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J. Phys. Chem. C, **Just Accepted Manuscript** • DOI: 10.1021/acs.jpcc.8b05342 • Publication Date (Web): 09 Oct 2018

Downloaded from <http://pubs.acs.org> on October 14, 2018

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Morphological Phase Diagram of Gadolinium Iodide Encapsulated in Carbon Nanotubes

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Abstract

The melt phase encapsulation of gadolinium iodide (GdI_3) in small internal diameter carbon nanotubes (CNT) was explored to understand how the tubular structure of the host could chemically stabilize a hygroscopic metal halide. However, given the distribution of diameters in the as-received CNTs, the final sample consisted of mixed encapsulation products. These varied from the mono-elemental iodine chain to the atomic layer deposition of the binary halide. Supported by density functional theory calculations, these observations led to the proposition of a morphological phase diagram for GdI_3 encapsulation in CNTs as a function of the host's internal diameter.

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1. Introduction

Soon after the 1991 report of Iijima¹, filling of the internal channel of carbon nanotubes (CNT) was investigated²⁻⁴. Since then, this confined space has been utilized to encapsulate numerous substances, ranging from molecules⁵ to atomic chains⁶⁻⁷. Furthermore, there has been increasing interest in using filled CNTs as chambers to perform reactions at the atomic scale⁸ or, more recently, as storage/delivery vehicles of inorganic materials⁹⁻¹⁰. For instance, exotic or high temperature metal compounds can be confined via the chemical reaction of pre-encapsulated metal precursor.¹¹⁻¹³ Apart from CNTs various inorganic materials such as chalcogenides, halides, oxides and metals can be synthesized in a form of nanotube and can also be encapsulated¹⁴⁻¹⁸.

There are various methods to encapsulate substances inside CNTs and these have been reviewed in the past¹⁹⁻²⁴. One of the most popular is the use of melts which relies on surface tension and capillary forces to drive inorganic compounds into the interior of the nanotube^{2, 25}. While quantifying and evaluating what filling yield constitutes is not trivial, literature often refers that several tens of nanotubes per cent can be filled using the melt method²⁶⁻²⁷. When materials are constrained by the restricted inner volume of the nanotubes, new structural phases may be generated²⁸⁻²⁹. These can show unexpected properties such as the transition from insulator-to-conductor that sulphur undergoes when arranged inside the narrow bore of a single-walled carbon nanotube (SWCNT)³⁰. Moreover, the host nanotube may also experience phenomena such as host-guest and guest-host charge transfers which may eventually change its properties³¹.

One system that has gathered attention is the inclusion of gadolinium species in CNTs. The ion Gd^{3+} is a known magnetic resonance imaging (MRI) contrast agent because it is intrinsically paramagnetic. In previous studies, the Gd and Gd^{3+} species have been identified inside SWCNTs³²⁻³³ and carbon nanohorns³⁴. As an example, Gd^{3+} clusters decorating defect sites in CNTs were shown to be 40 times more sensitive than conventional MRI contrast agents³². These so-called gadonanotubes were developed through the use of GdI_3 , a highly hygroscopic compound. More recently, this metal halide was encapsulated in the form of solid rods or tubes within multi-walled CNTs (MWCNT)³⁵ and WS_2 nanotubes³⁶. These $GdI_3@NT$ systems (where @ means encapsulated in) represent promising moisture-protective storage vehicles³⁷ for the paramagnetic Gd^{3+} ion.

Our previous observations of tube-in-tube configurations in GdI_3 filled MWCNTs³⁵, prompted the search for this type of novel structures in smaller diameter hosts such as double- and triple-walled CNTs. In the following, we describe the structure and composition of this and a number of other configurations, all of which were obtained with the melt-phase filling method.

2. Experimental

Synthesis:

The CNT sample was purchased from STREM Chemicals Inc. (CAS # 308068-56-6) and used as-received. The filling material was gadolinium (III) iodide, with a purity of 99.99%, procured from Sigma-Aldrich (CAS # 13572-98-0). This metal halide has a melting point of 926 °C and is hygroscopic. To fill the nanotubes, the following procedure was followed: firstly, the CNT and GdI_3 powders were mixed, in a weight ratio of 1:8, inside an Ar-filled glove box. This mix was packed into a quartz ampoule which was then sealed under vacuum (between 0.1 and 1 Pa) and placed inside a furnace. Since capillary forces drive the metal halide melt to the tube's interior, where it solidifies upon cooling, it is advisable to cycle the dwell temperature some tens of degrees (here, ± 50 °C) above and below the melting point in order to optimize the filling yield.^{26, 38} The heating process followed the profile shown in **Figure S1**. On completion, the furnace cooled naturally to room temperature, the sealed ampoule was opened and the products collected.

Characterization:

Transmission electron microscopy (TEM) was carried out in various instruments: 1) FEI Titan ChemiSTEM, operated at 80 kV, and equipped with a probe corrector, Super-X® energy dispersive

X-ray spectroscopy (EDS) windowless solid state detector (SDD) and a Gatan imaging filter (GIF) spectrometer for electron energy loss spectroscopy (EELS); 2) FEI Titan Cubed Themis, operated at 60 or 80 kV, and equipped with both probe and image correctors, monochromator, Super-X[®] EDS SDD detector and GIF spectrometer for EELS; 3) FEI Cs-corrected Cubed Titan G², operated at 80 kV, and equipped with a Gatan K2 direct electron detection camera. Fresh samples for TEM were prepared by dispersing the post-filling powder mixture in ethanol and drop-casting it to a holey carbon Cu grid. The EDS and EELS spectra were collected in scanning TEM (STEM) mode. This localized chemical analysis required a STEM probe of about 1-2 nm to balance spatial resolution and signal intensity (beam current). To carry out high resolution STEM, a high angle annular dark field (HAADF) detector was employed commonly in conjunction with a smaller electron probe (< 0.5 nm). Structure models were created with the Crystal Maker V9.2.7 software. The high resolution TEM (HRTEM) simulations were carried out using QSTEM³⁹ and employing similar microscope parameters to those used in the experimental work. To better understand the structure of the encapsulated materials, models of the confined crystals and filled CNTs are described in the Supporting Information.

Raman spectra of the as-received and filled CNTs were acquired in a WiTeC Alpha 300RA+ with laser wavelength of 532 nm and a 100x objective lens. The probe size and power were, respectively, 2-4 μm and less than 2 mW. The samples were prepared by pressing the powdered material between two clean glass slides. X-ray photoelectron spectroscopy (XPS) studies were carried out in a Kratos Axis Ultra DLD spectrometer equipped with a monochromatic Al K α X-ray source ($h\nu = 1486.6$ eV) operating at 150 W, a multi-channel plate and delay line detector under a vacuum of 10^{-9} mbar.

Computational details:

The spin-polarized calculations of all nanostructures were performed within the framework of the density-functional theory (DFT) as implemented in the SIESTA 4.0 software⁴⁰⁻⁴¹. The exchange-correlation potential within the Generalized Gradient Approximation (GGA) with the Perdew-Burke-Ernzerhof parametrization was used. The core electrons were treated within the frozen core approximation, applying norm-conserving Troullier–Martins pseudopotentials. The valence states were chosen as $6s^25d^14f^7$ for Gd, $5s^25p^5$ for I, $2s^22p^2$ for C. In all calculations double- ζ polarized basis set was used. The k-point mesh was generated by the method of Monkhorst and Pack. The real-space grid used for the numeric integrations was set to correspond to the energy cutoff of 300 Ry. For k-point sampling, a cutoff of 15 Å was used. All calculations were performed using variable-cell and atomic position relaxations, with convergence criteria corresponding to the maximum residual stress of 0.1 GPa for each component of the stress tensor, and the maximum residual force component of 0.05 eV/Å. Formation energies of composite nanostructures have been estimated from the total energies relative to the total energies of molecular I₂, the bulk *hcp* Gd and bare carbon part (graphene or nanotube).

3. Results and Discussion

As-received and filled CNTs

The as-received commercial nanotubes consisted of >70% double-walled CNT (DWCNT) and triple-walled CNT (TWCNT), with the remaining being SWCNT and MWCNT. Given the structural heterogeneity of the CNT in the raw sample, the inner nanotube diameter distribution was expectedly large, ranging commonly from 0.7 to 9 nm. Moreover, open ends were identified along with a noticeable absence of catalyst particles which indicates that the as-received CNTs were pretreated by the supplier (**Figure S2**). These circumstances are favorable for the purpose of filling nanotubes through the melt-phase method^{2,4}. Following the encapsulation procedure, repeated surveys with HRTEM and HAADF-STEM led to an estimate of >50% filling yield (**Figure 1**). This is quite noticeable from the bright lines in **Figures 1d** and **1e** which originate from the presence of

gadolinium halide and its byproducts encapsulated in CNTs. The length of the encapsulation varied greatly, from just a few (e.g. nanoparticles) to hundreds of nm (e.g. nanowires/nanotubes).

Figure 1 a-c) HRTEM micrographs of filled CNTs from different locations; d) and e) HAADF-STEM images of the as-produced sample illustrating the high filling yield obtained (>50%) and the presence of long, continuously filled nanotube sections; f) Raman spectra, with the main bands labeled, for filled (red curve) and empty (black curve) nanotubes.

In Raman spectroscopy of CNTs, the radial breathing mode (RBM) peaks are normally used to determine the diameter of CNTs with one or two walls⁴². **Figure 1e** shows that these were present in the spectral window 50-400 cm^{-1} for the filled (red curve) and empty (black curve) CNTs. The RBM peaks were deconvoluted with Lorentz curve fittings (**Figure S3**) which enabled the corresponding listing of the CNT diameters (**Table S1**). This analysis confirmed both the presence of single- and double-walled CNTs and the wide diameter distribution measured from TEM. Interestingly, comparison of the two spectra shows that the filled sample has more peaks in the low frequency region. Assuming that the synthesis conditions used did not result in disintegration of the host nanotubes (which would change the proportion of SWCNT-to-DWCNT in the sample and, consequently, the RBM intensities profile), it is plausible to state that shifts in peak position took place due to the encapsulated materials⁴³. In regards to the G-band (1588 cm^{-1}), no significant shifts or shape changes were observed. This implies an absence of charge transfer between the encapsulated material and the nanotubes³⁰⁻³¹. By contrast, the 2D band changed after filling. For guidance, peak-fitted Lorentzian curves for this spectral region are shown in **Figure S4**. The presence of excess halide material, around and between the outer walls of the CNTs (confirmed with high resolution TEM), might account for this as the 2D band is known to be sensitive to the surrounding environment⁴⁴. The high-temperature filling process did not alter the oxidation state of this excess halide as the presence of the paramagnetic Gd^{3+} species dominated the high-resolution Gd 3d XPS spectrum of the sample (**Figure S5**). The absence of impurities,

including oxygen or other secondary oxide phases, was also inferred from XPS and, as discussed later, confirmed locally with EDS/EELS.

3.1 Filled CNTs - structural and chemical analysis

Following the sample overview above, the chemical composition, morphology and structural phase of the nominally confined metal halide were analyzed. Below, the different systems identified are first divided according to their composition and then, their morphology.

Mono-elemental iodine fillings:

There have been previous reports of mono-elemental iodine assembled as linear chains inside SWCNT^{6, 45}. **Figure 2** illustrates well this type of filling in a DWCNT host. The continuous bright line in **Figure 2a** confirms that the filling is non-interrupted throughout the 30 nm long section shown (note that the contrast in HAADF-STEM is related to the atomic number of the elements observed⁴⁶). The corresponding HRTEM micrograph is shown in **Figure 2b**. The inner and outer diameters of the DWCNT were 7.6 ± 0.5 Å and 15 ± 0.5 Å, respectively. This implies that, when accounting for the radius of carbon atoms (0.68 Å)⁴⁷ and van der Waals interactions, the available cross-sectional space for encapsulation is close to 3 Å. Knowing that the expected size of an I atom is ~ 2.8 Å while that for Gd is 3.6 Å⁴⁷, it is possible to infer that the structure observed must be a monoatomic linear chain of iodine. Both the EDS (**Figure 2c**) and EELS (**Figure 2d**) spectra indicate the presence of pure iodine.

Figure 2 a) HAADF-STEM image of a 30 nm filled section of a nanotube; b) TEM micrograph of the system in a) confirming the presence of a DWCNT and a linear atomic chain filling; c) EDS spectrum of the system in a); d) EELS spectrum of a). The absence of Gd in c) and d) is clear; e) Structural models of the I@DWCNT, in longitudinal and cross-sectional views, where the I atoms are represented by violet spheres; f) Magnified view of b) with a matching simulated image superimposed and respective transverse image contrast intensity line profiles on the right; g) longitudinal intensity line profile of I@DWCNT.

To better understand the arrangement of the iodine atoms, image simulations were carried out. **Figure 2e** illustrates the structural model used while **Figure 2f** shows an overlap of the experimental and simulated images together with the respective intensity profiles taken along and across the nanotube. The average distance between I atoms was 3 ± 0.5 Å, close to the interatomic spacing of the iodine (I_2) molecule, 2.7 Å^{45, 47}. On the other hand, that value is almost two-thirds of the Gd-Gd bond length, as reported for a linear chain of Gd atoms (4.1 Å)²⁸. Overall, the structural and chemical analyses confirm a linear arrangement of I atoms and the absence of Gd intercalant species.

Mono-elemental gadolinium fillings:

In addition to linear chains of iodine, gadolinium fillings were identified inside triple-walled CNTs. As illustrated in **Figure 3**, these fillings were well-ordered. The host shown has an internal diameter of 15 ± 0.5 Å (**Figure 3a**). For this particular Gd@TWCNT, four rows of atom columns are visible (**Figure 3b**) and its EDS and EELS analyses revealed equivalent chemical signatures. The peaks derived from Gd are present in both **Figures 3c** and **3d**, while I is notoriously absent.

Figure 3 a) TEM micrograph of a Gd@TWCNT, the distance between the first and third (or second and fourth) rows of atoms is around 5.78 ± 0.5 Å; b) Top: magnified view of a), with a matching simulated image superimposed, bottom: structural models of the Gd@TWCNT with longitudinal and cross-sectional views, where Gd atoms are represented by pink spheres; c) EDS spectrum of the system in a); d) EELS spectrum of the system in a). Iodine was not identified.

To better understand the gadolinium filling, structural models for the Gd@TWCNT were constructed. These were then used to simulate the high resolution TEM micrographs. In standard conditions of temperature and pressure, the thermodynamically stable Gd phase is the hexagonal closed packed (*hcp*) structure (space group $P6_3/mmc$).⁴⁷ The *hcp* Gd structure has an ABAB type stacking with *c*- and *a*-axis lattice parameters of 5.78 Å and 3.64 Å, respectively. Based on the experimental and simulated images, an *hcp* crystal with the growth direction of the encapsulated Gd nanowire being [130] was best placed to explain the system observed (more details in **Figure S6**).

Compound gadolinium iodide fillings:

Besides mono-elemental fillings, the encapsulation of binary compounds was also observed and occurred in three morphologies: nanoparticles (either isolated or aggregated), nanowires and nanotubes.

Nanoparticles and Nanowires

Both crystalline and amorphous nanoparticle fillings were observed (**Figure 4a**). In average, the length of the particles was 6 nm. Structural analysis of the example shown in **Figure 4b**, points to the presence of a GdI_3 crystallite (space group $R\bar{3}$),⁴⁸ encapsulated in a TWCNT with inner and outer diameters of 19.6 ± 0.5 Å and 34.4 ± 0.5 Å, respectively. The $[310]$ direction of this confined particle is coincident with the tube's main axis, as shown in **Figure S7**. Comparing the simulated electron diffraction pattern obtained from the model used (**Figure S8a**) with the fast Fourier transform (FFT) pattern extracted from the HRTEM image (**Figure S8b**), lattice spacing deviations of $< \pm 5\%$ were observed. This is common for metal halides confined in CNTs^{35, 49}. The spectroscopic analysis of various nanoparticles showed the presence of iodine and gadolinium (**Figures 4c** and **4d**). However, quantification of the Gd:I ratio for individual nanoparticles was not possible due to their beam sensitive nature.

Figure 4 a) TEM micrograph with two particles filling a TWCNT; b) Top: superposition of experimental and simulated images for GdI_3 @TWCNT, bottom: structural model of the filled nanotube, I = violet spheres, Gd = pink spheres; c) EDS spectrum of the system in a); d) EELS spectrum of a), both I and Gd were identified; e) TEM micrograph of a DWCNT filled with gadolinium iodide (scale bar is 2 nm); f) HAADF-STEM image (scale bar is 2 nm) of the system in e); g) STEM-EDS elemental maps of the section marked in f) for C (green), Gd (red) and I (blue); h) EDS spectrum of the system in e), confirming the 1:3 ratio of the halide salt.

Multi-segmented chains of nanoparticles have been reported for CNTs encapsulating metal halides such as KI and CsI³⁸. Here, this same configuration was observed for gadolinium iodide nanoparticles. An example of these chains is shown in **Figures S9** and **S10**.

Nanowires are the most common type of filling for metal halides encapsulated in CNTs. A number of these structures were identified such as the one in **Figure 4e**. For this system, the inner and outer diameters of the DWCNT were 12 ± 0.5 Å and 19 ± 0.5 Å, respectively. In this case, the structure was stable enough under the electron beam to enable chemical mapping with EDS. Contrastingly, when STEM-EELS mapping was attempted, the nanowire disintegrated, as shown in **Figure S11**. A reason for this may be that the STEM-EDS mapping was performed with an advanced Super-X[®] EDS detector that collects more signal in a significantly shorter time than the EELS detector available⁵⁰. Besides confirming the presence of Gd and I, it was possible to calculate the stoichiometry of the binary crystal as GdI_3 . Interestingly, other systems showed nanowires with a stoichiometry close to GdI_2 and GdI_4 (**Figures S12** to **S14**). This corroborates previous observations using MWCNT hosts³⁵. The structural analysis of these confined nanowire systems was not straightforward as none of the attempted orientations for the $R\bar{3}$ GdI_3 crystal would fit the experimental images. We are likely in the presence of a new structural arrangement of gadolinium iodide whose detailed study will require further attention in the future.

Nanotube

Approximately 15% of all filled nanotubes observed were of the type “tube-in-tube”. In the literature, there are very few examples of inorganic tubes encapsulated in CNTs. Possibly, the first reference dates back to 2013 by a team that included one of the present authors³⁵. In that study, gadolinium iodide nanotubes encapsulated in MWCNTs were briefly mentioned but their structure and chemistry were not detailed. Apart from GdI_3 , other metal halides with this morphology have been identified more recently inside the cavity of CNT.^{23, 51-53} Generally, the highly crystalline confined inorganic tubes show diameters and morphologies that are governed by the templating host. In addition, it should be stated that the tube-in-tube configuration is not exclusive of carbon tubular hosts as analogous chalcogenide systems have been reported. For instance, using a WS_2 host nanotube, a variety of encapsulated materials crystallize with a tubular shape such as GdI_3 , BiI_3 , PbI_2 , SbI_3 and MoS_2 ^{36, 54-55}.

Figure 5 a) TEM micrograph of a tube-in-tube system; b) the corresponding HAADF-STEM image of a); c) and d) EDS and EELS point spectra, respectively, of a) - these confirmed the presence of Gd and I; e) TEM micrograph of a large GdI_3 NT@MWCNT; f) The model of the GdI_3 NT@TWCNT used to simulate the HRTEM image in g); g) Augmented view of the system in e), with a simulated HRTEM image superposed.

In **Figures 5a** and **5b**, the guest metal halide nanotube is single-walled with a diameter ranging from 2.1 to 3.2 nm. The visible layers of the encapsulated tube are seen, conforming to the shape of the templating CNT. The chemical analysis of this system indicates an overall Gd:I ratio of 1 to 3 (**Figures 5c** and **5d**). A number of similar tube-in-tube systems were studied using HAADF-STEM images (**Figures S15**). Some of these had internal double-walled tubes as shown in **Figure S15c**.

To better understand the structure of the encapsulated metal halide tube, HRTEM image simulations were performed for a wide tube-in-tube system (**Figure 5e**). Specifically, the diameter of this confined halide tube ranged from 5.8 nm to 8.1 nm (in fact, it was the largest tube we observed). Given software limitations (in regards to the number of atoms it can handle), the GdI_3 NT@CNT model created had three outer carbon walls and the internal single-walled tube was 6 nm wide. Models and image simulations for both zigzag (**Figures S16a to S16d**) and armchair (**Figures S16e to S16h**) halide guests were performed with 0° and 15° tilt. The experimental image matches well with a zigzag- GdI_3 NT at 15° tilt (**Figures 5f** and **5g**). The formation of a conformal GdI_3 single layer is confirmed by comparing the thickness of the shell modelled (3.7 Å) to that measured in the experimental micrograph (3.65 Å). Note that the monolayer of $R\bar{3}$ GdI_3 is composed of Gd cations sandwiched between two I sub-layers. In our work, the range of diameters for the guest halide coatings was between 1.8 and 8.1 nm.

Further orientation and structural parameters were determined from the FFT analysis of the experimental micrograph in **Figure 5g**. As showed in **Figure S17**, the d-spacings measured (3.71,

3.69 and 3.69 Å) compare well with the analogous values of the bulk material (3.77 Å). The 5% variation is common for confined halides in CNTs³⁵⁻³⁶ and can be accounted for either by lattice strain or distance measurement errors (due to the pixel size in the micrographs). Interestingly, we noticed that a constriction of the internal CNT wall was a common feature of these tube-in-tube systems.

3.2 Filled CNTs - DFT calculations

In order to get further insight for the morphologies and chemical bonding of the different systems observed, DFT calculations were employed. Several types of representative CNT-confined nanostructures have been considered: atomic chains of I, nanowires of Gd and nanotubes of GdI₃ (**Figure 6**). From the experimental TEM images, the inner-most SWCNT hosting the linear atomic chains of I should have a chirality of (5,5) or (8,2), as shown in **Figure 6a**. As for those systems with *hcp* Gd, the narrowest guest wire is likely confined by a (12,3) SWCNT (**Figure 6b**).

Figure 6 Ball-and-stick models of Gd-I-C nanostructures employed as prototypes for structural stability calculations. a) Side-on view of the structural model for an atomic chain of iodine encapsulated in a (8,2) SWCNT; b) Side-on view of the structural model for a *hcp* Gd nanowire encapsulated in a (12,3) SWCNT; c) Model of heterostructure composed of a GdI₃ nanostrip (NS) atop a graphene; d - e) End-on views of the models of single-walled GdI₃ NTs; f) Cross-sectional view of a nanostrip of GdI₃. The geometry of all structures was optimized using the DFT method. Gd, I and C atoms are painted in magenta, blue and black, respectively.

Figure 7 a) Energies of iodine intercalation into SWCNTs (black filled spheres) and DWCNTs (red open circles) as a function of the I-I interatomic distance - for clarity, the number of I atoms and unit cells of the host nanotube (which together make up the I@CNT supercell) is given; b) Strain energies for armchair and zigzag single-walled GdI₃ NTs (black open squares and circles) and zigzag GdI₃ nanostrip (red filled triangles) as a function of radii (here, the “radius” of a nanostrip is the width normalized by 2π).

Starting with the I@SWCNT composites, these can have different linear densities of iodine atoms along the host’s axial direction. Our calculations found that two supercells were particularly stable when considering their exothermic formation energies (E_{in}). Both the 2I@8,2 SWCNT and the 5I@6,5,5 SWCNT systems presented $E_{in} \approx -1.10$ eV/I-atom (**Figure 7a**). Therefore, notwithstanding the host nanotube’s chirality, an endohedral atomic chain of iodine should exist as a row of equidistantly ordered atoms with period of 3.0-3.3 Å. These values correlate well with the experimental TEM observations presented above.

To check quantitatively the possible influence of additional carbon shells on the intercalation energy, DFT calculations were performed for three systems of iodine encapsulated in DWCNT. **Figure 7a** includes the results of intercalating iodine into 8,2@16,4 and 5,5@10,10 CNT hosts (open red circles). For the least stable intercalates, the iodine interatomic distance (D_{I-I}) is merely 2.5 Å, implying a highly strained atomic chain. For this extreme case, the type of host nanotube (whether SWCNT or DWCNT) clearly influences the intercalation energy. However, when one considers the average interatomic distance experimentally measured (~ 3 Å), the systems stabilise considerably and differences in intercalation energy become negligible between DWCNT and SWCNT hosts (≤ 0.05 eV/I-atom). This trend is preserved for all other D_{I-I} considered (3.5 – 8.0 Å) and does not depend on the number of additional carbon walls (double, triple or multi).

The supercell of a Gd@SWCNT was assembled from the unit cells of a *hcp* Gd₆ nanowire (i.e. with 6 Gd atoms per cell in the direction [130]) and a (12,3) SWCNT (with a lattice parameter of 6.56 Å). The host-guest parameters ratio satisfies well the requirement for lattice commensurability resulting in a Gd₆@(12,3) SWCNT with a 6.5 Å long unit cell, after geometry optimization (**Figure 6b**). The formation of a bare *hcp* Gd₆ nanowire is exothermic with an energy of +1.54 eV/Gd-atom which indicates a highly reactive surface. Interestingly, the formation of the same nanowire within a (12,3) SWCNT, while still exothermic, bears the remarkably low energy of +0.68 eV/Gd-atom. In turn, an atomic chain of Gd within a SWCNT will be thermodynamically less stable. Calculations for a linear 2Gd@3(5,5) CNT composite revealed that the minimum formation energy is +1.50

eV/Gd-atom. Furthermore, there is a large interatomic Gd-Gd repulsion due to the transfer of charge from the Gd chain to the nanotube host (0.90 eV/Gd-atom). Therefore, and in contrast to the iodine case, it is unlikely that a confined linear atomic chain of Gd is ever found inside a CNT. Geometry optimization of the bulk and nanostrip of GdI_3 (space group $R\bar{3}$) did not reveal significant distortions to the hexagonal symmetry. The calculated equilibrium lattice parameters for bulk GdI_3 ($a = 7.39 \text{ \AA}$, $c = 19.69 \text{ \AA}$) were in fair agreement with the literature ($a = 7.54 \text{ \AA}$, $c = 20.83 \text{ \AA}$)⁵⁶. When isolated, the GdI_3 nanostrip undergoes a slight in-plane contraction, resulting in an equilibrium lattice parameter of $a = 7.35 \text{ \AA}$. Here, the nomenclature of single-walled GdI_3 NT follows that of the well-known CNTs. Two sets of halide nanotubes were studied: 1) the *armchair* (n,n) type, with indices varying from $n = 3$ to $n = 7$ and *zigzag* ($n,0$) with $n = 5$ to 8 , as shown in **Figure 6d** and **6e**. Note that the morphology integrity of all studied GdI_3 nanostructures was preserved after the geometry optimization, irrespective of the chirality type and the chosen indices. Accordingly, the halide nanotubes retain the structural units of GdI_6 as distorted octahedra.

Further to the above, the energies (ΔE) of the nanotubes were calculated relative to the total energy of an infinite nanostrip of GdI_3 . This allowed us to trace the relative stability of the GdI_3 NT as a function of both the radius and chirality. In fact, this quantity corresponds to the strain energy of these nanostructures. The values of ΔE per GdI_3 -unit are collected in **Figure 7b**. It is clear that they obey the classical $\sim 1/R^2$ rule in the elasticity theory for the bending of a layer and may thus be satisfactorily described using a single function. The proportionality factor between ΔE and $1/R^2$ for all considered GdI_3 NTs is equal to $12.57 \text{ (eV}\cdot\text{\AA}^2\text{)/unit}$ or $3.1 \text{ (eV}\cdot\text{\AA}^2\text{)/atom}$. Noteworthy, this factor is in-between the $0.5 \text{ (eV}\cdot\text{\AA}^2\text{)/atom}$ for SWCNTs and the $16.1 \text{ (eV}\cdot\text{\AA}^2\text{)/atom}$ for single-walled MoS_2 nanotubes⁵⁷. Overall, our calculations reveal that the elastic strain of the GdI_3 layers should not be the main constraint to a future mass synthesis of free-standing GdI_3 NTs. When the thermodynamic stability of a nanostrip (**Figures 6c** and **6f**) and that of a single-walled GdI_3 NT were compared, the latter was predicted to become more stable for GdI_3 nanotube diameters larger than $16 \text{ \AA}$ (**Figure 7b**).

In regards to the electronic properties of the confined GdI_3 NTs these are not altered from their free-standing counterparts. As it will be detailed in a follow-up communication, there is no host-guest charge transfer in these tube-in-tube composites (which concurs with the above Raman spectral observations).

3.3 Discussion

It was possible to stabilize, inside CNTs, metal halide nanostructures with varied composition, structure and morphology. The information about the internal diameter of more than 100 filled CNT as well as the corresponding type of encapsulation were collected from HRTEM images and compiled in the histograms show in **Figure S18**. Experimentally, the average inner diameter of CNT for the I@CNT was around $8 \text{ \AA}$. The iodine chains were successfully reproduced *in-silico* employing models of (5,5) and (8,2) host nanotubes. As for the confined Gd nanowires, it was predicted that the CNT host had to be slightly larger. This would reduce the structural instability of the Gd NW and avoid the formation of carbides. Experimentally, the *hcp* Gd phase was present in CNTs with diameters between 10 to $20 \text{ \AA}$. Beyond this point, larger diameters of the host nanotube seem to favor the encapsulation of the compound metal halide. However, the range of morphologies can differ. Nanoparticles (whether isolated or aggregated) or nanowires of GdI_3 form inside CNTs with an internal diameter of 12 to $55 \text{ \AA}$. Moreover, upwards from $20 \text{ \AA}$, the formation of the tube-in-tube configuration was registered. Especially for the larger CNTs (with internal diameters of $>30 \text{ \AA}$), long and continuous GdI_3 tubular structures were identified. In these, the conforming nature of the inner nanotubes to the host template is striking. The halide coats the inner walls of the CNTs with remarkable regularity and uniform thickness, to the point that closed ends of the GdI_3 NTs mirrored the templating sections of the host.

Figure 8 Schematic summary of the diameter effect of the host CNT on the structure and chemistry of filled CNTs. The models of I@CNT, Gd@CNT, GdI₃@CNT and GdI₃ NT@CNT are seen in cross-sectional view. The number of walls in the host CNT is merely representative. The colored rectangles mark the range of diameters in which a certain type of filling is observed.

Based on the above experimental and simulation results, it is confirmed that the diameter of the host nanotube influenced considerably the type of encapsulated crystals observed. Conventionally, phase diagrams show what structural phases are present at given conditions of temperature, pressure and composition. In the case of filled CNT, morphological phase diagrams have been plotted as a function of the internal diameter of nanotube hosts.⁵⁸⁻⁵⁹ As shown in **Figure 8**, there is a composition-CNT diameter relation for the present metal halide system. Different compositions (mono-elemental or binary) may overlap in diameter range. Statistically, and amongst the 114 filled CNT analyzed, 76% were filled with the binary compound. In the corresponding diameter range (>10 Å), additional morphological variations (from particles to tubes) were observed. Of these, less than 15% adopted the tube-in-tube (GdI₃ NT@CNT) configuration (**Figure S18**).

4. Conclusions

Melt-phase filling of as-received CNT with GdI₃ was demonstrated. The size of the host cavity played a pivotal role in determining the structure, morphology and chemical composition of the encapsulated materials. From linear atomic chains to conformal monolayer coatings, several types of inorganic crystals were identified. Overall, this amounts to the existence of a “morphological phase diagram” for this type of nanocomposite systems.

As concerns the “tube-in-tube” configuration, the GdI₃ NT@CNT represents a novel addition to a nascent family of internally-coated nanotubes. These could bring exciting developments to a number of engineering fields such as targeted drug delivery, medical imaging, fluid mechanics and nanoscaled porous membranes.

5. Conflicts of interest

There are no conflicts of interest to declare.

6. Acknowledgements

The authors are thankful for the financial support from KAUST (BAS/1/1346-01-01). NMB and JS thank KAUST for graduate scholarships. EA and FLD acknowledge the financial support by the N2020: Nanotechnology based functional solutions (NORTE-45-2015-02). AE acknowledges the support by Act 211 Government of the Russian Federation, contract No. 02.A03.21.0006.

7. Supporting Information

Melt synthesis temperature profile; TEM and size distribution histogram of as-received CNT; Raman analysis of empty and filled CNT; XPS of empty and filled CNT; Structural models of filled CNT; Structural, chemical and beam damage analysis of GdI₃NT@CNT; Statistical analysis of filled CNT.

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