

Spectroscopic Analysis of Single-Walled Carbon Nanotubes Sorted by Density-Gradient Ultracentrifugation

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Introduction

A significant barrier in efforts toward characterization of single-walled carbon nanotubes (SWNTs) is the inability to separate nanotubes by size, chirality and electronic type. Much of recent research focuses on post-production sorting of SWNTs. One promising method for post production sorting takes advantage of differences in buoyant densities of nanotubes and their interactions with different surfactant encapsulating agents¹⁻³.

Objectives

- Find experimental parameters ideal for isolation of SWNTs based on chirality
 - Investigate effect of surfactant type in dispersion
 - Investigate effectiveness of sorting SWNTs by different methods
 - Refine method for creating density gradient
- Evaluate effectiveness of separation through spectroscopy
 - Photoluminescence (PL)
 - Optical absorption

Background

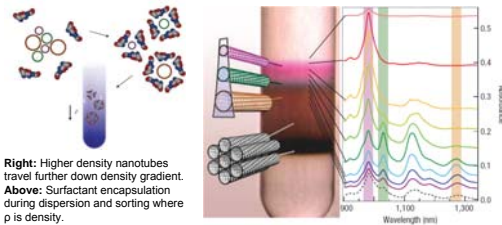
Two main factors contributing to sorting of SWNTs :

- Sedimentation coefficient**
 - Function of substance's distance from axis of rotation
 - Can be expressed by the Lamm equation⁴:

$$\frac{\partial c}{\partial t} = D \left[\left(\frac{\partial^2 c}{\partial r^2} \right) + \frac{1}{r} \left(\frac{\partial c}{\partial r} \right) - s \omega^2 r \left(\frac{\partial c}{\partial r} \right) + 2c \right]$$

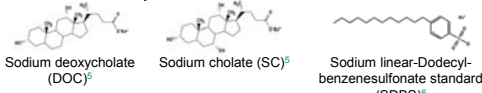
c = solute concentration
 t = time
 r = radius
 D = solute diffusion constant
 s = sedimentation coefficient
 ω = rotor angular velocity

- Buoyant density**⁵
 - Correlates to diameter and length of nanotubes
 - Takes into account effect of surfactant in dispersion procedure



Surfactant

Structural differences in surfactants used account for difference in interaction with SWNTs of different chirality.



Procedure

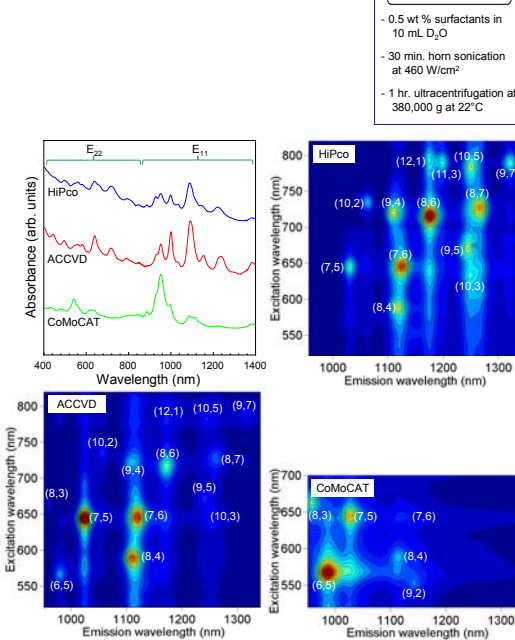
- Nanotube samples were dispersed in D₂O with different surfactants using horn sonication and ultra centrifugation with a fixed rotor
- After centrifugation, upper half of solutions were saved for later sorting
- Carbon nanotubes were then layered on top of a density gradient and placed in ultracentrifugation with a swing rotor for 10 – 12 hours.
- Layers of nanotubes were then extracted from top by layers and diluted as necessary for spectroscopy analysis
- PL and absorption spectroscopy were taken for each layer

Density gradient

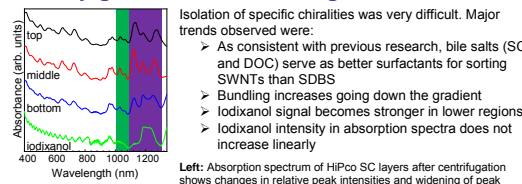
- 60% concentration w/v iodixanol solution diluted with D₂O to create concentrations between 7.5% and 22.5% with 2% w/v surfactants each layer²
- Layers were deposited from top with a micropipette
- Tubes were then covered and laid flat to allow for dispersion^{1,7}

Results

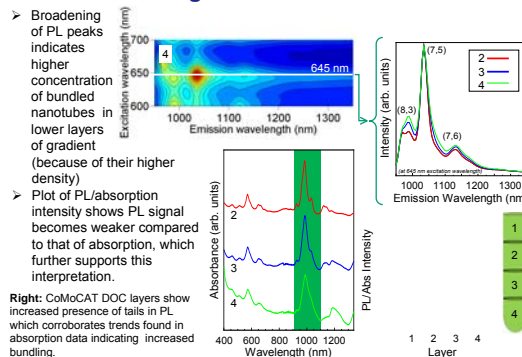
SWNT growth



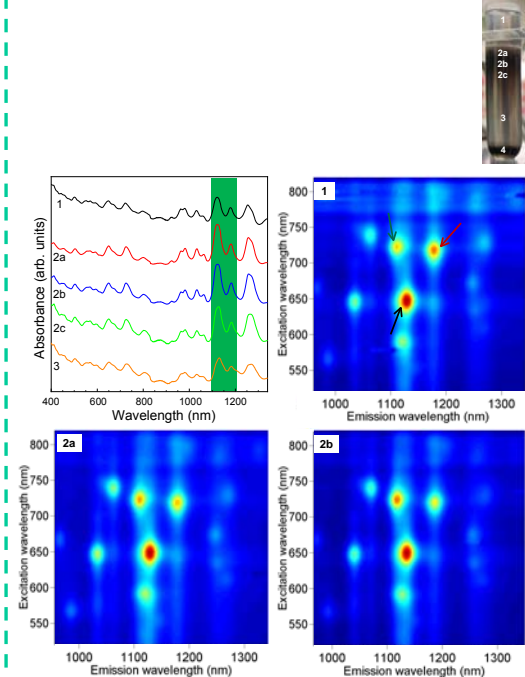
Density gradient ultracentrifugation



Effect of bundling



Partial sorting



Conclusion

- While spectroscopy analysis indicated partial sorting was accomplished, successive cycles may be necessary
- Effect of bundling observed even in the upper layers suggests inadequate dispersion or possibly rebundling during centrifugation process
- Higher concentrations of iodixanol draws out signals emitted by nanotubes in longer E₁₁ wavelength range

Improvements

- Surfactant mixtures and improvements in conditions in dispersion technique can decrease concentration of bundled nanotubes
- Density gradients of a narrower range should be used
- Centrifugation time should be optimized
- Fractionation should immediately follow sorting
- Improvement in fractionation needed to minimize post sorting mixing of layers
- Thinner layers should be extracted for spectroscopy analysis

References

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