**Electronic Supplementary Information**

# High-performance electrocatalyst based on polyazine derived mesoporous nitrogen-doped carbon for oxygen reduction reaction

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**S1. BET surface areas and pore volume variation with the pyrolytic temperature**

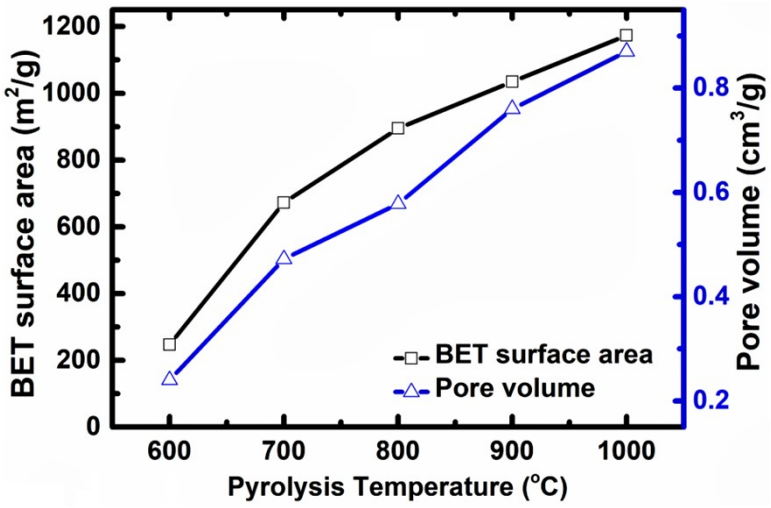


Figure S1 the BET surface areas and pore volume variation with the pyrolytic temperature

**S2 Pyrolysis behavior of F127/PAZ composite**

Figure S1 shows the thermal decomposition of F127, PAZ and their composite from 25 °C to 998 °C in a nitrogen atmosphere, respectively. As shown, a major weight reduction of above 99% for F127 takes place as the temperature reached 410 °C, suggesting that the template can be totally destroyed at this stage. For the PAZ without the F127 template, a rapid weight loss was observed at the temperature range of 150–300 °C (around 45% weight loss), which indicates the cleavage of small molecules from the further condensation of the linear polymer to form a framework structure and facilitate carbonization. In the range of 400–995 °C, the carbonization is improved, accompanied by the gradual decomposition of carbonaceous residue with approximately 40% of further weight loss. In contrast, the profile of the 127/PAZ composite colligated the pyrolytic behaviour of both the PAZ and F127. Two significant weight loss stages can be observed in the temperature range of 150–280 °C and 300–410 °C, which are attributed to the partial destruction of PAZ and the complete decomposition of F127, respectively. The final carbon yield (atom efficiency toward the desired carbon structure) is about 12% of the composite when it

is heated up to 995 °C.

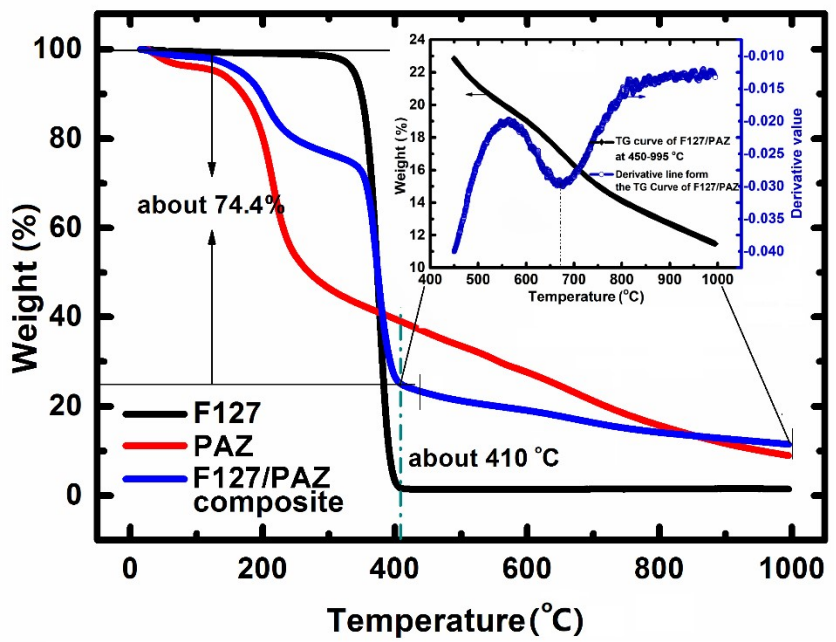


Figure S2 Thermogravimetric behaviors of the F127/PAZ composite compared to F127 and PAZ in $N_2$ atmosphere

Table S1 Comparison NMC–700 with previous reported metal free ORR catalytic in 0.1 M KOH at a scan rate of 5 or 10 mV/s with the RDE rotation rate of 1600 rpm.

| Materials | Precursors | Onset potential | [a] Relative half-wave potential | Tafel slopes | $H_2O_2$ yields | References |
|---|---|---|---|---|---|---|
| N-doped graphene | ammonia | ca. 25 mV positive | 43 mV positive | - | ca. 10% | [1] |
| N-doped Carbon/graphene composite | polydopamine | ca. 10 mV positive | 40 mV positive | - | 4.3-16.5% | [2] |
| N-doped carbon | ionic liquids | ca. 25 mV negative | - | - | - | [3] |
| N, S-dual-doped graphene | melamine, benzyl disulfide | ca. 30 mV negative | - | - | - | [4] |
| N-doped carbon | ZIF-8 | -0.13 V vs. SCE (not compare with Pt catalyst) | - | - | - | [5] |
| N-doped carbon/CNT composite | PANI | ca. 30 mV negative | 26 mV positive | 66 mV $decade^{-1}$ | | [6] |
| N-doped carbon | Polyazine | ca. 6 mV negative | 90 mV negative | 87 mV $decade^{-1}$ | ＜5% | This work |

a. Compared with the results from commercial Pt (20 at.%) catalyst

**S3 Normalization of kinetic current at 0.875 V to the exposure indexes of nitrogen species for ORR.**

Table S2 Physical and chemical characteristic parameter of materials prepared under different pyrolysis temperature (PT)

| PT (°C) | SSA ($m^2\ g^{-1}$) | Kinetic current densities at 0.875 V ($m$A $cm^{-2}$) | N-species containing (at.%)/*EI*[a] | |
|---|---|---|---|---|
| | | | pyridinic-N | pyrrolic-N |
| 600 | 247 | 0.29 | 8.21/430 | 1.74/2027 |
| 700 | 672 | 1.87 | 4.08/652 | 0.97/2742 |
| 800 | 895 | 1.70 | 2.46/438 | 0.49/2022 |
| 900 | 1034 | 0.62 | 0.76/300 | 0.29/786 |
| 1000 | 1174 | 0.60 | 0.56/235 | 0.2/657 |

a. The exposure indexes (*EI*) of the proposed active sites can be calculated as follows: *EI* = SSA×Nitrogen species containing (pyridinic–N or pyrrolic–N).

Normalization of $J_{0.875\ V}$ to *EI* can be carried out as follows:

$$\text{nominal}\, J_{0.875\ V} = \frac{J_{0.875\ V} \times S_{we}}{EI}\ (\mu\text{A g m}^{-2})$$

Where $S_{we}$ refers to the area of work electrode, the value is 0.19625 $cm^2$.

**S4 RRDE measurement**

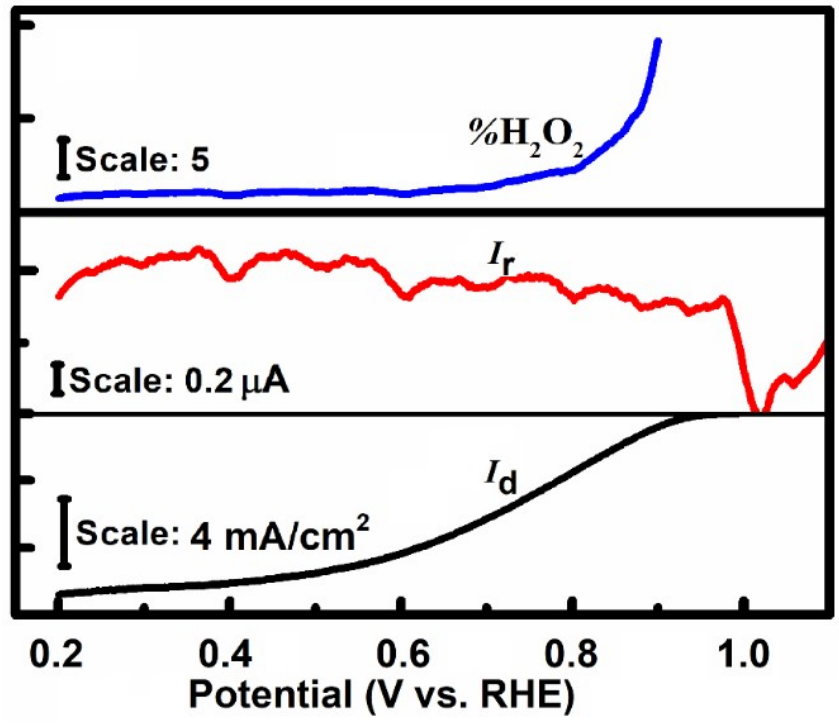


Figure S3 Rotating ring-disk electrode measurement combined with $H_2O_2$ yield over NMC-700 in $O_2$-saturated 0.1 M KOH solution at the rotation rate of 1600 rpm.

**References:**


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