

Synthesis of Carbon nanotubes

University of Parma

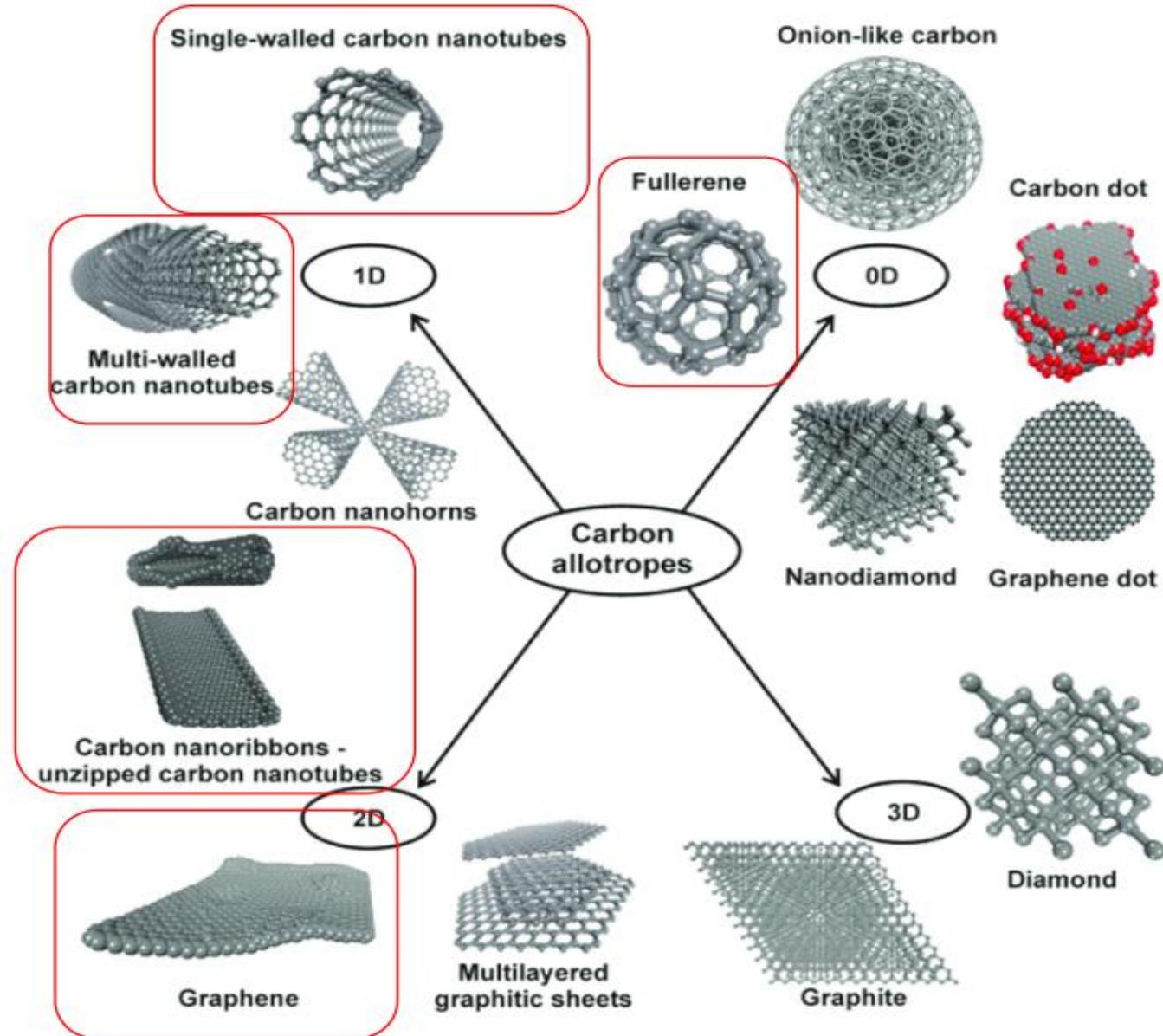
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Carbon based nanostructures

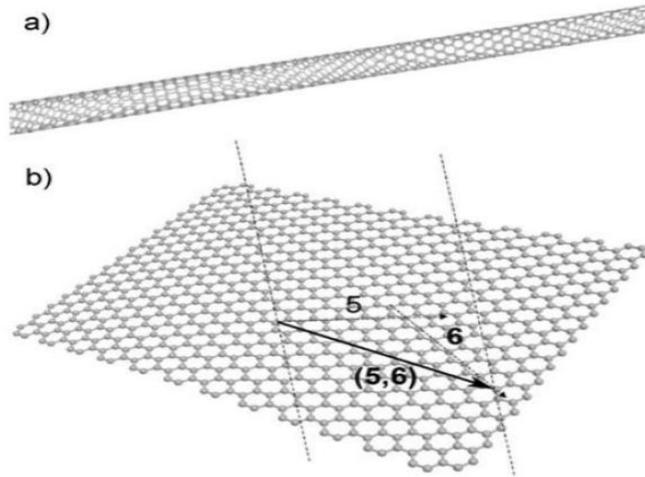
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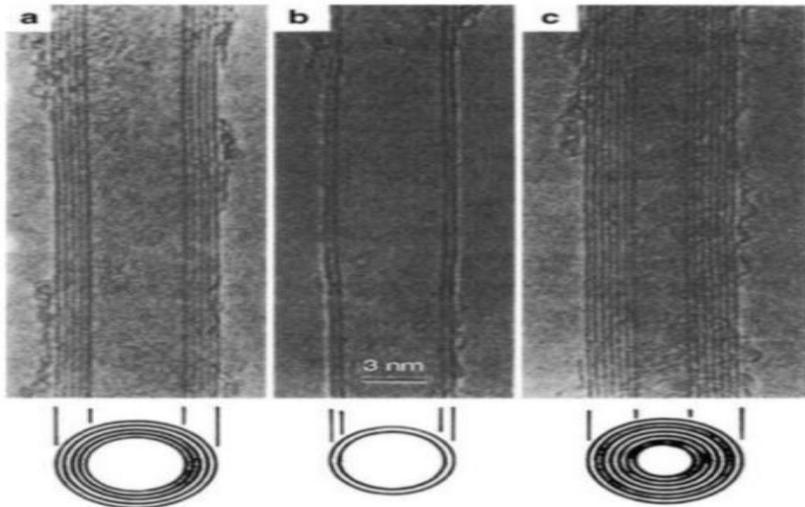
CARBON-BASED NANOMATERIALS



CNTs are rolled-up graphene sheets, defined by the chiral vector (n, m) .
CNTs: This chirality dictates their properties (metallic/semiconducting).
CNTs offer the highest recorded mechanical strength and exceptional thermal stability.

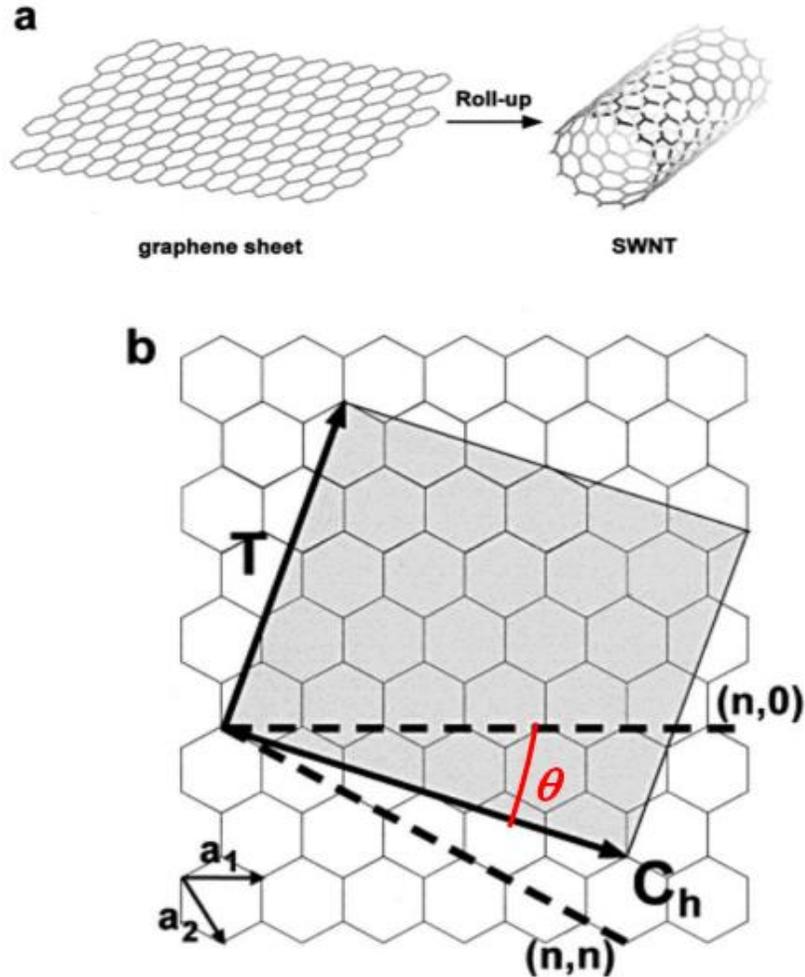


The idea structures of
a) a single walled-nanotube
and
b) a graphene sheet .



TEM images of MWNTs , formed from folding
a) 5
b) 2
c) 7
graphene layers

THE STRUCTURE OF CARBON NANOTUBES (CNTs);

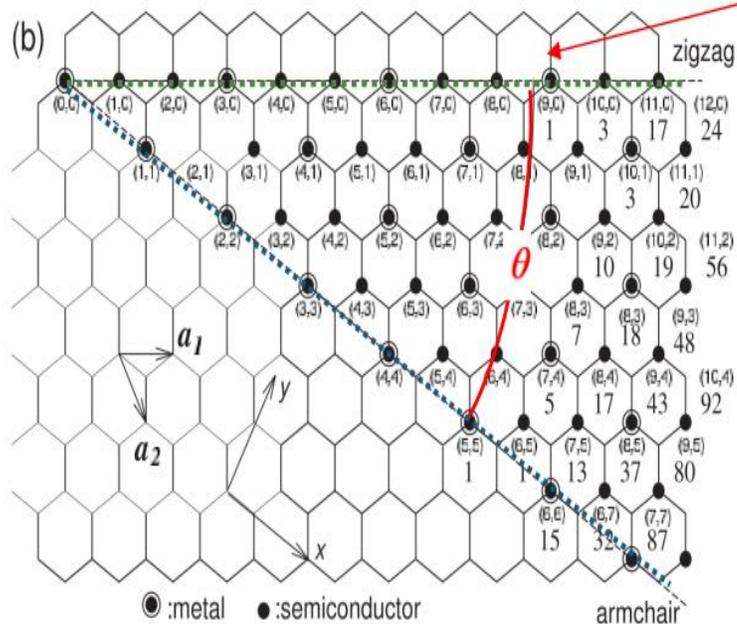


- The diameter and helicity of a SWNT are uniquely characterised by the roll-up (or chiral) vector:

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

- C_h connects crystallographically equivalent sites on a two dimensional (2D) graphene sheet, where a_1 and a_2 are the graphene lattice vectors and n and m are integers (also known as Hamada indices).
- The chiral angle Θ is defined by vector C_h and the “zigzag” direction (along the zigzag direction $\Theta = 0^\circ$)
- The limiting, achiral cases of $(n,0)$ zigzag and (n,n) armchair are indicated with dashed lines.
- The translation vector T is along the nanotube axis and defines the 1D unit cell. The shaded, boxed area represents the unrolled unit cell formed by T and C_h .
- The diagram is constructed for $(n,m) = (4,2)$.

Three distinct types of SWCNT structures can be generated by rolling up the graphene sheet into a cylinder:



$$\cos\theta = \frac{2n+m}{2\sqrt{n^2+nm+m^2}}$$

rolling toward $(n,0) \Rightarrow \theta = 0^\circ \Rightarrow$ zigzag

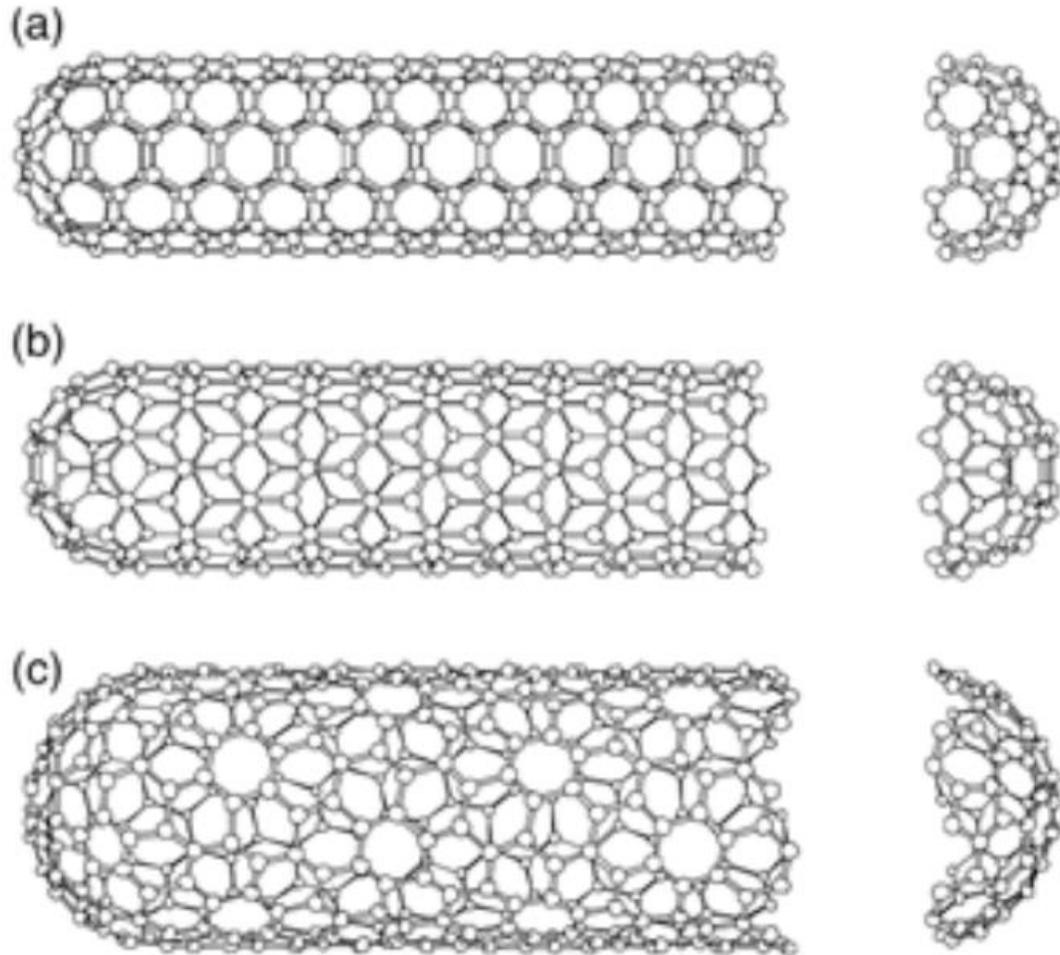
rolling toward $(n,m) \Rightarrow 0^\circ < \theta < 30^\circ \Rightarrow$ chiral SWCNT

rolling toward $(n=m) \Rightarrow \theta = 30^\circ \Rightarrow$ armchair

The roll-up vector C_h (and thus the Hamada index n and m) defines the diameter of the SWCNT:

$$D = \sqrt{3}d_{c-c} \frac{\sqrt{n^2 + nm + m^2}}{\pi} = \frac{C_h}{\pi} \quad \text{with } d_{c-c} = 1.421 \text{ \AA}$$

- SWCNT having chiral vectors with $n = m$ or $n-m =$ a multiple of 3 are metallic nanotubes .
- SWCNT with other chiral vectors are semiconductors whose band gap decreases with increasing diameter.
- MWCNT are always metallic .



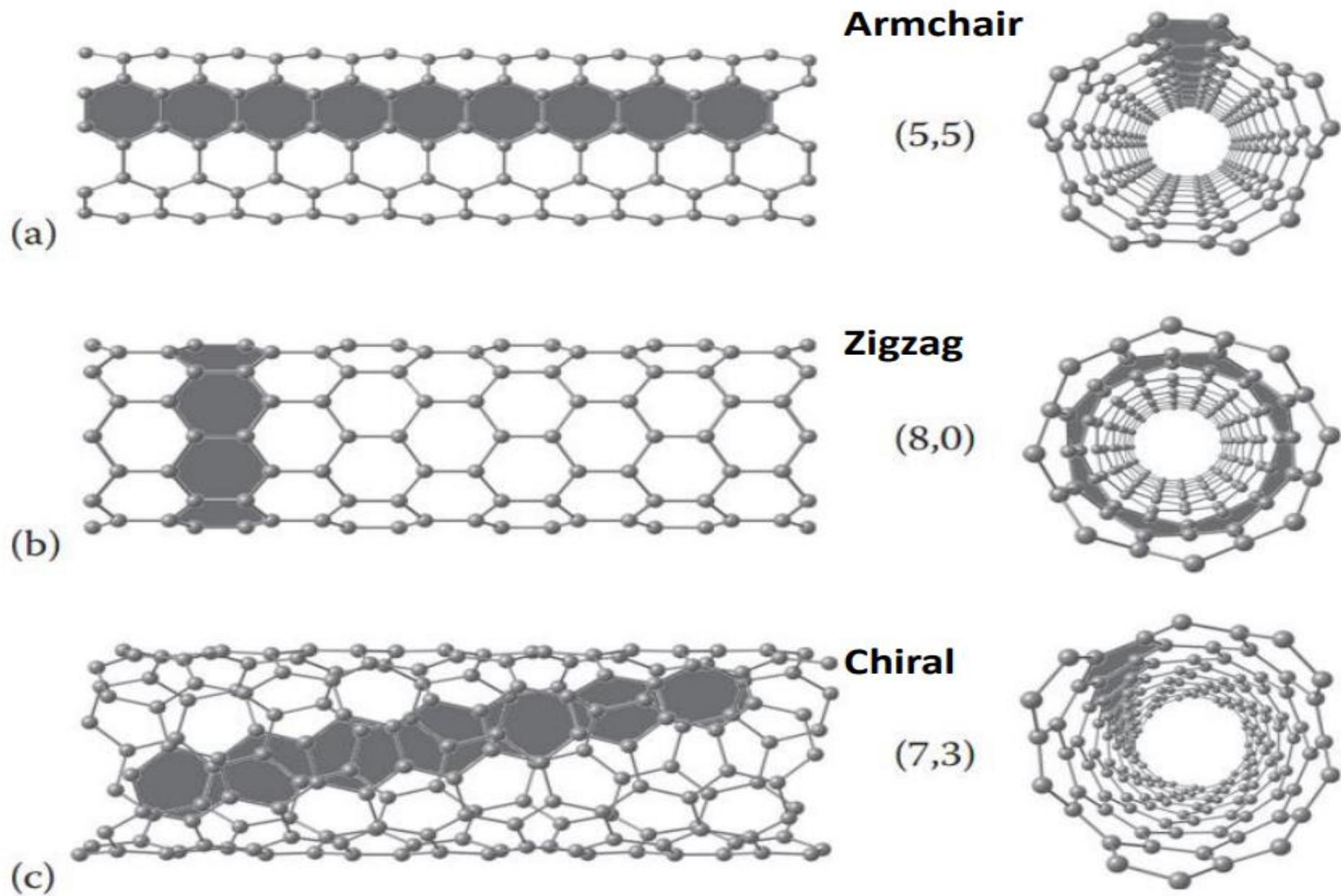
$\Theta = 30^\circ$ direction: “armchair” (n,n)
nanotube (metallic)

$\Theta = 0^\circ$ direction: “zigzag” (n,0)
nanotube

$0 < \Theta < 30^\circ$: “chiral” (n,m)
nanotube (semiconducting)

Chiral SWCNTs appear as mirror pairs of right-handed and left-handed structures with positive and negative chiral angles Θ , respectively.

The mirror degeneracy of chiral SWCNTs is often disregarded since right- and left-handed SWCNTs always share exactly the same electronic and optical properties.



THE SYNTHESIS OF CARBON NANOTUBES:

Several techniques



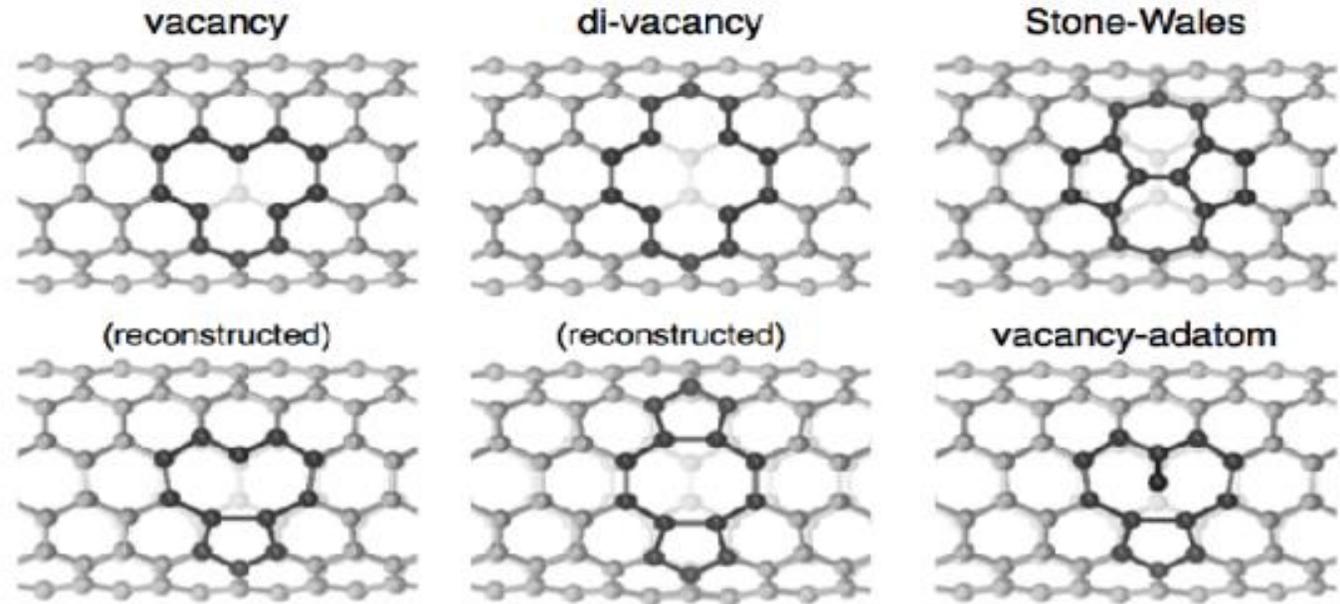
Defects



Purification

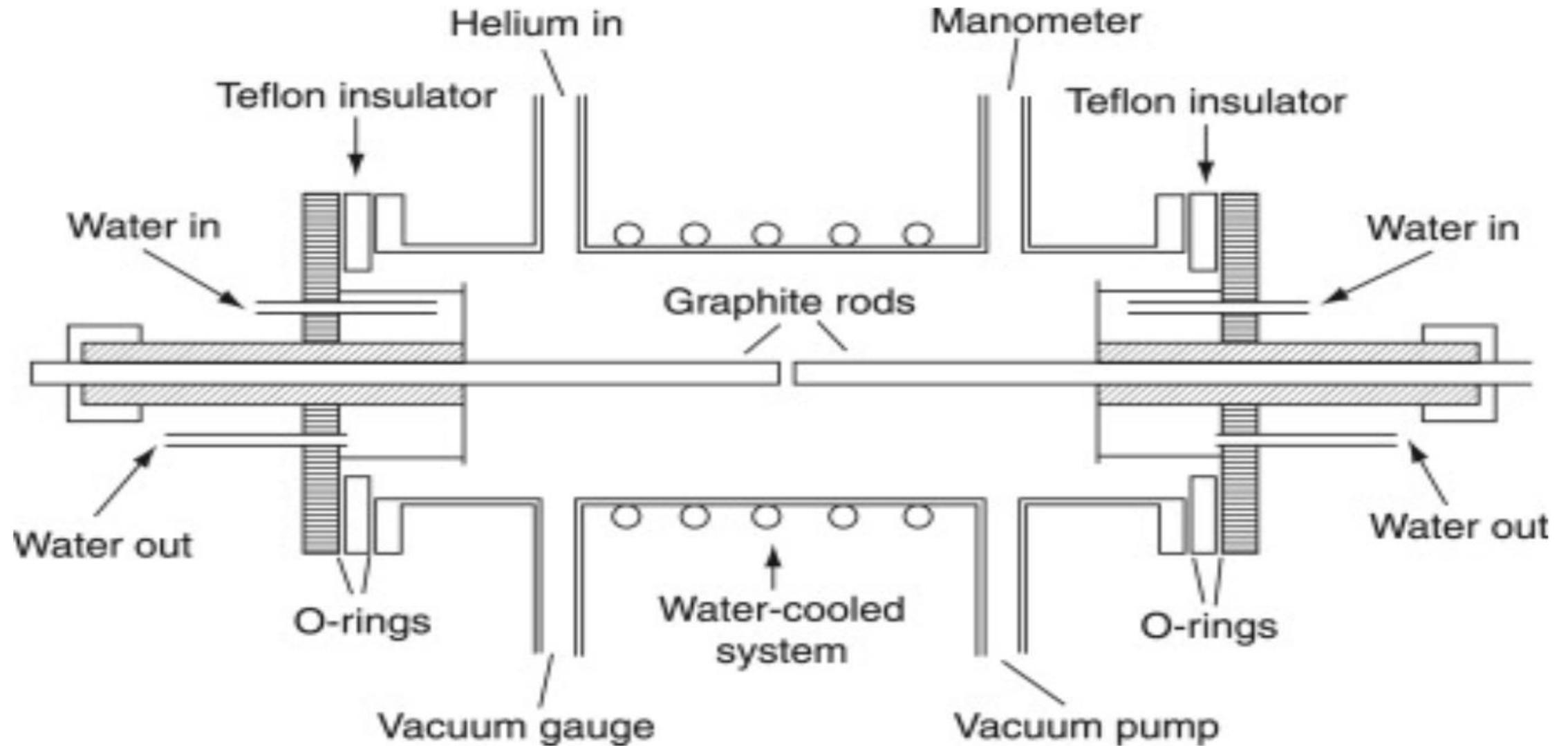


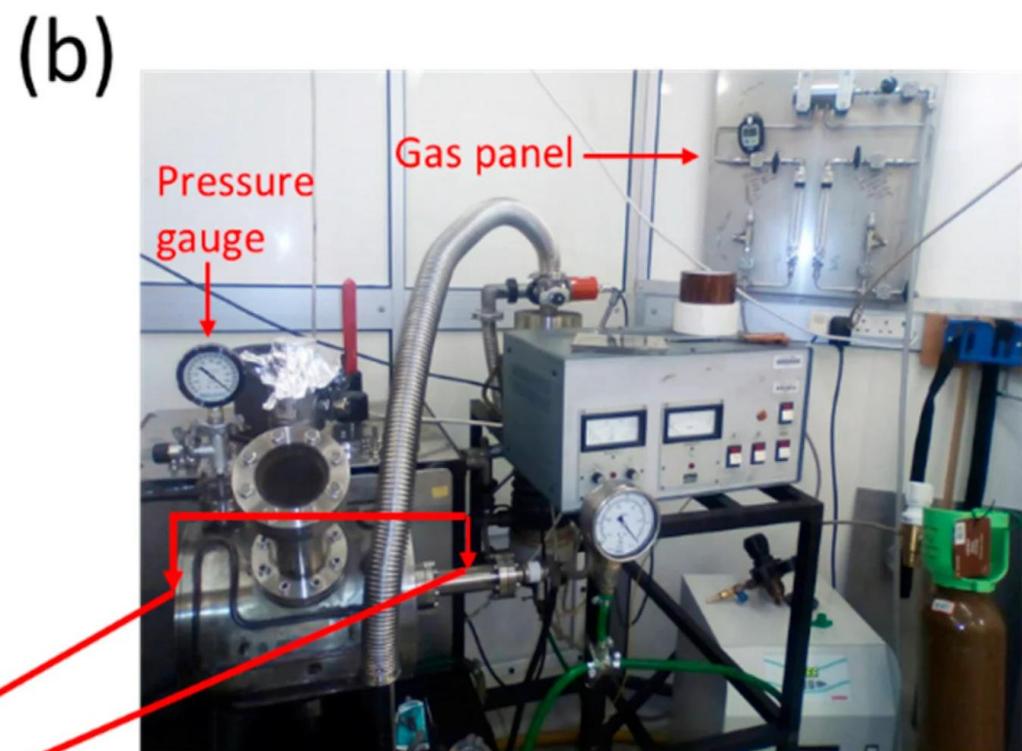
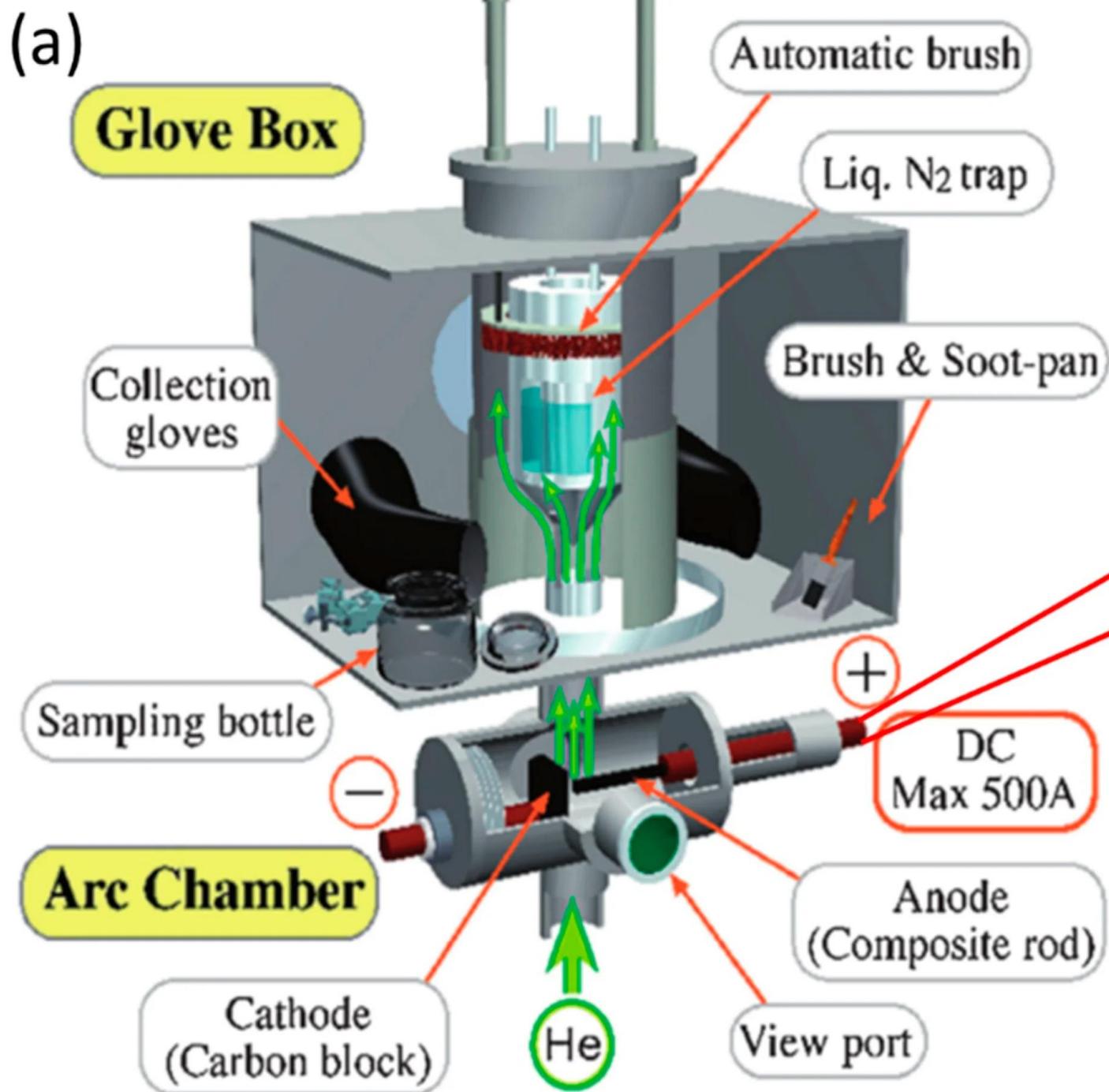
Costs



1. Electric-Arc Discharge Method
2. Laser Vaporization
3. Chemical Vapor Deposition (CVD)

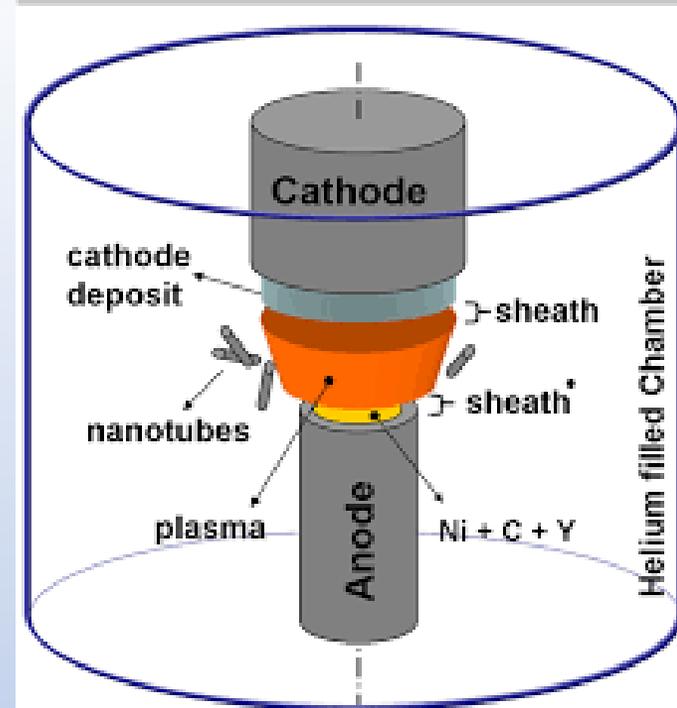
Electric-Arc Discharge Method





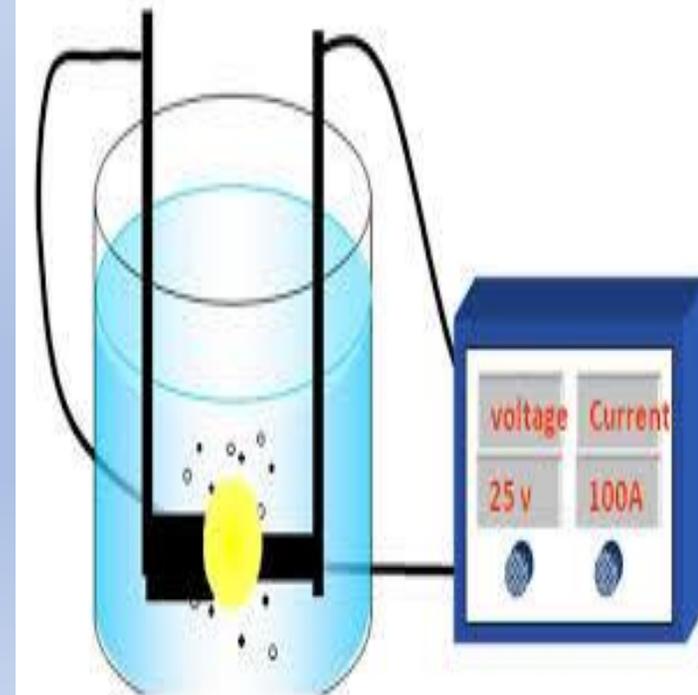
A) CARBON ELECTRODES (Iijima)

- Anode and Cathode made of graphite (5 to 20 mm diameter – 1 mm gap)
- Inert gas atmosphere (He, Ar) at 100 to 1000 torr.
- Voltage (12 to 25 V) and high current (50 to 120 amps) → arc discharge
- Deposit of the CNTs on the top of the cathode
- SWCNTs form when a metal catalyst is added to the anode (Fe:C or Co:C)
- By tailoring the Ar:He gas ratio, the diameter of the SWCNTs formed can be controlled, with greater Ar yielding smaller diameters



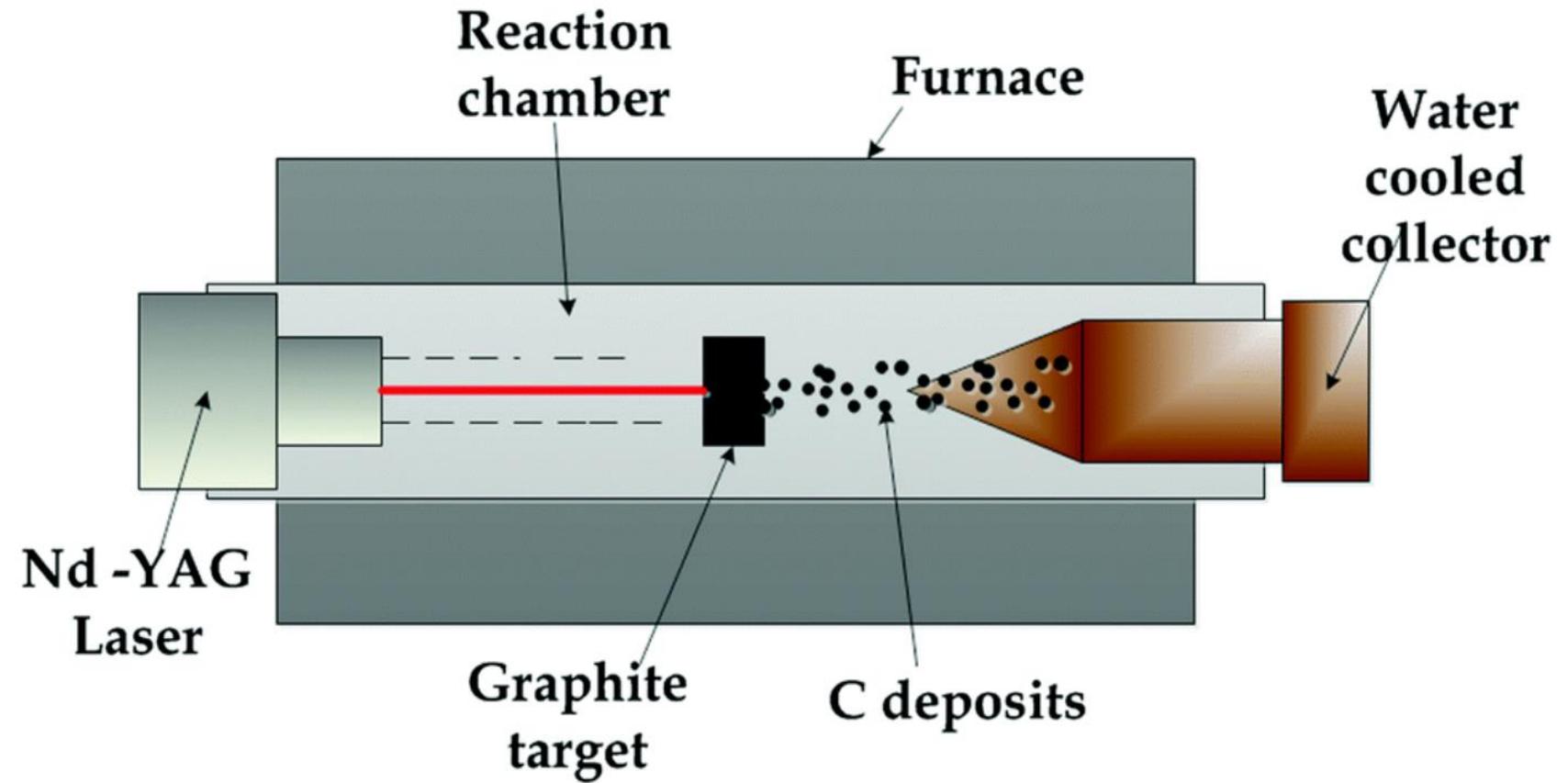
B) METAL CONTAMINATED ELECTRODES

- Electrodes made of metals (Ni)
- Hydrocarbon solvent (toluene)
- Voltage generates an Arc discharge
- Decomposition of toluene
- Deposit on the anode (oxidation)



Laser Vaporization

- Graphite target is vaporized by laser irradiation
- High temperature (1200 °C best quality)
- Inert atmosphere



SWNT : Transition metals (Ni, Co)

MWNT : pure graphite

1996 - Dual Pulsed Laser Vaporization

- 50:50 mixture of Co and Ni powder
- 1200 °C in Argon
- Heat treatment in vacuum at 1000 °C (to sublime C60)

1st LASER;

To ablate the carbon-metal mixture

2nd LASER;

To break up the larger ablated particles

Critical Factors in Dual-Pulse Laser Ablation:

•Time Delay & Spatial Overlap:

The most important parameters are the precise time delay (tens of nanoseconds) and the spatial alignment of the two pulses.

•Plasma Interaction:

The delay ensures the second pulse arrives exactly when the plasma plume is formed.

•Re-heating Mechanism:

instead of striking the solid target, the second pulse interacts with the plasma cloud, causing **re-heating and re-ionization**.

•Result:

This secondary heating is the key driver for maximizing both **yield** and **structural quality**.

The Dual Laser Vaporization Method

The study utilized a dual-laser setup to vaporize graphite targets within a high-temperature furnace. This method is designed to increase the **yield** and **quality** of the nanotubes compared to single-laser methods.

- The Setup:** Two pulsed Nd:YAG lasers were made **co-linear** and directed at a graphite target inside a quartz tube furnace. The first laser (532 nm) vaporizes the target surface. The second laser (1064 nm) is fired with a slight delay.

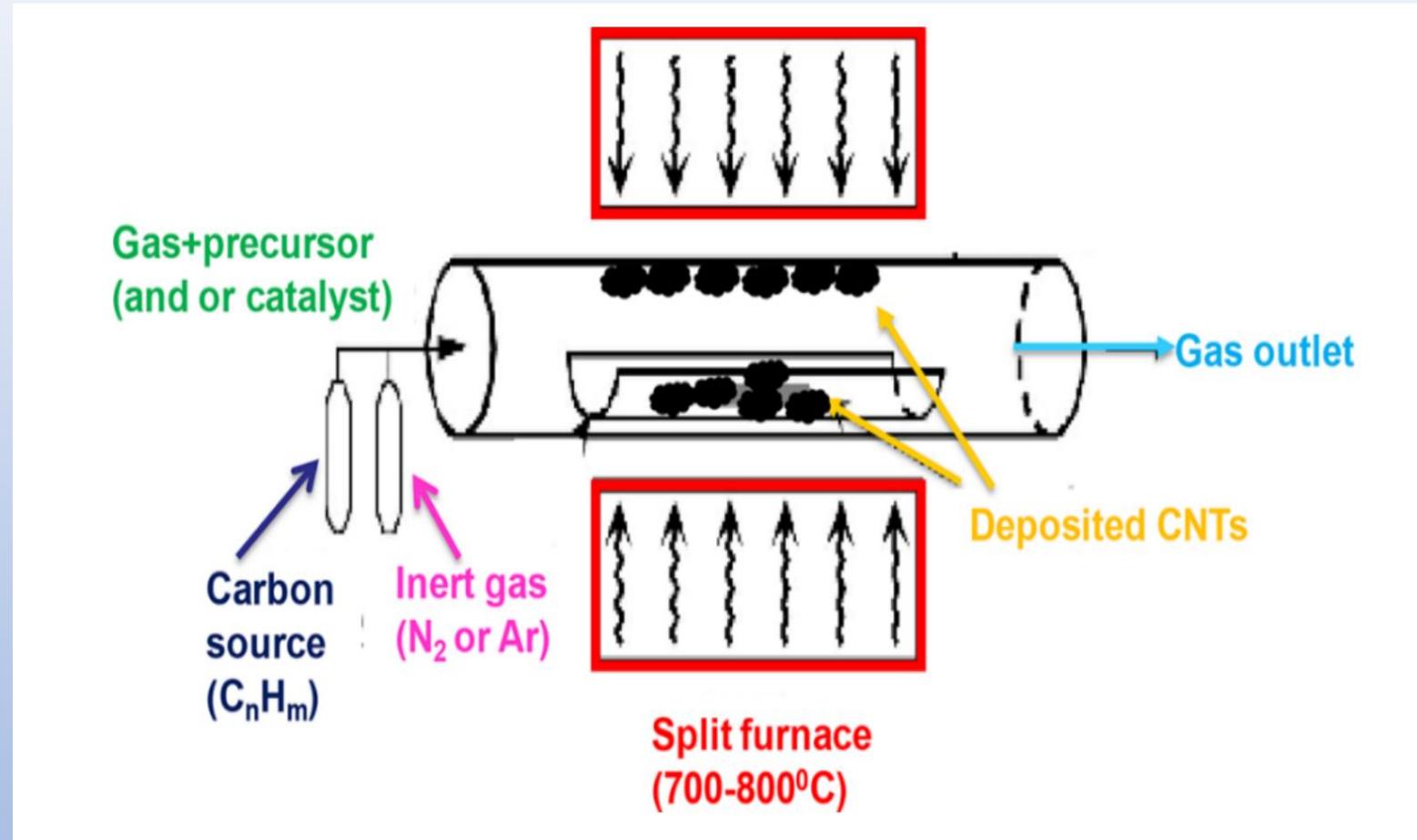
- The Mechanism:** The delay allows the second laser pulse to interact with the plasma plume created by the first pulse. The charged particles in the plasma absorb the photons from the second pulse (a process called reverse Bremsstrahlung). This rapidly increases the plasma temperature (up to 10,000°C) and ionization, which improves the conditions for carbon atoms to coalesce into nanotubes as the plume cools.

- Conditions:** The experiments were conducted in an Argon atmosphere at 500 mbar pressure. The furnace temperatures were set at either 1000°C or 1200°C to manage defect concentrations.

Chemical vapor deposition(CVD)

A) Thermal Chemical Vapor Deposition (Decomposition of Hydrocarbon Gas on Metal Catalysts)

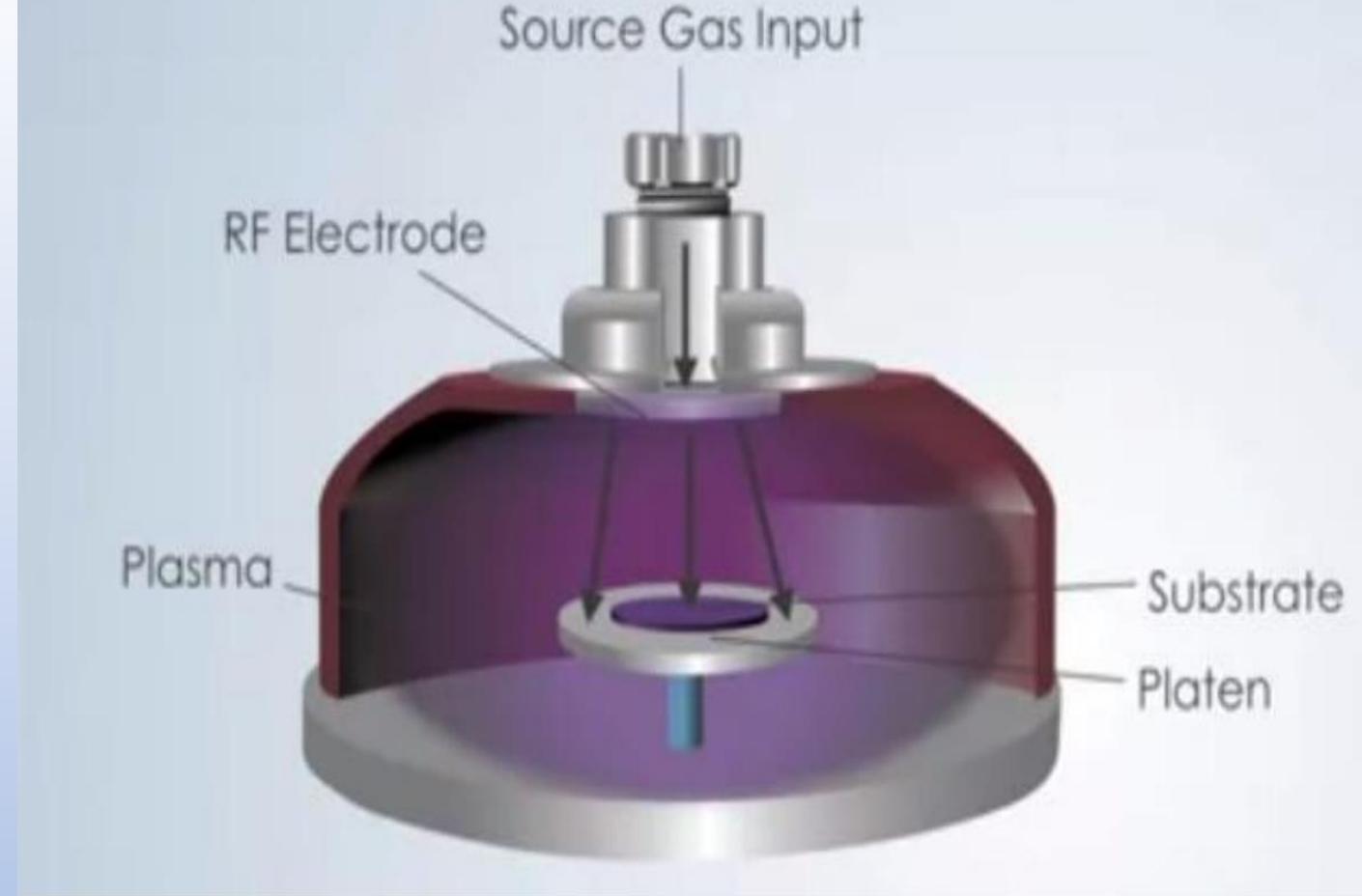
- Quartz tube enclosed in a furnace
- Acetylene (C_2H_2) or ethylene (C_2H_4) gas
- **Fe, Ni or Co** Nanoparticles as catalyst
- **Temperature** range: 500-900 °C



MWNTs diameters determined by the sizes of the metal particles

B) Plasma Enhanced Chemical Vapor Deposition

- Source of energy: plasma
- RF- Electrode generates a plasma
- Voltage applied to ionize gas molecules
- Molecules became chemically reactive
- Formation of a thin layer on the substrate
- Substrate (that cannot tolerate high temperatures)



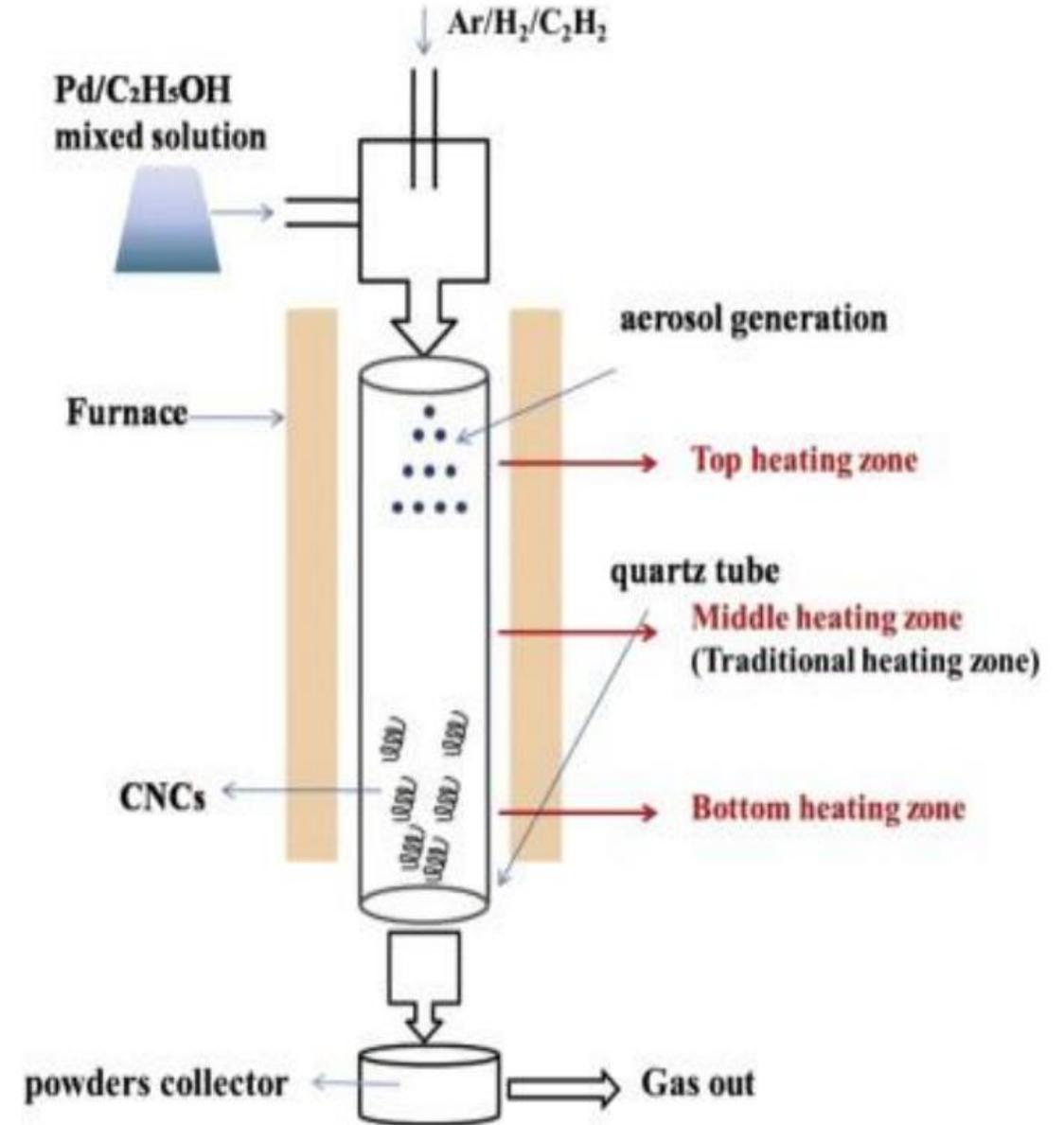
Technique for the selective vertical alignment of CNTs
(application in flat displays)

C) Catalytic Pyrolysis of Hydrocarbon

- Inject organometallic precursors
- Sublimation of precursor
- Formation catalyst nanoparticles in situ

DOUBLE STAGE FURNACE at different temperatures:

- 1) Sublimation of Organometallic compound
- 2) Nanotubes growth



Electrical Arc-Discharge (AD)	Laser Ablation (LA)
PROS	PROS
<ul style="list-style-type: none"> - Produces CNTs with the highest crystallinity and lowest structural defect density. 	<ul style="list-style-type: none"> - Achieves highly uniform SWNTs with a narrow diameter distribution.
<ul style="list-style-type: none"> - High product purity (95%) and production rates (>45 g/h) are achievable under controlled temperatures (600 C^). 	<ul style="list-style-type: none"> - Relatively high yield of quality product.
<ul style="list-style-type: none"> - Can avoid metal catalyst usage for MWNT synthesis. 	<ul style="list-style-type: none"> - Conditions are highly controlled and reproducible (e.g., dual laser method).
CONS	CONS
<ul style="list-style-type: none"> - Extremely high temperature requirement (>3000 C^) makes large-scale processing difficult. 	<ul style="list-style-type: none"> - Economically expensive due to the requirement for high-power lasers.
<ul style="list-style-type: none"> - Produces numerous initial impurities (soot, metal particles, fullerenes) requiring extensive and complex purification. 	<ul style="list-style-type: none"> - Not easily scalable for industrial bulk production.

Chemical Vapor Deposition (CVD)	Key Differentiators & Summary
PROS	QUALITY (Crystal Structure):
- Most suitable for large-scale production and industrial upscaling.	AD > LA >> CVD (CVD trades quality for scale due to lower temperatures).
- Cheapest and most practical method, utilizing common gas feedstocks like methane/acetylene.	SCALABILITY & COST:
- Operates at lower temperatures (500-1200 C^).	CVD >> AD > LA (CVD is the winner for mass production at the ton scale).
- Allows for controlled alignment (aligned arrays/forests) on substrates and targeted chirality growth with solid catalysts.	CONTROL FOCUS:
CONS	- LA offers the best control over diameter distribution/uniformity.
- Synthesized CNTs often contain more structural defects and amorphous carbon.	- CVD offers the best control over orientation (aligned films) and spatial placement on substrates.
- Requires essential post-synthesis purification to remove catalyst particles.	Final Verdict: The synthesis goal (quality vs. cost) dictates the method used.