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Facile electrospinning preparation of phosphorus and nitrogen dual-doped cobalt-based carbon nanofibers as bifunctional electrocatalyst

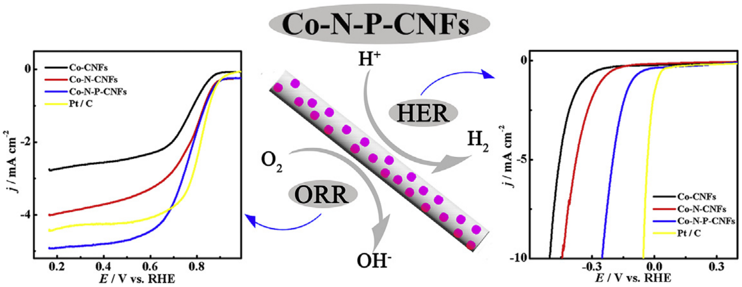
Zhuang Wang, Pengjian Zuo, Liquan Fan, Jianan Han, Yueping Xiong*, Geping Yin

School of Chemical Engineering and Technology, Harbin Institute of Technology, Harbin 150001, PR China

HIGHLIGHTS

- Novel Co-based CNFs catalysts were prepared by the electrospinning technique.
- The Co–N–P-CNFs catalyst exhibits the excellent ORR and HER catalytic activity.
- Synergy of N/P is responsible for the excellent catalytic performance.
- Pyridinic-N and Co-N$_x$ clusters of Co–N–P-CNFs were as catalytic active sites.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel electrochemical catalyst of phosphorus and nitrogen dual-doped cobalt-based carbon nanofibers (Co–N–P-CNFs) is prepared by a facile and cost-effective electrospinning technique. Excellent features of the porous carbon nanofibers with large amounts of Co atoms, N/P-doping effect, abundant pyridinic-N and Co–N$_x$ clusters as catalytic active sites, and the advantages of the structure and composition result in a high catalytic efficiency. In alkaline or acidic media, Co–N–P-CNFs exhibits remarkable electrocatalytic activities and kinetics for oxygen reduction reaction (ORR), superior methanol tolerance and stability, and a similar four-electron pathway. In addition, Co–N–P-CNFs also shows excellent performance for hydrogen evolution reaction (HER), offering a low onset potential of −0.216 V and a stable current density of 10 mA cm^{-2} at potential of −0.248 V. The mechanism of ORR and HER catalytic active site arises from the doping of N/P atoms in the Co-based CNFs, which is responsible for the excellent electrocatalytic performance. Due to the excellent catalytic efficiencies, Co–N–P-CNFs act as a promising catalyst material for fuel cells and water splitting technologies.

1. Introduction

Nowadays, the global environment pollution and energy crisis are becoming more and more severe [1]. It is greatly desirable to research and develop the green high-performance energy conversion and storage systems, such as metal-air batteries and fuel cells [2,3]. Oxygen reduction reaction (ORR), oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) play key roles in the various cell reaction processes, but they have the sluggish reaction kinetics and poor efficiencies [4–15]. It is necessary to investigate an efficient electrochemical catalyst to increase the reaction rate and improve the performance. As far as we know, Pt-based catalysts are

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[*] Corresponding author.
E-mail address: ypxiong@hit.edu.cn (Y. Xiong).

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considered to be the most efficient catalysts [4,5]. However, noble metals are expensive and unstable, which limits the widespread practical application. Therefore, it is important to explore efficient and low-cost alternatives to replace the noble metals.

Recently, due to the unique mechanical, electrical, magnetic, and chemical properties, carbon nanofibers (denoted as CNFs) have been widely investigated [6]. As expected, the CNFs have also been used in building the ORR, OER, or HER electrochemical catalyst. However, the catalytic performance of common CNFs is far from meeting the requirement because of the lack of surface active sites and fast mass transport pathways. In addition, the heteroatom-doped (N, Fe, Ni, Co) CNFs have been reported and found to exhibit excellent electro-catalytic performance [7–12]. Unfortunately, these catalysts are still far from meeting the requirements of combined high catalytic activity, strong durability, and low cost. New strategies to develop efficient catalysts are still desirable.

In these catalysts, nitrogen or phosphorus-coordinated transition metal (Fe, Co, Ni and Mn) co-doped CNFs or other carbon matrixes have been investigated and considered as the efficient ORR or HER catalyst [13–19]. But these catalysts remain some issues, including the corrosion of carbon at high potential, the poor intrinsic catalytic activity of a single active site compared with Pt [20], and the differences of the stabilities and kinetic rates in alkaline and acidic solutions [21]. The overall volumetric activity is the combination of a single site activity and the active site density. Thus, the principal strategy is in an effort to increase of active site density [22]. On the other hand, to convert the electronic structure and improve electrochemical properties of the catalysts, the co-doping of two nonmetal elements [23–27] with reverse electron negativity to that of carbon could lead to a unique electron-donor property of carbon by the synergetic effect between two kinds of heteroatoms [28]. However, the overall catalytic activity is much lower in comparison with Pt-based catalysts because of the lack of metal catalytic activity sites.

As mentioned above, some experimental conditions for the preparation of the catalysts are tedious and not cost-effective, which limits the practical industrial manufacture. Meanwhile, it is difficult for the simultaneous preparation of carbon matrices with the clusters as catalytic active sites, resulting in weak bonding of the catalytic active sites with carbon matrices, and even separation of the catalytic active sites from the carbon matrixes [29]. Electrospinning is a fascinating method for the preparation of CNFs, meanwhile, due to the presence of carbon source and a source of catalytic active sites [30], it is also a one-step preparation of carbon matrixes with catalytic active sites. It is simple and effective to limit the separation of the catalytic active sites from CNFs.

The previously reported carbon-based electrocatalysts exhibit excellent catalytic activity for ORR, HER, or OER, but high dual or triple activity for ORR, HER and OER using carbon-based electrocatalysts have rarely been reported [31–34]. In this article, we report a novel nitrogen and phosphorus co-doped cobalt-based CNFs (denoted as Co–N–P-CNFs) as bifunctional electrochemical catalyst. The catalyst was synthesized by a simple yet efficient method of electrospinning technique. The as-electrospun nanomaterial was sintered at 800 °C under N_2 atmosphere to prepare the final catalyst. The structures and morphologies of the as-prepared catalysts were characterized with X-ray diffraction (XRD), nitrogen adsorption-desorption isotherms, scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive X-ray (EDX) spectroscopy, X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy. The electrochemical performances of the catalysts were tested by cyclic voltammetry (CV), rotating disk electrode (RDE), and rotating ring-disk electrode (RRDE) techniques. Scheme 1 shows the illustration of the entire procedures for preparing Co-based CNFs catalysts.

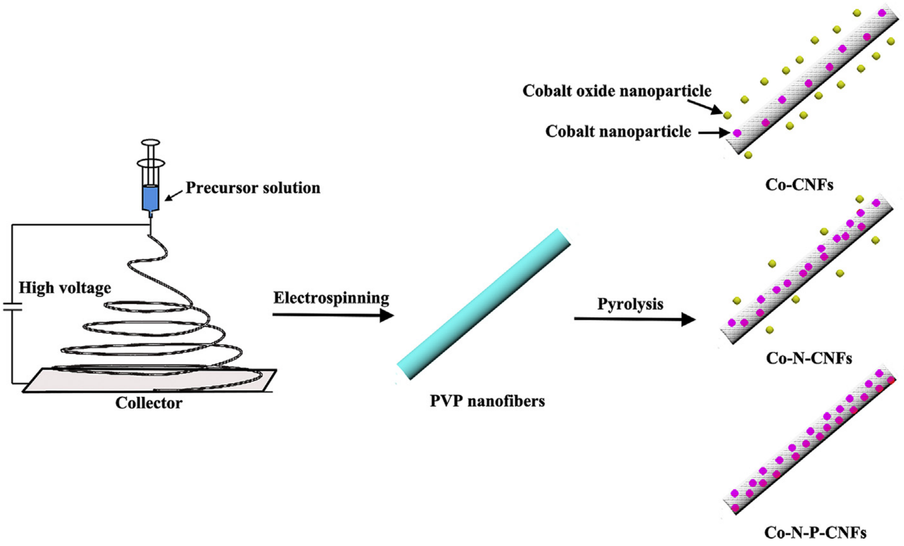
2. Experimental

2.1. Materials and reagents

Polyvinylpyrrolidone (PVP), N,N-dimethylformamide (DMF), $Co(NO_3)_2 \cdot 6H_2O$, urea, triphenylphosphine, and Nafion (5 wt% solution) were purchased from Sinopharm Chemical Reagent Co., Ltd. All other chemicals were analytical reagent grade and used as received. Ultrapure water (resistivity: $\rho \geq 18\ \Omega\mathrm{M\ cm^{-1}}$) was used to prepare the solutions.

2.2. Synthesis of Co-based CNFs

The catalysts Co–N–P-CNFs were synthesized by electrospinning technique. For the preparation of precursor solution, PVP and DMF were used as polymer and dispersant solvent, and



Scheme 1. Illustration of the preparation procedures for the Co-CNFs, Co–N-CNFs and Co–N–P-CNFs samples.