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Facile synthesis and excellent catalytic performance of nitrogen-doped porous carbons derived from banana peel towards oxygen reduction reaction

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ABSTRACT

In this paper, nitrogen-doped porous carbons have been synthesized by using a facile low-cost and accessible approach. The banana peels which regarded as discarded rubbish were reused and acted as carbon source. The typical sample possesses plenty of interconnected pores, and its BET surface area is as large as 1442 $m^2 g^{-1}$. Electrochemical measurements indicates that the typical samples exhibits considerable catalyticactivity and high four-electron route selectivity, which is comparable or even superior to Pt/C in alkaline and acid mediums. Excitingly, the typical sample can even endure methanol-poisoning effect,and long term electrolytic corrosion with only 9.41% current density attenuation after 5000 consecutive cycles, which exceeds the performance of Pt/C in alkaline mediums. What's more, this work demonstrates a successful example for turning discarded rubbish into valuable functional products as well as addresses the disposal issue of waste biomass and contributes to environment cleaning.

1. Introduction

Fuel cells (FCs) are one of the most promising and totally green energy conversion devices to replace the traditional fossil energy, which can address the problem of environmental pollution fundamentally [1–4]. Oxygen reduction reaction (ORR) is the crucial step in the reaction of FCs [5–7]. Nevertheless, it is essential to use excessive amounts of electrocatalysts at the cathode due to the sluggish kinetics of ORR. Hitherto,platinum (Pt) based catalyst has become the preferred materials to catalyze ORR and exhibited excellent electrochemical properties toward ORR. Whereas, Pt-based catalyst still suffer from multiple drawbacks. For instance, poor durability, methanol-poisoning effect intrinsically, high cost and scarcity of the noble Pt metal, which are the major factors to hinder the large-scale commercialization of FCs [8–11]. To address this issue and promote the development of FCs, one promising route is to exploit new types of catalyst with low cost and high efficiency such as non-precious metals or even metal-free catalysts. Carbon-based materials are considered to be scalable to replace Pt as ORR electrocatalysts because of excellent catalytic activities and good resistance to methanol poisoning. And various strategies have been developed for the nitrogen doped porous carbon. For example, Yu [12], Wang [13] and Zhao [14] successfully prepared porous carbon materials with comparable ORR activity by using g-C_3N_4, SiO_2 and polystyrene spheres as temples, respectively. Wang [15] prepared nitrogen-doped porous carbon from a bimetallic zeolitic imidazolate framework based on ZIF-8 and ZIF-67. Besides, Bing [16] presented an effective template-free synthesis of nitrogen-doped hierarchical porous carbonsby direct carbonization of melamine-resorcinol-terephthaldehyde networks. Among the carbon-based materials, biomass derived carbon materialshave emerged asfront runners to replace Pt, by virtue of its extensive available, renewable and environmentally [17–19]. And fungus [20], pomelo peel [21,22], watermelon peel [23] were also successfully used to synthesize electrochemical functional materials with excellent performance.

Banana is a most commonly eaten fruit all over the world. According to the FAOSTAT, the production of banana was more than 113 million tonnes in the year of 2016 (data from http://www.fao.org/faostat/en/#data/QC/visualize). And as a byproduct, banana peels represent 40% of the total weight of fresh banana, which are generally discarded and decayed, causing rigorous environmental pollution. Thus, it is necessary tomake full use of thiswaste biomass,develop their potential applications and convert into a high-value functional product for environmental purification. Gan and co-works synthesized the porous carbon foams through a novel strategy by reusing the banana peel as self-template strategy [24]. When used as supercapacitor electrodes, the product exhibits relative high specific capacitance

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(206 F g^{-1}) at a current density of 1 A g^{-1}, and excellent cycle stability. Besides, Mitlin and cooperators prepared a unique carbon material with low surface areas derived from banana peels [25]. The typical sample exhibits remarkable specific capacity, superior cycling stability and minimal charge-discharge hysteresis when used as sodium ion battery and lithium ion battery anodes. Nevertheless, as far as we know, employing banana peel derived carbon (BPDC) as a catalyst for ORR has not been reported up to now. More importantly, under the synergistic effect of H_3PO_4 treatment and nitrogen doping, the electrochemical catalysis of the final product toward ORR will be greatly improved by enhancing the electrical conductivity, BET surface area and active sites of BPDC.

In the present work, we synthesized a nitrogen-doped porous carbon material through a simple and economical method by the pyrolysis of H_3PO_4-treated BPDC. And related electrochemical measurements show that the typical sample possesses similar catalyze activity to Pt/C toward ORR, but superior stability and methanol tolerance compared to commercial Pt/C catalysts in alkaline and acid medium. It's a promising candidate catalyst to replace the Pt/C and accelerate the large-scale application of FCs.

2. Experimental section

2.1. Materials

Banana peel was recycled and washed with distilled water, and then cut into pieces. Phosphoric acid (H_3PO_4), methanol (CH_3OH), ethanol (C_2H_5OH), potassium hydroxide (KOH) and concentrated sulphuric acid (H_2SO_4) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, PR China). NH_3 (99.9%) was obtained from Shang Yuan Company (Nanjing, P R China). Deionized water was obtained from Millipore Milli-Q water purification system. All reagents are analytically pure and without further purification.

2.2. Synthesis of N-BPDC-H_3PO_4-1000

In a typical procedure (as shown in Scheme 1), 5 g of banana peel was placed in a 100 mL of Teflon-lined autoclave, 10 mL of H_3PO_4 and 50 mL of deionized water was added into the autoclave simultaneously, then the autoclave was sealed and kept at 180 °C for 12 h. The obtained precursor was washed with deionized water until the pH was neutral for the complete remove of H_3PO_4 before freeze-dried for 2 days. After that, the above precursor was carbonized in NH_3 atmosphere and labeled as N-BPDC-H_3PO_4-X, where X stands for the carbonized temperature (800 °C, 900 °C, and 1000 °C, respectively). Control samples were also prepared according to the method mentioned above without adding the H_3PO_4 or adding 5 mL and 15 mL of H_3PO_4 solutions, and then calcined in NH_3 atmosphere at 1000 °C, the products were marked as N-BPDC-1000, N-BPDC-H_3PO_4-1000 (5 mL) and N-BPDC-H_3PO_4-1000 (15 mL), respectively.

2.3. Characterization

The phase analysis of the as-synthesized products was performed using X-ray diffraction (XRD, DX-2700) with Cu-Kα radiation (λ = 1.54 Å). The morphologies of samples were examined byscanning electron microscope (SEM, Hitachi S-4800, Japan). Field emission transmission electron microscopy (FETEM, JEOL) images were obtained using a JEM-2100F instrument. BET surface area was carried out on a TrstarII3020 analyzer. Raman spectra were performed on a focusing Raman spectrometer (Renishaw inVia) with a 532 nm laser excitation. X-ray photoelectron spectroscopy (XPS) measurements were obtained on an X-ray photoelectron spectrometer (ESCALAB 250Xi).

2.4. Electrochemical measurements

For electrochemical measurements, the product was dispersed in the ethanol solution and sonicated to form a homogeneous ink with the concentration of 2 mg/mL. Afterwards,10 μL of the above ink was dropped onto the glass carbondisk electrode and 10 μL of Nafion solution (0.05 wt. %) was used to adherethe product. The related electrochemical measurements were carried outin a typical three-electrode cell by using a CHI 852C electrochemical workstation under a Pine electrochemical controlsystem.

For rotating disk electrode (RDE) tests, the counter electrode was platinum wire, and Hg/HgO and Ag/AgCl was used as a reference electrode in alkaline and acidic media, respectively.For rotating ring-disk electrode (RRDE) tests, a platinum wire and an Hg/HgO electrode were acted as the counter and reference electrodes, respectively. The electron transfer numbers (n) and peroxide yield (% H_2O_2) can be calculated from the RRDE curves by using the Eqs. (1) and (2), respectively [6,17].

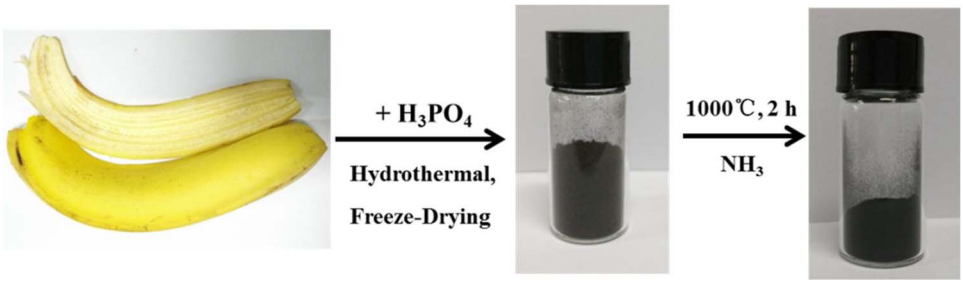
$$n = 4 \times \frac{I_d}{I_d + I_r/N} \quad (1)$$

$$\%H_2O_2 = 200 \times \frac{I_r/N}{I_d + I_r/N} \quad (2)$$

where I_r is the ring current, I_d the disk current, and N is the current collection efficiency of the Pt ring (N = 0.37).Accelerated durability test (ADT) was performed in O_2 saturated 0.1 M KOH solutionor O_2 saturated 0.5 M H_2SO_4 solution at room temperature to examine the stability of the typical sample. RDE polarization curves were recorded every 1000 cycles ranging from 1000 cycles to 5000 cycles.

3. Results and discussion

The XRD patterns of N-BPDC-1000, N-BPDC-H_3PO_4-800, N-BPDC-H_3PO_4- 900 and N-BPDC-H_3PO_4-1000 are shown in Fig. 1a. As can be seen, a broad band approximately located at 23° and 44° could be indexed as (002) and (100) planes of amorphous carbon in the products [17,26]. Fig. 1b shows the Raman spectra of these products,the carbon characteristic peak around 1342 cm^{-1} and 1596 cm^{-1} are ascribed to disordered carbon or defective graphitic structures (D band) and the



Scheme 1. Schematic illustration of the formation of N-BPDC-H_3PO_4-1000 composites.