A Layer-Structured Metal-Organic Framework-Derived Mesoporous Carbon for Efficient Oxygen Reduction Reaction

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Developing highly active and durable electrocatalysts for the oxygen reduction reaction (ORR) is crucial to large-scale commercialization of fuel cells and metal-air batteries. Here we report a facile approach for the synthesis of nitrogen and oxygen dual-doped mesoporous layer-structured carbon electrocatalyst embedded with graphitic carbon coated cobalt nanoparticles by direct pyrolysis of a layer-structured metal-organic framework. The electrocatalyst prepared at 800 °C exhibits comparable ORR performance to Pt/C catalysts but possesses superior stability to Pt/C catalysts. This synthetic approach provides new prospects in developing sustainable carbon-based electrocatalysts for electrochemical energy conversion devices.

Key words: Electrocatalysis, Oxygen reduction reaction, Mesoporous carbon, Cobalt nanoparticles

I. INTRODUCTION

Fuel cells and metal-air batteries are clean energy devices, in which the chemical energy of fuels can be transformed into electric energy by electrochemical reaction [1, 2]. However, the oxygen reduction reaction (ORR), an important process at the cathode of many electrochemical devices, is a kinetically sluggish reaction which greatly limits the chemical-electrical energy conversion efficiency [3, 4]. Therefore, the ORR electrocatalysts are very crucial to improve the performance of fuel cells and metal-air batteries in terms of energy conversion [5, 6]. Currently, most commonly used ORR electrocatalysts are noble metal-based materials such as Pt/C catalyst [7, 8]. Although noble metal-based catalysts possess high catalytic activities toward ORR, the high cost and scarcity of noble metals impede the large-scale applications of fuel cells and metal-air batteries. Moreover, noble metal-based catalysts suffer from insufficient durability and are not tolerant against methanol crossover [9–11]. In this context, developing efficient, low-cost and durable noble-metal free electrocatalysts are of great importance for large-scale commercialization of fuel cells, metal-air batteries, and other electrochemical devices.

Porous carbons are widely used as gas adsorbing mediums, electrode materials, and catalyst supports due to their low-cost, chemical stability, and good electrical conductivity [12–14]. Porous carbons also exhibit prominent ORR activity [15]. Recent studies show that the electrocatalytic performance of porous carbons can be finely controlled by doping heteroatoms (e.g. N, O, B, P etc.) [15–17] or introducing crystalline nanoparticles (e.g. Fe, Co, Fe3C) [18, 19]. Consequently, a number of carbon precursors have been developed to produce porous carbon-based ORR electrocatalysts. Metal-organic frameworks (MOFs), a unique kind of porous materials constructed by metal ions and organic ligands, should be ideal precursors to fabricate heteroatom-doped porous carbon materials [20]. Various MOFs have been used to prepare porous carbons for ORR [21–23]. However, few reports of MOF-derived catalysts have so far shown prominent ORR performance comparable to that of Pt/C catalyst due to the low content of heteroatom-doping and insufficient active sites [21].

Here we report the direct conversion of a two-dimensional (2D) layer-structured MOF which is assembled from cobalt (Co) ions and tetra-(4-carboxyphenyl)porphyrin (PPF-1Co) [24] into a layer-structured porous carbon materials under 800 °C for ORR without any special equipment or sacrificial templates (Scheme 1). The as-obtained mesoporous carbons (hereafter referred to as the PPF-1Co-800 catalyst, 800 stands for the pyrolysis temperature) are doped with nitrogen and oxygen elements and embedded with graphitic carbon coated Co nanoparticles. The unique mesoporous layered-structures could facilitate the diffusion of O2 and electrolyte. Meanwhile, the heteroatom-doping and incorporation of Co nanoparticles could increase the active sites for ORR [25, 26]. These fascinat-
II. MATERIAL AND METHODS

A. Preparation of PPF-1Co-X catalysts

2D layer-structured MOF (PPF-1Co) was synthesized by a solvothermal method reported previously [24]. In a typical synthesis, 291 mg Co(NO$_3$)$_3$·6H$_2$O and 790 mg meso-tetra(4-carboxyphenyl)porphine were dissolved in 10 mL mixed solution of N,N-dimethylformamide and ethanol (DMF:EtOH=3:1, volume ratio). The mixed system was sonicated for 10 min to ensure full dispersion and then 100 µL 1 mol/L HNO$_3$ was added. The solution was kept still and reacted at 80 °C for 24 h, followed by slow cooling to room temperature over 9 h. Purple crystals were formed from the solution. The crystals were centrifuged, washed by DMF over three times and dried under vacuum at 120 °C for 12 h to get the activated precursors.

Under Ar atmosphere, activated PPF-1Co was placed in a tube furnace and heated to 800 °C for 4 h with a heating rate of 3 °C/min. After naturally cooling to room temperature, black powders were obtained as PPF-1Co-800. No further treatments were employed.

B. Characterizations

Scanning electron microscopy (SEM) was performed on a JEOL JSM-6700 microscope. Transmission electron microscopy (TEM) was performed on a Hitachi Model 7560 microscope. High-resolution transmission electron microscopy (HRTEM) was conducted on a JEM-ARM 200F atomic resolution analytical microscope. Elemental mappings were collected using a Gatan GIF Quantum 965 instrument. Powder X-ray diffraction (PXRD) patterns were obtained using a Japan Rigaku DMax-γA rotation anode X-ray diffractometer equipped with graphite monochromatized Cu Ko radiation. The nitrogen adsorption-desorption experiments were carried out using the Micromeritics Tristar II 3020 instrument. X-ray photoelectron spectroscopy (XPS) measurements were performed on an X-ray photoelectron spectrometer (Thermo ESCALAB 250).

C. Electrochemical Measurements

All electrochemical measurements were performed in a three-electrode system on a PGSTAT302N electrochemical workstation (Metrohm Autolab). Pt wire and Ag/AgCl (KCl, 3.5 mol/L) served as the counter and reference electrodes, respectively. A 5 mm glassy carbon rotating disk electrode loaded with the electrocatalysts was used as working electrode and the electrolyte was 0.1 mol/L KOH aqueous solution. Before each test, the glassy carbon electrode was polished by 0.05 µm alumina slurry, and ultrasonically treated and rinsed in distilled water. To prepare the working electrode, 2 mg as-prepared samples were dispersed in 1 mL ethanol and sonicated to form suspension, followed by adding 10 µL 5% nafton solution. Then 30 µL suspension was drop-casted on the glassy carbon electrode and dried at ambient temperature. The linear sweep voltammetry (LSV) and cyclic voltammetry (CV) experiments were conducted at ambient temperature with a scan rate of 10 mV/s. Prior to the electrochemical measurements, O$_2$ flow was used to purge into the electrolyte for 30 min, and continuously bubbled over the electrolyte during the tests.

III. RESULTS AND DISCUSSION

SEM image of PPF-1Co crystals is shown in Fig.1(a) which clearly indicates the 2D layered-structure of PPF-1Co. PXRD pattern (Fig.1(b)) shows that PPF-1Co crystals are highly crystalline and the intensive peaks match well according to the previous report [24].

The PXRD pattern of pyrolysis products of PPF-1Co at 800 °C is shown in Fig.2(a). After carboniza-
tion under the elevated temperature, the characteristic peaks of precursors disappeared. The peak located at 26.1° can be assigned to the characteristic peak of graphitic carbon [26]. While other peaks can be attributed to the metallic Co (JCPDS 01-1255), indicating that cobalt ions are transformed into Co nanoparticles during high temperature carbonization [27]. SEM image of the PPF-1Co-800 catalyst (Fig.2(b)) shows that the pyrolyzed product could inherit the morphology from MOF precursor and also exhibits the stacked layered-structure. The results reveal that the carbon skeletons derived from MOFs are robust and can maintain integral structures under high temperatures. As shown in the TEM image (Fig.2(c)), the Co nanoparticles are uniformly distributed in the layered carbon matrix. High-resolution TEM image (Fig.2(d)) of the Co nanoparticles suggests that the lattice fringes (0.2 nm as labeled) are consistent with d-spacing value of (111) of metallic Co. In addition, graphitic carbons with interlayer spacing of 0.34 nm can be clearly observed. Moreover, the graphitic carbon coating is essential for stable ORR activity. It has been reported that Co nanoparticles can activate the surrounding carbon layers and make the outer carbons graphitic and catalytically more active [28, 29].

N$_2$ sorption isotherms and corresponding Barrett-Joyner-Halenda (BJH) pore size distribution of PPF-1Co-800 catalysts are shown in Fig.3(a). An obvious hysteresis loop can be observed, which reveals that carbonized samples are mesoporous with an average pore size of 4.1 nm. The BET specific surface area of PPF-1Co-800 catalysts is 197 m$^2$/g which is not a significant value compared to other porous carbons derived from MOFs. We surmise that the relatively low surface area is likely due to the presence of the large amount of Co nanoparticles in the carbon matrix. Nevertheless, the mesoporous layered-structure enables PPF-1Co-800 catalysts to expose more active sites and facilitate the diffusion of O$_2$ and electrolyte, both of which are beneficial for enhancing electrocatalytic activities [30, 31].

XPS analysis (Fig.3(b)) reveals the presence of C, N, O, and Co elements in the PPF-1Co-800 catalyst. High-resolution XPS spectra (Fig.3(c)) for N1s can be deconvoluted to five different signals that correspond to pyridinic-N, Co-N$_x$, pyrrolic-N, graphitic-N and oxidized-N. All of these N atoms play crucial roles in ORR except oxidized-N [26]. High-resolution Co2p spectra (Fig.4(d)) reveal that three types of Co species such as metallic Co, CoO$_x$ or CoC$_x$N$_y$, and Co-N$_x$ are present in the mesoporous catalyst. Co-N$_x$ has been identified as the catalytic sites for ORR [26, 29]. Elemental mapping of PPF-1Co-800 catalyst indicates that Co, N and O are dispersed uniformly throughout the carbon matrix (Fig.4). Given that Co nanoparticles can activate the surrounding carbon layers and make the outer carbons graphitic and catalytically more active, the homogeneously dispersed Co nanoparticles and N on the carbon matrix should promote ORR electroactivity [25–27].

In order to evaluate the electrocatalytic activity of PPF-1Co-800 catalyst, cyclic voltammetry (CV) measurements were first conducted in O$_2$- and Ar-saturated 0.1 mol/L KOH. As shown in Fig.5(a), noticeable cathodic peak can be observed in O$_2$-saturated electrolyte, whereas no obvious peak can be found in Ar-saturated electrolyte, implying that PPF-1Co-800 catalyst possesses enhanced ORR activity. Moreover, the peak potential of PPF-1Co-800 catalyst at 0.801 V versus reversible hydrogen electrode (RHE) is comparable to
FIG. 3 (a) Nitrogen sorption isotherms and the corresponding BJH pore size distribution (inset) of PPF-1Co-800. (b) XPS survey spectrum of PPF-1Co-800, and high-resolution XPS spectra for (c) N1s and (d) Co2p of PPF-1Co-800.

FIG. 4 HAADF-STEM image of the PPF-1Co-800 and the corresponding elemental mapping of C, Co, N and O.

that of commercial Pt/C catalysts (20wt%) as shown in Fig.5(b) (0.826 V). The linear sweep voltammetric (LSV) curves in Fig.5(c) confirm that PPF-1Co-800 catalyst exhibits prominent electrocatalytic activity with an onset potential \( E_{\text{onset}} \) of ~0.886 V vs. RHE and a half-wave potential \( E_{1/2} \) of ~0.773 V. These values are comparable to those of Pt/C tested under the same conditions \( E_{\text{onset}} \approx 0.926 \) V and \( E_{1/2} \approx 0.786 \) V), indicating the superior ORR activity of layer-structured mesoporous carbons. Furthermore, RDE measurements are conducted at different rotation rates for the LSV curves, which show the increasing current densities (Fig.5(d)). Based on the Koutechy-Levich (K-L) equation, the average electron-transfer number is calculated to be 3.95, suggesting the desired four-electron pathway for ORR.

To further evaluate the ORR performance of PPF-1Co-800 catalyst, stability and methanol tolerance tests are further performed in 0.1 mol/L KOH electrolyte. As shown in Fig.6(a), no discernible shift in the LSV curve can be observed for PPF-1Co-800 catalyst after 5000
FIG. 5 CV curves of (a) PPF-1Co-800 and (b) Pt/C in 0.1 mol/L KOH saturated with Ar and O$_2$ respectively. (c) LSV curves of PPF-1Co-800 and Pt/C in O$_2$-saturated 0.1 mol/L KOH at 1600 r/min. (d) LSV curves of PPF-1Co-800 in O$_2$-saturated 0.1 mol/L KOH at different rotation rates and (e) the corresponding K-L plots.

FIG. 6 Durability tests of (a) PPF-1Co-800 and (b) Pt/C for 5000 cycles in O$_2$-saturated 0.1 mol/L KOH. CV curves of (c) PPF-1Co-800 and (d) Pt/C before and after adding methanol in 0.1 mol/L KOH.
cycles. However, there is a 52 mV loss in $E_{1/2}$ for Pt/C catalyst after 5000 cycles. This comparison clearly shows that the PPF-1Co-800 catalyst possesses superior stability to the Pt/C catalyst. Moreover, no obvious change on the CV curves (Fig.6(c)) can be observed upon the addition of methanol into the electrolyte for the PPF-1Co-800. In contrast, the commercial Pt/C catalyst shows a typical methanol oxidation phenomenon upon the addition of methanol. Above results clearly demonstrate that the layer-structured mesoporous carbon catalyst derived from MOF has much better selectivity and stability than the commercial Pt/C catalyst in ORR.

IV. CONCLUSION

In summary, 2D layered PPF-1Co can be used as a unique precursor for layer-structured mesoporous carbon electrocatalyst. Due to the mesoporous layered structure, high graphitization, and homogeneous doping of N and O, the as-obtained carbon electrocatalyst exhibits excellent electrocatalytic performance in alkaline electrolyte. The measured onset potential, half-wave potential and diffusion-limiting current of PPF-1Co-800 are comparable to those of Pt/C catalysts. Moreover, PPF-1Co-800 catalyst possesses excellent stability and better tolerance to methanol than the Pt/C catalyst. The current work highlights the facile transformation of 2D structured MOFs into porous carbon materials without any sophisticated handling equipment and expensive chemicals, which have distinct advantages toward the mass production of non-precious metal-based M/N-C electrocatalysts in a cost effective and environmentally friendly manner. Thus, the materials used and the approach developed in this work hold great potential for the application in fuel cells and metal-air batteries.

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