CHIRALITY ASSIGNMENT: BAND GAP MODIFICATION OF SINGLE-WALLED CARBON NANOTUBES WITH STRAIN

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Single-walled carbon nanotubes (SWCNTs) offer a range of potential applications based on their unique one-dimensional structures. Theoretical calculations shows that their electronic structures depend strongly on their chiral vector indices (n,m) which determine the diameter and chiral angle. The graphite wrapping condition n-m=3p+q generates metallic tubes for q=0, while semiconducting tubes are found for q=$\pm$1 [1].

The recent development of methods to disperse nanotubes by surfactant wrapping has led to the observation of band gap luminescence providing a route to study the optical properties of spectrally resolved single nanotube species [2]. As a result there is a growing body of evidence to suggest that it is possible to assign a specific set of chiral indices to describe the properties of particular nanotubes. Modifications of the bandgap by mechanical deformation also offer a potential new route to characterize the tubes spectroscopically. It has been suggested theoretically [3] that the sign of strain-induced bandgap shift depends on their quantum number q and the magnitude varies strongly with different chiral angles. We demonstrate that it is possible to use strains produced by solution freezing or polymer swelling to deduce tube quantum number q. We also propose that this technique might be used to achieve bandgap engineering. This study also provides the first and direct proof for the theoretical formula of band gap shifts versus chiral angles proposed by Yang [3].

The effect of temperature on the band gap luminescence for polyvinylpyrrolidone(PVP)-wrapped SWCNTs excited with 633, 670 and 810nm radiation was studied. Variation of the excitation wavelength allows selective excitation of specific nanotubes by direct excitation into the E_{22} van Hove singularity(Fig.1). The temperature dependence of luminescence excited at 670nm is shown in Fig. 2. The change in temperature leads to a strain being induced in the nanotubes due to the difference in thermal expansion coefficients between the D_2O ice and nanotubes. All luminescence peaks fall into two classes, with bandgap energies shifting either up or down in response to strain, depending upon whether the value of q is $\pm$1. This allows us to assign the q values and also offers a possibility to correlate the E_{11} PL peaks to a specific (n,m) set.

A separate study of the strain effect on luminescence of PVP-wrapped SWCNTs was performed by drying the nanotube dispersion and using the change in hydration levels to apply the strain. With the increasing drying time the luminescence shows a similar evolution to that seen on cooling as shown in Fig.1. It is also concluded that the total shift from dry to wet which shows that the signs of the bandgap shift are identical for all peaks, and the total magnitude of the shifts are quite similar in two cases.

According to Yang's theory [3], the bandgap change of SWCNTs under small strain was derived as $\Delta E_g = \mathrm{sgn}(2q+1)\, 3\, t_0\, [(1+\nu)\, \sigma \cos 3\theta + \gamma \sin 3\theta\,]$ t_0 and ν denote the carbon-carbon transfer integral and the Poisson's ratio, and θ is the tube chiral angle. σ and γ are strains along tube axis and circumference, corresponding to uniaxial and torsional strains on nanotubes. $\sigma > 0$ means tubes are under uniaxial tension and $\sigma < 0$ for compression. Fig. 3 shows a compilation of both heating and swelling induced bandgap shifting versus chiral angles according to Weisman's chirality assignments [4]. The data were fitted after allowing for a small overall (constant) shift in the line positions of a few meV to take account of the effects of temperature or hydration state. With the assumption of $t_0 = 2.66$ eV and $\nu = 0.2$, a $0.253\pm0.022\%$ of uniaxial tension and a $0.091\pm0.018\%$ of torsional bond stretching are suggested for heating while a $0.204\pm0.018\%$ uniaxial and a $0.088\pm0.019\%$ torsional bond stretching are obtained for swelling.

References:

[1] R. Saito et al., in Physical Properties of Carbon Nanotubes (Imperial College Press, London, 1999), chap. 5.

[2] O'Connell et al., Science **297**, (2002) 593.

[3] L. Yang, J. Han, Phys. Rev. Lett. **85**, (2000) 154.

[4] S. M. Bachilo et al., Science **298**, (2002) 2361.

Figures:

Fig. 1

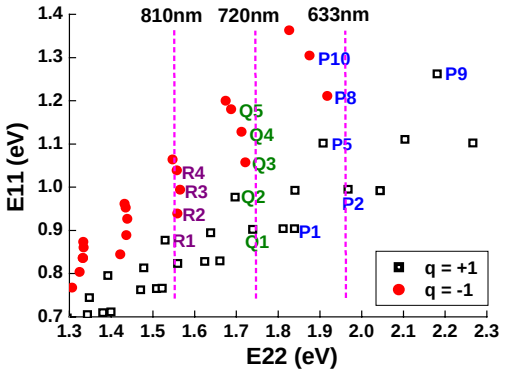

Fig. 2

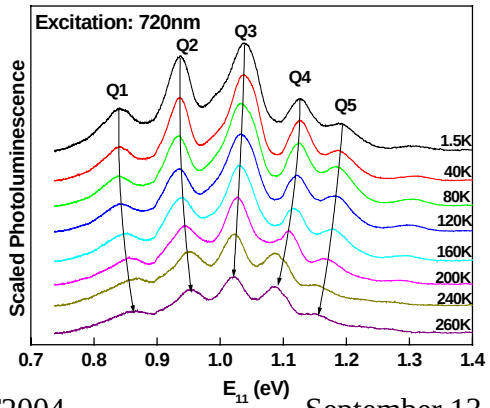

Fig. 3