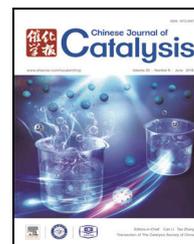


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## Article

# Simple synthesis of nitrogen-doped carbon spheres as a highly efficient metal-free electrocatalyst for the oxygen reduction reaction

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## ABSTRACT

In the present work, nitrogen-doped carbon spheres were synthesized through a simple hydrothermal treatment using glucose and melamine as inexpensive carbon and nitrogen sources, respectively. The ratio of melamine to glucose and annealing temperature were optimized. The final optimal sample exhibited a catalytic activity for the oxygen reduction reaction (ORR) that was superior than that of commercial 20%Pt/C in 0.1 mol/L KOH. It revealed an onset potential of  $-22.6$  mV and a half-wave potential of  $-133.6$  mV (vs. Ag/AgCl), which are 7.2 and 5.9 mV more positive than those of the 20%Pt/C catalyst, respectively, as well as a limiting current density of  $4.6$  mA/cm<sup>2</sup>, which is  $0.2$  mA/cm<sup>2</sup> higher than that of the 20%Pt/C catalyst. The catalyst also exhibited higher stability and superior durability against methanol than 20%Pt/C. Moreover, ORRs on this catalyst proceed through a more effective  $4e^-$  path. The above mentioned superiority of the as-prepared catalyst makes it promising for fuel cells.

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## 1. Introduction

As efficient clean energy suppliers, fuel cells have attracted increasing interest in recent years [1–4]. However, the large-scale application of fuel cells has been limited by the slow ORRs at the cathode, where highly efficient catalysts are demanded [5]. Pt catalysts have been considered among the best ORR catalysts; however, they suffer from some drawbacks such as sensitivity to current drift, CO deactivation, instability towards methanol, high cost, and limited supply of Pt [6,7].

To overcome the limitations of Pt-based catalysts, much effort has been made to identify alternatives to replace them.

Besides the development of nonprecious metal-based or precious metal alloy-based catalysts, efforts have been gradually focused on metal-free electrocatalysts [8,9], in particular, catalysts composed of heteroatom-doped carbon materials [10–12]. Carbon spheres have shown impressive surface permeability and high mechanical stability; hence, they have been extensively used in many areas such as catalysis, adsorption, drug delivery, and energy storage [13,14]. Lately, carbon spheres have been used as ORR catalysts [15,16]. However, their rather chemically inert surface and small surface area-to-volume ratio have limited their application in ORRs [16]. Diversified strategies have been adopted to modify the physical

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and/or chemical properties of the carbon spheres. Among them, doping the lattice structure of carbon with heteroatoms has turned to be the most effective method to take full advantage of the carbon sphere properties [17–20]. Doping of heteroatoms not only enhances surface adsorption ability but also increases catalytic activity and stability through the modification of the electron density distribution of carbon atoms [21]. In general, doping of nitrogen is mainly performed through three methods, including the post-processing method [22,23], hard template method [24,25], and soft template method [26,27]. Most of the reported methods are complicated and multistep and, consequently, have low production efficiency. Therefore, much simpler methods are desirable for the preparation of highly effective N-doped carbon spheres using cheap and abundant raw materials.

The present work uses glucose as the carbon source and melamine as the nitrogen source to develop a nitrogen-doped carbon sphere catalyst (NCS). The ORR tests indicate that the as-prepared catalyst possesses great catalytic activity, stability, and long-term durability against methanol-induced toxicity.

## 2. Experimental

### 2.1. Chemicals

Pt/C (20 wt% Pt on carbon black) and Nafion (5 wt%) were brought from Alfa Aesar. Mesoporous silica (average particle size 200 nm, specific surface area 300 m<sup>2</sup>/g, pore volume 0.5 cm<sup>3</sup>/g) was purchased from Sigma-Aldrich. All other chemicals and reagents are of analytical grade and were used as-received.

### 2.2. Preparation of the catalysts

Certain amount of glucose and melamine was dissolved in a 1.5% H<sub>2</sub>SO<sub>4</sub> solution (10 mL). After adding 2.0 g of mesoporous SiO<sub>2</sub>, the mixture was stirred for 15 min, followed by 30 min sonication. After being stirred for 3 h, the mixture was hydrothermally treated at 100 °C for 6 h and at 160 °C for another 6 h. The solid product was centrifuged, thoroughly washed by distilled water and ethanol, and then dried in vacuum at 100 °C. The dried sample was calcinated in a N<sub>2</sub> atmosphere for 3 h at 800 °C. After the heat treatment, the product was treated with HF solution to remove SiO<sub>2</sub>. The residual solid was collected upon centrifuging, thoroughly washed using distilled water and ethanol, and then dried in vacuum at 60 °C overnight. The finally obtained carbon sphere was labeled as N<sub>m</sub>C<sub>n</sub>S-T, where “S” denotes “sphere,” the units of “m” and “n” are grams, representing the amount of melamine and glucose used, and “T” refers to the annealing temperature (°C). Three N-doped samples were prepared and designated as N<sub>0.1</sub>C<sub>1.9</sub>S-800, N<sub>0.1</sub>C<sub>1.9</sub>S-900, and N<sub>0.2</sub>C<sub>1.8</sub>S-900. For comparison purposes, a sample without nitrogen was also prepared and denoted as C<sub>2.0</sub>S-900.

### 2.3. Characterization of the catalysts

The power X-ray diffraction (XRD) patterns of the samples were collected on a Shimadzu XRD-6000 diffractometer with

Cu K $\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ) operating at the voltage of 40 kV and current 200 mA. Scanning electron microscopy (SEM) images were obtained using a field-emission scanning electron microscope (JSM-6701F, FEOL) with the accelerating voltage of 5 kV. Transmission electron microscopy (TEM) images were taken on a JEM-2010 microscope operated at the accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) was performed using a Thermo Fisher Scientific's K-Alpha X-ray photoelectron spectrometer. Raman spectra of the samples were obtained on a Jobin-Yvon U1000 scanning double monochromator at a wavelength of 532 nm. The nitrogen adsorption-desorption characterization of the samples was performed on an ASAP 2020 Micromeritics instrument at -196 °C.

### 2.4. Electrochemical tests of the catalysts

For electrochemical testing, a CHI electrochemical workstation equipped with the software Versa Studio was used. A three-electrode cell assembly including a 3-mm glass carbon electrode or rotating disk electrode (RDE) as the working electrode, Ag/AgCl (in 3 mol/L KCl) as the reference electrode, and a graphite rod as the counter electrode was used for the linear sweep voltammetry (LSV) tests. Three milligrams of the catalyst were dispersed in 0.5 mL of ethanol containing 10  $\mu$ L of a Nafion solution (5 wt%), and the mixture was sonicated for more than 30 min. Afterwards, 3  $\mu$ L of the above solution were dropped onto the surface of a well-polished working electrode, and the electrode was dried at room temperature. The LSV tests were conducted in the potential range 0.2 to -0.8 V versus Ag/AgCl electrode at a scan rate of 10 mV/s in an oxygen-saturated 0.1 mol/L KOH at room temperature. The number of transferred electrons ( $n$ ) and kinetic current density ( $J_k$ ) were calculated according to the well-known Koutecky-Levich equation:

$$1/J = 1/J_L + 1/J_K = 1/(B\omega^{1/2}) + 1/J_k$$

$$B = 0.2nFA\nu^{-1/6}c(O_2)D(O_2)$$

where  $n$  indicates the number of transferred electrons;  $F$ , Faraday constant (96485 C/mol);  $c(O_2)$ , the bulk concentration of O<sub>2</sub> (1.2 $\times$ 10<sup>-6</sup> mol/cm<sup>3</sup>); and  $\nu$ , the kinematic viscosity of the electrolyte (0.01 cm<sup>2</sup>/s).

## 3. Results and discussion

### 3.1. Characterization of the catalysts

The XRD patterns of the as-prepared catalysts are shown in Fig. 1. The broad diffraction peak at  $2\theta \approx 22.5^\circ$  and  $44.5^\circ$  can be attributed to the (002) and (101) planes of graphitic carbon, respectively [28]. No other phases were detected in the samples.

Fig. 2 shows the Raman spectra of the samples. As can be seen, all the samples display two Raman scattering bands, a D band at 1350 cm<sup>-1</sup> and a G band at 1600 cm<sup>-1</sup>, of which the D band represents the degree of disorder and the defects of the graphite structure, and the G band reflects the degree of graphitization. Therefore, the relative intensity ratio between the D and G bands ( $I_D/I_G$ ) is a good measure of the degree of defects

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