



A resin-based methodology to synthesize N-doped graphene-like metal-free catalyst for oxygen reduction



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ABSTRACT

An ion-exchange resin-based methodology has been used to synthesize the N-doped graphene-like metal-free catalyst (NGMFC). This catalyst is hierarchical porous structured with high surface area. In acidic media, the NGMFC shows a high electrocatalytic performance and good stability towards oxygen reduction reaction (ORR) in rotating ring-disk electrode measurements. The onset potential of the catalyst for ORR is 0.99 V which is very close the onset potential of Pt/C catalyst. This research demonstrates that the ion-exchange resin-based methodology can be a potential alternative to produce efficient metal-free catalyst at extremely low cost for ORR.

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1. Introduction

Fuel cell is one of the key clean sustainable technologies which can replace the fossil energy in the near future. [1] The dependence on expensive Pt-based electrocatalysts in fuel cells remains a major obstacle for a widespread deployment of this technology. [2] In recent decades, the replacement of Pt by non-precious metals or non-metals has been a hot issue in electrocatalysis. [3–6] In alkaline medium, alternative catalysts much cheaper than Pt are available [7]. However, it becomes extremely tough in acidic media. For example, the Fe-N-C catalysts showed 1/3 volumetric activity for oxygen reduction reaction (ORR) compared with commercial Pt/C catalyst [8]. Even so, the Fe (Co)-N-C catalysts are regarded as the best alternative non-precious metal catalysts (NPMCs) at the moment. To synthesize Fe(Co)-N-C catalysts, different nitrogen-containing precursors like cyanamide [7], melamine [9], tripyridyltriazine [10] and many others have been investigated.

We have reported a three dimensional hierarchical porous material which combines an ultrahigh specific surface area and interconnected micro-, meso-, and sub-micrometer pores for fast and highly stable supercapacitors [11]. In this article, we report the synthesis of the N-doped large surface area material with porous structure by using nitrogen enriched D113 ion-exchange resin. The

final material has been applied for ORR as an N-doped graphene-like metal-free catalyst (NGMFC).

2. Experimental

2.1. Catalyst synthesis

In a typical experiment, pre-treated D113 resin (30 g, Shanghai Hualing Resin Co., Ltd, China) and nickel acetate (3 mM) dispersed in 400 ml deionized water. The solution was stirred for 6 h and then dried at 80 °C. The ion-exchanged resin (30 g) was added into a 1.2 L KOH/ethanol solution containing 30 g KOH and stirred at 80 °C until the mixture solution became an ‘ink-paste’, followed by 6 h of static soaking in ambient conditions. The mixture was heated at 850 °C for 2 h with a heating rate of 2 °C min⁻¹ in N₂ atmosphere. After cooling down to room temperature, the sample was added into 1 M H₂SO₄ (2 L) at 80 °C in oil bath for 12 h with magnetic stirring. Afterwards, the sample was washed and dried at 70 °C in ambient for 12 h. The mixture was then heated again at 850 °C for 2 h with a heating rate of 10 °C min⁻¹ in ammonia atmosphere.

2.2. Physical characterization of the materials

The crystalline structure of the sample was studied by X-ray diffraction (XRD) on a D/Max-III (Rigaku Co., Japan) using Cu-K α radiation ($\lambda = 0.15406$ nm) and operating at 40 kV and 30 mA. The graphitization degree of the sample was determined by

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Laser Micro-Raman Spectrometer (Renishaw in Via, Renishaw plc). The field-emission-scanning-electron-microscope (FESEM) images were collected on a JEOL JSM-6330F. The transmission electronic microscopy (TEM) investigations were carried out on a JEOL JEM-2010 at 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were conducted with two separate systems equipped with monochromatic Al K sources (ESCALab250, USA). The N₂ adsorption experiments were conducted by using an ASAP 2020 Surface Area Analyzer (Micromeritics Co., USA) to investigate the porosity of the samples. All the samples were nitrogen flowed for 4 h at 200 °C prior to the measurement. Nitrogen adsorption data were recorded at the liquid nitrogen temperature (77 K). The specific surface area of the samples was calculated according to the Brunauer-Emmett-Teller (BET) equation from the adsorption data in the relative pressure from 0.014 to 0.2. The pore volumes were estimated to be the liquid volume of adsorption (N₂) data relative pressure of 0.99. The pore size distribution was determined by the density functional theory (DFT) method. Thermo stability is conducted on a thermogravimetry (Netzsch).

2.3. RRDE measurements

Rotating ring-disk electrode (RRDE) measurements were conducted on a bipotentiostat (Pine instrument Company, USA) in the thermostat-controlled standard three-electrode cell at 25 °C with a reversible hydrogen electrode (RHE) as the reference electrode, a graphite rod as the counter electrode and a RRDE as the working electrode, respectively. The geometric area of the electrode was 0.2475 cm². In RRDE experiments, the ring potential was set to 1.2 V vs. RHE. The film electrocatalyst working electrode was prepared by mixing 10 mg electrocatalysts, 1 ml Nafion® solution (0.25 wt %, DuPont, USA) under ultrasonication for 30 min. The electrocatalyst ink was then quantitatively transferred onto the surface of the working electrode using a micropipette, and dried to obtain the electrocatalyst thin layer.

3. Results and discussions

The crystal structure of the NGMFC was investigated by XRD (Fig. 1a). The 2θ angular regions between 10° and 90° were operated at a scan rate of 10 ° min⁻¹. The characteristic peak of (002) demonstrated a high degree of graphitization. Raman spectroscopy is used to study the ordered/disordered crystal structures of carbonaceous materials. [12] The intensity of the D band of the Raman spectra is strongly associated with the disorder degree of carbon atoms, while the G band corresponds to the first-order scattering of the stretching vibration mode E_{2g} observed for sp² carbon domains. Generally, the intensity ratio of D band to G band (I_D/I_G) is used to estimate the disorder of carbon. [13,14] As shown in Fig. 1a, I_D/I_G ratio is 1.22. It is similar to the previously reported doped graphite materials. [9,15] Thermogravimetry (TG) and differential thermogravimetry (DTG) curves (Fig. 1b) of the NGMFC show a relatively high thermal stability of 630.6 °C, which is much higher than the graphene (502 °C) and N-doped graphene (531 °C) [15]. This may be due to both the resin-based methodology and reduction during the doping process.

The structure and surface morphology of the N-doped graphene-like materials were characterized by SEM and TEM. The thin flexible structure with disordered surface morphology can be observed in Fig. 2a. The N-doped graphene sheets are randomly distributed and overlapped to form a flexible interconnected conducting network with a porous structure. In an electrochemical condition, the pores can store electrolyte initially, providing a quick supply and short diffusion distance. It can be clearly observed the graphene-like structure by high-resolution TEM in Fig. 2b. The graphite shows

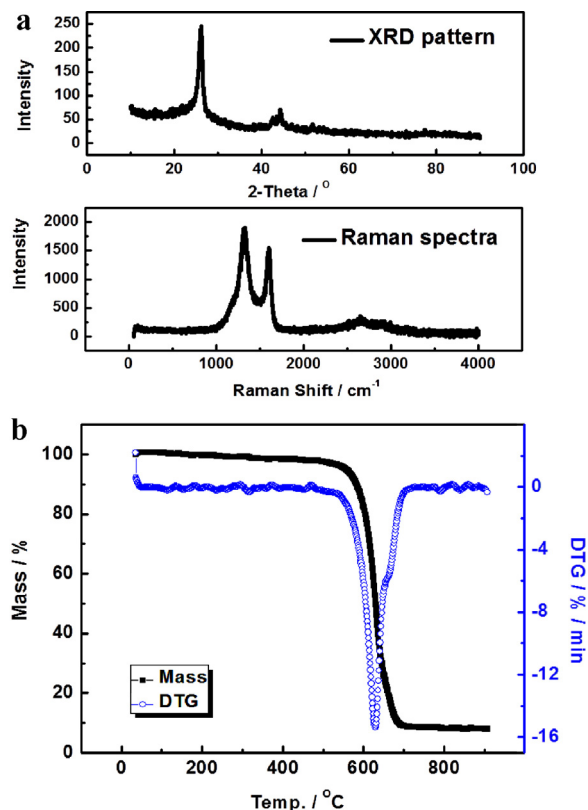


Fig. 1. (a) XRD pattern of the graphite structure and the Raman spectrum and (b) thermogravimetry (TG) and the differential thermogravimetry (DTG) curves of the NGMFC.

a high degree of curvature due to the activation by KOH as reported before. [16]

The pore-size characterization of the NGMFC was further investigated by measuring the nitrogen adsorption/desorption isotherms. The nitrogen adsorption/desorption curve (Fig. 3a) exhibits a combined characteristics of type II and type IV isotherms. The Brunauer-Emmett-Teller (BET) specific surface area is 1443.5 m² g⁻¹, micropore area 847.6 m² g⁻¹, mesopore area 476.3 m² g⁻¹, total pore volume 1.17 cm³ g⁻¹, micropore volume 0.42 m³ g⁻¹, mesopore (2–5 nm) volume 0.66 cm³ g⁻¹, micropore-to-total-pore-volume ratio 0.36 and mesopore-to-total-pore-volume ratio 0.56. The corresponding density functional theory (DFT) pore size distribution (Fig. 3a, inset) shows a predominant peak in the micro-scale of blew 2 nm with an average pore diameter of 1.18 nm and exhibits a hierarchical pore structure that includes micro-, meso- (2–5 nm), and macropores (> 50 nm).

The three types of N species including pyridinic N, graphitic N and pyrrolic N were formed predominately through substituting a carbon atom by N on edges or defect sites in the plane so such carbon atoms are much more chemically active than those within the plane [17,18]. The graphitic N refers to the N atoms replacing the C atoms inside of the graphite layers. The pyridinic N that contributes to the π system with one p electron corresponds to a tetrahedral nitrogen phase bonded to a sp³-hybridized carbon atom (N sp³ C). [19] The pyrrolic N atoms with two p electrons in the π system corresponds to a trigonal nitrogen phase bonded to a sp²-coordinated carbon atom (N sp² C). [19] To determine the content and types of N species in the catalyst, we performed XPS measurements. It revealed that the high-resolution N 1s spectrum (Fig. 3b) of the N-doped graphite is fitted to three main peaks of graphitic N (≈ 399.0 eV), pyridinic N (≈ 400.3 eV) and pyrrolic N (401 ~ 403 eV)

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