Highly effective oxygen reduction reaction electrocatalysis: Nitrogen-doped hierarchically mesoporous carbon derived from interpenetrated nonporous metal-organic frameworks

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ABSTRACT

Nitrogen-doped carbon materials with hierarchically mesoporous structure are synthesized in the present work *via* the pyrolysis of an interpenetrated non-porous metal-organic framework (MOF), *viz.* $[Zn_2(TPT)(BDC)_2] \cdot H_2O$ (SCUT-11, TPT = tris(4-pyridyl)triazine, BDC = 1,4-benzenedicarboxylate), as the precursor. X-ray diffraction reveals that the synthesized metal-organic framework (MOF) is of high purity of the crystalline phase, and its structure follows our previously reported SCUT-11. This triply-interpenetrated MOF features high density of Zn cations in their interwoven packing structure, which act as effective pore-forming agent to generate mesopores in final carbon. Physicochemical characterizations reveal that the resultant carbon has high specific surface area and bimodal mesopore size distribution, which originate from the removal of metal oxide and/or metal zinc. These textual features favour both oxygen mass transfer and accessibility of catalytically active sites. Electrochemical results confirm that the resultant carbon, synthesized by pyrolysis at 900 °C, shows a superior oxygen reduction reaction (ORR) activity, which is associated with high onset and half-wave potential up to 1.0 and 0.88 V, respectively. Further investigation suggests that the as-synthesized carbon catalyst exhibits a remarkable insensitivity towards anions, like sulphate and phosphate, compared with the Pt counterpart. The above features make this carbon catalyst promising to be widely used in different fuel cell types.

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1. Introduction

In the past few decades, metal-organic frameworks (MOFs), also known as coordination polymers (CPs), assembled by metal centres and organic linkers that extend "infinitely" in at least one dimension, are a new class of functional materials in the field of catalysis, chemical separation, sensors, gas storage, nonlinear optics, etc. [1–8]. The advantages of MOFs derive from their defined and ordered connections, controllable structures and surface area [9]. For the structural motifs, porous and interpenetrating modes are two common structural phenomena in MOF assemblies [10]. Topical research has been focused on the porous characters of MOF complexes [8,9,11–14]. Recently, pyrolysis of porous MOFs emerges as a novel self-sacrifice template way to prepare carbon materials for the electrochemical energy applications [15–19]. The carbon materials derived from MOFs present the following advantages: i) atom-level control over composition: uniform atom distribution in heteroatom-doped carbon due to the regular crystallization of organic linkers and definite structure of MOF precursors [20]; ii) pore structure: the formation of large specific surface area and hierarchical mesopores due to tuneable morphology and the

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uniformly distributed metal/metal oxide as pore-forming agent [15]. These characters may yield some favourable effects on both the kinetics and mass transfer in building non-Pt electrocatalysts for oxygen reduction reaction (ORR) [21–23]. Many porous nitrogen-doped carbon materials have been prepared by pyrolyzing traditional porous MOFs, *e.g.* ZIF-8, ZIF-67, ZIF-9, MOF-5 and MIL-100-Fe, which feature high specific surface area and decent electrocatalytic activity for ORR [16,24–30]. However, in contrast with the topical research towards using porous MOFs in preparing carbon catalysts, less attention has been paid to the use of interpenetrated nonporous MOF complexes as pyrolysis precursors until now. The removal of metal/metal oxide of coordination polymer frameworks after pyrolysis and acid leaching is believed to be effective in generating the final cavities of porous carbon materials [31]. As such, the pyrolysis of interpenetrated MOFs (metal-organic frameworks) may produce efficient porous channels in the resultant structure as they have high density of metal cations in the interwoven packing structure [10,32].

In this work, a N-doped hierarchically mesoporous carbon (NHMC) catalyst ranging from 2 to 30 nm was prepared, using a nitrogen containing triply-interpenetrated MOF [Zn$_2$(TPT)(BDC)$_2$]·H$_2$O (SCUT-11, TPT = tris(4-pyridyl)triazine, BDC = 1,4-benzenedicarboxylate) as precursor [33]. To our knowledge, this is the first report that N-doped hierarchically mesoporous carbon can be produced from an interpenetrated nonporous MOF precursor. The resulted material shows a better electrocatalytic activity than does Pt/C for the ORR with onset and half-wave potential up to 1.0 and 0.88 V, respectively. Anion-sensitivity test in three acid media (*viz.* HClO$_4$, H$_2$SO$_4$ and H$_3$PO$_4$) indicates that NHMC-900 exhibits a much higher anesthesia towards both SO$_4^{2-}$ and PO$_4^{3-}$ anions, than does the Pt counterpart, suggesting its applicability in different types of fuel cells [34,35].

2. Experimental

2.1. Material preparation

2.1.1. Preparation of SCUT-11

In a typical synthesis procedure, a mixture of Zn(NO$_3$)$_2$·6H$_2$O (150 mg, 0.50 mmol), tris(4-pyridyl)triazine (TPT, 62 mg, 0.20 mmol), 1,4-benzenedicarboxylate (BDC, 50 mg, 0.30 mmol), 4.0 mL H$_2$O and 6.0 mL ethylene glycol mono-ethyl ether were sealed in a 25 mL Teflon-lined stainless steel reactor and heated at 125 °C for 48 h. Yellow crystals were collected by filtration and washed with EtOH. After being dried at 60 °C in an oven, SCUT-11 crystal was obtained (81 mg, 51% yield based on TPT).

2.1.2. Preparation of N-doped hierarchically mesoporous carbon (NHMC)

The catalyst precursors were prepared as follows: 500 mg (0.63 mmol) of SCUT-11 was grinded in an agate mortar for 10 min. The obtained powder, together with dicyandiamide (DCD, 106 mg) and FeCl$_3$ (20 mg) with a molar ratio of 5:10:1, was dispersed into 10 mL EtOH. The dispersion was then left at room temperature under stirring for drying, and yellow mixture of powders were finally obtained.

The yellow powders were transferred into a quartz boat, which was subjected to pyrolysis at high temperatures for 1 h with a heating rate of 10 °C min^{-1} in Ar (99.999%). After cooling to room temperature, the black powders were washed with 1.0 M H$_2$SO$_4$ at 80 °C for 24 h to leach out the content of metal, metal oxide and other unstable species, followed by filtration and washing with deionized (D.I.) water. The as obtained samples are designated as NHMC-*x*, where *x* refers to the pyrolysis temperature, *viz.* 800, 900 and 1000 °C.

For comparison, N-doped mesoporous carbon merely derived from SCUT-11 was synthesized by the above method in the absence of FeCl$_3$ and DCD, which are referred to as NC-MOF in text.

2.2. Physicochemical characterization

Powder X-ray diffraction (PXRD) was carried out in the 2θ range of 5–60° using a Bruker AXS D8-Advanced diffractometer at 40 kV, 30 mA with Cu Kα radiation (λ = 1.5406 Å), a scan speed of 5° min^{-1} and a step size of 0.1° in 2θ. Raman spectrum was recorded on a LabRAM Aramis system. Scanning electron microscopy (SEM) images were taken by a Zeiss Merlin system at 5 kV. Transmission electrode microscopy (TEM) images were taken by a JEOL JEM-2100 system at 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were carried out with a Physical Electronics PHI 5600 multi-technique system using an Al monochromatic X-ray at a power of 350 W. Nitrogen adsorption/desorption isotherms were measured at 77 K using Micromeritics TriStar II 3020 analyzer. Before adsorption measurements, each sample was outgassed under vacuum for 8 h at 100 °C. The total surface area was analyzed with the well-established Brunauer-Emmett-Teller (BET) method, and the pore size distribution was analyzed by the Barrett-Joyner-Halenda (BJH) method (>5 nm) and the Classical Kelvin Equation (<5 nm, inset of Fig. 2 & S5).

2.3. Electrochemical characterization

The electrochemical tests were performed by the aid of an electrochemical workstation Zennium (Zahner) at room temperature. Saturated calomel electrode (SCE) was used as the reference electrode, and an Au gauze was used as the counter electrode. The working electrode was a rotating ring-disk (Glassy carbon disk: 5.0 mm in diameter, platinum ring: 6.5 mm inner diameter and 7.5 mm outer diameter, RRDE). The thin-film electrode on the disk was prepared as follows. 10 mg of the catalyst was dispersed in 1.0 mL Nafion/ethanol (0.84 wt% Nafion) by sonication for 120 min. Then, 10 μL of the dispersion was transferred onto the glassy carbon disk by using a pipette, yielding the catalyst loading of 0.50 mg cm^{-2}. For comparison, we also measured the ORR electrocatalytic activity of the commercial 40 wt% Pt/C catalyst (HiSPEC4000, Johnson Matthey) with a Pt loading of 20 μg cm^{-2}.

The electrolyte, including 0.10 M KOH, 0.10 M HClO$_4$, 0.050 M H$_2$SO$_4$ and 1.0 M H$_3$PO$_4$, was first bubbled with Ar for 60 min. Then, CV test was conducted at 20 mV s^{-1} in the potential range between 0 and 1.23 V (*vs.* reversible hydrogen electrode, RHE) for 20 cycles. If unspecified, the linear sweep voltammetry (LSV) curve was obtained by scanning the disk potential from 1.23 down to 0 V at 5 mV s^{-1} in the oxygen-saturated electrolyte solution under 1600 rpm; from this curve the ORR polarization curve was extracted by subtracting the capacitive current. During the data collection, the potential of the ring was set to be 0.5 V (*vs.* RHE) in alkaline and 1.2 V (*vs.* RHE) in acid environment to determine the yield of hydrogen peroxide, respectively. Herein, all potentials were calibrated by using a home-made reversible hydrogen electrode (RHE).

The H$_2$O$_2$ yield and the electron transfer number (*n*) were calculated by the following equation:

$$n = \frac{4|i_d|}{|i_d| + i_r/N} \tag{1}$$

$$H_2O_2 \, (\%) = \frac{2i_r/N}{|i_d| + i_r/N} \times 100 \tag{2}$$

where i_d is the disk current, i_r is the ring current, and N is the ring current collection efficiency (21.85%).