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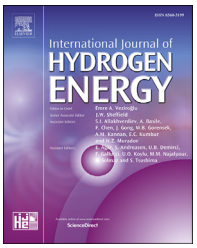

Highly microporous nitrogen doped graphene-like carbon material as an efficient fuel cell catalyst

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ABSTRACT

Nitrogen-doped carbon materials are known to be promising candidates as oxygen reduction reaction electrocatalysts used in fuel cells. However, developing metal-free catalysts with high performance and stability still remains a big challenge. Herein we report a new route by using the Maillard reaction, to caramelize ribose in a dispersing salt matrix, followed by carbonization of this caramel to synthesize metal-free catalysts. This catalytic material has the morphology of microporous nitrogen doped graphene-like carbon, and a highest surface area of 1261 $m^2 g^{-1}$ with a large amount of micropores. Such microporous structure offers numerous defects that generate a large number of reactive sites. As a result, when used as the cathode materials in fuel cells, the fuel cell shows a high power density of 547 mW cm^{-2} under 1.0 atm back pressure with good stability with only 12.5% loss after 250 h. Such catalyst has good performance in the class of metal-free oxygen reduction reaction catalysts, and is possible for commercial use.

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Introduction

Developing renewable energy resources with reduced carbon emission is one of the most urgent challenges to the sustainable development of human civilization [1–4]. Featured as zero emission with high energy efficiency, fuel cell is attracting growing scientific attention [5–7]. Electrocatalysts for oxygen reduction reaction (ORR) play a crucial role in many energy conversion systems, such as metal-oxygen batteries [8], photoelectrochemical cells [9], and especially proton exchange membrane fuel cells (PEMFCs) [10]. PEMFCs are treated as one of the major alternative power suppliers to replace fossil fuel use [11–14]. However, ORR-related energy devices are presently highly impeded by the Pt catalysts with high cost and scarcity [15,16]. The integration of graphene-based electrocatalysts in energy conversion systems offers

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opportunities to tackle the challenge driven by the contradiction of the increasing global energy demand and the applications of noble metal-based catalysts [17,18]. Graphene's two-dimensional nature gives it a high surface area, flexibility, and specific electronic properties, also making it a promising candidate for photovoltaic modules, batteries, supercapacitors and specifically for the ORR [19].

So far, there are mainly three methods to fabricate graphene, including chemical vapor deposition (CVD) [20], physical exfoliation [21], and chemical exfoliation [22]. These methods are relatively effective to fabricate graphene, though the widespread use of these methods has been hindered by their problematic issues, such as high requirements regarding fabrication conditions, low productivity, and/or environmental unfriendliness. Recently a modified Hummer's method [23] to fabricate reduced graphene oxide from graphite oxide has attracted most research attention [24]. This method considerably increases the productivity, and can be effectively used for various doping and modifications of graphene [25]. However, the purity and layer number of graphene produced via Hummer's method are greatly dependent on the pre-oxidation treatments. Graphene made via Hummer's method is generally stacked up with little single-layer graphene produced [26].

Fabricating graphene-based materials by means of polymerization and pyrolysis of organic molecular precursors offers great opportunities to synthesize high-quality graphene-like carbon material [27–29]. On account of the native ring structures that facilitate the production of sp^2 hybridized carbon materials, sugars, e.g. ribose, it is treated as an excellent candidate as the precursor [30–32]. Herein we take advantage of a typical reaction generally used in the food industry, the Maillard reaction between amino and carbonyl groups, to prepare caramels as the pre-reaction, and disperse these caramels into molten salt (MS) matrices to obtain graphene-like carbon material via the pyrolysis proces [33,34]. The nitrogen doped graphene-like carbon material prepared by this method is facile to produce, cost-effective, and uniform in thickness, which has potential for industrialization [35–37]. The produced nitrogen doped graphene-like carbon material has a highly microporous structure, leading to excellent ORR catalytic performance and stability, and can be used in fuel cells as a potential cathodic catalyst [9,38–40].

Experimental

Synthesis of catalysts

Ribose and ammonia chloride (NH_4Cl) were purchased from Aladdin Industrial Corporation (America) in China. Potassium chloride (KCl) and sodium chloride (NaCl) were purchased from Shanghai Chemical Reagent Co. (China). All the above chemicals were analytical grade and used as received. Pt/C (20 wt%) was purchased from Johnson Matthey Corporation.

In a typical synthesis process, 0.4 g of ribose and 0.2138 g of NH_4Cl as the carbon and nitrogen source, respectively, were evenly mixed with a certain amount of the eutectic mixture of 11.5 g of NaCl/13.5 g of KCl (weight ratio = 23/27), in which the eutectic salt was used as the dispersing agent to dilute the mixture of ribose and NH_4Cl [41]. The mixtures were thoroughly ground in a mortar and heated at 150 °C for 12 h in an autoclave. Then the pre-reacted brown mixture was transferred to a porcelain crucible and pyrolyzed at 1050 °C under N_2 for 1 h. After natural cooling to ambient temperature, the blacked products were thoroughly ultrasonically rinsed with distilled water and ethanol around 20 times. Acid leaching was then carried out ultrasonically in 0.5 M H_2SO_4 at 80 °C for 12 h to remove remnant salts and then rinsed with distilled water and ethanol 20 times again. The resulting sample collected by filtration was dried in a vacuum at 60 °C for 24 h, then pyrolyzed at various temperatures under NH_3 for 0.5 h to obtain the nitrogen doped graphene-like catalyst. Based on the weight ratio of dispersing salts and precursors, the as-synthesized samples were named MNG_50, MNG_25, MNG_10, and MNG_0, respectively.

Samples of MNG_50 synthesized at the nitridation temperatures of 950, 850 and 750 °C were respectively named MNG_50950 °C, MNG_50850 °C, and MNG_50 750 °C; MNG_50950 °C was shortened to MNG_50 for 950 °C as the commonly used nitridation temperature.

Characterizations

The samples were measured by field emission scanning electron microscopy (FE-SEM) (FEI NOVA NanoSEM230, USA) and transmission electron microscopy (TEM) (JEOL 3010, Japan). The structure was characterized by a powder X-ray diffractometer (XRD, Ultima III, Rigaku Corp., Japan) using Cu-Kα radiation (λ = 1.54178 Å, 40 kV, 40 mA). The surface composition was characterized by using X-ray photoelectron spectroscopy (XPS, ESCALAB 250). The specific surface area was collected through the Brumauer-Emmett-Teller (BET) method by N_2 adsorption (TriStar-3000, Micromeritics, USA) and O_2 adsorption (ASAP2020-M + C, Micromeritics, USA). Raman spectra were collected by a Jobin Yvon HR800 Raman scattering system with an excitation wavelength of 520 nm. The concentration of copper ions and ferric ions was detected by inductively coupled plasma (ICP, Optima 5300DV, USA).

Electrochemical measurements

The measurement of ORR performance and H_2O_2 production was conducted by using the rotating disk electrode (RDE) and rotating ring-disk electrode (RRDE) techniques in 0.1 M $HClO_4$ aqueous solution. All measurements were conducted under a mode of temperature control with a conventional three-electrode cell at room temperature. A reversible hydrogen electrode (RHE) [42], platinum plate and RRDE were used as the reference electrode, the counter electrode and the working electrode, respectively. The suspension was prepared ultrasonically for 1 h with a mix of 10 mg of catalyst with 95 μL of 5 wt% Nafion solution (Aldrich) and 350 μL of ethanol. And then 4.5 μL of the catalyst ink was dropped onto the RRDE (Diameter = 4 mm) for a catalyst loading of 717 μg cm^{-2}. For 20% Pt/C catalyst, 5 mg of Pt/C catalyst, 50 μL of 5 wt% Nafion solution and 1 mL of isopropanol were mixed to prepare the catalyst ink, and 6.3 μL of such ink was dropped onto the RRDE for a Pt loading of 50 μg cm^{-2}. Cyclic voltammetry test was

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