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SUPPORTING INFORMATION

Electrochemical Modification of Carbon Nanotube Fibres

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Materials. All reagents were used as received. 4-Nitrobenzendiazonium tetrafluoroborate, 4-bromobenzendiazonium tetrafluoroborate, 4-azidoaniline, 4-aminophenylacetic acid, tetrabutylammonium hexafluorophosphate ($TBAPF_6$), potassium ferricyanide and ethylene diamine were purchased from Sigma Aldrich. 4-Fluorobenzenediazonium tetrafluoroborate from TCI. Dry acetonitrile was purchased from ACROS. 10× PBS solution from Thermo Fisher. Raman spectra were collected on a Renishaw InVia Confocal Raman microscope with excitation wavelength at 785 nm, 633 nm and 532 nm on at least 50 random point per sample. XPS measurements have been recorded on a PHI Quantera XPS microprobe. All electrochemical measures were performed on a Garmy potentiostat/galvanostat "Reference 3000". EIS measures on fibres were recorded in a three-electrode cell (WE: functionalised fibre; RE: Ag/AgCl; CE: carbon fibre) in 10× PBS buffer solution and 0.005 M ferricyanide in 1× PBS.

General procedure for diazonium salt production. Diazonium salts not commercially available were synthetized adapting procedures already present in literature.[4] A portion of the selected aniline (1eq) was added to a round bottom flask with HBF_4 (6 eq) and dissolved in glacial acetic acid (50 ml per mmol of aniline). A solution of isoalmyl nitrite (3eq) was dropped in the flask. The system was left under stirring for 15 min and ethyl ether was slowly added to the solution. The product was collected as a crystal after 16 h at -22ºC (**2**: 75%; **4**: 88%).

4-Fluorobenzenediazonium tetrafluoroborate (2): FT-IR: 2290 cm^{-1}. ^1H NMR (500 MHz, DMSO) δ 8.82 (d, J= 9.20, 4.50 Hz, 2H); 7.90 (m, 2H).

4-Phenylaceticdiazonium tetrafluoroborate (4): red needle like crystals, 88% of yield. ^1H NMR (500 MHz, D_2O) δ 8.57 (d, J= 8.83 Hz, 2H); 7.92 (d, J= 8.81 Hz, 2H); 3.98 (s, 2H).

Preparation of carbon nanotube fibres. CNTFs were manufactured using a methodology previously reported.[1,2] Briefly, high-quality CNTs from Meijo NanoCarbon (Japan) were dissolved in chlorosulfonic acid (Sigma Aldrich, 99%) to form a liquid crystalline solution, extruded through a spinneret into a coagulant and collected onto a rotating drum. The CNTs were characterized by HR-TEM and found to be a mixture of SWCNTs and few-walled MWCNTs (average of 1.77 ± 0.50 walls measured from HR-TEM on 31 CNTs, 8 single-, 22 double-, and 1 triple-wall) with average diameter 2.01 ± 0.40 nm (Figure S1). The viscosity-average aspect ratio was found to be 3700 ± 200 using a technique previously described.[3] The as-produced fibres were washed in water

for 30 min at room temperature, dried in an oven at 115 °C overnight, washed in water at 60 °C for 3 h then dried in air under ambient conditions. Fibre diameters were measured using an FEI Quanta 400 scanning electron microscope (FEI). The tensile strength measurement was performed on an Ares-G2 Rheometer (TA Instruments) with a linear tension fixture at a constant strain rate of 0.05 s^{-1} on 10 samples, each of 20 mm length. The fibres had an average diameter of 21.0 μm, electrical conductivity of 7.14 ± 1.10 MS/m, and an ultimate tensile strength of 1.84 ± 0.34 GPa.

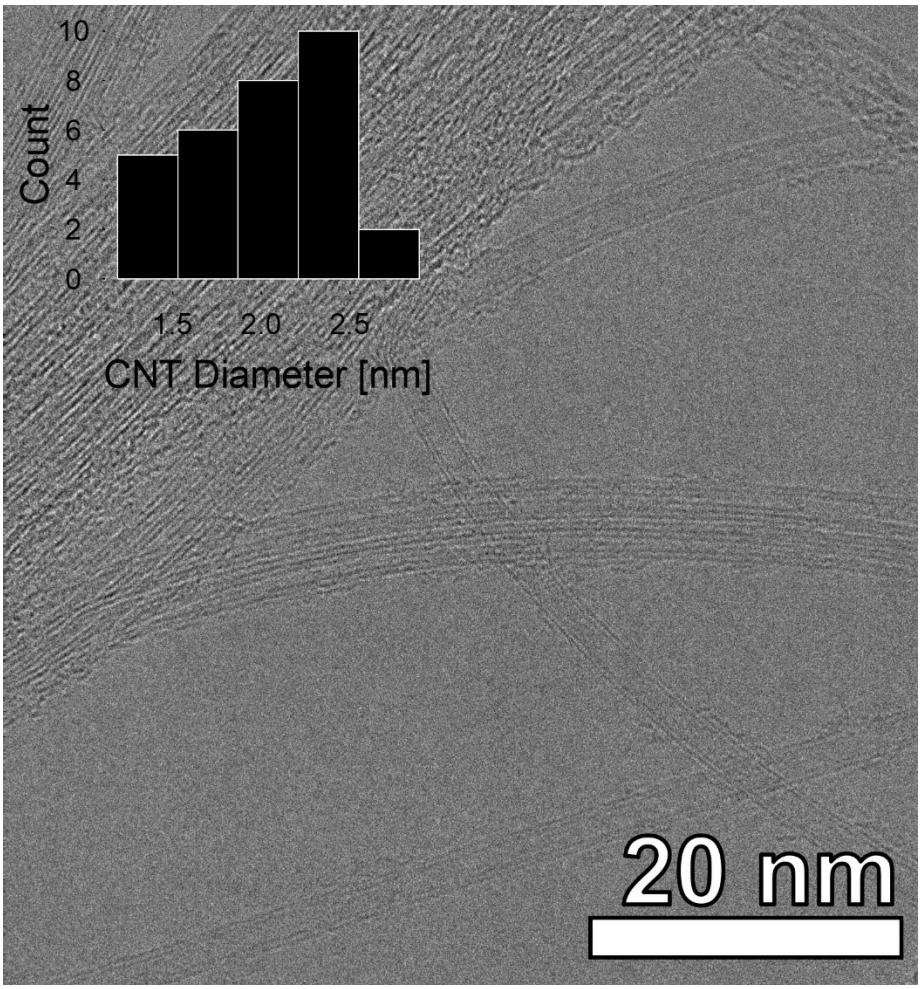


Figure S1. Representative HR-TEM image of few-walled MWCNTs with average diameter 2.01 ± 0.40 nm. The inset corresponds to average diameter distribution as bar graphic obtained from 30 measurements.

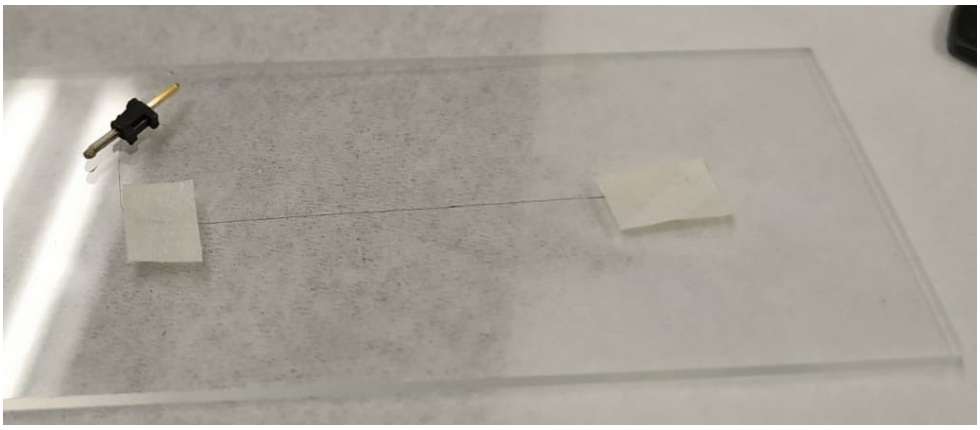


Figure S2. Picture of a CNTF fixed on a glass slide for Raman spectroscopy characterisation.

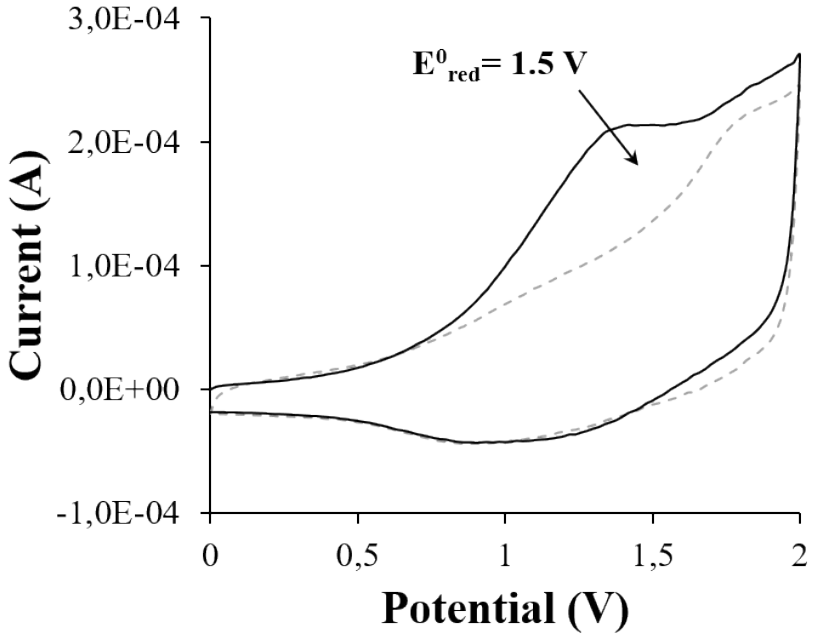


Figure S3. Cyclic voltammogram of ethylene diamine at 100 $mV \cdot s^{-1}$ scan rate to obtain **CNTF5**. First scan (black solid line) and second scan (grey dot line) correspond to the oxidation of ethylene diamine (5 mM) in ACN (40 mL) onto the CNTF electrodes.

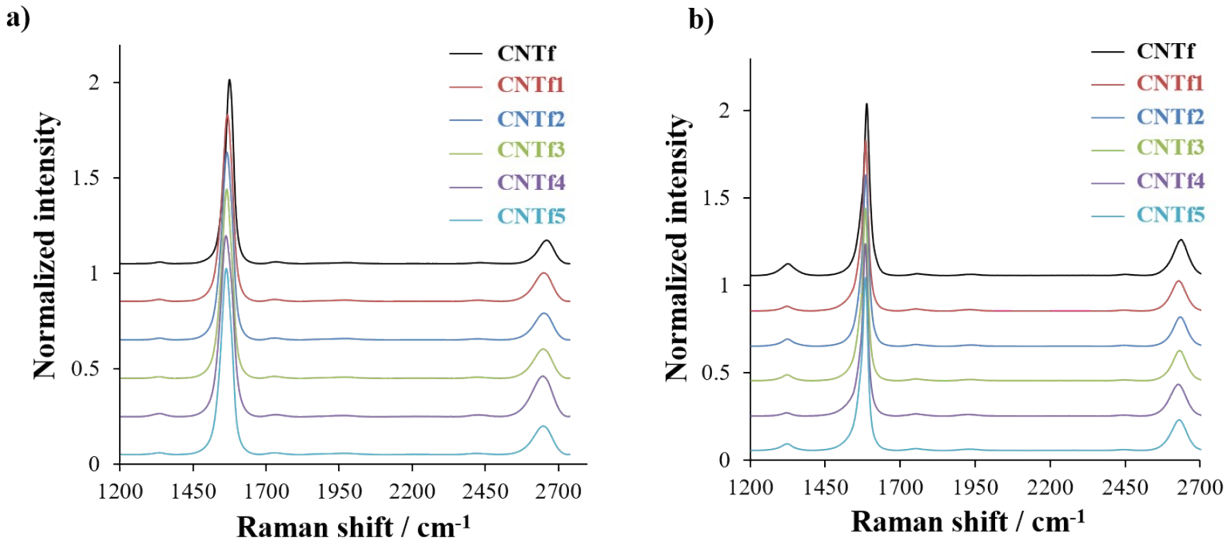


Figure S4. Raman average spectra of pristine CNTFs and functionalised CNTFs at a) 532 nm, b) 633 nm from line mapping mode of 180 points analysis, with time exposure of 1 s, and 10% power.

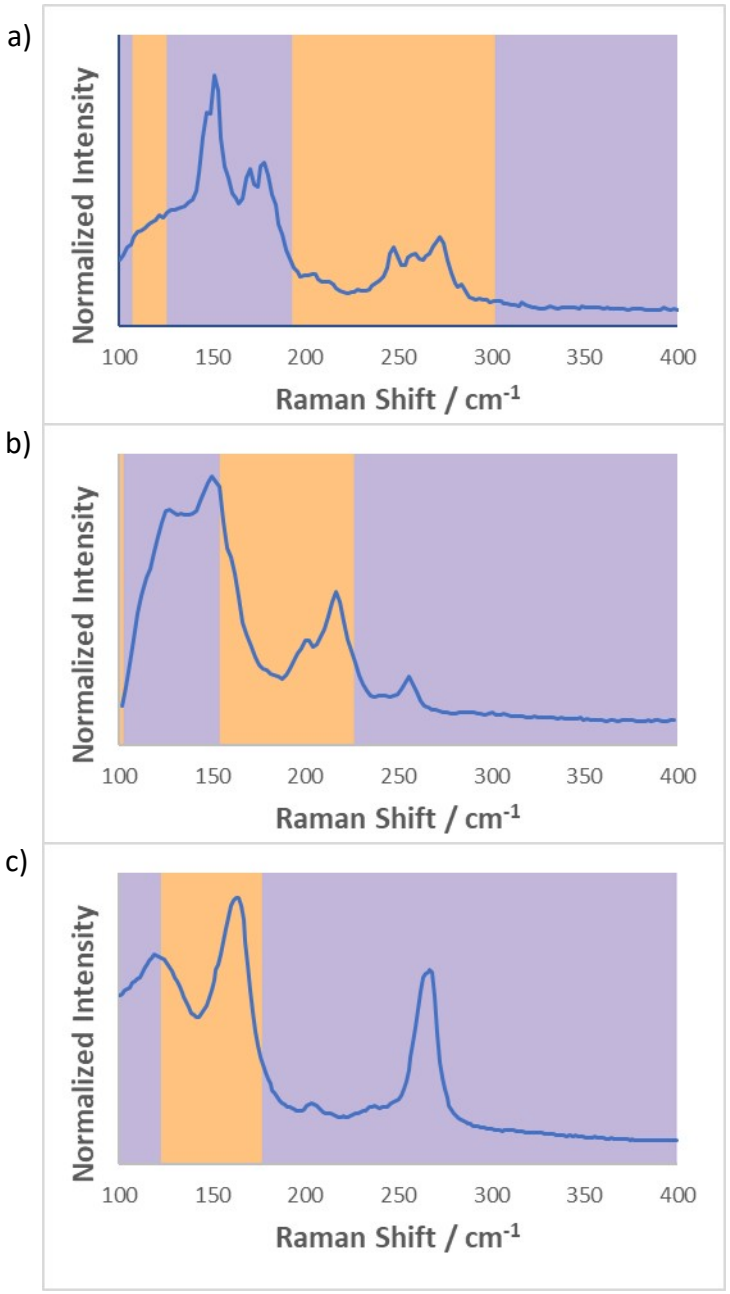


Figure S5. Resonant Raman average spectra of constituent CNTs in the radial-breathing-mode region. Spectra were taken with excitation wavelengths of a) 532 nm, b) 633 nm, and c) 785 nm. Light purple and orange regions serve as guides to expected resonance with semiconducting and metallic CNTs, respectively.

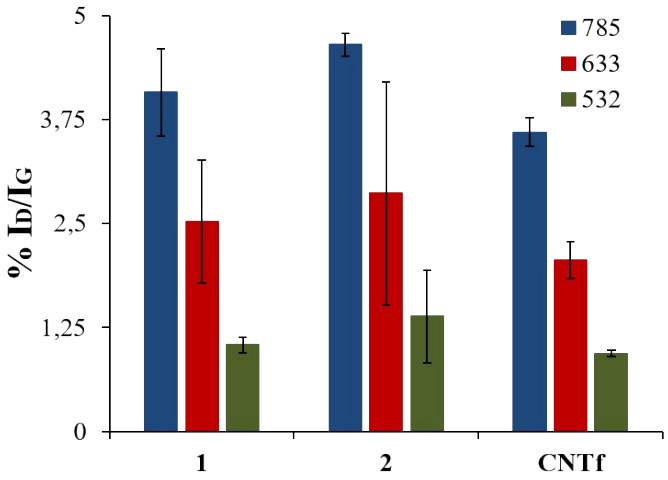


Figure S6. Percentage of I_D/I_G measured for control experiments: **1** for the electrochemical reduction of the aryl diazonium salt, **2** for the electrochemical oxidation of the ethylene diamine. Both control samples are compared with pristine CNTFs at different laser wavelengths.

Table S1. Raman I_D/I_G percentages measured on pristine and functionalised fibres using line mapping mode of 180 points analysis, with time exposure of 1 s, and 10% power, for three different laser sources, *i.e.* 532 nm, 633 nm and 785 nm.

Sample	I_D/I_G (%)			
	at 785 nm	at 633 nm	at 532 nm	Average
Pristine CNTF	3.6	2.1	0.9	2.2
CNTF1	5.5	2.8	1.2	3.2
CNTF2	6.6	4.3	1.0	3.9
CNTF3	6.2	3.6	1.0	3.6
CNTF4	5.3	3.4	1.5	3.4
CNTF5	7.0	4.1	1.1	4.1

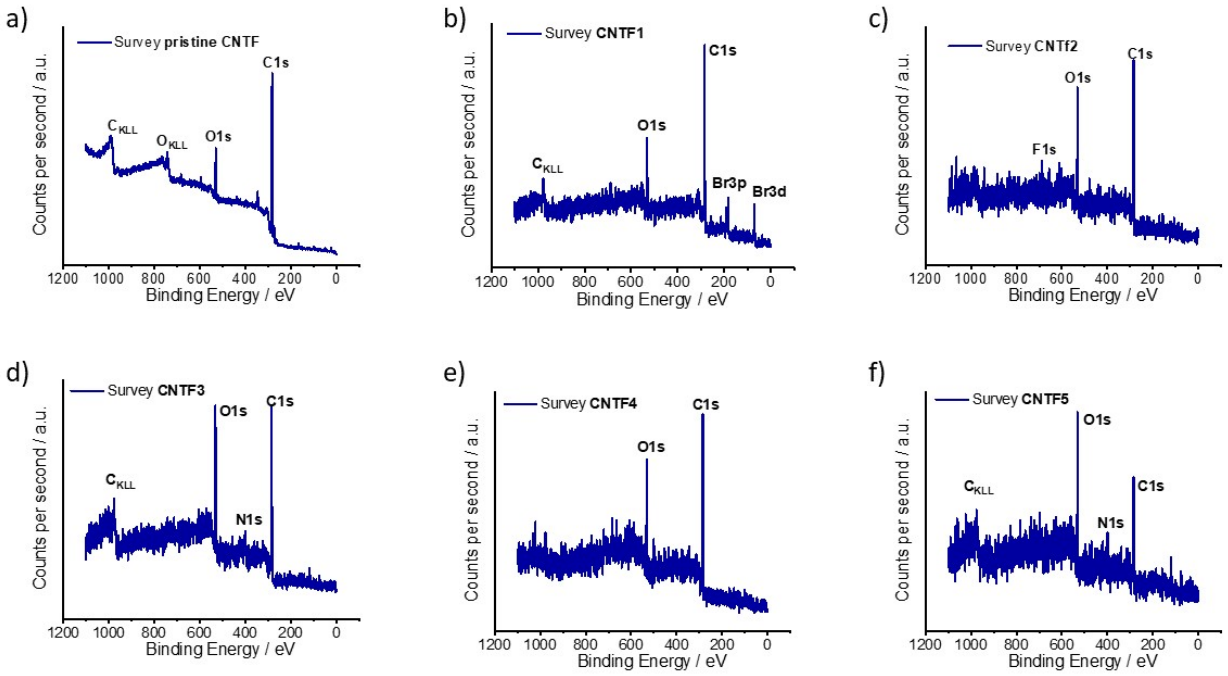


Figure S7. XPS survey spectra of a) pristine CNTFs, b) **CNTF1** c) **CNTF2** d) **CNTF3**, e) **CNTF4** and f) **CNTF5**.

Table S2. Atomic ratio of CNTFs obtained from XPS data analysis.

Sample	C at%	O at%	N at%	Br at%	F at%
Pristine CNTF	85.9	14.2	-	-	-
CNTF1	88.9	8.0	-	3.1	-
CNTF2	85.0	13.0	-	-	2.1
CNTF3	79.9	17.5	2.6	-	-
CNTF4	83.1	16.9	-	-	-
CNTF5	47.8	48.4	3.8		-

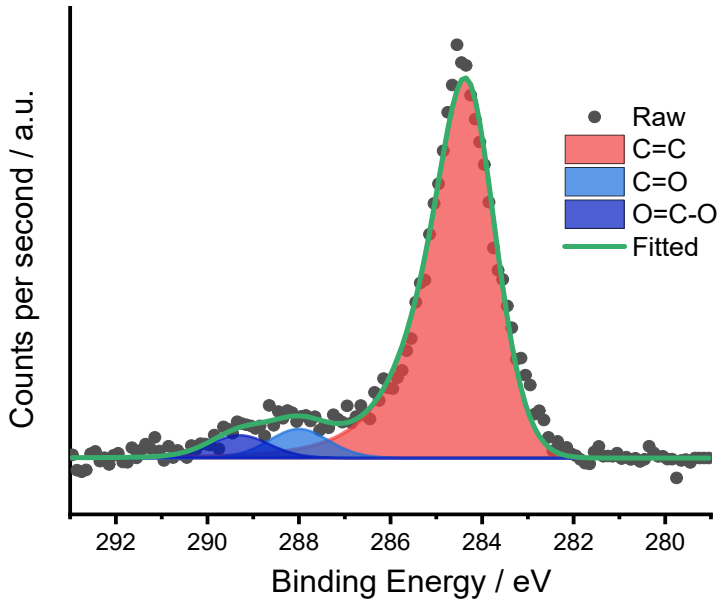


Figure S8. Deconvoluted Cs1 core level spectrum of **CNTF5**.

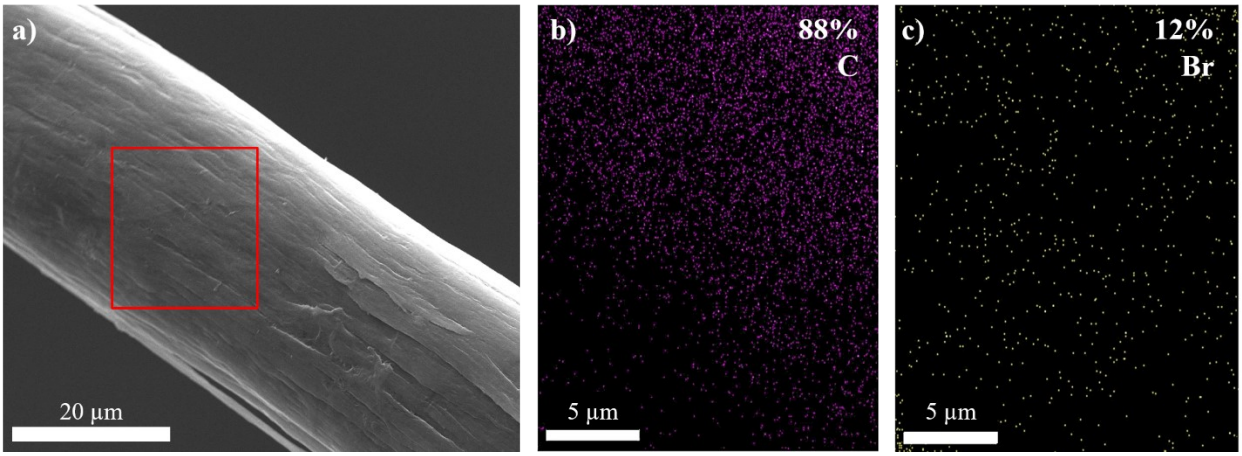


Figure S9. a) SEM and EDX images of **CNTF1** analysed within the area delimited by the red square, b) carbon and c) bromide element calculated percentages.

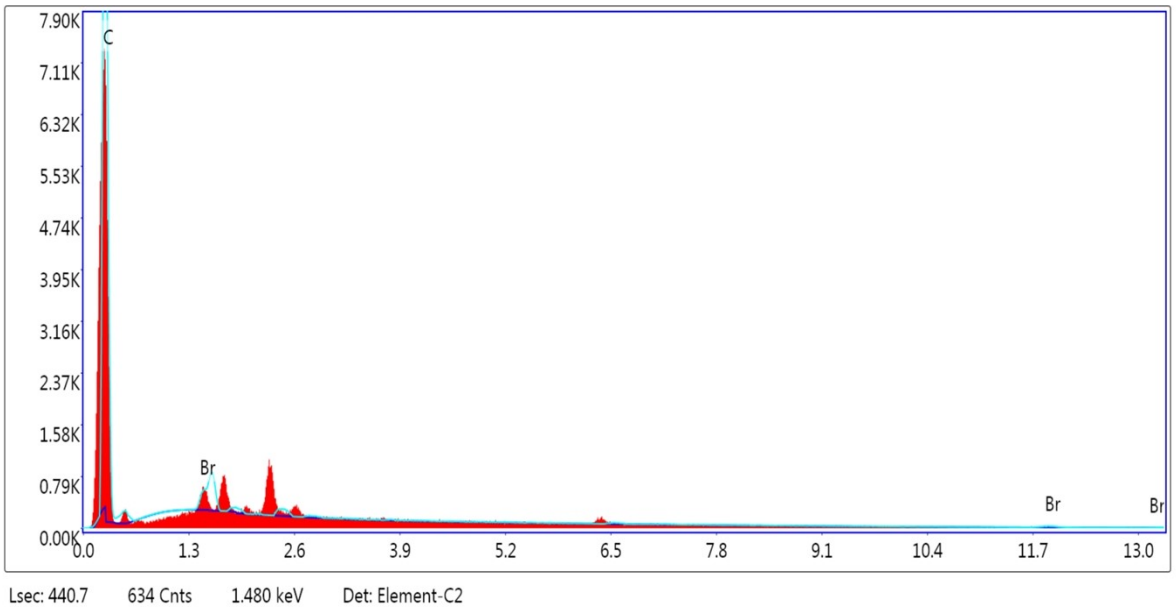


Figure S10. EDX spectrum of phenyl bromide functionalisation (**CNTF1**).

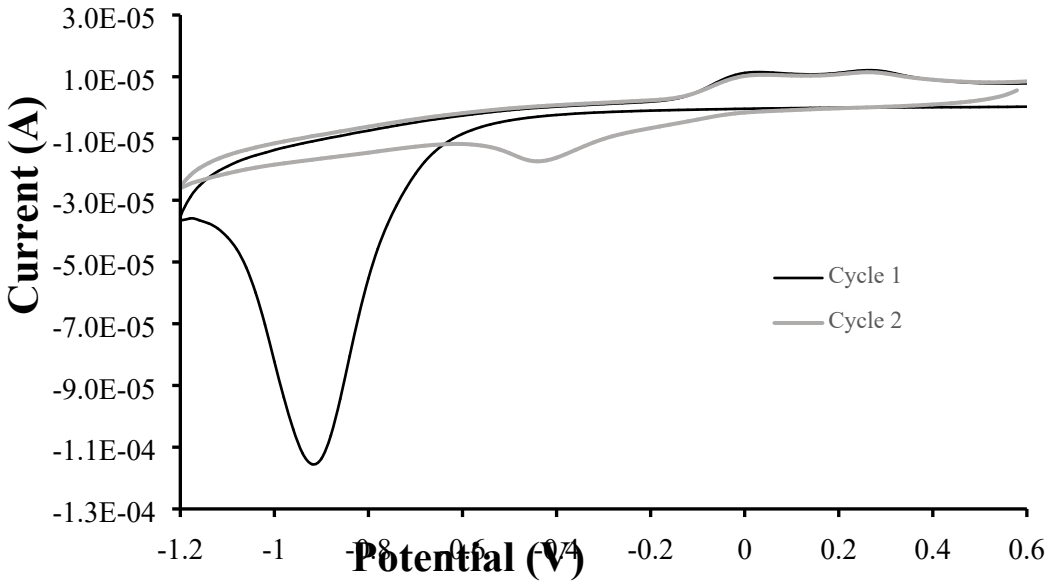


Figure S11. CV recorded from 0.6 to -1.2 V of the p-nitrophenyl functionalised **CNTF3** in 1× PBS. WE: **CNTF3**; RE: Ag/AgCl; CE: carbon fibres.

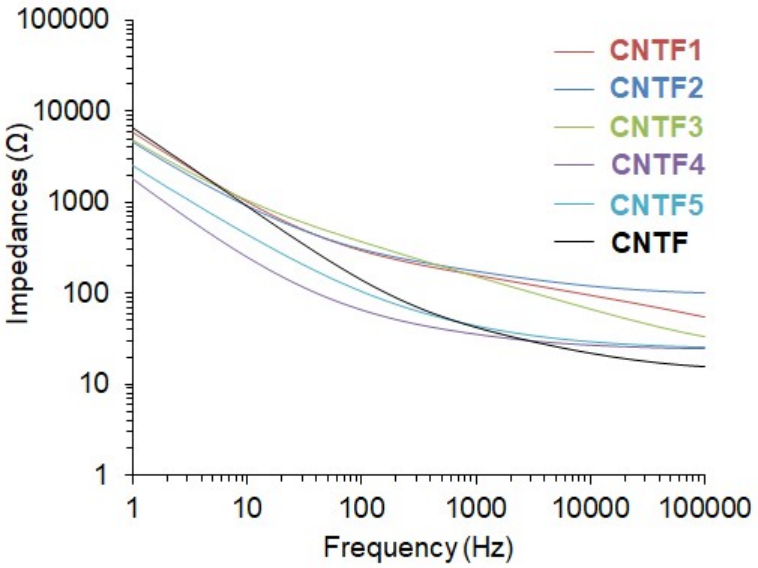
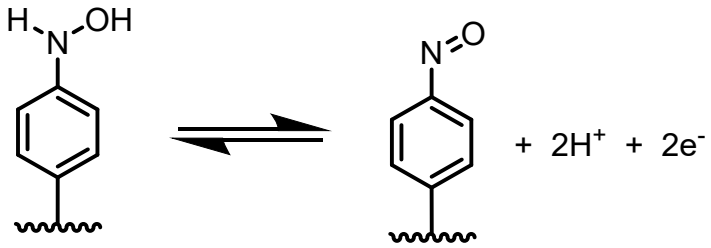


Figure S12. EIS measurement of relative impedance represented at logarithmic scale of functionalised CNTFs in PBS (pH=7.4, 0.1 M).



Scheme S1. Hydroxylamine/nitroso redox system.

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