

Synthesis and Characterization of WS₂ Inorganic Nanotubes with Encapsulated/Intercalated CsI

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ABSTRACT

WS₂ nanotubes have been filled and intercalated by molten phase caesium iodide. The presence of caesium iodide inside the WS₂ 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 WS₂ layers. The intercalation of CsI into the host concentric WS₂ 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 WS₂ nanotubes. In 1992, Tenne and coworkers first showed that WS₂ 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 WS₂ belong to the space group, *P6₃/mmc*. However, the structure of WS₂ is more complex than that of graphite. The WS₂ 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 WS₂ 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.

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2. Experimental

2.1 Synthesis of CsI@WS₂ NTs

WS₂ nanotubes and fullerene-like nanoparticles were prepared in a fluidized-bed reactor [10]. A mixture of the multi-walled WS₂ nanotubes (5%) in IF-WS₂ 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. 10⁻⁴–10⁻⁵ 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@WS₂ 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 WS₂ 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 WS₂ 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 WS₂ 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

WS₂ nanotubes, as confirmed by the fast Fourier transform (FFT) pattern. Remarkably, a Moiré pattern was found along the WS₂ 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 WS₂ 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

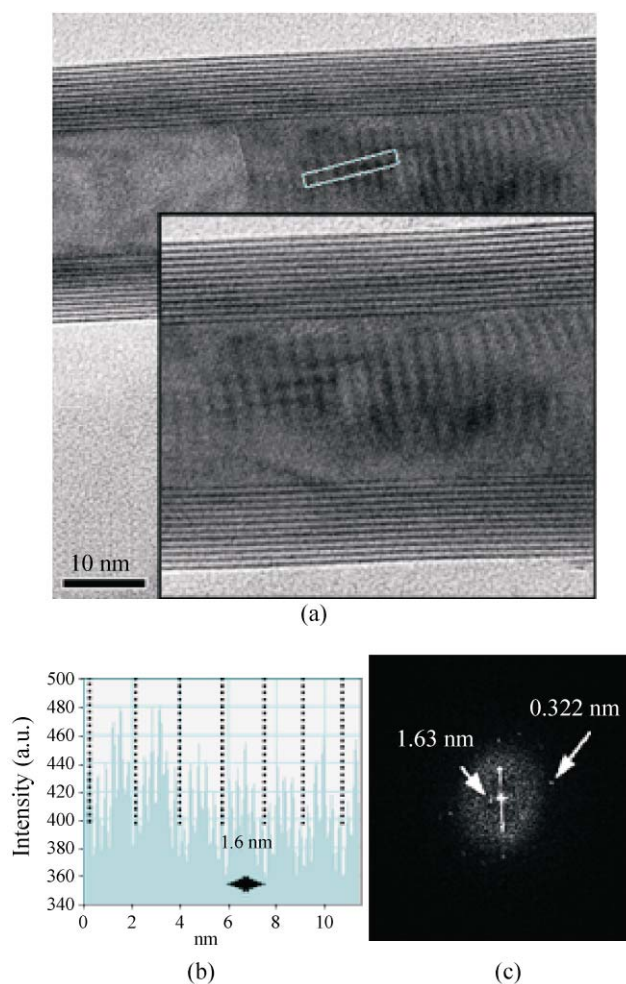


Figure 1 (a) Moiré pattern of HRTEM image of CsI filled WS₂ nanotube; (b) line profile integrated along the region enclosed in the rectangle; (c) FFT pattern

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 WS₂ nanotubes (< 10%) showed lattice expansion of the concentric WS₂ 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 WS₂ 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 WS₂ 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 WS₂. Molten phase wetting with CsI resulted in the formation of one-dimensional crystal structures inside WS₂ nanocapillaries. A Moiré pattern was observed in the CsI@WS₂ nanotubes due to the interference between CsI and WS₂ crystal layers. Moreover, the observation of an increase (ca. 0.7 nm) of the interlayer spacing between concentric WS₂ 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-WS₂ [15]. Unlike the previously described PbI₂@WS₂ nanotubes (PbI₂, two-dimensional layered) having a core-shell nanotubular structure [16], the CsI@WS₂ nanotube (CsI, 3-D CsCl archetype) has a one-dimensional stacking inside the WS₂ nanotube and also intercalation between concentric WS₂. This suggests that metal halides do not interact strongly with the WS₂ layers but instead

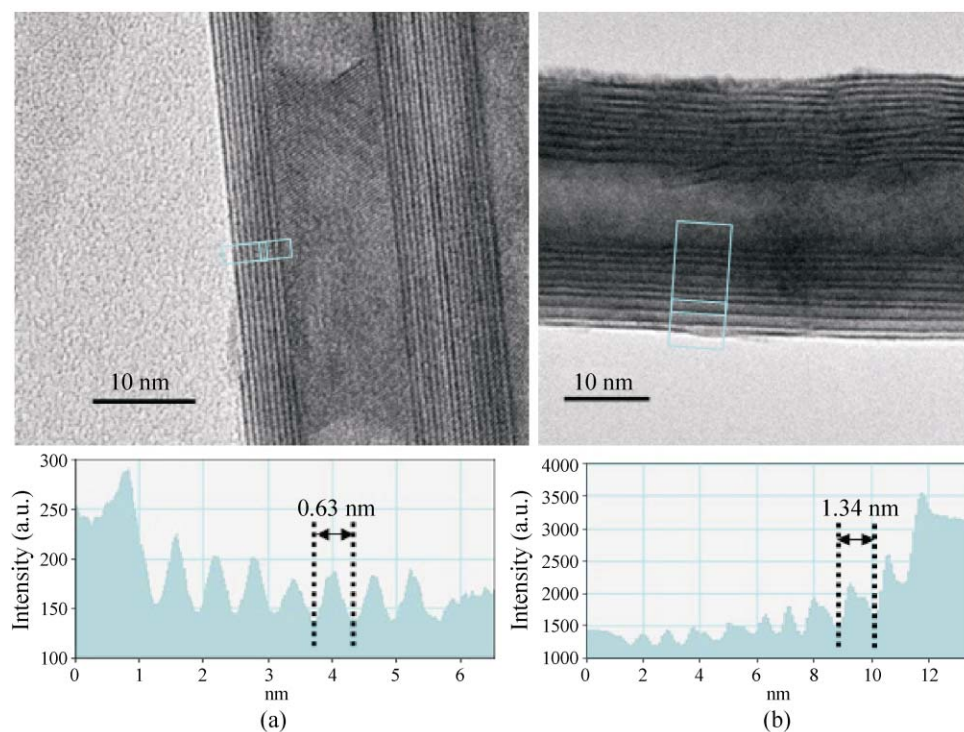


Figure 2 HRTEM images with line profiles: (a) non-intercalated WS₂ nanotube with encapsulated CsI; (b) WS₂ nanotube with intercalated CsI

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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