Nitrogen, phosphorus and iron doped carbon nanospheres with high surface area and hierarchical porous structure for oxygen reduction

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HIGHLIGHTS

- N, P and Fe co-doped carbon nanospheres were prepared by a facile method.
- The catalyst shows a high surface area and hierarchical porous structure.
- The catalyst exhibits excellent ORR performance superior to the Pt/C catalyst.

GRAPHICAL ABSTRACT
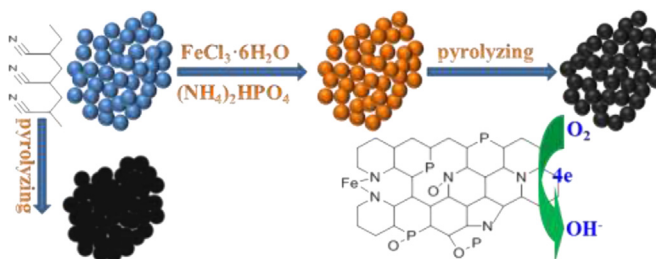
ABSTRACT

Nitrogen, phosphorus and Fe doped carbon nanospheres have been synthesized by a facile method in which polyacrylonitrile nanospheres are pyrolyzed in the presence of diammonium phosphate and iron trichloride hexahydrate. The specific surface area of the catalyst is high up to 771.3 m^2 g^{-1}, and it has a hierarchical micro-meso-macroporous structure. In an alkaline medium, the catalyst exhibits high electrocatalytic activity towards the oxygen reduction reaction (ORR) as well as excellent stability and methanol tolerance—superior in each case to commercial Pt/C catalyst. The effects that adding Fe salt and phosphorus on the structure and performance of the catalyst are also investigated. We suggest that the catalyst's excellent electrocatalytic performance may be attributed to: (1) the synergistic effect, which provides more catalytic sites for the ORR, due to the nitrogen and phosphorus co-doping; (2) the strong promotion by trace Fe residues; and (3) the high surface area and excellent mass transport rate arising from the hierarchical porous structure.

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1. Introduction

Pt-based electrocatalysts are regarded as the best catalyst materials developed, to date, for the ORR. However, they cannot meet the requirements of successful fuel cell commercialization for a number of reasons, including the scarcity and high cost of Pt, their poor stability and tolerance against poisons [1]. Considerable effort has therefore been invested in developing nonprecious-metal [2–14] and metal-free [15–19] catalysts for the ORR. Among such candidates, heteroatom-doped carbon materials have the distinct advantages of relatively low cost, long-term operational stability, and excellent methanol tolerance [20].

N-doped carbon materials exhibit superb electrocatalytic performance for the ORR [21,22], that may be attributed to the heteroatoms present in the carbon, which break the catalyst's

electroneutrality to create charged sites and consequently favor the molecular adsorption and reduction of oxygen. Recently, heteroatoms other than N have been used to dope carbon, including sulfur [19,23], boron [24,25], and phosphorus [26–28], and these also show enhanced catalytic activity for the ORR, but the performance is still lower than conventional Pt/C catalysts. To address this issue, some researchers have reported that doping carbon materials with two or more heteroatoms can further improve their ORR catalytic activity, due to the synergistic effects that arise between the heteroatoms by introducing larger asymmetrical spin and charge density than can be achieved by single heteroatom doping [29–31].

Although moderate ORR performance has been obtained with these multi-heteroatoms doped carbon materials, it is still far from satisfactory. Another promising way to improve the electrocatalytic properties of carbon catalysts is by modifying their porosity, as porosity can maximize the electroactive surface area and improve mass transport, yielding higher performance [32]. Carbon materials with hierarchical micro-meso-macroporous structures offer several advantages: (1) they have large surface areas for interfacial transport; (2) their active sites are dispersed amongst pores of different lengths; (3) they provide multidimensional electron transport pathways; and (4) they can shorten the diffusion paths or reduce the diffusion effect. They are therefore widely regarded as ideal ORR electrocatalysts [29,32,33]. So combining multi-heteroatoms doping with a hierarchical micro-meso-macroporous structure may be a way of achieving high catalytic activity for the ORR.

In this work, we report nitrogen, phosphorus and Fe doped carbon nanospheres ((Fe)N–P/Cns) with a hierarchical micro-meso-macroporous structure as an efficient electrocatalyst material for the ORR in an alkaline medium. The (Fe)N–P/Cns were synthesized by pyrolyzing polyacrylonitrile nanospheres that had been pretreated by immersion in an aqueous solution containing $FeCl_3 \cdot 6H_2O$ and $(NH_4)_2HPO_4$, followed by drying at 80 °C overnight. Remarkably, the resulting (Fe)N–P/Cns possess high surface area as well as a hierarchical micro-meso-macroporous structure, and in an alkaline medium they exhibit higher catalytic activity than a commercial Pt/C catalyst, and excellent methanol crossover tolerance and durability.

2. Experimental

2.1. Catalyst preparation

Polyacrylonitrile nanospheres (PANs) were prepared by soapless emulsion polymerization, as reported in our previous study [19]. The PANs were pretreated by immersion for 24 h in an aqueous solution containing $FeCl_3 \cdot 6H_2O$ and $(NH_4)_2HPO_4$ (the weight ratio of PANs:$FeCl_3 \cdot 6H_2O$:$(NH_4)_2HPO_4$ is 1:0.30:0.30. The content of Fe in precursor is 4.6 wt%.). After being dried in an oven at 80 °C, the mixtures were heated from room temperature to 900 °C with a heating rate of 5 °C min^{-1} and held at this temperature for 2 h for pyrolyzing under a N_2 atmosphere in a tubular furnace. Once the resulting product had cooled to room temperature, it was ground into powder and treated with 1.0 M H_2SO_4 solution at 80 °C for 12 h to remove leachable Fe from the catalyst. Finally, the sample was washed with deionized water until neutral pH was reached, then pyrolyzed again by the same procedure as described above. We denote the prepared catalyst as (Fe)N–P/Cns. For comparison, we also used the same procedures to prepare (Fe)N/Cns without P doping, and pristine N/C.

2.2. Physical characterization

Scanning electron microscopy (SEM) images were recorded on a Nova Nano 430 field emission scanning electron microscope (FEI, USA). Transmission electron microscopy (TEM) observation was performed with a JEM-2100HR transmission electron microscope (JEOL, Japan). X-ray photoelectron spectroscopy (XPS) was conducted on an ESCALAB 250 X-ray photoelectron spectrometer (Thermo-VG Scientific, USA). Specific surface areas were measured by Brunauer–Emmett–Teller (BET) nitrogen adsorption–desorption on a Tristar II 3020 gas adsorption analyzer (Micromeritics, USA).

2.3. Electrochemical measurements

Electrochemical measurements were carried out on an electrochemical workstation (Ivium, Netherlands) equipped with a rotating disk electrode (RDE) (Pine Research Instrumentation, USA) using a standard three-electrode system at room temperature. The electrolyte was 0.1 M aqueous KOH solution. A Pt wire and a Ag/AgCl solution (3 M KCl) were used as the counter and reference electrodes, respectively. The potential of the Ag/AgCl electrode (3 M KCl) was calibrated with respect to reversible hydrogen electrode (RHE) (in 0.1 M KOH, E (RHE) = E (Ag/AgCl) + 0.982 V). The working electrode was prepared by the following procedure. First, the catalyst ink was prepared by sonicating a mixture of 5 mg catalyst and 1 mL nafion ethanol solution (0.25 wt%) for half an hour. Then 20 μL catalyst ink was pipetted onto a glassy carbon (GC) electrode (5 mm diameter, 0.196 cm^2 geometric area), followed by drying under an infrared lamp. The mass loading of the catalyst on the electrode was 0.5 mg cm^{-2}. Before testing, the electrolyte was purged with high-purity N_2 or O_2 gas for at least 30 min. The scanning rate was 10 mV s^{-1} unless otherwise specified.

3. Results and discussion

Fig. 1 shows SEM images of all the samples and TEM images of the (Fe)N–P/Cns. As can be seen in Fig. 1a, the PANs have a uniform spherical morphology with an average diameter of about 400 nm. It is interesting that the N/C prepared by pyrolyzing PANs without Fe and P doping shows no distinct morphology (Fig. 1b), seeming to have lost the original PANs morphology during pyrolysis, possibly due to aggregation and melt caused by the temperature increase. However, the samples co-doped with either Fe or Fe and P maintain the nanospherical morphology of the PANs, albeit with some extent of adhesion (Fig. 1c, d), revealing that co-doping with Fe or Fe and P prevent to a certain extent the PANs from sintering and melting. In the TEM image of (Fe)N–P/Cns (Fig. 1e), we can see that the nanospheres appear transparent, implying that the catalyst has a porous structure [34].

The residue of Fe compounds can be observed on the high-resolution transmission electron microscopy (HRTEM) image of (Fe)N–P/Cns (See Fig. 1f). As shown by XRD (Fig. 2d), all FeP was removed during acid leaching. Thus, the residual Fe species may be existed as Fe nanoparticles coordinated to nitrogen to form Fe–N_x–C structure [35].

The hierarchical porous structure of the catalyst is supported by the N_2 adsorption–desorption results. Fig. 2a shows the N_2 adsorption–desorption isotherms of the N/C, (Fe)N/Cns, and (Fe)N–P/Cns catalysts. The N/C has type I characteristics, according to the IUPAC classification, with a steep initial region at P/P$_0$ = 0–0.03 indicating the catalyst's microporous structure. It is important that (Fe)N/Cns and (Fe)N–P/Cns have quite different isotherms, with type VI characteristics. There is a sharp slope with a hysteresis loop at high relative pressure, which is typically associated with capillary condensation, indicating the existence of plentiful mesopores, notably, when capillary condensation occurs at high relative pressure this indicates a larger pore-size distribution. The BET surface areas calculated from the isotherms follow the order of (Fe)N–P/