Supporting information

for

Identification of functionality of heteroatoms in boron, nitrogen and fluorine ternary doped carbon as robust nitrogen fixation electrocatalyst powered by zinc-air batteries

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Table S1 Quantitative analysis of BNFC-700, BNFC-800 and BNFC-900 electrocatalysts.

Electrocatalyst	B1s	N1s	F1s
BNFC-700	B_4C:1.88%	B-N: 10.36%	Ionic C-F:49.37%
	BC_3: 25.82%	Pyridinic N :28.94%	C-F:23.91%
	BC_2O: 54.21%	Pyrrolic N: 38.67%	Semi-ionic
	BCO_2: 14.34%	Graphitic N:9.37%	C-F:26.72%
	B-N: 3.75%	Oxidized N:12.66%	
BNFC-800	B_4C:14.20%	B-N: 5.33%	Ionic C-F:17.01%
	BC_3:37.56%	Pyridinic N: 29.67%	C-F:56.81%
	BC_2O:29.72%	Pyrrolic N: 29.02%	Semi-ionic
	BCO_2:10.68%	Graphitic N:22.45%	C-F:26.18%
	B-N: 7.84%	Oxidized N:13.53%	
BNFC-900	B_4C:12.95%	B-N: 10.24%	Ionic C-F:48.9%
	BC_3:22.82%	Pyridinic N:21.44%	C-F:9.12%
	BC_2O:29.50%	Pyrrolic N: 24.15%	Semi-ionic
	BCO_2:30.05%	Graphitic N:27.53%	C-F:41.98%
	B-N: 4.68%	Oxidized N:16.64%	

Table S2 Quantitative analysis of BNFC-800 electrocatalysts before and after stability test.

Electrocatalyst	B1s	N1s	F1s
BNFC-800	B_4C:14.20%	B-N: 5.33%	Ionic C-F:17.01%
	BC_3:37.56%	Pyridinic N: 29.67%	C-F:56.81%
	BC_2O:29.72%	Pyrrolic N: 29.02%	Semi-ionic
	BCO_2:10.68%	Graphitic N:22.45%	C-F:26.18%
	B-N: 7.84%	Oxidized N:13.53%	
BNFC-800 after 10 h NRR catalysis in 0.05 M H_2SO_4	B_4C:15.08%	B-N: 5.39%	Ionic C-F:17.89%
	BC_3:37.76%	Pyridinic N: 30.42%	C-F:57.60%
	BC_2O:28.13%	Pyrrolic N: 28.84%	Semi-ionic
	BCO_2:11.41%	Graphitic N:22.59%	C-F:24.51%
	B-N: 7.62%	Oxidized N:12.76%	
BNFC-800 after 10 h OER catalysis in 1 M NaOH	B_4C:13.74%	B-N: 5.16%	Ionic C-F:18.81%
	BC_3:34.79%	Pyridinic N:29.58%	C-F:56.76%
	BC_2O:29.68%	Pyrrolic N: 28.64%	Semi-ionic
	BCO_2:13.97%	Graphitic N:22.70%	C-F:24.43%
	B-N: 7.82%	Oxidized N:13.92%	

Table S3 Quantitative analysis of C, B, N, F elements in BNFC-800 electrocatalyst before and after stability test.

Element	BNFC-800	BNFC-800 after 10 h NRR catalysis in 0.05 M H_2SO_4	BNFC-800 after 10 h OER catalysis in 1 M NaOH
B	1.31%	1.26%	1.21%
N	5.79%	5.62%	5.73%
F	1.01%	0.94%	0.92%

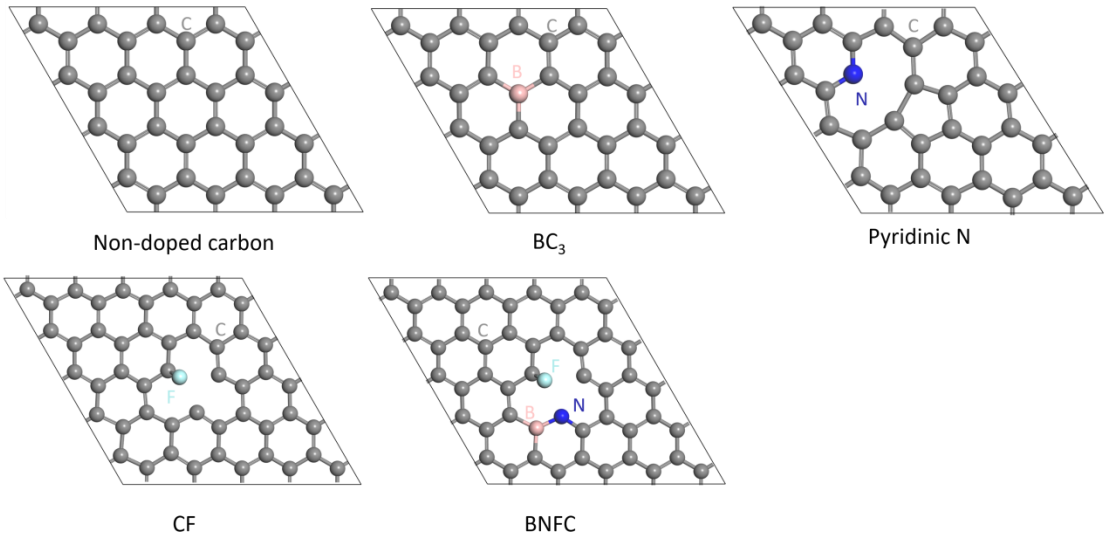

Figure S1 DFT calculated models of non-doped carbon, pyridinic N, BC_3, F doped carbon (FC) and B, N, F ternary doped carbon.

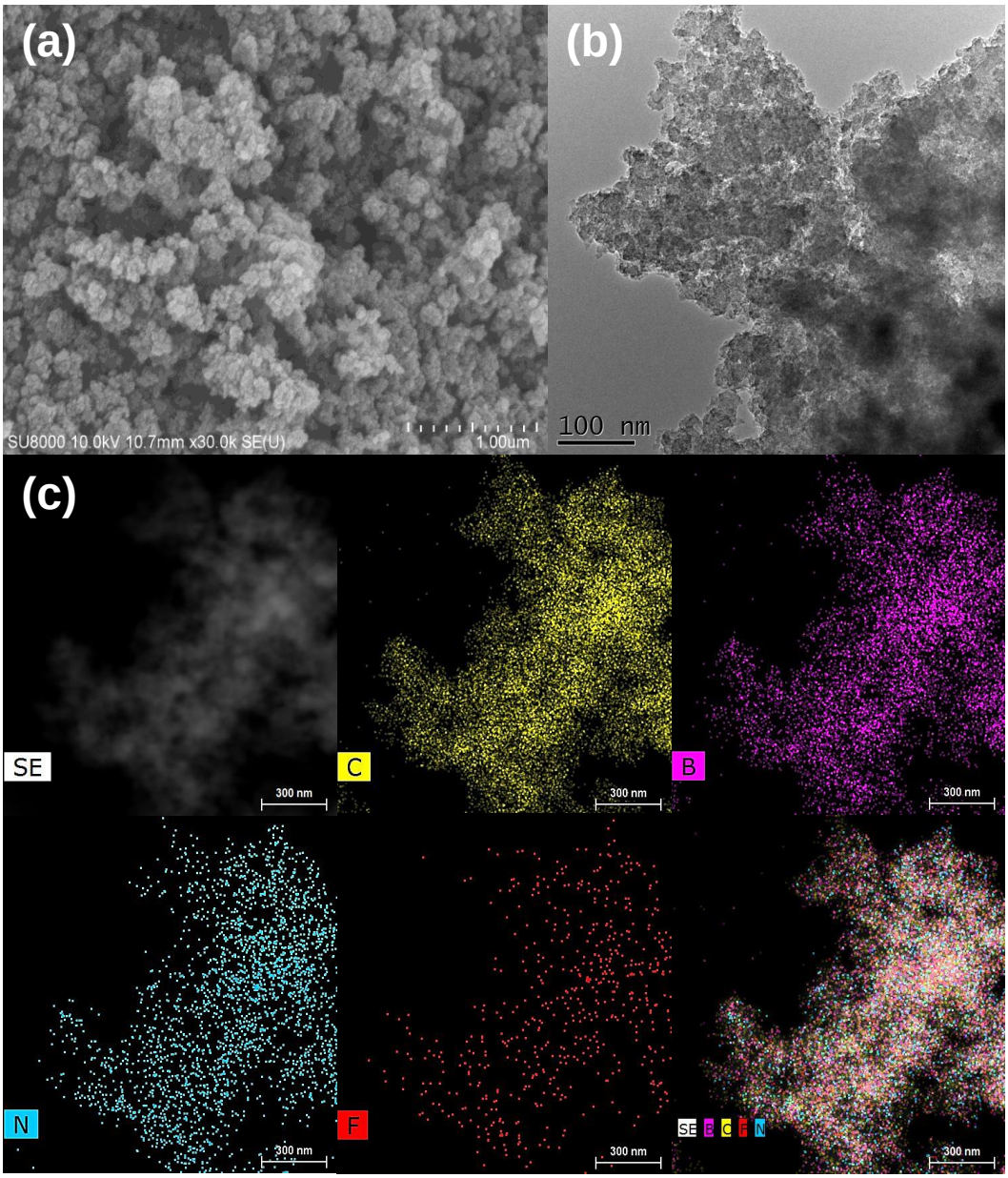

Figure S2 SEM (a), TEM (b), HAADF-STEM (c) images and relative EDS mappings of BNFC-700 electrocatalyst.

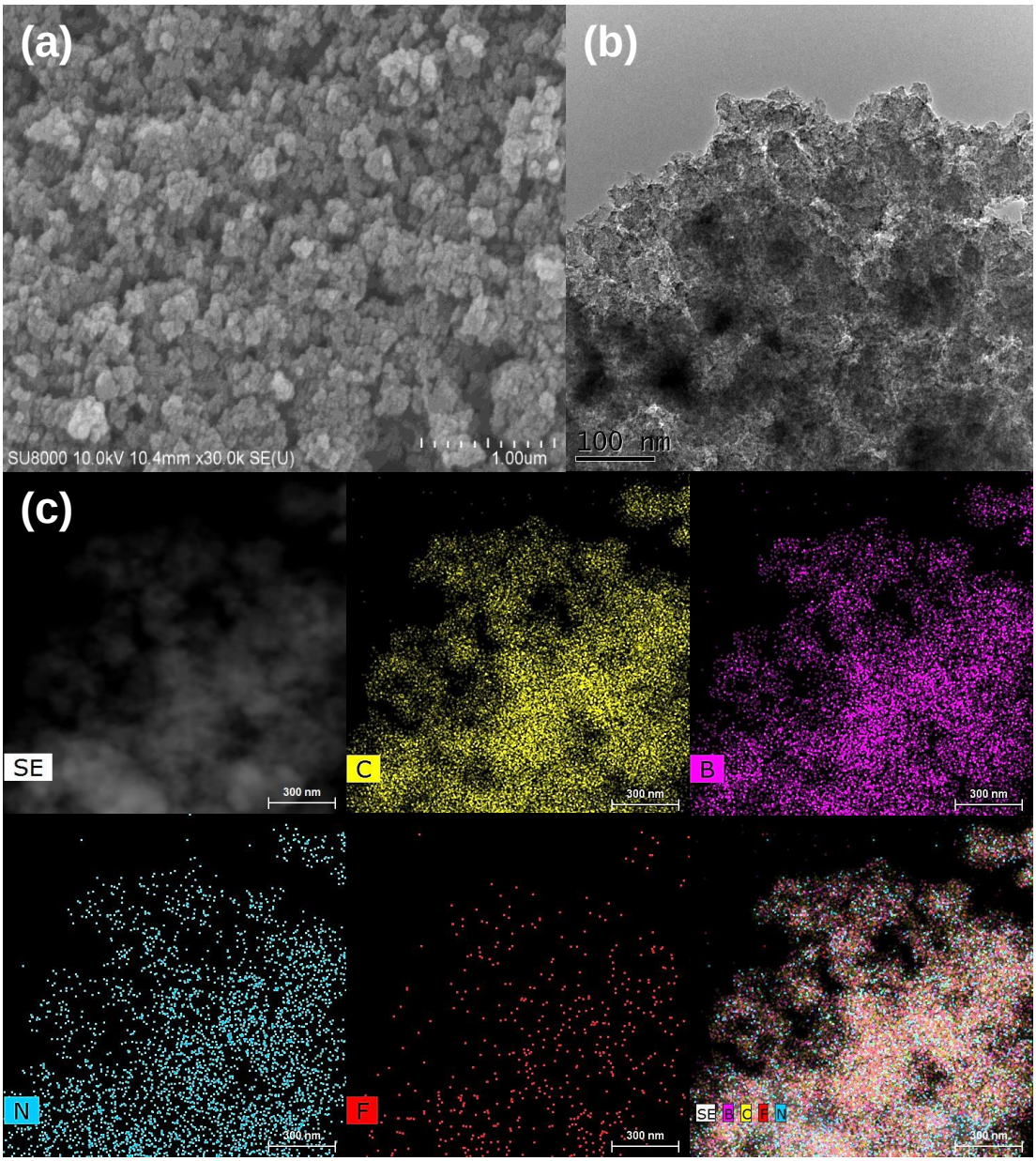

Figure S3 SEM (a), TEM (b), HAADF-STEM (c) images and relative EDS mappings of BNFC-900 electrocatalyst.

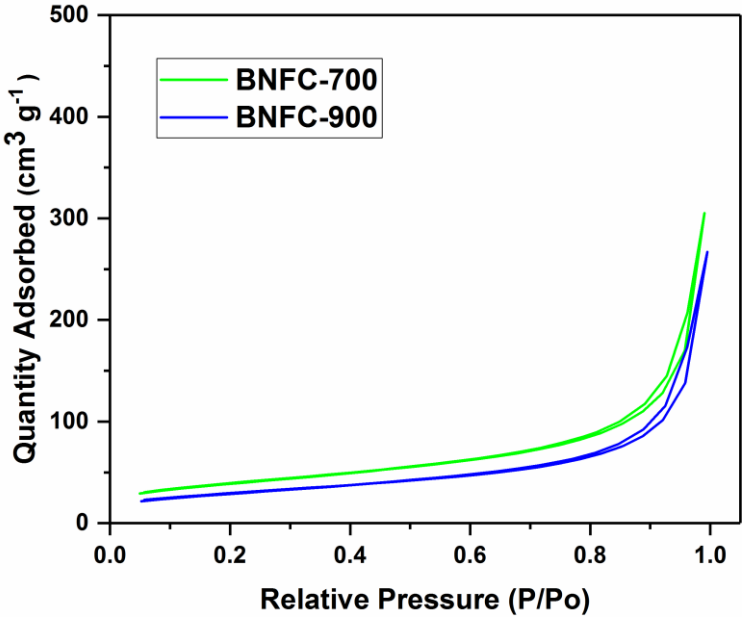

Figure S4 N_2 adsorption-desorption isothermal curves of BNFC-700 and BNFC-900 electrocatalysts.

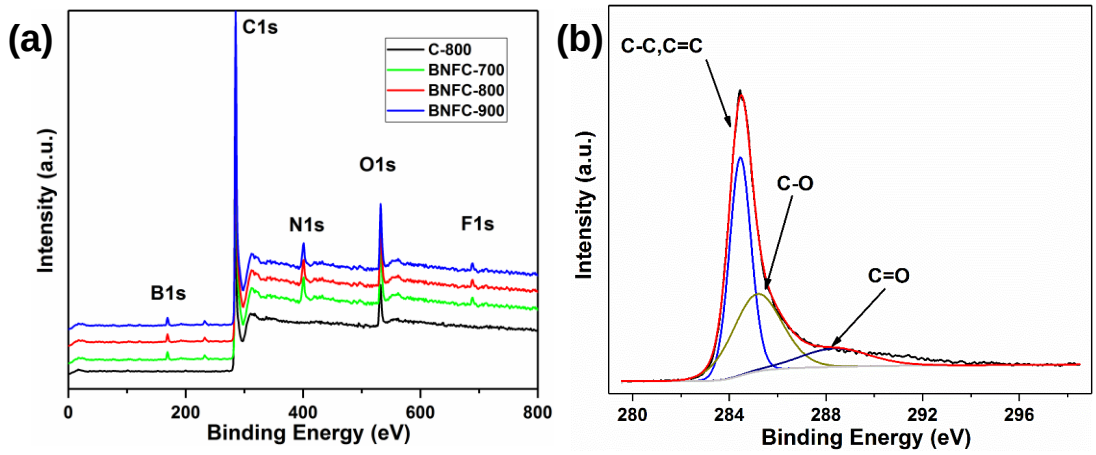

Figure S5 (a) XPS survey scan of C-800, BNFC-700, BNFC-800 and BNFC-900 electrocatalysts. (b) Deconvoluted C1s peak of C-800 electrocatalyst.

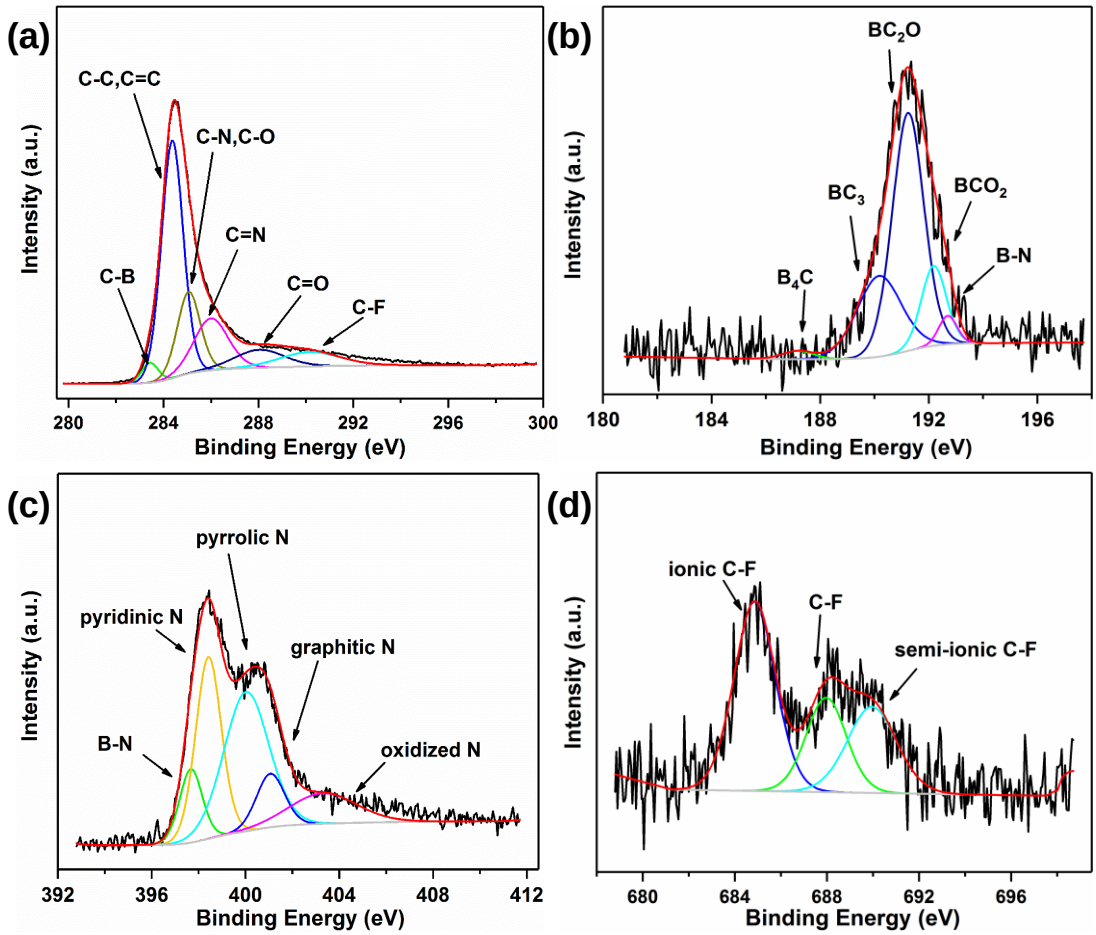

Figure S6 Deconvoluted C1s (a), B1s (b), N1s (c) and F1s (d) peaks of BNFC-700 electrocatalyst.

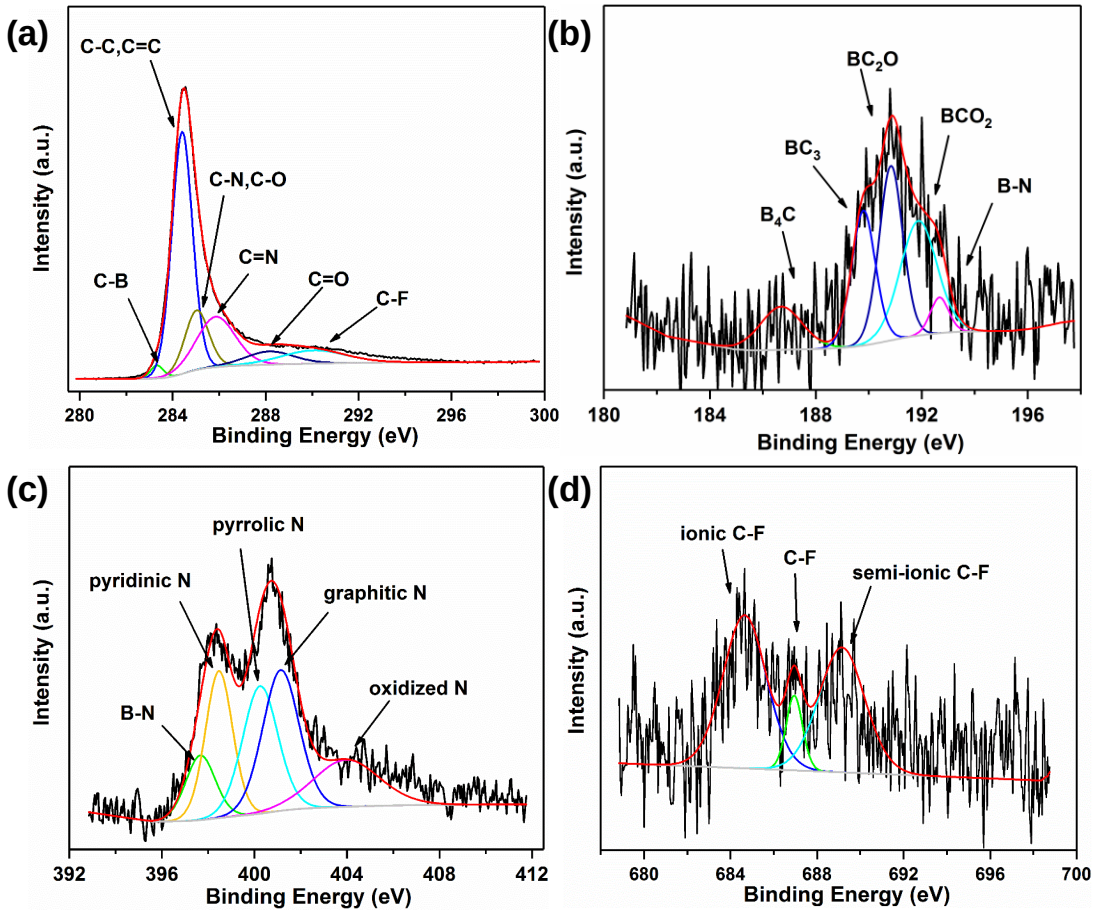

Figure S7 Deconvoluted C1s (a), B1s (b), N1s (c) and F1s (d) peaks of BNFC-900 electrocatalyst.

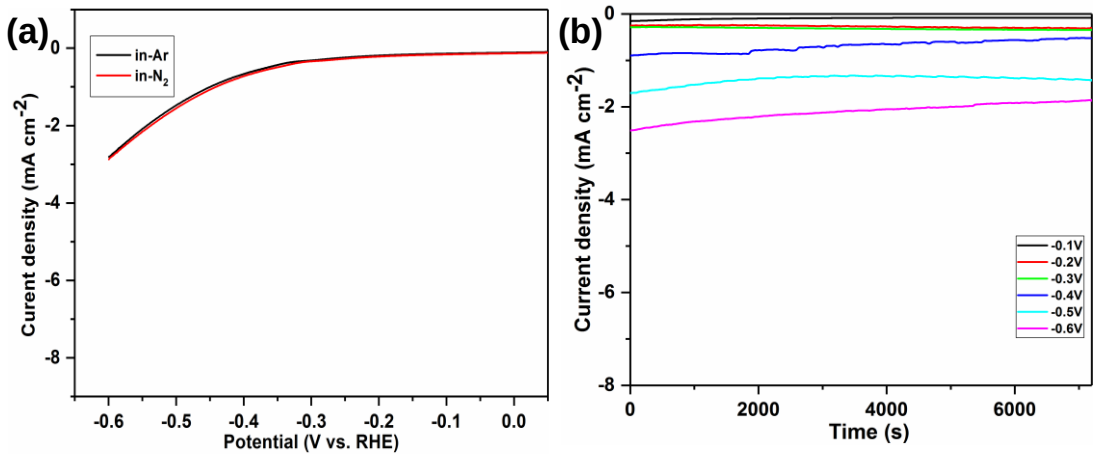

Figure S8 (a) LSV curves of C-800 electrocatalyst recorded in Ar- and N_2-saturated 0.05 M H_2SO_4 electrolyte. (b) Chronoamperometric curves of C-800 electrocatalyst with different applied potentials.

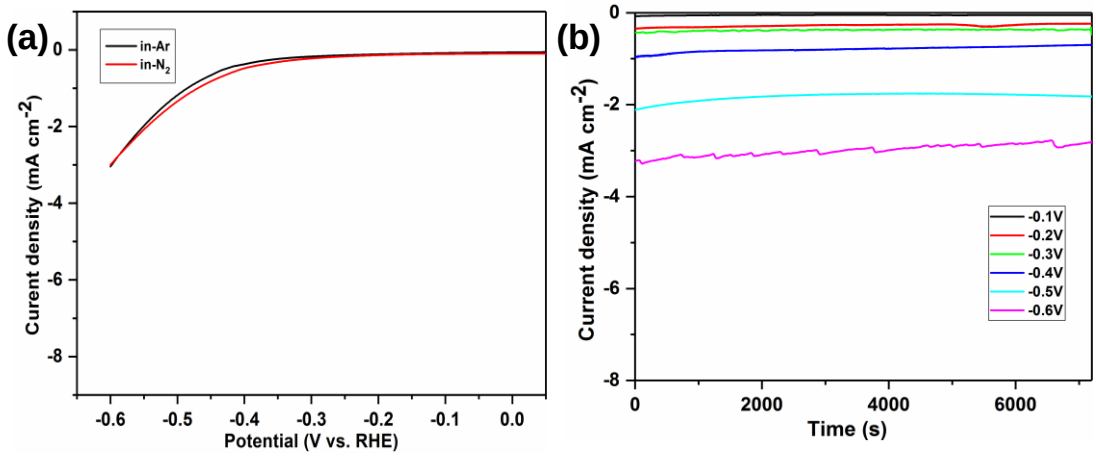

Figure S9 (a) LSV curves of BNFC-700 electrocatalyst recorded in Ar- and N_2-saturated 0.05 M H_2SO_4 electrolyte. (b) Chronoamperometric curves of BNFC-700 electrocatalyst with different applied potentials.

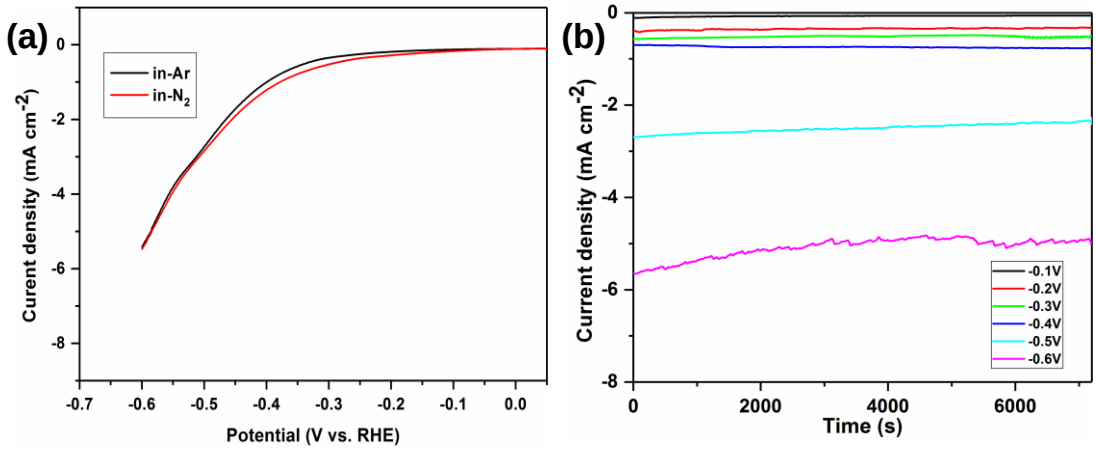

Figure S10 (a) LSV curves of BNFC-900 electrocatalyst recorded in Ar- and N_2-saturated 0.05 M H_2SO_4 electrolyte. (b) Chronoamperometric curves of BNFC-900 electrocatalyst with different applied potentials.

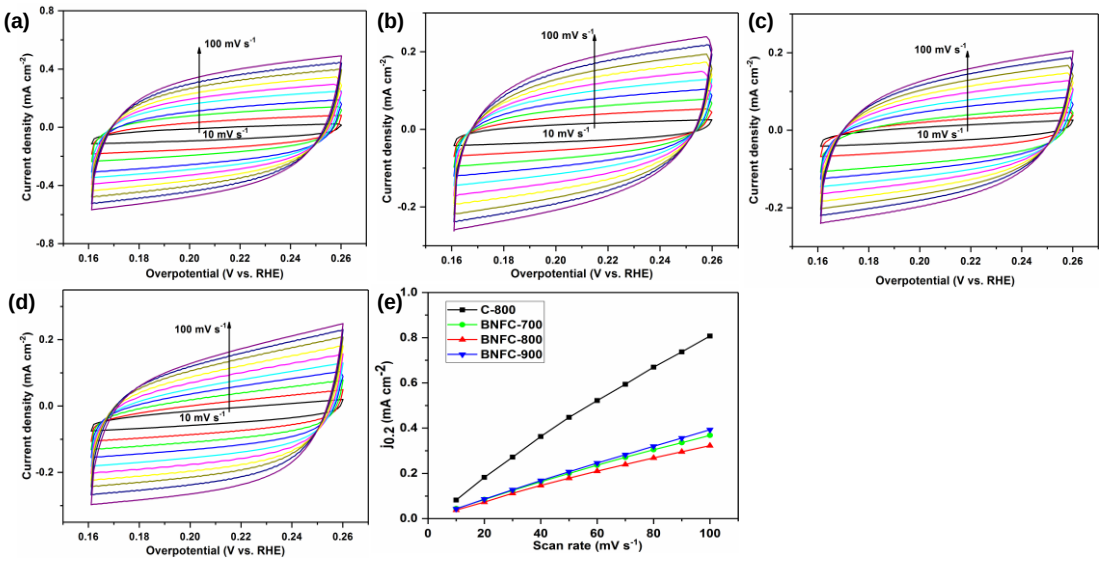

Figure S11 Cyclic voltammetry curves of C-800 (a), BNFC-700 (b), BNFC-800 (c) and BNFC-900 (d) electrocatalysts recorded from 0.16 V to 0.26 V vs. RHE. Double-layer capacitances (e) of C-800, BNFC-700, BNFC-800 and BNFC-900 electrocatalysts.

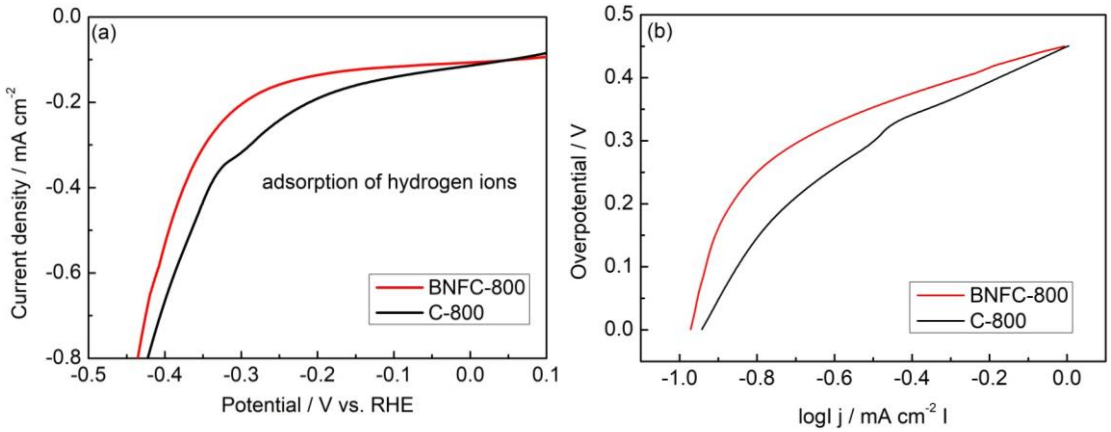

Figure S12 LSV curves and Tafel slope (b) of BNFC-800 and C-800 tested in Ar-purged 0.05 M H_2SO_4 electrolyte.

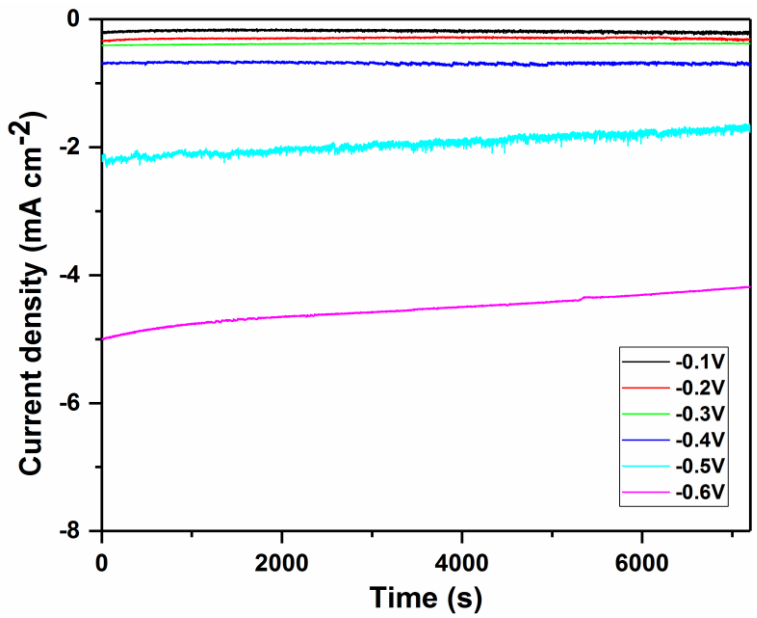

Figure S13 Chronoamperometric curves of BNFC-800 electrocatalyst with different applied potentials.

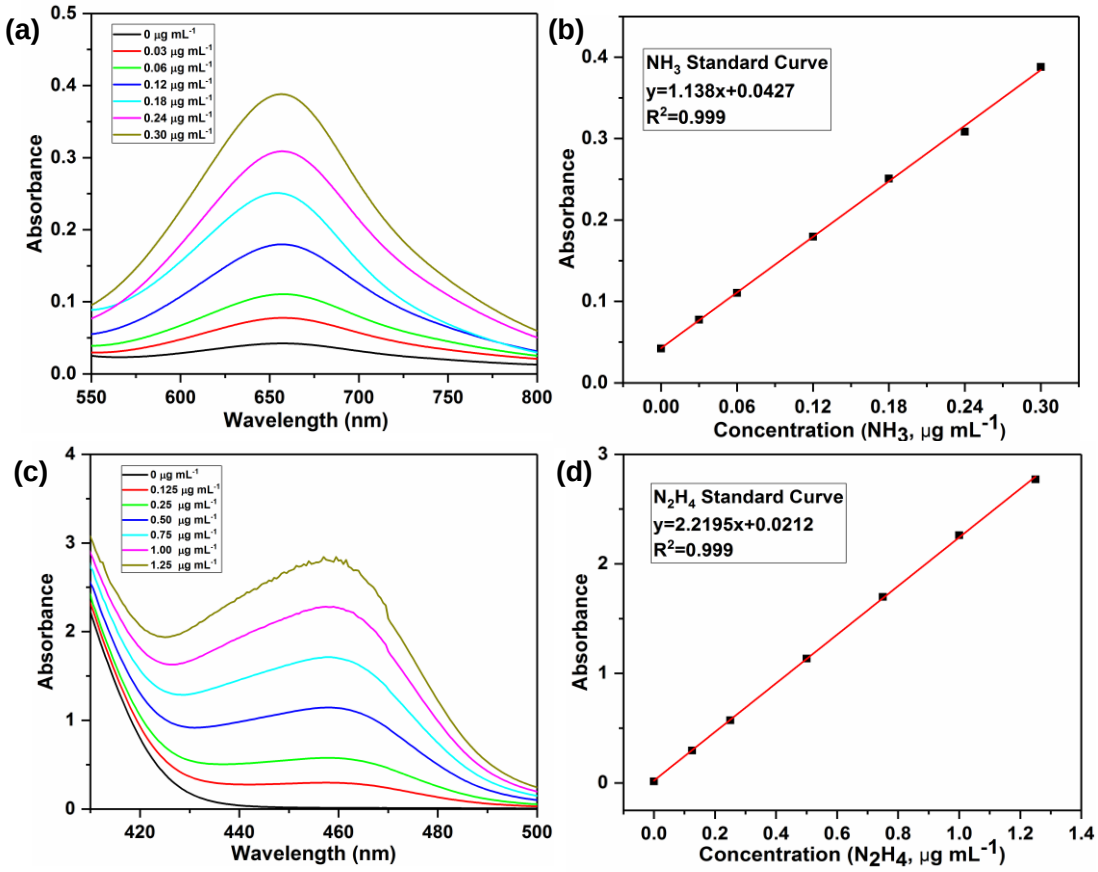

Figure S14 UV-vis spectroscopies of colorimetry and calibration of colorimetric NH_3 (a, b) and N_2H_4 (c, d) assay by salicylic acid spectrophotometry.

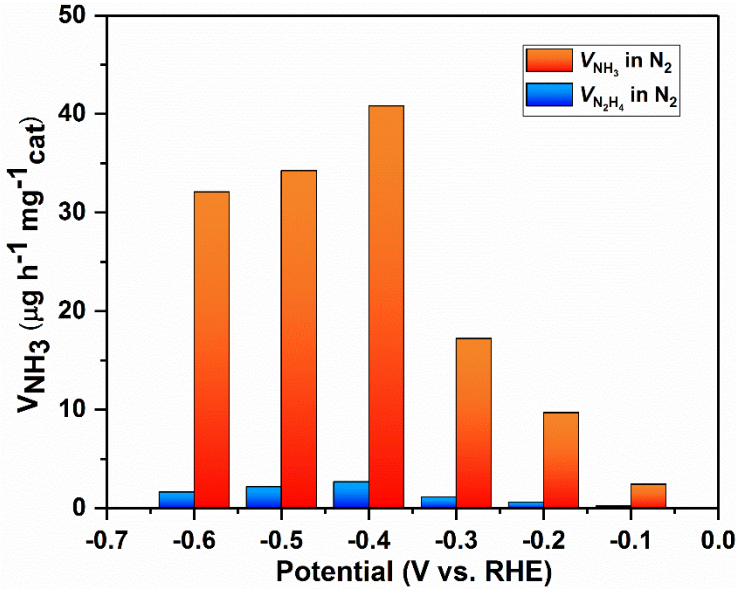

Figure S15 Calculated NH_3 and N_2H_4 yield rates of BNFC-800 electrocatalyst tested in 0.05 M H_2SO_4 electrolyte.

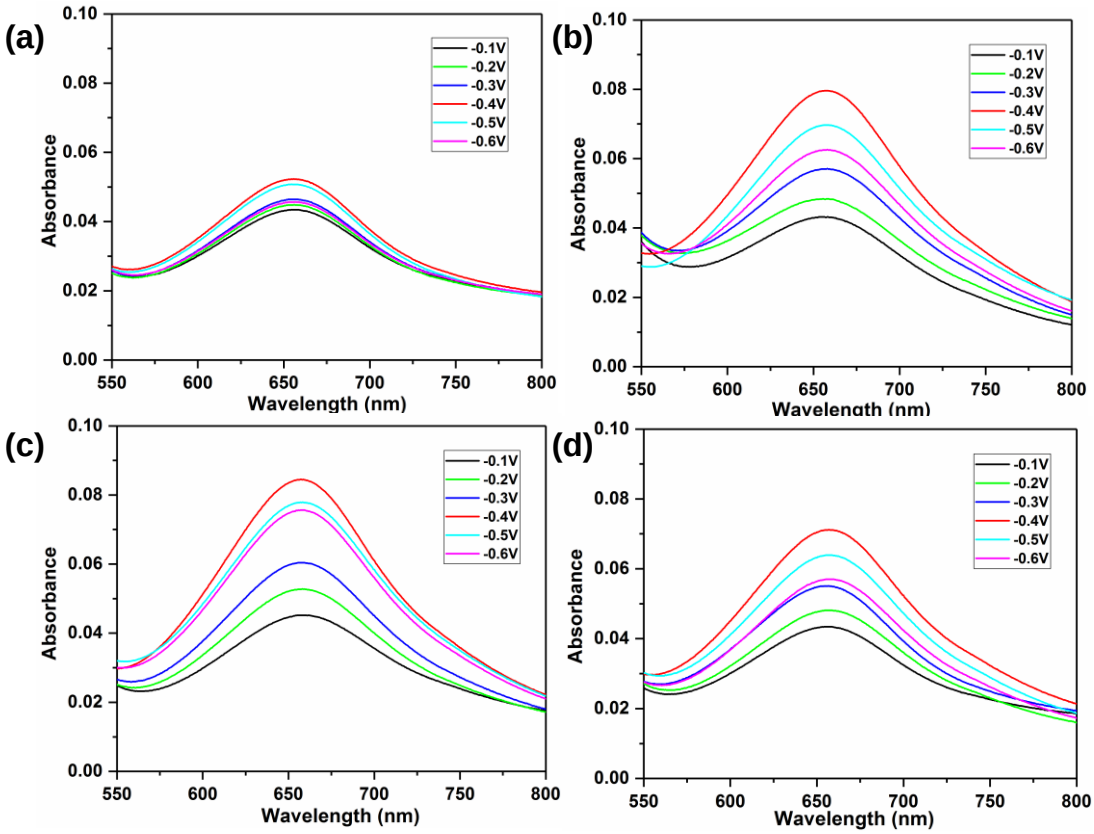

Figure S16 UV-vis spectroscopies of the electrolyte after testing with C-800 (a), BNFC-700 (b), BNFC-800 (c) and BNFC-900 (d) electrocatalysts for 2 h at different potentials in 0.05 M H_2SO_4 electrolyte.

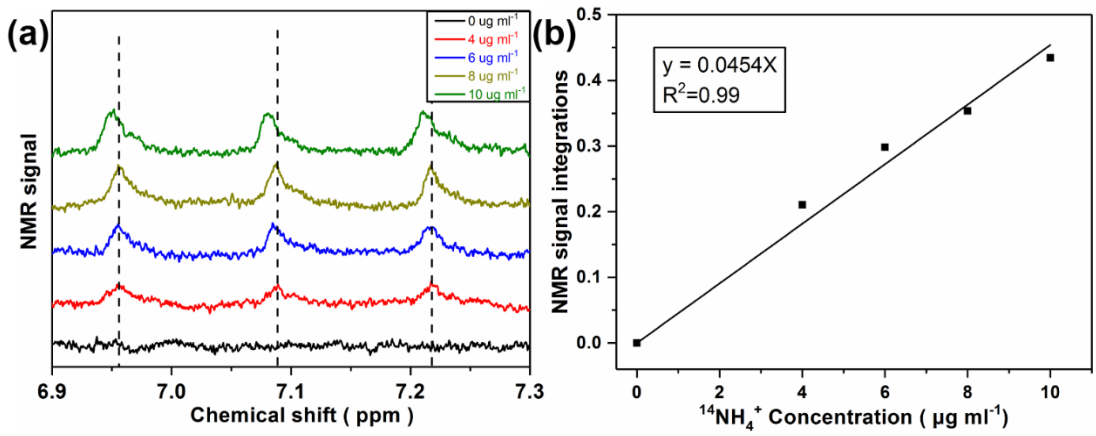

Figure S17 (a) NMR spectra of various $(NH_4)_2SO_4$ concentrations. (b) Plots of peak intensity as function of $(NH_4)_2SO_4$ concentrations.

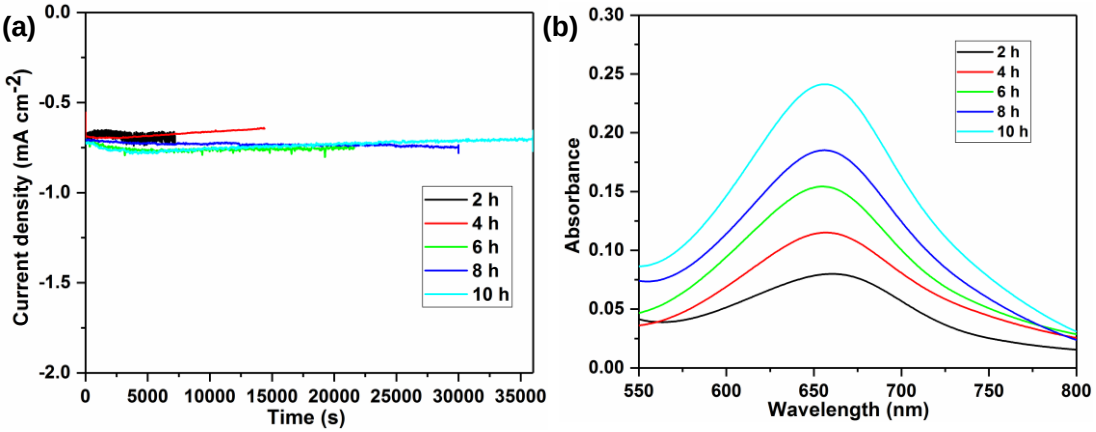

Figure S18 (a) Current densities recorded at -0.4 V vs. RHE for various durations. (b) UV-vis spectroscopies of the electrolyte after testing with BNFC-800 electrocatalyst for different times at -0.4 V vs. RHE in 0.05 M H_2SO_4 electrolyte.

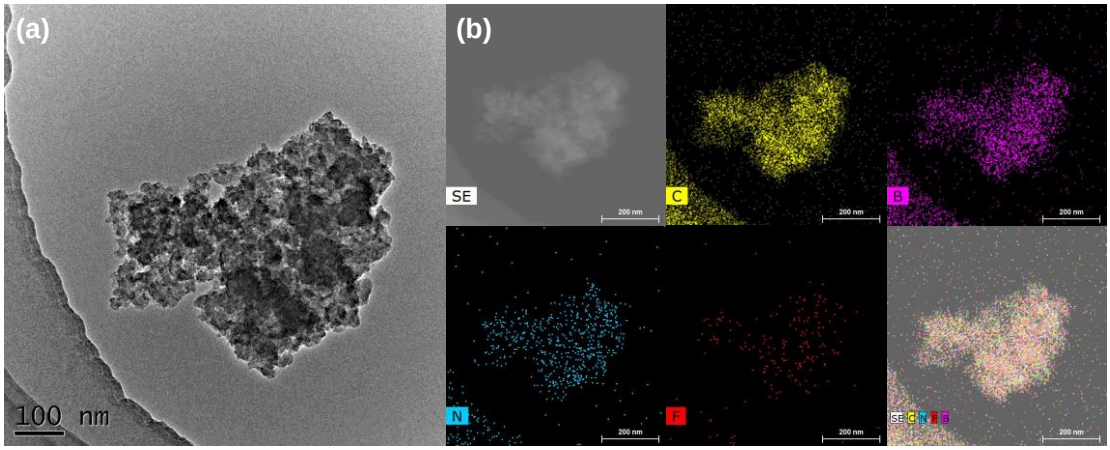

Figure S19 TEM (a), HAADF-STEM images (b) and relative EDS mappings of C, N, B and F elements in BNFC-800 electrocatalysts after stability test in 0.05 M H_2SO_4 electrolyte.

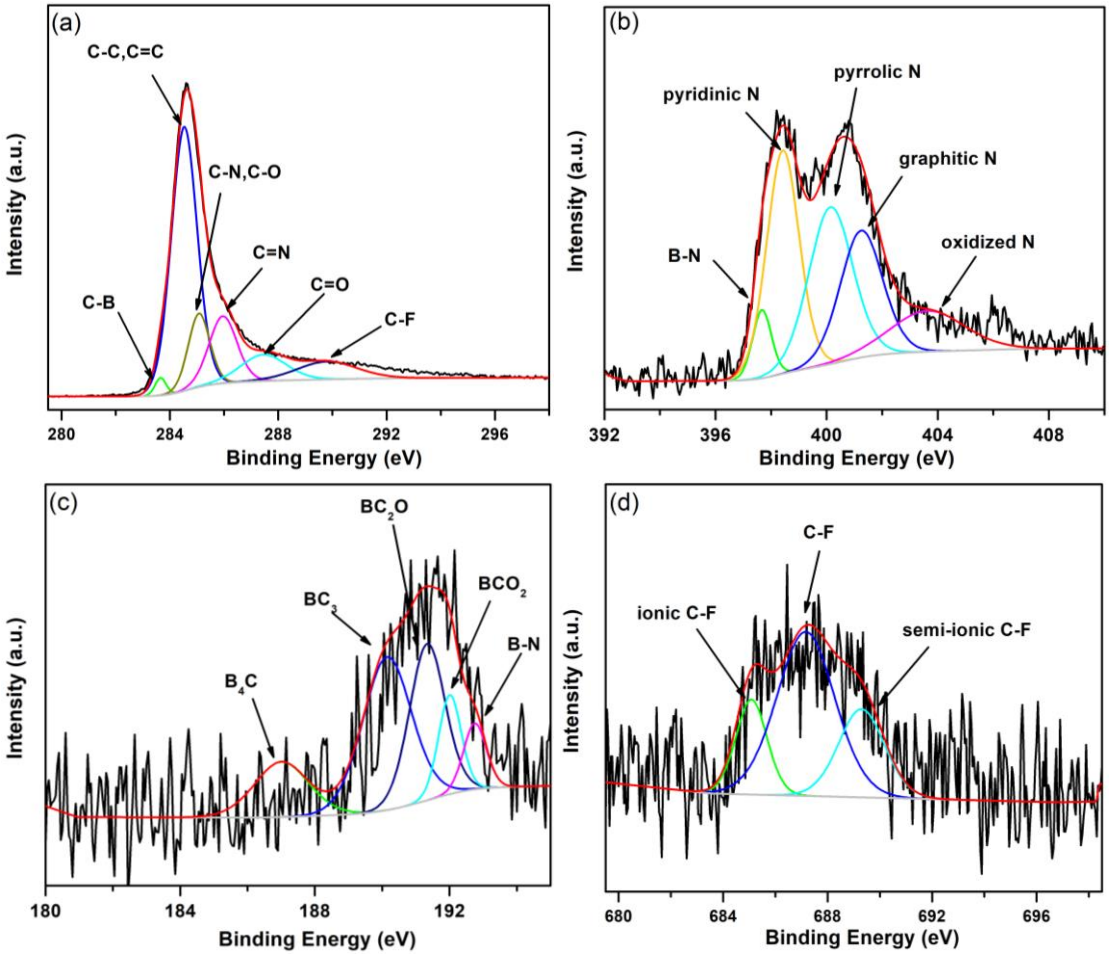

Figure S20 Deconvoluted C1s (a), N1s (b), B1s (c) and F1s (d) peaks of BNFC-800 after 10 h NRR catalysis in 0.05 M H_2SO_4 electrolyte.

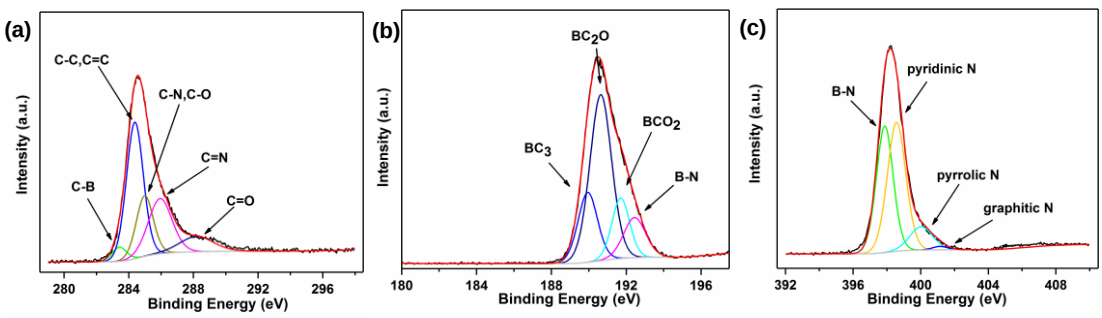

Figure S21 Deconvoluted C1s (a), B1s (b) and N1s (c) peaks of BNC-800 electrocatalyst.

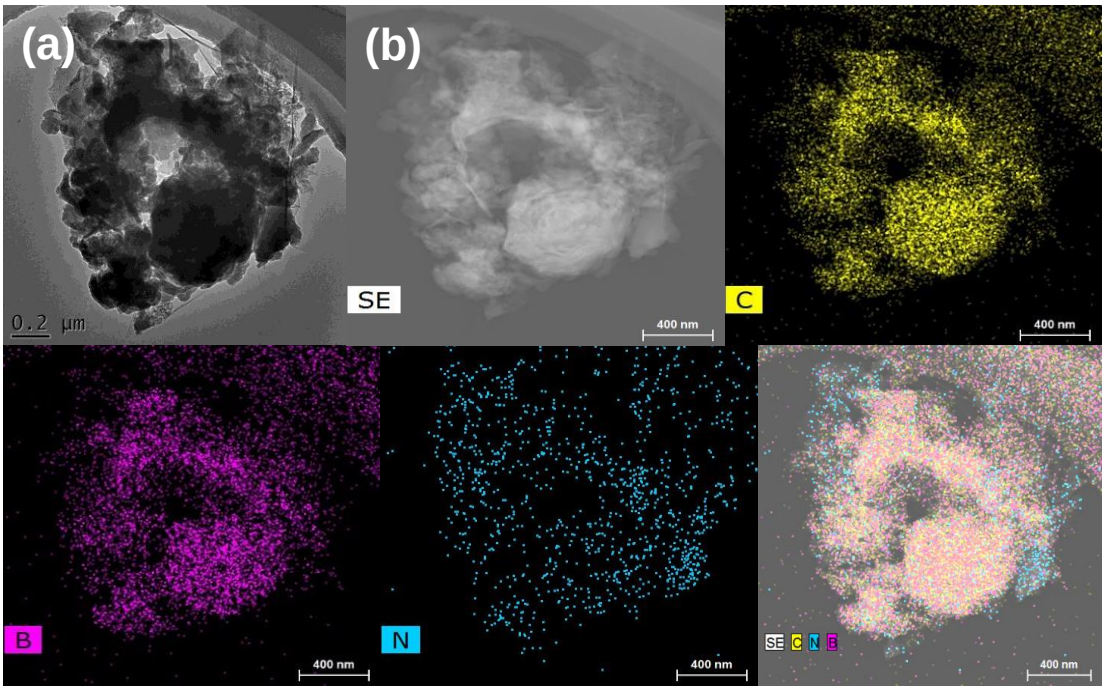

Figure S22 TEM (a), HAADF-STEM (b) images and relative EDS mappings of C, N and B elements of BNC-800 electrocatalyst.

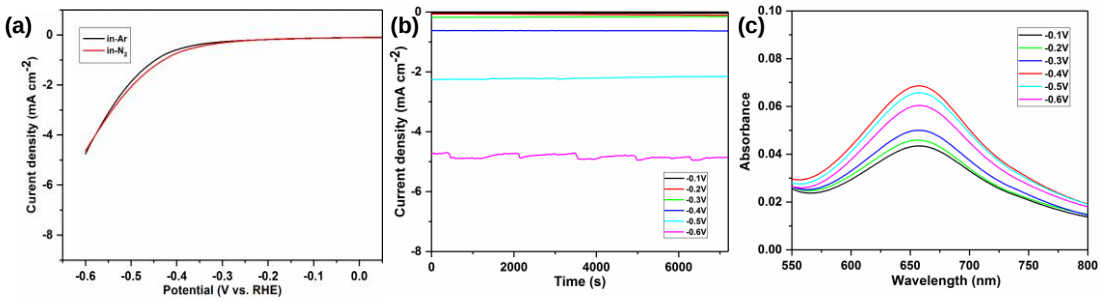

Figure S23 (a) LSV curves of BNC-800 electrocatalyst recorded in Ar- and N_2-saturated 0.05 M H_2SO_4 electrolyte. (b) Chronoamperometric curves of BNC-800 electrocatalyst with different applied potentials. (c) UV-vis spectroscopies of the electrolyte after testing with BNC-800 electrocatalyst for 2 h at different potentials in 0.05 M H_2SO_4 electrolyte.

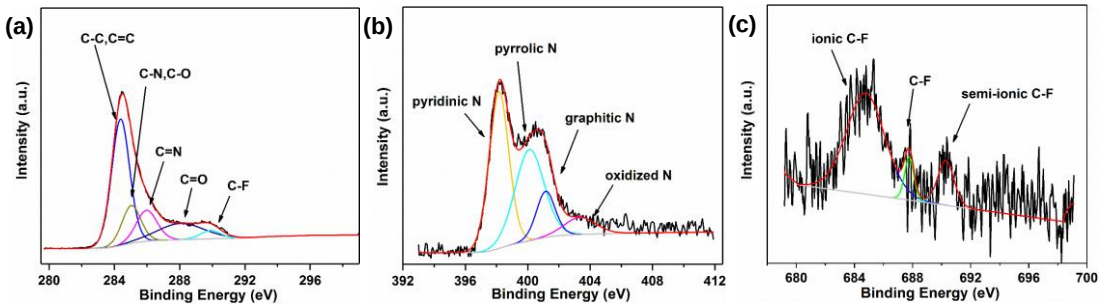

Figure S24 Deconvoluted C1s (a), N1s (b) and F1s (c) peaks of NFC-800 electrocatalyst.

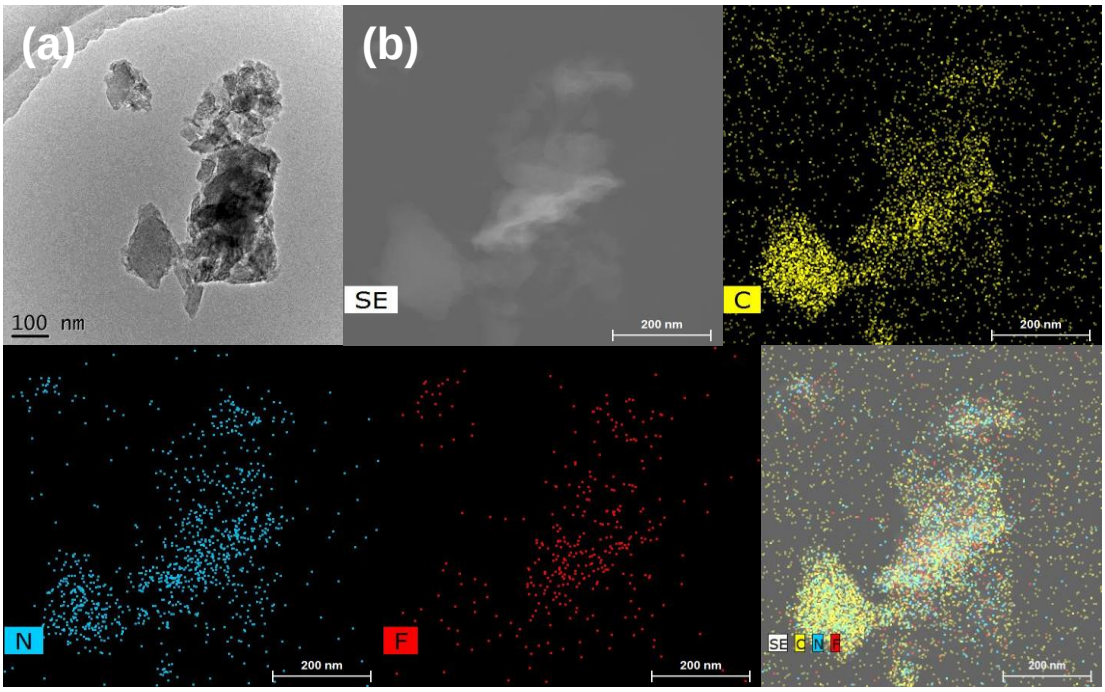

Figure S25 TEM (a), HAADF-STEM (b) images and relative EDS mappings of C, N and F elements of NFC-800 electrocatalyst.

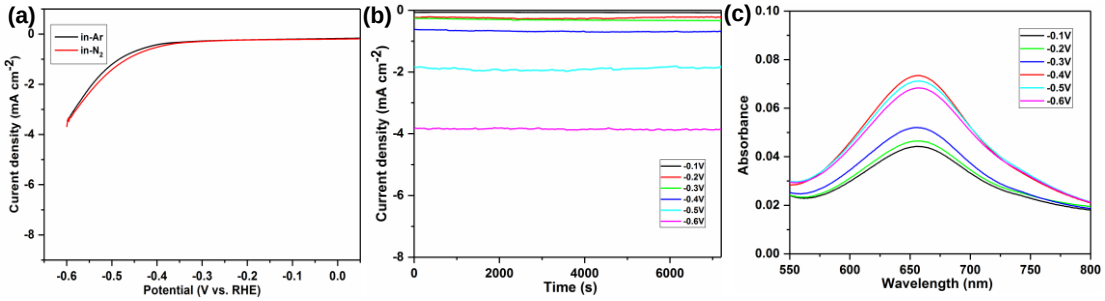

Figure S26 (a) LSV curves of NFC-800 electrocatalyst recorded in Ar- and N_2-saturated 0.05 M H_2SO_4 electrolyte. (b) Chronoamperometric curves of NFC-800 electrocatalyst with different applied potentials. (c) UV-vis spectroscopies of the electrolyte after testing with NFC-800 electrocatalyst for 2 h at different potentials in 0.05 M H_2SO_4 electrolyte.

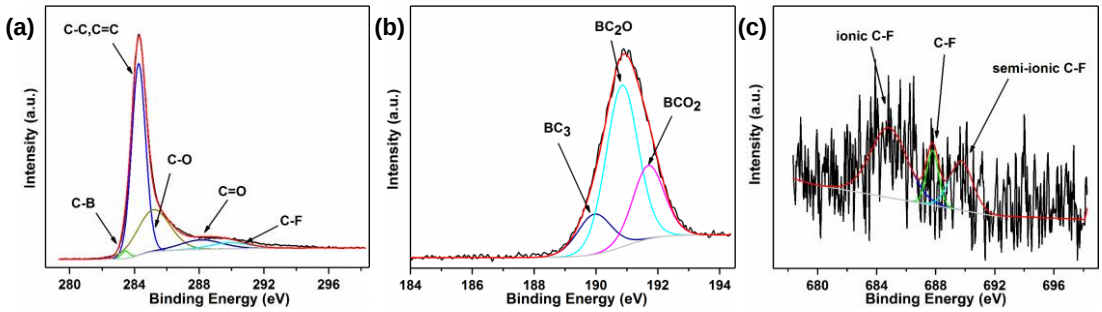

Figure S27 Deconvoluted C1s (a), B1s (b) and F1s (c) peaks of BFC-800 electrocatalyst.

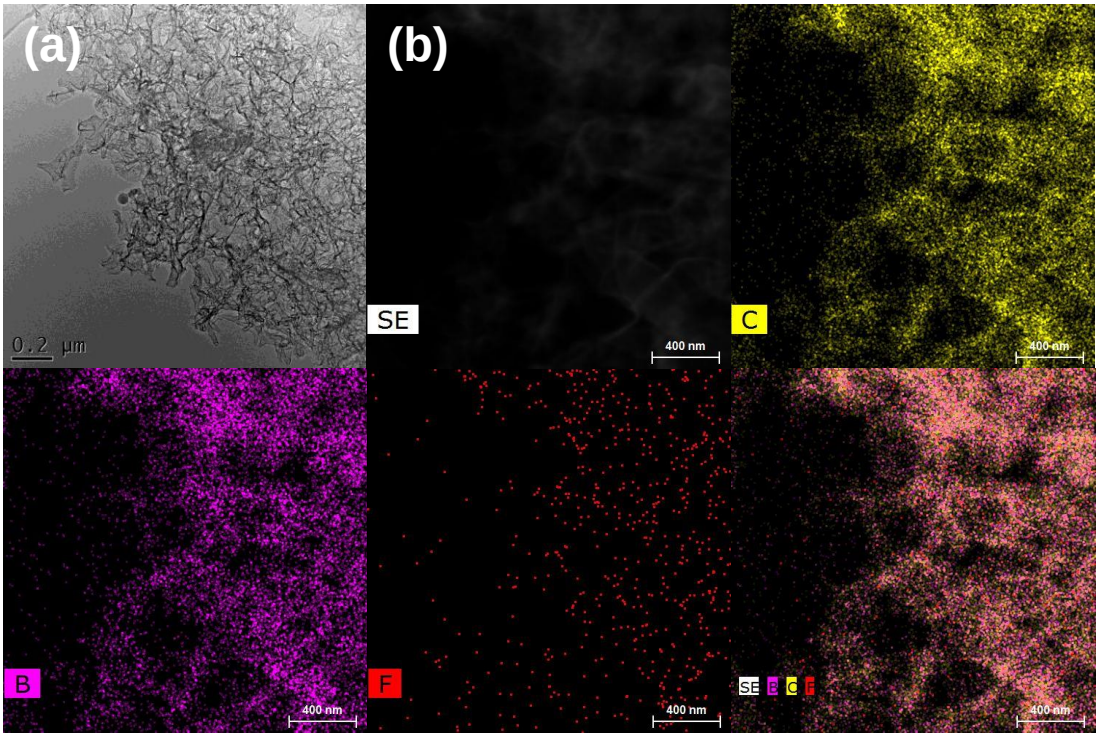

Figure S28 TEM (a), HAADF-STEM (b) images and relative EDS mappings of C, N and F elements of BFC-800 electrocatalyst.

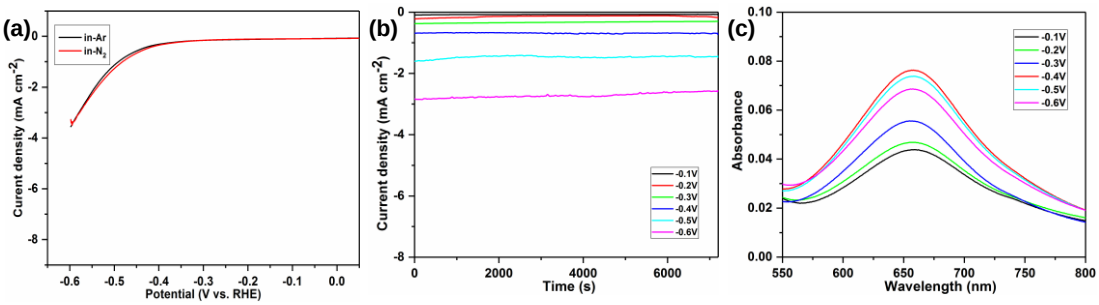

Figure S29 (a) LSV curves of BFC-800 electrocatalyst recorded in Ar- and N_2-saturated 0.05 M H_2SO_4 electrolyte. (b) Chronoamperometric curves of BFC-800 electrocatalyst with different applied potentials. (c) UV-vis spectroscopies of the electrolyte after testing with BFC-800 electrocatalyst for 2 h at different potentials in 0.05 M H_2SO_4 electrolyte.

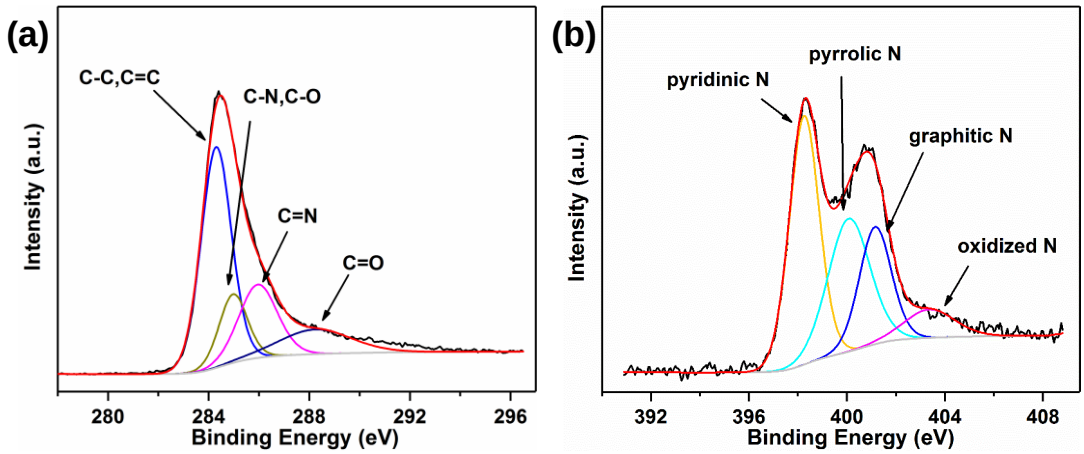

Figure S30 Deconvoluted C1s (a) and N1s (b) peaks of NC-800 electrocatalyst.

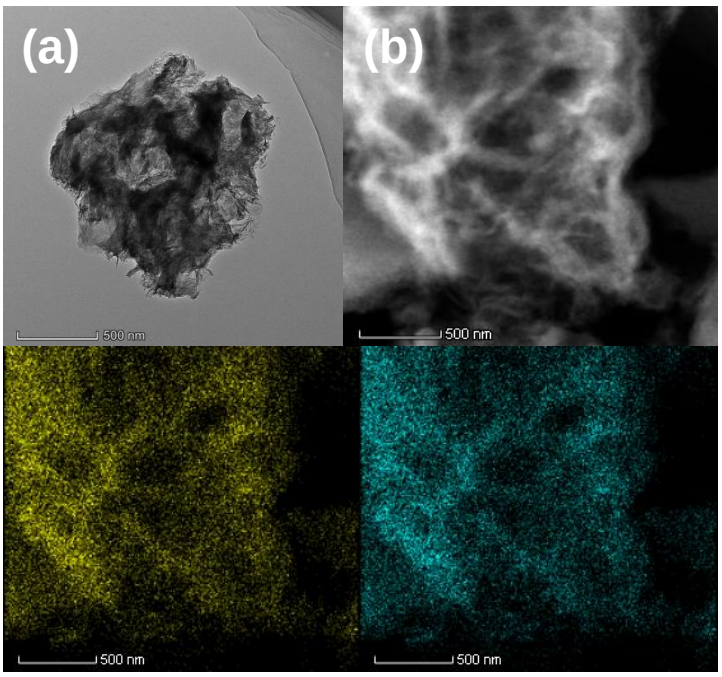

Figure S31 TEM (a), HAADF-STEM (b) images and relative EDS mappings of C and N elements of NC-800 electrocatalyst.

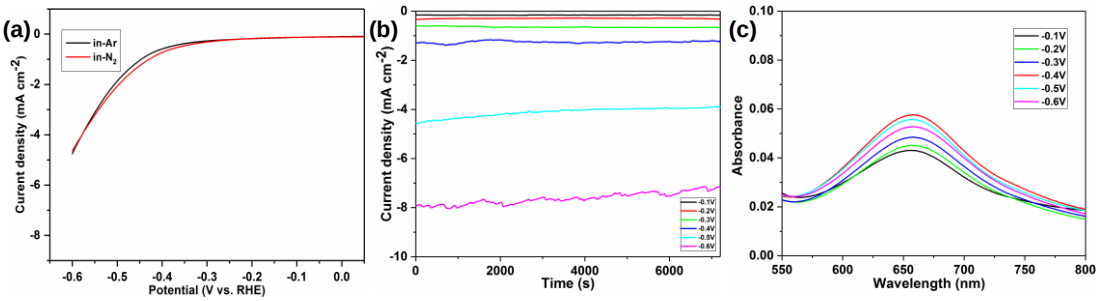

Figure S32 LSV curves of NC-800 electrocatalyst recorded in Ar- and N_2-saturated 0.05 M H_2SO_4 electrolyte. (b) Chronoamperometric curves of NC-800 electrocatalyst with different applied potentials. (c) UV-vis spectroscopies of the electrolyte after testing with NC-800 electrocatalyst for 2 h at different potentials in 0.05 M H_2SO_4 electrolyte.

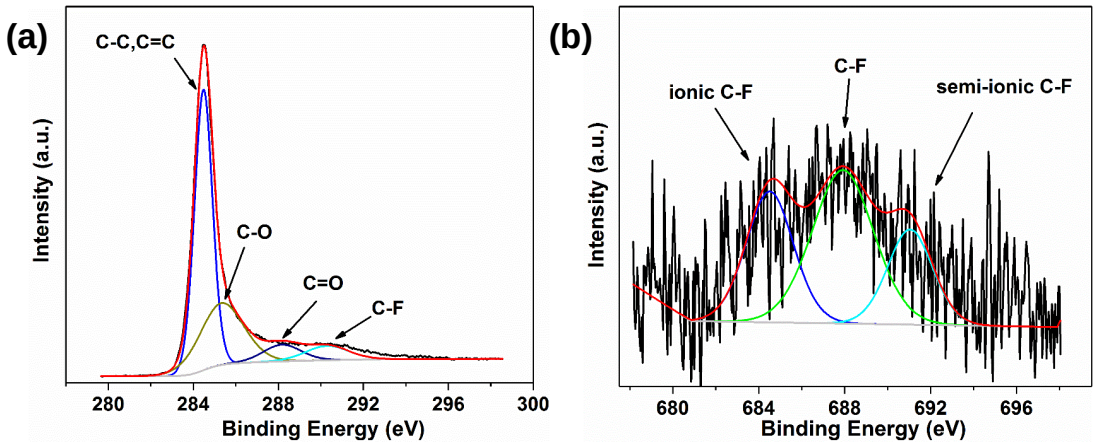

Figure S33 Deconvoluted C1s (a) and F1s (b) peaks of FC-800 electrocatalyst.

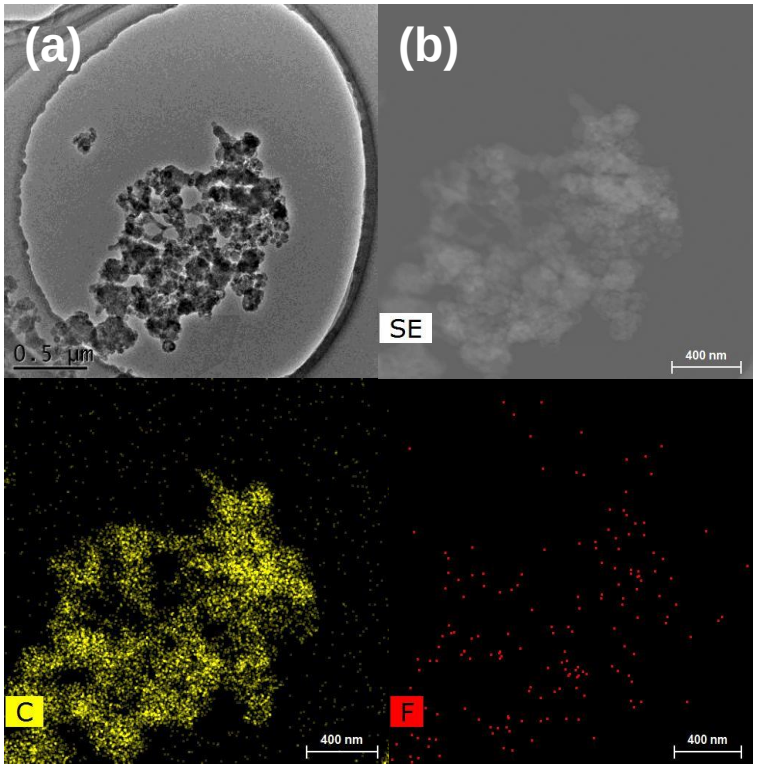

Figure S34 TEM (a), HAADF-STEM (b) images and relative EDS mappings of C and F elements of FC-800 electrocatalyst.

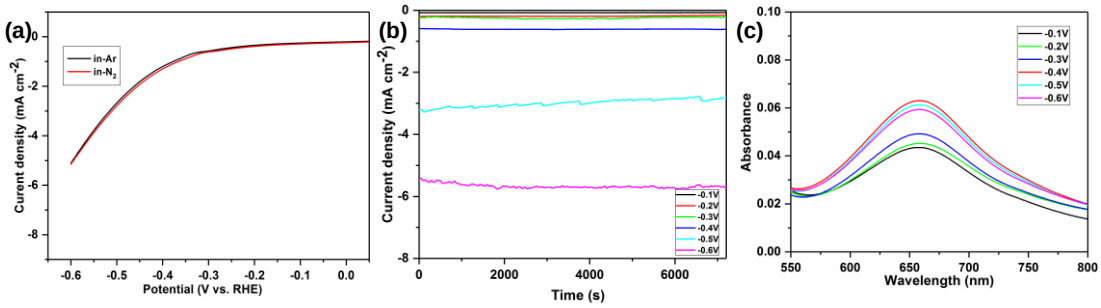

Figure S35 (a) LSV curves of FC-800 electrocatalyst recorded in Ar- and N_2-saturated 0.05 M H_2SO_4 electrolyte. (b) Chronoamperometric curves of FC-800 electrocatalyst with different applied potentials. (c) UV-vis spectroscopies of the electrolyte after testing with FC-800 electrocatalyst for 2 h at different potentials in 0.05 M H_2SO_4 electrolyte.

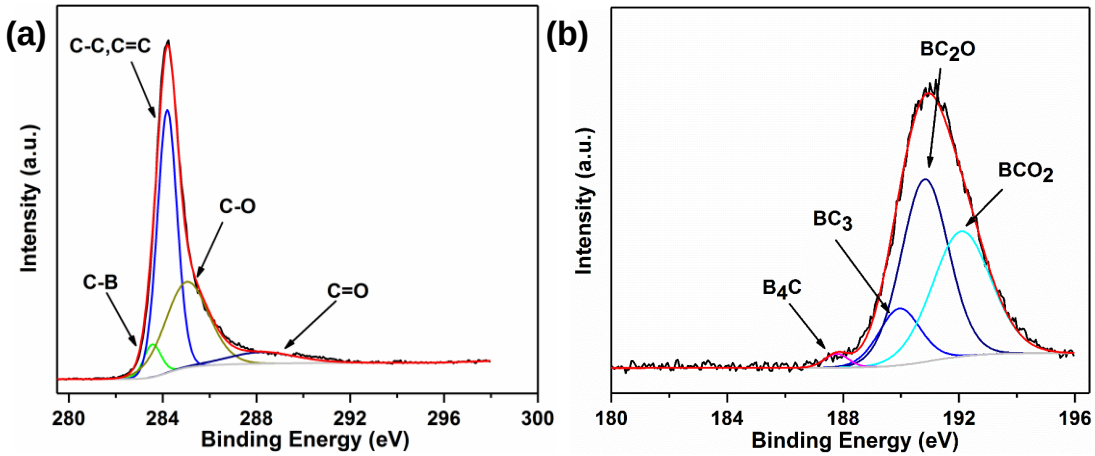

Figure S36 Deconvoluted C1s (a) and B1s (b) peaks of BC-800 electrocatalyst.

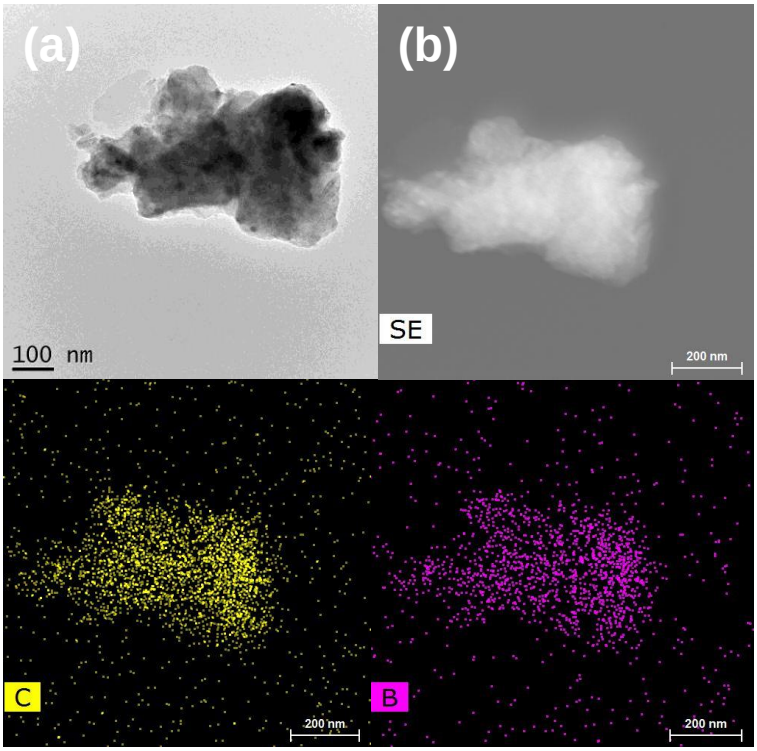

Figure S37 TEM (a), HAADF-STEM (b) images and relative EDS mappings of C and B elements of BC-800 electrocatalyst.

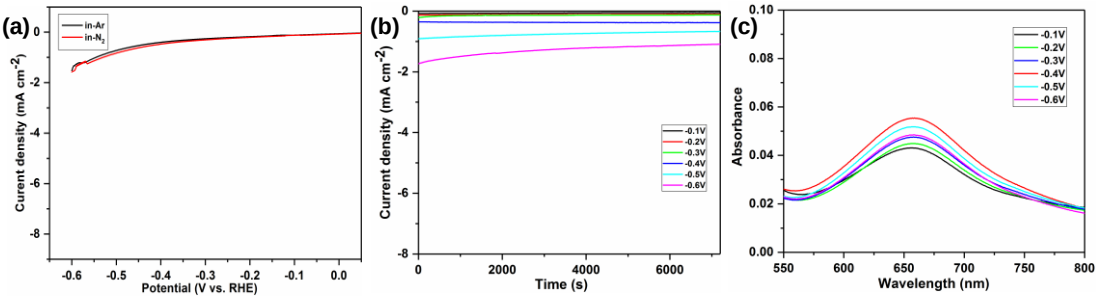

Figure S38 LSV curves of BC-800 electrocatalyst recorded in Ar- and N_2-saturated 0.05 M H_2SO_4 electrolyte. (b) Chronoamperometric curves of BC-800 electrocatalyst with different applied potentials. (c) UV-vis spectroscopies of the electrolyte after testing with BC-800 electrocatalyst for 2 h at different potentials in 0.05 M H_2SO_4 electrolyte.

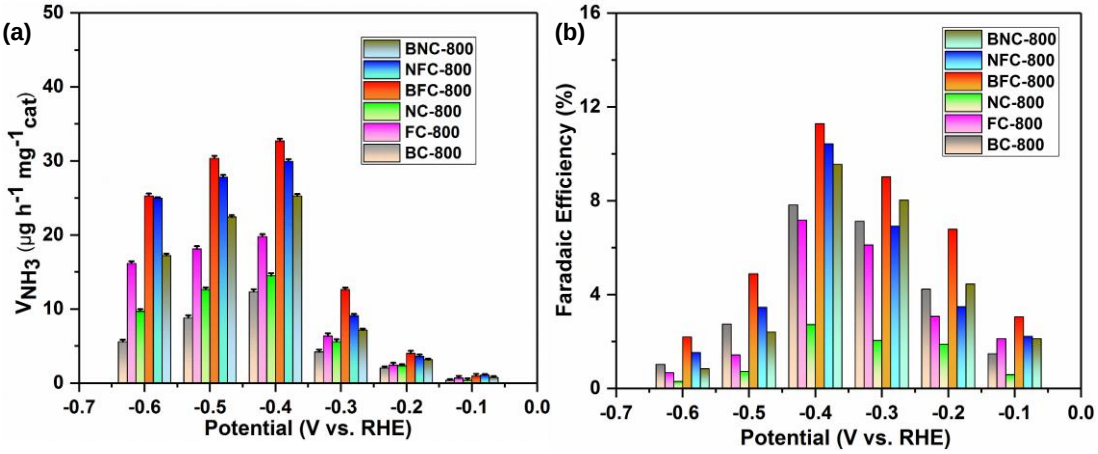

Figure S39 The NH_3 yield rates and Faradaic efficiencies of BNC-800, NFC-800, NC-800, FC-800 and BC-800 electrocatalysts at different potentials.

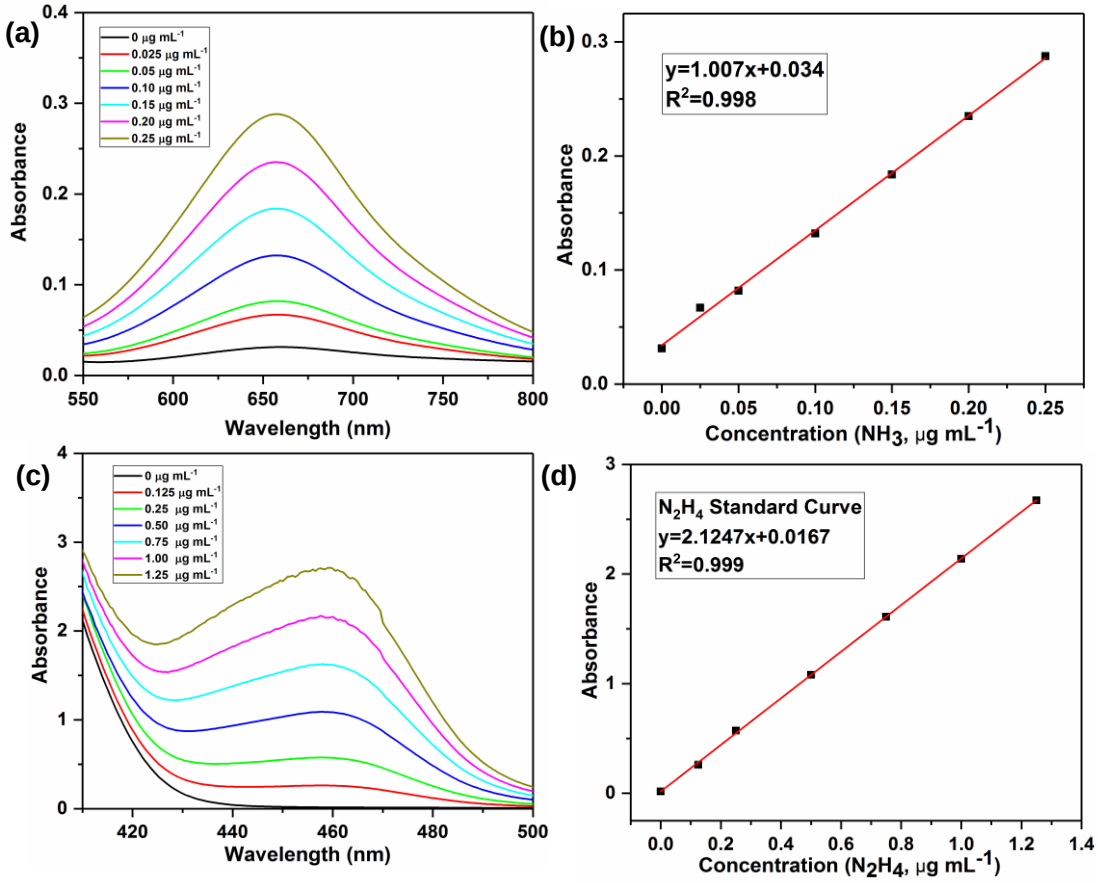

Figure S40 UV-vis spectroscopies of colorimetry and calibration of colorimetric NH_3 (a, b) and N_2H_4 (c, d) assay by salicylic acid spectrophotometry in 0.1 M NaOH electrolyte.

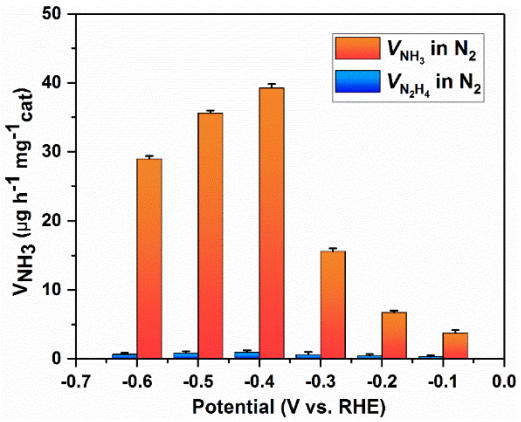

Figure S41 Calculated NH_3 and N_2H_4 yield rates of BNFC-800 electrocatalyst tested in 0.1 M NaOH electrolyte.

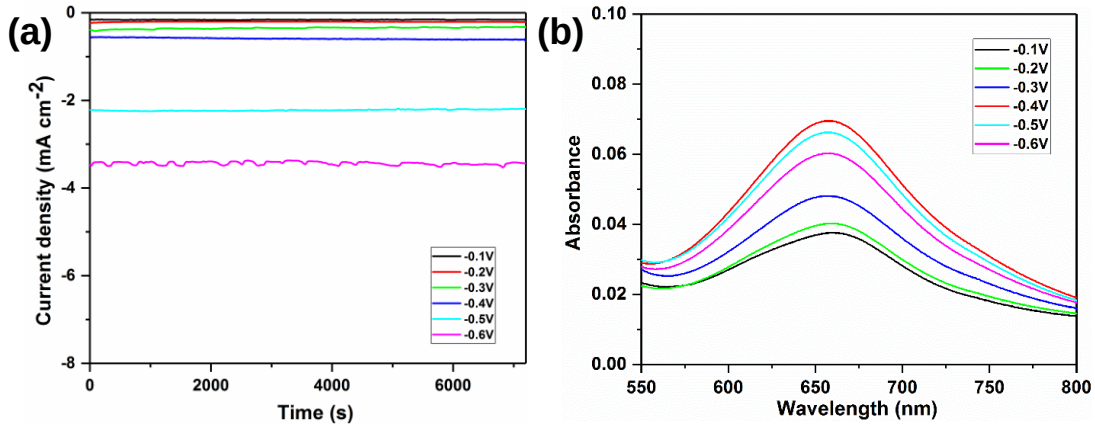

Figure S42 (a) Chronoamperometric curves of BNFC-800 electrocatalyst with different applied potentials. (b) UV-vis spectroscopies of the electrolyte after testing with BNFC-800 electrocatalyst for 2 h at different potentials in 0.1 M NaOH electrolyte.

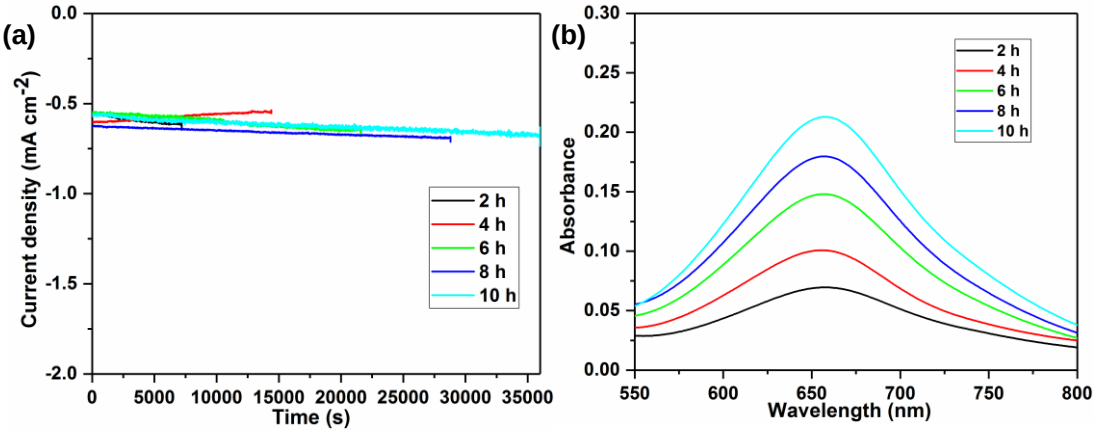

Figure S43 (a) Current densities recorded at -0.4 V vs. RHE for various durations. (b) UV-vis spectroscopies of the electrolyte after testing with BNFC-800 electrocatalyst for different times at -0.4 V vs. RHE in 0.1 M NaOH electrolyte.

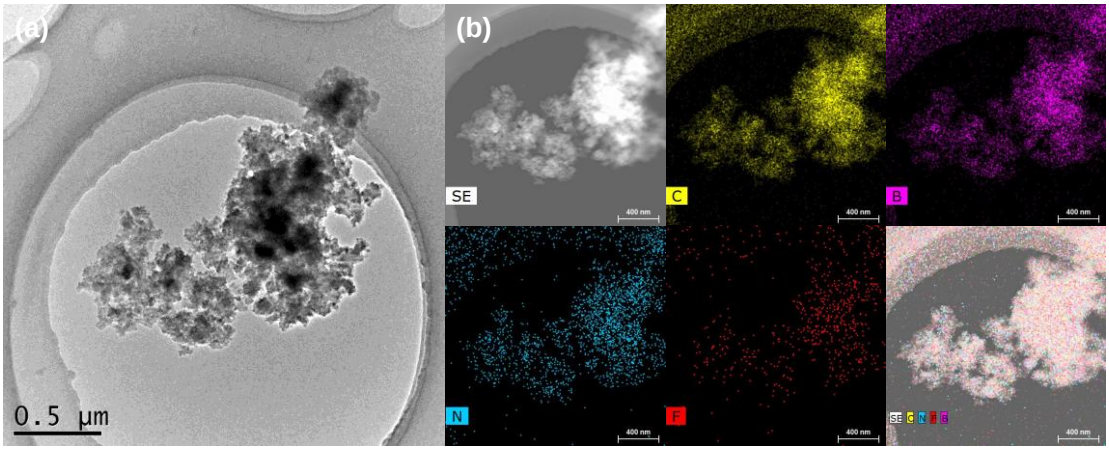

Figure S44 TEM (a), HAADF-STEM images (b) and relative EDS mappings of C, N, B and F elements in BNFC-800 electrocatalyst after stability test in 0.1 M NaOH electrolyte.

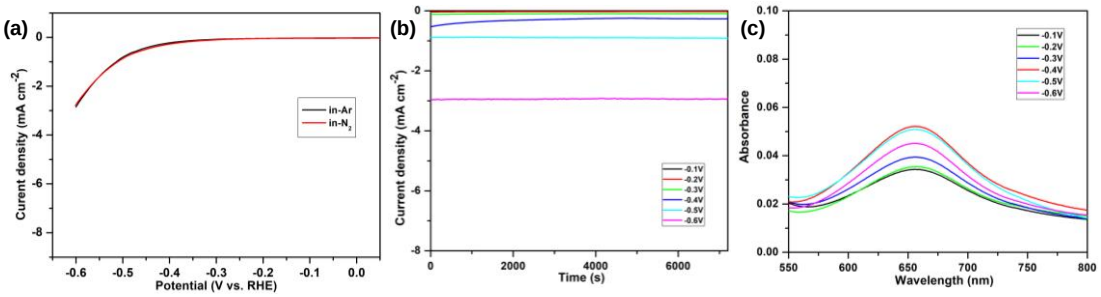

Figure S45 LSV (a) and Chronoamperometric (b) curves of BFC-800 electrocatalyst with different applied potentials. (c) UV-vis spectroscopies of the electrolyte after testing with BFC-800 electrocatalyst for 2 h at different potentials in 0.1 M NaOH electrolyte.

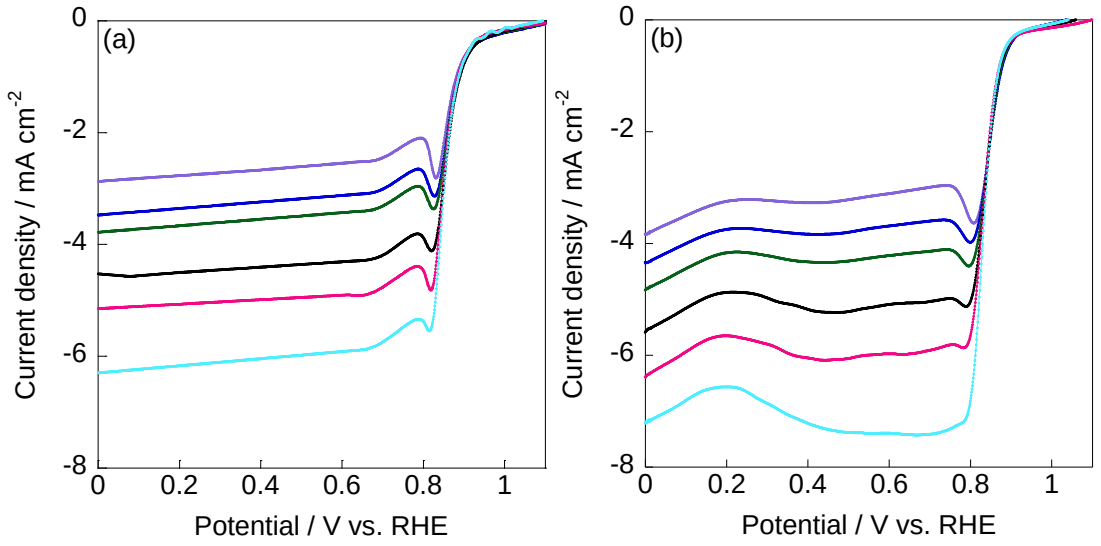

Figure S46 LSV curves of commercial Pt/C (a) and BNFC-800 (b) with various rotation speeds.

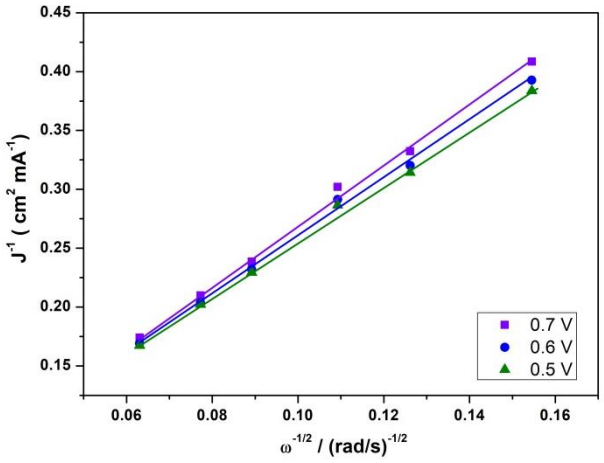

Figure S47 Number of electrons involved in ORR at various potentials of commercial Pt/C.

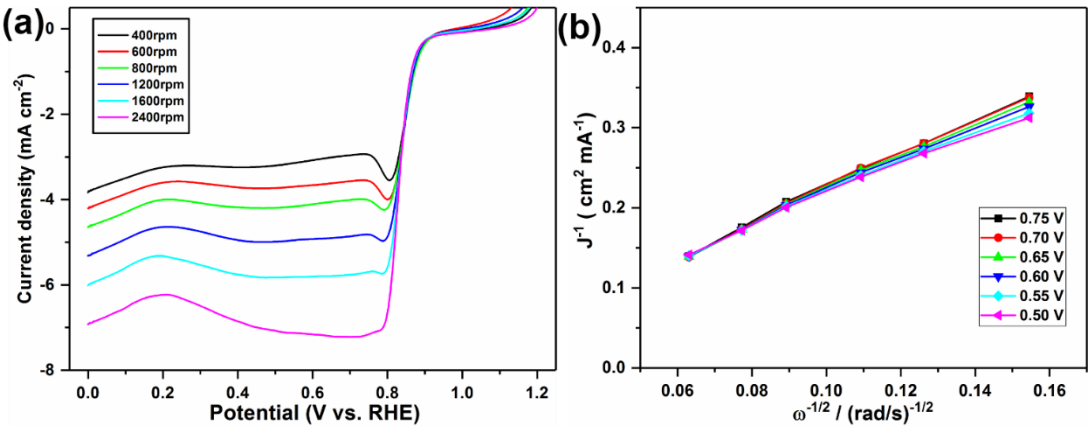

Figure S48 (a) LSV curves of BNFC-800 with various rotation speeds after 5000 potential cycles. (b) Number of electrons involved in ORR at various potentials after 5000 potential cycles.

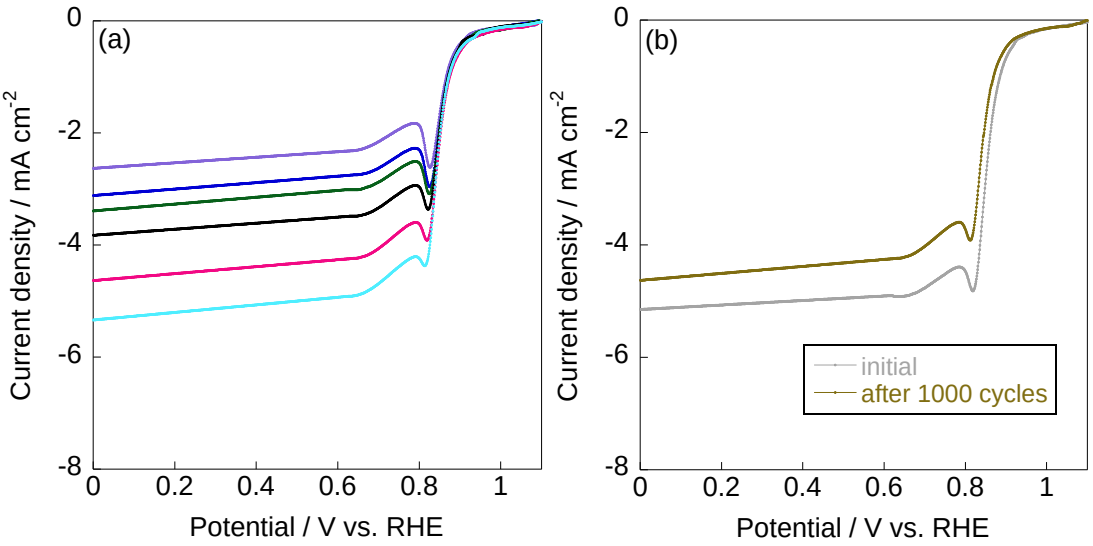

Figure S49 LSV curves of commercial Pt/C with various rotation speeds after 1000 potential cycles. (b) Comparison of ORR activity of commercial Pt/C before and after 1000 potential cycles.

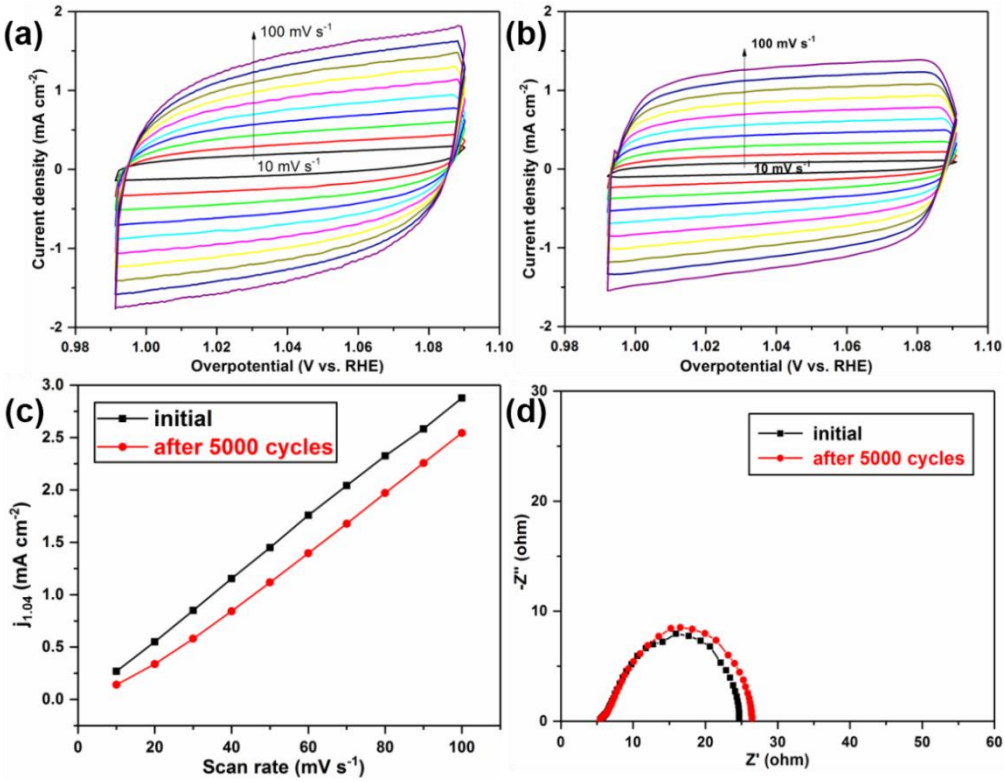

Figure S50 (a) Cyclic voltammetry curves, double-layer capacitances (b) and impedance spectroscopies (c) of BNFC-800 before and after 5000 potential cycles.

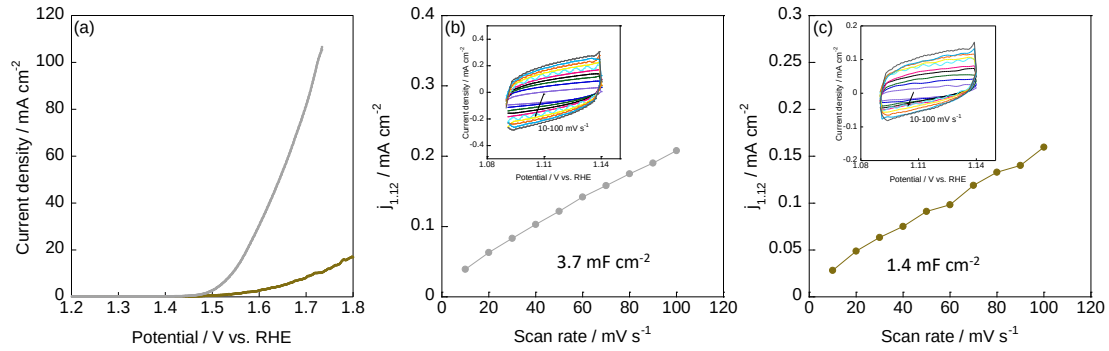

Figure S51 (a) Cyclic voltammetry curves and double-layer capacitances (b) of IrO_2 before and after 1000 potential cycles.

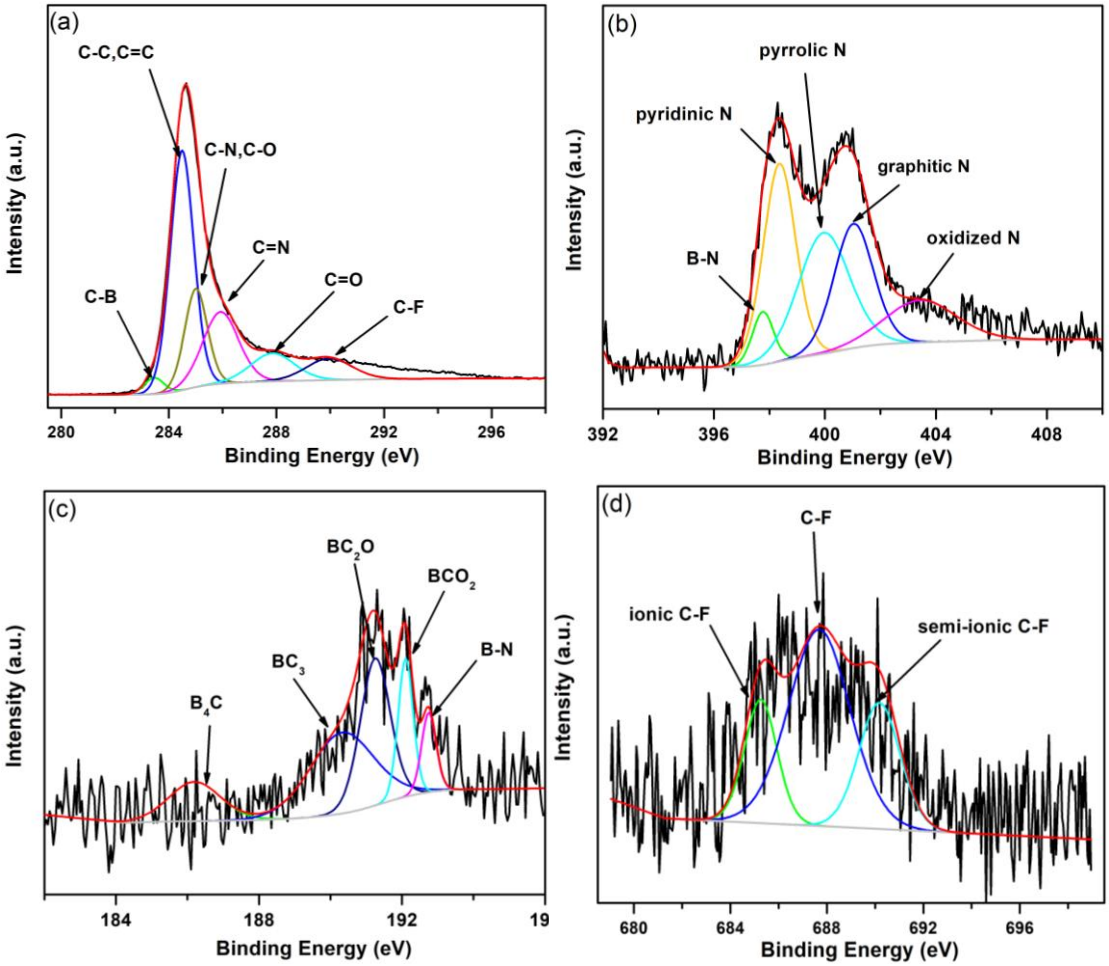

Figure S52 Deconvoluted C1s (a), N1s (b), B1s (c) and F1s (d) peaks of BNFC-800 after 10 h OER catalysis in 1 M KOH electrolyte.

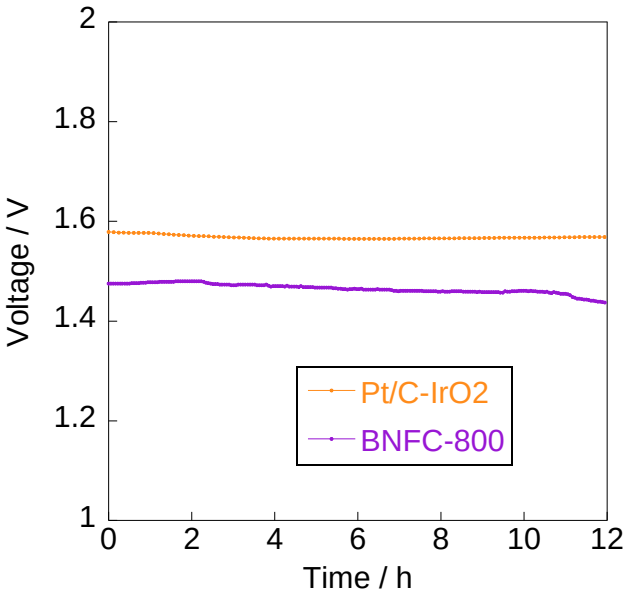

Figure S53 OCV test of Pt/C-IrO_2 and BNFC-800 based ZABs.