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Graphical abstract

Metal-organic frameworks templated nitrogen and sulfur co-doped porous carbons as highly efficient metal-free electrocatalysts for oxygen reduction reaction

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A novel kind of MOF-templated nitrogen and sulphur co-doped porous materials has been synthesized as efficient electrocatalysts for oxygen reduction reaction (ORR) firstly. The representative NS(3:1)-C-MOF-5 catalyst shows the highest onset potential, even comparable to commercial Pt-C catalyst, due to the synergistic effect of N and S co-doping.
A novel kind of MOF-templated nitrogen and sulphur co-doped porous materials has been synthesized as efficient electrocatalysts for oxygen reduction reaction (ORR) firstly. The representative NS(3:1)-C-MOF-5 catalyst shows the highest onset potential, even comparable to commercial Pt-C catalyst, due to the synergistic effect of N and S co-doping.

Fuel cells (FCs) have attracted a great deal of attention due to low operation temperature, long life span and so on. One of the technical challenges in FCs is the sluggish kinetics of oxygen reduction reaction (ORR) at the cathode, so developing efficient catalysts for ORR plays a significant role in various energy storage and conversion technologies. To date, platinum and its alloys have been the most effective metal catalysts for ORR. Nonetheless, some barriers and bottlenecks need be overcome by using catalysts containing platinum for ORR: the high cost, limited supply and intolerance to fuel crossover. To meet these targets, some innovative alternative materials have been obtained, such as non-precious metal, their alloys or oxides. In particular, the metal-free porous carbons have been employed as new Pt-alternative catalysts and shown the excellent electrocatalytic activity so far. Therefore, it is a novel research field to look for new raw materials or precursors to synthesize porous carbons for ORR.

On the other hand, porous metal-organic frameworks (MOFs), which are emerging as a new class of crystalline porous materials with multiple functionalities, have received great interests. MOF-templated porous carbons, which represent a kind of emerging porous material, have attracted tremendous attention in recent years. Xu’s group demonstrated the application of MOFs as a template for synthesis of porous carbons for the first time. Subsequently, other research groups have obtained some porous carbons using MOFs as a template, for gas separation or storage, and supercapacitor. Hitherto, only a limited number of MOF-templated porous carbons have been used as electrocatalysts for ORR, but these materials as metal-free catalysts have not been investigated. The porous carbons from carbonizing MOFs as electrocatalysts have two main advantages as follows: (i) the intriguing architectures and functions of porous carbons are tunable, because MOFs structures can be designed according to targeted properties by varying the types of metal ions and bridging organic ligands. (ii) larger surface areas and various pore distributions of MOFs are beneficial for adsorbing organic molecules, and then porous carbons doped with different elements and metals can be further obtained. Recently, the heteroatom-doped porous carbons (e.g., N, S and P) have been reported, which show good electrocatalytic activity toward ORR. But the MOF-templated nitrogen and sulfur co-doped porous carbons as metal-free catalysts have not been found yet. So it is a significant and challengeable task to synthesize heteroatom-doped metal-free porous carbons using MOFs as a template for ORR.

In this paper, we have first synthesized nitrogen and sulfur co-doped porous carbons (NS(A:B)-C-MOF-5, A:B : the N:S ratio of NS(A:B)-C-MOF-5) by encapsulating urea and dimethyl sulfoxide (DMSO) into MOF-5 as precursors (Table S1, ESI†). The most representative NS(3:1)-C-MOF-5 catalyst shows the highest onset potential as a metal-free electrocatalyst for ORR among all N and S co-doped porous carbons in the previous literatures, even comparable to commercial Pt-C catalyst, due to a synergistic effect caused by N and S co-doping.

According to the currently reported literatures, MOF-5 was chosen as a template and carbonized at 900 °C. The PXRD pattern of the synthesized MOF-5 is most identical with those simulated. The synthetic process for preparing MOF-5 templated N and S co-doped porous carbons as metal-free catalysts for ORR was illustrated in Scheme 1. Briefly, urea and DMSO were chosen as N and S precursors, respectively. The doping process was carried out by soaking the dried MOF-5 in methanol solution in the presence of urea and DMSO, and then carbonized at 900 °C in ultrapure N2. The obtained carbon materials were washed with dilute hydrochloric acid.
solution and distilled water, respectively. For comparison, the pristine (C-MOF-5), N or S solely doped porous carbons (N-C-MOF-5 or S-C-MOF-5) were also treated under similar conditions, respectively.

Further detailed structure data of these doped porous carbons were investigated by SEM (Fig. 1A and Fig. S2, ESI†), HRTEM (Fig. 1B and Fig. S3, ESI†), PXRD (Fig. S4A, ESI†), Raman spectroscopy (Fig. S4B, ESI†) and EDS (Fig. S5, ESI†), respectively. SEM and HRTEM images suggest the porous nature of the resulting carbon materials. The PXRD profiles for all porous carbons with two broad peaks at around 23 and 44° prove their amorphous characteristic. Remarkably, it was found that the JCPDS No. of NS(3:1)-C-MOF-5 was higher than the pristine and other doped carbons, showing the higher graphitic degree of NS(3:1)-C-MOF-5. The results coincide with the recently reported sulfur and nitrogen dual-doped mesoporous graphene.12b The peaks of C1s (Fig. S6, ESI†), N1s and S2p (Fig. 1C and D) XPS spectra demonstrate that N and S heteroatoms have been successfully incorporated into the frameworks of the samples, which are also supported by EDS measurement.

The nitrogen adsorption-desorption isotherms of all carbon materials are of type IV with distinct hysteresis loops (Fig. S7A, ESI†), which suggested the porous nature of the resulting carbon materials. The PXRD profiles for all porous carbons with two broad peaks at around 23 and 44° prove their amorphous characteristic. Remarkably, it was found that the JCPDS No. of NS(3:1)-C-MOF-5 was higher than the pristine and other doped carbons, showing the higher graphitic degree of NS(3:1)-C-MOF-5. The results coincide with the recently reported sulfur and nitrogen dual-doped mesoporous graphene.12b The peaks of C1s (Fig. S6, ESI†), N1s and S2p (Fig. 1C and D) XPS spectra demonstrate that N and S heteroatoms have been successfully incorporated into the frameworks of the samples, which are also supported by EDS measurement.

To examine electrocatalytic performances of all doped carbon materials for ORR, the electrocatalytic activities of the porous carbons were first evaluated by CVs at 0.1 M KOH aqueous solution saturated with N2 or O2, compared with the bare glassy carbon electrode (BGC), C-MOF-5 and the commercial Pt-C catalysts, respectively. As shown in Fig. S8 (ESI†), featureless voltammetric currents were observed in N2-saturated 0.1 M KOH solutions within the potential range of -1.0 to 0.2 V for BGC, C-MOF-5 and all doped carbon materials, respectively. In comparison, noticed reduction peaks emerged for O2-saturated solutions which suggested pronounced electrocatalytic activities of these catalysts for ORR. As far as we know, this is the first report of MOF-templated N and S co-doped porous carbons as metal-free electrocatalysts for ORR. The peak potentials shift positively by the following trend: NS(3:1)-C-MOF-5 > NS(2:1)-C-MOF-5 > NS(1:1)-C-MOF-5 > N-C-MOF-5 > C-MOF-5 > NS(1:2)-C-MOF-5 > NS(1:3)-C-MOF-5 > S-C-MOF-5 > BGC (Fig. 2A). However, the peak potentials of the samples are slightly negative compared with the commercial Pt-C (-0.13 V) (Fig. S8j, ESI†). Thus, it is believed that the remarkable graphitic degree and porous nature may provide proper channels for mass transport toward ORR. On the other hand, there is no linear relationship between the electrocatalytic activity with BET surface area and pore size of NS(A:B)-C-MOF-5. So it implies that the BET surface area and pore size distribution of NS(A:B)-C-MOF-5 have little impact on the electrocatalytic activity for ORR.
The representative LSVs of NS(3:1)-C-MOF-5 at different rotation rates were presented in Fig. 2C, and that of other samples were provided in Fig. S9 (ESI†), respectively. The corresponding Koutecky-Levich (K-L) plots and the electron transfer numbers involved in the ORR can be calculated (K-L equations are shown in ESI†). The electron transfer numbers of NS(3:1)-C-MOF-5 were calculated from the slopes of K-L plots to be 3.4-3.8 from -0.4 to -0.9 V (Fig. 2D), which were consistent with the rotating ring-disc electrode (RRDE) measurements (Fig. S10, ESI†). The above results exhibit that the NS(3:1)-C-MOF-5 catalyst is the high activity via an about 4e pathway for ORR.

The methanol tolerance ability was measured by CVs in O2-saturated 0.1 M KOH solution upon the addition of 1.0 M methanol for all the samples (Fig. S8, ESI†). After methanol addition, the ORR signal of the commercial Pt-C electrode disappeared at about -0.13 V in CVs and one new peak emerged at -0.08 V, which was attributed to methanol oxidation and indicated a strong crossover effect for the commercial Pt-C (Fig. S8, ESI†). As compared to the commercial Pt-C, no noticeable changes were observed for the other samples under similar conditions, indicating that all porous carbons have good selectivity for ORR and outperform the commercial Pt-C when methanol coexists. The electrochemical durability of typical NS(3:1)-C-MOF-5 was tested at -0.4 V for 20000 s in O2-saturated 0.1 M KOH solution at a scan rate of 10 mV s-1 and 1600 rpm. The corresponding current-time (i-t) chronoamperometric response of NS(3:1)-C-MOF-5 exhibited a much slower decay rate with a highly relative current of 80% after 20000 s, while the commercial Pt-C decreased about 27% of current density (Fig. S11, ESI†) due to the dissolution, sintering, and agglomeration of the commercial Pt-C catalysts.1, 2 The results confirm that the long-term stability and resistance to methanol crossover effect of NS(3:1)-C-MOF-5 are superior to that of the commercial Pt-C for ORR.

In summary, the nitrogen and sulfur co-doped porous carbons have been successfully synthesized by encapsulating urea and DMSO into MOF-5 as precursors for the first time. Owing to a synergetic effect of N and S, the most representative NS(3:1)-C-MOF-5 shows the highest onset potential as a metal-free electrocatalyst for ORR, even comparable to the commercial Pt-C catalyst. In terms of long-term stability and excellent resistance to methanol crossover effect for ORR, that of NS(3:1)-C-MOF-5 is superior to that of the commercial Pt-C. The results further pave a new way for achieving kinds of heteroatom-doped (e.g., N, S and P) porous carbon materials using different MOFs as a template for FC applications and other areas. Further research work is ongoing.

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Notes and references

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