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Active sites for oxygen reduction reaction on nitrogen-doped carbon nanotubes derived from polyaniline

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ABSTRACT

Understanding exact electronic configurations of carbon atoms bonded by nitrogen (N) functionalities at atomic-level may literally open a door to advance metal-free carbon materials as efficient catalysts for the oxygen reduction reaction (ORR). In this paper, a set of well-defined carbon nanotubes with controlled doping of various N species, such as pyrrolic, pyridinic and graphitic N, have been achieved by in-situ pyrolysis of polyaniline (PANI) nanotubes at different temperatures. Among these synthesized samples, the carbon nanotubes fabricated at 700 °C exhibit the highest electro-catalytic ORR activity, long-standing stability and good tolerance against methanol in alkaline medium. The improved activity is mainly attributed to the high nitrogen level of the active pyridinic and graphitic N. But, the pyridinic N possesses higher activity than the graphitic N because of their different sp^2 electronic structures. Pyridinic N, after bonding with two carbon(C) atoms, has two distorting N–C orbitals and one dangling orbital occupied by a lone electron pairs which are exposed, as the N sits at the edge of the carbon planes. Such unique electronic configuration makes the nitrogen and surrounding carbon atoms, bonded in the C–N bonds, can serve host of active sites or work as active sites for the ORR.

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1. Introduction

Oxygen reduction reaction (ORR) is one of the essential electrochemical reactions for several renewable energy systems, such as various fuel cells, metal-air batteries, and etc. [1–3]. Currently, the most common electrocatalyst for the ORR is platinum catalyst, but the high cost, resource scarcity and easy poisoning seriously restrict its commercialization in these above energy storage and conversion fields [4,5]. Hence, it is very urgent to develop alternative catalysts to Pt for the ORR. To date, metal-free carbon nanomaterials have gained intensively attention, because of their low cost and high-performance for the ORR [6,7]. Since pure carbon materials have relative low electro-catalytic activity, they should be doped by some heteroatoms, such as nitrogen (N) [8,9], boron (B) [10], sulfur (S) [11,12], and phosphorus (P) [13] as the active sites, which can help to improve their electro-catalytic ORR activity. Among these above heteroatoms doping into carbon materials, nitrogen has been considered to be the best candidate for carbon substitution, because of it having five valence electrons that are prone to form strong valence bonds with carbon atoms. As a result, the N-doped carbons have gradually become one of the most popular research hotspot by now. As reported in the published papers, N-doped carbon materials exhibited very high electrocatalytic activity and durability for the ORR in alkaline environments or acidic conditions [14,15], which is almost comparable with that obtained by a commercial Pt/C catalyst (E-TEK).

Although the essential origin of the improved activity is still under debate, the total nitrogen level and the types of the doped nitrogen species, such as graphitic and pyridinic nitrogen, should be responsible for the enhanced ORR activity of this type of catalysts. Jun Lou and co-workers [16] studied the relationship between the contents of the doped N and catalytic properties and found that the more N level is involved, the higher ORR activity can be achieved. So, controlling total nitrogen level is an important strategy to enhance activity of the ORR. Moreover, Takahiro Kondo et al. [17] researched the impact of different types of nitrogen species on the ORR activity, by using designed pyrolitic graphite doped with different N species, such as pyrrolic, pyridinic, and graphitic N groups. It is believed that the improved ORR activity may result

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from the pyridinic N atoms which serve as the active sites for the ORR. In this case, the ORR activity may be related with p-conjugated doping of larger electronegativity N atom into the sp^2 carbon lattice, which making it easy to adsorb of O_2 molecule and facilitating the O=O bond breaking of O_2 [18,19]. However, the ORR activity of this type of catalysts is not only simply related to the active pyridinic N atoms, but also governed by the graphitic N, as suggested by some investigators [14,20]. Some recently published papers [21,22] suggested that the graphitic N with n-conjugated configuration may be also of paramount importance for the ORR activity, except for the active pyridinic N atoms. You sung Jung et al. [23] used density functional theory (DFT) calculations to further identify the effect of the graphitic N on the ORR activity, and found that graphitic N can reduce the adsorption energy of oxygen and facilitates the first electron transfer of the oxygen reduction. So, the heteroatom (N) doping can efficiently alter the electronic and geometric properties of carbon atoms, providing more active sites and enhancing the interaction between carbon structure and active catalytic sites.

However, which type of these nitrogen species as the mainly catalytically active sites should be responsible for the improved ORR activity remains unclear by now, because each of them cannot unequivocally relate the ORR activity to a certain type of N sites [24]. This issue is mainly raised by a mixture of various types of N functionalities is inevitable for synthesis of N-doped carbon nanomaterials, even using various synthetic strategies, such as chemical vapor deposition [16], calcination [25] or biomass pyrolysis under high temperature condition [26]. Moreover, the inhomogeneous doping of N atoms, resulted from the local structure defects and the graphitization level of the original carbons, also decay the well-controlled doping of N species [17]. This drawback also makes it difficult to interpret which type of the nitrogen functionalities are mainly catalytically active sites for the ORR.

A smart idea to resolve this issue is to deeply study their electronic structures of these N species at the atomic-level, because the introduction of the N species can efficiently change the local electronic environment of the doped carbon materials which, in nature, decide the ORR activity. It is well known that pyridinic N species, which are incorporated in six-member rings, could donate one p-electron into the localized p-system (aromatic π system) in the carbon layers. On contrary, graphitic N species, which are coordinated to three carbon atoms in the carbon hexagonal rings by substituting the C atoms, could donate extra electrons into the delocalized n-system (delocalized π system) due to their same structural configuration with respect to carbon [27–32]. These two types of N species exhibit different sp^2 electronic configurations of C–N bonding existed in the carbon materials, which lead to different local electronic environments at the atomic-level, resulting in different contributions to the ORR kinetics. So, the exactly understanding the impact of the electronic configurations, raise by the heteroatom and carbon skeleton, is very important to explore the origin of the ORR kinetics for these N functionalities. However, the lack of the information about the electronic configurations of them at atomic-level has greatly obstructed the rational design and preparation of N-doped carbon nanomaterials as highly active catalysts for the ORR.

In this paper, a set of nitrogen-doping carbon nanotubes (NCNTs) have been fabricated by controlled pyrolysis of polyaniline (PANI) nanotubes at different temperatures (600, 700, 800 and 900 °C, respectively), through in situ incorporation of nitrogen atoms into the carbonized products. The direct pyrolysis of the polymer can not only achieve homogeneous incorporation of N species into the carbon skeleton at atomic-level, but also allow fine tuning of the types of the doped N species. The electro-catalytic performances for ORR on the NCNTs were characterized in an alkaline solution by using rotating ring-disk electrode. Also, we characterized the catalytically active sites for the ORR on the synthesized NCNT catalysts, through exploring the sp^2 electronic structures for different types of N spices after bonding with surrounding carbon atoms at atomic-level. Based on their electronic configuration of various C–N bonds, the possible kinetic mechanism of the ORR, catalyzed by the effective N specie, have been discussed deeply. This information is of great benefit to design and prepare N-doped carbon nanomaterials as catalysts for the ORR.

2. Experimental

2.1. Synthesis of N-doped carbon nanotubes

The synthesis of the N-doped carbon nanotubes (NCNTs) includes two steps: the preparation of polyaniline (PANI) nanotubes as precursors and the subsequent carbonization and activation of the precursors. The PANI precursors were obtained by oxidizing 0.1 M aniline with 0.1 M ammonium peroxydisulfate (APS) in the aqueous solution of succinic acid and the reaction was kept for 10 h at 5 °C [33]. Then, the products were filtered and washed with deionized water and ethanol for several times until the filtrate became colorless. Finally, dry these products at 60 °C for 24 h under vacuum to get PANI precursors.

Then, the as-synthesized PANI precursors were carbonized and activated under argon atmosphere with the flow rate of 50 sccm. The heating process as follows: the PANI precursors were firstly heated to 400 °C at a heating rate of 2 °C/min and maintained for 2 h at this temperature, then the temperature was increased to 600, 700, 800 and 900 °C with a heating rate of 1 °C/min and kept for 2 h at the target temperatures. After that, we obtained carbonized PANI. Followed, we used certain amount of KOH ($M_{(KOH)}$: $M_{(samples)} = 3:1$) to activate those samples at different temperatures (600, 700, 800 and 900 °C, respectively). The heating process was the same with the carbonization process. TGA measurements were carried out to show changes of the materials caused by different temperatures, as shown in Fig. S1.

2.2. Material characterization

The morphologies of the synthesized samples were observed by scanning electron microscopy (SEM) (JEOL 6701F) and transmission electron microscopy (TEM) (JEOL JMS-2100 microscope). Their structures were characterized via X-ray diffraction (XRD) (Rigaku-RINT 2200V/PC) operating with Cu Kα radiation ($\lambda = 1.5408$ Å) generated at 40 kV and 200 mA. Surface characterization of the samples was performed using an X-ray photoelectron spectroscopy (XPS) (Thermo ESCALAB250). The structural derivation and electronic state of the NCNTs are characterized by Raman spectroscopy here (LabRam HR800). Moreover, the special surface area of the NCNTs materials were calculated by Brunauer-Emmett-Teller (BET) method (Quadrasorb SI-MP-9).

2.3. Electrochemical measurement

Electrochemical experiments were performed using a rotating ring-disk electrode device (AFCBP1 type, PINE, USA) in 1 M NaOH electrolytic solution, with a typical three-electrode system using a platinum sheet as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. All the potentials were referred to a reversible hydrogen electrode (RHE), $E_{RHE} = E_{SCE} + 0.241V + 0.0591$ pH [34]. The working electrodes were prepared by depositing a thin-layer of the electrocatalyst ink over a glassy carbon (GC) electrode ($S = 0.247$ cm^2). The catalyst ink was prepared by dispersing 5 mg of catalyst and 50 μL of Nafion

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