Strain dependence of photoluminescense of individual carbon nanotubes.

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We have investigated strain dependence of photoluminescense (PL) spectra of single wall carbon nanotubes (SWNT). Nanotubes were sparsely dispersed in a thin PMMA film applied to acrylic bar, and strained in both compression and extension by bending this bar in either direction in a homebuilt four-point bending rig. The average surface strain was measured with high accuracy by a resistive strain gage applied on top of the film. The near – infrared imaging and spectroscopy were performed on the inverted microscope equipped with high numerical aperture reflective objective lens and InGaAs CCD cameras. PL was excited with a diode laser at either 658, 730 or 785 nm, linearly polarized in the direction of the strain. We were able to measure (n,m) types and orientation of individual nanotubes with respect to strain direction and strain dependence of their PL maxima. It was found that PL peak shifts with respect to the values measured in SDS micelles are a sum of three components. First, a small environmental shift due to difference in the dielectric constant of the surrounding media, that is constant and independent of the nanotube type. Second, shift due to isotropic compression of the film during drying. Third, shifts produced by the uniaxial loading of the film in the experiment. Second and third shifts follow expression based on the first-order expansion of the TB hamiltonian. Their magnitude is proportional to the nanotube chiral angle and strain, and direction is determined by the nanotube quantum number. PL strain dependence measured for a number of various nanotube types allows to estimate TB carbon-carbon transfer integral.

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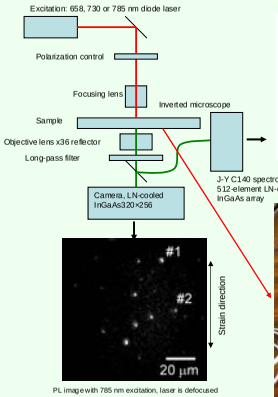
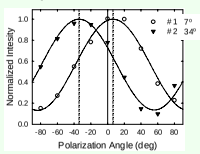
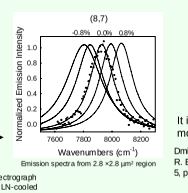
PL observations on individual nanotubes.



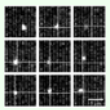
PL image with 785 nm excitation, laser is defocused





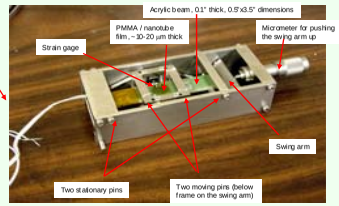
Emission spectra from 2.8 ×2.8 μm² region

J-Y C140 spectrograph
512-element LN-cooled InGaAs array



It is possible to observe Brownian motion of SWNT floating in liquid

Dmitri A. Tsyboulski, Sergei M. Bachilo, and R. Bruce Weisman, NanoLetters Vol. 5, No. 5, pp 975-979 (2005)



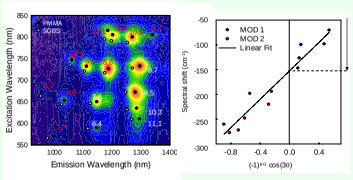
Four-point bending rig. Sample: SWNT dispersed in PMMA / Xylene and spin-coated onto ¼" acrylic beam, ~10 μm thick film. Bending in either direction produces uniaxial uniform strain in the PMMA film that is transferred to nanotubes. Strain σ is measured by resistive type strain gage attached to the film with high accuracy.

$\sigma_{NT} = \sigma \cos(\alpha)$, where α is the angle between strain and nanotube axis. For each nanotube, α was determined from the PL intensity dependence on the polarization angle.

Origin of the initial PL shifts

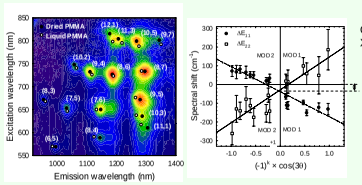
$$\Delta E_{gap} = \mathrm{sgn}(2p+1)3t_0\left[(1+\nu)\sigma\cos 3\theta + \gamma \sin 3\theta\right]$$

1. Environmental shift, ~155 cm^{-1}, uniform across SWNT types, related to change in the dielectric constant of the surrounding media SBDS/H_2O vs. PMMA vs. PMMA solution in Xylene
2. Shift related to the drying of the PMMA / Xylene film. Drying produces slight isotropic compressive strain in PMMA, and PL shifts are approximately proportional to cos(3θ) and have opposite signs for mod3=1 and mod3=2 SWNT



PL maps of NT dispersions in H_2O/SDBS and dry PMMA

Environmental shift, ~155 cm^{-1}.



Comparison of PL maps of NT dispersions in PMMA / Xylene solution and dry PMMA

Environmental shift, ~55 cm^{-1}.

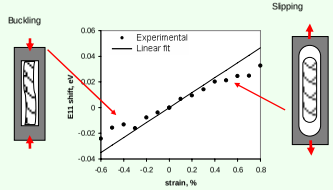
E_{11} and E_{22} shift in the opposite directions

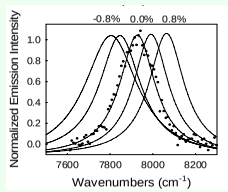
Measurements on the SWNT ensemble, using commercial J-Y Spex Fluorolog 3-211 spectrofluorometer with LN-cooled InGaAs detector, similar to S. Bachilo et. al., *Science* 298, p.2361 (2002)

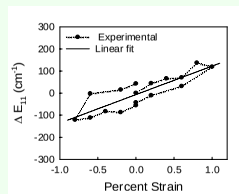
Measurements

Measurements for (8,4) SWNT
Slope is 320 ± 24 cm^{-1}/%
Buckling release of strain in compression at ~-0.3%

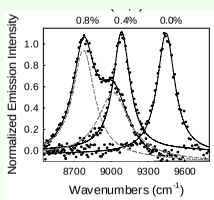
Slipping release of strain in extension at ~0.4%

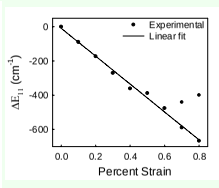


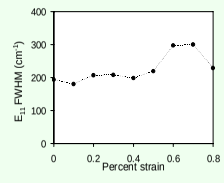




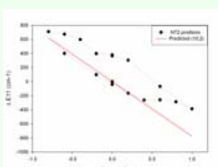
Measurements for the (8,7) SWNT. Slope is 129 ± 20 cm^{-1}/%
Hysterisis indicates some slipping of SWNT in PMMA



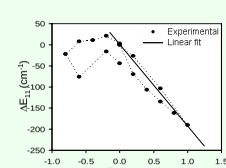


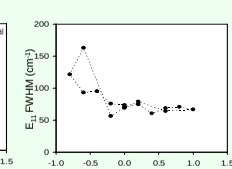


Measurements for (10,2) SWNT. Slope is -792 ± 28 cm^{-1}/%
At ~0.6 extension part of the nanotube starts slipping, and PL peak splits.
Increase in the linewidth also indicates that only part of it is slipping.



Measurements for the second (10,2) SWNT.
Slope is -808 ± 25 cm^{-1}/%
At ~0.4% extension nanotube starts slipping





Measurements for (8,6) SWNT. Slope is -190 ± 25 cm^{-1}/%
Anomalous behavior in compression

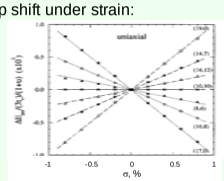
Theoretical prediction of the bandgap shift under strain:

Liu Yang and Jie Han, *PhysRevLett* 85, pp 154-157 (2000)

1st order expansion of TB Hamiltonian:

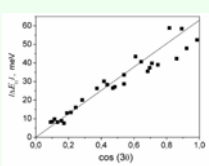
$$\Delta E_{gap} = \mathrm{sgn}(2p+1)3t_0\left[(1+\nu)\sigma\cos 3\theta + \gamma \sin 3\theta\right]$$

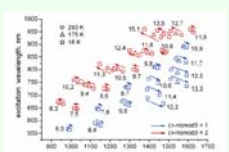
(2p+1)=1 for mod 3 = 1 (mod((n-m)/3)=1)
(2p+1)=-1 for mod 3 = 2 (mod((n-m)/3)=2)
t_0 – carbon-carbon transfer integral in TB theory, 2.55 eV (2.5 – 3.0 eV)
ν- Poisson ratio, ~0.15, θ - chiral angle
σ - axial strain, γ - torsional strain.



Earlier measurements: Strain induced by mismatch of the thermal expansion coefficients of SWNT and surrounding ice. PL shifts vs. temperature measured on the SWNT ensemble in frozen D_2O/SBDS/PVP

K Arnold, S Lebedkin, O Kiowski, F Hennrich, and M Kappes, *NanoLetters*, 4, 12, pp 2349-2354 (2004)



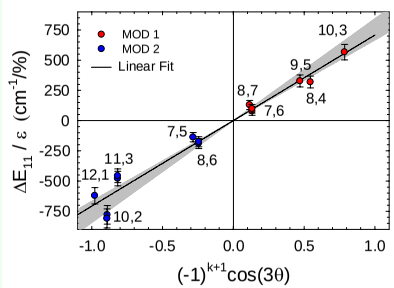


PL shifts upon cooling from 293K to 16K
σ was estimated ~-0.5%

Determining C-C transfer integral t_0 from experiment

$$\Delta E_{gap} = \mathrm{sgn}(2p+1)3t_0\left[(1+\nu)\sigma\cos 3\theta + \gamma \sin 3\theta\right]$$

$$\frac{|\Delta E_{gap}|}{|\sigma|} = 3t_0(1+\nu)\cos 3\theta$$



Slopes of experimental strain data for all SWNT

Predicted from the literature values:
t_0 = 2.66 eV, ν=0.15

Best fit with ν =0.15:
t_0 = 2.40 ± 0.23 eV.