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Metal–organic framework templated nitrogen and sulfur co-doped porous carbons as highly efficient metal-free electrocatalysts for oxygen reduction reactions†

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A novel MOF-templated nitrogen and sulphur co-doped porous material has been synthesized as an efficient electrocatalyst for oxygen reduction reactions (ORRs) for the first time. The representative NS(3 : 1)–C-MOF-5 catalyst shows the highest onset potential, and is 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 their low operation temperatures, long life spans and so on. One of the technical challenges for FCs is the sluggish kinetics of oxygen reduction reactions (ORRs) at the cathode, and therefore developing efficient catalysts for ORRs would be significant for various energy storage and conversion technologies.[1] To date, platinum and its alloys have been the most effective metal catalysts for ORRs.[2] Nonetheless, some barriers and bottlenecks that exist when using catalysts containing platinum for ORRs need to be overcome: high cost, limited supply and intolerance to fuel crossover. To meet these targets, some innovative alternative materials have been obtained, such as non-precious metals[3] and their alloys or oxides.[4] In particular, metal-free porous carbons have been employed as new Pt-alternative catalysts and have shown excellent electrocatalytic activity so far.[5] Therefore, looking for new raw materials or precursors to synthesize porous carbons for ORRs is a novel research field.

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 interest.[6] MOF-templated porous carbons, which are an emerging porous material, have attracted tremendous attention in recent years. Xu's group demonstrated the application of MOFs as templates for the synthesis of porous carbons for the first time.[7] Subsequently, other research groups have obtained some porous carbons using MOFs as templates,[8] for gas separation or storage,[7] and supercapacitors.[9] Hitherto, only a limited number of MOF-templated porous carbons have been used as electrocatalysts for ORRs,[10] but these materials have not been investigated as metal-free catalysts. The porous carbons from carbonizing MOFs as electrocatalysts have two main advantages: (i) the intriguing architectures and functions of porous carbons are tunable, because MOF structures can be designed according to targeted properties by varying the types of metal ions and bridging organic ligands.[8,10d] (ii) Larger surface areas and various pore distributions of MOFs are beneficial for adsorbing organic molecules, and porous carbons doped with different elements and metals can be further obtained.[7,9] Recently, heteroatom-doped porous carbons (*e.g.*, N,[5a] S[11] and P[12]) have been reported, which show good electrocatalytic activity toward ORRs. However, MOF-templated nitrogen and sulfur co-doped porous carbon metal-free catalysts have not been found yet. Hence, it is a significant and challengeable task to synthesize heteroatom-doped metal-free porous carbons using MOFs as a template for ORRs.

In this paper, we have synthesized nitrogen and sulfur co-doped porous carbons for the first time (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 ORRs among all N and S co-doped porous carbons in the previous literatures,[13] and is even comparable to commercial Pt–C catalyst, due to a synergistic effect caused by N and S co-doping.

According to a previous report,[7] in which MOF-5 was chosen as a template and carbonized at 900 °C, the PXRD pattern of the synthesized MOF-5 was almost identical with that from simulated data.[14] The synthetic process for preparing MOF-5 templated N and S co-doped porous carbons as metal-free catalysts for ORRs is illustrated in Scheme 1. Briefly, urea and DMSO

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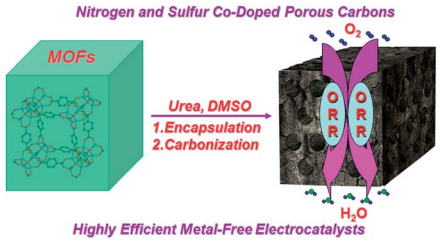

Scheme 1 Synthesis procedure for MOF-5 templated N and S co-doped porous carbons as metal-free electrocatalysts for ORRs.

were chosen as N and S precursors, respectively. The doping process was carried out by soaking the dried MOF-5 in a methanol solution in the presence of urea and DMSO, and then carbonized at 900 °C in ultrapure N_2. The obtained carbon materials were washed with dilute hydrochloric acid solution and distilled water. For comparison, the pristine (C-MOF-5) and soley N or S doped porous carbons (N–C-MOF-5 or S–C-MOF-5) were also treated under similar conditions.

Further detailed structural data of these doped porous carbons were investigated by SEM (Fig. 1A and S2, ESI†), HRTEM (Fig. 1B and S3, ESI†), PXRD (Fig. S4A, ESI†), Raman spectroscopy (Fig. S4B, ESI†) and EDS (Fig. S5, ESI†). The SEM and HRTEM images reveal 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 that they have amorphous characteristics. Remarkably, it was found that the I_G/I_D of NS(3 : 1)–C-MOF-5 was higher than the pristine and other doped carbons, revealing the higher graphitic degree of NS(3 : 1)–C-MOF-5. The results agree with a recent report on sulfur and nitrogen dual-doped mesoporous graphene.[13b] The peaks of C_{1s} (Fig. S6, ESI†), N_{1s} and S_{2p} (Fig. 1C and D) XPS spectra demonstrate that N and S heteroatoms have been successfully incorporated into the frameworks of the samples. This is also supported by EDS measurements.

The nitrogen adsorption–desorption isotherms of all of the carbon materials are of type IV with distinct hysteresis loops (Fig. S7A, ESI†). The detailed data of BET surface areas are summarized in Table S1 (ESI†) and the pore size distributions for the samples are shown in Fig. S7B (ESI†).

To examine electrocatalytic performances of all the doped carbon materials for ORRs, the electrocatalytic activities of the porous carbons were first evaluated in 0.1 M KOH aqueous solution saturated with N_2 or O_2 by cyclic voltammetry, and compared with a bare glassy carbon (BGC) electrode, C-MOF-5 and the commercial Pt–C catalysts. As shown in Fig. S8 (ESI†), featureless voltammetric currents were observed in N_2-saturated 0.1 M KOH solutions within the potential range of −1.0 to 0.2 V for the BGC electrode, C-MOF-5 and all doped carbon materials. In comparison, noticeable reduction peaks emerged for O_2-saturated solutions which suggested pronounced electrocatalytic activities of these catalysts for ORRs. 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 ORRs. 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 towards ORRs. On the other hand, there is no linear relationship between the electrocatalytic activity with the BET surface area and pore size of NS(A : B)–C-MOF-5. Hence, this 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 ORRs.

To gain more information on ORRs involving all doped carbon materials and the commercial Pt–C, linear sweep voltammograms (LSVs) were studied by using a rotating disk

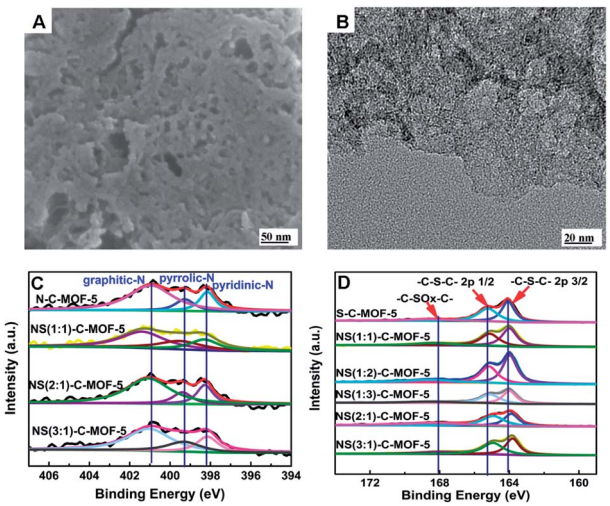

Fig. 1 (A) SEM and (B) HRTEM of the typical NS(3 : 1)–C-MOF-5 catalyst. (C) XPS-N_{1s} and (D) XPS-S_{2p} spectra of different samples.

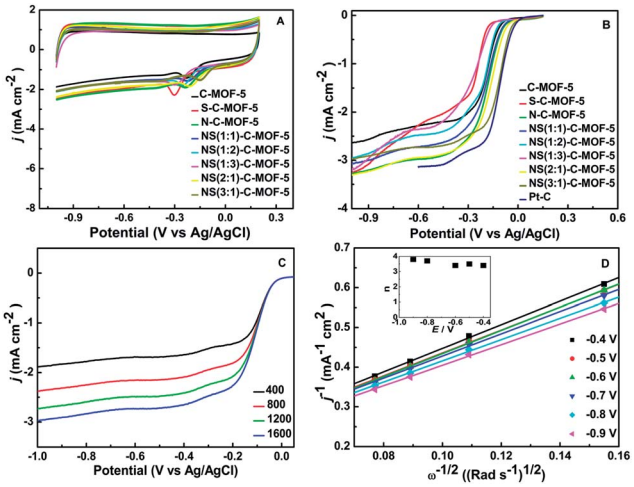

Fig. 2 (A) Cyclic voltammograms of different samples in O_2-saturated 0.1 M KOH solution; (B) LSVs of different samples at 1600 rpm; (C) LSVs of NS(3 : 1)–C-MOF-5 at different rotation rates; (D) K–L plots of NS(3 : 1)–C-MOF-5 from −0.4 to −0.9 V.

electrode (RDE). The onset potential of NS(3 : 1)–C-MOF-5 for the ORR is at about −0.005 V, which is more positive than those of NS(2 : 1)–C-MOF-5 (−0.01 V), NS(1 : 1)–C-MOF-5 (−0.02 V), N–C-MOF-5 (−0.023 V), C-MOF-5 (−0.03 V), NS(1 : 2)–C-MOF-5 (−0.06 V), NS(1 : 3)–C-MOF-5 (−0.09 V) and S–C-MOF-5 (−0.11 V) catalysts (Fig. 2B). Furthermore, the onset potential of NS(3 : 1)–C-MOF-5 is very close to that of the commercial Pt–C, exhibiting that the catalytic activity of NS(3 : 1)–C-MOF-5 is better than that of other carbon materials for ORRs. In particular, the onset potential of NS(3 : 1)–C-MOF-5 is the highest as a metal-free electrocatalyst among all N and S co-doped porous carbons described in the literatures.[13] The comparisons of electrocatalytic parameters are listed in the Table S2 (ESI†). Meanwhile, the electrocatalytic activity of NS(3 : 1)–C-MOF-5 is superior to those of graphene-supported metal catalysts.[15] All of the detailed data further prove that N and S in the N and S co-doped catalysts have synergistically enhanced electrochemical activities for ORRs, as is the case with the N and S co-doped mesoporous graphene.[13b] A possible mechanism is speculated as follows: the high activity of N doped porous carbons may be attributed to the larger electronegativity of N (3.04) with respect to C atoms (2.55), creating positive charge densities on the adjacent C atoms.[16] The electronegativity of sulphur (2.58) is similar to that of carbon.[17] When N and S are simultaneously doped into porous carbon materials, the spin and charge densities are changed, which results in an increase in the number of active C atoms and the very favourable adsorption of O_2.[13b] So the typical NS(3 : 1)–C-MOF-5 demonstrates excellent electrocatalytic activity for ORRs.

The representative LSVs of NS(3 : 1)–C-MOF-5 at different rotation rates are presented in Fig. 2C, and that of other samples are provided in Fig. S9 (ESI†). The corresponding Koutecky–Levich (K–L) plots and the electron transfer numbers involved in the ORRs 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 the 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-disk electrode (RRDE) measurements (Fig. S10, ESI†). The above results exhibit that the NS(3 : 1)–C-MOF-5 catalyst has high activity *via* a 4e pathway for ORRs.

The methanol tolerance ability was measured by cyclic voltammetry in O_2-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 the cyclic voltammograms 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. S8j, 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 ORRs and outperform the commercial Pt–C in the presence of methanol. The electrochemical durability of typical NS(3 : 1)–C-MOF-5 was tested at −0.4 V for 20 000 s in O_2-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 relatively high current of 80% after 20 000 s, while the commercial Pt–C decreased to about 27% current density (Fig. S11, ESI†) due to the dissolution, sintering, and agglomeration of the commercial Pt–C catalyst.[1,2] The results confirm that the long-term stability and resistance to the methanol crossover effect of NS(3 : 1)–C-MOF-5 are superior to that of the commercial Pt–C for ORRs.

In summary, 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 ORRs, and is even comparable to the commercial Pt–C catalyst. In terms of long-term stability and excellent resistance to the methanol crossover effect for ORRs, NS(3 : 1)–C-MOF-5 is superior to commercial Pt–C. The results further pave a new way for achieving heteroatom-doped (*e.g.*, N, S and P) porous carbon materials using different MOFs as templates for FC applications and other areas. Further research work is ongoing.

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