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A modular approach to the surface modification of carbon fibers for application in advanced materials

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Abstract: *A convenient and effective strategy to control the surface chemistry of carbon fibers is presented, comprising electrochemical reduction of aryl diazonium salts onto the surface, followed by 'click chemistry' to tether the desired surface characteristic of choice. The power of this approach was demonstrated by engineering a small-molecule interface between carbon fiber and an epoxy matrix improving interfacial shear strength by up to 220%, relative to unmodified control fibers. The techniques used in this work do not impede the fiber performance in tensile strength or Young's modulus. This work provides a platform upon which any carbon fiber-to-resin interface can be easily and rapidly designed and implemented.*

Contents

1. Experimental Procedures

1.1. Materials

Carbon fiber samples were supplied by Carbon Nexus at Deakin University, Australia. All chemicals, reagents and solvents were purchased from Sigma-Aldrich Chemical Company and used as received.

1.2. X-ray photoelectron spectroscopy

XPS analysis was performed using an AXIS Ultra-DLD spectrometer (Kratos Analytical Inc., Manchester, UK) with a monochromated Al K_α source ($h\nu$ = 1486.6 eV) at a power of 150 W (15 kV × 10 mA), a hemispherical analyzer operating in the fixed analyzer transmission mode and the standard aperture (analysis area: 0.3 mm × 0.7 mm). The total pressure in the main vacuum chamber during analysis was typically below 10^{-8} mbar.

Bundles of fibers were suspended across a custom-designed frame attached to standard sample bars. This ensured that only the sample to be analyzed was exposed to the X-ray beam and that any signal other than that originating from carbon fibers was excluded. Each specimen was analyzed at a photoelectron emission angle of 0° as measured from the surface normal (corresponding to a take-off angle of 90° as measured from the sample surface). However, since the microscopic emission angle is ill-defined for fibers the XPS analysis depth may vary between 0 nm and approx. 10 nm (maximum sampling depth).

Data processing was performed using CasaXPS processing software version 2.3.15 (Casa Software Ltd., Teignmouth, UK). All elements present were identified from survey spectra (acquired at a pass energy of 160 eV). To obtain more detailed information about chemical structure, C 1s, O 1s and N 1s high resolution spectra were recorded at 20 eV pass energy (yielding a typical peak width for polymers of 1.0 eV). If required these data were quantified using a Simplex algorithm in order to calculate optimized curve-fits and thus to determine the contributions from specific functional groups. The atomic concentrations of the detected elements were calculated using integral peak intensities and the sensitivity factors supplied by the manufacturer. Atomic concentrations are given relative to the total concentration of carbon as follows: the concentration of a given element X was divided by the total concentration of carbon and is presented here as the atom number ratio (or atomic ratio) X/C. This value is more robust than concentrations when comparing different samples. Binding energies were referenced to the aliphatic hydrocarbon peak at 285.0 eV. The accuracy associated with quantitative XPS is ca. 10%-15%. Precision (i.e. reproducibility) depends on the signal/noise ratio, but is usually much better than 5%. The latter is relevant when comparing similar samples.

1.3. Single fiber tensile testing

Samples were tested on a Favimat + Robot 2 single fiber tester (Textechno H. Stein) which automatically records linear density and force extension data for individual fibers loaded into a magazine (25 samples) with a pretension weight of (~100-150 mg) attached to the bottom of each carbon fiber.

Linear density was recorded using a gauge length of 25 mm and a pretension of 1.6 cN/tex (nominal L.D. of 0.65 per supplier specifications). It is reported in units of tex, where 1 tex equals 1g/km. Tensile load–extension curves were collected at 1 mm/min using a gauge length of 25 mm and a pretension of 1.6 cN/tex. Load data was normalized by dividing by the linear density to give specific stress strain curves from which tensile strength (ultimate specific stress or tenacity) and specific modulus could be determined. The mean values of tenacity and modulus were determined and since the statistical distribution of carbon fiber strengths is usually described by a weakest link model, the strengths were also analyzed by the two-parameter Weibull probability (*P*) equation:

$$P = 1 - \exp\left[-\left(\frac{\sigma}{\sigma_0}\right)^m\right]$$

where *P* is the cumulative probability of failure of a carbon fiber at applied tensile strength σ, m is the Weibull modulus or shape parameter of the carbon fiber and σ_0 is the Weibull scale parameter or characteristic stress.[1] P is determined for each point using the median rank method:

$$P = \frac{i - 0{\cdot}3}{n + 0{\cdot}4}$$

where n= no. of sample points and i is the rank. Rearrangement of the probability expression to a straight line form allows m and σ_0 to be obtained by linear regression.

1.4. Statistical analysis

A two-sample t-test, assuming equal variance, was used to test whether data was significantly different or not; a P-value less than 0.05 was considered statistically significant.

1.5. Preparation and functionalization of carbon fiber probe

Carbon fiber electrodes were prepared using approximately 5 cm of carbon fiber tow (for preliminary testing and analysis) or 20 cm (fibers functionalized for interface analysis) by affixing one end of the sample using adhesive copper tape to ensure contact between probe and terminal. All electrochemical measurements were conducted using Metrohm autolab Potentiostat (Kanaalweg, The Netherlands) and data processed using NOVA software (Kanaalweg, The Netherlands). A three-electrode system was employed using a Harvard Apparatus LF-2 leak free electrode (filling electrolyte 3M KCl) half-cell and a platinum counter-electrode. After degassing the samples, reductive coupling was performed using a carbon fiber working electrode cycled between +1.0 V and -1.0 V *vs* Ag/AgCl at a scan rate of 0.02 V s^{-1} in ACN, the specified concentration of aryldiazonium salt and 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as a supporting electrolyte. After functionalization, the fibers were then rinsed thoroughly with a series of organic solvents (ACN, chloroform, DCM, EtOH and acetone), followed by drying under reduced pressure for 24 hours to ensure removal of residual compound on the surface to yield an ‘alkyne’ functionalized fiber.

1.6. Solid-phase click reaction

Alkyne-functionalized carbon fibers were placed in a pressure vessel upright in a solution of dimethylformamide, copper sulfate, ascorbic acid and azide analogue. The mixture was then stirred at room temperature for exactly 2 hours to minimize variations in reaction completion/efficiency. The solution was then decanted and the fibers washed with EDTA solution, 1 M NaOH, chloroform, DCM, ethanol and acetone. The washed fibers were then dried under reduced pressure for 24 hours to yield the functionalized product.

1.7. Determination of click reaction efficiency on fiber surface

Three small probes were prepared from each sample with approximately 0.08 mg of fiber 5 cm in length. The samples were scanned at a slow scan rate (0.01 V s^{-1}, -0.1 V to +1.0 V). The ferrocene redox plots were processed using Originlab (Northampton, MA, USA), using a manual baseline subtraction for both oxidation and redox curves. The area under the CV was integrated to give area in coulombs s^{-1}, and divided by scan rate to give total charge (Q).

$$Surface\ coverage\ (moles\ cm^{-2}) = Q/nFA$$

The above equation represents the calculation of moles cm^2 where Q = charge in coulombs, n = number of electrons undergoing redox per molecule, F = Faradays number and A = area in cm^2. In the case of carbon fiber probes, sample area is extremely difficult to determine. As such, the area term was removed from the equation to give:

$$moles\ = Q/nF$$

In this case, n = 1 for ferrocene and F = 96485, so the calculated Q could be divided by F to give the total number of moles of ferrocene detected for each probe. This number was then divided by the average weight of the probes in mg (0.08) to give number of moles per mg. Three replicates were performed for each sample, and the average of all oxidation and reduction curves are presented in text, with standard error.

1.8. Reduction of surface bound nitro to amine

Click functionalized fibers were reduced using a three-electrode system of Ag/AgCl, Pt and functionalized carbon fiber. The reaction was performed in a 0.1 M KCl solution in H_2O:ethanol (10:1) with the CF working electrode cycled between 1 V and -1.5 V at a scan rate of 0.02 V s^{-1}. A total of 6 scans were performed, followed by chronoamperometry at -1.0 V for 5 min.

1.9. Formation and analysis of single fiber composites

Five individual fibers were prepared (for each different sample) by placing the fiber along the center of a dog-bone shaped mold, and adding 350 mg pretension weight to both ends of the fiber which were allowed to hang either side of the mold. This ensured the fiber would remain straight and centralized within the composite. Epoxy resin RIM935 was prepared along with hardener RIM937 (in a 10:4 w/w ratio as recommended by manufacturer), by stirring together at room temperature for 30 minutes to ensure even distribution, followed by storage under vacuum for 15 minutes to remove large bubbles from the solution. The resin mixture was then poured into the molds to ensure complete immersion of the fiber, and cured at room temperature for two days, followed by post-curing at 100°C for 12 hours. The samples were finally ground and polished to yield the final test coupon with the dimensions 25 mm × 5 mm × 1.5 mm.

The samples were extended to failure to ensure maximum fragmentation within the sample, using a tensile tester (Instron 5967, Instron Pty Ltd, USA) fitted with a 30 kN load cell. Each fragmentation test was monitored in real time using a digital microscope/camera (AD-4113ZT Dino-Lite, AnMo Electronics Co. Taiwan), and the fragments measured using a calibrated optical microscope (Olympus BX51M (Japan) equipped with Olympus DP70, images were processed using Olympus Stream image software). These data, along with values collected from Weibull analysis (experimental section 2.3) were then processed according to the Kelly-Tyson model,[2] where l is the average fragment length, and l_c is the critical length.

$$l_c = \frac{4}{3} l$$

Using the Weibull modulus m and the characteristic strength σ_0 at gauge length L_0, the characteristic strength at critical length $\sigma_f(l_c)$ can be calculated.

$$\sigma_f(l_c) = \sigma_0(L_0)\left(\frac{L_0}{l_c}\right)^{\frac{1}{m}}$$

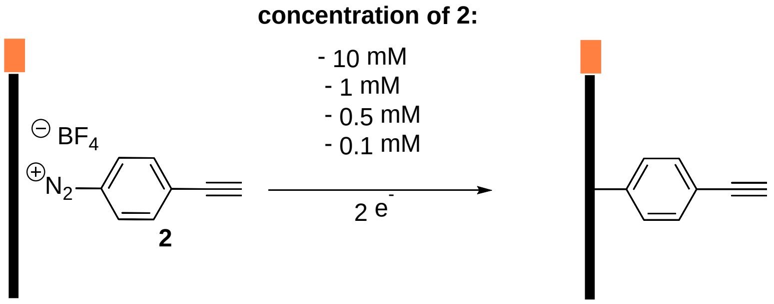
Finally, using the average fiber diameter d (determined to be 7 μm), the apparent interfacial shear strength τ can be calculated using the following equation:

$$\tau = \frac{\sigma_f(l_c)d}{2\, l_c}$$

Keeping in mind that for most impact to an industrial environment (i.e. large scale carbon fiber treatment), concentration of reagents is the most important aspect which must be considered. The goal being to employ a concentration to sufficiently decorate the fiber surface to illicit an interfacial improvement, while minimizing concentration and thus economy of synthesis and cost.

2. Electrografting of diazoalkyne

Optimization of the concentration of reagents for electrografting was investigated in the interest of scalability. To this end, a series of concentrations were proposed for the initial grafting reaction which included 10 mM (a standard literature treatment concentration), and three low concentration treatments of 1 mM, 0.5 mM and 0.1 mM (S1).



Scheme 1. Representation of electrografting reaction using diazoalkyne **2**.

Carbon fiber probes were prepared using adhesive copper tape at one end of a 5 cm carbon fiber tow. **Note that the samples were not agitated during electrografting, though this could result in enhanced surface modification if carried out in the future.** Grafting was performed by cyclic voltammetry, scanning from +1.0 V to -1.0 V at 0.1 V s^{-1}. In each case there was a reduction peak noted at approximately 0.3 V which was attributed to the reduction of the diazo to the corresponding reactive carbon, followed by rapid quenching at the carbon fiber surface. Interestingly, by the second scan there was little to no reduction peak remaining, indicating and irreversible reaction. This is consistent with observations made by Pinson and co-workers.[3] This concept of surface modification having an immediate effect then 'topping out' is not uncommon with carbon fiber surface treatments and was noted by Hughes as far back as 1991.[4] It was also noted that after agitating the solution followed by a second series of CVs, the initial reduction peak reappeared, but smaller in magnitude. These results suggest both diffusion and surface passivation may be playing a role during reduction.

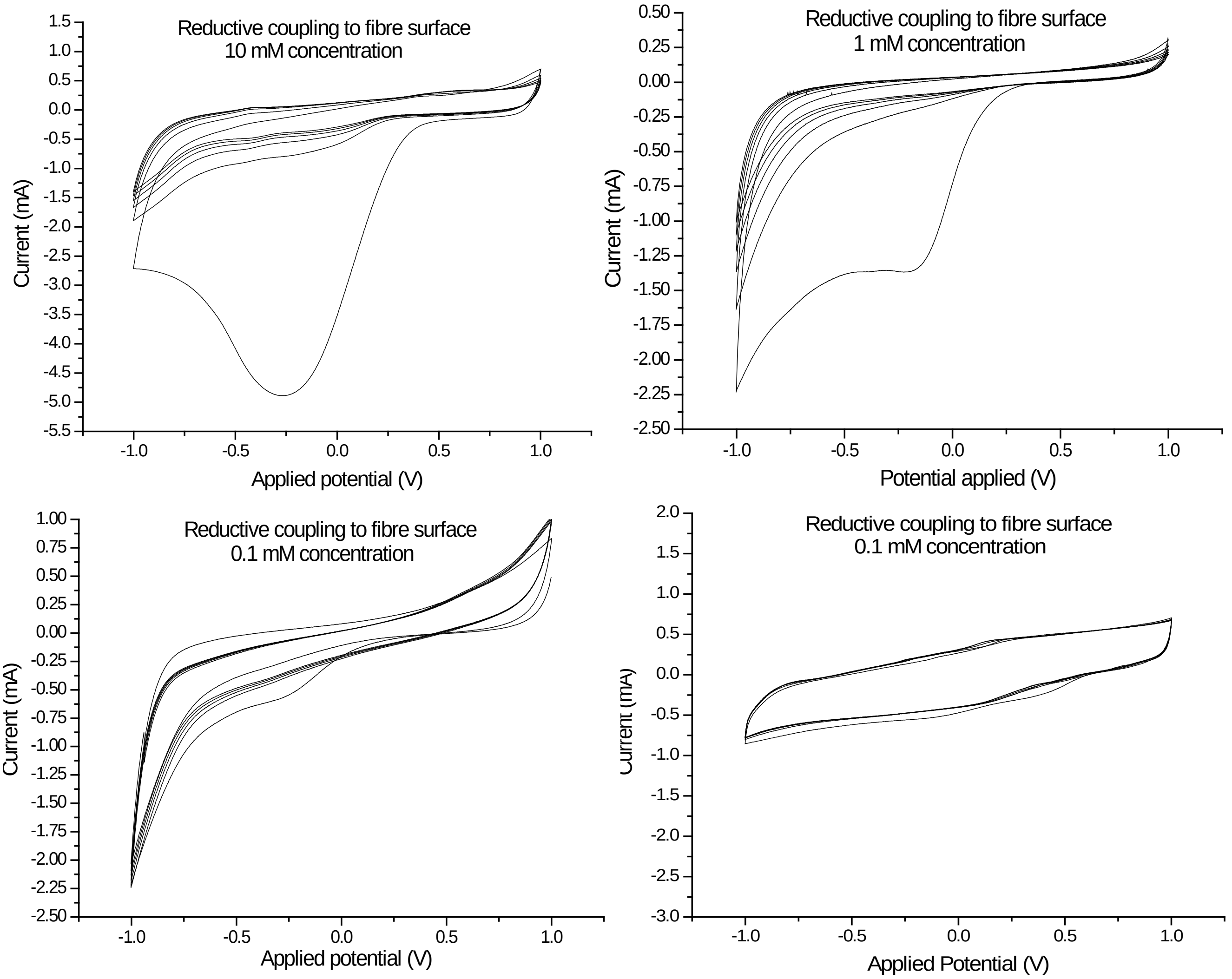
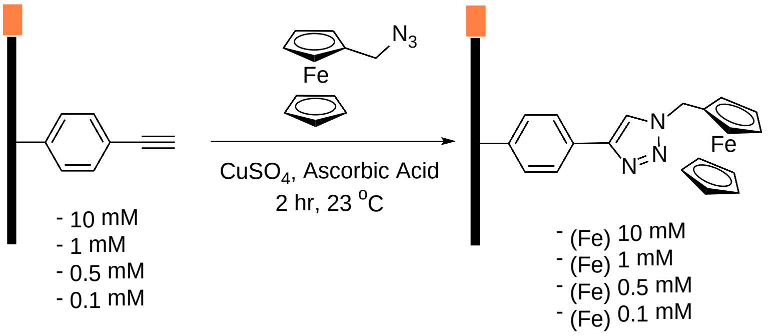


Figure 1. Reductive coupling of diazoalkyne **2** to carbon fiber probe at a 10, 1, 0.5 and 0.1 mM concentration in 0.1 M $TBAPF_6$ in MeCN.

3. Solid-phase click reaction and analysis

Using the established literature methodology, each of the alkyne functionalized fiber probes were then further treated using the click reaction with azido ferrocene. Special care was taken to ensure unreacted materials were removed from the fiber probes. Acidic aqueous and EDTA washes to remove residual copper were followed by extensive washing with 100 mL portions of chloroform, dichloromethane, ethanol and acetone, and finally drying under reduced pressure to ensure complete removal of trace material and residual solvent.



Scheme 2. Representation of proposed click reaction to yield ferrocene.

Subsequent analysis of the functionalized fiber probes (S1, (Fe) 10 – 0.1 mM) by XPS and integration of ferrocene redox curves led us to conclude that the optimal concentration for reductive grafting in this case was 1 mM. XPS analysis of the fibers was conducted to determine relative atomic ratios and detect the presence of the ferrocene and triazole functional groups introduced *via* the click reaction (Table 1). The first change noted was an increase in nitrogen relative to the control across the board, consistent with the presence of a triazole moiety post-click reaction. Additionally, there was a notable increase in iron attributed to the introduction of ferrocene to the fiber surface. Interestingly the ratio of iron to carbon detected was very similar across all of the samples (0.015, 0.019, 0.017 and 0.013). This semi-quantitative analysis indicated there may be comparable effectiveness between each of the four treatment concentrations.

Table 1. Atomic ratios determined by XPS relative to carbon

Element	**Control**		**10 mM**		**1 mM**		**0.5 mM**		**0.1 mM**	
	Mean	*Dev.*	Mean	*Dev.*	Mean	*Dev.*	Mean	*Dev.*	Mean	*Dev.*
C	1.000	*0.000*	1.000	*0.000*	1.000	*0.000*	1.000	*0.000*	1.000	*0.000*
N	0.016	*0.000*	0.069	*0.002*	0.071	*0.001*	0.043	*0.002*	0.042	*0.001*
O	0.040	*0.000*	0.123	*0.000*	0.141	*0.001*	0.168	*0.001*	0.105	*0.005*
Cl			0.002	*0.000*	0.002	*0.000*	0.006	*0.000*	0.003	*0.001*
F			0.001	*0.001*			0.029	*0.003*	0.032	*0.004*
Si	0.006	*0.000*	0.005	*0.001*	0.003	*0.000*	0.002	*0.000*	0.004	*0.000*
Na							0.001	*0.000*		
Cu			0.003	*0.001*	0.004	*0.000*	0.013	*0.000*	0.007	*0.001*
Ca			0.002	*0.000*			0.002	*0.000*	0.002	*0.000*
Fe			0.015	*0.001*	0.019	*0.001*	0.017	*0.001*	0.013	*0.000*
S							0.003	*0.000*	0.002	*0.000*

Values presented are an average of two spot analyses.

There was also a large increase in oxygen detected on the fiber surface which could not be attributed to the proposed grafted compounds. The most likely contributor was thought to be residual water, as there were a number of aqueous washing steps prior to analysis. Additional evidence of this is the small amount of water soluble copper detected on the surface along with a number of other trace elements found in water such as Ca and Na. There also appeared to be a fluorine anomaly with samples 0.5 and 0.1 mM. In general, the consistent presence of nitrogen and iron on the fiber surface are consistent with a successful grafting/click reaction to introduce the proposed triazole product.

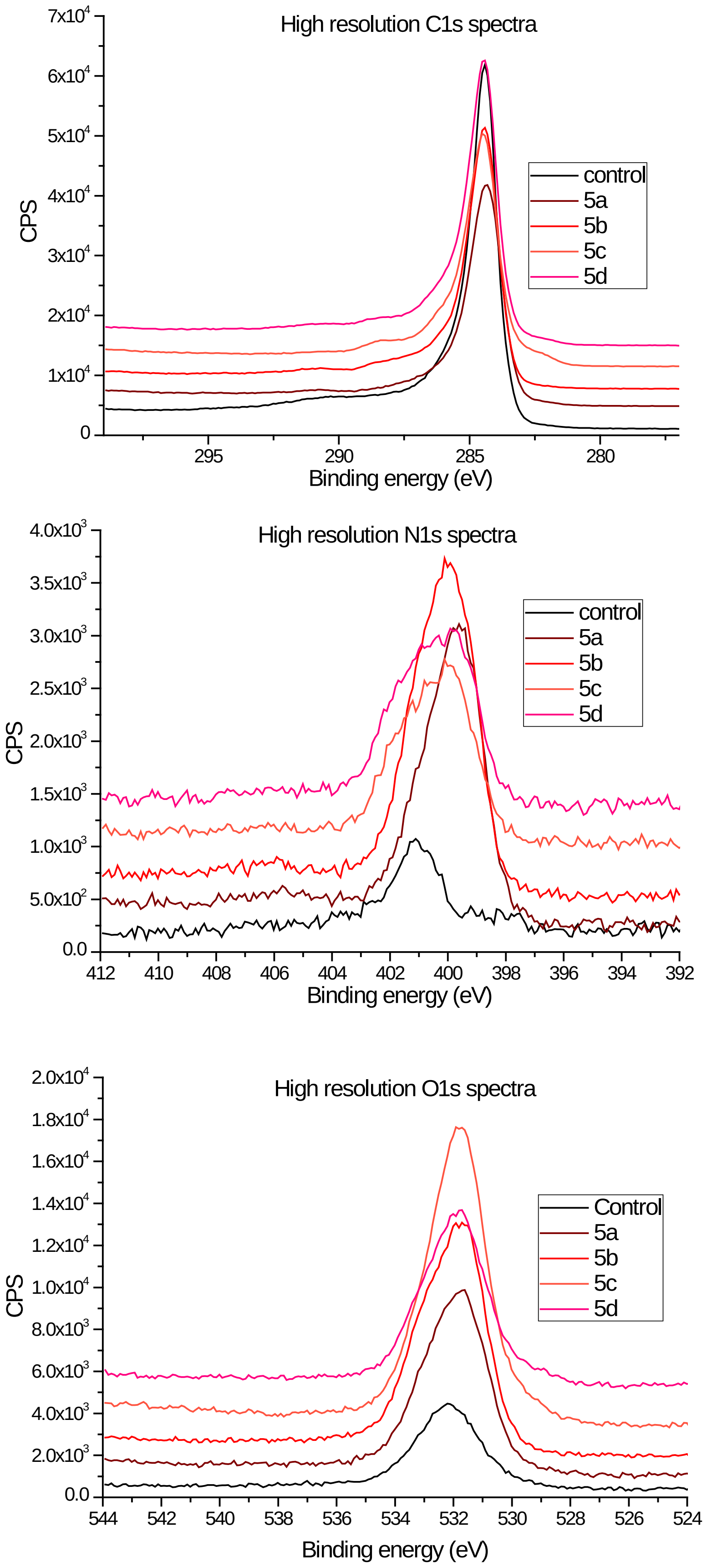
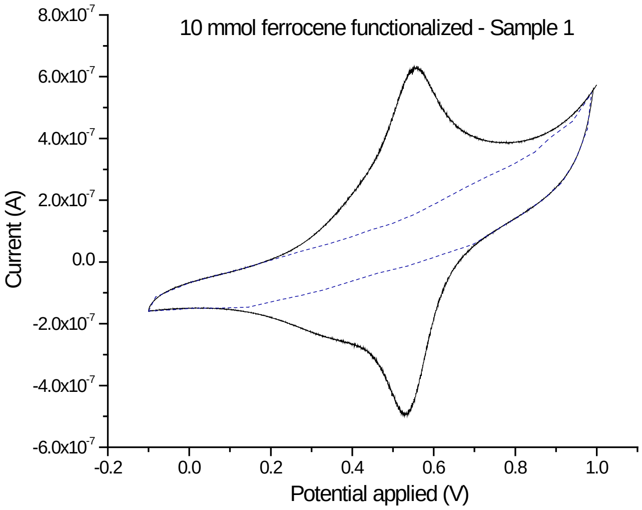
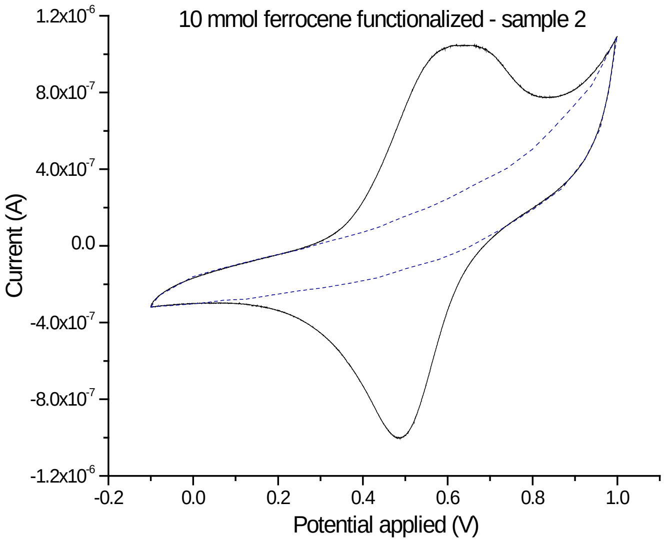


Figure 2. High resolution C1s, N1s, and O1s XPS spectra for treated samples

Few-fiber probes were then prepared in triplicate and scanned from -0.1 V to +1.0 V to detect the presence of ferrocene. CVs of the fiber probes exhibited a reversible redox peak attributed to ferrocene at approximately 0.43 V (red) and 0.59 V (ox). The fiber probes were scanned at a slow scan rate (0.01 V s^{-1}) in order to exhaustively oxidize the surface bound ferrocene.

The integrated current was used to quantify the number of electrons undergoing reaction, and subsequently the number of moles per mg of sample.





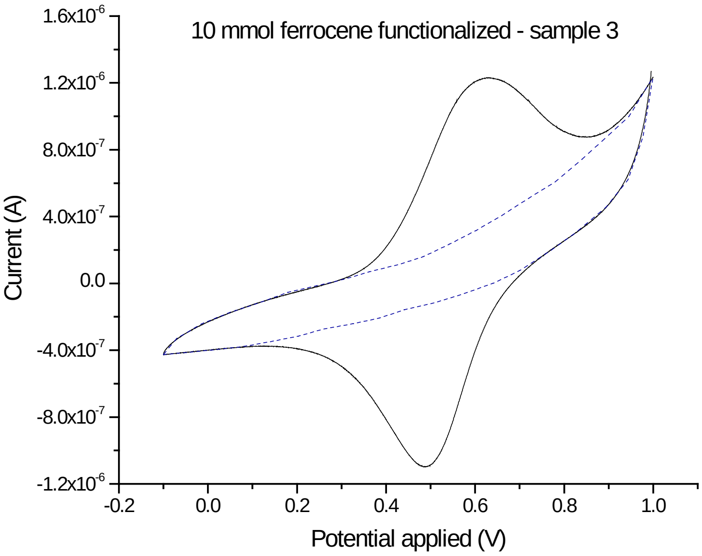


Figure 3. 10 mM ferrocene redox curve scanned at 0.01 V s^{-1} in 0.1 M TBA PF$_6$ in MeCN.

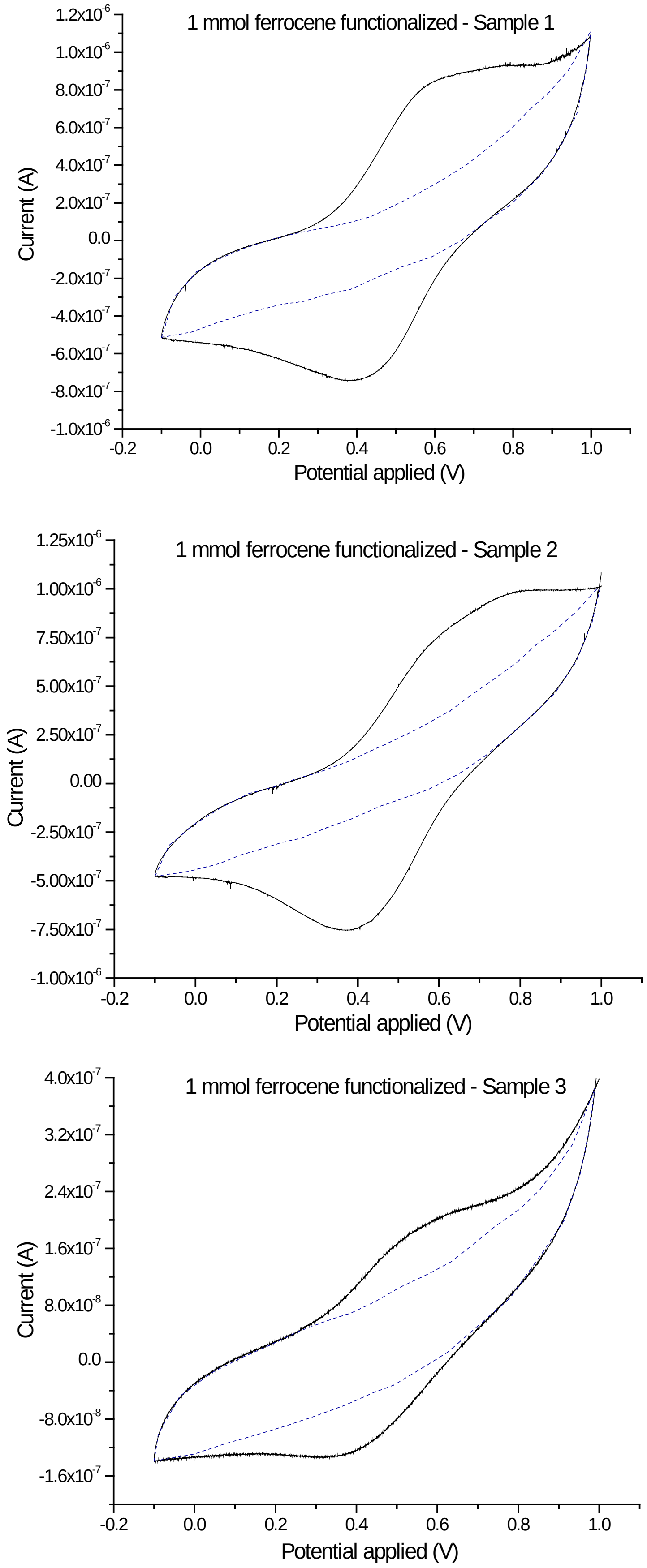
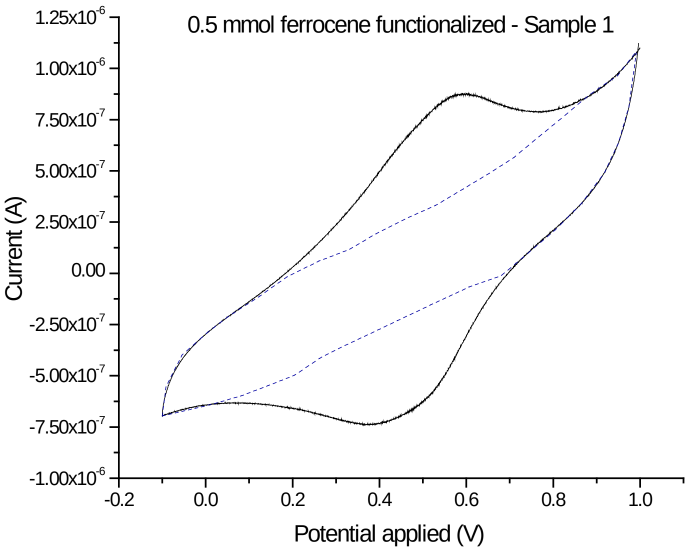
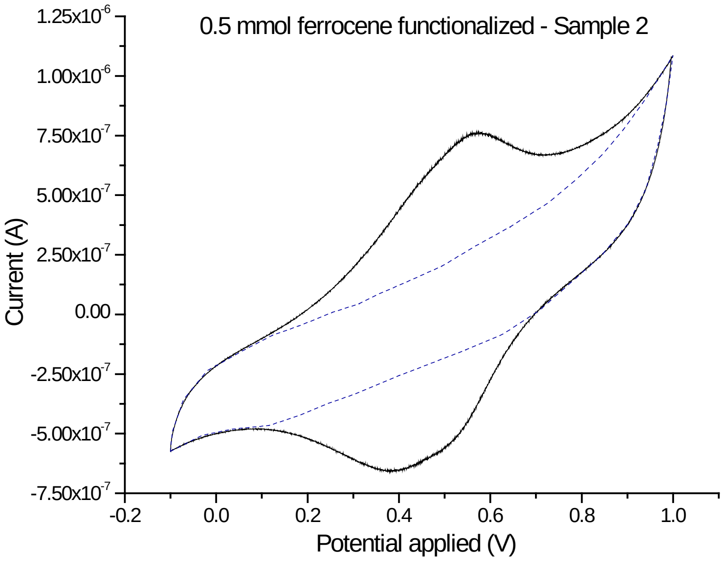


Figure 4. 1 mM ferrocene redox curve scanned at 0.01 V s^{-1} in 0.1 M TBAPF$_6$ in MeCN.





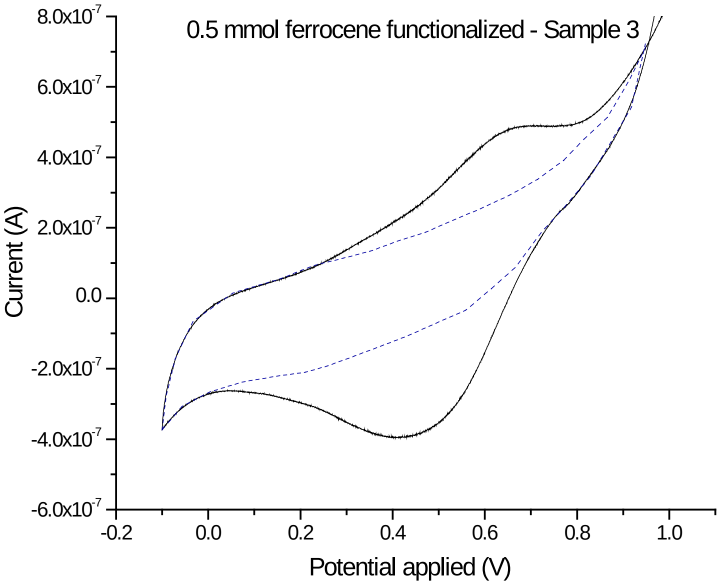


Figure 5. 0.5 mM ferrocene redox curve scanned at 0.01 V s^{-1} in 0.1 M TBAPF$_6$ in MeCN.

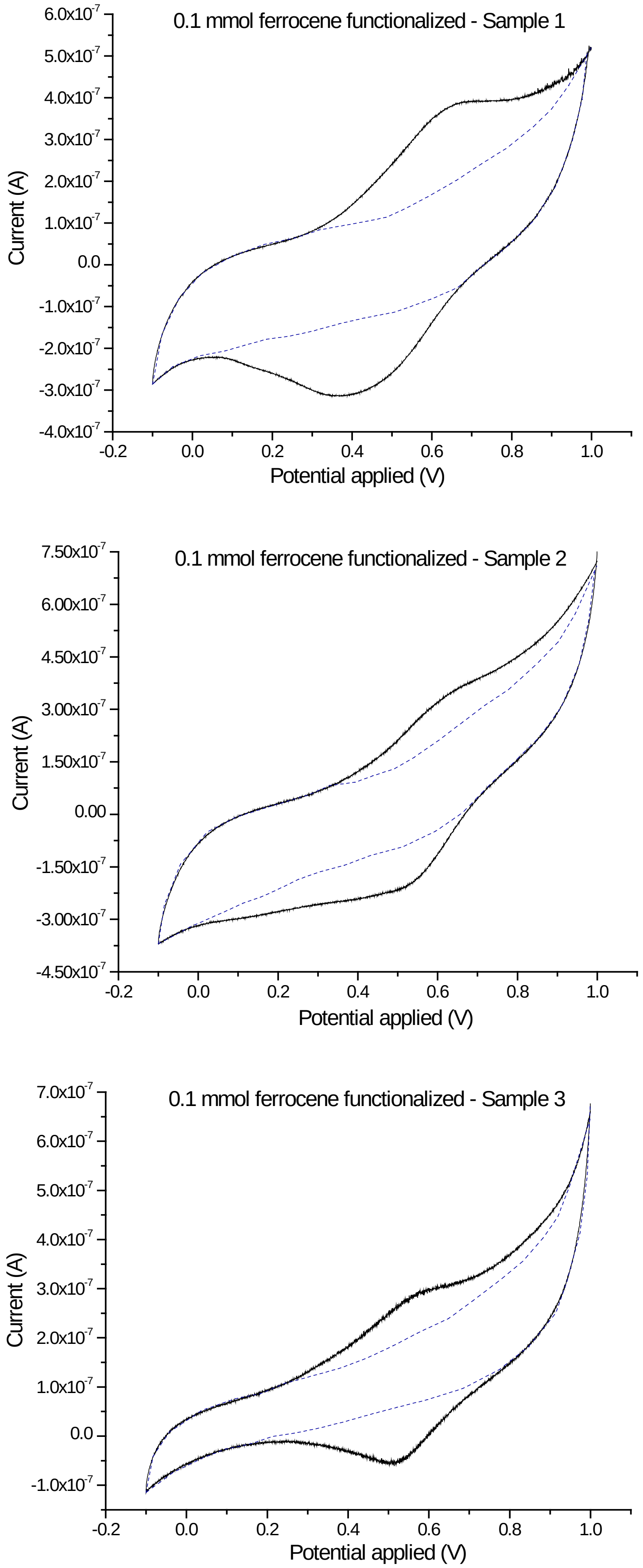


Figure 6. 0.1 mM ferrocene redox curve scanned at 0.01 V s^{-1} in 0.1 M $TBAPF_6$ in MeCN.

Manual baseline fitting (shown in blue dotted lines F3 to F6) was applied to each of the reduction and oxidation plots. The corrected curves were then plotted (F7), and integrated.

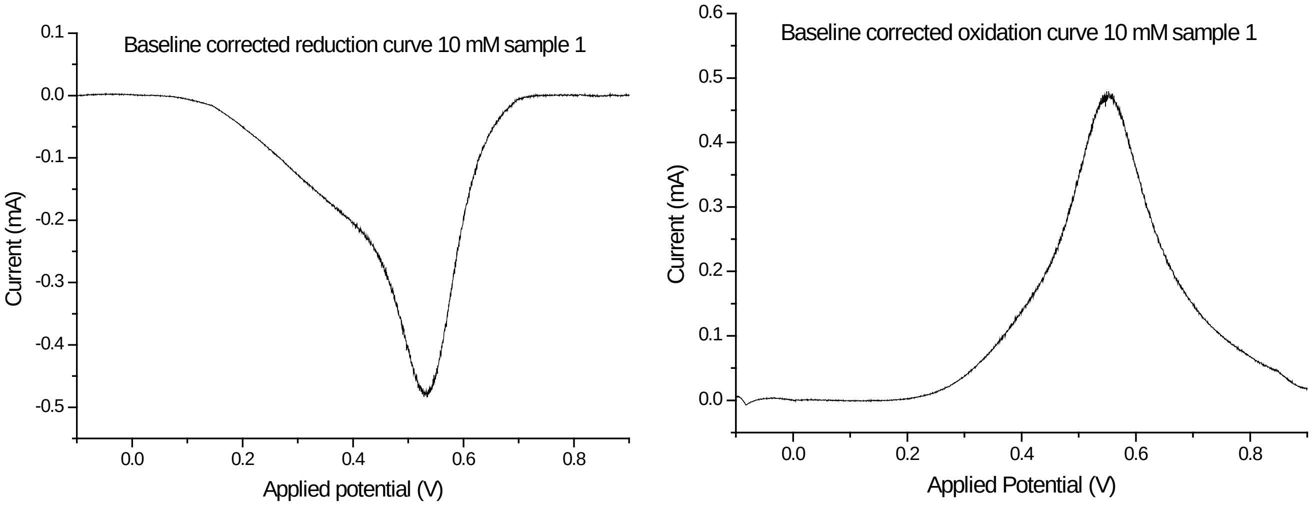


Figure 7. Baseline corrected reduction and oxidation curves.

The data from each curve was then converted to moles/mg for each curve (T2).

Table 2. Calculated number of moles of ferrocene detected per mg of material.

Sample		**10**	**1**	**0.5**	**0.1**
1	red	1.32E-09	2.57E-09	2.22E-09	8.24E-10
	ox	1.48E-09	2.79E-09	2.20E-09	8.77E-10
2	red	2.65E-09	2.73E-09	1.76E-09	6.69E-10
	ox	2.65E-09	2.23E-09	2.35E-09	5.60E-10
3	red	2.97E-09	3.45E-10	1.37E-09	3.68E-10
	ox	3.29E-09	3.62E-10	7.92E-10	3.97E-10
Average		**2.39E-09**	**1.84E-09**	**1.78E-09**	**6.16E-10**
Std. err.					

Examination of the graphed data (F8) highlighted an apparent downward trend from high to low concentration. However, statistical analysis of the data showed that while every sample was significantly different from the 0.1 mM sample, there was no significant difference between any of the other samples from 0.5 mM to 10 mM. When choosing a concentration at which to conduct the surface modifications, 10 mM was considered impractical due to the amount of starting material required per 100 mL of solvent (236 mg, compound **2**). As there was no benefit observed for higher graft density at higher concentrations, *i.e.* both 1.0 and 0.5 mM gave similar results (F8), 1 mM was considered to be the optimal concentration treatment of larger samples (30 cm), as this was both practical (24 mg of 2/100 mL) and was not at the edge of the observed grafting 'drop off'.

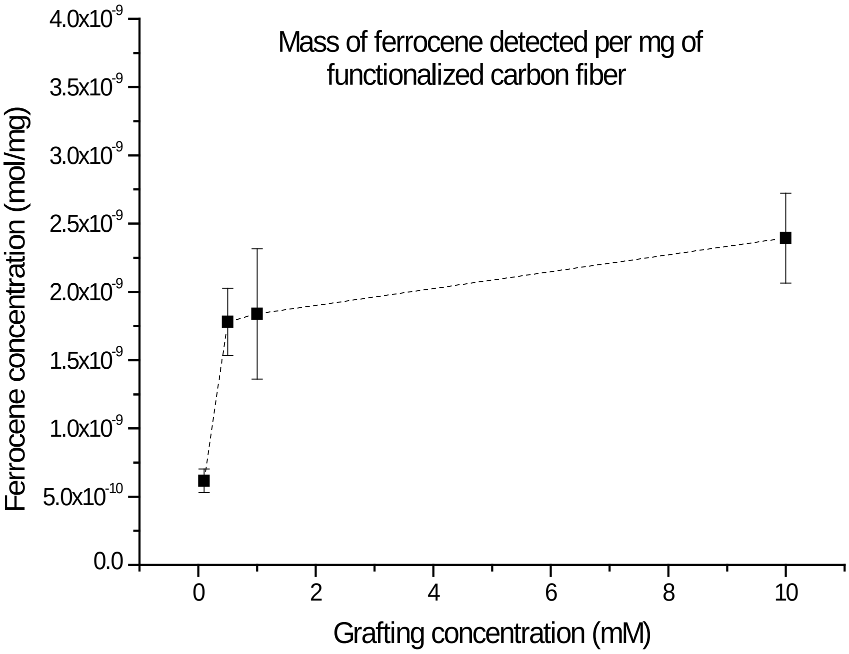
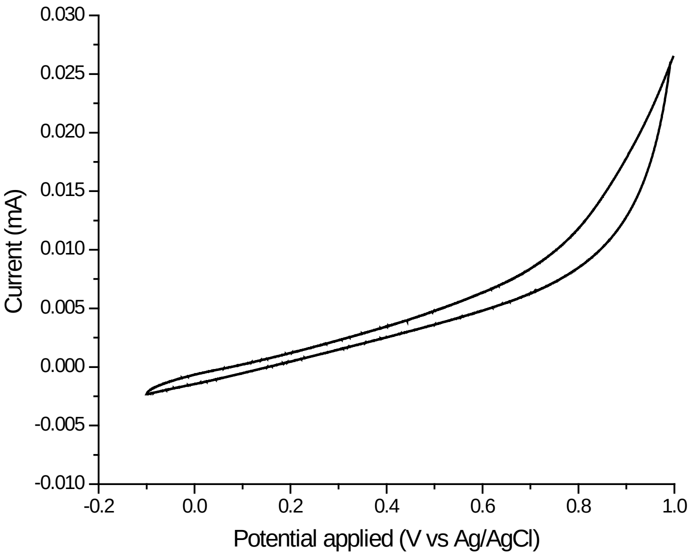


Figure 8. Average number of moles of surface bound ferrocene per mg of CF.

To ensure the redox couple observed for the funcitonalised fiber was attributed to covalently bound ferrocene and not simply adsorbed ferrocene a control experiment was conducted. Some ‘as received fibers’ were submerged in a DMF solution of ferrocene (as per the click reaction procedure) for 2 hours then removed and washed using the same protocol as for the functionalized fibres. These fibres were then connected to the potentiostat using adhesive copper tape and the redox activity of these fibres examined. The CV is shown below with no redox observed in any case. This supports the observed redox couple being tethered to the CF surface using this functionalization method.



4. Functionalization via the click reaction

Large scale functionalization ‘click’ reactions were then undertaken using a series of azides. The resulting functionalized materials (F9) were then subject to chemical and physical analysis.

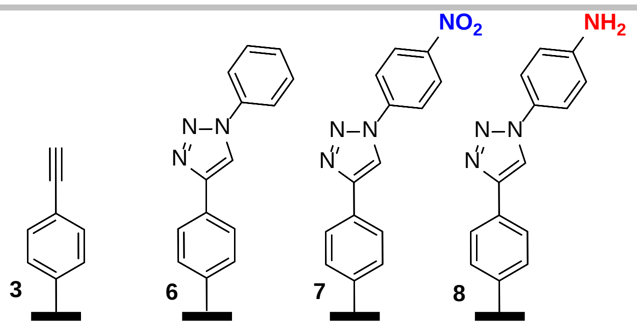
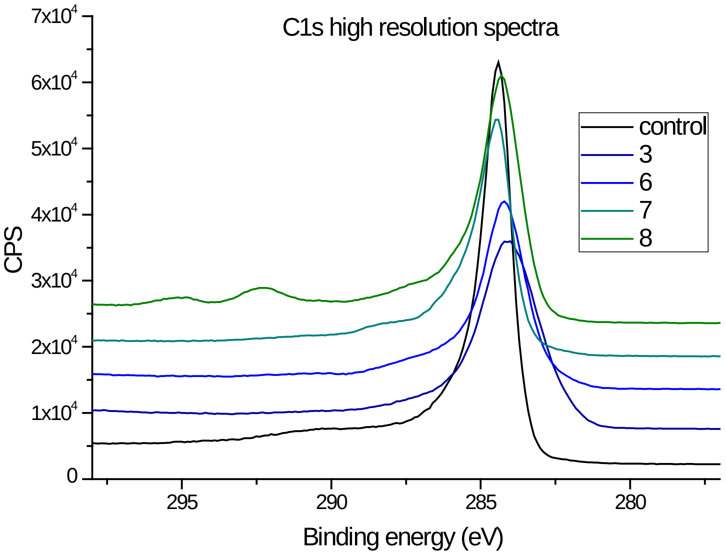


Figure 9. Representative chemical structures of functionalized fibers, after electrochemical grafting (**3**) and click reaction to give phenyl (**6**), nitro (**7**), and aniline (**8**) terminated samples.

Table 3. Atomic ratios at fiber surface as determined by XPS.

Element	**Control**		**3**		**6**		**7**		**8**	
	Mean	*Dev.*	Mean	*Dev.*	Mean	*Dev.*	Mean	*Dev.*	Mean	*Dev.*
C	1.000	*0.000*	1.000	*0.000*	1.000	*0.000*	1.000	*0.000*	1.000	*0.000*
N	0.016	*0.000*	0.052	*0.002*	0.070	*0.002*	0.076	*0.004*	0.058	*0.009*
O	0.040	*0.000*	0.169	*0.001*	0.223	*0.002*	0.195	*0.007*	0.151	*0.030*
Cl			0.003	*0.000*	0.005	*0.000*	0.003	*0.000*	0.003	*0.000*
F			0.006	*0.001*			0.008	*0.000*	0.003	*0.000*
Si	0.006	*0.000*	0.004	*0.000*	0.004	*0.001*	0.005	*0.000*	0.003	*0.000*
Na					0.018	*0.001*	0.037	*0.002*		
Cu			0.004	*0.000*	0.007	*0.000*	0.020	*0.003*	0.013	*0.002*
K									0.020	*0.004*
Ca			0.005	*0.001*	0.003	*0.000*				
Zn									0.002	*0.000*



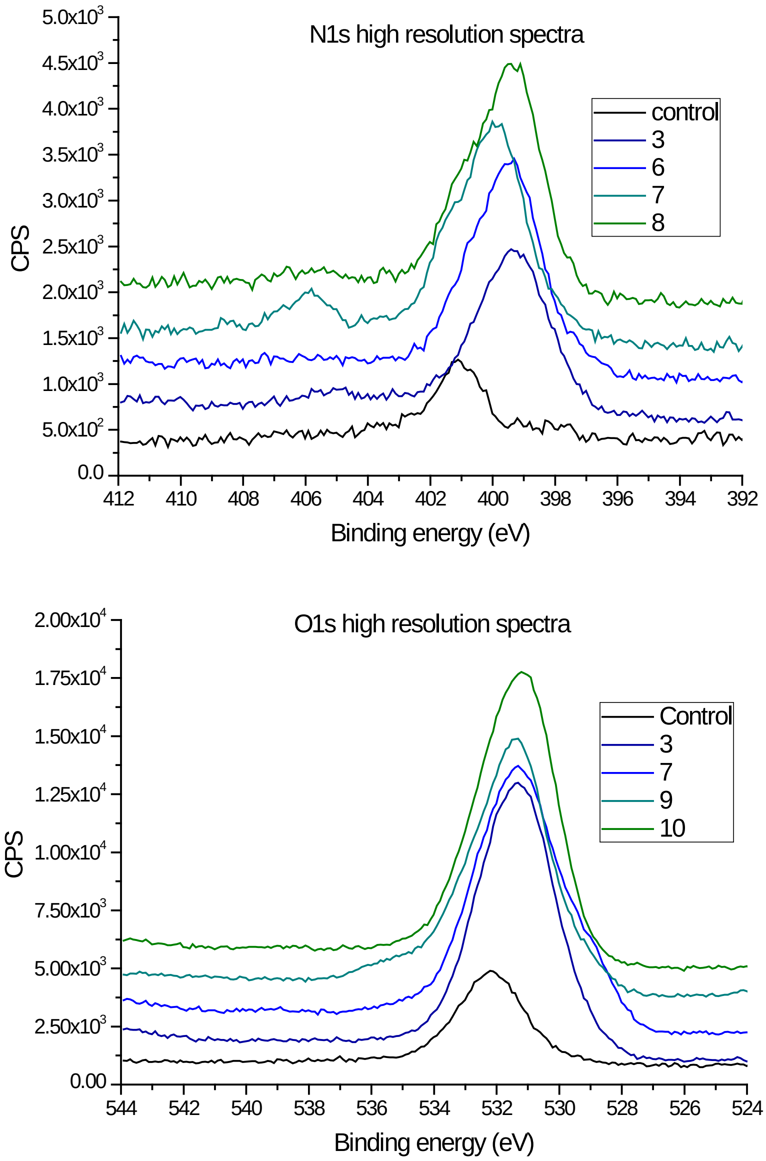
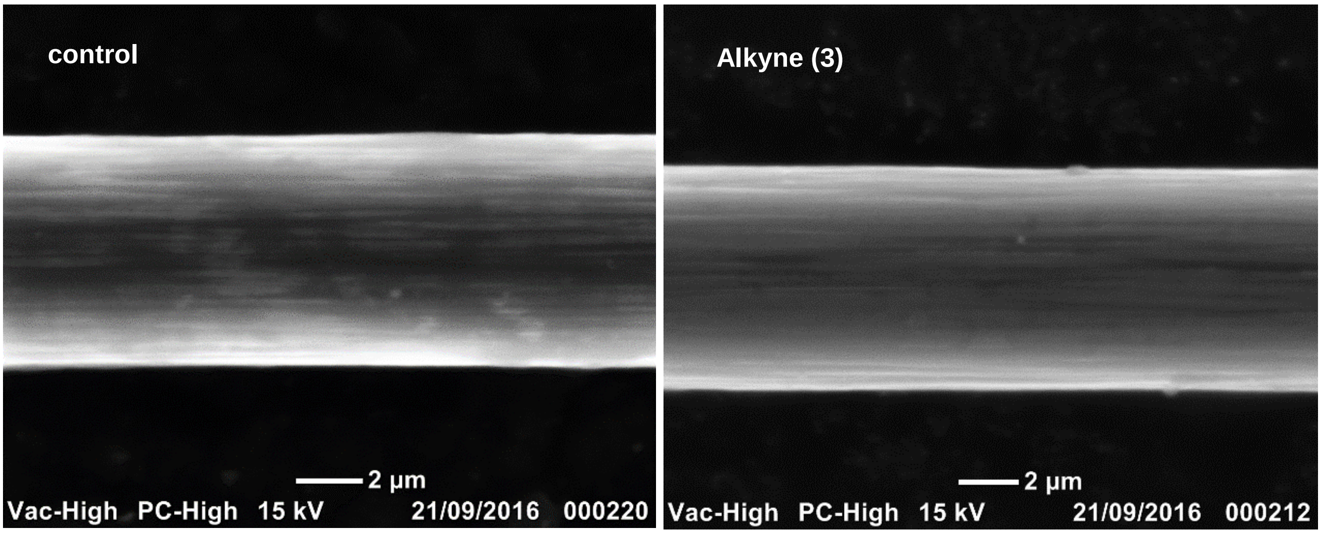


Figure 10. High resolution XPS data C1s, N1s and O1s.



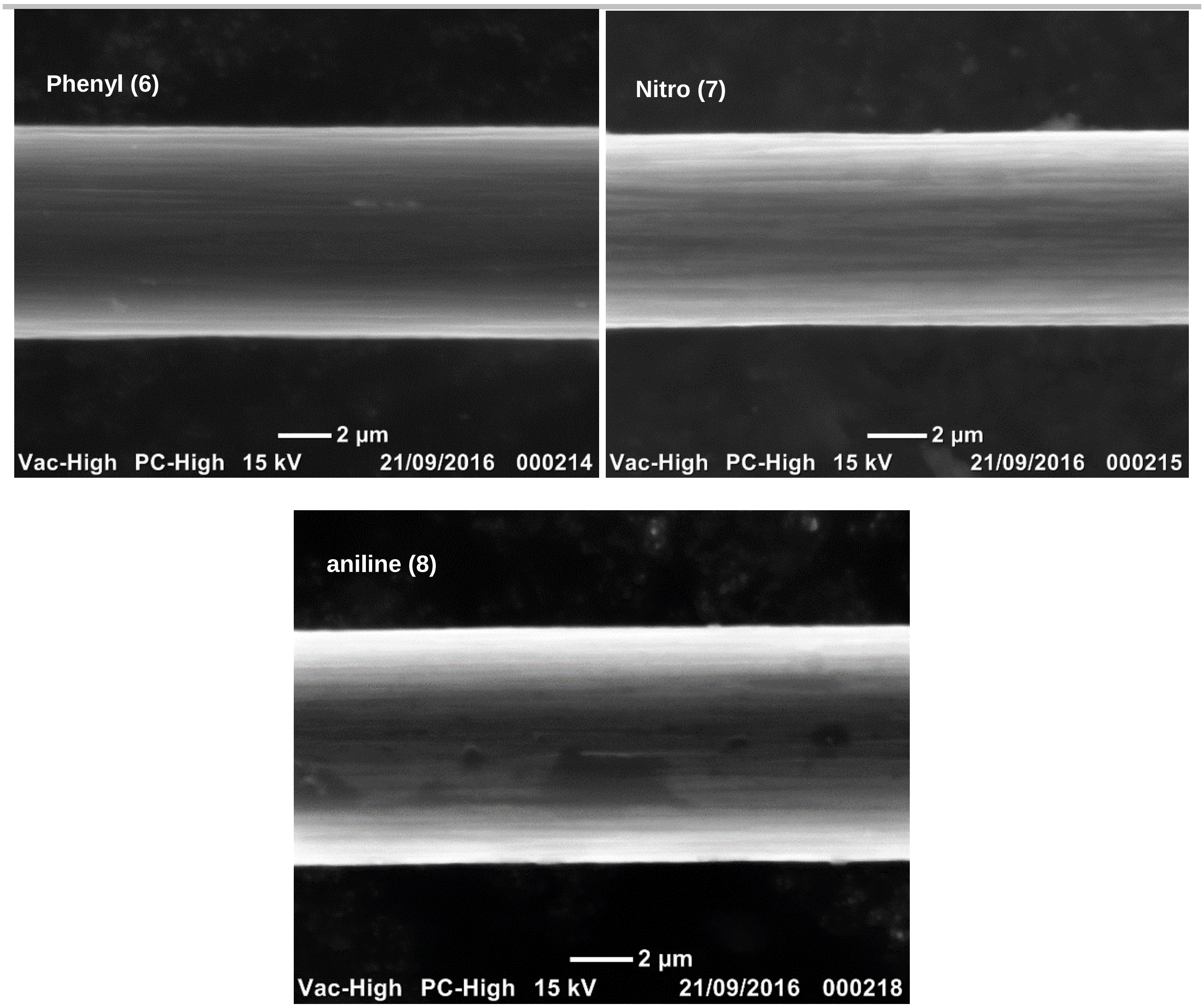
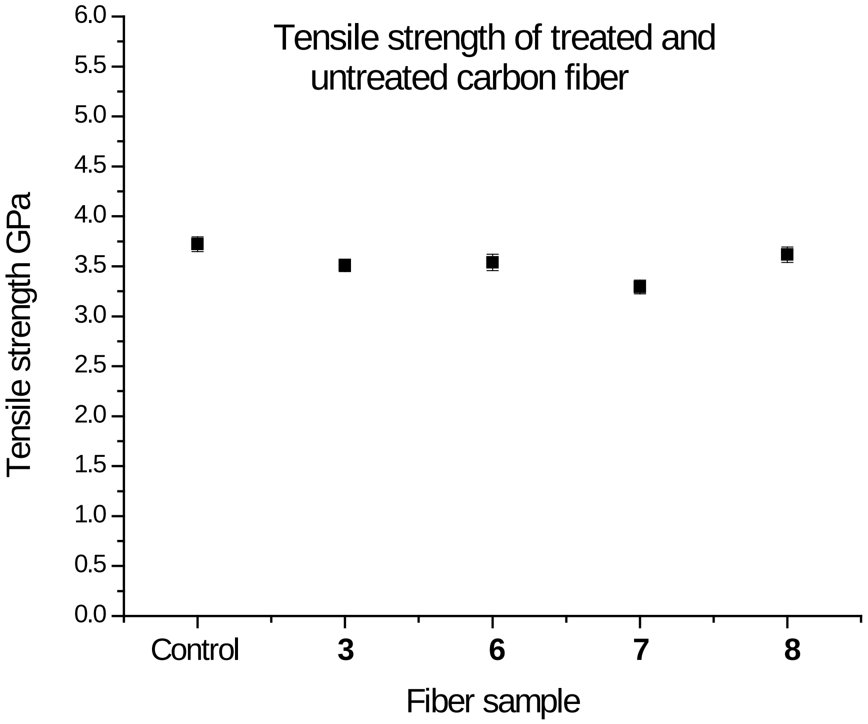


Figure 11. Electron micrographs of control and treated fibers 3, 6, 7 and 8.



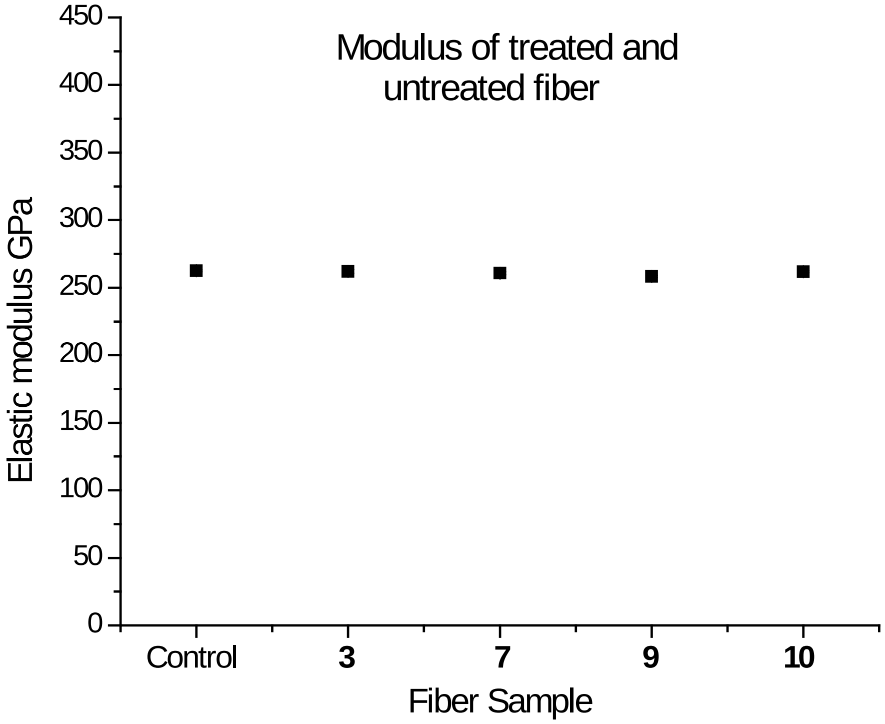
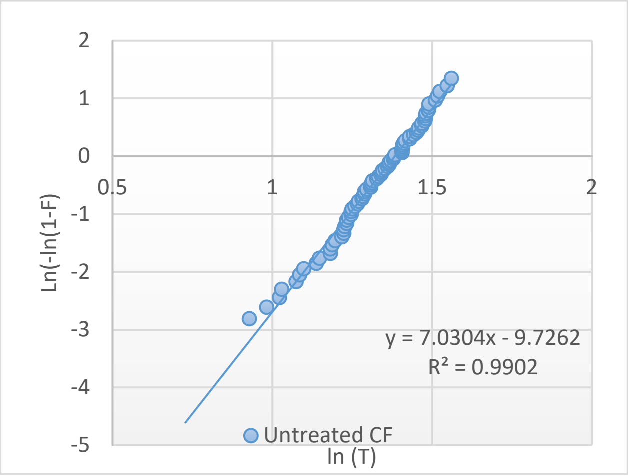
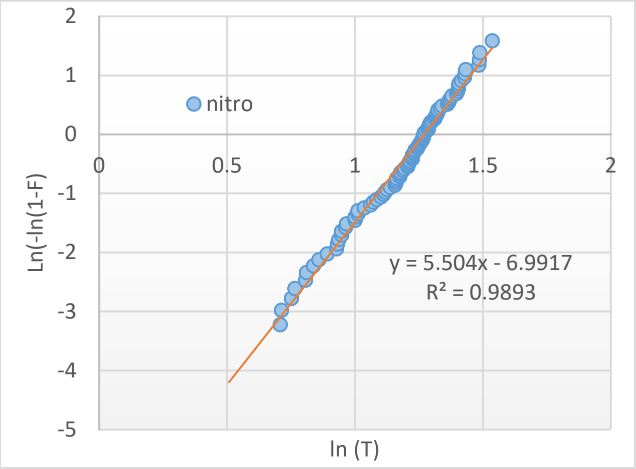
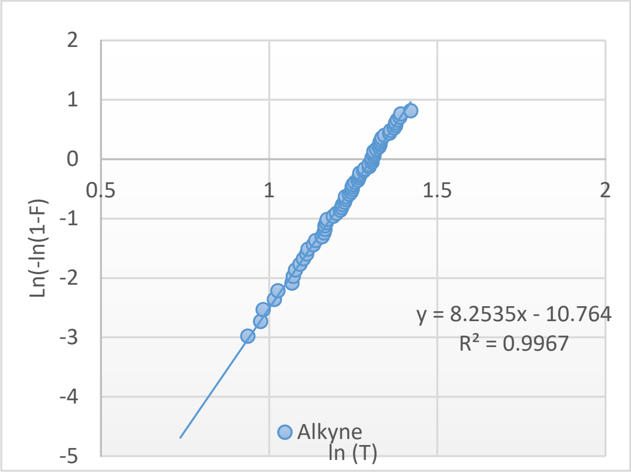
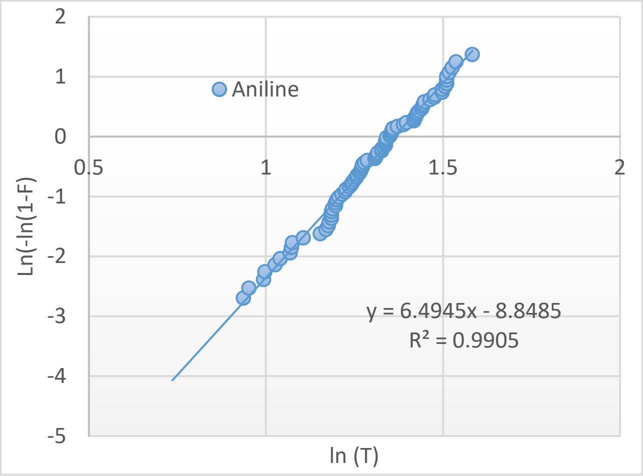


Figure 12. Tensile strength and modulus measured using a Favimat tensile tester (75 filaments per sample). Standard error presented (may be too small to see).









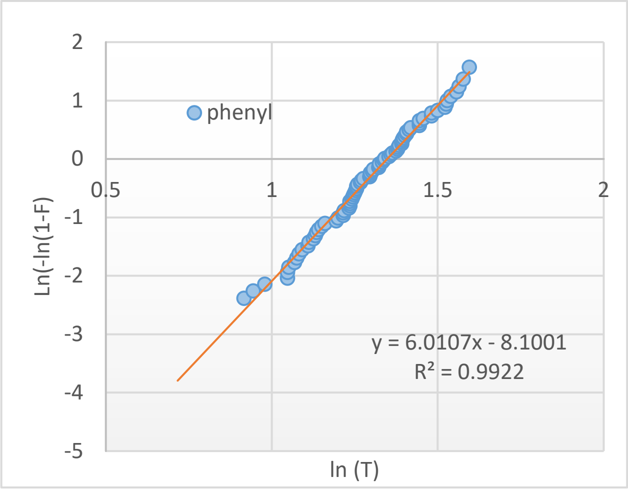


Table 4. Final data from single fiber fragmentation and Weibull analysis.

Sample	Av. fragment	σ0	m	IFSS (MPa)
control	883 ± 38	3.99	7.03	18 ± 1
3	491 ± 33	3.69	8.25	30 ± 3
6	484 ± 50	3.85	6.01	39 ± 5
7	380 ± 8	3.56	5.5	48 ± 2
8	490 ± 13	3.9	6.42	36 ± 1

5. Synthesis and analysis of new amine terminated samples

With the unexpected decrease in interfacial enhancement post reduction (from sample **7** to **8**), two new amines were proposed (a pre-synthesized azido aniline, and alkyl aniline). The fibers were then analyzed and evaluated for their interface performance.

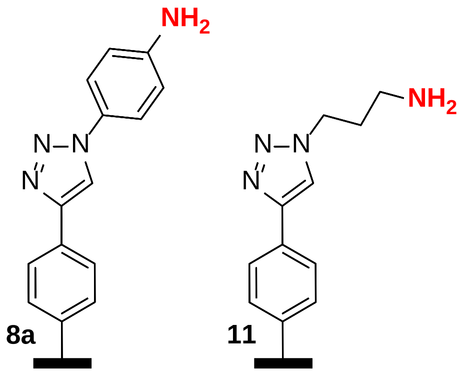
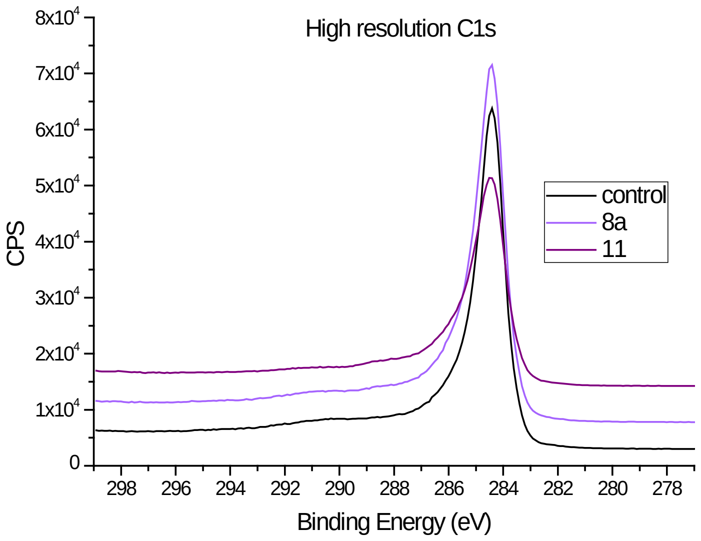


Figure 13. Chemical structures of proposed products after re-design of amine precursors.

Table 5. Atomic ratios at the fiber surface as determined by XPS.

Element	**Control**		**8a**		**11**	
	Mean	*Dev.*	Mean	*Dev.*	Mean	*Dev.*
C	1.000	*0.000*	1.000	*0.000*	1.000	*0.000*
N	0.016	*0.000*	0.046	*0.002*	0.075	*0.005*
O	0.040	*0.000*	0.068	*0.002*	0.149	*0.010*
Cl			0.002	*0.000*	0.002	*0.000*
F						
Si	0.006	*0.000*	0.004	*0.000*	0.005	*0.001*
Na			0.002	*0.000*		
Cu			0.003	*0.000*	0.003	*0.000*



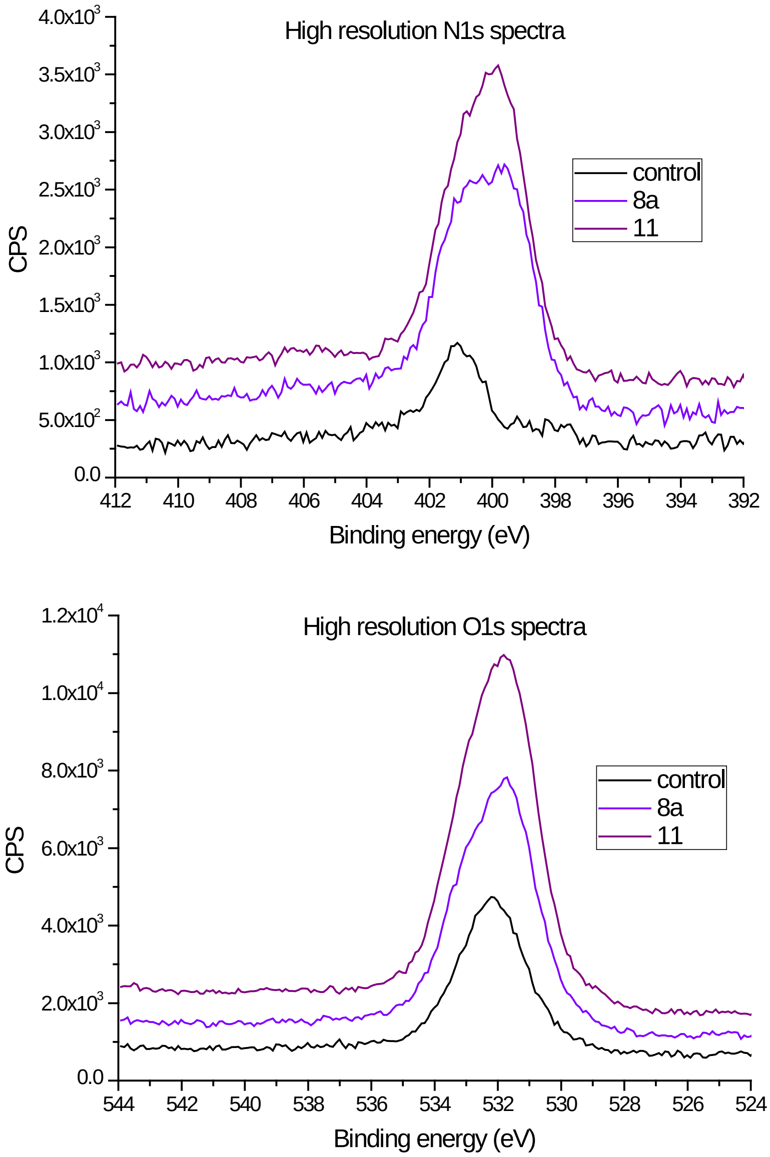


Figure 14. High resolution C1s, N1s and O1s spectra.

Table 6. Single fiber tensile properties.

Parameter	**Control**	**Aniline 8a**	**Amine 11**
Tensile strength (GPa)	3.72 ±0.07	3.78 ±0.10	3.65 ±0.08
Tensile modulus (GPa)	262.55 ±0.70	275.91 ±1.01	270.11 ±0.82

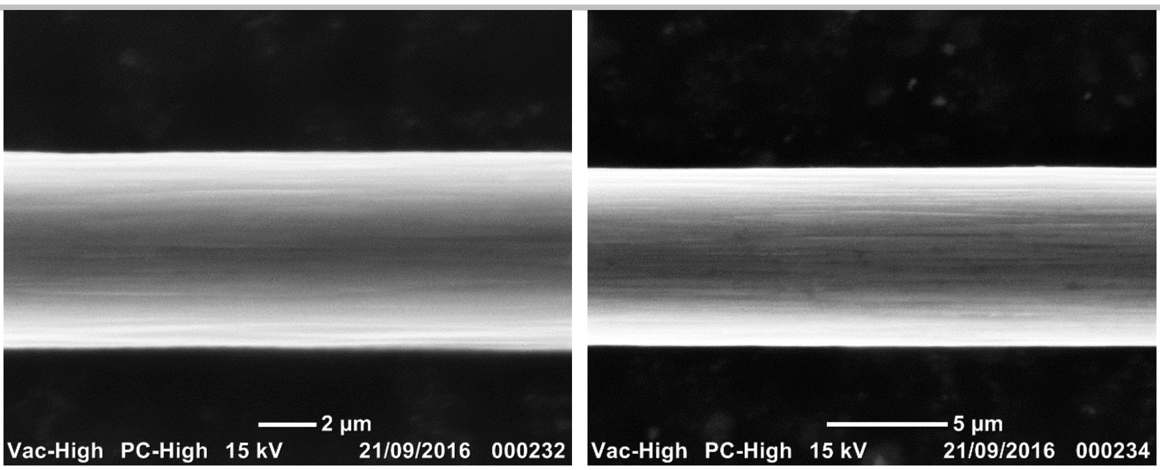


Figure 15. Electron micrographs of fibers after treatment (left) **8a**, and **11**.

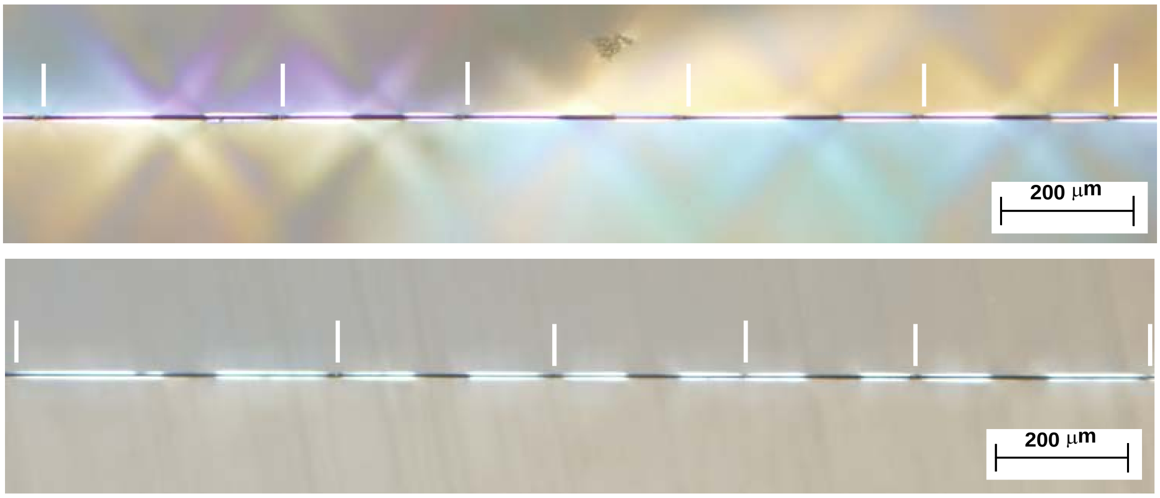
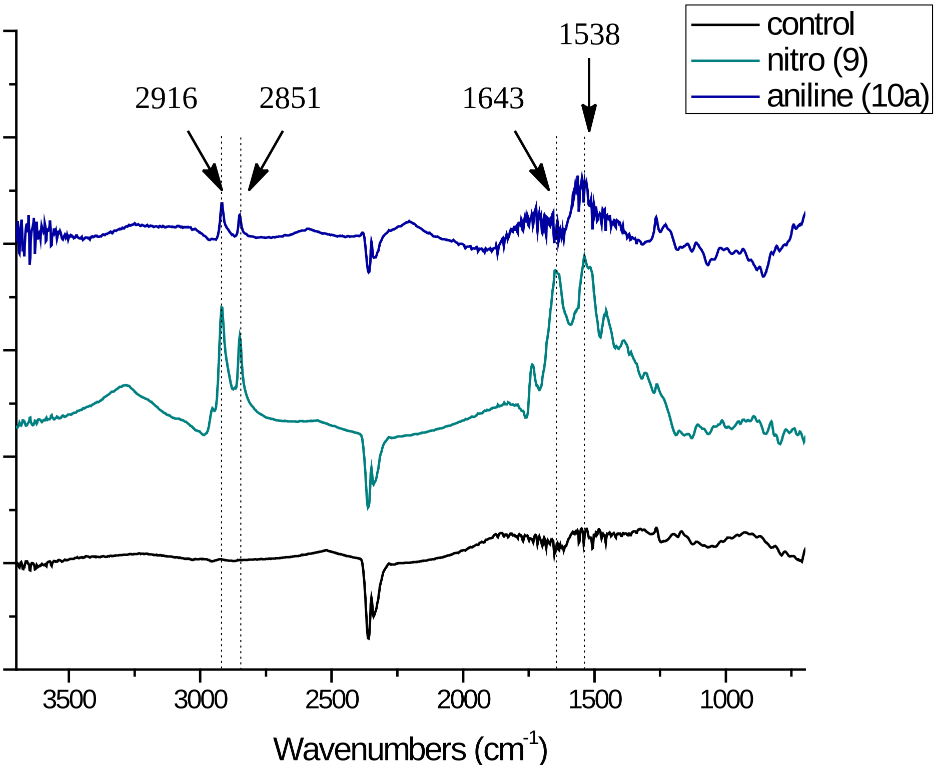


Figure 16. Representative optical microscope images of SFFT samples **8a** (top) and **11** fiber fragments denoted using vertical white lines. Average fragment size calculated for samples are: (**8a)** 397 µm, (**11**) 380 µm.

IR Spectra

Fibres were analysed using ATR-IR, using 256 scans of a fibre bundle bound to a glass slide using adhesive tape. A Bruker Lumos spectrometer, fitted with a germanium crystal was used.



The peaks at 2916 and 2851 cm^{-1} have been attributed to the 1,2,3-triazole present on the surface, while the peaks at 1643 an 1538 cm^{-1} have been attributed to the nitrophenyl group. These two spectra are clearly different and consistent with the XPS analysis presented on page 8 of the manuscript.

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Author Contributions

Linden Servinis (data acquisition, manuscript preparation, equal lead contributor); Kathleen M. Beggs (data acquisition, supporting contributor); Thomas R. Gengenbach (XPS acquisition and data interpretation, supporting contributor); Egan H. Doeven (electrochemistry, supporting contributor); Paul S. Francis (electrochemistry, manuscript preparation, supporting contributor); Bronwyn L. Fox (project administration, supporting contributor); Jennifer M. Pringle (electrochemistry, manuscript preparation, supporting contributor); Cristina Pozo-Gonzalo (electrochemistry, manuscript preparation, supporting contributor); Tiffany R. Walsh (project administration, manuscript preparation, supporting contributor); Luke C. Henderson (funding acquisition, project coordinator, writing of original draft and final draft, data analysis, equal lead contributor).