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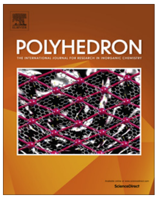

Synthesis of dry $SmCl_3$ from Sm_2O_3 revisited. Implications for the encapsulation of samarium compounds into carbon nanotubes

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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 $SmCl_3$.

1. Introduction

Inspired by the pioneering work of Prof. Malcolm L.H. Green on the encapsulation of materials into single-walled carbon nanotubes, and taking into account that filled carbon nanotubes (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

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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 applications, 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 °C 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 °C to sublime off the excess of NH_4Cl. Rapid heating should be avoided since not only it 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 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.

2. 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 °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 °C. The resulting product consisted of 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 h.

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 color 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