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# Nitrogen-doped carbon nanotube encapsulating cobalt nanoparticles towards efficient oxygen reduction for zinc–air battery

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## ABSTRACT

Nitrogen-doped carbon materials encapsulating 3d transition metals are promising alternatives to replace noble metal Pt catalysts for efficiently catalyzing the oxygen reduction reaction (ORR). Herein, we use cobalt substituted perfluorosulfonic acid/polytetrafluoroethylene copolymer and dicyandiamide as the pyrolysis precursor to synthesize nitrogen-doped carbon nanotube (N–CNT) encapsulating cobalt nanoparticles hybrid material. The carbon layers and specific surface area of N–CNT have a critical role to the ORR performance due to the exposed active sites, determined by the mass ratio of the two precursors. The optimum hybrid material exhibits high ORR activity and stability, as well as excellent performance and durability in zinc–air battery.

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## 1. Introduction

Zinc–air batteries have attracted extensive attentions due to their high specific energy, environmental friendliness and ample resource of raw material [1–5]. Zinc is the fourth abundant metal in the earth crust. Unlike conventional batteries, zinc–air battery is completely free of toxic metal species such as lead, mercury and cadmium, making it less expensive and pollution-free. Importantly, the active species for the positive branch of zinc–air battery is oxygen directly supplied from the atmosphere, thus tremendously simplifies the battery structure [6]. Up to now, the development of zinc–air battery is mainly hindered by the sluggish kinetics of oxygen reduction reaction (ORR) in the air electrode [7,8].

To decrease the polarization loss during the ORR process, many efforts have been made to develop effective and durable ORR catalysts including metals, metal oxides, metal–organic complexes and carbon based materials [9–12]. Among various catalysts, the well-designed non-precious transition metals (Fe, Co, Ni et al.) doped within graphene or carbon nanotubes (CNTs), with large

surface area, high electronic conductivity and structural tunability, are promising alternatives to substitute for the most active but expensive Pt catalysts [13–15]. Furthermore, the electron configuration and structural properties of the carbon framework can be well adjusted by heteroatoms (such as N, P, S, B, and F) doping, which in turn prospectively enhances their electrocatalytic performance [16–20]. Liang et al. have developed cobalt oxide/CNTs coupled hybrid as efficient ORR catalyst by growing nanocrystals on nitrogen-doped oxidized multiwall CNTs using a two-step method [21]. Recently, Thangasamy et al. have made attempt to anchor Co<sub>3</sub>O<sub>4</sub> nanoparticles (NPs) on CNTs to catalyze the ORR utilizing a supercritical fluid process under rigorous and complicated preparation conditions [22]. Therefore, convenient strategies are highly desired to fabricate CNT-supported metal/metal oxides hybrid materials.

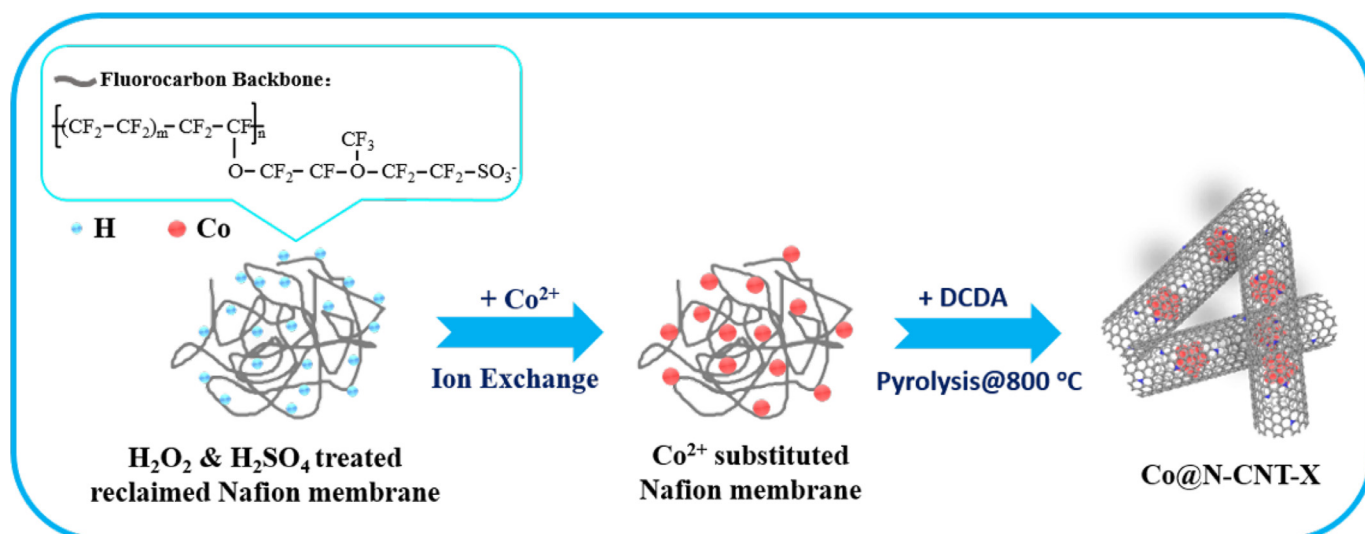
In our previous work, nitrogen and fluorine co-doped graphene/CNTs supported FeNi hybrid material was prepared using iron and nickel substituted perfluorosulfonic acid/polytetrafluoroethylene (PFSA/PTFE) copolymer with uniform distribution and conveniently adjustable ratios of metal ions [20]. The optimum hybrid material demonstrated excellent electrocatalytic activity in alkaline medium and high performance in zinc–air battery. Inspired by this, herein we explore to

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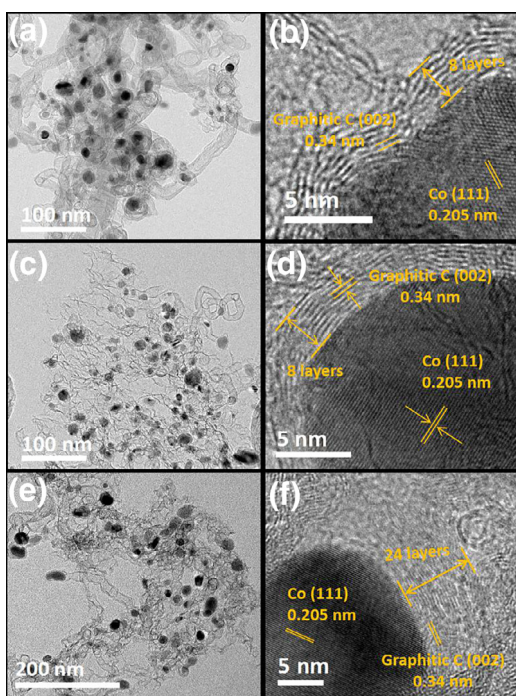
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**Scheme 1.** Schematic illustration of the synthesis process of different Co@N-CNT catalysts.



**Fig. 1.** TEM and HRTEM images of (a, b) Co@N-CNT-4, (c, d) Co@N-CNT-8 and (e, f) Co@N-CNT-12.

prepare nitrogen-doped CNTs (N-CNTs) encapsulating Co NPs using Co-substituted PFSA/PTFE copolymer by a simplified route. High exposure of N-C species is beneficial for the ORR activity by decreasing the carbon layers and increasing the specific surface area of N-CNTs. The hybrid material shows high activity and stability for ORR, as well as excellent performance and durability in zinc-air battery.

## 2. Experimental

### 2.1. Material synthesis

The perfluorosulfonic acid/polytetrafluoroethylene copolymer was prepared by soaking the reclaimed Nafion 211 membranes in boiled 15 wt% H<sub>2</sub>O<sub>2</sub> solution and 1 M H<sub>2</sub>SO<sub>4</sub> solution for 1 h,

respectively (denoted as PFSA/PTFE-H). The obtained PFSA/PTFE-H was then soaked in 800 mL 0.1 M CoSO<sub>4</sub> aqueous solution at room temperature for 24 h followed by washing with deionized water thoroughly to remove the residual CoSO<sub>4</sub> on the membrane (denoted as PFSA/PTFE-Co). The PFSA/PTFE-Co was cut into pieces and adequately mixed with dicyandiamide (DCDA) with mass ratios of 1:4, 1:8 and 1:12, respectively. The mixture was heated to 800 °C in a furnace at a rate of 10 °C min<sup>-1</sup> and kept at 800 °C for 2 h in Ar atmosphere at a flow rate of 50 mL min<sup>-1</sup>, and then cooled to room temperature. The obtained hybrid materials were denoted as Co@N-CNT-4, Co@N-CNT-8, and Co@N-CNT-12, respectively, according to the mass ratio of dicyandiamide to PFSA/PTFE-Co.

### 2.2. Physicochemical characterizations

Transition electron microscopy (TEM) and high-resolution TEM (HRTEM) characterizations were performed to investigate the morphology of catalysts using an FEI Tecnai G<sup>2</sup> microscope at 120 kV and a JEM-2100 microscope at 200 kV, respectively. X-ray diffraction (XRD) was performed on an Empyrean-100 diffractometer (PANalytical B.V., Netherlands) with Cu K $\alpha$  radiation source at 40 kV and 40 mA at a scan rate of 11 °/min. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Thermo Scientific spectrometer with an Escalab 250 Xi X-ray as excitation source. Nitrogen adsorption/desorption measurements were conducted using a Quantachrome QUADRASORB SI system at 77 K. Specific surface areas of the samples were calculated by the Brunauer-Emmet-Teller (BET) equation. Nonlocal density functional theory (NLDFT) was used to obtain pore size distribution based on equilibrium model of cylinder pore. The bulk contents of cobalt in the catalysts were analyzed with inductively coupled plasma-optical emission spectroscopy (ICP-OES, 7300DV, PerkinElmer).

### 2.3. Electrochemical measurements

The ORR electrocatalytic activities of the catalysts were evaluated in a three-electrode cell (AKCELL3, Pine Research Instrumentation) in O<sub>2</sub>-saturated 0.1 M KOH solution at 25 °C. A commercial glassy carbon (GC) electrode (AFE2M050GC, 5 mm in diameter, 0.196 cm<sup>2</sup>, Pine Research Instrumentation) covered by a catalyst layer, a graphite rod electrode (Wuhan Gaoss Union Co. Ltd.) and a Hg/HgO electrode (Shanghai Yueci Electronic Technology Co. Ltd.) were used as the working electrode, the

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