Encapsulating WS$_2$ Nanoribbons in Single-walled Carbon Nanotubes

Ellen Park$^{1,2}$, Yusuke Nakanishi$^{3,4}$, Motoki Aizaki$^4$, and Hisanori Shinohara$^{3,4}$

$^1$Dept. of Chemical and Biological Engineering, Cornell University, Ithaca New York, USA
$^2$Nakatani RIES: Research & International Experiences for Students Fellowship in Japan, Nakatani Foundation, Tokyo, Japan
$^3$Institute for Advanced Research, Nagoya University, Nagoya 464-8601, Japan
$^4$Department of Chemistry, Nagoya University, Nagoya 464-8601, Japan

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.

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-D Material Formation
- Allows for synthesis of hollow spaces in CNTs
- Nano-test-tube reaction

WS₂ Nanoribbon Peapods

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

Research Question:
Can we synthesize higher yields of WS₂ nanoribbon peapods in order to study the material’s electronic and magnetic properties?

WS₂ Electronic and Magnetic Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Bulk WS₂</th>
<th>Nonmagnetic semiconductor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zigzag-edged</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Most stable</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nonmagnetic or magnetic metal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Depends on edge passivation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Armchair-edged</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nonmagnetic semiconductor</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Average Measured W-W Distance (nm) vs. Calculated W-W Distance (nm)

<table>
<thead>
<tr>
<th>Distance (nm)</th>
<th>Measured</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.355</td>
<td>0.354</td>
<td>0.355</td>
</tr>
<tr>
<td>0.318</td>
<td>0.316</td>
<td>0.316</td>
</tr>
<tr>
<td>0.318</td>
<td>0.316</td>
<td>0.316</td>
</tr>
<tr>
<td>0.318</td>
<td>0.316</td>
<td>0.316</td>
</tr>
<tr>
<td>0.318</td>
<td>0.316</td>
<td>0.316</td>
</tr>
<tr>
<td>0.551</td>
<td>0.551</td>
<td>0.551</td>
</tr>
<tr>
<td>0.551</td>
<td>0.551</td>
<td>0.551</td>
</tr>
<tr>
<td>0.551</td>
<td>0.551</td>
<td>0.551</td>
</tr>
<tr>
<td>0.551</td>
<td>0.551</td>
<td>0.551</td>
</tr>
<tr>
<td>0.551</td>
<td>0.551</td>
<td>0.551</td>
</tr>
</tbody>
</table>

Tungsten Nanowire Peapods

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

- Crystal Orientation
  - L<sub>x</sub>/nm
  - L<sub>y</sub>/nm
  - L<sub>z</sub>/nm
- Measured Spacing Between Atoms Along CNT Diameter (nm)
- Measured Spacing Between Atoms Along CNT Wall (nm)

Results
- Successfully encapsulated WS₂ nanoribbon peapods 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
- MoS₂ nanoribbon obtained by annealing MoSCl<sub>2</sub> cluster NR
  - MoS₂ NR has similar crystal structure to WS₂ NR
- Hope to synthesize WS₂ NR of similar length to MoS₂ NR

Future Plans
- Obtain higher-resolution images of WS₂ nanoribbons using STEM
- Anneal sample in attempts to synthesize longer WS₂ nanoribbons

References


Acknowledgements

I would like to thank my mentors Prof. Yusuke Nakanishi and Motoki Aizaki for helping me with this project. I would also like to thank Prof. Shinohara and the Shinohara lab for hosting me this summer. This research was conducted as part of the Nakatani Foundation’s 2018 Nakatani RIES Fellowship for U.S. students in Japan. For more information see http://nakatani-ries.rice.edu/.