Electron and phonon in carbon nanostructures: a local study with scanning tunneling spectroscopy

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Spectroscopy on atomic scale

Scanning Tunneling Spectroscopy:
- Co and H-Co on Cu(111)
- TbPc2 on Cu(111)

Inelastic electron tunneling spectroscopy:

Point contact spectroscopy:

Self-assembling, lithography, transport, …
Carbon allotropes

3D
- diamond (3D)

1D
- single-walled carbon nanotube (1D)

2D
- graphene

0D
- C_{60} (0D)

1985

2004
Novel fascinations on Carbon

Fullerenes
Metallic, superconducting, isolating transition (doping level), Endohedral fullerenes (Metal or N): Magnetism and superconductivity

CNT
Electronic, mechanical and electrical new properties: Quasi 1D (model system for physicists!), metallic or semiconductor, supports large current flux, high carrier mobility, electron field emitters, CNT-FET, Single electron transistors
high young modulus, high tensile strength, gas sensors, gas storage, …,

Graphene
2D conductor, linear electron band, electron velocity independent on energy, high carrier mobility, QHE at RT, gas sensor, …,
Semiconducting SWCNTs as components of FETs


Donor-acceptor hybrids: natural photosynthesis

Integrated Logic Circuit Assembled on a Single Carbon Nanotube

Z. Chen et al., Science 5768, 1735 (2006)

NT-based Ultra-capacitors

UES:
- High Efficiency
- Ultra-capacitors
- Biological and Chemical Sensors
- Fuel Cells
Scanning Tunneling Microscopy & Spectroscopy

\[ \frac{dI}{dV} \sim \rho_{el} \]
Structure of single-wall carbon nanotubes (SWCNTs)

roll-up vector:

\[ \mathbf{C}_h = n\mathbf{a}_1 + m\mathbf{a}_2 \equiv (n,m) \]

metallic if \((n-m) = 3q\)  \(q:\text{integer}\)

semiconducting if \((n-m) \neq 3q\)
\[ \omega(k) = 2 \sqrt{\frac{K}{M}} \sin \frac{1}{2}ka \]

- Impurity atom
- Strain, different bond strength
Spatial resolution


Raman Spectroscopy


Confocal Raman Spectroscopy

A.Hartschuh et al. PRL.90.095503.2003

Near-Field Raman Spectroscopy

10 Å

Near Field Raman Spectroscopy

Confocal Raman Spectroscopy

Raman Spectroscopy

Near Field Raman Spectroscopy

Inelastic Electron Tunneling Spectroscopy

nm

1

10

100

1000

10 Å

10 Å

10 Å

10 Å
Spectroscopy technique: Local probe of lattice dynamics (vDOS)

Inelastic Electron Tunneling Spectroscopy

- Carbon nanotubes (SWCNT)
- Graphite (HOPG)
Electron Tunneling Spectroscopy

Elastic tunneling

\[ \frac{dI}{dV} \sim \rho_{el} + \rho_{in} \]

Inelastic tunneling
Recipe:
Disperse SWCNT in Dichlorehane, Sonicate and centrifuge.
Deposit the solution on Au substrates

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From STM images....

....to tube diameter?
Determinations of (n,m)

Metallic tube
\[ \Delta E = 6\gamma_0 a_{C-C}/d \]
\[ \Delta E \approx 1.38\text{V} \]
Diameter \( \approx 15.4\text{Å} \)

(14,8) tube

Energy separation between the first vHs singularities:

\[ \Delta E = 2\gamma_0 a_{C-C}/d \text{ semiconducting} \]
\[ \Delta E = 6\gamma_0 a_{C-C}/d \text{ metallic} \]

\( \gamma_0 = 2.5\ \text{eV} \) tight-binding overlap energy
\( a_{C-C} = 1.42\text{Å} \) lattice constant
Dependence of the radial breathing mode on the SWCNT diameter

\[ \omega_{\text{RBM}} = \frac{C}{d} \]

- \( d_t = 9.02\text{Å} \)
- \( d_t = 10.51\text{Å} \)
- \( d_t = 12.26\text{Å} \)
- \( d_t = 16.47\text{Å} \)
- \( d_t = 18\text{Å} \)
- \( d_t = 19.32\text{Å} \)
- \( d_t = 19.78\text{Å} \)
- \( d_t = 21.45\text{Å} \)
- \( d_t = 21.5\text{Å} \)

\( C = 262\text{meV} \times \text{Å} \)

C~270-290meV*Å

D.Sanchez-Portal et al PRB.59.12678.1999
J.Kurti et al. PRB.58.R8869.1998
Local properties:

Intramolecular-junction

Tube cap

Fig. 2: A few examples of nanotube connections. From left to right: straight connections between two armchair nanotubes, a honeycomb tube formed by joining a zigzag to an armchair nanotube, and a tube connected to two chiral nanotubes. The pentagons and hexagons are indicated by the p and h letters, respectively.

Local probe: Intra-molecular junction or 5/7 pairs
Local probe: Intra-molecular junction or 5/7 pairs
Local probe: Nanotube capping

Cap

Intermolecular junction

„Neck“
Nanotube capping: $d^2I/dV^2$

PRL.93.136103.2004
Theory for RBM  
(powered by C.S.Jayanthi et al)

-finite length:  
A tube can sustain an RBM only if its length exceeds 3.5nm.

-capped region:  
Transforms from radial to tangential character inside the tube.

PRL. 93. 136103. 2004
Crossed Nanotube Junction
pressure induced local metallization

If a (9,2) tube crosses a bundle...

1. DOS

PRL 96, 086804 (2006)
1.1 DOS: Local pressure-induced metallization

\[ d(9,2) = 8.2 \text{Å} \]

bundle \( \sim 15 \text{Å} \)

\[ \text{Tube compressed of } \sim 35\% \text{ at the crossing junction} \]

Pressure at crossing junction = 15GPa

(Assuming Bulk modulus = 35GPa)

PRL 96, 086804 (2006)
1.2 DOS: Image-charges

Contact potential
\[ \Delta = \Delta_{\text{holes}} - \Delta_{\text{image}} \]

\[ \Delta V = \Delta Q / C_{TS} \]

\[ \Delta V = 60 \text{meV} \]
\[ C_{TS} \approx 0.1 \text{aF} \]

\[ \Delta Q = \text{additional 0.025 hole/nm} \]
\[ (= \approx 25\% \text{ total charge transferred}) \]
2. Vibrational density of states

- **G-band**
- **RB-mode**
FIG. 1. Graphite $\pi$-band structure near some relevant points $M$, $\Gamma$, and $K$ in the energy range considered in this work.
The total density of phonons can be detected with STM-IETS.
Phonon assisted tunneling process

-Enhancement of the phonon modes at K
Take home message

- Inelastic Tunneling Spectroscopy as probe of lattice dynamics (vDOS)
  1. HOPG (phonon assisted tunneling process)
  2. SWCNT: RBM + G band

- Map of the vibration frequencies along the tube
  1. vibrational modes vs. tube structural changes (i.e. 5/7 pairs or tube deformations)
  2. charge transfer
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You for your attention!