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Nitrogen-doped porous carbon nanosheets made from biomass as highly active electrocatalyst for oxygen reduction reaction

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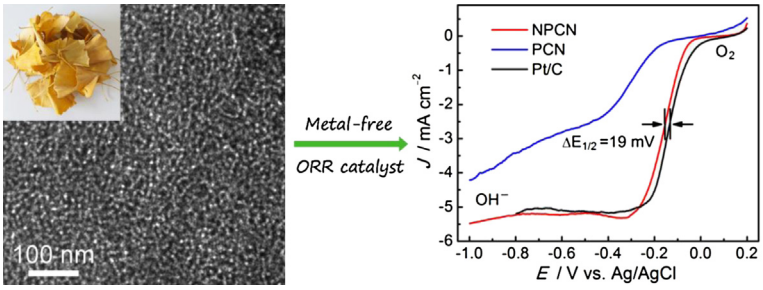
HIGHLIGHTS

- Naturally dead leaves are used to fabricate nitrogen-doped porous carbon nanosheets (NPCN).
- NPCN possesses hierarchical porous structure and a high surface area of 1436.02 $m^2 g^{-1}$.
- NPCN can serve as efficient metal-free catalyst for the oxygen reduction reaction.
- The excellent electrocatalytic performance originates from favorable structure and chemical composition.

GRAPHICAL ABSTRACT



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ABSTRACT

The successful commercialization of fuel cells requires the efficient electrocatalyst to make the oxygen reduction reaction (ORR) fast because of the sluggish nature of ORR and the high cost of the platinum catalysts. In this work, we report the excellent performance of metal-free nitrogen-doped porous carbon nanosheets (NPCN) with hierarchical porous structure and a high surface area of 1436.02 $m^2 g^{-1}$ for catalyzing ORR. The active NPCN is synthesized via facile high-temperature carbonization of natural ginkgo leaves followed by purification and ammonia post-treatment without using additional supporting templates and activation processes. In O_2-saturated 0.1 M KOH solution, the resultant NPCN exhibits a high kinetic-limiting current density of 13.57 mA cm^{-2} at −0.25 V (vs. Ag/AgCl) approaching that of the commercial Pt/C catalyst (14 mA cm^{-2}) and long-term electrochemical stability. Notably, the NPCN shows a slightly negative ORR half-wave potential in comparison with Pt/C ($\Delta E_{1/2}$ = 19 mV). The excellent electrocatalytic properties of NPCN originate from the combined effect of optimal nitrogen doping, high surface area, and porous architecture, which induce the high-density distribution of highly active and stable catalytic sites.

1. Introduction

The high O═O bond energy and slow nature of the oxygen reduction reaction (ORR) are two main obstacles to the successful commercialization of fuel cells, which can directly convert the chemical energy into electrical energy by the rapid electrochemical oxidation of fuel at the anode and sluggish electrochemical reduction of oxygen at the cathode [1,2]. Because of their high efficiency and environmental friendliness, fuel cells are considered promising energy-converting devices. Thus, the advanced electrocatalyst to accelerate the ORR kinetic process is significantly crucial for the sake of propelling the wide-spread application of fuel cells. At present, although platinum nanoparticle supported on high surface area carbon black (Pt/C) is the most commonly used

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material to catalyze ORR in current fuel cells, its large-scale application is hampered by the high cost and limited reserves, together with poor tolerance to fuel and time-dependent deactivation [3–5]. Recently, the ongoing researches are mainly focusing on certain structure/composition noble metal [6,7], non-precious metal [5,8,9], and metal-free materials [10–12] to reduce oxygen.

Nanostructured carbon materials have attracted tremendous attention in that they possess remarkable properties and exhibit promising potential in a variety of important application areas related to sensing [13], catalysis [14,15], and energy conversion/storage [16,17]. Recent reports have demonstrated that doping heteroatom (such as, B, N, S, and P) into carbon lattice to break the electroneutrality of carbon was an effective strategy to transform nanocarbon into active electrocatalyst for ORR [18–22]. The active carbon materials were found to display platinum-like ORR catalytic behavior, outstanding fuel selectivity and electrochemical stability. Commonly, the metal-containing catalysts often suffer from the time-dependent degradation of ORR activity owing to the leaching of metal particles from the electrode surface [23–25], suggesting that metal-free carbonaceous materials have great potential to meet the practical application. Till now, although numerous efforts have been made in enhancing catalytic performance, the ORR activities of metal-free carbon materials are still less than that of commercial Pt/C catalyst [26–28]. The key strategies that can enhance the catalytic capacity of carbon catalyst are to improve the turnover frequency (TOF) per active site and catalytic site density [29]. The TOF can be improved by tuning the doping atom chemical states to achieve certain bonding configuration that is intrinsically more active toward ORR. The introduction of nitrogen atoms into carbon lattice can mainly create four types of nitrogen functional groups, namely, pyridinic, pyrrolic, graphitic, and oxidized nitrogen species [16,18]. Among them, the pyridinic and graphitic nitrogen are regarded as ORR active centers. The pyridinic nitrogen with a lone electron pair can form side-on adsorption of oxygen molecule to weaken O–O bonding, and the graphitic nitrogen facilitates electron transfer from the carbon electronic bands to the antibonding orbitals of oxygen [30,31]. The active site density is largely dependent on the high surface area and porous nature, which guarantee a dense distribution of C–N catalytic centers and increase the effective interfacial area between active sites and reactant. Therefore, constructing porous carbon with large exposed surface and optimal nitrogen doping can provide a great opportunity to improve their catalytic activity. Now, the commonly used approaches to synthesize porous carbon are the hard template and chemical activation (KOH, $ZnCl_2$ activation) routes. These synthetic methods involve cost/toxic precursors, preparation of template, complicated activation and template removal processes, limiting their mass production in practical application [32–35]. For examples, SiO_2-based templates have been used to fabricate the porous carbon, which exhibited only low surface area and/or moderate ORR activities [36–38]. Therefore, developing the facile and low-cost approaches to prepare porous carbon with high surface area and excellent ORR performance is still challenging and of great importance.

In the present work, we describe a general route to the large-scale production of hierarchical nitrogen-doped porous carbon nanosheets (NPCN) via high-temperature carbonization of dead ginkgo leaves followed by washing with HCl and post-treatment with NH_3. This synthetic strategy possesses the following desirable advantages: 1) naturally sustainable ginkgo leaves, mainly consisting of organic components (cellulose, protein, and carbohydrate) and a small amount of inorganic minerals (Fig. S1, Supporting information), are used as precursors, 2) simple synthetic method without using additional templates and activation processes, 3) the resultant NPCN possesses hierarchical porous distribution, high surface area of 1436.02 $m^2\ g^{-1}$, uniform nitrogen doping, as well as the high content of pyridinic and graphitic nitrogen species. The above favorable features make NPCN a highly active ORR electrocatalyst in alkaline media, exhibiting low overpotential comparable to commercial Pt/C and high durability superior to Pt/C catalyst. The renewable raw materials, even waste, facile preparation, and superb ORR performance render NPCN a promising candidate to replace costly platinum as efficient cathodic ORR electrocatalyst in fuel cells.

2. Experimental

2.1. Synthesis of NPCN

The dead ginkgo leaves, collected from the campus of our institute, were used as the precursors (see photograph in graphical abstract). In a typical synthetic process, the ginkgo leaves were heated at 60 °C to get dried leaves, which were ground into uniform powder. Then, the powder in an alumina crucible with a cover was annealed in a tube furnace at 1100 °C for 5 h at a heating rate of 5 °C min^{-1} under Ar flow to produce carbonized sample, which was subsequently washed in 3 M HCl, distilled water, and ethanol to completely remove minerals residues and then warmed at 60 °C to obtain porous carbon nanosheets (denoted as PCN). To prepare nitrogen-doped porous carbon nanosheets, the PCN in an alumina boat was further thermally treated under flowing NH_3 (80 sccm) with a heating rate of 5 °C min^{-1} to 1000 °C. After heating for 1 h, the furnace was naturally cooled down to room temperature in NH_3. The sample was carefully taken out of the tube furnace and ground to yield final sample, named as NPCN.

2.2. Physical characterizations

The morphology and microstructure of the samples were investigated by transmission electron microscopy (TEM, TECNAI G2 TF20), high resolution TEM (HRTEM, TECNAI G2 TF20), STEM (TECNAI G2 TF20), and X-ray diffraction (XRD, X' PERT PRO). Thermogravimetric analysis (TGA) was conducted using a DSC200F3 analyzer under constant nitrogen flow with a heating rate of 10 K min^{-1}. Nitrogen absorption/desorption isotherms were measured on ASAP 2020 at 77 K, and the pore size distribution was calculated using density functional theory method. Raman spectrum was collected on a Raman spectrometer (LabRam HR800) with 532-nm laser. X-ray photoelectron spectroscopy analysis was carried out on ESCALAB 250Xi to obtain surface compositions.

2.3. Electrochemical measurements

All electrochemical tests were conducted on an Autolab electrochemical workstation (μ Autolab III) in a typical three-electrode cell at room temperature. A platinum wire and a saturated Ag/AgCl electrode were used as counter and reference electrode, respectively. A glassy carbon electrode (GCE, 3 mm in diameter) coated with the catalyst served as working electrode. In brief, the catalyst ink was prepared by ultrasonically blending (>3 h) 5 mg NPCN or PCN in a solution consisting of 0.4 mL of H_2O, 0.1 mL of ethanol, and 20 μL of 5% Nafion to get a uniform ink. The 5 μL of well-dispersed ink was carefully dropped on the prepolished GCE surface with a mass loading of 0.71 mg cm^{-2}, which was dried naturally for more than 10 h for subsequent electrochemical tests. To evaluate the ORR activity, cyclic voltammetry (CV) technique was carried out from 0.2 to −1.0 V with a scan rate of 50 mV s^{-1} in 0.1 M KOH solution saturated with O_2 or Ar gas. Rotating disk electrode (RDE) measurement was performed to obtain the LSV curves with a scan rate of 5 mV s^{-1} at different rotating speeds from 400 to 2400 rpm in