Hierarchical porous iron and nitrogen co-doped carbons as efficient oxygen reduction electrocatalysts in neutral media

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HIGHLIGHTS

- Hierarchical porous iron and nitrogen co-doped carbons have been successfully prepared.
- The synthesized HP−Fe−N−Cs show efficient ORR catalytic activities in neutral media.
- The HP−Fe−N−C-900 shows comparable MFCs performance to the commercial Pt/C catalyst.

GRAPHICAL ABSTRACT
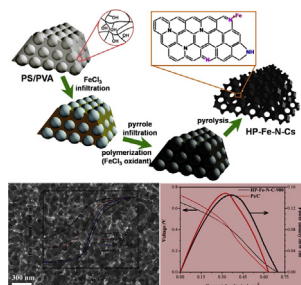
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ABSTRACT

Hierarchical porous iron and nitrogen co-doped carbons (HP−Fe−N−Cs) as efficient cathode catalysts for oxygen reduction reaction (ORR) in neutral media are reported. The HP−Fe−N−Cs are prepared by using polypyrrole as nitrogen source and poly(vinyl alcohol) (PVA) hydrogel-based composites as in-situ templates. In studying the effect of the iron and the hierarchical porous structure on the nitrogen-doped carbon support for ORR, we find that HP−Fe−N−Cs show more positive onset potential, higher cathodic current density, and higher electron transfer number for the ORR in neutral media than iron-free hierarchical porous nitrogen-doped carbon (HP−N−C) and non-hierarchical porous iron and nitrogen co-doped carbon (Fe−N−C), highlighting the importance of the iron and the hierarchical porous structure for improving the ORR performance. Furthermore, HP−Fe−N−Cs show better durability than the commercial Pt/C catalysts in neutral media, and the microbial fuel cells (MFCs) equipped with HP−Fe−N−Cs catalysts on cathodes exhibit comparable power outputs with those of MFCs with commercial Pt/C cathode catalysts.

1. Introduction

The oxygen reduction reaction (ORR) on the cathode plays a key role in energy-conversion devices such as fuel cells (FCs) and metal−air batteries [1,2]. Pt and Pt based catalysts have long been regarded as the most efficient catalysts for ORR [3,4]. However, the issues of increasing scarcity, high cost and poor stability hinder Pt cathode application [5,6]. Therefore, developing sustainable Pt-free catalysts is essential for the commercialization of fuel cells and metal-air batteries technology [7,8].

Currently, heteroatom-doped carbon materials, especially N-doped carbon materials are demonstrated to be a new kind of

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promising non-Pt electrocatalyst for ORR [9–11]. The nitrogen doping in carbon materials can significantly enhance the number of active sites for improved ORR activity [12,13]. For instance, vertically aligned N-doped carbon nanotubes exhibit outstanding electrocatalytic activity, and better stability than 20 wt% Pt/C for ORR in alkaline media [9]. However, for most N-doped carbon materials, the ORR activities are still on a less competitive level compared to Pt catalysts. It is proposed that an important limitation for enhancing the catalytic activity of these systems is the low surface density of catalytic active sites [14,15]. In this regard, an effective solution is to synthesize electrocatalysts with high-surface-area and porous structure. The high-surface-area characteristic could increase the volumetric surface area and thus to improve the surface density of catalytic active sites, while the porous structure could improve the transport properties of ORR-relevant species (H^+, OH^-, e^-, O_2, H_2O) [12,16]. Unfortunately, this solution usually need some specific pore-forming templates such as colloidal silica and mesoporous silica SBA-15 to produce the porous structure and high-surface-area, which may result in relatively complicated preparation processes due to the etching treatment [14,17,18]. Another potential solution is to incorporate transition metals into nitrogen-doped carbon materials, which are commonly known as non-precious metal (NPM) catalysts [19]. The transition metals could not only promote the formation of graphitized carbon framework, but also be conducive to the formation of more catalytic active sites [20]. What's more, the intrinsic active sites of Me–N_x may also form between the transition metals and the doped nitrogen atoms, which could significantly improve the ORR activity of the transition metals based nitrogen-doped carbon materials [21,22].

Therefore, considering that both high-surface-area, porous structure and transition metals incorporation are in favor of promoting the ORR performance for catalysts, it would be encouraging and significant to synthesize porous NPM catalysts with high-surface-area and investigate their performances toward ORR. Just recently, some NPM catalysts with porous structure have been developed and demonstrated to show enhanced ORR activity and superior stability, including pyrolyzed Fe-polypyrrole mesoporous spheres, hierarchical interconnected macro-/mesoporous Co-containing N-doped carbon and mesoporous cobalt–nitrogen-doped carbon etc [15,23,24]. These studies indicate that hierarchical porous materials with interconnecting macro-/mesoporous structures are ideal ORR electrocatalysts, as they provide multidimensional electron transport pathways, large surface areas for reaction, interfacial transport, or dispersion of active sites at different length scales of pores, and shorter diffusion paths or reduce the diffusion effect [25]. However, despite tremendous progress in NPM catalysts for ORR, developing a convenient, economical, and scalable method to prepare NPM catalysts with hierarchical porous structure is still urgently required. Furthermore, to the best of our knowledge, there are no studies are devoted to investigating the ORR performances of hierarchical porous NPM catalysts in neutral solution and even their practical applications in biological systems.

In this article, a facile and simple strategy for preparing hierarchical porous iron and nitrogen co-doped carbons (HP–Fe–N–Cs) has been reported by using polypyrrole (PPy) as a nitrogen source and poly(vinyl alcohol) (PVA) hydrogel-based composites as in situ templates, which were prepared by the solvent-assisted freezethaw method we previously developed. The presence of PVA hydrogel endows the templates with the hydrophilic character and hydroxyls of PVA allow for easy adsorption of metal cations due to complexing action between hydroxyls and metal cations, which facilitate the infiltration process. Remarkably, the resulting HP–Fe–N–Cs possess high surface area, hierarchical porous structure, and a certain amount of possibly existed Fe–N_x moieties which could act as active sites in the ORR catalytic process. Consequently, the as-prepared HP–Fe–N–Cs display excellent electrocatalytic performance for a four-electron pathway ORR and long-term stability superior to the commercial Pt/C catalyst in neutral media. Moreover, the feasibility of HP–Fe–N–C composite as cathode catalyst in MFCs was also evaluated by comparing with the commercial Pt/C catalyst, which manifests a comparable performance to Pt/C.

2. Experimental section

2.1. Materials

Poly(vinyl alcohol) (PVA, 99% hydrolyzed, DP = 1750 ± 50) was purchased from Sinopharm Chemical Reagent Co. All other chemicals were purchased from Shanghai Lingfeng Chemical Reagent Co. Styrene (St) was purified by treatment with a 5% (w/w) aqueous NaOH solution to remove the inhibitor. Ultrapure water (18 MΩ cm) was used in all experiments.

2.2. Synthesis

PVA hydrogel-based composites templates were synthesized by the solvent-assisted freeze–thaw method we developed previously [26]. Typically, a 10% (w/w) PVA dimethyl sulfoxide (DMSO) solution was mixed with a 10% (w/w) latex (v/v = 1/1) of monodisperse polystyrene (PS) colloids with a diameter of 160 nm. Then the pregel solution gelled at −20 °C for 4 h, thawed at room temperature for 1 h, and then chemically cross-linked in 0.75% glutaraldehyde aqueous solution for 4 h to form PVA hydrogel-based composites. For the synthesis of hierarchical porous iron and nitrogen co-doped carbon materials (HP–Fe–N–Cs), 5 g of PVA hydrogel-based composites were pre-impregnated into 20 mL of 0.1 M $FeCl_3$ ethanol solution by stirring for 5 h at room temperature. Afterward, the PVA hydrogel-based composites were transferred into an ethanol solution (0.2 M) of pyrrole monomer and stirred for 30 min. Then, 30 mL of aqueous solution (0.1 M) of $FeCl_3$ was added to the suspension followed by stirring for 24 h at 4 °C. The resulting solid was washed with water and ethanol to remove the residual oxidant and precipitation on the surface for several times. The obtained sample was dried under vacuum at 40 °C for 12 h and then pyrolyzed under argon at 800 °C, 900 °C and 1000 °C for 2 h. To remove excess metal elements, the pyrolyzed sample was treated with 0.5 M H_2SO_4 solution at room temperature for 12 h and then washed thoroughly with ultrapure water. For comparison, iron free hierarchical porous nitrogen-doped carbon materials (HP–N–Cs) and non-hierarchical porous iron and nitrogen co-doped carbon materials (Fe–N–Cs) were also synthesized. The preparation of HP–N–Cs was the same as described above except for no pre-impregnation step and replacing the $FeCl_3$ oxidant with ammonium persulfate (APS). The non-hierarchical porous sample (Fe–N–Cs) was prepared with PVA hydrogel without polystyrene (PS) colloids as templates under the same preparation processes.

2.3. Characterization

The morphology and microstructure of the samples were investigated by High-transmission electron microscopy (TEM: JEM-2100, operated at 200 kV) and Scanning electron microscopy (FE-SEM: S-4800). X-ray diffraction (XRD) patterns were collected on a powder X-ray diffractometer (RIGAK, D/MAX 2550 VB/PC, Japan). Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) models were used to determine the specific surface areas, pore volume, and the pore sizes of the samples, respectively. Raman spectra were recorded with a Bruker RFS 100/S spectrometer. X-ray photoelectron spectroscopy (XPS) was conducted using VG ESCA