Encapsulating WS_2 Nanoribbons in Single-walled Carbon Nanotubes

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Transition metal dichalcogenides (TMD) carbon nanopeapods have unique electronic and magnetic properties that result from electron interactions between the carbon nanotubes (CNTs) and encapsulated low-dimensional TMDs. The hollow space of CNTs serves as a nano-test-tube to synthesize one-dimensional TMDs as opposed to two-dimensional TMDs that can be synthesized via other conventional methods. This is important because one-dimensional TMDs, like WS_2 nanoribbons, have interesting properties that are different from those of the bulk material due to quantum confinement. For example, according to previous research calculations, zigzag-edged WS_2 nanoribbons can be magnetic or nonmagnetic metals depending on the edge passivation, while bulk WS_2 is a nonmagnetic semiconductor[1] . Encapsulation of WS_2 nanoribbons inside CNTs was successfully achieved in other studies but at low yields. This research seeks to find a method to synthesize higher yields of WS_2 nanoribbon peapods to further study the electronic and magnetic properties of the resulting material when the nanoribbon is encapsulated and then determine possible device applications. Additionally, because this TMD nanostructure cannot be synthesized via other methods, another goal is to extract the material from the CNT because the nanoribbon has possible applications for spintronics. In this study, transmission electron microscopy was used to analyze and compare the results of different heating temperatures and times on encapsulation yields of materials inside single-walled CNTs via sublimation. From initial inter-atomic distance measurements, it appears that WS_2 nanoribbons were successfully encapsulated.

[1] Z. Wang, K. Zhao, H. Li, *et. al.* J. Mater. Chem., 2011, 21, 171.

Synthesizing WS_2 nanoribbon peapods

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Peapods & 1-D Material Synthesis

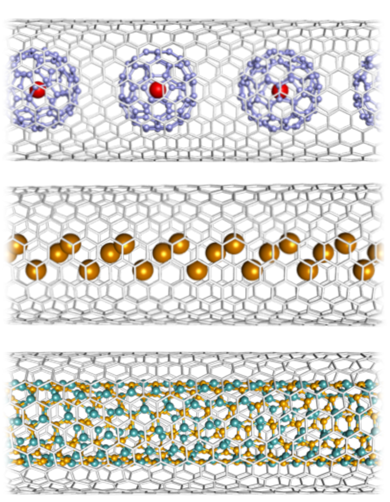
Peapods

- Carbon nanotubes (CNTs) with material encapsulated inside
- Unique electron and magnetic properties due to electron interactions between encapsulated material and CNTs

1-D Material Synthesis

- Nano-test-tube reaction
- Hollow spaces of CNTs serve as template
- Allows for synthesis of structurally precise 1D materials [1]

Family of Nanopeapods [2]



Metallofullerene

Metal nanowire

Boron-nitride nanotube

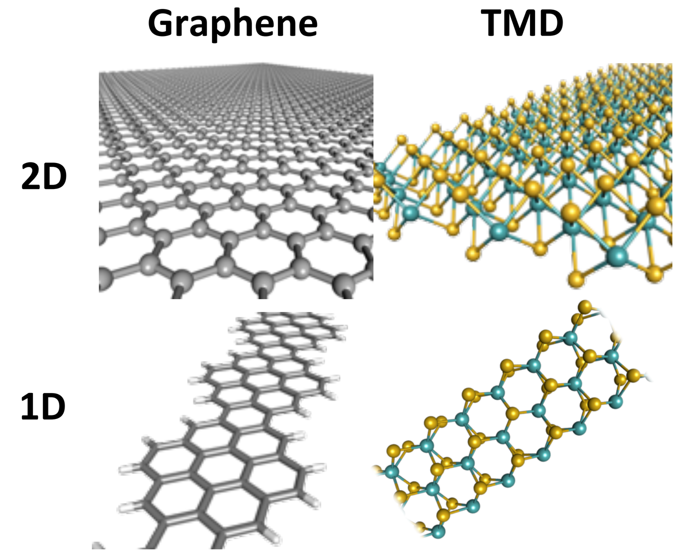
Transition Metal Dichalcogenide (TMD) Nanoribbon Peapods

Low-Dimensional TMDs

- Quantum confinement results in interesting electronic and magnetic problems

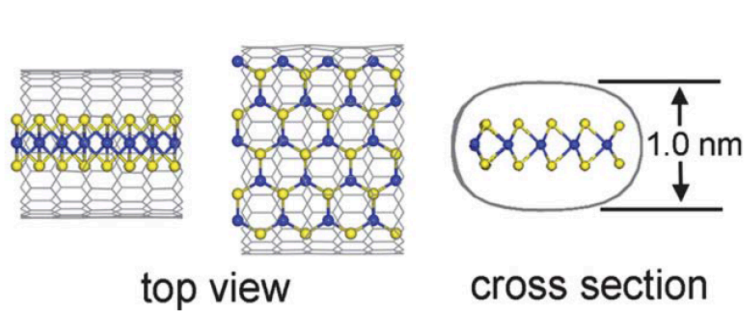
1D TMD Synthesis

- Only possible via nano-test-tube reaction
- Conventional methods yield 2D materials



Different types of 2D materials and their associated 1D nanoribbon structures. Made by Y. Nakanishi

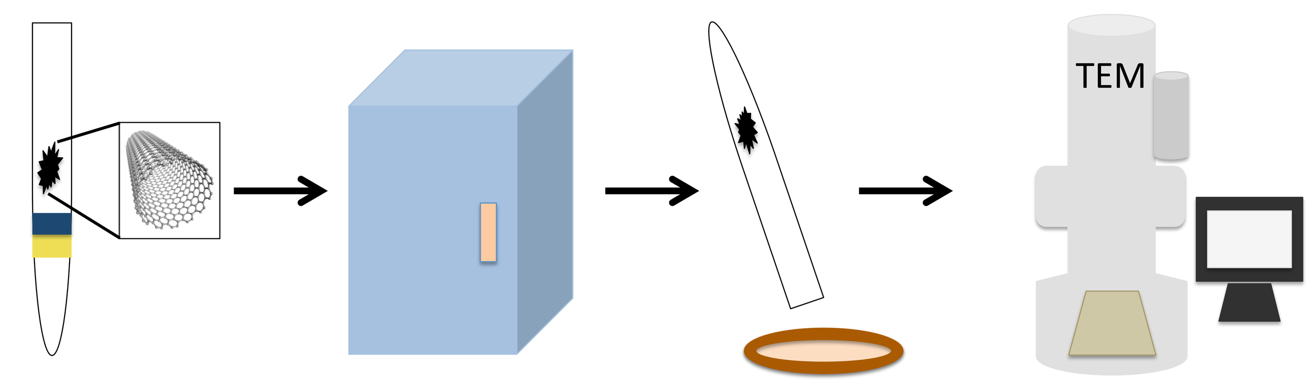
Research Question:
Can we synthesize higher yields of WS_2 nanoribbon peapods in order to study the material's electronic and magnetic properties?



WS_2 Nanoribbon Peapod [3]

WS_2 Electronic and Magnetic Properties [3]	
Bulk WS_2	Nonmagnetic semiconductor
WS_2 nanoribbon	*Zigzag-edged* – Most stable – Nonmagnetic or magnetic metal – Depends on edge passivation *Armchair-edged* – Nonmagnetic semiconductor

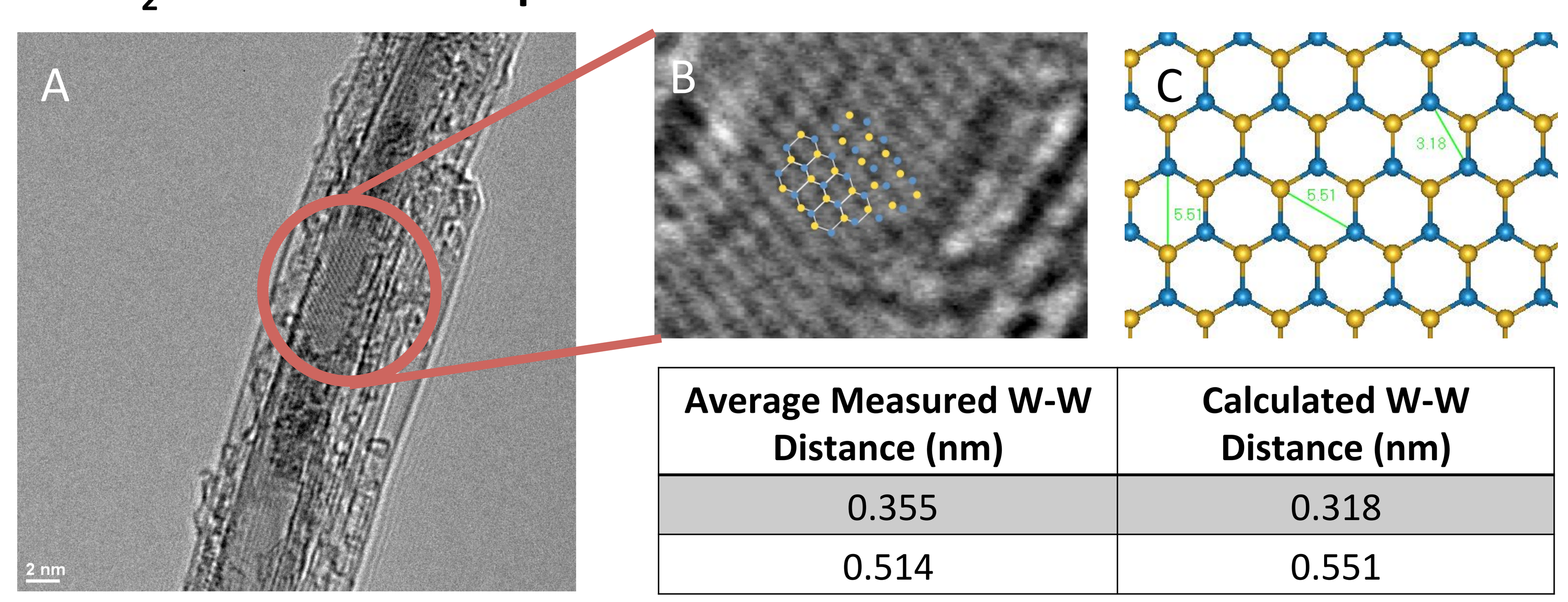
Encapsulation Method via Sublimation



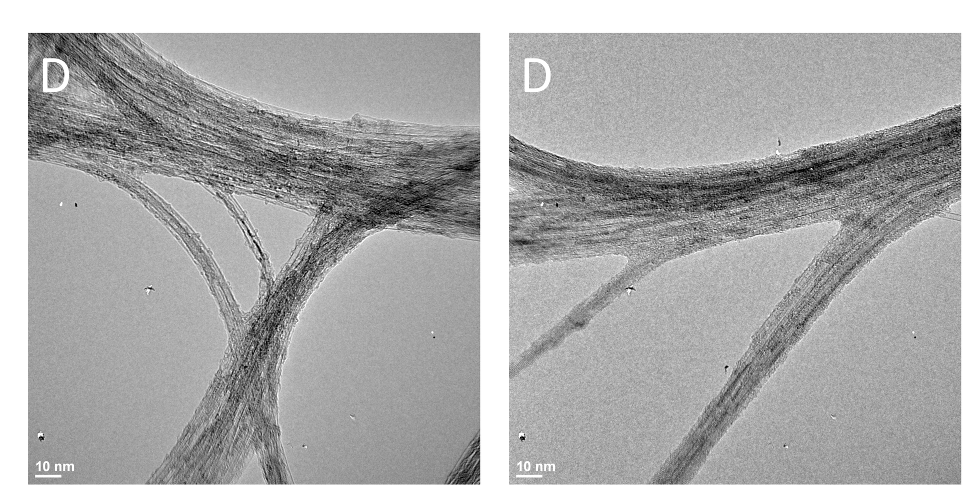
Add and seal reactants (WCl_6, S, & SWCNT) in a vacuum tube → Heat and sublime reactants for 24 hours → Prepare TEM grid with CNT sample → Analyze CNTs using TEM

WS_2 Nanoribbon Synthesis

WS_2 Nanoribbon Peapod



Average Measured W-W Distance (nm)	Calculated W-W Distance (nm)
0.355	0.318
0.514	0.551

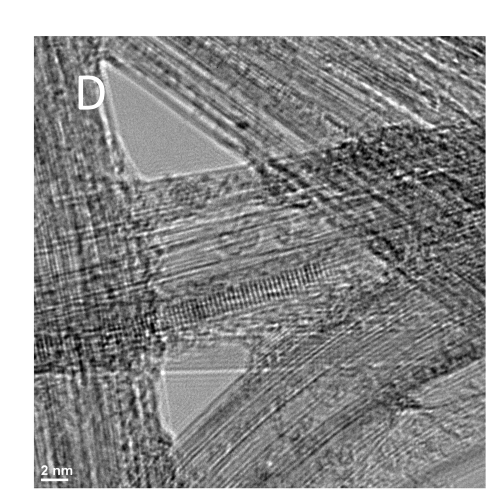


(A) *Encapsulated WS_2 NR with 2.8 nm diameter (600ºC for 24 hours)*
(B) *Labeled atoms in WS_2 NR*
(C) *Model of WS_2 NR with W-W atomic spacing (Å). Made by M. Aizaki*
(D) *TEM images of 600ºC for 24 hours encapsulation yields*

Tungsten Nanowire Peapod

Surface atom distances of single-crystal tungsten nanowires with different crystal orientations along x, y and z directions [4]

Crystal Orientation	L_x/nm	L_y/nm	L_z/nm
<100>	0.316	0.316	0.316
<110>	0.447	0.447	0.316
<111>	0.548	0.447	0.516



Measured Spacing Between Atoms Along CNT Diameter (nm)	Measured Spacing Between Atoms Along CNT Wall (nm)
0.353	0.48

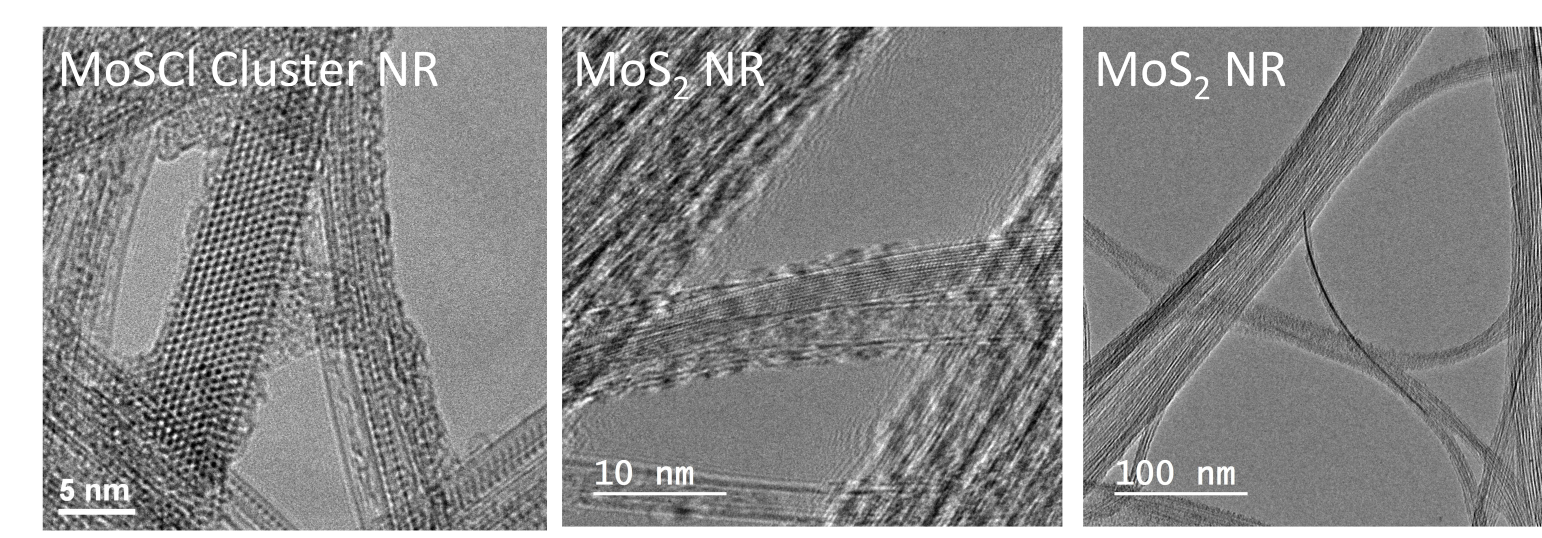
Discussion and TEM Analysis

Results

- Successfully encapsulated WS_2 nanoribbons under higher temperature conditions
- Yields too low to detect via Raman Spectroscopy
- Confirmed zigzag-edged nanoribbon encapsulated
- Tungsten nanowires also encapsulated under all reaction conditions
- Higher temperatures resulted in cleaner CNTs and greater amounts of encapsulation

Comparing TMD Nanoribbon Peapods

- MoS_2 nanoribbon obtained by annealing MoSCl cluster NR
  - MoS_2 NR has similar crystal structure to WS_2 NR
- Hope to synthesis WS_2 NR of similar length to MoS_2 NR



MoSCl cluster nanribbon and MoS_2 nanoribbon synthesis and TEM images by M. Aizaki

Future Plans

- Obtain higher-resolution images of WS_2 nanoribbons using STEM
- Anneal sample in attempts to synthesize longer WS_2 nanoribbons

References

[1] H. Shinohara, Jpn. J. Appl. Phys. 57, 020101 (2018).
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[3] Z. Wang *et. al.* J. Mater. Chem., 2011, 21, 171.
[4] B. Ma *et. al.* Nonferrous Met. Soc. China 24(2014) 2904-2910.

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