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# Inorganically filled carbon nanotubes: Synthesis and properties\*

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Abstract: Since the discovery of carbon nanotubes (CNTs) in 1991, widespread research has been carried out to understand their useful physical and electronic properties and also to explore their use in devices. CNTs have many unique properties such as tunable electrical resistance, mechanical robustness, and high thermal conductivity, which when combined with other inorganic materials such as phosphors or superconductors could lead to heterostructures with diverse functionality. We have been able to obtain mass production of such materials wherein CNTs form core-shell heterostructures with metals, semiconductors, insulators, and even metal-semiconductor heterojunctions. The emerging strategy employs a high-temperature chemical vapor deposition (CVD) technique and high heating rates. Interestingly, due to their high temperature stability, CNTs can act as a nanoreactor for production of exotic materials inside it. In this article, we take ZnS-filled CNTs as an example to explain our synthesis strategy. We explore the optical behavior of these complex materials, analyzing both their luminescence and degradation upon exposure to an electron beam. In addition, the mechanical response of filled CNTs has been evaluated individually inside a transmission electron microscope fitted with an atomic force microscopy-transmission electron microscopy (AFM–TEM) sample holder. Many applications can be envisioned for these nanostructures ranging from nanothermometers to photo-protective storage and delivery devices.

*Keywords*: carbon nanotubes; cathodoluminescence; heterostructures; mechanical properties; nanowires.

## INTRODUCTION

During the last two decades, the discovery of carbon nanotubes (CNTs) has been followed by intense research leading this field to continuous evolution [1]. The basic structural unit of a nanotube is a sin-

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gle graphitic sheet rolled up into a cylinder with lengths of micrometers and diameters up to 100 nm [2]. In practice, CNTs can be broadly classified in two classes based on their number of walls, i.e., single- and multi-walled CNTs. Several strategies have been developed for their synthesis, such as laser ablation, arc discharge, and chemical vapor deposition (CVD) techniques [1]. Depending on the way the graphene has been assembled, single-walled CNTs can be either metallic or semiconducting. Because of their exotic properties, CNTs have emerged as an attractive candidate in diverse technological applications, such as in polymer composites, sensors, and several others [3].

An interesting aspect of the CNTs is their inner cavity, which can be filled with another material in order to create novel heterostructured nanomaterials [4]. In fact, the cavity may act as a template for other elongated structures. These will have extremely large interface areas, which may well induce unusual properties in the ensemble [5]. Moreover, the CNTs could be used as a storage medium for airor moisture-sensitive materials. Led by such motivations, the prospect to fill their inner cavities with different materials such as fullerenes, metals, alloys, fluids, and biomolecules has been extensively investigated [5–7]. The filling procedure is based on two methods, (a) wet chemical methods, where chemicals dissolved in solvent are used as precursors and (b) physical methods, where tip-open CNTs are infiltrated with molten materials [5]. However, a major drawback for these techniques is that they cannot be used for many important functional materials (semiconducting ZnO or ZnS, for instance) since these are insoluble in solvents and become reactive at higher temperatures. Moreover, the fillings obtained by these conventional techniques are often partial and polycrystalline.

Herein, we present a novel method that has been successfully employed to obtain a variety of CNT-based core-shell heterostructures where the core is made of selected inorganic materials such as metals and semiconductors [8,9]. To illustrate this process, we take ZnS-filled CNTs (a.k.a. ZnS@CNT) as a model system. Further to growth conditions, we analyzed some properties such as reactivity, luminescence, and mechanical behavior.

#### ZnS@CNT SYSTEM

Zinc sulfide (ZnS) is a II-VI semiconductor with a direct bandgap of 3.8 eV. It has a high refractive index and transmittance in the visible range and has been extensively investigated for a number of applications including light-emitting devices and phosphors [10,11]. It has been reported that by doping with Group III elements, the conductivity of ZnS can be greatly improved [12].

The synthesis of ZnS@CNT materials was carried out in a high-temperature induction furnace. Details of the procedure and the furnace employed can be found elsewhere [8]. The morphology and composition of the product can be tuned by varying the composition of the reactant mixture and the synthesis temperature. It was also found that the addition of Ga or In to the synthesis process greatly improves the reaction yield. In a typical synthesis for Ga-doped ZnS-filled CNTs, a.k.a. Zn(Ga)S@CNT, 0.20 g of ZnS, 0.10 g of GaS, and 0.01 g of activated carbon powder were mixed in a graphite crucible and placed inside the induction furnace. The furnace was repeatedly evacuated and then filled with 99.99 % nitrogen gas, generating an inert atmosphere. The synthesis was carried out within the temperature range of 1300–1450 °C for 45 min while simultaneously maintaining a N<sub>2</sub> carrier gas flowing at a rate of 0.2 l/min. After the furnace was switched off, a wool-like product was collected at the outlet graphite tube placed at the top of the reaction chamber.

Figure 1a is a low-magnification scanning electron microscopy (SEM) image (JSM-6700F) of the as-synthesized Zn(Ga)S@CNT. At the micron-scale, the nanostructures show uniform length and diameter. Notably, we also obtained similar nanostructures when no Ga-dopant was added to the reaction mixture. Unfortunately, the reaction yield considerably decreased, resulting in a large proportion of by-products. In Fig. 1b, we show a high magnification image of the Zn(Ga)S@CNT, wherein two structures are visible. Uncommonly, one of the tubes is partially filled as indicated by the contrast difference along its length. A schematic representation of the ZnS-CNT core-shell structures is shown in Fig. 1c. Detailed examination of the product showed that one end of the filled CNTs is open while the other is

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**Fig. 1** (a) Low-magnification SEM image showing Zn(Ga)S@CNT. (b) High-magnification SEM image showing a partially empty CNT. A schematic of the nanostructure is shown in (c). (d) XRD pattern of the as-synthesized product.

closed. The composition of the product was confirmed by X-ray diffraction measurements (Fig. 1d, Rint 2200 diffractometer, Cu K $\alpha$  radiation). The diffraction peaks in the pattern can be indexed to wurtzite ZnS (h-ZnS, a = 3.82 Å and c = 6.25 Å, JCPDS card: 79-2204). There is, however, an additional peak at ~33°, which appears due to the cubic ZnS phase. This has been assigned partially to a thin cubic ZnS phase present near the interface with the shell CNT [8a].

Figure 2a shows a transmission electron microscopy (TEM) image of a Zn(Ga)S@CNT with regular thickness along its length. In Fig. 2b and its inset, the corresponding high-resolution TEM (HR-TEM) images and selected-area diffraction (SAED) pattern along the [-12-16] zone axis of wurtzite ZnS are given. All the spots on the SAED pattern can be indexed to wurtzite ZnS, showing that the structure is single-crystalline. In the HR-TEM image, the spacing between the fringes parallel to the nanowire growth direction is 3.2 Å. This corresponds to the set of lattice planes characteristic of the growth direction of the Zn(Ga)S@CNT along the [10-10] direction. It should be noted that the common growth direction for hexagonal systems like ZnS and ZnO is along the [0001] [13]. This unusual orientation can be explained by considering the growth of the ZnS phase proceeding from the walls of a CNT toward the center of the cavity rather than along the CNT length, as previously explained [8a]. Figure 2c shows the HR-TEM image of a CNT shell. The thickness of the CNT shell varies from 3 to 5 nm, and the graphitic layers are turbostratic. Figure 2d shows a typical energy-dispersive X-ray spectroscopy (EDS) fingerprint of the structure. The Zn(Ga)S@CNTs are fairly uniform in composition throughout their length, with the Ga composition varying in the sample batch within the interval of 2-4%.



**Fig. 2** (a) Low-magnification TEM image of a Zn(Ga)S@CNT nanowire. (b) HR-TEM image of the core structure. Inset shows an SAED pattern. (c) HR-TEM image of the CNT wall. (d) EDS pattern of the nanostructure.

The reaction conditions can be changed in order to tune the morphology of the product. For example, the thickness of the carbon layers covering the Ga-doped ZnS nanowires can be controlled by changes in the reaction temperature. Figure 3a is an SEM image of the nanostructures with a thicker carbon-shell (about 20 nm) obtained via a high reaction temperature of ~1500 °C. Additionally, the length of the Zn(Ga)S@CNT can be increased by reducing the carrier gas flow-rate (this raises the residence time of the reacting vapor in the hot zone). Finally, it is also possible to increase the diameter of the Zn(Ga)S@CNT by large extents. As an example, Fig. 3b shows SEM images of a ZnS-CNT system where the shell structure is considerably wide, about 1  $\mu$ m. Moreover, the overall shape resembles a collapsed tubular structure. These materials are obtained by using similar synthetic conditions to those described above, apart from employing  $In_2S_3$  instead of GaS. It should be noted that while we have been able to tune the size of the carbon shell, which is relevant for storage purposes, our effort to obtain pure micron-sized products under these experimental conditions is still on. Nonetheless, important insight into the growth mechanism of these ZnS-CNT systems was found by close examination of this specific product. The inset in Fig. 3b shows a large Zn(In)S@CNT structure where the core is visibly empty is shown. This further supports our proposal that the growth of the core takes place from the side walls of the shell CNT. Consequently, the first step in this synthesis is proposed to be the generation of Zn vapor



Fig. 3 (a) SEM images showing a Zn(Ga)S@CNT with a thicker CNT wall structure. (b) Collapsed carbon microtubes. The inset shows a microtube with a partially empty core.

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and  $CS_2$  gas. We base this assumption on the observation that when ZnS and C are kept separately in the furnace, rather than being thoroughly mixed, no product was obtained.

Apart from ZnS, this synthesis procedure can be extended to several other inorganic materials, such as oxides, nitrides, and phosphides [14–16].  $Ga_2O_3$  nanowires with average core diameter of 40 nm wrapped in CNTs with a wall thickness of 6 nm were generated by co-evaporation of GaO and activated carbon powder [14]. The nanostructures had a length of several micrometers. Mechanistically, GaO and carbon generate gaseous  $Ga_2O$  and CO at high temperature, which then recombine to form the core-shell product. The CNT coating of ultrafine InP nanowires has been realized in a similar manner [15]. The crystalline InP core was about 13–15 nm in diameter with the carbon layers just a few nanometers in thickness. The sheathing can be manipulated to obtain up to 10 carbon layers by simply adjusting the deposition parameters. Other systems successfully produced in our laboratory include the encapsulation of metal as well as metal-semiconductor heterojunctions [8b,17,18]. Taken together, the range of materials for which the outlined synthesis procedure can be employed is significantly broad.

Some of these nanostructures can also be used as unique precursors for other functional materials. ZnO and  $ZnGa_2O_4$  are two important phosphors having notorious stabilities in acidic and basic environments. Previously, we demonstrated that tubes containing these two materials can be obtained by controlled oxidation of Zn(Ga)S@CNT nanostructures at high temperature [8a]. Figures 4a,b show typical SEM images of such tubular structures. The transition from sulfide to oxide materials takes place by dint of diffusion of the cations and anions (Fig. 4c). The oxide anions created at the outer surface of the Zn(Ga)S@CNT diffuse into the core nanowire due to the difference in partial pressure, while



**Fig. 4** (a, b) SEM images of the  $ZnO/GaZn_2O_4$  nanotubes, (c) Schematic showing the formation mechanism of the oxide nanotubes. (d) An oxide tube after a long period of oxygen exposure of the Zn(Ga)S@CNT. The arrows highlight the presence of octahedral crystals. (e, f) DF-STEM images acquired at different orientations of the structure in (d). (All scale bars are 100 nm.)

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the cations move toward the surface. The smaller cations can diffuse out faster than the bulky anions into the core, thus creating a net outward movement of the charged species. The non-equilibrium interdiffusion leads to depletion of the nanowire core, while the new phase is generated at the outer surface of the nanowire, creating the tube-like material. Naturally, the diameter of the structures increases, thereby pointing to a mechanism similar to void formation in metal-alloys, known as the Kirkendall effect [21]. The HR-TEM images show that, upon extended periods of oxidation, the tube framework evolves into a complex network of mixed-size particles. Bigger particles decorate the outer surface, probably due to the fact that the surface particles are formed first and thus are sintered for a longer time. Figure 4d and inset show a selected region of a sintered structure. The smaller particles appear to be fused with each other without distinct morphology, whereas the bigger ones measure about 50 nm. What is interesting is that the latter have well-defined octahedral shapes, as indicated in Fig. 4d. The detailed morphology of this structure could be further comprehended from dark field (DF) scanning transmission electron microscopy (STEM) images acquired at two different orientations (Figs. 4e,f).

The CNT-based core-shell structures are promising for many applications. Crucially, the suggestion of using the carbon tube as a protective container has been illustrated in the elegant synthesis of single-crystalline nanowires of  $Mg_3N_2$  [16]. It is common knowledge that  $Mg_3N_2$  is extremely sensitive. Because it readily decomposes to  $Mg(OH)_2$  in air, its synthesis had been a major challenge. The synthesized  $Mg_3N_2$  nanowires were homogeneously sheathed, with protective carbon tubular layers rendering them air-stable. In 2002, Gao and Bando demonstrated how the height of a continuous, unidimensional column of liquid Ga inside a CNT varies linearly and reproducibly in the temperature range of 50–500 °C, making it the smallest existing thermometer [19]. The nanothermometers can be grown by a similar method to the described above and are about 10  $\mu$ m long and 75 nm wide. Ga was chosen as the thermal indicator because it has one of the greatest liquid ranges of any metal and a low vapor pressure at elevated temperatures. This nanothermometer should be suitable for uses in a wide variety of microenvironments. In addition, the resistance of a single Ga-filled CNT core-shell structure varies with the thermal expansion of the Ga column, which can be calibrated to measure local temperatures [20].

## Optical properties of the Zn(Ga)S@CNT system

ZnS has a bandgap of 3.7 eV and generally appears white to the naked eye. However, our Zn(Ga)S@CNTs have gray coloration and do not show any luminescence when irradiated with photons. Figure 5a shows a typical photoluminescence (PL) spectrum of the sample, showing none of the ZnS-related emissions. This could be due to the presence of the carbon shells. Hence, to investigate this system's optical properties, we have used cathodoluminescence (CL). CL is the emission of light under the excitation by a beam of electrons. These have stronger penetration depth as compared to photons. CL has several advantages for nanostructure characterization due to its local excitation, spatial and depth distribution of the luminescence centers [22]. Moreover, the electron excitation can activate most of the luminescence centers in the materials, from the deep ultraviolet to the infrared [23]. Finally, since the interaction between the incident electrons and the materials can generate different signals, it is possible to correlate the optical properties with the structural, chemical, and electrical properties [24].

An ultra-high vacuum scanning electron microscope (UHV-SEM) with a Gemini electron gun (Omicron, Germany) equipped with a CL system was utilized. Figure 5b shows the CL spectrum of a highly dense ensemble of Zn(Ga)S@CNT structures at an accelerating voltage of 5 kV and beam current of 1.0 nA. The CL spectrum consists of a broad Gaussian band at 475 nm with a shoulder at 530 nm. Investigation of the CL properties of the ZnS nanostructures is limited. Due to the presence of vacancies and interstices, ZnS electronic states contain shallow energy levels, e.g., donor levels of valance state, namely, interstitial Zn sites, Zn<sub>i</sub>, as well as acceptor level of V<sub>Zn</sub>, Zn vacancy states [11,25]. Thus, the two luminescence bands can be attributed to recombination within the intrinsic defects as well as recombination involving the impurity Ga ions. Group III dopants in ZnS create a self-

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Fig. 5 (a) PL and (b) CL spectra of the Zn(Ga)S@CNT. Inset in (b) shows an SEM image (above) and the corresponding CL image acquired at 475 nm.

activated emission band at 2.65 eV that shows red-shift to 1.94 eV in the case of Ga. The extent of the red-shift can be within 2.02 eV (615 nm) to 1.86 eV (670 nm) depending on the synthetic conditions [26]. Thus, we attribute the lower energy one (at 530 nm) to the Ga impurities. On the other hand, luminescence arising out of the intrinsic defects appears at a higher energy and hence we attribute the emission band at 475 nm to intrinsic defects [27]. The inset in Fig. 5b shows the corresponding SEM and CL images taken at 475 nm emission. The comparison of these clearly demonstrates that the CL signal originates from the nanostructures alone.

Figure 6 shows the CL spectra of the encapsulated Zn(Ga)S nanowires ensemble taken with different electron energy but with a constant beam current of 1.0 nA. The intensity of the 475-nm peak emission increases to around 200 counts-per-second (cps) at 10 kV and then saturates. On the other hand, the shoulder at 530 nm becomes more obvious with the increase of the electron energy. Since the size of the nanowires is much smaller than the penetration depth of the incident electrons (from 100 nm at 3 kV to 2000 nm at 20 kV), such variations cannot be attributed to core-shell structure related distribution of defects. In fact, the light generated from deep inside the assembly is absorbed by other nanowires along its path outside the materials [28]. It may lead to the re-emission of photons at lower energy. Such re-absorption being more effective for lower wavelength than higher ones, it explains why the 530 nm increases more with the increase of the electron energy than the 475 nm.



Fig. 6 CL spectra acquired at various accelerating voltages showing continuous evolution of the two defect luminescence emissions.

Figure 7 shows the evolution of the 475-nm emission of the encapsulated ZnS nanowires ensemble under irradiation at 3, 5, 7, 10, 15, and 20 kV with a beam current of 1.0 nA. The CL intensity decreases exponentially from 120 to 50 cps at 3 kV, from 320 to 140 cps at 5 kV, from 420 to 190 cps at 7 kV, from 750 to 330 cps at 10 kV, from 870 to 380 cps at 15 kV, and from 850 to 450 cps at 20 kV. Overall, for each electron energy, the intensity decreases by 50–55 % of the initial values after 1 h of irradiation. Since the ZnS emitters are inside the CNTs and the irradiation is performed in UHV conditions, we assume that the degradation is not related to oxidation [29]. More likely, it is possibly the creation/reactivation of defects (which will act as non-radiative centers) and/or the formation of an electric field (which affects the recombination of electron-hole pairs) that account for the observed signal reductions [30].



Fig. 7 Plots showing CL degradation observed for an assembly of Zn(Ga)S@CNT at various accelerating voltages.

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## Mechanical properties of the Zn(Ga)S@CNT system

Considering the pertinence of mechanical properties for the application of nanotubes in devices such as commercially available high-resolution atomic force microscopy (AFM) cantilevers together with the predicted reinforcement effect derived from filling CNTs with assorted substances [31,32], the nanomechanics of the Zn(Ga)S@CNT materials was investigated. From the onset, several methods were possible candidates to realize this. However, we decided that a minimal requirement was to have enough spatial and time resolution to closely follow the effect of applying loads on the nanostructures. This justifies the preferential use of electron microscopes and, in particular, TEM. An often-used TEM-based technique to perform nanomechanics studies on nanotubes is the resonant frequency analysis [33]. However, this was unfeasible as it needs structurally uniform materials such as the CNTs made by arcdischarge. As mentioned above, the present Zn(Ga)S@CNTs have turbostratic graphite shells. Consequently, our first approach was to explore image-based techniques and finite element modeling (FEM) such as those usually employed for macroscale columnar structures [34]. The characteristics of the nanotube (length, diameter, displacement, and arc-length) were measured before, during, and after the application of a quasi-uniaxial compression load. These figures were then used to compare with the results of FEM simulations based on the elastic properties of a core-shell column composed of graphite and ZnS. Unfortunately, all our attempts failed. We assume that a significant error exists on the measures taken experimentally since a TEM image is, in fact, a 2D projection of a 3D object. Finally, experiences were performed with a novel TEM sample holder that contains an AFM-type sensor [35]. Within this sophisticated force-sensing instrument is a micro-electromechanical system (MEMS) device in which an AFM cantilever (electrically conductive or not) is mounted. The AFM-TEM holder provides high flexibility and precision for mechanical analysis at the nanoscale level and is commercially available from Nanofactory Instruments AB. Until the appearance of this holder, nanomechanics of 1D materials was restricted to a few groups worldwide. Today, and besides the present hyb-CNTs study, this holder is behind several other reports from our group that cover from bending stress analysis to tensile strength estimations of nanotubes [36].

Resorting to the AFM-TEM ultimately enabled the experimental confirmation of the predicted effect of the core filling on the mechanical behavior of filled CNTs [34,37–39]. These force-displacement measurements, however, are not trivial because the experimental conditions need to obey certain predicaments [38]. First, as shown in Fig. 8a, an individual nanotube is placed between the two clamps, i.e., the cantilever and the sample-loaded substrate wire. Once stable contacts are achieved, the careful displacement of the sample wire (via a piezo-controlled nanomanipulator) allows the controlled compression of the column-like structure. Because this procedure is done in parallel with the imaging process (and, if required, the spectroscopic analysis and video recording), it is possible to follow in detail the bending behavior of the Zn(Ga)S@CNT. However, due to technical limitations explained



**Fig. 8** (a) A Zn(Ga)S@CNT contacted to both clamps (cantilever and sample wire). (b) F-d curve resulting from the application of a compression load. (b) Corresponding stress–strain curve of (b).

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elsewhere [38], we could not take the analysis to the point of failure of the filled CNTs. In all cases, force-displacement (F-d) curves were acquired for the nanotubes subjected to compression loads (Fig. 8b). Once this raw data had been processed into stress–strain curves (Fig. 8c), the analysis of the bending response enabled the direct extraction of the Young's modulus.

In addition to the analysis of the filled structures, it is possible to perform "on demand" the equivalent study for empty (or almost empty) nanotubes. An essential condition for this is the presence of an electrically conductive cantilever. Then, if one forces a considerable current density across the structure, the resistive heating build-up (i.e., the Joule effect) may be high enough to selectively melt the core component. Temperatures well above 2000 °C can be attained by this method. Furthermore, due to the presence of the high electric field between the two electrodes (cantilever and sample wire), it becomes possible to guide the melt to the exterior of the host nanotube. This process could be fundamentally useful for the controlled delivery of the encapsulated material. However, this implies that the current density must be carefully manipulated. In fact, past a certain threshold (unique for each CNT-electrode system due to variables such as contact resistance and density of defects) the melting of the nanotube will start taking place with eventual collapse of the carbon structure via electrical breakdown.

Figure 9a shows a compressed Zn(Ga)S@CNT after it had part of its content discharged. This nanotube always bent at mid-length, i.e., where the empty section lies (Figs. 9b,c). Notice however that other sections of the nanotube are also empty or partially empty (Figs. 9b,d). The observation of various types of filling morphologies inside the carbon shell provides an informative view of the response of the columnar structure. First, it confirms that the totally empty sections are the weakest points in the structures. In this respect, partially empty sections such as in those in Fig. 9d are stiffer than the totally empty ones (which again confirms the reinforcing effect of the core in Zn(Ga)S@CNT). Second, if sev-



**Fig. 9** (a) 9-µm-long Zn(Ga)S@CNT after the partial removal of the core and application of a compressive load. (b) Magnified view of the region marked in (a) with two of the unfilled sections highlighted. (c) Zoom of region 1 in (b). Clear-cut cross-sections are visible on both sides of the kink. (d) Zoom of region 2 in (b). Various regions are partially empty.

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eral totally empty sections are present, those closest to the mid-length of the CNT are more likely to fail.

It is interesting also to observe the type of kinks developed in the turbostratic carbon shell. Besides the simple folds as seen in Fig. 9c, more complex patterns may evolve. Figure 10a shows a nanotube with a totally empty section. After contact and compression, two kinks are visible (Fig. 10b). One of these is located immediately after a part of the remaining core filling which has a clear cut cross-section. Ripples are observed, and the failure zone appears to effectively contain two consecutive folds shaped in zig-zag style (Fig. 10c). Despite this, the carbon shell shows a remarkable recovery capability since the nanotube retakes its initial configuration (Fig. 10a) when the compressing load in suppressed.



**Fig. 10** (a) Zn(Ga)S@CNT with a 550-nm-long empty section. The inset highlights the clear-cut cross-section of the core and overall structural constancy of the carbon shell following the discharge procedure. (b) The structure in (a) after being subjected to a compressive load. Two kinks are visible. (c) Zoom of the region boxed in (b). The complex folding of the nanotube is clear.

In the end, it was possible to successfully compare the response of the same Zn(Ga)S@CNT before and after the release of the core compound material. Furthermore, the above resistive heating procedure allows full control of the release of the ZnS material. Therefore, partially empty or totally empty structures may be achieved. As seen in Figs. 9 and 10, the carbon shell does not suffer considerable damage. These results are important for all those working in the development of nanodevices integrating CNTs.

# CONCLUSIONS

We have described a new synthesis approach to obtain CNTs filled with functional inorganic materials. The encapsulated materials include metals, oxides, sulfides, nitrides, phosphides, and complex heterojunctions. Unlike all other existing CNT filling methods, our one-step, high-temperature procedure results in almost quantitative filling yields. Additionally, the core nanowire extends full length and is, for the most part, a structurally sound single-crystal. The shell CNT is turbostratic, which implies large graphitic disorders. By taking ZnS-CNT materials, we showed that the size and morphology of the products can be tuned "on demand". Optically, we found that the CNT layer is very effective in shield-ing the core material from external light. As regards the mechanics of these systems, we concluded that while the turbostratic CNT shell is weak but flexible, the brittle core filling provides mechanical strength to the Zn(Ga)S@CNT structure.

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