Water solublisation of single-walled carbon nanotubes using *p*-sulfonatocalix[4]arene

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Single-walled carbon nanotubes (SWCNTs) are decorated with nanoparticles of *p*-sulfonatocalix[4]arene which render the nanotubes soluble in water. The nanocomposite 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 microscopy and thermogravimetric analysis.

1. Introduction

Single-walled carbon nanotubes (SWCNTs) are rolled-up graphene sheets, which possess remarkable electronic, thermal, optical and mechanical properties.[1–5] They have been intensely studied for various applications, especially for energy storage, and in nanoelectronics and nanodevices.[6–9] However, the strong van der Waals attraction between individual hydrophobic nanotubes results in the formation of large bundles, which are insoluble in water. This has limited the applications of SWCNTs, and necessitates the use of intricate processing.[4,10–13] SWCNTs are also poorly soluble in organic solvents, but this can be overcome using various methods of surface modification. Such methods can also render the SWCNTs soluble in water, which is important in biosensors and drug-delivery systems.[5] Another method to form solubilised SWCNTs in aqueous media is the introduction of amphiphilic molecules as dispersants, such as surfactants[4,13–17] and polymers.[4,5,18,19] Other methods of enhancing the solubilisation and suspension of SWCNTs in aqueous media include chemical modification at the side walls, defect sites and open ends,[4] as well as cutting the long entangled CNTs to short lengths.[20]

Attaching organic hydroxy[21,22] or amide[23–24] functional groups to SWCNTs is effective in dispersing them in water through extensive hydrogen-bond formation.[24] 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.[5] Covalent attachment of the organic groups on SWCNTs is most effective using cycloaddition and radical addition reactions.[19,25–27] A significant disadvantage of covalent functionalisation, however, is the perturbation of the electronic properties of the SWCNTs, and thus side-wall functionalisation techniques are less favourable compared to non-covalent functionalization.[19,28,29] Non-covalent attachment of functional groups to SWCNTs involves adsorption of polynuclear aromatic compounds (anthracene,[30] pyrene[31] and porphyrins[32] derivatives), synthetic polymers (polystyrene sulfonate and polyvinyl pyrrolidone),[11] and adsorption of biomolecules (DNA[33,34] and peptides[35,36]). In the non-covalent interaction, aromatic molecules are anchored on the walls of the SWCNT where the hydrophobic part is oriented towards the coplanar surface of the nanotubes *via* effective π–π stacking while the polar moiety interacts with the solvent regime.[4,19,27,37] The size of the aromatic moiety as well as the curvature of the nanotube surface determine the strength of the π–π interactions and for molecules containing heteroatoms, the heteroatom–π electron interactions contribute to the interplay of the two components.[4,38]

Polymers bearing sulfonated organic molecules are effective in encapsulating and solublising carbon nanotubes in water.[4,14,18,19,39] Instead of using a sulfonated polymer we chose a polysulfonated macrocycle, notably *p*-sulfonatocalix[4]-arene, to solubilise SWCNT in water. *p*-Sulfonatocalix[4]arene is a cyclic tetramer with hydroxy groups at the lower rim and sulfonate groups at the upper rim. Herein we show that it is effective in solublising SWCNTs 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 SWCNT involves *p*-sulfonatocalix[4]arene. This cup-shaped amphiphilic macrocycle is a cyclic tetramer comprised of four phenolic moieties joined by methylene bridges with hydroxy groups at the lower rim and sulfonate groups at the upper rim. Our findings are in direct contrast to a recent report that SWCNTs 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.[40] Interestingly *p*-sulfonatocalix[4 or 6]-arenes modified by alkyl substituents on the phenolic oxygen centre also water-solubilise SWCNTs,[41] as do

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'extended arm' upper rim functionalised (benzyl, phenyl) *p*-sulfonated calix[8]arenes, and *p*-phosphonated calix[*n*]arenes (n = 4, 6, 8),[42] for which the lower oligomer is isoelectronic to the sulfonated calixarene in the present study.[42] Interestingly. the phosphonated calixarene work also involves the use of the calixarenes in separating SWCNTs with different diameters and properties.[42]

2. Materials and methods

Single-walled carbon nanotubes (SWCNTs) were purchased from Aldrich (diameter: 1.2–1.5 nm, length: 2–5 μm) and used without further purification, and sodium *p*-sulfonatocalix[4]-arene was synthesized according to an adaptation of literature procedures.[43]

Synthesis of water-soluble SWCNTs

24 mg of *p*-sulfonatocalix[4]arene and 1 mg of SWCNT were mechanically ground using a 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 SWCNT (Fig. 1).

Characterization of the water-soluble SWCNTs

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

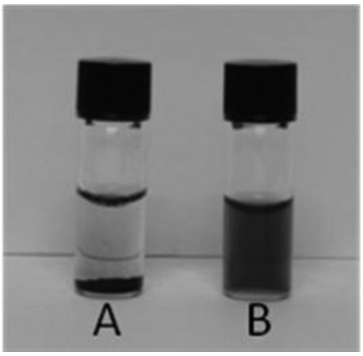

Fig. 1 (A) SWCNT in water, and (B) SWCNT-*p*-sulfonatocalix[4]-arene nanocomposite material in water.

3. Results and discussion

Synthesis

The synthesis of the SWCNT–sulfonated calixarene nanocomposite 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-SWCNT interactions, prior to the addition of water, and thus to maximise the amount and stability of the SWCNTs suspended in water. Additional calixarene had no effect on the solublising of the SWCNTs.

Raman spectroscopy

The Raman spectra of SWCNTs contain major characteristic regions: tangential modes (G-band) at 1540–1600 cm^{-1} (corresponding to the crystalline graphitic structures), the disorder-induced modes (D-band) at 1270–1350 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 cm^{-1}.[4,20,44] The ratio between the intensities of the D-band and G-band (Fig. 2) gives a semi-quantitative indication of the defect concentration or degree of functionalisation of the nanotubes.[4,20,44–46] 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 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 π-electrons on the nanotube walls[21,47,48] possibly with solublising other carbon nanoparticles.[44]

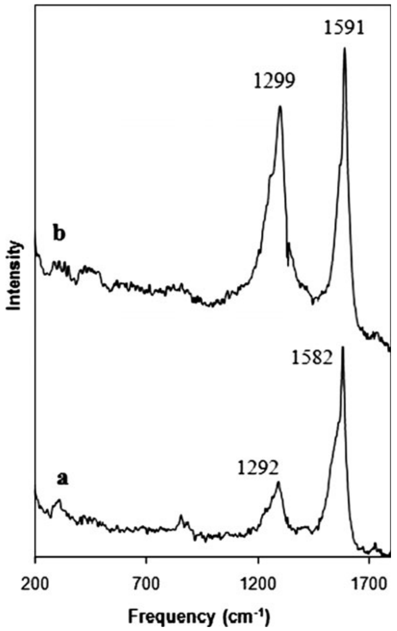

Fig. 2 Raman spectra of (a) pristine SWCNT and (b) SWCNT–*p*-sulfonatocalix[4]arene nanocomposite.

This maybe a consequence of the sonication process causing damage to the graphene sheets.[44] Broadening in the D-band was observed and this can be explained in terms of the nanotube phonon dispersion.[45] 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.[45] The peak frequency of the D-band in the nanocomposite was shifted to higher reciprocal wavenumbers compared with pristine SWCNT. In addition, the G-band peak for the nanocomposite was shifted from 1582 cm^{-1} to 1591 cm^{-1}. This reflects a significant interaction between the surface of a SWCNT and the nanoparticles of sulfonated calixarene decorated on the surface (see below). Such a shift has been noted for related phosphonated calixarenes shrouding SWCNTs.[42]

FTIR spectroscopy

FTIR spectroscopy gives less information about the vibrational properties of carbon nanotubes compared to Raman spectroscopy due to strong absorption of SWCNTs in the IR range.[49] The FTIR spectra have a weak and broad band at 3400 cm^{-1} which can be attributed to the presence of hydroxyl OH groups on the surface of the as-received SWCNTs, as well as ambient atmospheric moisture bound to the nanotubes (Fig. 3). Two weak C–H stretch peaks at 2909 and 2830 cm^{-1} 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 SWCNT side wall.[30] A prominent band at 1173 cm^{-1} from the sulfonate groups of $S{=}O$ stretching further supports 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[50] in the nanoparticles of the material decorating the surface of the SWCNTs.

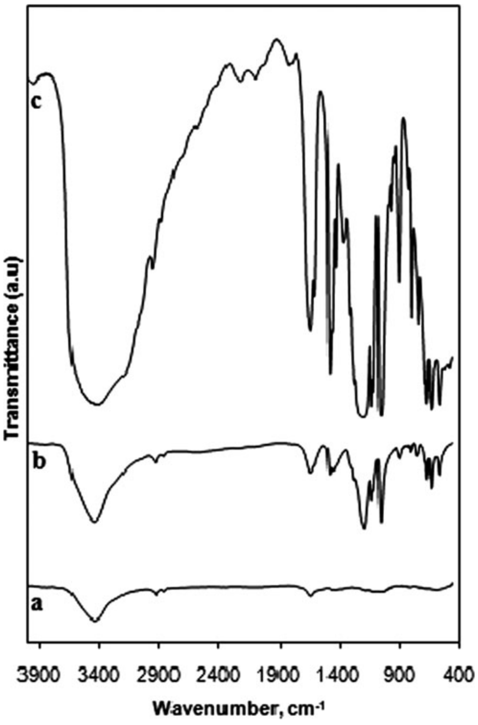

Fig. 3 FTIR spectra of (a) pristine SWCNT, (b) SWCNT–*p*-sulfonatocalix[4]arene nanocomposite, and (c) *p*-sulfonatocalix[4]arene.

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 (Fig. 4). The excimer fluorescence (above 450 nm) is less pronounced for the *p*-sulfonatocalix[4]arene compared to the functionalized SWCNT which signifies that *p*-sulfonatocalix[4]arene is adsorbed on the nanotube surface in some way.

Transmission electron microscopy (TEM)

TEM images show *p*-sulfonatocalix[4]arene particles randomly dispersed and adhered along the wall of the SWCNT (Fig. 5). The elemental mapping confirms the presence of the calixarene, with the sulfur map matching the nanoparticles adhering to the SWCNT, and noting that the only source of sulfur for the reaction and associated work-up is from the calixarene.

Thermogravimetric analysis (TGA)

Thermal degradation studies (Fig. 6) afford further evidence for some covalent side-wall functionalization of SWCNT. The TGA data plots showed a higher weight loss for pristine SWCNT (approx. 80%) compared to SWCNT–*p*-sulfonatocalix[4]arene (approx. 52%). Pristine SWCNT began to degrade at approximately 320 °C with SWCNT–*p*-sulfonatocalix[4]arene degrading at 380 °C and clearly shows enhanced thermal stability of SWCNT in the presence of the *p*-sulfonatocalix[4]arene. Pure sulfonated calixarene slowly decomposes at approximately 380 °C, as for the nanocomposite, but the weight loss thereafter is considerably less than for SWCNT. This presumably relates to the formation of

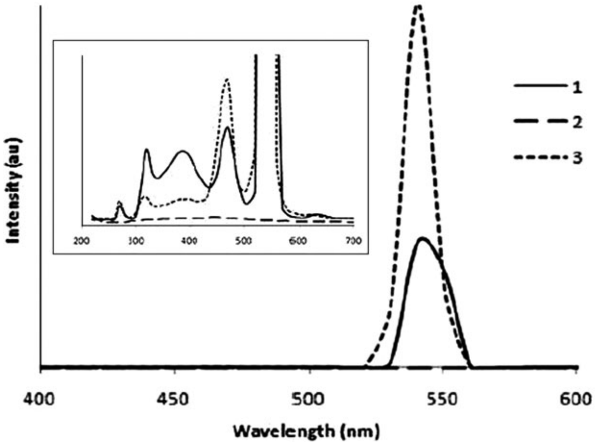

Fig. 4 Fluorescence emission (λ_{ex} = 540 nm) spectra of (1) *p*-sulfonatocalix[4]arene (6 μM, solid line), (2) pristine SWCNT (0.05 wt%, dashed line) and (3) SWCNT–*p*-sulfonatocalix[4]arene nanocomposite (6 μM, dotted line).

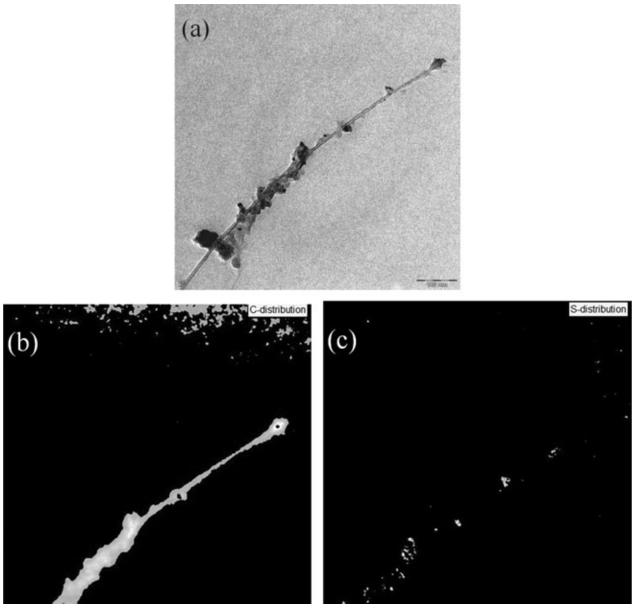

Fig. 5 (a) TEM images showing the coating of SWCNT by *p*-sulfonatocalix[4]arene, (b) carbon element mapping and (c) sulfur element mapping of the decorated SWCNT with *p*-sulfonatocalix[4]-arene nanoparticles.

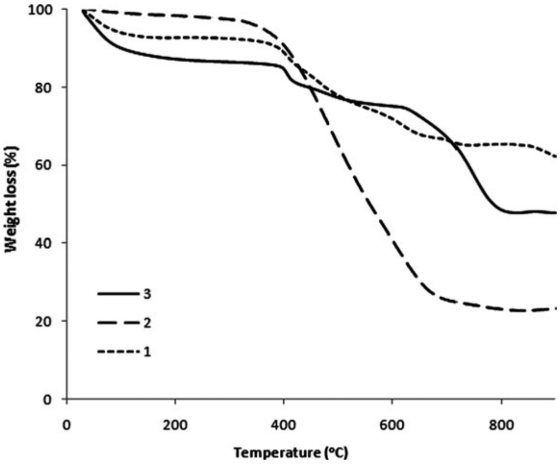

Fig. 6 TGA of (1) *p*-sulfonatocalix[4]arene, (2) pristine SWCNT, and (3) SWCNT–*p*-sulfonatocalix[4]arene nanocomposite.

polymeric material, and the formation of such material for the degradation of the nanocomposite is likely to form a protective coating around the SWCNTs. An initial weight loss of about 10% for both *p*-sulfonatocalix[4]arene and SWCNT–*p*-sulfonatocalix[4]arene is due to a loss of moisture in the samples. Overall, the TGA results support the protective effects of *p*-sulfonatocalix[4]arene in the nanocomposite.

4. Conclusions

SWCNTs can be solubilised in water by mechanical grinding the tubes with *p*-sulfonatocalix[4]arene, followed by sonication in water. The composite material has nanoparticles of the calixarene randomly arranged on the surface of the carbon nanotube. This approach has possibilities in using other amphiphiles in solublising 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.

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