Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Superiority of boron, nitrogen and iron ternary doped carbonized graphene oxide–based catalyst for oxygen reduction in microbial fuel cells

Chun Cao [ab], Liling Wei [a]*, Gang Wang [ab], Jianquan Shen [a]*

[a] *Beijing National Laboratory for Molecular Sciences, Key Laboratory of Green Printing, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P R China*

[b] U*niversity of Chinese Academy of Sciences, Beijing, 100049, P R China*

*Corresponding Author: E–mail: weill@iccas.ac.cn jqshen@iccas.ac.cn

Table S1 The details of feeding raw for preparation of different catalysts

Catalysts	GO content (mg)	PAN content (g)	Mass ratio (PAN/GO)	H_3BO_3
NFe–C	0	0.6	Non	Non
BNFe–C	0	0.6	Non	Y
BNFe–C–G1	10	0.6	60	Y
BNFe–C–G2	20	0.6	30	Y
BNFe–C–G3	40	0.6	15	Y
BNFe–C–G4	80	0.6	7.5	Y

Non represents H_3BO_3 was not introduced, while Y means H_3BO_3 was introduced.

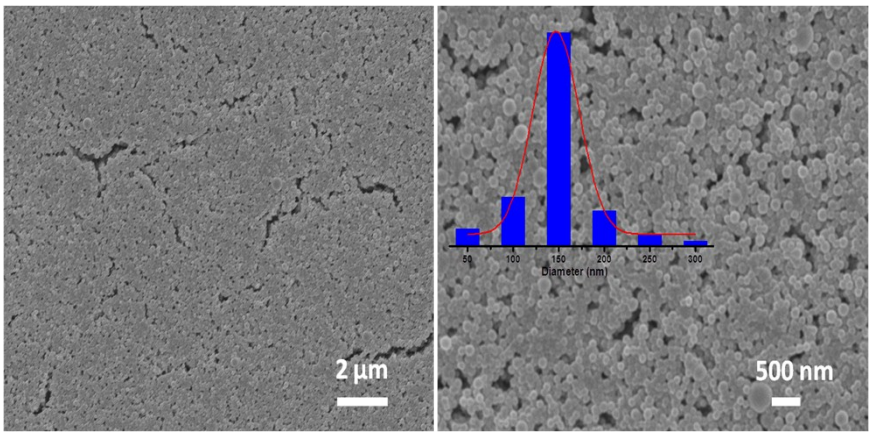

Fig. S1 SEM images of PAN microsphere and the particle size distribution (insert graph).

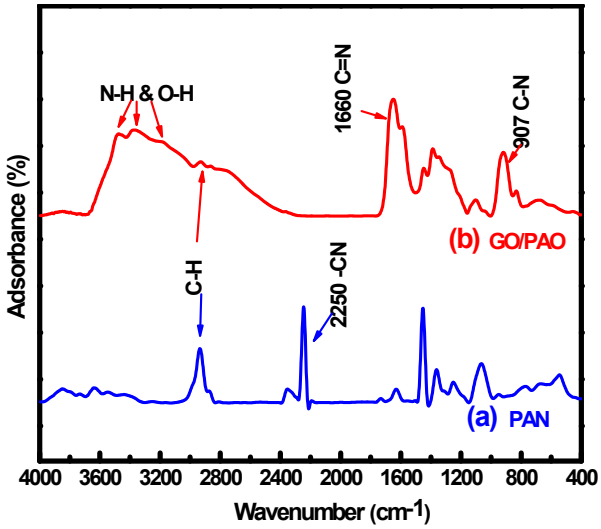

Fig. S2 The FTIR spectrum of PAN (a) and GO/PAO (b).

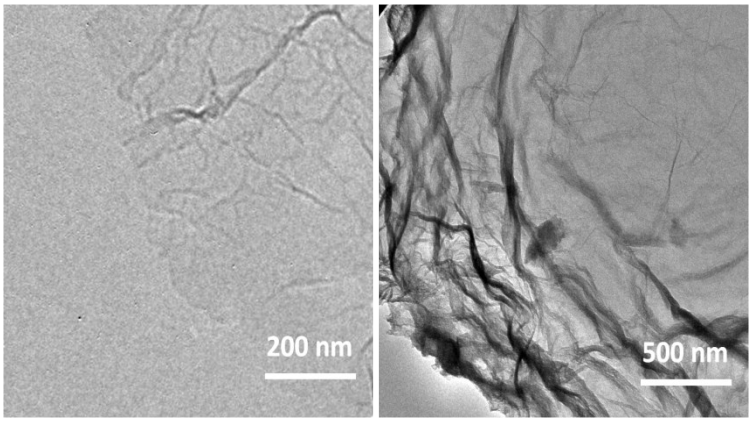

Fig. S3 TEM images of GO.

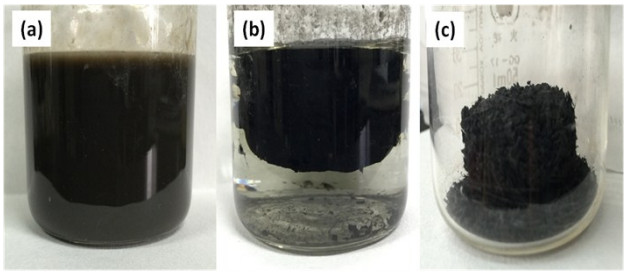

Fig. S4 the images of (a) GO/PAN, (b) G/PAO and (c) BNFe–C–G.

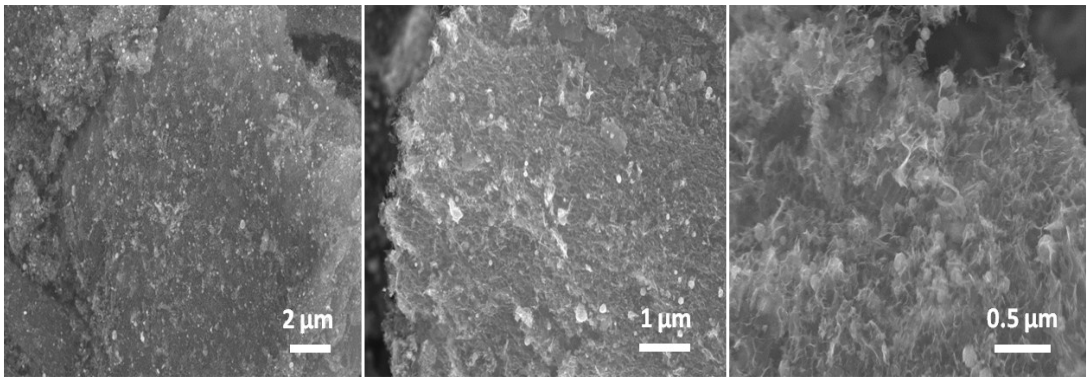

Fig. S5 The low‐magnification SEM images of BNFe–C–G.

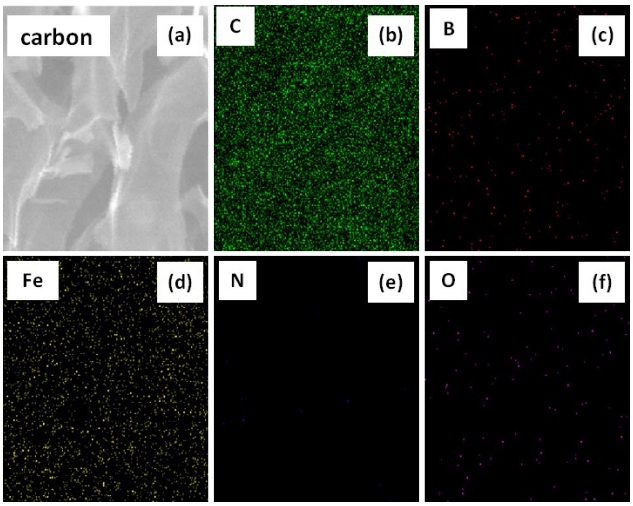

Fig. S6 The SEM–EDS images of carbon layer in BNFe–C–G: (a) SEM image, (b) C element, (c) B element, (d) Fe element, (e) N element and (f) O element.

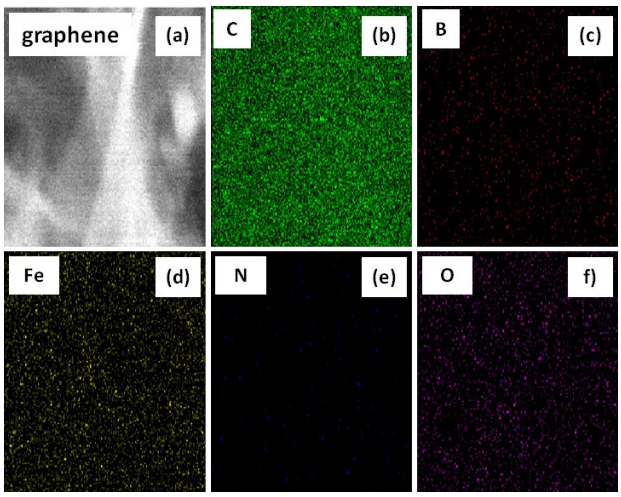

Fig. S7 The SEM–EDS images of graphene that introduced in BNFe–C–G: (a) SEM image, (b) C element, (c) B element, (d) Fe element, (e) N element and (f) O element.

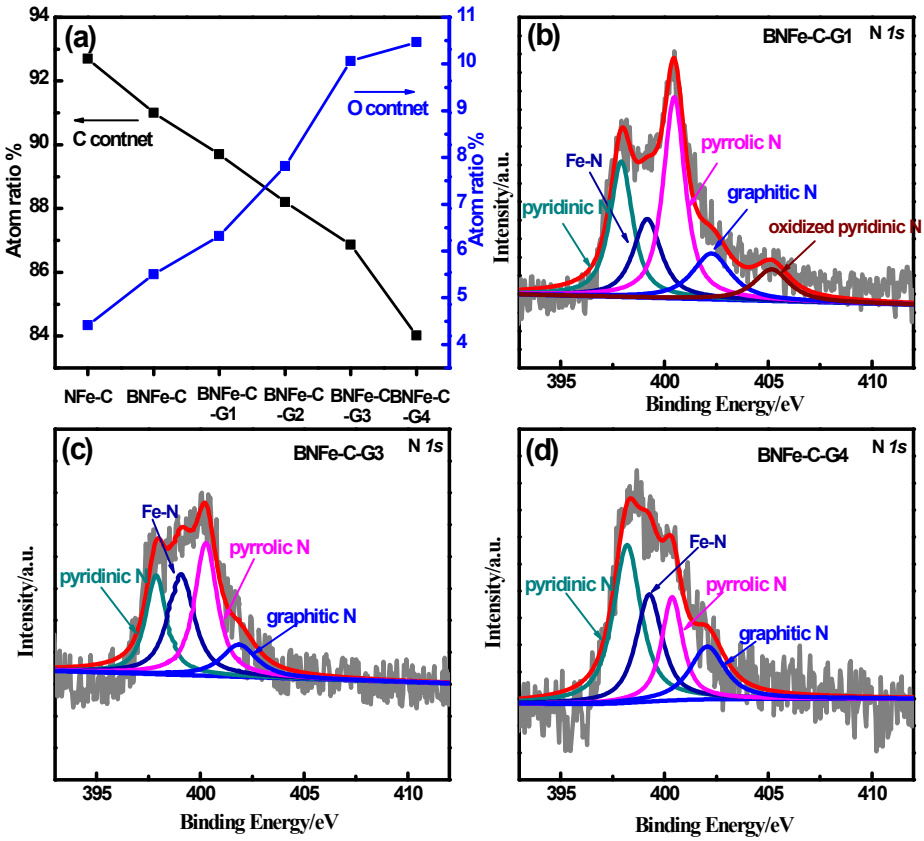

Fig.S8 (a) the variation of C and O in different catalysts; the high–resolution XPS of nitrogen for BNFe–C–G1 (b), BNFe–C–G3 (c) and BNFe–C–G4 (d).

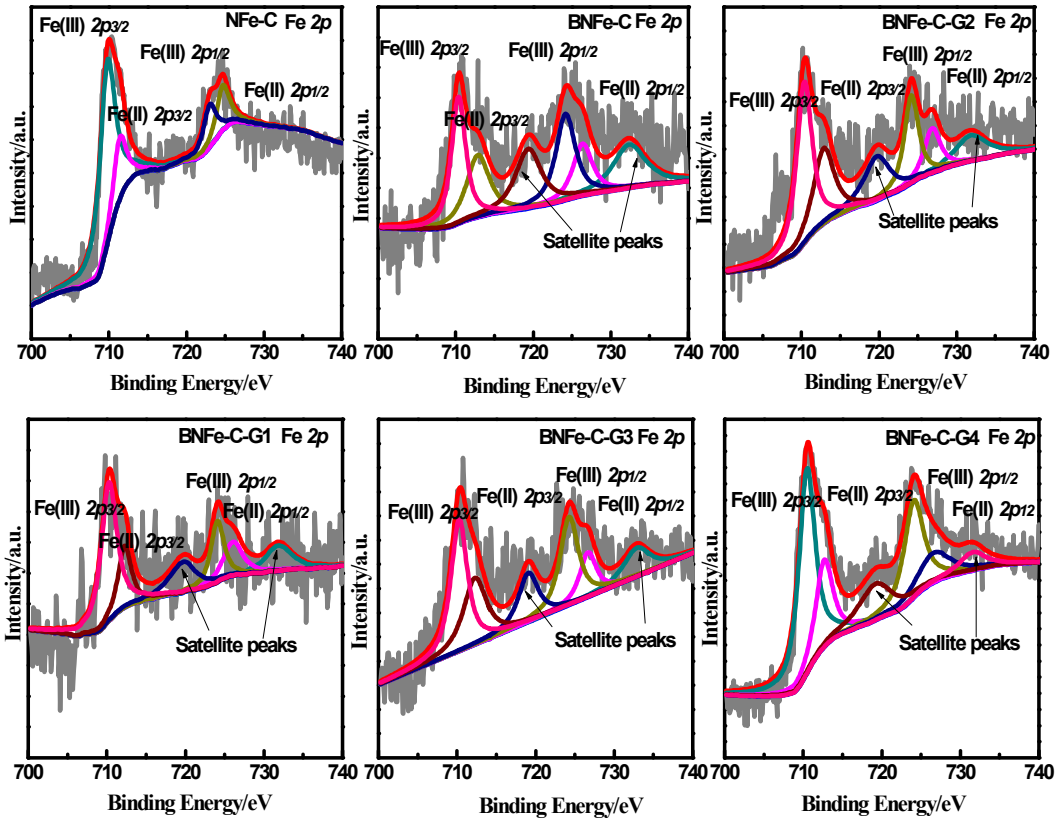

Fig. S9 The high–resolution XPS of Fe 2p within different catalysts.

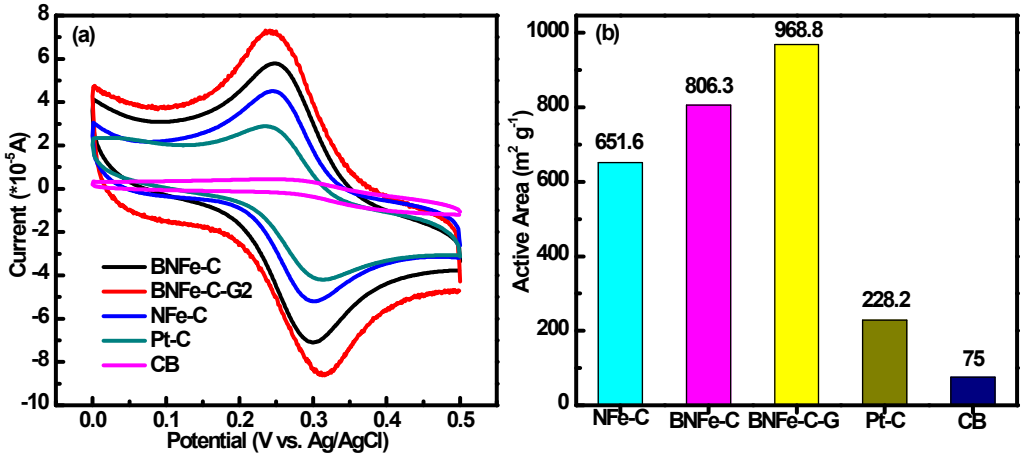

Fig. S10 The CV curves (a) and electrochemical BET (b) of different catalysts measured by well–known Matsuda's equation. The electrolyte was a mixed solution of 5mM potassium ferrocyanide and 0.2 M Na_2SO_4, and the scan potential window was 0 – 0.5 V (vs. Ag/AgCl) with the scan rate of 10 mV s^{-1}.

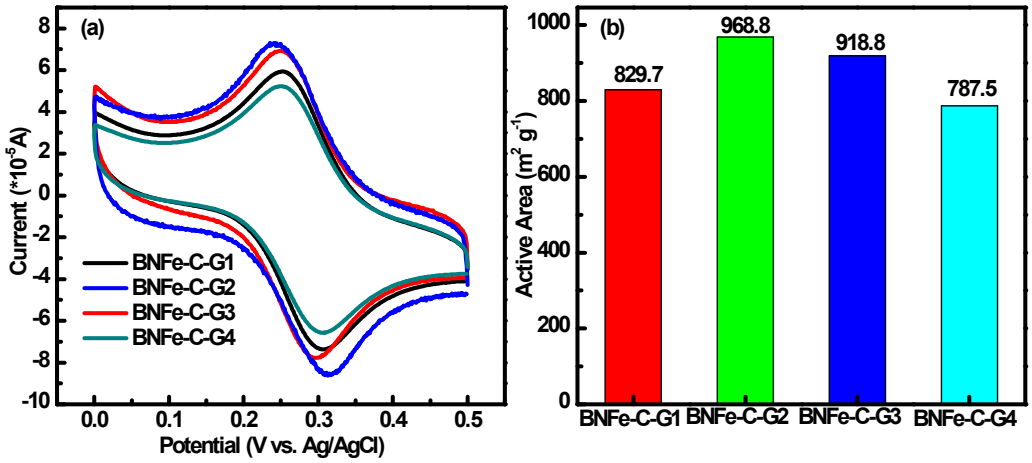

Fig. S11 The CV curves (a) and electrochemical BET (b) of different catalysts measured by well–known Matsuda's equation. The electrolyte was a mixed solution of 5mM potassium ferrocyanide and 0.2 M Na_2SO_4, and the scan potential window was 0 – 0.5 V (vs. Ag/AgCl) with the scan rate of 10 mV s^{-1}.

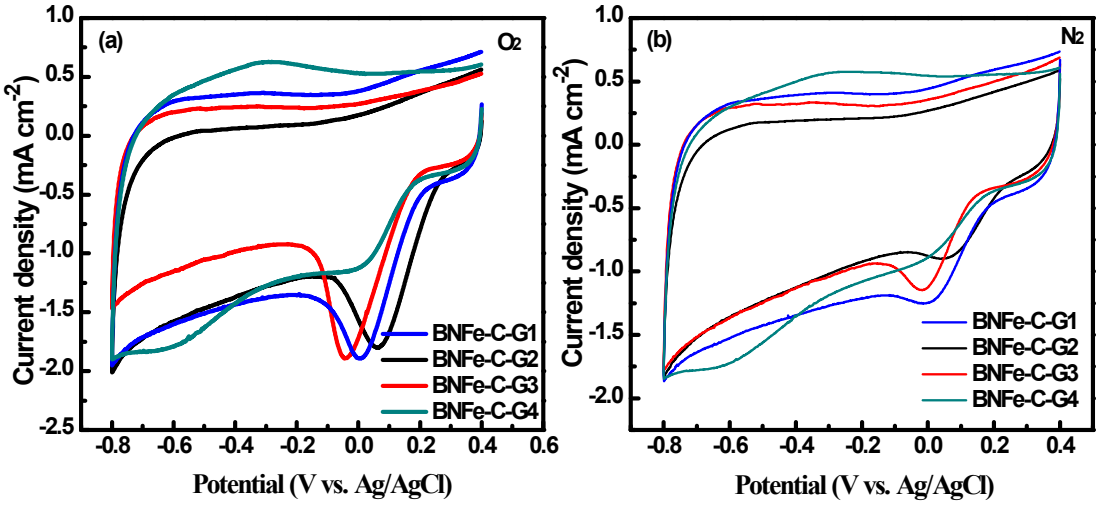

Fig. S12 The CV curves of different catalysts in O_2–saturated (a) and N_2–saturated (b) PBS solution.

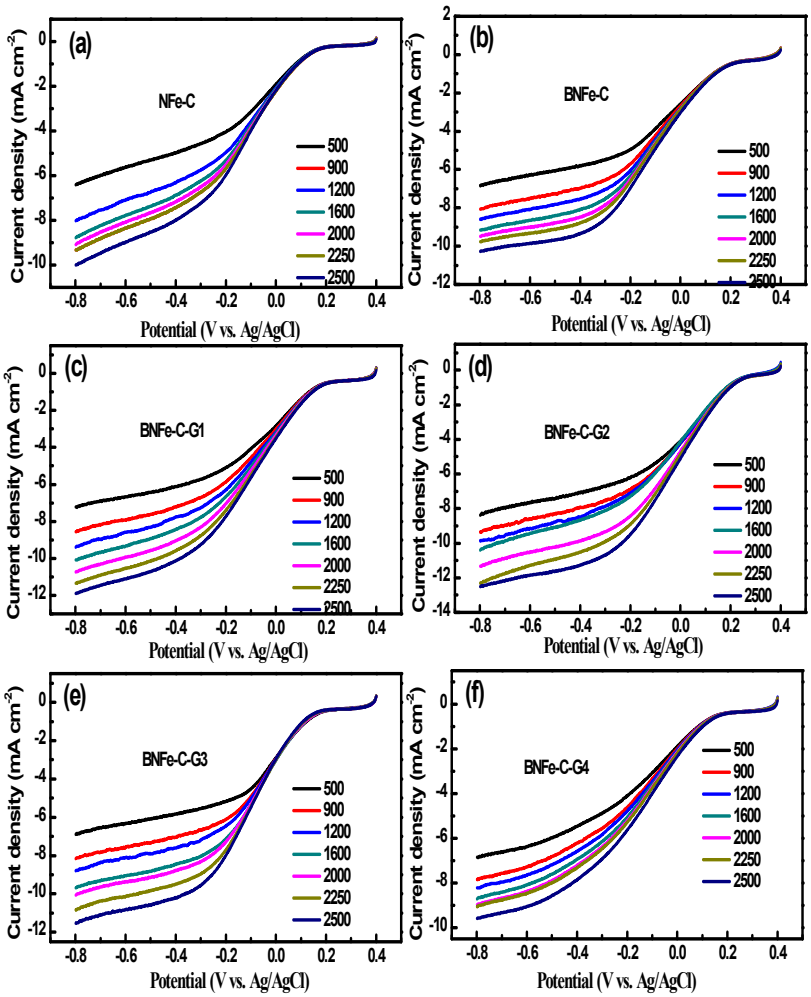

Fig. S13 The LSV curves of different catalysts in O_2–saturated PBS solution at different rotation speeds: (a) NFe－C, (b) BNFe－C, (c) BNFe－C－G1, (d) BNFe－C－G2, (e) BNFe－C－G3, (f) BNFe－C－G4.

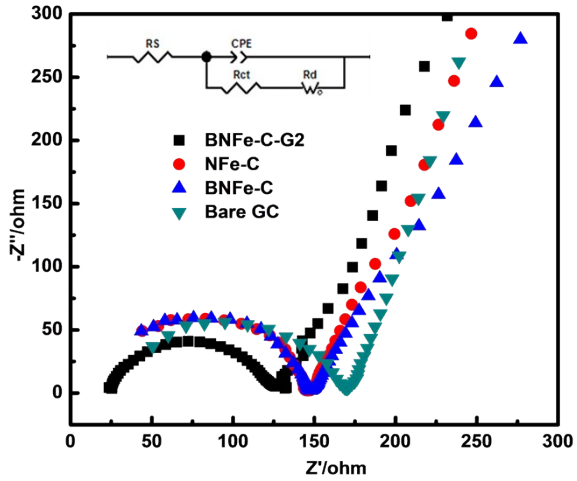

Fig. S14 The EIS plots of different catalysts on RDE (electrolyte: 50 mM PBS).

Table S2 the internal resistance (Rs) and the charge transfer resistance (Rct) of different catalysts on RDE (electrolyte: 50 mM PBS).

Samples	Rs (ohm)	Rct (ohm)
NFe－C	125	38
BNFe－C	121	32
BNFe－C－G2	105	27

Koutecky–Levich equations:

$$\frac{1}{j}=\frac{1}{j_k}+\frac{1}{j_L}=\frac{1}{j_k}+\frac{1}{B\omega^{1/2}} \qquad \text{Eq. S(1)}$$

Where, j represents the measured current density; ω is the angular velocity of the disk ($\omega=2\pi N$, N represents the linear rotation speed (rpm s^{-1})); j_L and j_k represent the limiting diffusion and kinetic current density, respectively; B can be determined from the slope of the Koutecky–Levich plots based on the Levich equation as follows, Eq. (2):

$$B = 0.62nFC_0(D_0)^{2/3}\nu^{-1/6} \qquad \text{Eq. S(2)}$$

Where, n represents the overall number of electrons transferred in oxygen reduction; the constant 0.62 is adopted when the rotating speed is expressed in rad s^{-1}; C_0 is the bulk concentration of O_2 ($C_0=1.2\times10^{-3}$ mol L^{-1}); F is the Faraday constant (F=96,485 C mol^{-1}); ν is the kinetic viscosity of the electrolyte (ν=0.01 cm^2 s^{-1} in 0.1 M PBS); and D_0 is the diffusion coefficient of O_2 in 0.1 M PBS ($D_0 = 1.9\times10^{-5}$ cm^2 s^{-1}).

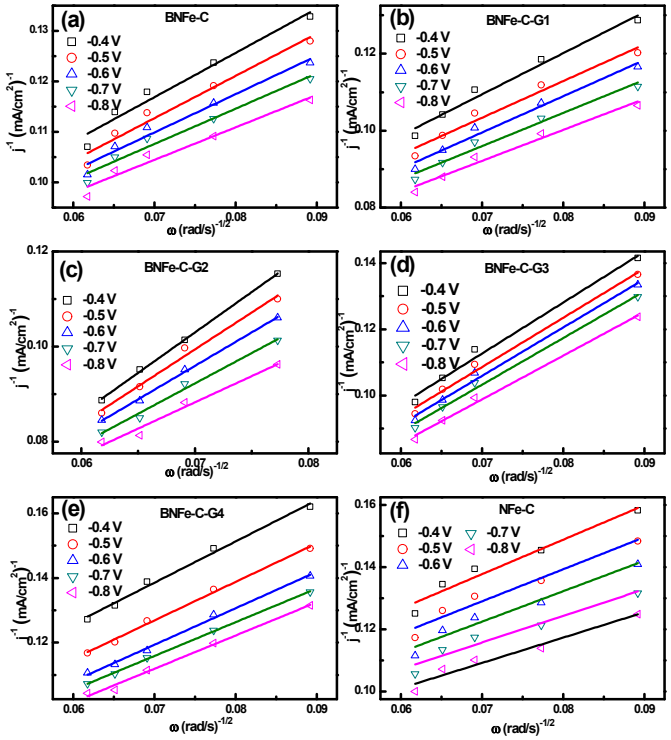

Fig. S15 The Koutecky–Levich plots of different catalysts: (a) BNFe－C, (b) BNFe－C－G1, (c) BNFe－C－G2, (d) BNFe－C－G3, (e) BNFe－C－G4, (f) NFe－C.

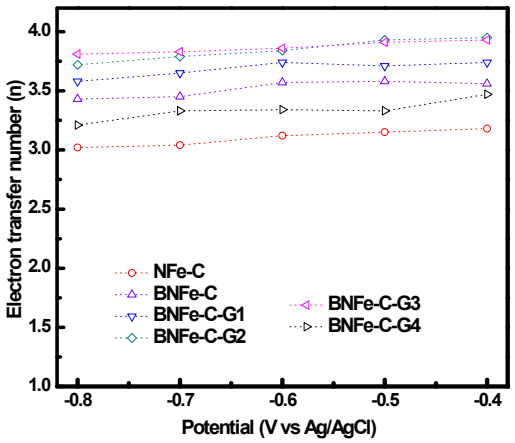

Fig. S16 The electron transfer number of different catalysts calculated from Koutecky–Levich plots.

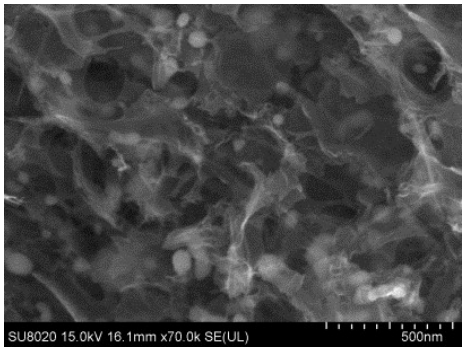

Fig. S17 The SEM image of BNFe–C–G2 after stability testing.

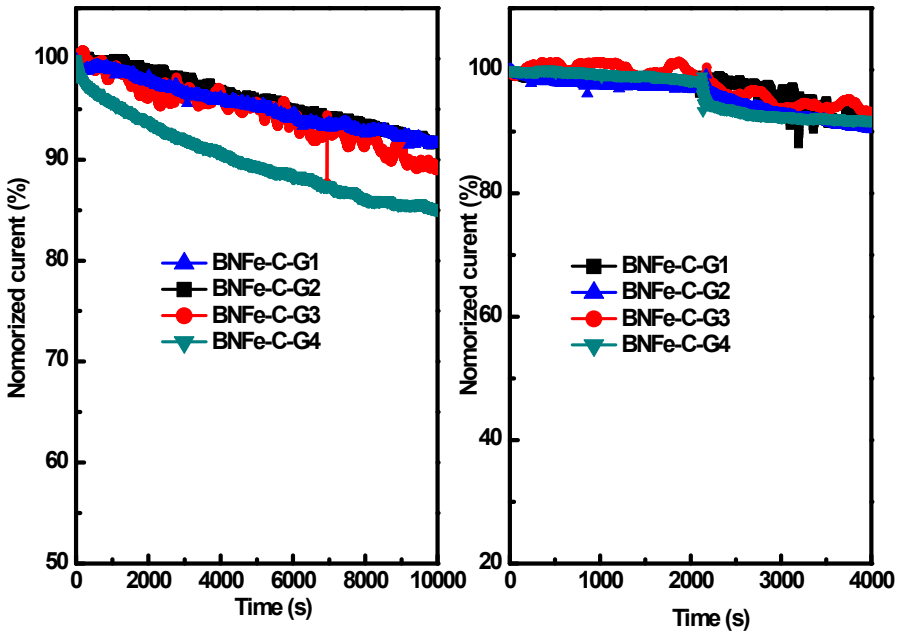

Fig. S18 i–t technique: the stability and resistance to poisoning of BNFe–C–G1, BNFe–C–G2, BNFe–C–G3 and BNFe–C–G4.