Dispersion of Single-Walled Carbon Nanotubes by Density Gradient Ultracentrifugation

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Single-walled carbon nanotubes (SWNTs) have been of interest for their unique material properties. Their high thermal and electrical conductivity, metallic or semiconducting nature, as well as chemically stable structure make them ideal for numerous applications. However, development of potential applications has been limited due to the inability to consistently separate SWNTs by chirality, diameter, or conductivity which would allow for optimal utilization of their electronic properties. In this study, we investigate the separation of SWNTs using a density gradient centrifugation (DGC) approach on SWNTs synthesized by the high-purity alcohol catalytic chemical vapor deposition (ACCVD) method. Surfactant encapsulation of the SWNTs is thought to help enhance buoyancy forces, which would thus result in better separation under ultracentrifuge settings. While sodium dodecyl sulfate (SDS) and sodium cholate (SC) are commonly used in DGC techniques, the addition of sodium deoxycholate (DOC) has recently been shown to enhance semiconducting/metallic separation. It is thought that DOC selectively attaches to metallic SWNTs thus changing the density of the encapsulated nanotubes. In order to enhance the separation between metallic and semiconducting SWNTs, we utilized three co-surfactants: SDS, SC, and DOC. This method was successful in separating SWNTs, but considerable improvement is expected upon further refinement.

Separation of (6,5) Single-Walled Carbon Nanotubes by Density Gradient Centrifugation

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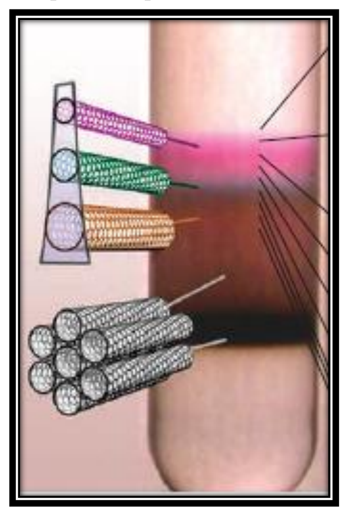
Introduction

Global Objective: develop methods to optimize growth and properties of single-walled carbon nanotubes (SWNTs)



- ❖The alcohol catalytic chemical vapor deposition (ACCVD)[1] method produces high-purity SWNTs, dia. ~1.0±0.3nm
- ❖Heterogeneous samples inhibit property optimization
- ❖Density gradient centrifugation sorts SWNTs by slight differences in density (right)[2]

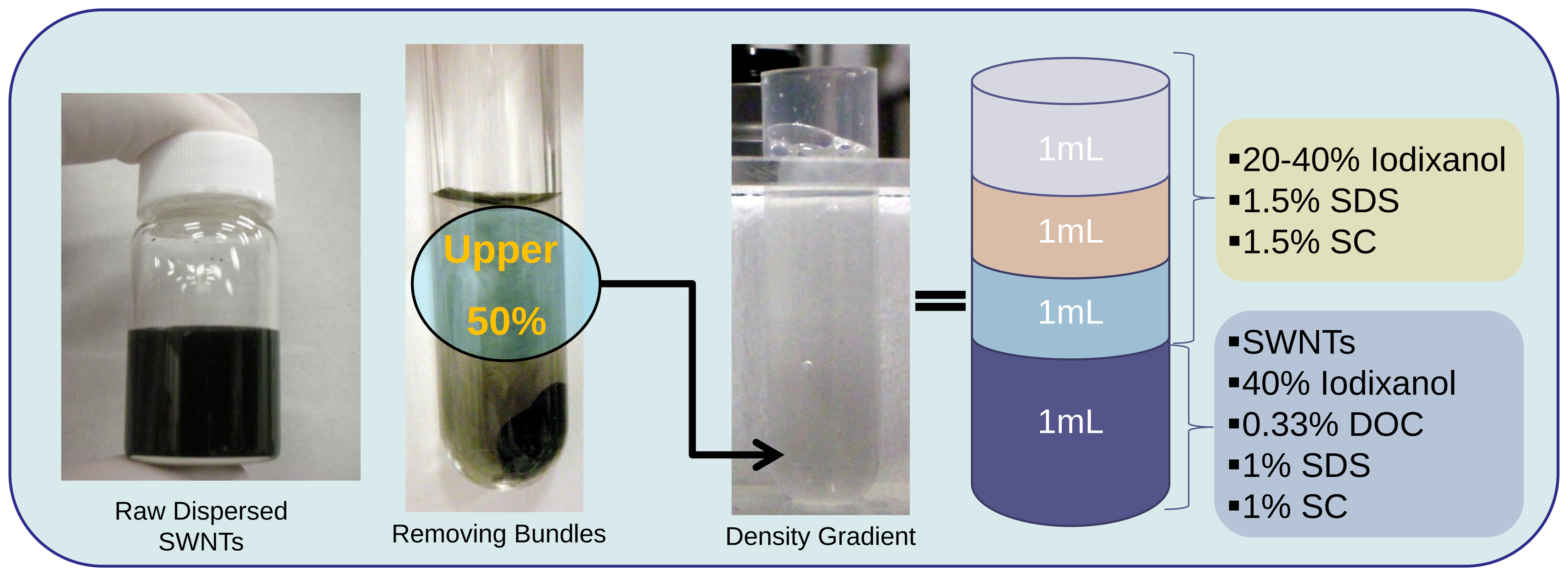
- ❖Encapsulation with sodium deoxycholate (DOC) enhances separation by electronic properties (left)[3]

This experiment shows separation of (6,5) SWNTs using DGC

1. S. Maruyama *et al.*, Chem. Phys. Lett. **360**, 229 (2002)
2. M. Arnold *et al.*, Nature Nanotech. **1**, 60 (2006)
3. K. Yanagi *et al.* App. Phys. Exp. **1**, 034003 (2008)

Methods

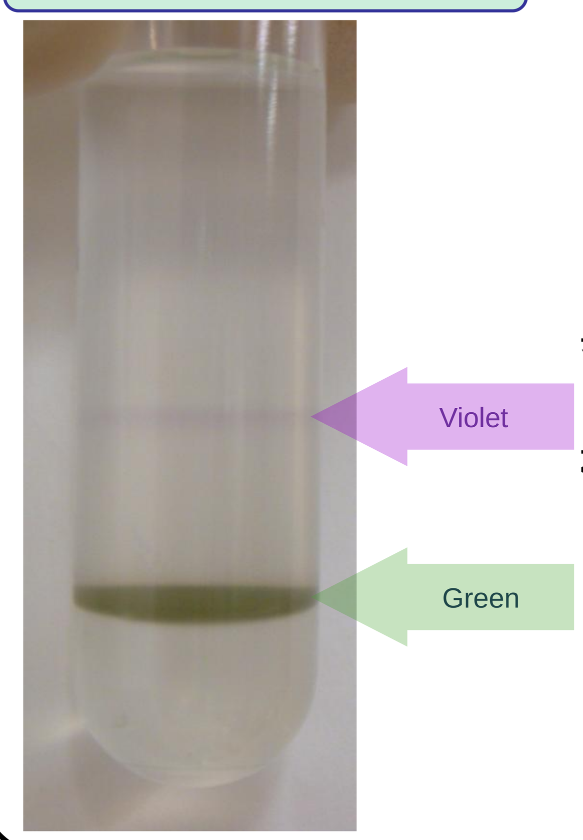
- ❖To remove bundles, SWNTs were dispersed in D_2O and 0.33% DOC, and ultra-centrifuged for 1hr at 275,000*g* using a stationary rotor
- ❖A linear density gradient was manually made as follows:



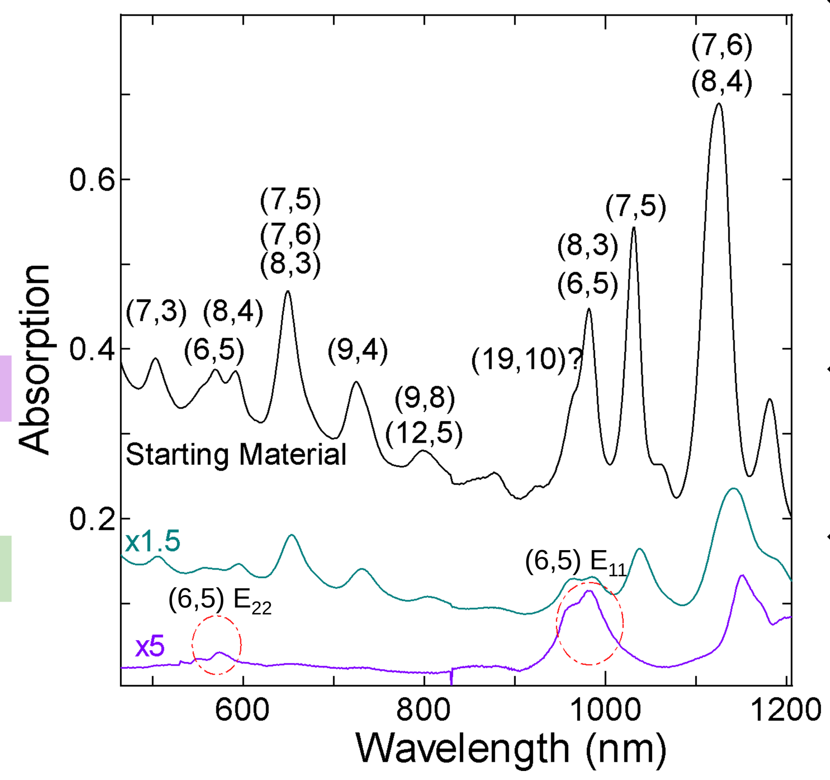
- ❖Samples were ultracentrifuged for 20hrs at 197,000*g* using a swinging rotor
- ❖Manual fractionation

Results

After Centrifugation



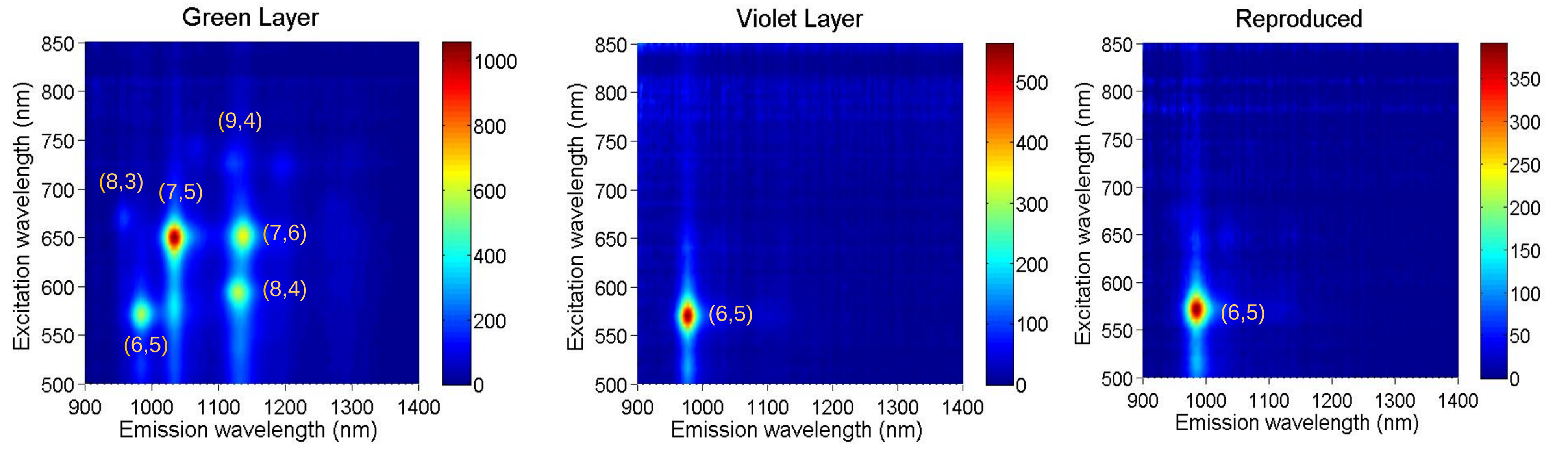
Absorption spectroscopy



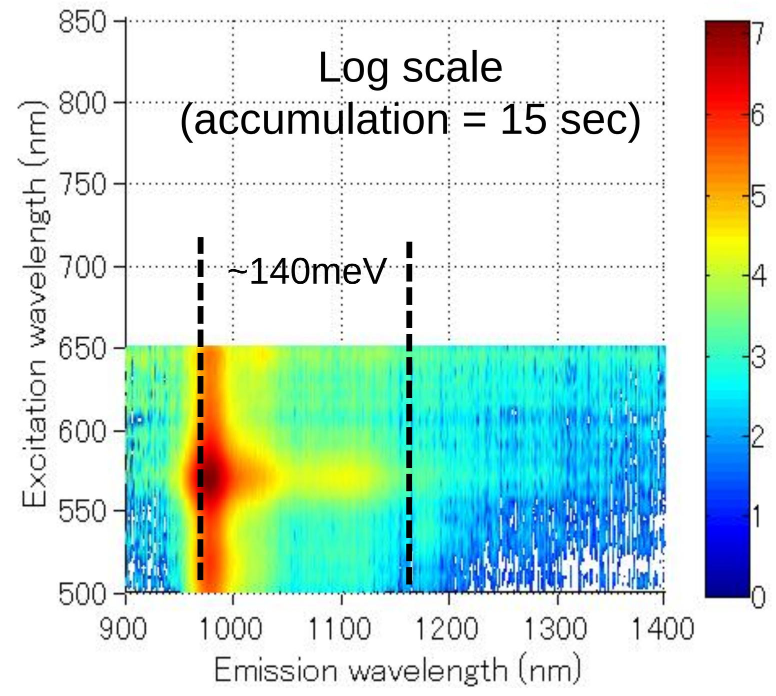
- ❖Violet layer shows (6,5) E_{11} and E_{22} peaks
  - ▪Peak near 1150 nm may be impurity
- ❖Peaks broadened by surfactant encapsulation
- ❖Relative intensities are lower, but may be improved with larger starting sample size

Results cont'd.

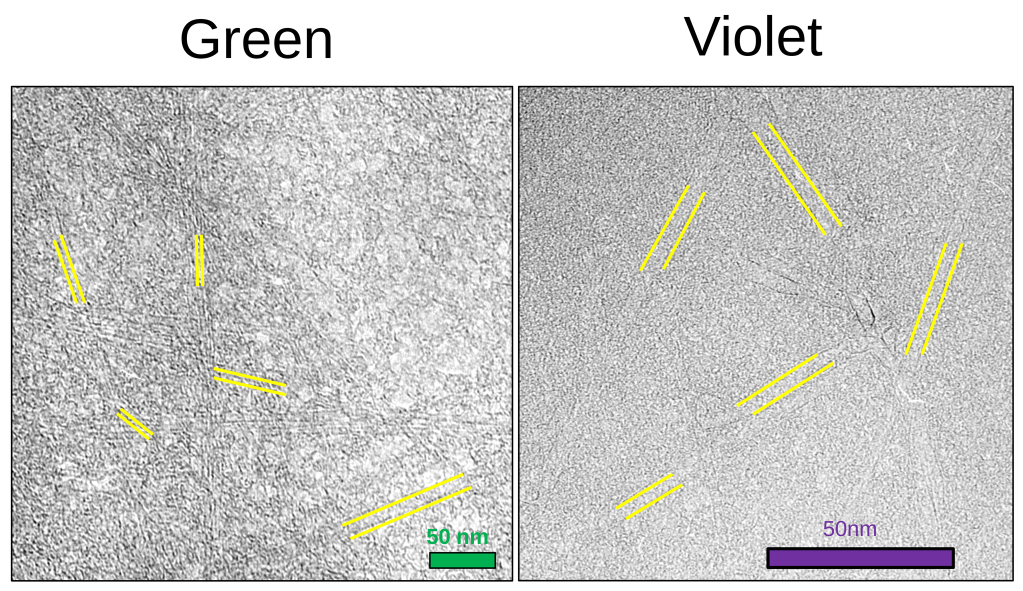
Photoluminescence excitation spectroscopy



- ❖Green layer shows multiple chiralities
- ❖Violet layer shows only (6,5) and corresponding non-resonant streaks
- ❖(6,5) enrichment was reproducible (above right)
- ❖Due to the high purity of the sample, successful measurement of side-band was possible (right)
- ❖The side-band measured was different[4] than previously reported[5]



TEM



- ❖Chirality assignment is difficult due to surfactant encapsulation
- ❖Green sample has mixed diameters
- ❖Violet sample diameters appear to be more uniform

4. Y. Murakami *et al.*, *in preparation*
5. S. Lebedkin *et al.*, Phys. Rev. B **77**, 165429 (2008)

Conclusions

1) Unlike previous processes, clear separation of (6,5) SWNTs was achieved through a one-time ultracentrifugation process
2) High sample purity allowed for accurate measurement of the side-band
3) Side-band emission was shown to be different from previously measured[4,5]
4) Evaluation by TEM imaging and Raman spectroscopy is inhibited by surfactant encapsulation
5) Although produced in small quantities, (6,5) SWNT yield can be improved

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