH = 7, and dried in air at 383 K overnight.

In order to adjust the microstructure of CNTs, a series of post-treatments were carried out as follows. Firstly, 300 mg CNTs were thermally treated from room temperature to 1073 K at 6 K min^{-1} in a flow of Ar (160 ml min^{-1}) and maintained at 1073 K in a flow of H_2 (160 ml min^{-1}) for 2 h, and then cooled down to room temperature in Ar flow. The obtained samples were correspondingly denoted as F-CNTs- H_2 and P-CNTs- H_2 . Secondly, 300 mg CNTs were ultrasonicated for 30 min, and then refluxed in 9 M HNO_3 at 383 K for 2 h. The resulting products were filtered and washed to pH = 7 by distilled water, and then dried at 383 K overnight. The obtained samples were correspondingly denoted as F-CNTs- HNO_3 and P-CNTs- HNO_3 . Afterwards, these samples were annealed at 1073 K under Ar for 2 h. The obtained samples were denoted as F-CNTs- H_2 -Ar, F-CNTs- HNO_3 -Ar, P-CNTs- H_2 -Ar and P-CNTs- HNO_3 -Ar. Moreover, P-CNTs were also treated physically by ball-milling, which were denoted as P-CNTs-M.

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The prepared samples were characterized with transmission electron microscope (TEM, JEOL, JEM2010) and Fourier transform infrared (FTIR) spectra (Nicolet 6700 FTIR spectrometer). The BET specific surface areas were measured by N_2 adsorption at 77 K using a TriStar 3000 (Micromeritics, USA).

The ORR activity of the samples was evaluated by cyclic voltammetry (CV) in O_2 -saturated 0.1 M KOH solution, according to our previous report [12]. The electrochemical approach for quantifying the defect density (edge sites) of carbon nanomaterials was employed with 10 mM ferricyanide as an electrochemical probe by CV in 0.1 M KCl at the scan rates of 60–200 $mV s^{-1}$. [13].

The DFT calculations were carried out in DMol3 package using spin-polarized generalized-gradient approximation with Perdew–Burke–Ernzerhof function and double numerical basis set including polarization function [14]. The adsorption energy (E_a) of O_2 molecule on CNTs was defined as $E_a = E_{total}[CNTs + O_2] - E_{total}[CNTs] - E_{total}[O_2]$, where E_{total} is the total energy of the calculated systems in the bracket.

3. Results and discussion

Fig. 1a and b shows that the graphene layers of CNTs are ordered with different angles to the central axis. The graphene layers of F-CNTs are about 15° inclining to the central axis, leading to many edge atoms exposing on the surface. For P-CNTs, the graphene layers are parallel to the central axis with almost all the surface composed of basal atoms. When F-CNTs were treated by H_2 or HNO_3 , several layers of edge carbons could be removed and some surface groups, such as CH_3 or $-COOH$ were introduced onto the edge of F-CNTs, thus shielding the electrocatalytic activity of edge carbons of F-CNTs [15,16]. After annealing, the surface groups were removed and edge carbons were uncovered again [17]. The results of FTIR (not shown here) evidently confirmed the peaks at 2900 and 2850 cm^{-1} , which correspond to the C–H and can be attributed to $-CH_3$, were obviously much stronger for F-CNTs- H_2 than for F-CNTs and then became significantly weaker for F-CNTs- H_2 -Ar. Similarly, the peaks at 1720 cm^{-1} and 1580 cm^{-1} ,

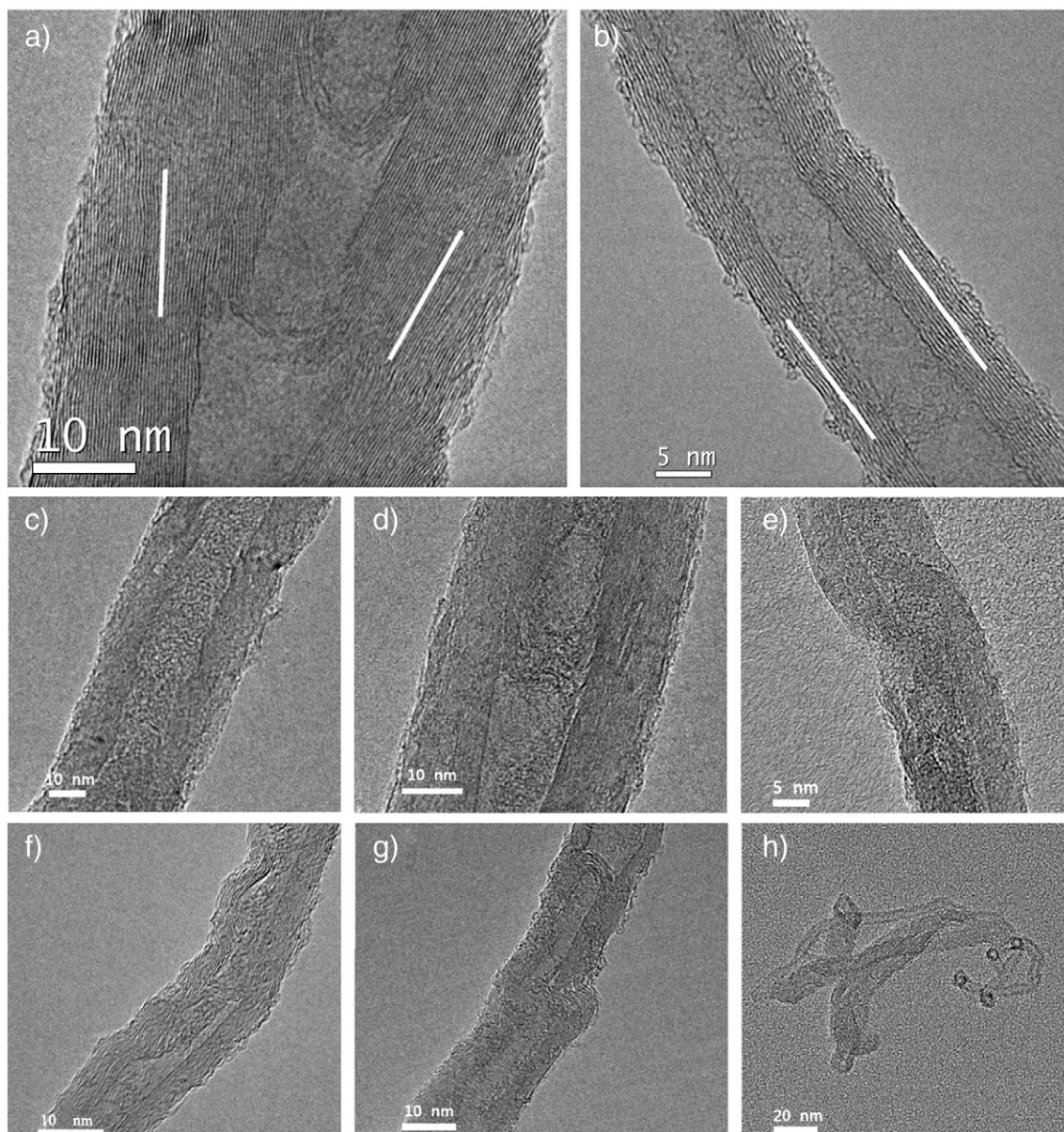


Fig. 1. TEM images of F-CNTs (a), P-CNTs (b), F-CNTs- H_2 -Ar(c), F-CNTs- HNO_3 -Ar(d), P-CNTs- H_2 -Ar(e), P-CNTs- HNO_3 -Ar(f) and P-CNTs-M(g, h).

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