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 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

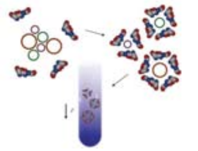
Two main factors contributing to sorting of SWNTs :

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

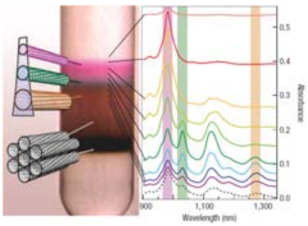
$$\frac{\partial c}{\partial t} = D\left[\left(\frac{\partial^2 c}{\partial r^2}\right) + \frac{1}{r}\left(\frac{\partial c}{\partial r}\right)\right] - s\omega^2\left[r\left(\frac{\partial c}{\partial r}\right) + 2c\right]$$

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



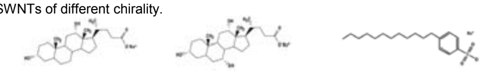
Right: Higher density nanotubes travel further down density gradient. **Above:** Surfactant encapsulation during dispersion and sorting where ρ is density.



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

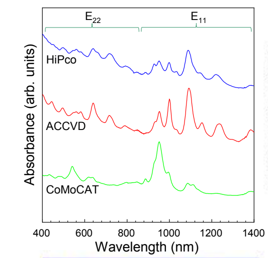
Density gradient

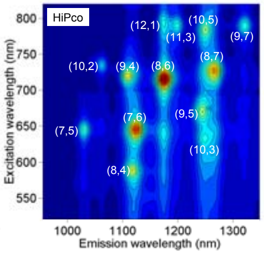
- 60% concentration w/v iodixanol solution diluted with D_2O to create concentrations between 7.5% and 22.5% with 2% w/v surfactants each layer[2]
- Layers were deposited from top with a micropipette
- Tubes were then covered and laid flat to allow for dispersion[4,7]

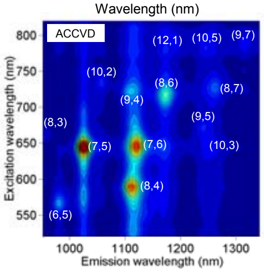
Results

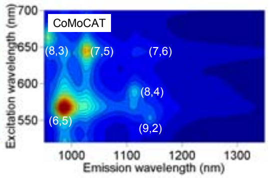
SWNT growth

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

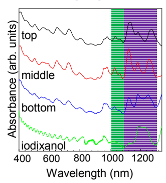








Density gradient ultracentrifugation



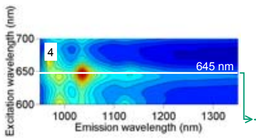
Isolation of specific chiralities was very difficult. Major trends observed were:

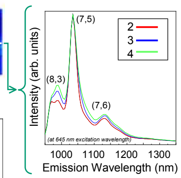
- As consistent with previous research, bile salts (SC and DOC) serve as better surfactants for sorting SWNTs than SDBS
- Bundling increases going down the gradient
- Iodixanol signal becomes stronger in lower regions
- Iodixanol intensity in absorption spectra does not increase linearly

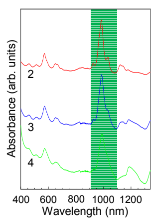
Left: Absorption spectrum of HiPco SC layers after centrifugation shows changes in relative peak intensities and widening of peak

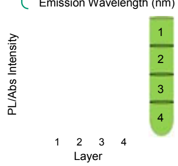
Effect of bundling

- 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.



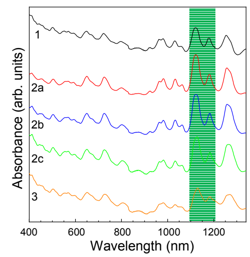


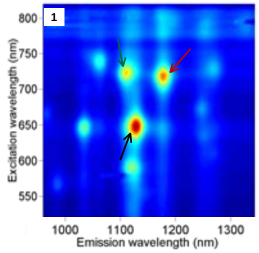


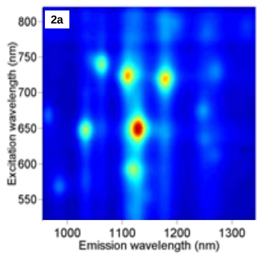


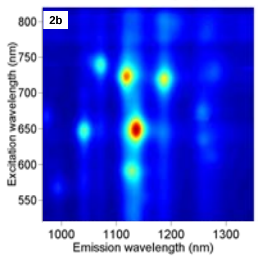
Right: CoMoCAT DOC layers show increased presence of tails in PL which corroborates trends found in absorption data indicating increased bundling.

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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