

# Supporting Information

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## Elemental Quantification and Residues Characterisation of Wet Digested Certified and Commercial Carbon Materials

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## Experimental Section

### Nuclear Magnetic Resonance

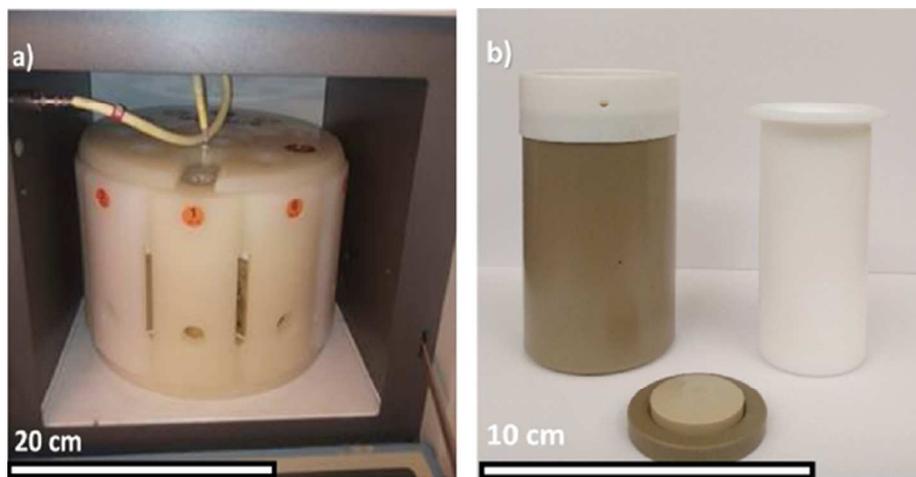
The carbon nanotube <sup>13</sup>C MAS spectrum without <sup>1</sup>H decoupling was obtained using a 2 second recycle delay, 3 microsecond <sup>13</sup>C  $\pi/2$  pulse, 20,000-40,000 transients and spinning speeds of 9 and 14 kHz. The digested nanotube <sup>13</sup>C MAS spectrum with 62.5 kHz <sup>1</sup>H decoupling field was obtained using a 2 second recycle delay, 3 microsecond <sup>13</sup>C  $\pi/2$  pulse, 25,000 transients, and spinning speed of 8.8 kHz. All spectra were collected using a 30-degree radio frequency pulse sequence at room temperature and referenced against the chemical shifts of adamantane at 38.48 and 29.45 ppm. The <sup>13</sup>C -<sup>1</sup>H cross-polarization was not efficient due to the conductive and ionic nature of the samples.

### ICP-OES Characterization

**Fig. S1a** shows the microwave assisted digestion system configured for acid digestion including the temperature sensor (inserted in the reference vessel). Before the digestion runs, the Teflon vessels (**Fig. S1b**) were cleaned and dried in an oven for two days at 80 °C.

The digestion protocol employed is as follows: 10 mg of the powder material (SWCNT-1, SRM2483, SWCNT, DWCNT, MWCNT, graphite or graphene) were accurately weighted and poured into a vessel,

then mixed with 4 mL HNO<sub>3</sub> and 1 mL H<sub>2</sub>O<sub>2</sub>. Next, the closed vessel was inserted in the polypropylene rotor (Fig. S1a) and the microwave-assisted digestion program started.



**Figure S1.** a) Microwave acid digestion system showing the rotor used along with the temperature sensor; b) Disassembled digestion vessel.

Two runs were performed each taking place in two stages, as detailed in **Table S11**. After the first run, the vessel cooled down to room temperature and an additional 4 mL of HNO<sub>3</sub> and 1 mL H<sub>2</sub>O<sub>2</sub> were added. The second microwave run was initiated, under the same two-stages conditions. At the end of this second step, the cooled vessel was transferred to a fume hood. There, the resulting digested mixture was transferred to 50 mL vials and diluted with Mili-Q water to a volume of 25 mL.

Note that this procedure was adopted after an exhaustive study where parameters like temperature, acids (type, ratios and volumes) were evaluated in order to provide a high digestion efficiency and best overall recoveries for the set of elements certified in the two CRMs. A key point was the limit of temperature at which the equipment could be safely operated (230°C). For this reason, the maximum temperature for the microwave-assisted digestions was capped at 220°C. In one trial, 200°C for 30 min (one-stage) was insufficient to digest the SWCNT samples. After several other attempts, we finally settled in performing a two-stages 30 min program (at 200 and 220 °C) but varying the ratio of time between the two temperatures. It was found that employing two iterations (“two-steps”) of the program with 10 min at 200°C followed by 20 min at 220°C resulted in clear digested solutions (for the SWCNT samples) while still retaining excellent recoveries for the set of targeted elements.

**Table S11.** Operating conditions for the microwave-assisted acid digestion

Stage	Time (min)	Power (W)	Temp (°C)
1	10	1100	200
2	20	1100	220

For the ICP-OES analysis, a Varian 720-ES spectrometer, bearing a dual detector assembly and covering a wavelength window between 165 nm and 782 nm was employed. The parameters used during the measurements are shown in **Table S12**.

The calibration of the ICP-OES was carried out with single-element solutions of Al, Ca, Ce, Co, Cr, Dy, Eu, Fe, Gd, K, Mg, Mn, Mo, Na, Ni, Sm, Ti and V at the concentrations of 1, 10 and 100 mg/L. All were derived from the respective 1000 ppm single-element standards (Inorganic Ventures, Inc).

**Table S12.** Operating parameters for ICP-OES

RF Power	1.2 kW
Plasma Ar gas flow	16 L/min
Auxiliary Ar gas flow	1.5 L/min
Nebulizer gas flow	0.7 L/min
Sample uptake rate	1 mL/min
Sample rinse time	50 sec
Sample pump rate	15 rpm
Stabilization delay	10 sec

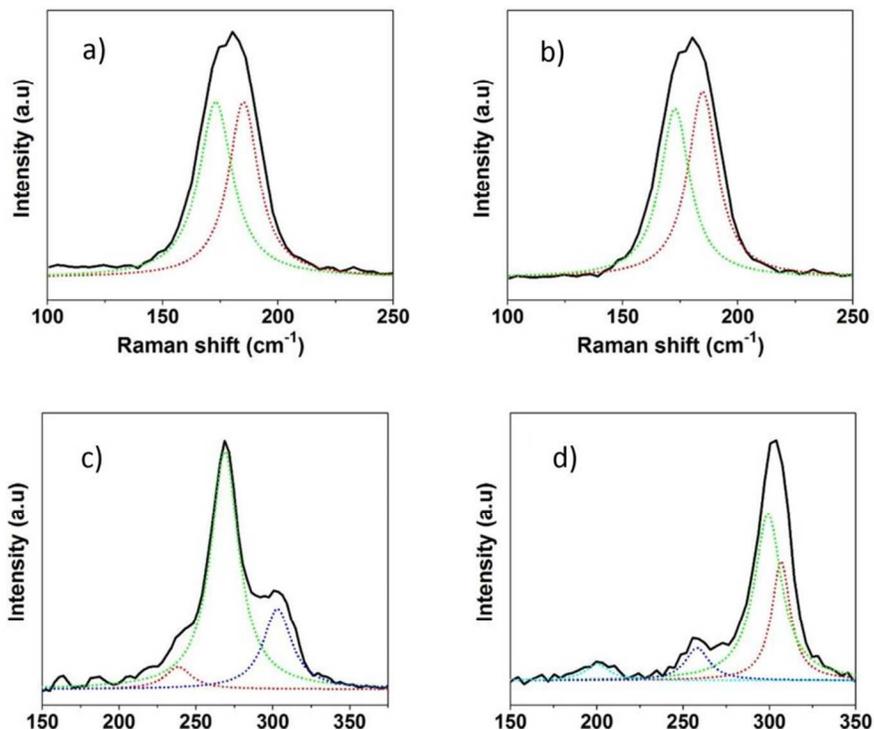
For the present experiments, the recovery of the analytes was evaluated through the use of certified reference materials and analyte spikes. This last procedure was used for the commercial SWCNT and followed the method 200.7, created by the US Environmental Protection Agency (EPA) [1]. Accordingly, a known volume of a solution containing all the analytes of interest in pre-determined concentrations was added to the SWCNT sample vessel. After cooling, the digested mixture was diluted to a volume of 25 mL and analyzed with ICP-OES. The concentration readings obtained for this “fortified” sample were used to calculate the recovery of the analytes via the following relation

$$R = \frac{C_s - C}{s} \times 100$$

Where R = percent recovery,  $C_s$  = fortified sample concentration,  $C$  = sample background concentration and  $s$  = concentration equivalent of analyte added to fortify the sample.

Further to the above, quality control sample (5 mg/L) and continuing calibration verification (1 mg/L) solutions were prepared in order to check the instrument performance and ensure that this was not degrading over the period of the analysis.

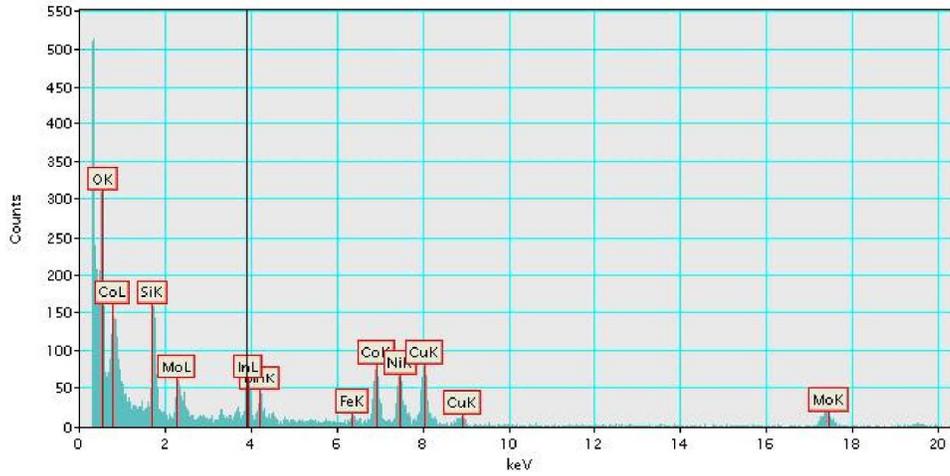
## Certified Reference Materials



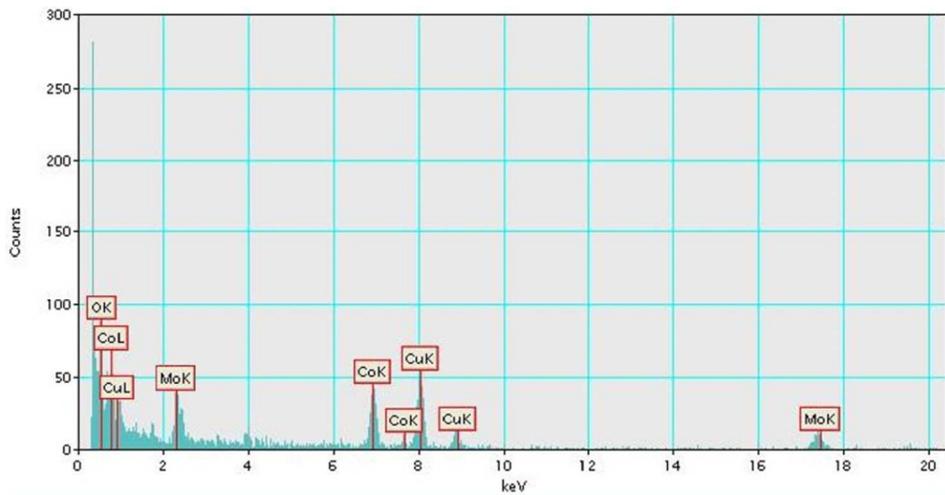
**Figure S2.** RBM peak fitting for: SWCNT-1 at a) 532 nm and b) at 488 nm, SRM2483 at c) 532 nm and d) 488 nm.

**Table S13.** - Diameters of the SWCNTs in the CRMs, according to the excitation laser wavelength. The peak wavenumbers were extracted from the above fitting (**Fig. S2**).

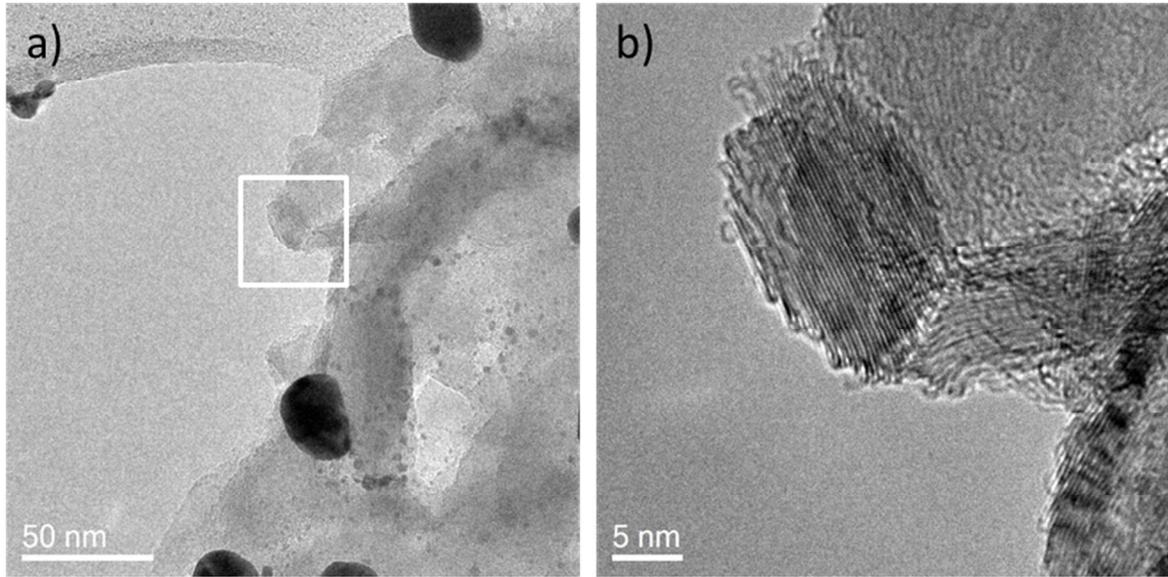
Sample	Laser (nm)	Wavenumber (cm <sup>-1</sup> )	Diameter (nm)
SWCNT-1	488	172.6	1.27
SWCNT-1	488	184.8	1.19
SWCNT-1	532	172.6	1.27
SWCNT-1	532	185.1	1.18
SRM2483	488	199.8	1.10
SRM2483	488	257.3	0.85
SRM2483	488	299.5	0.73
SRM2483	488	306.9	0.72
SRM2483	532	238.8	0.92
SRM2483	532	269.2	0.81
SRM2483	532	303.1	0.72



**Figure S3.** EDX spectrum of SWCNT-1 showing the presence of Fe, Co, Ni and Mo.



**Figure S4.** EDX spectrum of SRM2483 showing the presence of Co and Mo.

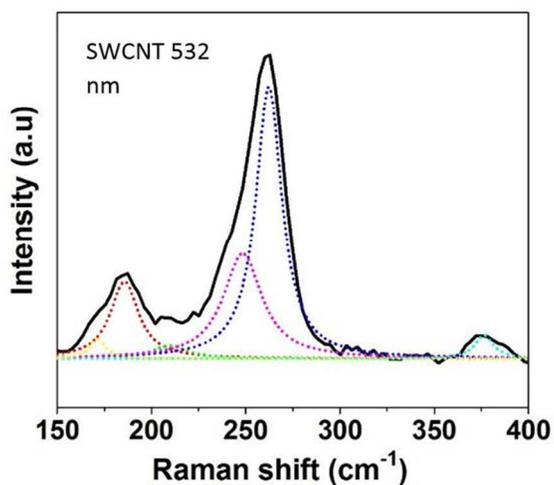


**Figure S5.** TEM images of the SWCNT-1 residues: a) graphitic shells and various Au particles are visible, b) a high mag view of the region boxed in c) where the structure of the graphite planes is clear.

## Commercial Samples



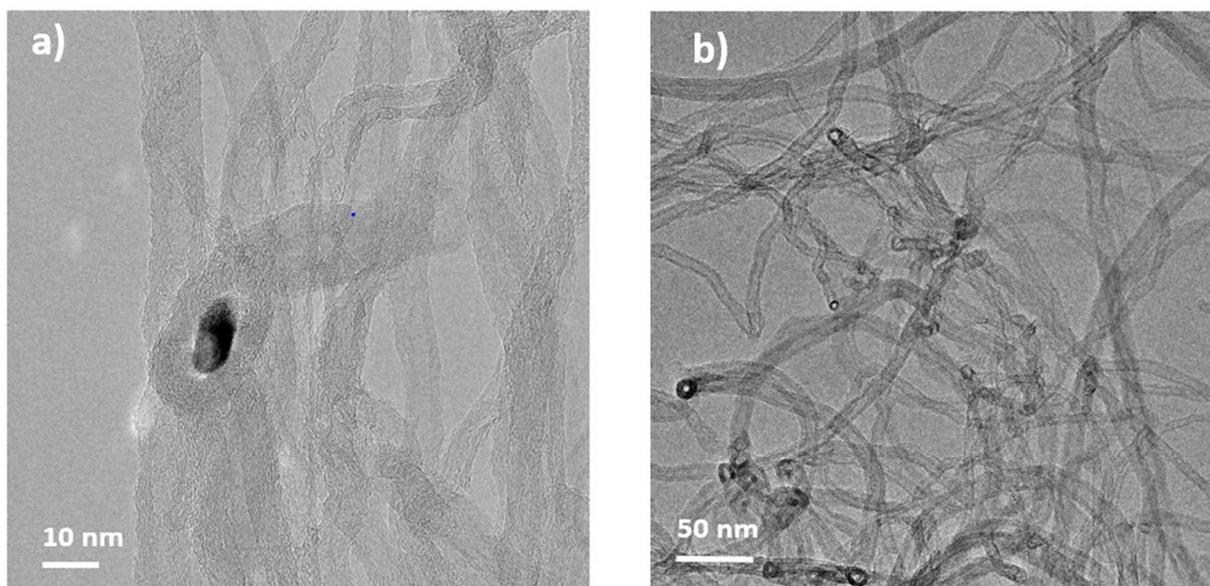
**Figure S6.** Post-digestion MWCNT sample, highlighting the yellowish color of the liquid.



**Figure S7.** RBM of commercial SWCNT, taken with a 532 nm laser.

**Table S14.** Diameters of the commercial SWCNT sample for the 532 nm excitation laser. The wavenumbers were extracted from the above peak fitting (**Fig. S7**).

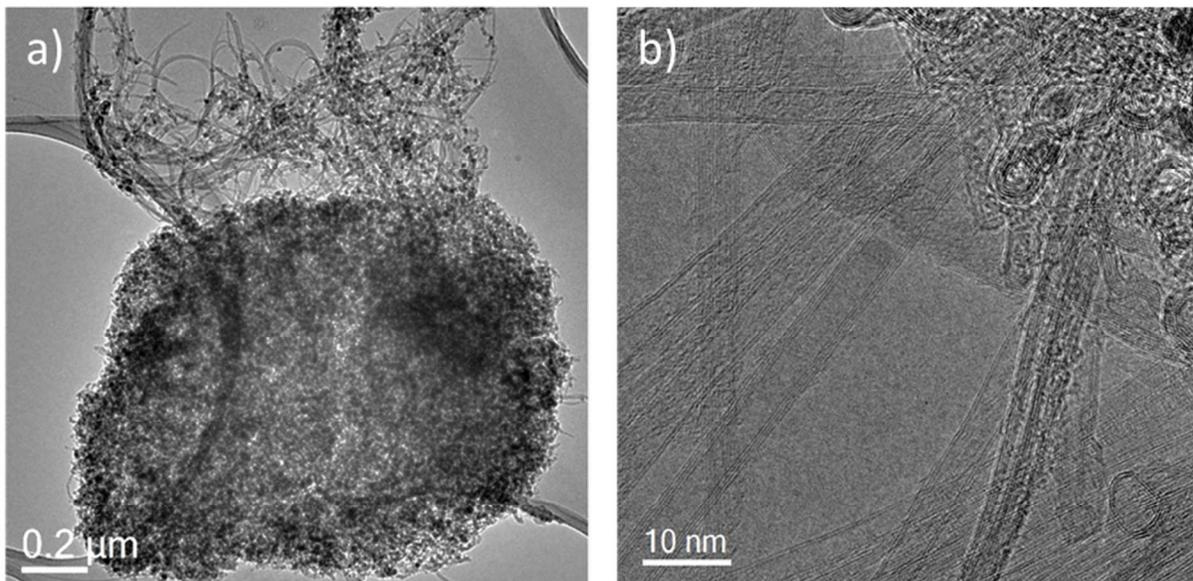
Sample	Laser (nm)	Wavenumber (cm <sup>-1</sup> )	Diameter (nm)
SWCNT	532	170.6	1.29
SWCNT	532	185.3	1.19
SWCNT	532	248.7	0.88
SWCNT	532	261.5	0.84
SWCNT	532	375	0.58



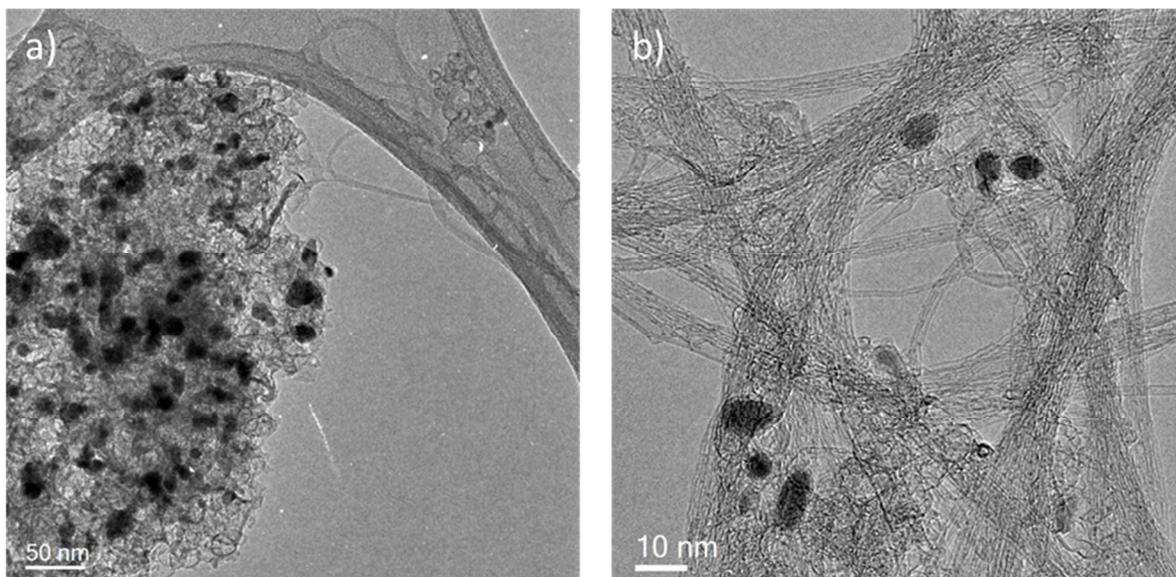
**Figure S8.** TEM micrographs of the as-received MWCNT. The wall texture of the nanotubes is characteristic of pyrolytic nanotubes, where the density of structural defects is high.

**Table S15.** Intensity ratios of D and G bands for the different commercial materials investigated, pre- and post-digestion.

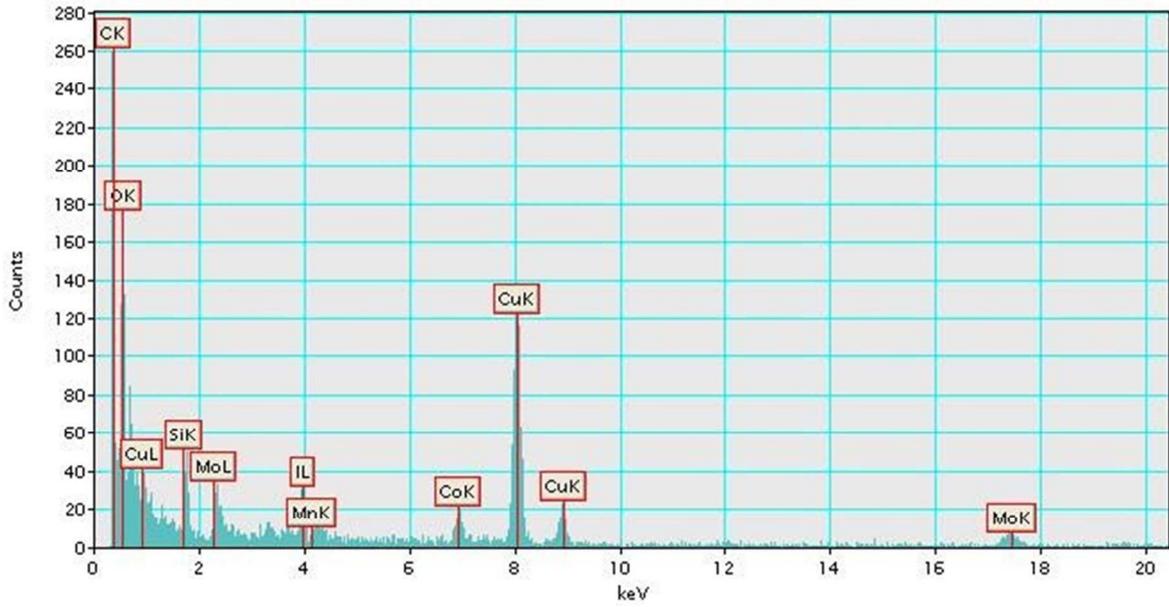
Sample	$I_D/I_G$ (as-received)	$I_D/I_G$ (after digestion)
SWCNT	~0	0.61
DWCNT	0.08	~0
MWCNT	1.28	1.51
Graphite	~0	0.07
Graphene	0.19	0.26



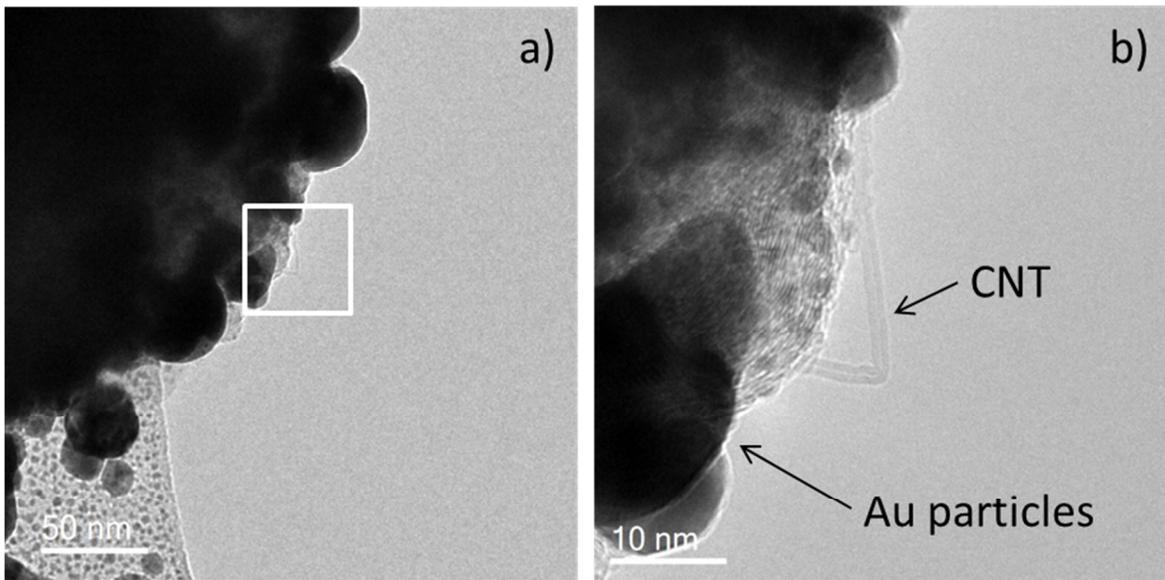
**Figure S9.** TEM images of the as-received DWCNT: a) the presence of by-products and lumps of non-graphitized carbon is visible in low mag micrographs; b) DWCNTs are mixed with single- and multi-walled nanotubes as well as other types of carbon particles.



**Figure S10.** TEM images of the as-received commercial SWCNT: a) low mag micrograph showing the presence of a high density of catalyst particles, b) high mag view showing the widespread presence of SWCNT bundles.



**Figure S11.** EDS spectrum of the commercial SWCNT material showing the presence of Co and Mo.



**Figure S12.** TEM micrographs showing the post-digestion residues of the commercial SWCNT.

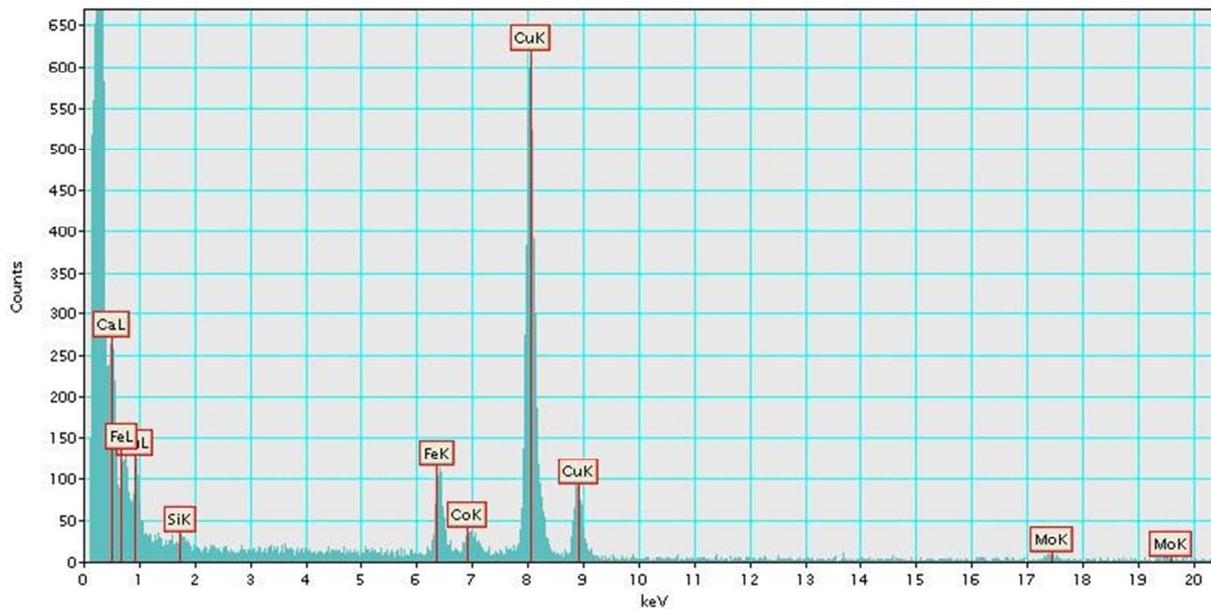


Figure S13. EDS spectrum of the commercial MWCNT material showing the presence of Fe, Co and Mo.

## References

[1] U.S. EPA. Method 200.7: Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry, Revision 4.4. (1994).