

# Wiring-up Catalytically Active Metals in Solution with Sulfonated Carbon Nanotubes

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**Materials:** SWCNTs were received from SouthWest NanoTechnologies (CG-100, >90% carbon content, lot # CG100-000-0012) and used without further purification. MWCNTs were obtained from Aldrich (>95% purity, for small-scale reactions) and Bayer Group (Baytubes<sup>®</sup>C 150 P, >95% purity, for large-scale reactions) and used as received. All solvents were of spectroscopic grade unless otherwise noted. Sodium 3-azidopropane-1-sulfonate<sup>1</sup> and dipropargyl acetylenedicarboxylate<sup>2</sup> were synthesized following reported procedures. All other chemicals were of reagent grade and used as received.

**General Methods and Instrumentation:** Fourier transform infrared (FT-IR) spectroscopy was performed on a Perkin-Elmer model 2000 FT-IR spectrophotometer using the Spectrum v. 2.00 software package. Raman spectra were measured on a Horiba LabRAM HR Raman Spectrometer using the excitation wavelength of 785 nm for SWCNTs and 532 nm for MWCNTs. The spectra in the UV-Vis range were obtained using an Agilent 8453 UV-visible spectrophotometer. TGA analyses were performed with a TGA Q50 apparatus (TA instruments). The thickness of thin films was measured using a Dektak 6M stylus profiler by Veeco and their conductivities were measured utilizing a Signatone four point probe with a 1.27 mm spacing connected to a Keithley 2400 source meter. Experiments were carried out under nitrogen. Samples were heated at 15 °C/min from 50 °C to 900 °C. XPS spectra were recorded on a Kratos AXIS Ultra X-ray Photoelectron Spectrometer. Gas chromatography (GC) was performed on an Agilent Technologies 7890A GC system. Optical

micrographs were recorded using a Leica DMRXP optical microscope with an attached Sony DXC-970MD camera. All synthetic manipulations were carried out under an argon atmosphere using standard Schlenk techniques unless otherwise noted.

**Synthesis of propargyl SWCNTs 1a.** A suspension of SWCNTs (240 mg, 20 mmol of carbon) in 1,4-dioxane (240 mL) was sonicated for 3 h. The mixture was heated to 60 °C and a solution of dipropargyl acetylenedicarboxylate (11.2 g, 59 mmol) in 1,4-dioxane (30 mL) and a solution of 4-dimethylaminopyridine (8.4 g, 69 mmol) in CHCl<sub>3</sub> (30 mL) were added simultaneously via syringe pump over 36 h. Subsequently, propargyl alcohol (9 mL, 8.7 g, 156 mmol) was added and the mixture was stirred at 60 °C for another 3 h. The reaction mixture was then cooled to room temperature and centrifuged at 3500 rpm for 20 min. The supernatant was discarded and the residue was extracted in a Soxhlet apparatus with *N,N*-dimethylformamide (DMF) at reduced pressure for 3 days. Afterwards, the obtained black solid was washed by dispersing, centrifuging and decanting using acetone, water, ethanol and hexanes as solvents upon which it was dried at high vacuum overnight. See figures S1-S4 for TGA, XPS, FT-IR and Raman characterization data.

**Synthesis of propargyl MWCNTs 1b.** A suspension of MWCNTs (1.2 g, 100 mmol of carbon) in 1,4-dioxane (1.2 L) was sonicated for 3 h using an ultrasonic probe. The mixture was heated to 60 °C and a solution of dipropargyl acetylenedicarboxylate (57 g, 300 mmol) in 1,4-dioxane (75 mL) and a solution of 4-dimethylaminopyridine (42.7 g, 350 mmol) in CHCl<sub>3</sub> (150 mL) were added simultaneously via syringe pump over 36 h. Subsequently, propargyl alcohol (45 mL, 43.7 g, 780 mmol) was added and the mixture was stirred at 60 °C for 3 more hours. The reaction mixture was then cooled to room temperature and centrifuged at 3500 rpm for 20 min. The supernatant was discarded and the residue was washed in a Soxhlet apparatus with DMF at reduced pressure for 2 days. Afterwards, the obtained black solid was washed by dispersing, centrifuging and decanting using DMF, *N*-methyl-2-pyrrolidone (NMP), dichloromethane (DCM) and hexane as solvents upon which it was dried at high vacuum overnight. See figures S5-S8 for TGA, XPS, FT-IR and Raman characterization data.

**Synthesis of sulfonate SWCNTs 3a.** A suspension of propargyl SWCNTs (**1a**, 150 mg) in water/*tert*-butanol (1:1, 15 mL) was sonicated for 15 minutes. Sodium 3-azidopropane-1-sulfonate (**2**, 735 mg, 3.9 mmol), sodium ascorbate (78 mg, 0.39 mmol) and copper(II) sulfate pentahydrate (10 mg, 0.04 mmol) were added and the mixture was sonicated for 50 more minutes. After stirring at room temperature for 4 days, the reaction mixture was centrifuged and the supernatant was discarded. The black residue was transferred into an ultrafiltration cell equipped with a polycarbonate membrane (Millipore, Isopore membrane, 50 nm pore size) and washed with water until the filtrate was clear. The resulting black solid was washed by dispersing, centrifuging and decanting using ethanol and hexane as solvents before it was dried at high vacuum overnight. See figures S9-S12 for TGA, XPS, FT-IR and Raman characterization data.

**Synthesis of sulfonate MWCNTs 3b.** Propargyl MWCNTs (**1b**, 1 g) were suspended in a 1:1 mixture of water and *tert*-butanol (100 mL) by sonication for 10 min. Subsequently, sodium 3-azidopropane-1-sulfonate (**2**, 4.9 g, 26 mmol), sodium ascorbate (520 mg, 2.6 mmol) and copper(II) sulfate pentahydrate (65 mg, 0.26 mmol) were added and the mixture was sonicated for 50 more minutes. The mixture was stirred at room temperature for 12 days and sonicated for 2 h every 2 days during this period. Afterward, the reaction mixture was centrifuged, the supernatant was discarded and the residue was transferred into an ultrafiltration cell equipped with a polycarbonate membrane (Millipore, Isopore membrane, 50 nm pore size). It was washed with water until the filtrate was clear upon which it was dried at high vacuum overnight. See figures S13-S16 for TGA, XPS, FT-IR and Raman characterization data.

**Determination of the mass extinction coefficient of sulfonate MWCNTs (3b).** Sulfonate MWCNTs (**3b**, 8 mg), were dissolved in MilliQ water (8 mL) by sonication for 5 min. Subsequently, the solution was diluted with MilliQ water to obtain concentrations of 0.1, 0.05, 0.025, 0.01 and 0.005 mg/mL. The UV-vis spectra of these solutions were measured and the mass extinction coefficient was determined using the Beer-Lambert law with the absorbance at 650 nm yielding a mass extinction coefficient of  $1.65 \times 10^3 \text{ mL m}^{-1} \text{ g}^{-1}$ .

**Measurement of sulfonate MWCNT (3b) solubility.** Sulfonate MWCNTs (**3b**, 130 mg) were added to MilliQ water (2 mL) and sonicated for 1 h. Aggregates were allowed to settle for 24 h upon which a sample was taken from the supernatant, diluted 1:1000 with MilliQ water and its UV-vis spectrum was immediately measured. Another sample was taken, diluted and analyzed by UV-vis spectroscopy after allowing aggregates to settle for 24 more hours. Subsequently, the mixture was centrifuged for 10 min at 5000 rpm, another sample from the supernatant was taken and treated similarly. The last sample was taken from the supernatant after centrifugation for 30 more minutes at 5000 rpm. It was diluted and the UV-vis absorption spectrum was recorded. The concentration of **3b** in all samples was determined using the absorption at 650 nm and the experimentally obtained mass extinction coefficient of  $1.65 \times 10^3 \text{ mL m}^{-1} \text{ g}^{-1}$  (see figure 1a).

**General procedure for the Wacker-type oxidation of 1-decene (4) to 2-decanone (5).** Palladium bistrifluoroacetate (1.5 mg,  $4.5 \mu\text{mol}$ ) and copper(II) triflate (53.5 mg, 0.148 mmol) were dissolved in a 7:1 mixture of DMF and water (0.5 mL) containing biphenyl (11.5 mg, 0.0746 mmol) as an internal standard. Sulfonate MWCNTs (**3b**, 20 mg) were added and the mixture was sonicated for 1 min. The reaction tube was purged with oxygen, sealed and an oxygen-filled balloon was attached. 1-Decene (28  $\mu\text{L}$ , 21 mg, 0.15 mmol) was added via syringe. The mixture was stirred at room temperature for 3 h upon which it was filtered through glass wool. Brine (1 mL) was added and the mixture was extracted with diethyl ether (2 x 1 mL). The organic phase was run through a short silica plug and then analyzed by gas chromatography (GC) to determine the yield of 2-decanone vs. the internal standard. GC-yield vs. biphenyl: 29 % (in the presence of 20 mg of **3b**), 16 % (without addition of **3b**).

**Wacker-type oxidation of 1-decene (4) to 2-decanone (5) using PdCl<sub>2</sub> and CuCl as the catalysts.** The reaction was performed analogous to the general procedure using PdCl<sub>2</sub> (0.80 mg,  $4.5 \mu\text{mol}$ ) and CuCl (14.6 mg, 0.147 mmol; oxidized prior to the addition of 1-decene by stirring for 1 h in an oxygen atmosphere) as the catalysts. GC-yield vs. biphenyl: 41 % (in the presence of 20 mg of **3b**), 41 % (without addition of **3b**).

**Wacker-type oxidation of 1-decene (4) to 2-decanone (5) using palladium bistrifluoroacetate and CuCl as the catalysts.** The reaction was performed analogous to the general procedure using palladium bistrifluoroacetate (1.5 mg, 4.5  $\mu$ mol) and CuCl (14.6 mg, 0.147 mmol; oxidized prior to the addition of 1-decene by stirring for 1 h in an oxygen atmosphere) as the catalysts. GC-yield vs. biphenyl: 34 % (in the presence of 20 mg of **3b**), 42 % (without addition of **3b**).

**Wacker-type oxidation of 1-decene (4) to 2-decanone (5) using PdCl<sub>2</sub> and copper(II) triflate as the catalysts.** The reaction was performed analogous to the general procedure using PdCl<sub>2</sub> (0.80 mg, 4.5  $\mu$ mol) and copper(II) triflate (53.5 mg, 0.148 mmol) as the catalysts. GC-yield vs. biphenyl: 5 % (in the presence of 20 mg of **3b**), 10 % (without addition of **3b**).

**Wacker-type oxidation of 1-decene (4) to 2-decanone (5) using palladium bistrifluoroacetate and copper(II) triflate as the catalysts in the presence of pristine SWCNTs.** The reaction was performed analogous to the general procedure using palladium bistrifluoroacetate (1.5 mg, 4.5  $\mu$ mol) and copper(II) triflate (53.5 mg, 0.148 mmol) as the catalysts and pristine SWCNTs (20 mg) as an additive instead of **3b**. GC-yield vs. biphenyl: 21 %.

**Wacker-type oxidation of 1-decene (4) to 2-decanone (5) using palladium bistrifluoroacetate and copper(II) triflate as the catalysts in the presence of pristine MWCNTs.** The reaction was performed analogous to the general procedure using palladium bistrifluoroacetate (1.5 mg, 4.5  $\mu$ mol) and copper(II) triflate (53.5 mg, 0.148 mmol) as the catalysts and pristine MWCNTs (20 mg) as an additive instead of **3b**. GC-yield vs. biphenyl: 21 %.

**Wacker-type oxidation of 1-decene (4) to 2-decanone (5) using palladium bistrifluoroacetate and copper(II) triflate as the catalysts in the presence of sulfonate SWCNTs (3a).** The reaction was performed analogous to the general procedure using palladium bistrifluoroacetate (1.5 mg, 4.5  $\mu$ mol) and copper(II) triflate (53.5 mg, 0.148 mmol) as the catalysts and sulfonate SWCNTs (**3a**, 20 mg) as an additive instead of **3b**. GC-yield vs. biphenyl: 1 %.

**Wacker-type oxidation of 1-decene (4) to 2-decanone (5) using palladium bistrifluoroacetate and copper(II) triflate as the catalysts in the presence of sodium polystyrene sulfonate.** The reaction

was performed analogous to the general procedure using palladium bistrifluoroacetate (1.5 mg, 4.5  $\mu$ mol) and copper(II) triflate (53.5 mg, 0.148 mmol) as the catalysts and sodium polystyrene sulfonate (20 mg) as an additive instead of **3b**. GC-yield vs. biphenyl: 10 %.

**Wacker-type oxidation of 1-decene (4) to 2-decanone (5) using palladium bistrifluoroacetate and copper(II) triflate as the catalysts in the presence of sulfonated polystyrene beads.** The reaction was performed analogous to the general procedure using palladium bistrifluoroacetate (1.5 mg, 4.5  $\mu$ mol) and copper(II) triflate (53.5 mg, 0.148 mmol) as the catalysts and sulfonate polystyrene beads (Amberlyst 15, 20 mg) as an additive instead of **3b**. GC-yield vs. biphenyl: 14 %.

**Determination of the influence of sulfonate MWCNTs on the 2-decanone to biphenyl ratio.** In six sealable test tubes, Palladium bistrifluoroacetate (1.5 mg, 4.5  $\mu$ mol) and copper(II) triflate (53.5 mg, 0.148 mmol) were dissolved in a 7:1 mixture of DMF and water (0.5 mL) containing biphenyl (11.5 mg, 0.0746 mmol) as an internal standard. 2-decanone (15  $\mu$ L, 0.079 mmol) was added via pipette. To three test tubes, sulfonate MWCNTs (20 mg) were added and all test tubes were sonicated for 1 min. The reaction tubes were purged with oxygen, sealed and an oxygen-filled balloon was attached. All mixtures were stirred at room temperature for 4 h, before brine (1 mL) was added. The mixtures were extracted with diethyl ether (2 x 1 mL) and the organic phases were run through a short silica plug. Subsequently the ratio of 2-decanone to biphenyl was determined via GC. Ratio 2-decanone to biphenyl:  $1.14 \pm 0.02$  (without sulfonate MWCNTs),  $1.12 \pm 0.05$  (with sulfonate MWCNTs).

**General procedure for the determination of conductivities of pristine and sulfonate SWCNTs and MWCNTs.** A CNT sample was sonicated in water (sulfonate CNTs) or DMF (pristine CNTs) for 1 min. Subsequently, 20  $\mu$ L of the suspension were drop-cast onto a glass slide and air-dried to create a thin film. Using a four point probe setup, the electric potential was measured at a current of 2  $\mu$ A at three different positions for each film. Subsequently, the thickness of the film was measured using a profilometer and the conductivity was calculated using equation 1

$$\sigma = I / (V \cdot t \cdot CF) \text{ (for } t/s < 0.4) \quad (1)$$

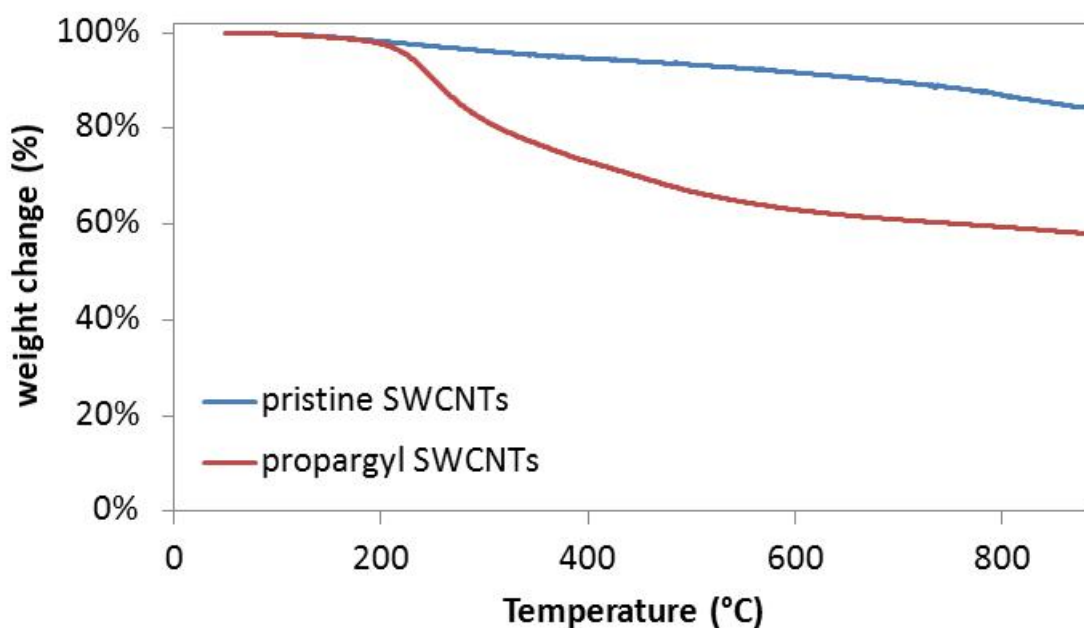
where  $I$  is the current,  $V$  is the voltage,  $t$  is the sample thickness,  $CF$  is the sheet resistance correction factor,<sup>3</sup> and  $s$  is the four point probe spacing.

**Conductivity of pristine SWCNTs** The conductivity of a drop-cast film of pristine SWCNTs was determined to be  $21.8 \text{ S cm}^{-1}$  (average of five films and three measurements each).

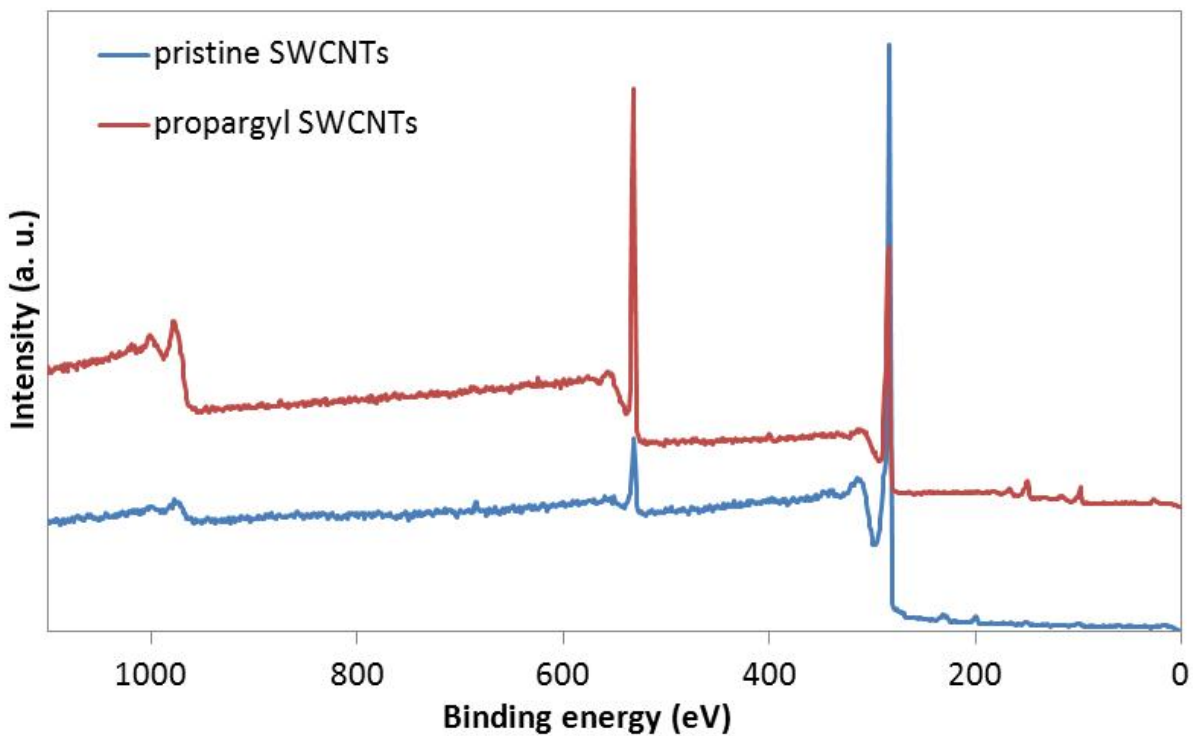
**Conductivity of pristine MWCNTs** The conductivity of a drop-cast film of pristine MWCNTs was determined to be  $3.9 \text{ S cm}^{-1}$  (average of five films and three measurements each).

**Conductivity of sulfSWCNTs (3a)** The conductivity of a drop-cast film of sulfSWCNTs was determined to be  $0.6 \text{ S cm}^{-1}$  (average of five films and three measurements each).

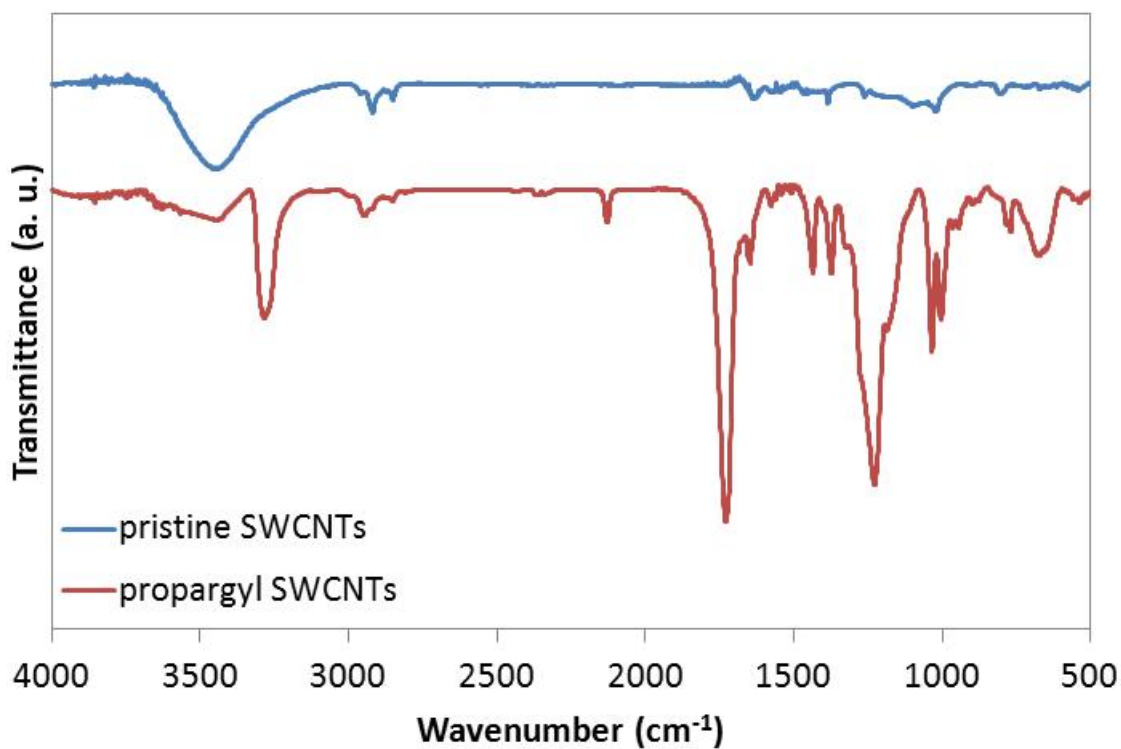
**Conductivity of sulfMWCNTs (3b)** The conductivity of a drop-cast film of pristine SWCNTs was determined to be  $2.8 \text{ S cm}^{-1}$  (average of five films and three measurements each).



**Figure S1.** TGA of propargyl SWCNTs (**1a**) and pristine SWCNTs

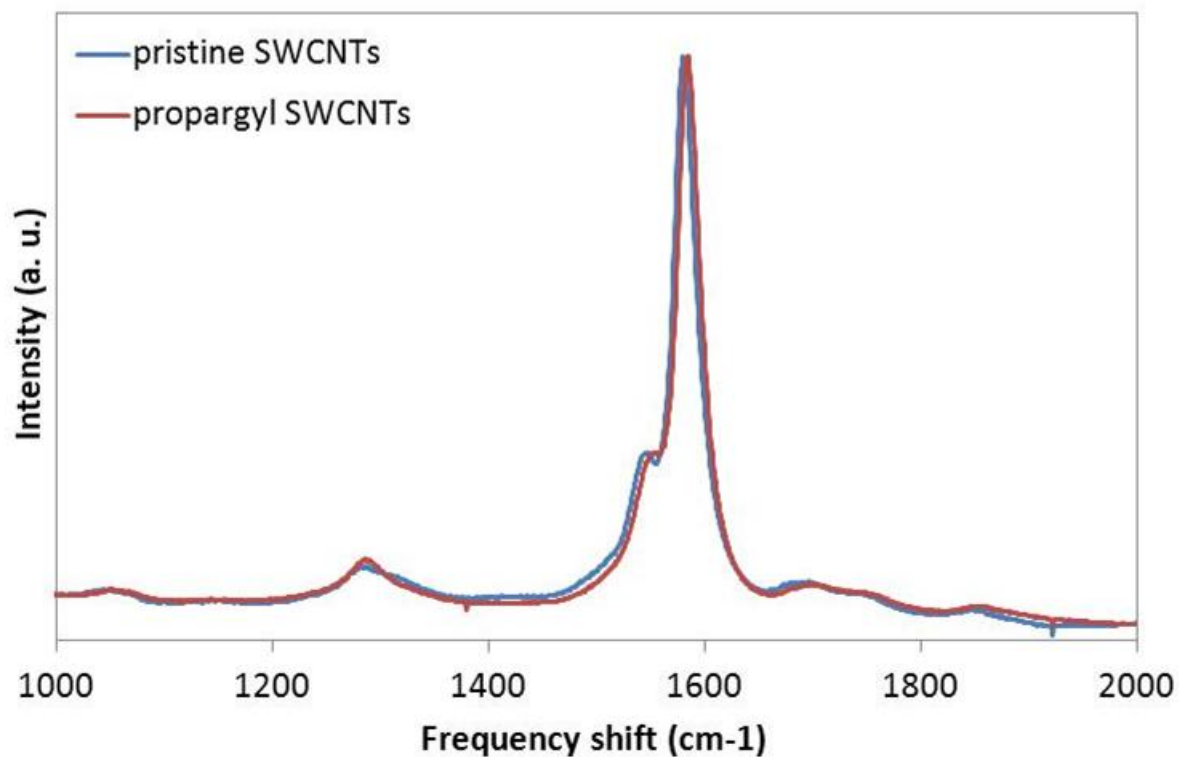


**Figure S2.** XPS spectra of propargyl SWCNTs (**1a**) and pristine SWCNTs

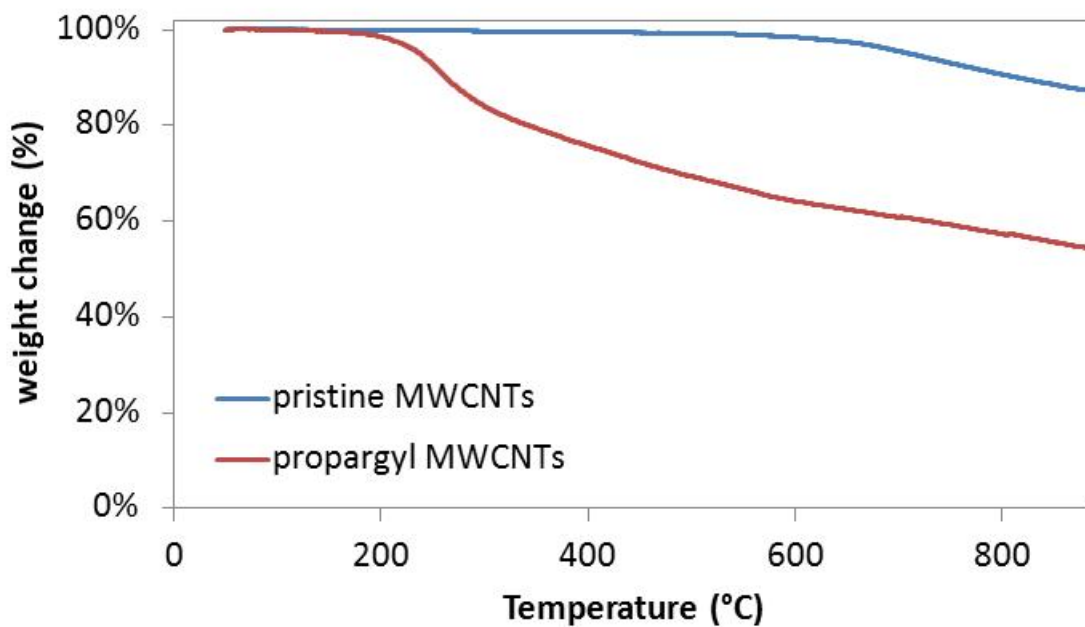


**Figure S3.** FT-IR spectra of propargyl SWCNTs (**1a**) and pristine SWCNTs

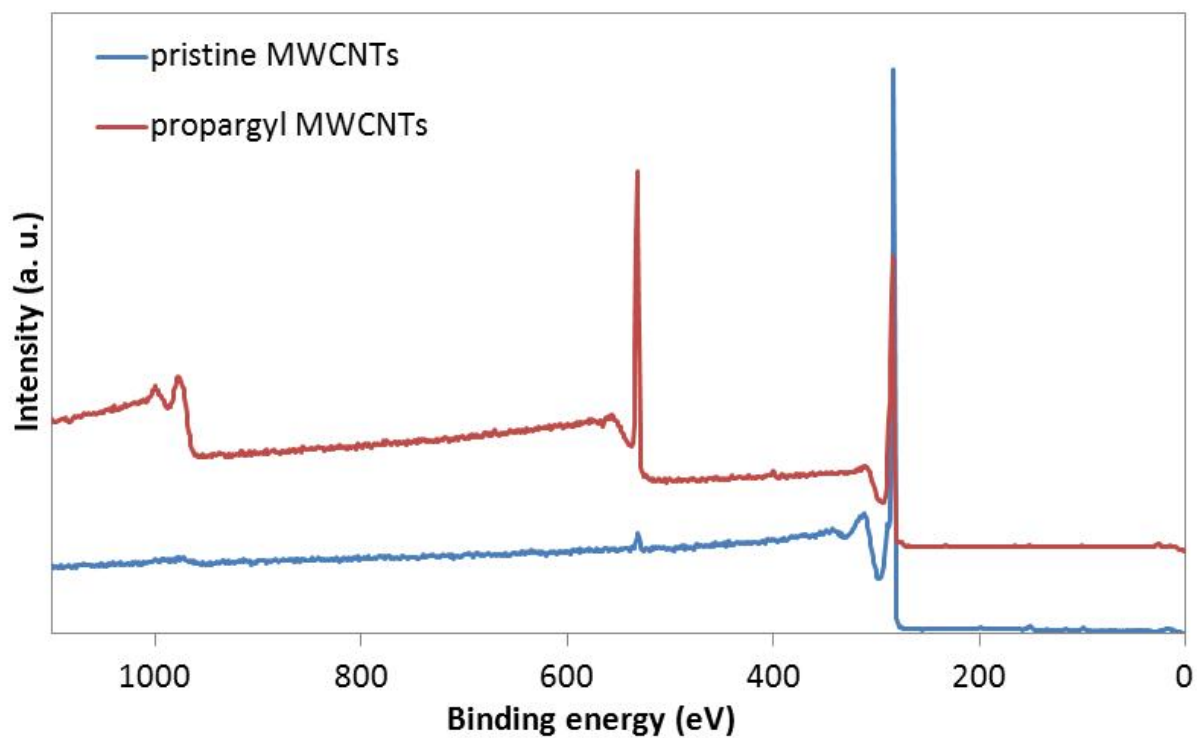




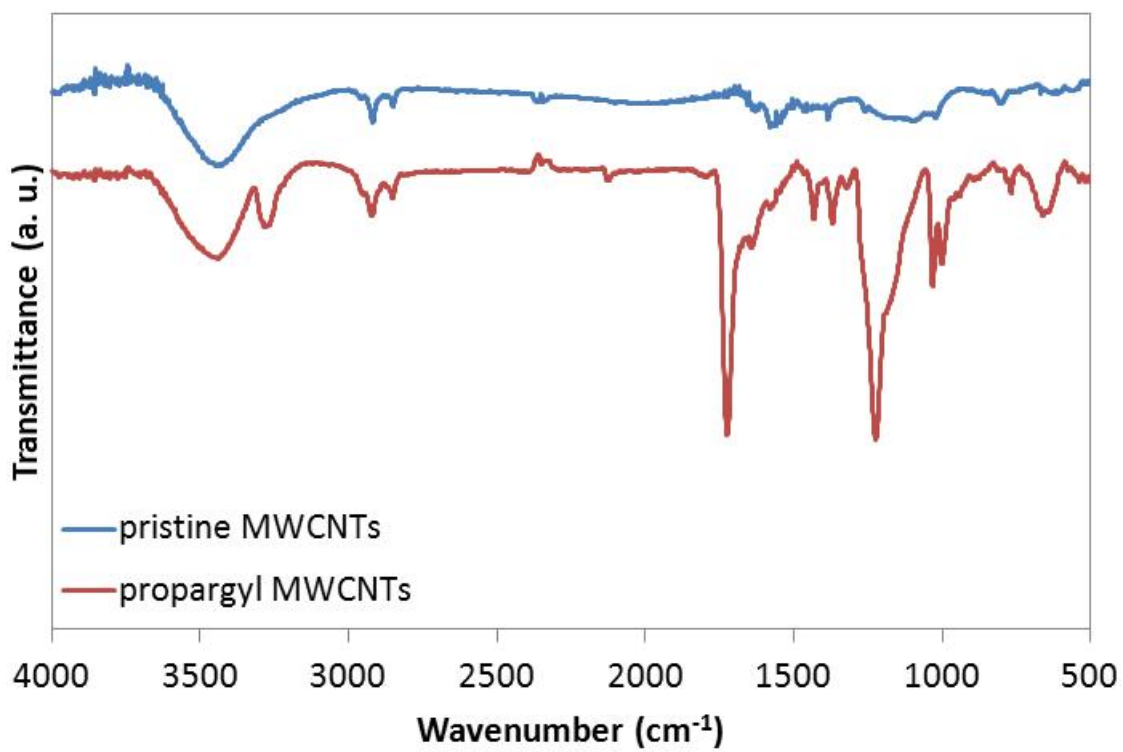
**Figure S4.** Raman spectra of propargyl SWCNTs (**1a**) and pristine SWCNTs



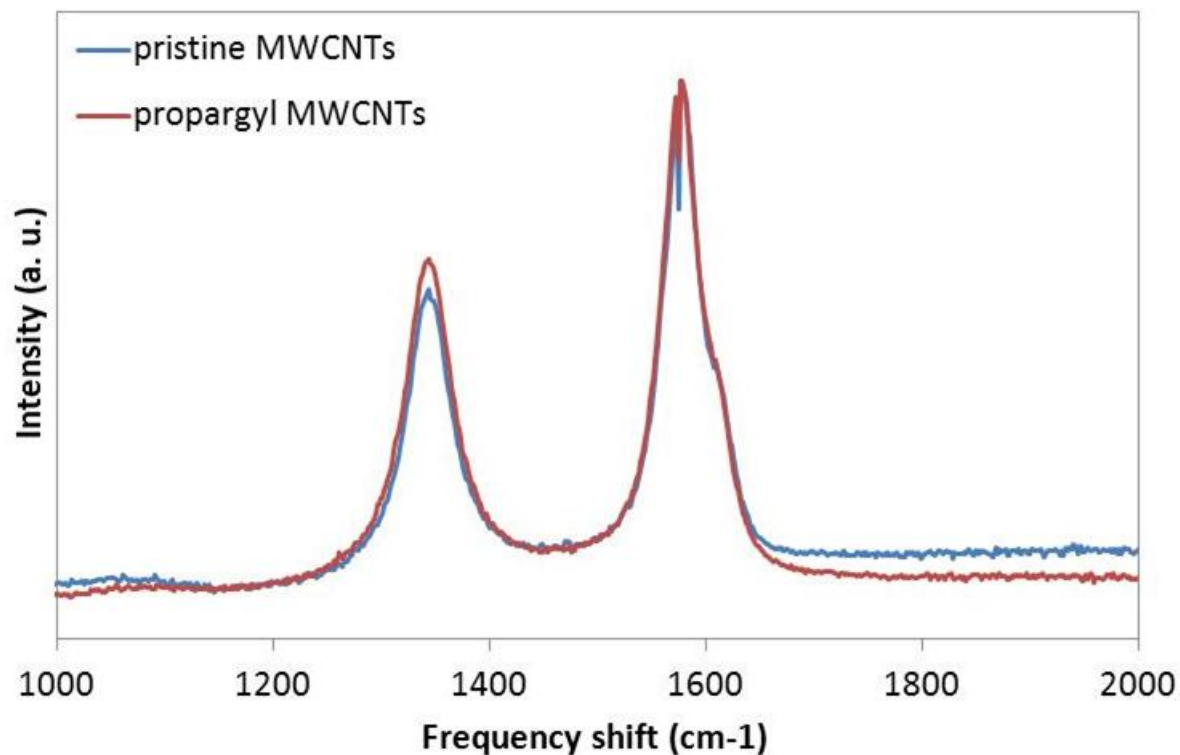
**Figure S5.** TGA of propargyl MWCNTs (**1b**) and pristine MWCNTs



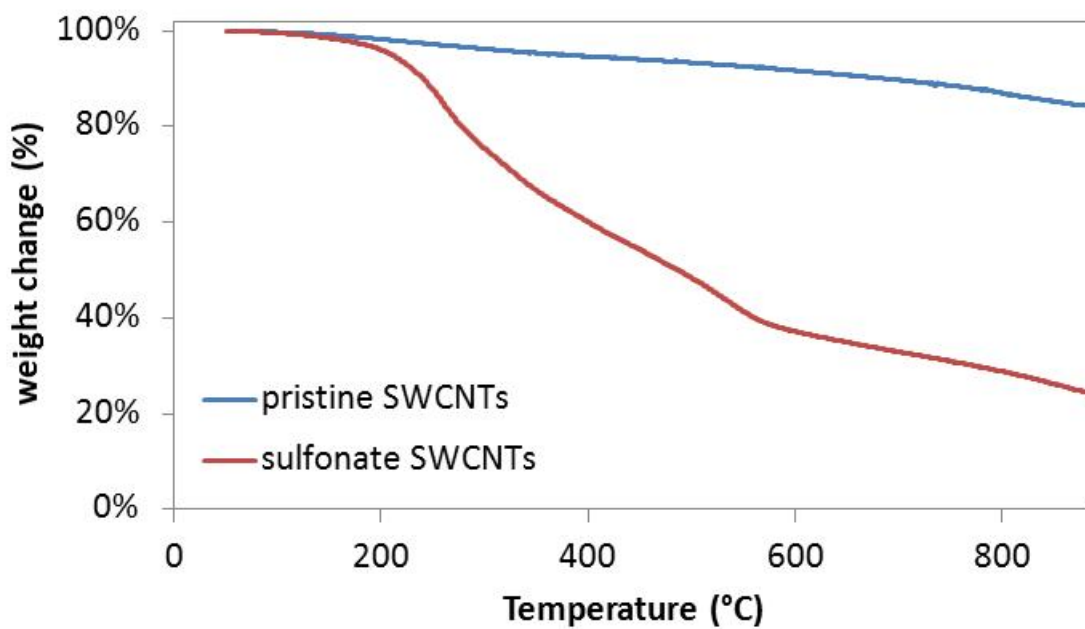
**Figure S6.** XPS spectra of propargyl MWCNTs (**1b**) and pristine MWCNTs



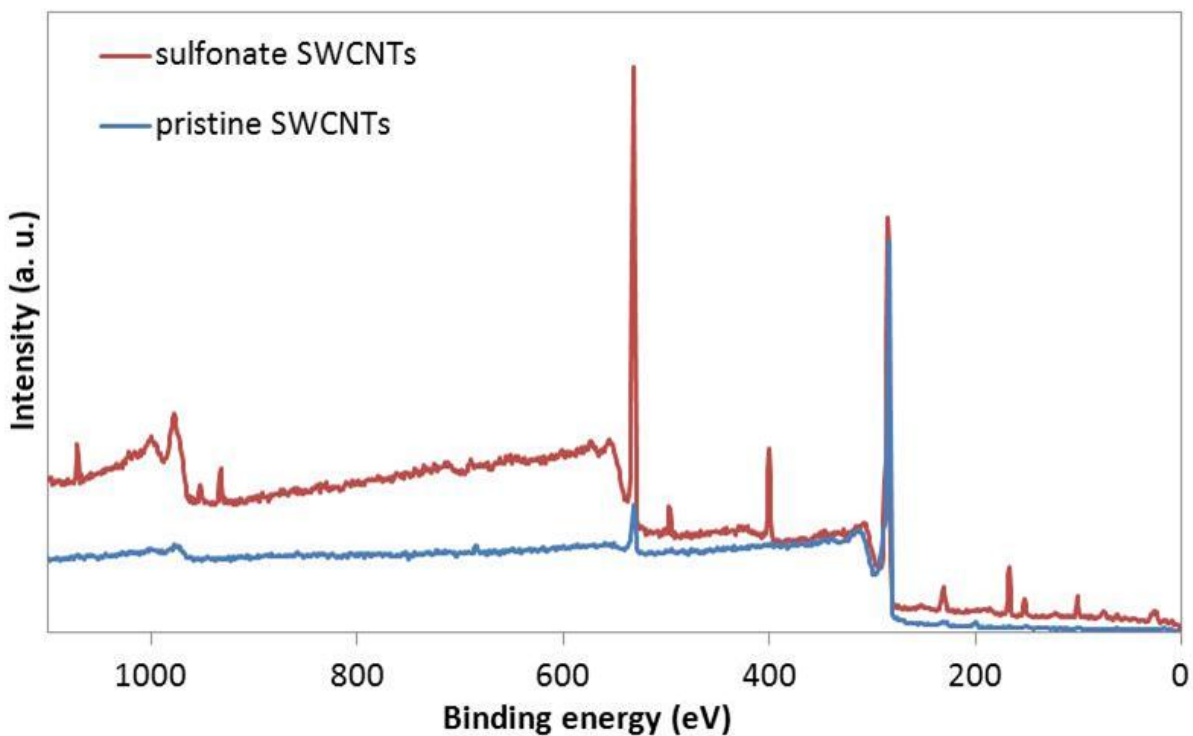
**Figure S7.** FT-IR spectra of propargyl MWCNTs (**1b**) and pristine MWCNTs



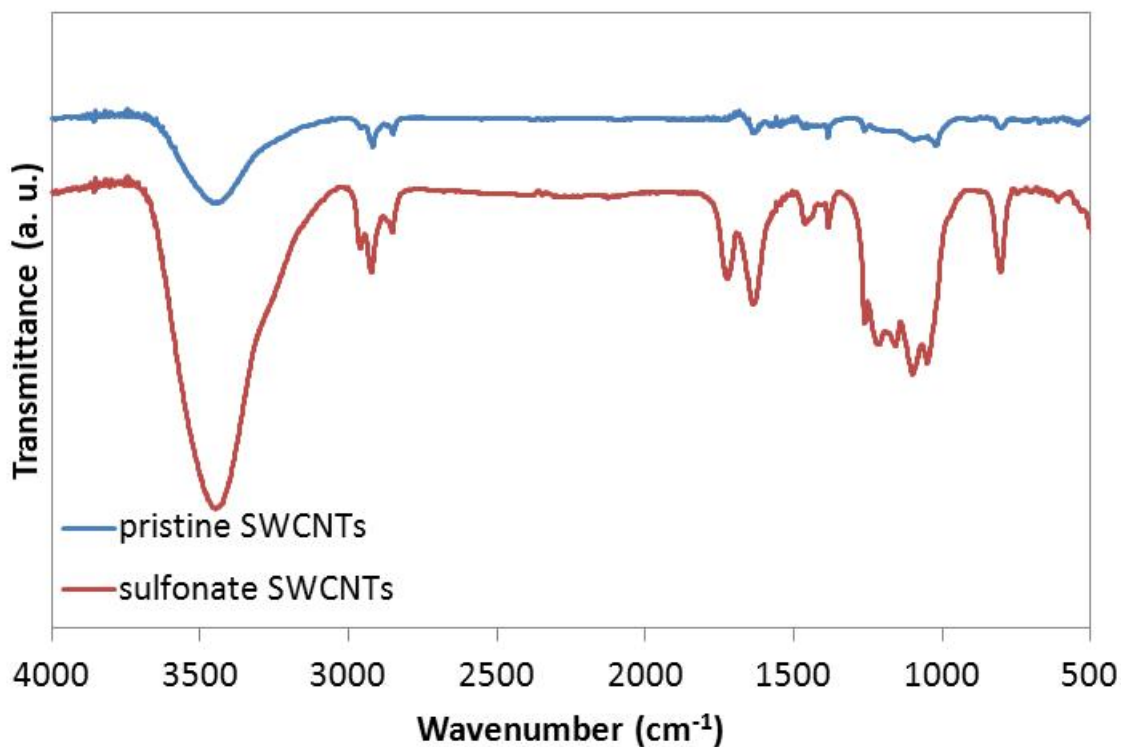
**Figure S8.** Raman spectra of propargyl MWCNTs (**1b**) and pristine MWCNTs



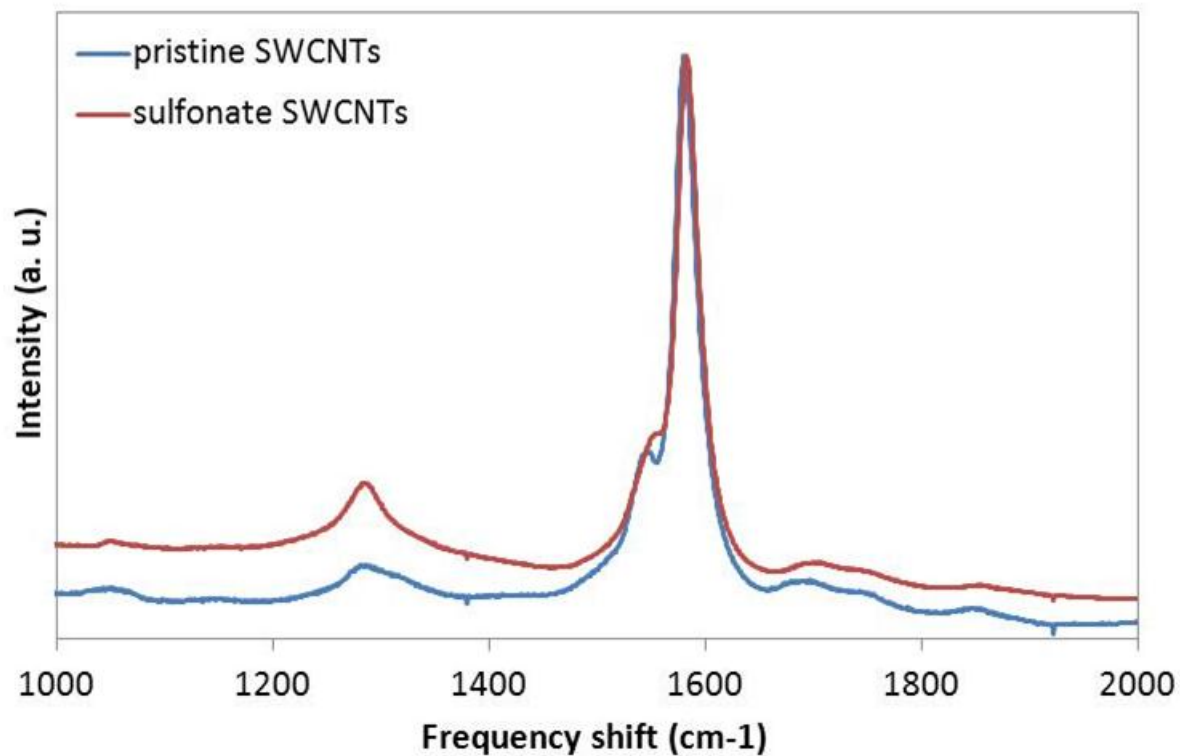
**Figure S9.** TGA of sulfonate SWCNTs (**3a**) and pristine SWCNTs



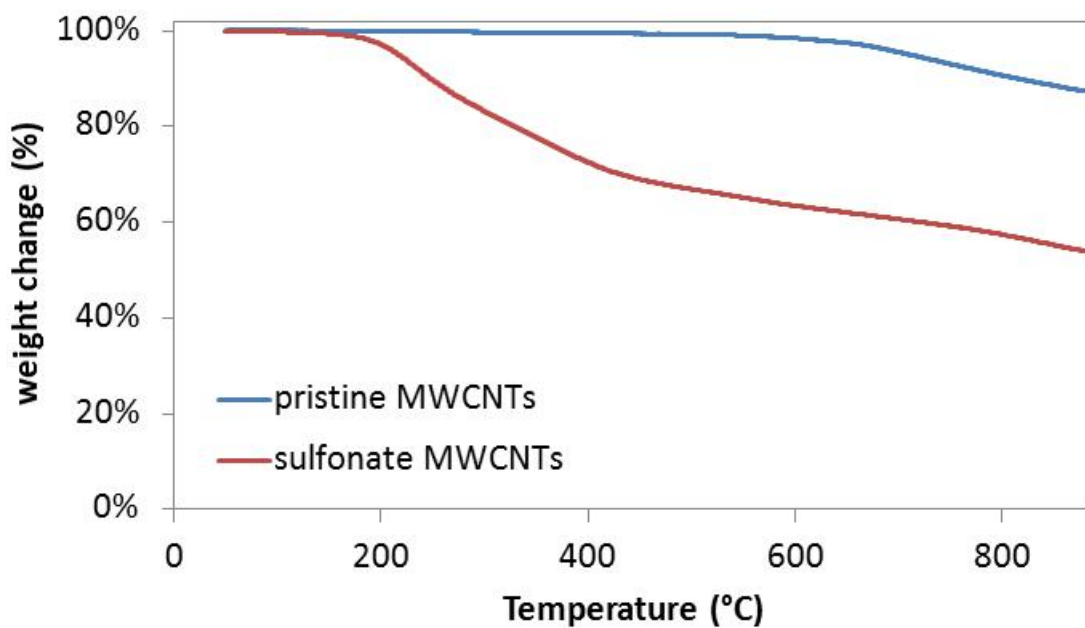
**Figure S10.** XPS spectra of sulfonate SWCNTs (**3a**) and pristine SWCNTs



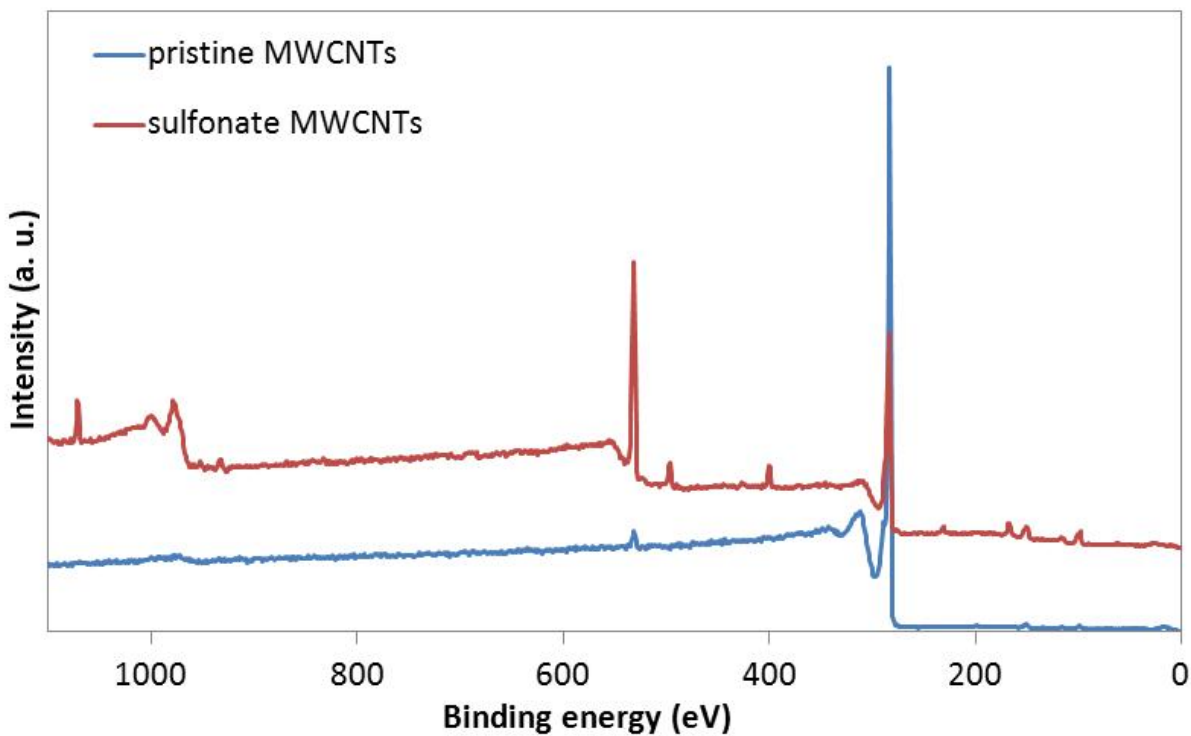
**Figure S11.** FT-IR spectra of sulfonate SWCNTs (**3a**) and pristine SWCNTs



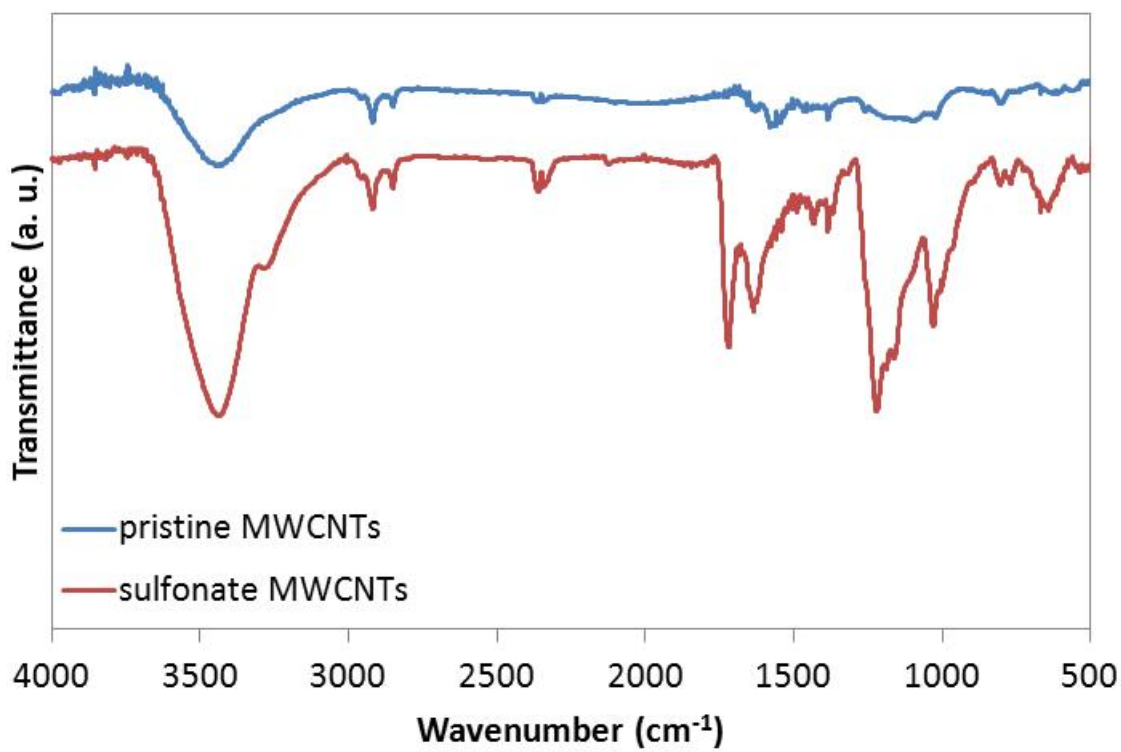
**Figure S12.** Raman spectra of sulfonate SWCNTs (**3a**) and pristine SWCNTs



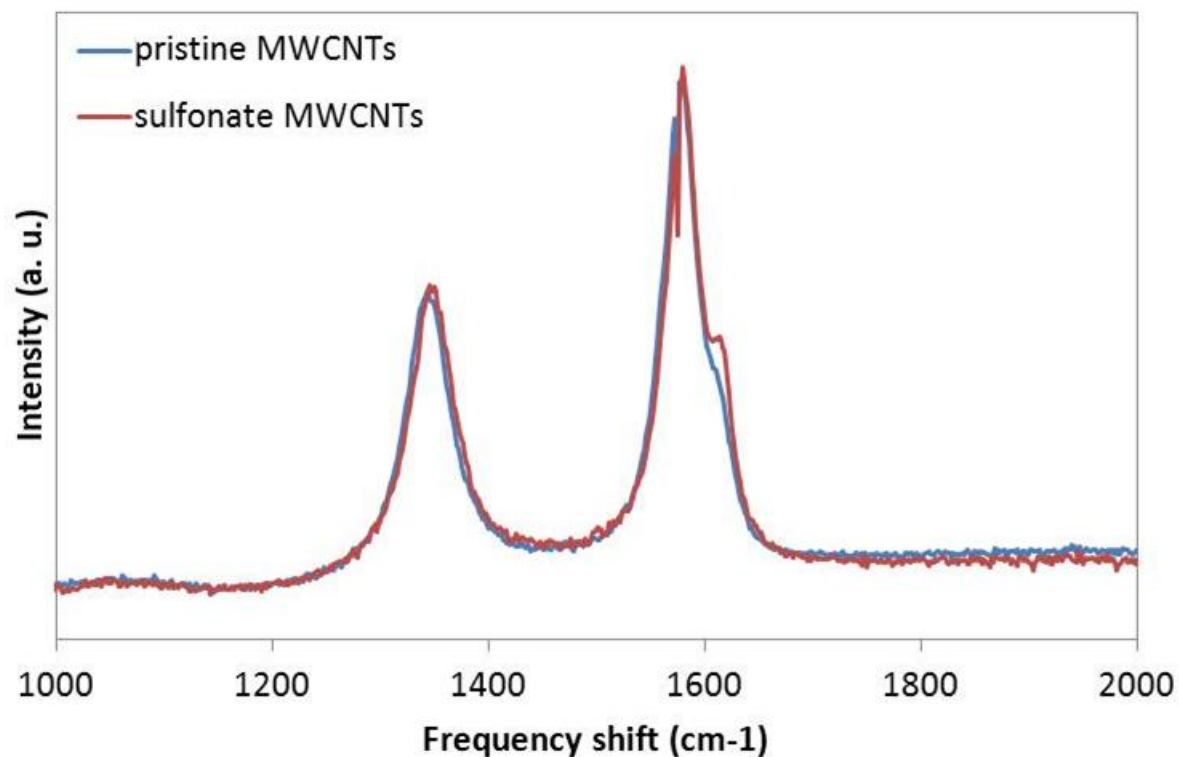
**Figure S13.** TGA of sulfonate MWCNTs (**3b**) and pristine MWCNTs



**Figure S14.** XPS spectra of sulfonate MWCNTs (**3b**) and pristine MWCNTs



**Figure S15.** FT-IR spectra of sulfonate MWCNTs (**3b**) and pristine MWCNTs



**Figure S16.** Raman spectra of sulfonate MWCNTs (**3b**) and pristine MWCNTs

- 1 X. Kong, D. Migneault, I. Valade, X. Wu, and F. Gervais, *WO 2004/113275*, 2004.
- 2 W. Zhang, J. K. Sprafke, M. Ma, E. Y. Tsui, S. A. Sydlik, G. C. Rutledge, and T. M. Swager, *J. Am. Chem. Soc.*, 2009, 131, 8446-8454.
- 3 L. J. Swartzendruber, *National Bureau of Standards*, 1964, Technical Note 199.