



# Nitrogen-doped carbon nanotubes as catalysts for the oxygen reduction reaction in alkaline medium



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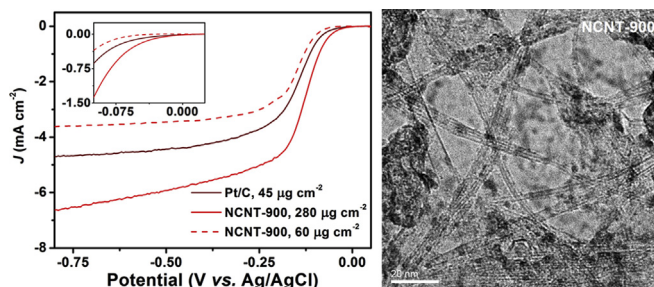
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## HIGHLIGHTS

- A novel electrocatalyst for the oxygen reduction reaction (ORR) was prepared.
- The electrocatalyst (NCNT) was fabricated by direct annealing CNTs and TPT in N<sub>2</sub>.
- The NCNT shows excellent catalytic activity towards ORR in alkaline medium.
- The as-synthesized NCNT is a very promising cathode material for AFCs.

## GRAPHICAL ABSTRACT



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## ABSTRACT

A novel electrocatalyst for the oxygen reduction reaction (ORR) is fabricated by directly annealing oxidized carbon nanotubes and tripyrrolyl[1,3,5]triazine in nitrogen. The structural and chemical properties of the resultant N-doped carbon nanotubes (NCNTs) are systematically investigated. The electrocatalytic activity of the NCNTs towards ORR in O<sub>2</sub>-saturated 0.1 M KOH electrolyte is evaluated using rotating disk electrode voltammetry. The results demonstrate that the as-prepared NCNT-900 (annealed at 900 °C) exhibits excellent electrochemical performance towards ORR in alkaline medium with an onset potential of  $-0.038$  V (vs Ag/AgCl), a high kinetic current density of  $31.26$  mA cm<sup>-2</sup> at  $-0.25$  V, a dominant four-electron transfer mechanism ( $n = 3.88$  at  $-0.25$  V), and excellent methanol tolerance and durability. The results obtained are significant for the development of N-doped carbon-based electrocatalysts for alkaline fuel cells.

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## 1. Introduction

The development of new and sustainable energy sources and relevant technologies is of great importance due to the rapidly

escalating energy crisis and the worsening environmental pollution. Fuel cells are currently considered to be clean and high-efficient energy conversion devices because they can convert chemical energy from fuel into electricity in an environmentally-benign manner [1–3]. On the other hand, the performance of fuel cells is hampered by the cathode due to the sluggish oxygen reduction reaction (ORR), which impacts the energy efficiency significantly and results in very low cell potentials [4,5]. Therefore, the demand for developing novel catalysts with both high selectivity and high efficiency for ORR has become urgent.

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Conventionally, Pt and Pt-based electrocatalysts are used in proton exchange membrane fuel cells (PEMFCs) due to their excellent electrocatalytic activity and stability. However, Pt-based electrocatalysts often suffer from CO poisoning and are expensive [6,7]. At present, considerable research efforts have been devoted to the development of non-precious metal and non-metal electrocatalysts for fuel cell applications [8–13]. Among various candidates, the carbon-based electrocatalysts have been proved to meet the practical application requirements of alkaline fuel cells (AFCs), because they exhibit much higher ORR activity in alkaline media than in acid solution [14–16]. Thereby most of nanostructured, carbon-based electrocatalysts are employed in AFCs rather than in PEMFCs. Considering the lower-cost electrocatalysts and less corrosive electrolyte in AFCs, the AFCs show great promise from the price point of view as compared to PEMFCs.

Recent studies have demonstrated that heteroatom-doped carbon nanomaterials, *i.e.*, carbon nanotubes (CNTs) [17–25], graphenes [26–29], graphites [30,31], graphitic, and amorphous carbons [32], hold great promise as non-metal electrocatalysts for ORR in AFCs. Among these carbon nanomaterials, CNTs by virtue of high electrical conductivity, good mechanical strength, and huge specific surface area are of particular interest, which make them ideal candidates for heteroatom-doping. As a matter of fact, heteroatom-doped CNTs [17–25] have been demonstrated both experimentally and theoretically to possess very high electrocatalytic activity towards ORR. One prominent example is the N-doped CNTs (NCNTs), which exhibits excellent electrocatalytic activity and high CO tolerance for ORR in AFCs in comparison to conventional Pt-based catalysts [33,34]. The motivation of preparing NCNTs is due to the electron accepting ability of N dopants. The incorporation of electron-rich N atoms into the graphitic network of CNTs has been predicted to have n-type dopant activity for electron conductivity, hence altering the route of reactions and improving the surface chemical reactivity [35]. In addition, *ab initio* calculations have also proved that N in CNTs increases the Fermi energy at the donor state and results in larger current emissions at considerably lower voltages, thereby increasing the catalytic activity for ORR [36–38].

Currently, two main strategies including direct growth and post-synthesis method have been used to prepare NCNTs, in which the direct synthesis involves NCNTs growth on catalytic templates under relatively harsh conditions, while the post-synthesis method involves the heat-treatment of CNTs with N dopants at relatively high temperature. The major direct NCNTs synthesis routes include chemical vapor deposition (CVD) [39–42] and arc-discharge [43]. Although the direct growth approach (particularly CVD) has shown promising success, however, it can be relatively expensive and difficult to scale. In addition, the unavoidable metal species remaining in the CNTs result in uncertainty in understanding the intrinsic electrocatalytic properties. On the contrary, the post-treatment of prefabricated CNTs implies advantages [44], for example, the as-grown CNTs can be purified, shortened, or functionalized before doping. In this manner, the metal catalysts can be completely removed from CNTs. Furthermore, the versatility of N dopants allows for control over the final electrocatalytic activity of the NCNTs, which may be dictated by the chemical and physical characteristics of the N dopants. From this point, post-treatment methods maybe more feasible for certain applications and are viewed as closer to commercialization. Hitherto, ammonia [45], cyanamide [46], urea [47,48], dicyandiamide [49], and polymers such as polyaniline [50] and polypyrrole [51], have been adopted as N dopants. As can be seen, there are only a few examples of N dopants used for preparing NCNTs. It is still a challenge to screen or design/synthesize new N dopants.

Herein, we demonstrate a novel dopant, namely tripyrrolyl

[1,3,5]triazine (TPT), for the synthesis of NCNTs by directly annealing CNTs and TPT in nitrogen. Compared to usually used N dopants, the novel TPT dopant endows NCNTs with enhanced electrocatalytic activity as well as long-term stability for ORR (*vide infra*). The as-synthesized NCNT is a very promising cathodic material for AFCs.

## 2. Experimental

### 2.1. Materials

Single-walled carbon nanotubes with purity of 95% were purchased from the Chengdu Organic Chemicals Co., Chinese Academy of Science. The raw materials were oxidized with concentrated  $\text{H}_2\text{SO}_4/\text{HNO}_3$  (3/1 by volume) at room temperature as described previously [52], and the oxidized products are denoted as CNTs. Thermogravimetric analysis (TGA) indicated that the carboxylic acid incorporation density was about 3.98 mmol per gram of neat CNTs (Fig. S4, see Supporting Information, SI). Tripyrrolyl[1,3,5] triazine (TPT) was prepared according to procedures outlined in the literature [53] (see SI).

### 2.2. Synthesis of NCNTs

NCNTs were synthesized by directly annealing the mixture of CNTs and TPT in  $\text{N}_2$ . The detailed procedure is as follows: CNTs (10 mg) and TPT (45 mg) were ultrasonically dispersed in ethanol for 3 h. The suspension was spread onto an evaporating dish and dried. The mixtures were then placed into a ceramic tube and annealed at 800–1000 °C for 2 h in  $\text{N}_2$  with a heating rate of 4 °C  $\text{min}^{-1}$ , and the products are denoted as NCNT-800, NCNT-900, and NCNT-1000, respectively. For comparison, pure CNTs without any dopants were also treated under optimal conditions and the obtained material is denoted as CNT-900. Their physical and electrochemical properties as well as corresponding experimental data are listed in Table 1.

### 2.3. Electrochemical measurements

Electrochemical measurements were carried out on an electrochemical workstation (CHI760D, Shanghai Chenhua Co., China) with a typical three-electrode cell at room temperature. A platinum wire and Ag/AgCl were used as counter and reference electrode, respectively. Working electrode was prepared according to follow procedure: catalyst ink was first made by dispersing 2.0 mg of the resulting NCNT catalysts or commercial 20 wt% Pt/C catalyst (Johnson Matthey) in a 2.0 mL mixture of ethanol and Nafion (Aldrich, 5.0 wt%) with a volume ratio of 98.5/1.5. The ink was then further sonicated to form a uniform, well-dispersed ink with a concentration of 1.0 mg  $\text{mL}^{-1}$ . Subsequently, 20  $\mu\text{L}$  of the catalyst ink was carefully deposited on a glassy carbon electrode (GCE, 3 mm diameter) and dried in air for 10 h, resulting in an NCNT loading of 283  $\mu\text{g cm}^{-2}$  (for 20 wt% Pt/C, the catalyst loading is 56.6  $\mu\text{g}_{\text{Pt}} \text{cm}^{-2}$ ). The ORR activity was then evaluated by cyclic voltammetry (CV) and linear sweep voltammetry (LSV) techniques on rotating disk electrode (RDE, ATA-1B) in  $\text{O}_2$ -saturated 0.1 M KOH solution. Methanol crossover and durability testing were conducted by chronoamperometric technique at the bias potential of  $-0.25 \text{ V}$  (*vs.* Ag/AgCl) in  $\text{O}_2$ -saturated 0.1 M KOH electrolyte with a rotation rate of 1600 rpm.

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