Module VII: Fullerene, carbon nanotubes, and graphene

Course: CSO203
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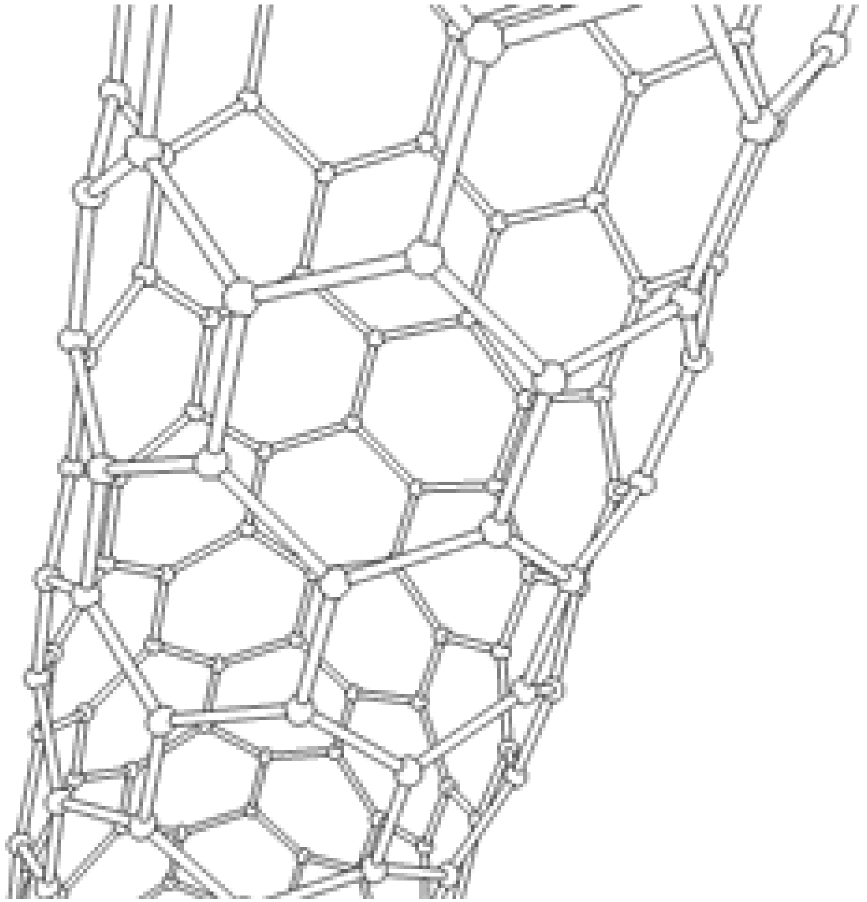
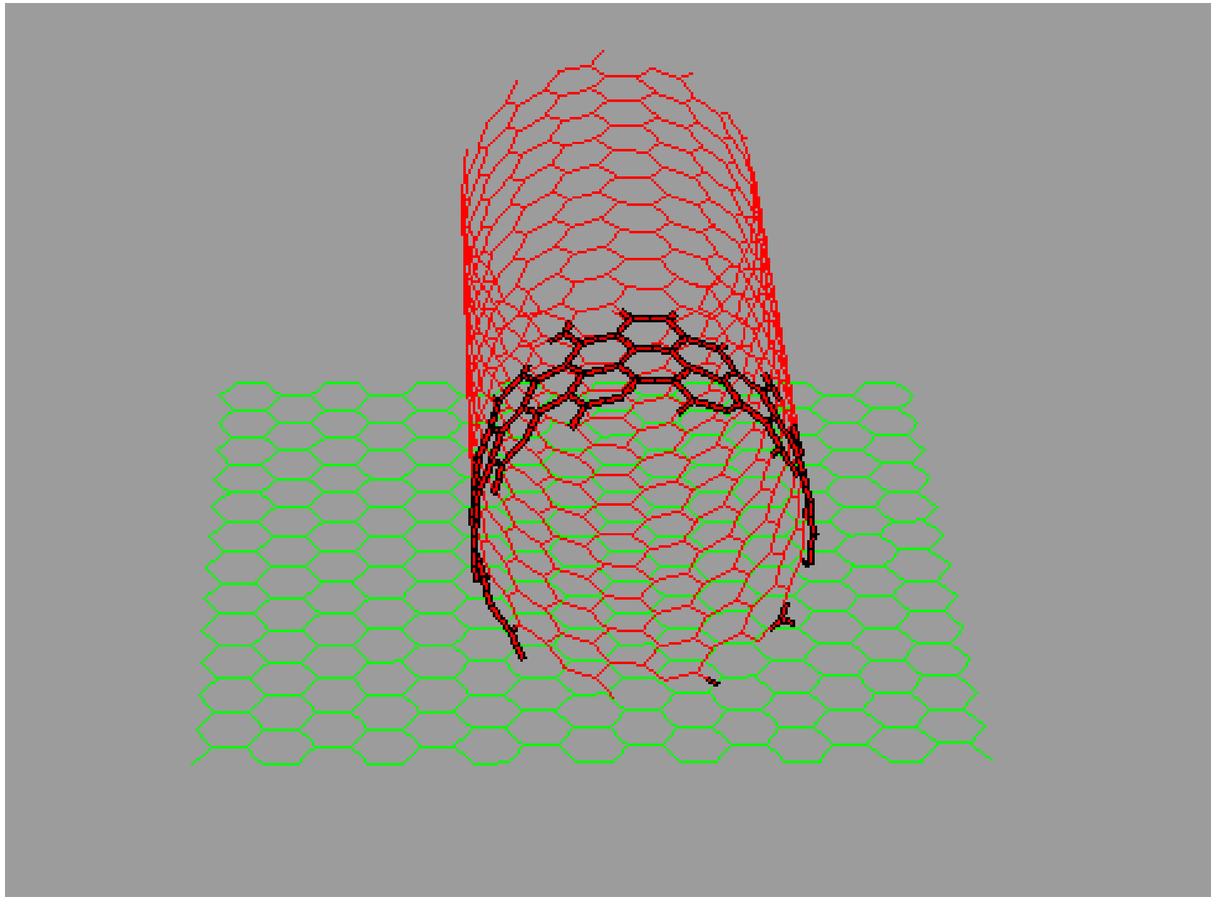
Carbon nanotubes





Carbon nanotubes

A **carbon nanotube, known as CNT,** is a tube made of carbon.

The diameter of the CNT is in the nanometre range (< 100 nm).

CNTs are one of the allotropes of carbon.

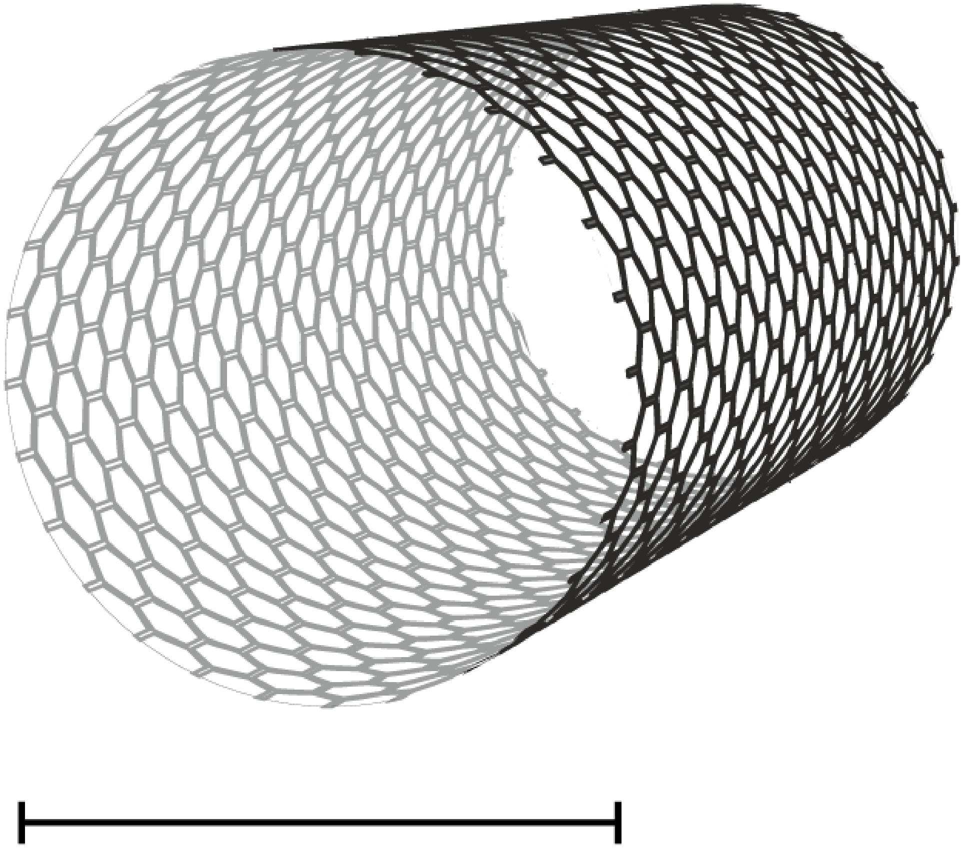
CNTs are classified into two:

(i) **<u>Single-walled carbon nanotubes (SWCNTs):</u>** It has a diameter in the range of 0.5–2.0 nanometres. SWCNTs are built of a single cylindrical layer of carbon atoms. It’s 100,000 times smaller than the width of a human hair.

(i) **<u>Multi-walled carbon nanotubes (MWCNTs):</u>** They consist of nested single-wall carbon nanotubes in a nested, tube-in-tube structure. The diameter of MWCNTs is larger than that of SWCNTs. For example, double- and triple-walled carbon nanotubes.

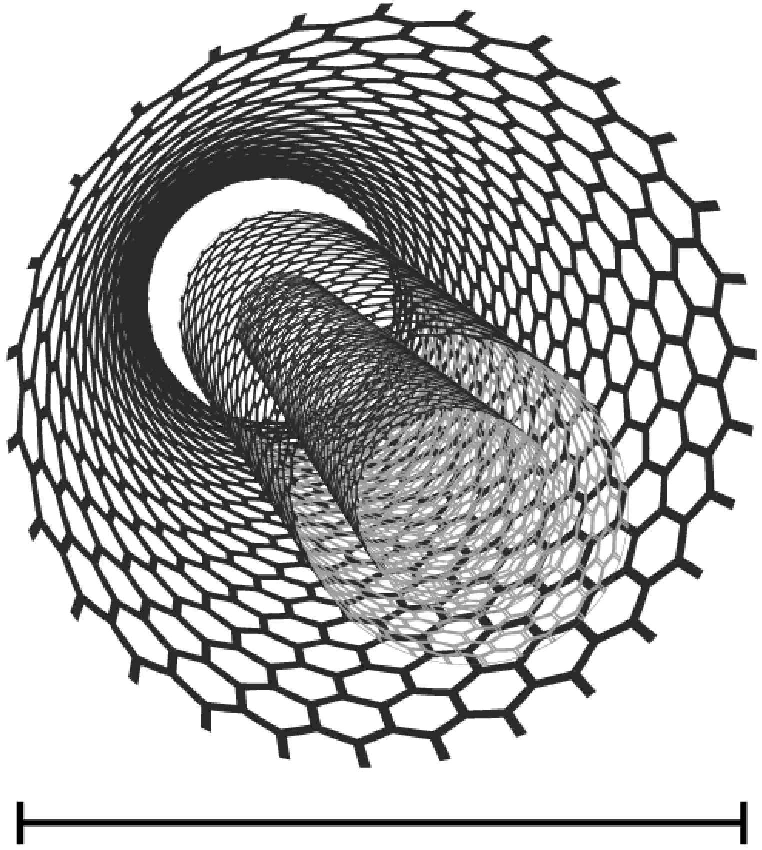
SWCNT & MWCNT

SWCNT



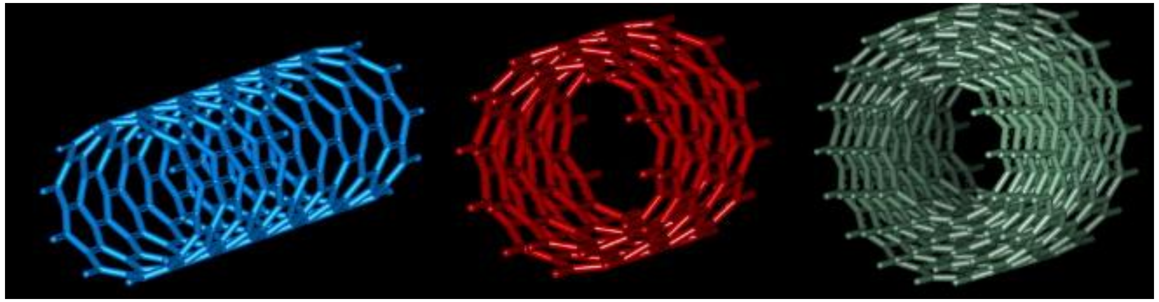
0.5–2.5 nm

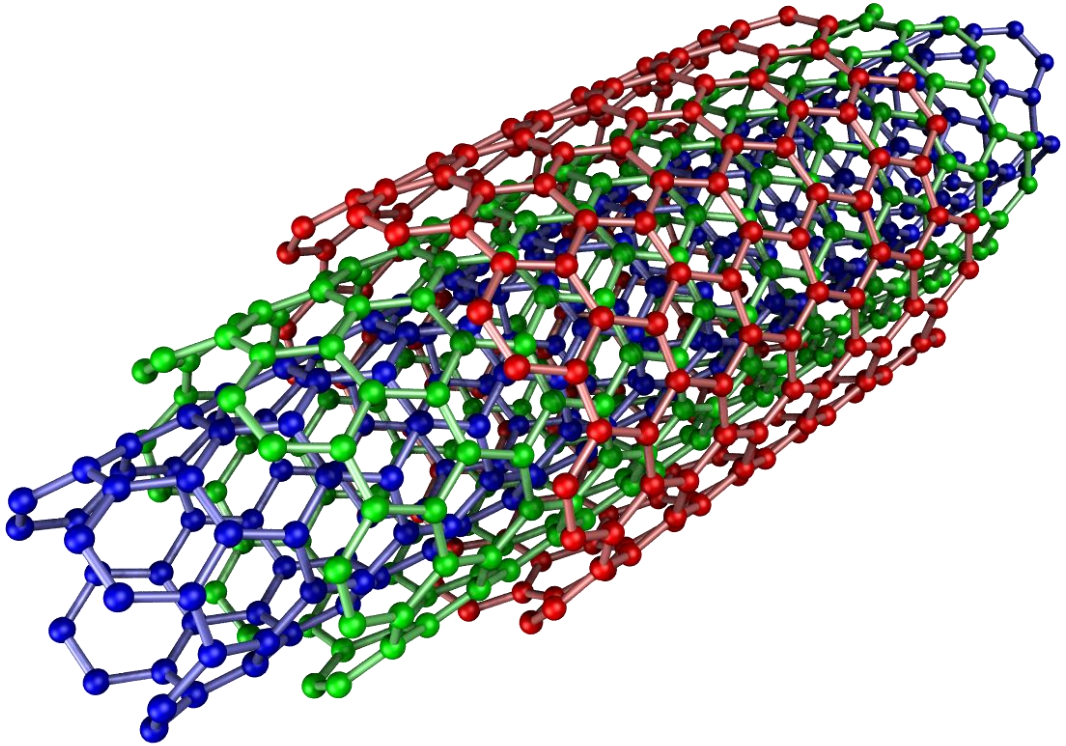
MWCNT



7–100 nm

Triple-walled CNT

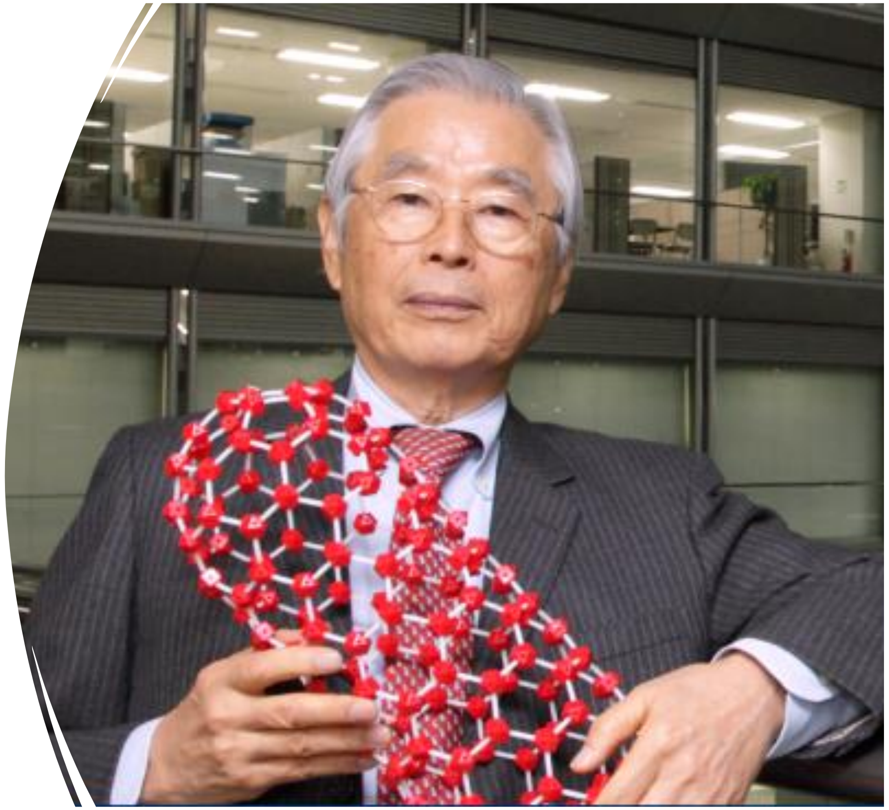




Discovery of CNT

Sumio Iijima, a Japanese physicist and inventor, is often cited for his discovery of **carbon nanotubes**.

Although carbon nanotubes had been observed before his "invention", Iijima's 1991 paper generated unprecedented interest in the carbon nanostructures and has since fueled intense research in the area of nanotechnology.



Discovery of CNT

LETTERS TO NATURE

Helical microtubules of graphitic carbon

Sumio Iijima

NEC Corporation, Fundamental Research Laboratories, 34 Miyukigaoka, Tsukuba, Ibaraki 305, Japan

THE synthesis of molecular carbon structures in the form of C_{60} and other fullerenes[1] has stimulated intense interest in the structures accessible to graphitic carbon sheets. Here I report the preparation of a new type of finite carbon structure consisting of needle-like tubes. Produced using an arc-discharge evaporation method similar to that used for fullerene synthesis, the needles grow at the negative end of the electrode used for the arc discharge. Electron microscopy reveals that each needle comprises coaxial tubes of graphitic sheets, ranging in number from 2 up to about 50. On each tube the carbon-atom hexagons are arranged in a helical fashion about the needle axis. The helical pitch varies from needle to needle and from tube to tube within a single needle. It appears that this helical structure may aid the growth process. The formation of these needles, ranging from a few to a few tens of nanometres in diameter, suggests that engineering of carbon structures should be possible on scales considerably greater than those relevant to the fullerenes.

Solids of elemental carbon in the sp^2 bonding state can form a variety of graphitic structures. Graphite filaments can be produced, for instance, when amorphous carbon filaments formed by thermal decomposition of hydrocarbon species are subsequently graphitized by heat treatment[2,3]. Graphite filaments can also grow directly from the vapour-phase deposition of carbon[4,5], which also produces soot and other novel structures such as the C_{60} molecule[6–8].

Graphitic carbon needles, ranging from 4 to 30 nm in diameter and up to 1 μm in length, were grown on the negative end of the carbon electrode used in the d.c. arc-discharge evaporation of carbon in an argon-filled vessel (100 torr). The gas pressure was much lower than that reported for the production of thicker

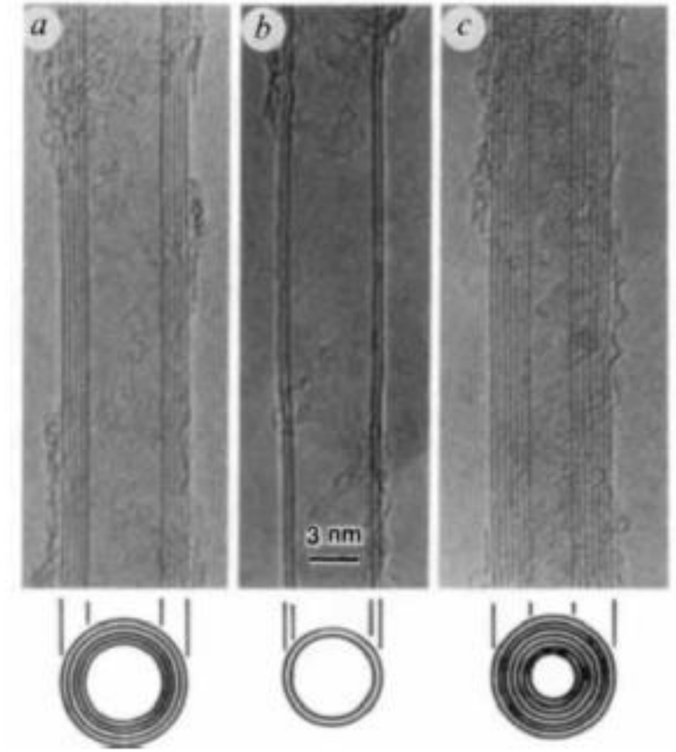
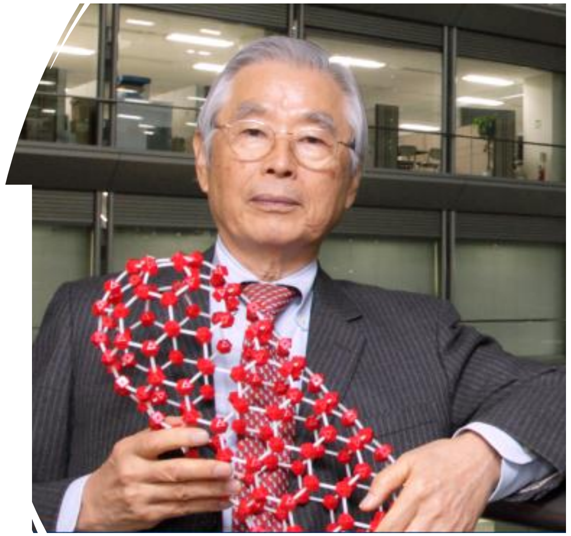


FIG. 1 Electron micrographs of microtubules of graphitic carbon. Parallel dark lines correspond to the (002) lattice images of graphite. A cross-section of each tubule is illustrated. *a*, Tube consisting of five graphitic sheets, diameter 6.7 nm. *b*, Two-sheet tube, diameter 5.5 nm. *c*, Seven-sheet tube, diameter 6.5 nm, which has the smallest hollow diameter (2.2 nm).



Salient features of CNT

- Carbon nanotube (CNT), also known as Bucky tube, is a class of nanomaterials composed, which is of a two-dimensional hexagonal lattice of carbon atoms

- They are bent in one direction and also combined to form a hollow cylinder

- Carbon nanotubes are allotropes of carbon, which are described between Fullerene (0-dimensional) and Graphene (2-dimensional)

Properties of CNT

- **Mechanical Strength**
  Carbon nanotubes can handle enormous tensile loads and outperform steel by a wide margin while staying extremely light

- **Low Density**
  They pack serious strength without the weight, which is why they are made from advanced composites

- **Electrical Behavior**
  Their electrical conductivity shifts depending on how the tube is rolled, allowing them to behave like metals or semiconductors

Properties of CNT

- **Thermal Conductivity**
  Heat flows along their length with remarkable efficiency, making them useful in heat-management applications

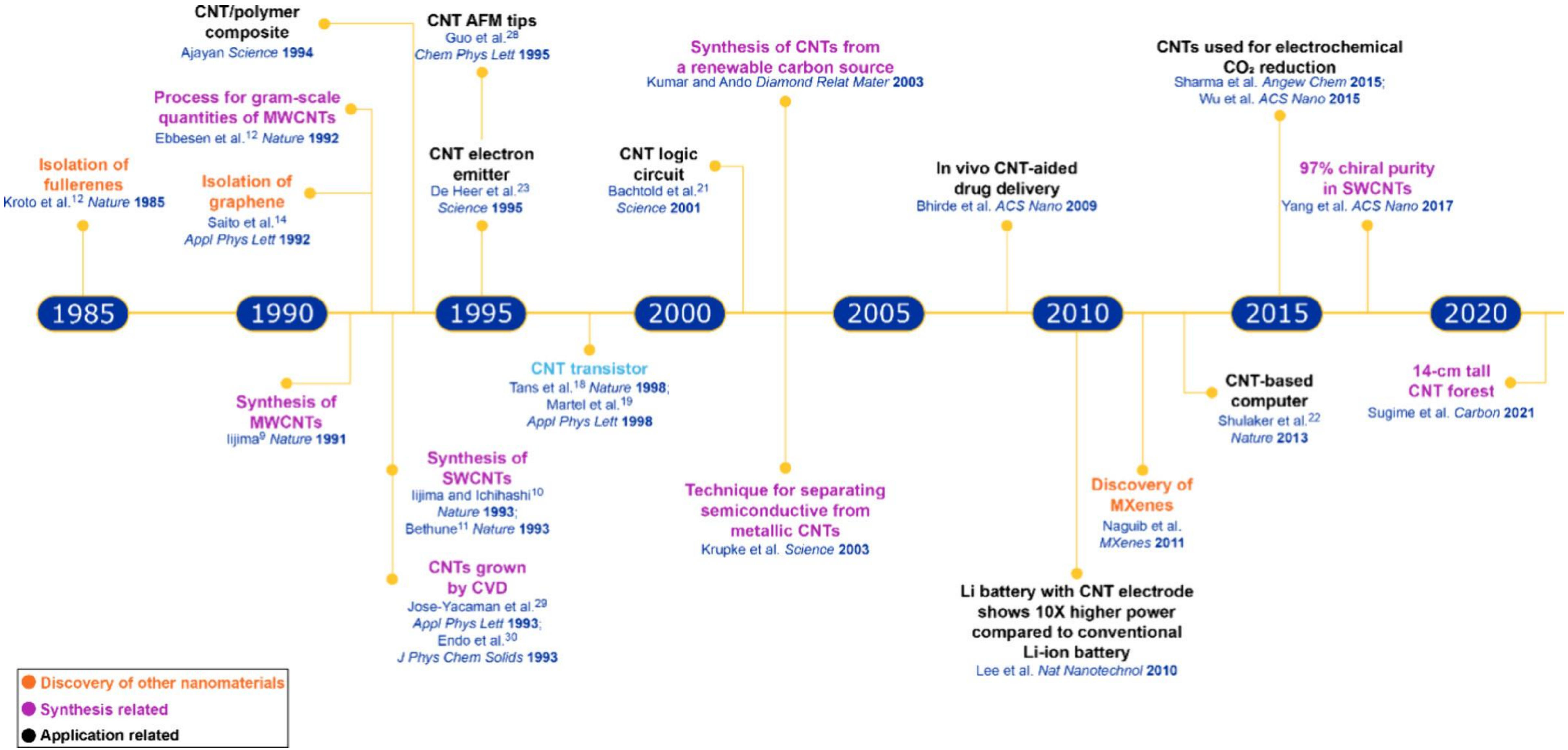
- **Chemical Stability**
  They resist most chemical reactions, which keeps them durable. Upon surface functionalization, they undergo chemical reactions.

- **High Surface Area**
  Their structure provides a large reactive or adsorptive surface area packed into a small footprint

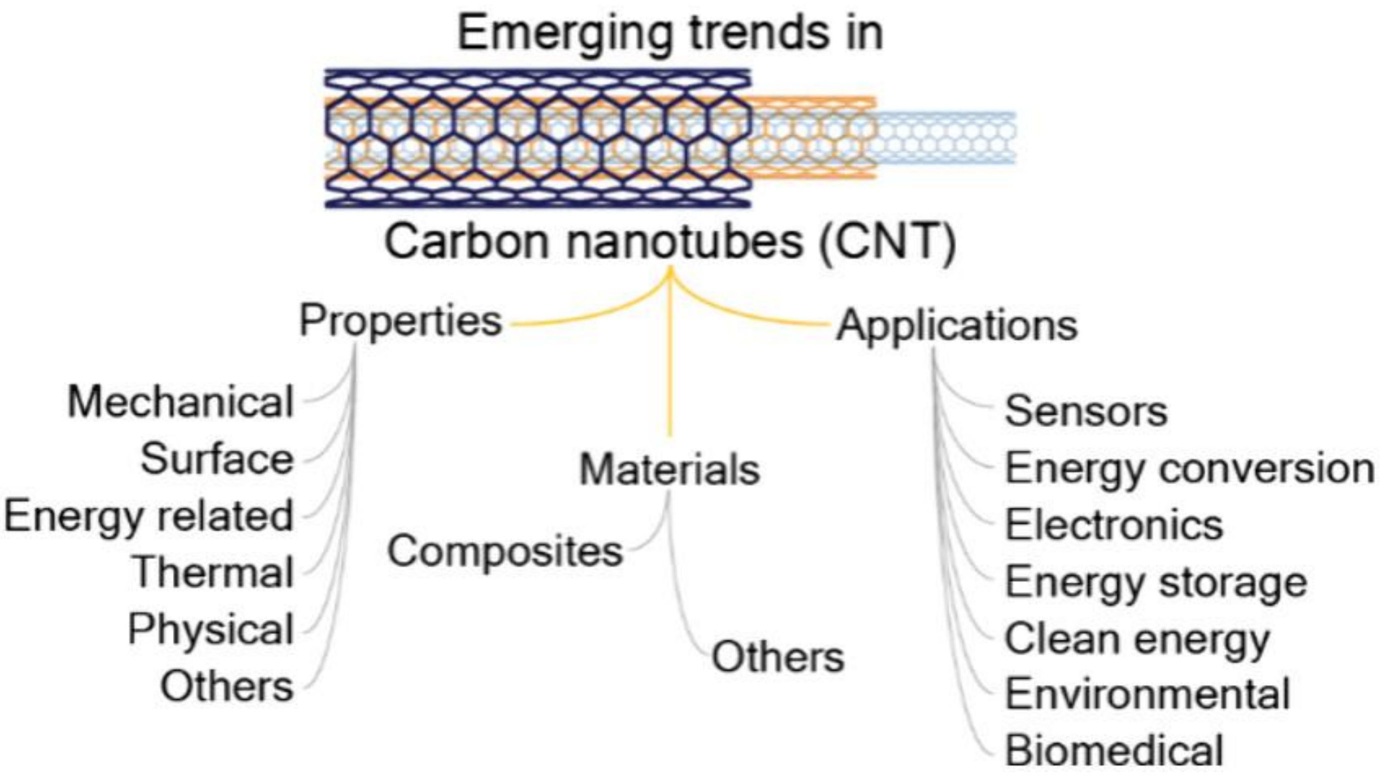
Preparation of CNT

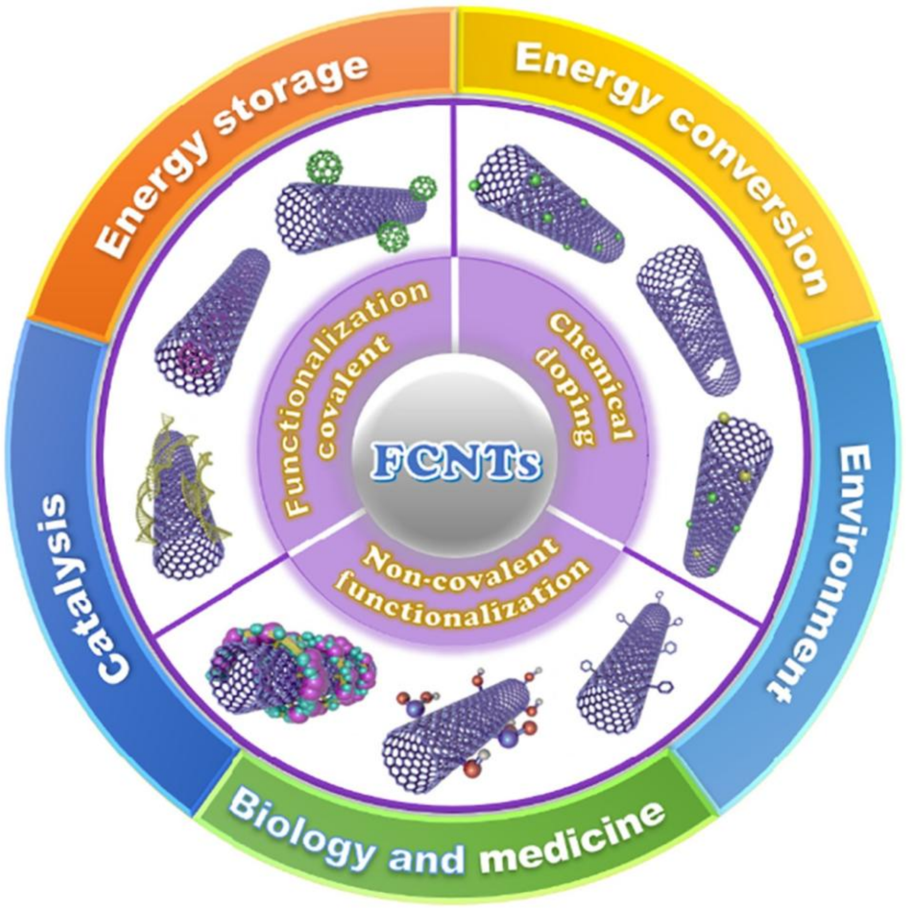
Method	Are Discharge	Laser Ablation	Chemical Vapor Deposition
Description	Arc evaporation of graphite in the presence of inert gas; CNT formed; CNT formed on electrodes during quenching	Vaporization of graphite target by laser; CNT formed on receiver during quenching.	Decomposition of hydrocarbons over transition metal catalyst to form CNT.
Operating Temperature	>3000 °C	>3000 °C	<1200 °C
Operating Pressure	50-7600 Torr generally under vacuum	200-750 Torr generally under vacuum	760-7600 Torr
Advantages	Good quality	Good quality; single conformation SWNT formed;	Easy scale up; it is possible to synthesis on templates;
Disadvantages	Difficult to scale it up	Difficult to scale it up; expensive	Quality is not that good

Applications of CNT



Applications of CNT

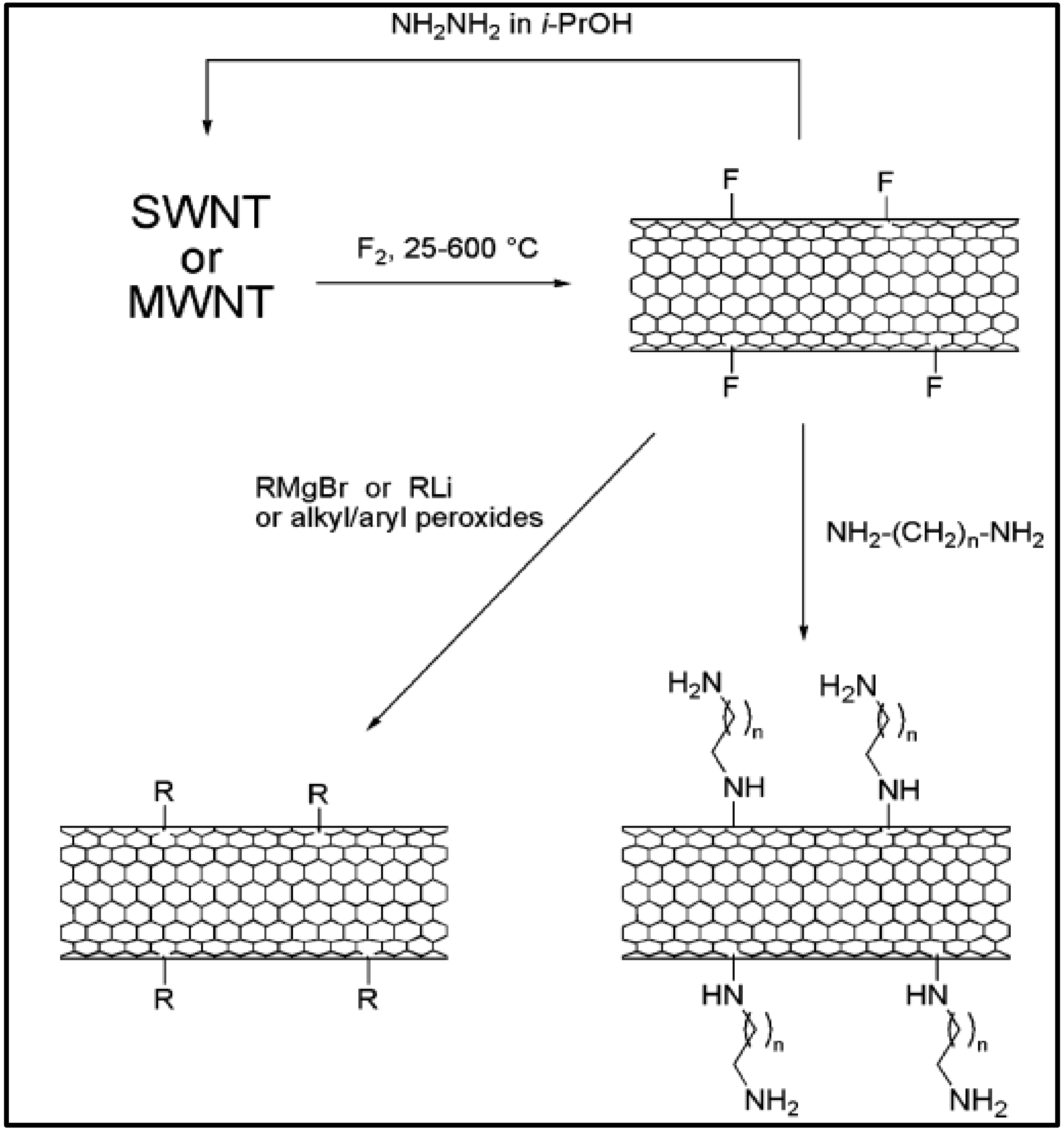




Trends in Chemistry

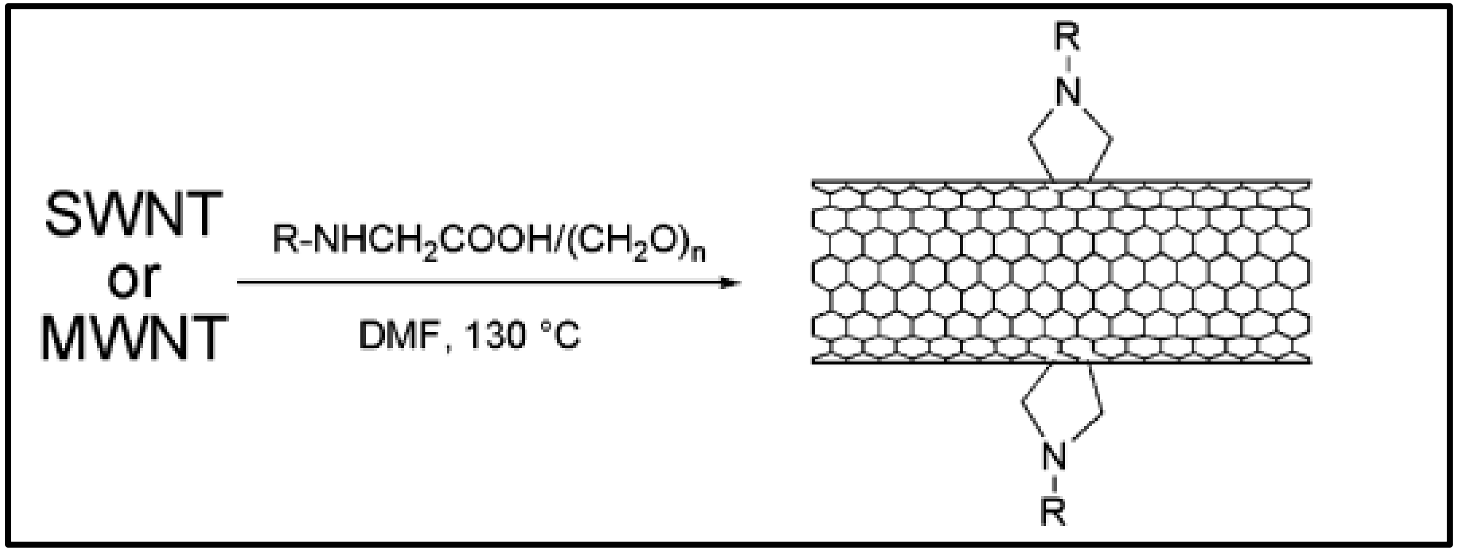
Fluorination of CNT

- Several diamines or diols were reported to react with fluoro nanotubes via nucleophilic substitution reactions
- Because of the presence of terminal amino groups, the amino alkylated CNT is soluble in diluted acids and water
- In addition, primary amines can be employed to further bind various biomolecules to the sidewalls of CNT for biological applications



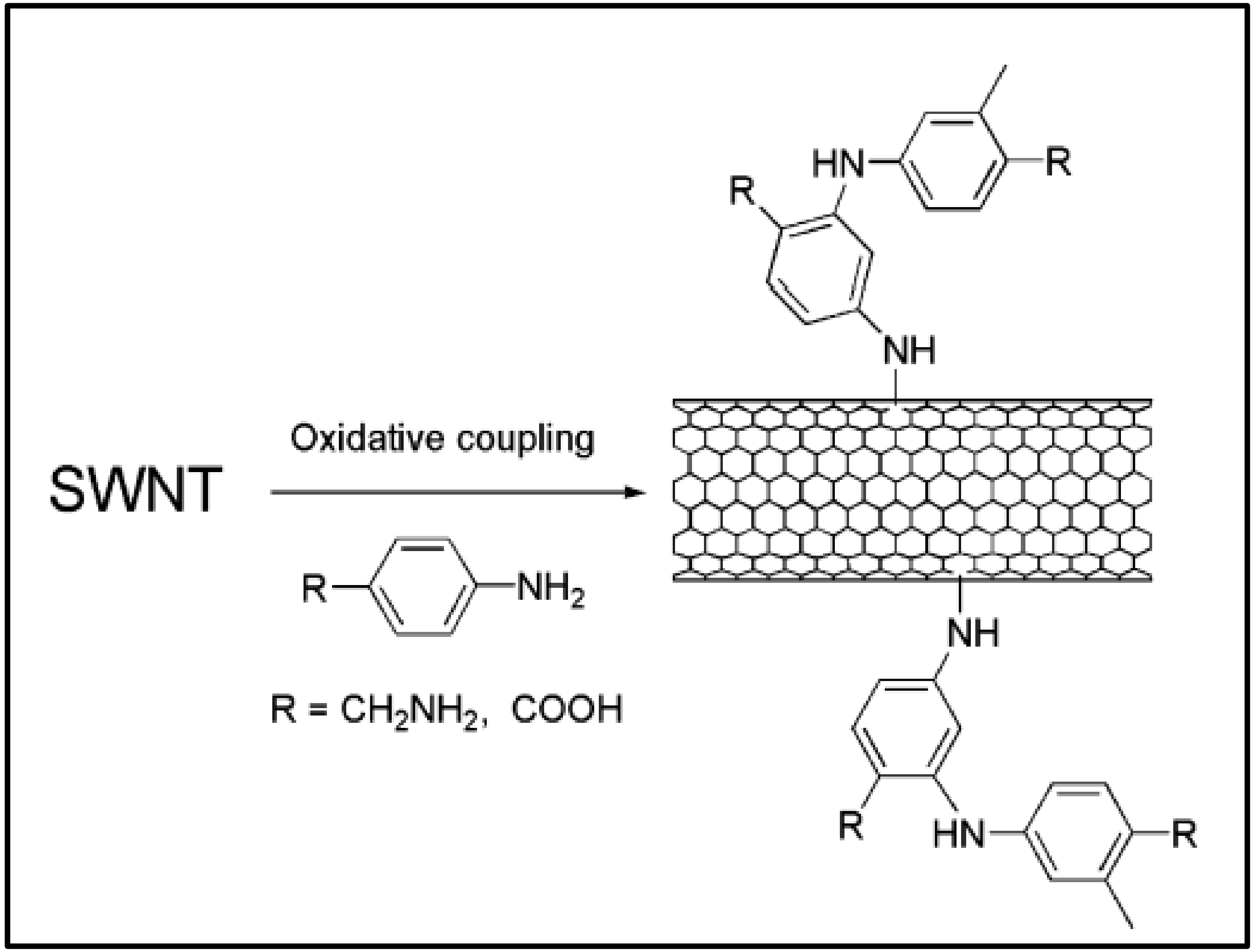
1,3 cycloaddition of CNT

- **A simple method for obtaining soluble CNT was developed. The azomethine ylides, thermally generated in situ by condensation of an R-amino acid and an aldehyde, were successfully added to the graphitic surface via a 1,3-dipolar cycloaddition reaction, forming pyrrolidine-fused rings**

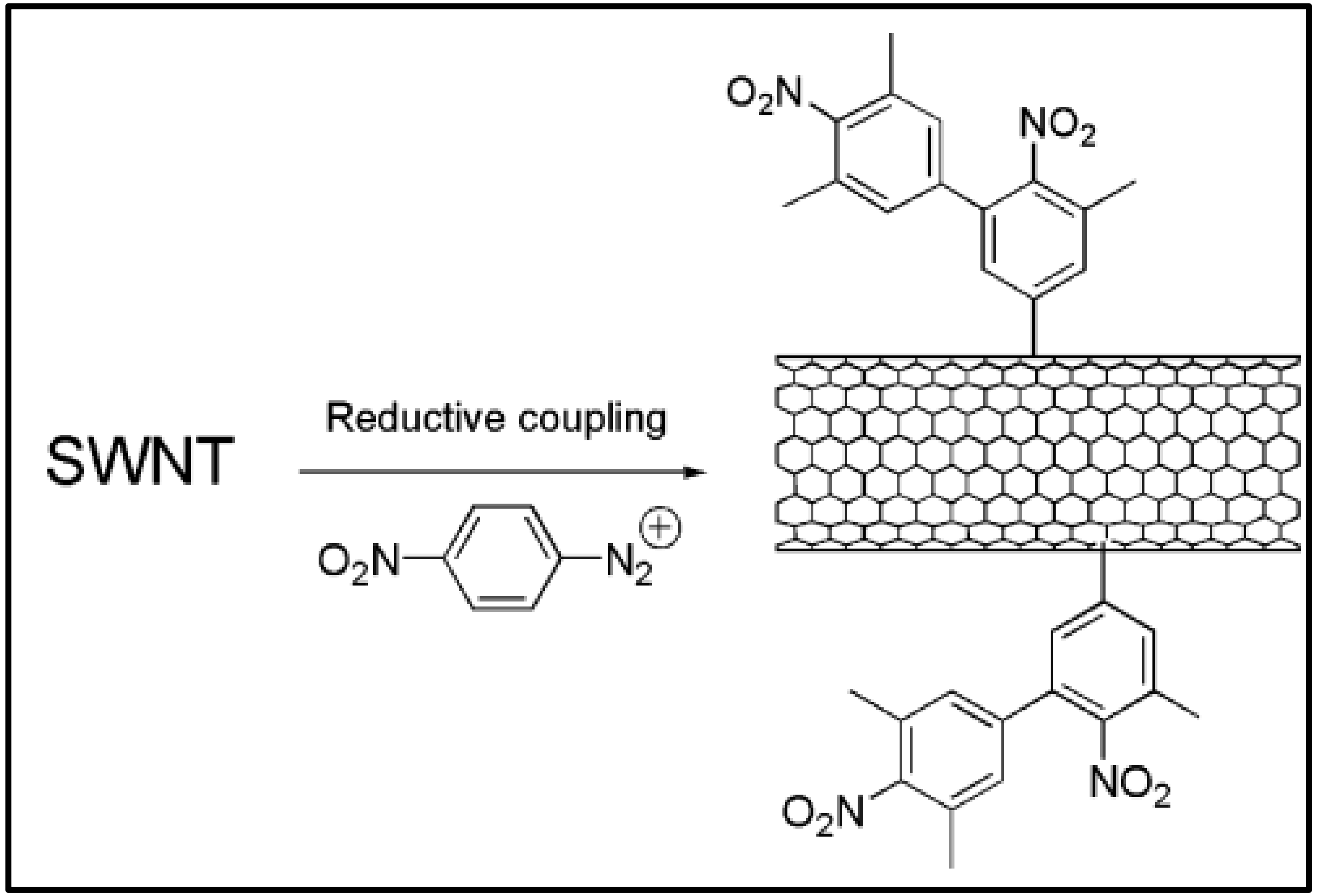


1,3-Dipolar cycloaddition of azomethine ylides

Oxidative coupling of CNT



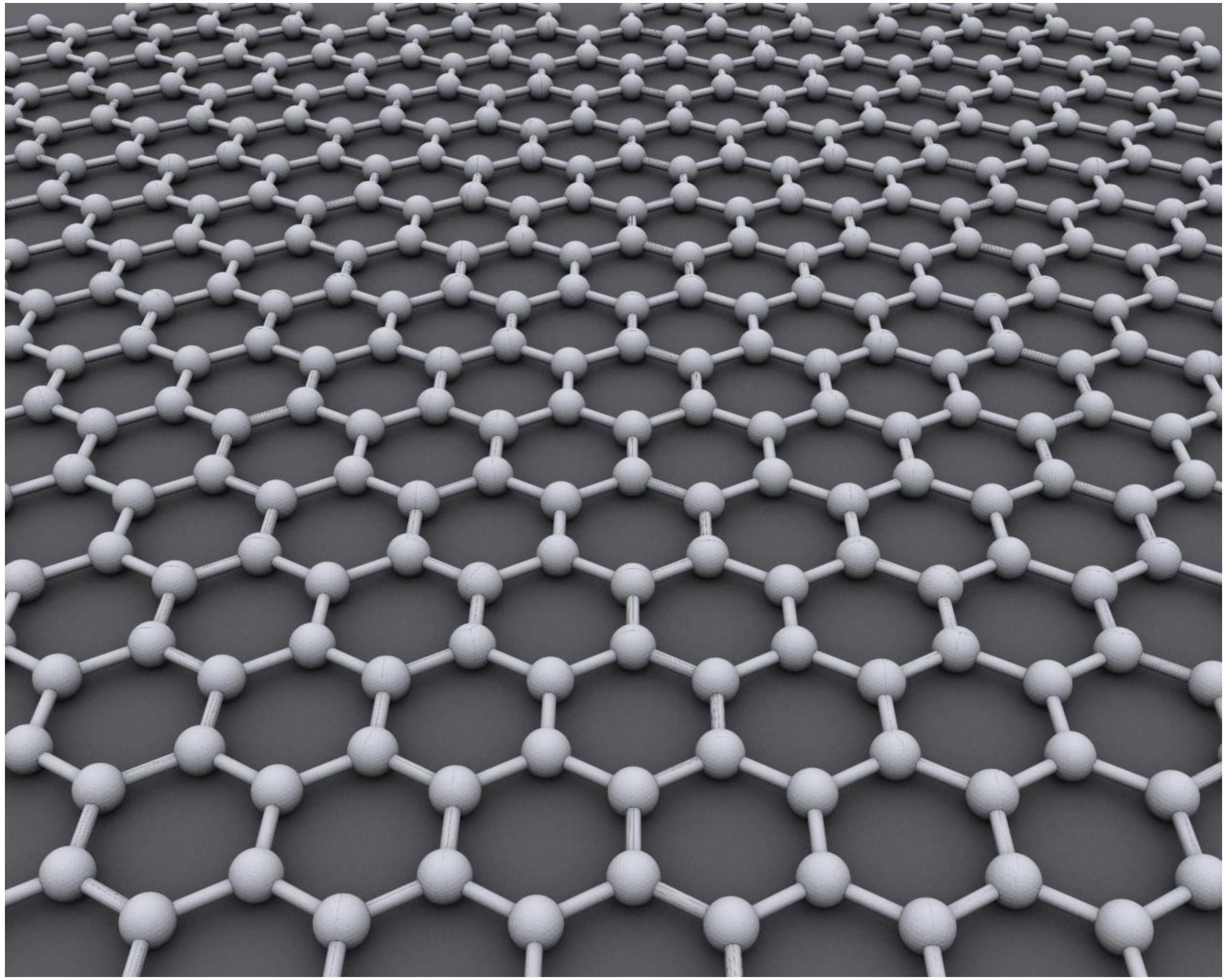
Chemical or electrochemical grafting on CNT



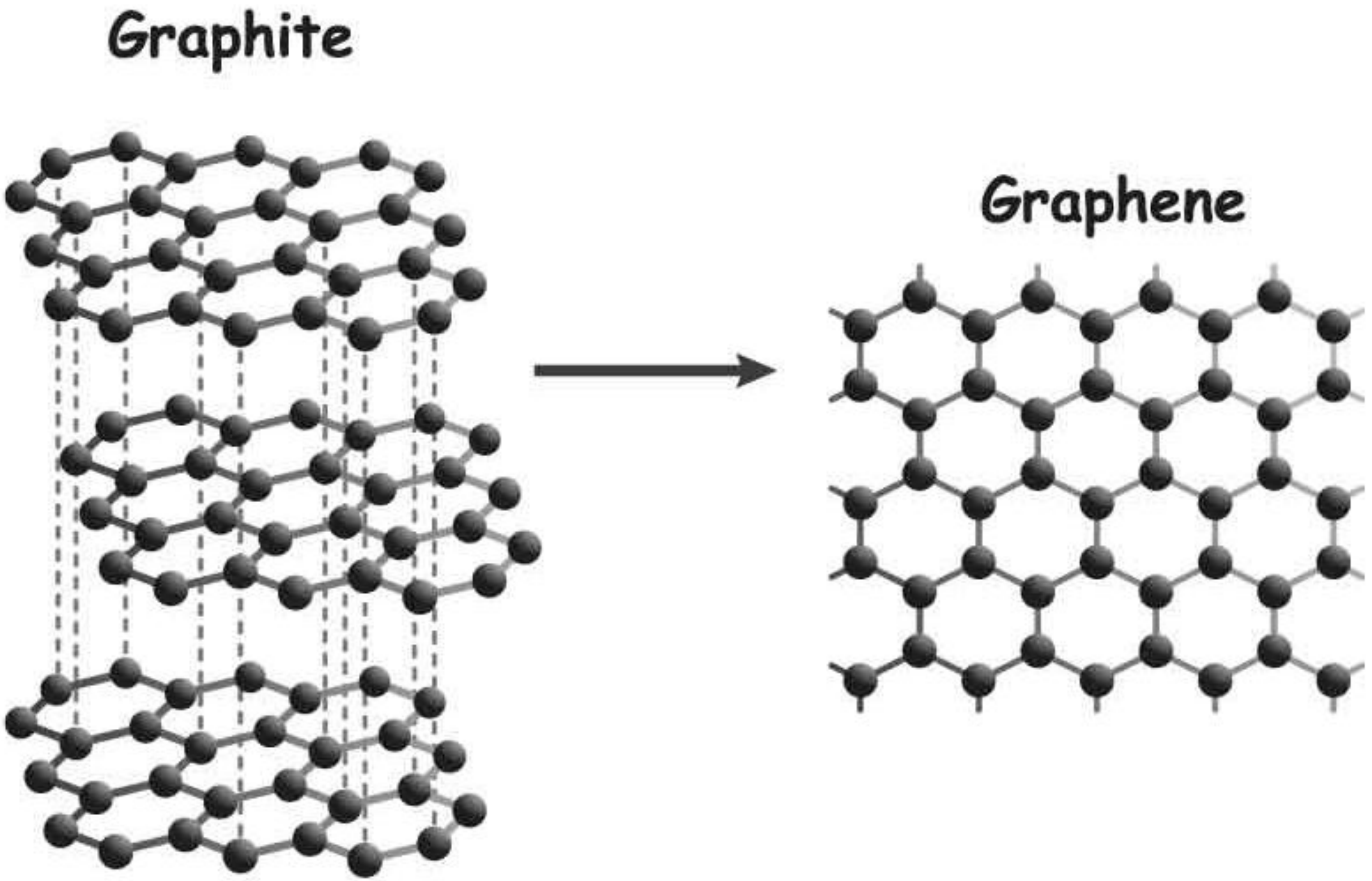
- **Electrochemical functionalization by oxidative coupling resulting in C-C bond formation**

- **Reductive coupling of aryl diazonium salts reaction resulted in a C-C bond formation at the graphitic surface**

Discovery of graphene



Discovery of graphene



Discovery of graphene

5 October 2010

The Royal Swedish Academy of Sciences has decided to award the Nobel Prize in Physics for 2010 to

Andre Geim
University of Manchester, UK

and

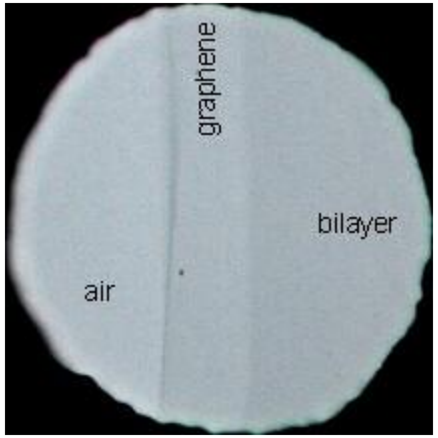
Konstantin Novoselov
University of Manchester, UK

"for groundbreaking experiments regarding the two-dimensional material graphene"

Discovery of graphene

Graphene – the perfect atomic lattice

A thin flake of ordinary carbon, just one atom thick, lies behind this year's Nobel Prize in Physics. Andre Geim and Konstantin Novoselov have shown that carbon in such a flat form has exceptional properties that originate from the remarkable world of quantum physics.



Graphene is a form of carbon. As a material it is completely new – not only the thinnest ever but also the strongest. As a conductor of electricity it performs as well as copper. As a conductor of heat it outperforms all other known materials. It is almost completely transparent, yet so dense that not even helium, the smallest gas atom, can pass through it. Carbon, the basis of all known life on earth, has surprised us once again.

Electrochemical exfoliation of graphene