



# Nitrogen-doped and nanostructured carbons with high surface area for enhanced oxygen reduction reaction



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## ABSTRACT

The development of highly-efficient, inexpensive, and stable electrocatalysts as alternatives to platinum-based materials for the oxygen reduction reaction (ORR) is crucial to various energy storage and conversion systems, such as metal–air batteries and fuel cells. Herein, we have successfully prepared three kinds of hierarchically porous nitrogen-doped carbons with different morphologies (particles, nanowires, and nanoribbons) through a carbon dioxide activation process. The porous properties and catalytic performance of the nitrogen-doped porous carbons are dramatically and clearly improved through changing the morphology of polypyrrole precursors. Among these nitrogen-doped porous carbons, the nitrogen-doped and nanostructured carbon with the morphology of nanoribbons possesses the highest specific surface area ( $1130 \text{ m}^2 \text{ g}^{-1}$ ) and displays the best ORR activity with the largest electron transfer number (3.67) and the most positive onset potential (0.86 V vs. RHE) in oxygen-saturated aqueous KOH solution (0.1 M). This enhanced ORR performance can be attributed to nitrogen-doping, a hierarchically porous structure, and large specific surface area.

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## 1. Introduction

Developing green sustainable energy storage and conversion technology has become very important in the twenty-first century because of the depletion of fossil fuels and increasing environmental problems associated with fossil fuels. The oxygen reduction reaction (ORR) is a critical step in electrochemical energy conversion and storage systems such as metal–air batteries and fuel cells [1]. Successful development of efficient catalysts for the ORR is regarded as key to realize optimal performance. As is well known, platinum (Pt) has been considered the most active catalyst on the basis of the desired four-electron transfer ORR process [2,3]. However, high cost, sluggish kinetics, limited stability, and low tolerance to methanol largely inhibit development and commercialization of Pt-based ORR catalysts [4]. In this regard, much effort has been devoted to reducing Pt loading or even completely replacing Pt, thus leading to development of more abundant and

less expensive electrocatalysts. These electrocatalysts include Pt-based alloys [5,6], transition metal oxides and chalcogenides [7,8], carbon-based non-noble metal composite catalysts [9,10], and metal-free carbonaceous catalysts [11–13].

Carbon-based metal-free materials have been considered as ideal electrocatalysts for ORR owing to their good corrosion resistance, low cost, high electronic conductivity, and excellent surface properties [14–16]. Heteroatom-doped carbons have drawn tremendous attention in the last few years. The heteroatom species play a vital role in modifying chemical properties and improving the catalytic activity of carbon-based materials [17]. In particular, nitrogen-doped porous carbons have been widely investigated as efficient metal-free electrocatalysts [18]. Generally, nitrogen-doped porous carbon catalysts can be obtained through direct doping in the preparation of porous carbons or post-treatment of the as-prepared carbon materials with a nitrogen-containing agent, such as ammonia and nitrogen [19–21]. Nitrogen-doped porous carbons usually possess many excellent properties, such as high porosity and outstanding surface polarity, which can promote the adsorption and diffusion of  $\text{O}_2$  molecules and increase the number of catalytic sites [22–24]. Therefore, nitrogen-doped porous carbons

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are excellent candidates for the ORR. For example, Graglia et al. prepared a hierarchically porous nitrogen-doped carbon using sustainable lignin as a precursor via an ionothermal carbonization method. The obtained porous carbon as an electrocatalyst displayed an outstanding catalytic activity for the ORR [25].

In addition to heteroatom doping, it has been proved that creating novel structures with large specific surface area can increase the density of active sites, thus improving the catalytic activity of catalysts [26,27]. For example, Chen et al. obtained nitrogen-doped carbon nanocages with a specific surface area of up to  $1393 \text{ m}^2 \text{ g}^{-1}$  through an in situ template method [28]. Yang et al. synthesized a series of nitrogen-doped mesoporous carbon spheres with tunable specific surface areas ( $67\text{--}1295 \text{ m}^2 \text{ g}^{-1}$ ) through a soft template method [29]. These nanostructured porous carbons as ORR electrocatalysts exhibited excellent activity and stability in alkaline medium. Therefore, structural design of the catalysts plays a vital role in the preparation and optimization of ORR catalysts.

Polypyrrole (PPy) is a widely available, low-cost, and common conducting polymer, which has been investigated in the fields of supercapacitors and batteries [30,31]. Especially, nanostructured PPy is attractive because of its unique physical and chemical properties [32]. Herein, we prepared three kinds of hierarchically porous nitrogen-doped carbons with different morphologies through carbon dioxide activation of polypyrrole (PPy) particles, nanowires, and nanoribbons. A nitrogen-doped and nanostructured carbon with the morphology of nanoribbons possesses the highest specific surface area ( $1130 \text{ m}^2 \text{ g}^{-1}$ ) and displays the best ORR activity in aqueous KOH solution (0.1 M).

## 2. Experimental section

### 2.1. Materials

Ammonium persulfate and pyrrole were purchased from Sina-pharm Chemical Reagent Co. Ltd., China. Cetyl trimethylammonium bromide (CTAB) was commercially available from Beijing Chemical Works, China. Carbon dioxide (99.5% purity) and nitrogen (99.999% purity) gases were obtained from Beijing Haik Yuanchang Gas Co. Ltd., China. Ultrapure water ( $18 \text{ M}\Omega \text{ cm}$ ) was produced by an UPT-II-

10T water purification system (Sichuan Ulupure Science and Technology Co. Ltd., China).

### 2.2. Synthesis of PPy particles

PPy particles were synthesized through an oxidative polymerization method [32]. The experimental procedure is as follows. Pyrrole monomer (600  $\mu\text{L}$ ) was added into ultrapure water (300 mL) and cooled to  $4^\circ\text{C}$ . Subsequently, precooled aqueous ammonium persulfate solution (9 mmol dissolved in 65 mL ultrapure water) was added into the mixture with simultaneous vigorous stirring. The mixture was kept in a refrigerator at  $4^\circ\text{C}$  for 24 h. The as-prepared mixture was filtered and washed with ultrapure water and ethanol for several times. Finally, PPy particles were collected by vacuum drying in an oven at  $80^\circ\text{C}$ .

### 2.3. Synthesis of PPy nanowires and nanoribbons

PPy nanowires and nanoribbons were synthesized through a modified oxidative template assembly method [32]. The experimental procedures are as follows. CTAB (3 mmol) was dissolved in 300 mL ultrapure water to obtain a homogeneous solution. Then, 600  $\mu\text{L}$  (for nanowires) or 300  $\mu\text{L}$  (for nanoribbons) pyrrole monomer was put into the above CTAB solution. After stirring for 10 min, the resultant mixture was cooled to  $4^\circ\text{C}$ . Subsequently, precooled aqueous ammonium persulfate solution (4.5 mmol for nanoribbons or 9 mmol for nanowires dissolved in 65 mL ultrapure water) was slowly added into the mixture with vigorous stirring. Then the mixture was kept in a refrigerator at  $4^\circ\text{C}$  for 24 h. The as-prepared mixture was filtered and washed with ultrapure water and ethanol several times. Finally, PPy nanowires and nanoribbons were collected by vacuum drying in an oven at  $80^\circ\text{C}$ .

### 2.4. Preparation of nitrogen-doped porous carbons

Three kinds of nitrogen-doped porous carbons were prepared through carbon dioxide activation of PPy particles, nanowires, and nanoribbons, respectively. In a typical experiment, PPy particles, nanowires, or nanoribbons were heated to  $950^\circ\text{C}$  in a tube furnace

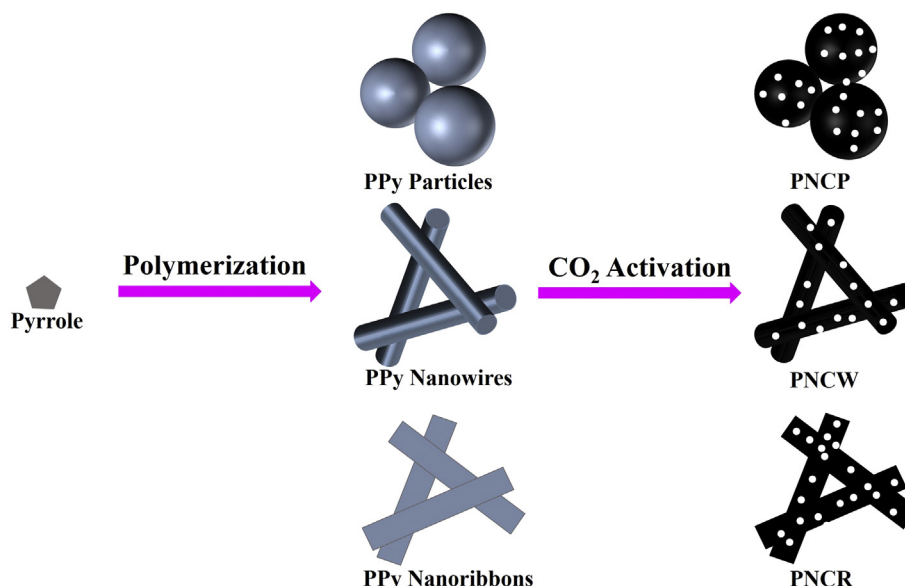


Fig. 1. Illustration of the preparation processes of PNC, PNCW, and PNCR. (A colour version of this figure can be viewed online.)

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