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Maximizing the utilization of Fe-N_xC/CN_x centres for air-cathode material and practical demonstration of metal-air batteries

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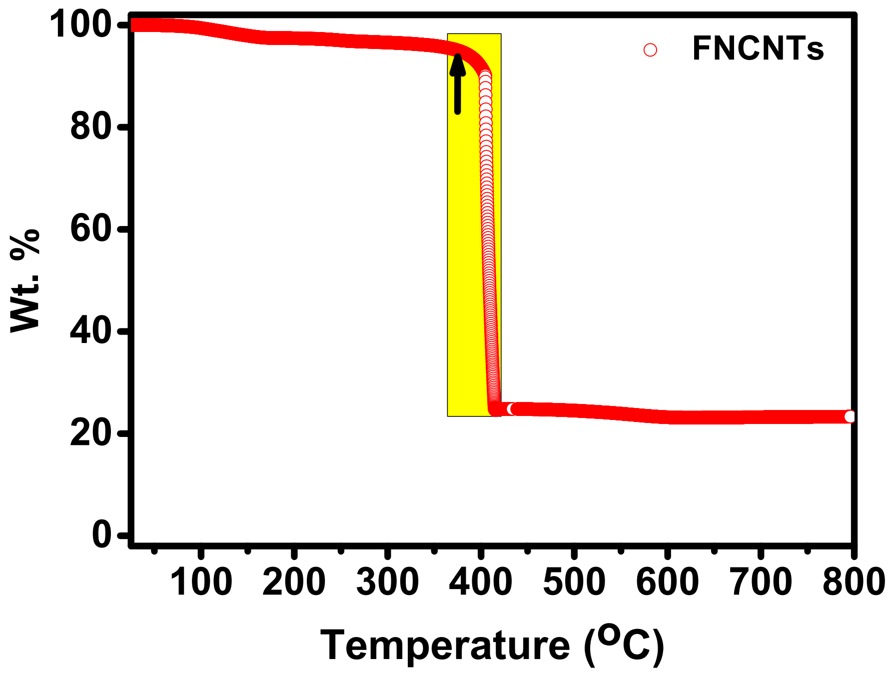

Figure S1. Thermogravimetric (TGA) curve for FNCNTs in presence of oxygen. The arrow indicates the annealing temperature used.

The TGA study suggest that in the temperature window of 40~45 ^{o}C (as depicted by yellow box) the most of the carbon get oxidised. Based on this study the temperature and the dwelling time of our experiment (for the partial exposure of Fe-Fe_3C nanoparticles) has been optimised which is 375 ^{o}C (ramping rate 10 ^{o}C per minute, oxygen gas flow rate 5 sccm).

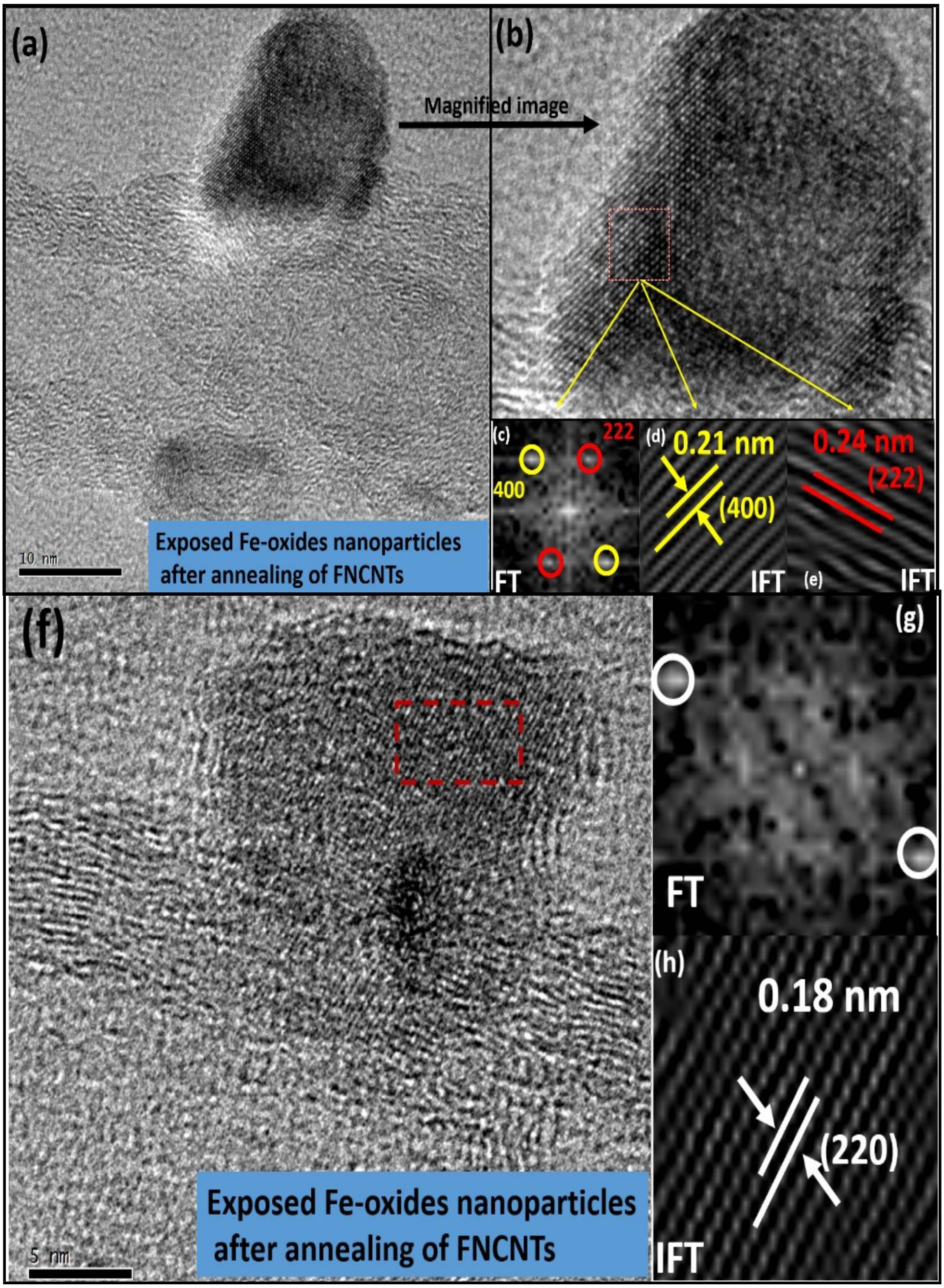

Figure S2. (a) (a) HRTEM image of annealed FNCNTs, (b and f) the magnified image of iron-oxide nanoparticles. (c-e and g-h) The corresponding FT and IFT patterns of the selected region as indicated by boxes, respectively.

HRTEM images of annealed FNCNTs are shown in Fig. S2. It is evident that the nanoparticles in annealed FNCNTs sample are either Fe_3O_4 or Fe_2O_3 and are in consort with the XRD pattern as shown in figure 2a. The boxes indicate the region of interest in the HRTEM image which are selected and processed (fast Fourier transformation-FFT and inverse Fourier transform-IFT). Figures S2 d and e suggest the presence of Fe_3O_4 and fig. S2 h suggests the presence of Fe_2O_3 nanoparticles.

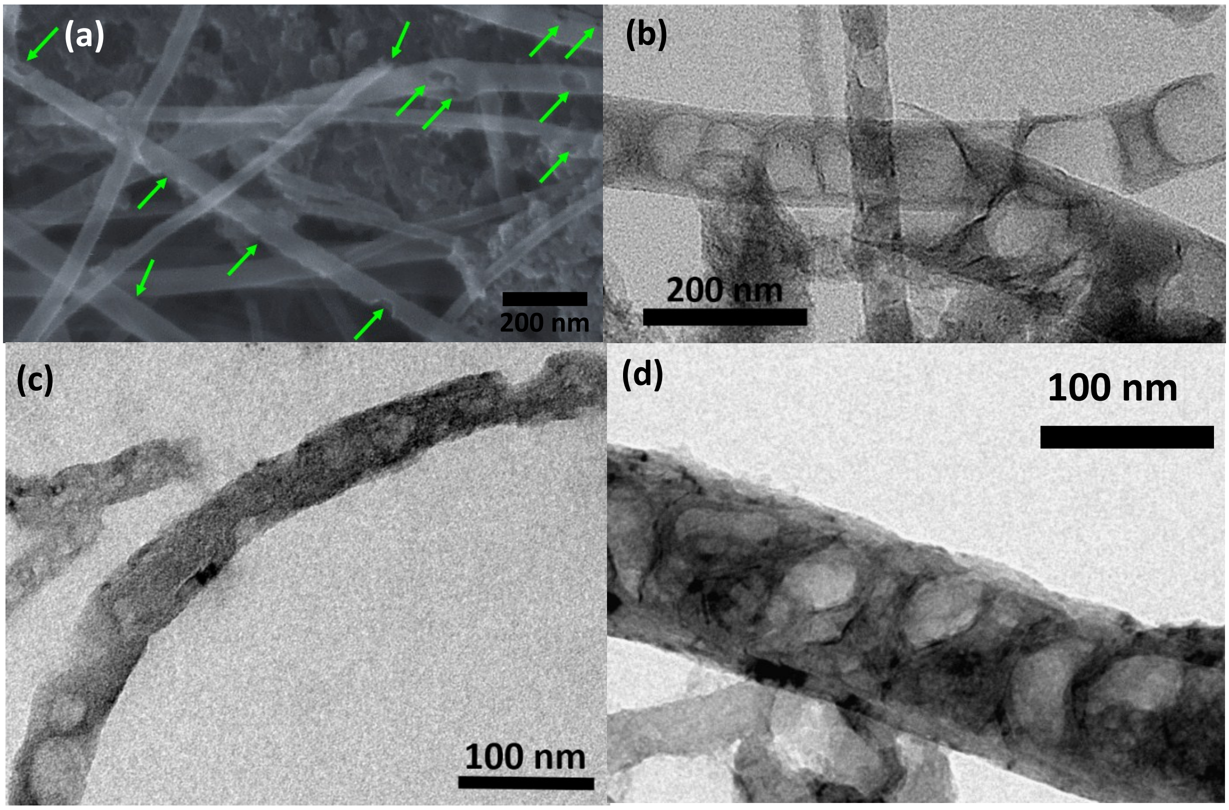

Figure S3. (a) SEM, and (b-d) TEM images of ANCNTs.

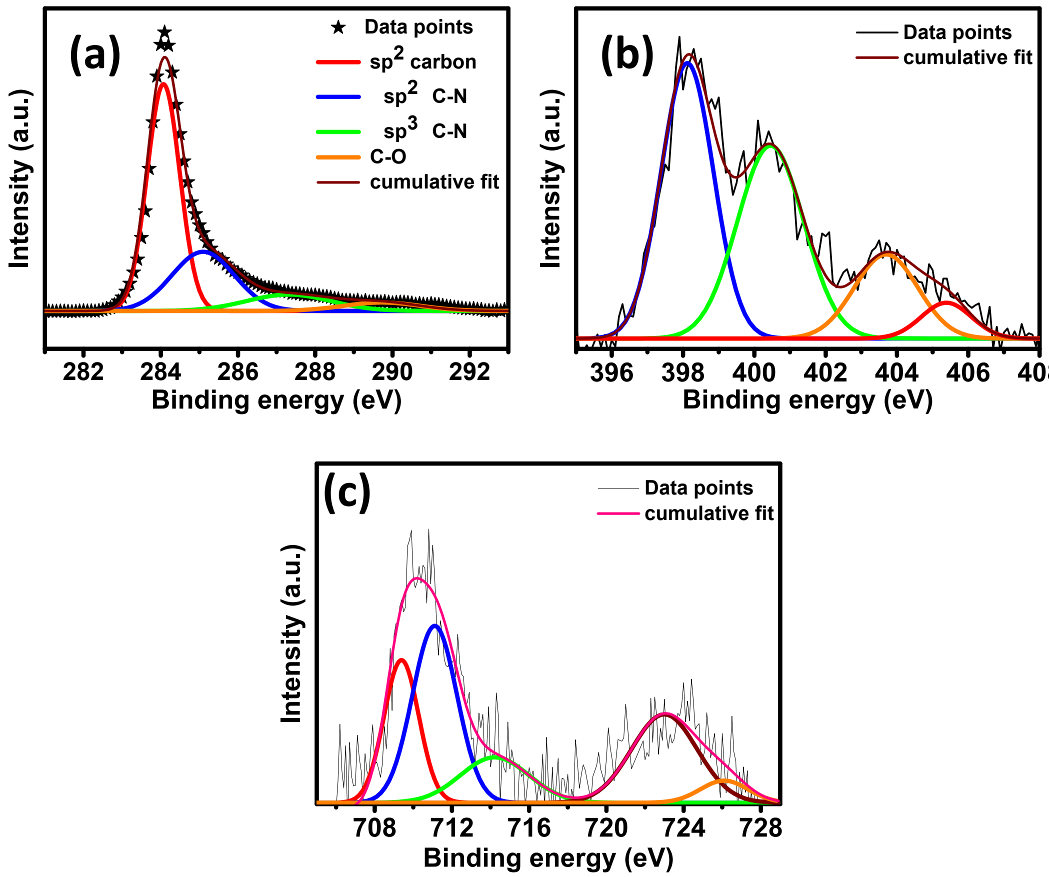

Figure S4. (a-c) Deconvoluted core spectrum of C1s, N1s and iron present in FNCNTs.

The deconvoluted C1s core spectrum comprises of peaks centred around 284.1, 285, 287.3 and 289.3 eV that correspond to sp^2 carbon, sp^2 carbon-nitrogen, sp^3 carbon-nitrogen and carbon-oxygen interactions, respectively.[1-3] Similarly the deconvoluted peaks for N1s core spectrum centred around 398.1, 400.7 eV represents the presence of pyridinic, quaternary nitrogen species along with 403.7 and 405 eV which can be attributed to the different form of nitrogen oxides interactions.[1-3] Further, for Fe 2p profile in addition to the peaks centred around 711.1, 714.2 eV (correspond to Fe^{2+} & Fe^{3+} $2p_{3/2}$ contributions) and 723.2 & 726 eV (correspond to Fe^{2+} & Fe^{3+} $2p_{1/2}$ contributions) there exist a satellite peak

709 eV corresponding to Fe^{o} state.[1-3] The change in the XPS profile of Fe in ANCNTs as compared to that of FNCNTs is believed to be due to the change in the kind of interactions Fe with other atoms in the vicinity. In the FNCNTs, the nature of interaction (as suggested by the XRD study) is due to presence of Fe-Fe3C nanoparticles whereas the contributions mainly come through the Fe-Nx/C interaction in ANCNTs. This is further validated by the electrochemical poisoning studies on ANCNTs using NaSCN.

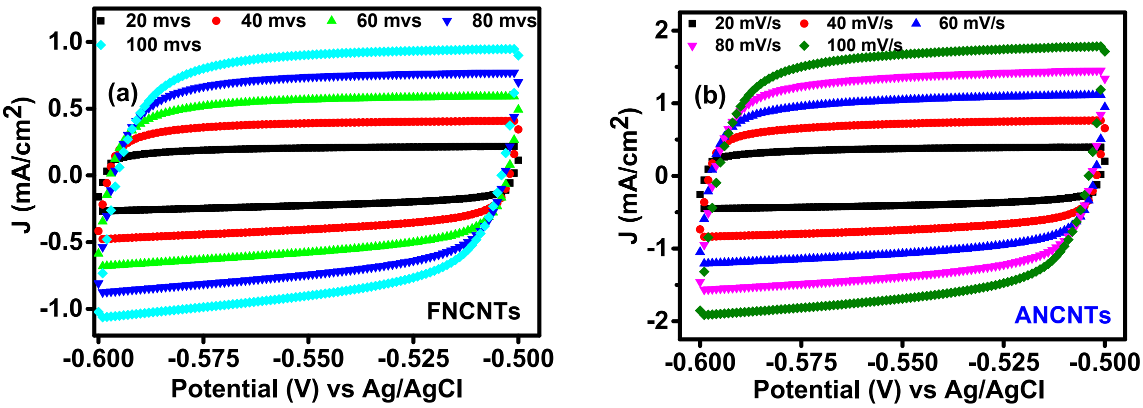

Figure S5. (a,b) Cyclic voltammograms of FNCNTs and ANCNTs in 0.3 M NaOH nitrogen-saturated aqueous solution at different scanning speed in Faradic-silent region.

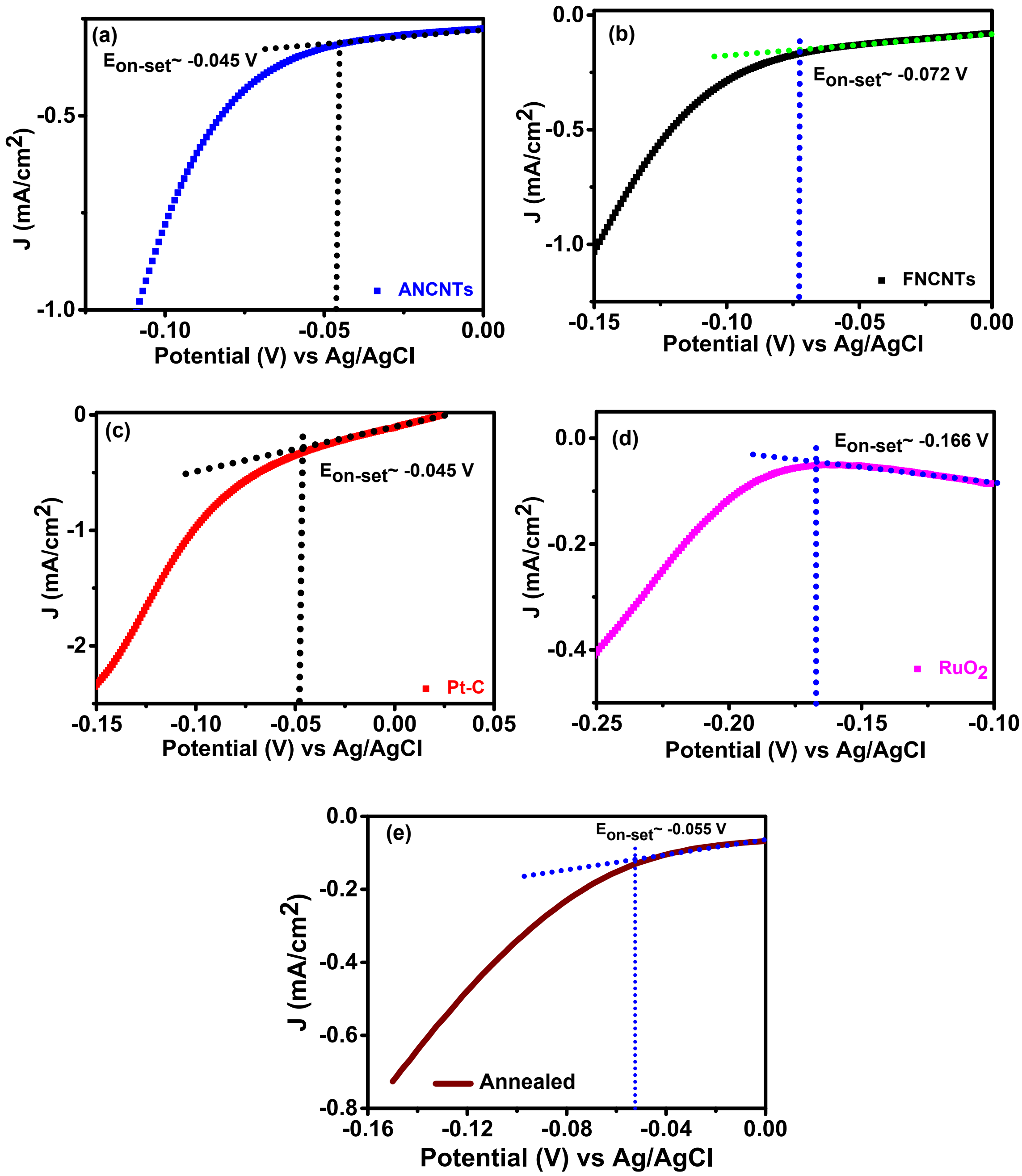

Figure S6. (a-e) Magnified portions of LSV-RDE curves of ANCNTs, FNCNTs, Pt-C, RuO_2 and annealed sample for ORR at 1600 rpm for $E_{on\text{-}set}$ determination.

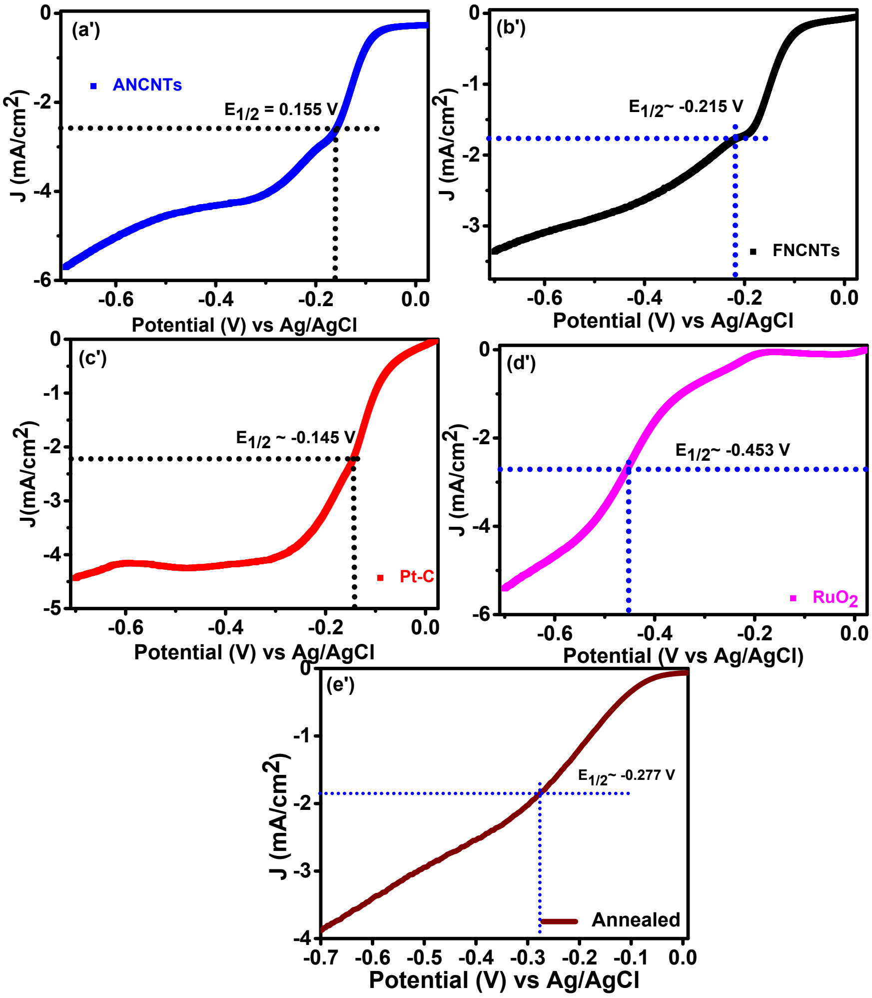

Figure S7. (a'-e') LSV-RDE curves of ANCNTs, FNCNTs, Pt-C, RuO_2 and annealed sample for ORR at 1600 rpm for $E_{1/2}$ determination.

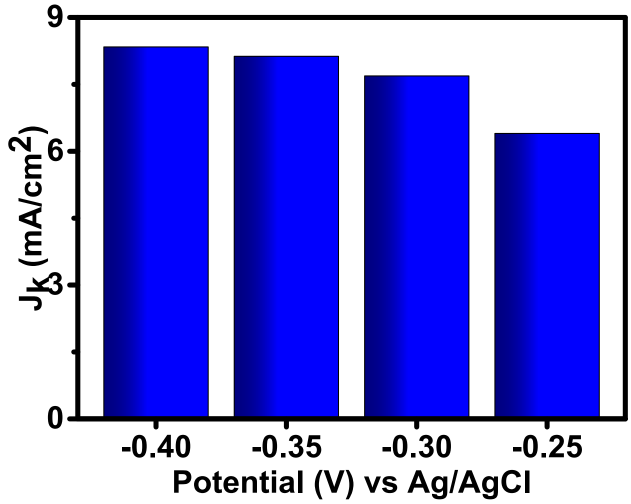

Figure S8. Kinetic current density (J_k) on ANCNTs deduced from K-L plot.

Table S1. ORR activity summary for various carbon-based electrocatalyst.

Electrocatalyst	Experimental Medium and loading of electrocatalyst	Eon-set (mV) Vs (Ag/AgCl)	E1/2 (mV) (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
$FeCo_2O_4$-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
NGPC/NCNT-900	0.1 M KOH, 0.105 mg/cm^2	-51	~ -171	*Chem. Mater.*, 2015, *27* (22), pp 7610–7618
S,N,Fe-porous carbon	0.1 M KOH, 0.100 mg/cm^2	-50	~ -200	Green Chem., 2016, **18**, 4004-4011
BFNCNTs	0.1 M NaOH 0.75 mg/cm2	-30	~ -225	*J. Mater. Chem. A*, 2017, 10.1039/C7TA04597B.
N-doped Fe-Fe_3C@ graphitic layer	0.1 M KOH, 0.710 mg/cm^2	-50	~ -200	Green Chemistry 18 (2016), 427-432
$CoFe_2O_4$/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
NCNTs	2M NaOH 4 mg/cm^2	-115	---	*J. Mater. Chem. A*, 2013, **1**, 3133
BCNTs	0.1 M NaOH 1 **mg/cm^2**	-45	-290	*Appl. Energy*, 2017, **205**, 1050–1058.
FNCNTs	**0.3 M NaOH 0.9 mg/cm^2**	**-72**	**-215**	Present Study
ANCNTs	**0.3 M NaOH 0.9 mg/cm^2**	**-45**	**-155**	Present Study

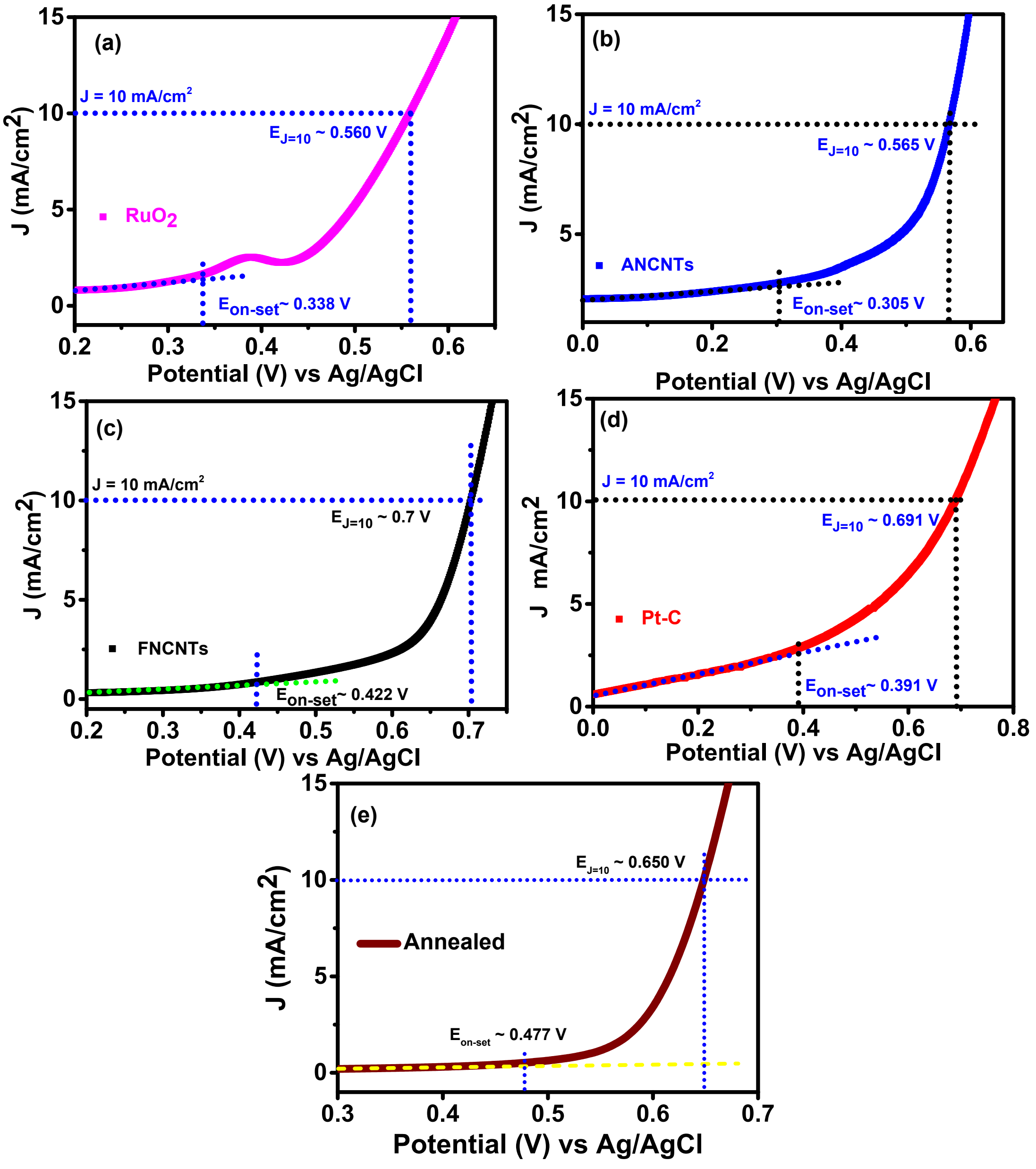

Figure S9. (a-e) OER $E_{on\text{-}set}$ and $E_{j=10}$ evaluation for RuO_2, ANCNTs, FNCNTs, Pt-C and annealed sample, respectively.

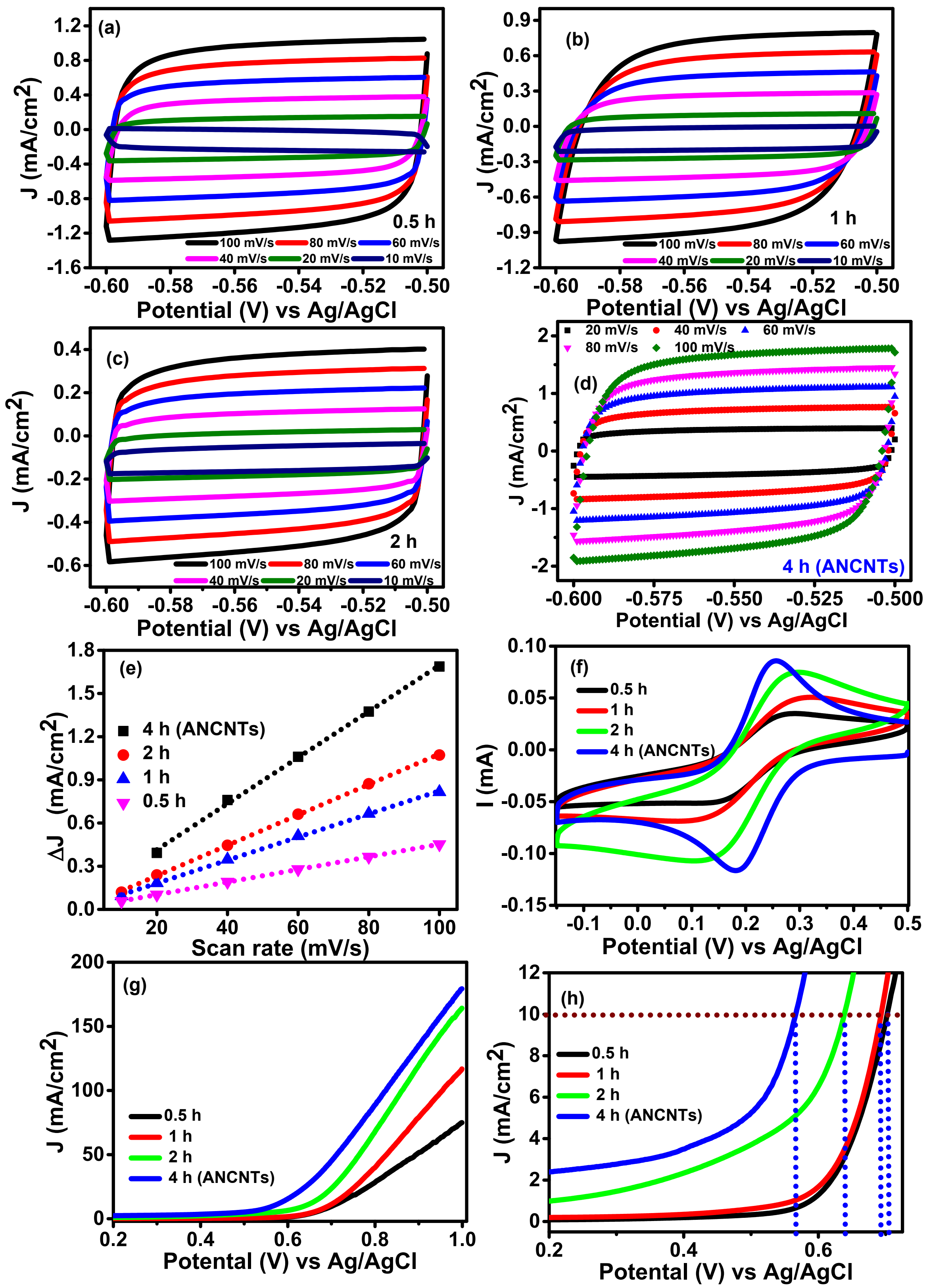

Figure S10. (a-d) CVs on various ANCNTs samples with different acid treatment time (0.5, 1, 2, 4 h) in 0.3 M NaOH nitrogen-saturated aqueous solution at different scanning speed in Faradic-silent region. (e) Double layer capacitance deduced from figure a-d. (f) CV curves of 10 mM $Fe(CN)_6^{3-/4-}$ in 0.5 M KCl aqueous solution using catalyst coated RDE electrodes at scan speed of 20 mV/s. (g) LSV curves for OER study in nitrogen saturated 0.3 M NaOH aqueous solution at 1000 rpm and 10 mV/s scan speed. (h) Magnified portion of figure (g) for $E_{j=10}$ determination.

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**
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
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
crumpled grapheme CoO	1 M KOH 0.7 mg/cm^2	----	580	Energy Environ. Sci., 2014, 7, 609-616
FNCNTs	**0.3 M NaOH 0.9 mg/cm^2**	**422**	**700**	Present Study
ANCNTs	**0.3 M NaOH 0.9 mg/cm^2**	**305**	**565**	Present Study

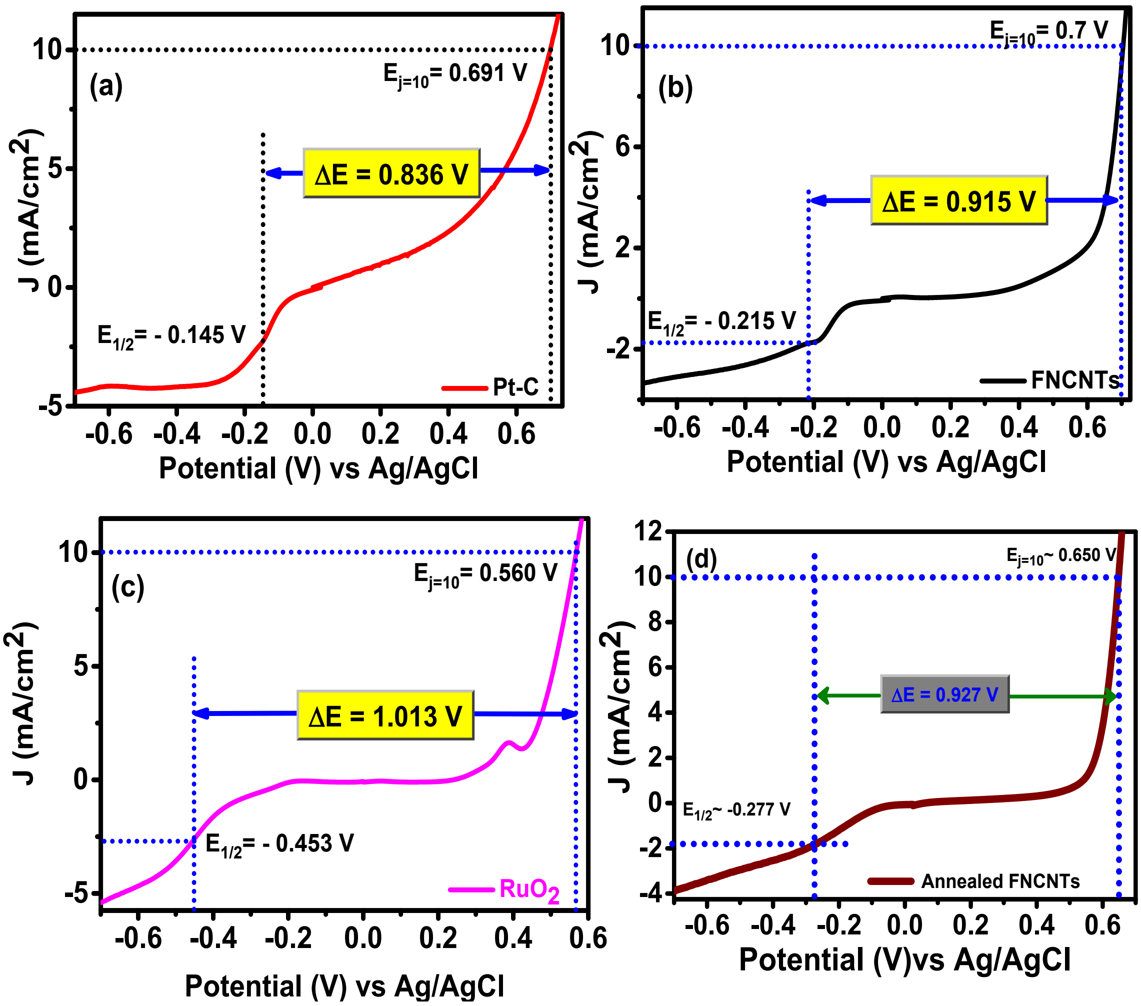

Figure S11. (a-d) Evaluation of total oxygen electroactivity $\Delta E = E_{j(OER)=10} - E_{1/2(ORR)}$ efficiency of Pt-C, FNCNTs, RuO_2 and of annealed FNCNTs.

Table S3. Overall oxygen electroactivity 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
CoO/Ngraphene	0.76	Energy Environ.Sci., *7*, 609(2014).
P,N-Graphene framework	~ 0.795 & 0.705	*Energy Environ. Sci.*, 2017, DOI: 10.1039/C6EE03446B
BFNCNTs	~ 0.788	*J. Mater. Chem. A*, 2017, 10.1039/C7TA04597B.
N,S-CNS, ΔE	~ 0.81 & 0.72	*Energy Environ. Sci.*, 2017, **10**, 742.
FNCNTs	**0.915**	Present Study
ANCNTs	**0.72**	Present Study

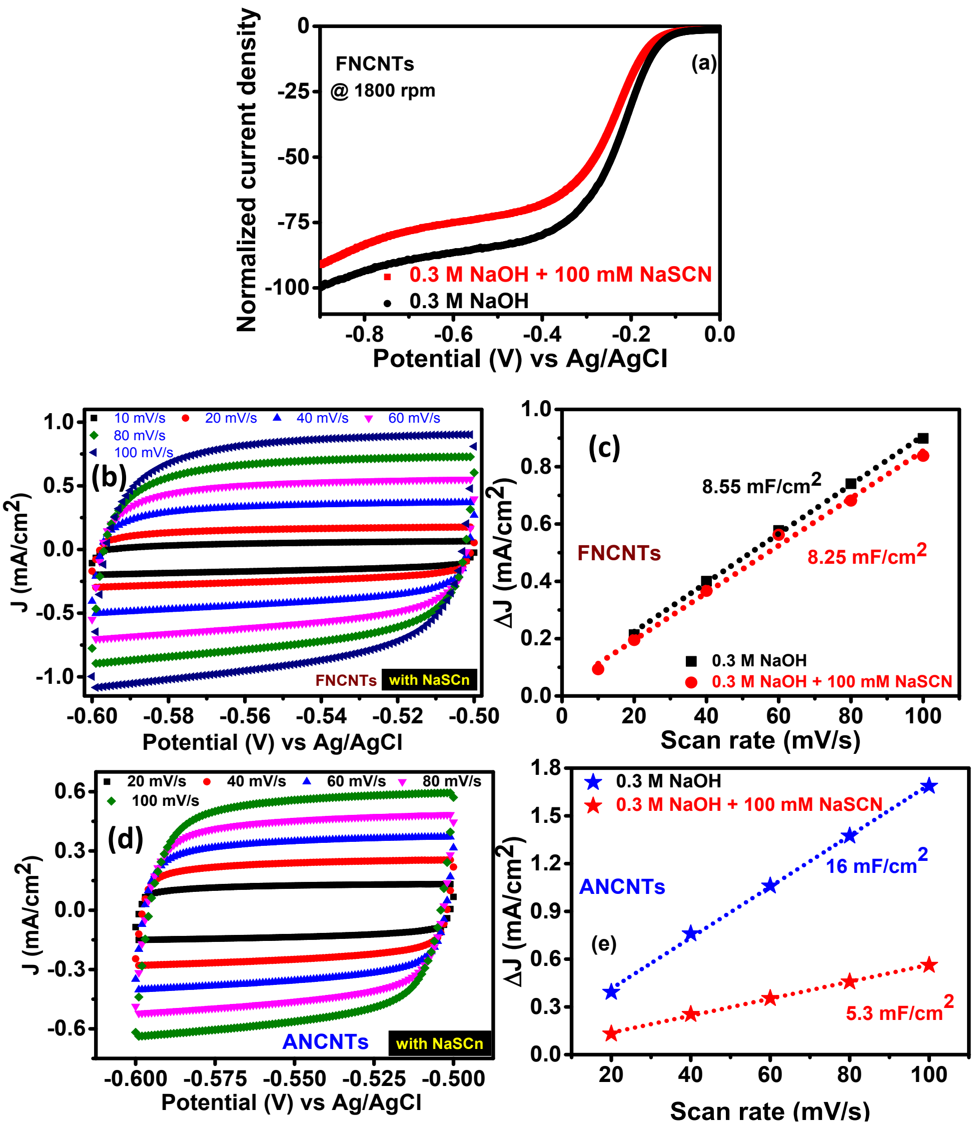

Figure. S12 (a-c) ORR polarization curves (@ 1800 rpm), CV and C_{dl} in 0.3 M NaOH and 0.3 M NaOH + 100 mM NaSCN aqueous solution on FNCNTs. (d and e) CV and C_{dl} on ANCNTs.

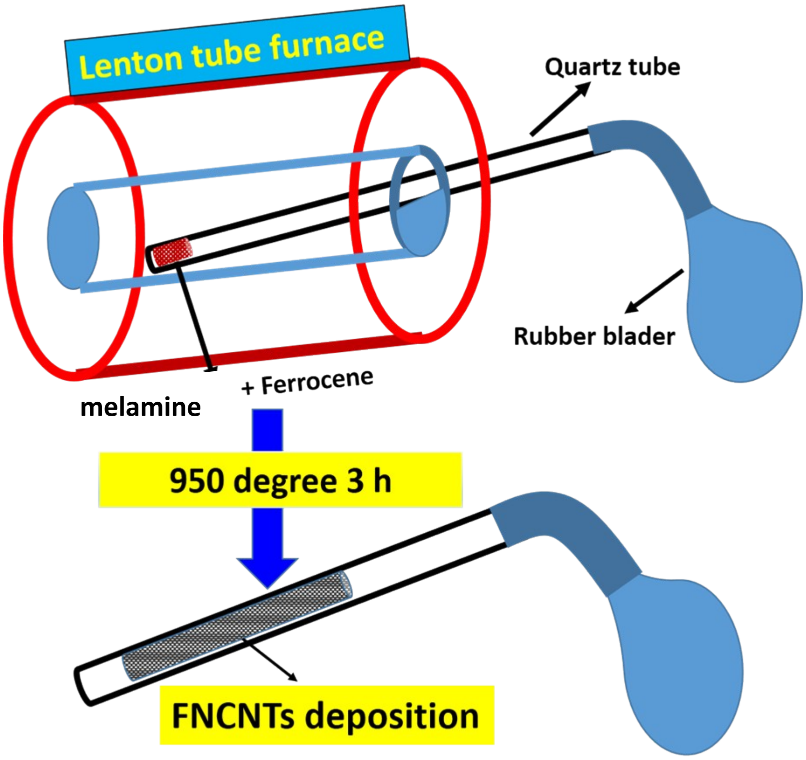

Figure S13. Synthesis schematic for FNCNTs

References

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