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Synthesis of dry SmCl₃ from Sm₂O₃ revisited. Implications for the encapsulation of samarium compounds into carbon nanotubes

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Abstract

Samarium is a rare-earth metal with several applications in materials science. It is used in organic chemistry as a reducing agent and it is the active payload in samarium-153 lexidronam, a drug being used for palliative treatment of bone metastases. Recently, the encapsulation of samarium compounds into the cavities of carbon nanotubes has attracted interest for the development of the next generation of radiopharmaceuticals. In the present study, we explore different routes to afford the encapsulation of samarium based materials into single-walled carbon nanotubes. Anhydrous samarium(III) chloride, despite being highly hygroscopic, raises as an excellent candidate to achieve a high filling efficiency. We provide a protocol that allows the synthesis of anhydrous samarium(III) chloride starting from samarium(III) oxide in a fast and simple manner. Synchrotron X-ray powder diffraction confirmed the crystallinity and purity of the synthesized SmCl₃.

Keywords
Samarium(III) chloride; thermogravimetric analyisis; X-ray powder diffraction; synchrotron beam irradiation; carbon nanotubes; electron microscopy

Introduction

Inspired by the pioneering work of Prof. Malcolm L.H. Green on the encapsulation of materials into carbon nanotubes (CNTs), and taking into account that filled CNTs have been advocated as promising nanocarriers in the biomedical field for drug delivery, imaging and therapy,[1] we have investigated the encapsulation of samarium compounds into their cavities. Samarium is an interesting payload since it is the active component in samarium lexidronam, a chelated complex of radioactive samarium with ethylenediamine tetra(methylene phosphonic acid), that is used with a palliative aim to relieve the pain of patients with bone metastases.[2] Radioactive samarium is produced at cyclotron facilities by neutron irradiation of samarium(III) oxide. However, direct encapsulation of samarium(III) oxide by molten phase capillary filling into carbon nanotubes is not feasible because the material presents a high melting point (2269 °C).[3] Solution filling, an alternative route for the encapsulation of

compounds into carbon nanotubes, requires the material to be soluble in either aqueous or organic solvents. Samarium(III) oxide is not soluble in water but it dissolves in mineral acids, forming salts upon evaporation and crystallization. Amongst the different samarium salts, samarium chloride arises as an interesting compound because a wide variety of metal halides have been filled inside carbon nanotubes. In fact, the first example on the encapsulation of materials into single-walled carbon nanotubes was reported by Green et al. back in 1998[4, 5]. In this initial study, single crystals of ruthenium were observed inside the cavities of single-walled CNTs (SWCNTs) after reduction of previously encapsulated $RuCl_3$. The same year the incidental discovery of the ability of fullerenes to enter SWCNTs was also reported.[5, 6] Since then, SWCNTs have been used as templates for the growth of low-dimensional materials whose structures and properties often differ greatly from those of the bulk.[7] A wide range of materials, including both organic and inorganic based, have been filled but metal halides have always received special attention. The reason could lie on their relative low melting points and wetting capabilities, once molten, thus making them good candidates for their encapsulation via molten phase filling. For instance $AgBr$-$AgCl$,[8] KI,[9] BaI_2,[10] CoI_2[11], NaI[12] and metal lanthanides, including $SmCl_3$,[13] have all been confined within the cavities of SWCNTs. A remarkable example, also from the Green group, on the application of filled tubes in the biomedical field is the encapsulation of NaI (using radioactive iodide) into the cavities of steam shortened SWCNTs.[12] The high density of radioemitting crystals allowed ultrasensitive imaging and the delivery of an unprecedented radiodosage *in vivo*. These promising results prompted us to carry out further investigations on the design of antibody-functionalized SWCNTs filled with radioactivable metals, including $SmCl_3$, for a targeted anticancer therapy.[14] The work was performed with commercial 'cold' non-radioactive $SmCl_3$. For this approach to be useful for biomedical application, though, the transformation of radioactive Sm_2O_3 to $SmCl_3$ using a fast, simple, safe and scalable method, as required when dealing with 'hot' samarium, needs to be addressed.

The synthesis of rare-earth metal trichlorides ($RECl_3$) from their parent oxides, including $SmCl_3$, is in general well documented but the reported protocols to date do not meet the mentioned requirements for their use with radioactive Sm_2O_3. The hydrated salts are commercially available products or are easily prepared from the oxides or carbonates by reaction with hydrochloric acid.[15] However, special processes need to be utilized for the production of the anhydrous halides $RECl_3$ since simple dehydration can easily lead to a hydrolytic loss of halogen (formation of REOX and RE_2O_3).[15] A major difficulty in the production of anhydrous $RECl_3$ is the ease of formation of metal oxychlorides and their highly hygroscopic character. Direct dehydration of hydrated $SmCl_3$ was actually reported back in the early 60s by annealing the hydrated form at 400 ℃ for 1.5 h under vacuum.[16] However, to the best of our knowledge this one-step synthesis process did not receive further attention and researchers focused their efforts in the use of chlorine-containing reagents to aid the dehydration process, aiming to achieve high purity anhydrous $RECl_3$ products.[15] Two main routes have been employed for the synthesis of anhydrous $RECl_3$, namely the ammonium chloride route and the thionyl chloride route. The ammonium chloride route consists on heating a chosen lanthanide oxide with an excess of ammonium chloride.[17, 18] Once the reaction is completed, the temperature is slowly raised to approx. 400 ℃ to sublime off the excess of NH_4Cl. Rapid heating should be avoided since not only increases the danger of hydrolysis but also decreases the yield because some trichloride is carried away mechanically by the subliming NH_4Cl.[15] When high purity is needed, the

2

reaction can be performed in a molybdenum or tantalum boat to exclude reaction with the glass walls.[15] It is also possible to employ the hydrated chlorides as starting material rather than the metal oxides. The use of ammonium chloride as dehydrating agent proved not to be efficient to prepare the chlorides of higher lanthanides, including $SmCl_3$, because the products contained varying amounts of oxide and oxychloride.[19] The hydrated chlorides of various RE metals can also be dehydrated by heating with thionyl chloride, through the so called thionyl chloride route.[19] On completion of the reaction, the remaining thionyl chloride can be distilled off or decanted.[19] However, a high degree of purity is not guaranteed without a subsequent sublimation of the products.[15] The ease of dehydration, which determines the time needed for the synthesis of the $RECl_3$, corresponds roughly to the heat of hydration of the chloride.[19] For instance 5 h are needed for the synthesis of anhydrous $SmCl_3$ via this route.[19] Although less explored, the thionyl chloride route can also be applied to RE_2O_3 as starting materials.[20]

As detailed above, metal halides can be readily filled into SWCNTs, leading to high encapsulation efficiencies.[21] Therefore, $SmCl_3$ arises as an ideal compound to achieve a high loading of Sm into the SWCNTs.[22] Unfortunately, neither the use of ammonium chloride nor thionyl chloride can be applied when working with radioactive compounds to afford anhydrous 'hot' $SmCl_3$, because they are based on multi-step and lengthy reactions that in turn need purification of the obtained products. In the present work, the direct one-step dehydration of $SmCl_3$ will be revisited and both solution and molten phase filling of SWCNTs will be investigated aiming to achieve a high filling yield of Sm encapsulation required for biomedical applications.

Material and methods
Samarium(III) oxide (Sm_2O_3) and samarium(III) chloride hexahydrate ($SmCl_3 \cdot 6H_2O$) were purchased from Sigma Aldrich and used without further purification. Hydrochloric acid (HCl) was purchased from Panreac. Chemical vapor deposition (CVD) grown Elicarb® single-walled carbon nanotubes were provided by Thomas Swan & Co. Ltd. As-received SWCNTs contain a mixture of both single-walled and double-walled carbon nanotubes (DWCNTs). Both SWCNTs and DWCNTs can be filled by solution and molten phase capillary wetting.[22, 23] We will refer to the sample as SWCNTs. The as-received material also contains impurities of amorphous carbon, graphitic particles and metal catalyst. Therefore, before proceeding to the bulk filling of the SWCNTs, the sample was steam purified at 900 ^{0}C for 4 h and HCl treated following a previously reported protocol.[24] The resulting SWCNTs have a median length of 420 nm, useful for biomedical applications.[25]
The synthesis of dry samarium(III) chloride was performed as follows. Samarium(III) oxide (about 50 mg per synthesis) was initially dissolved in 3 mL of 12 M HCl. Then the sample was dried by heating the dissolution at 80 ºC. The resulting product consisted in samarium(III) chloride hexahydrate as determined by X-ray diffraction (XRD) analysis. The one step dehydration process was performed by placing 50-70 mg of the obtained samarium(III) chloride hexahydrate inside a silica ampoule of 1 cm in diameter. The ampoule was connected to a vacuum line and pump-filled three times with Ar. The closed-end of the silica tube holding the sample was introduced into a tubular furnace. To accurately monitor the temperature at which the sample was exposed, and despite the furnace already had an internal thermocouple, an additional thermocouple was directly attached to the external wall of the silica tube at the position of the sample. The sample was annealed under dynamic vacuum at a heating rate

between 5 and 10 °C/min up to 240 °C. The sample was held at this temperature until no additional water was observed to evolve from the system (approx. 40 min). Then the sample was left to cool down to room temperature. The silica tube was filled with argon and transferred into an argon filled glovebox.

Solution filling of SWCNTs was performed by dissolving 300 mg of Sm_2O_3 in 5 mL of 12 M HCl. Purified nanotubes (30 mg) were added to the solution and stirred overnight. The sample, consisting of open-ended filled SWCNTs, was collected as a solid powder by filtration on top of a 0.2 μm polycarbonate membrane. Next, it was annealed in a vacuum sealed silica ampoule at 5 °C/min until 900 °C and kept at this temperature for 12 h. After this period of time, the furnace was cooled down to room temperature at 5 °C/min. It has been reported that high temperature annealing results in closure of the nanotubes ends upon cooling.[26] Having closed ends allows the removal of the external non-encapsulated compounds, while preserving the filled materials. The external samarium compounds were removed by washing the sample 3 times in 200 mL of acidic water (10 mL of HCl) at 80 °C for 24 hours.

Molten phase capillary filling of the prepared anhydrous samarium(III) chloride was performed as follows. $SmCl_3$ (300 mg) and purified SWCNTs (30 mg) were finely ground together inside a glovebox until a uniform homogeneous colour was obtained. The mixture was placed inside a silica ampoule and sealed under vacuum. The sample was heated in a tubular furnace at 5 °C/min up to 900 °C. The sample was kept at this temperature for 12 h and left to cool down to room temperature at a rate of 5 °C/min. As already mentioned this treatment results in closed-ended filled SWCNTs.[26] The sample was then washed following the protocol employed for the solution filled SWCNTs. An initial prewashing step, that consists in soaking the nanotubes in 200 mL of acidic water followed by filtration was applied to this sample due to the larger amount of external material present compared to the solution filling protocol. This prewashing step already removes the majority of non-encapsulated compounds.[22]

Thermogravimetric analysis (TGA) was performed using a TA instrument TGA Q5000-IR in MATGAS. The analyses were performed by placing around 5 mg of SWCNTs or 10 mg of samarium(III) chloride hexahydrate on a high temperature 100 μL platinum pan. A heating rate of 10 °C/min was employed with flowing air at 25 mL/min. TGA-MS data was acquired in a TGA/SDTA851e/LF/1600 coupled to a THERMOSTAR GSD301T detector at the Universidad de Alicante. Synchrotron X-ray powder diffraction (SXRPD) patterns were acquired on MSPD beamline at ALBA synchrotron (Cerdanylola del Vallès, Spain) using mythen bank of detectors.[27] Fine powders of as-synthesized anhydrous $SmCl_3$ where sealed inside a borosilicate glass capillary of 0.5 mm in diameter, that was rotated during data collection. To diminish the absorbance, a short wavelength (λ=0.620013 Å) was selected by the double cut Si (111) monochromator, and calibrated by measuring powder Si NIST standard. To prevent contact with air, capillary filling and sealing were performed in an argon filled glovebox. The measured pattern was analyzed by Rietveld method using FullProf_Suite of programs.[28] For Rietveld refinement, we started from the structure of isomorphous UCl_3 (ICSD-202333).[29] For the in-house X-ray diffraction analysis (XRD) the samples, in powder, were placed on top of a small glass window which was then covered with a Kapton film, thus preventing contact of the samples with air. Samples that are not air sensitive were analyzed directly on a silica support. High angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), high resolution transmission electron microscopy (HRTEM) images and energy dispersive X-ray spectra were acquired on a FEI TecnaiG2 F20 HR(S)TEM operated at 200 kV and

equipped with an EDAX superultra-thin window (SUTW) X-ray detector. Samples were deposited on lacey carbon Cu TEM grids (Agar).

Results and discussion

The aim of the work was to develop a protocol that allows the encapsulation of radioactive samarium compounds into the cavities of SWCNTs starting from samarium(III) oxide. Therefore in the present study model compounds ('cold') that have the same molecular formula and structure than their radioactive ('hot') analogues were employed.

As-received SWCNTs were steam and HCl treated to remove undesired carbonaceous impurities, catalytic particles and to open the ends of the SWCNTs.[24] The thermogravimetric analysis (TGA) of the purified SWCNTs is presented in Figure 1a. Since the analysis is performed in air, all the carbonaceous species present in the sample are completely oxidized and the solid residue obtained at the end of the analysis corresponds to inorganic ash. Iron is employed as catalyst material for the growth of the SWCNTs. Assuming that there are no other inorganic species present, an inorganic solid residue of 1.7 wt. %, that would be present as Fe_2O_3 at the end of the TGA, corresponds to a 1.2 wt. % of Fe in the purified sample.

We employed this sample of open-ended purified SWCNTs to explore the encapsulation of samarium compounds starting from samarium(III) oxide. In an initial approach, Sm_2O_3 was dissolved in hydrochloric acid until the solution became saturated. At this point, open-ended SWCNTs were added and left stirring overnight to allow the dissolved samarium to enter the capillaries of the nanotubes. Next, the sample was collected by filtration. This approach, known as solution filling, has been widely investigated for the encapsulation of a wide variety of materials into SWCNTs.[30, 31] It is well established that unless the ends of the nanotubes are closed or sealed, forming the so called "carbon nanocapsules", the encapsulated materials can be washed out from their interior using an appropriate solvent.[26, 32] Therefore, we next annealed the sample at 900 ºC under vacuum since it has been reported that after annealing SWCNTs at high temperature the ends of the tubes close on cooling.[26] Having closed ends allows the removal of the large amount of external material employed during the filling step whilst preserving the encapsulated compounds. The sample was thoroughly washed with an acidic solution and collected by filtration as a solid powder. The resulting sample was characterized by thermogravimetric analysis (TGA) and by HAADF scanning transmission electron microscopy (STEM). As it can be seen in Figure 1a, the solid residue obtained after the TGA in air of the filled sample (2.1 wt. %) is quite similar to the residue recorded for the purified SWCNTs, indicating a low filling degree. The presence of water (from the hydrated $SmCl_3$) inside the ampoule during the annealing step might prevent the closure of the ends, allowing the removal of encapsulated material during the washing. The low degree of filling was also confirmed by STEM inspection of the sample where only few filled SWCNTs could be observed (Figure 1b). A Z-contrast image is formed in STEM by focusing an electron probe on the specimen and detecting electrons that scatter out to a high angle annular dark-field (HAADF) detector. The intensity offered by an element present in the sample is proportional to its atomic number. Therefore, carbon appears as a pale grey and the encapsulated material, containing samarium, as bright lines following the shape of the carbon nanotube bundles. As it can seen in the image there are only few bright lines, corresponding to the filling material.
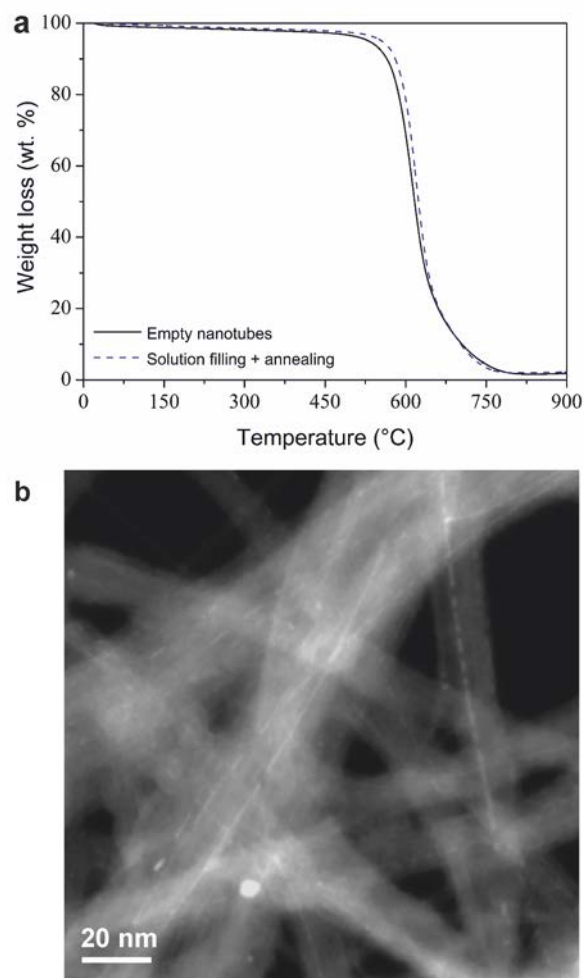
Figure 1. a) Thermogravimetric analysis in air of empty (purified SWCNTs) and solution filled SWCNTs. b) HAADF-STEM image of solution filled SWCNTs.

To determine the nature of the filled compounds, the protocol employed for the dissolution of samarium(III) oxide and post annealing at 900 °C after the solution filling was performed on samarium(III) oxide alone, without adding SWCNTs. Samarium(III) oxide was dissolved in HCl, which, after slow evaporation of the solvent lead to the formation of samarium(III) chloride hexahydrate in powder (XRD not shown). The solid powder was sealed under vacuum in a silica ampoule, heated to 900 °C for 12 h and allowed to cool down to room temperature. The ampoule was opened inside the glovebox and then the sample was protected with a Kapton film for XRD analysis. Figure 2 presents the XRD pattern of the obtained solid which is in good agreement with samarium oxychloride. Therefore, if we consider that SmOCl has been encapsulated inside SWCNTs after the solution filling process, it is possible to quantitatively determine the filling yield (FY) from the TGA data presented in Figure 1a,[21] which corresponds to a FY = 0.5 wt. %.
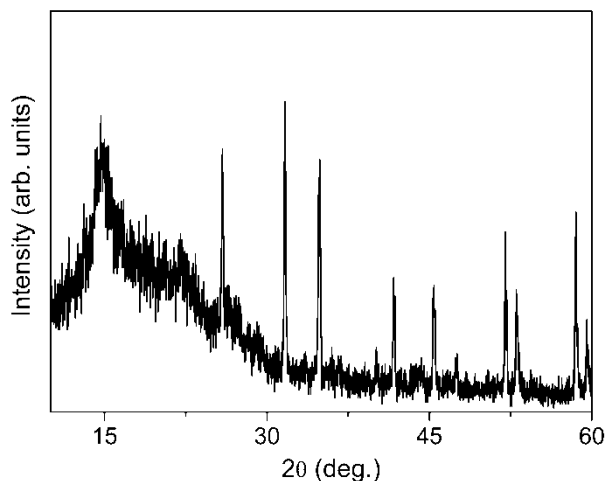
Figure 2. XRD pattern of annealed samarium(III) chloride hexahydrate at 900 °C under vacuum with the described protocol. The Kapton film employed to protect the sample from air contact contributes to the background up to about 30°. The XRD pattern is in good agreement with samarium oxychloride; PDF 00-012-0790 (ICDD, 1962).

The filling yield obtained is well below what has been obtained for most encapsulated metal halides.[21] In particular, the encapsulation of commercially available anhydrous samarium(III) chloride by molten phase filling has been recently reported to lead to a filling yield of about 20 wt. %.[22] Therefore, we next revisited the synthesis of anhydrous samarium(III) chloride starting from samarium(III) oxide. As discussed in the introduction the ammonium chloride and thionyl chloride routes do not meet the requirements for the transformation of 'hot' materials, which is the thread behind the present study. Since Sm_2O_3 can be easily dissolved in mineral acids leading to $SmCl_3 \cdot 6H_2O$ upon evaporation of the solvent, the direct dehydration of the metal halide, although less investigated, is an interesting approach. Figure 3 presents the TGA-MS data of commercially available samarium(III) chloride hexahydrate. The TGA of samarium(III) chloride hexahydrate in inert atmosphere reveals well defined weight losses that can be attributed to water removal, in agreement with the MS (m/z = 18). A small release of HCl is also recorded (m/z = 36) at certain temperatures. The amount of water removed at each of the weight losses can be quantified from the TGA curve. Each water molecule would result in a weight loss of 4.94 wt. %. Therefore, the weight loss of 24.9 wt. % recorded until the plateau at 160 °C corresponds to the removal of 5 water molecules. This is in good agreement with the expected theoretical value of 24.7 wt.%. The sixth coordinated molecule is removed between 160 °C and the plateau at about 240 °C with a weight loss of 5.32 wt. %. The small differences between the experimental and theoretical values for water removal could account for experimental error and for a small release of HCl, as detected by MS. Different inert gasses (helium/argon, nitrogen) have been employed for the analysis always leading to the same plateau at around 240 °C. Thus, at this temperature we would expect to have dehydrated the $SmCl_3 \cdot 6 H_2O$ thus obtaining the anhydrous form. Interestingly, the only study in which anhydrous $SmCl_3$ was prepared by simple dehydration employed 400 °C for 1.5 h.[16] According to the TGA-MS data, after the plateau at around 240 °C (approx. 230 °C to 320 °C) a continuous drop in mass is observed due to the release of HCl. To verify the

7

interpretation performed so far on the TGA-MS data, two samples were prepared at the two points of interest, by stopping the heating experiment at 240 ºC and at 400 ºC. XRD analysis of the powder obtained at 400 ºC (not shown) reveals the coexistence of samarium(III) chloride and samarium oxychloride, the latter being an undesired secondary product. In contrast, samarium oxychloride is not detected in the XRD pattern of the sample prepared at 240 ºC. Therefore, we focused on the treatment at 240 ºC and analyzed the sample by SXRPD (Figure 4).
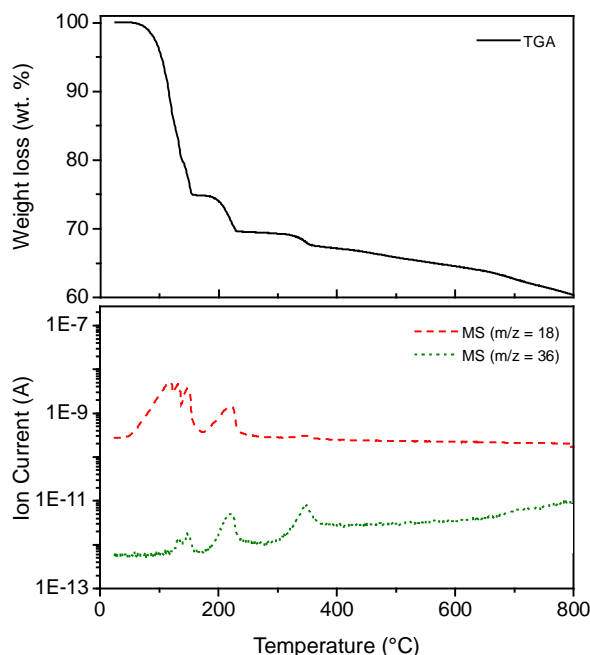
Figure 3. TGA-MS data of commercially available samarium(III) chloride hexahydrate showing the removal of water (m/z = 18). A small release of HCl (m/z = 36) can also be detected.

Rietveld refinement of SXRPD data was performed starting from the structure reported for $NdCl_3$[33], isostructural to $SmCl_3$. The refinement rendered very good agreement parameters (χ^2=4.51, R_{wp}=4.27%, R_B=1.38%), confirming the formation of dry samarium(III) chloride. In addition to diffraction peaks indexed by $SmCl_3$ structure, only very tiny peaks (around 200 counts versus 300000 counts of the most intense peak of $SmCl_3$) were detected thanks to a very good signal to noise ratio of the synchrotron data. Those peaks do not correspond to $SmCl_3 \cdot 6H_2O$, SmOCl nor Sm_2O_3 (in cubic or monoclinic form). Also, the flat background indicates that no significant amorphous phases are present. The results of the refinement are presented in Figure 4 and structural details are listed in Table 1. Sm-Cl bond distances obtained [2.918(2) and 2.850(1) Å] are slightly smaller than Nd-Cl ones reported for $NdCl_3$ [2.937 and 2.929 Å][33] what

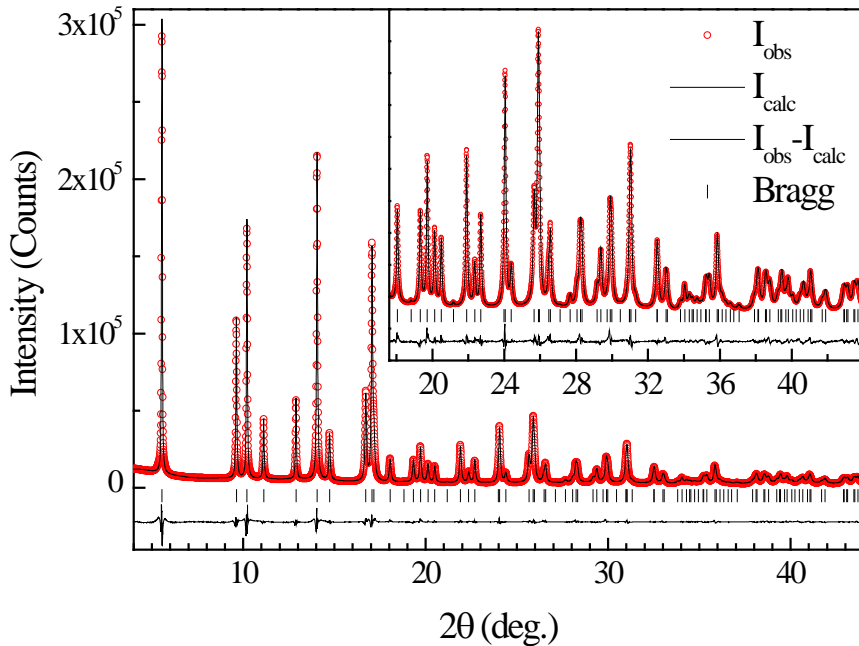resembles the smaller size of Sm when compared with Nd.

Figure 4. Rietveld refinement of SXRPD data of the synthesized anhydrous SmCl$_3$. Inset shows an enlargement of the high angle region.

Table 1. Structural details of SmCl$_3$ obtained by the Rietveld refinement. Space group is hexagonal $P6_3/m$ (no. 176), Sm occupies Wyckoff position 2c (1⁄3 2⁄3 1⁄4) and Cl position 6h (x y 1⁄4).

			Cl		
	a (Å)	7.3842(1)	Cl	x	0.3879(6)
	c (Å)	4.1536(1)		y	0.3016(6)
Sm	B_{iso} (Å^2)	0.36(5)	B_{iso} (Å^2)		0.74(5)

Having developed a fast and simple protocol for the synthesis of anhydrous SmCl$_3$ we next studied the molten phase filling of SWCNTs with the as-synthesized material. For ease of comparison, we employed the same batch of steam treated SWCNTs that has been used for the solution filling experiment. Anhydrous samarium(III) chloride was ground together with SWCNTs inside the glovebox. The resulting mixture was then vacuum sealed inside a silica ampoule and annealed at 900 ºC to allow the SmCl$_3$ to melt and enter the capillaries of the SWCNTs. The sample was then thoroughly washed to remove the non-encapsulated compounds and analyzed by TGA and HAADF STEM (Figure 5). TGA reveals an inorganic solid residue of 11.7 wt. %. Therefore, if the encapsulated material is SmCl$_3$, and taking into account the solid residue recorded for the purified SWCNTs (also included in Fig. 5a), this would correspond to a filling yield of 15 wt. % using the formula reported elsewhere.[21] This filling yield is an order of magnitude higher than that obtained by solution filling. The HAADF-STEM analysis of the sample is also in agreement with the TGA analysis. As mentioned, HAADF images are formed with the intensity proportional to the atomic number of the element. Hence, the bright lines visible on the micrograph in Figure 5b

correspond to samarium(III) chloride. The surrounding SWCNTs are visible but with much lower contrast. Comparison of the HAADF-STEM images of both filled samples reveals that the filling yield of the sample prepared by capillary melting is much higher than that prepared by solution filling.
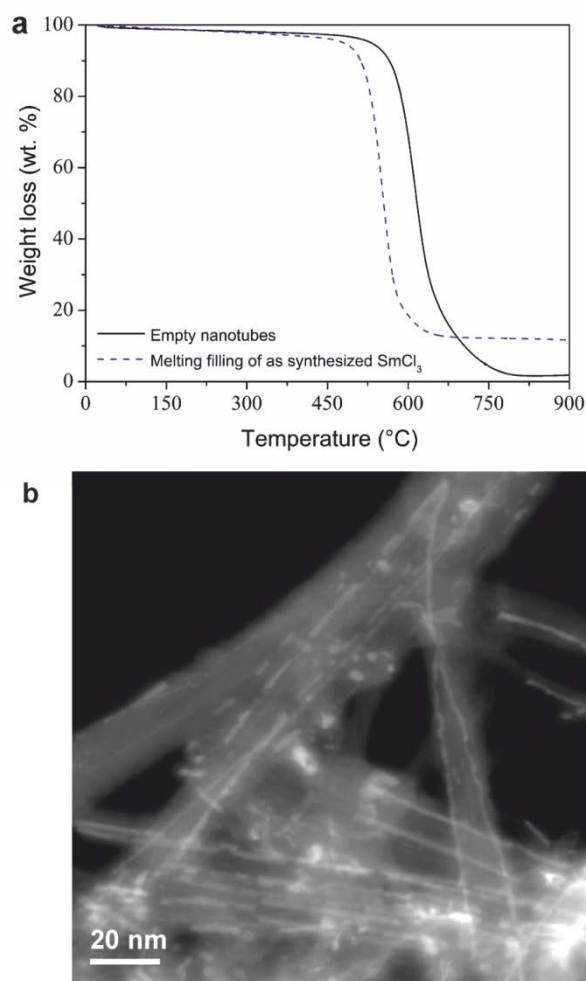

Figure 5. Characterization of molten phase filling of SWCNTs with the as-synthesized anhydrous $SmCl_3$. a) Thermogravimetric analysis in air of empty (purified SWCNTs) and melt filled $SmCl_3$@SWCNTs. b) HAADF-STEM image of melt filled $SmCl_3$@SWCNTs.

HRTEM studies on the sample prepared by molten phase filling confirm that the encapsulated $SmCl_3$ keeps the hexagonal $P6_3/m$ structure once at interior of the carbon nanotubes. Interplanar spacings of 3.2 Å, which are in good agreement with the (200) plane of the hexagonal $SmCl_3$, are clearly visible in the HRTEM image in Figure 6. The EDX spectrum confirms the presence of both Sm and Cl from the filling material. The Cu, C, O and Si peaks arise from the carbon nanotubes, the lacey carbon support grid and the detector.
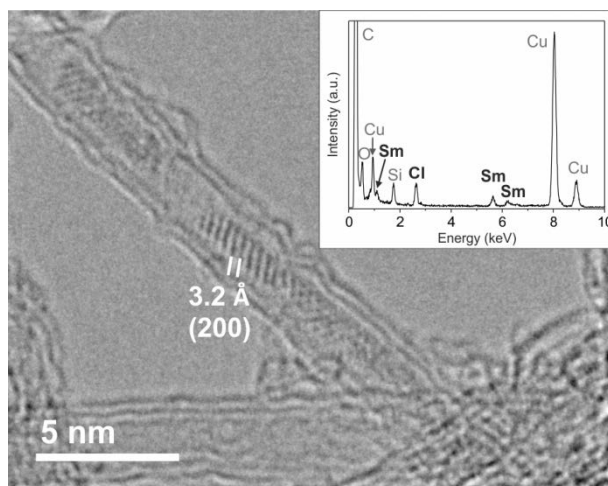
Figure 6. HRTEM image of $SmCl_3$ confined in the cavities of a double-walled carbon nanotube prepared by molten phase filling with the corresponding EDX analysis (inset).

Conclusions

To conclude, we have developed a fast, simple and economic protocol that allows the synthesis of anhydrous samarium(III) chloride from samarium(III) oxide. The production of dry samarium(III) chloride has been assessed by high resolution SXRPD analysis, which confirmed the successful formation of the material and the absence of significant impurities in the sample. The as-synthesized $SmCl_3$ has been subsequently filled into the cavities of SWCNTs by molten phase capillary wetting with a high filling yield. The amount of radioactive material that could be encapsulated with the developed approach overpasses that achieved by current strategies using external radiolabelling of carbon nanotubes. The present study opens up new possibilities for the development of novel samarium-based radiopharmaceuticals.

Appendix A. Supplementary data

CCDC 1458307 contains the supplementary crystallographic data for $SmCl_3$. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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