



Nitrogen/phosphorus dual-doped hierarchically porous graphitic biocarbon with greatly improved performance on oxygen reduction reaction in alkaline media

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ARTICLE INFO

Keywords:

N, P-doped biocarbons
Metal free catalysts
Alkaline fuel cell
Oxygen reduction reaction

ABSTRACT

The N, P dual-doped hierarchically porous graphitic biocarbons were prepared via a simple pyrolysis of the precursors derived from hydrothermal treatment of natural polymer chitosan and triphenyl phosphine (P(Ph)₃). The characterization using scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and N₂ adsorption-desorption analysis indicated the samples doping with P exhibited smaller crystal size and more defect sites. The electrocatalytic activities of the as-prepared samples were evaluated with oxygen reduction reaction (ORR) in alkaline media. The results showed that the catalytic properties of N, P dual-doped samples were greatly enhanced compared with the phosphorous free ones. The optimized catalysts exhibited nearly equivalent catalytic performances to the commercial Pt/C (20%) with respect to onset potential, halfwave potential and limit current density.

1. Introduction

With its important role in the development of more effective fuel cells, the ORR catalyst has drawn considerable attentions [1–6]. Limited by its cost, slow electron-transfer kinetics, low durability, and poor stability, platinum-based precious metal catalysts have not made their way to the large scale commercialization [4,7–11]. Thus, it has been in great demand to develop the non-noble metal or even non-metal ORR catalysts with high efficiency that can be used in fuel cell. Over the past few years, many alternative materials have been investigated including non-precious metal oxide, doped carbon nano-materials [2,12–16]. Heteroatom, such as N, P, S doped carbon materials have received much more interests due to their low cost and prominent catalytic performances, such as nitrogen doped carbon sheets, nitrogen and sulfur co-doped carbon nanospheres and phosphorus-doped graphite layers [7,12–22]. A nitrogen-doped ordered graphitic mesoporous catalyst developed by Liu et al. [23] exhibited superior performance to that of commercially available Pt/C catalyst. N-doped carbon spheres developed through direct pyrolyzing a nebulized solution of xylene and ethylenediamine although achieved the onset potential close to Pt/C catalyst, showed higher current density [24]. Using SBA-15 as template, Yang et al. synthesized phosphorus-

doped ordered mesoporous carbons that possessed enhanced stability and methanol tolerance compared to Pt/C catalyst [25]. Among the various doping strategies in the development of more effective ORR catalysts, N, P dual doped functionalized carbon materials have exhibited excellent thermal stability and chemical inertness, high conductivity, large specific surface area and high stability than Pt-based catalysts [26–29].

So far, doped or not, the majority mesoporous carbons used as ORR catalysts have developed from either hard or soft template [30–32]. However, the reported functionalized carbon materials ORR catalyst were mostly prepared by multistep process using organic chemicals as raw materials under harsh conditions with low yields [33]. On the other hand, biomass has been found its application in the preparation of the carbon-supported catalyst. In particular, biomasses such as sucrose, glucose, cyclodextrins, cellulose, and starch have been used as the precursors to develop porous carbon materials [34–37]. Each year, there are considerable amount of biomasses produced in the world, however, the utilization of the biomass has not been very effective, and a significant amount of biomass ends up to be rotten and become pollutants [38]. Therefore, it is a significant, sustainable and environmentally friendly way to develop carbon material ORR catalysts using biomass as raw materials.

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Chitosan, an abundant biomass, is made by treating the chitin shells of shrimp and other crustacean with an alkaline substance. Chitosan contains a large number of amino groups and can be used as a source of carbon and nitrogen for the preparation of nitrogen self-doped biocarbon, such as chitosan modified screen printed electrode, chitosan based porous carbon and carbon nanosheets [39–41]. Moreover, amino group in chitosan has a strong coordination ability and can coordinate with metal ions to form complexes. This facilitates the controlling of the structures and properties of the catalysts at the molecular level [39,42,43]. In addition, other heteroatoms can be introduced to chitosan to achieve synergetic and additive interactions [17,22,25].

In the present work, N, P dual doped hierarchically porous biocarbon catalysts were prepared by using chitosan as carbon and nitrogen source, triphenyl phosphine as phosphorus donor, and ZnCl_2 as activator. To make N and P be homogeneously doped in the catalysts at molecular level, the precursors were first synthesized by coordination of chitosan and triphenyl phosphine with Fe (III) formed metal complexes. The precursors were then pyrolyzed at high temperature in the presence of ZnCl_2 . The final catalysts were obtained by etching the pyrolyzed sample with acid to remove the metal species. The as-prepared catalysts have shown hierarchically porous structures, high surface areas and stabilities, and comparable catalytic activities for ORR with commercial Pt/C (20%).

2. Experimental section

2.1. Reagents and materials

Chitosan and triphenyl phosphine were purchased from Aladdin chemical reagent company. Pt/C (20 wt% Pt on carbon black) and Nafion (5 wt%) were purchased from Alfa Aesar. All reagents were analytical grade and were used directly without any further purification.

2.2. Synthesis of the catalysts

In the typical synthesis of the N, P dual-doped graphitic carbons, 1.0 g chitosan and 30 mL 0.5 M FeCl_3 aqueous were added into a beaker and continuously stirred on an oil bath at 50 °C for 3 h. Then, 0.75 g of P(Ph)_3 was added under stirring. The mixture was then transferred to a 50 mL Teflon-lined stainless steel autoclave and hydrothermally treated at 180 °C for 12 h. After naturally cooled to room temperature, the obtained brown precipitation was collected by filtration, washed with deionized water for several times and then dried in vacuum at 100 °C overnight to obtain the precursor. 0.5 g of the precursor was then mixed with 2.0 g ZnCl_2 and pyrolyzed at 900 °C for 2 h with a heating rate of 5 °C/min [18,44,45]. The pyrolyzed sample was treated with 1 M HCl at 60 °C for 3 h, thoroughly washed with deionized water and dried in vacuum at 100 °C overnight to obtain the final catalyst denoted as NPC@0.75, where 0.75 represents the quantity of added P(Ph)_3 in preparation of the precursor. To investigate the effect of P(Ph)_3 amount, another two catalysts NPC@0.5 and NPC@1.0 were also prepared. For comparison purpose, the catalyst without P doping was also prepared and denoted as NC.

2.3. Physical characterization

Scan electron microscope (SEM) images and energy-dispersive X-ray (EDS) spectrum were collected using a field-emission scanning electron microscope (JSM-6701F, FEOL) with an accelerating voltage of 5 kV. Transmission electron microscopy (TEM) images were taken with a JEM-2010 transmission electron microscope operated at an accelerating voltage of 200 kV. The X-ray power diffraction (XRD) patterns of the samples were obtained on a Shimadzu XRD-6000 diffractometer with Cu $\text{K}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$) at 40 kV and 200 mA of the operation voltage and current, respectively. The nitrogen adsorption-desorption characterization were performed with an ASAP2020 Micromeritics Instrument at 77 K and each sample was degassed at 350 °C for 4 h prior

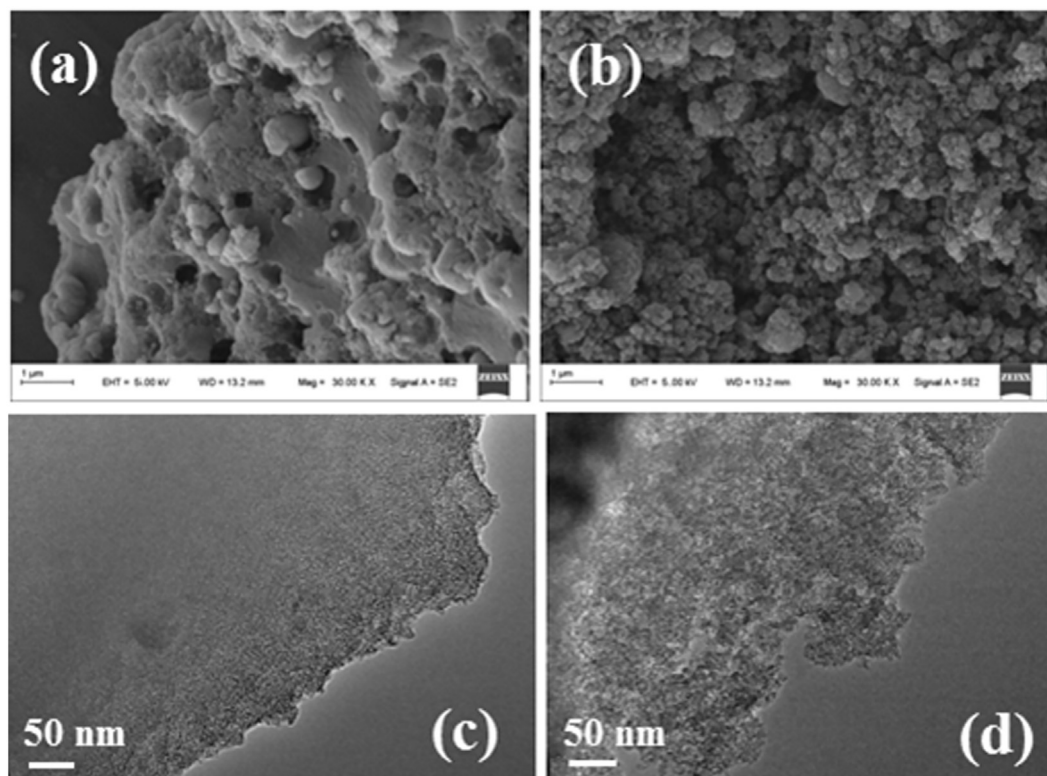


Fig. 1. Typical SEM and TEM images of NPC@0.75 (a, c) and NC (b, d).

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