Colorful Carbon: Photophysics of Carbon Nanotubes

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Small systems, big concerns

The Washington Post

Sunday, 21. January 2007:

“Nanotechnology is the hot new science of the very small, in which researchers are engineering materials and devices as tiny as a billionth of a meter across. At those scales, even mundane materials such as carbon perform extraordinary feats - conducting electricity, for example, or triggering chemical reactions - that they'd never do in their chunkier forms.”

“Already, hundreds of products containing nanomaterial are on the market, including stain-resistant fabrics, high-tech tennis rackets, cosmetic creams and sunscreens, computer hard drives and even a "Nanoceuticals Slim Shake," which claims to deliver nutrition directly into your cells in the form of "CocoaClusters" 100,000 times smaller than a grain of sand.”

Nanotechnology warning sign contest by the Erosion, Technology and Concentration (ETC) group.
A new nanotech warning sign
In the eye of the public ...

Economist.com
Thursday February 14th 2008
The risk in nanotechnology

A little risky business
Nov 22nd 2007
From The Economist print edition

The unusual properties of tiny particles contain huge promise. But nobody knows how safe they are. And too few people are trying to find out.

Illustration by Bill Butcher
Today’s menu

• Low-dimensional photophysics 101
• Optically excited states in CNTs
• Preparative developments
• Dynamics: introduction and some gory details
• Outlook


Now also to be found in Germany’s high school standard for Chemistry "Elemente Chemie 1 – Unterrichts-Werk für die Sekundarstufe II“, Band 4179, page 175 B6, Klett Verlag.
Size matters

Carbon Nanotubes

Molecules & Clusters

Nanocrystals, nanoparticles, ...
Optical band gap of carbon nanotubes
Low dimensional photophysics 101
Excited states in semiconductors

Electron energy

Band-gap $E_g$

Electron momentum $k$

free e-h pairs

Excitons

e-h pair momentum $q_{i,k}$

Nagoya, February 2008
Excited states in semiconductors

Commonly used notations in carbon nanotubes

- \( E_{22} \) exciton
- \( E_{11} \) exciton
- Free e-h pairs
- Ground state

Nagoya, February 2008
Sommerfeld factors
(see for example Ogawa and Takagahara, PRB 43 (1991) 14325)

\[ \alpha_{\text{cont}}(\omega) = \alpha_{\text{free}}(\omega) C'(\omega) \]
Excitons: 3D $\rightarrow$ 1D

Effective medium Hamiltonian

$$H = \frac{p^2}{2\mu} - \frac{e^2}{(4\pi\varepsilon_0)\varepsilon r}$$

Binding energy of the 1s state:

$$E_{1s}^b = \left(\frac{\mu}{m_e}\varepsilon^2\right)\left(\frac{2}{\alpha - 1}\right)^2 E_H$$

$\alpha$ - dimensionality (see He, PRB 43, 2063 (1991))
1D systems are different

3-dimensional

Conduction-band

Valenceband

Free e-h pairs

Excitons

\( \alpha(\omega) \)

1-dimensional

Conduction-band

Valenceband

Free e-h pairs

Excitons

\( \alpha(\omega) \)

See for example:
Quantum theory of the optical and electronic properties of semiconductors
Carbon allotropes

The heritage
• Strong bonds, stiff orbitals
• Inert surfaces (sp$^2$)

Derived properties
• Mechanical, chemical, thermal, electrical and photostability

New qualities
• Variable electronic character
• Variable band-gap
• Unsurpassed transport properties
• Sensitivity to environment
The promise

Most researched

• Electronics
• Composites
• Field emission sources
• Membranes and host materials
• ...

Our interests

• Photosensing
  – specific surface area, chemical stability
• Imaging & microscopy
  – luminescence in the water window, chemical- and photostability
• Agents and reporters in biological systems
  – benign surface chemistry, low cytotoxicity
Practical challenges

• **Solubilization for use in various environments**
  – CNT soot is hydrophobic and insoluble in practically all organic solvents

• **Purification, structural sorting**
  – CVD synthesized material is polydisperse
  – Mixed metallic and semiconducting tubes

• **Soft functionalization**
  – Graphitic surfaces not biocompatible
  – Graphitic surfaces have no chemical specificity
Optically excited states in CNTs
Wrapping graphene

Chiral vector: 
\[ C = n a_1 + m a_2 \]
Chirality and diameter make a difference

$sp^2$ orbitals

$p_z$ derived graphene bands

3 examples

quantization

character

metallic

$(n-m) \ mod(3) = 0$

semiconducting

$(n-m) \ mod(3) = \pm 1$
Tight binding example

(2,1) \( \pi \)-subbands
Band gap in semiconducting SWNTs

Diameter dependence of optical band gap

Free parameter: nearest neighbor hopping or transfer integral:

\[ t = \langle p_a^A(r)\mid H\mid p_z^B(r - r_{C-C}) \rangle \]

Deviation from 1/d scaling because of curvature and chirality effects on π-π overlap.
Coulomb interactions give birth to excitons

Many particle problem with Coulomb interaction:
Solution of the Bethe-Salpeter equation

\[ \Delta_k A_k^S \sum_{k'} K_{k,k'}^{eh} A_{k'}^S = \Omega_S A_{k'}^S \]

\( \Delta_k \) - quasiparticle energy (not WW)
\( K_{k,k'}^{eh} = K_{k,k'}^d + 2K_{k,k'}^x \) - direct and exchange terms
\( A_k^S \) - exciton amplitude

(6,5) tube

\[ \Phi_0 A^0_0 (r_e, r_h) \]
Simplified energy level scheme

- $E_{22}$ exciton
- $E_{11}$ exciton
- Free e-h pairs
- Ground state

Levels:
- $S_0$
- $S_1$
- $S_2$
Including spin and band degeneracy

\[ \frac{1}{\sqrt{2}} \left( |KK\rangle - |K'K'\rangle \right) \]

\[ \frac{1}{\sqrt{2}} \left( |KK\rangle + |K'K'\rangle \right) \]

\[ \frac{1}{\sqrt{2}} \left( |KK\rangle + |K'K'\rangle \right) \]

\[ \frac{1}{\sqrt{2}} \left( |KK\rangle - |K'K'\rangle \right) \]

\[ \chi_{0,0}^1 = \frac{1}{\sqrt{2}} \left( |\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle \right) \]

\[ \chi_{1,+1}^3 = |\uparrow\uparrow\rangle \]

\[ \chi_{1,0}^3 = \frac{1}{\sqrt{2}} \left( |\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle \right) \]

\[ \chi_{1,-1}^3 = |\downarrow\downarrow\rangle \]

Wavefunctions

\[ |v_e\rangle \]
\[ |v_h\rangle \]
\[ |K\rangle \]
\[ |K'\rangle \]

Spin components

Symmetr. WF.

Antisymmetr. WF.

Term scheme

S\(_1\) Singlets
s=0

T\(_1\) Triplets
s=1

\[ 0E_\mu^\pm \]

\[ \omega A_0^- \]

Dipole allowed

\[ \omega B_0^- \]

Spectroscopic assessment

Absorption and photoluminescence

Photoluminescence excitation spectrum, poly-disperse CNT material

\[ S_0 \rightarrow S_1 \rightarrow S_2 \]

Excitation wavelength / nm

Emission wavelength / nm

\[ (n-m)\text{mod}(3)=-1 \quad \text{and} \quad (n-m)\text{mod}(3)=+1 \]
Absorption spectroscopy: samples 1999-2007

1999  Laseroven material: $\bar{\varnothing} \approx 1.4$ nm
1999  Laseroven material: $\bar{\varnothing} \approx 1.2$ nm
2000  CVD material (HIPCO): $\bar{\varnothing} \approx 1.0$ nm
2002  HIPCO colloidal
2003  CVD material (CoMoCAT) colloidal:
       $\bar{\varnothing} \approx 0.8$ nm
2005  CoMoCAT material: isopycnic fractionation.
2006  Fractionation of metallic tubes
       (isopycnic)

Energetic landscape

Known to some degree

- Energetics of singlet manifold

Unresolved

- Decay of excited states?
- Coupling to vibrations?
- Exciton size?
- Branching ratios?
- Energetics of triplet manifold?
- ...
Sample preparation
Colloidal Nanotube suspensions

CNT soot

SWNT-rope

SWNT micelles

\[ \eta \approx 10^{-4} - 10^{-3} \]

Mixture


soap & water

energy (ultrasound)

supernatant

sedimentation 100,000g, 4h
Density gradient ultracentrifugation (DGU)

- Additives generating density gradients
  - CsCl: 1.0-1.9 g/cm³
  - Sucrose: 1.0-1.35 g/cm³
  - Iodixanol: 1.0-1.6 g/cm³
  - ...

- Ultracentrifugation at high accelerations
  - 100,000g - 200,000g

- Fractionation by buoyancy (isopycnic fractionation)
The supernatant is polydisperse

- Starting material contains in excess of 70 wt.% of small aggregates.
- Single tube fractions have η > 1%.

Crochet, Clemens, Hertel, JACS 129, p8058 (2007)
The supernatant is polydisperse

Comocat & Na-cholate in iodixanol gradient

- Starting material contains in excess of 70 wt.% of small aggregates.
- Single tube fractions have $\eta > 1\%$.

Crochet, Clemens, Hertel, JACS 129, p8058 (2007)
Cosurfactants introduce new flavor

- **Zero order energetics: amphiphilics in water with nanotube soot**
  - Minimization of hydrophobic interactions (CNT-H₂O)
  - Non-specific to tube metallicity or band-gap

- **Second order effects**
  - Optimization of van der Waals interactions
  - Hamaker constants can be shown to depend on polarizabilities (Lifshitz theory)

\[
F(D) = -\frac{A(\epsilon_{\text{CNT}}, \epsilon_S, \epsilon_{\text{water}}) R}{12D^2}
\]

- Selectivity towards band-gap and metallicity

SC + SDS + SWNT
Better samples through cosurfactant DGU

Better diameter selectivity
(4:1 mixture of SC:SDS, 2 wt%)

Separation of metallic and semiconducting SWTNs

sample by M. Arnold & M. Hersam
Kinetics and dynamics
Kinetics and dynamics: relevance

Selected applications
- Light emitting devices
- Fluorescent tags
- Saturable absorbers
- Photosensors

Role of excited state dynamics
- determines efficiency (electroluminescence)
- determines quantum yields (photoluminescence)
- power, rep. rate, etc (modelocked ultrafast lasers)

Questions
- rate constants for different relaxation channels
- branching ratios
- ...
Kinetics and dynamics: overview

Processes of interest

- Internal conversion (IC)
- Intersystem crossing (ICS)
- Trapping
- Branching
- Radiative decay
- Non-radiative decay
- Ground state recovery
- ....
Radiative and non-radiative decay

\[ \eta = \frac{\tau_{PL}}{\tau_{rad}} \]

PL quantum yields

Photon counting

\[ \eta = \frac{N_{PL}}{N_{abs}} \]

Kinetics

\[ \eta = \frac{k_{rad}}{k_{rad} + k_{nr}} \]

Lifetimes
Non-radiative decay $k_{nr}$ is efficient

$$\eta = \frac{k_{rad}}{k_{rad} + k_{nr}} \approx 3\%$$

$k_{nr} \approx 30 \times k_{rad}$

Crochet, Clemens, Hertel, JACS 129, p8058 (2007)
Rajan, Strano, Heller, Hertel, Schulten, JPCB (in press)
Radiative decay $\tau_{PL}$ is on the order of ps

\[
\eta = \frac{\tau_{PL}}{\tau_{rad}}
\]

\[k_{PL} \approx (30\text{ps})^{-1}\]

Inhomogeneities affect non-radiative decay

Time-correlated single photon counting of (6,4) tubes.

$$k_{nr}(\text{tube 1}) \neq k_{nr}(\text{tube 2}) \neq k_{nr}(\text{tube 3})$$

What kind of inhomogeneities? Defects, Bundles? ...

Hagen et al.,
PRL 95, 197401 (2005)
Long tubes shine brighter

Electrophoretic length fractionation

Rajan, Strano, Heller, Hertel, Schulten, JPCB (in press)

Non-radiative decay at tube ends!
Diffusion is crucial!

Is diffusion one-dimensional?
Determining the exciton size

Phase space filling model
Schmitt-Rink, Chelma, Miller, PRB 32, 6601 (1985)

\[ f_e(k) = f_h(k) = \frac{\Delta \tilde{n}}{2} |\Psi_x(k)|^2 \]

\[ \Delta x \Delta k \approx \frac{\hbar}{2} \]

delocalized exciton saturates easily
localized exciton saturates later

single particle energy

\[ f_e(k) : 0 \to 1 \]

\[ f_h(k) : 1 \to 0 \]
Exciton size is about $5 \times$ the tube diameter

- Nonlinear-response $\Delta T/T = -\Delta \tilde{n}/\tilde{n}_s$  
  $\tilde{n}_s$ - Saturation density
  $\Delta \tilde{n}$ - Electron-hole density

(6,5) tube

$\Phi^+ A^- \left( r_e, r_h \right)$

Hole-position

$\sim 3 \text{ nm}$

Lüer, Hoseinkhani, Crochet, Hertel, Lanzani, (submitted)
Radiative and non-radiative decay

Now, do we know the radiative lifetime?

\[ \eta = \frac{N_{PL}}{N_{abs}} + \eta = \frac{\tau_{PL}}{\tau_{rad}} \implies k_{rad} = \frac{1}{\tau_{rad}} \]

\[ k_{nr} \approx (30 \text{ ps})^{-1} \]

Ground state
Now, do we know the radiative lifetime? 

No!

\[ k_{nr} \approx (30 \text{ ps})^{-1} \]
The $S_2$ resonance is short lived

Hertel, Crochet, Perebeinos, Arnold, Kappes and Avouris, (Nano Lett. 8, 87 (2008))
No $S_2$ decay into the $e_1$-$h_1$ continuum

Perturbation theory

$$W_{22} \propto |\langle \psi_{22} | V | \psi_{e-h} \rangle|^2 \rho_{e-h}(E_{22})$$

Rate should scale with DOS in final state

Hertel, Crochet, Perebeinos, Arnold, Kappes and Avouris, (Nano Lett. 8, 87 (2008))
Phonons scatter $S_2$ into higher $S_1$ states

Using Su-Schrieffer-Heeger model with matrix element:

$$t = t_0 - g \delta R_{C-C}$$

$$g = 5.3 \text{ eV} / A$$

→ phonon coupling to dark $S_1$ exciton via zone-boundary optical phonon.

Su et al., PRL 42 (1980) 1698.

Hertel, Crochet, Perebeinos, Arnold, Kappes and Avouris, (Nano Lett. 8, 87 (2008))
**S_2** relaxation summary

Hertel, Crochet, Perebeinos, Arnold, Kappes and Avouris, (Nano Lett. 8, 87 (2008))
so far

\[ k_{IC} \approx (10 \text{ fs})^{-1} \]

\[ k_{nr} \approx (30 \text{ ps})^{-1} \]

\[ k_{rad} \approx (1 \text{ ns})^{-1} \]
Pump-probe spectroscopy: (6,5) DGU material

Extinction coefficient:
\[ \Delta \alpha_{S_0 \rightarrow S_1} \propto \Delta \rho_{S_0} - \Delta \rho_{S_1} \]

\( \alpha \) first decreases (photobleach, PB)
then \( \alpha \) recovers because of decay of the \( S_1 \) state

Pump-probe spectroscopy: (6,5) DGU material

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\( \alpha \) first decreases (photobleach, PB)
then \( \alpha \) recovers because of decay of the \( S_1 \) state

Ground state recovery is diffusion limited

Optical transients

Survival probability scales like power law in time

\[ [A] \propto t^{-\gamma} \]

Zhu, Crochet, Resasco, Arnold, Hersam, and Hertel,

Exciton wavefunctions

Exciton diffusion should be 1-dimensional.
### diffusion limited reactions in 1D

Educt-survival probabilities scale with time:

\[ [A] \propto t^{-\gamma} \]

<table>
<thead>
<tr>
<th>Reaction type</th>
<th>Exponent</th>
<th>Exponent</th>
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<tbody>
<tr>
<td>Bimolecular reaction</td>
<td>$A + A \rightarrow B$</td>
<td>$\frac{1}{4}$</td>
</tr>
<tr>
<td>Particle-antiparticle annihilation</td>
<td>$A + \bar{A} \rightarrow B$</td>
<td>$\frac{1}{2}$</td>
</tr>
<tr>
<td>Trapping by defects</td>
<td>$A + D \rightarrow D^*$</td>
<td>$1$</td>
</tr>
</tbody>
</table>

Experiment: 0.45±0.03

Overview

\[ k_{IC} \approx (10 \text{ fs})^{-1} \]

\[ k_{nr} \approx (30 \text{ ps})^{-1} \]

\[ k_{rad} \approx (1 \text{ ns})^{-1} \]

\[ [A] \propto t^{-1/2} \]

possibly triplet-triplet annihilation
Outlook
Imaging with Si-detectors

- DGU purification of (6,5) suspension
  - PL QY ~ 1%
  - Emission at 980 nm

PL image (right) of SWNT suspension recorded with Si hole accumulation diode (HAD) CCD array.

Si hole accumulation diode (HAD) CCD sensitivity
Soft functionalization

Replacement of surfactants with single stranded DNA by dialysis

Na-cholate
Nucleotide sequence

thermal stability of DNA-CNT hybrids ~ oligomer length
Re-Aggregation
Engineering of crystallites

- Lateral exciton delocalization
- Metallic impurities
- Semiconducting impurities
Funding

- NSF
- American Chemical Society
- Max-Kade Foundation
- VINSE

THANKS
Thanks

Current and recent

- F. Bonnacorso (summer student) DGU, aggregates
- M. Clemens (graduate student) TCSPC
- D. Stich (graduate student) nonlinear dynamics
- J. Crochet (graduate student) nonlinear-optics
- K. Müller (summer student) DGU
- S. Novikov (summer student) DGU, solvatochromism
- J. Thompson (graduate student) outreach
- Z. Zhu (graduate student) nonlinear-optics

Collaborations

- University of Oklahoma Resasco
- Northwestern University Arnold, Hersam
- Polytechnical Univ. de Milano Lanzani, Lüer
- Technische Universität München Hartschuh
- Universität Karlsruhe Kappes, Richert
- MIT Strano, Heller
- IBM Yorktown Heights Avouris, Perebeinos

Interested to join?

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