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Research Article

# Synthesis and Characterization of WS<sub>2</sub> Inorganic Nanotubes with Encapsulated/Intercalated CsI

Sung You Hong<sup>1</sup>, Ronit Popovitz-Biro<sup>2</sup>, Gerard Tobias<sup>3</sup>, Belén Ballesteros<sup>3</sup>, Benjamin G. Davis<sup>1</sup>, Malcolm L. H. Green<sup>3</sup>, and Reshef Tenne<sup>4</sup> (✉)

<sup>1</sup> Department of Chemistry, Chemistry Research Laboratory, University of Oxford, Mansfield Road, Oxford, OX1 3TA, UK

<sup>2</sup> Electron Microscopy Unit, Weizmann Institute of Science, Rehovot 76100, Israel

<sup>3</sup> Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, OX1 3QR, UK

<sup>4</sup> Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot 76100, Israel

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## ABSTRACT

WS<sub>2</sub> nanotubes have been filled and intercalated by molten phase caesium iodide. The presence of caesium iodide inside the WS<sub>2</sub> nanotubes has been determined using high-resolution transmission electron microscopy (HRTEM) coupled with electron energy-loss spectroscopy (EELS) and energy-dispersive X-ray spectroscopy (EDS). Noticeably, a Moiré pattern was observed due to the interference between encapsulated CsI and WS<sub>2</sub> layers. The intercalation of CsI into the host concentric WS<sub>2</sub> lattices resulted in an increase in the interplanar spacing.

## KEYWORDS

Inorganic nanotubes, transmission electron microscopy, intercalation, encapsulation

## 1. Introduction

The discovery of carbon nanotubes (CNTs) initiated the exploration and discovery of inorganic layered compounds with related tubular structures [1]. A wide variety of metal oxides, metal halides, and other materials have been introduced into CNTs by capillary wetting [2–5]. For example, Green and coworkers reported one-dimensional crystals of various metal halides in both multi-walled and single-walled carbon nanotube capillaries [3, 6, 7]. By analogy, filling by use of nanocapillaries was also explored for the inorganic WS<sub>2</sub> nanotubes. In 1992, Tenne and coworkers first showed that WS<sub>2</sub> material of nanometer scale in a platelet form could spontaneously form closed cage structures known as inorganic fullerene-like (IF)

nanoparticles and inorganic nanotubes [8], which are akin to carbon fullerenes and carbon nanotubes. The structures of graphite and WS<sub>2</sub> belong to the space group, *P6<sub>3</sub>/mmc*. However, the structure of WS<sub>2</sub> is more complex than that of graphite. The WS<sub>2</sub> layer contains a layer of metal atoms, sandwiched between two sulphur layers, with the metal atom bonded to six sulphur atoms in a trigonal prismatic coordination [9]. Folding and bonding of edge atoms on the periphery of the quasi two-dimensional planar nanostructure leads to the formation of closed cages with polyhedral or nanotubular shapes [1]. The inner diameters of WS<sub>2</sub> inorganic nanotubes range between 15–30 nm and the tips are inherently open-ended [10], so this nanotubular structure is suitable for capillary filling using molten metal halides.

Address correspondence to [reshef.tenne@weizmann.ac.il](mailto:reshef.tenne@weizmann.ac.il)

## 2. Experimental

### 2.1 Synthesis of CsI@WS<sub>2</sub> NTs

WS<sub>2</sub> nanotubes and fullerene-like nanoparticles were prepared in a fluidized-bed reactor [10]. A mixture of the multi-walled WS<sub>2</sub> nanotubes (5%) in IF-WS<sub>2</sub> nanoparticle powder (30 mg) and CsI (120 mg, Acros, 99.9%, m.p. 621 °C) were ground using a mortar and pestle and transferred to a silica quartz ampoule 10 mm in diameter. The mixture was dried under high vacuum (approx. 10<sup>-4</sup>–10<sup>-5</sup> torr) for 2 h, and the ampoule was then sealed. The ampoule was heated to 640 °C for 4 h. The furnace was cooled to room temperature overnight.

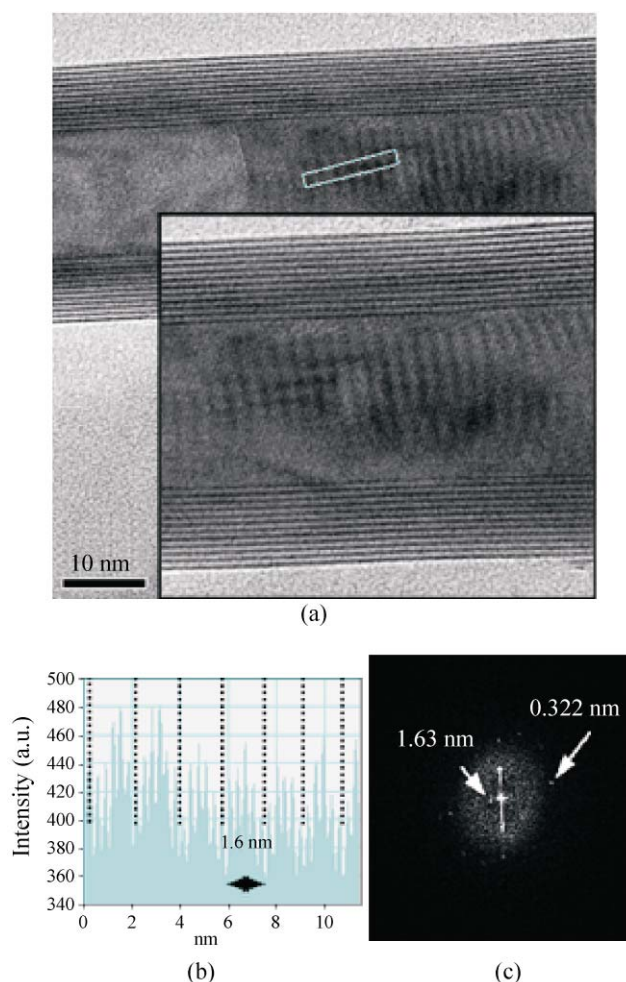
### 2.2 TEM analysis of CsI@WS<sub>2</sub> NTs

The product was sonicated in ethanol, placed on a carbon/collodion-coated Cu grid, and analyzed by transmission electron microscopy (TEM) (Philips CM-120, 120 kV) and high-resolution TEM (HRTEM) (FEI Tecnai F-30 with electron energy-loss spectroscopy (EELS) or JEOL JEM-3000F field emission gun, 300 kV). Images were acquired digitally on a Gatan model 794 (1000 × 1000) charge coupled device (CCD) camera, the magnification of which was calibrated with the Si [110] lattice spacing. Energy-dispersive X-ray spectroscopy (EDS) was performed with an electron probe 0.5 nm in diameter.

## 3. Results and discussion

Compared to the carbon nanotubes, the inorganic WS<sub>2</sub> nanotubes have heavier elements (W, Z = 74; S, Z = 16). Therefore, there is a severe limitation to the visualization of light elements, which may be filled within WS<sub>2</sub> nanotubes. For this reason caesium iodide was the metal halide of choice, because of the strong electron-scattering power of Cs (Z = 55) and I (Z = 53) which it was anticipated would allow observation of CsI crystal structures within the WS<sub>2</sub> nanotubes using HRTEM analysis. We note that CsI is one of a group of alkali halides that adopt the *Pm3m* CsCl structural archetype (*a* = 0.4520 nm) [11]. An HRTEM micrograph of the resulting composite is presented in Fig. 1, where the (110) lattice plane of CsI with lattice interplanar spacing of 0.32 nm is observed within the core of the

WS<sub>2</sub> nanotubes, as confirmed by the fast Fourier transform (FFT) pattern. Remarkably, a Moiré pattern was found along the WS<sub>2</sub> nanotube surface. The Moiré *d* spacing was calculated based on the two lattice spacings with a mismatch of 0.049 or 0.056 nm from the (100) or (101) spacings of the WS<sub>2</sub> crystal, respectively. The calculated Moiré spacing was 1.5–1.8 nm, which was in good agreement with the corresponding Moiré spacing measured from the line profile recorded on the HRTEM image (ca. 1.6 nm). Stacking of the caesium iodide crystals inside the nanocapillary exhibited various orientations, such as (110) and (100) lattice planes (see Figs. S-1 and S-2 in the Electronic Supplementary Material (ESM)). Further, EELS analysis performed (Fig. S-3 in the ESM) on such nanotubes gave a Cs:I ratio fairly close to 1:1, consistent with the existence of CsI layers. EDS analysis also confirmed

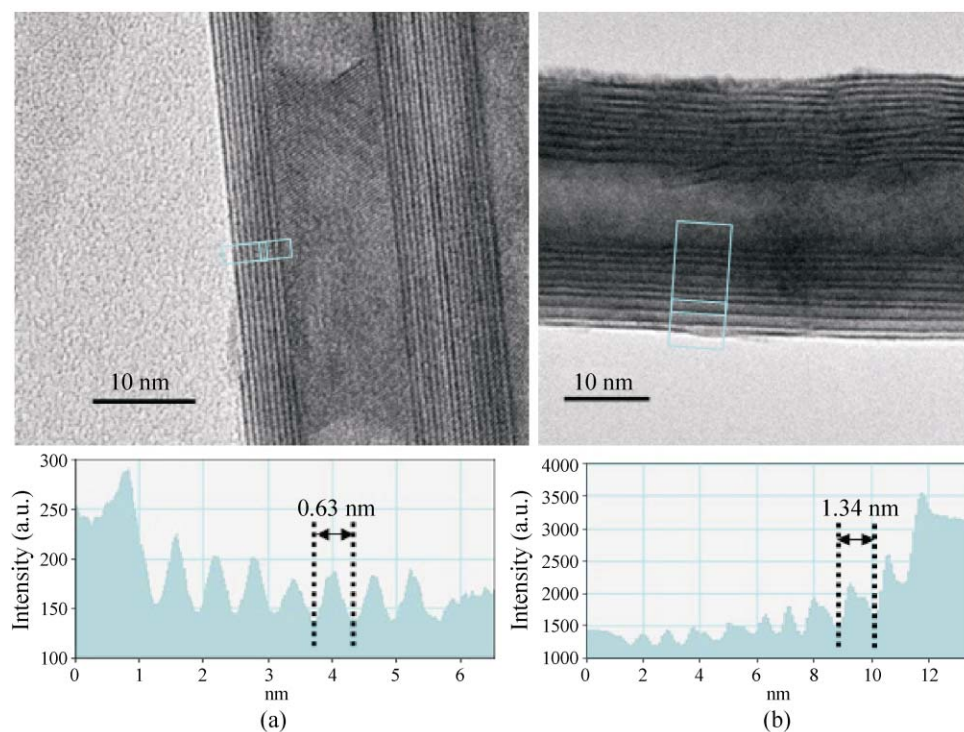


**Figure 1** (a) Moiré pattern of HRTEM image of CsI filled WS<sub>2</sub> nanotube; (b) line profile integrated along the region enclosed in the rectangle; (c) FFT pattern

the presence of W, S, Cs, and I (Fig. S-3 in the ESM). In addition to the nanotubes filled with CsI rod-like crystals, occasionally, some of WS<sub>2</sub> nanotubes (< 10%) showed lattice expansion of the concentric WS<sub>2</sub> layers and revealed a substantial increase (ca. 0.7 nm) in the interlayer spacing (Fig. 2). While the encapsulation is induced by nanocapillarity, the intercalation mechanism is not clearly understood. Presumably, it involves diffusion from both inner and outer walls of WS<sub>2</sub> nanotubes: such a significant increase in layer spacing can be attributed to the uptake of water into these intercalated layers during exposure to the atmosphere. A similar behavior of hydration of intercalated layers has been described earlier for WS<sub>2</sub> materials intercalated by alkali metals [12, 13]. Also, alkali metal atom intercalated CNTs show a similar hydration expansion [14]. The occurrence of intercalation of CsI into the layers may be associated with the weak interlayer van der Waals interaction between the tungsten metal dichalcogenide layers [15]. However, more extensive studies are required to explain the interlayer expansion.

#### 4. Conclusions

We have shown that filling of nanotubes by nanocapillarity is not limited to carbon nanotubes but can be applied to the inorganic nanotubes of WS<sub>2</sub>. Molten phase wetting with CsI resulted in the formation of one-dimensional crystal structures inside WS<sub>2</sub> nanocapillaries. A Moiré pattern was observed in the CsI@WS<sub>2</sub> nanotubes due to the interference between CsI and WS<sub>2</sub> crystal layers. Moreover, the observation of an increase (ca. 0.7 nm) of the interlayer spacing between concentric WS<sub>2</sub> layers of inorganic nanotubes indicates that intercalation has occurred and the expansion with the CsI is larger than that (0.3–0.5 nm) found for alkali metal intercalated IF-WS<sub>2</sub> [15]. Unlike the previously described PbI<sub>2</sub>@WS<sub>2</sub> nanotubes (PbI<sub>2</sub>, two-dimensional layered) having a core-shell nanotubular structure [16], the CsI@WS<sub>2</sub> nanotube (CsI, 3-D CsCl archetype) has a one-dimensional stacking inside the WS<sub>2</sub> nanotube and also intercalation between concentric WS<sub>2</sub>. This suggests that metal halides do not interact strongly with the WS<sub>2</sub> layers but instead



**Figure 2** HRTEM images with line profiles: (a) non-intercalated WS<sub>2</sub> nanotube with encapsulated CsI; (b) WS<sub>2</sub> nanotube with intercalated CsI

adopt their preferred ionic structures.

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**Electronic Supplementary Material:** Additional HRTEM images and details of elemental analysis by EDS and EELS are available in the online version of this article at <http://dx.doi.org/10.1007/s12274-010-1018-0> and are accessible free of charge.

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