

# CHAPTER 11

## *Nano-Chemistry: Water solubalisation of single-walled carbon nanotubes using p-sulfonatocalix[4]arene*

*Single-walled carbon nanotubes (SWNT) are decorated with nanoparticles of p-sulfonatocalix[4]arene which render the nanotubes soluble in water. The nano-composite was prepared by a solventless grinding method, followed by the additional of water then sonication. The non-covalently modified carbon nanotubes have been characterized using Raman, FTIR spectroscopy, fluorescence spectroscopy, transmission electron microscope and thermogravimetric analysis.*

## 11.1 Introduction

Attaching organic hydroxyl<sup>[287,288]</sup> or amide<sup>[289,290]</sup> functional groups to SWNTs is effective in dispersing them in water through extensive hydrogen bond formation<sup>[290]</sup>. The incorporation of these functional groups involves a variety of approaches, which includes covalent side wall coupling reactions, end-group reactions and non-covalent interactions<sup>[289]</sup>. Covalent attachment of the organic groups on SWNTs is most effective using cycloaddition and radical addition reactions<sup>[287, 288, 292]</sup>. A significant disadvantage of covalent functionalization, however, is the perturbation of the electronic properties of the SWNTs, and thus side-wall functionalization techniques are less favourable compared to non-covalent functionalization<sup>[289, 292, 293]</sup>. Non-covalent attachment of functional groups to SWNTs involves adsorption of a polynuclear aromatic compounds (anthracene<sup>[294]</sup>, pyrene<sup>[295]</sup>, and porphyrins<sup>[296]</sup>, derivatives), synthetic polymers (polystyrene sulfonate and polyvinyl pyrrolidone)<sup>[295]</sup>, and adsorption of biomolecules (DNA<sup>[298, 299]</sup> and peptides<sup>[300, 301]</sup>). In the non-covalent interaction, aromatic molecules are anchored on the walls of the SWNT where the hydrophobic part is oriented towards the coplanar surface of the nanotubes via effective  $\pi$ - $\pi$  stacking while the polar moiety interacts with the solvent regime<sup>[292, 302, 303, 304]</sup>. The size of the aromatic moiety as well as the curvature of the nanotube surface determine the strength of the  $\pi$ - $\pi$  interactions and for molecules containing heteroatoms, the heteroatom- $\pi$  electron interactions contribute in the interplay of the two components<sup>[13, 302]</sup>.

Polymers bearing sulfonated organic molecules are effective in encapsulating and solubilising carbon nano-tubes in water<sup>[244, 292, 302, 305, 306]</sup>. Instead of using a sulfonated polymer a poly-sulfonated macrocycle, notably *p*-sulfonatocalix[4]arene, was exploited to solubilise SWNT in water. *p*-Sulfonatocalix[4]arene is a cyclic tetramer with hydroxy groups at the lower rim and sulfonate groups at the upper rim. It is shown in this work

that it is effective in solubilising SWNTs in water, which are surprisingly decorated with nanoparticles of the calixarene on the surface of the nanotubes, rather than the calixarene acting as a surfactant with the molecules assembled over the entire surface.

The non-covalent functionalisation of SWNT involves *p*-sulfonatocalix[4]arene. Interestingly the finding is in direct contrast to a recent report that SWNTs are insoluble in the presence of *p*-sulfonatocalix[4]arene, and also *p*-phenol sulfonic acid, but not so for the corresponding calix[6 or 8]arene analogues <sup>[67]</sup>. It is noteworthy that *p*-sulfonatocalix[4 or 6]arenes modified by alkyl substituents on the phenolic oxygen centre can also water solubilise SWNTs <sup>[245]</sup>, as do ‘extended arm’ upper rim functionalised (benzyl, phenyl) *p*-sulfonated calix[8]arenes, and *p*-phosphonated calix[*n*]arenes (*n* = 4, 6, 8) <sup>[247]</sup>, for which the lower oligomer is isoelectronic to the sulfonated calixarene in the present study. The phosphonated calixarene work also involves the use of the calixarenes in separating SWNTs with different diameters and properties <sup>[247]</sup>.

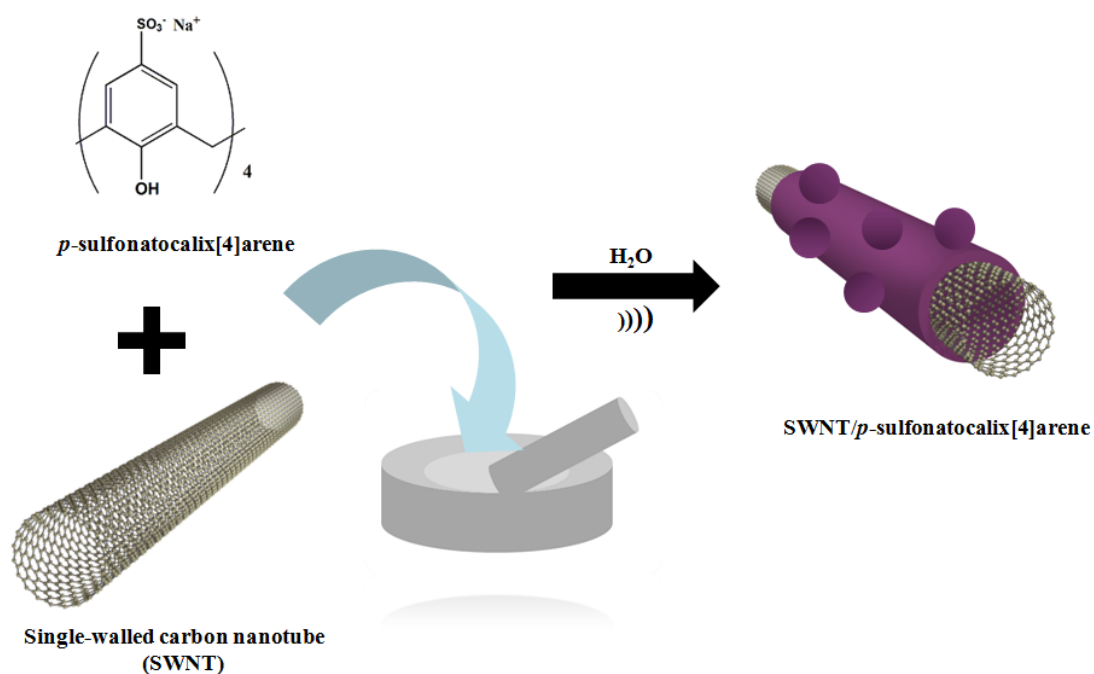
## 11.2 Materials and methods

Single-walled carbon nanotubes (SWNTs) were purchased from Aldrich (diameter: 1.2-1.5 nm, length: 2-5  $\mu$ m) and used without further purification, and sodium *p*-sulfonatocalix[4]arene was synthesized described in Section 3.4.

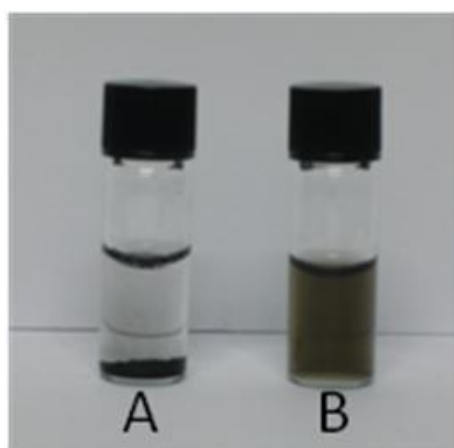
### 11.2.1 Synthesis of water soluble SWNTs

24 mg of *p*-sulfonatocalix[4]arene and 1 mg of SWNT were mechanically ground using mortar and pestle for 25 minutes whereupon 4 mL of deionized water (pH 7.1) was added. The resulting mixture was sonicated in an ultrasonic bath (frequency: 37 kHz,

power: 320 W) for half an hour and then centrifuged for 30 minutes to obtain the dark supernatant of dispersed SWNT, Figure 11.1 and Figure 11.2.



**Figure 11.1** Synthesis procedure for SWNT-*p*-sulfonatocalix[4]arene nano-composite.



**Figure 11.2.** (A) SWNT in water, and (B) SWNT-*p*-sulfonatocalix[4]arene nano-composite material in water.

### 11.2.2 Characterization of the water-soluble SWNTs

Dried solid samples from the supernatant were used for analysis and characterization. Raman spectra were obtained using the excitation wavelength of 785 nm from Raman Systems R-3000CN. FTIR spectra were recorded on Perkin Elmer Spectrum 2000 FTIR spectrometer from 4000 to 400  $\text{cm}^{-1}$  using KBR plates. Fluorescence spectra were collected using Hitachi Fluorescence Spectrophotometer F2000 within 10-mm quartz cuvettes. Transmission Electron Microscope (TEM) images were obtained from samples which were prepared by drop cast of dispersed nanotubes on copper grid carbon film (300 mesh), with Leo Libra 120 microscope operating at an accelerating voltage of 120 kV. Thermogravimetric analysis (TGA) was recorded with a Perkin Elmer Pyris 6 instrument in nitrogen environment at scan rate of 20°C/min from room temperature to 900°C.

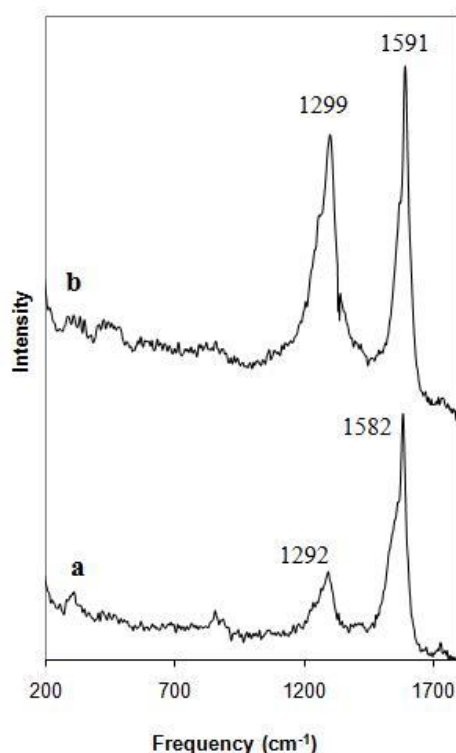
## 11.3 Results and discussion

The synthesis of the SWNT/sulfonated calixarene nano-composite involved grinding the two components with an excess of the calixarene, followed by the addition of water and sonication. The use of excess calixarene was deemed necessary to encourage the formation of material devoid of any inter SWNT interactions, prior to the addition of water, and thus to maximise the amount and stability of the SWNTs suspended in water. Additional calixarene had no effect on the solubilising of the SWNTs.

### 11.3.1 Raman spectroscopy

The Raman spectrum of SWNTs contains major characteristic regions: tangential modes (G-band) at 1540-1600  $\text{cm}^{-1}$  (corresponding to the crystalline graphitic structures), the disorder-induced modes (D-band) at 1270 - 1350  $\text{cm}^{-1}$  (corresponding to

vacancies, substitutional heteroatoms,  $sp^3$  defects, finite-size effects and possibly bending and other carbon nanomaterials) and the radial breathing modes (RBM) at 250-350  $\text{cm}^{-1}$  [302, 307, 308]. The ratio between the intensities of the D-band and G-band, Figure 11.3, gives semi-quantitative indication of the defect concentration or degree of functionalisation of the nanotubes [302, 307, 308-310]. A significant increase in the ratio between the intensities of the D-band and G-band was observed for non-covalent functionalised nanotubes. For the present study, the intensity of the peak in the 1280-1300  $\text{cm}^{-1}$  region increases on association with *p*-sulfonatocalix[4]arene. This reflects a large content of  $sp^3$  hybridized carbon associated with disruption of the aromatic system of the  $\pi$ -electrons on the nanotube walls [287, 311, 312] possibly with solublising other carbon nano-particles [308].



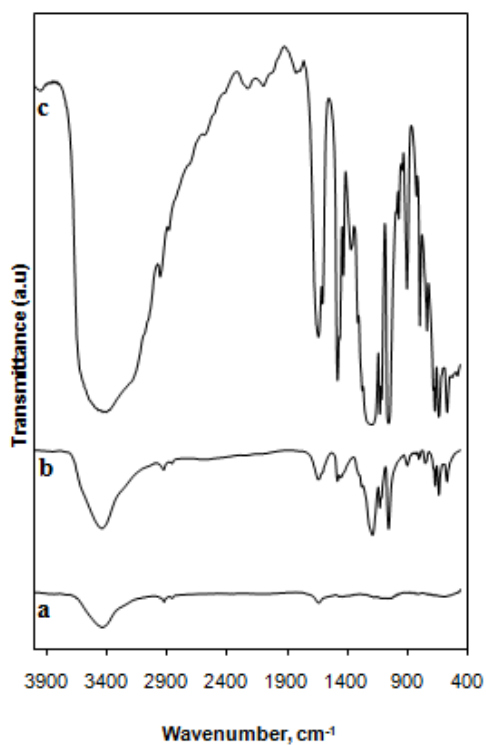
**Figure 11.3.** Raman spectra of (a) pristine SWNT and (b) SWNT/*p*-sulfonatocalix[4]arene nano-composite.

This may be a consequence of the sonication process causing damage to the graphene sheets<sup>[308]</sup>. Broadening in the D-band was observed and this can be explained in terms of the nanotube phonon dispersion<sup>[309]</sup>. High levels of functionalisation caused a large number of defects on the nanotube wall which produces a large number of symmetry-prohibited phonon modes between the D-band and G-band<sup>[309]</sup>. The peak frequency of the D-band in the nano-composite was shifted to higher reciprocal wavenumbers compared with pristine SWNT. In addition, the G-band peak for the nano-composite was shifted from 1582 cm<sup>-1</sup> to 1591 cm<sup>-1</sup>. This reflects a significant interaction between the surface of a SWNT and the nano-particles of sulfonated calixarene decorated on the surface. Such a shift has been noted for related phosphonated calixarenes shrouding SWNTs<sup>[247]</sup>.

### 11.3.2 FTIR spectroscopy

FTIR spectroscopy gives less information about the vibrational properties of carbon nanotubes compared to Raman spectroscopy due to strong absorption of SWNTs in the IR range<sup>[313]</sup>. The FTIR spectra have a weak and broad band at 3400 cm<sup>-1</sup> which can be attributed to the presence of hydroxyl OH groups on the surface of the as-received SWNTs, as well as ambient atmospheric moisture bound to the nanotubes, Figure 11.4. Two weak C-H stretch peaks at 2909 and 2830 cm<sup>-1</sup> are consistent with the stretching modes of C-H stretch peaks of the calixarene, but nevertheless they are consistent with C-H stretch peaks for aliphatic hydrogen on defects of the SWNT side wall<sup>[294]</sup>. A prominent band at 1173 cm<sup>-1</sup> from the sulfonate groups of S=O stretching further supports that the presence of *p*-sulfonatocalix[4]arene in the composite material. FTIR analysis is inconclusive in ascertaining the mode of interaction of the calixarenes at the surface of the nanotube, either through the lower rim hydroxyl groups or the upper rim

sulfonate groups interactions, or most likely through both. This is consistent with the presence of bilayers of self-assembled sulfonated calixarenes themselves<sup>[314]</sup> in the nano-particles of the material decorating the surface of the SWNTs.

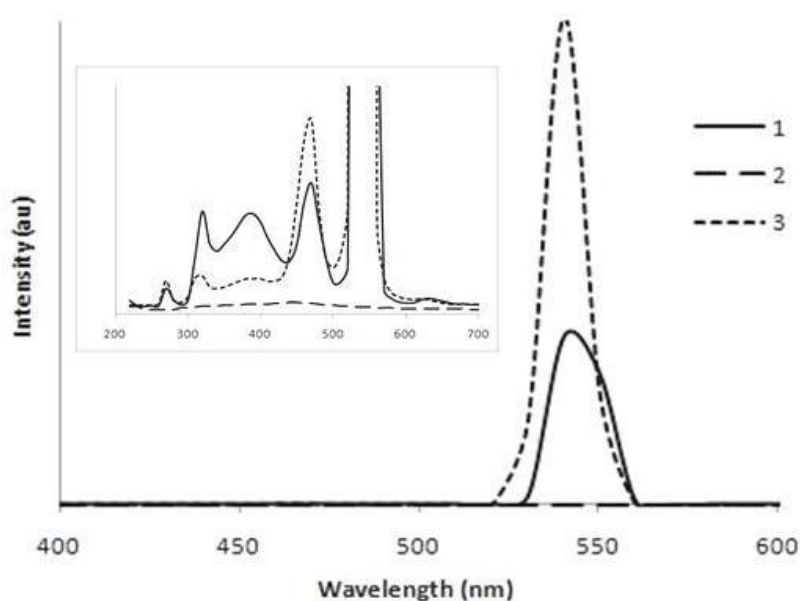


**Figure 11.4.** FTIR spectra of (a) pristine SWNT, (b) SWNT/*p*-sulfonatocalix[4]arene nano-composite, and (c) *p*-sulfonatocalix[4]arene.



### 11.3.3 Fluorescence spectroscopy

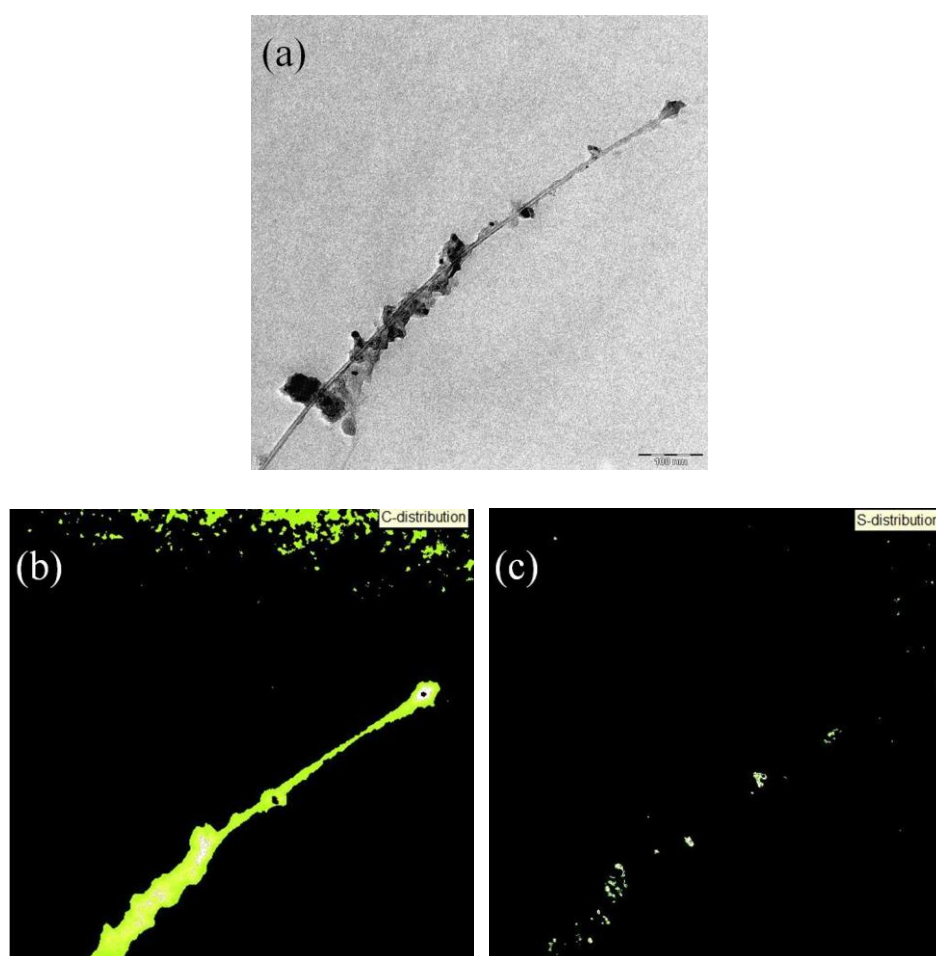
The fluorescence spectrum is shifted by approximately 4 nm, which can be ascribed to electronic communication between the *p*-sulfonatocalix[4]arene particles and nanotubes, Figure 11.5. The excimer fluorescence (above 450 nm) is less pronounced for the *p*-sulfonatocalix[4]arene compared to the functionalized SWNT which signifies that *p*-sulfonatocalix[4]arene is adsorbed on the nanotube surface in some way.



**Figure 11.5.** Fluorescence emission ( $\lambda_{\text{ex}} = 540 \text{ nm}$ ) spectra of (1) *p*-sulfonatocalix[4]arene (6  $\mu\text{M}$ , solid line), (2) pristine SWNT (0.05 wt%, dashed line) and (3) SWNT/*p*-sulfonatocalix[4]arene nano-composite (6  $\mu\text{M}$ , dotted line).

### 11.3.4 Transmission electron microscopy (TEM)

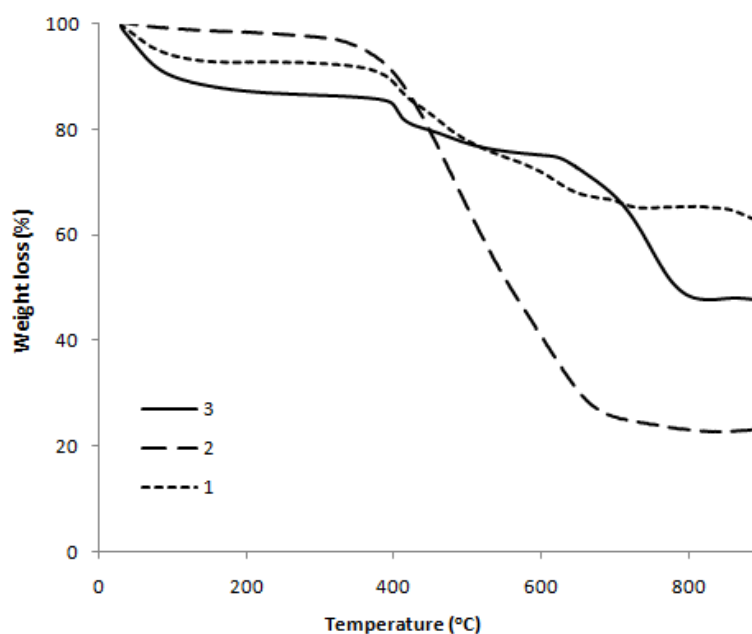
TEM images show *p*-sulfonatocalix[4]arene particles randomly dispersed and adhered along the wall of the SWNT, Figure 11.6. The elemental mapping confirms the presence of the calixarene, with the sulphur map matching the nano-particles adhering to the SWNT, and noting that the only source of sulphur for the reaction and associated work up is from the calixarene.



**Figure 11.6.** (a) TEM images showing the coating of SWNT by *p*-sulfonatocalix[4]arene, (b) carbon element mapping and (c) sulphur element mapping of the decorated SWNT with *p*-sulfonatocalix[4]arene nanoparticles.

### 11.3.5 Thermogravimetric analysis (TGA)

Thermal degradation studies, Figure 11.7, afford further evidence for some covalent sidewall functionalization of SWNT. The TGA data plots showed a higher weight loss for pristine SWNT (approx. 80%) compared to SWNT/*p*-sulfonatocalix[4]arene (approx. 52%). Pristine SWNT began to degrade at approximately 320°C with SWNT/*p*-sulfonatocalix[4]arene degrading at 380°C and clearly shows enhanced thermal stability of SWNT in the presence of the *p*-sulfonatocalix[4]arene. Pure sulfonated calixarene slowly decomposes at approximately 380°C, as for the nano-composite, but the weight loss thereafter is considerably less than for SWNT. This presumably relates to the formation of polymeric material, and the formation of such material for the degradation of the nano-composite is likely to form a protective coating around the SWNTs. An initial weight loss of about 10% for both *p*-sulfonatocalix[4]arene and SWNT/*p*-sulfonatocalix[4]arene is due to loss of moisture in the samples. Overall, the TGA results support the protective effects of *p*-sulfonatocalix[4]arene in the nano-composite.



**Figure 11.7.** TGA thermogram of (1) *p*-sulfonatocalix[4]arene, (2) pristine SWNT, and (3) SWNT/*p*-sulfonatocalix[4]arene nano-composite.

## 11.4 Conclusions

SWNTs can be solubilised in water by mechanical grinding the tubes with *p*-sulfonatocalix[4]arene, followed by sonication in water. The composite material has nano-particles of the calixarene randomly arranged on the surface of the carbon nanotube. This approach has possibilities in using other amphiphiles in solubilising carbon nanotubes in general, where other techniques for dispersing such material are limited. The same approach may also be applicable to stabilising and solubilising other forms of carbon including carbon quantum dots, and composites of different forms of carbon.