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Quantitative monitoring of the removal of non-encapsulated material external to filled carbon nanotube samples

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Markus Martincic,[a] ElzbietaPach,[b] Belén Ballesteros[b] and Gerard Tobias*[a]

The endohedral functionalization of carbon nanotubes with both organic and inorganic materials allows the development of tailored functional hybrids which properties benefit from the synergies of the constituent compounds. Bulk filling of carbon nanotubes (CNTs) results in samples that contain a large amount of non-encapsulated material external to the CNTs. The presence of the external material is detrimental for the processing and application of the resulting hybrids. Here we introduce the use of UV-Vis spectroscopy to monitor the cleaning process, i.e. the elimination of non-encapsulated compounds. Chrome Azurol S has been employed to assess the bulk removal of external samarium(III) chloride from filled single-walled carbon nanotubes. Chrome Azurol S is of interest since it can be used to quantify a large variety of materials in a fast, accurate and reliable manner. The parameters that control the cleaning process have been optimized, including time, temperature, volume and sonication, to achieve a fast and complete removal of the external material.

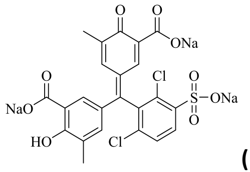
Introduction

Carbon nanotubes (CNTs) have intrigued the scientific community since the report by Iijima in 1991,[1] showing a continuous increase of published papers and patents over the years. Their unique properties make them suitable materials for many applications including electronics, photonics, and nanomedicine.[2-4] The availability of the external wall and inner cavity for exohedral and endohedral functionalization respectively makes them a singular nanoplatform for targeting, protection and delivery of desired compounds.

Since the first theoretical report by Pederson and Broughton back in 1992 highlighting the potential of carbon nanotubes to host materials in their interior,[5] a wide variety of organic and inorganic compounds have been experimentally encapsulated inside carbon nanotubes.[6-10] Filled carbon nanotubes find their applications in different fields such as drug delivery and medical diagnostics,[8] magnetoelectronics,[11] molecular electronics,[12] cell tracking,[13] nanothermometry[14] and controlled growth of layered materials[15] to name some.

Regardless of the method employed for the encapsulation of materials into carbon nanotubes, bulk filling always results in a large amount of undesired external material (impurities). Electron microscopy is being widely employed to confirm both the filling and the presence/absence of external material. However, it is generally time-consuming and provides local information of the sample. The aim of this work was to establish a versatile, quick, easy and cheap methodology that allows monitoring of the cleaning process of bulk samples of filled carbon nanotubes.

There are various analytical spectrophotometric methods described that allow the determination of ions in solution (both anions and cations). The range of ions that can be determined can be greatly expanded by coupling with specific organic ligands.[16, 17] For instance, a combination of Chrome Azurol S (CAS) **(1)**, an organic colorimetric reagent, with surfactants has been widely used for colorimetric analysis of different metal salts such beryllium,[18] aluminium,[19] iron,[20] europium[21] and samarium.[22] Cetylpiridinium chloride (CPC) **(2)**, a cationic surfactant, is one example of such materials that enhance significantly the sensitivity and detection limit of the analysis.



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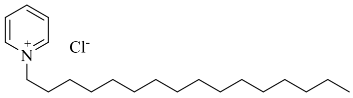

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In this work we present a quantitative monitoring and optimization of the washing protocol used for the removal of non-encapsulated samarium(III) chloride from a sample of

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[a] Institut de Ciencia de Materials de Barcelona (ICMAB-CSIC), Campus de la UAB, 08193 Bellaterra, Barcelona, Spain. E-mail: gerard.tobias@icmab.es; Tel. +34 935 801 853, Fax. +34 935 805 729

[b] Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and The Barcelona Institute of Science and Technology, Campus UAB, Bellaterra, 08193 Barcelona, Spain.

Electronic Supplementary Information (ESI) available: Thermogravimetric analyses. Raman spectra of $SmCl_3$ filled SWCNTs. HAADF STEM image of a partially washed sample. Method for the determination of filling yield. See DOI: 10.1039/x0xx00000x samarium(III) chloride filled single-walled carbon nanotubes ($SmCl_3$@SWCNTs). Samarium is a rare earth metal that naturally occurs in several minerals such as samarskite, gadolinite, monazite, cerite and bastnasite. A relatively low toxicity of its compounds and radionuclides makes it a suitable candidate for cancer therapy. One of such compounds is samarium lexidronam (^{153}Sm) used for treating bone metastases in hormone-refractory prostate cancer.[23] In this context, $^{153}SmCl_3$@SWCNTs arise as promising nanocarriers for nuclear medicine for both diagnosis and cancer treatment. We have recently shown that the confinement of radionuclide crystals within the cavities of carbon nanotubes allows ultrasensitive imaging and the delivery of unprecedented radio-dose densities.[24] Therefore, the complete removal of external non-encapsulated material is important in order to achieve high purity carbon nanocapsules[25] (filled carbon nanotubes) for further *in-vitro* and *in-vivo* studies. The methodology reported herein will allow not only an optimum cleaning of radionuclide-filled nanotubes, which is imperative when dealing with radioisotopes, but also the monitoring and cleaning of samples of filled tubes with a wide variety of materials of interest not only for biomedicine but also for electronics, sensors and optical devices, to name a few.

Experimental

Anhydrous samarium(III) chloride, samarium(III) chloride hexahydrate, Chrome Azurol S and cetylpiridinium chloride were all purchased from Sigma Aldrich. Aqueous solutions of chrome azurol S and cetylpiridinium chloride (0.2 % w/v) were prepared separately by dissolving 100 mg in 50 mL of distilled water in a volumetric flask. For the calibration curve, 18.2 mg of samarium(III) chloride hexahydrate was transferred into a 100 mL calibrated flask and dissolved with distilled water up to the mark. UV-Vis spectroscopy was performed in a Cary 5.0 UV-Vis double beam spectrophotometer using 10-mm optical path quartz cells. The pH of the solutions was checked by a Mettler Toledo FE20/EL20 pH meter with a glass electrode.

Single-walled carbon nanotubes (SWCNTs) were provided by Thomas Swan Co. Ltd. (Elicarb®). As-received SWCNTs contain impurities of amorphous carbon, graphitic particles and metal catalyst. Therefore, before proceeding to the bulk filling of the SWCNTs with the selected compound, the sample was steam purified following a previously reported protocol.[26] Steam has been reported to open the ends of the carbon nanotubes whilst preserving the integrity of the tubular structure.[27, 28] Thus steam treated CNTs are suitable for the containment of chosen payloads. For the steam purification, 400 mg of SWCNTs were placed into a tubular furnace and heated up to 900 ºC for 4 hours under an argon/steam flow. The purification process was repeated twice to obtain the amount of purified SWCNTs required for the filling experiments. The steam treatment results in the removal of the CNT ends, the amorphous carbon and some graphitic shells that might be in turn covering catalytic particles. Therefore, a subsequent treatment in 6 M HCl was performed overnight at 110 ºC to remove the now exposed metal nanoparticles.[27] The sample was filtered, neutralized with water and left for drying overnight at around 80 ºC. In an argon-filled glovebox, purified single-walled carbon nanotubes (around 400 mg) were ground with an agate mortar and pestle with dry samarium(III) chloride, in a mass ratio of 1 to 10 respectively, until the mixture presented a uniform color. The sample was then split and vacuum sealed in four silica tubes, that were annealed at 900 ºC for 12 hours leading to SWCNTs filled with samarium(III) chloride ($SmCl_3$@SWCNTs); see Fig. 1 for an schematic representation of the filling process. We employed 900 ºC since this temperature is above the melting point of $SmCl_3$, a requirement for the molten filling of carbon nanotubes, and it leads to closed-ended filled SWCNTs.[29] Since both the encapsulated and external material are of the same nature, it is necessary to seal the ends of the nanotubes to allow the removal of the external material whilst preserving the encapsulated compounds.[29-31] We have previously shown that when performing the filling experiment under high temperature melting condition, as in the present case, the ends of the tubes seal during cooling and therefore the cooled filling material is sealed inside closed-ended SWCNTs.[25, 29] After the filling process, the silica tubes were opened and the four samples were ground together leading to a large homogenous sample that was employed for this study.

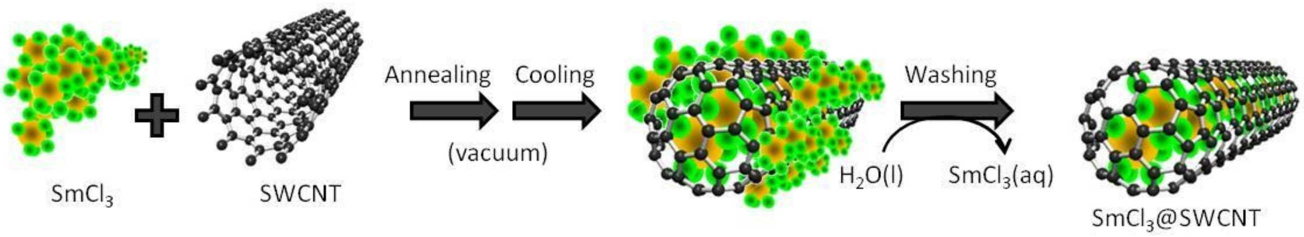

Fig. 1 Schematic representation of the filling of carbon nanotubes (carbon atoms represented as grey spheres). The encapsulation of samarium(III) chloride (green and yellow spheres) inside carbon nanotubes consists of molten phase filling and cooling down the sample. This process leads to close-ended filled nanotubes with a large amount of external material. Finally the sample is washed in water in order to remove the non-encapsulated samarium(III) chloride.

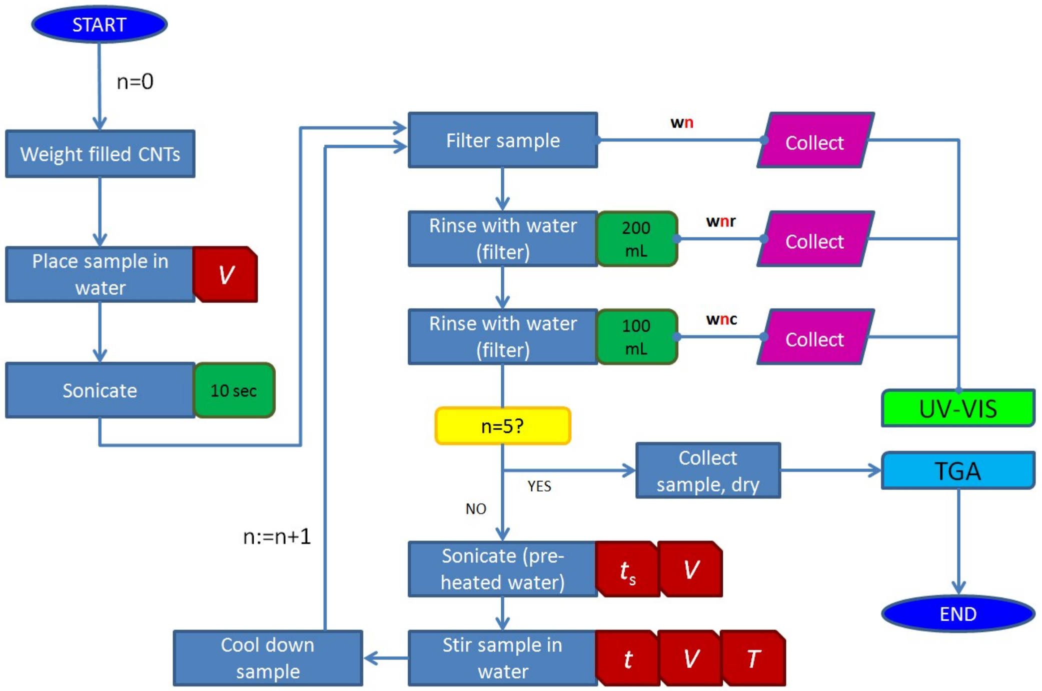

Fig. 2 Algorithmic scheme of the washing protocol used to monitor the washing efficacy in the removal of external samarium(III) chloride from SmCl$_3$@SWCNTs. The variable parameters are marked in the rectangles and changed between different washings systematically. Volume (*V*), time of sonication (t_s), time of stirring (*t*) and temperature (*T*) are parameters that have been changed during the washing protocols. The sample was placed in water (*V*) and sonicated for 10 seconds (w0), filtered and rinsed first with 200 mL of water (w0r) and then rinsed with 100 mL of water (control; w0c). This pre-washing step (n=0) was performed whilst keeping the sample on top of the filter membrane. The sample was next sonicated (t_s) and left for stirring in a given amount of water (*V*), at a given temperature (*T*) for a given time (*t*). After cooling down (the operator := increases, therefore n=1), the protocol was repeated by filtering (w1), rinsing (w1r and w1c) the sample with water, stirring it and cooling it down. This was repeated until w5c was collected (n=5).

The experimental parameters involved in the removal of external samarium chloride were optimized using the algorithmic scheme presented in Figure 2. For each optimization, 150 mg of filled carbon nanotubes, with external material present, were dissolved in a given volume of water (*V*) and sonicated for 10 seconds (pre-washing) in order to remove large amounts of external non-encapsulated material. The sample was then filtered through a 47 mm polycarbonate membrane with 200 nm pore size, and the filtrate collected (wn). Without collecting the solid sample from the membrane, the sample was rinsed with 200 mL of water and the resulting filtrate was again collected for further analysis (wnr). Finally an additional 100 mL were passed through the sample and the filtrate collected as a control (wnc). The solid sample was then collected from the membrane and placed in the same volume of water employed during the initial pre-washing step (*V*). The employed water was already pre-heated at a chosen temperature (*T*). The sample was initially sonicated for a given period of time (t_s) followed by a continuous stirring (for time *t*) while keeping the temperature *T* constant. The sample was then cooled down in ice to room temperature, filtered (collected filtrate: w1) and rinsed on top of the filter membrane with 200 mL of water (collected filtrate: w1r). As described in the pre-washing steps, an additional rinsing with 100 mL was performed that served as control to confirm the absence of samarium in the filtrate (collected filtrate: w1c). The solid powder was collected from the membrane and this protocol was repeated five times as shown in the algorithmic scheme. After the fifth washing procedure was completed, the sample was dried and analyzed by thermogravimetric analysis (TGA) under flowing air in a TA instrument TGA Q5000-IR, using around 5 mg of sample for the analysis, 10 ˚C/min heating rate and 25 mL/min of gas flow for the analysis. All the collected solutions were characterized by UV-Vis spectroscopy. Prior to sample collection, all vials were rinsed with the solution of interest. Fresh CPC and CAS solutions were always prepared before UV-Vis analysis. The measurements were performed at 509 nm for Sm-CAS-CPC complex against blank CAS-CPC of the same concentration.

An additional sample of SmCl$_3$@SWCNTs was independently prepared that was employed to test the washing protocol using the optimized parameters. This sample underwent the same purification and filling protocols.

Electron microscopy characterization was performed in a FEI Magellan 400L XHR SEM at 20 keV in transmitted electrons mode using a high angle annular dark field (HAADF) STEM detector and specially adapted holder. Energy dispersive X-Ray (EDX) spectra were acquired using a FEI Tecnai G2 F20 operated at 200 keV and equipped with an EDAX super ultra-thin window (SUTW) X-ray detector. The samples were deposited on a copper grid coated with a lacey carbon film (Agar Scientific) from a dispersed solution in hexane (Sigma Aldrich).

Results and discussion

The calibration curve for Sm^{3+} in the presence of CPC and CAS is presented in Figure 3. Samarium(III) chloride hexahydrate was employed to prepare the calibration curve because dry samarium(III) chloride is moisture and air sensitive and therefore unsuitable to prepare solutions of a given known concentration. Following the work by *Soylak et al.*,[22] CPC and CAS were added to each of the solutions to enhance the detection limit and sensitivity of the system. The pH of all the solutions was between 6.7 and 7.0 and no buffer was added in any of the analyzed samples. As it can be observed in Figure 3a, two distinctive peaks are clearly visible at 509 nm and 620 nm arising from the Sm-CPC-CAS complex. The maximum absorption values for each of the peaks upon dilution are presented in Figure 3b. Fitting this data to two independent regression lines the following equations can be derived: $y = 0.0840x + 0.0169$ at 509 nm ($R^2 = 0.9991$), and $y = 0.0612x – 0.0353$ at 620 nm ($R^2 = 0.9869$). The equation derived from the peak at 509 nm presents a higher degree of sensitivity and lower detection limit and thus will be employed for further analysis.

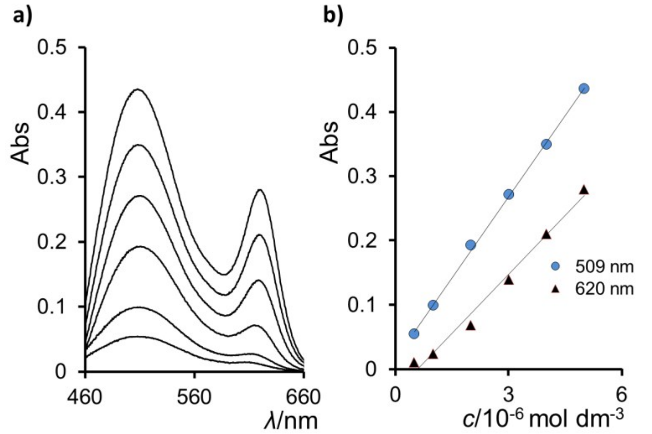

Fig. 3 a) UV-VIS spectra of the prepared samarium(III) standards with CPC and CAS showing two peaks present at 509 and 620 nm with a bathochromic shift in the latter one up to 10 nm; b) calibration plot for the two peaks showing an increased sensitivity and detection limit for the peak at 509 nm

Following the algorithmic scheme presented in Figure 2, we have investigated the role of several parameters employed for the removal of the external non-encapsulated material from samples of filled SWCNTs. First, we studied the effect of time (*t*) when stirring a sample in a given volume (100 mL) at a set temperature (80 °C). We used 10 min, 1 h and 24 h as control points (Fig 4a). Both 10 min and 1 h led to similar removal profiles, whereas in the case of one day (24 h), removal of external material was still visible after the second washing (w2). However, taking into account that 10 min and 1 hour treatments can be performed several times in 24 h, it seems sensible to employ shorter treatments to render a clean sample free of external material.

Next, using still the same volume of water (100 mL), the time was set to 10 min for each of the washing steps, and we investigated the effect of temperature (*T*), which was held at 50 °C, 80 °C and 110 °C. As it can be seen in Figure 4b, 50 °C turned out not to be efficient and removal of external material was observed only when the solution was heated to either 80 °C or 110 °C. Treatment of carbon nanotubes with boiling water is being employed for the purification of the material; it leads for instance to the disintegration of arc-discharged soot to submicron-sized particles, and the removal of aromatic carboxylic acids.[32, 33] Although these are both of interest for the removal of carbon based impurities, the use of milder conditions (80 °C) appear to be desirable in the present study, thus avoiding the use of boiling water. Volume (*V*) plays a specific role in the washings since it changes the concentration of the solutions. We kept the temperature of the solution and time of stirring constant (10 min at 80 °C), while employing volumes of 50 mL, 100 mL and 200 mL of water. As it can be seen in Figure 4c, the smaller the volume employed the more efficient turned out to be the washing step. The profile for 50 mL shows removal of external material even after the third washing (w3) making it the optimum volume for the case of study. We argue that the smaller volume leads to a better washing efficiency since if forces the sample to get closer to the stirrer achieving an improved dispersion of the non-encapsulated material.

To complete this study the role of sonication was also investigated since it is widely used to disperse and debundle SWCNTs. Different sonication times (t_s) were applied, namely 0, 5 and 10 min, while the rest of parameters where kept constant (Fig. 4d). Indeed by looking at the removal profile of external material in Figure 4d it becomes clear that sonication helps in detaching external samarium chloride material from the sample, since removal of external material can still be detected after the second washing (w2) for both 5 and 10 min of sonication. The efficacy of bath sonication in dispersing CNT samples is highly dependent on the position of the sample within the bath, and might account for the higher efficiency observed for 5 min with respect to the 10 min sonication treatment, which in principle seems contradictory. We suggest the use of 5 min to aid in the removal of external material. It has been reported that sonication might lead to structural damage of carbon nanotubes.[34] Therefore, we analyzed by Raman spectroscopy the three samples of $SmCl_3$@SWCNTs submitted to 0 min, 5 min and 10 min sonication (Fig. S1). The D to G band intensity ratios have a similar values irrespective of whether the sample has been subjected to sonication or not, indicating that no structural damage has been introduced during the sonication process employed in the present study.

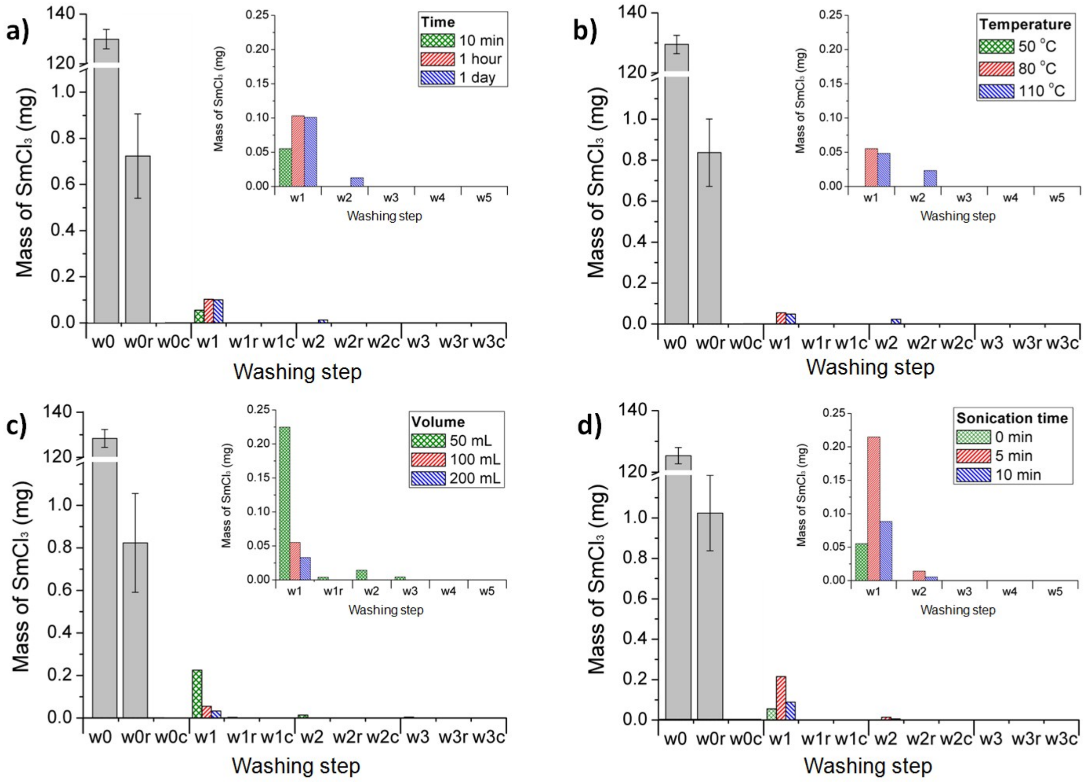

Fig. 4 Mass profile of removed non-encapsulated samarium(III) chloride from $SmCl_3$@SWCNTs after each of the cleaning/washing steps. Pre-washing step is marked in gray and is independent of the washing protocol employed. a) Effect of time of stirring (t) where the parameters V=100 mL, t_s = 0 min and T = 80 °C were kept constant, b) effect of temperature(T) where the parameters V = 100 mL, t_s = 0 min and t = 10 min were kept constant, c) effect of volume (V) where the parameters t = 10 min, t_s = 0 min and T= 80 °C were kept constant, d) effect of sonication time (t_s) where the parameters V = 100 mL, t = 10 min and T = 80 °C were kept constant. A detail of the mass profiled of $SmCl_3$ removed by each of the washing steps (w1 to w5) is included as an inset for each of the optimized parameters (up to n = 5).

To evaluate the efficacy of the washing protocols, thermogravimetric analysis (TGA) was next performed on the solid powder collected after the final (fifth) washing, as indicated in Figure 2. TGA being a bulk technique allows the quantitative assessment of the amount of material encapsulated in filled carbon nanotubes provided they are clean from non-encapsulated material.[35] During the TGA experiment on the filled samples in flowing air, the filled material reacts with oxygen forming samarium oxide, a solid residue. Any other inorganic material present in as-received nanotubes, will also contribute to the residue obtained after the complete combustion of the sample. In the present study, the steam purified nanotubes present a 2.1 wt% of inorganic solid residue after the TGA analysis in flowing air, which can be attributed to Fe_2O_3 from the oxidation of the Fe catalyst.[27] This implies an iron content of 1.5 wt. % in the purified sample. Since the ratio Fe/C will be preserved after the filling experiment, the major contribution to the residue obtained after the TGA of filled tubes will correspond to Sm_2O_3, to which both filled and non-encapsulated material would contribute. Therefore if the sample has not been properly washed, the presence of external material would lead to a higher TGA residue than expected. On the other hand, if the sample has been cleaned through harsh protocols that damage the tubular structure of the nanotubes, release of the encapsulated material would occur and a lower TGA residue would be observed. The error of the TGA measurement was determined by repeating five times the TGA analysis on one of the samples ($SmCl_3$@SWCNTs cleaned under the following conditions: t = 10 min; T = 80 °C; V = 100 mL; t_s = 0 min). The value of inorganic residue in this sample was determined to be 15.8 ± 0.41 wt.%. All the prepared samples of $SmCl_3$@SWCNTs free of external $SmCl_3$ lead to a similar TGA residue, within experimental error, indicating that in all the cases a clean sample was obtained (Table S1). Only the sample treated at 50 °C presented a slightly higher inorganic residue, outside the statistical window, indicating that this sample still had some external material. This is in agreement with the above analysis of Fig 4b where we observed that higher temperature was needed in order to remove the non-encapsulated material.

It is worth pointing out that despite several parameters have been optimized in order to remove the external material in a fast and efficient manner, namely time, temperature, volume and sonication, the pre-washing treatment (w0, areas marked in grey in Fig. 4) proved to be the most efficient step. This pre-washing removes over 99% of external samarium chloride. It consists of a short sonication step (10 s) of the as-filled SWCNT sample in water, followed by filtration of the sample (w0). Sonication is employed to disperse the nanotubes, at least partially, and detach the external material from their walls. The solid sample on top of the filter membrane is then rinsed twice with additional water (w0r and w0c). The first filtration (w0) results in the highest amount of removed material (127.25 ± 2.96 mg, average from 9 samples). A considerable quantity of material is still removed (1.07 ± 0.38 mg, average from 9 samples) when the sample is rinsed on top of the membrane (w0r). This corresponds to material that has been dissolved, but remained in the solvent wetting the carbon nanotubes and did not cross the polycarbonate membrane in the first filtering step. By performing an additional rinsing no further samarium chloride is detected in the filtrate (w0c). Therefore this second rinsing served to control that no additional samarium chloride could be removed from the sample just by passing additional water. At this point it is necessary to collect the sample and proceed to a new set of washing steps were the volume employed along with an adequate heating, stirring and sonication aids the detachment and dissolution of external, non-encapsulated compounds. Although water at room temperature is employed for the pre-washing steps, once this step is completed, stirring the sample at 50 ^{o}C in subsequent steps did not result in further removal of external material, at least to a detectable level by UV-Vis analysis of the filtrates. This suggests that to achieve a sample of purified filled tubes temperature plays an important role in ensuring the complete removal of external material. The solubility of a compound in a given solvent is temperature dependent and therefore it is worth paying special attention to this parameter when dealing with the removal of external material from filled tubes.

Next, two additional samples of $SmCl_3$@SWCNTs with external material were washed to test the efficacy of the optimized parameters. For the first sample, the amount of filled carbon nanotubes was kept at 150 mg (as per the optimization of the parameters) and the following parameters were employed: time of stirring (t) of 1 hour, volume of water (V) of 50 mL, temperature (T) of 80 ^{o}C and sonication time (t_s) of 5 minutes. The washing protocol was the same as described in the algorithmic scheme 2 and the removal of external material was followed by UV-Vis of the filtrate (Fig. 5). As it can be seen an efficient removal of external material is achieved under these experimental conditions. To get some insights on the scalability of the washing protocol, a larger sample (300 mg) of filled tubes was employed. In this case all the parameters were kept the same (T = 80 ^{o}C; t_s = 5 min) or proportional (V = 100 mL) than in the case of the previous sample with the exception of the time of stirring that was reduced to 10 min (t). There is a clear interest in minimizing the time of any process, but bearing in mind that filled tubes hold potential in nuclear medicine, we wanted to keep time to the minimum, a key parameter when dealing with radionuclides. The removal of external material was also monitored by UV-Vis spectroscopy analysis of the filtrates (Fig. 5). In both cases no detectable amount of samarium was present in the filtrates after the fifth wash indicating that purified samples, clean of external non-encapsulated material had been obtained. Therefore the non-encapsulated material can be efficiently removed in less than 1 h from a sample as large as 300 mg.

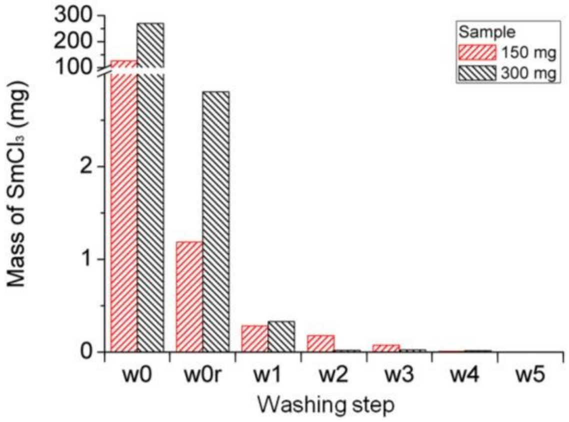

Fig. 5 Mass profile of removed non-encapsulated samarium(III) chloride from $SmCl_3$@SWCNTs from two independent samples of $SmCl_3$@SWCNTs using the optimized parameters. Starting with 150 mg and 300 mg of sample.

The purity of the prepared material was finally assessed by electron microscopy analysis. Whereas UV-Vis spectroscopy provides information on the bulk material, electron microscopy provides local information down to the atomic scale and has been widely used for the investigation of filled carbon nanotubes.[36, 37] HAADF STEM images of the sample before and after washing with the optimized parameters are presented in Fig. 6a and b. In this imaging modality, the contrast offered by an element scales with its atomic weight. Therefore, the brighter contrast corresponds to the samarium chloride or any residual catalytic iron nanoparticles, whereas carbon appears as a pale grey. Before the washing procedure large particles of external $SmCl_3$ are clearly visible on the bundles of filled carbon nanotubes (Fig. 6a). In contrast, a careful examination of the sample after employing the optimized washing protocol reveals the absence of external material (Fig. 6b), that would appear as bright particles. Also, white strings along the carbon nanotube bundles are clearly observed confirming the encapsulation of samarium(III) chloride inside the nanotubes. Analysis of a sample that has been partially washed shows the presence of both external material and filled SWCNTs (Fig. S2). Energy dispersive X-ray spectroscopy (EDX) confirms the presence of Sm and Cl in the samples of $SmCl_3$@SWCNTs before and after being thoroughly washed (Fig. 6c). As expected, the washed sample presents a lower intensity of both the Sm and Cl peaks due to the absence of external material. The performed electron microscopy analyses proved the encapsulation of samarium(III) chloride and removal of external, non-encapsulated, material with the optimized protocol.

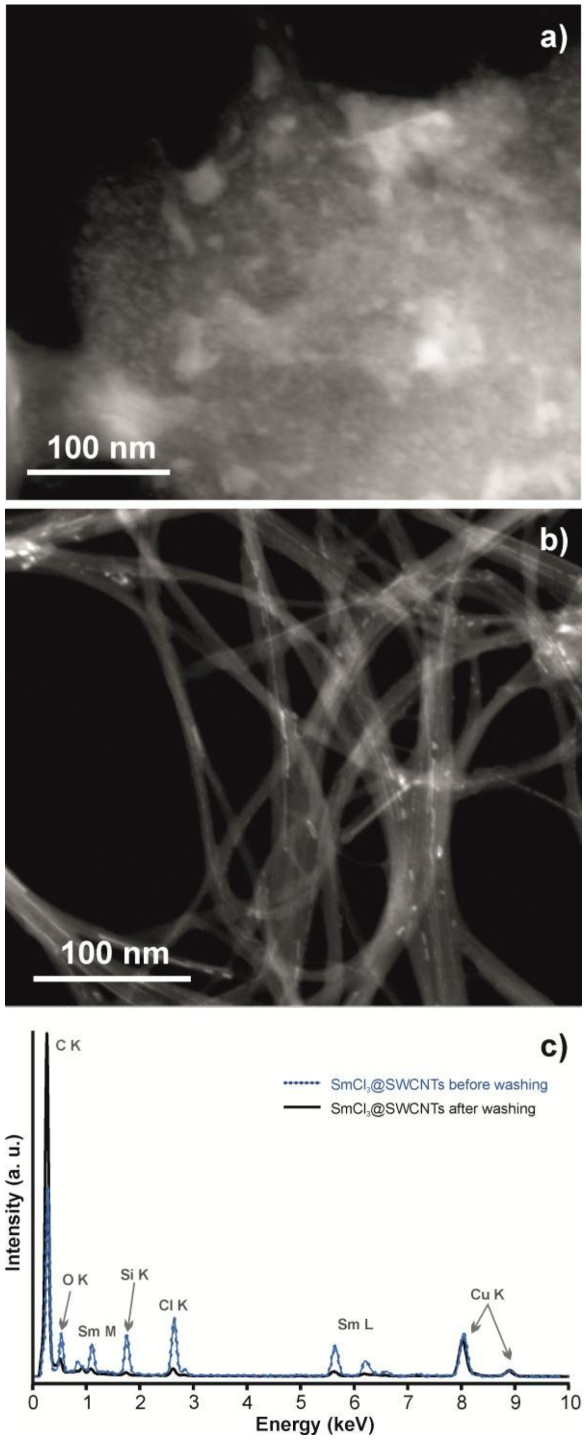

Fig. 6 HAADF STEM images of $SmCl_3$ filled single-walled carbon nanotubes before (a) and after (b) the optimized washing procedure (on a sample of 150 mg). The external material on (a) is visible as bright crystals that are found outside of the nanotubes. Bright spots of few nanometers in size present both in (a) and (b) correspond to iron catalyst protected by graphitic shells. (c) EDX spectra of both samples before and after washing showing the presence of samarium and chlorine, with a decrease in their intensity after the washing.

Conclusions

We have presented an efficient, fast and reliable monitoring method to assess the cleaning process of samples of filled carbon nanotubes that relies of UV-Vis analysis of the filtrates obtained from the washing steps. The optimum parameters that lead to a clean sample have been determined. Despite most filling experiments are performed with few mg of carbon nanotubes, we have shown that a sample of filled tubes as large as 300 mg can be efficiently purified from external material within 1 hour. This is of special relevance for instance for nuclear medicine, a field where filled carbon nanotubes are being actively investigated. The monitoring approach presented herein can be easily extended to other filling materials, with or without the use of complexing agents, making this study an important asset in future development of filled carbon nanotubes for a wide variety of applications.

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