Nanomaterials

Lecture 8: Carbon Nanomaterials
Carbon Nanomaterials

STM Image

7 nm

AFM Image
Characterization of Stimulated Emission from Encapsulated SWNTs

Characterization of Stimulated Emission from Encapsulated SWNTs

**Experimental setup**

- **Pulsed pump** from Ti:sapphire laser (300 fs pulse width)
- **Probe** from CW fiber laser (λ=1053 nm)
- **Sample** (stirred)
- **60dB**
- **ESA or oscilloscope**

**Graphs**

- **Probe modulation in frequency domain**
- **Temporal response of probe modulation**
Effect of Aggregation and pH

- Aggregation of isolated nanotubes by lyophilization and re-suspension drastically reduces probe modulation intensity by a factor of 122.
- Photobleaching disappears at acidic pH and is reversibly restored at neutral and basic pH, consistent with protonation of nanotube sidewalls at acidic pH.

• The measured $E_{22}$ transition width of 65 meV is consistent with fast electron-electron scattering on the 300 fs time scale.

• The feature near 1.4 eV is likely due to a Raman effect (the measured difference between pump and probe energies is $\sim 1600 \text{ cm}^{-1}$, which matches the G-band Raman mode in SWNTs).

Probe Spectral Dependence

- The probe modulation spectrum is slightly red-shifted from the absorbance spectrum by 45 cm\(^{-1}\).

- From a Lorentzian fit, the width of the \(E_{11}\) transition is only 10 meV compared with 65 meV as measured for the \(E_{22}\) transition.

Co-polarized pump and probe lead to greater photobleaching than cross-polarized as expected for a 1-D system.

At low pump intensities below 10 W/cm², linear behavior is observed.

Saturation of the probe modulation is consistent with:

- Increased multi-particle Auger recombination for large carrier densities.
- Exciton-exciton annihilation effects.
- Saturation and filling of a finite number of states.

Probe Saturation Effects

- $x_s$ corresponds to the probe intensity for which the rate of stimulated recombination is equal to the intrinsic rate of recombination.

- An increase in $x_s$ at large pump intensities is consistent with an increase in the effective interband recombination rate due to enhanced Auger recombination for large carrier densities.

Degenerate Pump-Probe Measurements

Degenerate pump-probe optical setup.

Time-resolved relaxation at $E_{11}$ (975 nm) and $E_{22}$ (740 nm) optical transitions.
Temporal Relaxation at $E_{11}$

Semi-log relaxation at $E_{11}$ (975 nm)

$\tau = 116$ ps
An Estimate of the Optical Gain

To reach optical transparency, SWNTs need to be separated by electronic bandstructure.

~ 10% instantaneous decrease in absorption
Optical Absorption Spectra for DNA Encapsulated SWNTs

Optical absorbance spectrum:
**E\textsubscript{22} Transition:**

![Graph showing absorption spectrum for E\textsubscript{22} transition with wavelengths 652.1 nm, 651.4 nm, and 645.5 nm.

**E\textsubscript{11} Transition:**

![Graph showing absorption spectrum for E\textsubscript{11} transition with wavelengths 973.4 nm, 983.5 nm, and 987.2 nm.

<table>
<thead>
<tr>
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<th>E\textsubscript{11} red-shift</th>
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<tbody>
<tr>
<td>SDS-NT in D\textsubscript{2}O</td>
<td>0 meV</td>
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Characterization of Stimulated Emission from Encapsulated SWNTs

### Optical Absorption Spectra for DNA Encapsulated SWNTs

#### E\textsubscript{22} Transition:

![Graph showing E\textsubscript{22} transition](image)

#### E\textsubscript{11} Transition:

![Graph showing E\textsubscript{11} transition](image)

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Density of DNA Encapsulated SWNTs

Density of SWNTs in vacuum:

\[ \rho_{NT} := \frac{4 \rho_s}{D} \]

Density of DNA encapsulated SWNTs:

\[ \rho_{NT} := \frac{\rho_s \pi D + \rho_{ext} \pi \left( \frac{D}{2} + t \right)^2 - \frac{D^2}{4}}{\pi \left( \frac{D}{2} + t \right)^2} \]

\( \rho_s = \) areal density of graphite = 7.66\times10^{-8} \text{ g/cm}^2

\( \rho_{ext} = \) volume density of hydrated DNA in iodixanol = 1.12 g/cm³

Density Gradient Centrifugation of DNA Encapsulated SWNTs

Density of DNA encapsulated SWNTs: $1.11 – 1.17 \text{ g/cm}^3$

$\rightarrow$ DNA hydration layer thickness of 2 – 3 nm

Separation of DNA Encapsulated SWNTs by Diameter

Correlating Diameter and Density

- Density of DNA encapsulated SWNTs increases with increasing diameter.
- Separation is most effective at small diameters.