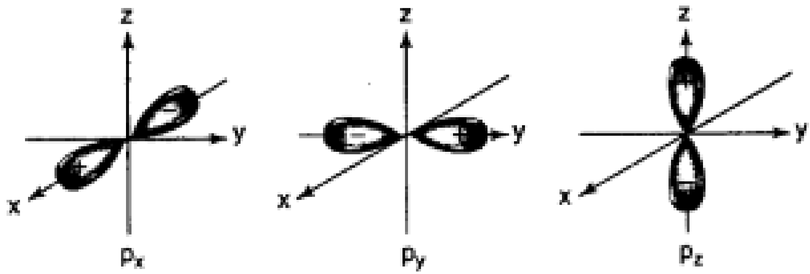
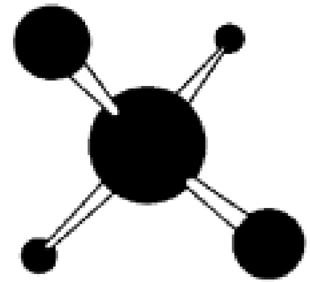
# Introduction to Nanotechnology
# Chapter 5 Carbon Nanostructures
# Lecture 1

ChiiDong Chen
Institute of Physics, Academia Sinica
chiidong@phys.sinica.edu.tw
02 27896766

**Carbon contains 6 electrons: $(1s)^2$, $(2s)$, $(2p_x)$, $(2p_y)$, $(2p_z)$**



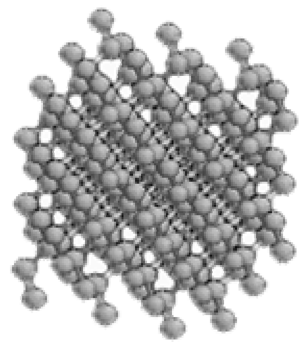

**$p_x$, $p_y$, $p_z$ orbitals of carbon atom**



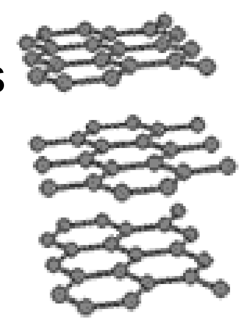
**$sp^3$ hybridization in $CH_4$**

$$\Psi = s + \lambda_x p_x + \lambda_y p_y + \lambda_z p_z$$

Diamond : tetrahedral bond through $sp^3$ hybrid bonds



Graphite sheet: hexagon bond through $sp^2$ hybrid bonds



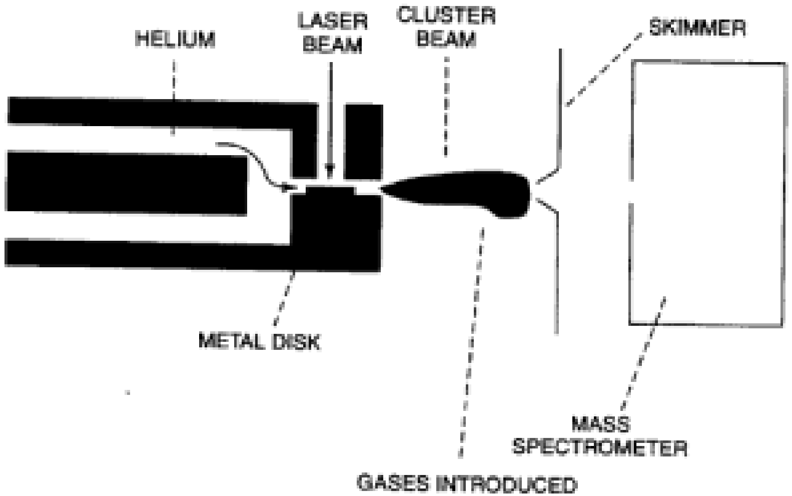



**Fig. 4.2 Apparatus for laser evaporation of nanoparticles**

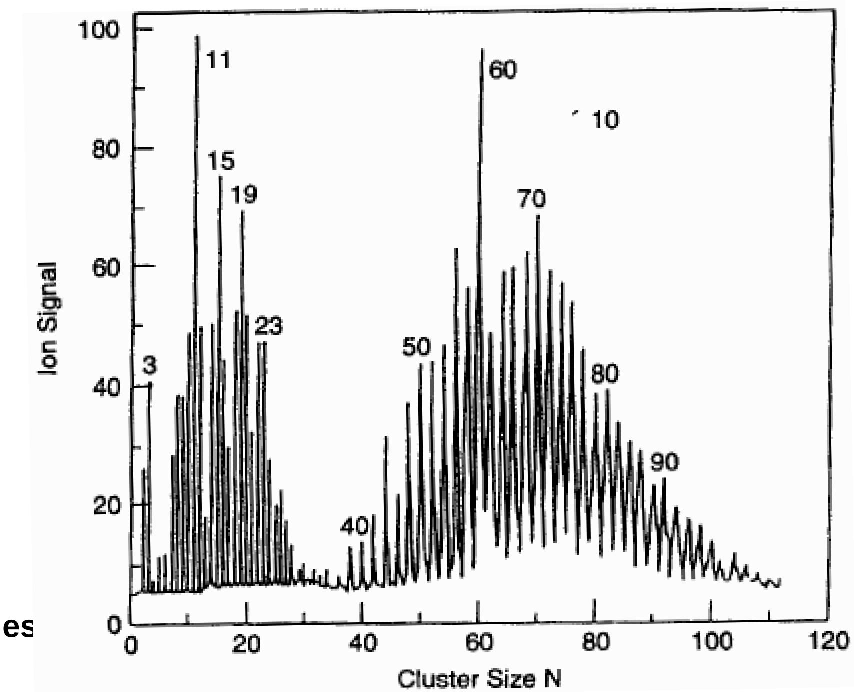
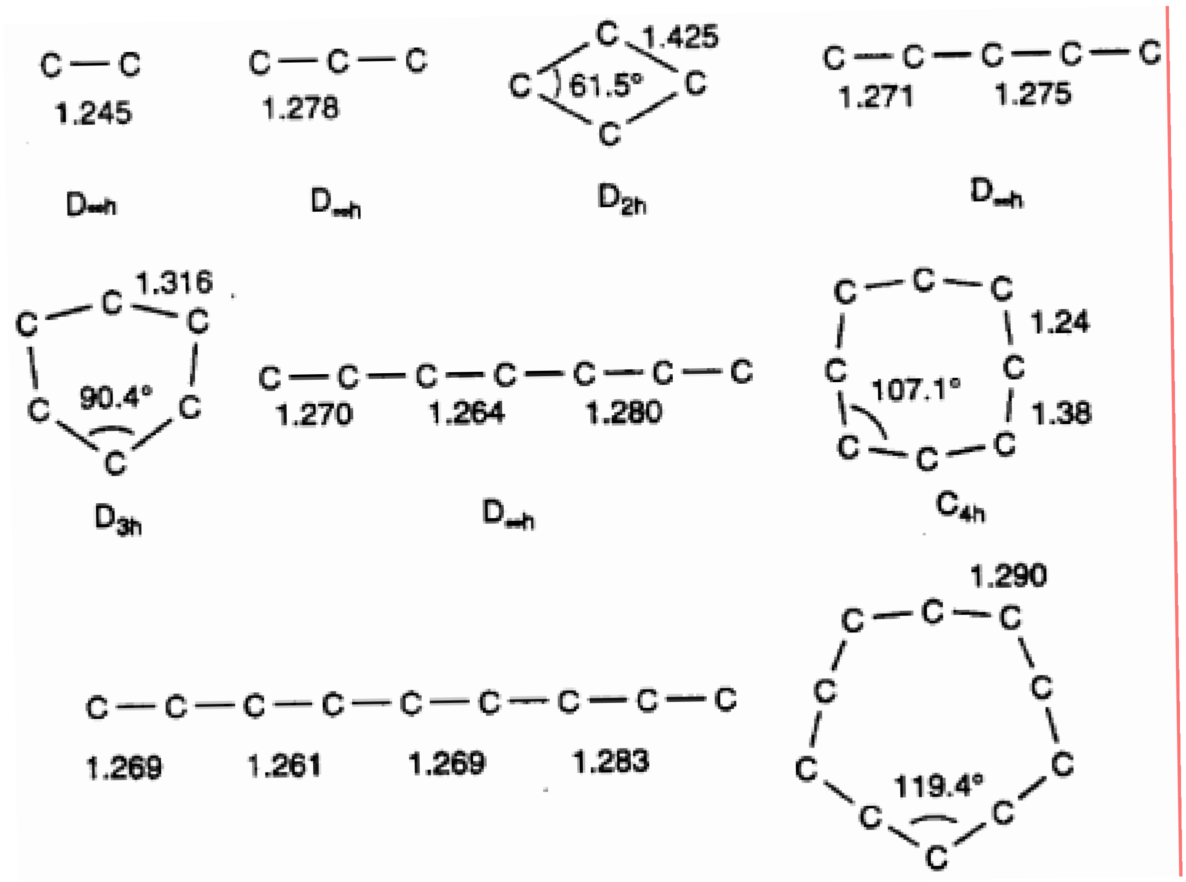



**Fig. 5.3 Mass spectrum of Carbon clusters. The $C_{60}$ and $C_{70}$ peaks are evident.**

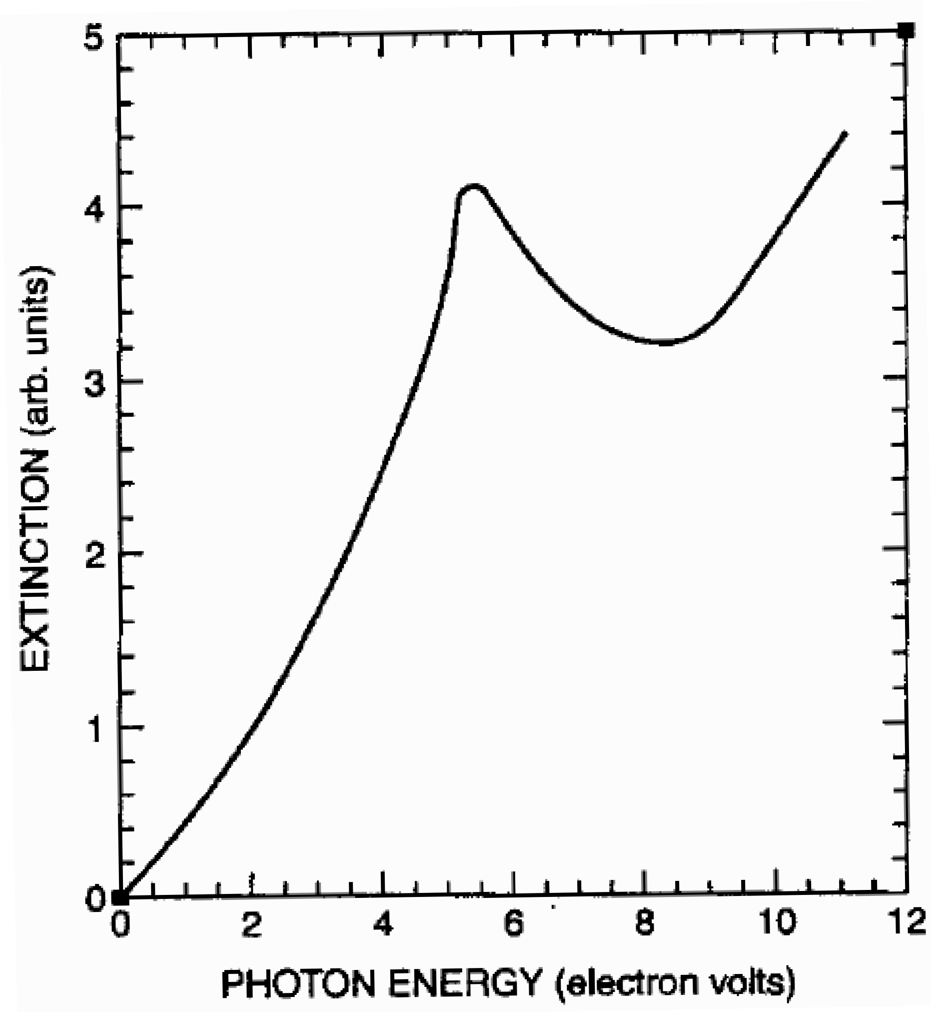
Fig. 5.4 Result of molecular orbital theory for the structure of small clusters




Odd N: linear structure, sp hybridization

Even N: closed structure

# Optical extinction




**Carbon Star (Red giant)**

$C_{60}$ molecules are created in the outer atmosphere of a “red giant”

**Optical spectrum of light coming from stars in outer space. The peak at 5.6eV (220nm) is due to absorption from $C_{60}$ presented in interstellar dust.**

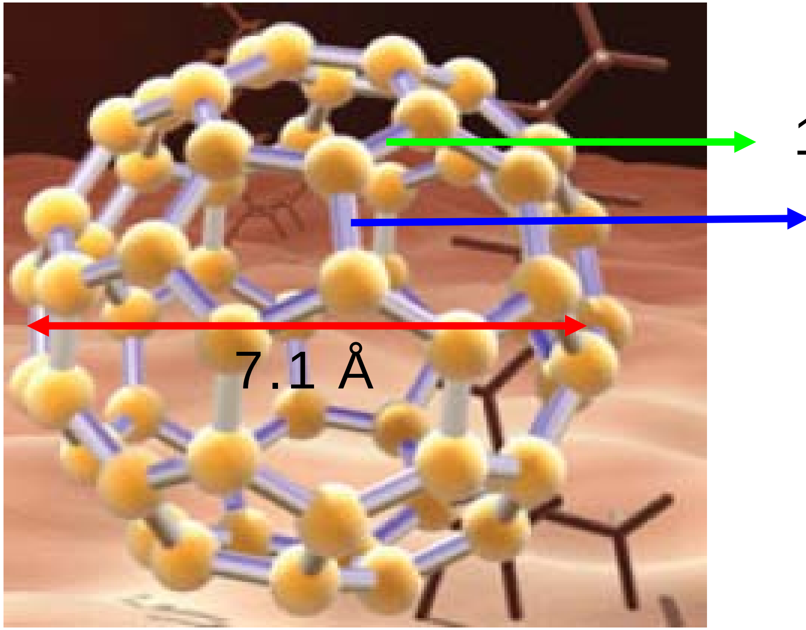
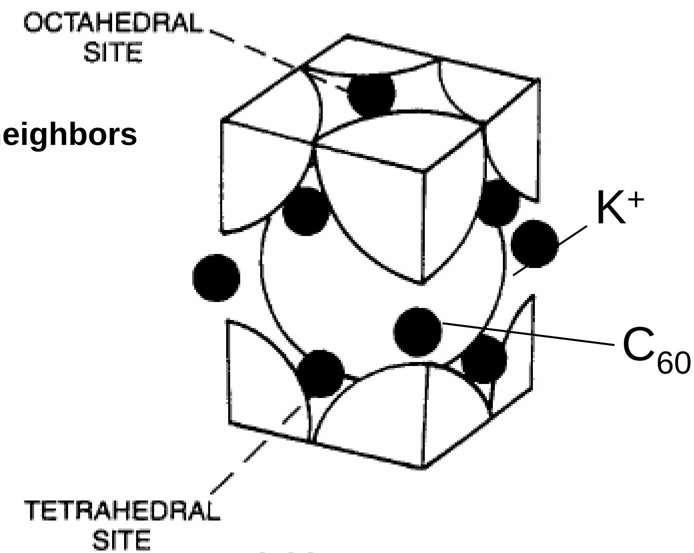



**Fig. 5.6 structure of $C_{60}$ fullerene molecule**

- Atoms are held together by van der Waals forces
- contains 12 pentagonal and 20 hexagonal
- The pentagons are needed to produce closed ( convex ) surfaces, and hexagons lead to a planar surface.

- **Dissolves in common solvents like benzene, toluene, hexane**
- **Readily vaporizes in vacuum around 400°C**
- **Low thermal conductivity**
- **Pure $C_{60}$ is an electrical insulator**
- **$C_{60}$ doped with alkali metals shows a range of electrical conductivity:**
  - **Insulator ($K_6$ $C_{60}$) to superconductor ($K_3$ $C_{60}$) < 30 K!**

**6 neighbors**




**4 neighbors**

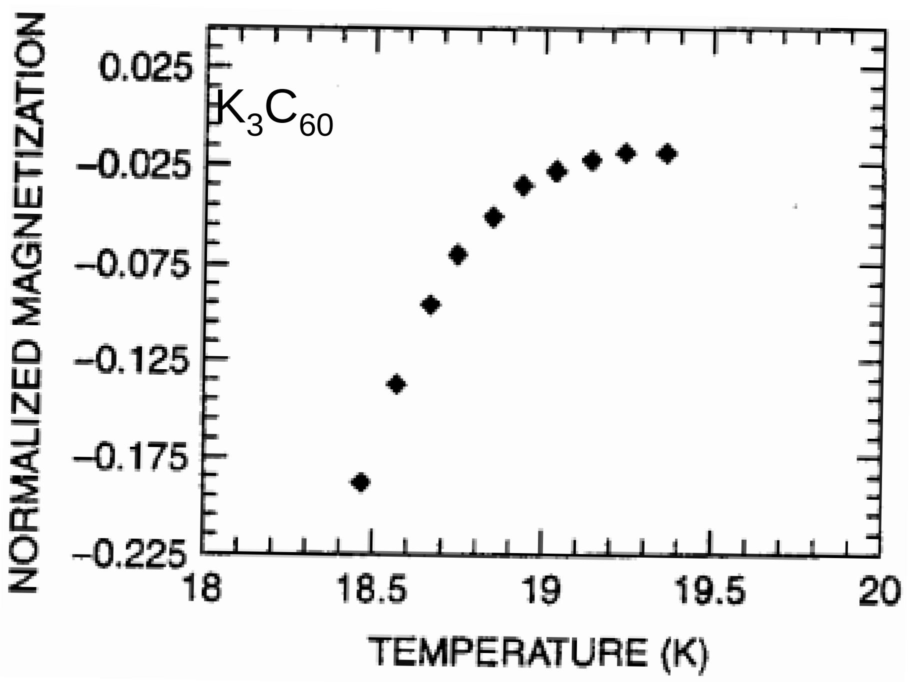
$C_{60}^{3-}$ with 3 ionized $K^+$

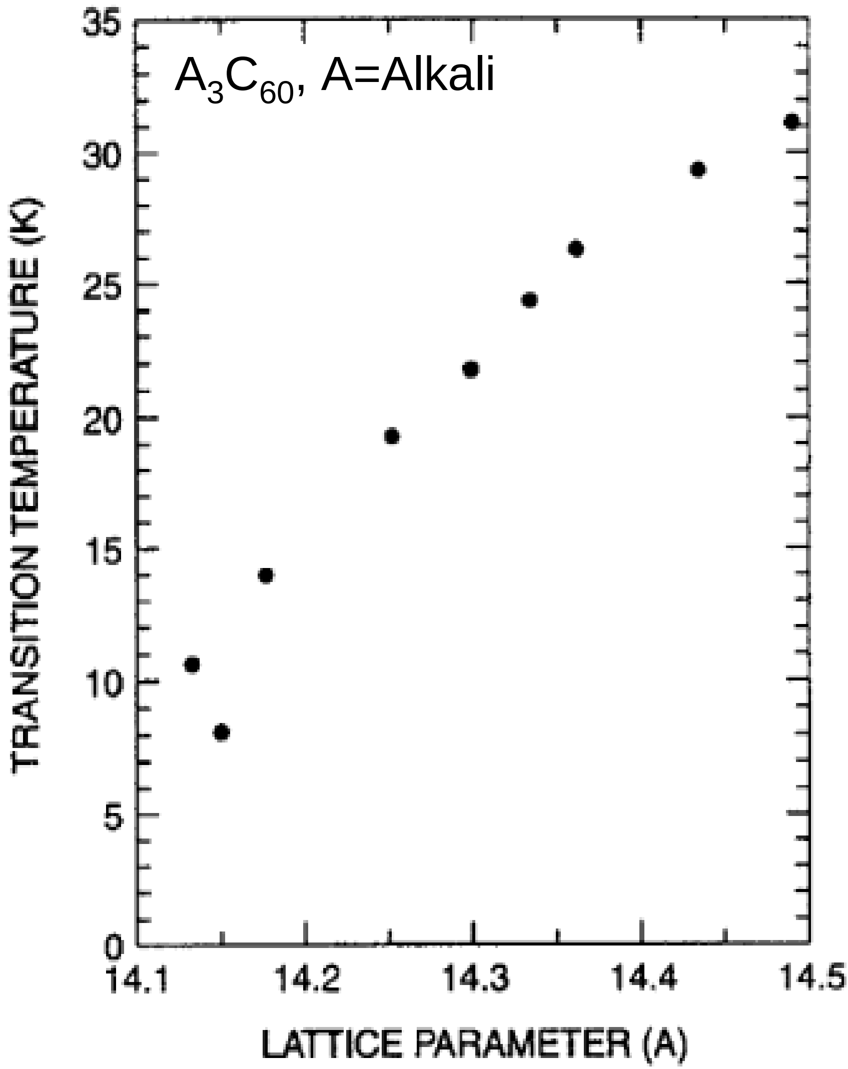
Highly disordered material

Other superconducting compounds:
$Rb_3C_{60}$, $Cs_3C_{60}$, $Na_3C_{60}$

# Superconductivity in $K_3C_{60}$

**$K_3C_{60}$ :18K**
**$Cs_2RbC_{60}$ : 33K**

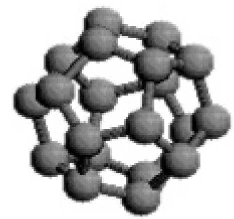


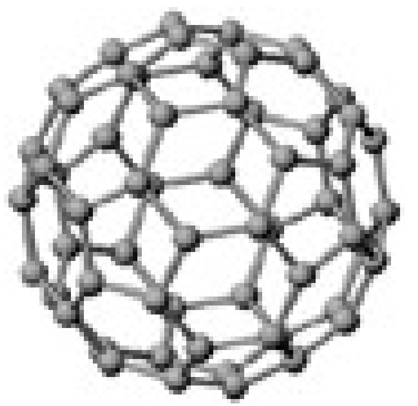
# Various sizes of fullerenes

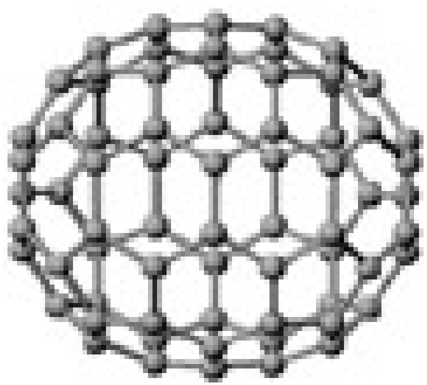
**The Smallest Fullerene**

**$C_{20}$**

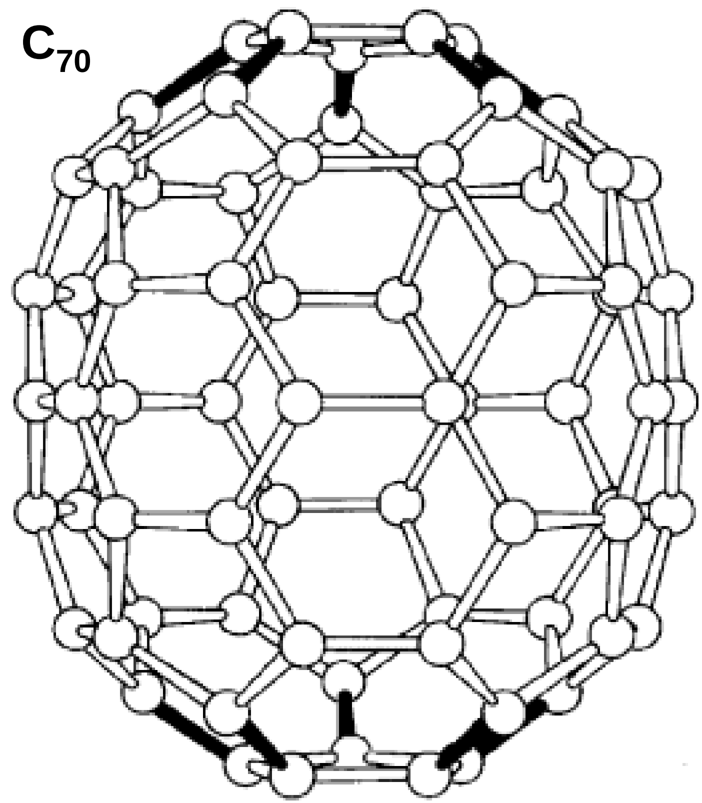


**Gas-phase production and photoelectron spectroscopy of the smallest fullerene, $C_{20}$ [Nature, 407, 60 (2000)]**

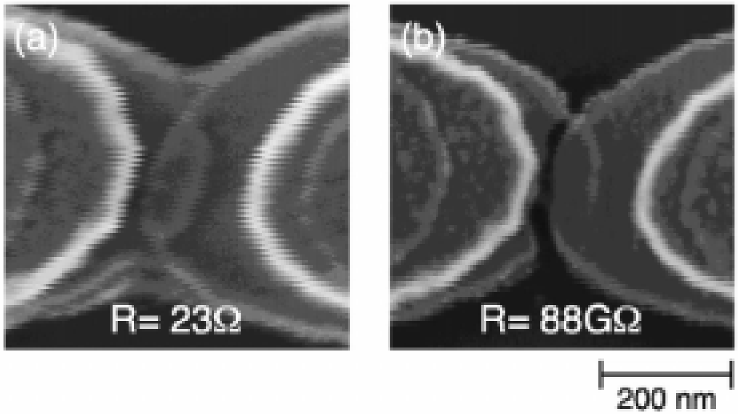




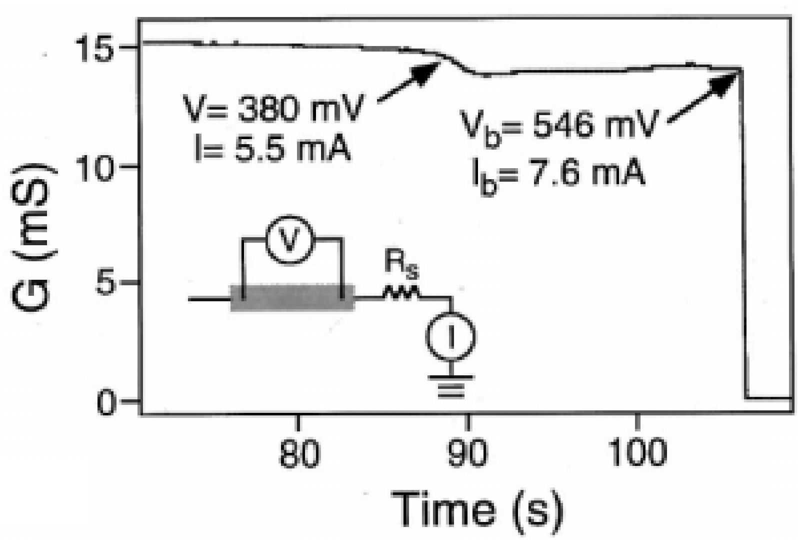
**$C_{70}$**



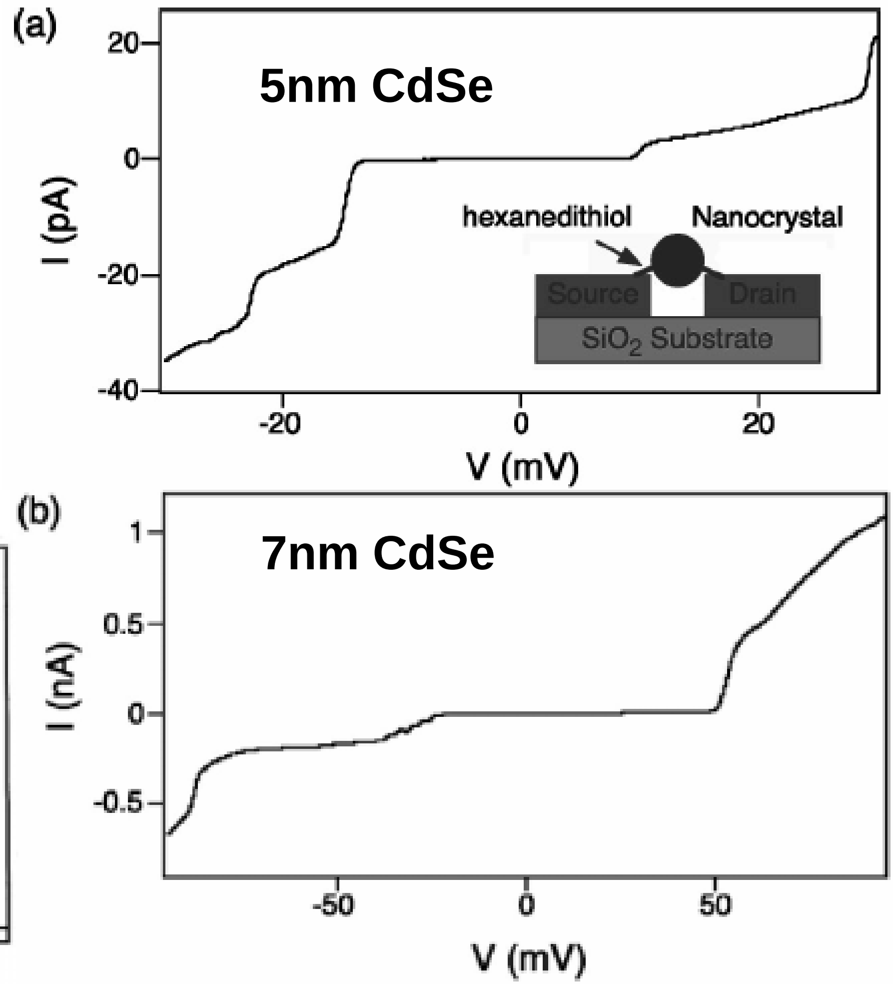
# Break junction approach for electrical measurement of a single nano-particle



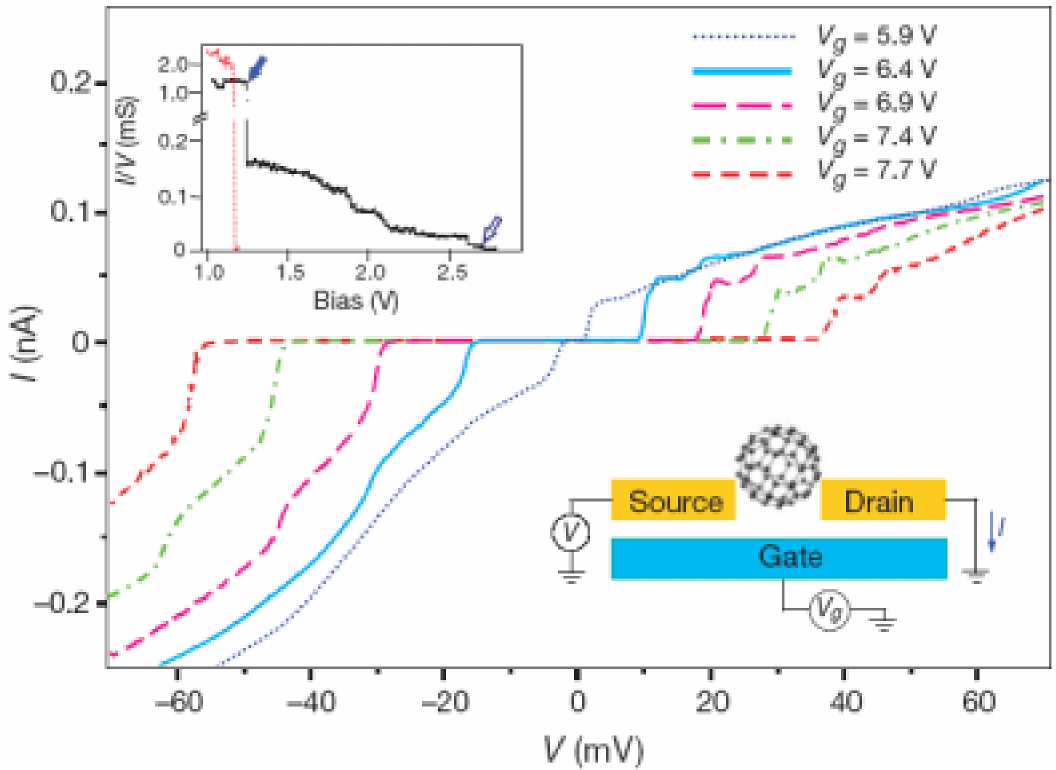

**Fabrication of metallic electrodes with nanometer separation by electromigration [APL, 75, 301 (1999)]**




**IV at 1.5K**



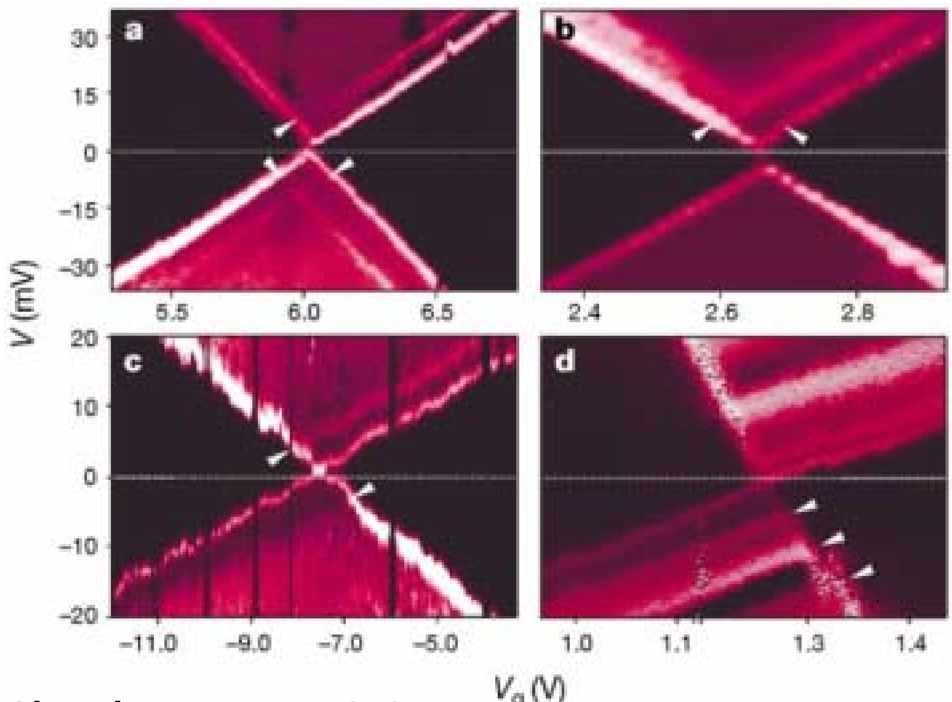
# IV characteristics of a single $C_{60}$ transistor at 1.5K

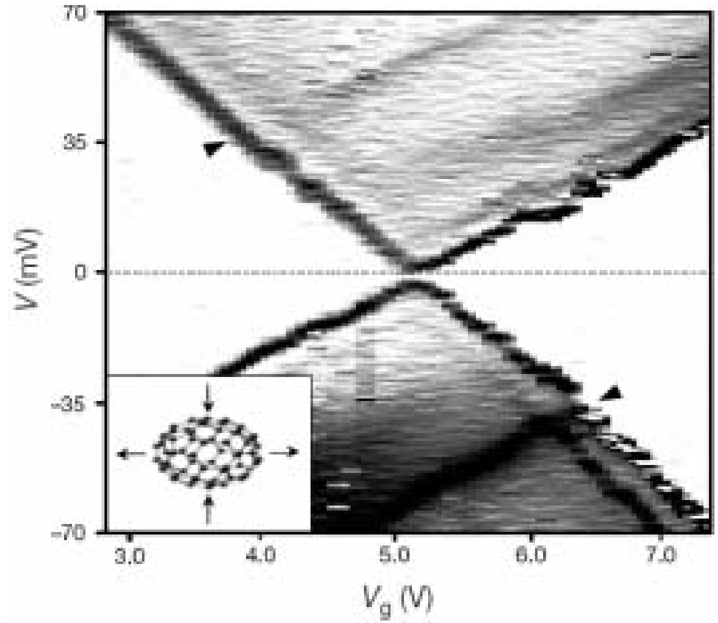



Nature 407, 58 (2000)

**Figure 1 Current–voltage ( I–V) curves obtained from a single-$C_{60}$ transistor at T= 1.5 K. Five I–V curves taken at different gate voltages ( Vg) are shown. Single-$C_{60}$ transistors were prepared by first depositing a dilute toluene solution of C60 onto a pair of connected gold electrodes. A gap of,1 nm was then created using electromigration-induced breaking of the electrodes. Upper inset, a large bias was applied between the electrodes while the current through the connected electrode was monitored (black solid curve). After the initial rapid decrease (solid arrow), the conductance stayed above ,0.05 mS up to ,2.0 V . This behaviour was observed in most single-$C_{60}$ transistors, but it was not observed when no $C_{60}$ solution was deposited (red dotted curve). The bias voltage was increased until the conductance fell low enough to ensure that the current through the junction was in the tunnelling regime (open arrow). The low bias measurements shown in the main panel were taken after the breaking procedure. Lower inset, an idealized diagram of a single C60-transistor formed by this method.**

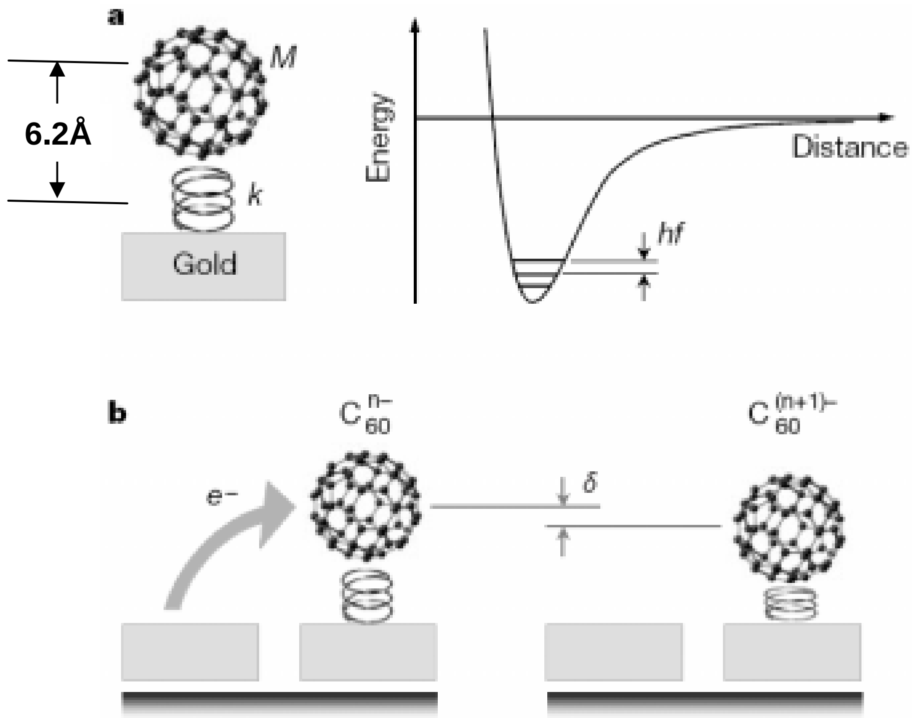
In large bias range




**Charging energy > 270meV**

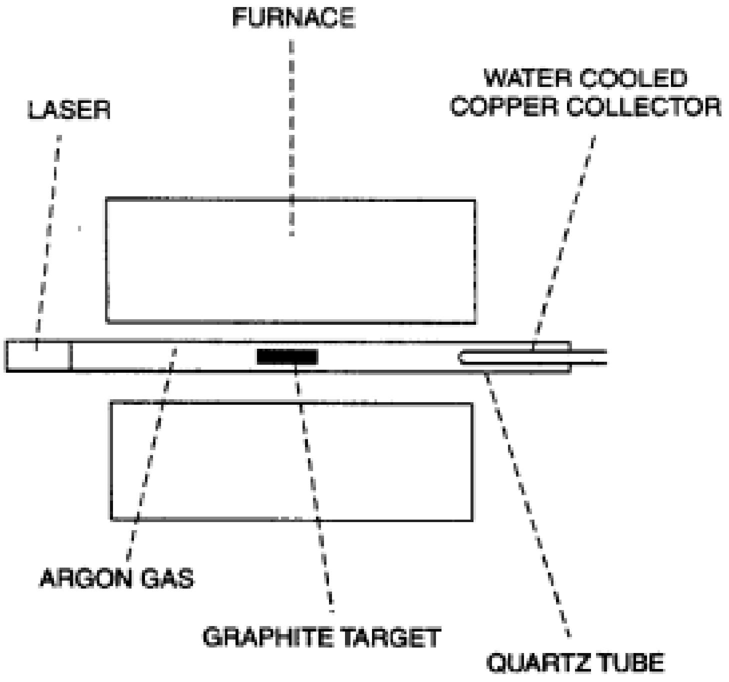
**Two-dimensional differential conductance (∂I/∂V) plots as a function of the bias voltage (V) and the gate voltage ($V_g$). Data were obtained from four different devices prepared from separate fabrication runs. The dark triangular regions correspond to the conductance gap, and the bright lines represent peaks in the differential conductance. a–d, The differential conductance values are represented by the colour scale, which changes from black (0 nS) through pink to white (white representing 30 nS in a, b and c and 5 nS in d). The white arrows mark the point where ∂ I/∂ V lines intercept the conductance gap. During the acquisition of data in d, one 'switch' where the entire ∂ I/∂ V characteristics shift along the $V_g$ axis occurred at $V_g$ = 1.15 V. The right portion of the plot d is shifted along the $V_g$ axis to preserve the continuity of the lines.**




$K \approx 70$N/m
$f \approx 1.2$THz
$hf \approx 5$meV
$\delta \approx 4$pm

**Figure 4 Diagram of the centre-of-mass oscillation of $C_{60}$. a, A $C_{60}$ molecule is bound to the gold surface by the van der Waals and electrostatic interaction. The interaction potential is shown schematically alongside. The potential near the equilibrium position can be approximated well by a harmonic potential with a force constant k. This harmonic potential gives quantized energy levels with frequency $f= 1/2\pi(k/ M)^{1/2}$. Here M represents the mass of $C_{60}$ and his the Planck constant. b, When an electron jumps on to $C^{n-}_{60}$, the attractive interaction between the additional electron and its image charge on gold pulls the C60 ion closer to the gold surface by the distance d. This electrostatic interaction results in the mechanical motion of C60.**

Laser evaporation

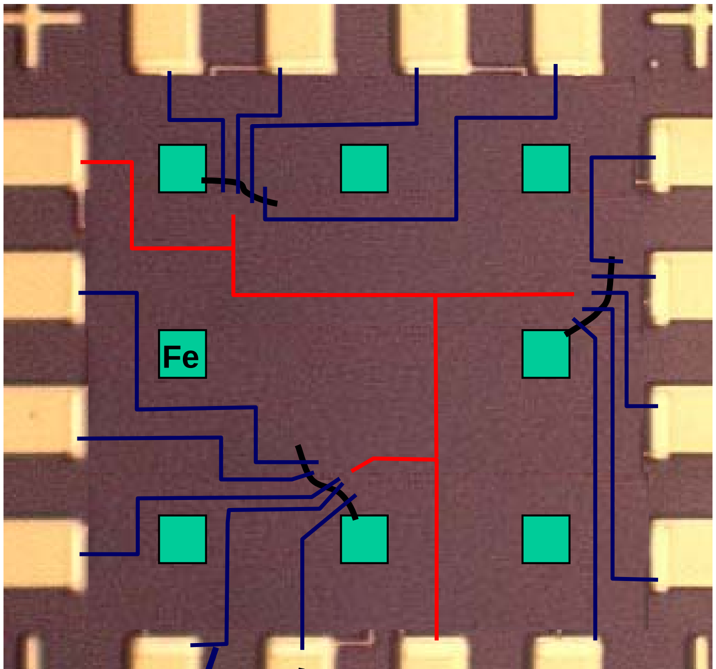



Chemical vapor deposition: method: methane ($CH_4$) 1100ºC

Catalyst Co or Ni

# Fabrication of the nanotube devices

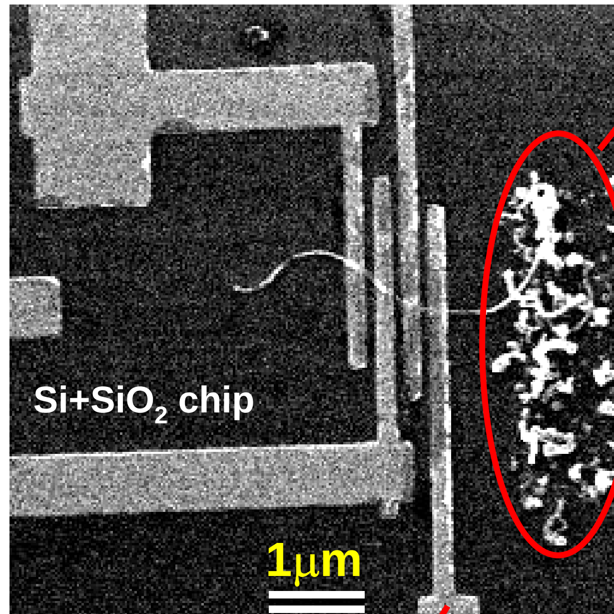
Fe catalyst + multiwalled carbon nanotubes grown by CVD




10 μm

Cr leads

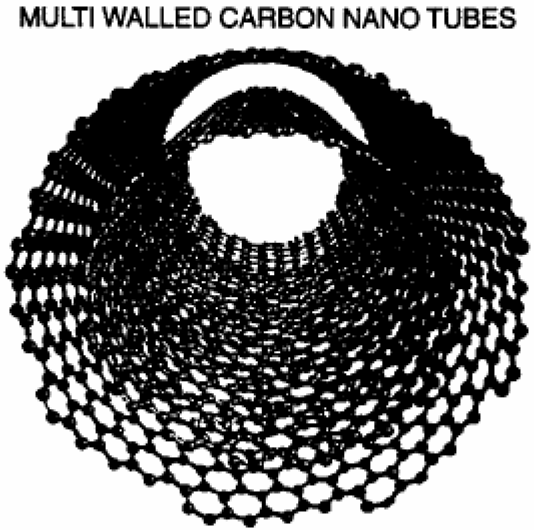
Au leads made by photo-lithography

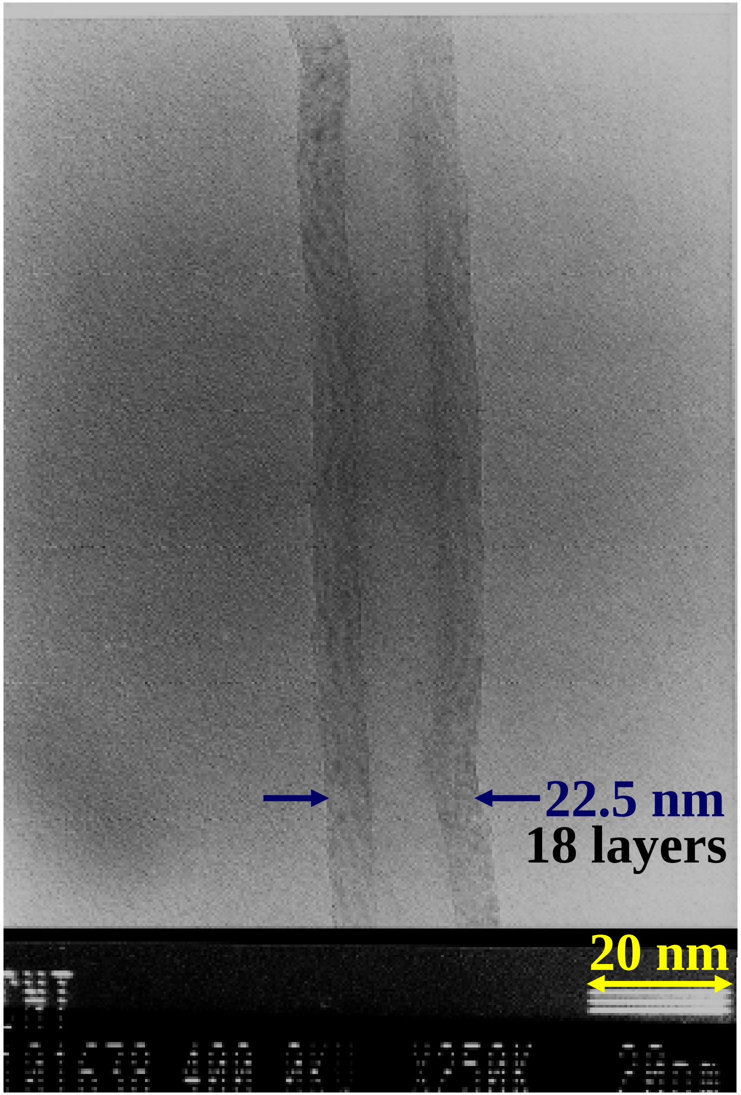


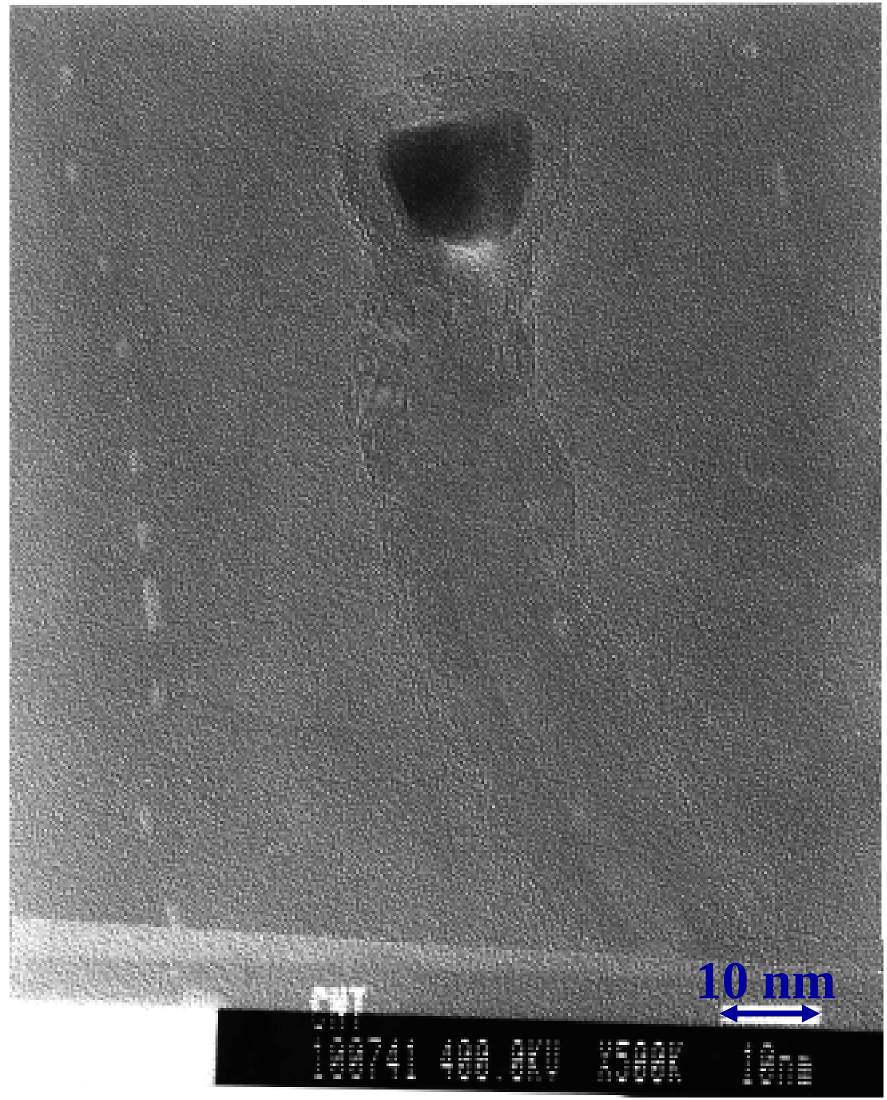

Cr electrodes made
by e-beam lithography

# Growth Conditions:

- **Substrate: 300nm thermally grown $SiO_2$**
- **Catalyst: 9-nm-thermally evaporated iron pads**
- **Pretreatment: 1mBar hydrogen, ~700°C, 5 min**
- **Growth: 1mBar ethylene, ~750°C, 5 min**






TEM 相片：陳貴賢，林麗瓊

Multiwall nanotube consists of capped concentric cylinders separated by ~ 3.5 Å.

- Typically, outer diameter of carbon nanotubes prepared by a carbon arc process ranges between 20 and 200 Å, and inner diameter ranges between 10 and 30 Å. Typical lengths of the arc-grown tubules are about 1 μm, giving rise to an aspect ratio (length-to-diameter ratio) of $10^2$ to $10^3$.

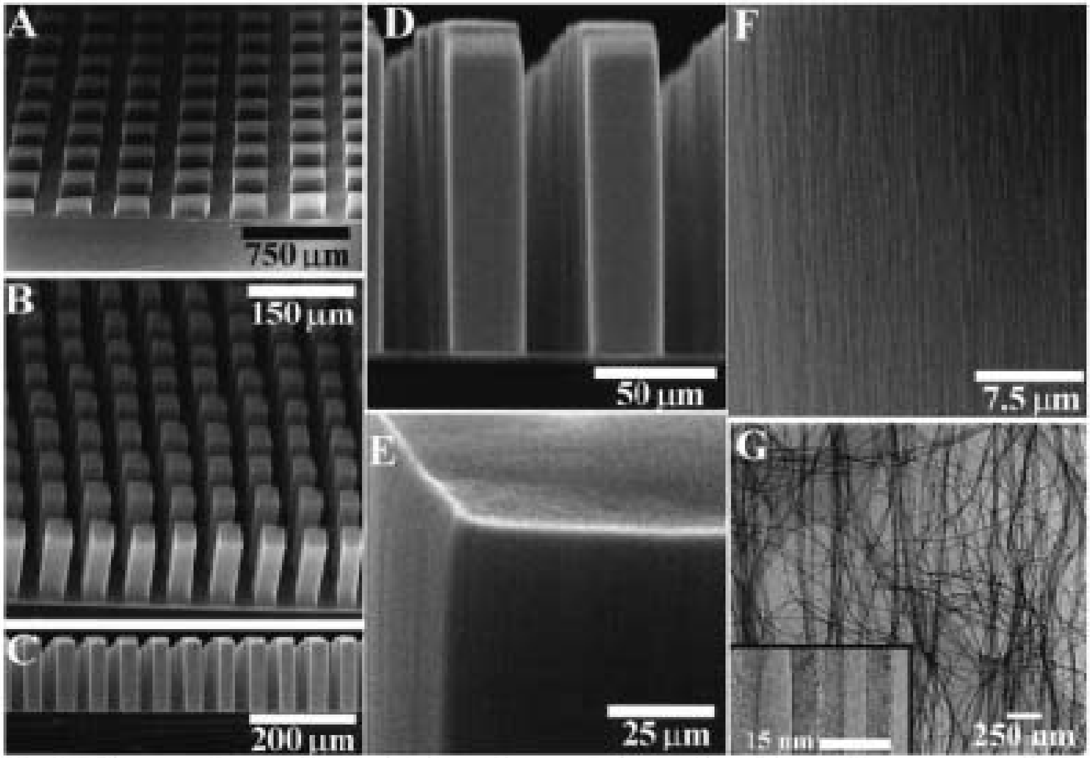
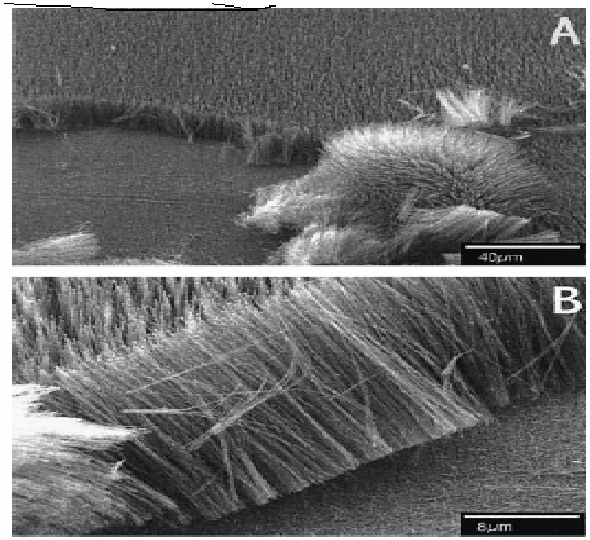
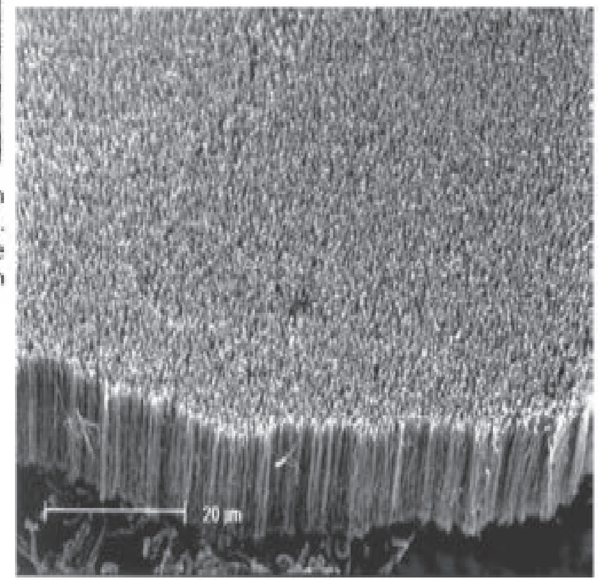



**Fig. 2.** Electron micrographs of self-oriented nanotubes synthesized on n$^{+}$-type porous silicon substrates. (**A**) SEM image of nanotube blocks synthesized on 250 µm by 250 µm catalyst patterns. The nanotubes are 80 µm long and oriented perpendicular to the substrate [see (F)]. (**B**) SEM image of nanotube towers synthesized on 38 µm by 38 µm catalyst patterns. The nanotubes are 130 µm




Forests of multiwalled carbon nanotubes



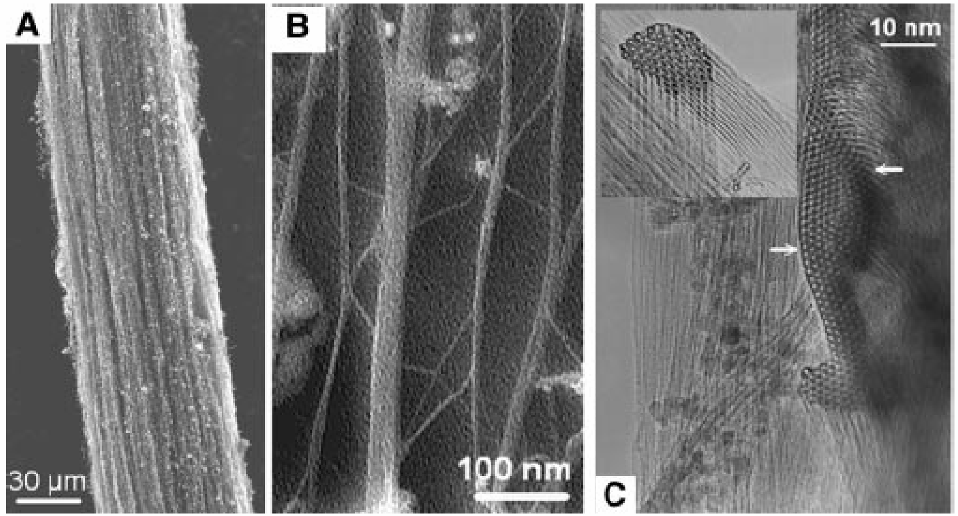



**Fig. 2.** (**A**) Low-magnification SEM image of a long SWNT strand. When the strand is peeled carefully along the length, a thinner SWNT rope is obtained. (**B**) High-resolution SEM of an array of SWNT ropes peeled from the strand. (**C**) HRTEM image of a top view of a SWNT rope. For HRTEM observation, we selected a SWNT rope, tore it with tweezers, and affixed it on the HRTEM grid by wetting it with a drop of ethanol or acetone. White arrows indicate the arrangement of the triangle lattice of a large area in a SWNT strand. The inset shows a cross-sectional view of a polycrystalline bundle.