SEPARATION OF SINGLE-WALLED CARBON NANOTUBES BY SURFACTANT SELECTION AND DENSITY GRADIENT ULTRACENTRIFUGATION

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Carbon nanotubes (CNTs) have received significant attention due to their unique material properties, for their nanostructure enables them to have high electrical and thermal conductivity, along with chemical stability and other properties. With these beneficial characteristics, CNTs can be used for a wide range of applications in electronics, optics, and sensing. However, current techniques of CNT fabrication cannot produce homogenous carbon nanotubes, and this prevents the widespread use of CNTs because their electrical nature (metallic or semiconducting) varies depending on the chirality. In this study, we explore a technique to separate CNTs by diameter and electronic type using the interaction of surfactants and CNTs. Surfactant encapsulation alters the buoyant density of the nanotubes, so the technique of density gradient ultracentrifugation (DGU) can be applied to separate nanotubes. In this technique, surfactants are added to nanotubes, placed in a density gradient, and then centrifuged at high speeds, causing the nanotubes to separate into colored bands of differing characteristics. We have successful recipes for electronic and chirality separation, and we are developing a recipe for separation of both types simultaneously. By analyzing the energy shift of the nanotubes with photoluminescence spectroscopy before and after surfactant wrapping, we are able to better understand the interaction between CNTs and surfactants. This will aid in knowing how different surfactants are selective for electronic type or diameter size, and this can help in further development of the separation process of DGU.

Separation of Carbon Nanotubes by Surfactant Selection and Density Gradient Ultracentrifugation

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Introduction

Objective: develop **methods** to separate single-walled carbon nanotubes (SWCNTs) based on electronic type or chirality and create a **model** to understand the process

Why Carbon Nanotubes?

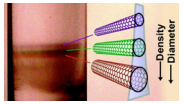
- Structure: hollow cylinders composed of carbon atoms arranged in hexagonal patterns; diameter = 0.7 – 2 nm[1]
- Properties: electrical and thermal conductivity, mechanical strength, and chemical stability
- Applications: nanoscale electronics, optics, and sensors

Challenges:

- CNTs currently produced are a heterogeneous mixture
- Separation is necessary to isolate CNTs by type

Separation Method: Density Gradient Ultracentrifugation (DGU)

- Sorts CNTs based on differences in buoyant density
- Structure-dependent surfactant selection can separate by electronic type or chirality[2]



Diameter-based separation by DGU[2]

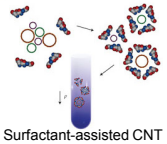
Goals:

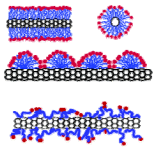
1. Investigate surfactant/nanotube interaction
2. Separate CNTs by chirality and electronic type
3. Create model for surfactant wrapping of CNTs

Key Concepts

Surfactant Selection:

- Amphiphilic molecules (hydrophilic head, hydrophobic tail)
- Disperse CNTs by attachment (hydrophobic attraction)
- Organize into micelles on surface of CNTs

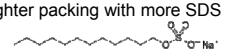

Surfactant-assisted CNT dispersion[2]



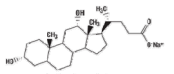
Possible micelle structures[3]

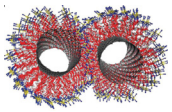
Surfactant Types:

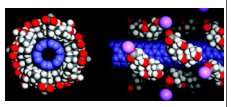
1. Sodium dodecylbenzene (SDS)
   - Stands on surface; tighter packing with more SDS



2. Sodium deoxycholate (DOC)
   - Benzene rings align with CNT wall structure; DOC lies along surface at a fixed angle



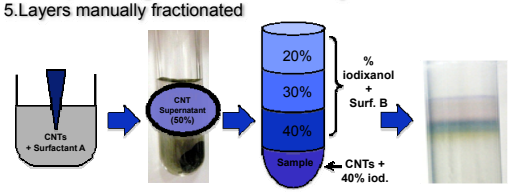

Tightly packed SDS wrapping morphology[5]


DOC-like wrapping morphology[4]

Methods & Results

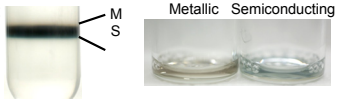
DGU process:

1. CNTs dispersed using surfactant A (sonication for 30 min)
2. Bundles removed after centrifugation (1 hr)
3. Density gradient (containing surf. B) created in centrifuge tube
4. CNTs placed in gradient and ultracentrifuged for 22 hrs
5. Layers manually fractionated



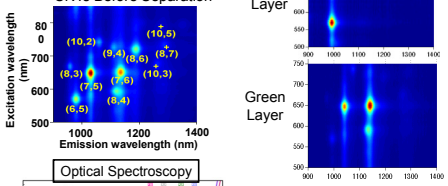
Electronic Separation:

- Surfactant A: SDS; Surfactant B: SDS
- Results:

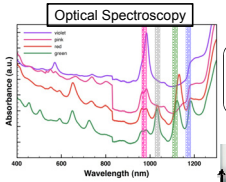


Chiral Separation:

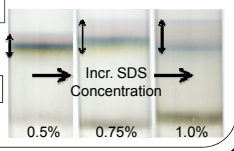
- Surfactant A: DOC; Surfactant B: SDS
- Results: rainbow separation



Optical Spectroscopy



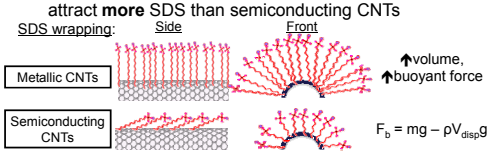
Rainbow Expansion:



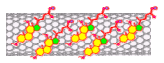
Discussion

Modeling Surfactant Wrapping:

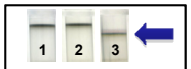
1. SDS wrapping (electronic separation):
   - Metallic CNTs have dielectric properties, causing them to attract **more** SDS than semiconducting CNTs



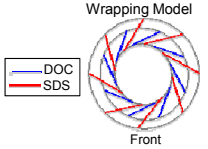
2. DOC wrapping (no separation):
   - Attachment is based on chirality
   - Wraps close to surface, difference in density is small



2. DOC & SDS wrapping (chirality separation):
   - SDS needed to create differences in density:



1 = No surfactant in DG
2 = DOC in DG
3 = SDS in DG

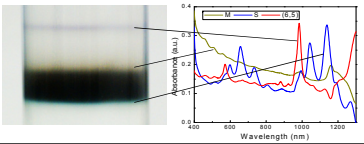


- Chiralities with smaller diameter tend to rise to the top (less mass → greater buoyant force)
- Evidence of this model:

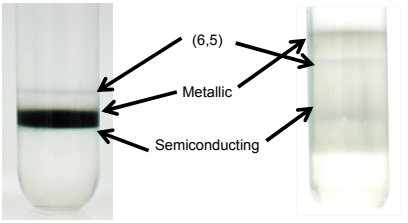
Sample	SDS wrapped	DOC wrapped	DOC + SDS wrapped
E11	979.6 nm	984.5 nm	992.4 nm

Future Work

- **Simultaneous** separation of CNTs by both electronic type and chirality is desired
- Progress has been made using co-surfactants (disperse with SDS + DOC)
- Further research is needed



Co-Surfactant Separation



Conclusions

- **DGU** = technique for CNT separation
  - Successful separation by chirality or elec. type
  - Procedures refined for optimum results
  - Future work in simultaneous separation
- **Surfactant selection** has been investigated
  - Models created to explain the phenomena
  - By understanding surfactant/nanotube interaction, we can control CNT separation

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