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# High-activity oxygen reduction catalyst based on low-cost bagasse, nitrogen and large specific surface area

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ABSTRACT

Developing low-cost oxygen reduction catalysts to replace expensive Pt-based materials and simultaneously cleaning our environment are still a considerable challenge. In this work, we display a green and turning waste into wealth route to prepare the typical material of nitrogen-doped nanoporous carbon sheets (N-NCS-1000) with a high BET surface area of 1284 $m^2$ $g^{-1}$ via thermal annealing discarded bagasse under flowing $NH_3$ atmosphere. Further tests indicate that N-NCS-1000 shows not only superior catalytic activity for oxygen reduction reaction (ORR) in alkaline media, but also decent catalytic ability in acidic media. Furthermore, it also exhibits excellent stability and methanol tolerance, suggesting a promising metal-free catalyst for ORR. We expect that this facile sustainable and cost-effective synthetic method would provide a worthy inspiration for making use of other discarded wastes to synthesize various functional materials.



## 1. Introduction

The oxygen reduction reaction (ORR) plays a considerable role in fuel cells, and has attracted the widespread attention of many researchers in recent years [1]. Because of its sluggish kinetics, efficient ORR catalysts are needed in order to enhance the reaction rate [2,3]. Currently, precious Pt-based materials are considered for most effective ORR catalysts [4–7]. Unfortunately, low abundance and high cost of Pt are a serious impediments for commercial application. Developing cheap, resource-rich and high-performance ORR catalysts with abundant elements in the earth is of great significance, which will accelerate the commercial application of fuel cells [8,9].

Common element of carbon is based on the existence of various forms in the earth, such as various carbon-containing minerals, vegetation, and so on. However, raw carbon materials have poor catalytic activity towards ORR, which is not suitable for using as ORR catalysts. Numerous studies showed that the effective way of heteroatom doping, especially nitrogen doping, can effective enhance the catalytic activity for ORR [10,11]. Further studies showed that the nitrogen-doped carbon materials not only display excellent catalytic activity for ORR, but also good stability and methanol tolerance [12,13]. Remarkable catalytic activity towards ORR of nitrogen-doped carbon materials is attributed to the following reasons. Some reports indicated that nitrogen doping can create positively charged sites on adjacent carbon atoms, which are conducive for oxygen adsorption and reduction [14,15]. In particular, studies have shown that nitrogen-doped carbon materials with high ORR activity may be attributed to the graphitic N species [16]. In addition, the large specific surface area is also key parameter for improving ORR activity, which can provide more active sites [17]. Developing nitrogen-doped carbon materials with high specific surface area is highly desirable for improving the catalytic activity [18]. Recently, 3D nitrogen-doped graphene [19], heteroatom (N or S)-doped graphene [20], nitrogen-doped carbon nanofibers [21] have been reported as excellent metal-free catalysts. However, researchers have been continuously explored better preparation approaches. Such as, Chen et al. reported that nitrogen-doped nanoporous carbon nanosheets as a superior oxygen reduction catalyst derived from *Typha orientalis* [18]. Looking for more cheap carbon source, more simple synthetic method and simultaneously cleaning our environment for expandable production of nitrogen-doped carbon materials as high-activity oxygen reduction catalysts have great potential to meet the practical application of fuel cells.

Bagasse as environmental waste is low-cost and renewable biomass resource, and mainly from the daily life and sugar industry.

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China is one of countries with the most abundant sugarcane resources in the world, but most of bagasse has not been effectively re-used and became rubbish. The abundant bagasse resource of our country has great potential for low-cost and large-scale production of the metal-free catalyst for ORR.

Herein, we successfully developed a smart strategy and easy route to prepare nitrogen-doped nanoporous carbon sheets via high-temperature carbonization discarded bagasse in an $NH_3$ atmosphere. More interesting, the typical material has excellent catalytic activity for ORR in both alkaline and acidic media, and presents superior stability and methanol tolerance. This work displays a good example for turning waste into valuable products, and is very meaningful in low-cost development of new materials and environmental cleaning.

## 2. Experimental section

### 2.1. Materials

The discarded bagasse was collected from our daily life and used as carbon source (see photograph in Scheme 1a). As we all know, sugarcane is an herbaceous plant, and is widely cultivated in Brazil, India, China, and so on. Generally, sugarcane is a raw material for making sugar, which will produce a lot of bagasse as environmental waste. Therefore, the bagasse is low-cost, sustainable and resource-rich. For turning waste into valuable products, we chose the discarded bagasse as starting material for the preparation of oxygen reduction catalysts.

### 2.2. Material syntheses

Scheme 1 illustrates the preparation process of N-NCS-1000. In order to make better use of low-cost environmental wastes to prepare an efficient oxygen reduction catalyst, we chose the discarded bagasse as starting material. Briefly, the bagasse (Scheme 1a) was cut into pieces, immersed into boiling water and washed for several times to remove the soluble sugar and impurities. Then, the dried bagasse was obtained by freeze drying for 3 days (Scheme 1b). Finally, the dried bagasse was carbonized at 1000 °C for 2 h in a tube furnace under flowing $NH_3$ atmosphere. This typical product is marked as N-NCS-1000 (Scheme 1c). In sample preparation process, the main equipment was shown in Fig. S1a (see Supplementary Material), which is the high temperature furnace. Easy to see, this method adopts inexpensive bagasse as precursor, simple equipment and one-step fabrication, and can offer the potential expandable production.

For comparison, N-NCS-800 and N-NCS-900 were prepared at 800 °C and 900 °C in an $NH_3$ atmosphere for 2 h, and NCS-1000 was obtained at 1000 °C in an Ar atmosphere for 2 h, respectively, when other conditions were unchanged.

### 2.3. Characterization

Scanning electron microscopy (SEM) and Transmission electronic microscopy (TEM) images were characterized by field emission scanning electron microscope (FE-SEM, Hitachi S-4800, Japan) and JEM-2100 instrument. The BET surface area was obtained on a Micrometrics ASAP2020 analyzer. Raman spectrum was performed on an inVia-Reflex Spectrometer (Renishaw) with a 532 nm laser excitation. X-ray photoelectron spectroscopic (XPS) measurements were carried out on an X-ray photoelectron spectrometer (ESCALAB 250Xi, Thermo, USA).

### 2.4. Electrochemical measurements

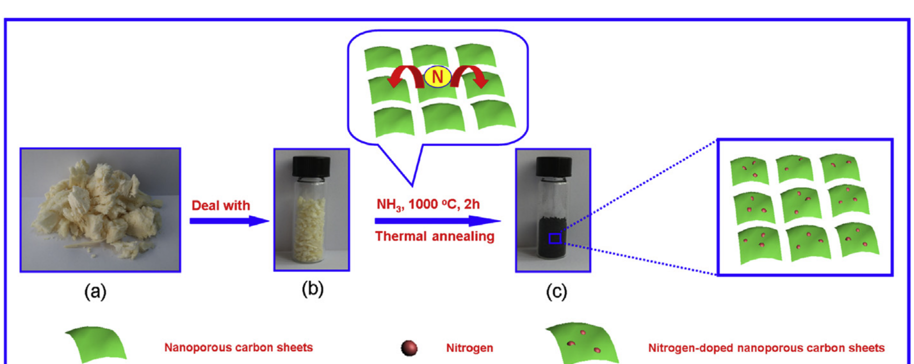
The electrochemical tests were conducted on a CHI 852C electrochemical workstation in a three-electrode cell at room temperature. In alkaline media, a Pt wire and Hg/HgO were used as counter electrode and reference electrode, respectively. The rotating disk electrode (RDE, 5 mm in diameter) and rotating ring-disk electrode (RRDE, 5.61 mm in diameter) served as the working electrode. 8.0 mg of the catalyst (or other catalysts) was dispersed in ethanol (4.0 mL) by ultrasonic dispersion. Then, 10 μL of the prepared ink was dropped onto the glassy carbon (GC) disk electrode, and 15 μL of Nafion solution (0.05 wt %) was adhered on the electrode and dried thoroughly at room temperature. The RDE and RRDE measurements were conducted in $O_2$-saturated 0.1 M KOH at room temperature.

In acidic media, the ORR measurements were performed in $O_2$-saturated 0.5 M $H_2SO_4$ at room temperature. A Pt wire and Ag/AgCl were used as counter electrode and reference electrode, respectively. In electrochemical measurements process, the main instrument was shown in Fig. S1b (see Supplementary Material), which is the ORR tests equipment system.

## 3. Results and discussion

### 3.1. Characterization of catalysts

Fig. 1a, b show the SEM images of N-NCS-1000. It is clearly observed that the typical product is composed of some carbon sheets and a two-dimensional sheet structure. The morphology of the section carbon sheets presents a curved shape, which is quite significant to prevent carbon sheets from stacking, resulting in better exposure of the active sites of the catalyst. TEM images further confirm the morphology of the carbon sheets. From Fig. 1c,




**Scheme 1.** Preparation process of N-NCS-1000.