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Encapsulation of two-dimensional materials inside carbon nanotubes: Towards an enhanced synthesis of single-layered metal halides

Stefania Sandoval [a], Elzbieta Pach [b], Belén Ballesteros [b, **], Gerard Tobias [a, *]

[a] Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus de la UAB, 08193, Bellaterra, Barcelona, Spain
[b] Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and The Barcelona Institute of Science and Technology, Campus UAB, Bellaterra, 08193 Barcelona, Spain

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ABSTRACT

The unique properties of two-dimensional (2D) nanomaterials make them highly attractive for a wide range of applications. As a consequence, several top-down and bottom up approaches are being explored to isolate or synthesize single-layers of 2D materials in a reliable manner. Here we report on the synthesis of individual layers of several 2D van der Waals solids, namely CeI_3, $CeCl_3$, $TbCl_3$ and ZnI_2 by template-assisted growth using carbon nanotubes as directing agents, thus proving the versatility of this approach. Once confined, the metal halides can adopt different structures including single-layered metal halide nanotubes, which formation is greatly enhanced by increasing the temperature of synthesis. This opens up a new strategy for the isolation of individual layers of a wide variety of metal halides, a family of 2D materials that has been barely explored.

1. Introduction

The formation of low dimensional systems is a powerful tool for tuning the physical properties of materials. As a consequence, a wide variety of approaches have been explored to synthesize and control their size, morphology and crystal structure. Template-directed synthesis represents a convenient and versatile route for the growth of low dimensional systems and both organic and inorganic-based materials are being employed as templates. In this sense, carbon nanotubes (CNTs) are an attractive host since they can have a variety of diameters and lengths and their inner hollow cavity can be filled with a large variety of compounds [1–6]. Among them, metal halides have received widespread attention since the resulting hybrids are of interest for instance for biomedical imaging [7–9], even allowing mapping of cellular organelles [10]. In general, confinement of materials within the walls of CNTs results in the formation of molecular entities, nanoclusters or nanowires. For the vast majority of applications removal of the carbon template is not desired since the resulting hybrid typically presents a high stability. Furthermore, the presence of CNTs might create synergistic effects with the filling material resulting in unique properties and superior performance [11]. Actually, the application of filled CNTs expands from molecular magnets [12] to biomedicine [13] going through sensors [14]. More recently, the possibility of isolating individual layers of two-dimensional (2D) materials inside CNTs has attracted a great deal of attention. Nanoribbons of graphene [15] and metal dichalcogenides (MoS_2, WS_2) [16] have been synthesized within the cavities of single- and double-walled CNTs, whereas single-layered PbI_2 nanotubes have been grown using multi-walled CNTs as templates [17]. A recent theoretical study by Zhou et al. reveals that these heterostructures, consisting of single-layers of PbI_2 and a carbon layer can substantially enhance the visible light response, suggesting potential applications in novel 2D optoelectronics and photovoltaics [18]. Despite their interest, the number of reports on single-walled inorganic nanotubes is limited because the formation of their multi-walled counterparts is favored during the synthesis [19]. Therefore, the possibility of growing single-layered nanotubes using CNTs as directing agents opens up a new synthetic strategy for the development of advanced nanomaterials that combine the characteristics of both 1D and 2D systems [20]. Here we show that the templating strategy is versatile by reporting on the synthesis of single-layered nanotubes of $TbCl_3$, CeI_3, $CeCl_3$ and ZnI_2. Furthermore, by controlling conditions of the synthesis it is possible to enhance the formation of these single layered structures. The present approach expands the strategies available for the

* Corresponding author.
** Corresponding author.
E-mail addresses: belen.ballesteros@icn2.cat (B. Ballesteros), gerard.tobias@icmab.es (G. Tobias).

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isolation and growth of individual layers of 2D van der Waals solids, which can go via bottom-up (e.g. chemical vapor deposition) and top down (e.g. liquid phase exfoliation) approaches [21,22]. Among the different morphologies that 2D materials can adopt, the formation of nanoscrolls [23], concentrically rolled-up 2D layers, is getting an increased attention. For instance, highly thermal-stable paramagnetism has been recently reported by rolling up MoS_2 nanosheets [24], and an enhanced photon absorption has been observed in spiral nanostructured solar cells [25]. The formation of nanoscrolls also opens up new opportunities in composite materials [26]. When both longitudinal edges of an individual 2D nanoscroll are seamlessly joined, a single-layered nanotube is formed, typically referred to as single-walled nanotube. The concept of using edgeless 2D rolled-up sheets is for instance being investigated for the development of ultracompact plasmon circuitry at the nanoscale because plasmons along 2D ribbons suffer from scattering at edges [27].

Noteworthy, within the several families of van der Waals solids, metal halides have received little attention when it comes to the individualization of their constituent layers and will be the focus of the present study.

2. Experimental

2.1. Filling of MWCNTs with $TbCl_3$, $CeCl_3$, CeI_3 and ZnI_2

Multiwalled carbon nanotubes (CVD, Thomas Swan Co. Ltd.) were steam treated in order to remove amorphous carbon and graphitic nanoparticles and to open their ends [28]. Additionally, the sample was treated with a 6 M HCl solution to remove the catalytic metal nanoparticles [29], filtered and dried overnight at 60 °C. In an argon-filled glove box, purified CNTs and the corresponding salt ($TbCl_3$, CeI_3, $CeCl_3$ or ZnI_2) were ground with an agate mortar and pestle until the mixture presented a uniform color. The mixture was then transferred into a silica ampoule, evacuated and sealed under vacuum. The ampoule was placed into a furnace where it dwelled at temperatures above the melting point of the salt, during 12 h. The respective temperature was obtained after a controlled heating rate (5 °C.min^{-1}). Finally, the samples were cooled at 0.42 °C.min^{-1} until temperatures under the melting point and subsequently at 5 °C.min^{-1} until room temperature. In order to tailor the nature of the inner structure obtained inside the template, ZnI_2 was treated at temperatures ranged between 475 °C and 1000 °C. Time of treatment and heating ramp were kept constant (12 h and 5 °C.min^{-1}, respectively).

2.2. Characterization

The morphology and the distribution of the inorganic structures grown within the MWCNTs was studied recording TEM, HRTEM images and high-angle annular dark field (HAADF) images in scanning transmission electron microscopy (STEM) mode. TEM images were obtained using a JEOL 1210 microscope, operating at 120 kV. HRTEM was carried out in a FEI Tecnai F20 microscope operating at 200 kV. Samples were prepared by sonicating and dispersing in hexane. Afterwards, they were placed dropwise onto a lacey carbon coated Cu support grid. EDX analysis was performed on a FEI Quanta SEM by placing the Cu grid on top of an aluminium support.

3. Results and discussion

Single-layered nanotubes of several 2D van der Waals solids, namely $TbCl_3$, CeI_3, $CeCl_3$ and ZnI_2, were prepared by molten phase capillary wetting [30], using steam purified and open-ended multiwalled CNTs (MWCNTs) as templates (see experimental details). A mixture of MWCNTs and the metal halide was annealed under vacuum at temperatures above the melting points of the selected materials (475 °C-1000 °C) [31]. The successful formation of single-layered inorganic nanotubes was confirmed by analysis of the resulting sample by high-resolution transmission electron microscopy (HRTEM) and scanning transmission electron microscopy (STEM). Fig. 1 shows a HRTEM image of a single-layered $TbCl_3$ nanotube synthesized within the cavity of a MWCNT at 650 °C. The metal halide layer is easily differentiated from the walls of the carbon nanotube due to the difference of contrast.

Next, to provide evidence of the versatility of this approach, the growth of individual layers of cerium based 2D systems was attempted. CeI_3 and $CeCl_3$ were the materials of choice being filled at 900 °C and 850 °C respectively. Since the constituent elements of the employed salts are heavier than carbon (from CNTs) it is possible to easily discern the filling material by means of high-angle annular dark field (HAADF) STEM imaging. The intensity of HAADF-STEM images (also called Z-contrast imaging) scales approximately with the square of the atomic number. Thus heavy elements, metal halides in our case, will appear brighter than light elements, such as carbon from the CNTs. Therefore, the bright lines observed in Fig. 2 (a) and Fig. S1 (a) along the inner walls of the CNTs can be attributed to the metal halides. The diameter of the inorganic nanotubes displayed in the HAADF-STEM images is in the range of 3.5–6.9 nm. The thermal annealing of metal halides in the presence of CNTs also results in the formation of other nanostructures inside the CNTs (Fig. S2), which mainly take the form of nanorods but nanoparticles have also been observed inside few CNTs. When nanorods are present, these can either completely (Fig. S2 (a)) or partially (Fig. S2 (b)) fill the hollow cavity of the CNTs, the latter adopting a polycrystalline snake-type morphology. To discern between both types of structures we will refer to the former as nanorods and to the latter as “nanosnakes”. In most cases crystalline structures are observed for the confined metal halides. The spacing of the lattice fringes in the HRTEM image of the CeI_3 nanorod in Fig. S2 (a) is in good agreement with the (130) plane of bulk CeI_3 presenting an orthorhombic structure, thus confirming the successful encapsulation of this material [32].

The coexistence of different types of inorganic nanostructures inside an individual CNT has also been observed. For instance, in Fig. 2(b) a fragment of an inorganic nanorod of CeI_3 has grown within the walls of a single-layer nanotube of the same material. Both types of structures can be easily discerned by visual inspection of the Z-contrast STEM image (Fig. 2 (b)), but further evidence can be provided by intensity profiles across an area presenting a single-layered inorganic nanotube (red line, *A*) and an area containing a nanorod fragment (green line, *B*). Marked differences between the intensity profiles become evident. When the inner nanorod is present, the highest intensity is detected in the central space of the analyzed area, confirming the complete filling of the host. In contrast, the intensity profile of the tubular fraction shows the highest intensity at the edges, with a diameter and shape determined by the inner cavity of the carbon nanotube. A much weaker intensity is registered in the intensity profile of an empty area where only carbon, from the CNT walls, is present (blue line, *B*; Fig. S3). Although most of the CNTs have opened ends, the presence of some closed tips has allowed the formation of CeI_3 caps which are visible in the Z-contrast STEM image in Fig. S3. A clear differentiation between the inorganic nanotubes and nanorods is also visible by TEM analysis (Fig. S4).

Temperature being a key factor in the molten filling process [33], we decided to investigate the role of this parameter towards the formation of nanotubes and other types of nanostructures. Therefore we analyzed the encapsulation of CeI_3 at 800 °C and 900 °C.