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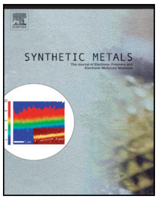

Bacterial cellulose derived iron and phosphorus co-doped carbon nanofibers as an efficient oxygen reduction reaction electrocatalysts

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ABSTRACT

Heteroatom-doped carbon materials as efficient electrocatalysts for oxygen reduction reaction have been attracted a lot of research interest. For its low cost, high selectivity and excellent stability, heteroatoms-doped carbon materials have been considered as the candidate for replacing Pt-based catalysts. We had designed an iron and phosphorus co-doped carbon nanofibers (Fe-P/CNFs) derived from bacterial cellulose for oxygen reduction reaction, which not only showed a three-dimensional (3D) porous network structure, but also possessed large surface area. The unique 3D porous network could accelerate oxygen diffusion and electron transfer, and meanwhile enlarge specific surface area. Accordingly, the obtained material had more active sites for electrocatalysis. More importantly, the unusual synergistic effects between the doped Fe and P atoms could efficiently improve the electrocatalytic performance of oxygen reduction reaction. As expected, the Fe-P/CNFs showed a high ORR electrocatalytic activity with a more positive onset potential of 1.01 V, similar with 1.03 V at 20 wt% Pt/C, and a good long-term stability (94% retention of current density after chronoamperometry 20,000s).

1. Introduction

Today fossil fuel burning brings many severe problems such as energy crisis and environmental destruction obviously [1–3]. Thus, the development of clean, sustainable, reliable and technical viable energy conversion and storage is one of the biggest challenges of the 21st century. Fuel cell, an appealing device for sustainable energy conversion and storage, can largely alleviate energy pressure and reduce the negetive impact of climate change [4]. Unfortunately, the sluggish oxygen reduction reaction (ORR) in the cathode reaction of fuel cells intensely has limited its working efficiency [5–8]. Platinum (Pt)-based materials are so far the most efficient electrocatalysts for ORR, while a series of disadvantages including high cost, scarcity, poor durability and undesirable crossover deactivation hindered the practical applications on fuel cells [9–13]. Accordingly, exploring affordable and efficient electrocatalysts to replace Pt-based catalysts in ORR is crucial for commercial applications of fuel cells [14,15].

Note that heteroatom-doped carbon materials have been explored as alternative electrocatalysts for the ORR due to their advantages of abundance, low-cost and high catalytic activity. Expecially doping heteroatoms into carbon materials can change the physical and chemical properties and modify the surface of carbon, thus provide more new active site to enhance ORR catalytic activity [14,16,17]. Additionally, worldwide researchers have devoted to prepare the heteroatom-doped carbon materials via changing carbon precursors and anealing temperature to improve ORR electrocatalytic performance. Recent many studies had reported that Fe-N/C catalysts exhibited superior performance toward ORR. It had been predicted on the basis of molecular orbital theory that Fe atom in Fe-N/C can adsorb the O_2 on the surface of catalysts, which resultd in an increase of O—O bond distance and avails O_2 decomposing [18,19]. Furthermore, in despite of the exact role of N in Fe-N/C still exist many disagreements, density fanctional theory (DFT) and experimental observations have suggested that the carbon atoms adjacent to N could possess high positive spin density and atomic charge density and thus become the active catalytic sites for ORR [14]. Accordingly, as an element of the nitrogen group, phosphorus atom also has attracted tremendously attention, which is believed to be the same number of valence electrons and similar chemical properties with nitrogen [20]. For instance, Yu et al. have reported a new species Fe-P introduced into the carbon matrix, which exhibited promising the activity for ORR in alkaline and acid media that depends highly on

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the presence of both Fe-P species and C-P bond [21]. Liao et al. have delivered a Fe-P-N doped carbonspheres as the efficient electrocatalysts for ORR which can be attributed to the synergistic effect of nitrogen and phosphorus [22]. More importantly, these studies uniformly demonstrated the possibility for the Fe-P/C nanomaterials as alternatives to Pt-based fuel cell electrocatalysts [23].

Due to its low cost and 3D nanonetwork architecture, bacterial cellulose (BC) had been reported as an excellent precursor to obtain carbon nanofibers materials for many applications, especially for electrocatalysis. As the carbon precursor, BC endowed three predominant advantages, namely, i) abundant and cheap raw materials, ii) the adequate functional groups (carboxylic/hydroxy group) decided efficient absorbability of ions, iii) 3D network structure [16,24–26]. Herein, we reported a novel iron and phosphorus co-doped carbon nanofibers derived from BC, denoted as Fe-P/CNFs. The obtained carbon nanofibers materials not only inherited 3D nanonetwork architecture of BC but also provided a large surface area [27–30]. Notably, the unusual synergistic effects between the doped Fe and P atoms can also improve the ORR catalytic performance. Consequently, the as-prepared Fe-P/CNFs exhibited excellent ORR activity, high selectivity, superior stability and good tolerance to methanol poisoning effects in the alkaline media.

2. Experimental sections

2.1. Synthesis of Fe-P/CNFs

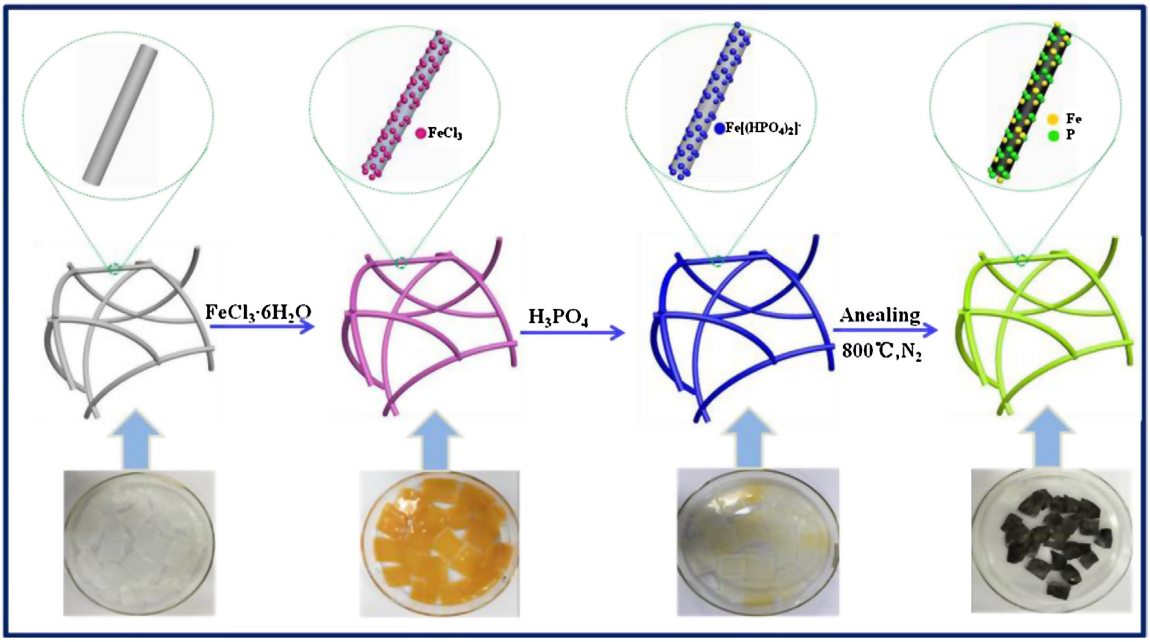
Purified BC pellicles with thickness of 2 mm were kindly provided by Ms CY Zhong (Hainan Yeguo Foods Co., Ltd., Hainan, China). The BC pellicles were first washed by deionized water and then cut into small pieces (2 cm × 2 cm) with a sharp blade. And then 10 pieces of BC pellicles were dipped into 50 mL 0.01 M $FeCl_3 \cdot 6H_2O$ solution for 12 h at the room temperature. The color of BC pellicles turned into orange because of absorption of Fe^{3+}. Subsequently, 50 mL 0.02 M H_3PO_4 solution was added to reacted with Fe^{3+} which generated the colorless $Fe[(HPO_4)_2]^-$ ($Fe^{3+} + 2HPO_4^{2-} = Fe[(HPO_4)_2]^-$). Finally, the obtained BC was freeze-dried in a bulk tray dryer at a sublimating temperature of −48 °C and a pressure of 0.06 mbar. The freezed-dried BC was pyrolyzed under flowing N_2 atmosphere to form Fe-P/CNFs. In brief, the temperature was slowly increased to 350 °C at a rate of 1.5 °C min^{-1} and kept for 1 h to stabilize the BC structure, and then was increased to 800 °C for another 1 h to obtain the Fe-P/CNFs. The as-obtianed Fe-P/CNFs was washed by 1 M HCl solution to remove residual Fe and dried at 60 °C for 12 h. The synthetic procedure of Fe-P/C was depicted in Scheme 1. For comparison, the P-CNFs were prepared as above steps without $FeCl_3$ $6H_2O$ addition and the CNFs were obtianed by anealing freezed-dry BC directly.

2.2. Characterization

The samples were characterized by a MSAL-XD2 X-ray diffractometer (XRD, Cu Ka, 40 kV, 20 mA, $\lambda = 1.5406$ Å). The morphologies were examined by field emission scanning electron microscope (FESEM, ZEISS Ultra 55) and JEM2010 high resolution transmission electron microscopy (HRTEM) operating at 200 kV. The X-ray photoelectronic spectroscopy (XPS) was carried out using an ESCALab250 spectrometer with Alumina Ka (1486.6 eV) source. Nitrogen sorption isotherms of as-prepared materials were studied by a Micromertics TriStar 3000 analyzer at 77 K. The plot of specific surface area was deduced from the isotherm analysis of adsorption data at the relative pressure (P/P_0) of 0–1.0 and the average pore diameters were collected from the peak value on the pore diameter distribution. The degree of crystalline structure of as-prepared samples were investigated by a Raman spectroscopy, which was recorded in a backscattering configuration using the 514.5 nm line of an Ar^+ ion laser and a Renishaw in Via Plus Raman spectrometer.

2.3. Electrochemical measurement

A CHI660D electrochemical workstation (CH Instruments, China) was used to measure the electrochemical performance of the sample at room temperature in three-electrode system. Platinum foil (1.0 × 1.0 cm^2) and Ag/AgCl (saturated KCl) were used as counter electrode and reference electrode, respectively. A rotating ring disk electrode (RRDE) system (Pine Instrument Co,



Scheme 1. Schematic representation of the synthesis of Fe-P/CNFs.