Supporting Information for

Spin-coated Carbon

James P. Blinco, Benjamin A. Chalmers, Alison Chou, Kathryn E. Fairfull-Smith and

*Steven E. Bottle**

ARC Centre of Excellence for Free Radical Chemistry and Biotechnology, Faculty of Science and Technology, Queensland University of Technology, GPO Box 2434, Brisbane, QLD, 4001, Australia

s.bottle@qut.edu.au

General

Air-sensitive reactions were carried out under an atmosphere of ultra-high purity argon. 5-amino-1,1,3,3-tetramethyl-2,3-dihydroisoindol-2-yloxyl was prepared using established literature procedures. All other reagents were purchased from commercial suppliers and used without further purification.

ESI-high resolution mass spectra were obtained using an Agilent QTOF LC high resolution mass spectrometer which utilized electrospray ionisation (recorded in the positive mode). An Agilent 1100 Series diode array was connected in-line with the mass selective detector (using an m/z range of 28-1000). LC flow (100% methanol at 1 mL min^{-1}) was introduced into the ESI interface after detection by the photo-diode-array. Fourier transform infrared (FTIR) spectra were recorded on a Fourier Transform Infrared Spectrometer equipped with a DTGS TEC detector and an ATR objective. The electrochemical experiments were conducted in a sealed, three-electrode glass cell, controlled by a Princeton Applied Instruments 273A Potentiostat galvanostat. A platinum wire and solid Ag/Ag+ electrode were used as a counter and reference electrode, respectively. Redox potentials were measured in acetonitrile, using 0.1M tetrabutylammonium tetrafluoroborate (TBAF) as the supporting electrolyte. The TBAF was recrystallized and dried under vacuum prior to use. Single spot Raman spectra were recorded at room temperature using a Renishaw inVia Raman microprobe spectrometer with a laser source emitting at 785 nm or 633nm, and a 50× objective (Leica) lens. Each spectrum was collected as a single scan with 10s exposure time. Raman images were recorded using a WITec alpha300 R (WITech, Ulm, Germany) with at 532nm laser. Melting points were measured on a Variable Temperature Apparatus by the capillary method and are uncorrected. Thermogravimetric analysis (TGA) was performed at a heating rate in Ar on a METTLER TOLEDO STAR.thermogravimetric analyser. XPS measurements were performed on a K-Alpha spectrometer (ThermoFisher Scientific, East Grinstead, U.K.) using a microfocused, monochromated Al Kα X-ray source (200 μm spot size). Up to 30 separated spots were measured to limit damage to the samples from the X-ray irradiation, and each measurement was run for the minimum acquisition time. All spectra were finally collapsed to one single spectrum when a sufficient signal/noise ratio was attained. The kinetic energy of the electrons was measured by a 180° hemispherical energy analyzer operated in the constant analyzer energy mode (CAE) at 50 eV pass energy for elemental spectra. The photoelectrons were detected at an emission angle of 0° with respect to the normal of the sample surface. The K-Alpha charge compensation system was employed during analysis, using electrons of 8 eV energy and low-energy argon ions to prevent any localized charge build-up. Data acquisition and processing were undertaken using the CASAXPS software. The analyzer transmission function, Scofield sensitivity factors,[1] and effective attenuation lengths (EALs) for photoelectrons were applied for quantification. EALs were calculated using the standard TPP-2M formalism.[2] All spectra were referenced to the C1s peak of hydrocarbon at 284.6 eV binding energy controlled by means of the well-known photoelectron peaks of metallic Cu, Ag, and Au, respectively. EPR spectroscopy was carried out on a Magnettech, MiniScope EPR spectrometer. Samples were suspended in DI ethanol and the spectra were recorded at 5°C.

Synthesis of Aryl Diazonium Ion Nitroxide 2 (ADIN)

A portion of nitrosonium tetrafluoroborate (1.2 mol equiv) was weighed out in round bottomed flask inside a glovebag and the flask was then sealed. After removal from the glovebag, acetonitrile was added to the flask (3 mL/mmol of nitroxide) using a syringe, and the solution was cooled to -30 °C (dry ice/acetonitrile). A solution of the 5-amino-1,1,3,3-tetramethyl-2,3-dihydroisoindol-2-yloxyl derivative (1 mol equiv) in acetonitrile (ca. 1 mL/mmol) was added dropwise using a syringe to the stirring nitrosonium tetrafluoroborate solution. After complete addition, stirring was continued for 30 min, at which time the cold bath was removed. After stirring for a total of 1 h, the reaction mixture was diluted with a 2x volume of diethyl ether and stirred. This resulted in the precipitation of a tan solid. The precipitate was collected by filtration and washed thoroughly with ether. Yield 85%, m.p. 137 °C (dec).

A number of complimentary techniques were used to confirm the formation of ADIN **2**. TLC confirmed complete consumption of the starting nitroxide, and the appearance of an extremely polar compound that could not be moved from the baseline of the plate. Melting point of the isolated powder showed a sharp decomposition temperature with evolution of a gaseous byproduct which is common for diazonium salts as they readily undergo Schiemann thermal reactions to give alkyl halides with the evolution of nitrogen.[3] FTIR (Figure S1) shows evidence for the formation of the diazonium ion with the characteristic infra-red band visible at 2300 cm^{-1} attributed to the N-N stretching.[4]

Electrospray Mass Spectrometry was also used to further confirm the structure of ADIN **2**. While the molecular ion was not observed (as expected with highly reactive species such as diazonium ions), all the major spectral peaks could be assigned to fragments from this parent structure. The fragments at m/z 190 and 213 arise from loss of molecular nitrogen to give the aryl cation species and its sodium salt adduct respectively. The peaks at m/z 221 and 243 are formed through reaction of the aryl cation with the flow solvent (methanol) to give a methoxy-ether product and its sodium salt adduct.[5]

General Procedure for Grafting of ADIN to Carbon Surfaces Using Electrochemical-Reduction

The apparatus used for the electrochemical derivatization experiments was a three-electrode cell, with Ag/$AgNO_3$ reference electrode and platinum wire counter electrode. The working electrode was comprised of either glassy carbon set into a PET housing, or unidirectional carbon fibre tape that had one end coated with conductive paste. The electrode was held with an alligator clip that had previously been coated with conductive paste and the electrode was immersed in an acetonitrile solution that contained 1,1,3,3-tetramethyl-2,3-dihydroisoindol-2-yloxyl-5-diazonium tetrafluoroborate (0.05M) and tetra-n-butylammonium tetrafluoroborate (TBAF, 0.05 M). A potential of -1.0 V was applied for a period of 30 min. Care was taken to exclude light, and argon was bubbled through the solution during the experiments to limit oxygen side reactions. After completion of the reaction, the electrode was soaked in acetonitrile for 4 h and then washed with further acetonitrile then chloroform and finally ethanol.

General Procedure for Grafting of ADIN to Carbon Surfaces Using Spontaneous Single Electron Transfer

HiPco single wall carbon nanotubes (0.048mg, NanoIntegris) were stirred in an aqueous sodium dodecyl sulphate solution (35μM, 200ml) for 1h at room temperature. After this time ADIN **2** (5 mg) was introduced into the mixture and the stirring was continued for a further 3h. The reaction mixture was then filtered through a PTFE (0.2μm) membrane and washed with acetone and water to remove the SDS surfactant. The ADIN **2** grafted SWNTs were dried in a vaccum dessicator overnight. A similar procedure was followed for grafting ADIN **2** onto graphene. CVD graphene on SiO_2 (ACS Material) was immersed in an aqueous solution of SDS (35μM, 200 ml) and ADIN **2** (5mg/250ml). The reaction solution was kept at 45°C with stirring for 8h following a published procedure.[6] The modified graphene was removed from the reaction solution at the end of 8h, rinsed with acetone and water and dried in a stream of dry nitrogen.

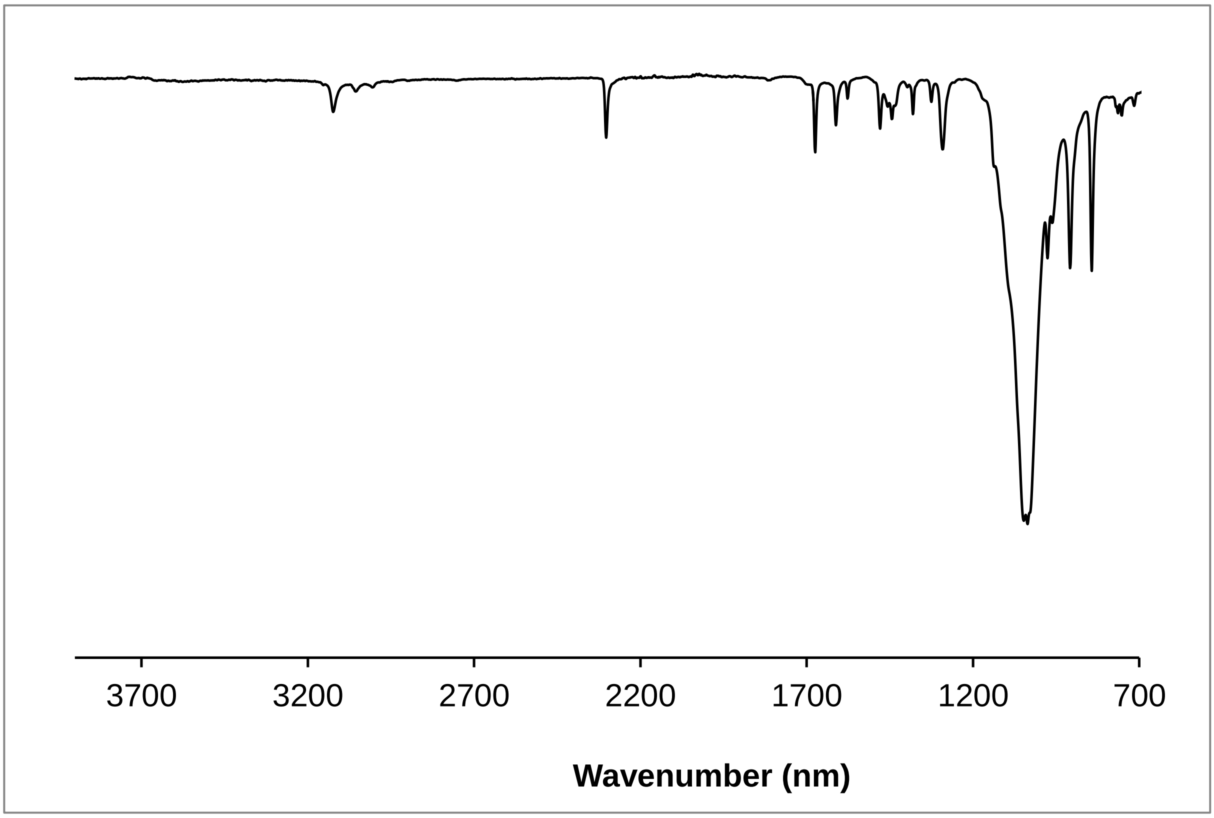

Figure S1. FTIR spectrum of ADIN **2**

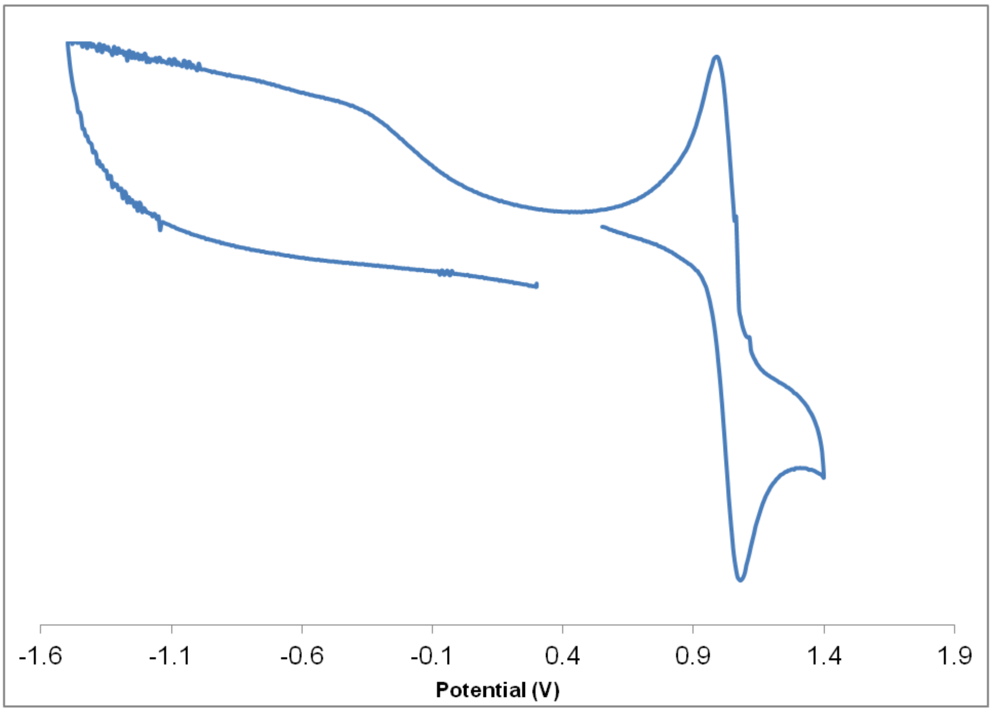

Figure S2. Cyclic Voltammogram of ADIN **2**

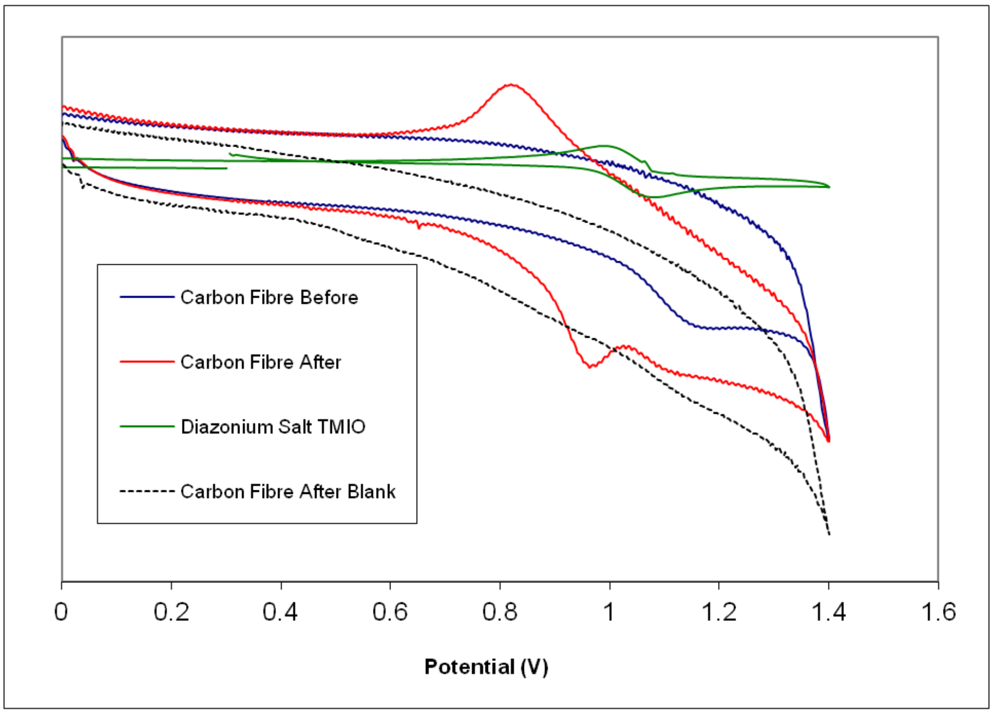

Figure S3. Cyclic Voltammogram of ADIN **2** (green), pristine carbon fibre tape (blue), carbon fibre tape that has been electrochemically treated with ADIN **2** (red) and carbon fibre tape treated under identical electrochemical conditions, but in the presence of a nitroxide without a diazonium moiety (black).

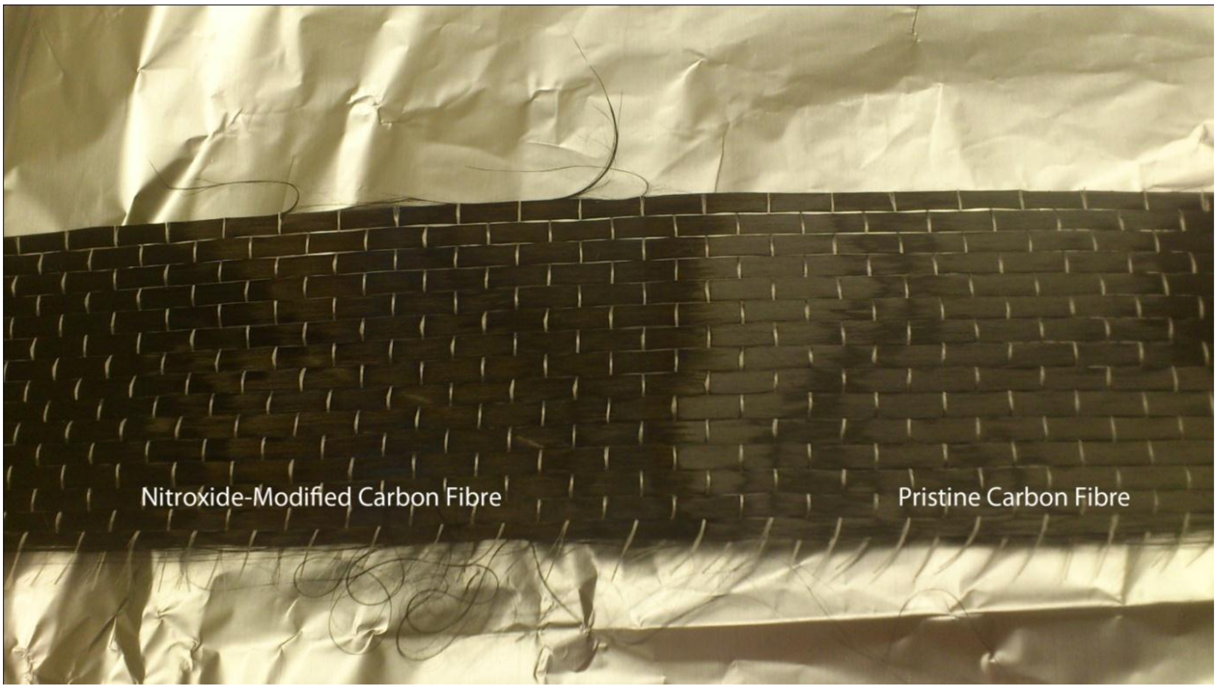

Figure S4. Photograph of carbon fibre tape after electrochemical treatment. Regions are clearly defined as to where exposure to ADIN **2** has taken place decreasing the surface gloss.

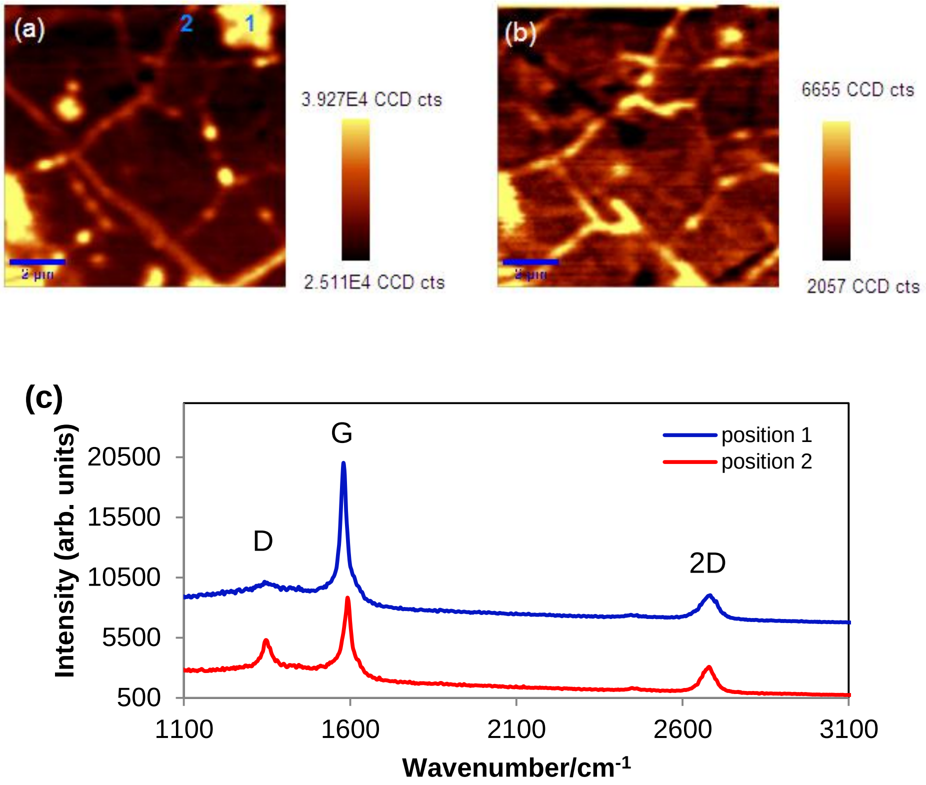

Figure S5. Micro Raman mapping of ADIN **2** modified CVD graphene showing the distribution of G, sp^2 sites (a) and D, sp^3 sites (b) as indicated by the contrast; brighter yellow areas denote larger intensity, therefore higher concentration of the signal from G or D. The similarity between these two maps reveals that graphene has disorder-related D band intensity expected to arise from the attachment of ADIN **2** to the surface during the grafting process. (c) Raman spectra taken from the position marked in (a) and (b).

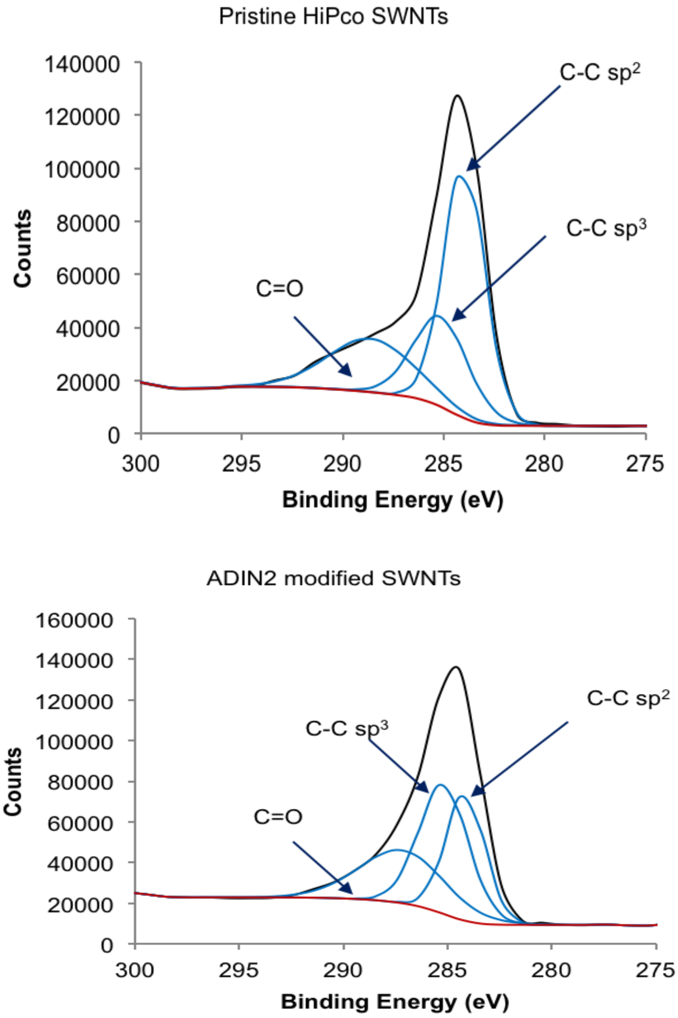

Figure S6 Scan of the C1s region of Pristine SWCNT and ADIN modified SWCNT.

Component percentage

	Pristine	ADIN **2** modified
Graphitic (284eV, sp^2)	52	31
Defects (285eV, sp^3)	25	40

After reaction with ADIN **2**, there is an increase in the FWHM of the C1s peak. The observed FWHM for the ADIN **2** sample is 3.3 and 3 for the pristine SWNTs. The 1eV binding energy shift is in accordance with the chemical shift between sp^2 and sp^3 hybridized carbon species in carbon nanotube materials. [7]

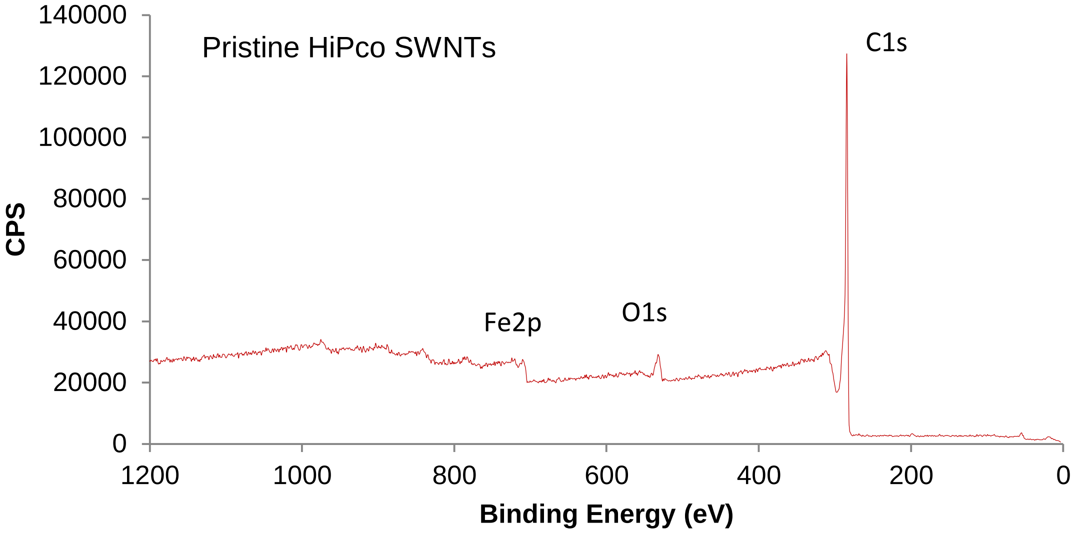

Figure S7. XPS Survey Scan of Pristine SWCNT.

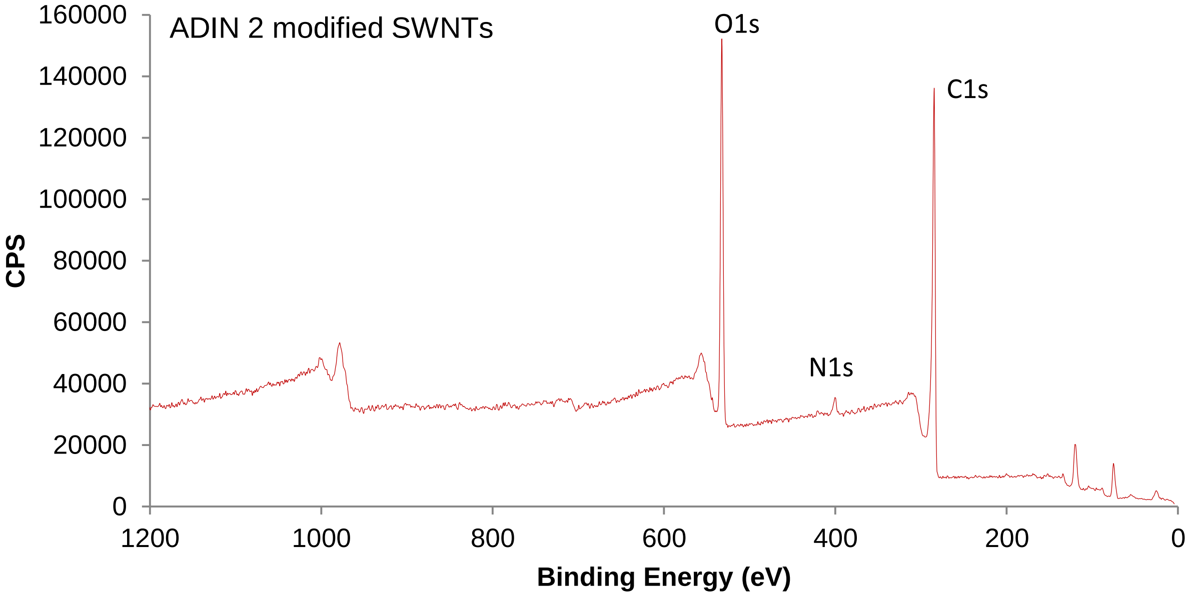

Figure S8. XPS Survey Scan of SWCNT modified with ADIN **2**.

References

---

[1] Scofield, J. H. *J. Electron Spectrosc. Relat. Phenom.* **1976**, *8*, 129-137.

[2] Tanuma, S.; Powell, C. J.; Penn, D. R. *Surf. Interface Anal.* **1994**, *21*, 165-176.

[3] Swain, C. and Rodgers, R. *J. Am. Chem. Soc.* **1975**, *97*, 799–800.

[4] Nuttal, R.H., Roberts E. R. and Sharp D. W. A. *Spectrochemica Acta*,**1961**, *17*, 947–952 .

[5] Broxton, T. J., Colton, R. and Traeger, J. C. *J. Mass Spectrom*. **1995**, *30*, 319–323.

[6] Jin, Z.; McNicholas, T.P.; Shih, Wang, Q.H.; Paulus, G.L.C; Hilmer, A.J.; Shimizu, S. and Strano, M.S. *Chem. Mater.* **2011**, *23*, 3362-3370.

[7] Okpalugo, T.I.T.; Papakonstantinou, P.; Murphy, H.; McLaughlin, J. and Brown, N.M.D.; *Carbon* **2005**, *43*, 153.