Supporting Information

Carbon Nanohorn-Derived Graphene Nanotubes as a Platinum-Free Fuel Cell Cathode

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Material Characterization: FEI Technai G2 T30 operated at 300 kV and Quanta 200 3D FEI were used respectively for high resolution transmission electron microscopic (HR-TEM) and scanning electron microscopic (SEM) analysis. LabRam spectrometer (HJY, France) was used for Raman analysis with a laser wavelength of 632 nm. VGMicrotech Multilab ESCA 3000 spectrometer was used for X-ray photoelectron spectroscopic analysis by employing a monochromatic Mg K_α X-ray source ($h\nu$ = 1253.6 eV). Brunauer-Emmet-Teller (BET) nitrogen adsorption-desorption experiment was performed on Quantachrome Quadrasorb automatic volumetric measurement system at 77 K using ultra pure nitrogen gas.

Electrochemical Measurements: Biologic electrochemical workstation (VMP3) was used for all the electrochemical measurements by using a three-electrode set-up. 0.1 M $HClO_4$, 0.5 M H_2SO_4 and 0.1 M KOH were used as the electrolytes for the electrochemical measurements. Catalyst coated glassy carbon disc (0.196 cm^2 area, Pine Instruments. Inc.) was used as the working electrode. Different reference electrodes were used for the electrochemical measurements which are Ag/AgCl in 0.1 M $HClO_4$, $Hg/HgSO_4$ in 0.5 M H_2SO_4 and Hg/HgO in 0.1 M KOH. For the purpose of comparison, all the potentials are converted to reference hydrogen electrode scale and used in the manuscript. A graphite rod was used as the counter electrode in all the three electrolytes. For the preparation of the catalyst ink, 10 mg of the catalyst was ultrasonically dispersed in a mixture of 1 ml of water-isopropyl alcohol (3:1) and 40 µl of 5 wt. % Nafion solution for 1 h. 20 µl of the catalyst slurry was drop coated on the glassy carbon electrode to get a total catalyst loading of 1 mg cm^{-2}. The glassy carbon electrode was polished using 0.05 µm polishing alumina powder prior to drop coating of the catalyst ink. The catalyst ink was dried under an IR lamp for electrochemical analysis. Commercial Pt/C (40 wt. % from Johnson Mattey (Alpha Acessar)) was also studied for the comparison purpose. Catalyst ink for Pt/C was prepared by dispersing 10 mg of Pt/C in 1 ml of water and 40 µl of Nafion (5 wt. % in water) using an

ultrasonic bath for 1 h. 5 µl of the resulting ink was drop coated on the glassy carbon electrode in order to get a total Pt loading of 100 μg_{Pt} cm^{-2}. Linear sweep voltammograms (LSVs) were recorded using a rotating disk electrode (RDE, 0.196 cm^2, Pine Instruments) at different electrode rotation speeds (400, 900, 1200, 1600 and 2500 rpm) in an oxygen saturated electrolyte with a scan rate of 5 mV s^{-1} at room temperature. For the durability analysis, accelerated durability test (ADT) was performed for 5000 cycles for FeGNT in all three electrolytes. CV was performed at 100 mV s^{-1} scan rate in between a potential window of 0.60 to 1.0 V under oxygen purging. LSV was taken before and after ADT at 1600 rpm with a scan rate of 5 mV s^{-1}.

Hydrogen peroxide percentage and number of electron transfer during the oxygen reduction reaction were measured using a rotating ring disc electrode (RRDE, 0.245 cm^{-2}, Pine Instruments) voltammogram using the following equations:

$$n = 4 \times \frac{I_d}{I_d + \frac{I_r}{N}} \quad \text{..... (1)}$$

$$H_2O_2(\%) = 200 \times \frac{\frac{I_r}{N}}{I_d + \frac{I_r}{N}} \quad \text{.....(2)}$$

where, I_d is the disc current, I_r is the ring current, and N is the collection efficiency of the Pt ring (0.37).

Single cell analysis

Nafion 212 membrane (DuPont, USA) was used as the proton exchange membrane. Initially the Nafion membrane was boiled in con. HNO_3 for 1 h. This was followed by boiling the membrane in DI water, 1 M H_2SO_4, and DI water for another 1 h each. This pretreated membrane was used for the membrane electrode assembly (MEA) fabrication.

Electrodes were prepared by conventional brush coating method. For the cathode layer, a slurry of FeGNT and 20 wt. % Nafion (Dispersion in water, DuPont, USA) with a Nafion to carbon ratio (N/C) of 0.50 in isopropyl alcohol (IPA) was used. 2 mg cm^{-2} of the catalyst loading was used on a gas diffusion layer (GDL, SGL CC, Germany). The anode electrode comprises of 40 wt. % Pt/C with a catalyst loading of 0.50 mg cm^{-2} (N/C is 0.5). For comparison, the Pt/C cathode layer was also made with a Pt loading of 0.50 mg cm^{-2} and an N/C ratio of 0.50.

MEA was prepared by keeping the Nafion membrane in between the cathode and anode followed by applying 0.25 ton pressure for 1 min. at 130 ^{o}C. 4 cm^2 is the active electrode area of the MEA. A standard test fixture (Fuel Cell Technologies Inc, USA) was used for the MEA performance analysis. The testing was done by using a fuel cell test station (Fuel Cell Technologies Inc, USA) by purging H_2 and O_2 with a flow rate of 50 sccm and 100 sccm respectively at the anode and cathode by maintaining a relative humidity of 100 % without applying back pressure and a cell operating temperature of 65 ^{o}C.

Table S1: Elemental composition of the different samples calculated from XPS.

Sample	C (At.%)	O (At.%)	N (At.%)	Fe (At.%)
FeGNT	88.87	7.64	3.10	0.39
FeNCNT	91.95	6.18	1.42	0.45
NCNH	88.67	10.26	1.10	0.00

Table S2: ORR activity comparison of FeGNT catalyst with reported non-precious metal catalyst in acidic medium

Catalyst	Preparation method	Electrolyte	Catalyst loading (mg cm^{-2})	Onset potential (V *vs* RHE)	$E_{1/2}$ difference compared to Pt/C (mV)	reference
FeGNT	High temperature annealing of nanohorn, melamine and iron acetate	0.1 M $HClO_4$	1	0.9	150	Present study
FeGNT	High temperature annealing of nanohorn, melamine and iron acetate	0.5 M H_2SO_4	1	0.9	100	Present study
Fe-P-C[1]	High temperature annealing of phytic acid and Fe salt.	0.1 M $HClO_4$	0.039	0.84	~210	4
Fe-N-C catalyst[2]	Annealing of bidppz molecule and $FeSO_4$ at 800 ^{O}C	0.1 M $HClO_4$	0.1	~ 0.9	59	5
Carbon supported Fe-N catalysts[3]	Annealing of 2,4,6-tris(2-pyridyl)-1,3,5- triazine and Mohr's salt at 800 ^{O}C	0.5 M H_2SO_4	0.2	0.88	~140	6
Co and Fe loaded N doped carbon[4]	Annealing of 2,6-diaminopyridine in with Co and Fe salt at 700 ^{O}C in presence of NH_3	0.5 M H_2SO_4	0.5	0.84	110	7
Fe-N-C catalyst[5]	Annealing of carbendazim and $FeCl_3$ mixture with silica template at 800 ^{O}C	0.5 M H_2SO_4	0.6	~0.89	-------	8
Carbon Nanotube/ Fe_3C nano particle[6]	annealing a mixture of PEG-PPG-PEG Pluronic P123, elamine, and $Fe(NO_3)_3$ at 800 °C in N_2.	0.1 M $HClO_4$	1.2	0.88	~170	9
Fe-N-HCMS[7]	Silica template mediated annealing of EDA and iron	0.5 M H_2SO_4	0.25	0.80	~180	10

	nitrate					
Carbon nanotube-graphene complex[8]	Partial unzipping of carbon nanotube	0.1 M $HClO_4$	0.5	~ 0.89	~ 100	11

Table S3: Electrochemical performance of the different catalysts including Pt/C in 0.1 M $HClO_4$, 0.5 M H_2SO_4 and 0.1 M KOH.

	Catalyst loading (mA cm^{-2})	Onset potential (V vs RHE)	Half wave potential (V vs RHE)	Tafel slope (mV $decade^{-1}$)	Peroxide yield at 0.5 V vs RHE	Number of electron transfer at 0.5 V vs RHE
0.1 M $HClO_4$						
Pt/C	0.1	0.99	0.87	66.84	2.80	3.95
FeGNT	1	0.90	0.71	77.40	5.30	3.89
FeNCNT	1	0.77	0.46	132.21	6.03	3.88
NCNH	1	0.80	0.49	146.04	6.02	3.88
0.5 M H_2SO_4						
Pt/C	0.1	0.98	0.85	64.23	1.47	3.97
FeGNT	1	0.90	0.75	77.94	2.30	3.95
FeNCNT	1	0.77	0.48	114.98	7.37	3.85
NCNH	1	0.71	0.41	211.19	7.37	3.85
0.1 M KOH						
Pt/C	0.1	1.00	0.86	91.00	3.45	3.94
FeGNT	1	1.00	0.85	84.84	5.01	3.90
FeNCNT	1	0.92	0.75	84.86	9.95	3.80
NCNH	1	0.92	0.75	91.14	3.01	3.94

Table S4: Half wave potential ($E_{1/2}$) of FeGNT and Pt/C in 0.1 M$HClO_4$, 0.5 M H_2SO_4 and 0.1 M KOH before and after ADT.

	FeGNT		Pt/C	
Electrolyte	Before 5000 cycles, $E_{1/2}$ (V vs RHE)	After 5000 cycles, $E_{1/2}$ (V vs RHE)	Before 5000 cycles, $E_{1/2}$ (V vs RHE)	After 5000 cycles, $E_{1/2}$ (V vs RHE)
0.1 M $HClO_4$	0.71	0.67	0.87	0.82
0.5 M H_2SO_4	0.75	0.73	0.00	0.00
0.1 M KOH	0.85	0.84	0.86	0.83

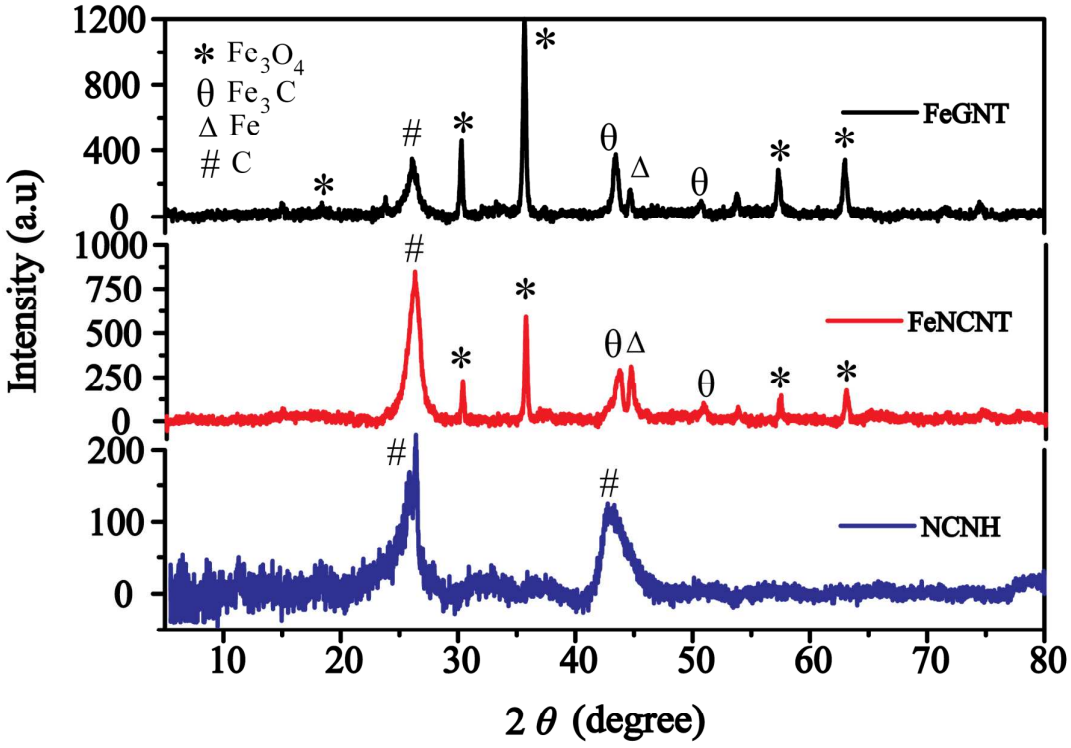

Figure S1. X-ray diffraction patterns of FeGNT, FeNCNT and NCNH.

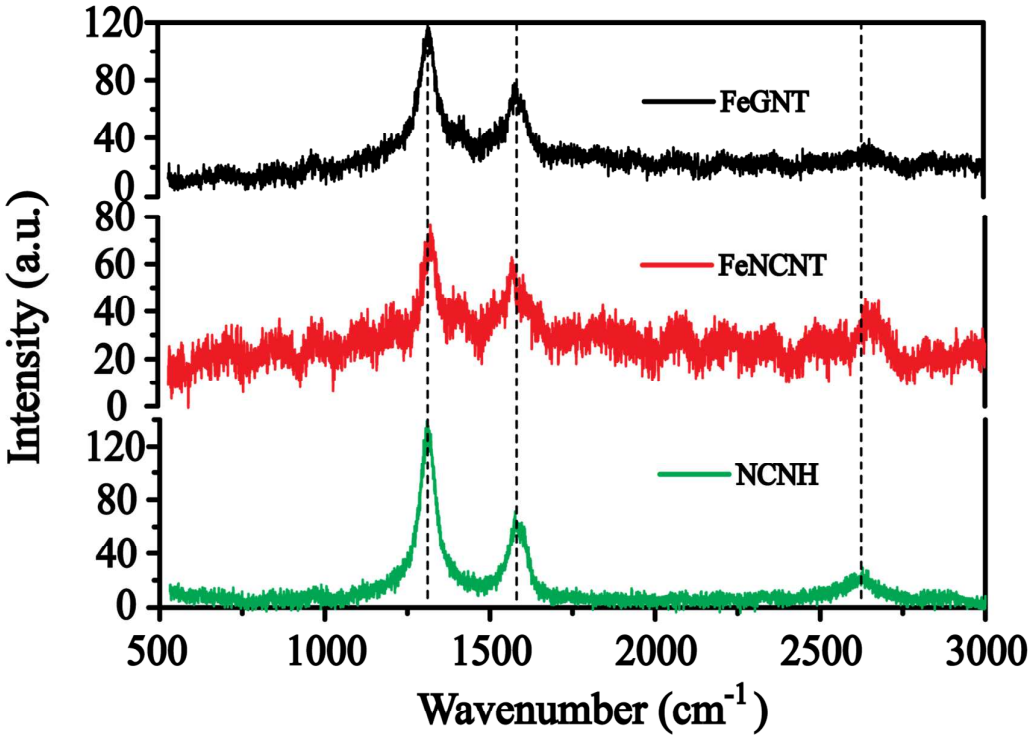

Figure S2. Raman analysis of FeGNT, FeNCNT and NCNH.

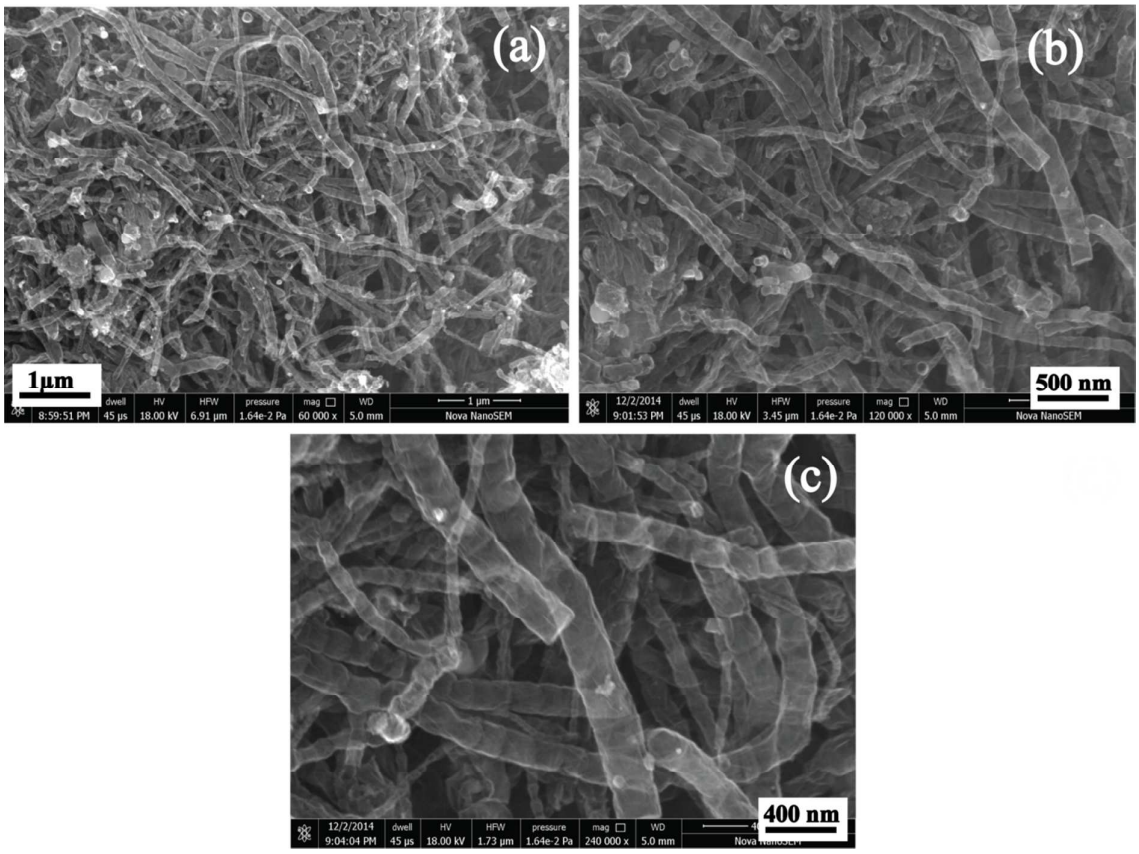

Figure S3. FE-SEM images of FeGNT at different magnifications ((a) scale: 1µm, (b) scale: 500 nm and (c) scale: 400nm).

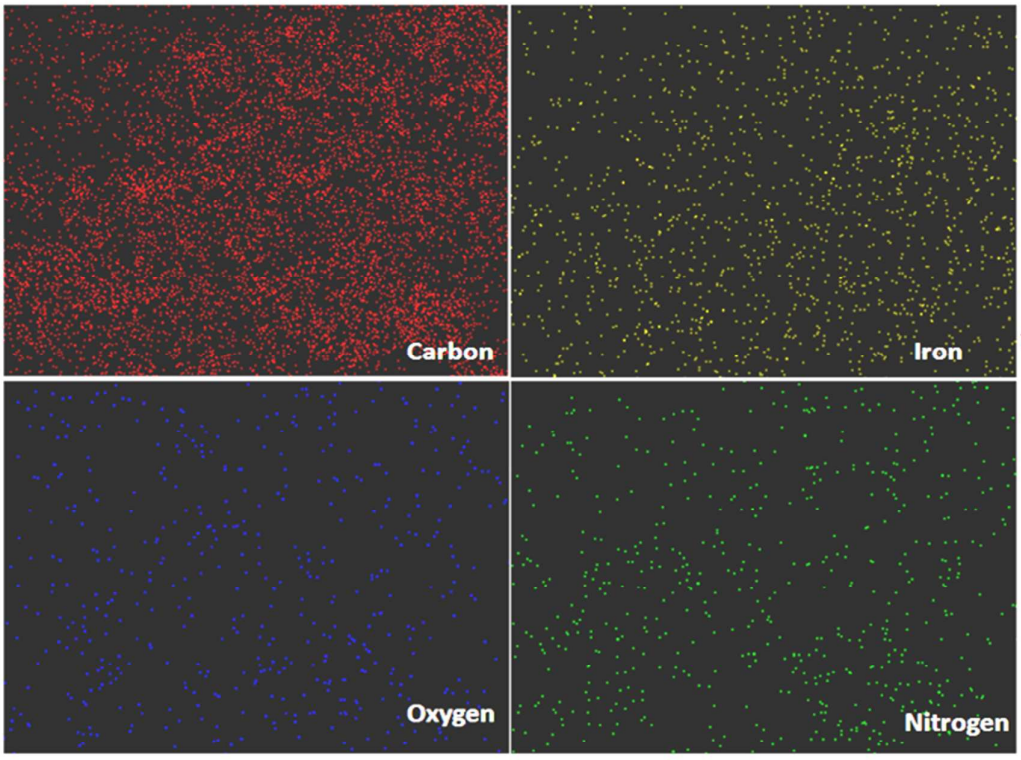

Figure S4. Elemental mapping of FeGNT using FE-SEM in a scale bar of 1 μm.

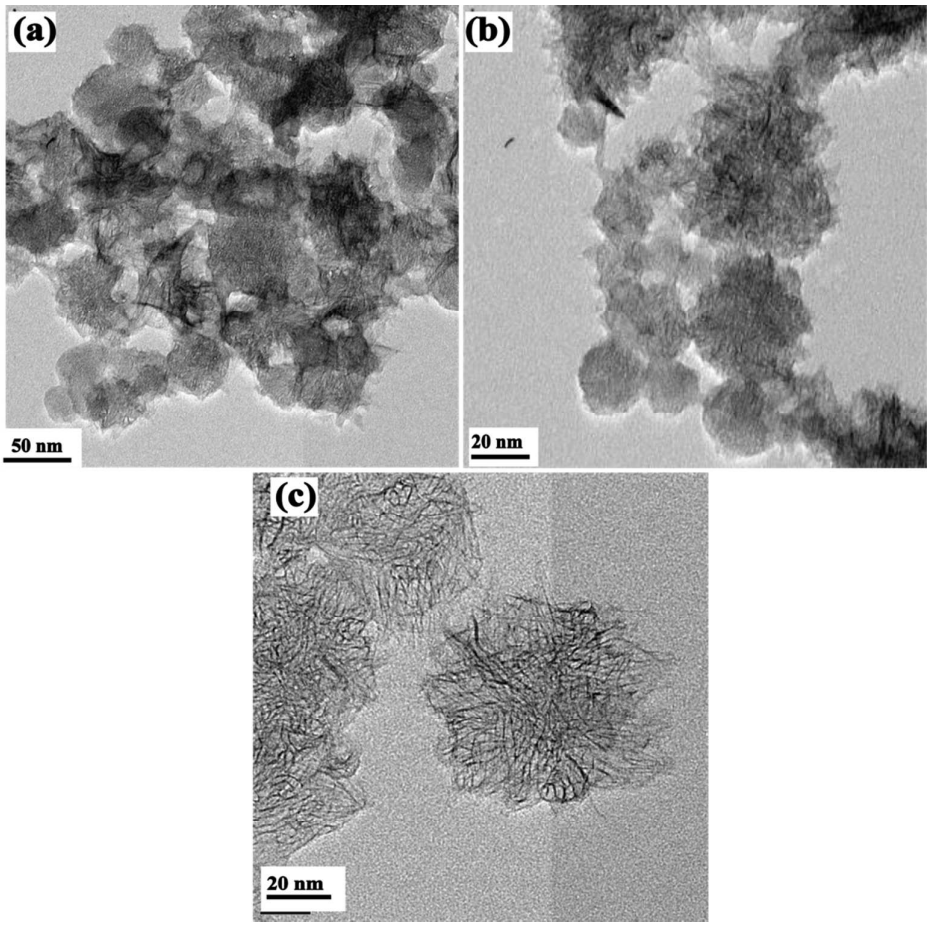

Figure S5. HR-TEM images of (a) FeCNO, (b) NCNH and (c) SWCNH.

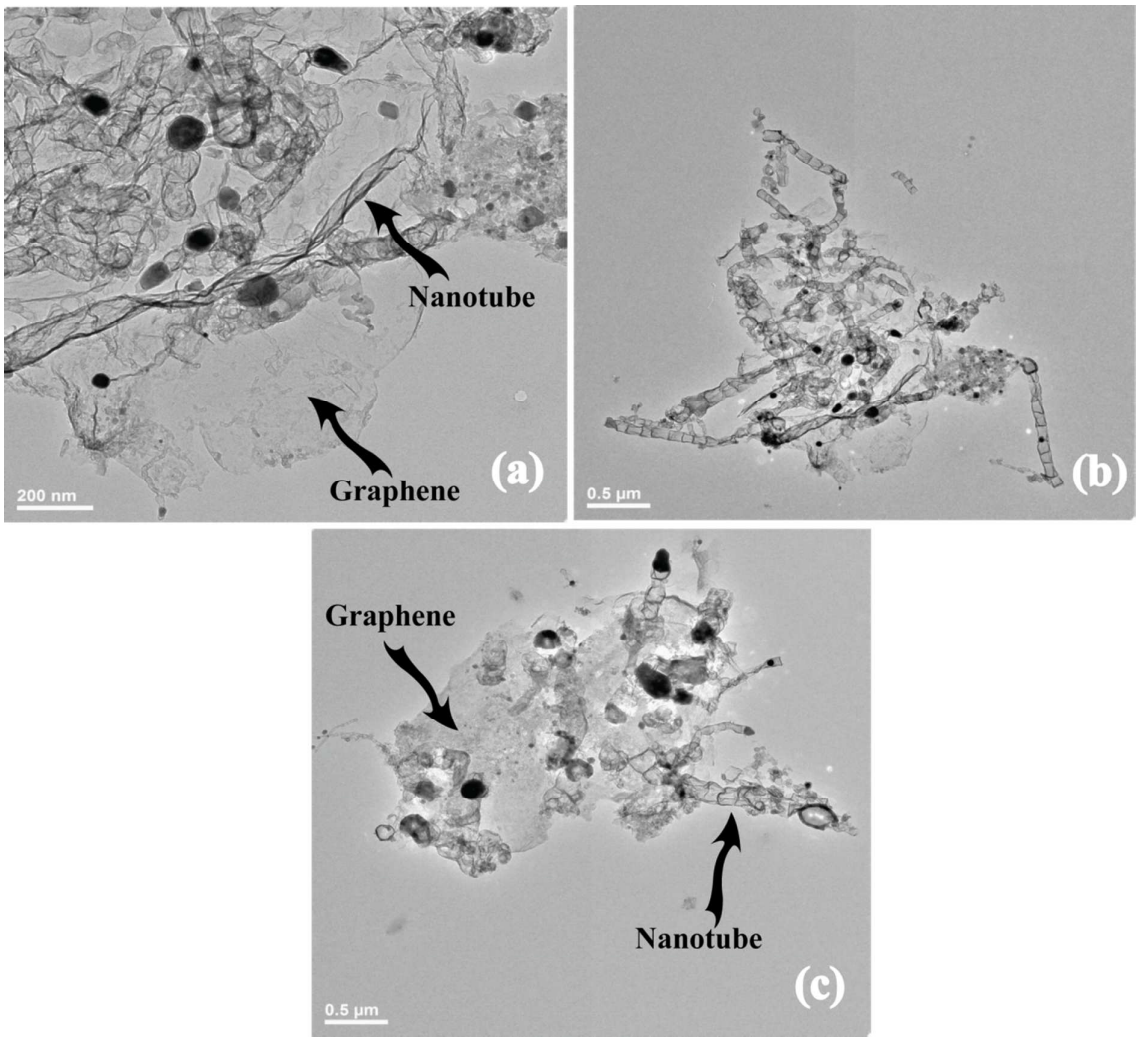

Figure S6. HR-TEM images of the nanotube grown on graphene sheets at different magnifications ((a), (b) and (c)).

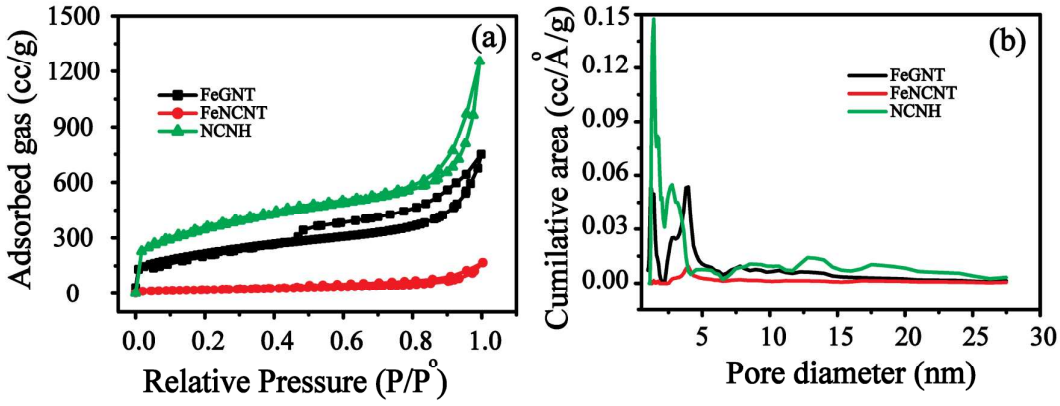

Figure S7. (a) Nitrogen adsorption–desorption isotherms and (b) pore size distribution profiles of FeGNT, FeNCNT and NCNH.

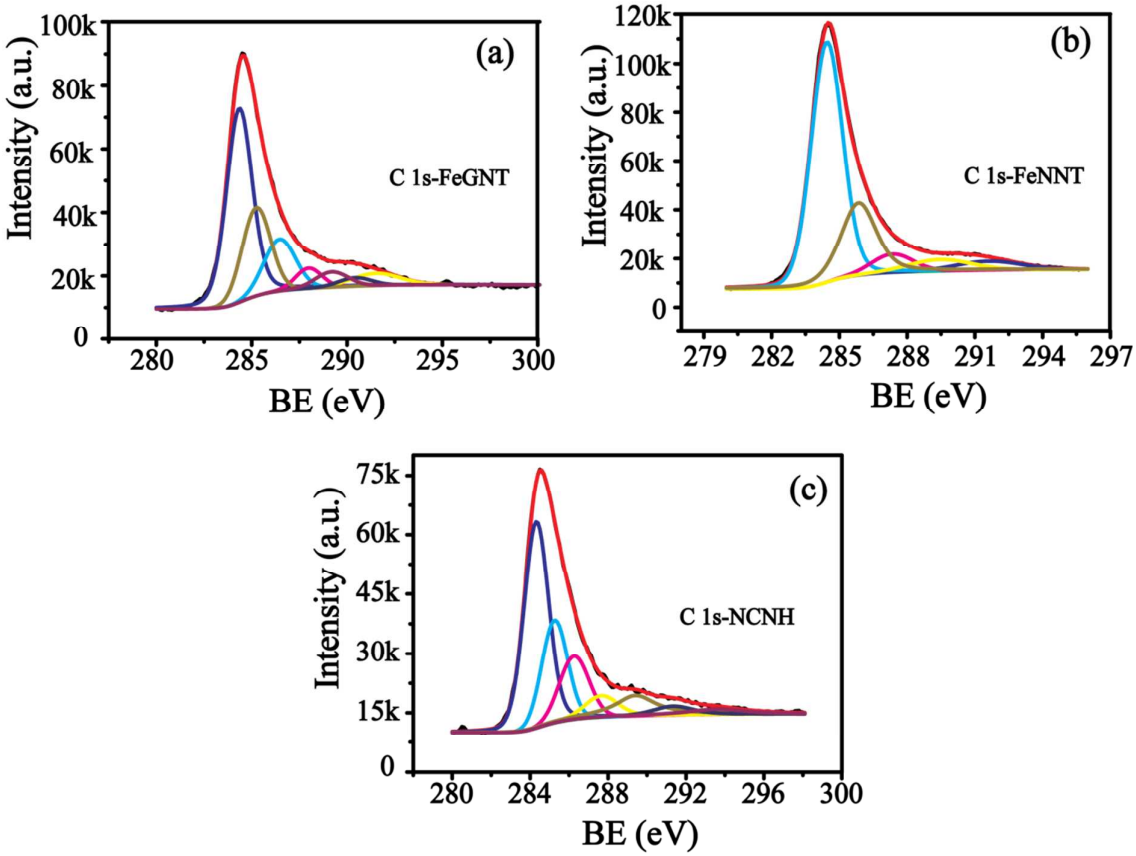

Figure S8. Deconvoluted C1s spectra of (a) FeGNT, (b) FeNCNT and (c) NCNH.

Fitted C1s spectra of FeGNT show a peak at 284.34 eV corresponds to the sp^2 carbon. Similarly, the peaks at 286.51 eV and 289.38 eV indicate different mode of C-O interactions in the carbon nanostructure.[9] The peak at 285.23 eV indicates the carbon nitrogen interaction where nitrogen is bonded with a sp^2 carbon.[10] Similarly, the peak at 287.98 eV indicates the C-N bond where 'N' is attached to the sp^3 carbon.[10] Similar peaks are also observed in FeNCNT and NCNH. Fitted C1s spectra of all the three catalysts give information about the nitrogen doping in the carbon matrix.

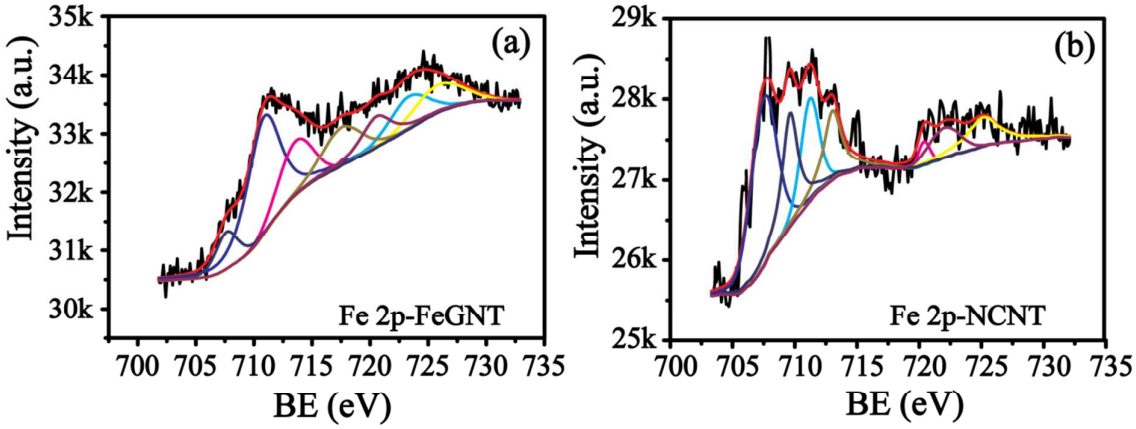

Figure S9. Deconvoluted Fe 2p spectra of (a) FeGNT and (b) FeNCNT.

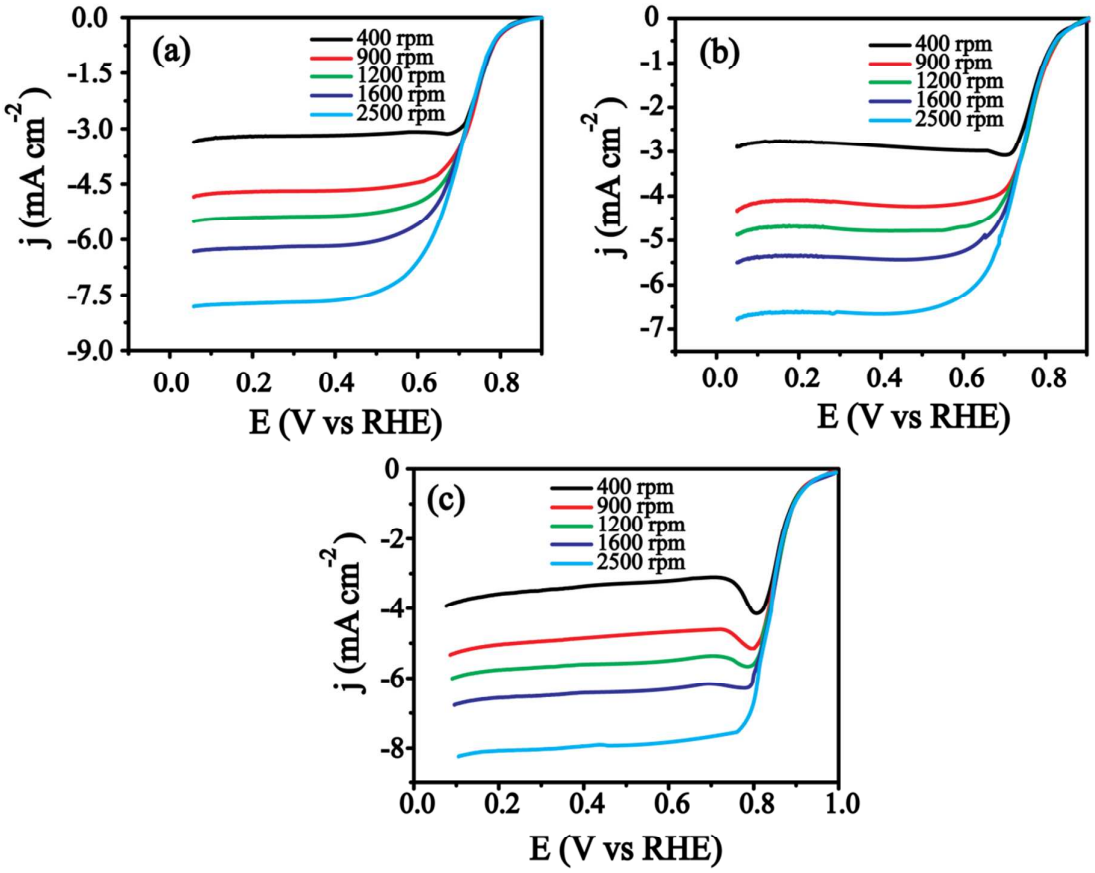

Figure S10. Linear sweep voltammograms of FeGNT at different electrode rotation rates in (a) 0.1 M $HClO_4$, (b) 0.5 M H_2SO_4 and (c) 0.1 M KOH.

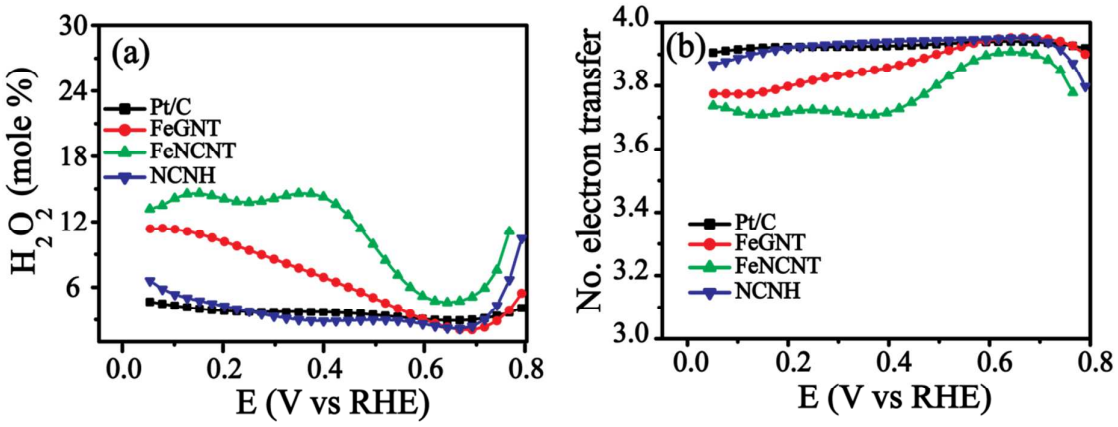

Figure S11. (a) Hydrogen peroxide yield and (b) number of electron transfer of the samples at different potentials in 0.1 M KOH calculated from RRDE.

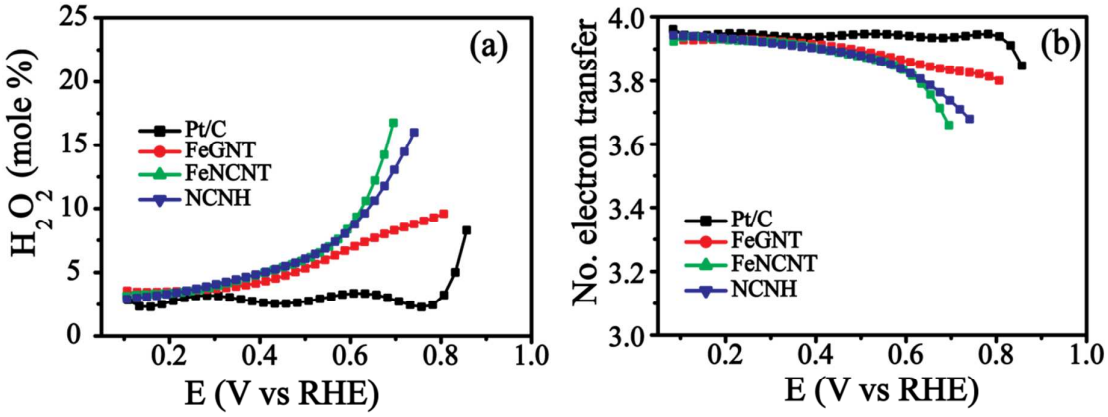

Figure S12. (a) Hydrogen peroxide yield and (b) number of electron transfer of the samples at different potentials in 0.1 M $HClO_4$ calculated from RRDE.

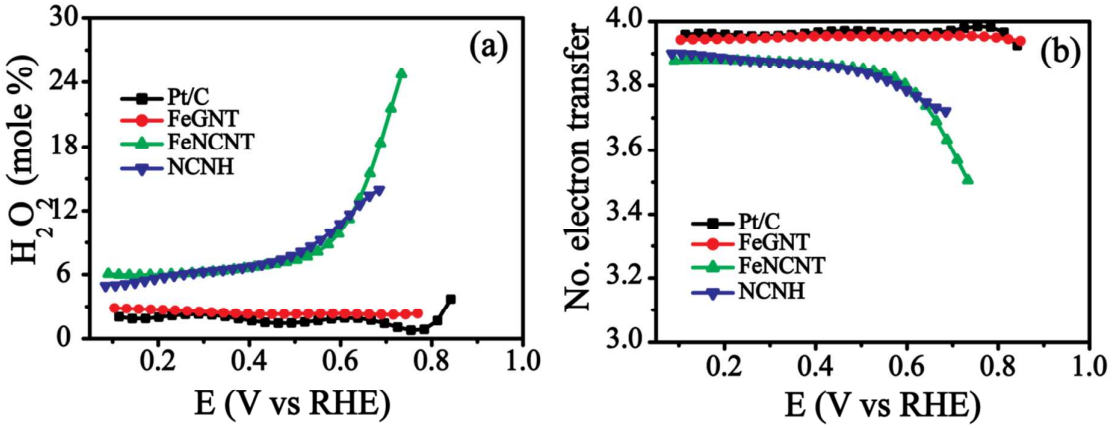

Figure S13. (a) Hydrogen peroxide yield and (b) number of electron transfer of the samples at different potentials in 0.5 M H_2SO_4 calculated from RRDE.

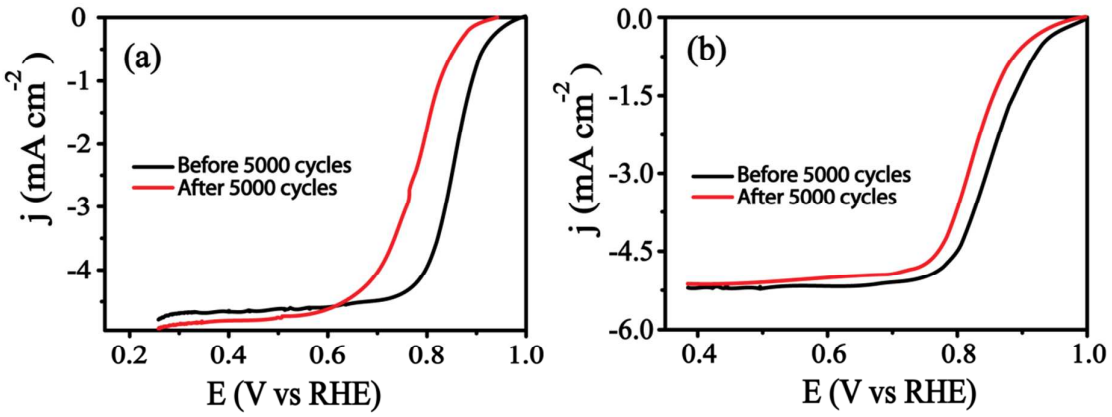

Figure S14. LSVs of Pt/C before and after ADT in (a) perchloric acid and (b) 0.1 M KOH with an electrode rotation rate of 1600 rpm and a scan rate of 5 mV s^{-1}.

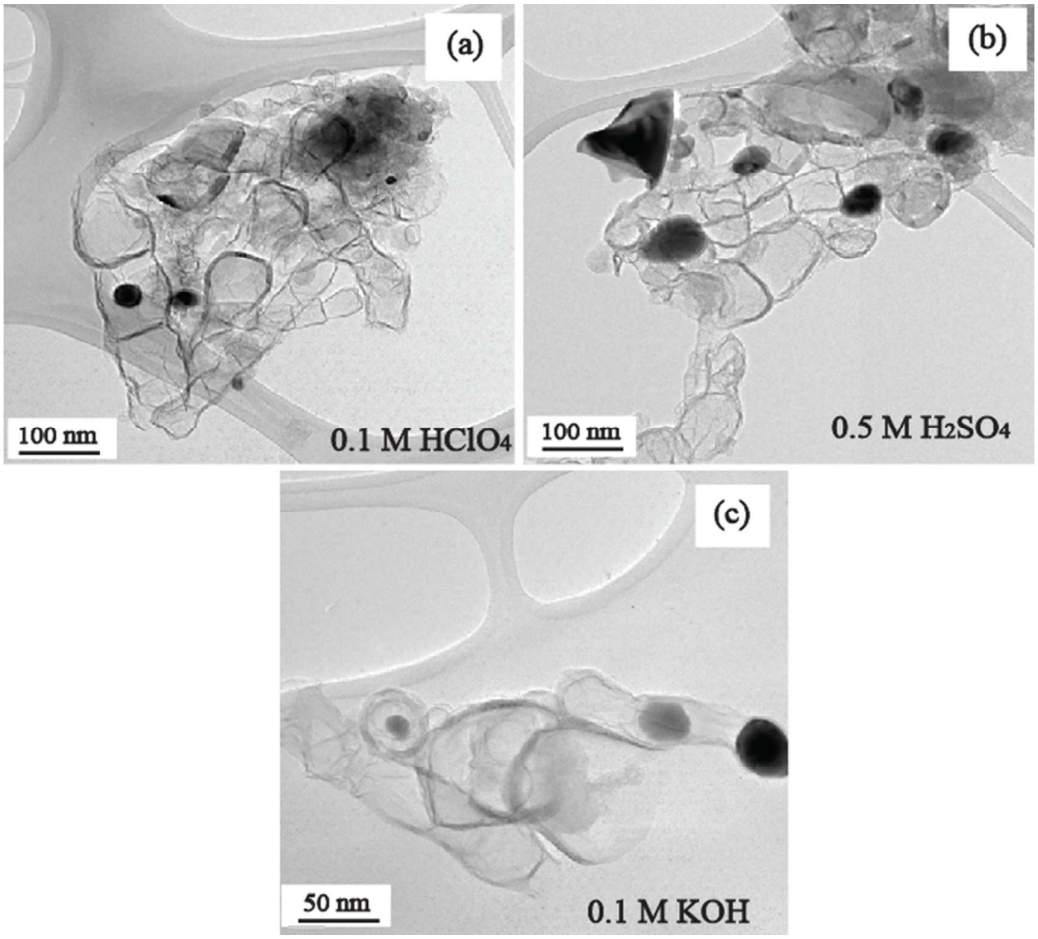

Figure S15. TEM images of FeGNT after ADT in (a) 0.1 M $HClO_4$, (b) 0.5 M H_2SO_4 and (c) 0.1 M KOH.

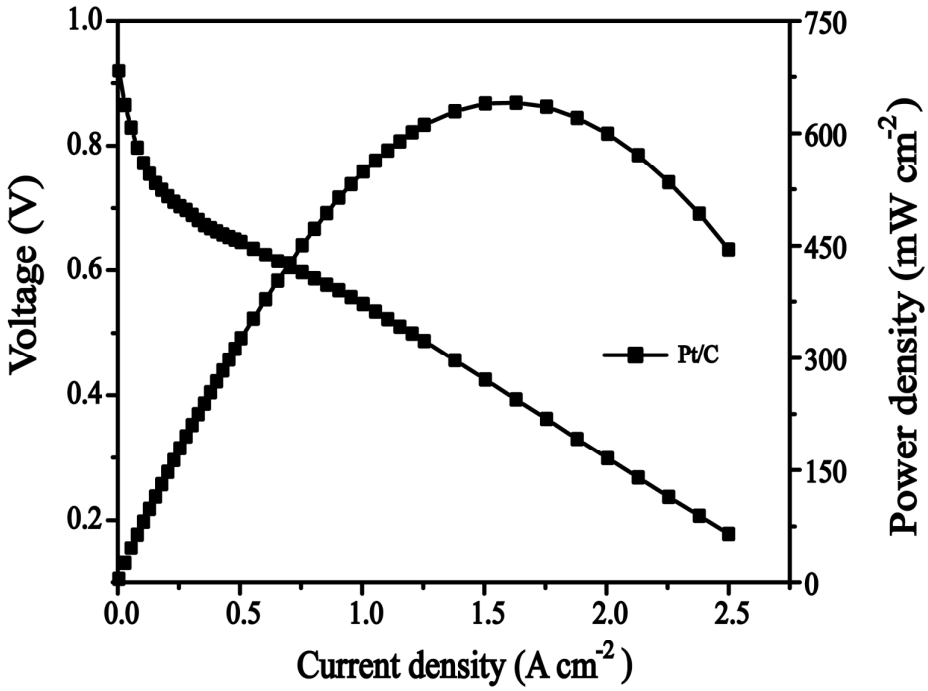

Figure S16. Single cell polarization plots recorded (active area is 4 cm^2) at 65 ^oC of a PEMFC with 0.5 mg cm^{-2} of Pt/C on both anode and cathode with Nafion 212 as the proton conducting membrane. H_2 and O_2 were used as the fuel and oxidant with flow rates of 50 sccm and 100 sccm, respectively without applying any back pressure.

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