

Electronic Supplementary Information

**Pyrazinium Ionic Liquid for Preparing A 0D/2D
Hybridized N, P-codoped Carbon Enriched with Pyridinic
N and Enhanced Electrocatalytic Performance toward
Oxygen Reduction Reaction**

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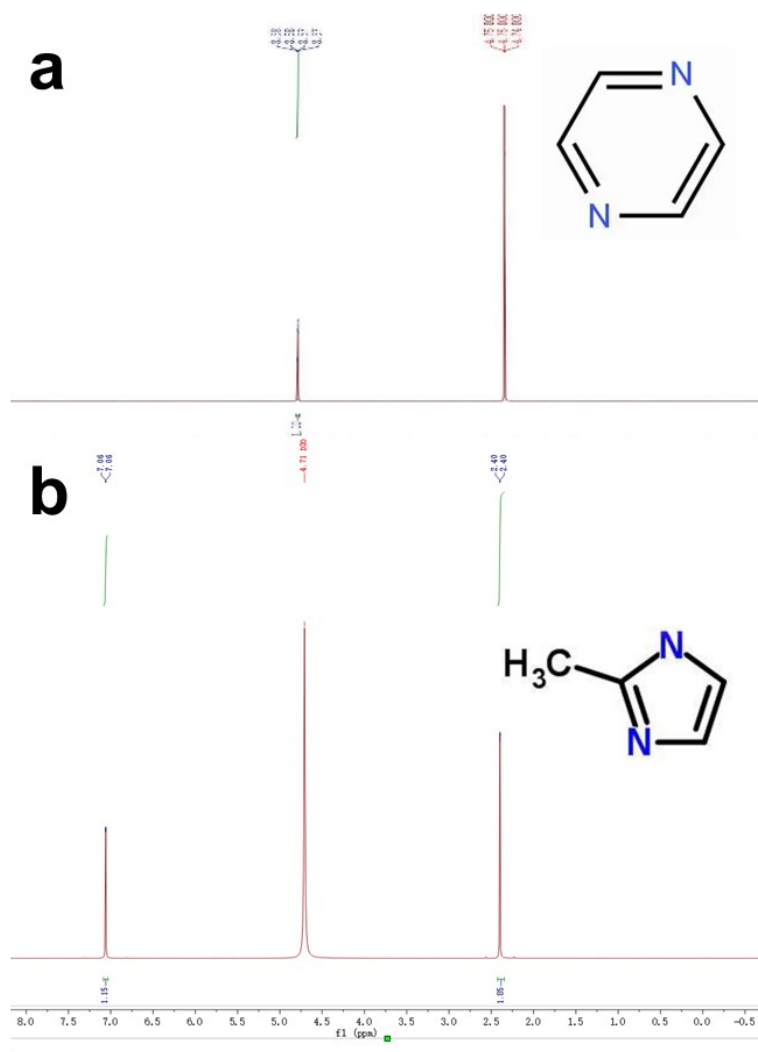
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Fig.S1 ^1H NMR for (a) [Hpyraz] H_2PO_4 and (b) [2-Mim]DHP.

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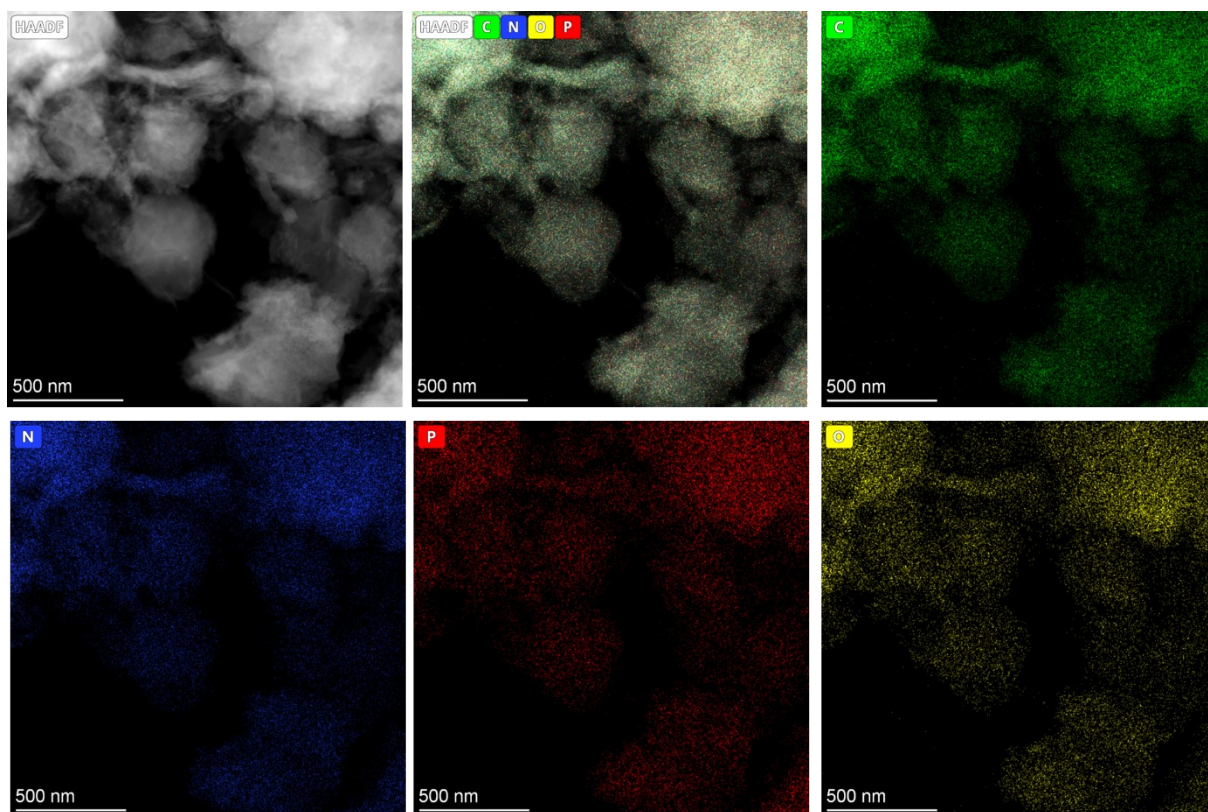


Fig. S2 HAADF STEM image of C_{mim} and corresponding EDS elemental mappings.

Table S1 Weight contents of C, N, and H in the C_{pyr} and C_{mim} obtained by EA results

Sample	C (wt. %)	H (wt. %)	N (wt. %)
C_{mim} -700	76.74	1.16	1.89
C_{mim} -800	85.38	0.59	0.95
C_{mim} -900	89.43	0.36	0.24
C_{mim} -1000	89.23	0.29	0.24
C_{pyr} -700	85.07	0.52	0.16
C_{pyr} -800	91.23	0.30	0.19
C_{pyr} -900	90.34	0.40	0.17
C_{pyr} -1000	89.13	0.31	0.10

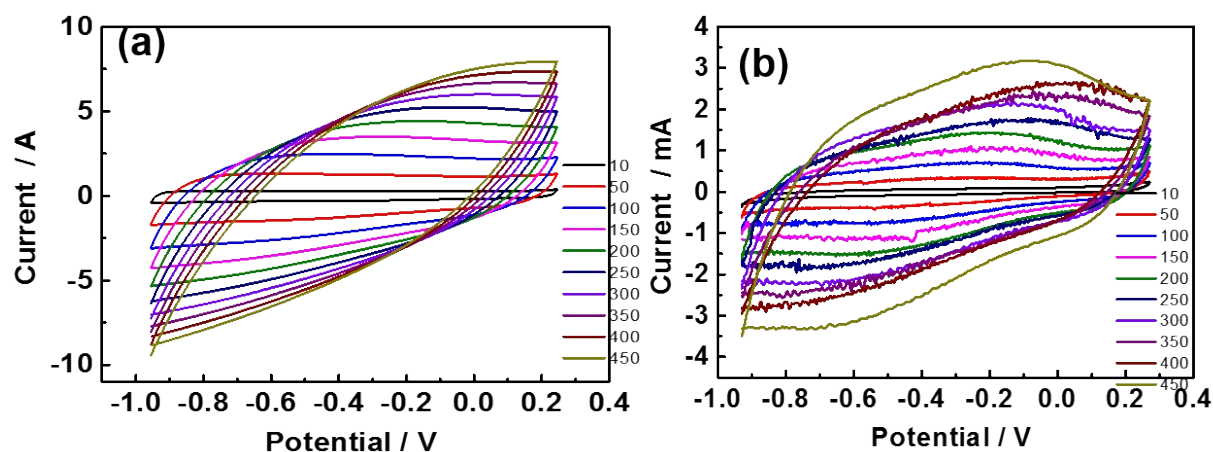


Fig. S3 CV curves for (a) C_{pyr} and (b) C_{mim} .

Table S2 ORR performance of various catalysts reported in recent years.

	Catalyst	Precursor/condition	Onset Potential/ V_{RHE}	Half wave potential V_{RHE}	Specific current V_{RHE}	Reference
1	N-doped carbon	Silica-supported polyaniline/900 °C, Ar, 2h	~0.94	0.71	4.8	1
2	N-Ketjenblack/Fe/Fe ₃ C-Functionalized Melamine Foam	FeCl ₂ , ketjenblack, melamine foam/800°C, Ar, 2h	~0.93	0.78	12	2
3	N-doped carbon	Melamine/phenol formaldehyde (M-PF) resin/900 °C, Ar, 3h.	~0.97	0.84	19.02	3
4	N-doped carbon	Ethyl linked bis(N-(2-cyanoethyl)-imidazole bis(pentafluoroethylsulfonyl)-imide/950 °C, Ar, 2h	~0.95	0.80	18	4
5	N,P co-doped carbon	Polyaniline aerogel and phytic acid/1000 °C, Ar, 2h	0.94	0.85	20.9	5
6	Fe-N-C-HNS-750	Fe ³⁺ -PDA/SiO ₂ /750°C, Ar, 2h	0.89	0.72	0.58	6
7	Graphene Quantum Dots/Graphene Nanoribbons	Na, Methylbenzene, hexabromobenzene/1000°C, Ar, 2h	~0.97	0.78	19.6	7
8	N-doped porous graphene foam	GO, FeCl ₂ , dicyandiamide, silica sphere/900 °C, N ₂ 1h	1.02	0.86	12.4	8

9	N,P co-doped carbon	Melamine, phytic acid, graphene oxide/1000°C, Ar, 1h.	~0.95	~0.81	22.9	9
10	Graphene quantum dots	graphitized carbon nanofibers/120 °C, reflux, 2h	~0.84	0.67	1.3	10
11	Co ₃ O ₄	Co(NO ₃) ₂ , glycerol/700 °C, Ar, 200 min	0.93	0.84	13.7	11
12	N-doped carbon	polyimide (PI) film/1000 °C, Ar, 1h	0.97	0.82	29.4	12
13	N,S co-doped carbon	pyrrole, aniline, ammonium persulfate/various temperatures, N ₂ , 2	0.93	0.81	7.13	13
14	N-doped carbon	ZIF-67, 900 °C, N ₂ , 1h.	0.91	0.84	37.8	14
15	Co-N-doped Hollow Carbon Spheres	poly(methyl methacrylate), cobalt acetate/800 °C, N ₂ , 5h	0.96	0.86	16.7	15
16	N-doped GO	GO/5 °C, ultrasonic treatment, 5 min	0.84	0.7	0.98	16
17	Co-N-C	Co(NO ₃) ₂ , HvimNO ₃ /600 °C, N ₂ , 1h	0.96	0.8	7.85	17
18	Mn ₃ O ₄ /Ti ₃ C ₂	Ti ₃ C ₂ Mxene, Mn(AC) ₂ /150 °C, 3h	0.89	0.8	25	18
19	N,P co-doped carbon	[Hvim]H ₂ PO ₄ /560°C, N ₂ , 1h (Fe(NO ₃) ₃ , nicarbazin, methylimidazole, glucoril ,	0.93	0.75	7.7	19
20	Fe-N-C	zinc, carbon nanotube and LM150 fumed silica/975 °C, N ₂ , 45 min	0.96	0.83	10.7	20
21	N, P dual-doped carbon	melamine–diphenylphosphinic acid/1100 °C, N ₂ , 1h	0.91	0.79	7.85	21
22	N, S copded carbon	Acetylene black, melamine and sluphur template/900 °C, vacuum, 1h	0.99	0.82	9.44	22
23	N-doped holey carbon	GO, zinc gluconate/900 °C, Ar	0.97	0.82	17.6	23
24	Fe-N-C	glycine, citric acid, and FeCl ₃ /800 °C, N ₂ , 2h	0.93	0.75	8	24
25	Graphdiyne doped with N	few-layer oxidised graphdiyne, melamine/900 °C, Ar, 3h	~1.0	0.87	9.32	25
26	Pyridinic-N-doped graphene	C ₃ N ₄ -GO/900 °C, N ₂ , 3h	0.98	0.85	27.2	26
27	FeN ₄ Moiety/MXene	Ti ₃ C ₂ Tx MXene and FePc/ stirred 20h	~0.93	0.86	20.8	27
28	Fe-N ₄ -carbon fabric	GO, polyacrylonitril, FeCl ₃ /900 °C, NH ₃ , 1h	0.93	0.73	Not Available	28
29	N-doped carbon	Citric acid and NH ₄ Cl/1000 °C,	0.95	0.82	19.62	29

		Ar, 3h				
30	N-doped porous carbon	D-gluconic acid sodium/700°C, Ar, 1h	0.94	0.864	19	30
		Bio-MOF-1				
31	N-doped porous carbon	Zn ₈ (Ad) ₄ (Bpdc) ₆ O·2Me ₂ NH ₂ ·8 DMF·11H ₂ O/1000°C, Ar, 1,2,3,4h.	0.96	0.84	9	31
32	S,N,F triple-doped carbon	Superfine PTFE, thiourea/800 °C, Ar, 1h	0.98	0.86	11.77	32
33	Pichlorohydrin-dimethylamine copolyme modified CNT	Pichlorohydrin-dimethylamine copolyme modified CNT/700 °C, 24h	0.87	0.7	0.2	33
34	N-doped CNT in Fe-Nx/Fe ₂ O ₃ /Fe ₃ O ₄ -encapsulated carbon sheet	Fe-Nx/Fe ₂ O ₃ /Fe ₃ O ₄ - encapsulated carbon	0.95	0.85		34
35	N, P-doped carbon	[H ₂ pyraz]2H ₂ PO ₄ /900 °C, N ₂ , 1h	0.93	0.75	3.0	This work

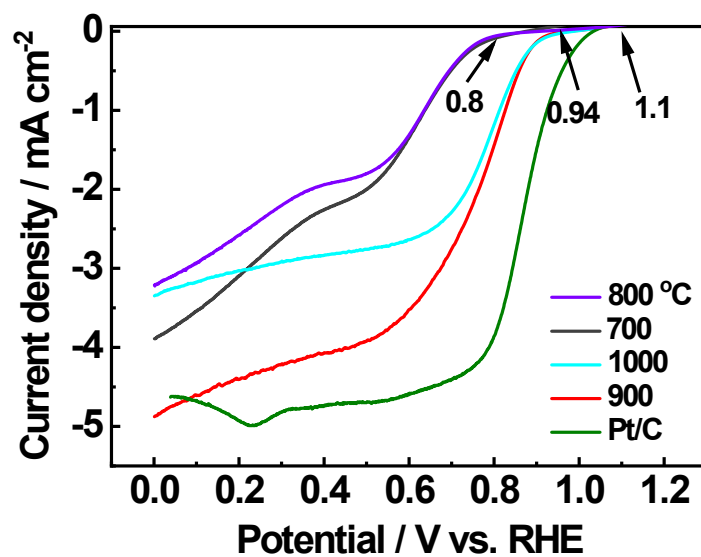
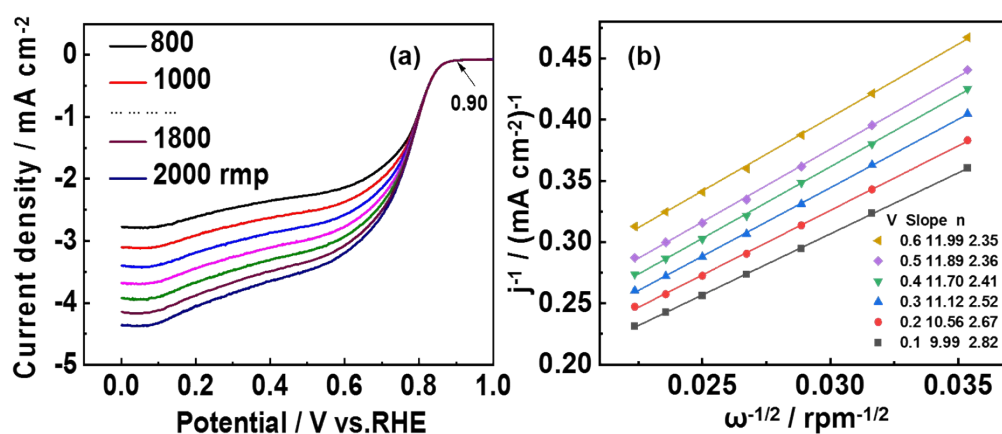


Fig. S4 LSVs for C_{pyr} prepared at various temperatures.

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60 Fig. S5 (a) LSV curves at various rotational speeds for C_{mim} , (b) K-L-plots for C_{mim} .

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65 **Table S3** Peak power density of ZABs with some reported ORR catalyst

	Catalyst	PPD (mW·cm ⁻²)	Reference
1	Pt/C+RuO ₂	80	34
2	Fe, N-doped 3D porous carbon	112	35
3	Pt/MoC/ nitrogen-doped carbon	100	36
4	Pt/C+RuO ₂	50	37
5	Conjugated aromatic/Co-Fe	88	38
6	N,P co-doped carbon	117	This work

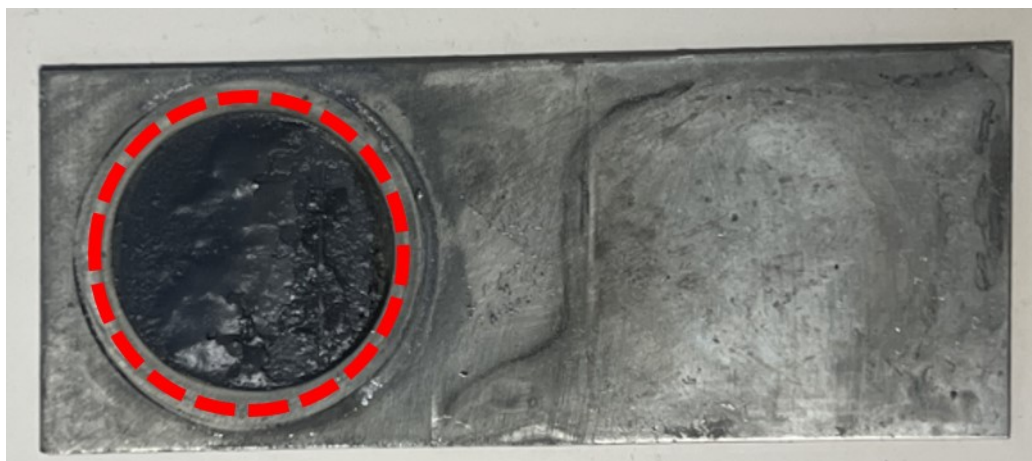
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73 Fig. S6 Picture of the Zn foil after discharging for 4 hours, the circled area is the working area.

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78 References

79 (1) Silva, R.; Voiry, D.; Chhowalla, M.; Asefa, T. Efficient metal-free electrocatalysts for
80 oxygen reduction: polyaniline-derived N- and O-doped mesoporous carbons. *J. Am. Chem.*
81 *Soc.* **2013**, *135*, 7823-7826.

82 (2) Lee, J. S.; Park, G. S.; Kim, S. T.; Liu, M. L.; Cho, J. A Highly Efficient Electrocatalyst
83 for the Oxygen Reduction Reaction: N-Doped Ketjenblack Incorporated into Fe/Fe₃C-
84 Functionalized Melamine Foam. *Angew. Chem. Int. Ed.* **2013**, *52*, 1026-1030.

85 (3) He, W.; Jiang, C.; Wang, J.; Lu, L. High-Rate Oxygen Electroreduction over
86 Graphitic - N Species Exposed on 3D Hierarchically Porous Nitrogen - Doped Carbons.
87 *Angew. Chem. Int. Ed.* **2014**, *53*, 9503-9507.

88 (4) Zhang, Z. Y.; Veith, G. M.; Brown, G. M.; Fulvio, P. F.; Hillesheim, P. C.; Dai, S.;
89 Overbury, S. H. Ionic liquid derived carbons as highly efficient oxygen reduction catalysts:

90 first elucidation of pore size distribution dependent kinetics. *Chem. Commun.* **2014**, *50*, 1469-
 91 1471.

92 (5) Zhang, J.; Zhao, Z.; Xia, Z.; Dai, L. A metal-free bifunctional electrocatalyst for oxygen
 93 reduction and oxygen evolution reactions. *Nat. Nanotechnol.* **2015**, *10*, 444-452.

94 (6) Zhou, D.; Yang, L.; Yu, L.; Kong, J.; Yao, X.; Liu, W.; Xu, Z.; Lu, X. Fe/N/C hollow
 95 nanospheres by Fe(iii)-dopamine complexation-assisted one-pot doping as nonprecious-metal
 96 electrocatalysts for oxygen reduction. *Nanoscale* **2015**, *7*, 1501-1509.

97 (7) Jin, H. L.; Huang, H. H.; He, Y. H.; Feng, X.; Wang, S.; Dai, L. M.; Wang, J. C.
 98 Graphene quantum dots supported by graphene nanoribbons with ultrahigh electrocatalytic
 99 performance for oxygen reduction. *J. Am. Chem. Soc.* **2015**, *137*, 7588-7591.

100 (8) Zhou, X.; Bai, Z.; Wu, M.; Qiao, J.; Chen, Z. 3-Dimensional porous N-doped graphene
 101 foam as a non-precious catalyst for the oxygen reduction reaction. *J. Mater. Chem. A* **2015**, *3*,
 102 3343-3350.

103 (9) Zhang, J.; Qu, L.; Shi, G.; Liu, J.; Chen, J.; Dai, L. N,P-Codoped Carbon Networks as
 104 Efficient Metal-free Bifunctional Catalysts for Oxygen Reduction and Hydrogen Evolution
 105 Reactions. *Angew. Chem. Int. Ed.* **2016**, *55*, 2230-2234.

106 (10) Wang, M. R.; Fang, Z.; Zhang, K.; Fang, J.; Qin, F. R.; Zhang, Z. A.; Li, J.; Liu, Y. X.;
 107 Lai, Y. Q. Synergistically enhanced activity of graphene quantum dots/graphene hydrogel
 108 composites: a novel all-carbon hybrid electrocatalyst for metal/air batteries. *Nanoscale* **2016**,
 109 *8*, 11398-11402.

110 (11) Li, G.; Wang, X. L.; Fu, J.; Li, J. D.; Park, M. G.; Zhang, Y. N.; Lui, G.; Chen, Z. W.
 111 Pomegranate-inspired design of highly active and durable bifunctional electrocatalysts for

112 rechargeable metal-air batteries. *Angew. Chem. Int. Ed.* **2016**, *55*, 4977-4982.

113 (12)Liu, Q.; Wang, Y.; Dai, L.; Yao, J. Scalable fabrication of nanoporous carbon fiber films
114 as bifunctional catalytic electrodes for flexible Zn-Air batteries. *Adv. Mater.* **2016**, *28*, 3000-
115 3006.

116 (13)Wu, Z.; Liu, R.; Wang, J.; Zhu, J.; Xiao, W.; Xuan, C.; Lei, W.; Wang, D. Nitrogen and
117 sulfur co-doping of 3D hollow-structured carbon spheres as an efficient and stable metal free
118 catalyst for the oxygen reduction reaction. *Nanoscale* **2016**, *8*, 19086-19092.

119 (14)Jia, G.; Zhang, W.; Fan, G.; Li, Z.; Fu, D.; Hao, W.; Yuan, C.; Zou, Z.
120 Three - Dimensional Hierarchical Architectures Derived from Surface - Mounted Metal-
121 Organic Framework Membranes for Enhanced Electrocatalysis. *Angew. Chem. Int. Ed.* **2017**.

122 (15)Cai, S.; Meng, Z.; Tang, H.; Wang, Y.; Tsiakaras, P. 3D Co-N-doped hollow carbon
123 spheres as excellent bifunctional electrocatalysts for oxygen reduction reaction and oxygen
124 evolution reaction. *Appl. Catal. B-Environ.* **2017**, *217*, 477-484.

125 (16)Tao, H.; Yan, C.; Robertson, A. W.; Gao, Y.; Ding, J.; Zhang, Y.; Ma, T.; Sun, Z. N-
126 Doping of graphene oxide at low temperature for the oxygen reduction reaction. *Chem.*
127 *Commun.* **2017**, *53*, 873-876.

128 (17)Gao, J.; Ma, N.; Zheng, Y.; Zhang, J.; Gui, J.; Guo, C.; An, H.; Tan, X.; Yin, Z.; Ma, D.
129 Cobalt/nitrogen-doped porous carbon nanosheets derived from polymerizable ionic liquids as
130 bifunctional electrocatalyst for oxygen evolution and oxygen reduction reaction.
131 *ChemCatChem* **2017**, *9*, 1601-1609.

132 (18)Xue, Q.; Pei, Z.; Huang, Y.; Zhu, M.; Tang, Z.; Li, H.; Huang, Y.; Li, N.; Zhang, H.; Zhi,
133 C. Mn₃O₄ nanoparticles on layer-structured Ti₃C₂ MXene towards the oxygen reduction

134 reaction and zinc-air batteries. *J. Mater. Chem. A* **2017**, *5*, 20818-20823.

135 (19)Gao, J.; He, C.; Liu, J.; Ren, P.; Lu, H.; Feng, J.; Zou, Z.; Yin, Z.; Wen, X.; Tan, X.

136 Polymerizable ionic liquid as a precursor for N, P co-doped carbon toward the oxygen

137 reduction reaction. *Catal. Sci. Tech.* **2018**, *8*, 1142-1150.

138 (20)Hossen, M. M.; Artyushkova, K.; Atanassov, P.; Serov, A. Synthesis and characterization

139 of high performing Fe-NC catalyst for oxygen reduction reaction (ORR) in Alkaline

140 Exchange Membrane Fuel Cells. *J. Power. Sources* **2018**, *375*, 214-221.

141 (21)Zhu, J.; Xiao, M.; Song, P.; Fu, J.; Jin, Z.; Ma, L.; Ge, J.; Liu, C.; Chen, Z.; Xing, W.

142 Highly polarized carbon nano-architecture as robust metal-free catalyst for oxygen reduction

143 in polymer electrolyte membrane fuel cells. *Nano energy* **2018**, *49*, 23-30.

144 (22)Xiang, Q.; Li, S.; Zou, X.; Qiang, Y.; Hu, B.; Cen, Y.; Xu, C.; Liu, L.; Zhou, Y.; Chen, C.

145 Self-assembly porous metal-free electrocatalysts templated from sulfur for efficient oxygen

146 reduction reaction. *Appl. Surf. Sci.* **2018**, *462*, 65-72.

147 (23)Sun, J.; Lowe, S. E.; Zhang, L.; Wang, Y.; Pang, K.; Wang, Y.; Zhong, Y.; Liu, P.; Zhao,

148 K.; Tang, Z. Ultrathin Nitrogen - Doped Holey Carbon@ Graphene Bifunctional

149 Electrocatalyst for Oxygen Reduction and Evolution Reactions in Alkaline and Acidic Media.

150 *Angew. Chem. Int. Ed.* **2018**, *130*, 16749-16753.

151 (24)Li, C.; He, C.; Sun, F.; Wang, M.; Wang, J.; Lin, Y. Incorporation of Fe₃C and Pyridinic

152 N Active Sites with a Moderate N/C Ratio in Fe–N Mesoporous Carbon Materials for

153 Enhanced Oxygen Reduction Reaction Activity. *ACS Appl. Nano Mater.* **2018**, *1*, 1801-1810.

154 (25)Zhao, Y.; Wan, J.; Yao, H.; Zhang, L.; Lin, K.; Wang, L.; Yang, N.; Liu, D.; Song, L.;

155 Zhu, J.; Gu, L.; Liu, L.; Zhao, H.; Li, Y.; Wang, D. Few-layer graphdiyne doped with sp-

156 hybridized nitrogen atoms at acetylenic sites for oxygen reduction electrocatalysis. *Nature*
 157 *Chemistry* **2018**, *10*, 924-931.

158 (26) Wang, Q.; Ji, Y.; Lei, Y.; Wang, Y.; Wang, Y.; Li, Y.; Wang, S. Pyridinic-N-dominated
 159 doped defective graphene as a superior oxygen electrocatalyst for ultrahigh-energy-density
 160 Zn-air batteries. *ACS. Energy. Lett.* **2018**, *3*, 1183-1191.

161 (27) Li, Z.; Zhuang, Z.; Lv, F.; Zhu, H.; Zhou, L.; Luo, M.; Zhu, J.; Lang, Z.; Feng, S.; Chen,
 162 W.; Mai, L.; Guo, S. The Marriage of the FeN₄ Moiety and MXene Boosts Oxygen
 163 Reduction Catalysis: Fe 3d Electron Delocalization Matters. *Adv. Mater.* **2018**, *30*.

164 (28) Li, B.; Sasikala, S. P.; Kim, D. H.; Bak, J.; Kim, I.-D.; Cho, E.; Kim, S. O. Fe-N₄
 165 complex embedded free-standing carbon fabric catalysts for higher performance ORR both in
 166 alkaline & acidic media. *Nano Energy* **2019**, *56*, 524-530.

167 (29) Jiang, H.; Gu, J.; Zheng, X.; Liu, M.; Qiu, X.; Wang, L.; Li, W.; Chen, Z.; Ji, X.; Li, J.
 168 Defect-rich and ultrathin N doped carbon nanosheets as advanced trifunctional metal-free
 169 electrocatalysts for the ORR, OER and HER. *Energy Environ. Sci.* **2019**, *12*, 322-333.

170 (30) Han, H.; Noh, Y.; Kim, Y.; Jung, W. S.; Park, S.; Kim, W. B. An N-doped porous carbon
 171 network with a multidirectional structure as a highly efficient metal-free catalyst for the
 172 oxygen reduction reaction. *Nanoscale* **2019**, *11*, 2423-2433.

173 (31) Yang, L.; Xu, G.; Ban, J.; Zhang, L.; Xu, G.; Lv, Y.; Jia, D. Metal-organic framework-
 174 derived metal-free highly graphitized nitrogen-doped porous carbon with a hierarchical
 175 porous structure as an efficient and stable electrocatalyst for oxygen reduction reaction. *J.*
 176 *Colloid Interf. Sci.* **2019**, *535*, 415-424.

177 (32) Lv, Y.; Yang, L.; Cao, D. Sulfur, Nitrogen and Fluorine Triple-Doped Metal-Free Carbon

178 Electrocatalysts for the Oxygen Reduction Reaction. *Chemelectrochem* **2019**, 6, 741-747.

179 (33) Yu, Y.; Zhang, Z.; Dai, L.; Wang, F. Copolymer-induced intermolecular charge transfer:
 180 Enhancing activity of metal-free catalysts for oxygen reduction. *Chem-Euro. J.* **2019**, 25,
 181 5652-5657.

182 (34) Gan, R.; Song, Y.; Ma, C.; Shi, J. In situ growth of N-doped carbon nanotubes in Fe-
 183 Nx/Fe₂O₃/Fe₃O₄-encapsulated carbon sheets for efficient bifunctional oxygen catalysis. *Appl.*
 184 *Catal. B-Environ.* **2023**, 327, 122443-122452.

185 (35) Huang, Y.; Liu, K.; Kan, S.; Liu, P.; Hao, R.; Liu, W.; Wu, Y.; Liu, H.; Liu, M.; Liu, K.
 186 Highly dispersed Fe-Nx active sites on graphitic-N dominated porous carbon for synergetic
 187 catalysis of oxygen reduction reaction. *Carbon* **2021**, 171, 1-9.

188 (36) Wang, X.; Gong, X.; Hu, L.; Fan, J.; Chen, R.; Jia, Y.; Cheng, Y.; Jiang, B.; Geng, H.
 189 Constructing Pt and Pt/MoC Co - anchored on nitrogen - doped carbon toward excellent
 190 methanol - resilient oxygen reduction performance for Zinc - Air batteries. *ChemNanoMat*
 191 **2023**, 9, e202200365.

192 (37) Tang, C.; Wang, B.; Wang, H. F.; Zhang, Q. Defect engineering toward atomic Co-Nx-C
 193 in hierarchical graphene for rechargeable flexible solid Zn-air batteries. *Adv. Mater.* **2017**, 29,
 194 1703185-1703194.

195 (38) Yang, S.; Yu, Y.; Dou, M.; Zhang, Z.; Dai, L.; Wang, F. Two - dimensional conjugated
 196 aromatic networks as high - site - density and single - atom electrocatalysts for the oxygen
 197 reduction reaction. *Angew. Chem. Int. Ed.* **2019**, 58, 14724-14730.

198