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Supporting Information

Designing N-doped carbon nanotubes and Fe-Fe_3C nanostructures co-embedded in B-doped mesoporous carbon as endurant cathode electrocatalyst for metal-air batteries

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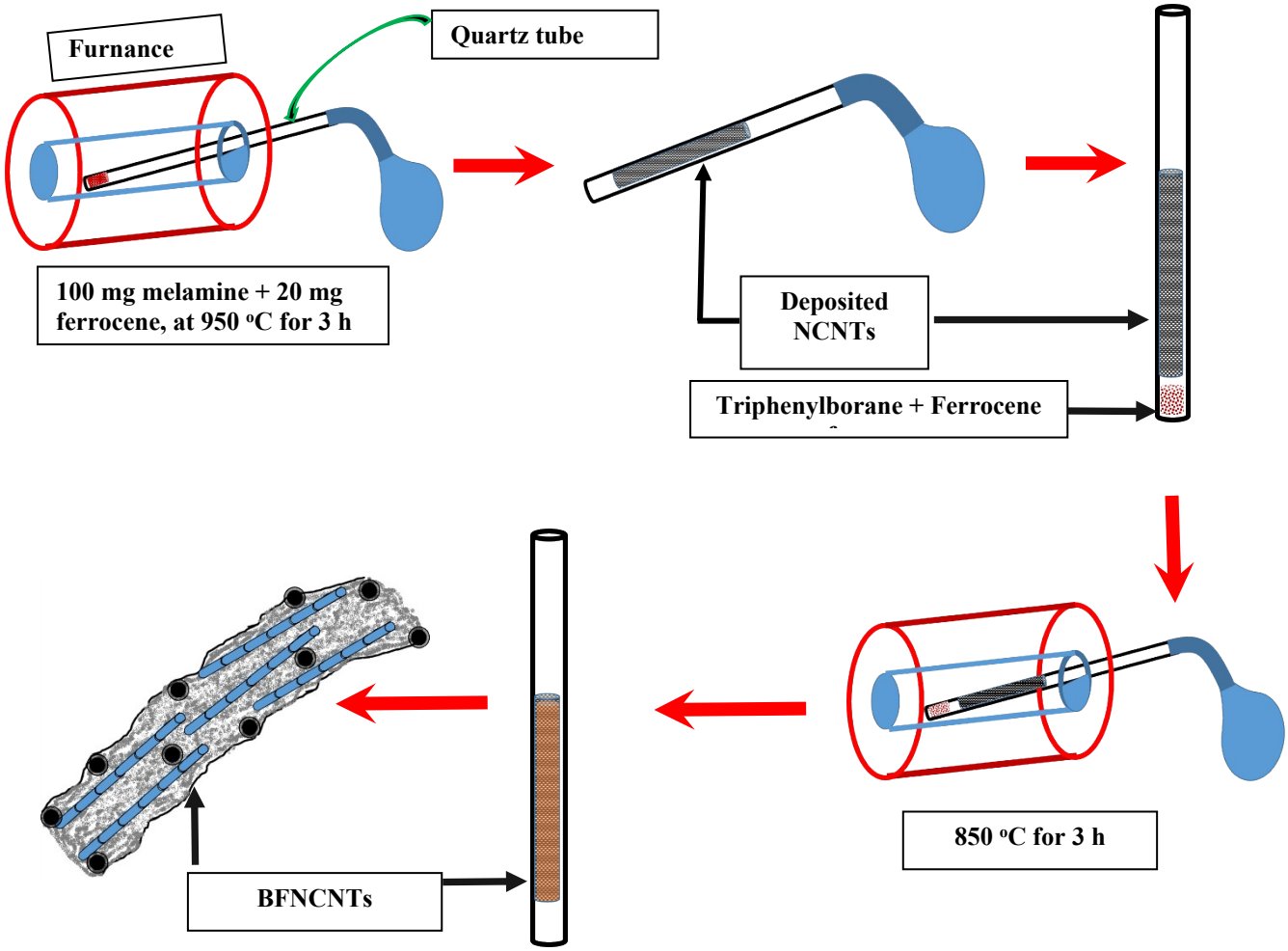

Figure S1. Schematic representation of synthesis procedure of NCNTs, Fe-Fe_3C co-embedded BFNCNTs

1st Step (950 °C for 3 h)	2nd Step (followed by 1st Step) (850 °C for 3 h)	Final Product
Melamine + Ferrocene	Triphenylborane	BNCNTs
Melamine + Ferrocene	Ferrocene	FNCNTs
Melamine + Ferrocene	Triphenylborane+ Ferrocene	BFNCNTs

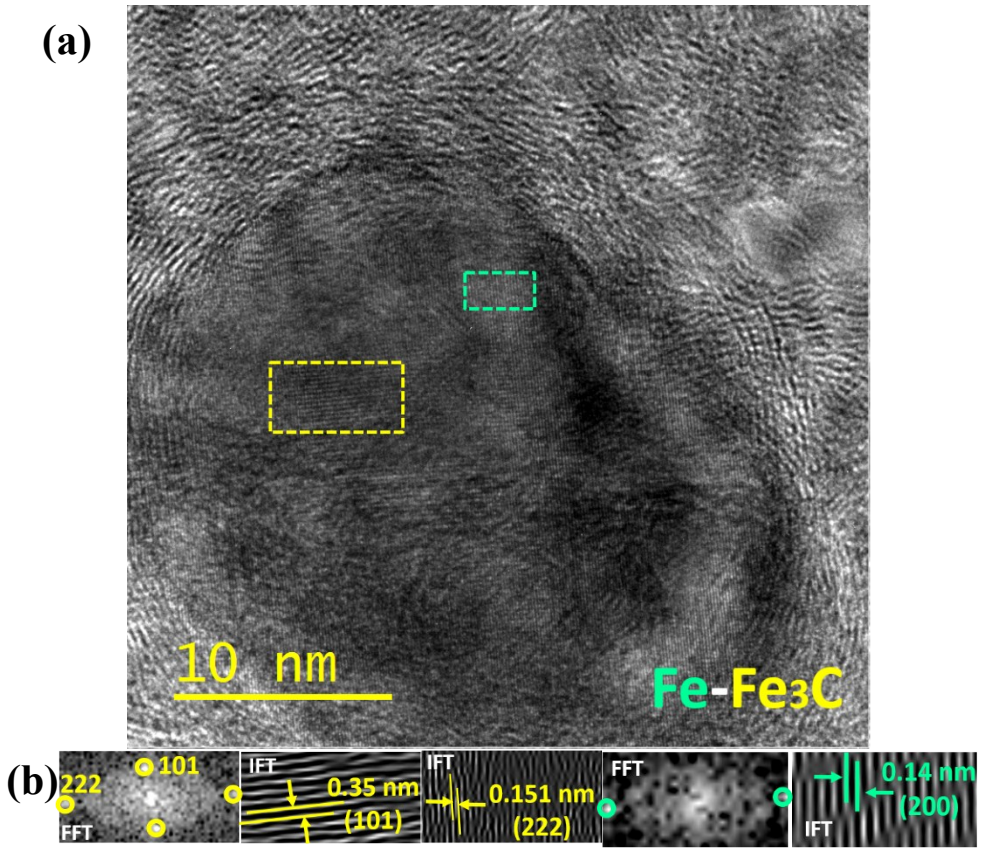

Figure S2. (a) HRTEM image of Fe-Fe_3C nanostructure from BFNCNTs, boxes show the simultaneous presence of planes correspond to Fe (green) and Fe_3C (yellow) in the structure. (b) Shows the corresponding FT and IFT patterns of the selected regions.

In order to elucidate the presence of Fe-Fe_3C in the structure, HRTEM image (figure S2) indexing of Fe-Fe_3C nanoparticle has been done. The two regions as shown by boxes in the HRTEM image are selected and processed (fast Fourier transformation-FFT and inverse Fourier transform-IFT). It is evident from figures that the structures comprise of planes that correspond to Fe-Fe_3C species which is in consort with the XRD pattern as shown in figure 3a.

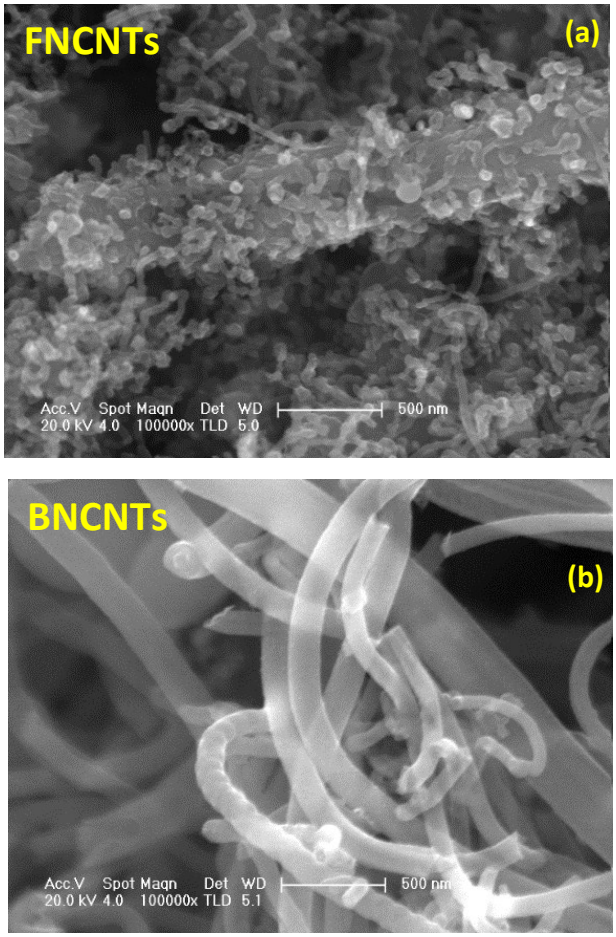

Figure S3. SEM images of (a) FNCNTs and (b) BNCNTs.

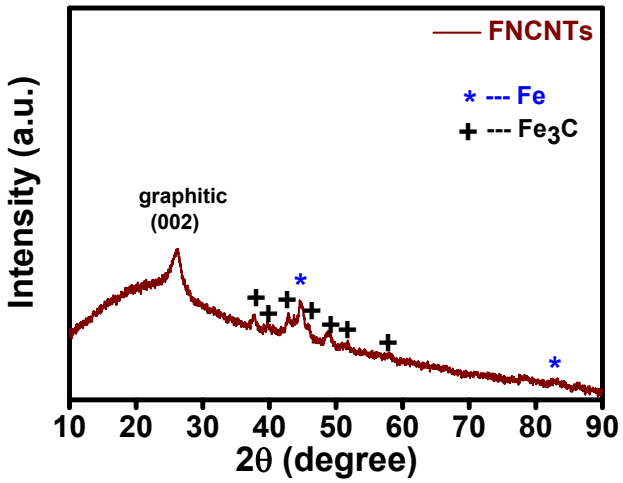

Figure S4. XRD pattern of FNCNTs.

Figure S4 shows the XRD pattern of FNCNTs. Alike to NCNTs and BFNCNTs the peak centred around 26° can be attributed to (002) carbon peak, whereas the peaks centred around 44.7 and 82.5 ^{o} can be attributed to (110) and (211) planes of Fe (ICSD no. 52258). In addition, peaks centred around 37.78, 39.8, 42.9, 43.8, 45.8, 48.9, 51.8, 58.15 ^{o} correspond to (121), (002), (211), (102), (112), (131), (122), (301), respectively for Fe_3C (ICSD no. 99002). Thus, XRD pattern of FNCNTs suggests the presence of Fe- Fe_3C species.

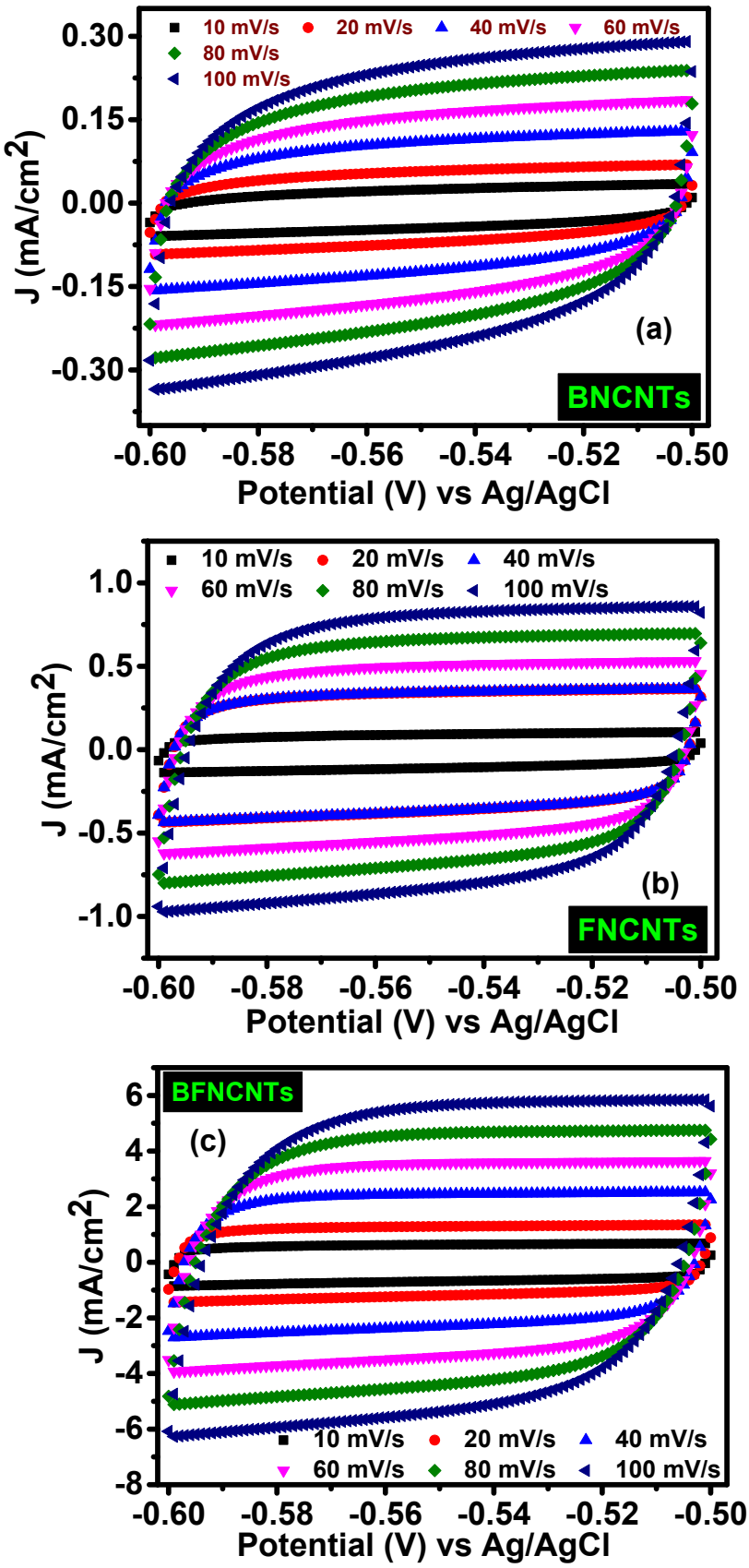

Figure S5. (a-c) Cyclic voltammograms of BNCNTs, FNCNTs and BFNCNTs in 1 M NaOH nitrogen-saturated aqueous solution at different scanning speed in Faradic-silent region.

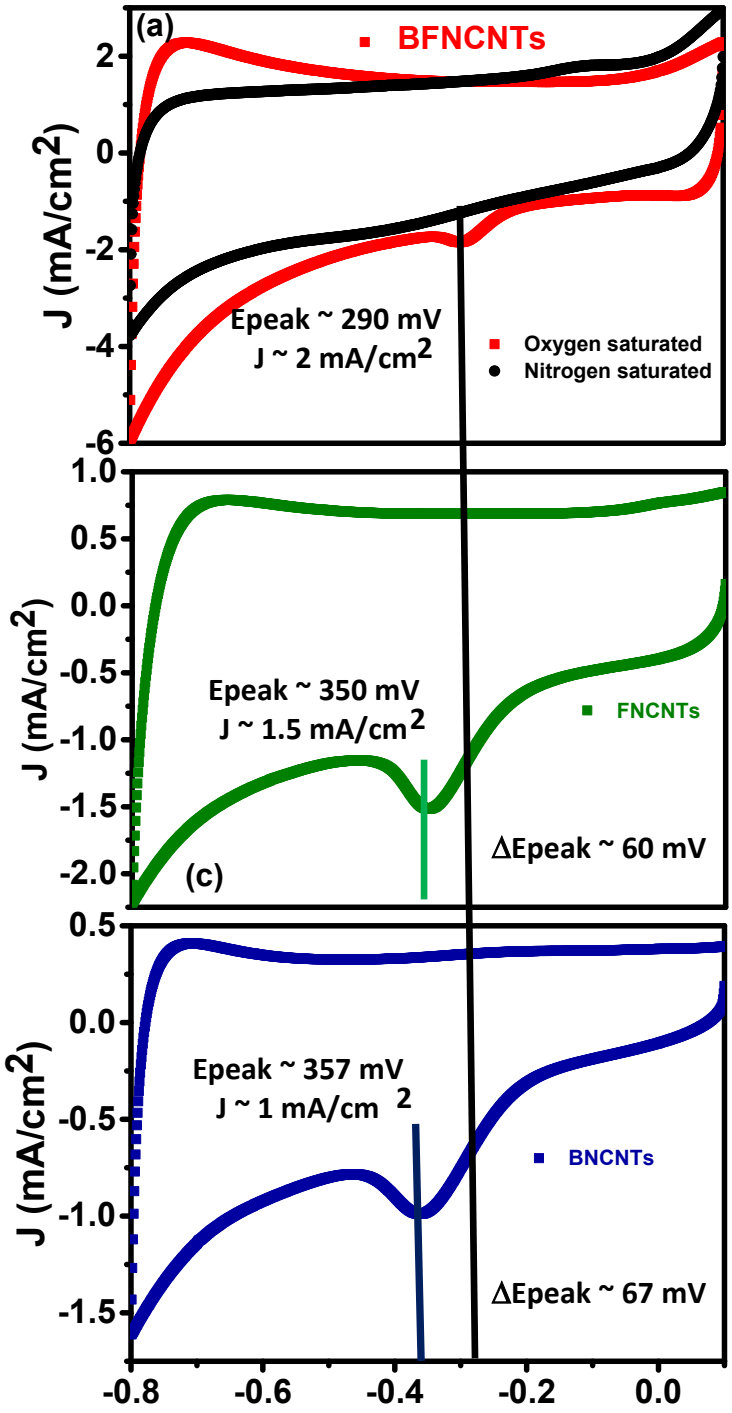

Figure S6. CV curves for ORR on BFNCNTs, FNCNTs, BNCNTs in oxygen/nitrogen saturated alkaline solution at scan speed of 50 mV/s

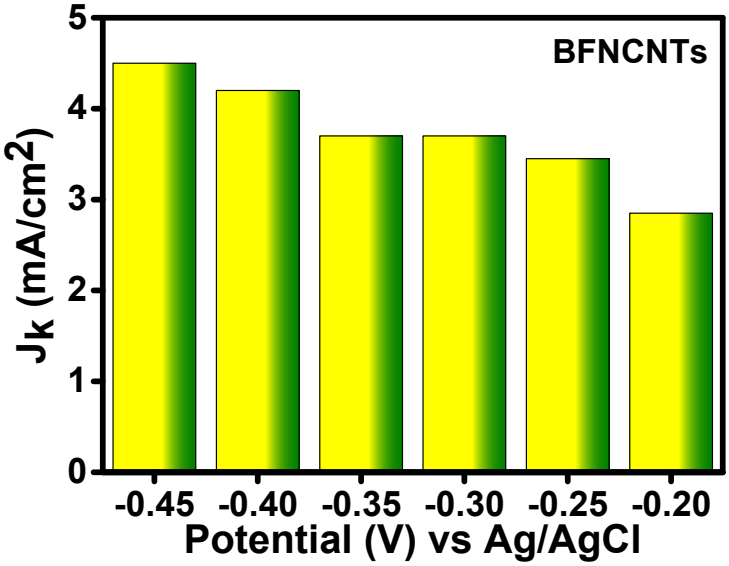

Figure S7. Normalized kinetic current density (J_k) with respect to geometrical electrode area at different potential obtained from the intercept of corresponding K-L plots in mixed control region for BFNCNTs.

Table S1. Summarise the BET surface area for some carbon based oxygen electrocatalysts.

Catalyst	BET surface area	Reference
$NiCo_2O_4$/Graphene	**77** m^2g^{-1}	*J. Mater. Chem. A* **2013**, *1*, 4754.
$CoFe_2O_4$/N-P-biocarbon	79.84 m^2g^{-1}	*J. Mater. Chem. A* **2014**, *2*, 18012.
MWCNT@S–N–C	121 m^2g^{-1}	*New J. Chem.* **2015**, *39*, 6289.
CoFe2O4/rGO	173.12 m^2g^{-1}	*Journal of Power Sources* **2014**, *250*, 196.
Fe/Fe3C@NGL-NCNT	210 m^2g^{-1}	*Chem. Commun.* **2015**, *51*, 2710.
BFNCNTs	**272** m^2g^{-1}	**Present study**

Table S2. OER activity summary for various carbon-based electrocatalyst.

Electrocatalyst	**Experimental Medium and loading of electrocatalyst**	**E_{on-set} (mV) Vs Ag/AgCl**	**$E_{J=10}$ (mV) Vs Ag/AgCl**	**Reference**
CoFe2O4/rGO	0.1 M KOH, 1.006 mg/cm^2	540	700	Journal of Power Sources 250 (2014) 196e203
FeCo2O4-HrGOS	0.1 M KOH, 1.006 mg/cm^2	570	750	Carbon 92 (2015) 7 4 –8 3
CoFe2O4/CNTs	0.1 M KOH, 1.006 mg/cm^2	600	700	Electrochimica Acta 177 (2015) 65–72
MWCNT@S–N–C	0.1 M KOH, 0.200 mg/cm^2	600	700	*New J. Chem.,* 2015, 39, 6289--6296
S,N,Fe-porous carbon	0.1 M KOH, 0.100 mg/cm^2	----	650	*Green Chem.*, 2016, **18**, 4004-4011
N-doped Fe-Fe3C@ graphitic layer	0.1 M KOH, 0.710 mg/cm^2	600	778	Green Chemistry 18 (2016), 427-432
Nitrogen-doped Fe/Fe3C@graphitic layer/carbon nanotube	0.1 M KOH 0.103 mg/cm^2	500	850	*Chem. Commun.,* 2015, **51,** 2710-2713
NiCo2S4@N/SrGO	0.1 M KOH 0.283 mg/cm^2	600	720	*ACS Appl. Mater. Interfaces*, 2013, *5* (11), pp 5002–5008
BFNCNTs	**1 M NaOH 0.75 mg/cm^2**	**422**	**562**	Present Study

Table S3. ORR activity summary for various carbon-based electrocatalyst.

Electrocatalyst	**Experimental Medium and loading of electrocatalyst**	**Eon-set (mV) Vs (Ag/AgCl)**	**E1/2 (Vs Ag/AgCl)**	**Reference**
MWCNT@S–N–C	0.1 M KOH, 0.2 mg/cm^2	-200	~-350	*New J. Chem.,* 2015, 39, 6289--6296
$CoFe_2O_4$/CNTs	0.1 M KOH, 1.006 mg/cm^2	-124	~ -300	Electrochimica Acta 177 (2015) 65–72
$CoFe_2O_4$/rGO	0.1 M KOH, 1.006 mg/cm^2	-136	~ -260	Journal of Power Sources 250 (2014) 196e203
Co–N–GN	0.1 M KOH, 0.1 mg/cm^2	-98	-162	J. Mater. Chem. A, 2013, **1**, 3593-3599
N,P,S-rGO/*E. coli*	0.1 M KOH, 0 0.510 mg/cm^2	-90	~ -220	J. Mater. Chem. A 2015,3, 12873-12879
$FeCo_2O_4$-HrGOS	0.1 M KOH, 1.006 mg/cm^2	-90	~ -200	C A R B ON 9 2 (2 0 1 5) 7 4 –8 3
N-graphene/CNT hybrids	0.1 M KOH, 0.430 mg/cm^2	-80	~ -200	Angew. Chem. Int. Ed. 2014, 53, 6496 - 6500
N-CNTs	0.1 M KOH, 0.306 mg/cm^2	-60	-220	Carbon 50 (2 0 12) 2620-2627
N,S-Graphene	0.1 M KOH, 0.43 mg/cm^2	-60	-300	*Angew. Chem., Int. Ed.*, 2012, 51, 11496
BFNCNTs	**0.1 M NaOH 0.75 mg/cm^2**	**-30**	**-225**	Present Study

Table S4. Overall oxygen electroactivity (ΔE) summary for various carbon-based electrocatalyst.

Catalyst	Overall oxygen electrode activity ΔE ($E_{j=10(OER)} - E_{1/2(ORR)}$)(V)	Reference
S-N-C@MWNCNTs	~1.25	*New J. Chem.* **2015**, *39*, 6289.
NCNF-1000	~1.02	Adv. Mater. 2016, 28, 3000−3006.
Fe/Fe3C@NGL-NCNT	~1	*Chem. Commun.* **2015**, *51*, 2710.
N-Graphene/CNTs	~1.00	*Small*, **2014**, *10*, 2251.
B-MWNCNTs	~1.00	*Electrochimica Acta* **2014**,*143*, 291.
$CoFe_2O_4$/rGO	~0.98	*J. Power Sources* **2014**, *250*, 196.
$CoFe_2O_4$/N-P-biocarbon	~0.98	*J. Mater. Chem. A* **2014**,*2*,18012.
N,P-Carbon paper	~ 0.96	*Angew. Chem. Int. Ed.* **2015**, *54*, 4646.
P-doped g-C3N4 /CF	~0.96	Angew. Chem. Int. Ed. 2015, 54, 4646−4650.
Fe/Fe3C@ N-graphitic layer	~ 0.97	*Green Chemistry* **2015**, DOI: 10.1039/c5gc01405k
Pt@C	~0.94	*Angew. Chem. Int. Ed.* **2014**, *53*, 8508.
Mn_xO_y/N-Carbon	~0.93	*Angew. Chem. Int. Ed.* **2014**, *53*, 8508.
Ir@C	~0.92	*J. Am. Chem. Soc.* **2010**,*132*, 3612.
$NiCo_2O_4$/Graphene	~0.915	*J. Mater. Chem. A* **2013**,*1*,4754.
N, S, O carbon nanosheet	0.88	Nano Energy 19 (2016) 373–381
Fe@N-C	0.88	Nano Energy 2015, 13, 387−396.
NiO/CoN PINWs	0.8	*ACS Nano*, **2017**, *11* (2), pp 2275–2283
Fe/N/C@BMZIF	0.79	*ACS Appl. Mater. Interfaces*, **2017**, *9* (6), pp 5213–5221
BFNCNTs	**0.788**	Present Study