Electronic Supplementary Information
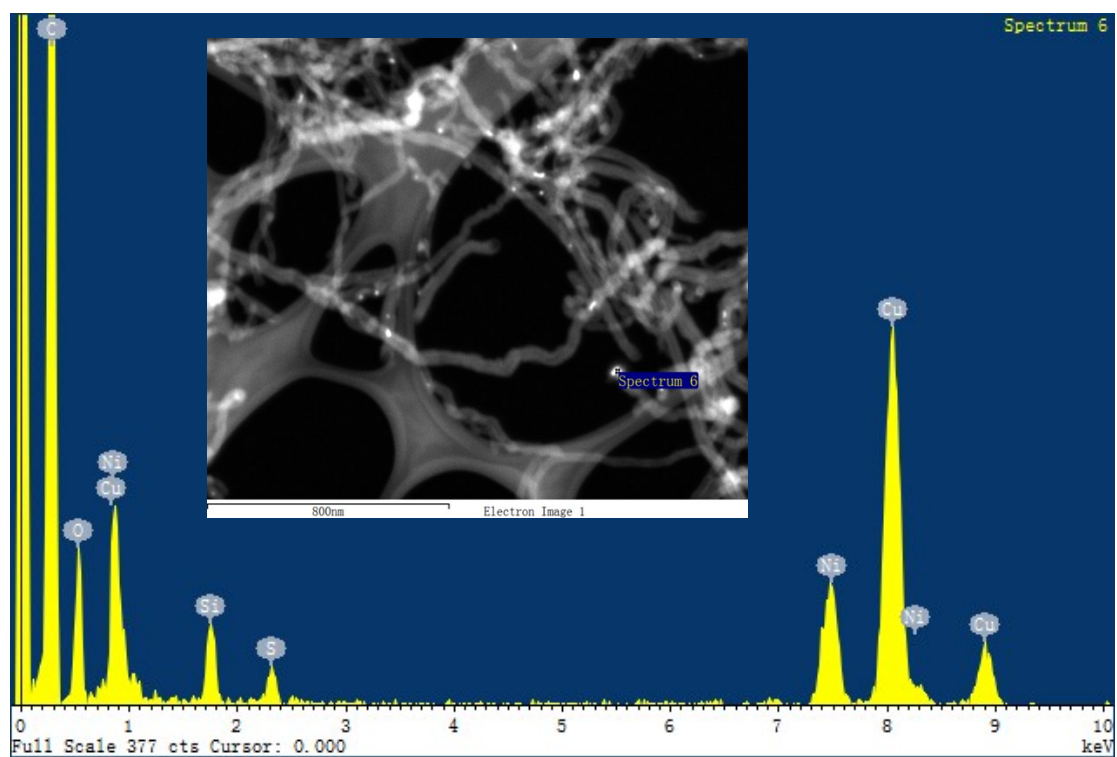
Effect of Oxygen Functionalisation on the Electrochemical Behaviour of Multiwall Carbon Nanotube for Alcohol Oxidation Reactions

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## 1. Transmission electron microscopy coupled EDS

Figure S1. TEM coupled EDS was focused at metal impurities found inside the core of MWCNT, the EDS spectra shows that the impurities was Ni.

2. X-ray photo electron spectroscopy

Table S1. XPS quantitative elemental analysis for O 1s peak of MWCNT samples

Functional groups	Peak (eV)	Atomic %					
		pMWCNT	moMWCNT	hoMWCNT	eo-pMWCNT	moMWCNT-180	pMWCNT$_{900}$
Ketonic (C=O)	531.3	0.64	1.54	0	Cannot be resolved	1	0.3
Hydroxyl, Epoxy (C-O)	532-533.3	0.83	1.77	22.4	11.91	0.95	0.44
Total		1.47	3.31	22.4	11.91	1.95	0.74
Ratio ($I_{(C=O)}/I_{(C-O)}$)		0.77	0.87	0	0	1.05	0.68
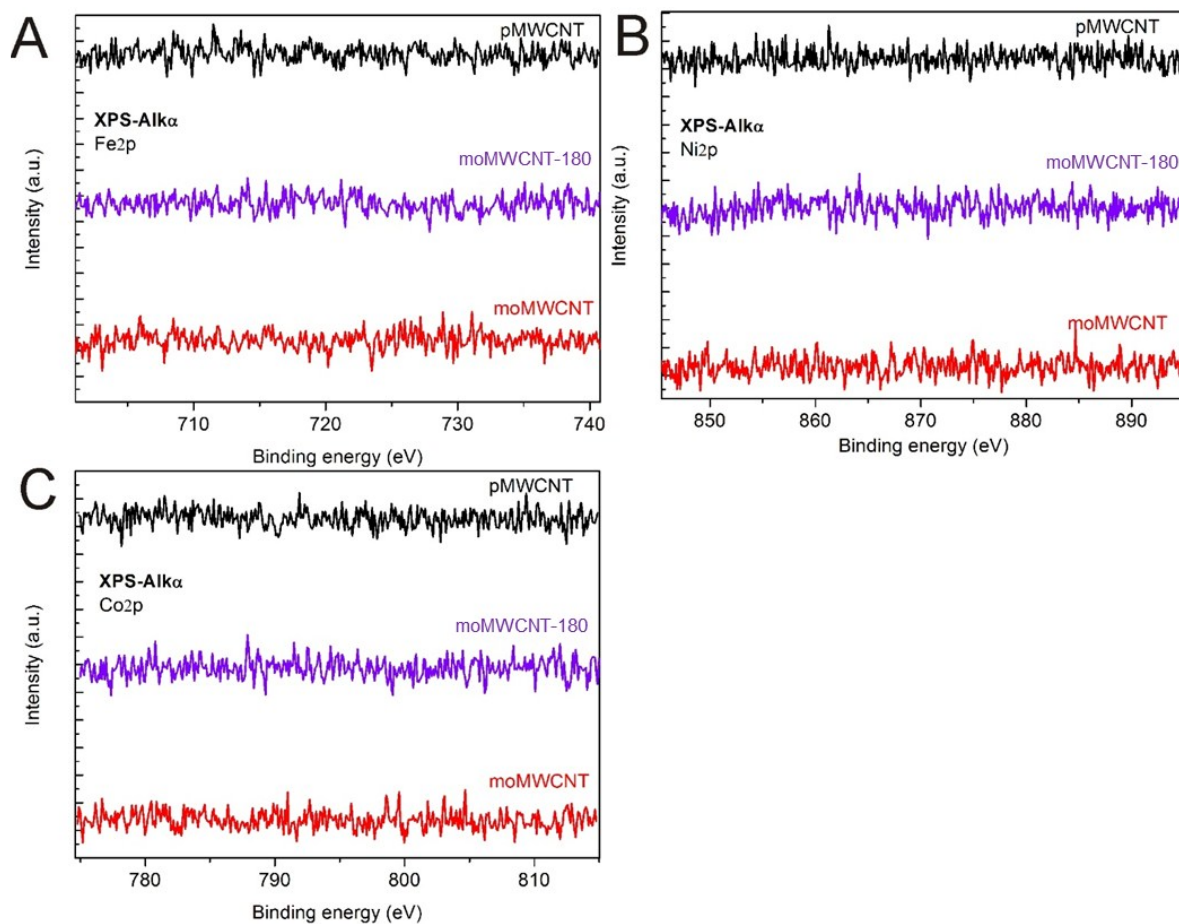
Figure S2. Deconvolution of Ni_{2p}, Fe_{2p} and Co_{2p} peaks from the XP spectra of MWCNTs samples
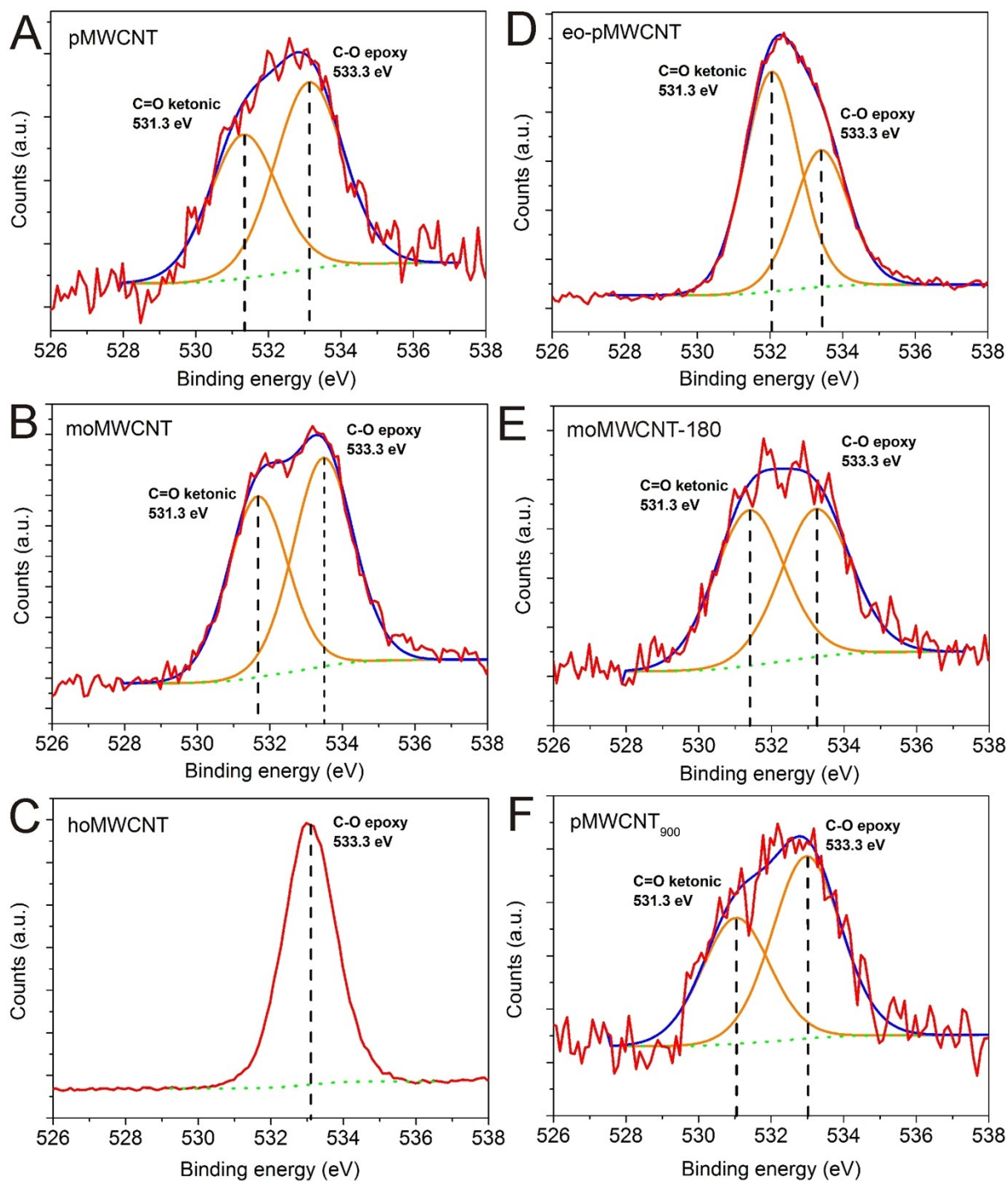
Figure S3. Deconvolution of high resolution XPS O 1s peaks from all MWCNT samples.

3. Raman spectroscopy

Table S2. Summary of I_G/I_D values from the Raman spectra of MWCNTs samples.

| Sample	I_G/I_D	D'-band (integrated surface area)
pMWCNT	0.90	3.00
moMWCNT	1.01	7.15
hoMWCNT	0.81	3.20
moMWCNT-180	1.20	4.36
eo-pMWCNT	1.07	4.91
pMWCNT$_{900}$	0.95	4.36

4. Electrochemical data

Table S3. Electrochemical parameters from cyclic volmtammetric analysis of the electrochemical oxidation of alcohols using MWCNTs and oxidized MWCNTs in 0.1 M KOH with 0.2 mg cm^{-2} catalyst loading.

Catalyst	Alcohol	pKa	Onset potential (E_o / V)	Peak I		Peak II		Tafel slope (mV/dec)
				E_p (V)	j_p (mA cm^{-2})	E_p (V)	j_p (mA cm^{-2})	
pMWCNT	EtOh	15.9	1.44	1.58	0.14	1.57	0.07	177
eo-pMWCNT	EtOH	15.9	1.43	1.58	0.51	1.58	0.56	-
moMWCNT	EtOH	15.9	1.43	1.59	1.21	1.57	1.40	46
hoMWCNT	EtOH	15.9	1.51	1.65	1.14	1.61	1.10	114
	MeOH	15.5	1.46	1.65	5.90	1.64	6.16	49
moMWCNT-180	EtOH	15.9	1.44	1.59	4.00	1.58	4.23	51
	PrOH	16.5	1.44	1.56	1.43	1.56	1.54	63.5
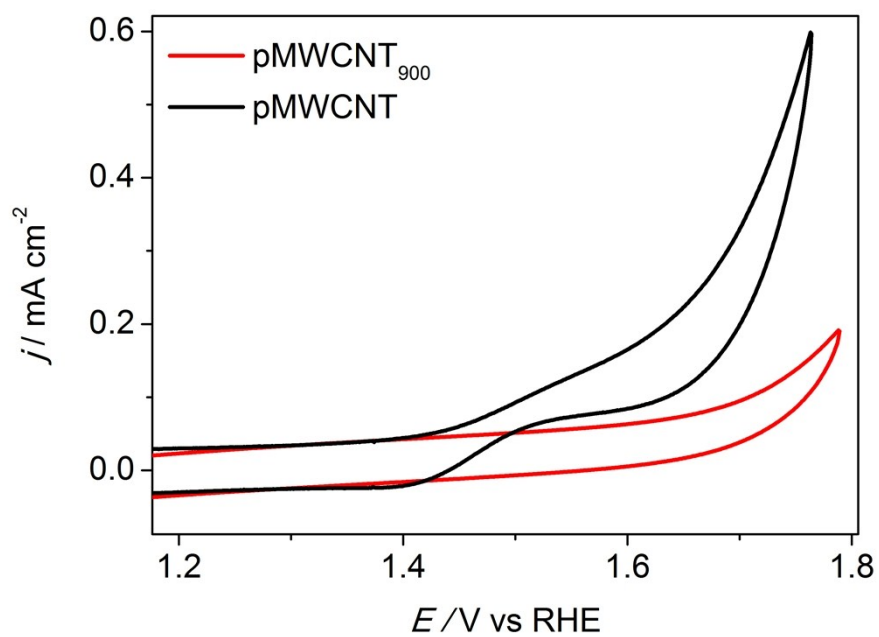
Figure S4. Cyclic voltammetries of pMWCNT and pMWCNT$_{900}$ in 0.1 M KOH containing 1M EtOH. (scan rate : 50 mV s^{-1})
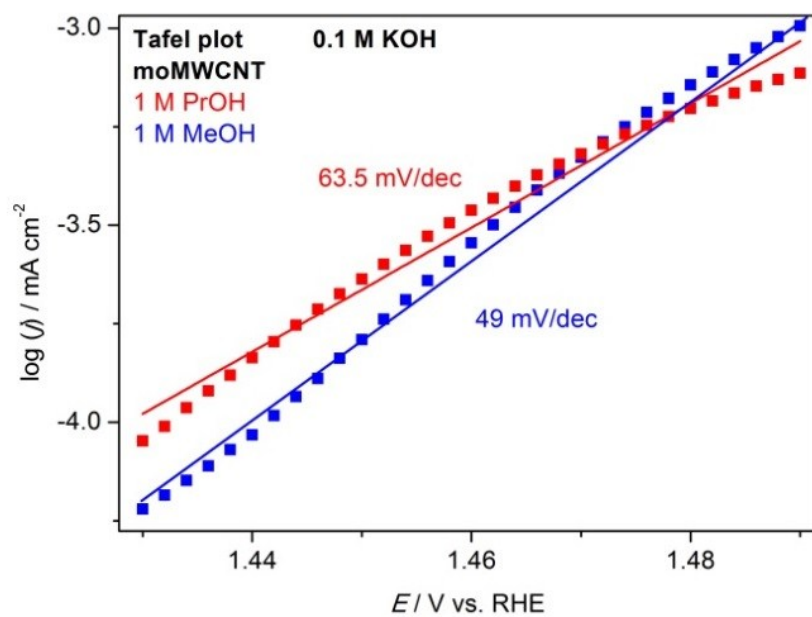
Figure S5. The tafel plots for oxidation of MeOH and PrOH using moMWCNT-180.

5. Determination of ECSA

The electrochemically active surface area (ECSA) of pMWCNT sample was determined using the following equation:

$$ECSA = C_{DL}/C_S$$

The value of double-layer capacitance (C_{DL}) can be obtained by cyclic voltammetry. Typically, the cyclic voltammetric scan is performed within the region where Faradaic current is absent. In Fig. S6a, the scans were done within a range of 0.1 V from 0.1 V to 0.2 V (Ag/AgCl), and the potential was held for 10 s at each vertex with a series of different scan rates, ranging from 5 mV s^{-1} to 200 mV s^{-1}. By assuming the current from the scan is originated from double layer charging, the slope from the plot of current at centre of the scan (0.15 V) vs. scan rate (v) is the value of C_{DL}.
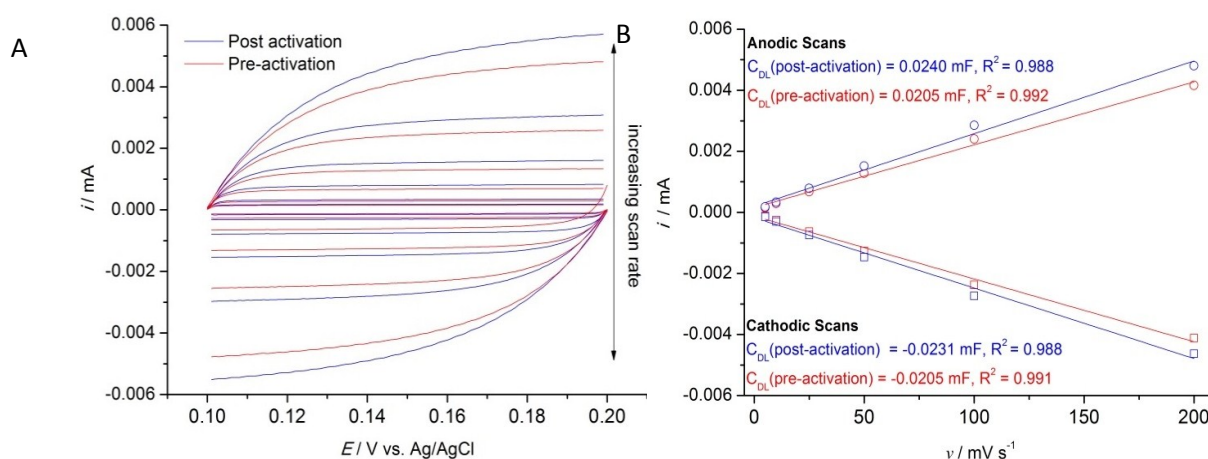

Figure S6. Determination of the electrochemically active surface area (ECSA) of the pMWCNT and the electrochemically activated pMWCNT was performed using cyclic voltammetric double-layer capacitance measurements in 0.1 M KOH. (A) Cyclic voltammograms were measured in non-Faradaic region with scan rates ranging from 5 mV s^{-1} to 200 mV s^{-1} and (B) The cathodic (square) and anodic (circle) capacitance currents measured at 0 V vs. Ag/AgCl plotted as a function of scan rate.

6. UV-Vis spectra
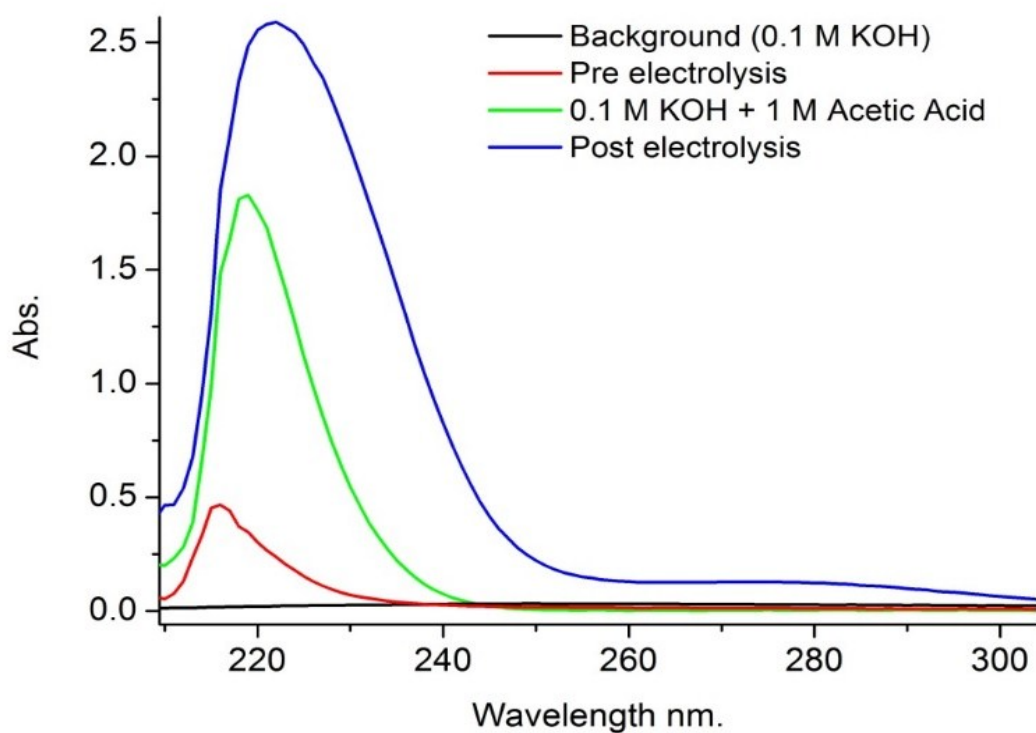
Figure S7. UV-visible spectra obtained from the pre-electrolysis and post-electrolysis electrolyte in the range of 200 nm to 300 nm. 1 M acetic acid in 0.1 M KOH was used as external control.

7. Alcohol bulk electrolysis
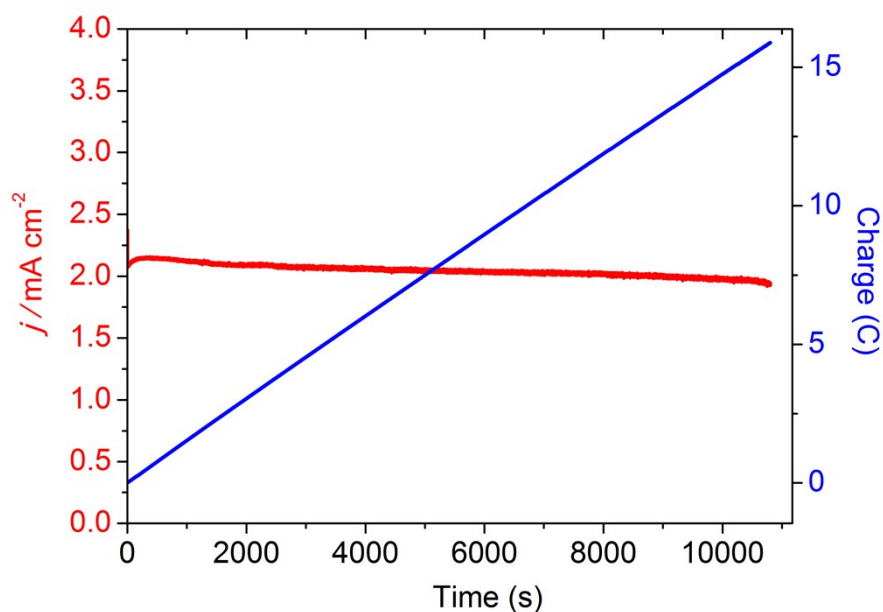
Fig S8. Extended bulk EtOH electro-oxidation at E = 1.62 V for 3 h. Blue line represents the charge consumed during the bulk electrolysis.

Faradaic efficiency was calculated according to the Faraday's law $n = Q/zF$, F is faraday's constant which equal to 96,485 C mol^{-1} and $z = 4$ is the number of electron involved in oxidation of EtOH into acetic acid. From the charge vs time plot we can calculate that the amount of acetic acid produced during the electrolysis is 41.45 µmol.

8. Gas chromatography (GC) measurement

Gas chromatography measurement was done using Shimadzu GC-2010 equipped with an AOC-20i autosampler and SGE Solgel-wax premium capillary column, the system was connected to a PC and operated using GC solution software. Flame ionisation detector (FID) was used as the primary sensor. For this measurement the injection and FID temperatures were set at 210 °C and operated under linear velocity mode, other parameters were to the following values: total flow rate was set at 65.8 ml/min, linear velocity was set at 45.0 cm/s, column flow at 2.66 ml/min, purge flow at 3.0 ml/min and pressure was set at 100 kPa with an injection volume of 1 µl. Prior to analysis with GC the sample from alcohol EOR was distilled to remove all of the electrolyte and non-volatile compound using a standard distillation set-up composed of 2 round bottomed flasks connected to a water condenser (closed system), the distillation chamber was then heated to 150 °C.

The GC analysis in Fig. S9 show that following the electrolysis, a new peak is formed at the retention time of 2.428min which corresponds to acetic acid while the peaks at 1.550 min belong to the ethanol from the electrolyte and residual methanol from syringe wash. To determine the concentration of acetic acid in the sample, glacial acetic acid (AJAX APS) was used as an external standard and was used to build a calibration plot (Fig. S6), where the y-axis corresponds to value of integrated area under the curve between 2.4 to 2.5 min. and the x-axis is the concentration of external standards in mM unit. The yielded equation was used to determine the concentration of Acetic acid in the sample.
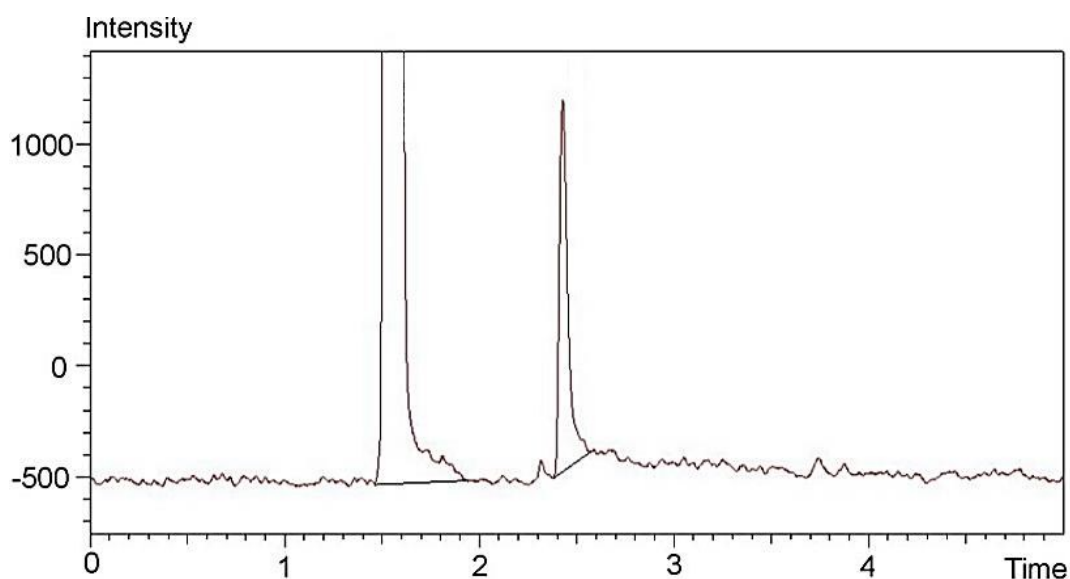
Figure S9. The GC chromatogram of the post alcohol EOR electrolyte sample.
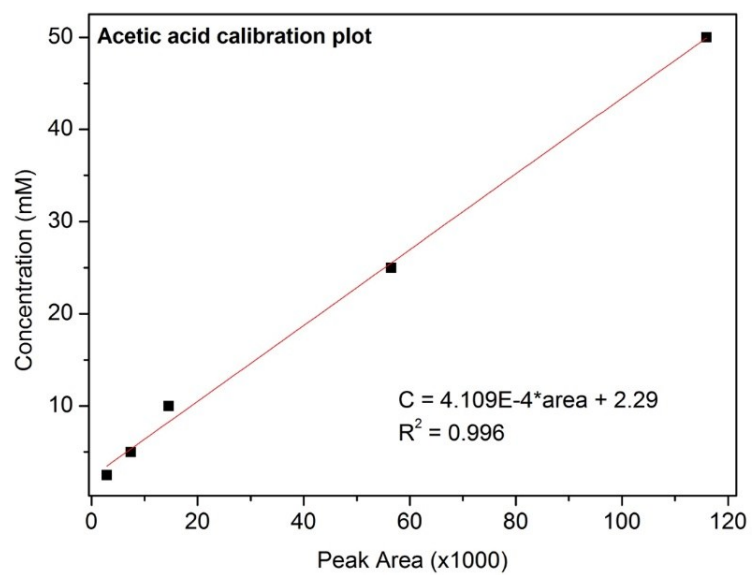
Figure S10. The calibration curve from the acetic acid external standard.