9th August 2017 Update: Please note that this version of the Supporting Information replaces the version that was originally published on 19th January 2016 and contains updated versions of Fig. S9 and Table S1, as described in the associated Correction Notice.

Supporting Information:

A Versatile Strategy to Fabricate MOFs/Carbon Materials Integrations and Their Derivatives for Enhanced Electrocatalysis

Xiao Ma,[a,b] Xue Zhao,[a,b] Jian Sun,[a] Dehui Li,[a,b] and Xiurong Yang[a]*

Experimental details

Preparation of ZC (means the hybrid of ZIF-8 and MWCNTs)

Purified MWCNTs (0.17 g) were put in methanol (15 mL) followed by sonication for 10 min. $Zn(NO_3)_2 \cdot 6H_2O$ (0.2231 g) and 2-MeIM (0.4926 g) were dissolved in above solution followed by transferring it into a 50 mL Teflon-lined stainless steel autoclave and crystallized for 24 h at 140 °C.[1] After cooling down to room temperature, the solution was filtered and rinsed with MeOH followed by drying in a vacuum oven overnight at 50 °C.

Preparation of ZC-900 (means the ZC pyrolyzed at 900 °C)

The as-prepared ZC was put in a ceramic boat and then transferred it to a tube furnace for pyrolysis at 200 °C for 2 h and then 900 °C for 5 h under argon flow. Next, the resultant sample was immersed in H_2SO_4 (1 M) with stirring for 24 h followed by washing and drying.[2]
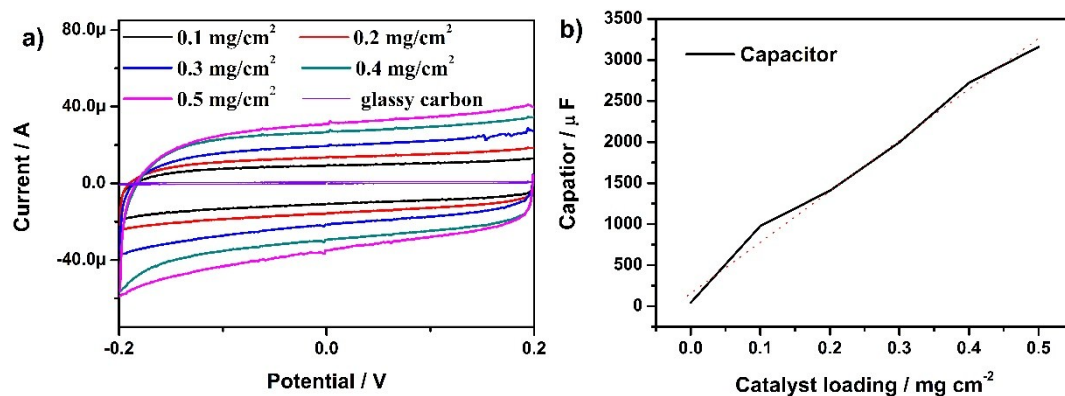
Fig. S1~S11:

Figure S1 a) The measured CVs of different amounts of ZPC-1/1-900 on GCEs; b) The relationship between capacitors and loading amounts of ZPC-1/1-900. (Scan rate: 10 mV s^{-1}, electrolyte: 0.1 M KOH)
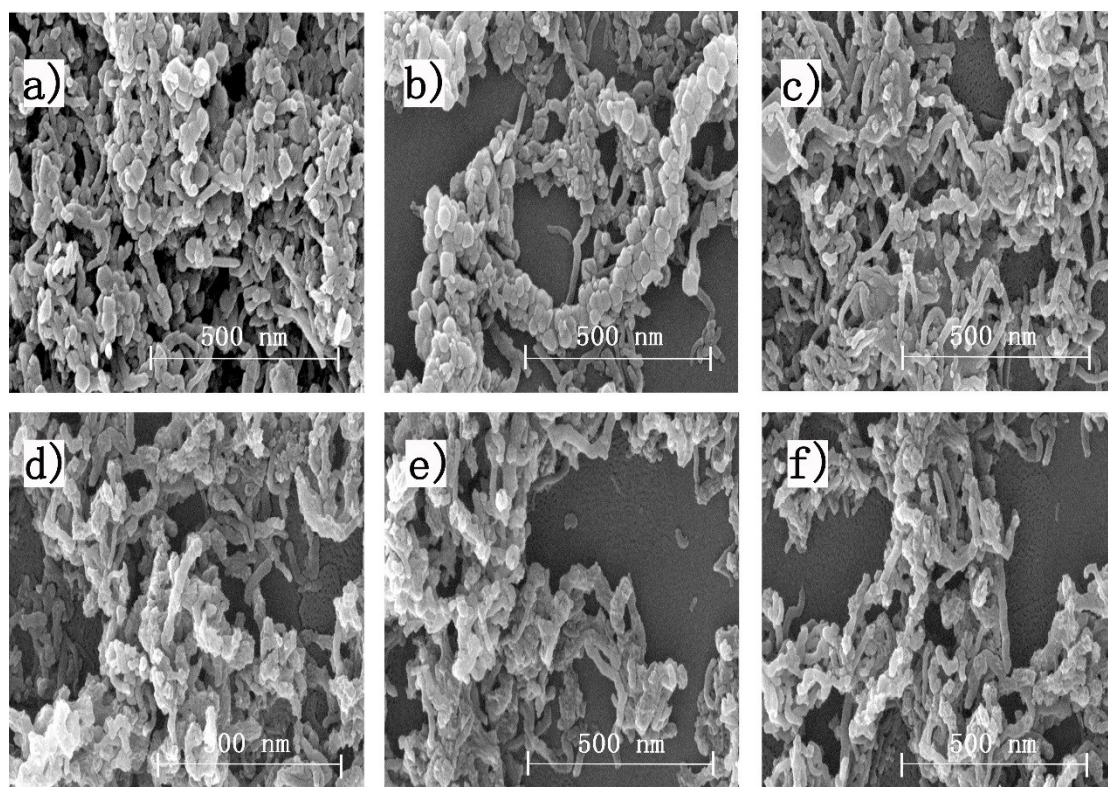

Fig. S2 SEM images of a) ZPC-0.5/1, b) ZPC-1/1, c) ZPC-2/1, d) ZPC-0.5/1-900, e) ZPC-1/1-900 and f) ZPC-2/1-900.
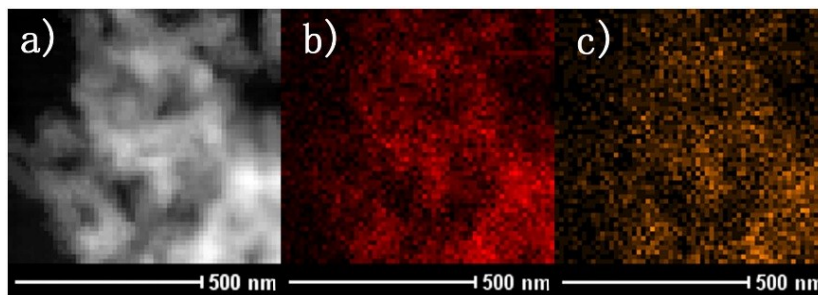
Fig. S3 a) HAADF-STEM image of ZPC-1/1-900; b) corresponding C elemental mapping image; c) corresponding N elemental mapping image.
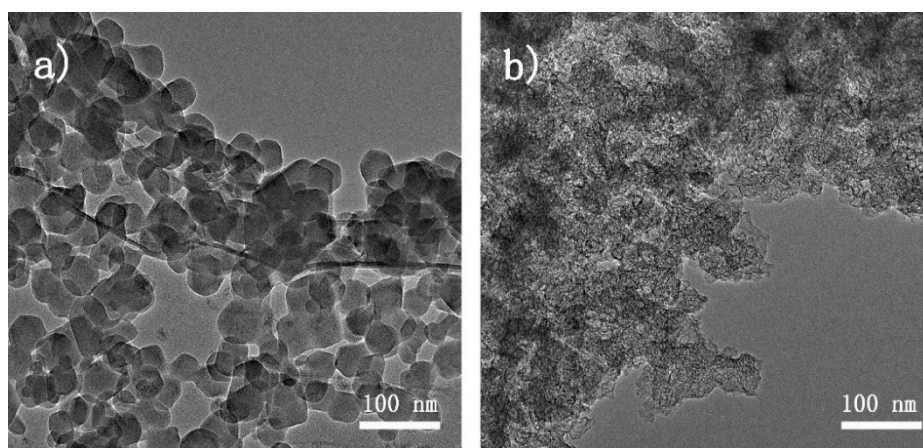

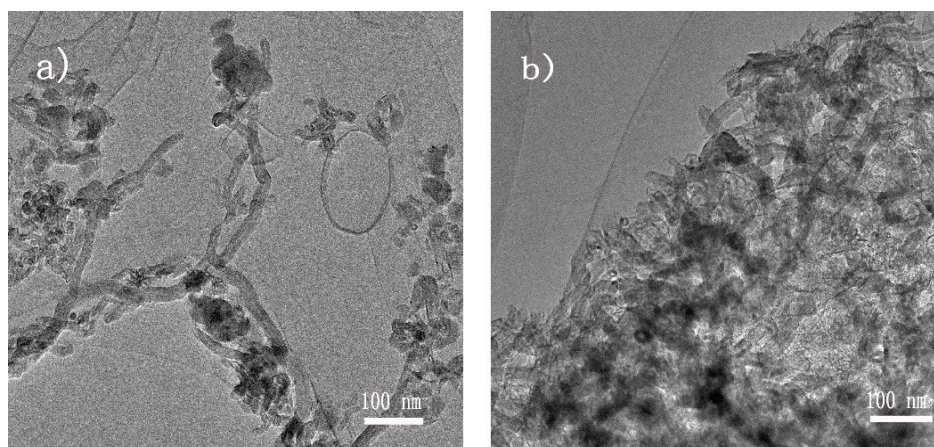**Fig. S4** TEM images of a) pure ZIF-8 and b) ZIF-8-900.

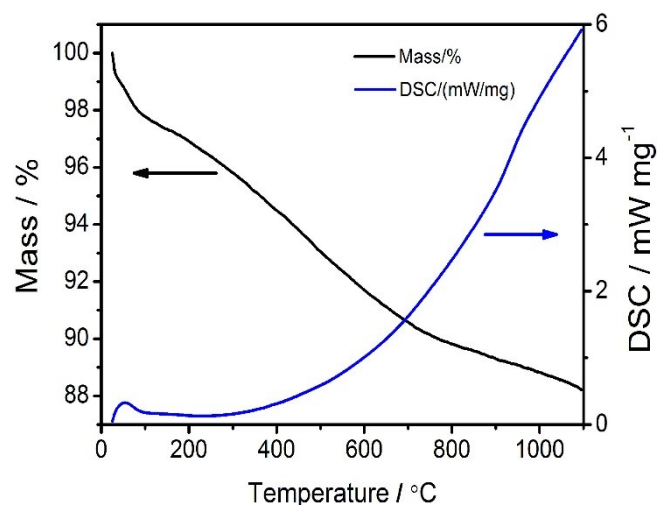
Fig. S5 TEM images of a) ZC and b) ZC-900.
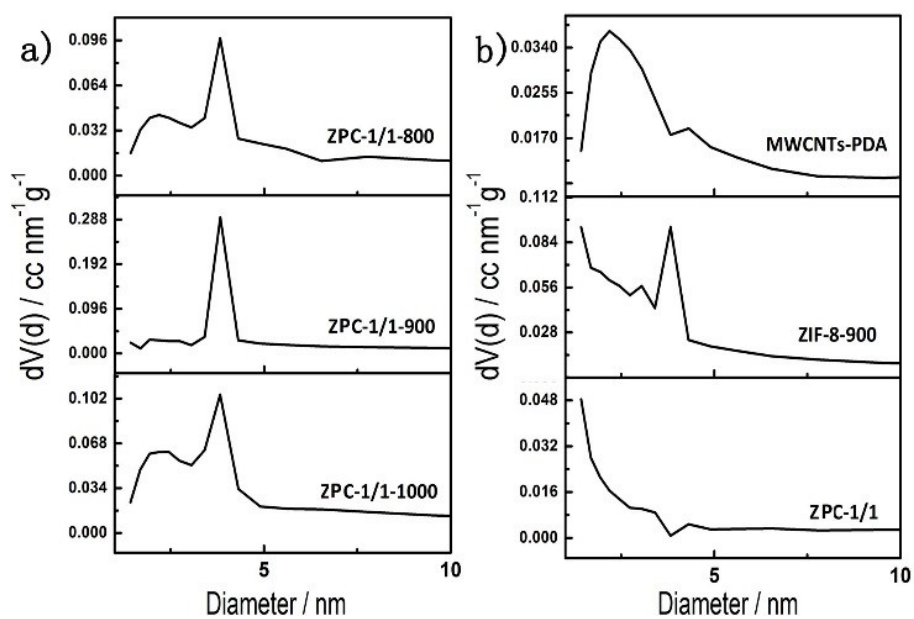
Fig. S6 TGA and DSC curves of MWCNTs-PDA.

Fig. S7 PSD data of ZPC-1/1-800, ZPC-1/1-900, ZPC-1/1-1000, MWCNTs-PDA, ZIF-8-900 and ZPC-1/1 respectively.
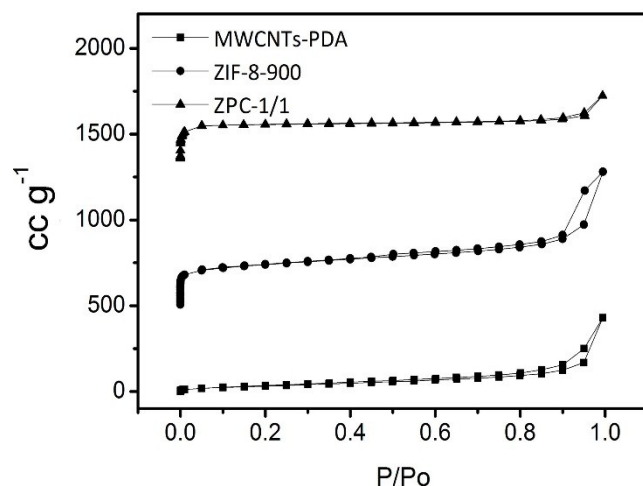
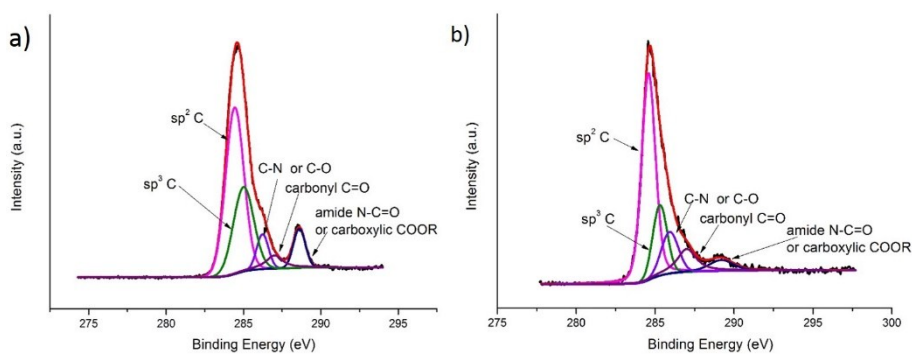**Fig. S8** Nitrogen adsorption/desorption isotherms of MWCNTs-PDA, ZIF-8-900 and ZPC-1/1.

Fig. S9 High-resolution C 1s spectra of a) ZIF-8-900 and b) ZPC-1/1-900.
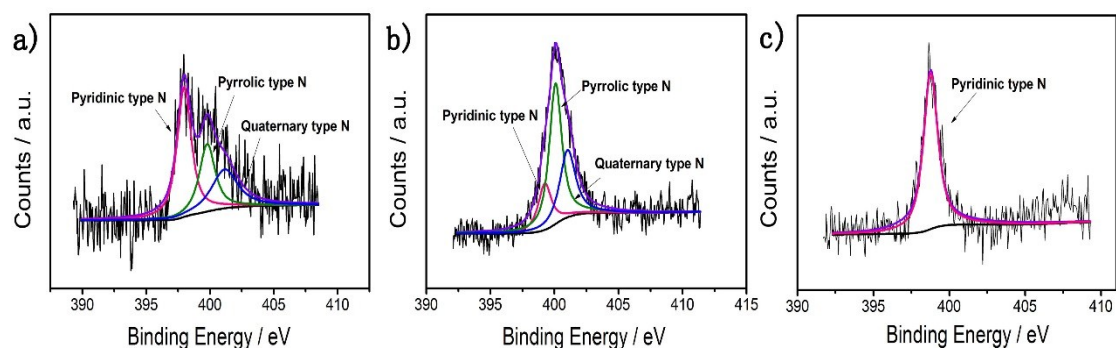

Fig. S10 High-resolution N 1s spectra of a) ZIF-8-900, b) MWCNTs-PDA and c) ZPC-1/1.
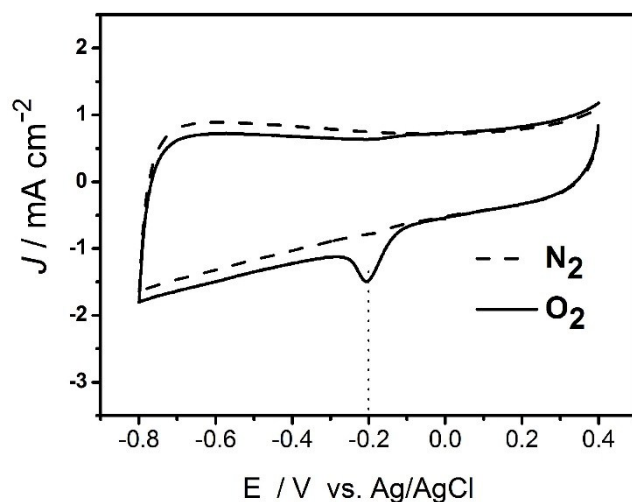
Fig. S11 CV curves of ZPC-1/1-900 in N_2 and O_2- saturated KOH (0.1 M). The scan rate is 100 mV s^{-1}.
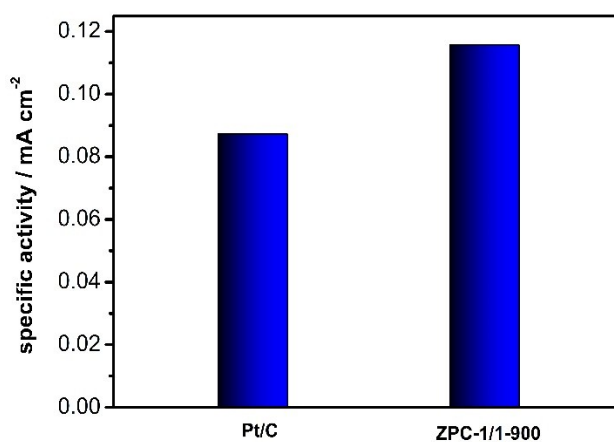
Fig. S12 The specific activities of commercial Pt/C and ZPC-1/1-900 at -0.164 V (vs. Ag/AgCl, saturated KCl, reference electrode).

Table S1. The content of different types of N and Ca

catalyst	*N1*	N2	N3	N(total)	C1	C2	C3	C4	C5	C(total)
ZPC-1/1-800	2.89	1.02	1.05	4.96	43.15	26.29	4.54	5.74	4.22	83.94
ZPC-1/1-900	1.61	0.97	1.40	3.98	48.58	15.70	11.01	9.66	4.75	89.7
ZPC-1/1-1000	0.68	0.50	0.53	1.7	35.40	27.54	13.95	9.01	6.20	92.09

Note: N1: pyridinic-N, N2: pyrrolic-N and N3: quaternary-N; C1: sp^2 C, C2: sp^3 C, C3: C–N or C–O, C4: carbonyl C=O and C5: amide N–C=O or carboxylic COOR.

Table S2. Summary of the metal-free porous doped carbon electrocatalysts reported in correlative literatures.

electrocatalyst	Electron transfer number	Half-potential	Reference
ZPC-1/1-900	3.8	0.774 V	Present work
N3B3-900	3.3	0.674 V	S3
NC900	3.3	0.680 V	S4
Carbon-L	3.7	0.697 V	S5
NGPC-1000-10	3.8	0.764 V	S6
N,S-GN	3.1	0.614 V	S7
N,S-mesoporous GN	3.6	0.664 V	S8
PC-Al-1000	3.4	0.704 V	S9
N-doped carbon nanocages	3.3	0.704 V	S10
g-C3N4@CMK-3	4.0	0.729 V	S11

Note: All potentials are versus to reversible hydrogen electrode (RHE) based on the standard calculation method: in 0.1 M KOH solution (pH = 13), E (RHE) = E (Ag/AgCl) + 0.964, E (RHE) = E (Hg/HgO) + 0.932

Notes and references

[a]*State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, Jilin, China.*
E-mail: xryang@ciac.ac.cn
[b]*University of the Chinese Academy of Sciences, Beijing 100049,China.*

1. K. S. Park, Z. Ni, A. P. Cote, J. Y. Choi, R. Huang, F. J. Uribe-Romo, H. K. Chae, M. O'Keeffe and O. M. Yaghi, *P. Natl. Acad. Sci. USA,*, 2006, **103**, 10186-10191.
2. W. Zhang, Z.-Y. Wu, H.-L. Jiang and S.-H. Yu, *J. Am. Chem. Soc.*, 2014, **136**, 14385-14388.
3. S. Wohlgemuth, T. Fellinger, P. Jaker and M. Antonietti, *J. Mater. Chem. A,* 2013*, 1, 4002-4009.*
4. A. Aijaz; N. Fujiwara and Q. Xu, *J. Am. Chem. Soc.*, 2014, **136**, 6790-6793.
5. P. Zhang, F. Sun, Z. Xiang; Z. Shen, J. Yun, and D. Cao, *Energy Environ. Sci.*, 2014, *7*, 442-450.

6. L. J. Zhang, Z. X. Su, F. L. Jiang, L. L. Yang, J. J. Qian, Y. F. Zhou, W. M. Li and M. C. Hong, *Nanoscale*, 2014, **6**, 6590-6602.

7. W. Ai, Z. Luo, J. Jiang, J. Zhu, Z. Du, Z. Fan, L. Xie, H. Zhang, W. Huang, and T. Yu, *Adv. Mater.* 2014, **26**, 6186–6192.

8. J. Liang, Y. Jiao, M. Jaroniec, S.-Z. Qiao, *Angew. Chem. Int. Ed.* 2012, **51**, 11496-11500.

9. X. Zhao, H. Zhao, T. Zhang, X.Yan, Y. Yuan, H. Zhang, H. Zhao, D. Zhang, G. Zhu and X. Yao, *J. Mater. Chem. A,* 2014, **2**, 11666-11671.

10. S. Chen, J. Bi, Y. Zhao, L. Yang, C. Zhang, Y. Ma, Q. Wu, X. Wang and Z. Hu, *Adv. Mater*. 2012, **24**, 5593-5597.

11. Y. Zheng, Y. Jiao, J. Chen, J. Liu, J. Liang, A. Du, W. Zhang, Z. Zhu, S. C. Smith, M. Jaroniec, G. Q. Lu, and S. Qiao, *J. Am. Chem. Soc.* 2011, **133**, 20116–20119.