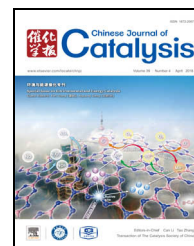


available at [www.sciencedirect.com](http://www.sciencedirect.com)journal homepage: [www.elsevier.com/locate/chnjc](http://www.elsevier.com/locate/chnjc)

Article (Special Issue on Environmental and Energy Catalysis)

# Paper-derived cobalt and nitrogen co-doped carbon nanotube@porous carbon as a nonprecious metal electrocatalyst for the oxygen reduction reaction



Gaopeng Liu <sup>a</sup>, Bin Wang <sup>a</sup>, Li Xu <sup>a</sup>, Penghui Ding <sup>a</sup>, Pengfei Zhang <sup>b,c</sup>, Jiexiang Xia <sup>a,b,\*</sup>, Huaming Li <sup>a,#</sup>, Junchao Qian <sup>d</sup>

<sup>a</sup> School of Chemistry and Chemical Engineering, Institute for Energy Research, Jiangsu University, Zhenjiang 212013, Jiangsu, China

<sup>b</sup> Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge 37830, USA

<sup>c</sup> School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, China

<sup>d</sup> Jiangsu Key Laboratory for Environment Functional Materials, Suzhou University of Science and Technology, Suzhou 215009, Jiangsu, China

## ARTICLE INFO

### Article history:

Received 21 November 2017

Accepted 23 December 2017

Published 5 April 2018

### Keywords:

Oxygen reduction reaction

Waste paper

Biomass

Porous carbon

Cobalt

## ABSTRACT

The oxygen reduction reaction (ORR) is a vitally important process in fuel cells. The development of high-performance and low-cost ORR electrocatalysts with outstanding stability is essential for the commercialization of the electrochemical energy technology. Herein, we report a facile synthesis of cobalt (Co) and nitrogen (N) co-doped carbon nanotube@porous carbon (Co/N/CNT@PC-800) electrocatalyst through a one-step pyrolysis of waste paper, dicyandiamide, and cobalt(II) acetylacetonate. The surface of the hierarchical porous carbon supported a large number of carbon nanotubes (CNTs), which were derived from dicyandiamide through the catalysis of Co. The addition of Co resulted in the formation of a hierarchical micro/mesoporous structure, which was beneficial for the exposure of active sites and rapid transportation of ORR-relevant species (O<sub>2</sub>, H<sup>+</sup>, OH<sup>-</sup>, and H<sub>2</sub>O). The doped N and Co formed more active sites to enhance the ORR activity of the electrocatalyst. The Co/N/CNT@PC-800 material exhibited optimal ORR performance with an onset potential of 0.005 V vs. Ag/AgCl and a half-wave potential of -0.173 V vs. Ag/AgCl. Meanwhile, the electrocatalyst showed an excellent methanol tolerance and a long-term operational durability than that of Pt/C, as well as a quasi-four-electron reaction pathway. The low-cost and simple synthesis approach makes the Co/N/CNT@PC-800 a prospective electrocatalyst for the ORR. Furthermore, this work provides an alternative approach for exploring the use of biomass-derived electrocatalysts for renewable energy applications.

© 2018, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

## 1. Introduction

Fuel cells are one of the most promising energy conversion devices for providing sustainable and clean energy [1,2]. The

oxygen reduction reaction (ORR) is the cathode reaction in fuel cells and is usually catalyzed by precious metals, especially by state-of-the-art platinum (Pt)-based catalysts, because of their excellent catalytic performance [3]. However, the Pt materials

\* Corresponding author. Tel: +86-511-88791108; E-mail: [xjx@ujs.edu.cn](mailto:xjx@ujs.edu.cn)

# Corresponding author. Tel: +86-511-88791108; E-mail: [lhm@ujs.edu.cn](mailto:lhm@ujs.edu.cn)

This work was supported by the National Nature Science Foundation of China (21476098, 21471069, 21576123) and International Postdoctoral Exchange Fellowship Program of China Postdoctoral Council (20150060).

DOI: 10.1016/S1872-2067(17)62982-6 | <http://www.sciencedirect.com/science/journal/18722067> | Chin. J. Catal., Vol. 39, No. 4, April 2018

are expensive and suffer from limited natural reserves, sluggish kinetics, poor durability, the crossover effect, and low tolerance to methanol, which pose a key obstacle to its development and commercialization [4–7]. Therefore, the development of low-cost, high-performance non-Pt catalysts to replace Pt-based catalysts is considered as one of the best ways to achieve large-scale commercialization of fuel cells.

To endow non-Pt catalysts with superior ORR performance, various carbon-based materials are a great choice. Carbon-based materials have some unmatched versatility for electrocatalysis including good electrical conductivity, chemical inertness, versatile morphology, and large surface area. Various carbon-based materials have been extensively applied for the ORR such as graphene [8], carbon nanotubes (CNTs) [9], and carbon microspheres [10]. However, pure carbon materials have few active sites and display poor ORR activity. Numerous studies have demonstrated that the doping of heteroatoms (B [11,12], N [13,14], P [15,16], S [17,18]) within the skeleton of carbon materials can change their electron donor properties and form active sites to boost the ORR [19,20]. Specifically, N-doped carbon materials with unique structures, favorable flexibility, and excellent mechanical and electrochemical properties have been widely used as effective electrocatalysts for the ORR [21]. In N-modified carbon materials, the nitrogen atoms have a higher electronegativity than that of the carbon atoms. The electron density of the carbon atoms adjacent to the nitrogen atom is lowered, which favors the dissociative chemisorption of oxygen [22]. Furthermore, the earth-abundant transition metals (Fe [23], Co [24], Ni [25], Cu [26]) have also been introduced to enhance ORR activity, which could immobilize the dissociative oxygen species and promote electrical conductivity [23,27]. In particular, transition metals (such as Co) in N-doped carbon can effectively improve the ORR properties by constructing Co–N<sub>x</sub> active sites [28]. Cao *et al.* [29] synthesized Co and N co-doped bamboo-like CNTs (NBCNT), which showed an enhanced ORR performance compared with individual Co- or N-doped materials. The synergistic effect of the co-doped Co and N promoted the ORR process.

Recently, carbon-based materials derived from carbon-enriched biomass (seaweed [30], fermented rice [31], typha orientalis [32]) have also been widely exploited for the ORR. Biomass is sustainable, renewable, ecofriendly, cheap, and ubiquitous in nature. All these merits imply that biomass is a potential candidate for the ORR for large-scale applications. Paper is one of the most common biomass-derived materials used in daily human life, but its recycling rate is still very low. Wei *et al.* [33] have prepared Fe-based N-doped carbon materials as ORR catalysts using tissue and filter paper. Carbon materials prepared from waste paper have a large specific surface area. The large specific surface area is favorable for the transmission of ORR-related species (O<sub>2</sub>, H<sup>+</sup>, OH<sup>−</sup>, and H<sub>2</sub>O) and accelerates the reaction rate. Furthermore, it is an environmentally friendly process, which would not only reduce the cost but would also be conducive to large-scale preparation.

Herein, we designed a readily scalable approach for the fabrication of Co and N co-doped porous carbon (Co/N/CNT@PC-800) electrocatalysts, which were prepared

through a simple annealing of a mixture of waste paper, dicyandiamide, and cobalt(II) acetylacetonate at 800 °C. Because of the catalytic effect of cobalt, the Co/N/CNT@PC-800 catalyst with a porous structure had many nanotubes on its surface. The numerous micropores and mesopores are beneficial for exposure of the active sites and the transportation of ORR-relevant species. The Co and N co-doped carbon materials can generate more active sites to enhance the ORR activity. For these reasons, the low-cost catalyst exhibited good ORR performance with a quasi-four-electron reaction pathway, good stability, and methanol tolerance in an alkaline medium. This work will open up a new way to utilize biomass waste to obtain value-added materials through an economic and environmentally friendly method.

## 2. Experimental

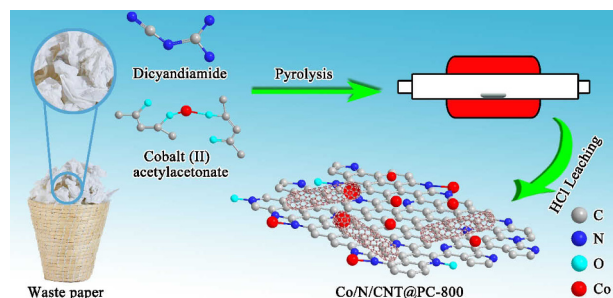
### 2.1. Chemicals

Cobalt(II) acetylacetonate (99%), dicyandiamide, and methanol were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Nafion (10% wt%) was obtained from Sigma-Aldrich (Missouri, USA). Commercial 20 wt% Pt/C was obtained from Alfa Aesar (China) Chemicals Co., Ltd. (Shanghai, China). The waste paper obtained from our laboratory. (Zhenjiang, China). All these chemicals were used as delivered without further treatment.

### 2.2. Material synthesis

The shredded paper was washed with an appropriate amount of distilled water to remove the impurities. Then, the paper pulp was filtered by suction and vacuum dried at 60 °C before further use.

The synthesis of Co/N/CNT@PC-800 is shown in Scheme 1. In a typical synthesis, 2.0 g dicyandiamide and 0.5 g of cobalt(II) acetylacetonate were dissolved in 50 mL methanol and defined as solution A. Then, 1.0 g pretreated paper was distributed in 50 mL of distilled water to obtain mixture B. Solution A was added into mixture B and then stirred for 12 h. The intermediate product was dried in an oven. Afterwards, the obtained dark-green material was ground and placed into a ceramic boat. The material was heated to 500 °C for 2 h with a ramp rate of 5 °C min<sup>−1</sup> under an argon atmosphere in a tubular furnace. Then, the temperature was raised to 800 °C and main-



**Scheme 1.** Schematic of the synthesis process for the Co/N/CNT@PC-800.

Download English Version:

<https://daneshyari.com/en/article/6505695>

Download Persian Version:

<https://daneshyari.com/article/6505695>

[Daneshyari.com](https://daneshyari.com)