Optical Spectroscopy of Single-Walled Carbon Nanotubes

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Groups: Heinz, O’Brien, Hone, Turro, Friesner, Brus
1. SWNT Luminescence dynamics – psec pump-probe spectroscopy (F. Wang, G. Dukovic)
   - Radiative lifetime ~ 100ns
   - Efficient Auger recombination

   - Neutral and protonated endoperoxides

5. Rayleigh scattering from individual metallic and semiconducting SWNTs (M. Sfeir, F. Wang, L. Huang, C. Chuang)
Constructing a (10,10) SWNT

- Unit cell: $dt = 1.375 \text{ nm}$
- $\theta = 30^\circ$
- Aspect ratio: $L > 1 \text{ mm}$
- Aspect ratio: $> 10^6$
Nanotube:
- Ideal 1-D system;
- Many unique properties: Electrical, mechanical and optical.
10 frontier orbitals of (5,5) Nanotube fragments

Energy (eV)

# of sections (10 C each sect.)
Light Emission from SWNTs

Band Gap Fluorescence [1]

- Photonic application.
- Useful tool for probing electronic structure and carrier dynamics.

Electroluminescence [2]


Hartschuh, Pedrosa, Novotny, Krauss  [Science 301 1354 (2003)]
Psec dynamics in SWNT ensembles

Isolated SWNTs in aqueous micelles

Ref. [1]

A single nanotube embedded in SDS micelle

AFM Image

Micellar Fluorescence Spectra

Pump wavelength 800 nm

[(n,m) assignment according to S.M. Bachilo et al. Science 298, 2361 (2002)]
Spectrally Integrated Time-Resolved Fluorescence

- Fluorescence decay: Principal decay time $\sim 7$ ps
- Also fluorescence in long-time tails.
Radiative Recombination Lifetime

Absolute fluorescence Q. E. (fast comp.):
\[ \eta = 0.7 \times 10^{-4} \]

\[ \gamma_{\text{total}} = 7 \text{ps}^{-1} \]

\[ \gamma_{\text{rad}} = \eta \cdot \gamma_{\text{total}} \]

\[ \tau_{\text{rad}} = \frac{1}{\gamma_{\text{rad}}} \approx 110 \text{ ns} \]
Implication of the Radiative Lifetime

\[ \tau_{rad} \sim 100 \text{ ns} \]

- Comparable to CdSe semiconductor nanoparticles with high fluorescence quantum yield:

→ Low fluorescence efficiency is due to the fast trapping

In 10 ps carrier at thermal velocity travels \( \sim 3 \, \mu\text{m} \)
New Channel with Multiple e-h Pairs

- Additional fast decay initially for multiple excitation per nanotube
- Similar decay at later times, which saturates at high excitation density.

Similar results recently reported by Fleming et al., UC Berkeley
Auger Recombination

**Multi-Carrier Interaction: Auger Process**

At low excitation density:

Fluorescence $\propto$ # of excitated nanotubes $\propto$ pump fluence

At high excitation density:

Fast auger process until one excitation per nanotube

Initial decay differs, tail part of decay is equivalent.
Modeling vs. Experiment

Two electron-hole pairs in 400nm long tube:
Auger rate $\sim 0.8 \text{ ps}^{-1}$
Theoretical Estimation of Auger Rate

Simplified model:

\[ V(r_e - r_h) = -U \delta (r_e - r_h) \]

Simplified Coulomb interaction:

Exciton binding energy: \( E_{\text{bind}} = -\frac{\mu U^2}{2\hbar^2} \approx 200\, \text{meV} \)
Auger Recombination Processes

Feynman Diagrams:

\[ + (K \leftrightarrow P) \]
Calculation Results

M determined by U and Feynman diagrams

\[ \Gamma_{K,p} = \frac{2\pi}{\hbar} \sum_{k_e, k_h} |M|^2 \cdot \delta(E_K + E_P - \varepsilon_{c,k_e} - \varepsilon_{v,k_h}) \]

\[ \tau_{Auger}^{-1} = \Gamma_{Auger} = \frac{0.8 (ps^{-1})}{l} \]

Doesn’t depend strongly on temperature.

In comparison, Auger rate for free electron picture without including excitonic effect has an activated temperature behavior, and is orders of magnitude smaller.
Implication of the Rapid Auger Recombination Rate

• Limit on e-h pairs density:
  *Constraints for population inversion and light amplification.*

• Auger recombination due to the presence of free electrons or holes arising from defects or surface molecular species:
  *Environmental sensitivity of photoluminescence.*

• Rapid Auger recombination:
  *Limit electroluminescence efficiency at high electron-hole injection rate.*
**Summary: Carrier Dynamics in SWNT**

**Experimental Observations:**

- Intraband: $< 200\text{fs}$
- Nonradiative: Defect $\sim 7\text{ps}$
- Radiative: $\sim 100\text{ns}$
- Auger $\sim 1\text{ps}$

**Some Implications:**

- *Fast defect trapping limits the fluorescence yield*
- *Efficient Auger process excludes multiple sustained electron-hole pairs in nanotube, constraint for light emission and amplification in nanotubes*
Absorption bleaching and luminescence quenching at low pH

- Overall increase in intensity with increasing pH – hole doping at acid pH due to a protonated surface oxide (also observed by Strano et al, J. Phys. Chem, 2003, 107, 6979)
- Luminescence more sensitive to H\(^+\) than optical absorption
Direct observation of oxygen desorption
(surface oxide in equilibrium with atmospheric oxygen)

- Heating to 97 °C under argon results in luminescence recovery – surface oxide decomposition
- Data fits unimolecular decomposition kinetics after induction period
- Estimate of $E_a$ for concerted decomposition – 1.2eV
What is the structure of SWNT surface oxide?

**B3LYP DFT calculation**

**ENDOPEROXIDE**

**PROTONATED OXIDE**

Positive charge delocalized on SWNT

carbocation
SWNT re-oxidation with $^1\Delta O_2$ at pH 3

**endoperoxide**

\[ \text{endoperoxide} \xrightarrow{\text{heat}} \text{benzene} + ^1\Delta O_2 \]

**Luminescence quenched**

**Absorption NOT bleached**

- [DMN] = 0.3 mM (control)
- [DMN-O$_2$] = 0.1 µM
- [DMN-O$_2$] = 1.0 µM
- [DMN-O$_2$] = 3.3 µM

- pH 3; air-equilibrated
- pH 3; oxygen removed; [DMN-O$_2$] = 3.7 µM; t = 0
- pH 3; [DMN-O$_2$] = 3.7 µM; t = 18 hours
Effect of oxide on SWNT optical properties

First quantitative study of SWNT oxidation and its effect on SWNT optical properties

- **Fluorescence quenching** – ~ 10 holes per 400 nm tube

- **Absorption bleaching** – ~ 250 holes per 400 nm tube

Difference in sensitivities to holes in absorption and luminescence explained by the Auger effect

Non-radiative recombination: $e^- - h^+ + h^+ \rightarrow h^+ + \text{kinetic energy}$
Optical Spectroscopy of Single Nanotubes

Existing techniques:

• Resonance Raman spectroscopy.
• Fluorescence Excitation Spectroscopy.

We perform single tube *Rayleigh scattering spectroscopy.*

Advantages:

• Direct probe of electronic transitions, intrinsically stronger than Raman Scattering.
• Present for both semiconductor and metallic nanotubes.
Previous Work: (Z. Yu 2001)

- Ensemble Rayleigh scattering from laser-ablation material.
- Shown to closely resemble ensemble absorption spectra.
- Intensity of features shown to be highly polarization dependent.

**Challenge**: Characterize and identify an individual carbon nanotube by their Rayleigh scattering.
Scaling of Nanotube Rayleigh Cross Section

Sphere

\[ \sigma \propto \frac{r^6}{\lambda^4} \left| \frac{\varepsilon - 1}{\varepsilon + 2} \right| \]

Infinite Cylinder

\[ \sigma \propto \frac{r^4 |\varepsilon - 1|^2}{\lambda^3} \]

\( \sigma (d_t = 2 \text{ nm}) \sim 10^{-14} \text{ cm}^2 \)
Supercontinuum Radiation

- High brightness – like laser
  Large spectrum bandwidth – like a light bulb

Spectral range: 450 - 1450 nm

Microstructured fiber: core ~ 2 m
Experimental Setup

Supercontinuum Generation

- Mode-locked Ti:Saph coupled to microstructured fiber optic.
- Spectrograph and CCD
  - Scattered light is corrected by the supercontinuum spectral profile giving the Rayleigh spectrum.
- Laser system
  - Linear fiber
  - Laser brightness
  - Spectral range: 450-1550 nm
- Reference beam
  - Polarizers
  - Polarizers
- Excitation and collection objectives
- Sample
- Scattered light
- Transmitted light
- Spatial filter (pinhole)
Growth and Imaging

CVD Growth Process

Si/SiO$_2$ substrates with slits patterned by optical lithography and wet etching.

Directional growth determined by flow direction of feed gas, lengths > 100 microns:

- CO, methane, and ethanol gas
- Fe, FeMo, and CoMo catalysts

Imaging

Look at total integrated intensity on CCD to find tubes. Correlates to SEM images.

Single tubes scatter light much less than bundles. Distinguishable from the number of peaks in the spectra and width of features.
Types of Rayleigh Spectra from Individual Nanotubes

- Sharp, well-separated two peaks
- Two closely-positioned peaks.
Interpreting the Rayleigh Spectra

Rayleigh scattering from an infinitely long cylinder:

$$\sigma \propto \frac{|\varepsilon - 1|^2}{\lambda^3}$$

$E_{33}$ and $E_{44}$ of semiconductor nanotubes
$E_{22}$ of metallic nanotubes in our dt range

- Resonance structure corresponds to van Hove singularities of nanotube, reflecting the electronic signature of specific nanotubes.
Rayleigh Spectra

**Semiconducting Carbon Nanotube**

Two well separated $E_{33}$ and $E_{44}$ transitions for larger diameter tubes, $E_{33}$ and $E_{22}$ for smaller diameters.

**Metallic Carbon Nanotube**

Single $E_{22}$ transition observed in the visible – sometimes split into two very close peaks by trigonal warping effect.
Polarization Dependence of The Rayleigh Scattering

Light scattering is strongly polarized along the nanotube.

\[ P'' = ( -1 ) E''_0 \]

\[ P = ( -1 ) \frac{2}{+1} E_0 \]
Scattering Spectra along the Nanotube: Single Tube

Does the nanotube keep the same chirality along the entire length?

Yes. At least up to 40 μm, a chain of several millions of carbon atoms.
Scattering Spectra along the Nanotube: Single Tube to Small Bundle

Small Carbon Nanotube Bundle

Four or more peaks, broadened compared to single nanotube spectra.

Bundling Effect, Tube Interactions

When in bundles, spectra broaden and red-shift by approximately 15 meV.
Correlated Raman and Rayleigh Scattering from the Same Nanotube

Rayleigh →

Resonance Raman

Radial breathing mode → $d=1.89\text{nm}$

(21,4) nanotube: $d=1.85\text{nm}$, $E_{33}=1.87$, $E_{44}=2.10$ (tight binding model)
Summary

• Nonradiative Auger recombination is extremely fast in SWNTs

• Nanotubes exposed to air form surface endoperoxides which can protonate to quench luminescence by hole-doping
  – Just a few holes in a 400 nm tube sufficient for quenching
  – Excited state sensitive along the entire length

• In open-slit geometry, it is possible to detect very strong Rayleigh scattering in short times
  – Rayleigh scattering clearly shows strong resonant optical transitions and distinguishes between metallic and semiconducting tubes and provides a structure identification tool