Supporting information

The synthesis of atomic Fe embedded in bamboo-CNTs grown on graphene as a superior CO_2 electrocatalyst

Huinian Zhang,[a, b] Jie Wang,[a, b] Zheng Zhao,[a, b] Huifang Zhao,[a, b] Miao Cheng,[a, b] Anni Li,[a] Congwei Wang,[a] Junying Wang*[, a] and Junzhong Wang**[, a]

a CAS Key Laboratory of Carbon Materials, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, China

b University of Chinese Academy of Sciences, Beijing 100049, China

**Corresponding Author: Junying Wang, E-mail: wangjy@sxicc.ac.cn;*

***Corresponding Author: Junzhong Wang, E-mail: wangjz@sxicc.ac.cn.*

Chemicals and materials

Graphite paper (99.95%, Qingdao Huarun Graphite Co., Ltd.), 1-buty-3-methylimidazolium Tetrachloroferrate ([BMIM]$FeCl_4$) (98%, Linzhou Keneng Materials Technology Co., Ltd), hydrochloric acid (HCl, 37%), sulfuric acid (H_2SO_4, 18 mol/L), melamine (Sinopharm Chemical Reagent Co., Ltd.) Nafion solution (5 wt%) and Nafion 117 membrane were supplied by Alfa Aesar, carbon paper (Toray TGP-H-060, Toray Industries Inc).

Additional Figures

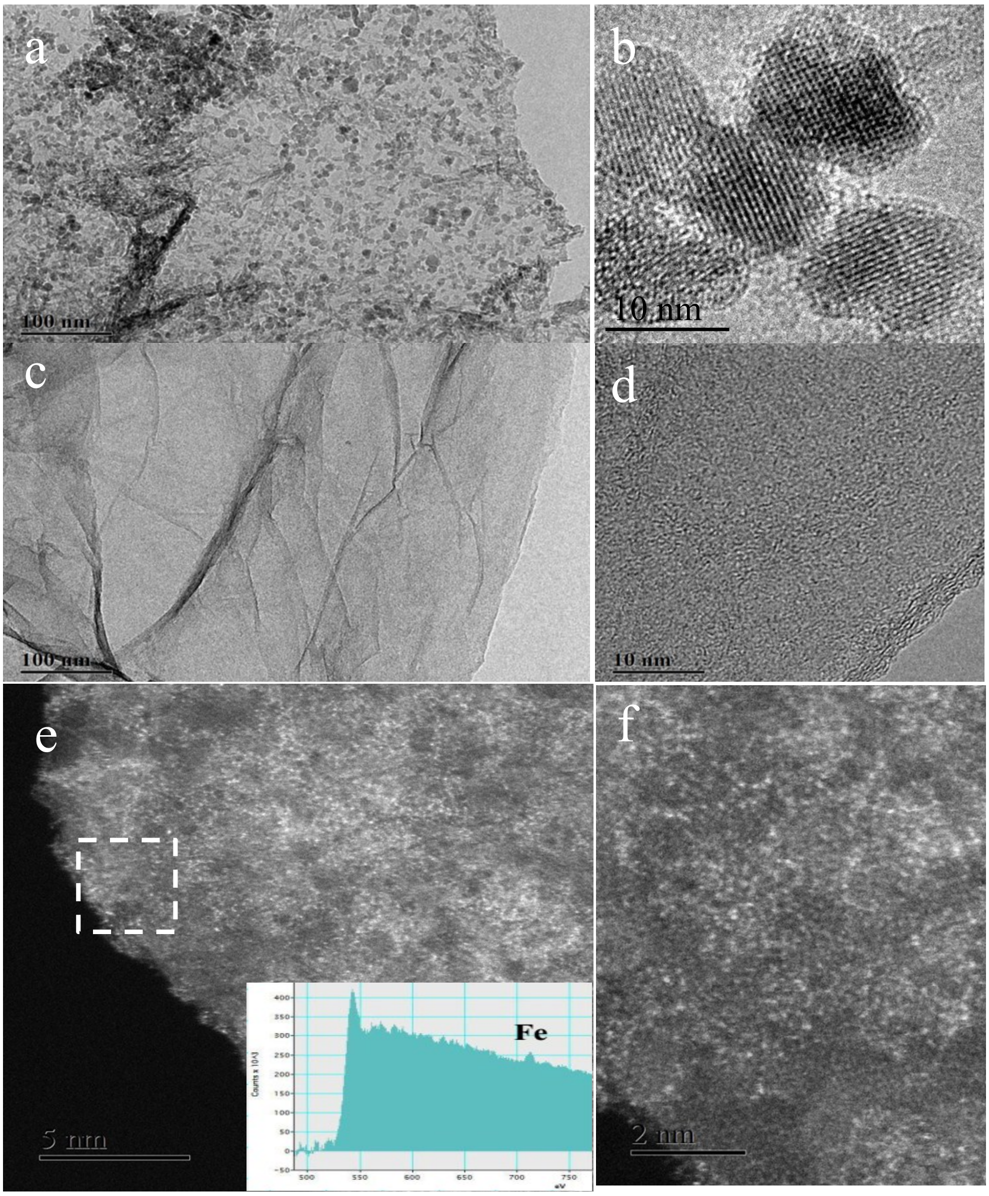

Fig. S1 TEM images of the samples of Fe/G that was prepared by electrochemical process of atomic Fe into graphene in the ionic liquid [BMIM]$FeCl_4$. (a, b) before washing with HCl, (c, d) after washing with HCl, (e, f) HRTEM images of Fe/G after washing with HCl (inset: EELS atomic spectrum of the Fe element of marked area in (e)).

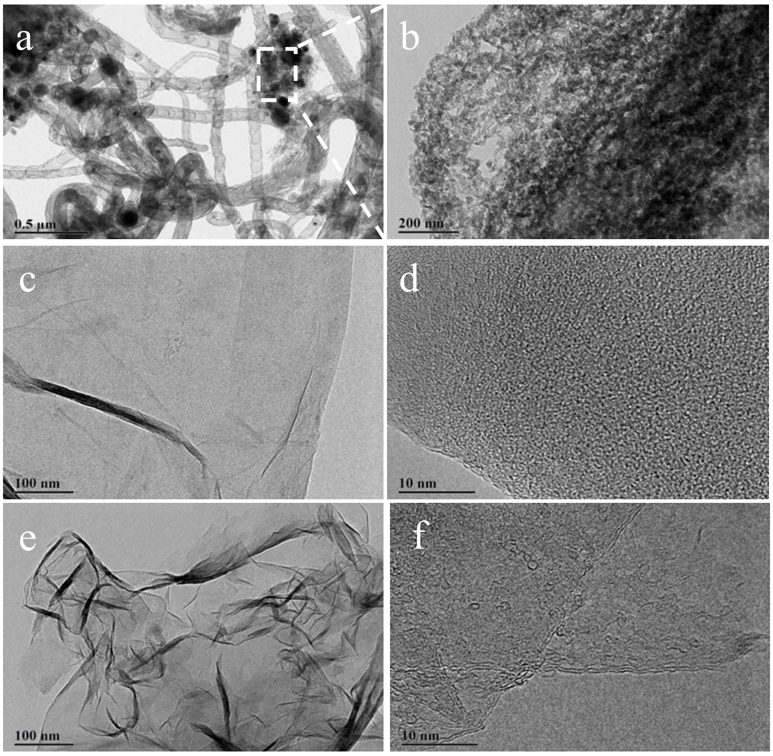

Fig. S2 TEM images of control samples: (a, b) Fe-N/bC, (c, d) Fe-N-G, (e, f) G-N.

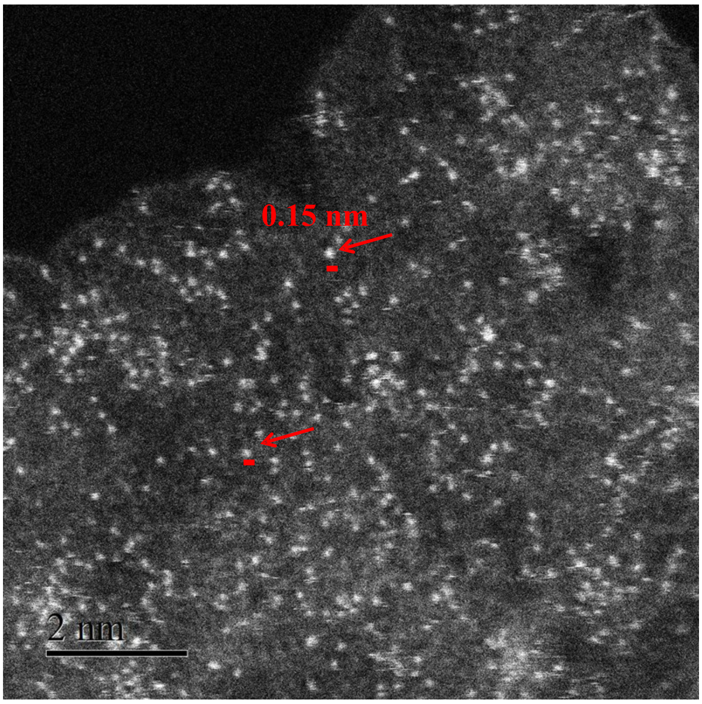

Fig. S3 HAADF-STEM analysis of Fe-N-G/bC catalyst. Atomic Fe was clearly observed in graphene nanosheet.

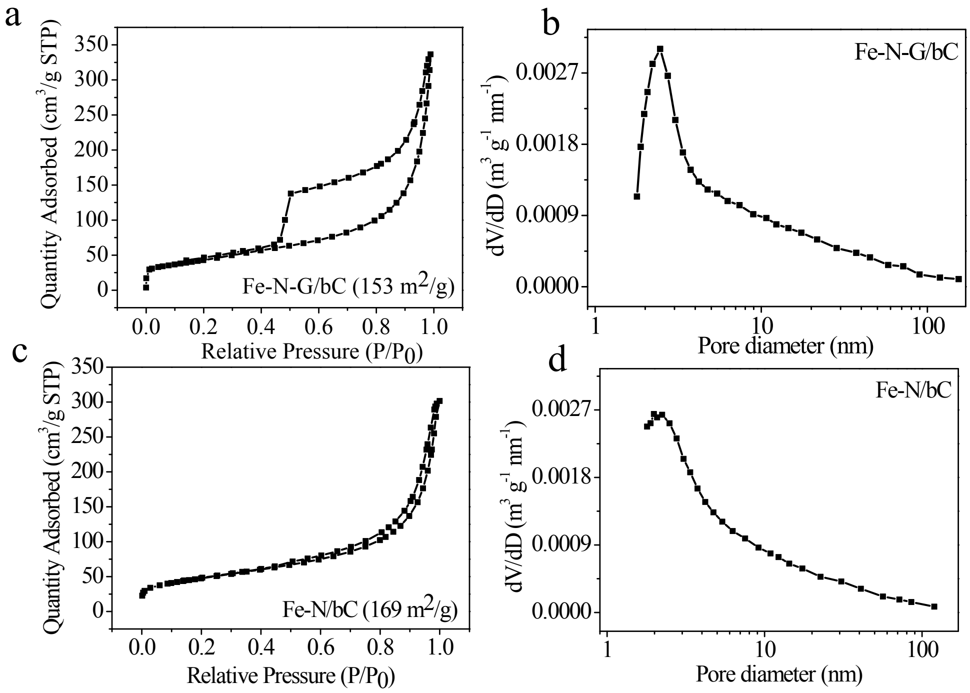

Fig. S4 N_2 adsorption-desorption isotherms and its pore size distribution (right) of Fe-N-G/bC compared with control sample prepared without using graphene: (a, b) Fe-N-G/bC and (c, d) Fe-N/bC.

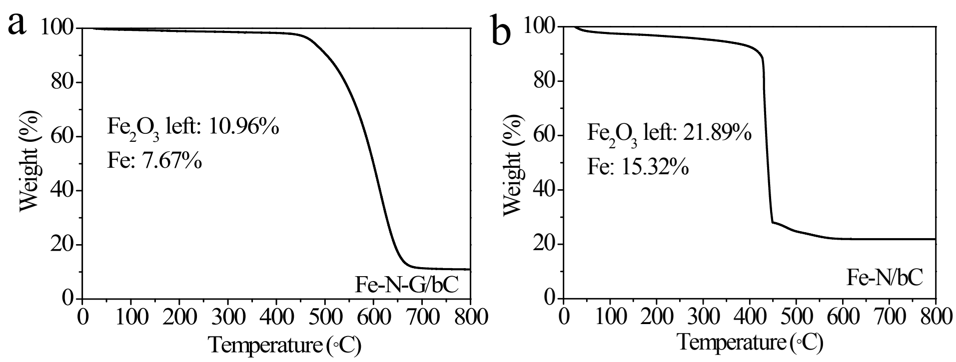

Fig. S5 TGA spectra in air of (a) Fe-N-G/bC compared with control sample (b) Fe-N/bC prepared without using graphene.

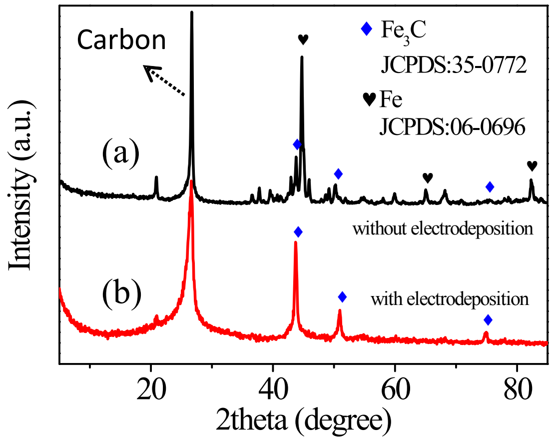

Fig. S6 XRD patterns of Fe-N-G/bC sample synthesized with the graphene electrodeposited by atomic Fe as the starting material and control sample synthesized with blain graphene as the starting material without electrochemical processing. ((a) black line: control sample; (b) red line: Fe-N-G/bC sample).

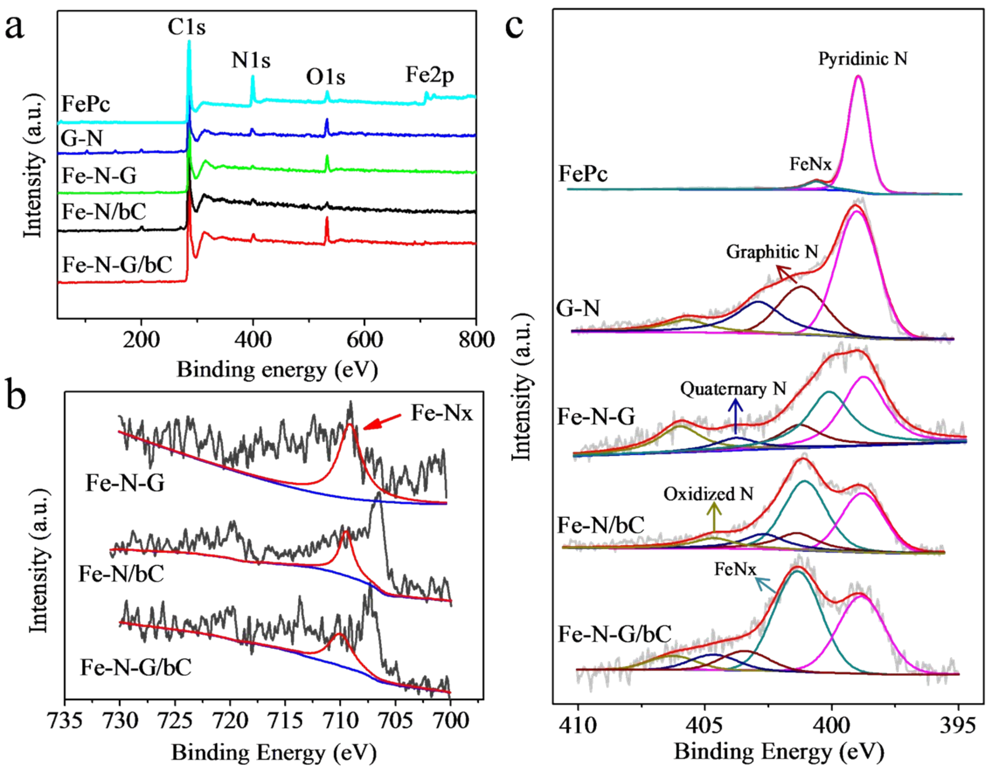

Fig. S7 XPS spectra of Fe-N-G/bC catalyst compared with control samples. (a) XPS full spectra of Fe-N-G/bC compared to G-N, Fe-N-G and Fe-N/bC, (b) XPS spectra of

Fe2p peaks with the deconvolution, (c) XPS spectra of N1s peaks with the deconvolution.

Table S1 Atomic ratios (at. %) of C, N, Fe and O elements in G-N, Fe-N-G, Fe-N/bC and Fe-N-G/bC based on XPS analysis.

Sample	C content (at%)	N content (at%)	Fe content (at%)	O content (at%)
G-N	90.85%	4.20%	-	4.94%
Fe-N-G	91.95%	2.35%	0.33%	5.37%
Fe-N/bC	90.44%	2.82%	0.38%	6.37%
Fe-N-G/bC	94.47%	2.30%	0.52%	2.70%
FePc	75.71%	15.45%	3.54%	5.29%

Table S2 Atomic contents of pyridinic N, Fe-N_x, graphitic N, quaternary N and oxidized N based on fine scan of N 1s of XPS.

Sample	Pyridinic N (at%)	Fe-Nx (at%)	Graphitic N (at%)	Quaternary N (at%)	Oxidized N (at%)
G-N	2.08%	-	0.90%	0.87%	0.35%
Fe-N-G	0.80%	0.73%	0.31%	0.16%	0.34%
Fe-N/bC	0.83%	1.10%	0.35%	0.31%	0.22%
Fe-N-G/bC	0.81%	1.00%	0.19%	0.15%	0.14%
FePc	14.03%	1.42%	-	-	-

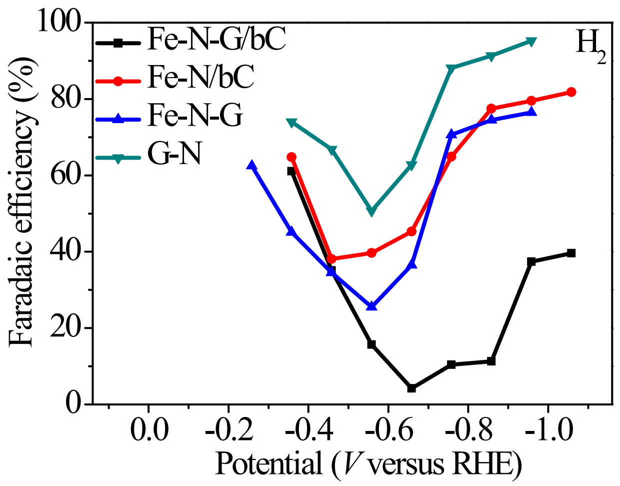

Fig. S8 FE of H_2 at different potentials on Fe-N-G/bC, Fe-N/bC, Fe-N-G and G-N catalysts.

Table S3 Comparison data of the CO_2RR catalytic performances of various materials reported in the literature (references listed in the following) with this work of Fe-N-G/bC catalysts.

Catalyst	Electrolyte	Maximum FE_{CO}	Experimental conditions	overpotential	Reference
Fe-N-G/bC	0.1 M $KHCO_3$	95.8%	-1.3 V (SCE)	-0.55 V	This work
Fe-N-G/bC	0.1 M $KHCO_3$	84.3%	-1.2 V (SCE)	-0.45 V	This work
NCNT	0.1 M $KHCO_3$	80%	-0.8 V (RHE)	-0.69 V	[1]
NCNT-3-700	0.5 M $NaHCO_3$	90%	-0.9 V (RHE)	-0.79 V	[2]
NG	0.1 M $KHCO_3$	85%	-0.58 V (RHE)	-0.47 V	[3]
Fe-N-C	0.1 M $NaHCO_3$	91%	-0.60 V (RHE)	-0.49 V	[4]
Fe-N-C	0.1 M $KHCO_3$	80%	-0.60 V (RHE)	-0.49 V	[5]
Ni-N-G	0.1 M $KHCO_3$	90%	-0.70 V (RHE)	-0.59 V	[6]

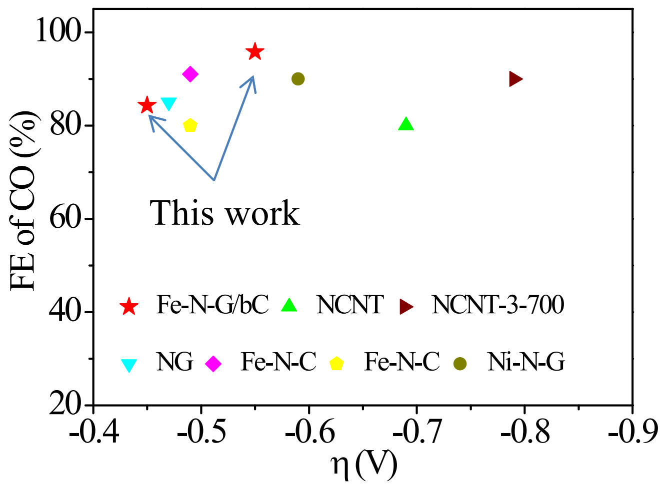

Fig. S9 Comparison of the CO_2RR catalytic performances of various materials reported in the literature (references listed in the following) with this work of Fe-N-G/bC catalysts.

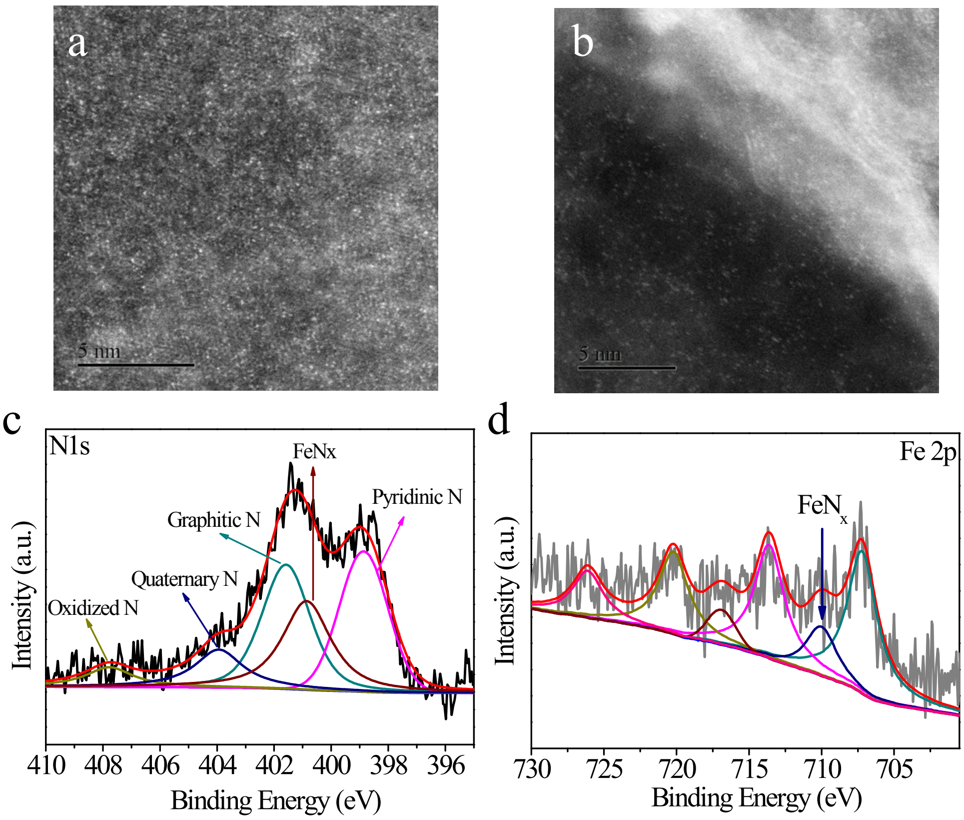

Fig. S10 The high-resolution HAADF-STEM images of Fe-N-G/bC catalyst after durability test for 12 h: (a) atomic Fe on the graphene and (b) atomic Fe in both the nanotubes walls and the interior of the bC; (c) XPS spectra of Fe-N-G/bC catalyst after durability test for 12 h: XPS spectra of N1s peaks with the deconvolution and (d) XPS spectra of Fe2p peaks with the deconvolution.

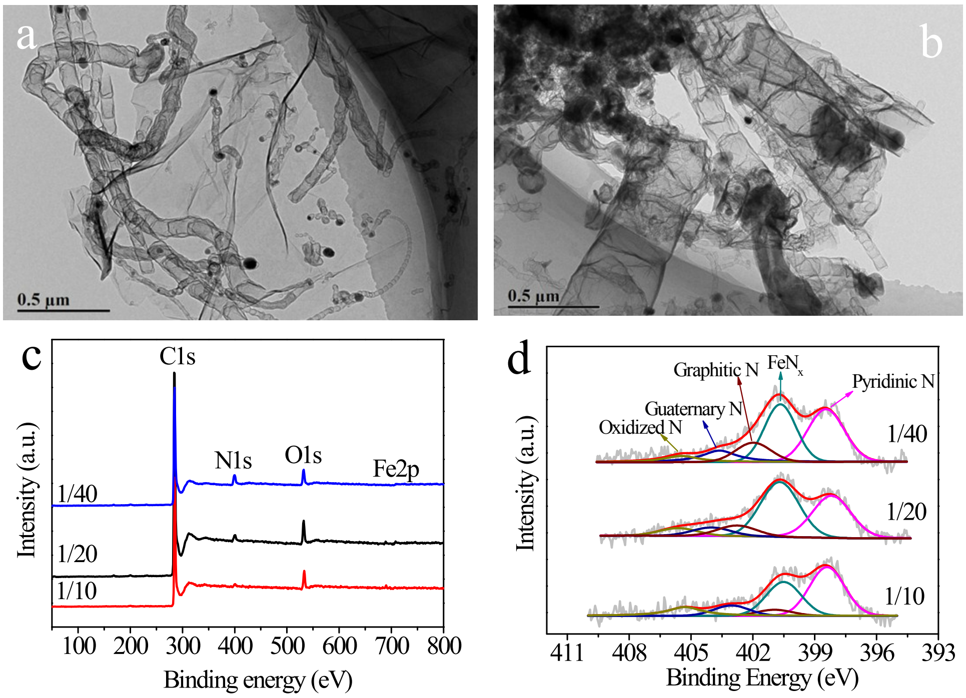

Fig. S11 TEM images of Fe-N-G/bC catalyst synthesized with different mass ratios of graphene and ionic liquid [BMIM]$FeCl_4$ (G/IL) in the starting material (a) 1/10 and (b) 1/40; XPS spectra of Fe-N-G/bC catalyst with different G/IL ratios, (c, d) XPS spectra of (c) survey and (d) N1s with the deconvolution.

Table S4 Atomic ratio (at%) of C, N, Fe and O elements in Fe-N-G/bC with different mass ratios of graphene and ionic liquid (G/IL) in the starting material based on XPS analysis.

Sample	C content (at%)	N content (at%)	Fe content (at%)	O content (at%)
1/10	94.56%	2.04%	0.43%	2.97%
1/20	94.48%	2.30%	0.52%	2.70%
1/40	93.35%	3.14%	0.68%	2.83%

Table S5 Atomic contents of pyridinic N, Fe-N_x, graphitic N, quaternary N and oxidized N based on fine scan of N 1s of XPS.

Sample	Pyridinic N (at%)	Fe-Nx (at%)	Graphitic N (at%)	Quaternary N (at%)	Oxidized N (at%)
1/10	0.89%	0.62%	0.11%	0.19%	0.23%
1/20	0.81%	1.00%	0.19%	0.15%	0.14%
1/40	1.12%	1.05%	0.39%	0.34%	0.23%

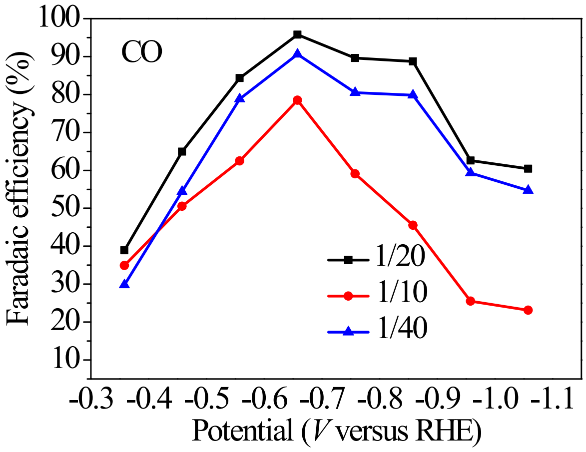

Fig. S12 FE of CO at different potentials of Fe-N-G/bC electrode with different mass ratios (1/10, 1/20 and 1/40) of graphene and ionic liquid (G/IL) in the starting material.

References for Table S3 and Fig. S9

1. J. J. Wu, R. M. Yadav, M. J. Liu, P. P. Sharma, C. S. Tiwary, L. L. Ma, X. L. Zou, X. D. Zhou, B. I. Yakobson, J. Lou and P. M. Ajayan, *ACS Nano*, 2015, **9**, 5364-5371.

2. J. Y. Xu, Y. H. Kan, R. Huang, B. S. Zhang, B. L. Wang, K. H. Wu, Y. M. Lin, X. Y. Sun, Q. F. Li, G. Centi and D. S. Su, *ChemSusChem*, 2016, **9**, 1085-1089.

3. J. J. Wu, M. J. Liu, P. P. Sharma, R. M. Yadav, L. L. Ma, Y. C. Yang, X. L. Zou, X. D. Zhou, R. Vajtai, B. I. Yakobson, J. Lou and P. M. Ajayan, *Nano Lett.* 2016, **16**, 466-470.

4. T. N. Huan, N. Ranjbar, G. Rousse, M. Sougrati, A. Zitolo, V. Mougel, F. Jaouen and M. Fontecave, *ACS Catal.*, 2017, **7**, 1520-1525.

5. A. S. Varela, N. R. Sahraie, J. L. Steinberg, W. Ju, H. S. Oh and P. Strasser, *Angew. Chem. Int. Ed.*, 2015, **54**, 10758-10762.

6. P. P. Su, K. Iwase, S. J. Nakanishi, K. Hashimoto and K. Kamiya, *Small*, 2016, **12**, 6083-6089.