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Direct synthesis of nitrogen and phosphorus co-doped hierarchical porous carbon networks with biological materials as efficient electrocatalysts for oxygen reduction reaction

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ABSTRACT

We described a process of the preparation of N, P co-doped hierarchical porous carbon by one-step pyrolysis of the chitosan/phytic acid (CS/PA) precursor without extra activation processes, and the nitrogen and phosphorus were successfully incorporated into the carbon framework. Experimentally, the best performance was identified with NPC-1000 which possessed the highest BET specific surface area of 1117.2 m² g⁻¹. This NPC-1000 showed a half-wave potential of 50 mV difference with commercial Pt/C, better tolerance to methanol and a superior stability comparable to commercial Pt/C catalyst. The results suggest that it is a simple, feasible, and economical route to synthesis of hierarchical porous carbon which can be used as metal-free catalysts for oxygen reduction.

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Introduction

Polymer electrolyte membrane fuel cells (PEMFC) are environmentally friendly and renewable energy technologies,

which are the most popular energy resource at present [1,2]. When hydrogen is fed as fuel, it combines hydrogen and air to generate electricity through a chemical catalyst, the only products are heat and water [3]. The oxygen reduction

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reaction (ORR) is a key process to catalyze the reaction of oxygen in the air at the cathode. A direct four-electron ORR would lead to the high performance [4]. Although platinum-base catalysts have a higher activity, the platinum resource is scarce and very expensive. Low-cost and efficient catalysts for ORR are indispensable.

As a promise catalysts, heteroatom doped carbon nano-materials have revealed excellent electrocatalytic activities towards ORR owing to their distinct advantages of low cost and long term stability [5,6]. Charge delocalization of the carbon atoms is a significant characteristic related to the ORR activity of carbon-based catalysts by inducing heteroatom into carbon [7,8]. Specifically, experimental researches and theoretical calculations have confirmed N-doped carbons own higher activities than other heteroatom-doped carbons [9,10]. Generally, the pyridinic and graphitic nitrogen are regarded as ORR active centers among the four types of nitrogen functional groups [11,12]. In addition, introduction of multiple heteroatoms into the graphitic structures such as N, P co-doping can further improve ORR activity in view of the synergistic effects between the dopants which bring out abundant active sites [13–17]. P is another doping heteroatom which has the same number of valence electrons as N and it is an electron donor which can be incorporated into carbon [18,19]. In addition, P possesses lone pair electrons in the 3p orbitals for inducing local charge density which facilitates O₂ adsorption in the oxygen reduction reaction [20–22].

As for sites utilization and mass delivery, a hierarchically porous nanoarchitecture (micro-, meso-, and macropore) with high surface area is highly desired except the intrinsic feature of N, P co-doping [23–25]. It has been demonstrated that the porous carbon materials with large surface area was beneficial to catalytic activity [26]. However, carbon obtained from pyrolysis biological materials directly usually have low specific surface area [27]. An additional chemical activation treatment is a traditional method to improve it. For example, H₃PO₄ [24], KOH [28], and ZnCl₂ [29] have been reported as typical agents for chemical activation. Nevertheless, chemical processes require multiple steps involving pore-making and/or activation, or relatively expensive and difficult to scale up. Therefore, a simple and facile strategy is still highly desired to synthesize heteroatoms co-doped hierarchical porous carbon with high surface area.

Various kinds of biological materials with many advantages such as cheap, naturally abundant, cyclically sustainable and rich in heteroatoms, have the ability to transform into heteroatom-doped carbon materials [30]. Chitosan (CS), a well known natural aminopolysaccharides riched in nitrogen with many bio-functional groups, such as –NH₂ and –OH [31,32], is very abundant and low-cost resources on the earth, existing in the cells of various crustaceans such as shrimp, crab, and insect [33]. In the acidic condition, a large amount of amino of chitosan polymer chain combines with a hydrogen ion in the solution, and forms electropositive macromolecular polymer electrolyte [34]. Phytic acid (PA) contains twelve acidic protons on six P-containing units on a single six-carbon molecule, which is negatively charged over a wide pH range of pH > 2.0 [35,36]. It is a green material as C precursor and P precursor which mainly exists in the seeds, roots and stems of plants. Thus, P-rich PA as negatively charged partner to pair

with N-rich CS [37] to form self-assembling chitosan-phytic acid super-molecular aggregate.

Herein, we describe a process of the preparation of N, P co-doped hierarchical porous carbon by one-step pyrolysis of the CS/PA compound without extra activation processes. The resulting catalyst exhibited high electrocatalytic activity and long-term stability which can be applied to metal-free catalysts for oxygen reduction, due to the nanopores in the hierarchical porous carbon networks with numerous edges sites increase the topological defects and N, P doping causes the distortion of sp² conjugated carbon atoms [5,38].

Experimental section

Sample preparation

The preparation of N, P co-doped hierarchical porous carbon was summarized in Scheme 1. Refer to the method of Zhang et al. [39], the precursor was prepared by chitosan and phytic acid. 3 g chitosan powders were stirred in 150 mL 1 wt% acetic acid solution for 2 h. 4 wt% phytic acid solution was added into the chitosan solution dropwise to form the white precipitate completely. After collecting by centrifugation and repeatedly washed with deionized water to neutral, the precipitates dried under vacuum at 80 °C for 1 day as precursors. The precursors were then heated in a tube furnace under N₂ atmosphere at 700, 800, 900 and 1000 °C with a heating rate of 5 °C min⁻¹, and maintained at that temperature for 2 h. The final products were grounded to fine powders, named as NPC-700, NPC-800, NPC-900 and NPC-1000.

Physical characterizations

The morphology of the samples were measured by the field emission scanning electron microscope (FESEM, JSM-6700F) and Transmission electron microscopic (TEM, JEOL JEM-2100, with an accelerating voltage of 200 kV). X-ray diffraction (XRD) patterns were performed on Bruker AXS D8 (Cu K α radiation; $\lambda = 0.1541$ nm), the diffraction angle ranging from 10 to 80°. Raman spectra were performed on HR Evolution Raman spectrometer instrument with a 514 nm laser. The specific surface area and the pore structure of the samples were analyzed by adsorption/desorption measurements using Quantachrome Quadrasorbevo. Surface area was examined by Brunauer-Emmett-Teller (BET) method, pore volume and pore size distribution were calculated using the DFT method. The elemental composition was conducted on an energy dispersive spectroscopy (EDS). The elements binding environment of the samples were carried out on X-ray photoelectron spectroscopy (XPS) by Escalab 250Xi (Thermo Scientific, with Al K α radiation, $h\nu = 1486.6$ eV).

Electrochemical measurements

To study the ORR activity of the catalysts, all tests were recorded on a Pine electrochemical system using the RRDE technique with a standard three-electrode electrochemical cell in 0.1 M KOH solution at room temperature. Pt wire, Ag/AgCl (3 M KCl) electrode and the catalyst coated RRDE were

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