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Facile synthesis of N, S co-doped porous carbons from a dual-ligand metal organic framework for high performance oxygen reduction reaction catalysts

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ABSTRACT

Heteroatom doped porous carbons have been regarded as one of most promising candidates for Pt-free oxygen reduction reaction (ORR) catalysts. The proper heteroatom bonding configuration and synergistic effect of multiple atom co-doping are very important for improving their catalytic activity. In this work, a series of N, S co-doped porous carbons (NSCs) with excellent ORR performance were prepared by rationally using a dual-ligand metal organic framework as a carbon precursor. The interconnected porous structure, high surface area, N, S co-doping and high graphitization-N dopant, significantly contribute to the enhanced catalytic performance of ORR. The electrocatalyst studies indicated that the obtained materials have comparable ORR activity to that of the commercial Pt/C in both alkaline and acidic media, and superior long-term durability than that of Pt/C. This work can provide some guidance for synthesizing other multiple atom co-doping carbons for energy storage and conversion applications through target oriented synthesis of metal organic frameworks with different ligands.

1. Introduction

For energy conversation and storage devices such as fuel cells and metal-air batteries, the oxygen reduction reaction (ORR) is a significant reaction that influences the performance of the whole device [1,2]. However, a large amount of precious Pt metal is required to enhance the reaction kinetics of ORR, and the large-scale commercialization of such electrical chemical energy conversation devices is greatly restricted by the limiting resources reserve and high cost of Pt [3,4]. In addition, supported Pt-based catalysts are prone to aggregation and loss activity during long-term operations. Therefore it is necessary to develop novel catalysts with high reaction activity and durability to address the cost and the stability issues [5]. Among the many candidates for ORR catalysts, porous carbons stand out because of their high electronic conductivity, good corrosion resistance, excellent surface properties and low cost [6–8]. Recent reports show that by incorporating of nitrogen atoms into porous carbons, the charge distribution and electron spin density of the carbons can be effectively turned, improving the oxygen adsorption and reduction properties [9–12]. For nitrogen doped porous carbons, the bonding configuration of nitrogen greatly affects their catalytic activity. It is generally considered that pyridine-like N and graphite-like N (also named quaternary N) are highly catalytically active N species, whereas the catalytic activity of pyrrole-type N is relatively low [13,14]. Thus, it is necessary to improve the active N species content of nitrogen doped carbons by the rational design of the carbon precursor.

Metal-organic frameworks (MOFs) are a kind of porous material composed of metal centers and organic ligands, and have attracted wide attention in many fields due to their high surface area and tunable structures. [15,16] Having diverse structures and compositions, MOFs can act as good precursors to fabricate nanostructured porous carbon, metal/carbon composite or metal oxides. MOFs-derived materials have shown great potentials in various fields such as catalysis, gas sorption, supercapacitors and batteries [17–26]. Using N-containing ligand MOFs as precursors, nitrogen doped porous carbons with good performance for ORR can be obtained [27–30]. However, the generally used imidazole-based MOF makes it difficult to control the bonding configuration of

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nitrogen species. It should be pointed out that the structure of MOFs can be designed at the molecular level, and by careful choosing proper N containing ligands, it is possible to control the nitrogen bonding configuration in the porous carbons and fabricate porous carbons with highly active N dopants [31].

On the other hand, the ORR activity of carbons can be further improved through the introduction of other heteroatoms, such as B, P, and S into the N containing carbon materials [32–36]. The synergistic effect arising from the co-doping of heteroatoms can significantly improve the ORR activity. By introducing other heteroatom precursors into the MOFs during the thermal annealing process, N, S co-doped and N, P co-doped porous carbons can also be obtained [37–39]. However, it should be noted that the diverse compositions of MOFs make it possible to prepare multiple-heteroatom co-doped carbons with dual-ligand MOFs as precursors. Undoubtedly, using dual organic ligands to synthesize MOFs with precise crystalline structure for use as carbon precursor could lead to a more uniform composition of the porous carbons, and meanwhile avoid the complex preparation processes and a compromise of experimental repeatability.

Based on the viewpoint of designing multiple heteroatoms co-doped carbons with highly active N dopant sites, in this work, we chose a dual-ligand MOF as the precursor to prepare N, S co-doped porous carbon by using a direct pyrolysis method (Fig. 1). The MOF was synthesized facilely via solid state grinding with Zn $(OAc)_2.4H_2O$, 2,5-thiophenedicarboxylic and 4,4'-bipyridine as the raw materials. During the thermal annealing process, the organic ligands 2,5-thiophenedicarboxylic and 4,4'-bipyridine act as C, N and C, S source, yielding nitrogen and sulfur co-doped porous carbons (NSCs). The structure and components of the resulting carbons can be turned easily by altering the pyrolysis temperature. The obtained porous carbons show great potential for ORR in both alkaline and acidic media because of their high surface areas, N, S co-doping and highly active graphite-like N species. The optimized catalyst NSC-1000 shows dominate four electron transfer mechanism with an onset ORR potential of 0.913 V (vs. RHE)/half-wave potential of 0.829 V in 0.1 M KOH and an onset ORR potential of 0.705 V/half-wave potential of 0.553 V in 0.1 M $HClO_4$. Moreover, it also exhibits distinct advantages concerning long-term stability and methanol poisoning tolerance in comparison to commercial Pt/C catalyst.

2. Experimental Section

2.1. Synthesis of MOF Zn(tdc)(bpy)

All the reagents in this experiment were used directly without further treatment. The original MOF was prepared according to a modified method. [40] $Zn(OAc)_2 \cdot 2H_2O$, 4,4'-bipyridine, and 2,5-thiophenedicarboxylic with 1:1:1 mole ratio were ground in an agate mortar for 10 minutes, followed by washing with DMF and CH_3OH several times to remove any unreacted reagents. Then the obtained white Zn(tdc)(bpy) crystals were dried at room temperature for further use.

2.2. Synthesis of NSCs

The porous carbon catalysts were prepared by direct carbonization of the Zn(tdc)(bpy) in a horizontal tube furnace at different temperatures. In a typical procedure, 200 mg of Zn(tdc)(bpy) was weighed into a quartz boat and heated to the target temperature in a tube furnace at a ramping rate of 5 °C min^{-1}. Then the temperature was maintained for 2 h under N_2 flow (100 mL min^{-1}). Subsequently, the furnace was allow to cool to room temperature naturally. The obtained samples are denoted as NSC-x, where x is the carbonized temperature.

2.3. Characterization

Powder X-Ray diffraction (PXRD) measurements were recorded on a Rigaku D/MAX2550 diffractometer using Cu-Ka radiation (35 kV, 25 mA) with scanning rate of 10° min^{-1} (2θ). Raman spectra of the NSCs were measured by using Renishaw inVia Raman spectrometer, with the 514.5 nm line of an Ar ion laser as the excitation source. The data were recorded from 500–2500 cm^{-1}. Field Emission Scanning Electron Microscopy (FE-SEM) images were obtained by using a Nova NanoSEM 450 (FEI) instrument. X-ray photoelectron spectroscopy (XPS) was conducted with an ESCALAB 250Xi (ThermoFisher) to analyze the surface states of chemical elements. Nitrogen adsorption/desorption measurements were carried out at −196 °C with an Autosorb-iQ2 (Quantachrome Instruments) to determine surface area and pore size distribution. Before sorption analysis, the sample was evacuated at 200 °C for 10 h with a turbo molecular vacuum

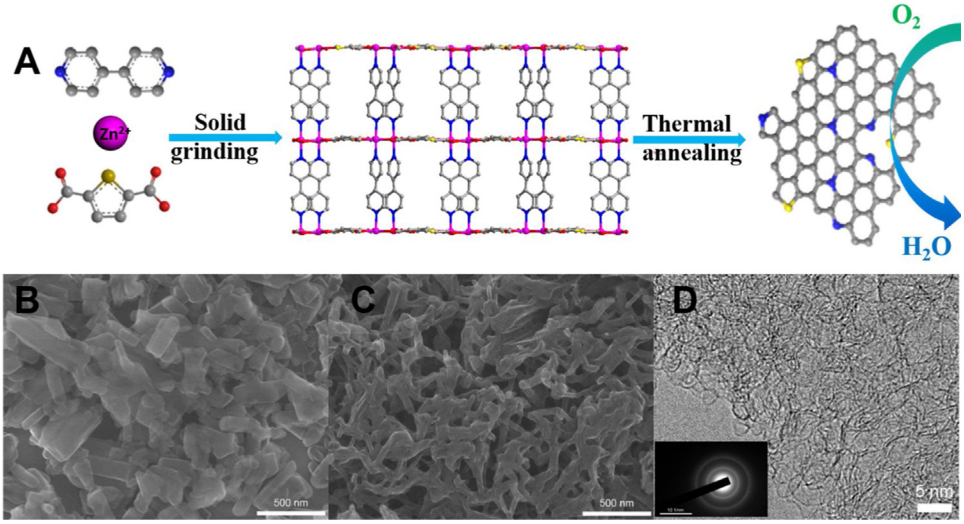

Fig. 1. (A) Schematic illustration for the synthesis of Zn(tdc)(bpy) and their nitrogen-doped porous carbon materials by the pyrolysis of Zn(tdc)(bpy). (B) SEM images of the Zn (tdc)(bpy) crystals. (C) SEM image of NSC-1000; (D) TEM image of NSC-1000. The inset in D is the selected area electron diffraction pattern.