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# Nanocubic-Co<sub>3</sub>O<sub>4</sub> coupled with nitrogen-doped carbon nanofiber network: A synergistic binder-free catalyst toward oxygen reduction reactions



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## ARTICLE INFO

## Article history:

Received 27 January 2016

Received in revised form

13 June 2016

Accepted 7 July 2016

## Keywords:

Nanocubic-Co<sub>3</sub>O<sub>4</sub>

Nitrogen-doped carbon nanofiber

Binder-free

Oxygen reduction reactions

## ABSTRACT

High-performance electrocatalysts with excellent catalytic activity and long durability competitive to Pt are urgently necessary for fuel cell development. Here, a novel self-standing membrane of nitrogen-doped carbon nanofibers (NCNF) has been developed, acting as a three-dimensionally networked and conductive template for immobilization of electrochemically active Co<sub>3</sub>O<sub>4</sub> particles. Thus, nanocubic-Co<sub>3</sub>O<sub>4</sub> coated NCNF (NCNF@Co<sub>3</sub>O<sub>4</sub>) composite fiber membrane with hierarchical structures is obtained, which subtly combines the synergistic effects between the electroactive nanocubic-Co<sub>3</sub>O<sub>4</sub>, efficient surface nitrogen doping and highly conductive NCNF network. Therefore, the NCNF@Co<sub>3</sub>O<sub>4</sub> composite exhibits excellent catalytic activity toward oxygen reduction reactions with positive  $E_{\text{peak}}$  potential, high current density and superior durability over the commercial Pt/C catalyst, being a promising noble metal-free catalyst for practical fuel cell applications.

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## 1. Introduction

The increasing demand for clean and sustainable energy has inspired extensive exploration of advanced energy conversion and storage systems with high efficiency, low cost and environmental benignity, such as supercapacitors, lithium-ion batteries, fuel cells, and metal–air batteries [1,2]. Nevertheless, the sluggish kinetics of oxygen reduction reaction (ORR) on the cathode side definitely limits the successful commercialization of high efficiency fuel cells and metal–air batteries. Pt-based materials have been considered as the most active noble metal ORR electrocatalysts, but largely constrained in practical applications due to their scarcity, poor durability and severe crossover effects [3,4]. Therefore, non-precious metal-based and even metal-free electrocatalysts, such as transition metal oxides (TMOs), metal chalcogenides and carbon-based materials are newly emerging as promising candidates for high-performance fuel cell and metal–air battery applications [5–7].

Co<sub>3</sub>O<sub>4</sub>, as a typical kind of TMOs, has attracted increasing attention as a relatively active ORR catalyst with natural abundance, low cost, and environmental compatibility [8–10]. Nevertheless, poorly conductive Co<sub>3</sub>O<sub>4</sub> nanoparticles always suffer from

inevitable dissolution and agglomeration during the reaction processes, thus leading to compromised kinetics and reduced ORR activity. Directly growing or immobilizing Co<sub>3</sub>O<sub>4</sub> nanocrystals on various carbon-based supporting materials, like graphene, carbon nanotubes (CNTs) or porous carbon, is proved to be an effective strategy to construct hybrid materials with largely increased surface active sites, optimized electrical and chemical coupling between Co<sub>3</sub>O<sub>4</sub> and the supporting substrates [11–13]. For example, N-doped graphene/Co<sub>3</sub>O<sub>4</sub> composites [11], N-doped graphene/carbon nanotube/Co<sub>3</sub>O<sub>4</sub> composites [14], and Co<sub>3</sub>O<sub>4</sub> nanocrystals/O-/N-doped carbon nanoweb [15] have been demonstrated to show high activity and long-term stability as ORR catalysts. However, carbon-based nanoparticles like CNTs and graphene easily tend to restack or aggregate due to the strong van der Waals interactions between individual particles, which ultimately results in decreased surface area and electrochemical active sites to take part in efficient catalytic processes. For this reason, it is urgently needed to explore novel conductive carbon-based frameworks with synergistically enhanced mechanical stability and electrochemical performance.

Electrospinning is considered as a simple and versatile technique to produce self-standing carbon nanofiber membranes with unique three-dimensional (3D) fiber network, good structural stability and high flexibility [16–18]. The interconnected 3D macroporous architecture can act as a highly conductive core for fast

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electron transport, as well as provide sufficient surface active sites for further immobilization of electrochemically active nanoparticles [19,20]. Herein, nitrogen-doped carbon nanofibers (NCNFs) have been facilely obtained through the combination of electrospinning, in-situ polymerization and high-temperature carbonization. Subsequently, the free-standing membrane of nanocubic- $\text{Co}_3\text{O}_4$  coated NCNF (NCNF@ $\text{Co}_3\text{O}_4$ ) composite is fabricated via a simple hydrothermal reaction (Fig. S1), which combines the superior electroactivity of nanocubic- $\text{Co}_3\text{O}_4$ , the efficient doping effect of nitrogen, and the good conductivity of NCNF network. Hence, the NCNF@ $\text{Co}_3\text{O}_4$  composite membrane exhibits excellent catalytic performance toward oxygen reduction reactions, being a promising noble metal-free ORR catalyst in fuel cell applications.

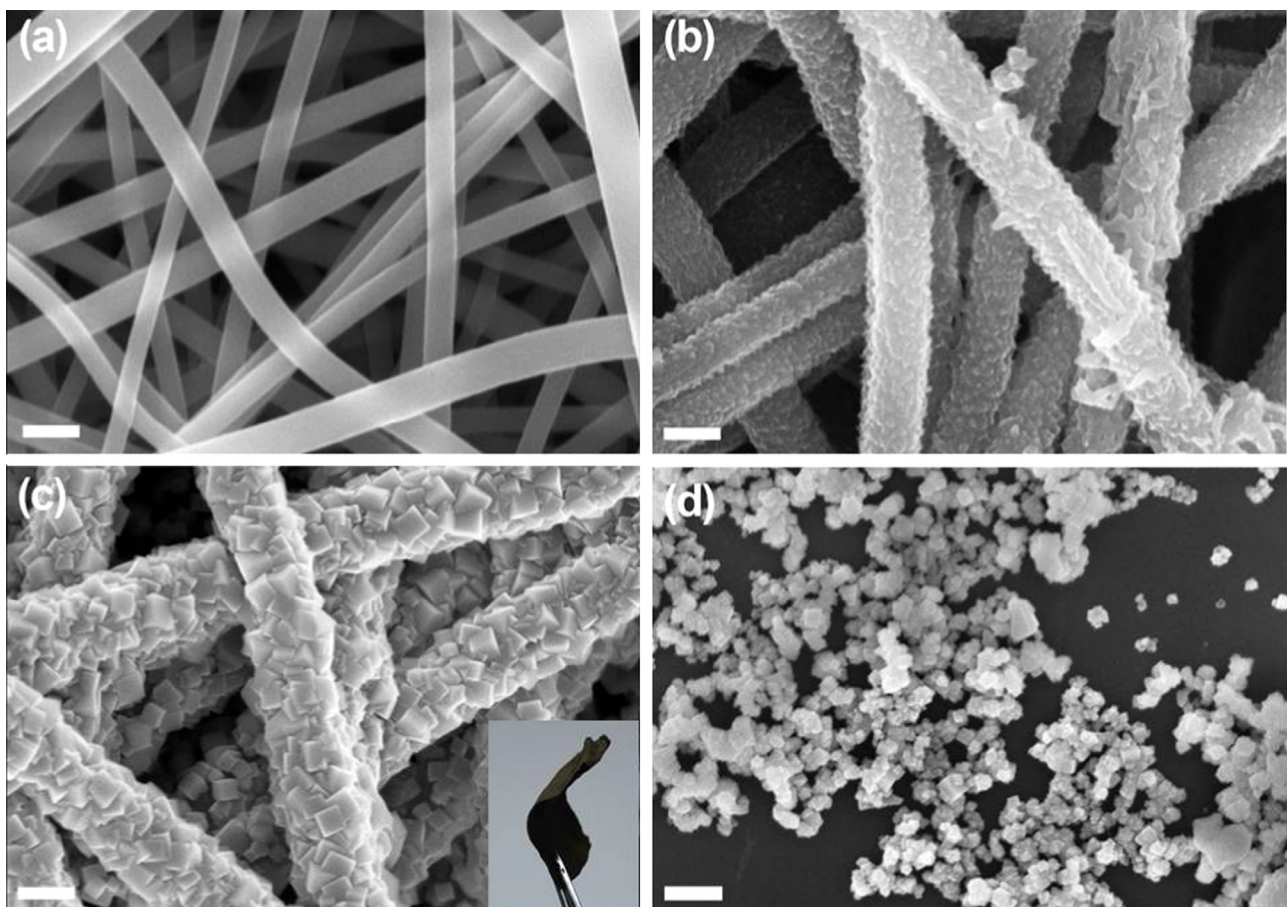
## 2. Results and discussion

As shown in Fig. 1a, electrospun poly(amide acid)-derived carbon nanofibers (CNFs) show uniform diameter with an average size of about 140 nm. In order to introduce nitrogen into CNFs, in-situ polymerization of aniline was carried out in the presence of poly(amide acid) fiber template, followed by a high-temperature carbonization treatment. Under an initial aniline concentration of 0.02 M, nitrogen-doped CNFs (denoted as NCNF-0.02) are obtained, which exhibit an increased fiber diameter of about 215 nm with uniformly distributed needle-like nanoparticles on the fiber surface (Fig. 1b). Satisfyingly, the homogeneous bump structure of NCNF-0.02 can provide more catalytic active sites and be beneficial to faster ion diffusion compared with the smooth surface of CNFs.

Subsequent deposition of  $\text{Co}_3\text{O}_4$  nanoparticles was achieved by the hydrothermal reaction of cobalt acetate ( $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ ) in the presence of NCNF-0.02 template. As expected, nanocubic- $\text{Co}_3\text{O}_4$  particles with a mean size of 20–30 nm are uniformly distributed on the surface of NCNF-0.02 at a proper concentration of  $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ , forming NCNF-0.02@ $\text{Co}_3\text{O}_4$ -0.2 composite fibers with an obvious coaxial structure (Fig. 1c), which can effectively prevent the severe agglomeration of  $\text{Co}_3\text{O}_4$  powder as obtained in the absence of NCNF-0.02 template (Fig. 1d). Furthermore, the NCNF-0.02@ $\text{Co}_3\text{O}_4$ -0.2 composite fiber membrane exhibits distinct free-standing feature (as shown in the inset of Fig. 1c), coincidentally omitting the usage of insulating binders required for powdery materials and thus effectively avoiding unwanted inner resistance for oxygen reduction reactions.

The structure of CNF, NCNF-0.02, NCNF-0.02@ $\text{Co}_3\text{O}_4$ -0.2 fiber membranes, and  $\text{Co}_3\text{O}_4$  powder was further investigated by X-ray diffraction (XRD) patterns. As shown in Fig. 2a, both of pure CNF and NCNF-0.02 fiber membranes exhibit amorphous structure while sharp peaks at  $2\theta = 19.5^\circ$ ,  $31.6^\circ$  and  $37.2^\circ$  are observed for NCNF-0.02@ $\text{Co}_3\text{O}_4$ -0.2 fiber membrane and  $\text{Co}_3\text{O}_4$  powder, which correspond to the (111), (220) and (311) crystal facets of cubic  $\text{Co}_3\text{O}_4$  with good crystalline structure.

X-ray photoelectron spectroscopy (XPS) characterization was carried out to further analyze the elemental composition of NCNF-0.02 and NCNF-0.02@ $\text{Co}_3\text{O}_4$ -0.2 fiber membranes. As shown in Fig. 2b, the survey spectrum of NCNF-0.02 indicates the existence of C, O and N elements, confirming the successful incorporation of nitrogen into the carbon nanofibers through the in-situ polymerization of aniline and carbonization process. The high-resolution XPS spectrum of N 1s (Fig. 2c) reveals that nitrogen atoms exist in three



**Fig. 1.** FESEM images of electrospun CNF (a), NCNF-0.02 (b), NCNF-0.02@ $\text{Co}_3\text{O}_4$ -0.2 (c) fiber membranes, and  $\text{Co}_3\text{O}_4$  powder (d). Scale bar: 100 nm. The inset of (c) shows the distinct free-standing feature of NCNF-0.02@ $\text{Co}_3\text{O}_4$ -0.2 fiber membrane.

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