Wondrous World of Carbon Nanotubes

Appendix B: Overview of purification techniques

B.1 Method for purifying single wall carbon nanotubes [54]

Patent on a method for purifying SWNTs. SWNTs, produced with arc discharge, Ni:Y:Ti:graphite = 2:2:2:94, are purified with two oxidation steps.

First oxidation step:

1. Thermal oxidation: heating from 350 - 600 °C.

   Metal catalyst acts as oxidation catalyst for the graphite carbon layers.

2. Wet oxidation: reflux in hydrogen peroxide solution between 60-120 °C.

   Metal catalyst surface is cleared, so the metal can be solvated in acid, the SWNTs remain suspended.

3. Wet oxidation: reflux in nitric acid.

   The metal catalyst is exposed to acid and solvated; the SWNTs remain suspended.

Second oxidation step:

1. Wet oxidation: reflux in hydrogen peroxide solution

   Metal catalyst acts as oxidation catalyst; both SWNT and carbon oxidise. Because there is only a small amount of catalyst left, this step does not affect the yield very much.

2. Wet oxidation: reflux in hydrochloric acid.

   The metal catalyst is exposed to acid and solvated; the SWNTs remain suspended.

A sonication step was performed between all steps. Smaller catalyst diameter and thinner carbon layers are beneficial for the method. No records of characteristic measurements, yield or purity are given.

B.2 Reduced diameter distribution of SWNTs by selective oxidation[55]

Both a chemical treatment in HNO_3 and oxidation in a reduced O_2 atmosphere lead to a selective burning of the narrower SWNTs in bulk samples and to a diameter distribution which is smaller by a factor two.

Reduced oxygen atmosphere

1. The sample is annealed in high vacuum (5×10^{-6} mbar) at 873 K in a quartz tube to remove the remaining fullerene particles and amorphous carbon.
2. Into the same quartz tube, pure oxygen is fed with a partial pressure of $1.5 - 5 \times 10^{-6}$ mbar, within a temperature range of 723 - 873 K. Total annealing time is 70 h. This step selectively burns SWNTs with smaller diameter.
3. The sample is annealed in high vacuum (1×10^{-7} mbar) at 1023 K to remove the oxygen.

In this method there is still metal catalyst in the sample.

Chemical oxidation

1. The sample is annealed in high vacuum (5×10^{-6} mbar) at 873 K to remove the remaining fullerene particles and amorphous carbon.
2. The material is then refluxed in 2 M HNO_3 for 43 h at room temperature. This selectively oxidises the narrower SWNTs and also removes the metal catalyst.
3. The solution is neutralised and filtrated 6 h using crossflow filtration.
4. The sample is annealed in high vacuum at 873 K for 0.5 h to remove the remaining solvent and acid.
5. The sample is annealed in high vacuum at 1073 K for 0.5 h to remove the remaining solvent and acid.

Regarding the metal content a purity of 99.9 % is reached.

The samples are checked with *AAS* (atomic absorption spectroscopy) and *TEM* pictures. This shows that the metal content in the samples is reduced from 31 wt% to 0.1 wt% and that the diameter distribution is narrowed. A narrower size distribution is created, with a larger average diameter.

B.3 Plasma etching for purification and controlled opening of aligned carbon nanotubes[56]

For the usage of aligned MWNTs in FED display industry, a thin layer (ca. 0.1 - 0.5 µm) of amorphous carbon film has to be removed. Most of the techniques known are tedious, have low yields and damage the vertical alignment.

The unique layered structure of the amorphous carbon film formed on top of the aligned MWNTs, makes the radio frequency glow-discharge plasma etching[139] a good method for purification.

1. The substrate is exposed to a water-plasma under vapour pressure in the range of 0.3 - 0.5 Torr. (80 min)
2. The power needed for the plasma is supplied by a radio frequency of 250 kHz
3. The plasma leads to a high concentration of atomic oxygen.
4. This oxygen will controllably oxidise a thin carbon layer on top of the vertically aligned tubes.
5. As a result purified aligned one-end opened nanotubes are obtained.

The result is confirmed by *SEM* and *TEM* images, which clearly show that the end-caps with the metal catalyst have been removed.

B.4 Purification and characterisation of SWNTs[57]

This method has been developed for the removal of metal catalyst and carbon impurities from the laser grown SWNTs and initially cleaned with nitric acid. It describes two studies of a relatively high temperature gas phase oxidation process.

The first study:

1. Water reflux for removing aromatic carboxyl acids produced by the cleaning with nitric acid.

2. The sample was heated in a 5 % O_2/Ar, 1 atm mixture for 1 h. The temperature was varied from 300 - 500 °C in four steps.

3. After each heating step, a sonication in concentrated HCl followed

4. Best steps were the oxidations at 300 and 500 °C.

The second study was done with a two-step oxidation to produce the best results for metal removal with minimum loss of nanotubes:

1. Water reflux for removing aromatic carboxyl acids produced by the cleaning with nitric acid.

2. The sample was heated at 300 °C in a 5 % O_2/Ar, 1 atm mixture for 1 h.

3. After this heating step a sonication in concentrated HCl was performed.

4. The sample was heated at 500 °C in a 5 % O_2/Ar, 1 atm mixture for 1 h.

5. Another sonication step in concentrated HCl.

6. The final metal content in 0.1 % relative to the carbon content. The last step, the oxidation is metal catalysed.

7. Finally, annealing at 900 °C follows.

The samples were checked with *SEM* and *TEM* images. *TGA* indicated that the samples that were heated showed the best temperature resistance. Also the effect of more metals was checked with *TGA*. From the *Raman* spectra, it can be seen that the annealing step increased the intensity of the SWNT peak. Looking at the van Hove peaks gained with *UV-vis-near-IR*, it can be concluded that this oxidation removes smaller diameter SWNT preferentially. Also the intensities of the van Hove peaks increased.

B.5 Purification of SWNTs by selective microwave heating of catalyst particles[58]

Steps:

1. Microwave treatment at 500 ^{o}C for 20 min.

The sample (100 mg of arc-discharge SWNTs) was placed in a quartz tube that passed through a cavity. The microwaves couple to the residual metal catalyst, raising significantly the local temperature, leading to both the oxidation and rupturing of the carbon passivation layer over the catalyst particles.

2. Mild acid treatment

With this protective carbon coating weakened or removed, a mild acid treatment (4 M HCl reflux for 6 h) is then sufficient to remove most of the metal in the sample, leaving the nanotubes in tact.

Optimal conditions:

- Flow (dry air) = 100 sccm
- Frequency = 2,45 GHz
- Power = 150 W
- Temperature = 500 °C

The entire process was monitored by *TEM* and *HRTEM* pictures. *TGA* showed that a apparent three differential peak structure was obtained, which indicated that the metal catalyst partially oxidised the tubes, to form amorphous carbon and multi shell carbons. *Raman* spectrometry indicated that the microwave process gave a small broadening of the SWNT peak, the HCl

treatment hardly damaged the SWNT and the HNO_3 reflux step gave a significant peak broadening.

Using microwave processing and a mild acid treatment it is possible to remove residual metal to a level lower than 0,2 wt%. The total yield for the two-step purification procedure is about 35 wt%.

B.6 Length sorting cut SWNTs by high performance liquid chromatography[59]

Previously cut SWNTs by an acid base process are sorted by length by HPLC based, size exclusion chromatography (SEC). The SWNTs were grown by pulsed laser vaporisation.

Purifying and cutting SWNTs

1. Wet oxidation with reflux in HNO_3
2. Crossflow filtration
3. First cutting was affected by 24 h ultrasonication in a 3:1 mixture of HNO_3-:H_2SO_4 at 45 °C.
4. Next to further shorten the tubes and to consume sidewall defects, the SWNT reacted in a 4:1 mixture of H_2SO_4:H_2O_2 for 10 min.

HPLC

1. The cut SWNTs are run over a SEC-HPLC.
2. The biggest SWNTs leave the HPLC first (after ± 20 min).
3. At the end, when all the SWNTs have already past, the C_{60}, C_{70} etc, come out (after ± 30 min).

The results above could be concluded from *AFM* (atomic force microscopy) pictures and the *UV-vis* measurements from the HPLC.

B.7 Purification of SWNTs synthesised by the hydrogen arc-discharge method[60]

SWNTs synthesised with the hydrogen arc-discharge method have been purified with ultrasonication in alcohol, oxidation in fixed air and soaking in hydrochloric acid. The yield of the method is ~ 41% of the as-produced soot which contained ~55% SWNTs. The obtained purity is 96%.

1. Ultrasonication in alcohol for 30 min to cleave off impurities from the SWNTs.
2. Dried to air at room temperature.

3. The sample is oxidised in fixed air at 540-550 °C for 40 min, which oxidises the carbon impurities.
4. The product is then soaked in hydrochloric acid.
5. Afterwards, the sample is washed with de-ionised water and dried in an oven at 150 °C.

The *TEM* pictures showed that almost no visible impurities remained in the sample. This was confirmed by *TGA* (thermo graphic analysis), which included *TG* (thermogravimetry), *DTG* (differential thermogravimetry) and *DTA* (differential thermal analysis). *Raman* spectrometry showed the removal of the carbon impurities peak and sharpening of the SWNT-peak.

Further is stated that the carbon impurities start to combust at 528 °C and the SWNTs start to combust at 600 °C. This is why a temperature of 550 °C is chosen.

B.8 High-quality SWNTs from arc-produced soot[61]

A three-step process, for purifying the raw soot, which contained 33 % metal and 67 % carbon.

Steps:

1. *Soft oxidation*. The as-produced soot (150 mg) was subjected to 120 ^{o}C reflux in a 2,8 N HNO_3 solution (200 ml) for 6, 12 or 24 hours. The solution was filtered and washed with distilled water several times, followed by drying at 100 ^{o}C for more than 10 hours. In this first step an oxide layer was formed on the surface of the metal catalyst and damage to the amorphous carbon occurred.

2. *Air oxidation*. The dried sample was heated in air at 550 ^{o}C for ten min to remove the amorphous carbon.

3. *High-temperature vacuum treatment*. The sample was heat-treated at 1600 ^{o}C at a pressure of 10^{-3} Pa for three hours. In this final step the graphitic carbon and metals are removed, the oxide layer decomposes and the rearrangement of SWNT walls occurred.

After the final step, about 20 % of the weight of the initial raw soot remained and the final product contained less than 1 % metal.

TEM images are analysed. *TGA* samples of the different steps have been made, which show the loss in metal and carbon. *Raman* spectra give information on the diameter size (RBM peaks) and the SWNT content (G/D values) by comparing peaks.

B.9 High-yield purification process of SWNTs[62]

A two step process for the purification of as-produced SWNTs from the catalytic arc discharge process (Ni/Co/FeS=1:1:1). The process involves rotating thermal oxidation in air and an acid treatment.

1. The as-produced SWNTs were grinded and heated at 470°C for 50 min while rotated at 30 rpm. This step removes the carbonaceous particles, weight was reduced to 40 wt% of the initial sample.
2. The oxidised powder was immersed and filtered in 6 M HCl to dissolve the metal catalyst. The yield was 70 wt%.
3. To unbundle the SWNTs, the sample was refluxed in 30 % HNO_3 for 4-6 hours.
4. The obtained suspension was filtered with a PTFE (poly-(tetrafluoroehtylene)) membrane in de-ionised water.

The final yield was 25-30 wt% with a purity of ~ 96 %, containing 1 % metal atoms (initially 8%).

SEM and *TEM* images, *Raman* spectra and *TGA* of the process samples were taken. The *Raman* spectra clearly show that the samples purity and defects content are improved by the various processes. The ratio of the peaks at 1600 cm^{-1} and 1300 cm^{-1} increases.

B.10 Purification and characterisation of SWNTs obtained from the gas-phase decomposition of CO (HiPco process)[63]

Steps:

1. Raw HiPco tubes compressed onto a dry filter paper (vacuum).

2. SWNTs are placed in a quartz tube furnace.

3. Mixture of O_2 in Ar is passed trough a water bubbler and run over the sample.

4. Nanotubes and a continuous flow of wet Ar and O_2 are heated at 225 ^oC for 18 h. This heating step oxidises the metal. This metaloxide has a lower density, which causes the carbon shells to break open and exposes the metal. This could also be done at 325 ^oC (1,5 h) or 425 ^oC (1 h).

5. Sonication (15 min.) or prolonged stirring in concentrated HCl solution (overnight).

6. Filtered onto a 47 mm (1 mm pore size) Teflon membrane.

7. Washed several times with de-ionised water and methanol

8. Dried in a vacuum oven at 100 ^{o}C (minimum of 2 h).

9. Annealing at 800 ^{o}C in Ar for 1 h.

From the *TGA* measurements it can be seen that the samples first gain weight, because of oxidation of the metal and then loose weight because of the (catalysed) carbon removal. *UV-vis-near-IR* indicate the preferential loss of smaller diameter during the cleaning process and give insight in the van Hove features during the process. With *Raman* spectra the loss of intensity due to the process and recovery due to annealing is shown. *SEM* en *TEM* images show the raw and the purified SWNTs. A large reduction of impurities can be seen. Also a comparison is made with laser-grown SWNTs by comparing the *UV-vis-near-IR* and *Raman* spectra.

The reference shows the different outcomes for the different temperatures. This method oxidises the metal and the carbon impurities. SWNTs with smaller diameters are oxidised preferentially.

B.11 Ultrasonic reflux system for one-step purification of carbon nanostructures[64]

Patent for one-step purification of SWNTs. Soot containing amorphous carbon, metal catalyst and carbon nanostructures is purified in one system.

First step:

1. Sonication, to solve soot in the first flask.
2. Solvated soot is run over a filtering membrane and removed from the sonication area, non-solvated soot remains in flask.

Second step:

1. Solvated soot is further purified in second flask with a reflux column.
2. Oxidising gas is inserted to oxidise the amorphous carbon.
3. In the second flask acid removes metal catalyst.

No records of characteristic measurements, yield or purity are given.

B.12 Purification of SWNTs by microfiltration[65]

This technique allows us to separate the as-prepared SWNT mats into three separate fractions without the use of acid, heat, or oxidative treatment.

Steps:

1. The sample (SWNTs prepared by pulsed laser ablation) is soaked into CS_2.

2. The CS_2 insolubles are then trapped in a filter.

3. Sonication of the insoluble solids in aqueous solution (0,1 % surfactant).

4. Micro filtration. Most of the carbon nano spheres (CNS, C_{60} and C_{70}) and metal nanoparticles are passing through the filter, while the SWNTs and a small amount of residual CNS and metal nanoparticles are trapped. The microfiltration process is repeated for three cycles to minimise the amount of residual CNS and metal nanoparticles trapped between the ropes of the SWNTs.

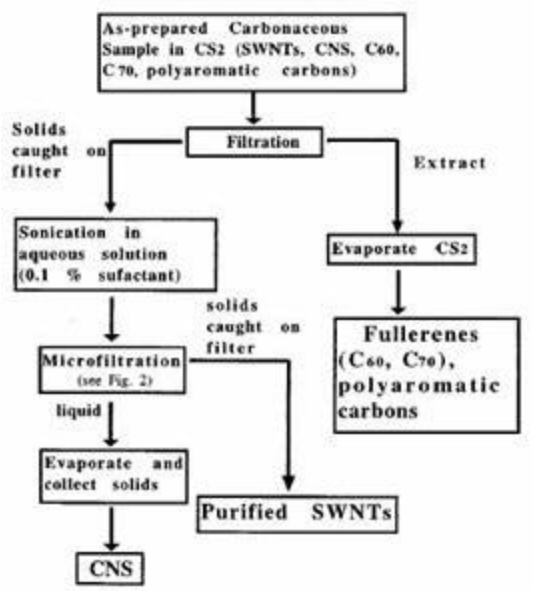

Figure 7-8: Scheme of the purification process. [65]

HRSEM and *TEM* pictures gave proof of that what is stated above. The *Raman* spectra of the CS_2 extracts, the as-produced and the purified SWNTs show that C_{60} and C_{70} are removed.

The individual weight percentages of the separated fractions are 6, 10 and 84 wt% for the CS_2 extract, CNS and SWNTs respectively.

B.13 Purification of HiPco carbon nanotubes via organic functionalisation[66]

Steps

1. Organic functionalisation of the as-produced nanotubes (p-SWNTs) based on 1,3-dipolar cycloaddition of azomethineylides in DMF suspension.

2. Purification of the soluble functionalised nanotubes (f-SWNTs). The purification is based on the improved solubility of the nanotubes and the

insolubility of the metal particles. To further purify f-SWNTs, basically removing the amorphous carbon particles, a slow precipitation process is employed, occurring when diethyl ether is added to a chloroform solution of f-SWNTs (85 mg in 300 ml).

3. Removal of the functional groups and recovery of the purified nanotubes (r-SWNTs) by thermal treatment at 350 ^{o}C, followed by annealing to 900 ^{o}C.

4. The metal content was reduced from 26 % to 0.4 %.

TEM images of the purified and as-produced nanotubes were taken. *DSC* (differential scanning calorimetry) showed that the purification process had few impact on the structure of the SWNTs, as the curves were almost the same. The DSC curve of the f-SWNTs were quite different. *NIR* (near-infrared) showed that functionalisation altered the electronic properties of the tubes. Further could be seen that some peaks after purification became less intense, due to the fact that more SWNTs with smaller diameter were oxidised. The same result was found with *Raman*. From the *AAS* measurement could be seen that the metal content was reduced from 26 % to 0.4 %.

B.14 Purification of SWNTs by ultrasonically assisted filtration[67]

This process generates material with a purity of more than 90% and yields of 30-70%. Ultrasonically assisted filtration technique allowed us to purify up to 150 mg SWNT soot in 3-6 h.

Steps

1. The soot was suspended in toluene and the suspension was filtered to extract soluble fullerenes. The toluene-insoluble fraction was then re-suspended in methanol. A typical concentration of the raw material in the suspension was 1 g/l.

2.The suspension was then transferred into a 47 filtration funnel. A 25,4 mm ultrasonic horn was inserted into the funnel and was placed about 1 cm above the surface of the filter membrane.

- Pore size membrane: 0,8 µm
- Amplitude horn tip vibrations: 33µm
- Power diss. by horn: 12 W/cm^2
- Temperature funnel: 0 °C
- Pressure: 50 Torr

Ultrasonication applied to the samples during filtration maintains the material in suspension. It also prevents formation of a cake of the material on the filter surface.

Methanol was continuously added to the filtration funnel to maintain a constant filtration volume.

3.After filtration, the material was washed with 6 M sulphuric acid to remove traces of metal, introduced into the sample by the ultrasonic horn.

TEM and *SEM* images of the purified samples have been made. Next to that they were characterised by *Raman* spectroscopy. The method substantially decreased the amorphous carbon peak. *TGA* showed that the purified SWNTs had more defects. The 50 % oxidation point is reached 30 °C earlier as for purification.

B.15 Mechanical purification of SWNT bundles from catalytic particles[68]

The basic principle of the purification method is like a snooker game, where we use the energy of elastic impact between encapsulated catalysts and small hard inorganic particles to eject the metal kernels and trap them with a strong magnet.

Steps:

1.SWNTs are first suspended either in soap solution or in toluene and then are dispersed in various solvents such as toluene, N,N-dimethylformamide or 30 % nitric acid.

2.A powder of nanoparticles (ZrO_2, NH_4Cl, $CaCO_3$ or diamond), that is not soluble in the given medium, was then added to the suspension. This slurry was sonicated typically for 24 hours. The ultrasonic bath mechanically removes the ferromagnetic particles from their graphitic shells.

3.The magnetic particles are trapped with permanent magnetic poles and with a subsequent chemical treatment A high purity SWNT material is obtained.

The samples were checked with *ESR* (electron spin resonance) and *TEM* images, which proved that the main part of the metal catalyst was removed. This method is typically developed for lab-sized purifications.

B.16 Cutting SWNTs by fluorination[69]

This process describes the fluorination of purified HiPco SWNTs (~1.0 nm, no amorphous carbon, no metal), followed by pyrolysis of the partially fluorinated tubes (CF_x, $x < 0.2$). This gives short tubes with average lengths of < 50 nm. The initial length was ~1 µm.

1. Purified SWNTs are fluorinated for 2 hours to a stoichiometry of CF_x, ($x < 0.2$).
2. The partially fluorinated SWNTs are pyrolised up to 1000 °C (TGA control, 10 C/min) in an argon atmosphere.
3. In this step the fluorine is driven off the sidewall of the tubes to form CF_4 or COF_2.
4. This leaves behind chemically cut SWNTs in a yield of 55 %, with average lengths of ~ 40 nm. The yield is based on the amount of SWNTs.

The length of the tubes was measured by *AFM* imaging. *TGA, elemental analysis* and *IR* show that during pyrolysis the fluorine is completely driven off the nanotube. The elements that appear due to pyrolysis are also shown in a derivative weight percentage. *Raman* spectra of the purified, fluorinated and cut SWNTs indicate that the defects in the carbonaceous species increase.

B.17 Enhanced saturation lithium composition in ball-milled single-walled carbon nanotubes[70]

The nanotubes are grinded for several minutes up to 20 min, what will induce breaking and disordering the carbon nanotubes. This process is highly time dependent, as longer ball-milling will eventually tear down all the SWNT structures.

The results of ball-milling have been monitored with *TEM* and *SEM* images and with *Raman* spectra. The tubes are shortened and *Raman* spectra indicate that more disordered carbon is produced.

B.18 Chromatographic purification of soluble SWNTs[71]

SWNTs (1.4 nm and lengths of 100 - 300 nm) produced by arc-discharge, after several purification steps, are dissolved and run over a gel permeation chromatographic column:

1. Short SWNTs are functionalised with octadecylamine and solvated in THF.
2. The solution is run over a gel permeation chromatographic column, styragel HMW7.
3. Two main fractions are obtained.
4. The first fraction gives semi-conducting SWNTs.
5. The second fraction does not contain SWNTs, but contains nanoparticles and amorphous carbon.

AFM images have been made of the different fractions. The three HPLC fractions were analysed with continuous *UV-vis* measuring and a complete spectrum of each fraction was made. *NIR* spectra suggest that fraction 1 hardly contains metallic tubes. The yield was estimated with *NIR*. The *Raman spectra, AFM and NIR* show the purity of the fractions.

This method claims to separate and purify semi-conducting and metallic SWNTs. Finally, an estimate of 50% of the initial amount of SWNTs in the soot is recovered, with a high purity.

B.19 Chromatographic purification and properties of soluble SWNTs[72]

SWNTs (1.4 nm and lengths of 100 - 300 nm) produced by arc-discharge, after several purification steps, are dissolved and are run over a gel permeation chromatographic column:

1. Short SWNTs are functionalised with octadecylamine and solvated in THF.
2. The solution is run over a gel permeation chromatographic column, PLgel MIXED-A.
3. Three main fractions have been obtained.
4. The first fraction gives semi-conducting SWNTs.
5. The second fraction gives traces of SWNTs and nanoparticles.
6. The third faction gives amorphous carbon.

AFM images were made from the different fractions. The three fractions were seen with continuous *UV-vis* measuring and a complete spectrum of each fraction was made. The yield was estimated with *NIR*. The *Raman spectra, AFM and NIR* show the purity of the fractions. The *fluorescence* en *NIR* spectra suggest that fraction 1 hardly contains metallic tubes.

This method also claims to separate and purify semi- and metal-conducting SWNTs. The estimated yield is a lot higher than with the technique above. This one recovers 74 % of the initial amount of SWNTs in the soot with high purity.