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# Three-dimensional nitrogen-doped carbon nanotubes/carbon nanofragments complexes for efficient metal-free electrocatalyst towards oxygen reduction reaction

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## ABSTRACT

Heteroatom-doped carbon materials as one of the most promising oxygen reduction reaction (ORR) catalysts have attracted much attention. Rational design and exploration of suitable heteroatom-doped carbon materials greatly affects their ORR performance. Herein, we successfully prepared nitrogen-doped carbon nanotubes/carbon nanofragments (NCNT/CNF) complexes by a pyrolysis process using oxidized open-ended carbon nanotubes (OCNT)/oxidized carbon nanofragments (OCNF) hybrids as carbon precursors. The effect of carbon precursors on the synthesis of the corresponding nitrogen-doped carbon products was systematically investigated. The result showed the OCNT retained good conductivity, while the OCNF offered adequate structure defects for efficient post-doping. Benefiting from the co-merits of sole constitute, the obtained NCNT/CNF<sub>1-15</sub> (1–15 refers to the mass ratio) complexes possessed a typical three-dimensional architecture and much increased specific surface area, which facilitated reactant/electrolyte infiltration and ion/electron transfer. More importantly, they built the most optimized balance on ORR catalytic sites and conductivity. Thus, the NCNT/CNF<sub>1-15</sub> complexes showed much enhanced ORR performance. Clearly, our work provides a good guidance on the design of advanced heteroatom-doped carbon-based ORR catalysts.

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## Introduction

The oxygen reduction reaction (ORR) plays a crucial role in determining the electrochemical performance of many energy

conversion and storage devices, such as fuel cells, metal-air batteries, chlor-alkali electrolyzers and so forth [1,2]. However, common ORR process often suffers from very sluggish kinetics, which greatly affects the chemical-electrical energy-

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conversion efficiency [3,4]. Thus, rational design and development of highly efficient and durable ORR electrocatalysts to accelerate ORR dynamics makes much sense for us. To date, platinum (Pt) or its alloys treated as the state-of-the-art ORR<sup>1</sup> electrocatalyst has received much attention due to its excellent catalytic activity, but the prohibitive cost,<sup>2</sup> low abundance, poor durability and susceptibility to methanol crossover greatly restrict its further advancement and broader application [5,6]. Accordingly, exploiting non-precious metal or even metal-free electrocatalysts with low cost, high activity and good stability to replace these Pt-based electrocatalysts is desperately desired.

Metal-free heteroatom-doped carbon materials with competitive catalytic activity and low price have been regarded as one of the most prominent candidates for advanced ORR catalysts [7,8]. In the heteroatom family, N atom, next to C atom in the periodic table with similar atom size, have been testified to play the most important role in altering electronic structure and promoting intrinsic ORR activity of carbon materials. Both experiments and theoretical calculations demonstrate that doping N into carbon framework can induce a charge redistribution around the N atoms due to the difference in electronegativity between C and N, and such charge redistribution creates a net positive charge on the adjacent C atoms, which changes O<sub>2</sub> chemisorption mode and weakens O–O bonding [9–12]. Generally, to doping N into carbon framework, post-doping methods (including thermal annealing, hydrothermal process etc.) are more preferred due to their lower expenditure, higher output, more facile operation when compared with *in-situ* doping approaches [13,14]. Careful selection of carbon precursors proves very crucial before post-doping process. Generally, pristine carbon materials (such as carbon nanotubes, graphene and so on) with very stable and inert sp<sup>2</sup>-type structure are unqualified to achieve effective N doping, while carbon materials equipped with structure defects (oxygen-containing functional groups) can be used as suitable carbon precursors for subsequent N doping [15–17]. Feng et al. [18] adopted graphene oxide (GO) as carbon precursor, and prepared N-doped graphene (NG) by thermal annealing GO/cyanamide composites under Ar atmosphere. Meanwhile, Yin et al. [19] synthesized NG by a hydrothermal method by using ammonia and GO as N source and carbon precursor, respectively. The structure defects in carbon precursors are always considered as the doping reactive sites and promise effective N doping. Moreover, more structure defects often bring about higher doping amounts, which indicates more ORR catalytic sites [20–22]. Hence, pristine carbon materials need to acquire structure defects by pre-oxidation treatment before N doping [23]. But if excessive oxidation is imposed, it will result in adequate structure defects and harshly sacrificed conductivity simultaneously for the obtained carbon precursor [24]. As demonstrated previously [25–28], adequate catalytic sites and good conductivity are both vital for excellent ORR performance. One hand, adequate catalytic sites can alter electron density and make charge redistribution, which are in favor of strengthening O<sub>2</sub> adsorption capability and weakening O–O bonding, and further boosting the ORR process. On the other hand, good conductivity guarantees fast electron transfer and ion transport, effectively elevating the ORR dynamics. In view of this, it

is essential to build a good balance on catalytic sites and conductivity of N-doped carbon materials by rationally regulating the structure defects in the corresponding carbon precursors.

As far as we know, most reports about N-doped carbon materials focus on regulating the doping conditions (including doping methods, selected N sources and so forth.) [20–25], only few works reported the controllable synthesis of N-doped carbon materials from the perspective of carbon precursors. Kuang et al. [26] firstly prepared a series of oxidized carbon nanotubes (O-CNTs) by oxidizing pristine carbon nanotubes (CNTs) for different times, and obtained the corresponding N-doped carbon nanotubes (N-CNTs) by using these O-CNTs as carbon precursors. They found that the ketone (C=O) and carboxyl (COOH) groups in O-CNTs were favorable to form the pyridinic N in N-CNTs, while the hydroxyl (–OH) and epoxy (–C(O)C–) groups in O-CNTs tended to produce graphitic N in N-CNTs. Meanwhile, Zhou et al. [29] adopted graphene oxide (GO)/oxidized unzipped carbon nanotubes (O-UCNT) hybrid as carbon precursor, and found that carbon precursor with three-dimensional (3D) morphology and large specific surface area contributed to fabricating nitrogen-doped carbon material with high nitrogen content. In our work, we utilized pristine carbon nanotubes as the initial carbon source, and prepared two distinct carbon precursors, oxidized open-ended carbon nanotubes (OCNT) and oxidized carbon nanofragments (OCNF). The two sole carbon precursors were integrated into a carbon precursor hybrid (named as OCNT/CNF<sub>1-15</sub>, where 1–15 referred to the mass ratio), which then reacted with urea by a pyrolysis process to obtain the final product, nitrogen-doped carbon nanotubes/carbon nanofragments complexes (NCNT/CNF<sub>1-15</sub>). Among them, the one-dimensional (1D) OCNT prepared by a mild oxidation strategy were decorated with few structure defects and retained the good conductivity of pristine CNTs, while the quasi-2D OCNF synthesized by a harsh oxidation way were modified with plenty of structure defects and offered adequate doping reactive sites. Benefiting from the co-merits of individual constituent, the obtained NCNT/CNF<sub>1-15</sub> complexes showed a typical 3D architecture and increased specific surface area, which promoted reactant/electrolyte infiltration and ion/electron transfer during ORR process. More significantly, they built the most optimized balance the ORR catalytic sites and conductivity. As a consequence, the 3D NCNT/CNF<sub>1-15</sub> complexes exhibited much enhanced catalytic activity and stability towards ORR than other counterparts. Clearly, our work not only develops a promising candidate for commercialized ORR catalysts, but also provides us a good guidance on the design and exploration of metal-free ORR catalysts with optimized structure and excellent performance.

## Experimental section

### Chemicals and materials

All reagents (Sinopharm Chemical Reagent Co., Ltd., China) were of analytical grade without further purification. Ultra-pure water was employed in this work. Multi-walled carbon nanotubes (MWCNTs, >97% purity) with 5–15 μm in length

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