2.57 Nano-to-Macro Transport Processes

Fall 2004 - Lecture 15

Guest lecture by Prof. Dresselhaus

1. Outline
-Overview
-Synthesis
-Structures and Symmetry
-Electronic Properties
-Transport Properties
-Phonon Properties
-Resonant Raman Effect
-Applications

2. Unique Structure and Properties of Single Wall Carbon Nanotubes (SWNTs)
A SWNT can be viewed as a cylinder formed by rolling up a graphene sheet.

Image removed for copyright reasons.

A SWNT is an ideal model of 1D systems for nanoscience. It has the following interesting characteristics:

(1) Size
SWNTs are nanostructures with dimensions of ~1 nm diameter (~20 atoms around the cylinder). The smallest SWNT has a diameter of only 0.4 nm.

(2) Electronic Properties
They can be either metallic or semiconducting depending on the diameter or orientation of the hexagons.

(3) Mechanical
SWNTs have very high strength, Young's modulus, and good properties on compression and extension.

SWCNs can be used to make heat pipes and electromagnetic antennas. Its structure can be determined by single nanotube (as one molecule) spectroscopy. Due to the unique properties, currently many applications are being attempted worldwide for CNs.

3. Synthesis
Three methods are utilized to grow CNs:
(1) Arc Discharge
In the following figure, two graphite rods (5-20 mm in diameter) are used as the cathode and anode, between which arcing occurs when 50-120A DC is supplied. By electron collision into the anodic rod, carbon clusters from the anodic graphite rod are condensed on the surface of the cathodic graphite rod and carbon nanotubes are formed along with other products.

Image removed for copyright reasons.

Y. Saito *et al, Phys. Rev*. 48 1907 (1993)

(2) Laser Ablation
The experimental setup is shown as following, where Nd-Yb-Al-garmet Laser is utilized at 1200 ℃.

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A. Thess *et al. Science* 273 483 (1996)

(3) Chemical Vapor Deposition (CVD) method

For the laser ablation method, we always get many twisted "wires", which are bundles of SWCNs and thus difficult to use. Isolated single wall carbon nanotubes can be by grown by the Chemical Vapor Deposition (CVD) method. By depositing catalyst on the specified positions, we can control the location of grown CNs. This brings tremendous convenience to the research. Some work has also been conducted to control the average diameter and diameter distribution by changing the catalysts and furnace temperature (H. Kataura et al., 2000).

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N. Wang *et al. Nature* 408, 50 (2000)

The above figure shows the smallest SWNT with a diameter 0.42 nm. It is a (5,0) zigzag nanotube and has metallic electronic structure. Under 15 K it becomes a superconductor.

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Peapod Empty SWNT

H. Kataura et al, unpublished (2001)

A new material, fullerene-peapods can also be made based on SWCNs. Baking fullerenes with CNs in a quartz ampoule at 650 ºC for 2 ~ 6 h, the fullerenes can fit into CNs and form this new structure. From the above figure, we can see its electronic structure is similar to empty SWNTs especially near the Fermi level. By Heating at higher termperatures, C_{60} fullerenes inside the nanotubes can merge and form double wall carbon nanotubes (DWNTs).

4. Structures and Symmetry

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Chiral Vectors : *(n,m)*
R. Saito *et al., Phys. Rev*. **B46**, 1804 (1992)

$$C_h = na_1 + ma_2 \equiv (n,m)$$

a_1, a_2 : primitive lattice vectors

$$T = t_1 a_1 + t_2 a_2 \equiv (t_1, t_2)$$

$$t_1 = \frac{(2m+n)}{d_R},\ t_2 = -\frac{(2n+m)}{d_R}$$

$$d_R = \gcd(2n+m, 2m+n)$$

$$d_t = \frac{L}{\pi} = \frac{a\sqrt{n^2+nm+m^2}}{\pi}$$

$$L = |C_h|$$

Although there can be other ways to define the primitive lattice vectors in a hexagon sheet, the method presented in the above figure is widely used in all current publications. The chiral vector (equator of nanotube) is the vector OA or C_h in the figure; the translational vector of 1D material is vector OB and marked as T. Here C_h denotes the perimeter of the SWCN, while the translational vector is along the axis direction of the rolled up SWCNs. For one Unit Cell OAB'B, C_h and T are always expressed with the lattice vectors a_1 and a_2. Three special CN structures are defined as

• Symmorphic (mirror symmetry)
–Armchair Nanotube (n,n), n=m
–Zigzag Nanotube (n,0), m=0
• Non-Symmorphic (axial chirality)
–Chiral Nanotube (n,m), n≠m

In the above figure, the chiral angle θ ($0 < \theta < \pi/6$) is defined as the included angle between C_h and a_1. The diameter d_t of SWNTs can be calculated from the length of C_h.

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P. Kim et al., PRL 82, (1999) 1225.

J. W. G. Wildoer et al,
Nature, 391 (1998) 59

Using a STM, the structure of a SWNT can be observed. In the right above figure, we can barely see the hexagons. SWNTs can be metallic or semiconductive. The transition happens when the conduction band and valence band touch each other at six K points in the k space. The energy contours are also drawn in the left above figure.

5. Electronic Properties

A unit cell and the corresponding Brillouin zone are drawn in the following two figures. The point K is at the corner of the hexagon, while M is the edge midpoint.

Image removed for copyright reasons.

P. R. Wallace, *Phys. Rev*, **71** 622 (1947).

Image removed for copyright reasons.

R. Saito *et al., Phys. Rev*. **B46**, 1804 (1992)

In the above three cases, an energy gap appears in a (10,0) SWNT, indicating semiconductor. The density of states depends on the chirality of the SWNT. The general law to judge the electronic property (metallic, semiconductive) is summarized in the embedded equation of the following figure.

Image removed for copyright reasons.

$$n - m = \begin{cases} 3p & \text{metal} \\ 3p \pm 1 & \text{semiconductor} \end{cases}$$

R. Saito *et al., Appl. Phys. Lett.* **60**, 2204 (1992)

The width of DOS split depends on the chirality of the SWNT. In the following figures, we find the Zigzag SWNT exhibits splitting DOS compared with an Armchair SWNT.

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(a) Metal (b) Semiconductor

R. Saito *et al, Phys. Rev.* **B61**, 2981(2000)

The wave vector k for one-dimensional carbon nanotubes is shown in the two-dimensional Brillouin zone of graphite hexagon. In the direction of K_1, discrete k values are obtained by periodic boundary conditions for the circumferential direction of the carbon nanotubes, while in the direction of the K_2 vector, continuous k vectors are shown in the one-dimensional Brillouin zone. For metallic nanotubes, the bold line intersects a

K point (corner of the hexagon) at the Fermi energy of graphite. For the semiconductor nanotubes, the K point always appears one third of the distance between two bold lines and no DOS splitting occurs for any chirality.

6. Transport Properties

When two SWNTs with different atom numbers on the circumference meets, a pair of pentagon and heptagon will form at the junction and thus makes smooth transition between different geometries. Junctions such as a diode are measured in experiments.

Image removed for copyright reasons.

S. Iijima, NEC Symp.(1992) (a) Metal-metal (b) Metal-semiconductor

The following figures are the first electrical measurement of carbon nanotube, where the gate voltage is used to change the electronic structure of a SWNT.

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S.J. Tans *et al. Nature*, 393, 49 (1998)

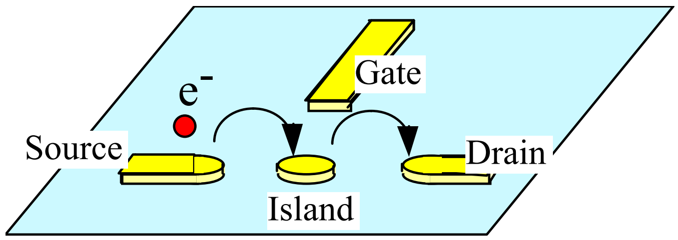
Resonant tunneling transport is demonstrated in the left bottom figure. The energy levels in a SWNT can be compared with a particle in a box. By changing the applied gate voltage, the energy level can be shifted and tunneling will happen at discrete levels. In addition, quantized conductance is also observed in this experiment, which is a multiple of

$$G_0 = \frac{2e^2}{h} = (12.9\,\mathrm{k}\Omega)^{-1}$$

Image removed for copyright reasons.

W. Liang Harvard Univ.

Ballistic transport of electrons in a metallic carbon nanotube is also measured. For metallic SWNTs, the Fermi level just across the intersection point of two bands.



The above figure demonstrates the idea of CNT single electron transistor by AFM nicking. The nanotube is broken at two locations and electrons will transfer from source to drain under specified applied tip voltage.

7. Phonons and Raman Spectroscopy

The Raman Spectroscopy is the major characterization method for SWNTs. It is non-destructive, contactless measurement and can be conducted in air at ambient pressure. Additionally it is quick (1 min) and accurate in energy.

The Raman Spectroscopy measures the wavelength and intensity of inelastically scattered light from molecules. When light is scattered, a small fraction of light is scattered at optical frequencies different from, and usually lower than, the frequency of the incident photons. This inelastic scattering can occur with a change in vibrational, rotational or electronic energy of a molecule. Since Resonant Raman Effect is diameter selective (also chirality dependent), it is used to determine the size of SWNTs.

Image removed for copyright reasons.

"Physical Properties of Carbon Nanotubes" R. Saito, G. Dresselhaus, and M.S. Dresselhaus, Imperial College Press, (1998)

$$N = \frac{2(m^2 + n^2 + nm)}{d_R}$$

$$d_R = \begin{cases} 3d & \text{if } n - m = 3d \cdot p \\ d & \text{otherwise} \end{cases}$$

$2N$ carbon atoms
$6N$ phonon modes (three directions of vibrations)

Image removed for copyright reasons.

Phonon modes -- (10,10) Armchair
R.Saito *et al*. *Phys. Rev.* **B57** (1998) 4145

In the following figures, the result for SWNTs is presented.

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A.M. Rao et al, Science **275** (1997) 187

In the following figures, the PL absorption and emission spectra in S-SWNTs provides $E11^{S}$, $E22^{S}$, and additional information about the SWNT electronic structure. Compared to resonance Raman Spectroscopy, PL is a complementary technique to characterize a large number of semiconducting SWNTs in solution.

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M. O'Connell et. al. Science **297** 593 (2002)

8. Challenges for Carbon Nanotube Synthesis and Separation
It is important to control synthesis process to produce tubes with the same diameter and chirality (n,m). Before the control of synthesis process is achieved, we need to develop effective separation methods to separate metallic SWNTs from semiconducting ones by

diameter and chirality. For applications, it is significant to develop method for large-scale, cheap synthesis, and improve nanotube characterization and manipulation.

Separation processes reported till now include:
(1) Precipitation of SWNTs non-covalently functionalized with ODA
(2) Ion-exchange liquid chromatography of ssDNA wrapped SWNTs
(3) Alternating current dielectrophoresis in an aqueous SWNT suspension
(4) Selective functionalization with diazonium salts
(5) Centrifugation after addition of diluted bromine

It should be noted that many of these processes separate SWNTs by diameter in addition to metallicity.

9. Applications
The wide applications of SWNTs include:
(1) STM/AFM tips (advanteous in scanning sharp-trench topography)
(2) Direct Analysis of DNA
(3) Semiconductor devices
(4) Field Emitters
(5) Filler for enhancing lifetime in Li ion batteries (to eliminate the electrode gap change in the charging and recharging processes)
(6) Filler for enhancing conductivity of polymer composites
(7) Ultimate strong fiber (space elevator made of SWNTs)
(8) Hydrogen Storage for fuel cells (as in the following figure)