Electronic Supplementary Material (ESI) for Materials Advances.

Supporting Information

Green Synthesis of Hierarchical Carbon Coupled with Fe_3O_4/Fe_2C as Efficient Catalyst for Oxygen Reduction Reaction

Ling Zhang[a†], Lili Fan[a†]*, Pu Yang[a], Mengfei Li[a], Haobing Zhang[a], Yucheng Tang[a], Zixi Kang[a], Hailing Guo[b], Rongming Wang[a]* and Daofeng Sun[a]

[a] School of Materials Science and Engineering, College of Science, China University of Petroleum (East China), Qingdao 266580, P. R. China

[b] State Key Laboratory of Heavy Oil Processing, Key Laboratory of Catalysis, China National Petroleum Corp. (CNPC), China University of Petroleum (East China), Qingdao 266580, P. R. China.

* Corresponding author (email: lilifan@upc.edu.cn; rmwang@upc.edu.cn)

† These authors contributed equally to this work.

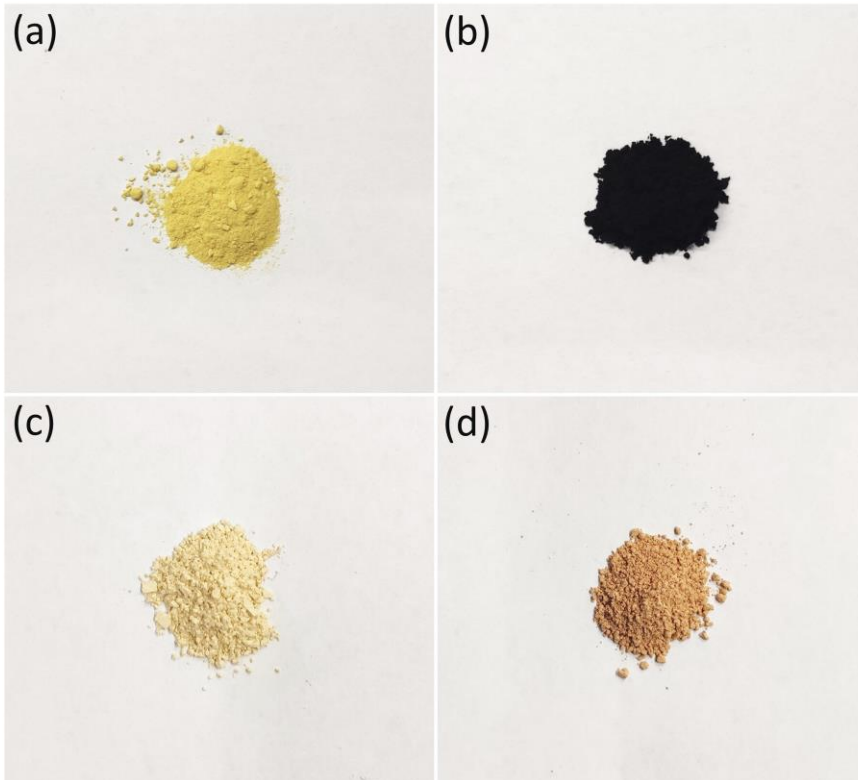


Fig. S1 Digital photos of (a) BM-Fe@NC-120 precursor, (b) BM-Fe@NC-120, (c) BM-IM-120 and (d) Fe-MIL-101 from hydrothermal synthesis.

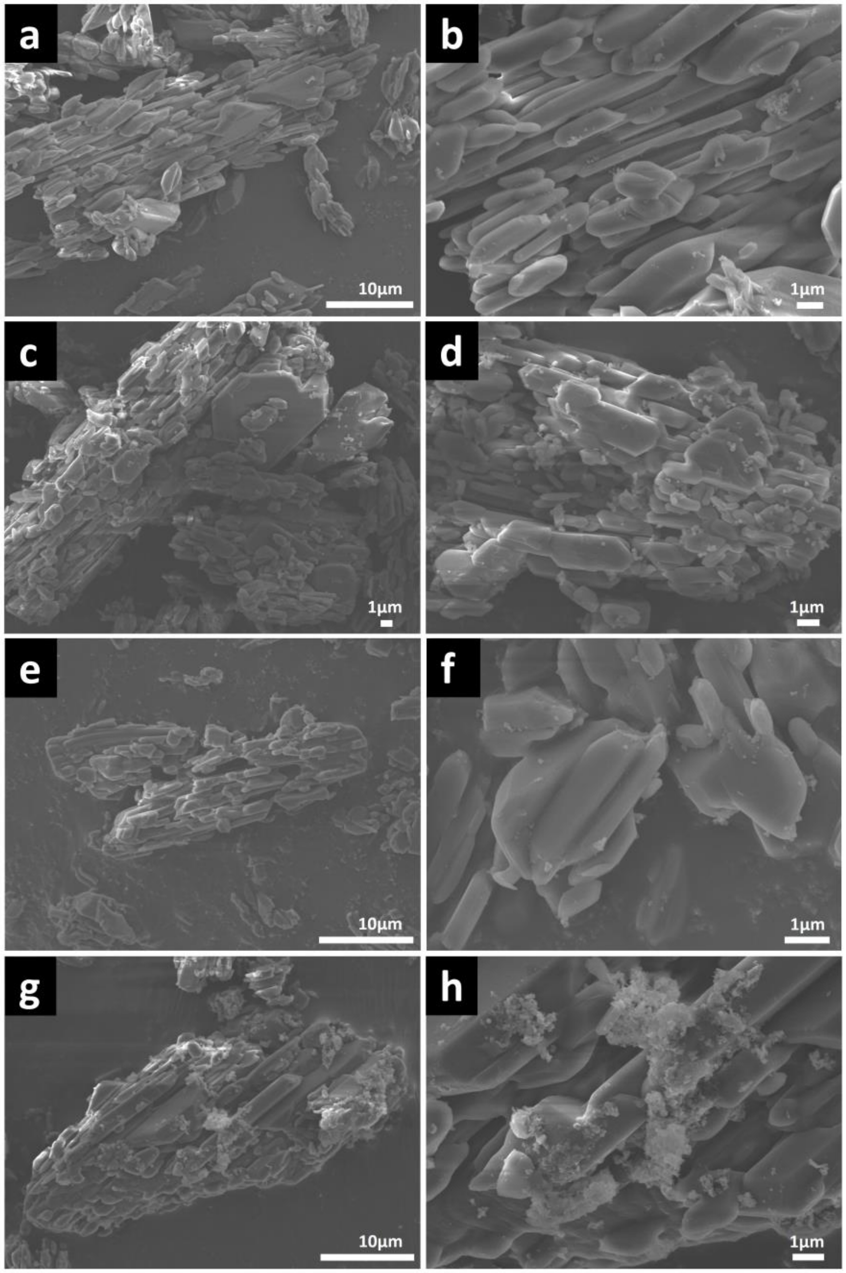


Fig. S2 Different magnification SEM images of (a-b) BM-IM-30, (c-d) BM-IM-60, (e-f) BM-IM-90 and (g-h) BM-IM-150.

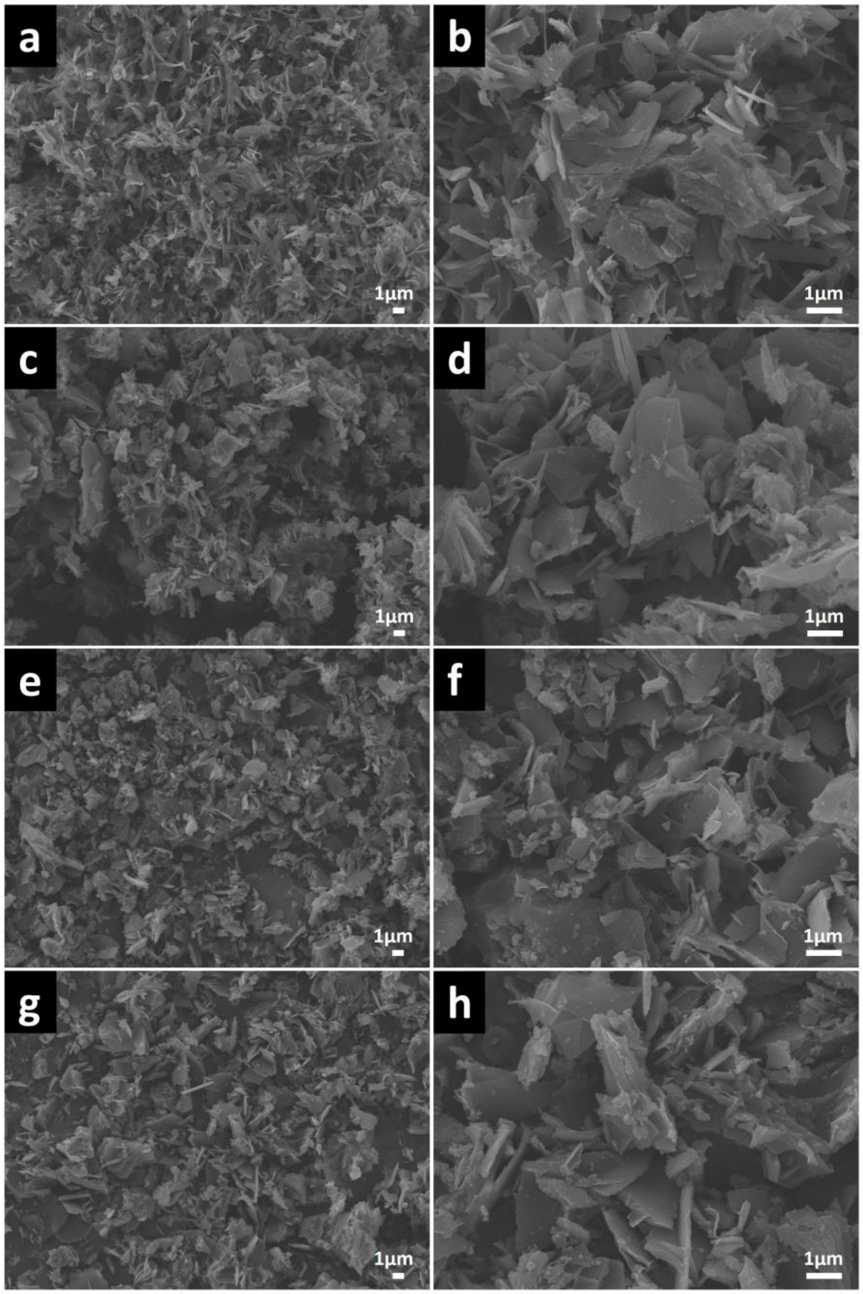


Fig. S3 Different magnification SEM images of (a-b) BM-Fe@NC-30, (c-d) BM-Fe@NC-60, (e-f) BM-Fe@NC-90 and (g-h) BM-Fe@NC-150.

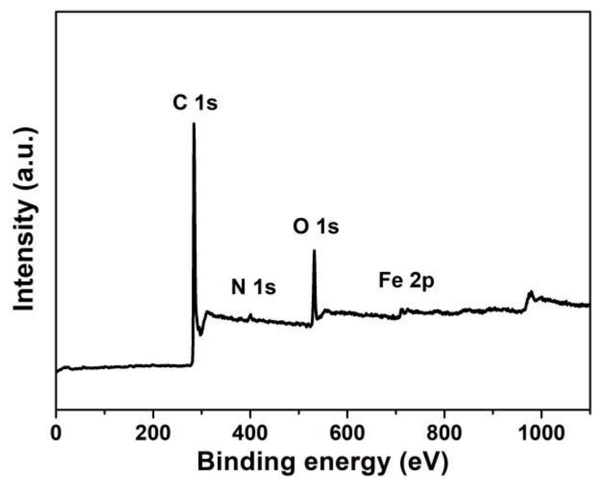


Fig. S4 XPS survey spectrum of BM-Fe@NC-120.

Table S1 XPS results of the surface elemental composition of BM-Fe@NC-120.

Element	C	N	O	Fe
Atomic %	85.27	1.89	12.01	0.84

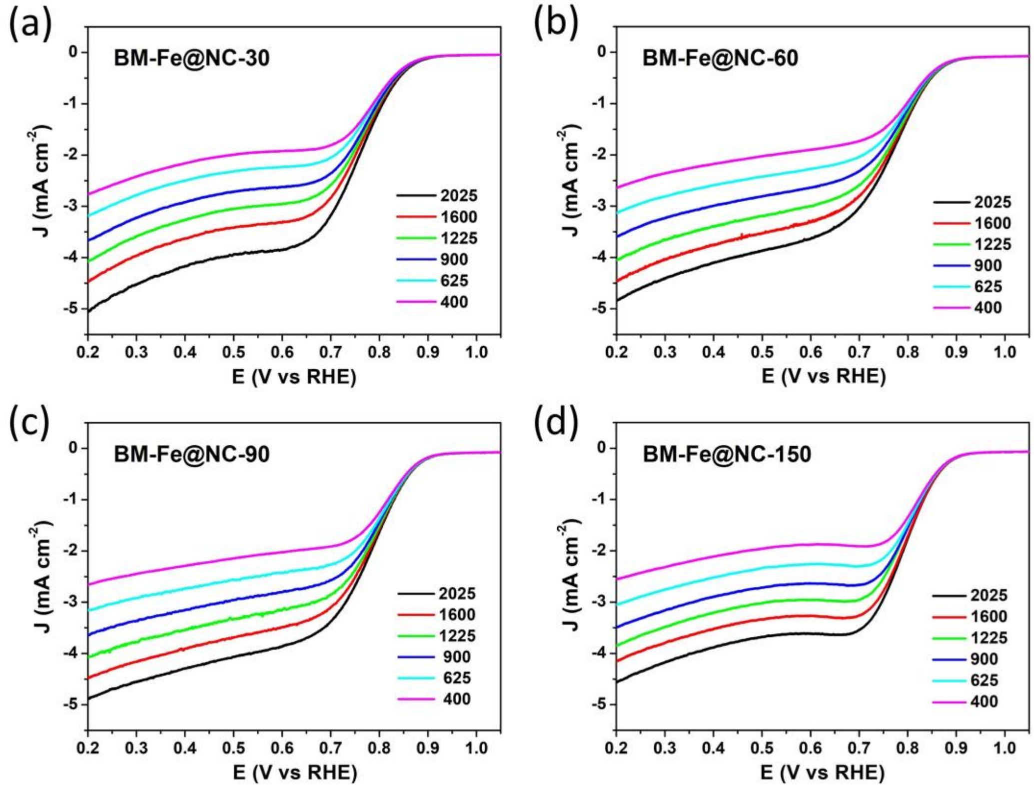


Fig. S5 LSV curves of (a) BM-Fe@NC-30, (b) BM-Fe@NC-60, (c) BM-Fe@NC-90 and (d) BM-Fe@NC-150 at different rotation rates.

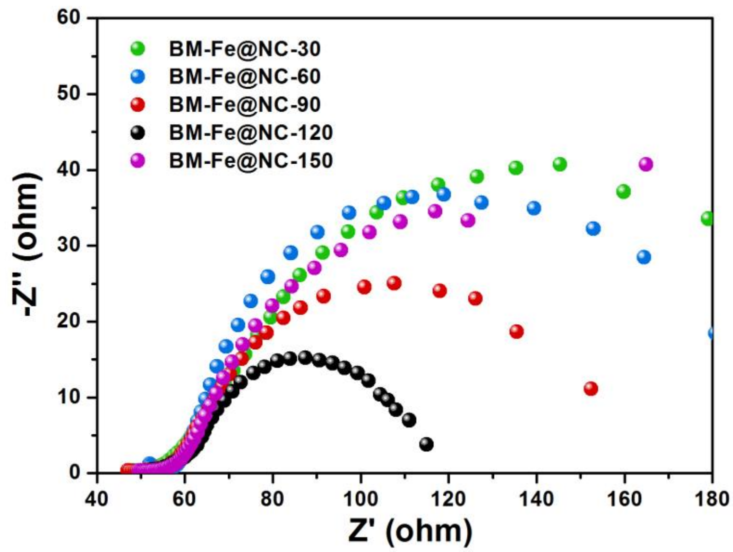
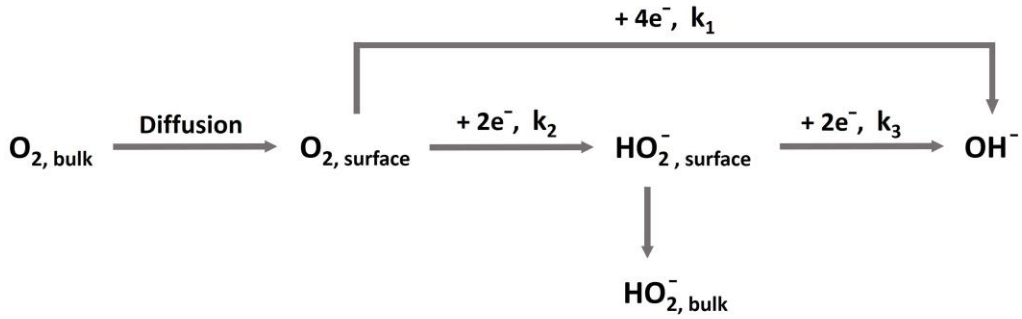


Fig. S6 Nyquist plots of BM-Fe@NC-30, BM-Fe@NC-60, BM-Fe@NC-90, BM-Fe@NC-120 and BM-Fe@NC-150.



Scheme 1 Reaction scheme for the electrochemical reduction of oxygen in alkaline medium.

The following series of Equations proposed by Damjanovic *et al.* and Hsueh *et al*. were used to calculate the rate constants k_1, k_2 and k_3 for BM-Fe@NC-90, BM-Fe@NC-120 and BM-Fe@NC-150:

$$\text{For } O_{2^*}\text{: } z_1\omega^{1/2}(c_{1b} - c_{1^*}) - (k_1 + k_2)c_{1^*} = 0 \quad \text{(S1)}$$

$$\text{For } H_2O_2\text{: } k_2c_{1^*} - \left(k_3 + z_2\omega^{1/2}\right)c_{2^*} = 0 \quad \text{(S2)}$$

$$I_d = 2S_DF[(2k_1 + k_2)c_{1^*} + k_3c_{2^*}] \quad \text{(S3)}$$

$$I_r = 2S_DFNZ_2\omega^{1/2}c_{2^*} \quad \text{(S4)}$$

$$c_{1^*} = c_{1b}\left[1 - \frac{I_r/N + I_d}{I_{rl}/N + I_{dl}}\right]$$

As $I_r \ll I_d, I_d \ll I_{dl}$, the equation simplified to:

$$c_{1^*} = c_{1b}\left[1 - \frac{I_d}{I_{dl}}\right]$$

$$\frac{I_d}{I_r} = \frac{1 + 2k_1/k_2}{N} + \frac{2(1 + k_1/k_2)}{Nz_2}k_3\omega^{-1/2} \quad \text{(S5)}$$

$$\frac{I_{dl}}{I_{dl} - I_d} = 1 + \frac{k_1 + k_2}{z_1}\omega^{-1/2} \quad \text{(S6)}$$

$$k_1 = Z_1S_2\frac{I_1N - 1}{I_1N + 1} \quad \text{(S7)}$$

$$k_2 = \frac{2Z_1S_2}{I_1N + 1} \quad \text{(S8)}$$

$$k_3 = \frac{NZ_2S_1}{I_1N + 1} \quad \text{(S9)}$$

where I_d is the disk current, I_r is the ring current, I_{dl} is the disk diffusion limited current determined by RDE treatment, I_1 and S_1 are respectively the intercept and slope of the plot of I_d/I_r

vs $\omega^{-1/2}$, S_2 is the slope of the plot of $\frac{I_{dl}}{I_{dl}-I_d}$ vs $\omega^{-1/2}$, $Z_1 = 0.2D_{O_2}^{2/3}v^{-1/6}$ and $Z_2 = 0.2D_{H_2O_2}^{2/3}v^{-1/6}$. The $D_{H_2O_2}$ presents the diffusion coefficient of H_2O_2 ($D_{H_2O_2} = 1.18 \times 10^{-5} cm^2\, s^{-1}$ in 0.1 M KOH)

Table S2 Comparison of the electrocatalytic performance of BM-Fe@NC-120 with other reported carbon materials in 0.1 M KOH solution.

Catalysts	Half-wave Potential (V)	Current density (mA cm^{-2})	Onset Potential (V)	Electron transfer number	Reference
CoO@Co/N-rGO	0.81	4.6	0.95	3.97	J. Mater. Chem. A, 2017 [1]
Co_9S_8/C	0.778	--	0.892	3.7	Nanoscale, 2019 [2]
Fe-N-CNTs	0.784	5.443	0.980		Appl. Surf. Sci., 2019 [3]
Co−C_3N_4/ CNT	0.83	5	0.9	4	J. Am. Chem. Soc., 2017 [4]
Fe_3O_4@NHCS	0.875	5.85	--	4.02	Nano Res., 2019 [5]
Fe-N_x-C	0.91	5.44	1.05	3.9	Adv. Funct. Mater., 2018 [6]
CIAC-126&CMK	0.786	3.86	0.874	3.76	ACS Appl. Nano Mater. 2019 [7]
Co/CoP–HNC	0.82	7.78	0.95	4.0	Mater. Horiz., 2018 [8]
CoNC-CNF	0.80	5.9	--	3.96	Small, 2018 [9]
Co@Co_3O_4/N-C	0.81	5.5	0.89	3.83	Chem. Commun., 2018 [10]
C@CoC_x	0.8	5.4	0.92	3.92	ACS Appl. Nano Mater., 2019 [11]
Cu@Cu-N-C	0.85	5.4	0.97	3.9	Small, 2019 [12]
BM-Fe@NC-120	0.80	5.08	0.89	3.95	This work

References:

1. X. X. Liu, J. B. Zang, L. Chen, L. B. Chen, X. Chen, P. Wu, S. Y. Zhou and Y. H. Wang, *J. Mater. Chem. A*, 2017, **5**, 5865-5872.

2. L. Li, H. G. Li Song, W. Xia, C. Jiang, B. Gao, C. Wu, T. Wang and A. J. He, *Nanoscale*, 2019, **11**, 901-

907.

3. Z. Lu, B. Liu, W. Dai, L. Ouyang and J. Ye, *Appl. Surf. Sci.*, 2019, **463**, 767-774.
4. Y. Zheng, Y. Jiao, Y. Zhu, Q. Cai, A. Vasileff, L. H. Li, Y. Han, Y. Chen and S. Qiao, *J. Am. Chem. Soc.*, 2017, **139**, 3336-3339.
5. Y. Li, H. Huang, S. Chen, X. Yu, C. Wang and T. Ma, *Nano Res.*, 2019, **12**, 2774-2780.
6. J. Han, X. Meng, L. Lu, J. Bian, Z. Li and C. Sun, *Adv. Funct. Mater.*, 2019, **29**, 1808872.
7. X. Hang, W. Yang, S. Wang, H. Han, W. Liao and J. Jia, *ACS Appl. Nano Mater.*, 2019, **2**, 4232-4237.
8. Y. Hao, Y. Xu, W. Liu and X. Sun, *Mater. Horiz.*, 2018, **5**, 108-115.
9. W. Zhang, X. Yao, S. Zhou, X. Li, L. Li, Z. Yu and L. Gu, *Small*, 2018, **14**, 1800423.
10. Y. Wang, T. Hu, Y. Qiao, Y. Chen and L. Zhang, *Chem. Commun.*, 2018, **54**, 12746-12749.
11. S.A. Rasaki, H. Shen, T. Thomas and M. Yang, *ACS Appl. Nano Mater.*, 2019, **2**, 3662-3670.
12. T. Wang, R. Yang, N. Shi, J. Yang, H. Yan, J. Wang, Z. Ding, W. Huang, Q. Luo, Y. Lin, J. Gao and M. Han, *Small*, 2019, **15**, 1902410.