Filling Single-Walled Carbon Nanotubes with Lutetium Chloride: A Sustainable Production of Nanocapsules Free of Non-Encapsulated Material

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ABSTRACT

Filled carbon nanotubes are of interest for a wide variety of applications ranging from sensors to magnetoelectronic devices and going through the development of smart contrast and therapeutic agents in the biomedical field. In general, regardless of the method employed, bulk filling of carbon nanotubes results in the presence of a large amount of external non-encapsulated material. Therefore further processing is needed to achieve a sample in which the selected payload is present only in the inner cavities of the nanotubes. Here, we report on a straightforward approach that allows the removal of non-encapsulated compounds in a time efficient and environmentally friendly manner, using water as a 'green' solvent, whilst minimizing the residual waste. The results presented herein pave the way towards the production of large amounts of high-quality closed-ended filled nanotubes, also referred to as carbon nanocapsules, readily utilizable in the foreseen applications.

1. Introduction

Carbon nanotubes (CNTs) are currently used in many fields by virtue of their extraordinary physical and chemical properties. To name a few, they are extensively studied as functional parts of electronic devices, in energy conversion and storage applications, embedded in bulk matrices for structural reinforcement, thermal management, or even used as analytical tools for sensing.[1-5] Amongst their most inspiring goals, the employment of CNTs in nanomedicine currently holds enormous potential as a new generation of diagnostic and therapeutic agents, if properly processed and functionalized.[6-10] One of the earliest applications of CNTs takes advantage of their hollow tubular structure to host selected payloads.[11] The endohedral filling of CNTs is of interest, for instance, for the development of nanothermometers,[12] molecular magnets,[13] growth of graphene[14] and related layered materials,[15] and light harvesting.[16] One application that is receiving an increased attention is the use of filled tubes in the biomedical field,[17-19] since an imaging or therapeutic cargo can be encapsulated and thus shielded from the biological milieu while the external walls can be modified with biocompatible and targeting moieties. A proper cleaning of outer material is of crucial relevance when developing novel nanocarriers based on filled carbon nanotubes for either biomedical imaging or therapeutic purposes to reduce toxicity and undesired side-effects of the developed materials.

Filling of CNTs can be accomplished through plenty of means, including high temperature (molten phase, gas phase) and low temperature (solution phase, nanoextraction, supercritical CO_2) methods.[20-21] Regardless of the method employed, bulk filling of carbon nanotubes usually results in samples that contain a large amount of unwanted non-encapsulated material. In general, attempts to remove the material external to the CNT walls also result in the

removal of the encapsulated compounds, of the same nature. To overcome this problem, Wilson et al. have for instance developed "gadonanotubes" by using highly defective single-walled carbon nanotubes (SWCNTs) where superparamagnetic clusters of Gd^{3+} ions reside within the sidewall defects of the nanotubes.[22] The Gd^{3+} ion clusters are so tightly contained by the CNT platform that the ions do not leak out.[9] The success of this approach depends on the chemical nature of the agent to be encapsulated. Alternative protocols have been developed using CNTs with a low degree of structural defects. For instance, several authors have explored the use of solvent mixtures or micelles to allow the selective washing of the external material.[23-24] Another approach consists on coating the nanotubes with an inert material,[25] or to seal the ends of CNTs forming the so-called carbon nanocapsules,[26] to allow the selective removal of the external material whilst preserving the encapsulated payloads. In the case of SWCNTs, the latter can be achieved by either using fullerenes as corks[27-29] or by high temperature annealing of the carbon nanotubes, typically around 700-900 ºC.[30] In this respect, molten phase filling in this range of temperatures is of particular interest since it allows the simultaneous filling and end-closing in a single step. Among the different materials that have been encapsulated by the molten phase filling, metal halides (MX) have received special attention, since they can be incorporated in a high yield.[31-33] Novel crystal structures and charge transfer with the SWCNTs have been reported for these hybrid materials.[34-35] A more recent application resides in the use of 'hot' (radioactive) metal halides as *in vivo* radiotracers. For instance, ultrasensitive imaging and the delivery of an unprecedented amount of radiodose density has been achieved via de the encapsulation of radioactive $Na^{125}I$ inside SWCNTs.[36] Provided that external functionalization ensured biocompatibility, and a secondary derivatization granted proper targeting, these nanocapsules have proven to be a unique nanoplatform towards the development of a targeted anticancer

therapy.[36-38] The removal of non-encaged external material whilst preserving the structural integrity of the nanocapsules becomes even more important when dealing with radioactive species. Besides, given the short half-life times of common clinically used radionuclides, rapidity is a must.

We were thus motivated to develop an approach which ensured an efficient and environmentally friendly external cleaning of MX@SWCNTs that could be directly transferable to the large scale production of an equivalent radioactive system. Water was the selected 'green' solvent and in order to minimize the radioactive waste, reduction of the volume employed in the cleaning process was also a targeted objective. Lutetium(III) chloride was the material of choice owing to the extended use of its radioisotope ^{177}Lu for the treatment of several cancer types including neuroendocrine tumors.[39] Furthermore, the low water solubility of $LuCl_3$ allowed a better appreciation of the effect that each of the different washing protocols had on the removal of the external $LuCl_3$. To our best knowledge this is the first comparative study on different methodologies for the removal of external, non-encapsulated material from samples of filled CNTs.

2. Experimental

2.1 *Materials and Reagents*

Chemical vapor deposition SWCNTs (Elicarb®) were provided by Thomas Swan & Co. Ltd. The as-received material contains a fraction of double-walled carbon nanotubes (DWCNTs), metal iron nanoparticles (from the catalyst employed for the growth of the nanotubes) and carbonaceous impurities (namely, graphitic particles and amorphous carbon). Milli-Q water was employed in all the washing protocols. Lutetium (III) chloride (anhydrous, powder, 99.99% trace

metals basis), cetylpiridinium chloride (CPC), chromeazurol S (CAS, dye content 50%) and dialysis sacks (cellulose, 12kDa MWCO) were purchased from Sigma Aldrich. Extraction thimbles (Whatman, cellulose) and filtration membranes (Whatman Cyclopore, polycarbonate, pore size 0.2 μm) were bought from Fischer Scientific.

2.2 *Filling carbon nanotubes with LuCl₃*

As-received SWCNTs were purified by a combined steam (4 h, 900 ºC) and HCl treatment, following a previously reported protocol.[40] Purified SWCNTs (300 mg) were ground together with LuCl$_3$ in a weight ratio 1:7 inside an argon filled glovebox until the sample presented a homogeneous color. Then, the mixture was divided into five equal portions that were vacuum-sealed inside silica ampoules. Ampoules were then placed together inside a tubular furnace, annealed at 950 ºC and dwelled at this temperature for 12 h. After cooling to room temperature they were opened in the air. In this way the whole batch of filled tubes was prepared under the same experimental conditions.

2.3 *Cleaning protocols*

In all the washing protocols large and equal amounts (480 mg) of LuCl$_3$@SWCNTs, collected after the filling experiment, were processed. All treatments were repeated for up to six days unless a clean sample was already achieved at an early stage. Hot water used in the protocols was in range 70-90 ºC.

2.3.1 *Sonication and Filtration (SF)*

LuCl$_3$@SWCNTs were dispersed in 150 mL of water at 90 ºC by bath sonication for 2 min, and filtered over a polycarbonate membrane. The sample was further rinsed with 900 mL of hot

water on top of the filter membrane. The whole process (sonication + filtration + rinsing) was repeated three times. Then, the sample was collected from the top of the membrane, dispersed in 150 mL of water (2 min sonication) and left stirring overnight at 70 ºC. Finally the solution was filtered and the solid sample was recovered from the top of the filter membrane. The whole process was repeated 6 times.

2.3.2 Sonication and Dialysis (SD)

Filled nanotubes were dispersed in 150 mL of water at 90 ºC by bath sonication for 2 min. The suspension was filtered over a polycarbonate membrane. The solid sample was transferred to a cellulose dialysis sack with 40 mL of water. The dialysis sack was placed in a beaker containing 900 mL of hot water, sonicated for 2 minutes and left for 2 hours. Next, the sample was recovered by filtration and transferred again with 40 mL of fresh water to a new dialysis sack. The hot water in the beaker was also replaced. Two additional cycles of dialysis were performed. The last dialysis step was carried out overnight in water at 70 ºC. This procedure was repeated 6 times.

2.3.3 Sonication and Centrifugation (SC)

$LuCl_3$@SWCNTs were dispersed in 150 mL of water at 90 ºC by bath sonication for 2 min. The sample was transferred to 30 mL tubes and centrifuged at a speed of 4000 r.p.m. for 10 min. The supernatant was separated from solid sample by decantation. All the steps (sonication + centrifugation + decantation) were repeated three times. The fourth cycle consisted of stirring $LuCl_3$@SWCNTs overnight in 150 mL of water at 70 ºC. The complete protocol was repeated systematically for 4 more cycles.

2.3.4 *Soxhlet with cellulose thimble (Sh)*

Filled SWCNTs were placed in a cylindrical cellulose thimble as solid powder and moistened with water. The thimble containing the sample was placed into a Soxhlet apparatus. The round-bottom flask underneath the thimble was filled with 200 mL of water. Water was refluxed using an electric heating mantle (set at 400 ºC). The water was allowed to circulate through the system for 5 days, with water replacements every 8-10 h. The sample was not removed from the thimble when placing fresh water and the same thimble was employed during the whole process. After completing the washing cycles, the thimble with the solid content was placed in the oven at 80 ºC and allowed to dry for few hours. LuCl$_3$@SWCNTs were poured out from the thimble as a dry solid powder by holding the thimble upside down.

2.3.5 *Soxhlet with dialysis sack (DSh)*

LuCl$_3$@SWCNTs were placed inside a dialysis sack and dispersed in 40 mL of water. The dialysis sack containing the sample was placed into the Soxhlet apparatus. The round-bottom flask underneath was filled with 200 mL of water and heated, with an electrical mantle (set at 400 ºC), to allow the circulation of water through the system. Both, water and the dialysis sack were replaced every 24 h. To do so, the sample was collected from the dialysis sack by filtration onto a polycarbonate membrane, and then transferred with 40 mL of water to new dialysis sack. The overall process was performed for 4 days.

2.4 *Equipment and characterization*

Thermogravimetric analysis (TGA) was performed in a Q5000 IR instrument under glowing air with a heating rate of 10 ºC min^{-1}. Scanning transmission electron microscopy (STEM) images

were acquired on FEI Magellan XHR SEM operated at 20 kV using a high angle annular dark field (HAADF) detector. High resolution TEM (HRTEM) images and energy-dispersive X-ray (EDX) spectra were acquired with a FEI Tecnai G2 F20 HRTEM at 200 kV equipped with an EDAX super ultra-thin window (SUTW) X-ray detector. All samples were deposited on lacey carbon Cu grids from Agar.

3. Results and discussion

As-received SWCNTs were steam and HCl treated in order to open their ends and remove carbonaceous and metal impurities, following a previously established protocol.[41] The resulting SWCNTs have a median length of 420 nm,[40] suitable for biomedical applications. The purified material was characterized by thermogravimetric analysis (TGA) and by electron microscopy. A representative HAADF STEM image of the purified sample is presented in Figure 1a. Apart from SWCNTs forming a web-like structure, small bright dots of few nanometers are visible, which correspond to the residual Fe catalytic particles remaining after the purification process. These metal particles are employed during the synthesis of SWCNTs and are partially removed by the HCl treatment. The amount of iron nanoparticles still present after the purification step is 1.2 wt. % as determined by TGA. Afterwards, we proceeded to the filling of the SWCNTs with $LuCl_3$ by molten phase capillary wetting. Electron microscopy analysis of the collected material after the filling process reveals the presence of a large amount of non-encapsulated salt (Figure 1b). SWCNTs appear to be mostly covered by large crystals of $LuCl_3$.
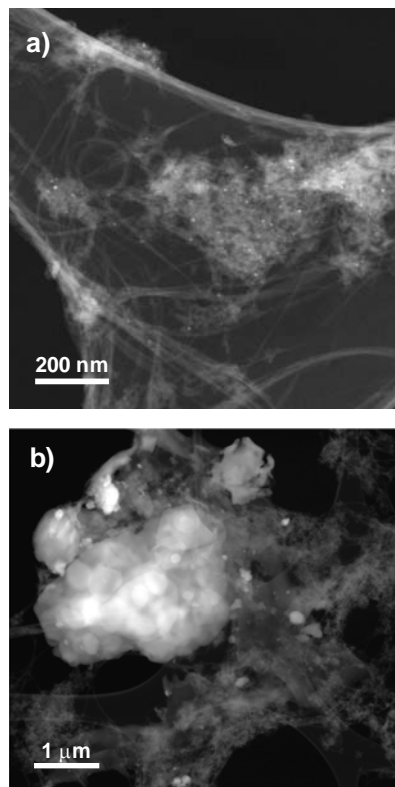
Figure 1. a) HAADF STEM image of steam and HCl purified SWCNTs. Small bright dots of few nanometers in diameter correspond to residual iron catalyst remaining after the purification process. b) HAADF STEM image of as-produced $LuCl_3$@SWCNTs (before washing). Huge bright crystals correspond to non-encapsulated $LuCl_3$.

The protocol employed for the encapsulation of $LuCl_3$ into SWCNTs leads to samples of filled tubes with closed ends.[30] This allows the removal of the non-encapsulated $LuCl_3$ using a solvent in which the salt is soluble, since the nanotubes protect the inner crystals from dissolution. We tested the solubility of $LuCl_3$ and observed that at room temperature it presents a good solubility in hydrochloric acid and a poor solubility in water. A higher solubility was

achieved in hot water (≥ 70 ºC), which was preserved after cooling. We avoided the use of corrosive mineral acids, such as nitric acid, that can alter the tubular structure of the carbon nanotubes.[42] The presence of defects could result in the release of the encapsulated payload, which is indeed undesirable in the present study. On the other hand we also disregarded the use of surfactants or organic solvents, which have for instance been employed for the purification of filled SWCNTs[23-24] since the aim was to develop an environmentally friendly protocol. This drove us to the use of boiling water, which is a "green" innocuous solvent, for the cleaning of the non-encapsulated salt.

The most common protocol for the removal of external material consists on dispersing the sample of filled SWCNTs in a suitable solvent. After a given amount of time, which can involve or not stirring, the sample is collected as a solid powder by filtration.[24-25, 43-44] This process might be repeated several times to completely remove the non-encapsulated payload. The quality of the resulting material is in general determined by means of electron microscopy, but since the filtrate contains the dissolved external material, a fast monitoring of the cleaning process can be performed by visual inspection of the filtrate, provided a colored solution is obtained upon dissolution of the payload. The presence of a colorless filtrate serves then as an indication that the cleaning protocol is completed. This is for instance the case when iron chloride is removed from the exterior of filled tubes using hydrochloric acid, since iron cations give a yellow color to the solution.[45] To benefit from such fast qualitative monitoring, and despite LuCl$_3$ gives a colorless water solution, we used a salt complexation method and added CPC/CAS (Cetylpyridinium chloride/Chromeazurol-S) to the collected filtrates. CPC/CAS complexes have been reported for several metal and rare-metal salts.[43, 46-47] The color of the solution becomes dark royal blue if the lutetium complex is formed and yellow when the

lutetium salt is not present (Figure S1). This allows a quick and non-destructive *on-site* assessment of the removal of external salts.

A large sample of LuCl$_3$ filled SWCNTs (480 mg) was submitted to the above mentioned cleaning protocol, which consisted in sonication of the sample in hot water followed by filtration three times. Then to allow enough time for the salt to get dissolved, the sample was left stirring overnight in water at 70 ºC. We will refer to this treatment as "sonication and filtration" (SF). In the present case, cleaning of the sample was stopped after prolonged washing cycles, reaching up to 6 days and 18 fractions. It has been reported that the majority of external material is removed after the first washing step.[43] To check whether this was also the case in the present study, we analyzed the sample collected after the initial sonication and filtration by TGA. Analysis of the obtained data reveals that at this stage, 12.8 wt. % of the sample corresponds to non-encapsulated LuCl$_3$ external to the nanotubes (to work out this value a filling yield of 23 wt.% was employed, which will be determined later on for the sample washed using the optimized protocol). STEM analysis of the collected sample at the end of this process reveals the presence of contamination from an organic-type material (Figure 2a). It is likely that the sample has been contaminated with polycarbonate from the filter membranes due to the prolonged treatment at which the sample was subjected (18 cycles). The SF is the most classical method employed by most authors, with slight variations, and works well when using a "good" solvent, i.e. a solvent in which the material to be removed presents a high solubility. No previous observations of contamination have been reported using SF. Therefore, the eventual contamination observed in the present case is attributed to the prolonged processing of the material. Much shorter washing cycles are needed when the external material presents a high solubility in the employed solvent.
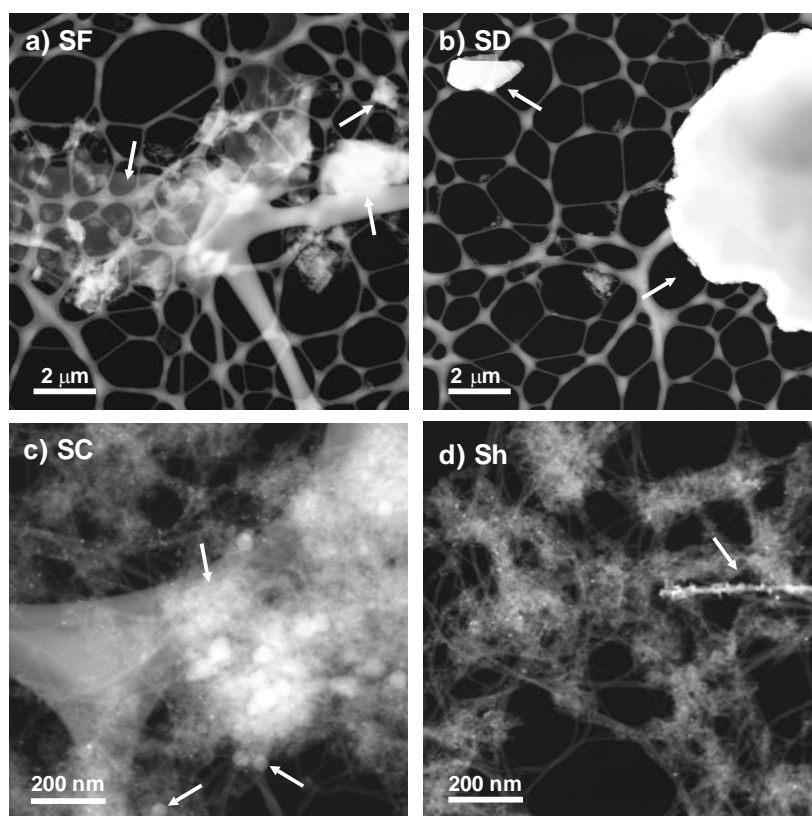
Figure 2. a-d) HAADF STEM images of LuCl$_3$@SWCNTs at the final stage of the different washing protocols. a) SF-sonication and filtration; b) SD-sonication and dialysis; c) SC-sonication and centrifugation; d) Sh-Soxhlet with cellulose thimble. Arrows point to external impurities.

An alternative cleaning protocol was thus needed. We next tested two variations of the SF, replacing the filtration step by either dialysis or by centrifugation. We will refer to the former as "sonication and dialysis" (SD) and to the latter as "sonication and centrifugation" (SC). The SD method was the least efficient in removing external material as shown in the HAADF STEM image (Fig. 2b), where micrometer-sized lumps of non-encapsulated LuCl$_3$ are visible even after several washing cycles. The number of washing fractions, time employed and a brief description of the obtained results are recorded in Table 1, for the different explored methods. The SC

method seemed to work well at the beginning but a complete cleaning of the sample was not reached even after prolonged treatment. STEM inspection of the final collected sample reveals the presence of external metal halide impurities. A major drawback of this methodology is that requires decantation of the supernatant after centrifugation, which results in a continuous loss of sample between cycles.

The use of a Soxhlet apparatus, which has been employed for the purification of as-produced nanotubes,[48] arises as an interesting alternative. First of all it reduces the amount of waste, since water is recirculated over the sample in a closed cycle. This is key for the envisaged application that aims to develop a "green" process that allows handling of radioactive systems (^{177}LuCl$_3$). On the other hand it requires minimal sample manipulation which is also of interest when dealing with radionuclides. Remarkably, using the Soxhlet approach (Sh) a clean sample was already achieved with only 6 cycles. Unfortunately, due to the difficulty in recovering the nanotubes after the reflux from the cellulose cartridge, contamination of the sample with cellulose seemed to have taken place, as it can be seen in the STEM image of Figure 2d. Encouraged by the efficiency of the Soxhlet system, we replaced the generally employed cellulose thimble with a dialysis sack, to facilitate the recovery of the sample and prevent its contamination. A schematic representation of the proposed "Soxhlet with dialysis sack" (DSh) system is presented in Scheme 1. After the initial DSh cycle the majority of external LuCl$_3$ is already removed. The collected sample contains only a 3.4 wt. % of non-encapsulated LuCl$_3$ (as determined by TGA and using the filling yield of 23 wt. %). A completely clean sample was already achieved with only three cycles of washing. According to the CPC/CAS test, the filtrate of the fourth washing was already free of LuCl$_3$ and thus this final washing would be unnecessary (Figure S2).
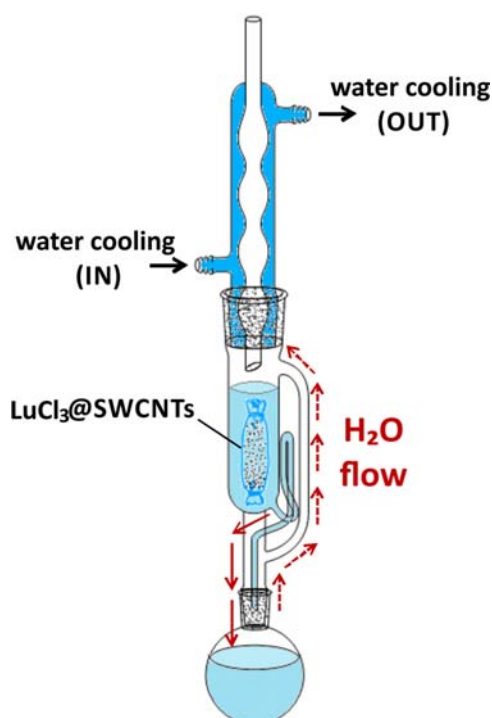
Scheme 1. Schematic representation of the "Soxhlet with dialysis sack" system. The sample to be cleaned from external material is sealed in a dialysis sack and placed into the Soxhlet apparatus. Boiling water goes through the sample in a continuous flow thus minimizing the amount of liquid waste at the end of the process.

Electron microscopy analyses confirm that a clean sample, free of external $LuCl_3$, was achieved by the DSh protocol (Fig. 3). No large lumps of $LuCl_3$ or additional impurities, which could arise from the processing of the sample, were detected either by HAADF STEM or by low magnification TEM imaging. This is further proven by EDX analysis (Fig. 3b) as only signals for Lu and Cl (from the encapsulated material), Fe (from the catalyst) and C are detected. Cu peaks arise from the TEM support grid.
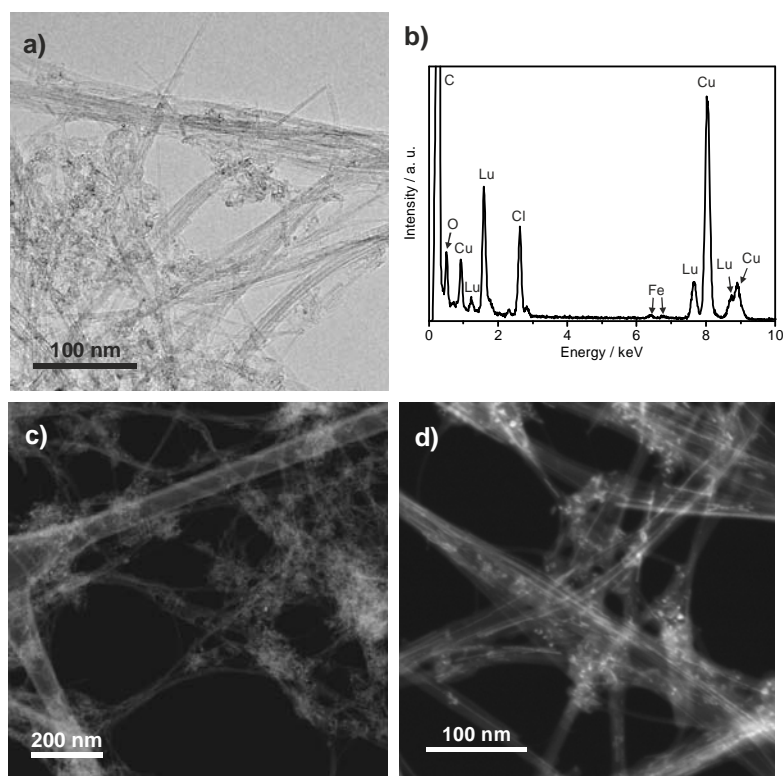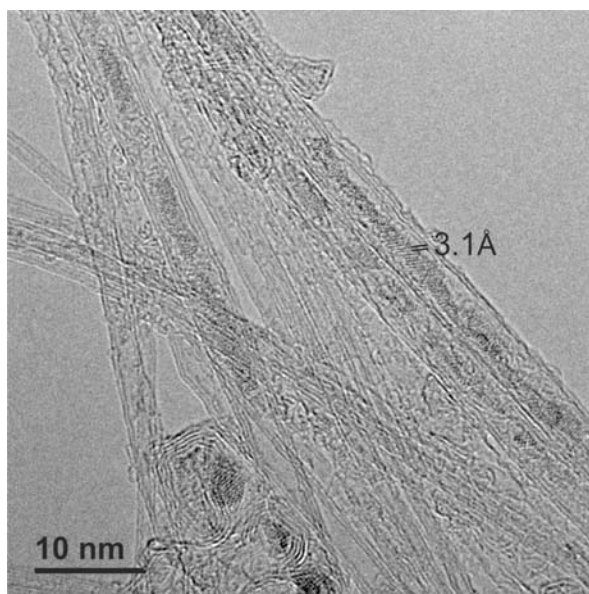
Figure 3. Analysis of the sample of LuCl₃@SWCNTs washed by the DSh protocol. a) TEM image, b) EDX analysis, c,d) HAADF STEM images

The LuCl₃ filling can be more easily seen in the HAADF STEM images. In this imaging modality, heavy elements (such as Lu, Cl) give a higher intensity than light elements (such as C). Therefore, the filled material appears as bright lines following the shape of the SWCNTs, which appear as pale grey.

A close inspection by HRTEM allowed excluding that LuCl₃ was present outside the CNTs in the form of small clusters or nanoparticles. Representative HRTEM images are shown in Figure 4 and Figure S3. All the LuCl₃ appears enclosed within graphitic shells, either in the form of nanowires or small nanoparticles. No external material is observed. Once encapsulated, LuCl₃ keeps its monoclinic C2/m crystal structure. Interplanar spacings of 3.1 Å, in good

agreement with the (002) planes of the monoclinic LuCl$_3$, are observed in the HRTEM image in Figure 4.

Figure 4. HRTEM image of the sample of LuCl$_3$@SWCNTs washed by the DSh protocol.

EDX analyses carried out on individual small nanoparticles, which appear dark in the HRTEM and bright in the HAADF STEM images, prove that these correspond either to Fe, from the catalyst impurities still buried inside graphitic shells after the steam treatment[49] - already observed in the purified sample of empty SWCNTs (Figure 1a) -, or to encapsulated LuCl$_3$ (Figure S4). The presence of round shaped LuCl$_3$ nanostructures can arise from LuCl$_3$ filling in the form of small nanoparticles but also from filled SWCNTs visualized in cross-section or from the filling of other graphitized nanomaterials, such as graphitic carbon nanoparticles which are side-products formed during the synthesis of carbon nanotubes.

A quantitative determination of the filling yield can be provided by TGA of the sample in air. The TGA curves of the purified (empty) SWCNTs and the DSh cleaned LuCl$_3$@SWCNTs are presented in Figure 5. During the TGA in air, carbon species are completely oxidized to CO_2. Thus the solid residue recorded in the sample of empty SWCNTs results from the oxidation of the Fe nanoparticles to Fe_2O_3. A 1.7 wt.% of iron oxide corresponds to a 1.2 wt.% of iron (value previously mentioned). The oxidation of the sample of filled tubes will still have a small contribution from these iron nanoparticles, but the main contribution to the inorganic solid residue collected at the end of the experiment will arise from the oxidation of LuCl$_3$ to Lu$_2$O$_3$ (17.6 wt.%). Although TEM has been widely employed to estimate the degree of filling, the amount of encapsulated payload (i.e. filling yield) can be quantitatively determined from the TGA residues of the purified SWCNTs and the filled LuCl$_3$@SWCNTs, using the formula reported elsewhere[45] (see also the Supporting Information). In this case, the filling yield of LuCl$_3$ turned out to be of 23 wt.%, which is similar to the filling yields achieved with other metal halides (as per TGA).[45]
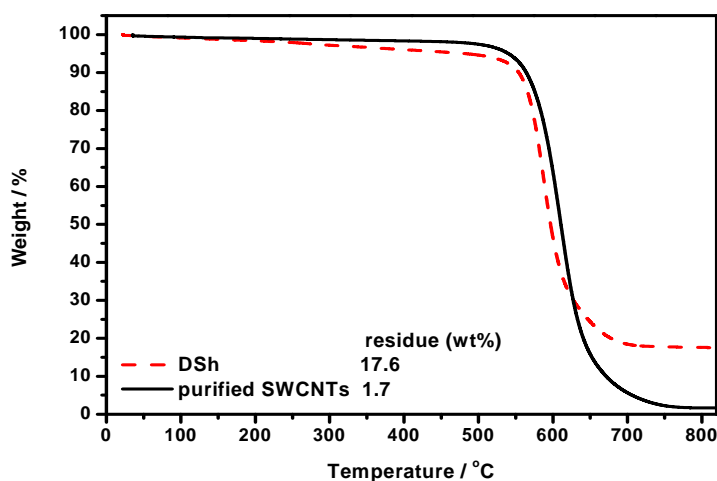
Figure 5. TGA of empty purified SWCNTs and LuCl$_3$@SWCNTs after being washed with the DSh protocol. Analyses were performed under flowing air at a heating rate of 10 °C min^{-1}.

Thus, only the DSh method was able to provide a clean product with a high filling yield. We believe that the superiority of the DSh method with respect to the other studied protocols lies in the fact that this setup provides a continuous flow of hot water resulting in the constant removal of external material whilst preserving the tubular structure of the nanocapsules. Furthermore, the use of a dialysis sack prevents sample contamination from the employed materials. Taking into account that we replaced the Soxhlet water every 24 h, we believe that the time employed for dissolving the external material can be further decreased with more frequent water replacements. A remarkable reduction of the liquid waste, which would be contaminated with radioactive materials when using ^{177}Lu, has been achieved with the developed protocol. As previously discussed, the widely employed SF process leads to clean samples when the material to be removed presents a good solubility in the employed solvent. In the present case, even if the SF did not result in a clean sample at the end of the process, the total volume of water employed (18 fractions) amounts to 18.90 L, in contrast to 0.96 L used for the optimized DSh. This represents a 95 % reduction in water waste, which gets contaminated with hazardous heavy (radioactive) elements. It is also worth noting that the use of dialysis sacks is compatible with both acidic and basic conditions and a wide range of organic solvents further expanding the range of application of the proposed process.

Table 1 summarizes the different investigated protocols for the removal of material remaining on the exterior of filled SWCNTs after the bulk filling process.

Table 1. Comparison of different washing protocols.

Protocol	Brief Description	Number of fractions	Time (days)	Comments
SF	sonication and filtration	18	6	Eventual contamination
SD	sonication and dialysis	18	6	Unable to completely clean sample, loss of sample during cleaning
SC	sonication and centrifugation	13	5	Unable to completely clean sample, loss of sample during cleaning
Sh	Soxhlet with cellulose thimble	6	6	Eventual contamination
DSh	Soxhlet with dialysis sack	4	4	Clean sample achieved, high filling

4. Conclusions

In summary, we have developed a sustainable system to process samples of filled SWCNTs with poor water soluble materials. The green protocol allows a 95 % reduction in water waste, which gets contaminated with hazardous heavy (radioactive) elements. The developed methodology benefits from a synergistic combination of both Soxhlet and dialysis. It allows the efficient removal of the large excess of non-encapsulated material present after filling carbon nanotubes. The methodology holds special interest for the manipulation of radioactive systems where reduction of the residual waste is a must, but can be employed for the external removal of other payloads. A quick *on-site* assessment the proper removal of external salts has been carried out by visual inspection of the filtrate, avoiding the consumption of the sample in the process. LuCl$_3$@SWCNTs has been the material of choice since the radioactive isotope ^{177}Lu is clinically employed in oncology. An efficient removal of the LuCl$_3$ remaining on the exterior of the SWCNTs after its encapsulation has been achieved whilst preserving the encapsulated

payload and structural integrity of the SWCNTs. We foresee the use of such optimized purification protocol as a path towards high-quality filled SWCNTs, exclusively endohedral, to be employed not only in the biomedical field but also in other applications where the presence of non-encapsulated material can be detrimental.

ASSOCIATED CONTENT

Supporting Information. $LuCl_3$ complex with CPC/CAS, CPC/CAS test of the DSh protocol, additional electron microscopy characterization, and calculation of filling yield (PDF).

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. [‡]These authors contributed equally.

ABBREVIATIONS

CNTs, carbon nanotubes; SWCNTs, single-walled carbon nanotubes; MX, metal halide; $LuCl_3$@SWCNTs, lutetium chloride filled SWCNTs.

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SYNOPSIS

A sustainable removal of non-encapsulated compounds from samples of filled carbon nanotubes is achieved using a soxhlet-dialysis system.

TOC
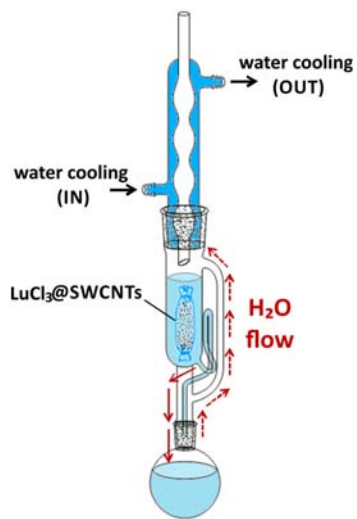
- Supporting Information –

Filling Single-Walled Carbon Nanotubes with Lutetium Chloride: A Sustainable Production of Nanocapsules Free of Non-Encapsulated Material

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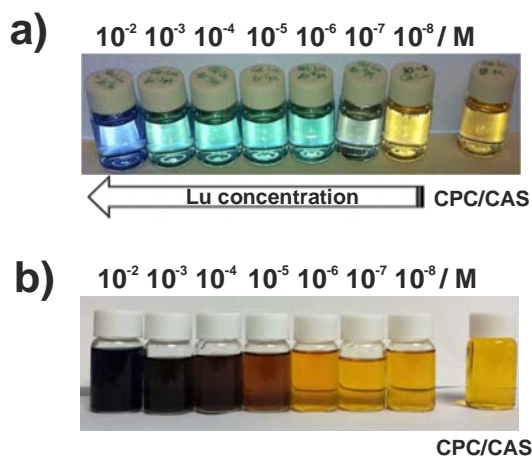[a]Institut de Ciència de Materials de Barcelona (*ICMAB*-CSIC), Bellaterra, 08193 Barcelona, Spain

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This Supporting Information has four pages and contains

five sections and four figures (Figs. S1- S4).

1. LuCl$_3$ complex with CPC/CAS

Aqueous solutions of 0.2 % (w/v) CPC and CAS were prepared, mixed in 1:1 ratio and diluted to $4 \cdot 10^{-3}$ %. A CPC/CAS solution (2 mL) was added to LuCl$_3$ aqueous solutions in the range of concentrations 10^{-2} to 10^{-8} M, keeping the final volume at 30 mL. Two different concentrations of CPC/CAS have been employed. From a qualitative point of view it is interesting to note that regardless of the concentration of CPC/CAS a royal blue color indicates the presence of lutetium chloride, not appreciable in the picture in b, and yellow indicates the absence of the metal salt (CPC/CAS in water has a yellow color). Greenish/reddish colors are observed between both stages.

a) 10^{-2} 10^{-3} 10^{-4} 10^{-5} 10^{-6} 10^{-7} 10^{-8} / M

Lu concentration — CPC/CAS

b) 10^{-2} 10^{-3} 10^{-4} 10^{-5} 10^{-6} 10^{-7} 10^{-8} / M

CPC/CAS

Figure S1. Vials containing 10^{-2}-10^{-8} M LuCl$_3$ in the presence of CPC/CAS showing a concentration-dependent change of color. A control sample of CPC/CAS is included on the right side of the photograph. The concentration of CPC/CAS is a) $4 \cdot 10^{-3}$% w/v and b) 0.2% w/v.
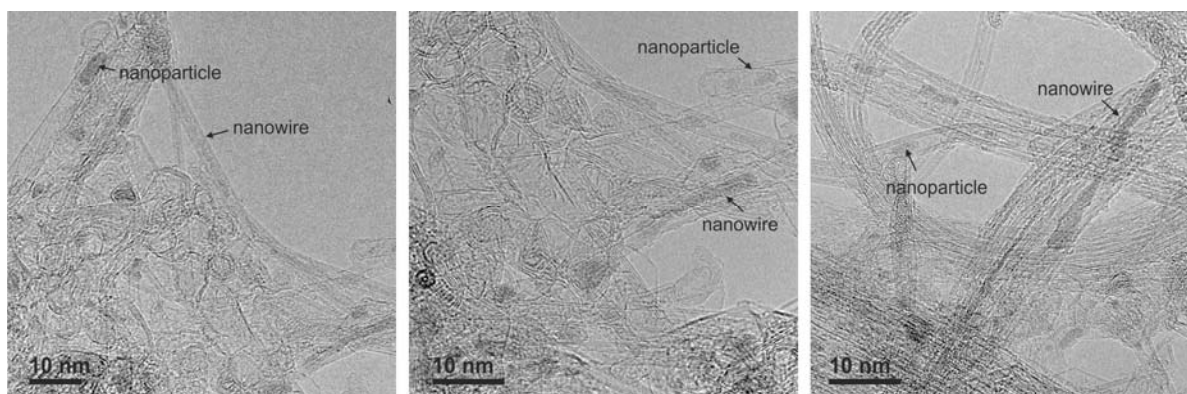
2. CPC/CAS test of the DSh protocol

Figure S2. Photos of aliquots after complexation with CPC/CAS using DSh for the removal of external LuCl$_3$ after first washing (left) and 4th final washing (right). The concentration of CPC/CAS is 0.2% w/v. Total volume of each fraction was 30 mL.

3. Additional HRTEM images of DSh sample

Figure S3. Additional HRTEM images of the sample of LuCl₃@SWCNTs after the final washing by the DSh protocol confirming that all the LuCl₃ is encapsulated within graphitic shells, as no external material is observed. Examples of small nanoparticles of LuCl₃ encapsulated within the CNTs as well as filling in the form of nanowires can be observed in the images.

4. EDX analyses on individual nanoparticles on DSh sample
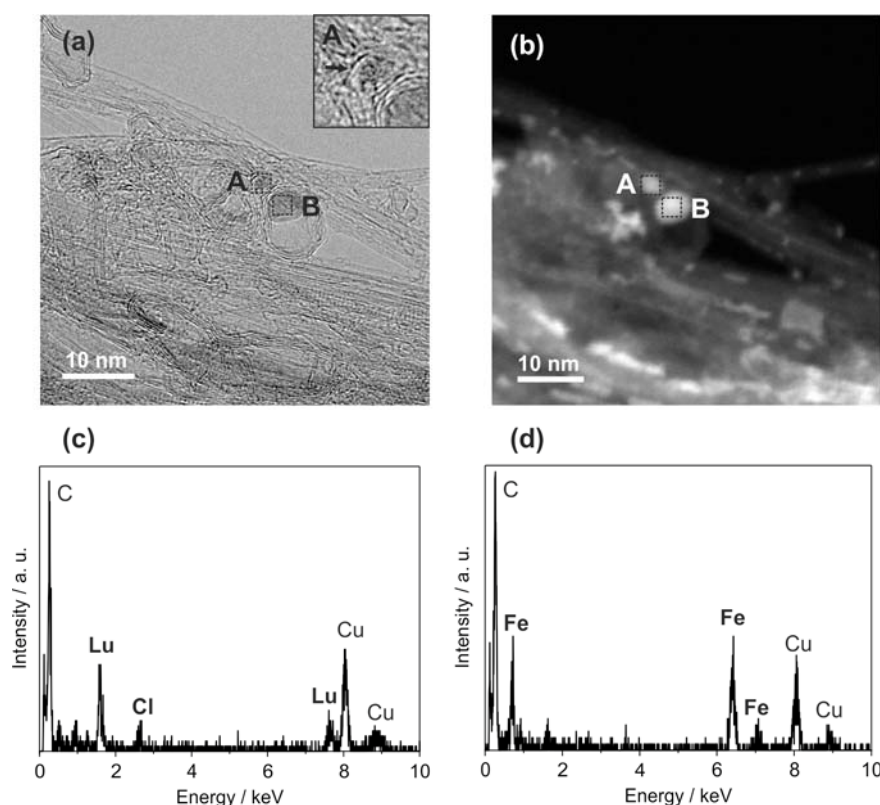
Figure S4. (a) HRTEM image on a bundle of CNTs showing nanoparticles **A** and **B** surrounded by graphitic shells. The inset shows nanoparticle **A** at higher magnification, with a black arrow pointing to the shell; (b) HAADF STEM images on the same area, where the nanoparticles appear with a bright intensity; (c) EDX analysis on nanoparticle **A** shows the presence of Lu and Cl, from the encapsulated material; (d) EDX analysis on nanoparticle **B** confirms that it is residual catalyst, as it is formed by Fe.

5. Calculation of filling yield[1]

Filling yield of $LuCl_3$@SWCNTs was calculated on the basis TGA residues in air: from empty nanotubes (R_1), clean filled nanotubes (R_2) and bulk material (R_A).

$$FY\ (wt\%) = \frac{100 \cdot (R_2 - R_1)}{R_A - R_1}\ (1)$$

Bulk material (W_B) is product of oxidation of lanthanide halide (W_A), where x and y are stoichiometric coefficients of reaction and M is molar mass. Thus residue can be calculated according to following formula:

$$R_A = \frac{100 \cdot y \cdot MW_B}{x \cdot MW_A}\ (2)$$

1. Ballesteros, B.; Tobias, G.; Ward, M. A. H.; Green, M. L. H., Quantitative Assessment of the Amount of Material Encapsulated in Filled Carbon Nanotubes. *J. Phys. Chem. C.* **2009,** *113* (7), 2653-2656.