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

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While the development of large scale synthesis of single walled carbon nanotubes (SWNTs) has steadily progressed, full understanding of electric and optical properties has not yet been achieved. Various schools of thought have developed in an attempt to explain optical features in SWNTs that theory alone cannot account for, such as the unassigned peaks in the Raman spectra of vertically aligned SWNTs that disappear in dispersed samples. Another interesting feature is the existence of features in contour mappings of the photoluminescence spectrum that do not correlate to assignments of chirality as per current research. To better understand these features, high resolution and polarized Raman and photoluminescence spectroscopy of various samples were taken and compared. Additionally, because the inability to separate nanotubes by size, chirality and electric type hinders efforts to understanding properties of SWNTs, post-production sorting methods were also examined. Previous research in sorting carbon nanotubes suggests taking advantage of differences in buoyant densities of nanotubes and their interactions with different surfactant encapsulating agents. Using this approach, the effectiveness of various surfactant mixtures and nanotube samples in the density-gradient ultracentrifugation process was examined to refine purification methods. Photoluminescence, absorption, and Raman spectra were then examined to confirm the effectiveness of the purification process and to investigate the existence of a π Plasmon peak for semiconducting SWNTs.

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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 agents[1-3].

Objectives

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

Background

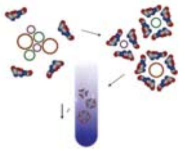
Two main factors contributing to sorting of SWNTs :

- *Sedimentation coefficient*[3]
  - Function of substance's distance from axis of rotation
  - Can be expressed by the Lamm equation[4]:

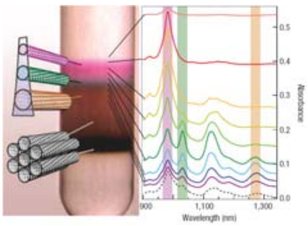
$$\frac{\partial c}{\partial t} = D\left[\left(\frac{\partial^2 c}{\partial r^2}\right) + \frac{1}{r}\left(\frac{\partial c}{\partial r}\right)\right] - s\omega^2\left[r\left(\frac{\partial c}{\partial r}\right) + 2c\right]$$

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

- *Buoyant density*[2]
  - Correlates to diameter and length of nanotubes
  - Takes into account effect of surfactant in dispersion procedure



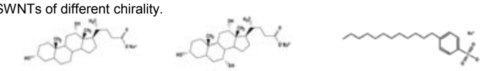
Right: Higher density nanotubes travel further down density gradient. **Above:** Surfactant encapsulation during dispersion and sorting where ρ is density.



M.S. Arnold et.al., *Nature Nanotechnology*, **1**, 60 (2006).

Surfactant

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



Sodium deoxycholate (DOC)[5] | Sodium cholate (SC)[5] | Sodium linear-Dodecyl-benzenesulfonate standard (SDBS)[6]

Procedure

- Nanotube samples were dispersed in D_2O 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

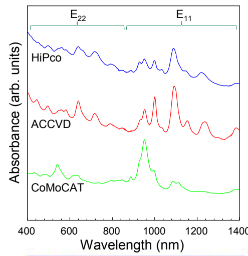
- 60% concentration w/v iodixanol solution diluted with D_2O to create concentrations between 7.5% and 22.5% with 2% w/v surfactants each layer[2]
- Layers were deposited from top with a micropipette
- Tubes were then covered and laid flat to allow for dispersion[4,7]

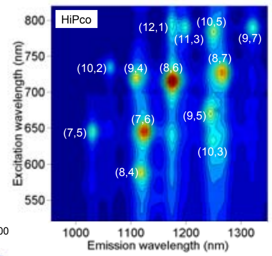
Results

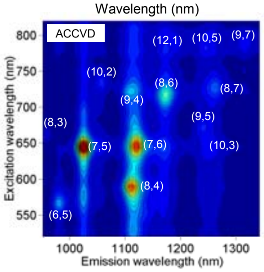
SWNT growth

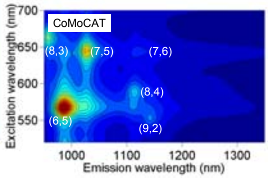
Standard Dispersion

- 0.5 wt % surfactants in 10 mL D_2O
- 30 min. horn sonication at 460 W/cm^2
- 1 hr. ultracentrifugation at 380,000 g at 22°C

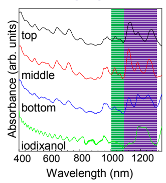








Density gradient ultracentrifugation



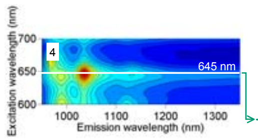
Isolation of specific chiralities was very difficult. Major trends observed were:

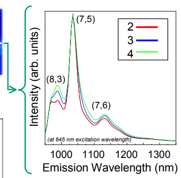
- As consistent with previous research, bile salts (SC and DOC) serve as better surfactants for sorting SWNTs than SDBS
- Bundling increases going down the gradient
- Iodixanol signal becomes stronger in lower regions
- Iodixanol intensity in absorption spectra does not increase linearly

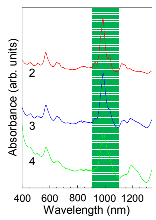
Left: Absorption spectrum of HiPco SC layers after centrifugation shows changes in relative peak intensities and widening of peak

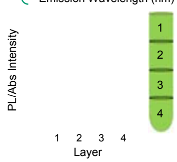
Effect of bundling

- Broadening of PL peaks indicates higher concentration of bundled nanotubes in lower layers of gradient (because of their higher density)
- Plot of PL/absorption intensity shows PL signal becomes weaker compared to that of absorption, which further supports this interpretation.



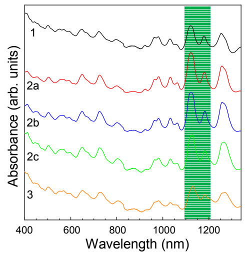


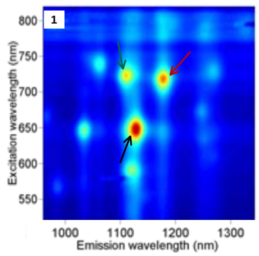


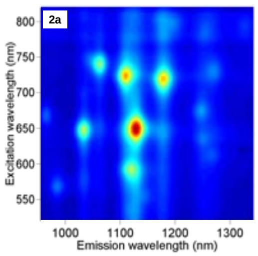


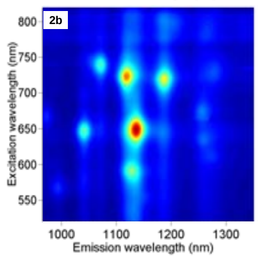
Right: CoMoCAT DOC layers show increased presence of tails in PL which corroborates trends found in absorption data indicating increased bundling.

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 drowns out signals emitted by nanotubes in longer E_{11} 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

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Acknowledgements

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