

Journal of Materials Chemistry A

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Graphical abstract

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

Jisen Li,^{a,b} Yuyun, Chen,^a Yujia, Tang,^a Shunli Li,^a Huiqing Dong,^a Kui Li,^a Min Han,^a Ya-Qian Lan,^{a*} Jianchun Bao^a and Zhihui Dai^{a*}

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.



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

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/MaterialsA

Jisen Li,^{a,b} Yuyun, Chen,^a Yujia, Tang,^a Shunli Li,^a Huiqing Dong,^a Kui Li,^a Min Han,^a Ya-Qian Lan,^{a*} Jianchun Bao^a and Zhihui Dai^{a*}

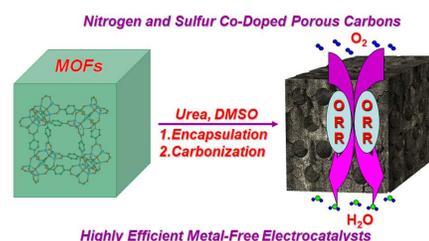
A novel kind of MOF-templated nitrogen and sulphur co-doped porous materials has been synthesized as efficient electrocatalysts for oxygen reduction reaction (ORR) firstly. The representative NS(3:1)-C-MOF-5 catalyst shows the highest onset potential, even comparable to commercial Pt-C catalyst, due 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.¹ To date, platinum and its alloys have been the most effective metal catalysts for ORR.² 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,³ their alloys or oxides.⁴ In particular, the metal-free porous carbons have been employed as new Pt-alternative catalysts and shown the excellent electrocatalytic activity so far.⁵ 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.⁶ 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.⁷ Subsequently, other research groups have obtained some porous carbons using MOFs as a template,⁸ for gas separation or storage,⁷ and supercapacitor.⁹ Hitherto, only a limited number of MOF-templated porous carbons have been used as electrocatalysts for ORR,¹⁰ 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.^{8,10d} (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.^{7,9} Recently, the heteroatom-doped porous carbons (e.g., N,^{5a} S¹¹ and P¹²) 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,¹³ even comparable to commercial Pt-C catalyst, due to a synergistic effect caused by N and S co-doping.



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

According to the currently reported literatures,⁷ 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.¹⁴ 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.

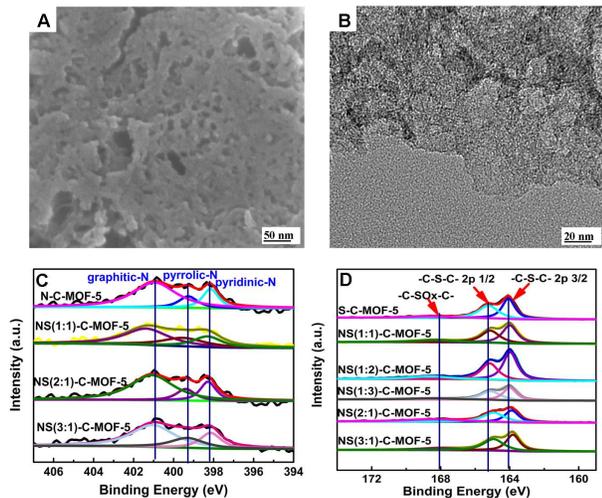


Fig. 1 (A) SEM and (B) HRTEM of the typical NS(3:1)-C-MOF-5 catalyst. (C) XPS-N_{1s} and (D) XPS-S_{2p} spectra of different samples.

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 I_G/I_D 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.^{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, 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[†]). The detailed data of BET surface areas were summarized in Table S1 (ESI[†]) and the pore size distributions for the samples were showed in Fig. S7B (ESI[†]).

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.

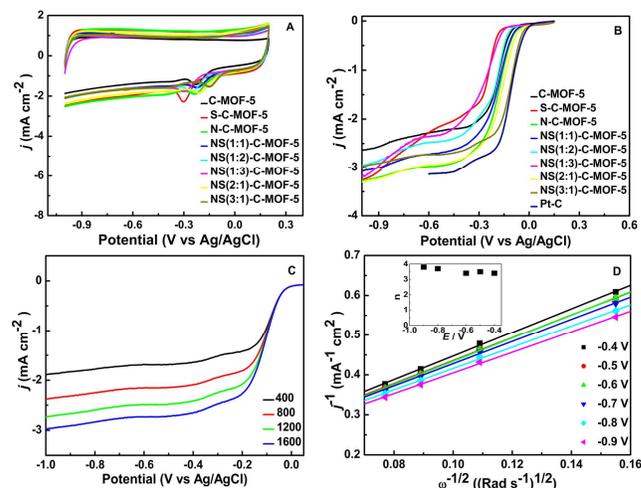


Fig. 2 (A) CVs of different samples in O₂-saturated 0.1 M KOH solution; (B) LSVs of different samples at 1600 rpm; (C) LSVs of NS(3:1)-C-MOF-5 at different rotation rates; (D) K-L plots of NS(3:1)-C-MOF-5 from -0.4 to -0.9 V.

For gain more information on ORR involving all doped carbon materials and the commercial Pt-C, LSVs were studied by using a rotating disk 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 ORR. In particularly, 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 were 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 the synergistically enhanced electrochemical activities for ORR, 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 (electronegativity of nitrogen: 3.04) with respect to C atoms (electronegativity of carbon: 2.55), and the creating of positive charge density on the adjacent C atoms.¹⁶ Sulfur (electronegativity of sulphur: 2.58) has a close electronegativity to carbon (electronegativity of carbon: 2.55).¹⁷ When N and S are simultaneously doped into the porous carbon materials, the spin and charge densities are changed, which result in an increase in the number of active C atom and the very favourable adsorption of O₂.^{13b} So the typical NS(3:1)-C-MOF-5 indicates the excellent 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-disk 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. 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 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 catalyst.^{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.

This work was financially supported by the NSFC (No. 21001020, 21171096 and 21371099) and University Postgraduate Research and Innovation Project in Jiangsu Province (CXLLX13_368).

Notes and references

^a Jiangsu Key Laboratory of Biofunctional Materials, College of Chemistry and Materials Science, Nanjing Normal University, Nanjing 210023, P. R. China. E-mail: yqlan@njnu.edu.cn; daizhihui@njnu.edu.cn

^b Department of Chemistry and Chemical Engineering, Jining University, Qufu 273155, P. R. China

Electronic Supplementary Information (ESI) available: Full experimental details, Figures and Tables. See DOI: 10.1039/x0xx00000x

- (a) M. Winter and R. J. Brodd, *Chem. Rev.*, 2004, **104**, 4245; (b) Y. J. Wang, D. P. Wilkinson and J. Zhang, *Chem. Rev.*, 2011, **111**, 7625.
- (a) V. R. Stamenkovic, B. Fowler, B. S. Mun, G. F. Wang, P. N. Ross, C. A. Lucas and N. M. Markovic, *Science*, 2007, **315**, 493; (b) H. W. Liang, X. Cao, F. Zhou, C. H. Cui, W. J. Zhang and S. H. Yu,

- Adv. Mater.*, 2011, **23**, 1467; (c) S. J. Yoo, S. K. Kim, T. Y. Jeon, S. J. Hwang, J. G. Lee, S. C. Lee, K. S. Lee, Y. H. Cho, Y. E. Sung and T. H. Lim, *Chem. Commun.*, 2011, **47**, 11414.
- (a) L. Xiao, L. Zhuang, Y. Liu, J. T. Lu and H. D. Abruna, *J. Am. Chem. Soc.*, 2009, **131**, 602; (b) T. N. Lambert, D. J. Davis, W. Lu, S. J. Limmer, P. G. Kotula, A. Thuli, M. Hungate, G. Ruan, Z. Jin and J. M. Tour, *Chem. Commun.*, 2012, **48**, 7931; (c) G. Wu, K. L. More, P. Xu, H. L. Wang, M. Ferrandon, A. J. Kropf, D. J. Myers, S. Ma, C. M. Johnston and P. Zelenay, *Chem. Commun.*, 2013, **49**, 3291.
 - (a) M. H. Shao, K. Sasaki and R. R. Adzic, *J. Am. Chem. Soc.*, 2006, **128**, 3526; (b) Y. Y. Liang, Y. G. Li, H. L. Wang, J. G. Zhou, J. Wang, T. Regier and H. J. Dai, *Nat. Mater.*, 2011, **10**, 780; (c) D. A. Slanac, W. G. Hardin, K. P. Johnston and K. J. Stevenson, *J. Am. Chem. Soc.*, 2012, **134**, 9812.
 - (a) S. Yang, L. Zhi, K. Tang, X. Feng, J. Maier and K. Müllen, *Adv. Func. Mater.*, 2012, **22**, 3634; (b) Y. Chang, F. Hong, C. He, Q. Zhang and J. Liu, *Adv. Mater.*, 2013, **25**, 4794; (c) F. Cheng, J. Liang, J. Zhao, Z. Tao and J. Chen, *Chem. Mater.*, 2008, **20**, 1889.
 - (a) J. R. Long and O. M. Yaghi, *Chem. Soc. Rev.*, 2009, **38**, 1213; (b) H. C. Zhou, J. R. Long and O. M. Yaghi, *Chem. Rev.*, 2012, **112**, 673; (c) S. Xiang, Y. He, Z. Zhang, H. Wu, W. Zhou, R. Krishna and B. Chen, *Nat. Commun.*, 2012, **3**, 954; (d) S. C. Xiang, Z. J. Zhang, C. G. Zhao, K. L. Hong, X. B. Zhao, D. R. Ding, M. H. Xie, C. D. Wu, M. C. Das, R. Gill, K. M. Thomas and B. L. Chen, *Nat. Commun.*, 2011, **2**, 1.
 - (a) B. Liu, H. Shioyama, T. Akita and Q. Xu, *J. Am. Chem. Soc.*, 2008, **130**, 5390; (b) H. L. Jiang, B. Liu, Y. Q. Lan, K. Kuratani, T. Akita, H. Shioyama, F. Zong and Q. Xu, *J. Am. Chem. Soc.*, 2011, **133**, 11854.
 - (a) L. Radhakrishnan, J. Reboul, S. Furukawa, P. Srinivasu, S. Kitagawa and Y. Yamauchi, *Chem. Mater.*, 2011, **23**, 1225; (b) H. L. Jiang and Q. Xu, *Chem. Commun.*, 2011, **47**, 3351; (c) M. Hu, J. Reboul, S. Furukawa, N. L. Torad, Q. M. Ji, P. Srinivasu, K. Ariga, S. Kitagawa, and Y. Yamauchi, *J. Am. Chem. Soc.*, 2012, **134**, 2864.
 - (a) A. Banerjee, R. Gokhale, S. Bhatnagar, J. Jog, M. Bhardwaj, B. Lefez, B. Hannoyer and S. Ogale, *J. Mater. Chem.*, 2012, **22**, 19694; (b) W. Chaikittisilp, M. Hu, H. Wang, H.-S. Huang, T. Fujita, K. C. W. Wu, L.-C. Chen, Y. Yamauchi and K. Ariga, *Chem. Commun.*, 2012, **48**, 7259.
 - (a) G. Goenaga, S. Ma, Yuan, S. Yuan, and D.-J. Liu, *ECS Trans.*, 2010, **33**, 579; (b) S. Ma, G. A. Goenaga, A. V. Call, and D.-J. Liu, *Chem. Eur. J.*, 2011, **17**, 2063; (c) D. Zhao, J.-L. Shui, C. Chen, X. Chen, B. M. Repragle, D. Wang, and D.-J. Liu, *Chem. Sci.*, 2012, **3**, 3200; (d) P. Su, H. Xiao, J. Zhao, Y. Yao, Z. Shao, C. Li, and Q. Yang, *Chem. Sci.*, 2013, **4**, 2941; (e) S. L. Li and Q. Xu, *Energy Environ. Sci.*, 2013, **6**, 1656.
 - I. Y. Jeon, H. J. Choi, S. M. Jung, J. M. Seo, M. J. Kim, L. Dai and J. B. Baek, *J. Am. Chem. Soc.*, 2013, **135**, 1386.
 - D. S. Yang, D. Bhattacharjya, S. Inamdar, J. Park and J. S. Yu, *J. Am. Chem. Soc.*, 2012, **134**, 16127.
 - (a) S.-A. Wohlgemuth, R. J. White, M.-G. Willinger, M.-M. Titirici and M. Antonietti, *Green Chem.*, 2012, **14**, 1515; (b) J. Liang, Y. Jiao, M. Jaroniec and S. Z. Qiao, *Angew. Chem. Int. Ed.*, 2012, **51**, 11496; (c) J. Xu, G. Dong, C. Jin, M. Huang and L. Guan, *ChemSusChem*, 2013, **6**, 493.

- 14 K. Koh, A. G. Wong-Foy and A. J. Matzger, *Angew. Chem. Int. Ed.*, 2008, **47**, 677.
- 15 (a) H. Yin, H. Tang, D. Wang, Y. Gao and Z. Tang, *ACS nano*, 2012, **6**, 8288; (b) R. Liu, X. Yu, G. Zhang, S. Zhang, H. Cao, A. Dolbecq, P. Mialane, B. Keita and L. Zhi, *J. Mater. Chem. A*, 2013, **1**, 11961.
- 16 Z. Yang, Z. Yao, G. Li, G. Fang, H. Nie, Z. Liu, X. Zhou, X. Chen and S. Huang, *ACS nano*, 2012, **6**, 205.
- 17 K. P. Gong, F. Du, Z. H. Xia, M. Durstock and L. M. Dai, *Science*, 2009, **323**, 760.