

Nanocarbons

- Elemental carbon is quite versatile, can be obtained in several forms.
- Until 1985, the known macroscopic allotropes of carbon were ***amorphous, graphite (one of the softest materials), and diamond (one of the hardest materials).***
- ***The precise molecular organization of the carbon can dramatically affect its macroscopic properties.*** In its bulk ***sp³-hybridized solid-state form, it is diamond;*** in its bulk ***sp²-hybridized solid-state form, it is graphite.***
- Over the past four decades, scientists have discovered that ***sp²-hybridized carbon can also form discrete (0D) molecules, one-dimensional (1D) nanoscale tubes, and two-dimensional (2D) nanoscale sheets.***
- The CNMs can be divided into 0D-NMs (i.e., fullerenes, particulate diamonds, and carbon dots), 1D-NMs [i.e., CNTs, CNFs, and diamond nanorods], 2D-NMs (i.e., graphene, graphite sheets, and diamond nanoplatelets), and 3D-NMs [i.e., nanostructured diamond-like carbon (DLC) films, nanocrystalline diamond (NCD) films, and fullerite.
- CNMs composed entirely of sp² bonded graphitic carbon are found in all reduced dimensionalities including fullerenes (0D-NMs), CNTs (1D-NMs), and graphene (2D-NMs).
- Each of these forms of carbon shows very ***interesting properties.***

- Carbon-based nanomaterials with different nanostructures as: Nanodiamonds, Carbon Quantum Dots, Fullerenes Nanostructures, Graphene Nanosheets, Carbon Nanotubes (CNTs), Carbon Nanofibers, etc.

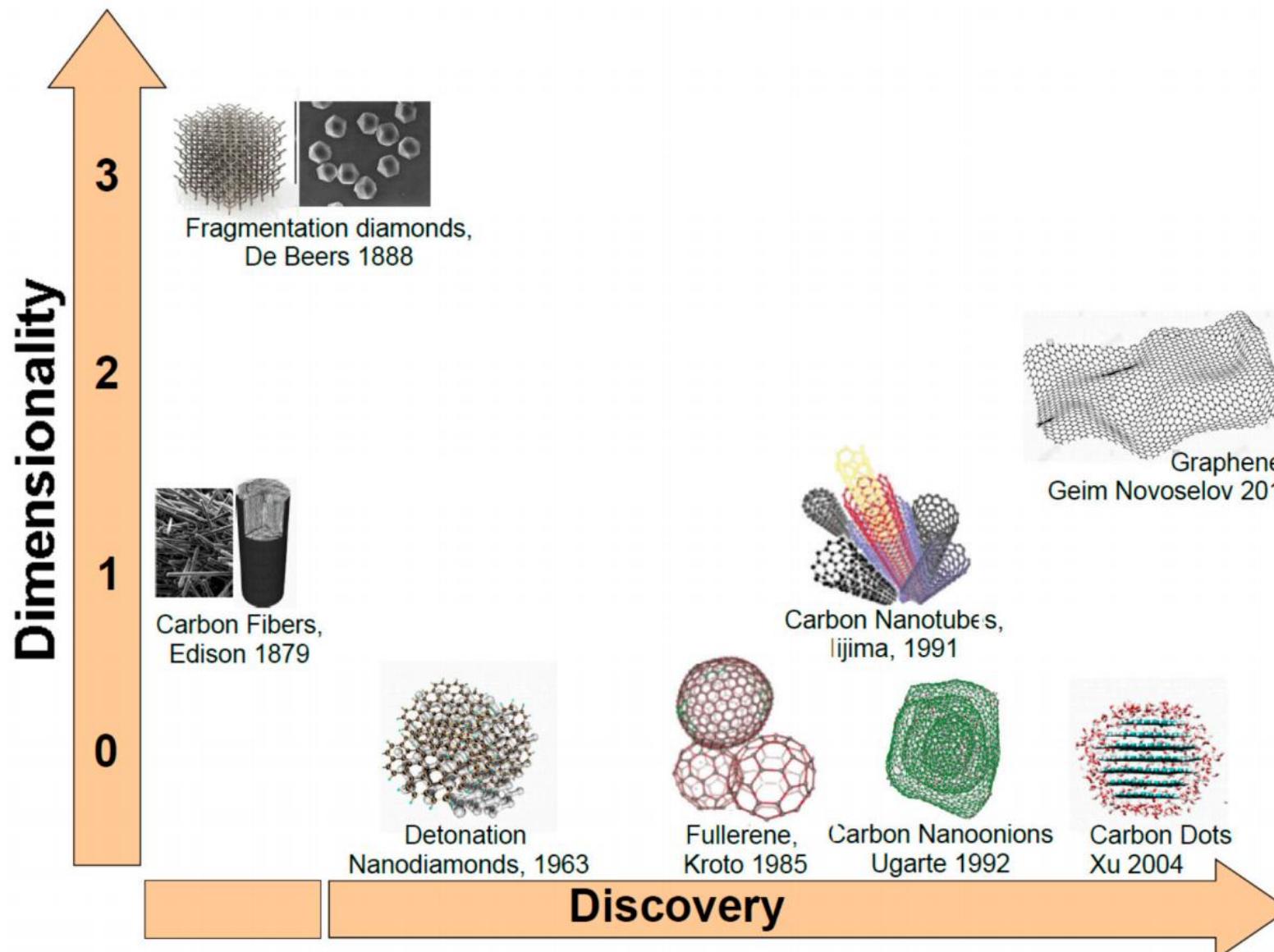


Figure 1. Carbon nanostructures ordered following dimensionality and discovery time.

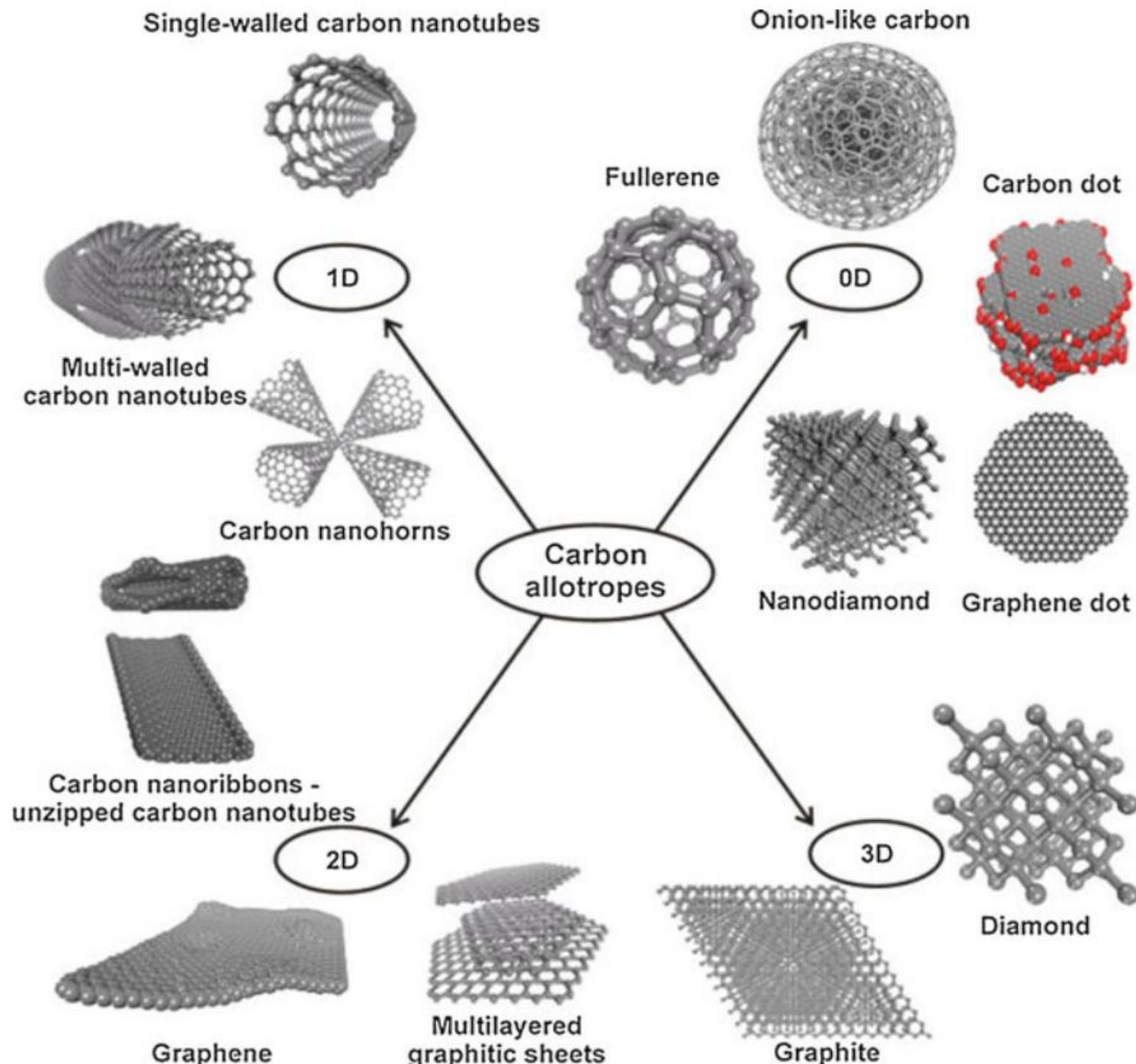
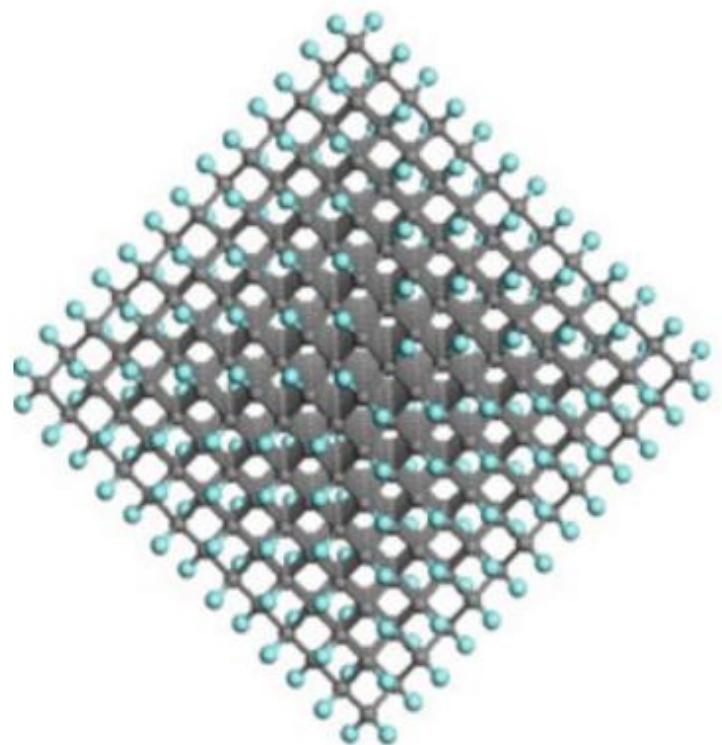
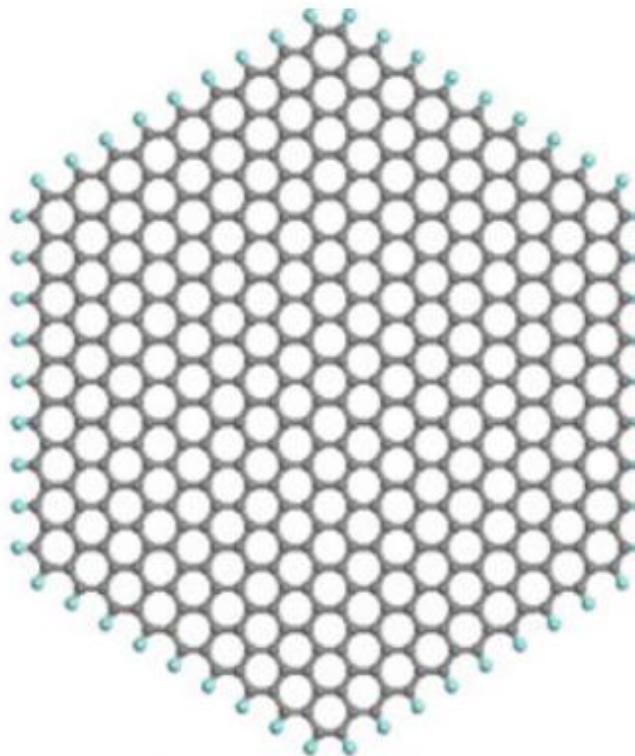


Fig. 1 Different structures carbon nanoallotropes: Carbon dots, nanodiamond, fullerenes, carbon nanotubes, carbon nanohorns, graphene, carbon nanoribbons, and combined superstructures.
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Nanodiamond: $C_{455}H_{196}$



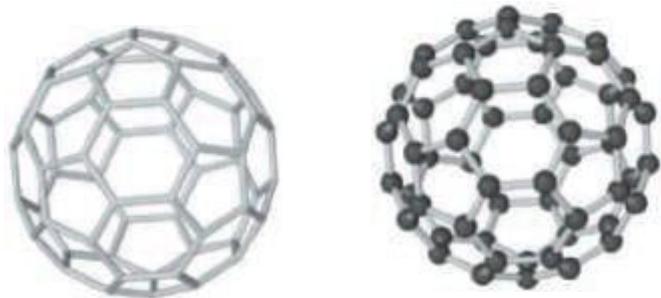
Nanographite: $C_{486}H_{54}$

Fig. 2 Representative atomic structures of the nanodiamond $C_{455}H_{196}$ and nanographite $C_{486}H_{54}$.
Carbon (Gray balls) and hydrogen (Light green balls).
(Copyright 2007, Elsevier)

- As mentioned before, carbon (C) atoms are able to organize themselves in different structures as depicted in Figure 1. When C atoms are arranged in a honeycomb lattice, they form the graphite crystal, a stack of two-dimensional single sheets.
- The single graphite layer constitutes the **graphene** atomic crystal. Graphene nanostructures (GNs) were firstly isolated by the Nobel-prizes Geim and Novoselov in 2010.
- Another carbon-based structure ***is carbon nanotube (CNT)***. Discovered by Iijima in 1991, it may be *regarded* as a single graphene layer rolled along an axis aligned along the graphene crystalline directions.
- Like CNTs, carbon fibers (CFs) are also unidimensional system. However, CFs are disordered, tangled structures possessing a two-dimensional long-range order of C atoms organized in planar hexagonal networks while in the direction orthogonal to these planes, CFs display only a shortrange order due to parallel plane stacking.
- If in unidimensional carbon structures we reduce their length to the nanometer size we will obtain nanocages. **Fullerenes** discovered by Kroto and Smalley in 1985 is a perfectly spherical nanocage formed by a number of pentagonal and hexagonal rings.
- **Carbon nano-onions** (CNOs) are cages with spherical or polyhedral shape formed by several fullerene-like overlapped carbon shells which are defective and disordered to a certain degree. They were discovered in 1992 by Ugarte during electron beam irradiation of an amorphous carbon sample using a TEM microscope.
- Another unidimensional carbon nanostructure (CNS) is represented by the **carbon dots** (CDs). CDs are nanoparticulate where graphitic and amorphous carbon phases coexist. Typically, the average dimension of carbon dots is about 5 nm. Quantum confinement effects induce excellent optical properties as highly tunable photoluminescence (PL), high photostability easy functionalization of their surface and biocompatibility make them good competitor of quantum dots based on toxic chemical elements such as cadmium.

- Another CNS with excellent degree of biocompatibility is the **nanodiamond**. Nanodiamonds (NDs) were discovered in the sixties. Depending on the synthesis process, NDs dimensions are in the 5–100 nm range. In NDs, C atoms are sp^3 hybridized orbitals leading to the formation of the hexagonal or cubic diamond lattices. In the case of diamond, the four bonding electrons produce a tetrahedral charge distribution around each atom and so the atoms come together along these mutual bonds forming a tetrahedral arrangement. The bonds (covalent σ bonds) are strong, giving diamond its extreme hardness.
- Since all the electrons are involved with bonding, they don't interact easily with light, thereby making diamond a good insulator and transparent though impurities and defects can give it an intrinsic color. NDs possess distinctive electronic and optical properties deriving from dopants (N, Si, Ge . . .) present in the structure as defect.

Nanocarbons



Buckminsterfullerene, C_{60} . The molecule has a highly symmetric structure in which the 60 carbon atoms sit at the vertices of a truncated icosahedron. The bottom view shows only the bonds between carbon atoms.

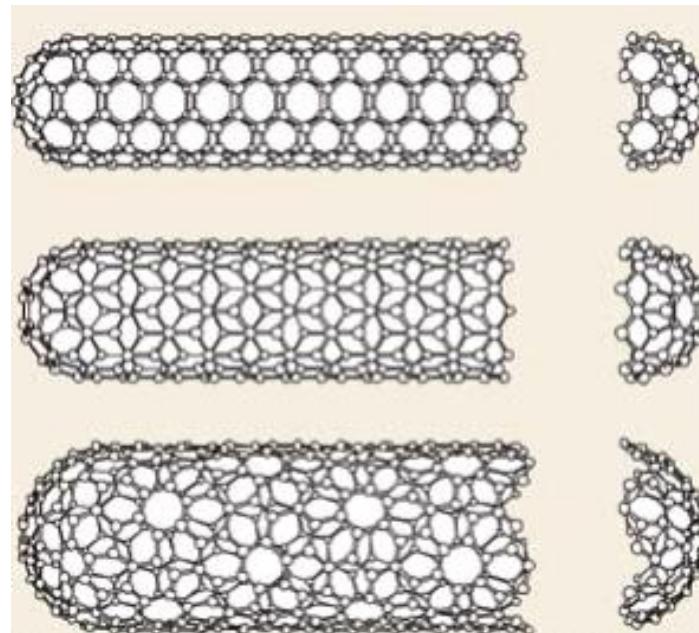


Figure 12.50 Atomic models of **carbon nanotubes (CNTs)**.

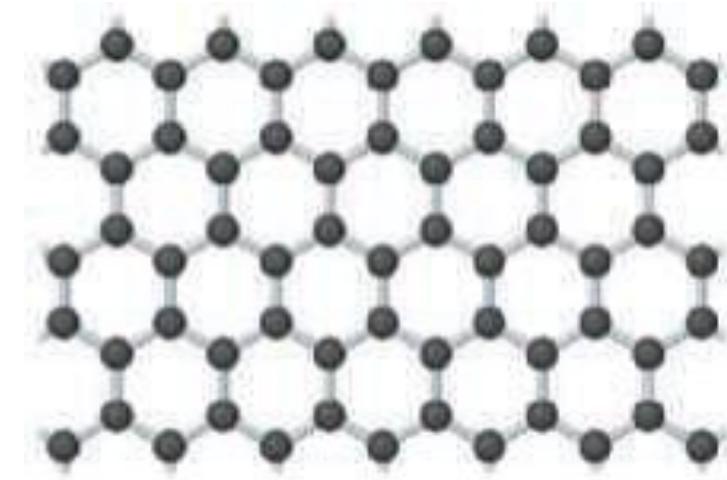


Figure 12.51 A portion of a two-dimensional **graphene** sheet.

❑ Fullerenes

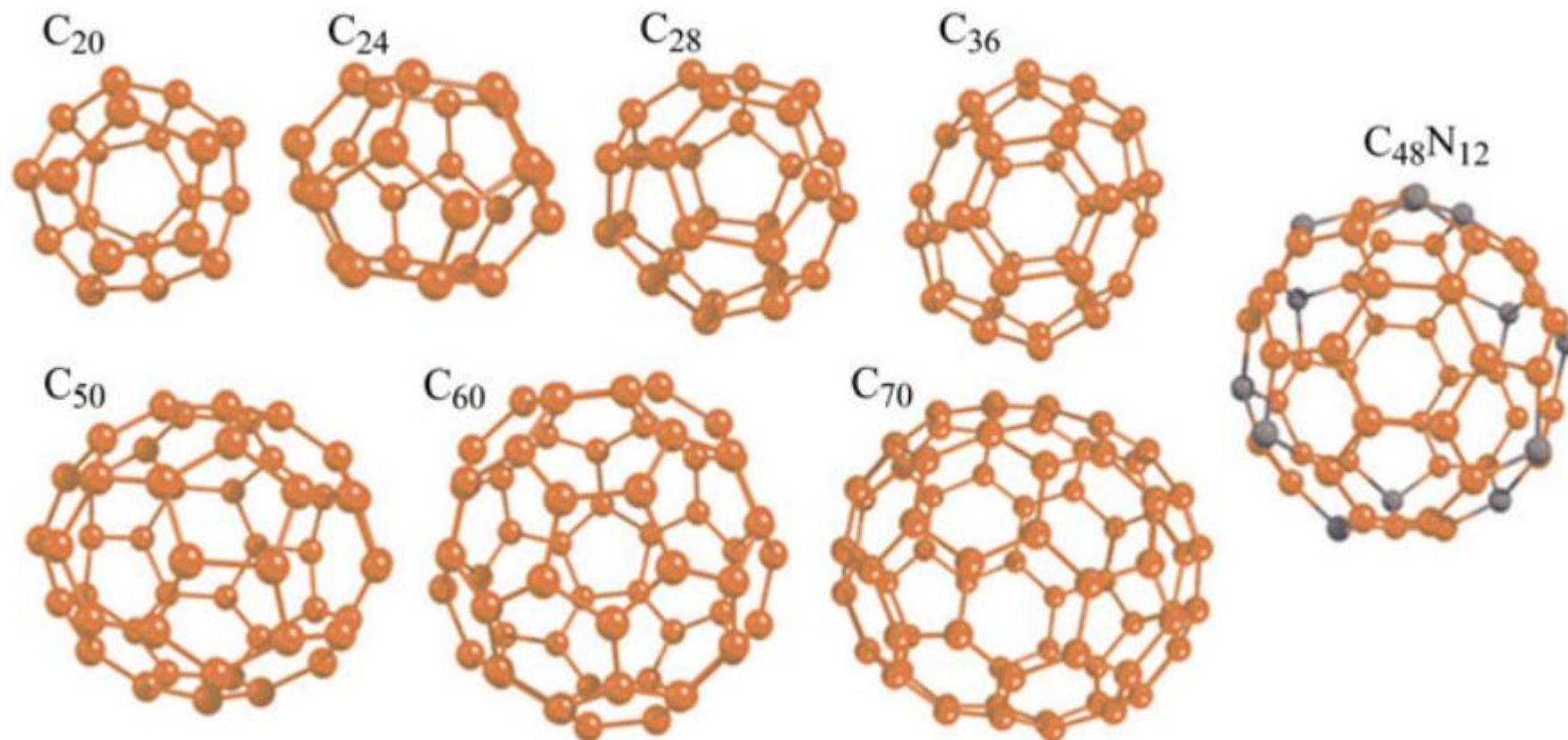


Fig. 3 A broad fullerene family of a range of atomic carbon clusters C_n (n > 20).
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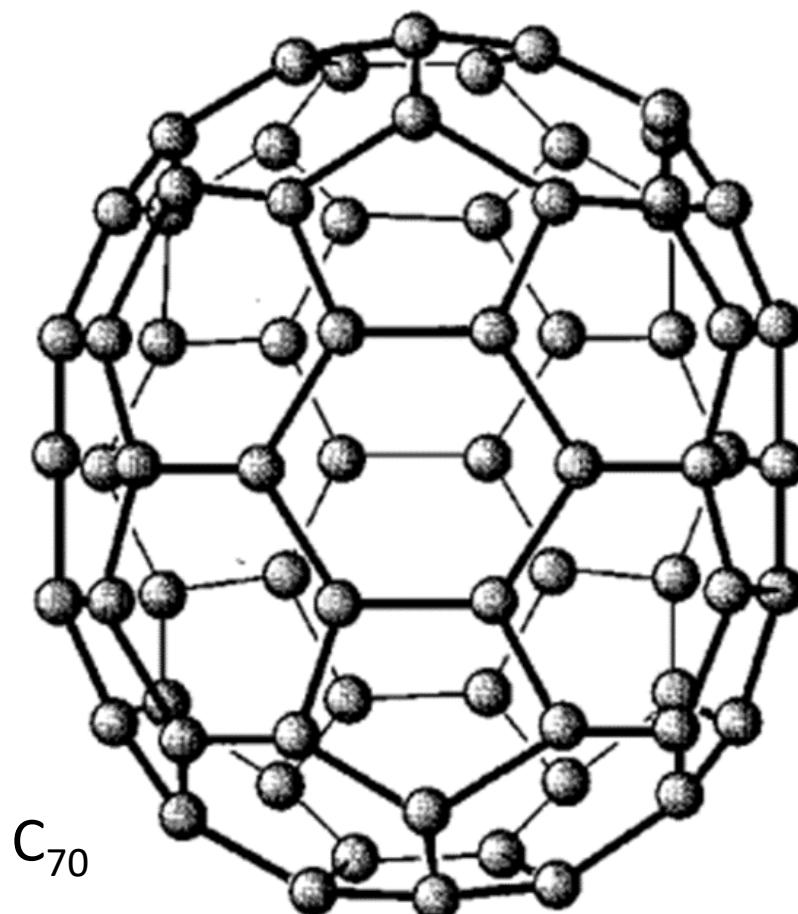
- If *h* (for “hexagons”) is ***the number of 6-membered carbon rings*** in the structure, ***the chemical formula of a fullerene is C_{20 + 2h}***.
- 20 indicates 12 pentagons-closed structure, the smallest fullerene. So larger fullerenes only have extra hexagons! The constant number of pentagons in the fullerene series has been confirmed by shrink-wrapping experiments.

Fullerenes

- A new form of carbon was identified in 1985 by Curl, Smalley, and Kroto who shared the 1996 Nobel Prize in Chemistry for this discovery.
- During experiments in which graphite was vaporized using a laser, new forms of carbon clusters were discovered.
- These clusters were in the form of *fullerenes, closed and convex cage molecules* formed by the *arrangement hexagonal and pentagonal faces*.
- The *most common and most stable carbon cluster* was the **buckminsterfullerene**, named after the architect R. Buckminster Fuller due to the resemblance of the carbon structure between Fuller's geodesic domes.
- This caged cluster is a *60 carbon atoms spheroidal molecule*, resembling a soccer ball in which hexagon carbons are arranged to form ordered closed structure pentagon carbon faces that serve as vertexes. Therefore, another popular name for buckminsterfullerene is **buckyball**.
- *This is in contrast to graphite* which is composed of a two-dimensional flat layer of hexagonal carbon arrangements.
- The C_{60} *Buckminsterfullerene* is the most abundant cluster of carbon atoms found in *carbon soot*. Larger carbon fullerenes that have 70, 76, 84, 90, and 96 carbon atoms were also found to be formed under similar experimental conditions.

- C_{70} is much less dominant than C_{60} . Its structure is similar to that of C_{60} with an extra band of 10 carbon atoms around the waist.
- The other species, with order of magnitude less abundance, are C_{76} , C_{78} , C_{84} , C_{90} , C_{92} , C_{96} , etc. Even smaller closed-cage carbon cluster are possible to obtain including C_{50} , C_{36} , and C_{20} .
- If h (for “hexagons”) is *the number of 6-membered carbon rings* in the structure, *the chemical formula of a fullerene is C_{20+2h}* . Up to large values of h , the fullerenes are found to be very stable as pure carbon-containing molecules. The most stable forms, consistent with the experimentally observed quantities, are those that avoid the strain energy of two adjacent 5-membered rings.
- *The smallest possible fullerene, C_{20} , consisting solely of 12 pentagons*, has been generated from a brominated hydrocarbon, dodecahedrane, by gas-phase debromination. Yet, *the lifetime of the C_{20} was only about 0.4 milliseconds*.

FIG. The structure of the fullerene C_{70}



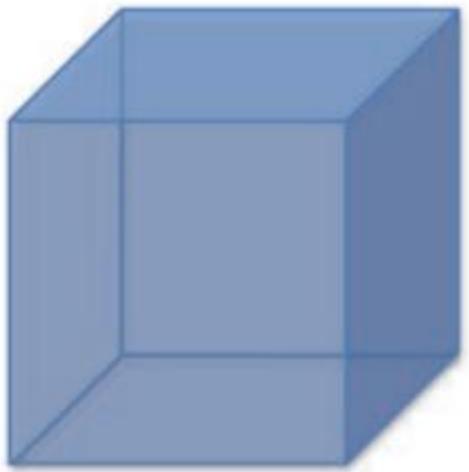
STRUCTURAL SYMMETRY OF THE CLOSED FULLERENES

- **Pentagonal rings** are the key to understanding the structural stability of C_{60} and other closed fullerenes. Examining the molecule closely, we see that it has 20 hexagonal and **12 pentagonal faces**.
- This is a particular member of a general class of polyhedral shapes constructed out of polygons that have engrossed mathematicians since ancient times. The fascination is in forming closed shapes out of polygonal tiles and finding rules for the formation of perfect closure with *no gaps or overlap* of tiles. In 1620, Descartes noticed a general rule connecting the number of **faces**, **edges**, and **corners** in a closed polyhedron that was later proved by Euler in 1752 and has since been known as **Euler's theorem**.
- If we manage to construct **a perfect closed shape with polygonal tiles**, then if **F** denotes **the number of faces** or **tiles**, **E the number of edges**, and **V the number of vertices or corners**, Euler proved that the formula
- $V - E + F = 2$ must be satisfied.
- Figure 3.5 shows a few examples that verify the formula for a cube, a tetrahedron, and a C_{60} molecule.
- **Euler's formula** can be used to determine whether it is possible to form a closed shape out of a given set of tiles. For example, it is easy to prove that it is **not** possible for a hexagonal sheet of graphene to close upon itself and form a spherical structure consisting entirely of hexagons as this goes against the Euler's theorem. If one imagines starting to build the three-dimensional structure with **n** hexagonal tiles brought together along their edges, it is easy to verify that each pair shares an edge ($E = nF/2$) and that each triple form a corner ($V = nF/3$) so that $V - E + F \neq 2$, proving that completing **a closed shape without gaps is impossible** unless one also uses tiles with a different shape. In fact, it was realized by the ancient Greeks that there are **only three polygons that can form closed shapes** on their own—that is, a **square**, a **triangle** and a **pentagon**.
- We can then find out that the **smallest fullerene has 12 pentagonal rings**. (...PROVE IT..)

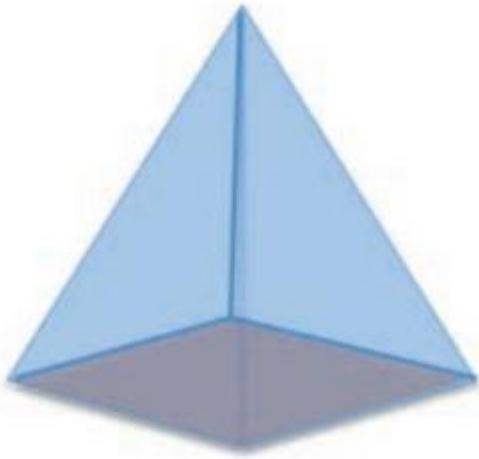
- Remembering that pentagonal rings are strained, as far as carbon bonding is concerned, it is clear that having adjacent pentagons will introduce a great deal of strain and decrease the stability of the molecule. The pentagons must be isolated from each other to minimize the strain. In the case of C_{60} we need to mix pentagonal faces with the hexagonal ones, and here again the power of Euler's theorem comes to the fore.
- ***It can be proved that there are exactly 12 pentagons in the closed cage, irrespective of the number of hexagons*** and carbon atoms; using more hexagons simply makes the cage larger.
- If we then inquire as to which is the smallest fullerene (with 12 pentagonal rings) that can be formed by having no adjacent pentagonal rings, the answer is the C_{60} structure. This elegant combination of chemistry and structural symmetry dictates that the molecule must take this structure.

□ USING EULER'S THEOREM TO PROVE A FULLERENE CAGE CONTAINS 12 PENTAGONS

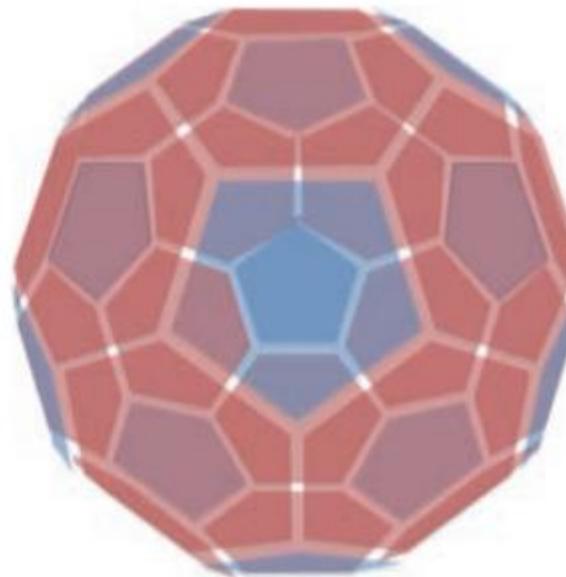
- Assume that fullerene is composed of p pentagons and h hexagons; then the number of faces is $F = p + h$.
- ***Each pair of adjoining tiles shares a single edge***, irrespective of whether the adjoining tiles are hexagons or pentagons, so the ***number of edges in the polyhedron must be half the number of edges*** presented by the isolated tiles; that is, $E = (5p + 6h)/2$.
- Every three edges from the isolated tile set (i.e., irrespective of whether they are shared) defines a single vertex, so $V = (5p + 6h)/3$.
- Thus, applying Euler's theorem gives $(5p + 6h)/3 - (5p + 6h)/2 + p + h = 2$
- that is, $p = 12$.
- Thus, the ***number of hexagons doesn't matter***, but there must be 12 pentagons if the tiling is to form a closed cage.
- 3- or 4-membered C ring structures are avoided as they are not as stable as 5- and 6-membered C rings!



Cube
6 square tiles
 $F = 6, E = 12, V = 8$
 $V - E + F = 2$



Pyramid
4 triangular tiles
1 square tile
 $F = 5, E = 8, V = 5$
 $V - E + F = 2$



C₆₀
12 pentagonal tiles
20 hexagonal tiles
 $F = 32, E = 90, V = 60$
 $V - E + F = 2$

Fig. 3.5 Euler's theorem. Verification of Euler's theorem for a cube, a pyramid and a C₆₀ molecule.

- It may be possible that in the future ways will be found to stabilize these sub-nm structures.
- On the other hand, much larger carbon clusters are also found. Such ***closed-cage structures*** contain hundreds of carbon atoms.
- There were also descriptions of “**carbon onions**” in which for example a C_{20} was placed inside a C_{240} cage which was in turn inside a C_{540} cluster cage.
- ‘**Carbon onions**’ are another form of carbon, related to the fullerenes with giant *nested closed-shell fullerene structures*.

It has been found possible to encapsulate moisture-sensitive materials, such as LaC_2 , inside these giant structures, thereby protecting them from atmospheric moisture.

- *The synthetic procedure for making fullerenes is deceptively simple and essentially involves striking an arc between two graphite electrodes in a low-pressure helium atmosphere.* In this regard it is highly surprising that the fullerenes were not discovered much earlier.

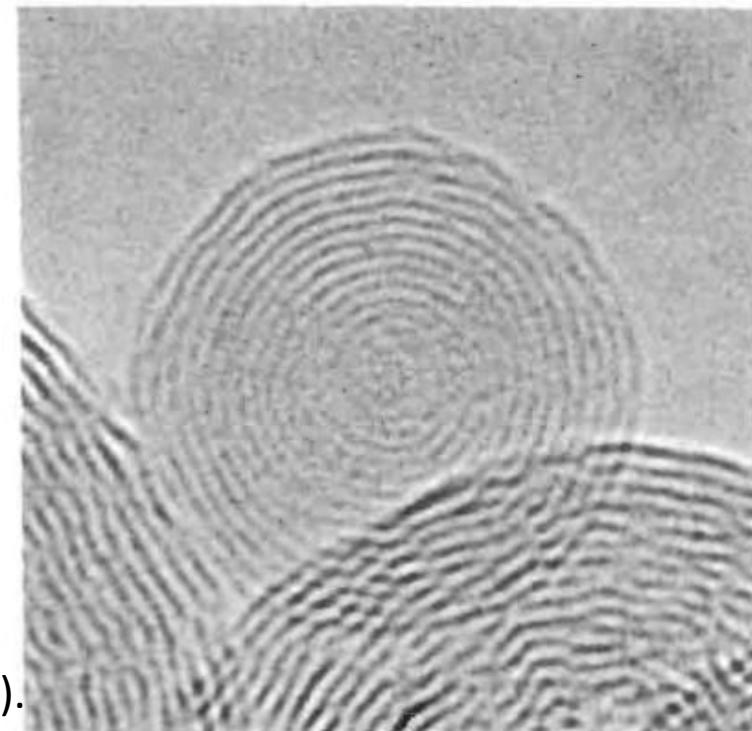
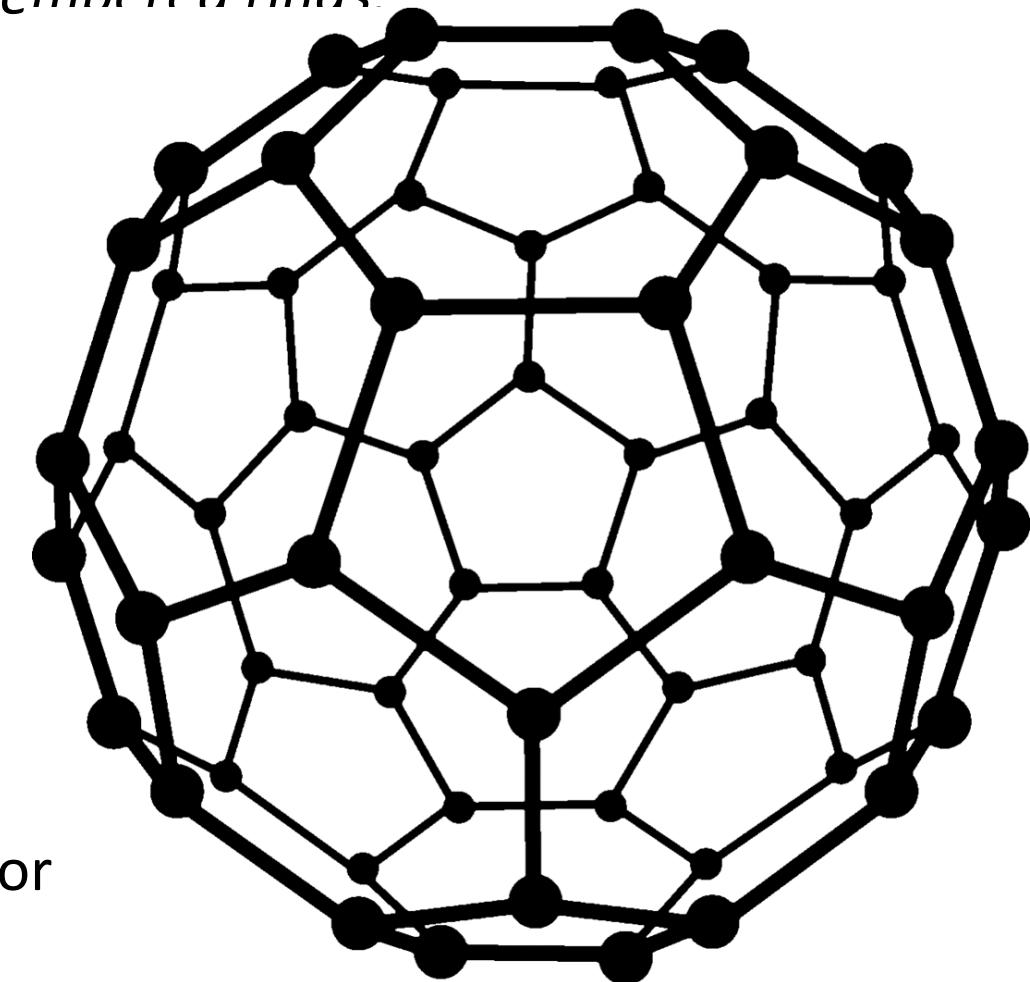


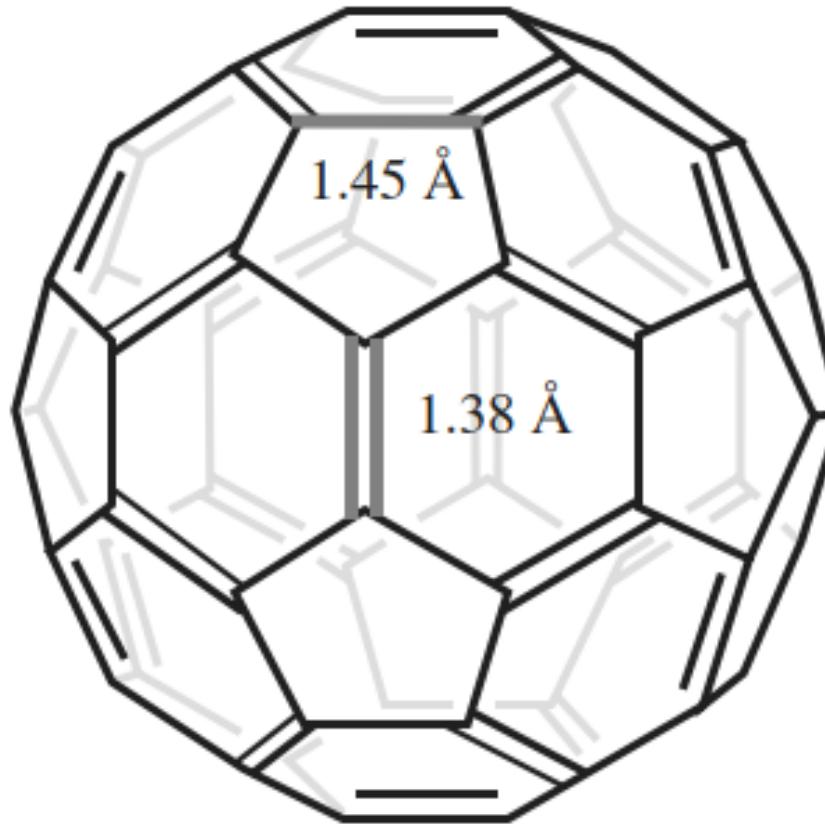
Fig. 2. HREM image of a quasi-spherical **onion-like graphitic particles** (dark lines represent graphitic shells, and distance between layers is 0.34 nm).

□ Structure:

- The C_{60} cluster is an elegant soccer ball-shaped structure (see Fig.). *This molecule, other similarly structured carbon clusters, and their derivatives are all collectively known as fullerenes.*
- *The fullerenes are based on any of several three-dimensional carbon structures with 12 five-membered carbon rings and a variable number of six-membered rings.*
- The C_{60} structure, the most stable of this family, is a perfect *truncated icosahedron*, a geometric solid having 20 6-membered rings and the considerable symmetry of the point group I_h : 6 \hat{C}_5 axes, 10 \hat{C}_3 axes, and 15 \hat{C}_2 axes. **The symmetry was first established by measuring the ^{13}C NMR spectrum of $^{13}C_{60}$ in which only one peak was observed, verifying that all 60 carbon atoms were chemically equivalent.**

Fig. 8.7. Structure of C_{60} ; the interatomic distance is **0.140 nm** for two carbon atoms shared by adjacent hexagons and **0.145 nm** for atoms shared by a hexagon and a pentagon.





In the previous Fig, the values given for the structure of C₆₀; the interatomic distance is **0.140 nm** for two carbon atoms shared by ***adjacent hexagons*** and **0.145 nm** for atoms shared by a hexagon and a pentagon.

- The size of a C_{60} fullerene is about 0.7 nm.
- The fullerenes share some properties with graphite, which is also built from 6-membered rings, but ***lack the extended delocalization of the p electrons*** that graphite has. As a result, ***the electrical conductivity*** across the ***fullerene surface is much lower***.
- C_{60} consists of a three-dimensional network of aromatic benzene rings. However, ***unlike benzene, the bonds in the 6-membered rings of C_{60} are not all equivalent***.
- Half carbon atoms lie between two 6-membered rings while the other half forms the border between one 5- and one 6-membered ring. As a result, C_{60} contains 'shorter' and 'longer' C-C bonds rather than having all bonds equal which would be expected if the molecule were fully conjugated. The interatomic distance is 0.140 nm for two carbon atoms shared by adjacent hexagons and 0.145 nm for atoms shared by a hexagon and a pentagon.
- Fullerene has ***hybridization intermediate between sp^2 and sp^3*** : Although the 6-membered rings would be most stable in a planar arrangement, each C-C bond on the surface lies at an angle only 11.6° from the plane of the 5- or 6-membered ring it joins to, resulting in ***relatively little strain***.
- Just as graphite has carbon *pi* orbitals perpendicular to the sheet, C_{60} has normal orbitals that extend perpendicular to the surface of the sphere. These normal orbitals are nearly pure ***p*** orbitals, with only 8% s-character.
- Two types of bonds *do not share p electrons equally*. This reduces the degree of resonance stabilization in C_{60} compared to benzene sufficiently that ***this and other fullerenes are not generally considered to be aromatic***.

- The fullerenes are easily isolated in large quantities. Because C_{60} is soluble in benzene, single crystals of it can be grown by slow evaporation from benzene solutions. *The C_{60} molecule can be dissolved in nonpolar solvents like toluene and can then be deposited into a film.*
- *They are stable and only mildly reactive*, because each carbon atom is bound to three other carbons *in a rigid geometry* that reaction would disrupt.
- The C_{60} **derivatives** that have atoms bound to the surface by these normal orbitals may have up to 20% *s*-character at the binding site, and the carbon atom at that site approaches the tetrahedral bonding of a pure sp^3 hybrid orbital, which has 25% *s*-character.
- *The large density of pi electrons results in a large polarizability and dispersion force, so the fullerenes are sticky molecules.* The C_{60} molecules arrange themselves in an FCC structure in the film with a spacing of 0.29 nm. This material is called **fullerite**. The bonding between the fullerenes is van der Waal's bonding so that the film is mechanically weak.
- A class of metal derivatives of the fullerenes is the **fulleride** salts formed by reaction of the fullerenes, e.g., C_{60} , with alkali metals.
- In the face-centered cubic fullerene structure, 26% of the volume of the unit cell is empty, so alkali atoms can easily fit into the empty spaces between the molecular balls of the material. When C_{60} crystals and potassium metal are placed in evacuated tubes and heated to 400°C, potassium vapor diffuses into these empty spaces to form the compound K_3C_{60} . The C_{60} crystal is an insulator, but when doped with an alkali atom it becomes electrically conducting. When C_{60} is doped with potassium to form K_3C_{60} , the potassium atoms become ionized to form K^+ and their electrons become associated with the C_{60} , which becomes a C_{60}^{3-} triply negative ion.

- Thus each C_{60} , has three extra electrons that are loosely bonded to the C_{60} , and can move through the lattice making C_{60} electrically conducting. In this case the C_{60} is said to be electron-doped.
- The many vacant molecular orbitals of the C_{60} molecule allow it to accept electrons (from the alkali metals) forming compounds containing the **fulleride** anions, e.g., M_3C_{60} and M_6C_{60} . *The former of these is of current interest since it has been found to **superconduct** at low temperatures.*
- ✓ The solid-state structure of M_3C_{60} is also worthy of comment. C_{60} itself, as might be expected of a highly symmetrical, pseudo-spherical molecule, packs together quite efficiently and the compound crystallizes in a *face-centered cubic* lattice. It will be recalled that for every atom in a close-packed lattice there are two tetrahedral holes and one octahedral hole per lattice unit, in this case, a C_{60} molecule. The structure of M_3C_{60} can therefore be derived based on a close-packed C_{60} array with all of the octahedral and tetrahedral holes filled by metal ions.
- Fullerenes can be reduced to form [60]fulleride salts, C_{60}^{n-} ($n = 1-12$). Fullerides of alkali metals are solids having compositions such as K_3C_{60} . The structure of K_3C_{60} consists of a face-centred cubic array of C_{60} ions in which K^+ ions occupy the one octahedral and two tetrahedral sites available to each C ion (Fig. below). The **compound is a metallic conductor at room temperature** and a superconductor below 18K. Other superconducting salts include Rb_2CsC_{60} , which has a superconducting transition temperature (T_c) of 33K, and Cs_3C_{60} , with $T_c = 40K$. The conductivity of M_3C_{60} compounds can be explained by considering that the conduction electrons are donated to the C_{60} molecules and are mobile because of overlapping C_{60} molecular orbitals.

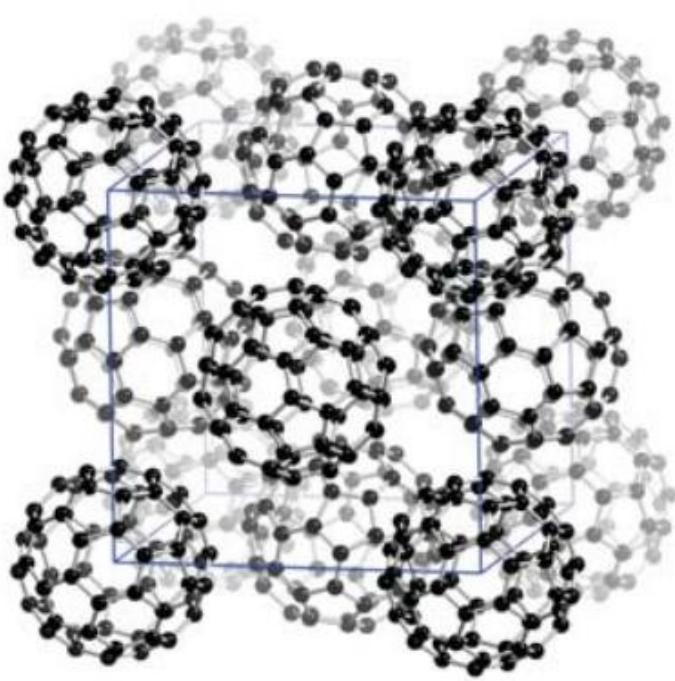


Figure 24.68* The arrangement of C_{60} molecules in a face-centred cubic lattice in the crystalline material. This material is called **fullerite**.

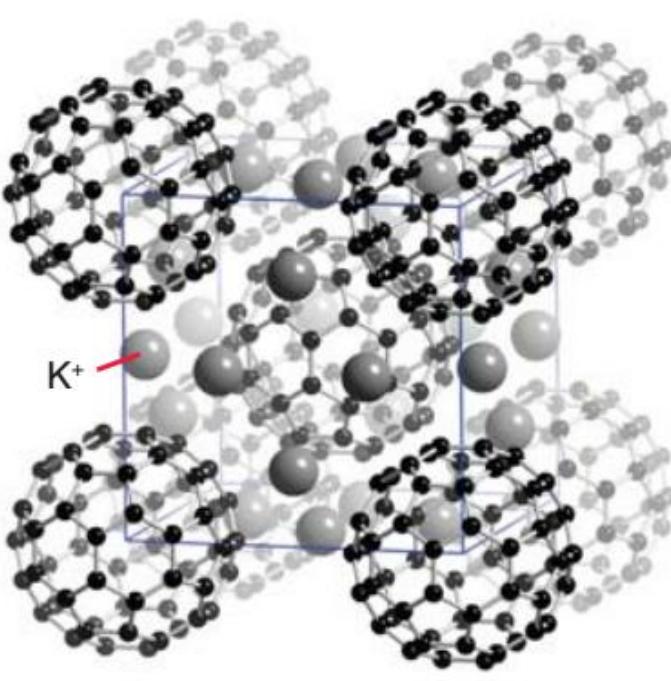


Figure 24.69* The structure of K_6C_{60} , with a body-centred cubic unit cell with C_{60}^{6-} molecular ions at the cell corners and body centre, and K^+ ions occupying half of the sites in the faces of the cell which have approximate tetrahedral coordination to four C_{60} molecular ions. This anionic material is called **fulleride**.

FIGURE...The structures of solid C_{60} showing the packing of C_{60} polyhedra in an fcc unit cell.

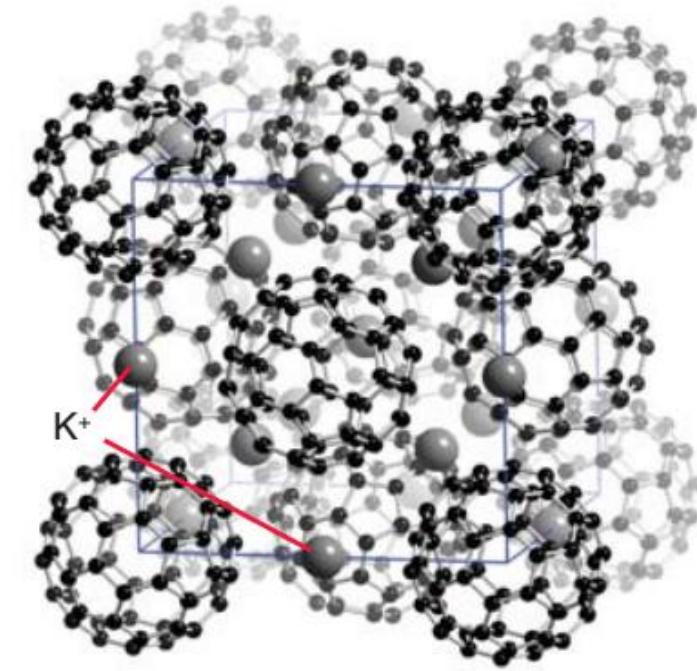


Figure 24.70* The structure of K_3C_{60} is obtained by filling all the tetrahedral and all the octahedral holes in the close-packed C_{60}^{3-} lattice with K^+ ions. This anionic material is called **fulleride**.

Superconductivity in C_{60} :

- ✓ Superconductivity is a state of matter in which the resistance of a sample becomes zero, and in which no magnetic field is allowed to penetrate the sample. The latter manifests itself as a reduction of the magnetic susceptibility χ of the sample to $\chi = -1$ (in the MKS system). In 1991, when A. E Hebard and his co-workers at Bell Telephone Laboratories doped C_{60} crystals with potassium by the methods described above and tested them for superconductivity, to the surprise of all, evidence was found for a superconducting transition at 18 K. A new class of superconducting materials had been found having a simple cubic structure and containing only two elements. Not long after the initial report it was found that many alkali atoms could be doped into the lattice, and the transition temperature increased to as high as 33 K in Cs_2RbC_{60} . As the radius of the dopant alkali atom increases, the cubic C_{60} lattice expands, and the superconducting transition temperature goes up.

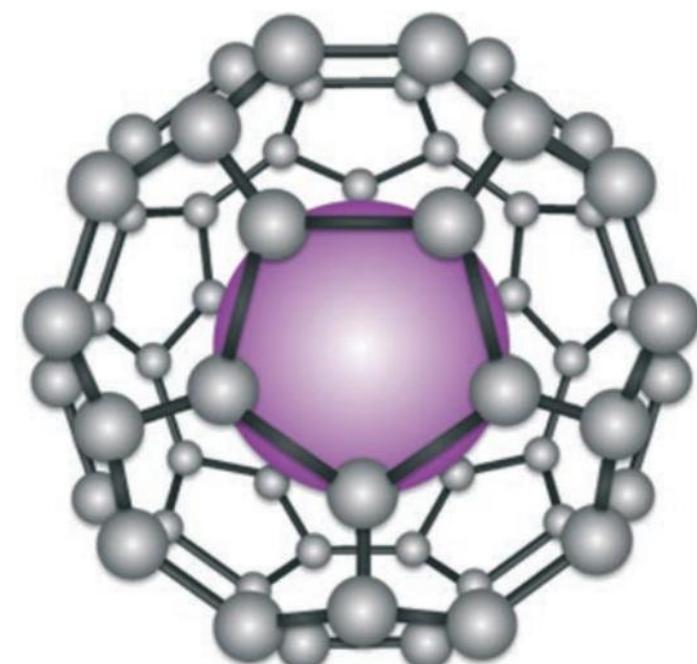
LARGER FULLERENES

- ✓ Larger fullerenes such as C_{70} , C_{76} , C_{80} , and C_{84} have also been found. A C_{20} dodecahedral carbon molecule has been synthesized by gas-phase dissociation of $C_{20}HBr_{13}$. $C_{36}H_4$ has also been made by pulsed laser ablation of graphite. One interesting aspect of the existence of these smaller fullerenes is the prediction that they could be superconductors at high temperatures when appropriately doped.
- ✓ C_{60} is the most stable molecule in the fullerene series; but as stated above and proved, using Euler's theorem, any closed shell will be produced by 12 pentagons, irrespective of the number of hexagons. Thus there should be a whole series of viable structures formed by increasing the number of hexagons, which for n atoms in the fullerene is the number $(n/2 - 10)$. Molecular stability depends not only on particularly symmetric geometric structures but also on the stability of the resulting electronic shells. It is found that there is a series of stable fullerenes containing $60 + (k \times 6)$ atoms, where the k represents the integers: 0,2,3,4,5..... (note that $k = 1$ is not included in this series). As the fullerene size increases, the average distance between the pentagons increases, and this continues all the way up to graphene (the "infinite fullerene"). Within this series, there are especially stable numbers of atoms—that is, special values of n when, for example, the closed shell has a low-energy morphology. These are known as magic numbers, with $k = 0$ (C_{60}) being the first magic number.
- ✓ The $60 + (n \times 6)$ series of fullerenes starting from C_{60} , described above, is only one of the possible series. It was observed, right from the first discovery of C_{60} , that C_{70} is also a highly stable molecule. Any mass spectrum showing the C_{60} peak always has C_{70} as well. It was soon realized that this structure, with 10 extra atoms, could be constructed by adding a belt of 5 extra hexagonal faces around the waist of the C_{60} molecule to produce the elliptical fullerene.

- ✓ Including elliptical and tubular fullerenes there are two extra series with stable numbers of atoms given by $70 + 30k$ ($k = 0, 1, 2, 3, \dots$) and $84 + 36k$ ($k = 0, 1, 2, 3, \dots$). Going from one size to the next involves a tubular extension about the long axis producing an increasing elongation. For large numbers these start to look like carbon nanotubes, described below, but in the case of nanotubes it makes more sense to consider the starting structure as a rolled-up graphene sheet.

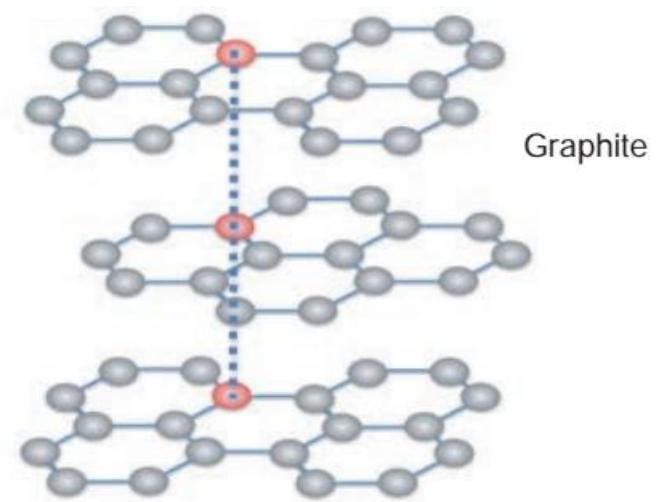
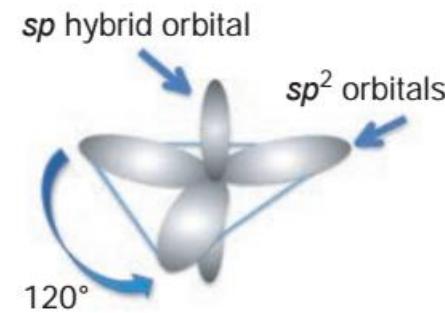
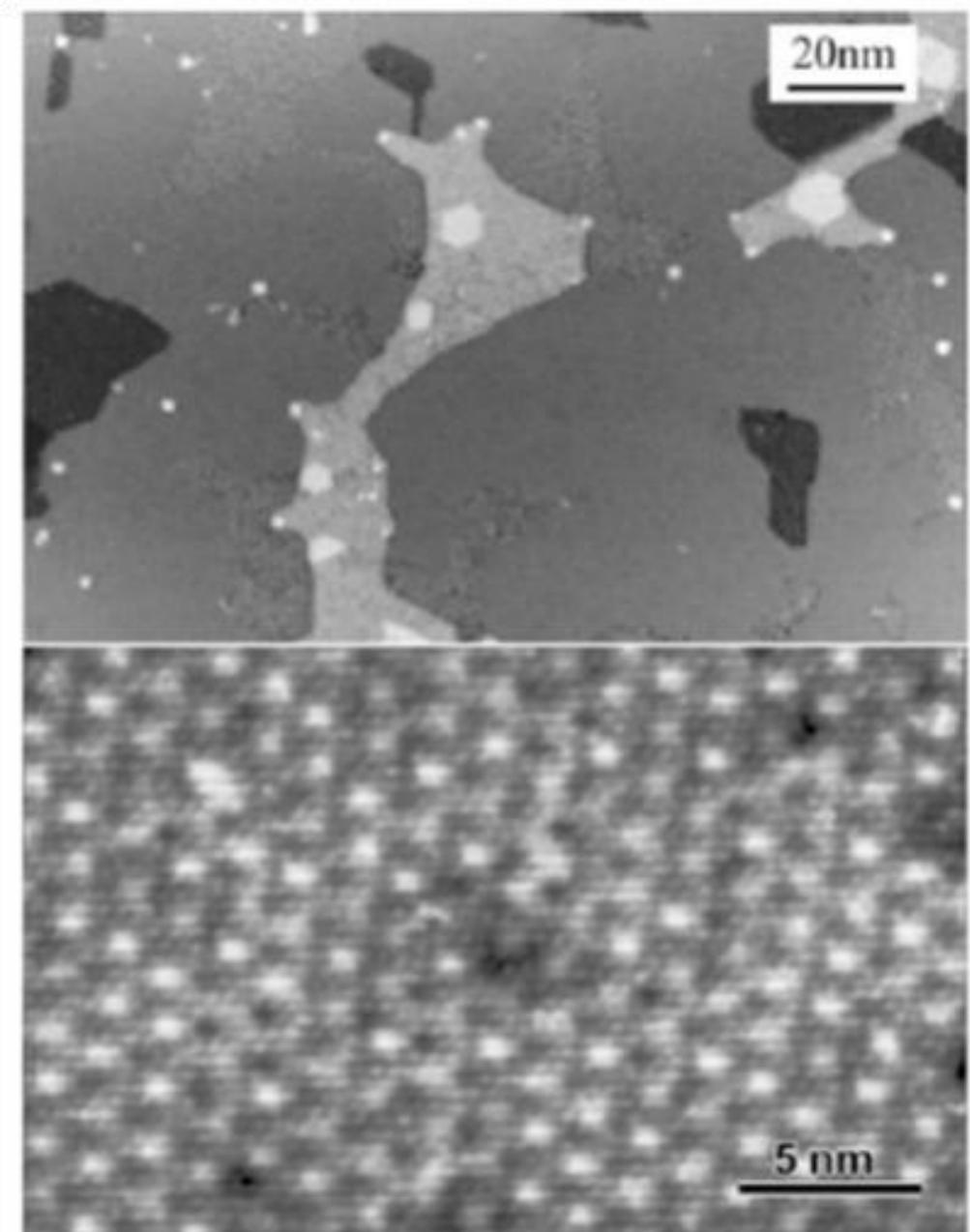
- Endohedral fullerenes containing various rare-earth atoms (terbium, thulium, neodymium, europium, and erbium) are now commercially available. As shown in Fig. 3.8.
- It was mentioned above that graphite consists of parallel planar graphitic sheets of carbon atoms. It is possible to put other atoms between the planes of these sheets, a procedure called *intercalation*. When intercalated with potassium atoms, crystalline graphite becomes superconducting at the extremely low temperature of a few tenths of a kelvin.
- ❖ Many applications have been suggested for the carbon fullerenes. Many of the biological or biotechnological ones are related to the ability of the assembly to serve as nano-containers for drug delivery or a reservoir to diagnostic agents. It was also demonstrated that modified fullerenes could serve as anti-viral agents. It was revealed that a modified C_{60} molecule could effectively inactivate human immuno-deficiency virus (HIV) at low micromolar concentrations.

Fig. 3.8 Endohedral fullerene. Introducing metal atoms into the vapor in which fullerenes are created produces metal atoms trapped inside the fullerene cage.



Graphenes and Carbon Nanotubes (CNTs): “Key Building Blocks” for Future Nanotechnological Applications

- Graphenes and Carbon Nanotubes (CNTs) are among the most prominent nanoscale materials currently studied.
- *The confinement to one or two dimensions and the high symmetry of these materials leads to interesting new properties and many potential applications.*
- **Graphene**, the youngest allotropes of elemental carbon, **is a one-atom-thick sheet of planar sp^2 -bonded carbon atoms in a hexagonal arrangement**. Graphene is a single layer of graphite (although the term is also used to collectively refer to a few layers of graphene) and is the two-dimensional form of carbon with bonding.
- Graphene is at the cutting-edge of materials science and condensed matter physics research. Geim and Novoselov were awarded the Nobel Prize in Physics in October 2010 for their work on graphene.
- It is the thinnest known material in the world and **conceptually** a basic build block for constructing many other carbon materials. It can be rolled into 1D CNTs and stacked into 3D graphite. With the addition of pentagons, it can be wrapped into a spherical fullerene. In one sense, it is the mother of all graphitic materials.



Graphene = 1 layer of graphite

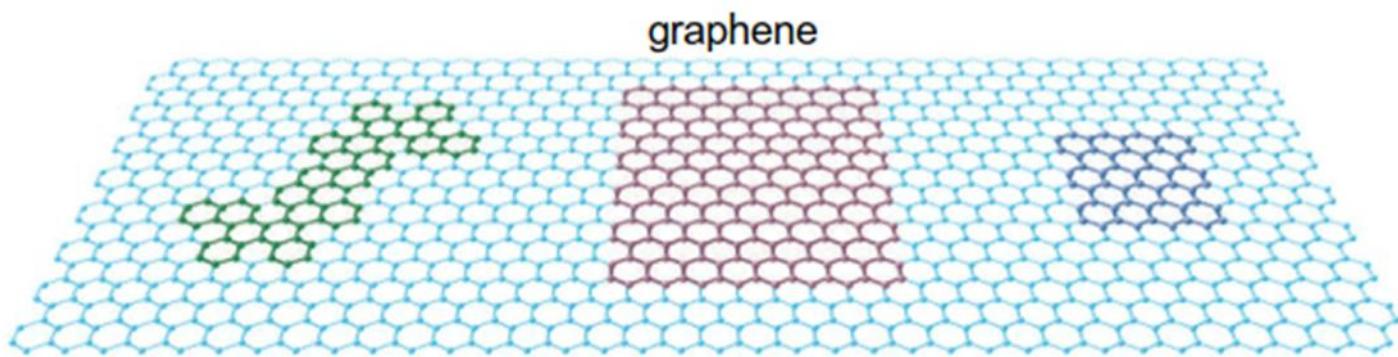


Figure 6.2 Scanning tunneling microscope (STM) images of epitaxial graphene growth on SiC.

- This novel material has received tremendous interest due to a large number of unique and exceptional properties. Here are **some basic parameters and properties of graphene**:
- ❖ Graphene (being an sp^2 -bonded carbon network; C-C bond distance of about 1.42 Å) *can easily be functionalized to interact with many chemical and biological agents, with the power tool set available from organic chemistry.*
- ❖ Thickness about 3.35 Å (this is close to the interplanar spacing in 3-D graphite).
- ❖ Weight per unit area is about **0.77 mg/m²**.
- ❖ Specific surface area of **2620 m²/g** (similar to that of activated carbon and significantly larger than that of CNTs).

High surface area: 2620 m²/g for *both sides* of graphene (e.g., suspended graphene) and 1310 m²/g for one side (e.g., supported on a substrate).

This also means that a graphene-based composite material can have a huge surface area. This property has also been used to demonstrate, for example, an “ultracapacitor” based on graphene.

❖ *Unique conducting properties:*

- ❖ From the viewpoint of its electronic properties, graphene is a zero-gap semiconductor with unique electronic properties.
- ❖ Graphene has the fastest electron mobility of $\sim 15,000 \text{ cm}^2/(\text{V cm})$ or $10^6 \Omega \text{ cm}$ (lower than Ag), a superhigh mobility of temperature-independent charge carriers of $200,000 \text{ cm}^2/(\text{V s})$ (200 times higher than Si), and an effective Fermi velocity of 10^6 m/s at room temperature, similar to the speed of light.
- Pure, **defect-free** (suspended monolayers) graphene has a **bulk electrical conductivity of $0.96 \times 10^6 \Omega^{-1} \text{ cm}^{-1}$** . This is somewhat higher than the conductivity of copper, which is $0.60 \times 10^6 \Omega^{-1} \text{ cm}^{-1}$.
- Pure, **defect-free** (suspended monolayers) graphene has a **thermal conductivity** of $2000\text{--}5000 \text{ W/m}^2 \text{ K}$ (vs. Ag: 430 W/m K). Copper at room temperature has a thermal conductivity of 401 W/(m K) . Thus, graphene conducts heat 10 times better than copper.

❖ **Mechanical properties** – tensile strength, Young's modulus, and fracture toughness:

More importantly, graphene possesses not only unique electronic properties but also excellent mechanical, optical, thermal, and electrochemical properties that are superior to other carbon allotropes such as graphite, diamond, fullerene, and CNTs.

- ✓ As yet, graphene appears to be one of the strongest materials ever tested. Measurements have shown that graphene has a breaking strength 200 times greater than steel. Pure, defect-free graphene has a *calculated tensile strength* (a stiffness) of about 130 GPa (19,000,000 psi) and *Young's modulus* of about 1035 GPa. These values have also been experimentally measured in very small samples; they may be *compared with those for standard stainless steel, of about 1.5 GPa and about 200 GPa*, respectively.
- ✓ However, *very few as-synthesized samples are defect-free*, so their tensile strength and Young's modulus do not approach these calculated numbers; and very few samples of graphene are large enough for their exceptional strength to be utilized in any practical manner.
- ✓ Nevertheless, such values have been used to accord superlative predictions to graphene, e.g., that *a 1 m² sample of graphene could “support up to 5 kg, but weigh only 0.77 mg, 1/10,000 of the weight of standard office paper of the same size”*.
- ✓ Conversely, pure, defect-free graphene is **very brittle**: it has a *fracture toughness* of about 4 MPa/m^{1/2} vs. about 20–50 MPa/m^{1/2} for most metals.

- ❑ **Unique optical properties:** Graphene is largely transparent (despite being highly conductive), with many distinctive optical properties and spectroscopic signatures (e.g., Raman). These properties are also often **affected by external perturbations and may be utilized in optical-based sensing**. Moreover, graphene has been shown to be able to strongly influence the optical/spectroscopic properties of objects (e.g., molecules) adsorbed on it, *opening many opportunities for various sensing and other applications*.
- Graphene is extremely thin and has an optical transmittance of $\sim 97.7\%$ (absorbing 2.3% of white light); but it is still a visible material, as it absorbs about 2.3% of white light (which is quite a lot for a 2D material). Combine this with graphene's amazing electronic properties, and it turns out that graphene can theoretically be used to make very efficient solar cells.
In addition, absorbing 2.3% of visible light still makes graphene very much transparent to the human eye, which may have various uses; it can be used to make transparent conductors, for example.

Graphene is almost transparent; it absorbs only 2.3% of the light intensity, independent of the wavelength in the optical domain. This number is given by $\pi\alpha$, where α is the fin structure constant. Thus, suspended graphene does not have any color.

- ❖ Graphene is also considered to have tremendous potential for a myriad of applications, like next-gen batteries, sensors, solar cells, and more - thanks to a wide array of properties.
- ❖ Many of these properties are *highly tunable* and *sensitively dependent on various parameters*.
 - ✓ *This, along with the fact that graphene is robust and typically exposed to the environment with an extraordinary specific surface area (2620 m²/g), makes graphene and graphene-based nanomaterials very promising for various applications.*
 - *Appealing properties of graphene as a sensor material* include high thermal conductivity, excellent mechanical properties, and relative ease of planar patterning using standard micro/nanofabrication (offering the outstanding potential to develop miniaturized sensors with high spatial resolution).
 - Graphene has an extremely high electrical current density (a million times that of copper) and intrinsic mobility (100 times that of silicon). Graphene has a lower resistivity than any other known material at room temperature, including silver. There are also some methods to turn it into a *superconductor* (it can carry electricity with 100% efficiency).

- Such exceptional and tunable (which can make it sensitive to external perturbations) electronic properties of graphene are appealing for graphene sensors based on conductivity measurement. For example, at room temperature, a graphene sensor that **detects the adsorption or desorption of single gaseous molecules has been demonstrated** based on the extraordinary sensitivity of graphene to local electrical perturbation.
- Graphene can also behave well in liquid and graphene field-effect transistors (FETs) operating in liquids have been demonstrated. Graphene has excellent electrical properties, especially high electrical conductivity and carrier mobility, and *ultralow electronic noise*. Moreover, **many electronic properties of graphene are highly tunable, including the bandgap, carrier type and density (field effect), and conductivity.**
- Due to its unique properties, it is speculated that in many applications graphene will outperform CNTs, graphite, metals, and semiconductors where it is used as an individual material or as a component in a hybrid or composite material.

□ Graphene is the basis of other carbon nanostructures.

- It can be wrapped up into **0D (zero-dimensional) fullerenes**, rolled into **1D nanotubes**, or stacked into 3D graphite crystal (see Figure 2).

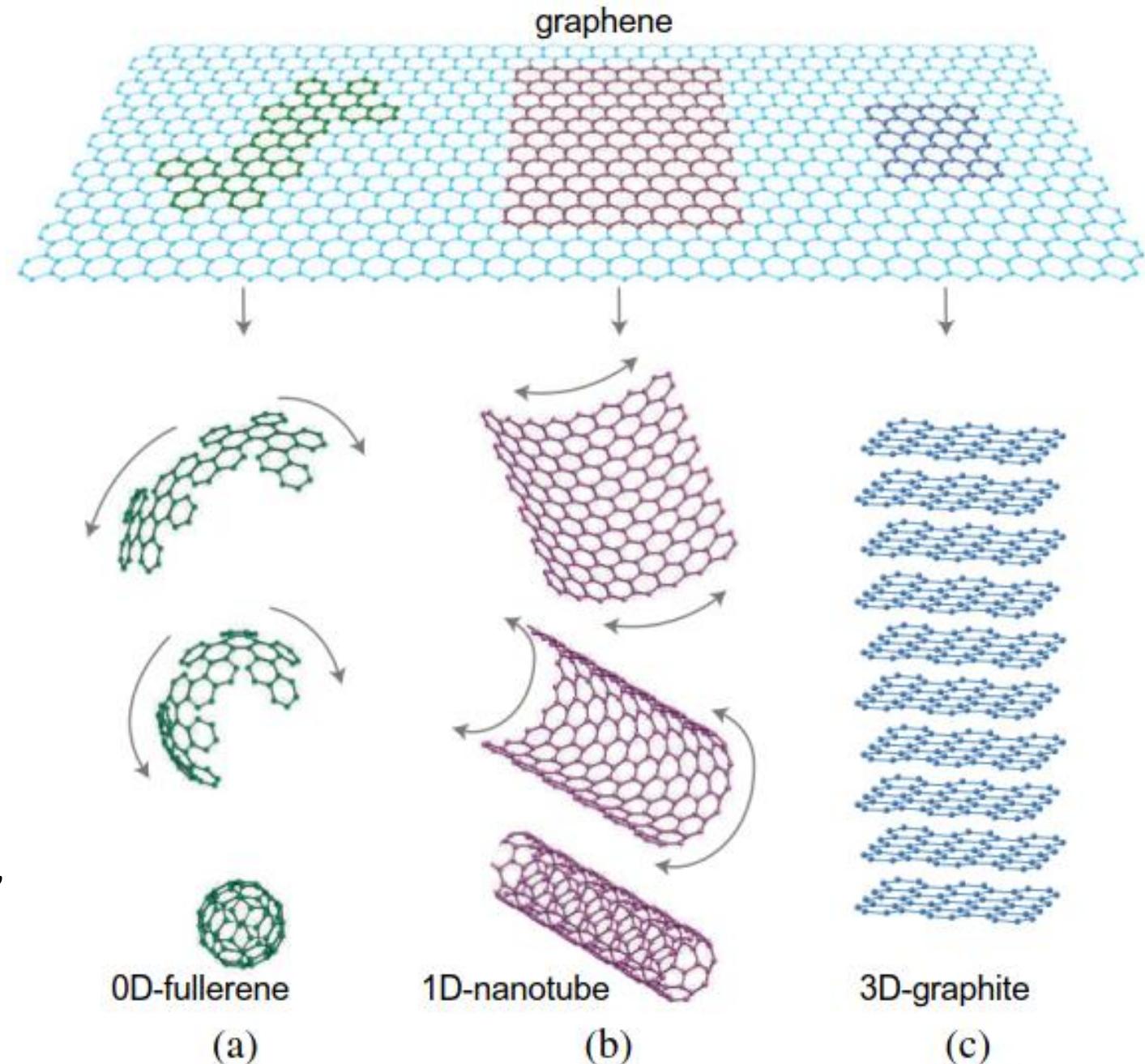


Figure 2. Graphene and its descendants,
(a) wrapped graphene = fullerenes;
(b) rolled graphene = nanotubes; and
(c) stacked graphene = graphite.

➤ A fullerene is a carbon sheet closed upon itself to form a sphere. As discussed in the next section, a carbon nanotube can be similarly seen as a graphene sheet folded into a cylinder. Such ***closure and folding of the graphene sheet occur because they lead to a decrease in energy***. At the ***edge of a graphene sheet***, the carbon atoms are bonded to only two other atoms and have one ***dangling bond***. As the size of the graphene sheet decreases, the ratio of the edge atoms (2-coordinated) to the inside atoms (3-coordinated) increases rapidly. The energy can be reduced if two dangling bonds join together to form a single bond. At small sizes of the graphene sheet, the number of the dangling bonds is large and the sheet structure becomes unstable with respect to a folded structure. ***Some elastic strain energy is introduced due to folding***; however, the ***reduction in energy*** due to the elimination of the ***dangling bonds more than compensates for this increase in energy***. The activation for the process is usually ***provided by heat available during the synthesis*** of fullerenes and the nanotubes.

- ❖ ***The remarkable physical properties of graphene lay in its honeycomb structure made out of hexagons*** (see Figure below). Each carbon atom is bonded to three others making an angle of 120° and a bonding length of 1.42 Å.
- ❖ The stability of this lattice is given by the sp^2 hybridization between one s orbital with two p orbitals that leads to the formation of σ bonds between C atoms. **The corresponding σ band is closed-shell** and gives robustness to the lattice. The remaining p orbital is oriented perpendicularly to the planar structure and can interact and form covalent bonds with the adjacent C atoms forming a π band. **This band is half-filled since each p orbital has one extra electron.**

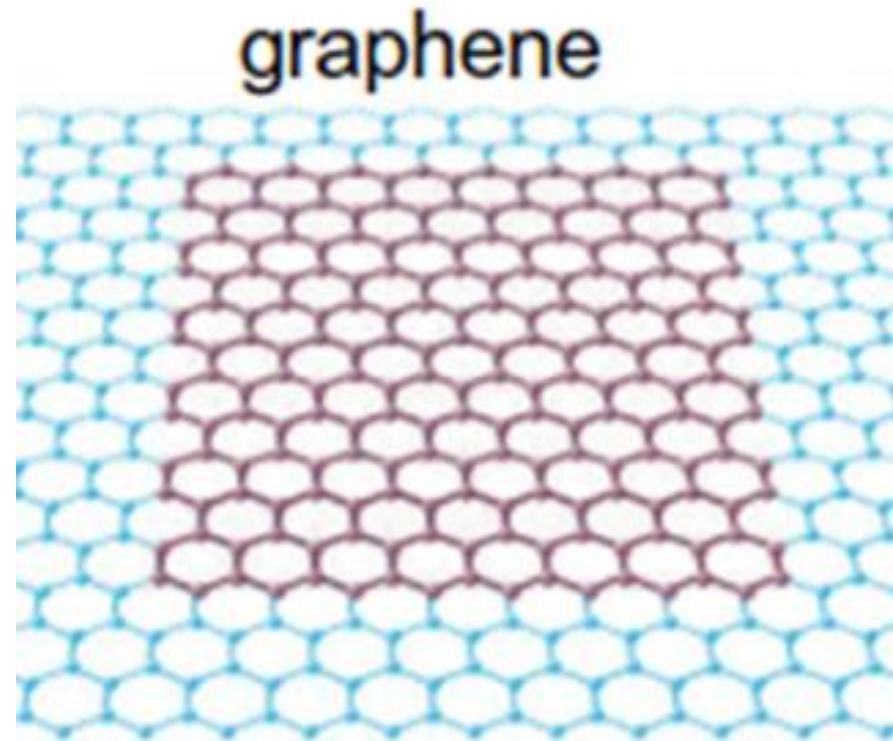


Fig. The structure of graphene showing its honeycomb arrangement.

- The structure of graphene consists of carbon atoms located at the corners of hexagons; each carbon atom being shared by three hexagons. **The unit cell is a hexagon with $6/3 = 2$ atoms per unit cell.**
- ✓ The structure can also be looked at as consisting of two interpenetrating triangular lattices (A) and
- ✓ *the unit cell can be taken as the parallelogram shown at B.*

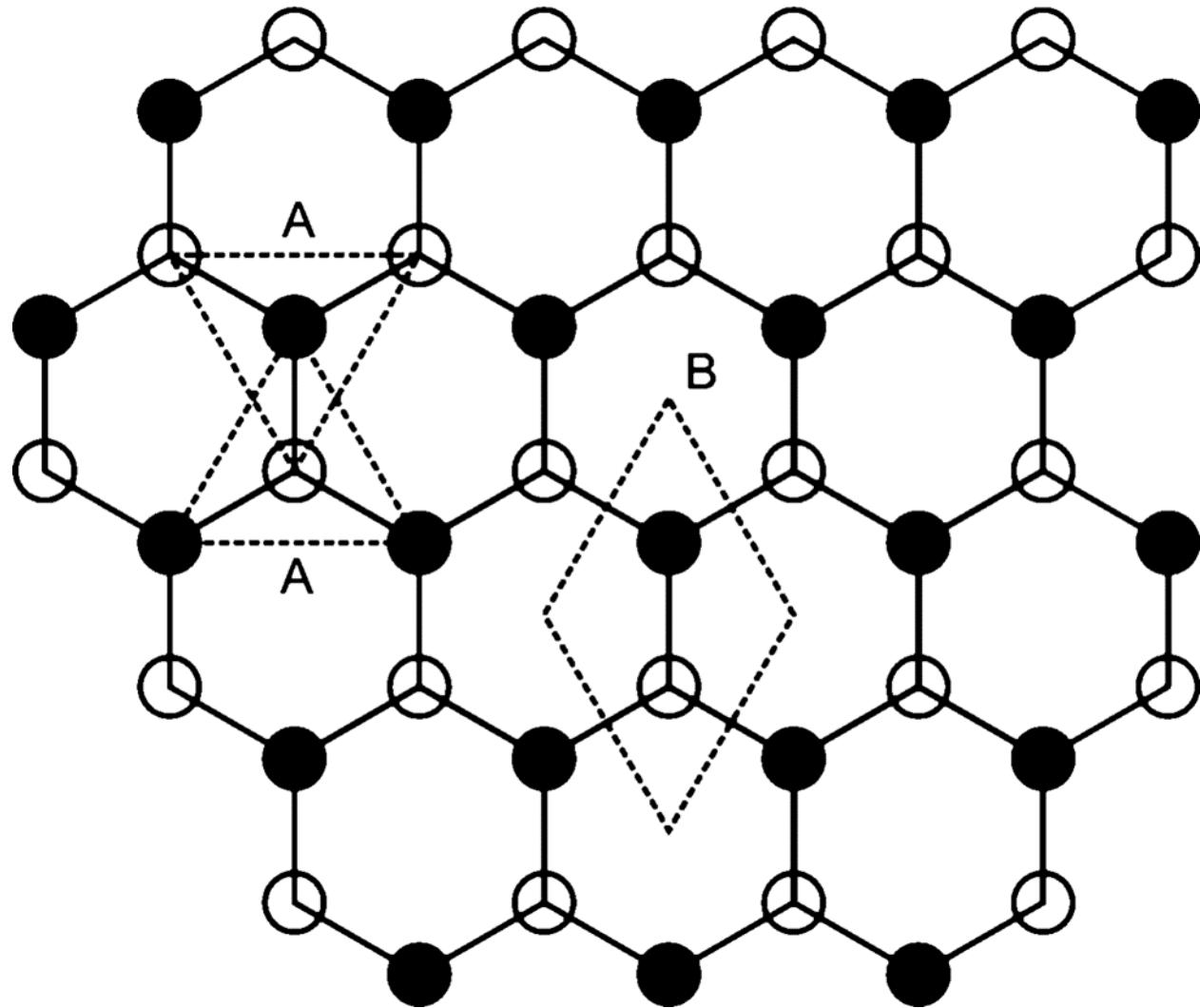


Fig. 8.3. The atomic structure of graphene and the unit cells.

➤ **The edge shape of graphene** is also of great interest **since the chirality and morphology of the edges are known to determine** the electronic properties, including the **band gap properties**, and **magnetic and optical behavior** of graphene.

➤ Graphene **edges** could be configured as either **zigzag** or **armchair based on morphology**, **open or closed depending on whether decorated with fully coordinated bonds or not or folded/unfolded upon edge terminations.**

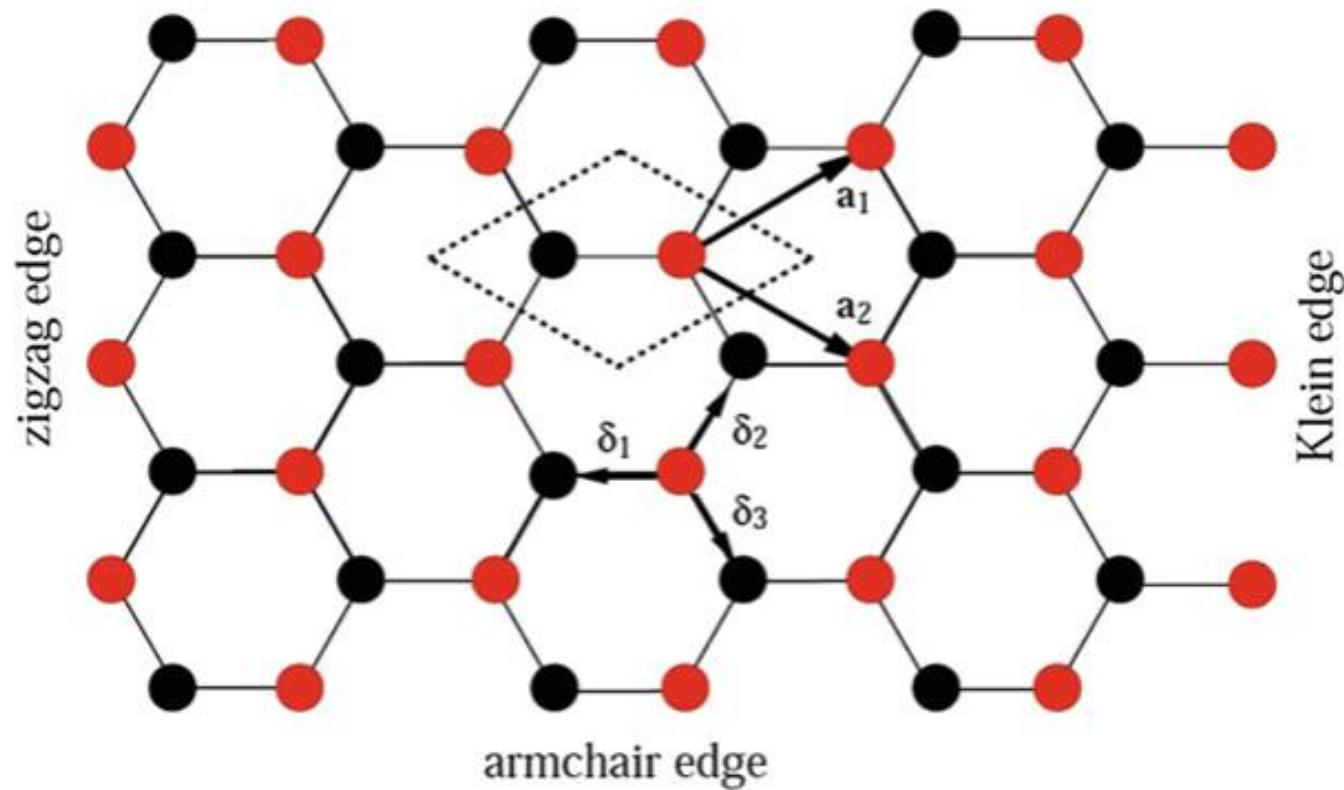


Fig. 16.1 Basic geometry of graphene lattice. Atomic structure of graphene showing its honeycomb arrangement, the dotted lines denote the **two-atom unit cell** with lattice vectors a_1 and a_2 ; the carbon atoms are represented by spheres. *The lattice can be also represented by two interpenetrated carbon triangular sublattices (red spheres and black spheres on a hexagon).*

The edge shape of graphenes

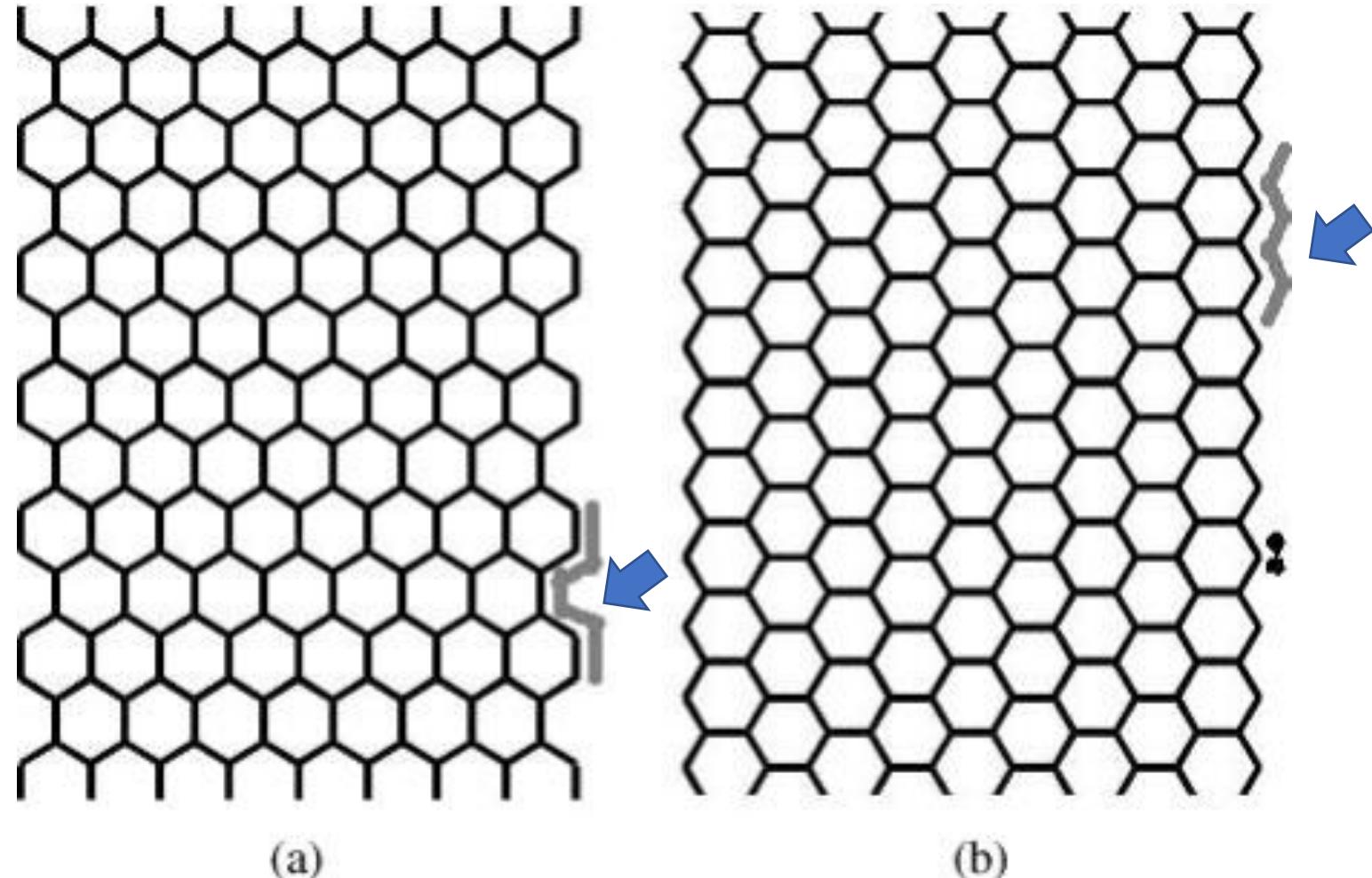
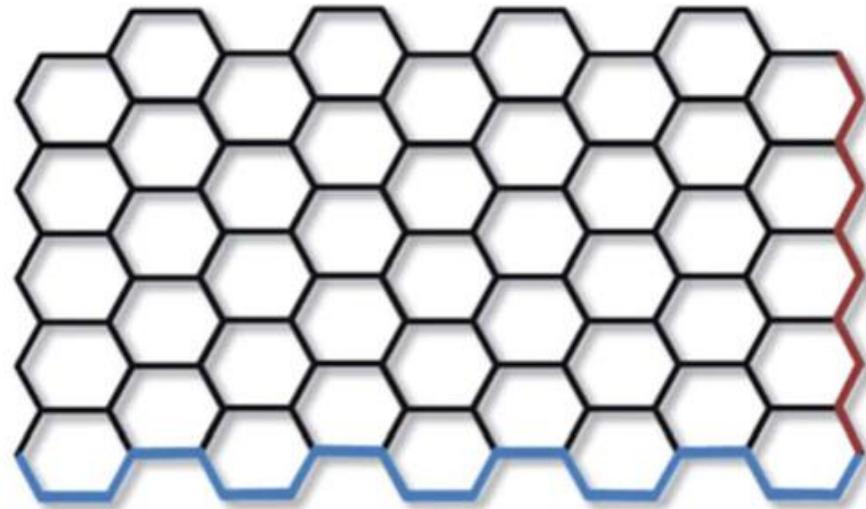
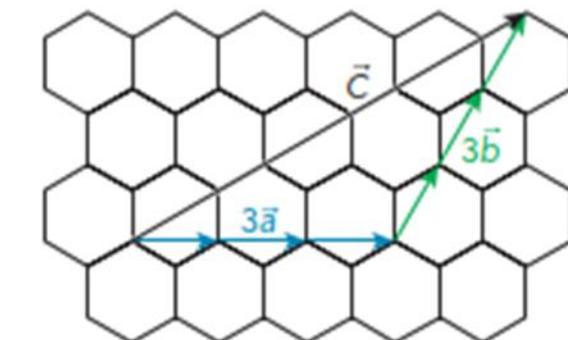
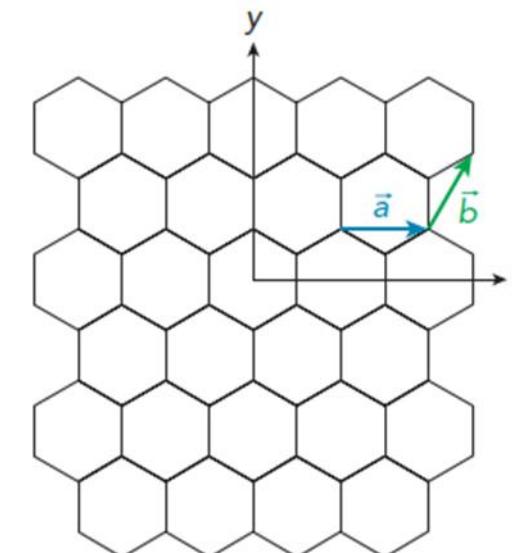
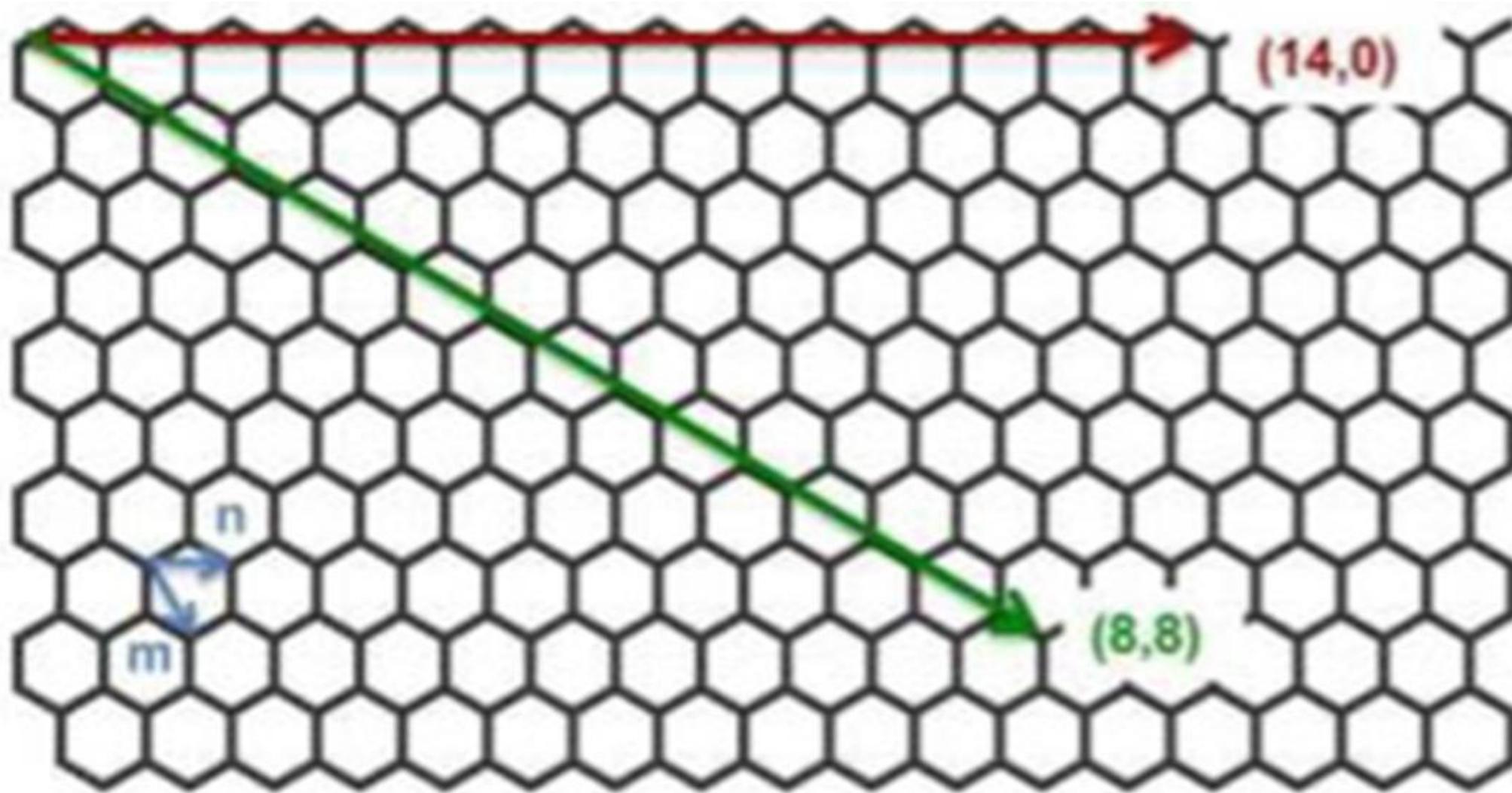


Figure 2. Graphene structures with (a) armchair and (b) zigzag edges.

- For the electronic properties, **the Zigzag graphene nanoribbon (GNR) is always metallic** while the **armchair GNR may be metallic or semiconducting** (depending on width) and **the Chiral GNR band structure depends on its chirality**.
- ❖ The way the graphene is cookie-cut from a large graphene sheet can then be defined by its **chirality vector**: $\vec{C} = na + mb$ where a and b are lattice vectors.
- ❖ n, m are positive integers ($0 \leq m \leq n$).
- ❖ If the **ribbon edge is cut along a chiral vector $(n, 0)$ it becomes a zigzag nanoribbon** and **if the cut is along (n, n) it results in an armchair nanoribbon**.
- ❖ If $n \neq m$ then it is an (n, m) **chiral nanoribbon** with electronic properties in-between the pure armchair and the pure zigzag GNRs.
- ✓ In the zigzag, the graphene is cut along the tops of the hexagons and $m = 0$, so this type of cut is designated $(n, 0)$; **in the armchair, it is cut along the centers of the hexagon and $n = m$, so this type of cut is designated (n, n)** ; and **in the chiral, it can be cut in almost any way**, defined by the chiral parameters.





- The single-layer graphene is a one-atom thick sheet of hexagonally arranged sp^2 -bonded carbon atoms.
- In addition to single sheets of graphene, i.e., monolayers, graphene as studied in the laboratory also comes in forms such as bilayer or few-layer, nanoribbons, and even quantum dots.
- With the impressive progress in research on graphene mono- and bilayers, recent attention has also turned to graphene ***few-layer graphene counterparts (FLG)***.
- In FLG, the crystallographic stacking of the individual graphene sheets provides an additional degree of freedom.
- The distinct lattice symmetries associated with different stacking orders of FLG have been predicted to strongly influence the electronic properties of FLG.
- Recent studies indicate distinct properties for these two types of graphene trilayers. **ABA**-stacked trilayers are semimetals with ***an electrically tunable band overlap***, while **ABC**-stacked trilayers are predicted to be semiconductors with ***an electrically tunable band gap***.

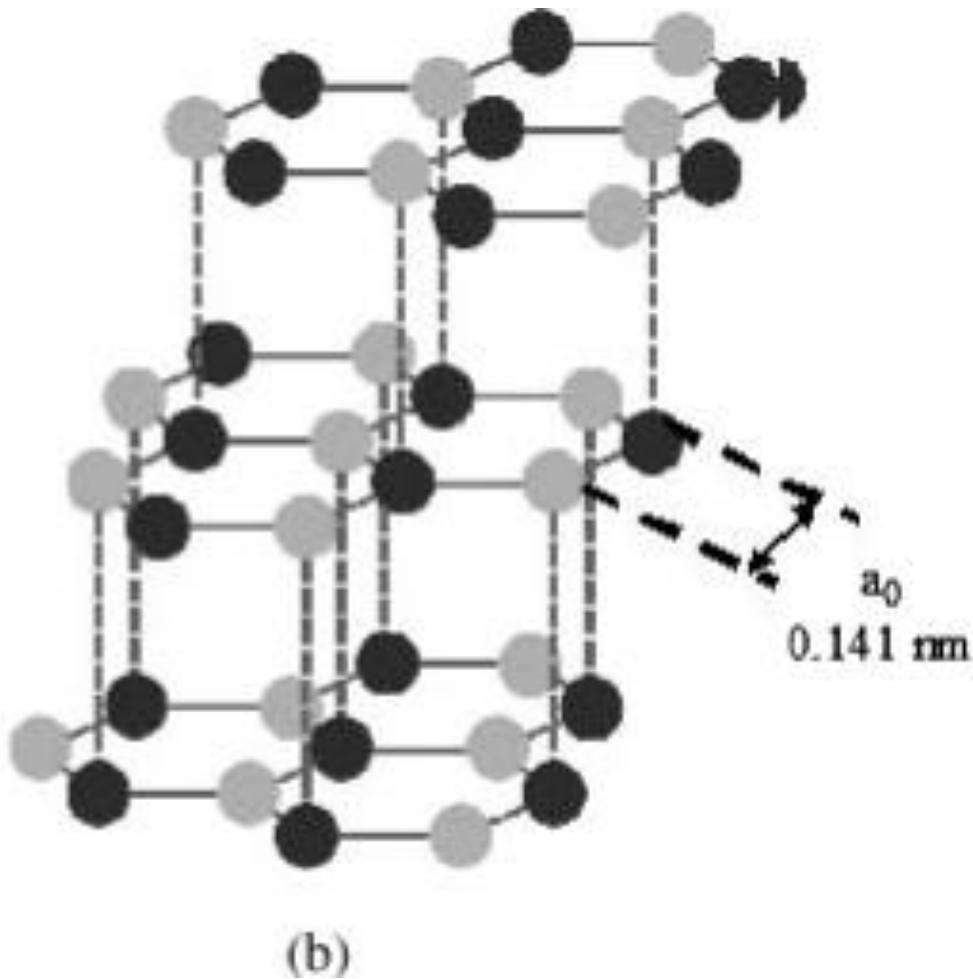
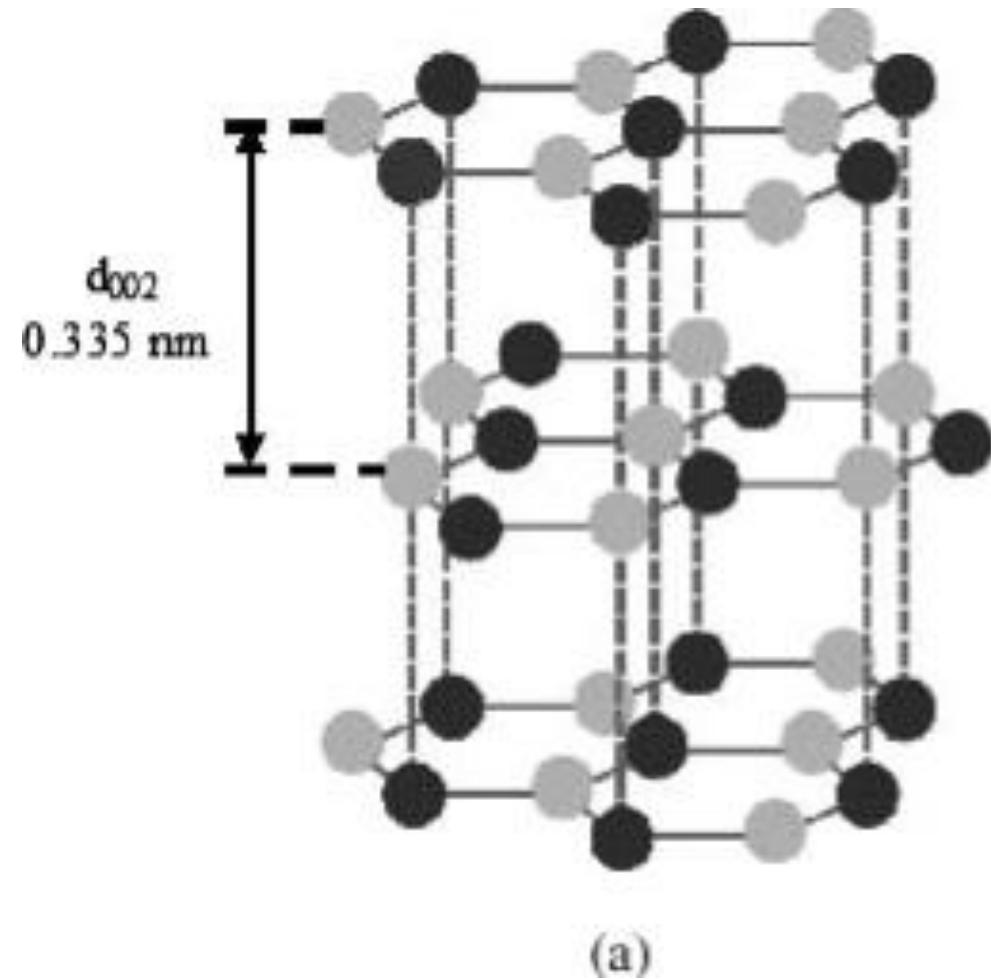
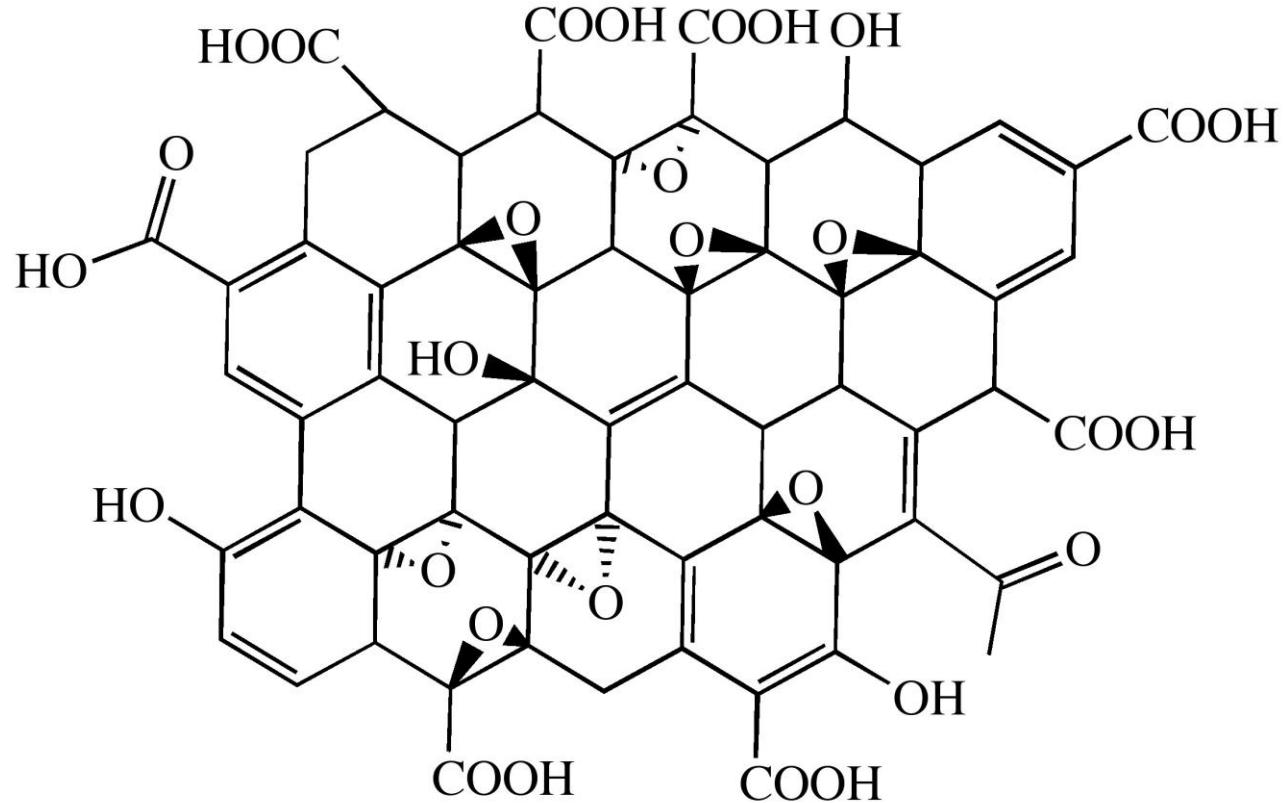


Figure 1. Lattice structure of trilayer graphene with (a) ABA and (b) ABC stacking sequence. The grey and black dots represent carbon atoms in the A and B sublattices of the graphene honeycomb structure.

- As an electronic material, graphene has the highest mobility at room temperature among all known materials. For this reason, graphene has been considered as one of the **most promising material for “post-silicon”** (beyond Moore’s law) **electronics** in semiconductor industry and a lot of ***work has started to explore the applications of graphene in high-speed, high-performance, and low-power electronic devices.***
- Due to graphene’s exceptional properties, it might revolutionize a wide range of fields.
- **Graphene-based electronics “graphenium” is an active field of application.** This material has already shown its potential as IBM scientists have developed a ***graphene field-effect transistor*** with an operation frequency of 26 GHz. ***A likely candidate to substitute the silicon-based technology is the development of graphenium technology.***
- Another field that is growing by the graphene discovery and the 2D crystals in general is the area of ***ultrathin and flexible devices applied to electronics.***

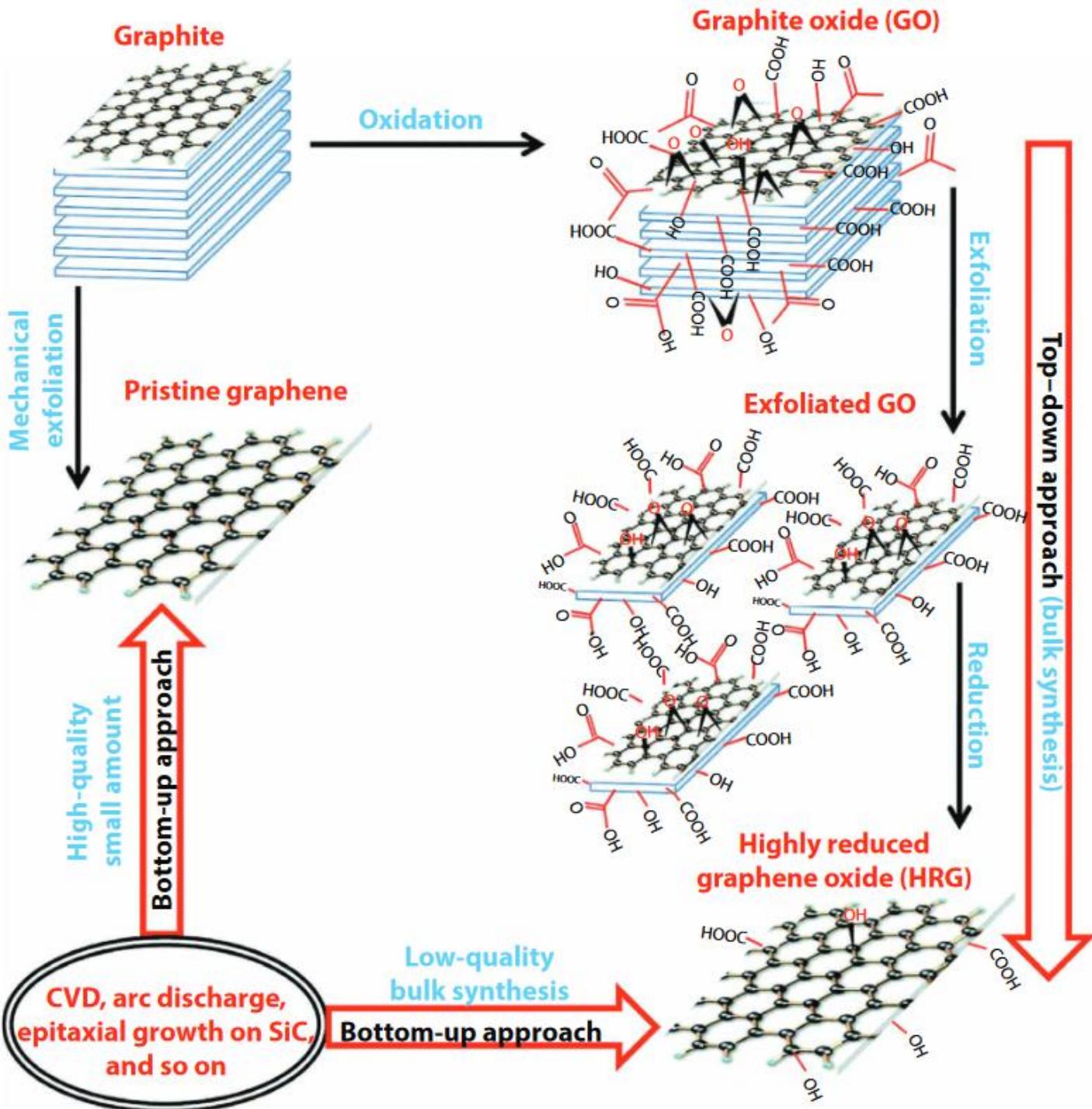
- One route to synthesize graphene is by the chemical reduction of graphene oxide (GO) as **graphite oxide (synthesized by oxidizing graphite with acids)** is water soluble and much easier to exfoliate. GO is hydrophilic (*in contrast to graphene*, which is *hydrophobic*), allowing stable aqueous dispersion in water.
- It is convenient to exfoliate GO into nano-sized single layers, which is the **promising mass production of both GO and graphene**.
- Various methods are being also developed to exfoliate graphite in solutions with appropriate chemical properties to obtain graphene or chemically functionalized graphene.
- Using such a method, one often obtains partially oxidized graphene or *graphene with chemical functional groups attached*.
- Many forms of graphene are produced using **graphene oxide (GO)**, which is relatively easy to synthesize from graphite, as the starting material. **GO is then reduced**. The reduction is however rarely 100% complete. Thus, the resulting in **reduced graphene oxide (RGO or rGO)** frequently possesses not only *impurities* (such as remnants of catalysts, if used in the reduction process) but also *some still-oxidized sites*, frequently in the form of $-\text{C}=\text{O}$ or $-\text{COOH}$ groups. Nevertheless, many researchers still use RGO in their work and believe their findings extend to pure graphene.

Figure 7.3.12: Idealized structure proposed for graphene oxide (GO).
Adapted from C. E. Hamilton, PhD Thesis, Rice University (2009).



- As graphene oxide is electrically insulating, it must be converted by chemical reduction to restore the electronic properties of graphene. Chemically converted graphene (CCG) is typically **reduced** by **hydrazine** or **borohydride**.
- The properties of CCG can never fully match those of graphene for two reasons:
 - Oxidation to GO introduces defects.
 - Chemical reduction does not fully restore the graphitic structure.
- As would be expected, CCG is prone to aggregation unless stabilized. Graphene materials produced from pristine graphite avoid harsh oxidation to GO and subsequent (incomplete) reduction; thus, *materials produced are potentially much better suited to electronics applications*.

Figure 11.1 Schematic representation of the methods used for the synthesis of graphene, which are classified into top-down and bottom-up approaches. The top-down approach is widely used for the scalable synthesis of graphene that produces a relatively low quality of a graphene-like material commonly known as reduced graphene oxide (rGO) or graphene in large quantity required for the preparation of graphene-based nanocomposites [18]. (Reproduced with permission of Royal Society of Chemistry.)



Carbon Nanotubes: Type, Structure and Properties

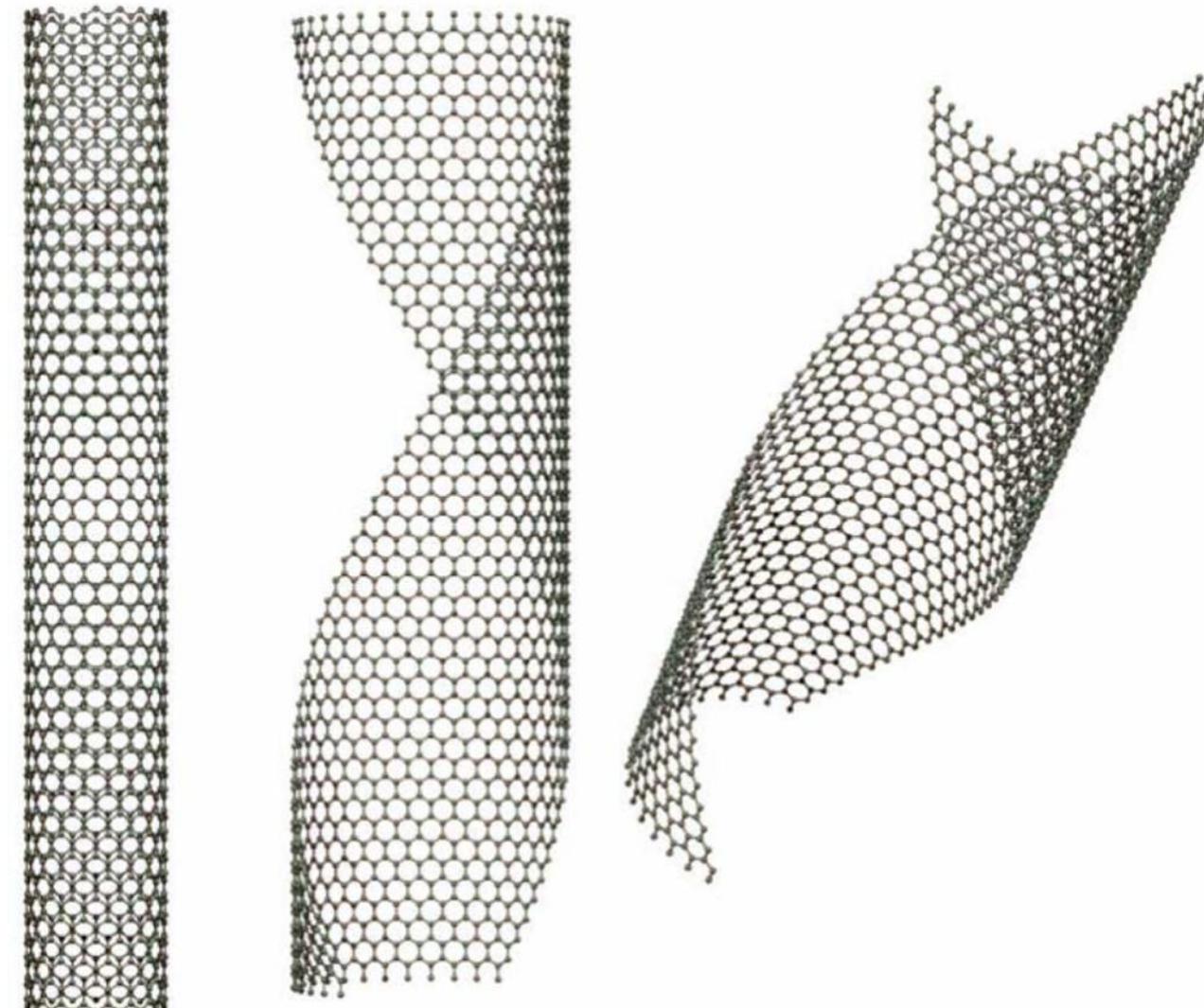
- The discovery of the closed-cage carbon structures was followed by the discovery in 1991, by Sumio Iijima of the NEC Corporation, of yet a new form of carbon at the nano-scale, the carbon nanotubes.
- Since then, research activities exploring their structure, properties, and applications have exploded across the world.
- *Carbon nanotubes exhibit unique electronic properties and extraordinary mechanical properties, and, hence, have received attention in nano-electronics, sensors, actuators, field emission devices, high strength composites and a host of other applications.*

Carbon Nanotubes

- These nanotubes, in their single-shell form (known as single-walled nanotubes - SWNTs) are elongated variants of the C_{60} fullerenes that described above. They practically resemble graphite sheets (graphenes) wrapped around into elongated cylinders with or without capping at their ends (Figure 2.5).

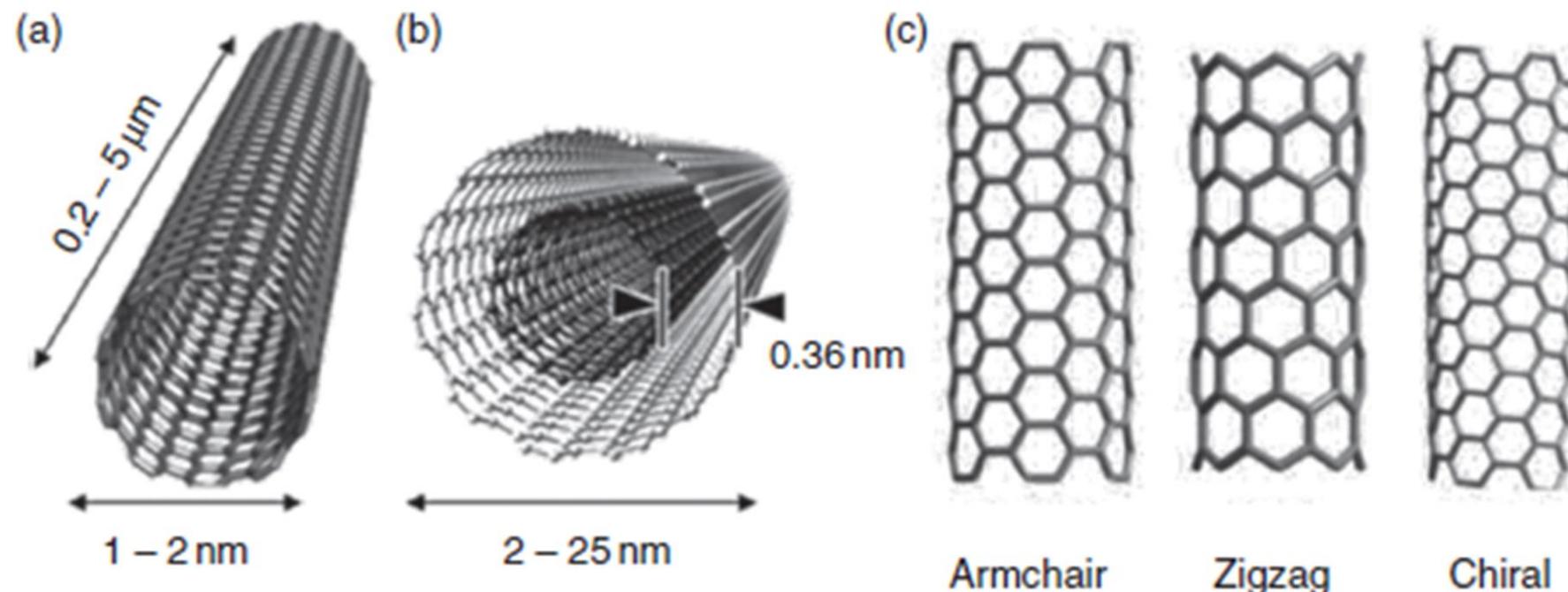
Figure 2.5: Model for the formation of carbon nanotubes by the two dimensional graphite-like layer. The tubes presented here are single-walled, although double-walled and multi-walled carbon nanotubes also present.

Courtesy of Chris Ewels (©Chris Ewels www.ewels.com).



Classifications: Based on (a) Wall Type and (b) Chirality

- (a) Wall Type:** CNTs are categorized depending on the number of concentrically arranged graphene layers:
(i) ***Single walled CNT*** (SWCNT); (ii) ***Double walled CNT*** (SWCNT); and (iii) ***Multiwalled carbon nanotube*** (MWCNT).
- (b) Chirality:** Three types of nanotube structures can be *classified* based on the chiral vector and the chiral angle:
(i) **Armchair**, (ii) **Zig-zag**, and (ii) **Chiral** CNTs.



16.1 Diagram showing typical dimensions of length, width and separation distance between layers of (a) SWCNT, (b) MWCNT and (c) different structures of CNTs. (Source: Adapted and modified from Iijima (2002). Used with permission from Elsevier.)

- **Single-walled CNTs** (SWCNTs) are composed of a unique graphene layer, usually produced with a random distribution of **diameters (0.7–2 nm)** in hexagonally close-packed bundles. The origin of these bundles is based on van der Waals forces among SWCNTs.
- *The smallest SWCNTs reported so far have a diameter of 0.4 nm, which corresponds to an armchair (2,2) CNT. It has a hemispherical fragment of the C_{20} dodecahedron.*
- **Double-walled CNTs** (DWCNTs) are composed of two concentric graphene layers and represent an intermediate structure between Multi-Walled CNTs (MWCNTs) and SWCNTs.
- A ***multiwalled carbon nanotube*** (MWCNT) is configurationally a stack of graphene sheets rolled up into concentric cylinders with the ends either closed with half-fullerenes or left open.
- *MWCNTs consist of several concentric graphene layers with their ends individually capped with fullerene-like hemispheres. Typically, their **outer diameter ranges from 2 to 100 nm**, while their **inner diameter is about 1–3 nm**. MWCNT **lengths may reach several μm** .*
- Figure 4.2 shows transmission electron microscopy (TEM) images of a SWCNT (Figure 4.2a) and a MWCNT (Figure 4.2b).
- The formed nanotubes could be remarkably long.
- One key property of the carbon nanotubes is their remarkable ***aspect ratio (their length to width ratio or length to diameter ratio)*** is extremely high (few nm in diameter and up to 1 mm in length).
- The **aspect ratio is** sometimes as high as 100,000:1; in some cases, aspect ratios as high as 132,000,000:1 have been claimed, with lengths of up to 0.5 m (meter).

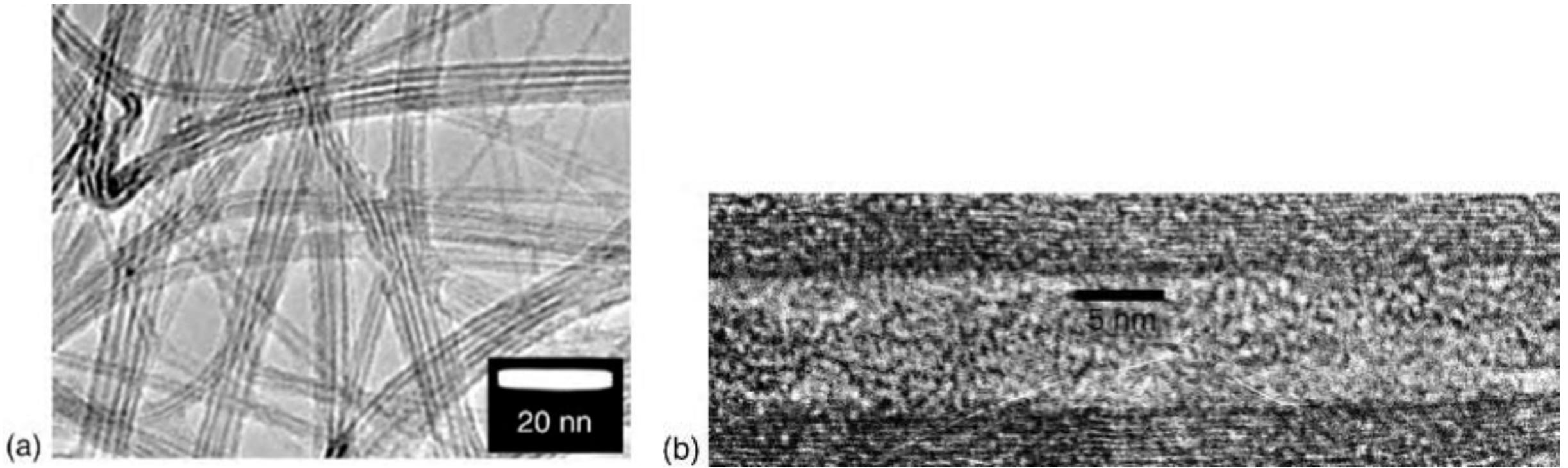


FIGURE 4.2 TEM images of (a) SWNT ropes; (b) a MWNT.
(Image courtesy of Lance Delzeit.)

Structures of Carbon Nanotubes

- The discovery of fullerenes led quickly to the development of techniques for manufacturing ***carbon nanotubes. These are cylindrically rolled, single or a few sheets of graphite that yield extremely strong tubes of very narrow diameter.***
- Variations of the procedure for forming fullerenes have led to carbon nanotubes, commonly known as ***buckytubes***. These can be thought of as being formed from a number of sheets of graphite folded round on themselves to form 'nested' cylinders.
- Configurationally, a carbon nanotube can be thought of as a two-dimensional graphene sheet rolled up in the form of a tube, the ends of which are closed with hemispherical fullerene-like caps, as shown in Fig. below. ***Yet again, 12 pentagons provide the curvature at the fullerene-like ends of the tubes.***
- Of particular interest is the manner in which their electronic properties can be tuned by adjusting the parameters for their construction.

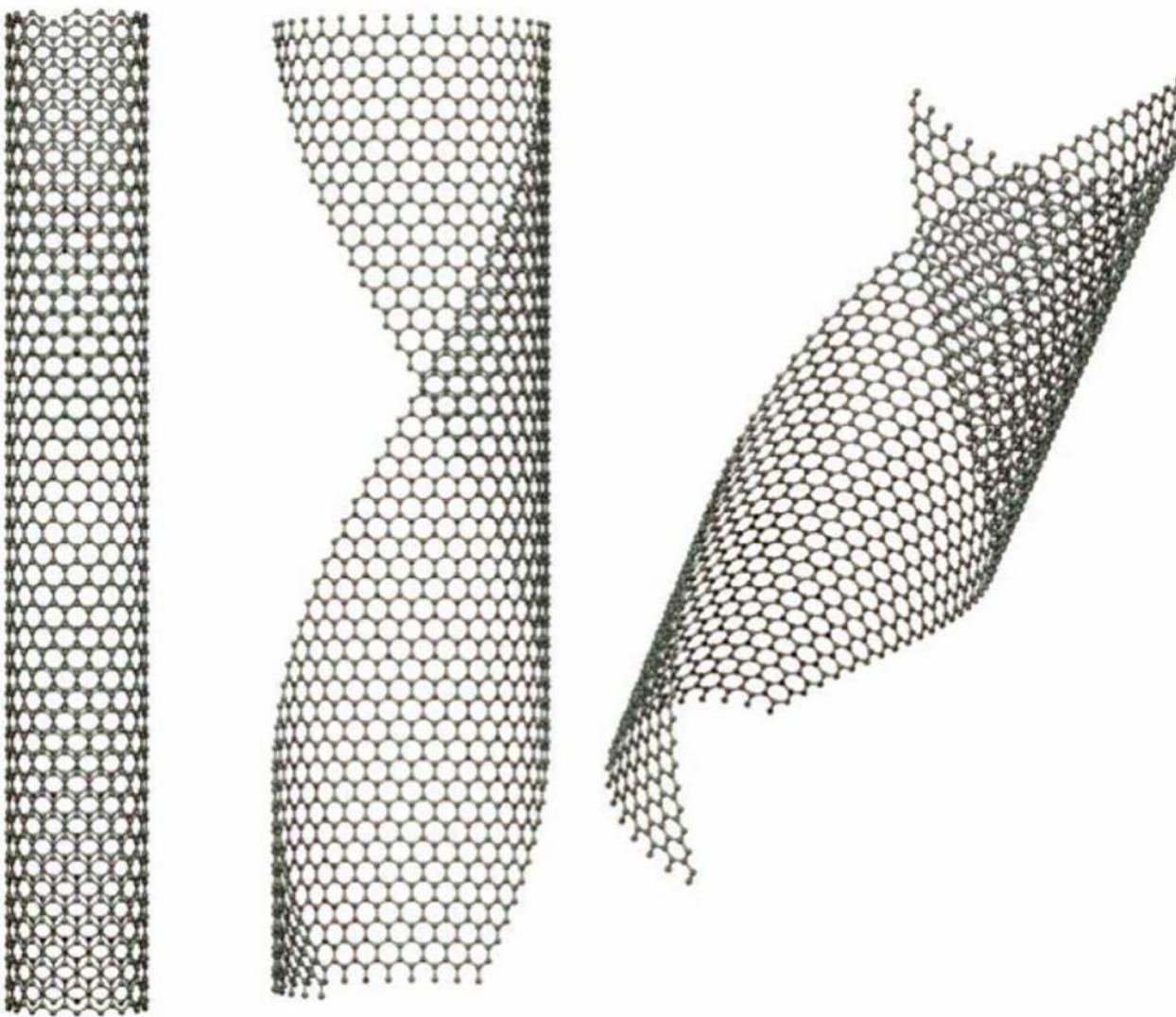
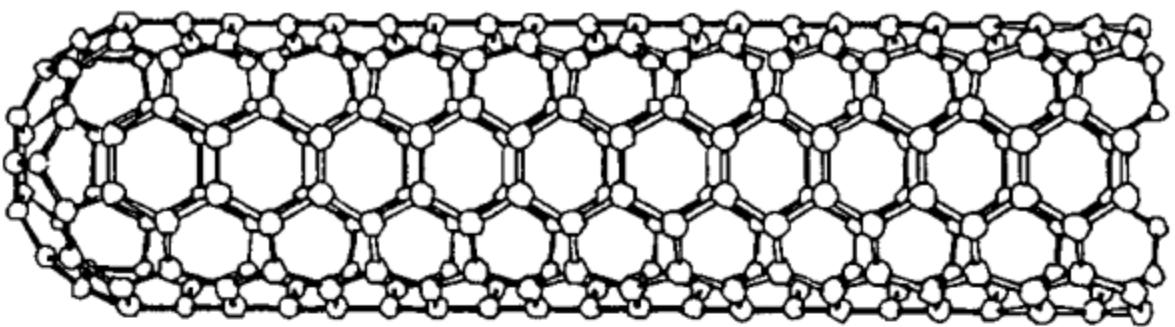
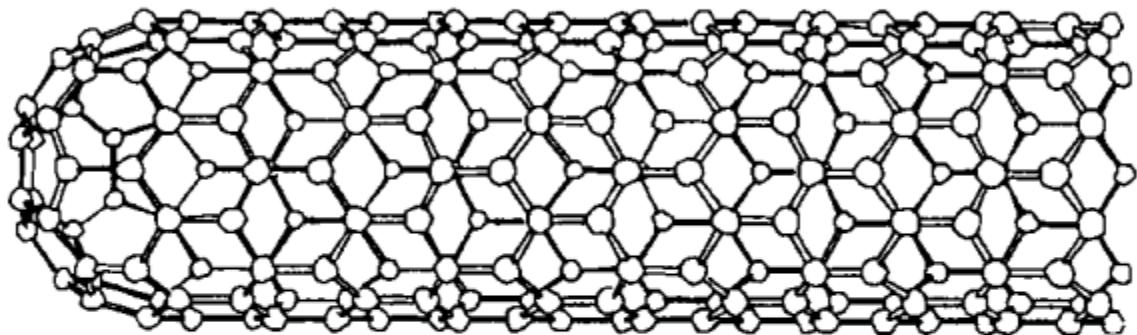


Figure 2.5: Model for the formation of carbon nanotubes by the two-dimensional graphite-like layer. The tubes presented here are single-walled, although double-walled and multi-walled carbon nanotubes also present.

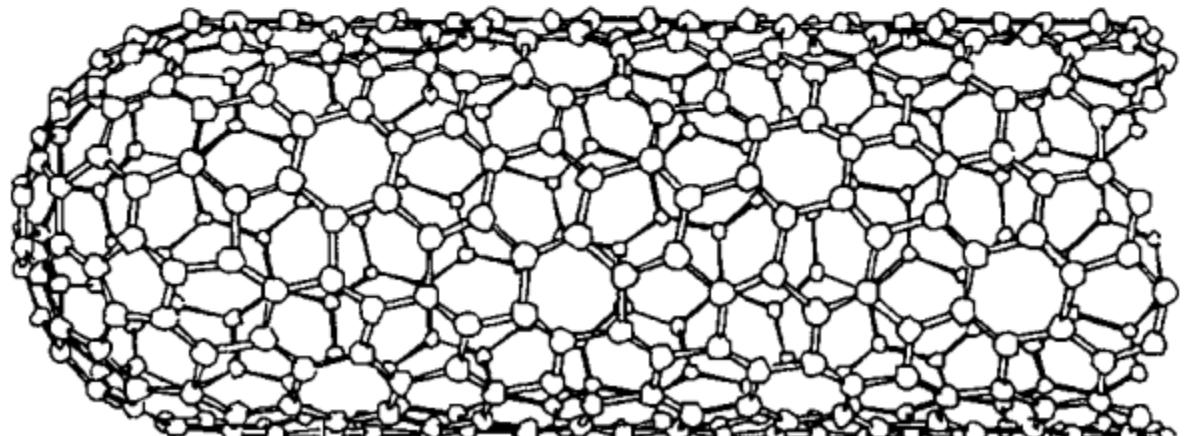
Courtesy of Chris Ewels (©Chris Ewels www.ewels.com).



(a)



(b)



(c)

Figure 5.11. Illustration of some possible structures of carbon nanotubes, depending on how graphite sheets are rolled: (a) armchair structure; (b) zigzag structure; (c) chiral structure.

- So far the structure has been described simply as a rolled graphene sheet, but there is still a choice of axis about which to roll as shown in Fig. 5.14.
- Starting from an infinite graphene sheet, one can cut a rectangle and roll the sheet to join at atoms so that the perfect hexagonal arrangement is maintained at a number of different angles. This allows the angle the hexagons make with the tube axis to vary, which may not seem to be a significant change; but as we will see below, ***the choice of the axis angle produces profound changes in the electronic properties of the tubes***. An alternative way of thinking of the rolling angle is to start with a high-symmetry roll, and then before joining bonds to atoms introduce a shift of n atoms along the join ***to generate a twist***. The choice of axis angle or n -shift is known as the ***chirality*** of the tube, and for each chirality there is an infinite family of tubes with different diameters and lengths, which also affect the tube properties. Thus there is a large degree of flexibility in the properties of nanotubes that can be exploited for applications.
- The formal method for specifying the ***chirality*** of a nanotube is based on the unit vectors of the hexagonal lattice, which are the vectors labeled a_1 and a_2 in Fig. 5.14. It is possible to specify any vector that connects two equivalent points on the graphene lattice in terms of these two by $na_1 + ma_2$, where m and n are integers and several examples are shown.
- The ***chirality of a nanotube*** is specified by the vector $na_1 + ma_2$, with the notation simplified to (m, n) .
- The tube is constructed by rolling the graphene sheet so that the beginning and end of the vectors meet, as indicated by the arrows. Two examples for the nanotubes $(8, 8)$ and $(12, 0)$ are shown in Figs. 3.17b and 3.17c, respectively. It is clear that any (n, n) nanotube will have the “***armchair***” pattern of carbon atoms at its end highlighted in red in Fig. 3.17b, and any $(n, 0)$ nanotube will have the “***zigzag***” pattern highlighted in Fig. 3.17c. Sometimes (n, n) and $(n, 0)$ tubes are referred to with these labels. The ends of nanotubes are not necessarily open and will often be terminated by a hemispherical dome, which is half a fullerene.

- There are a variety of structures of carbon nanotubes, and these various structures have different properties. Although carbon nanotubes are not actually made by rolling graphite sheets, it is possible to explain the different structures by consideration of the way graphite sheets might be rolled into tubes. A nanotube can be formed when a graphite sheet is rolled up about the axis T shown in Fig. 5.14. The C_h vector is called the **circumferential vector**, and it is at right angles to T . Three examples of nanotube structures constructed by rolling the graphite sheet about the T vector having different orientations in the graphite sheet are shown in Fig. 5.11.

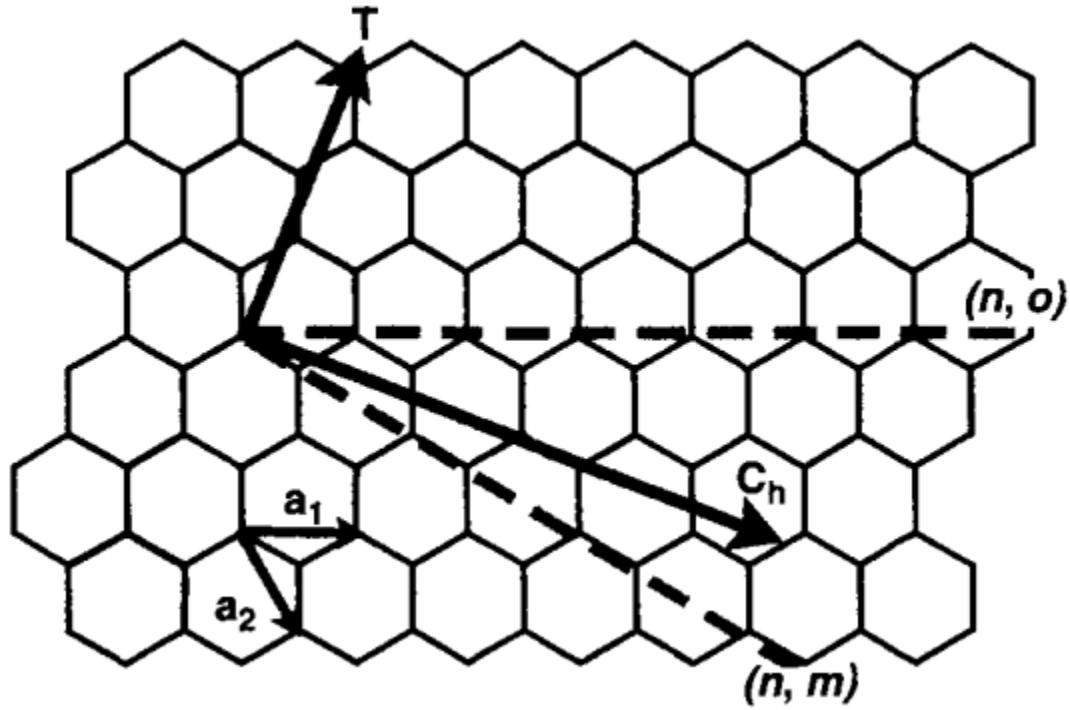


Figure 5.14. Graphitic sheet showing the basis vectors a_1 , and a_2 of the two-dimensional unit cell, the axis vector T about which the sheet is rolled to generate the armchair structure nanotube sketched in Fig. 5.11a, and the circumferential vector C_h at right angles to T . Other orientations of T on the sheet generate the zigzag and chiral structures of Figs. 5.11b and 5.11c, respectively.

- STRIP OF A GRAPHENE SHEET ROLLED INTO A TUBE

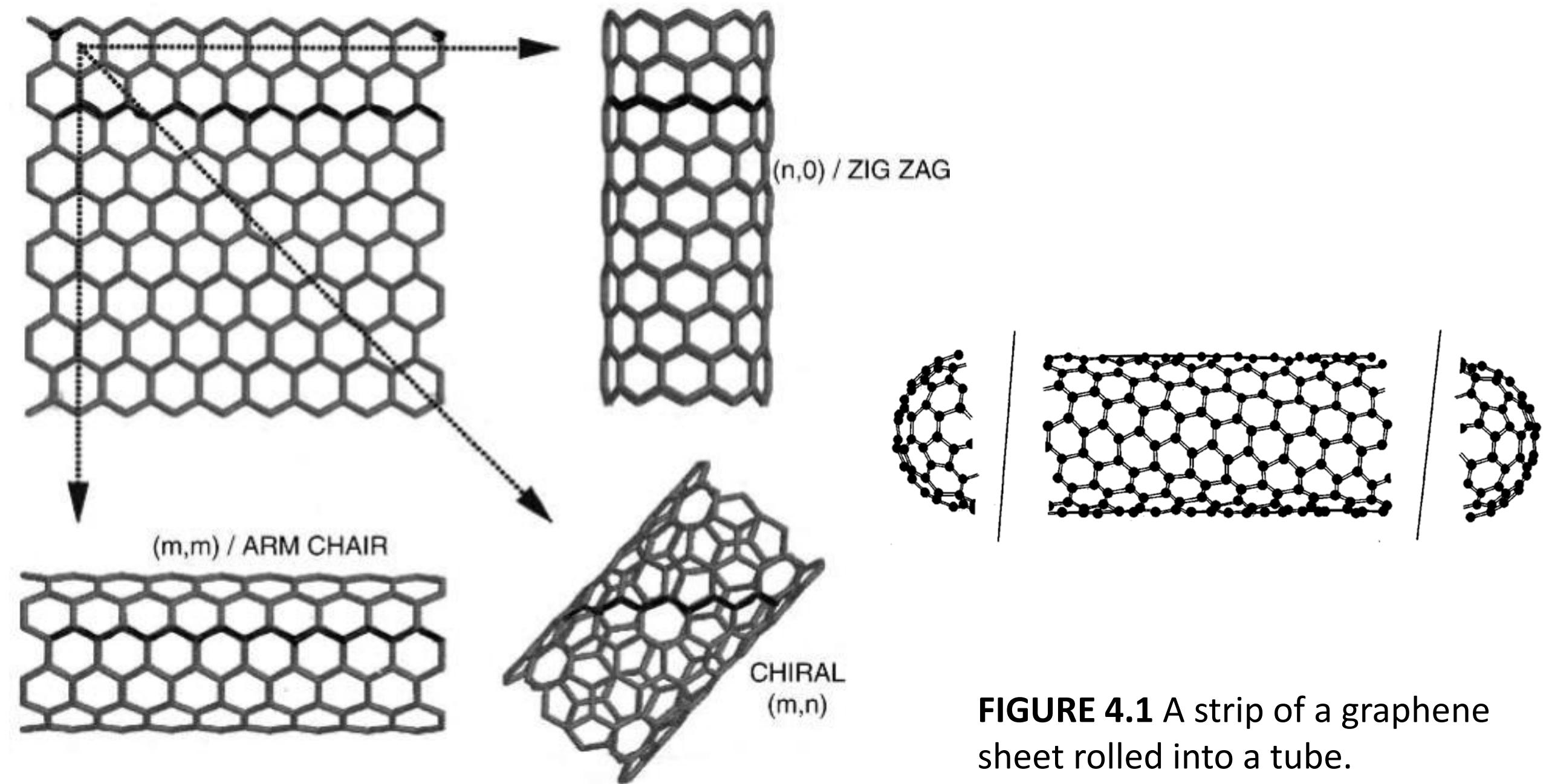
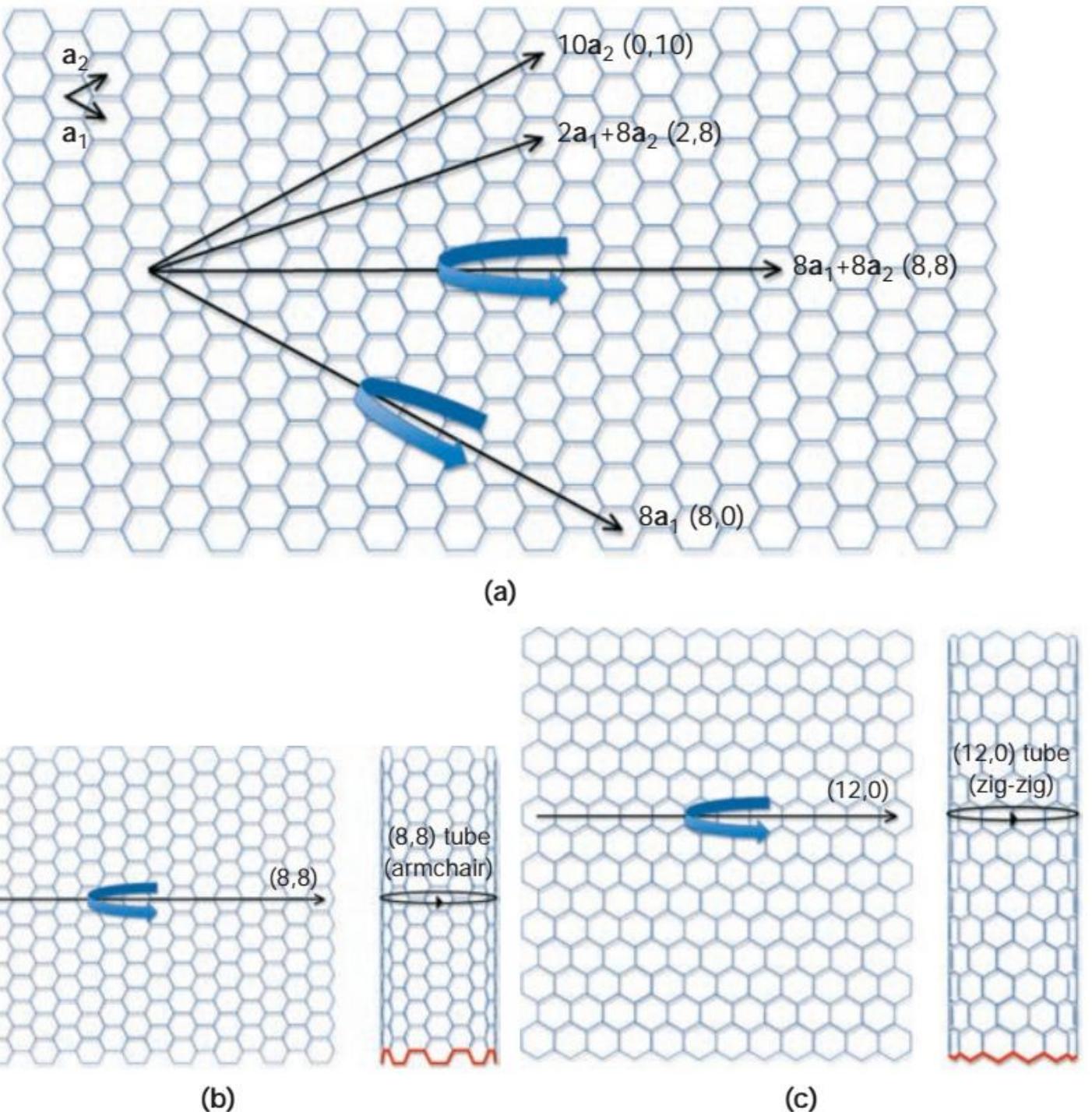


FIGURE 4.1 A strip of a graphene sheet rolled into a tube.

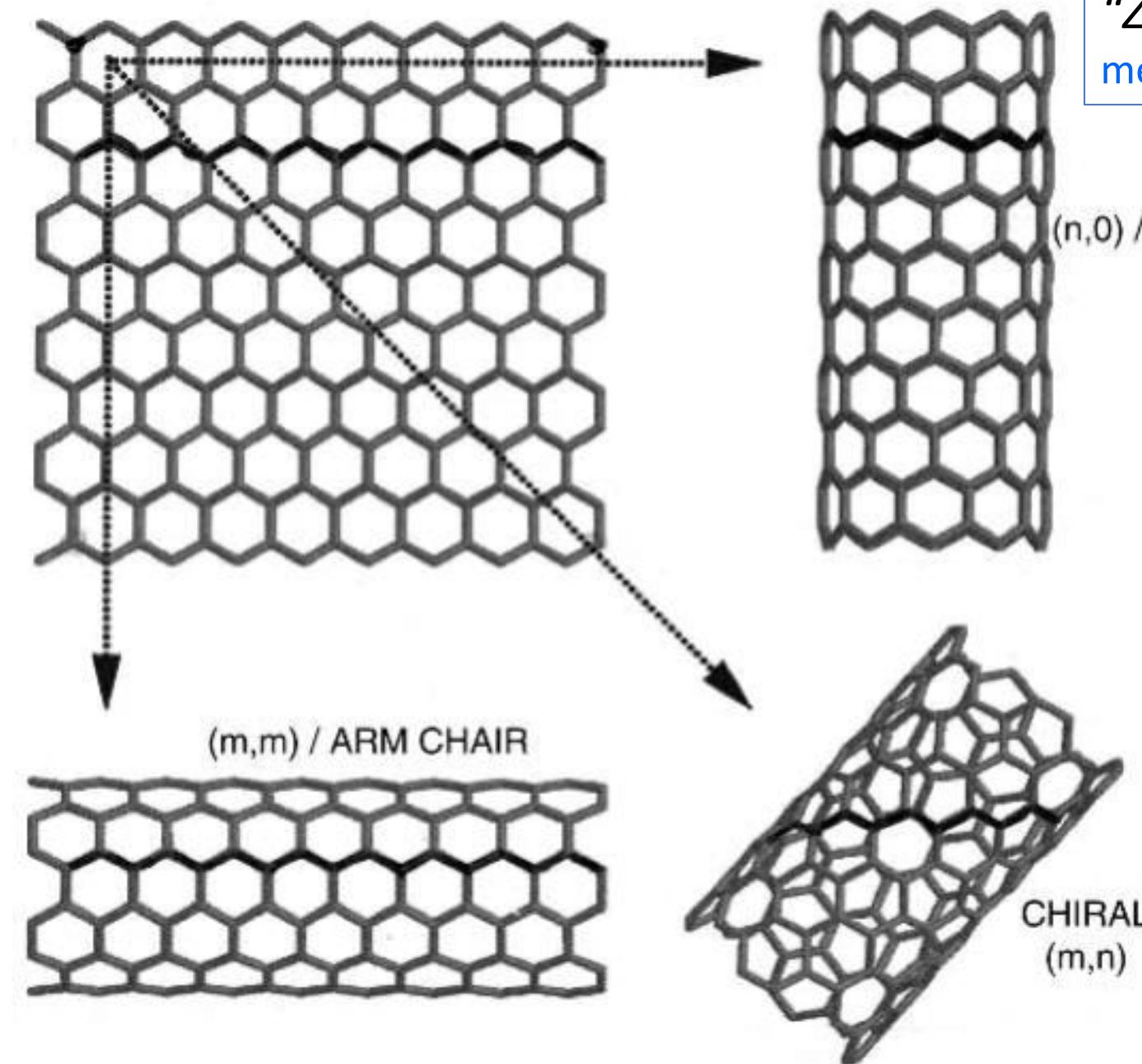
- When *T* is parallel to the C-C bonds of the carbon hexagons, the structure shown in Fig. 5.11a is obtained, and it is referred to as the "*armchair*" structure.
- The tubes sketched in Figs. 5.11b and 5.11C, referred to respectively as the zigzag and the chiral structures, are formed by rolling about a *T* vector having different orientations in the graphite plane, but not parallel to C-C bonds. Looking down the tube of the chiral structure, one would see a spiraling row of carbon atoms.
- Generally nanotubes are closed at both ends, which involves the introduction of a pentagonal topological arrangement on each end of the cylinder. The tubes are essentially cylinders with each end attached to half of a large fullerene-like structure. In the case of SWNTs metal particles are found at the ends of the tubes, which is evidence for the catalytic role of the metal particles in their formation.

Fig. 3.17 System for specifying nanotube chiralities. (a) The tube is specified by the circumferential vector $na_1 + ma_2$ denoting a vector joining two equivalent points on the graphene lattice in terms of the unit vectors a_1 and a_2 . The vector notation is simplified to (m, n) . The tube is generated by rolling the graphene lattice so that the vector lies on a circumference, as shown by the arrows, and joining the start and end points. (b) An example of an $(8,8)$ tube, also called an armchair tube because of the pattern of carbon atoms at the end. Any (n, n) tube will have an armchair configuration. (c) An example of a $(12,0)$ tube, also called a zigzag tube because of the pattern of carbon atoms at the end. Any $(n, 0)$ tube will have a zigzag configuration. For an excellent nanotube modeller that draws the geometry for any chirality see the website: <http://jcrystal.com/steffenweber/JAVA/jnano/jnano.html>.



- A single-walled carbon nanotube (SWNT) is a tubular shell made of hexagonal rings (in a sheet) of carbon atoms, with the ends of the shells capped by dome-like half-fullerene molecules.
- An *important feature in the carbon nanotube atomic structure* that is vital in deciding various physical properties is *the arrangement of the carbon hexagons around the tube surfaces*, in other words, **the “helicity” of the honeycomb lattice of graphene layer with respect to the tube axis**.
- *When a layer of graphene is rolled up to form a nanotube, the edges of the atomic layer that carry unbonded carbon atoms must join perfectly with each other in order to form a seamless cylinder.* Thus, the way the edges of graphene layer pair up result in specific directions of rolling and only from those directions can a tubular structure be formed. These specific directions can be characterized by the crystallographic orientations of the surface hexagons, which are noted by **helicity indices (m, n)**.
- The SWNTs are classified using a nomenclature (n, m) where n and m are integer indices of two graphene unit lattice vectors corresponding to the “**chiral vector, C_h** ” (or \vec{C} , also called **Helicity vector** or **Roll-up vector**) of a nanotube (see Figure 4.1).

- STRIP OF A GRAPHENE SHEET ROLLED INTO A TUBE



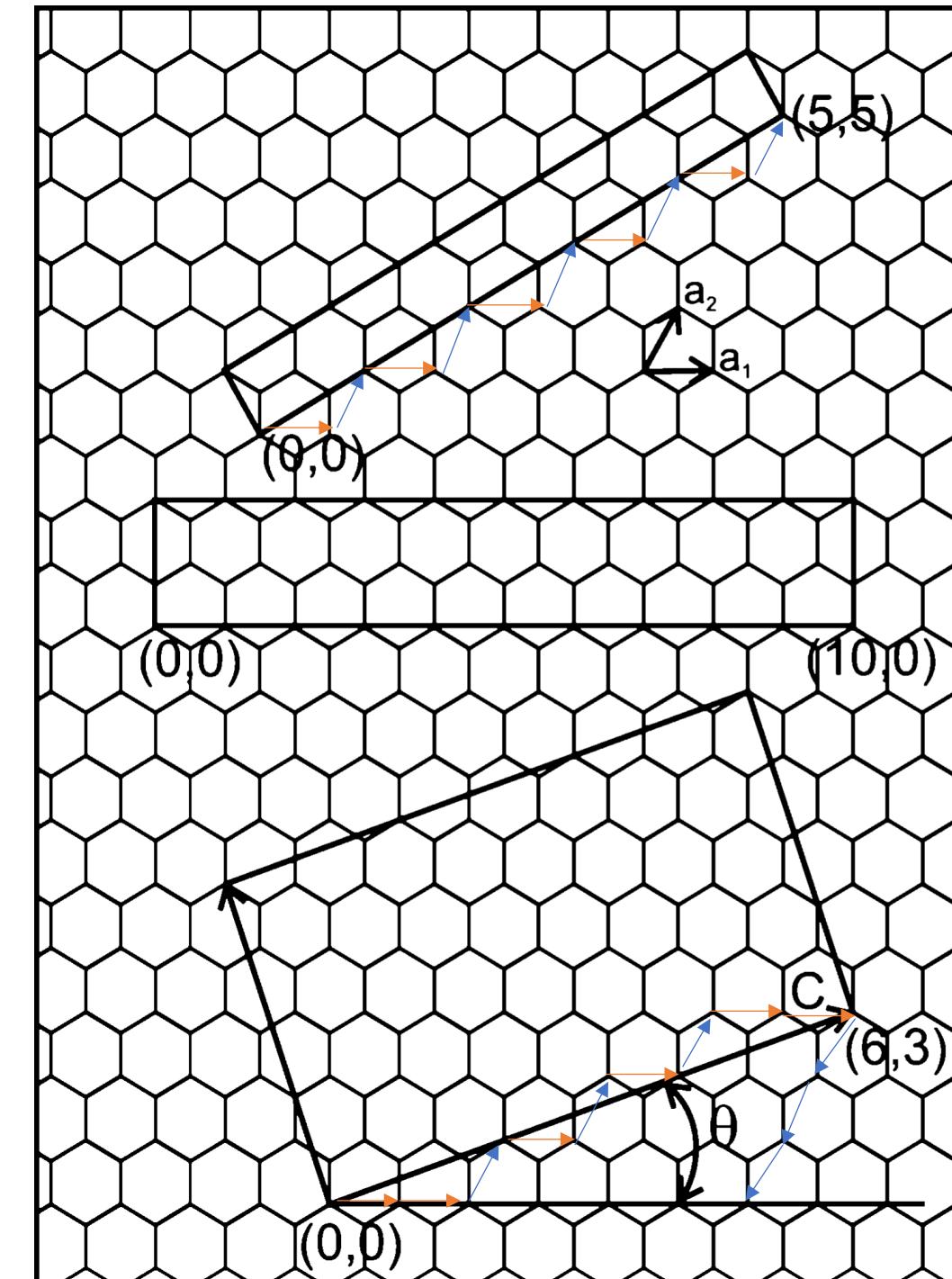
“Armchair” (m,m) CNT: shows metallic behavior.
“Zigzag” ($n,0$) CNT: can be either **semiconducting** or **metallic**, depending on *tube diameter*.

FIGURE 4.1 A strip of a graphene sheet rolled into a tube.

Structure of carbon nanotubes

A single wall carbon nanotube can be imagined to be made by *taking a rectangular strip of graphene sheet, rolling it into a cylinder and welding the two edges*. Adjoining Figure shows the arrangement of hexagons in a graphene sheet with two 'unit vectors' a_1 and a_2 . Any lattice point in the graphene sheet can then be obtained by a translation by integral numbers of a_1 and a_2 . A carbon nanotube is produced by choosing a vector $C = na_1 + ma_2$ and rolling the sheet so that the origin coincides with the end point of this vector, called the **chiral vector**, C .

The angle between the chiral vector and a_1 is called the **chiral angle** (θ).



ARM CHAIR

ZIG ZAG

CHIRAL

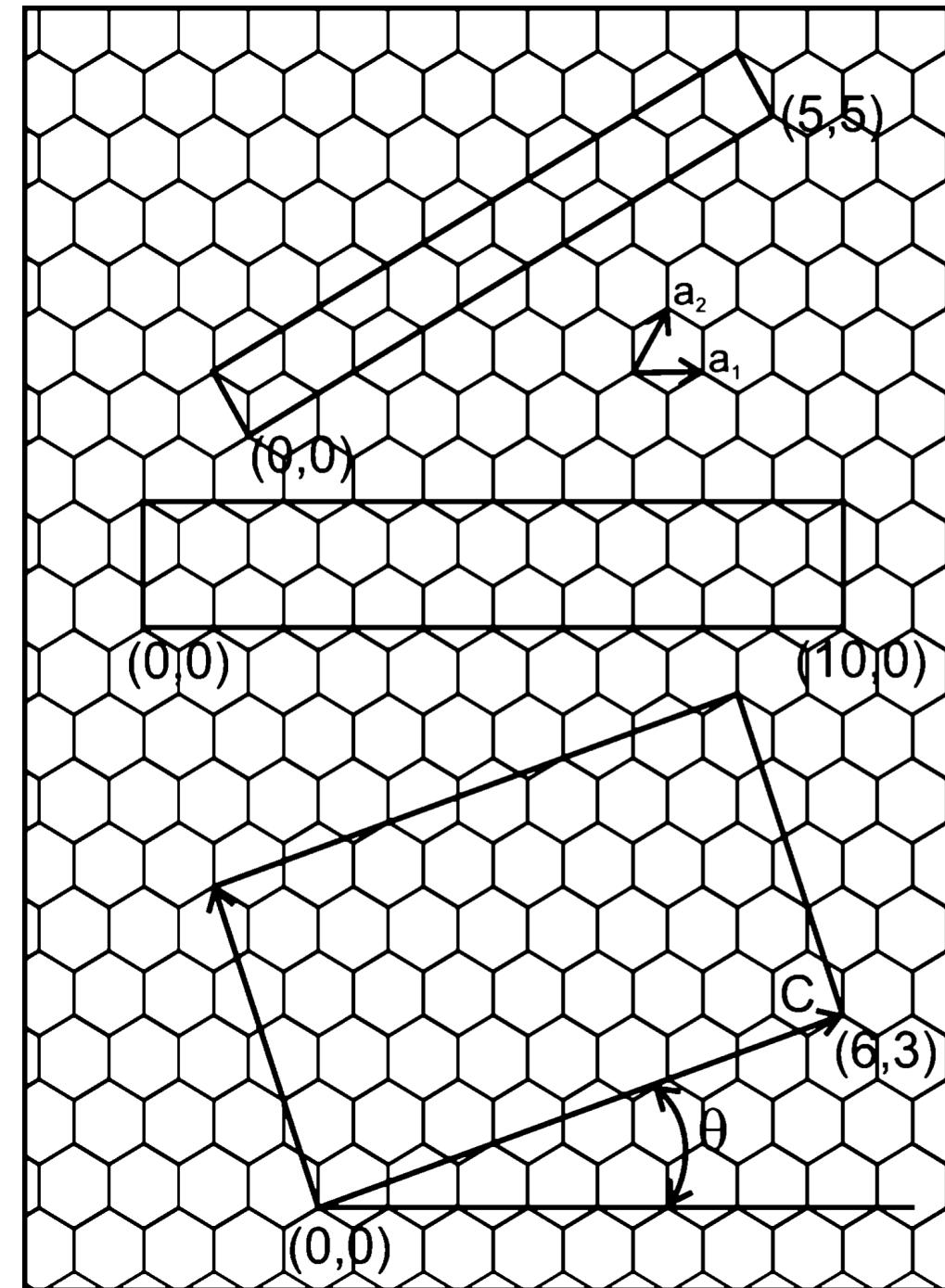
The chiral vector \mathbf{C} ($= n\mathbf{a}_1 + m\mathbf{a}_2$) is referred to by its indices as (n, m) .

If $\mathbf{C} = n\mathbf{a}_1$ then the hexagons in the resulting tube are arranged in a ***zig-zag*** fashion *along the axis of the tube*. The ***chiral angle*** in this case is **zero**. Such a tube is called a “zig-zag” tube (middle of the Fig. 8.8).

If $\mathbf{C} = n\mathbf{a}_1 + n\mathbf{a}_2$ (i.e., $n = m$), then the tube obtained is called an ***armchair*** tube as the hexagons are arranged in an armchair fashion along the axis of the tube (top of Fig. 8.8). In this case the ***chiral angle*** is **30°** .

In all the other cases, the tube is called a ***chiral*** nanotube (bottom of Fig. 8.8) and the *hexagons are arranged along a helix on the surface of the tube*. The chiral nanotubes can exist in two mirror related forms. Any arbitrary chiral vector lies between $\theta = 0^\circ$ (zig-zag tube) and $\theta = 30^\circ$ (armchair tube).

Fig. 8.8. Arrangement of hexagons in a graphene sheet; a_1 and a_2 are the lattice vectors with $|a_1| = |a_2| = a = 0.246$ nm; each side of the hexagon is 0.142 nm; if the sheet is rolled so that the origin coincides with the point (n,n) , e.g. $(5,5)$, then the hexagons are arranged in an **armchair** fashion along the axis of the tube and the tube is called an **armchair nanotube** (top); if the sheet is rolled so that the origin coincides with the point $(n,0)$, e.g. $(10,0)$, then the hexagons in the tube will be arranged in a **zig-zag** manner along the axis (vertical direction) of the tube and the tube is called a **zig-zag tube** (middle); rolling along any other direction $na_1 + ma_2$ with $n \neq m \neq 0$ gives a **chiral nanotube** in which the hexagons are arranged along a helix on the surface of the tube (bottom).



ARM CHAIR

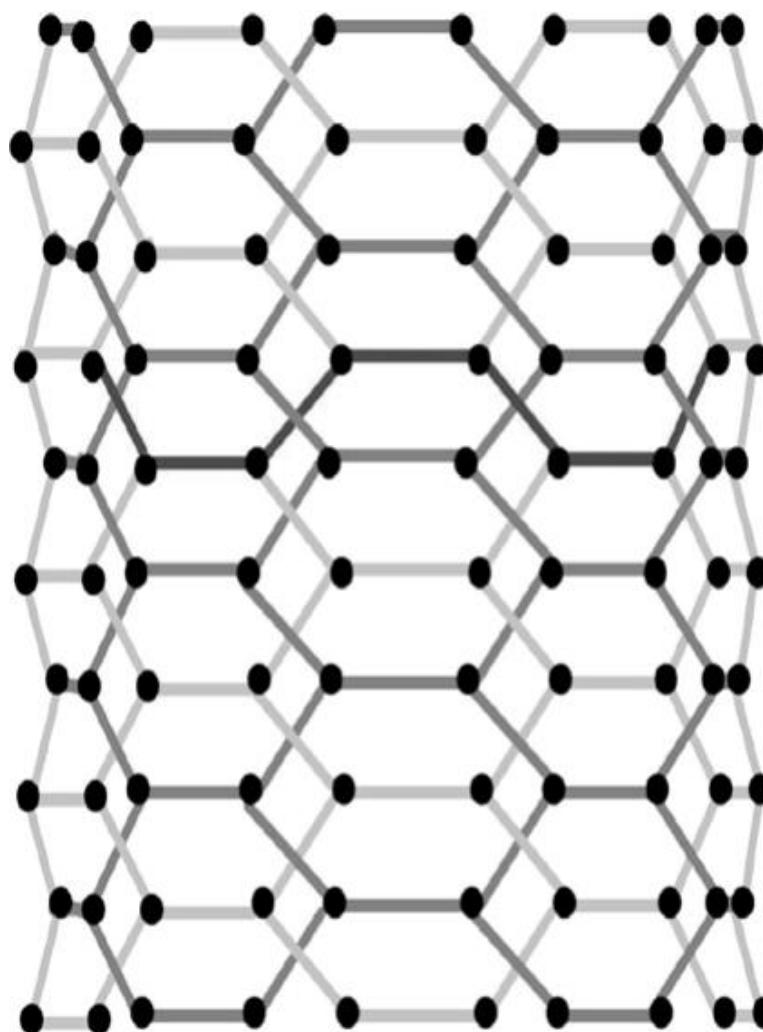
ZIG ZAG

CHIRAL

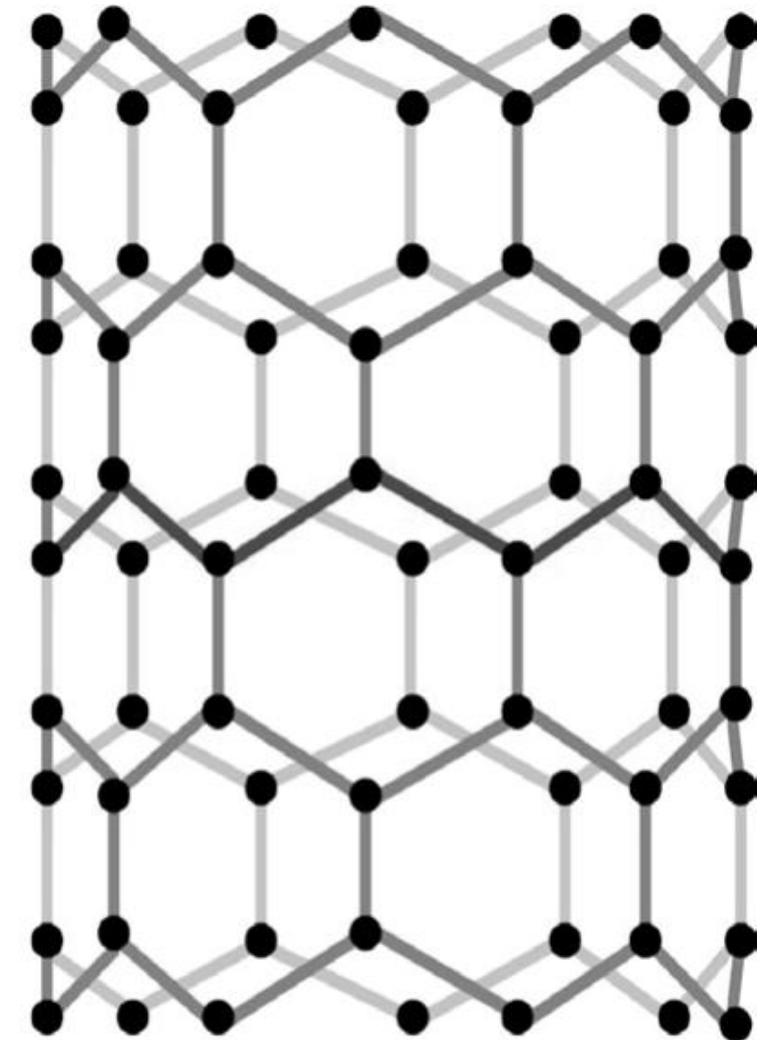
- A *chiral angle* θ is also defined in this figure, which is **the angle between the chiral vector C_h and the zigzag direction** ($\theta = 0$) parallel to the direction of unit vector of a_1 .
- Owing to the hexagonal structure of graphene $0^\circ \leq \theta \leq 30^\circ$). If $\theta = 0^\circ$ then the NT is zigzag, if $\theta = 30^\circ$ it is armchair, and all values in between are chiral CNTs.
- Nanotubes with chiral vectors of (n,n) and $(n,0)$ have no twist and are classified as *achiral* nanotubes. These two special cases are denoted armchair and zig-zag respectively, referring to the pattern of the carbon atoms around the nanotube circumference.

- Three types of nanotube structures can be *classified* based on the chiral vector and the chiral angle.
- Zigzag and *armchair* nanotubes are defined when the corresponding *chiral angles* are $\theta = 0$ and $\theta = 30^\circ$, respectively. These nanotubes are considered *achiral* nanotubes because they have mirror plane symmetry in the structures.
- The other type of nanotubes is **chiral nanotubes**, corresponding to chiral angles in the range $0 < \theta < 30^\circ$.
 - If the *helicity indices* (n, m) are used to label these nanotubes.
 - ✓ *Armchair* nanotubes are those corresponding to $n = m$.
 - ✓ When $m = 0$, a **zigzag** nanotube is formed.
- Three-dimensional models of the two types of achiral nanotubes are shown in Fig. 5.3. Chiral nanotubes correspond to helicity indices n and m in other permutations. In practice, *most carbon nanotubes do not form achiral structures* with high symmetry. Instead, *they like to form chiral nanotubes*, whose helicities can be individually addressed experimentally using electron microscopes and electron diffraction techniques.
- For multiwall nanotubes, constant interlayer separation of continuous tubes puts an additional constraint on the tube structures, requiring each tube layer to have its own helicity.

What kinds of CNTs are these?

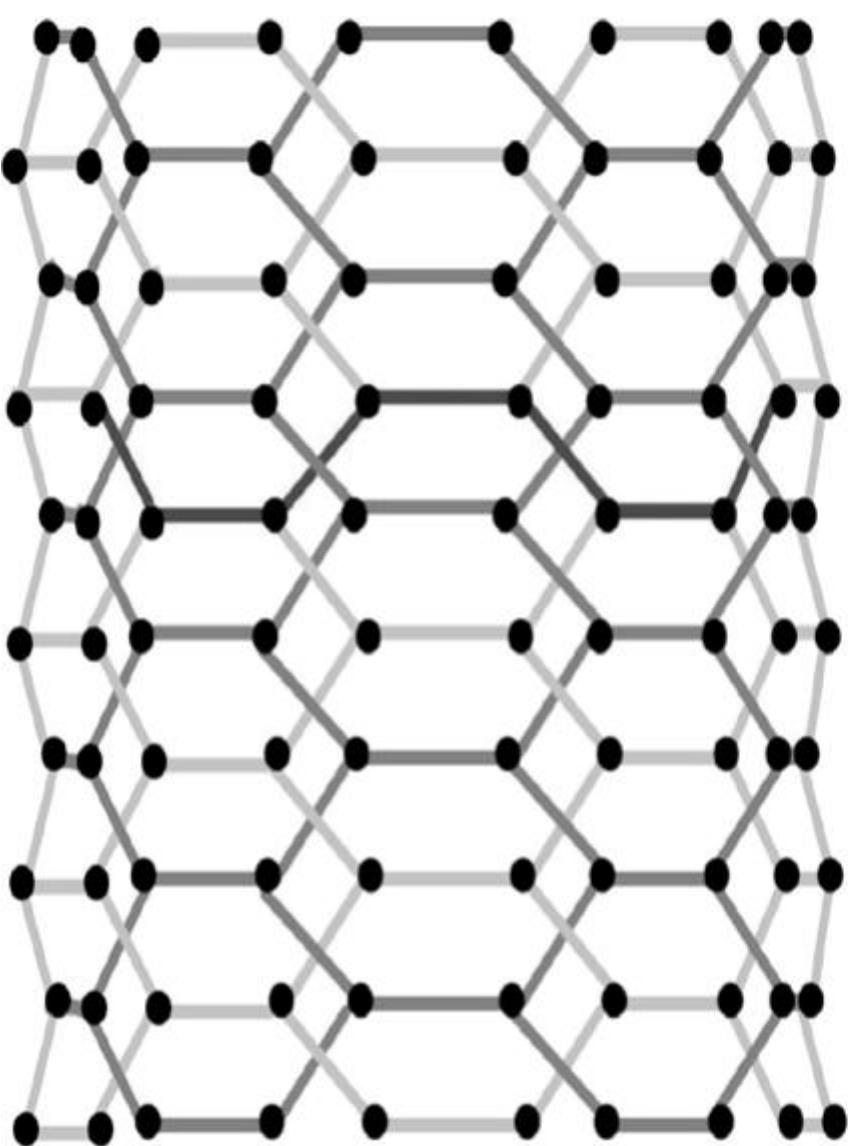


(a)

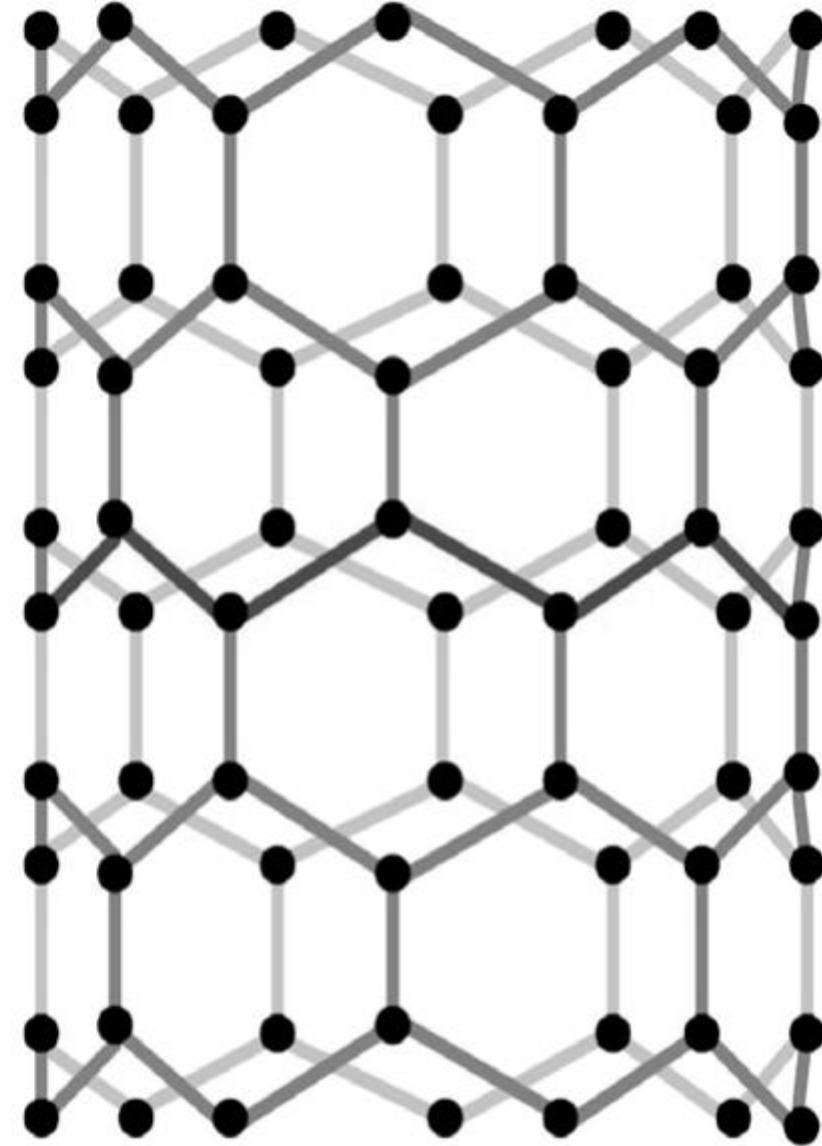


(b)

Figure 5.3 The models of
(a) an **armchair** nanotube
and
(b) a **zigzag** nanotube.



(a)



(b)

Calculation of diameter d of the nanotube: For example, the (3, 3) nanotube in Fig. 11.7 would be rolled along the \vec{C} axis shown, resulting in a tube that has *C–C bonds parallel to the circumferential vectors* and therefore perpendicular to the axis of the tube. Similarly, any (n, 0) tube—or equivalently any (0, m) tube—will have the *C–C bonds oriented parallel to the axis* of the tube.

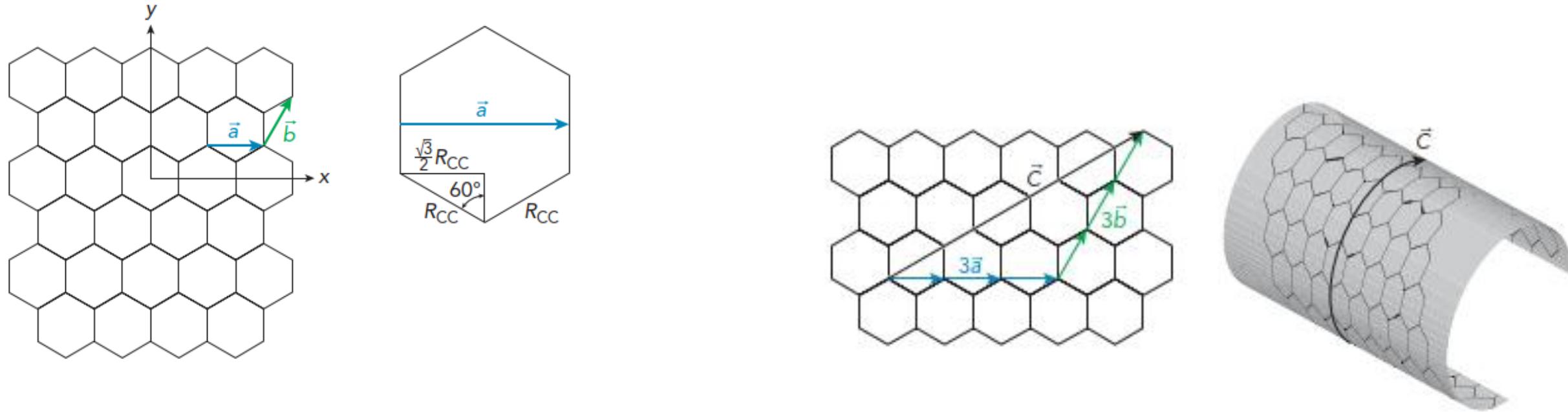


Figure 11.6 The circumferential coordinate vectors \vec{a} and \vec{b} (or the basis vectors of the graphene net, $\vec{a} = \vec{b} = a_g = 0.246$ nm and separated with an inter-angle of 60°) and their summation are shown on graphene, a single sheet of sp^2 covalently bonded carbon atoms. The circumferential vector \vec{C} for a (3,3) nanotube are shown.

Because \vec{a} and \vec{b} are not perpendicular, the length of \vec{C} must be calculated using the angle $\theta = \pi/6$ between the two coordinate vectors:

$$\begin{aligned}
 |\vec{C}|^2 &= |m\vec{a} + n\vec{b}|^2 = |m\vec{a}|^2 + |n\vec{b}|^2 + 2(m\vec{a}) \cdot (n\vec{b}) \\
 &= m^2|\vec{a}|^2 + n^2|\vec{b}|^2 + 2mn(\vec{a}) \cdot (\vec{b}) \\
 &= m^2|\vec{a}|^2 + n^2|\vec{b}|^2 + 2mn(\vec{a})(\vec{b}) \cos \frac{\pi}{3} \\
 &= m^2 + n^2 + 2mn(\sqrt{3}R_{CC})(\sqrt{3}R_{CC})\left(\frac{1}{2}\right)
 \end{aligned}$$

$$|\vec{C}| = \sqrt{3}R_{CC}\sqrt{m^2 + n^2 + mn} = a_g\sqrt{m^2 + n^2 + mn}$$

(where R_{CC} is the *neighboring* C–C bond distance)

If the **diameter** of the **nanotube** is d , then $\pi d = |\vec{C}|$

Therefore, the diameter d of the nanotube can then be calculated as:

$$d = \frac{|\vec{C}|}{\pi} = \frac{\sqrt{3}}{\pi} R_{CC}\sqrt{m^2 + n^2 + mn} = \frac{a_g}{\pi}\sqrt{m^2 + n^2 + mn}$$

The chiral angle, θ , is given by;
$$\theta = \tan^{-1}(\sqrt{3}n/(2m + n))$$

- **Estimate** the diameter of the (3, 3) carbon nanotube shown above, assuming a carbon–carbon bond length of 1.42 Å.

(Ans. 4.07 Å; ***This diameter is among the smallest possible for carbon nanotubes, but it has been observed in experiments.***)

- A SWCNT can be uniquely defined by its chiral vector. The word uniquely, in this context, means both geometrically and, as we will realize later, physical and chemical property wise. Hence nanotubes are usually referred to by the two vector multiples (n,m) defining their chiral vector.

- The CNTs are characterized by the vector (n, m) which is given in terms of the base vectors \mathbf{a}_1 and \mathbf{a}_2 (see Fig. 5.6) where ***the magnitude of the vector is the circumference of the tube***.
- The (n, m) indices can be determined experimentally by photoluminescence studies in conjunction with resonant Raman experiments. The $n = m$ tubes are of the armchair structure, whereas the $n = 0$ or $m = 0$ tubes are of the zigzag structure.

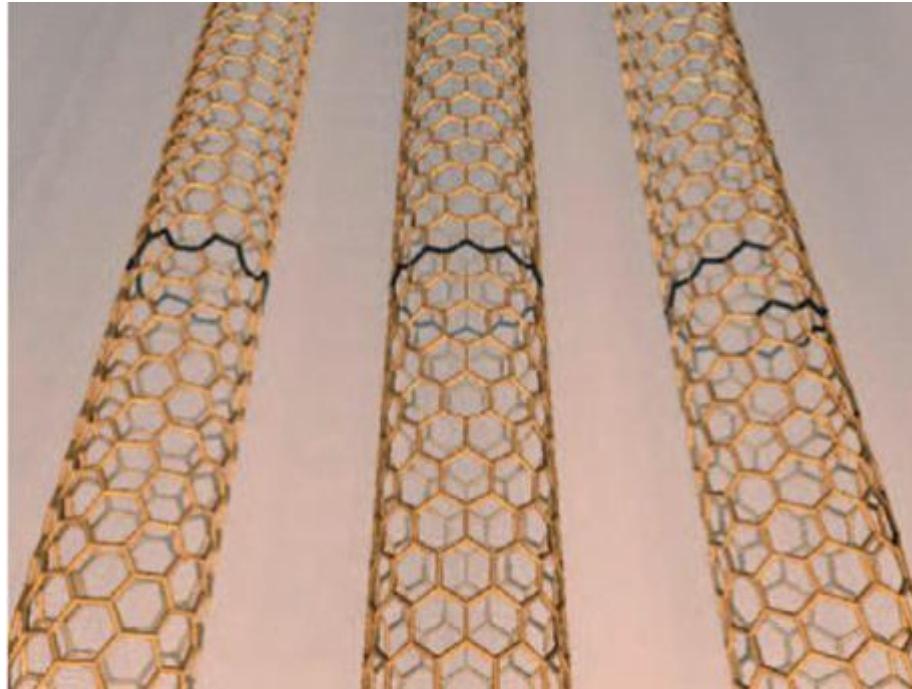


Fig. 5.5 The carbon nanotubes (CNTs) can be thought to be formed by seamless bending of graphene layers with triply coordinated C atoms. Three different types of CNTs can be differentiated as “armchair” (left), zigzag (center), and chiral (right).

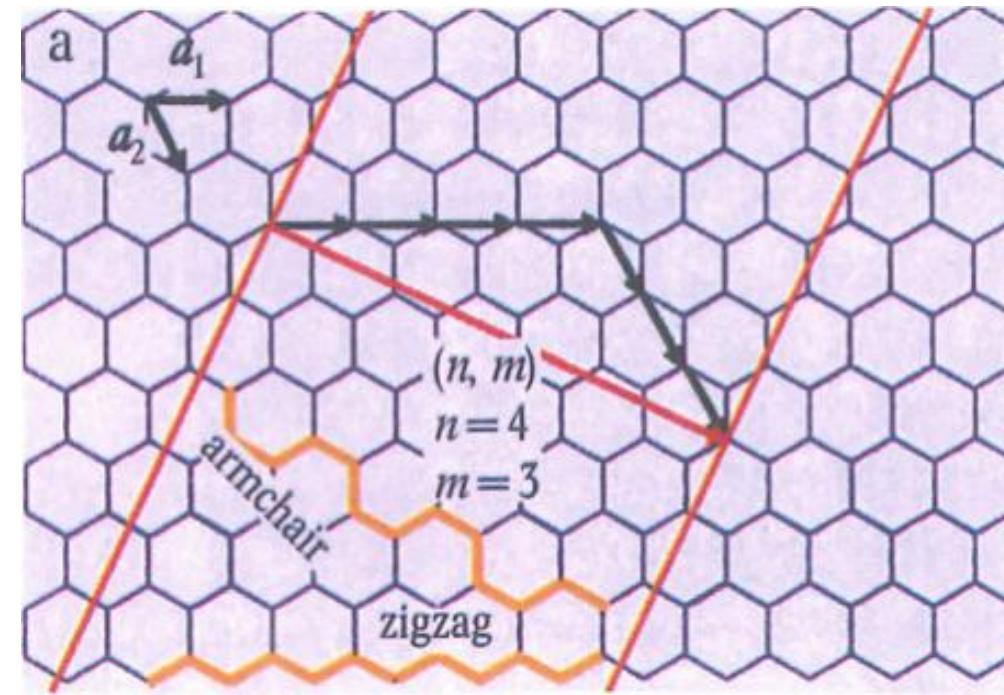
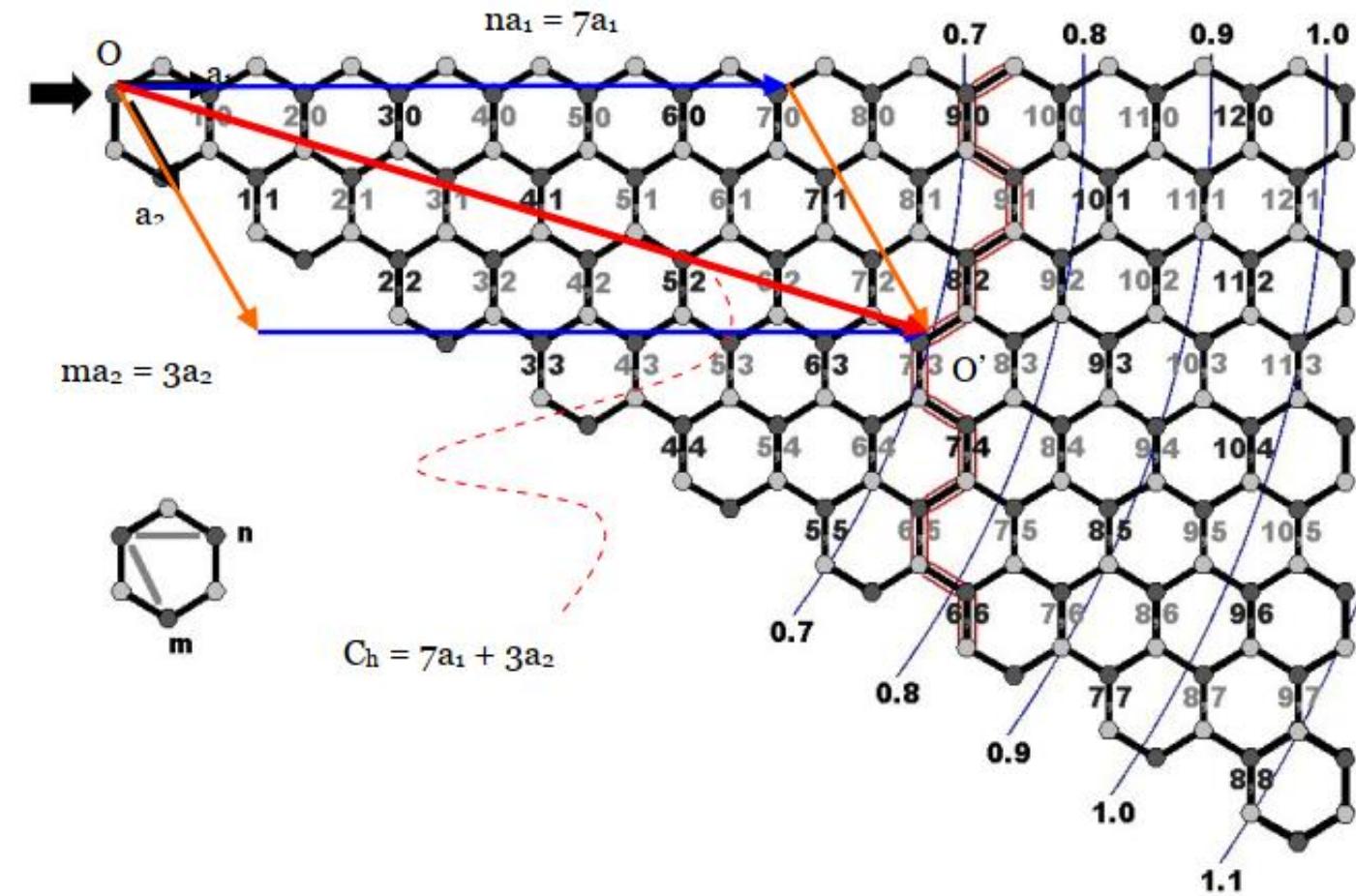


Fig. 5.6 The vector (n, m) perpendicular to the CNT axis, defined by the base vectors \mathbf{a}_1 and \mathbf{a}_2 .

FIGURE 2-3.

- Graphene sheet with indications of the possible “roll-up” (chiral) vectors;
- $C_h = na_1 + ma_2$.
- The atom marked with the black arrow, can only be identical, and therefore roll-up, to the other dark atoms.
- The $C_h (7,3)$ SWCNT is exemplified with the red arrow. This CNT can form superimposing the carbon atom at O onto the carbon atom at O'.
- Diameters of different C_h 's (0.7 to 1.1 nm are shown) are indicated with the blue lines.
- **The red-and-black line running from (9,0) to (6,6) indicates the smallest stable SWCNT.**



The way the graphene is cookie-cut can then be defined by its chirality vector (also sometimes known as the roll-up vector):

$$C_h = na + mb$$

where the (n,m) notation is used as shorthand, thus, e.g., defining a “(5,5) CNT.”

Certain values of n and m are in turn given further, shorthand names, zigzag, armchair, and the generic chiral, corresponding to the way in which the graphene edge appears to be cut. **In the zigzag, the graphene is cut along the tops of the hexagons and $m = 0$, so this type of cut is designated $(n,0)$;** **in the armchair, it is cut along the centers of the hexagon and $n = m$, so this type of CNT is sometimes designated (n,n) ;** and **in the chiral, it can be cut in almost any way**, defined by the chiral parameters.

This is also shown in Fig. 1.3. The **vector C_h is always perpendicular to the axis of the cylinder of the CNT.**

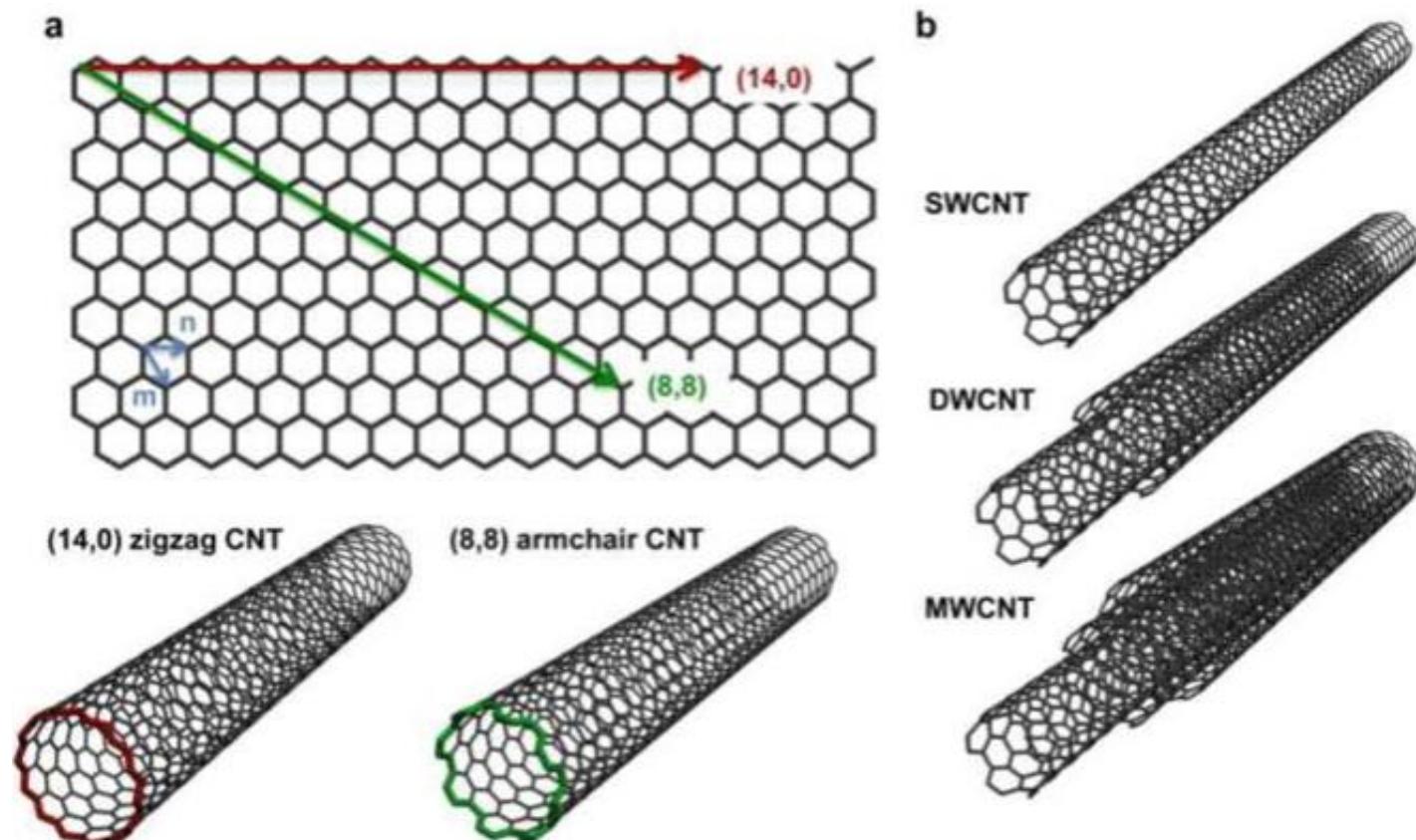
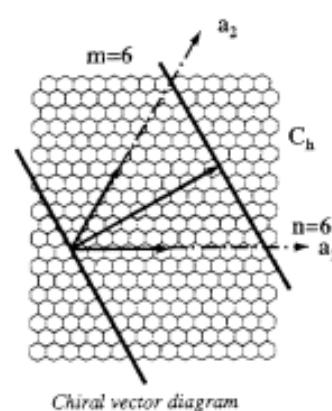
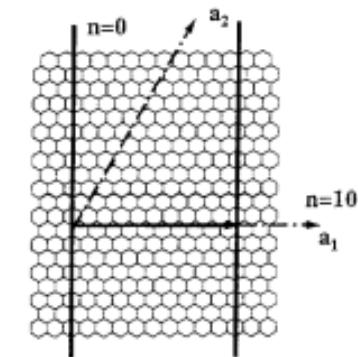


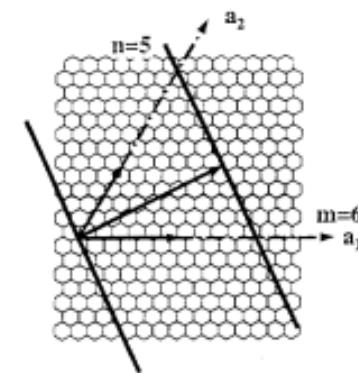
FIGURE 2.1. SWCN structure and example of nanotubes.



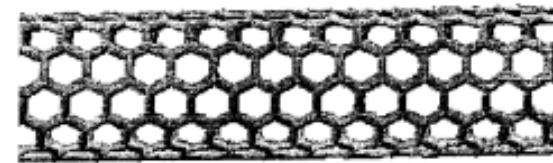
a) Armchair nanotube (6,6)



b) Zig zag nanotube (10,0)



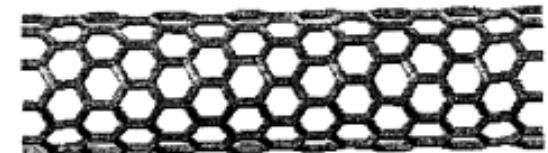
c) Chiral nanotube (6,5)



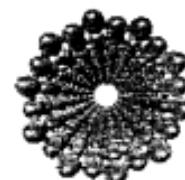
Side view



Front view



Side view



Front view



Side view



Front view

- A fullerene is a carbon sheet closed upon itself to form a sphere.
- A carbon nanotube can be similarly seen as a graphene sheet folded into a cylinder.
- ***Such closure and folding of the graphene sheet occur because they lead to a decrease in energy.***
- ***At the edge of a graphene sheet, the carbon atoms are bonded to only two other atoms and have one dangling bond.***
- ***As the size of the graphene sheet decreases, the ratio of the edge atoms (2-coordinated) to the inside atoms (3-coordinated) increases rapidly.***
- ***The energy can be reduced if two dangling bonds join together to form a single bond.***
- At small sizes of the graphene sheet, the number of the dangling bonds is large, and the sheet structure becomes unstable with respect to a folded structure.
- ***Some elastic strain energy is introduced due to folding; however, the reduction in energy due to the elimination of the dangling bonds more than compensates for this increase in energy.***
- The activation for the process is usually provided by heat available during the synthesis of fullerenes and the nanotubes.

- Carbon nanotubes are a new carbon allotropic form, composed of sp^2 carbon atoms, similar to graphite but arranged in a cylindrical fashion. The curvature that these graphene sheets possess gives rise to (i) an appreciable change in the pyramidalization angle and (ii) a misalignment of p -orbitals. Consequently, CNTs show an **increased reactivity** towards addition reactions. Due to these facts, **the CNT sidewalls are supposed to be more reactive than the planar sheets of graphene**. However, at the same time, they are found to be **less reactive than fullerenes, which have larger curvatures and therefore higher strains**.
- In graphite, the four valence electrons of carbon form three sp^2 -hybridized σ bonds and one π -orbital. If a graphene sheet is rolled up into a structure like a CNT, **the orbital structure of carbon is altered, because the bond length between carbon atoms decreases and the bond angle changes**. The σ - and π -orbitals are no longer perpendicular to each other. As a consequence, **the parts of the π -orbitals inside and outside of a nanotube rearrange, in a way that the outer contribution is larger than the inner one** (see Figure 6a). The curvature induces a mixed state of σ - and π -orbitals, called **rehybridization**.
- Nearly all CNTs display a C—C bond length of about 1.45 Å, representing an sp^2 -C to sp^3 -C bond.
- MWCNTs have intertubule spacings of about 3.4 Å, close to that of the inter-sheet spacing in graphite (3.35 Å).

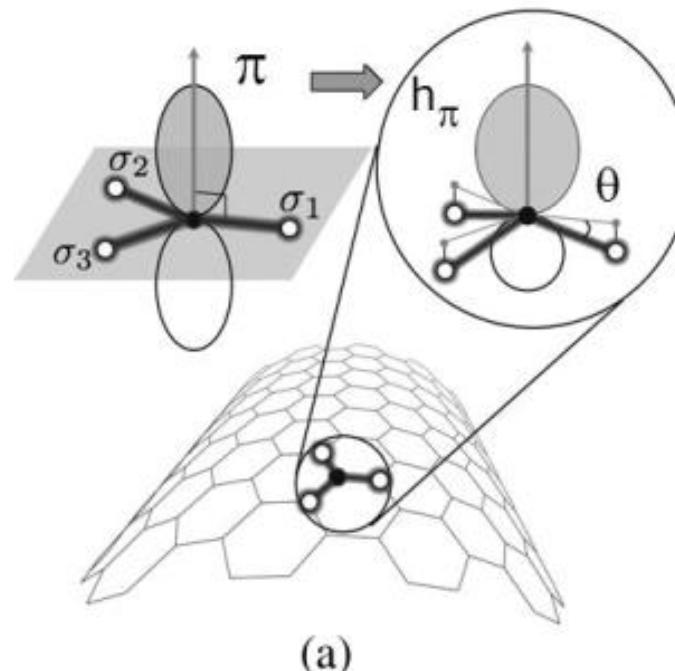


Figure 6. (a) Diagram showing the π -orbital in planar graphene and its change into h_π under bending together with the pyramidalization angle θ .

Electrical Properties

- Carbon nanotubes have the most interesting property that they are metallic or semiconducting, depending on the diameter and chirality of the tube. Chirality refers to how the tubes are rolled with respect to the direction of the T vector in the graphene plane, as discussed above. Synthesis generally results in a mixture of tubes two-thirds of which are semiconducting and one-third metallic.
- The metallic tubes have the armchair structure.
- Figure 5.15 is a plot of the energy gap of semiconducting chiral carbon nanotubes versus the reciprocal of the diameter, showing that as the diameter of the tube increases, the bandgap decreases.
- Electrons in the quantum theory can be viewed as waves. If the electron wavelength is not a multiple of the circumference of the tube, it will destructively interfere with itself, and therefore only electron wavelengths that are integer multiples of the circumference of the tubes are allowed. This severely limits the number of energy states available for conduction around the cylinder. The dominant remaining conduction path is along the axis of the tubes, making carbon nanotubes function as one-dimensional quantum wires. The electronic states of the tubes do not form a single wide electronic energy band, but instead split into one-dimensional sub-bands. These states can be modeled by a potential well having a depth equal to the length of the nanotube.

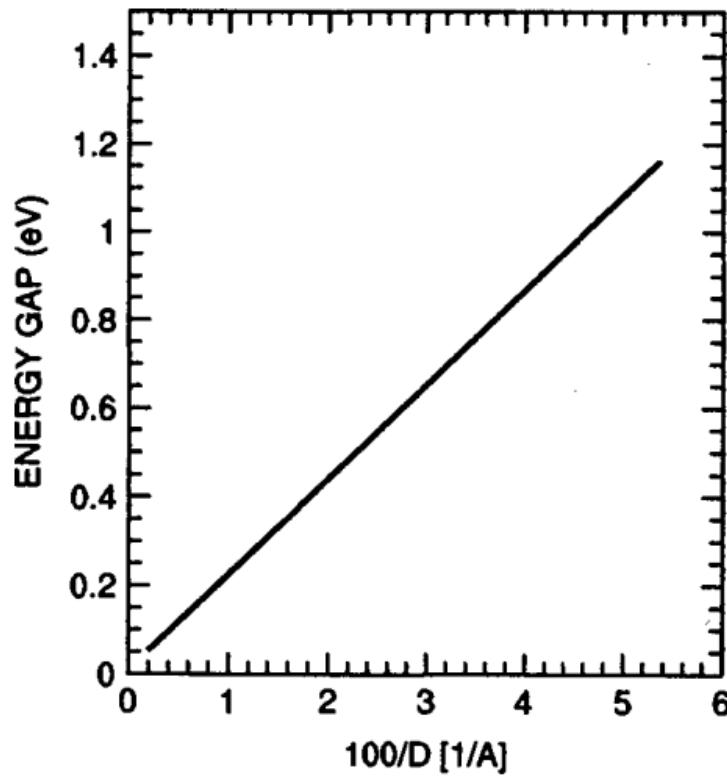


Figure 5.15. Plot of the magnitude of the energy band gap of a semiconducting, chiral carbon nanotube versus the reciprocal of the diameter of the tube ($10 \text{ \AA} = 1 \text{ nm}$).

[Adapted from M. S. Dresselhaus et al., Molec. Mater. 4, 27 (1994).]

- Carbon nanotubes have **unique physical properties**: both mechanical and electrical.
- Unlike a single sheet of graphite which is a semiconductor, carbon nanotubes are found as a random mixture of conductive and semiconductive entities.
- The conductivity of the tubes depends on the direction by which the sheet of carbon is wrapped to form the tube.
- The conductivity of tubes on the one hand and their small size on the other led to the suggestion of the use of the tubes as molecular wires, conductive composites, and interconnects.
- Furthermore, the electric properties of carbon nanotubes appear to be modulated by various gases, for example nitrogen dioxide. Thus, arrays of carbon nanotubes could serve as very sensitive gas sensors.
- They have a ***tensile strength that is about 10 times greater than steel***, yet at ***about one quarter the weight***. Therefore, **carbon nanotubes are considered the strongest known material for their weight**.
- Therefore, carbon nanotubes are expected to be used in the development of ultra-strong materials for the construction, car, and aviation industries.
- Moreover, carbon nanotubes are envisioned as thread for ultra-strong fabrics and clothing such as light weight bullet proof fabrics.
- CNTs are also said to possess ***exceptional physico-mechanical properties such as tensile strength (said to be greater than that of steel)*** and elastic modulus. However, it is also true that none of these exceptional mechanical properties have been converted to a “macro” product, i.e., a practical product that can be used in the real world, with anything close to the properties reported experimentally on nanotubes on a “nano-” or “micro-” scale, although incremental (20% to 60%) improvements to physico-mechanical properties have been obtained when CNTs are added to extant materials.

- CNTs are today found in niche applications, such as additions to composite bicycle parts to make them slightly (about 25%) stronger; additions to polymer-matrix composites to make them slightly more (about 30%) thermally conductive and thus quicker to cure, increasing the specific strength of carbon fiber composites (about 50%); and the like.
- One of the wildest ideas for the use of nanotubes is the assembly of an ultra-strong cable to be used for the construction of a space elevator.
- Other potential applications that have been proposed for carbon nanotubes includes energy storage and energy conversion devices; field emission displays and radiation sources; hydrogen storage media; and nanometer-sized semiconductor devices.
- However, many of the ***potential commercial uses of carbon nanotubes are limited by its high cost of production.*** A pure sample of carbon nanotubes cost *a few hundred dollars a gram*. Such a high price makes many of the suggested uses of carbon nanotubes commercially unrealistic. Yet, much efforts are being invested in the construction of industrial settings for large scale production of carbon nanotubes and their price is expected to be lowered in years to come.

Carbon nanotube properties: Electronic

➤ Electronic band structure is determined by symmetry:

- $n = m$: Metal
- $n - m = 3j$ (j non-zero integer): Tiny band-gap semiconductor (nearly metallic)
- Else: Large band-gap semiconductor.

➤ Band-gap is determined by the diameter (d) of the tube:

- For tiny band-gap tube: $E_g \propto \frac{1}{d^2}$
- For large band-gap tube: $E_g \propto \frac{1}{d}$ ($E_g \approx \frac{0.9}{d}$ (eV))

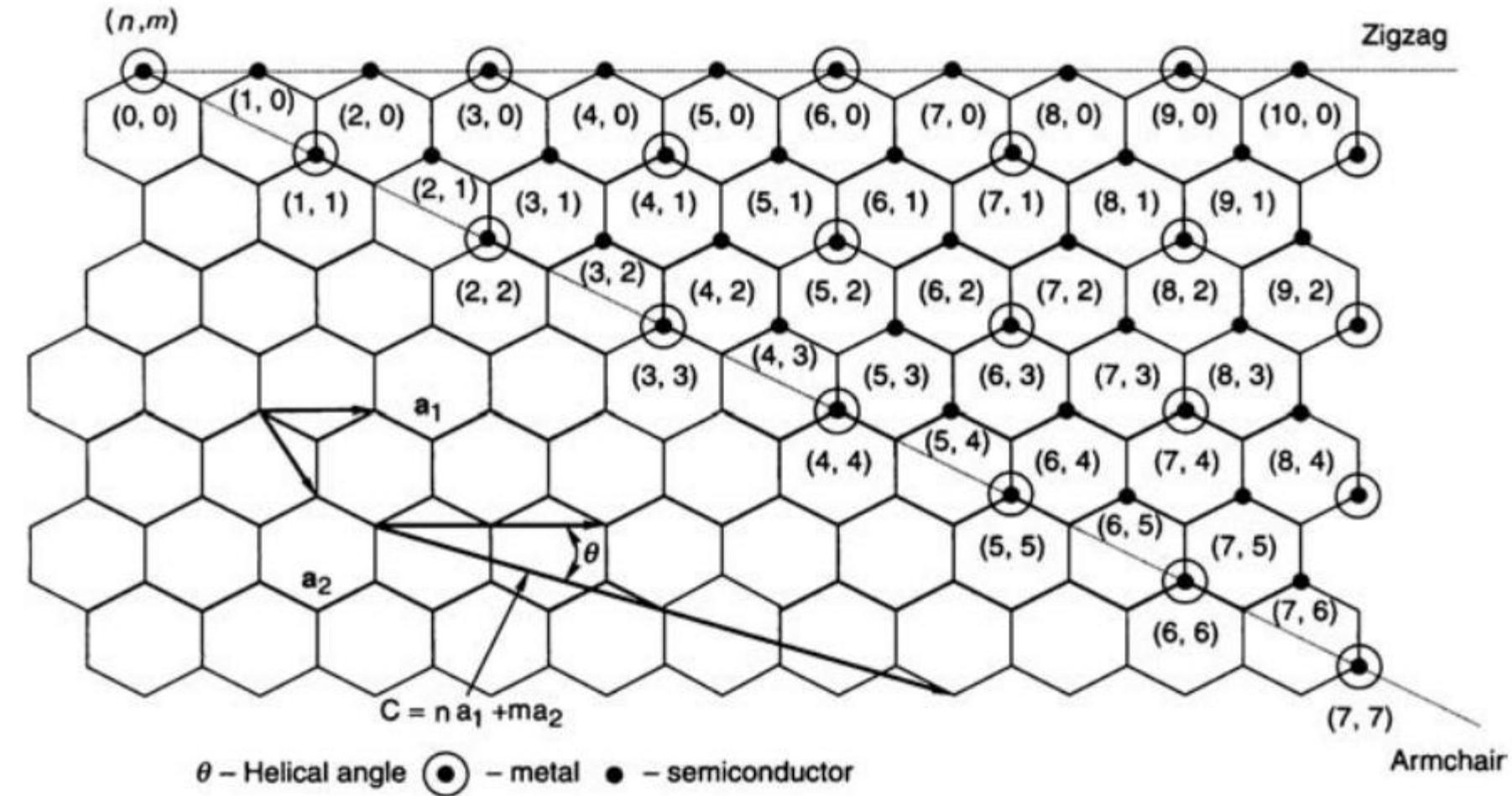
➤ The **diameter** of the nanotube is given by $d = (a_g/\pi) (n^2 + mn + m^2)^{0.5}$ where a_g (=0.246 nm) is the lattice constant of graphite.

➤ An important property of semiconducting nanotubes is that the *bandgap energy* (E_g), which is essential in determining the electronic and optical properties of carbon nanotubes, is *inversely proportional to the tube diameters*. The **bandgap tunability through diameters** is an **important merit of semiconducting nanotubes**.

➤ The density of electronic carriers as well as the absorption bandgap of nanotubes can be potentially tuned by the tube diameters to match certain electronic and optical applications.

- The electronic properties of SWCNTs are due to the wrapping angle of the graphene sheet.
- The electronic energy distribution depends strongly on the direction of the circumferential vector. Thus, SWCNTs are classified as **armchair**, **zigzag** and **chiral**, based on their hexagonal lattice structure.
- The zigzag and chiral nanotubes can be either metallic or semiconducting while **armchair** nanotubes are always **conducting (metallic)**.
- A SWNT can be either **metallic or semiconducting depending on its chirality**, i.e., the values of n and m .
- Of particular interest, the electrons in the π system formed from the p_z orbitals, perpendicular to the surface of the nanotube, find themselves in a **nearly metallic** environment only when $(n - m)$ is an integer multiple of 3.
- At these orientations, the lowest excited p -electron MO in the nanotube drops to the energy of the highest occupied MO, allowing the electrons to be excited with the tiniest push. These **excited state orbitals connect adjacent hexagons**, and the electrons can move freely from one end of the nanotube to the other.
- The same holds for the p electrons in ordinary graphite, so this is not terribly surprising. However, **as we change the value of $(n - m)$, we separate the HOMO and LUMO energies** so that the **nanotube becomes a semiconductor** requiring some additional energy to push the localized electrons into the excited state MOs.
- When $(n - m)/3$ is an integer, the nanotube is **nearly metallic (or tiny band-gap semiconductor)**; otherwise, it is **semiconducting**.
- As we expect, the nanotube returns toward the electrical conductance of graphite as the diameter of the tube increases and the surface of the tube becomes flatter.
- The resistance of a metallic CNT is $h/4e^2 \approx 6.5 \text{ K}\Omega$ where h is Planck's constant.

Fig. 3. The 2D graphene sheet is shown along with the vector which specifies the chiral nanotube. The pairs of integers (n,m) in the figure specify chiral vectors C_h . Below each pair of integers (n,m) is listed the number of distinct caps that can be joined continuously to the cylindrical carbon tubule denoted by (n,m) . The circled dots denote metallic tubules, and the small dots are for semiconducting tubules.



$$\overrightarrow{C_h} = n\overrightarrow{a_1} + m\overrightarrow{a_2} \equiv (n, m)$$

(Adapted from Dresselhaus et al. Copyright Elsevier, 1995.)

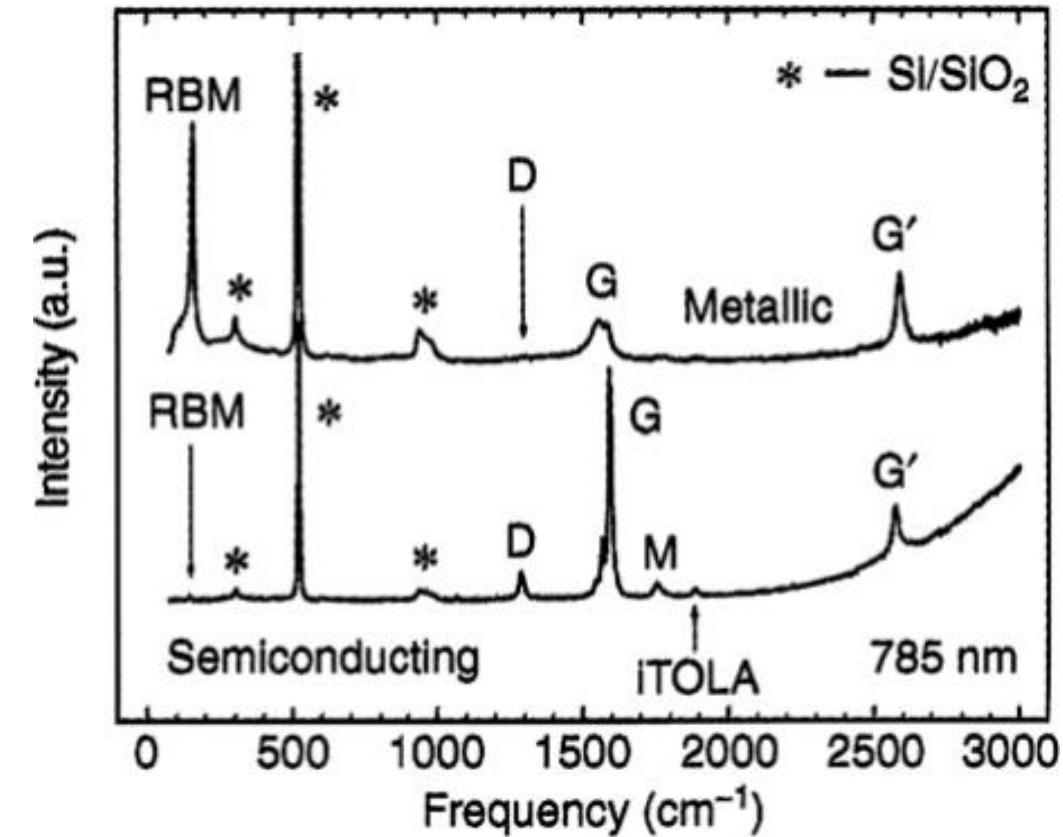
- Most currently available **synthetic methods** produce SWCNTs with a *random distribution of metallic and semiconducting nanotubes, in a ratio of 1:2*.
- Except for the sp^3 hybridized diamond structure, all of these forms of carbon conduct electricity (and the **fullerenes, with help from the alkali metals, can even become superconductors**, with zero electrical resistance).
- These **fascinating properties make CNTs unique materials with a high potential for molecular electronics**.
- In the metallic state the conductivity of the nanotubes is very high. A **rope** of SWCNTs has conductivity in the range 10000–30000 S cm^{-1} at room temperature. In fact, it has been reported that **SWCNTs can act as ballistic conductors, with high effective electron mobilities and can sustain very high current densities**. It is estimated that they can carry a billion amperes per square centimeter. Copper wire fails at one million amperes per square centimeter because resistive heating melts the wire. One reason for the high conductivity of the carbon tubes is that they have very few defects to scatter electrons, and thus a very low resistance. High currents do not heat the tubes in the same way that they heat copper wires. Nanotubes also have a very high thermal conductivity, almost a factor of 2 more than that of diamond. This means that they are also very good conductors of heat.
- These properties, combined with the material's nanosize, offer unique opportunities to develop miniature advanced sensors for rapid, label-free electronic detection of different biological materials. The fabrication of these sensors is supported by the exceptional mechanical strength — a useful feature for tissue scaffolds and engineering that is demonstrated by a Young modulus of ~ 1 TPa.
- Individual carbon nanotubes have an unusually high ratio of strength to weight, and at present this is the basis of their principal application, which is in the development of new lightweight construction materials.
- Their small size has also led to their use in probe tips for atomic force microscopes.

Optical Properties: Raman Spectra:

- The molecular structure of single-walled carbon nanotubes (SWCNTs) can be considered as graphene sheet of carbon atoms rolled into seamless hollow cylinder, and multi-walled carbon nanotubes (MWCNTs) are regarded as several co-axially arranged SWCNTs with varying diameter.
- In graphene, the Stokes phonon energy shift caused by laser excitation creates two main peaks in the Raman spectrum: **G (1580 cm⁻¹)**, a primary *in-plane vibrational mode*, and **2D (2690 cm⁻¹)**, a second-order overtone of a *different in-plane vibration*, **D (1350 cm⁻¹)**. *D and 2D peak positions are dispersive (dependent on the laser excitation energy)*.
- The G-mode is at about 1580 cm⁻¹ and arises from the stretching of the C-C bond in graphitic materials and is common to all sp² carbon systems.
- *The D-mode is caused by disordered structure of graphene.* The presence of disorder in sp²-hybridized carbon systems results in resonance Raman spectra, and thus makes Raman spectroscopy one of the *most sensitive techniques to characterize disorder in sp² carbon materials*.

- The peak appearing at $\sim 1750 \text{ cm}^{-1}$ is called the **M** band, which is an overtone of the out-of-plane transverse optical (oTO) phonon and has been observed in *graphite* and *single-walled nanotube* (SWNT) samples. **The M band, activated by strong coupling between graphene layers, is suppressed** for SLG.
- If there are some *randomly distributed impurities or surface charges* in the graphene, the G-peak can **split into two peaks**, G-peak (1580 cm^{-1}) and D'-peak (1620 cm^{-1}). The main reason is that the localized vibrational modes of the impurities can interact with the extended phonon modes of graphene resulting in the observed splitting.
- Although the D- and G-bands are found in Raman spectra of graphite, **the RBM (radial breathing mode)** is **specific to CNTs** and *is representative of the isotropic radial expansion of CNTs*.
- The *RBM corresponds to the coherent vibration of the carbon atoms in the radial direction*, and the RBM frequency of SWCNTs has been proved to be inversely proportional to the tube diameter.
- Therefore, *the Raman RBM is an important parameter for determining the distribution of diameters for CNT samples*.

Fig. 5.7 Raman spectra from a ***metallic*** and from a ***semiconducting*** isolated ***SWNT*** on a Si/SiO₂ substrate obtained with a 785 nm laser excitation. The strong first-order features – the *radial breathing mode* (RBM) and the *tangential G band-mode vibrations* – are assigned in the spectra. The D, M, iTOLA (**^{**}see below), and G' features are modes activated by defects (D) or combination of two modes. The features with an asterisk originate from the Si/SiO₂ substrate.



***iTOLA (in-plane Transverse Optical-Longitudinal Acoustic).

For a one-dimensional alternating array of two types of ion or atom of mass m_1 , m_2 repeated periodically at a distance, connected by springs, two modes of vibration result: so-called *optical* mode and the *acoustic* mode. In the optical mode two adjacent *different* atoms move against each other, while in the acoustic mode they move together.

Optical Properties: Raman Spectra:

- The phonon structure of SWNTs can be studied optically by using resonance Raman spectroscopy. In Fig. 5.7 the Raman spectra from two isolated SWNTs show features of ***the radial breathing mode (RBM)*** where all C atoms vibrate radially and the ***graphite-like G band mode characteristic for tangential vibrations***.
- The RBM frequency ω can be used for measuring the tube diameter d making use of the relationship $\omega = \alpha/d$.
- ***The G mode is different for metallic and semiconducting SWNTs due to the presence of plasmons in metallic SWNTs*** which couple to phonons.
- The peak in the above Figure appearing at $\sim 1750 \text{ cm}^{-1}$ is (a double peak feature) called the M band, which is an overtone of the out-of-plane transverse optica (oTO) phonon and has been observed in *graphite and single-walled nanotube* (SWNT) samples. The M band, which is activated by strong coupling between graphene layers, is suppressed for SLG.

□ Special Properties of Carbon Nanotubes

- Based on the rolling direction, CNTs can be semiconductors or conductors. CNTs show extraordinary mechanical, electrical, and thermal properties because of their C–C covalent bonding and seamless hexagonal network architecture. Electronic, molecular, and structural properties of CNTs are determined to a large extent by their nearly 1D structure. The most important properties of carbon nanomaterials and their molecular background are discussed as follows:
- ❖ **The chemical reactivity:** The chemical reactivity of a CNT is, compared with a graphene sheet, enhanced as a direct result of the curvature of the CNT surface. CNT reactivity is directly related to the π orbital difference caused by an increased curvature. Therefore, a difference must be made between the sidewall and the end caps of a nanotube. For the same reason, a smaller nanotube diameter results in increased reactivity. Covalent chemical modification of either sidewalls or end caps has shown to be possible. For example, the solubility of CNTs in different solvents can be controlled this way. However, direct investigation of chemical modification on nanotube behavior is difficult as the crude nanotube samples are still not pure enough.
- ❖ **Electrical conductivity:** Depending on their chiral vector, CNTs with a small diameter are either semiconducting or metallic. The differences in conducting properties are caused by the molecular structure that results in a different band structure and thus a different band gap. The differences in conductivity can easily be derived from the graphene sheet properties. A (n, m) nanotube is semiconducting if $n - m \neq 3 \times$ integer whereas shows metallic conductivity when $n = m$ or $n - m = 3 \times$ integer, where n and m are defining coordinates of the nanotube. The resistance to conduction is determined by quantum mechanical aspects and was proved to be independent of the nanotube length.

- ❖ **Optical activity:** Theoretical studies have revealed that the optical activity of chiral nanotubes disappears if the nanotubes become larger. Therefore, it is expected that other physical properties are influenced by these parameters too. Use of the optical activity might result in optical devices in which CNTs play an important role.
- ❖ **Mechanical strength:** CNTs have a very large Young modulus in their axial direction. The nanotube as a whole is very flexible because of the great length. Therefore, these compounds are potentially suitable for applications in composite materials that need anisotropic properties.

Synthesis: Although the rolled sheet is a convenient way to describe the structure of a carbon nanotube in terms of plane geometry, this is not the way the tubes are normally formed. Several different methods exist. Different methods to generate CNTs can be categorized as (a) *arc-discharge*, (b) *laser ablation*, (c) *chemical vapor deposition* (CVD), (d) *catalytic gas-phase growth* starting with carbon monoxide or other carbon sources (e.g., High Pressure Carbon Monoxide, HiPco, methods).

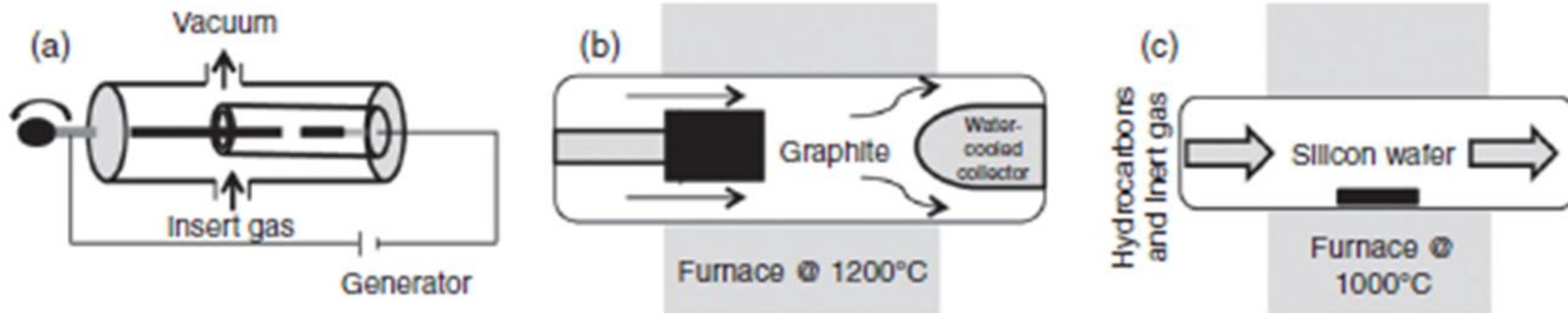
The first two methods involve the vaporization of carbon in an inert atmosphere, whereas CVD and HiPco are based on catalytic decomposition of hydrocarbons. The synthesis of CNTs has advanced to the point that patterns of aligned MWCNTs or SWCNTs can be engineered.

One common way to make carbon nanotubes currently is to grow them by plasma-enhanced chemical vapor deposition (PECVD) from metal nanoparticles attached to a solid surface in a vacuum chamber. An electric discharge runs through a combination of gases—a noble gas to provide the ions that maintain the discharge current, a hydrocarbon to provide the carbon atoms, and a process gas such as hydrogen or ammonia that helps suppress the formation of more stable graphite.

The earliest nanotubes produced were multiwalled nanotubes. In these tubes, more than one graphene cylinders are arranged concentrically. Subsequently, single walled nanotubes, consisting of a single tube, were also produced.

The single wall nanotubes require a **catalyst** for their growth while the multiwall tubes can be grown *without a catalyst*.

The dimensions of the SWNT depend sensitively on the catalyst used and the preparation conditions. Single wall nanotubes with much larger diameter, up to 6 nm, can be produced when, in addition to the catalyst (e.g., Co), some sulfur as elemental S or as metal sulfide is introduced in the anode.



16.2 Widely used methods for CNT fabrication: (a) arc discharge method, (b) laser vaporization method and (c) CVD.

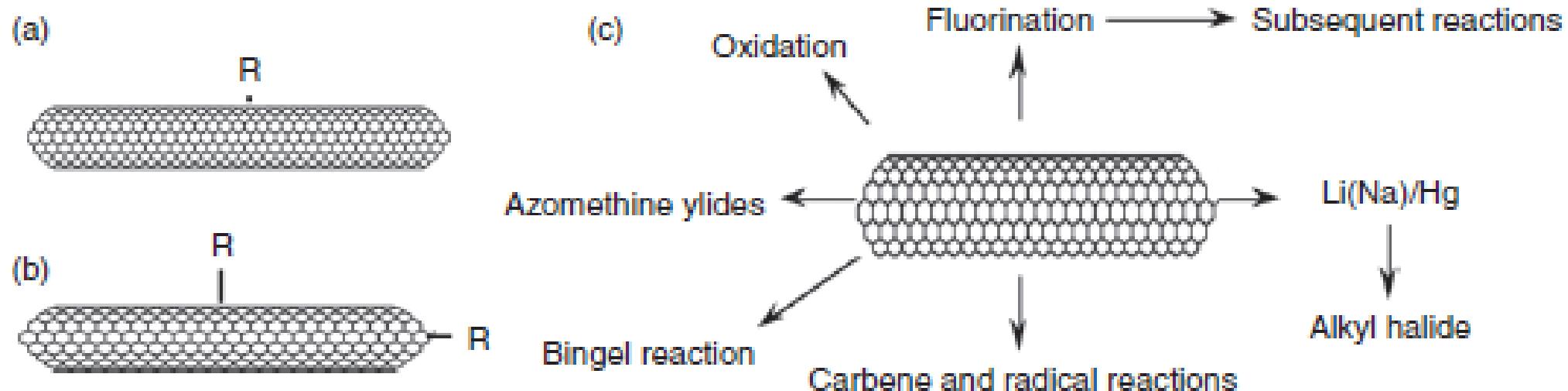
- The **mechanism of nanotube growth** is not understood. Since the metal catalyst is necessary for the growth of SWNTs, the mechanism must involve the role of the Co or Ni atoms. One proposal referred to as the “scooter mechanism” suggests that atoms of the metal catalyst attach to the dangling bonds at the open end of the tubes, and that these atoms scoot around the rim of the tube, absorbing carbon atoms as they arrive.
- Generally synthesis results in a mixture of tubes ***two-thirds of which are semiconducting and one-third metallic.***
- A group at IBM has developed a method to separate the semiconducting from the metallic nanotubes. The separation was accomplished by depositing bundles of nanotubes, some of which are metallic and some semiconducting, on a silicon wafer. Metal electrodes were then deposited over the bundle. Using the silicon wafer as an electrode, a small bias voltage was applied that prevents the semiconducting tubes from conducting, effectively making them insulators. A high voltage is then applied across the metal electrodes, thereby sending a high current through the metallic tubes but not the insulating tubes. This causes the metallic tubes to vaporize, leaving behind only the semiconducting tubes.

Functionalization:

Regardless of which synthesis method is utilized, the CNTs produced are considered pristine (or as is), which refers to their surface chemistry (unmodified). In combination with their nanoscale geometry, strong van der Waals forces and hydrophobicity, pristine nanotubes tend to bundle together forming agglomerates. The bundling effect, or lack of dispersion of CNTs, becomes a serious limitation in their usage, especially in biomedical applications such as tissue engineering and drug delivery. In order to improve CNT functionality, CNTs have been functionalized covalently and non-covalently with various hydrophilic and hydrophobic groups. Among these functional moieties are: carboxylic acid (COOH), hydroxyl (OH), poly m-aminobenzoic sulfonic acid (PABS), polyvinyl alcohol, polyimide, polymers, nucleic acid and proteins. In non-covalent functionalization (Fig.16.3a), different solubilizers (polymers, surfactants, aromatic solvents, superacids) are used to physically deposit molecules onto the CNTs' walls while being sonicated. Mechanical energy from the sonication helps to break the van der Waals forces and allows for loosening of CNTs bundles. This is a fairly easy method compared with the covalent functionalization (Fig. 16.3b), which requires chemical reactions and offer greater control of the chemistry and physics of CNTs. The covalent functionalization method used depends on whether the chemical modification is occurring at the side walls or open ends, as shown in Fig. 16.3c.

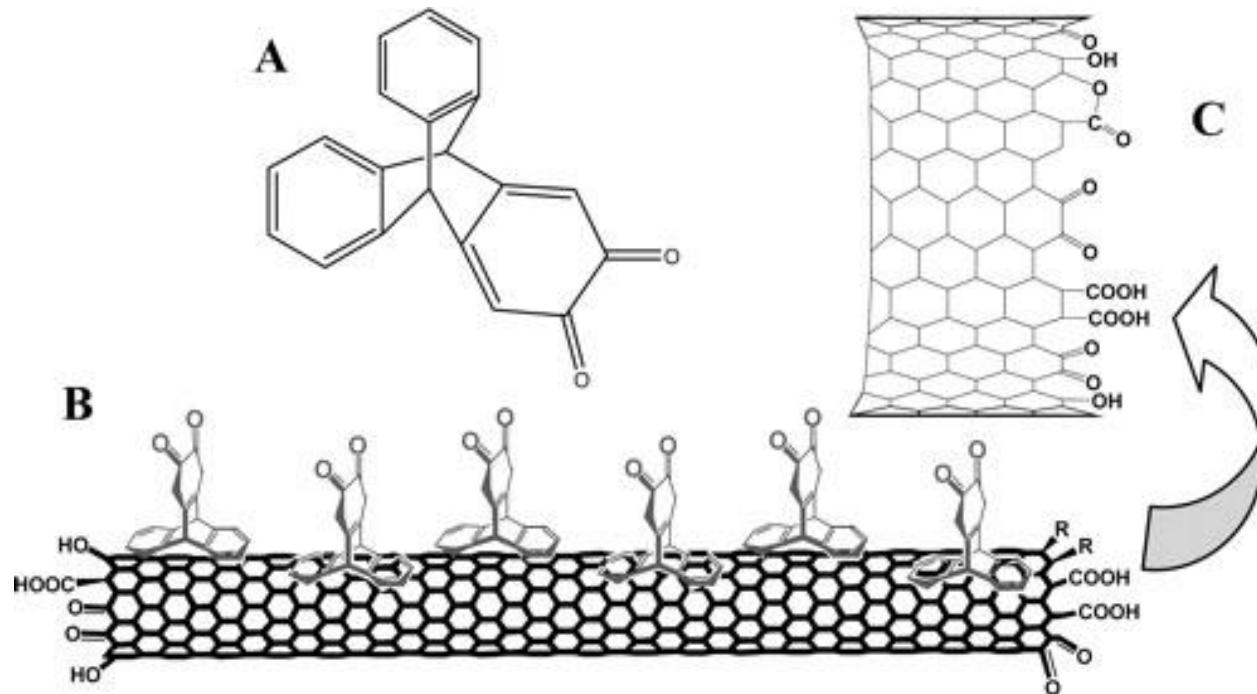
A number of novel applications can be envisaged—*on heating in air in the presence of lead, the caps are oxidized away, opening the tubes which then act as 'nanopipettes'* and fill with the molten lead. Such materials chemistry has enormous potential for the fabrication of nanowires which could be used in electronic devices and the like.

Due to (1) the close resemblance of CNTs to the native structures of tissues, (2) their large outer surface area that can be utilized to interact with active molecules and (3) the inner void that can encapsulate growth factors, drugs, or cells, CNTs are very desirable for biomedical applications. Moreover, the biocompatibility of functionalized CNTs offers a great advantage due to their ability to cross biological barriers and translocate into mammalian cells.



16.3 CNT functionalization: (a) non-covalent functionalization, (b) covalent functionalization (R: represents different functional groups) and (c) various covalent functionalization methods. (Source: Adapted and modified from Barron (2010).)

Functionalized Carbon Nanotubes



Structure of Triptycene Orthoquinone (TOQ, A), Schematic Illustration of Attachment of TOQ onto Carbon Nanotubes (B), and Enlarged Tube Ends with Oxygen-Containing Moieties (C) (Reprinted from Nanowerk Website (American Chemical Society) <http://www.nanowerk.com/spotlight/spotid=7288.php>

❖ ***The advantages of the carbon nanotubes*** are as follows:

- The carbon nanotubes are tiny and lightweight with excellent electrical, thermal and mechanical properties. They can be chemically modified or functionalized.
- The carbon nanotubes are resistant to the changes in temperature; their function remains same in both the cold and hot temperatures.
- The resources needed to generate carbon nanotubes are plenty and can be made by a little amount of material.

❖ **Uses of the Carbon Nanotubes:**

- Single-electron transistor
- Spacecraft
- Solar panels
- In the treatment of cancer
- Energy storage
- Optics
- Biosensing
- DNA sequencing
- LCDs
- Submicroscopic test tubes
- Functional AFM tips

- Their electrical qualities (as insulators, semi-conductors or, in certain cases, conductors) make these structures particularly attractive for the creation of electronic components at a level of miniaturization that has so far never been achieved by silicon technology. As a result, the smallest transistor in the world was made on a nanometric level.
- The use of nanotubes in the area of biosensors seems more likely. Chemists know how to transplant specific molecules to the biosensors which are able to bond with other molecules in a particular environment so that they can be analyzed. Consequently, high-quality detectors are created. These machines are used for the transportation of medicine inside the human body.
- Nanotubes are rather odd objects. Even if for the moment we are unable to produce nanotubes with homogenous electrical characteristics, we are, however, able to prepare a nanotube deposit on a substrate surface which is semi-conducting. We can make low-cost solar cells and circuits which can be used for transparent electrodes, flat screens with electroluminescent diodes and, once correctly adjusted, biocompatible substrates.

Carbon Nanotube Sensors Coated with ssDNA and Electronic Readout

Electronic nose and electronic tongue applications

➤ A new class of nanoscale chemical sensors are based on ssDNA as the chemical recognition site and single-walled carbon nanotube FETs (SWNT-FETs) as the electronic readout component. SWNT-FETs with a nanoscale coating of ssDNA respond to gas odors that do not cause a detectable conductivity change in bare devices. Responses of ssDNA/SWNT-FETs differ in sign and magnitude for different gases and can be tuned by choosing the base sequence of the ssDNA.

ssDNA/SWNT-FET sensors detect a variety of odors, with rapid response and recovery times on the scale of seconds. The arrays of nanosensors could detect molecules on the order of 1 ppm. The sensor surface is self-regenerating: samples maintain a constant response with no need for sensor refreshing through at least 50 gas exposure cycles. The nanosensors could **sniff** molecules *in the air* or **taste them in a liquid**. This remarkable set of attributes makes sensors based on ssDNA-decorated nanotubes promising for “**electronic nose**” and “**electronic tongue**” applications ranging from homeland security to disease diagnosis.

☐ Artificial Muscles Made of Carbon Nanotubes

- An aerogel – a lightweight (1.5 mg/cm^3), sponge-like material consisting of **bundles of multiwalled carbon nanotubes** (12 nm in diameter) – is **light as air, yet stronger than steel and more bendable than rubber**.
- **These characteristics are combined in a material that twitches like a bionic man's biceps when a voltage is applied.** Applying a voltage across the width of a ribbon of the material electrically charges the nanotubes that thread through the material. This **makes them repel one another** and the ribbon can **expand sideways** by up to three times its original width with an actuation rate of $3.7 \times 10^4\% \text{ s}^{-1}$, much faster than the $50\% \text{ s}^{-1}$ maximum rate of natural muscle. The maximum achieved work per actuation cycle is $\sim 30 \text{ J/kg}$, compared with the maximum capability of $\sim 40 \text{ J/kg}$ for natural muscle.
- Applying a voltage along the length of the ribbon has a very different effect. It triggers the nanotube structure **to contract**, making the material more dense and very stiff. The material can withstand extreme temperatures between 80 and 1900 K and, therefore, could be easily used in harsh environments.

Organic Nanomaterials

- *Nanoparticles can be considered as objects in-between the compact organic compounds and single molecules.*
- The progress in biochemistry and nanomedicine is determined by the properties of complex organic compounds, which, in addition to carbon and hydrogen, can include atoms of oxygen, sulfur, and halogens, and also by the mechanisms of processes involving these compounds.
- **Organic nanoparticles (NPs)** are templated upon *natural or synthetic organic molecules*.
- Nature provides a wide range of examples of organic NPs such as protein aggregates, lipid bodies, milk emulsions, or more complex organized structures such as viruses, to name a few.
- One of the most important features of organic NPs is that they offer relatively simple routes for the encapsulation of materials.
- This together with the fact that the molecules used for the fabrication of the organic NPs can be biodegradable makes organic NPs the most appealing systems for drug delivery and biomedical applications.

- Organic NPs are part of many *industrial products*, mostly **food** and **cosmetics**.
- Many food products such as creams, chocolate, and cakes present nanoemulsions in their formulation and that is also the case in the cosmetic industry.
- Organic NPs are used in **pharmaceutical formulations**, that is, liposome vectors, polymersomes, polymer–protein, or polymer–drug conjugates.
- Organic NPs are also used in agriculture.

IFFCO Nano Urea

IFFCO Nano Urea is a nanotechnology based revolutionary Agri-input which provides nitrogen to plants. Nano Urea is a sustainable option for farmers towards smart agriculture and combat climate change. These fulfil the plant nutrient requirement as a fertilizer since Nano urea is bio available to plants because of its desirable particle size about 20-50 nm and more surface area (10,000 times over 1 mm urea prill) and number of particles (55,000 nitrogen particles over 1 mm urea prill). Hence, Nano Urea increases its availability to crop by more than 80% resulting in higher Nutrient Use efficiency. In addition to this, Nano urea helps in minimizing the environmental footprint by reducing the loss of nutrients from agriculture fields in the form of leaching and gaseous emissions which used to cause environmental pollution and climate change.



DRIVING SUSTAINABILITY

DISCOVER IFFCO NANO UREA

Helping farmers fight climate change

Nano urea is a potential component of 4 R nutrient stewardship as it promotes precision and sustainable agriculture. It promotes clean and green technology as its industrial production is neither energy intensive nor resource consuming. In addition to this, Nano urea helps in minimizing the environmental footprint by reducing the loss of nutrients from agriculture fields in the form of leaching and gaseous emissions which used to cause environmental pollution and climate change.

- The methods for the preparation and physicochemical properties of nanoparticles containing complex organic molecules are studied to an *insufficient* extent yet.
- The low melting temperatures and lesser thermal stability of organic nanostructures as compared with those of inorganic compounds limit the methods for their synthesis and applications.
- This is partly associated with the fact that the intermolecular interactions are weaker than the interatomic ones and the size dependence of physicochemical properties of organic nanoparticles is less pronounced as compared with inorganic nanoparticles.
- It was believed that no size effect is manifested in organic nanomaterials. However, eventually it was shown that the size effect is typical of organic nanoparticles as well.

METHODS FOR THE PREPARATION OF ORGANIC NANOPARTICLES

- ❑ Organic NPs can also be fabricated both by “**top-down**” and by “**bottom-up**” approaches.
- The former approach relies on ***physical methods***, while the latter includes mainly the ***chemical methods*** for the fabrication of nanoparticles.
- In the “***top-down***” ***techniques involve grinding of coarse particles*** (molecular aggregates, powders, grains) to nanosized particles.
- ✓ the most common is the **mechanical milling**, although, recently, other more complicated techniques involving ***microfluidics and lithography*** have been used to produce organic nanomaterials.
- ✓ These processes are **mostly used to fabricate drug NPs from poor water-soluble compounds, and almost all the products in the market fabricated by this technique** are done by using the pearl mill that was developed by Liversidge and coworkers in 1995, today known as the **NanoCrystalTM** technology.
- ✓ The synthesis of organic nanoparticles is a laborious branch of chemistry, which is poorly explored so far. The use of physical methods, e.g., mechanical disintegration and laser ablation, is of limited application due to the low melting points and thermal instability of organic compounds.

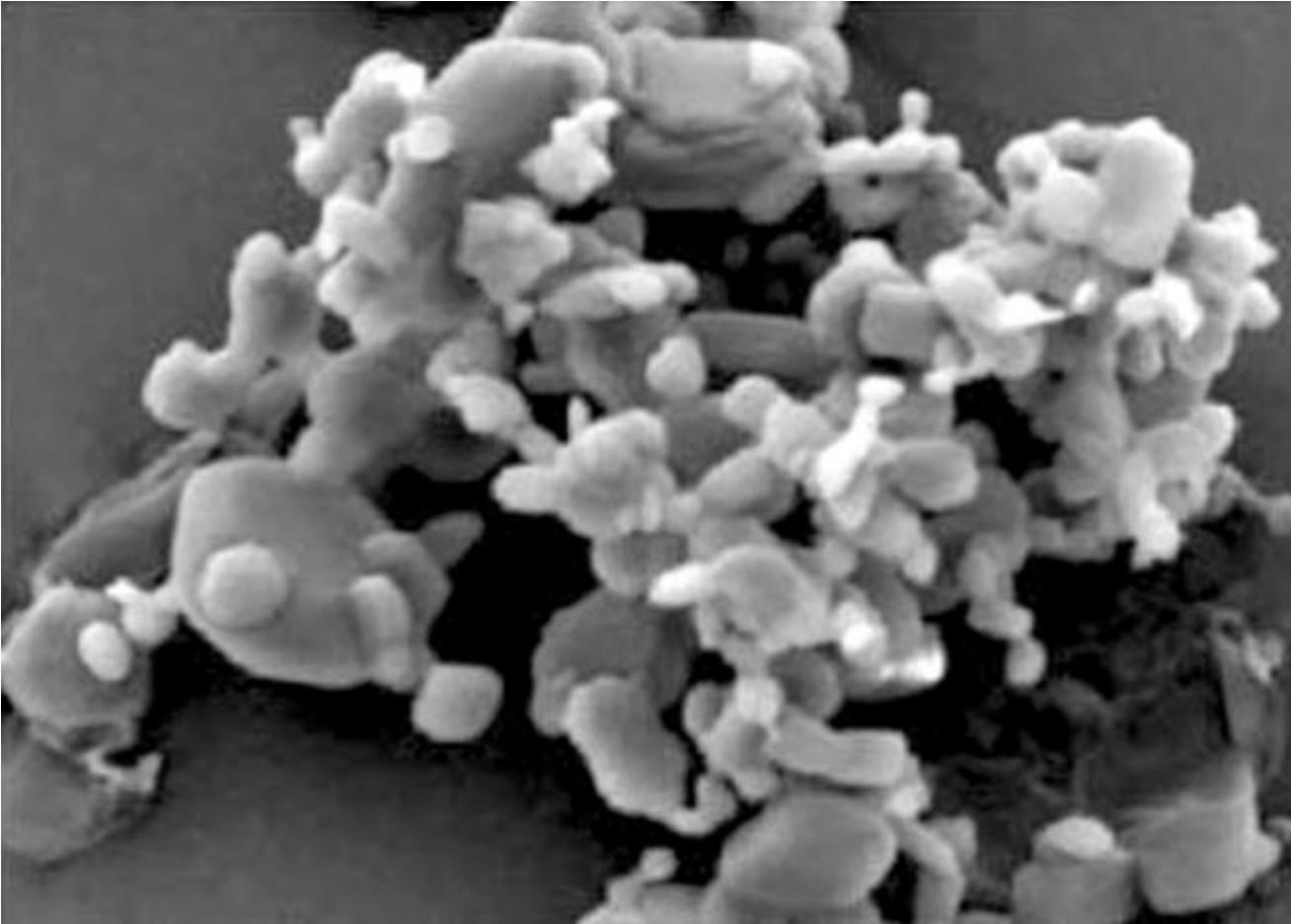


FIGURE 9.1 SEM image of ibuprofen particles produced by **mechanical grinding**.

- In “bottom-up” techniques involve coarsening of original species, i.e., single atoms and molecules, to form nanosized particles. **NPs are fabricated from atoms or molecules via synthetic chemistry and self-organization/assembly.**
- ✓ The “bottom-up” techniques are used for the generation of a wide range of nanomaterials such as ***micelles, vesicles and liposomes, polymersomes, polymer conjugates, dendrimers, capsules, and polymeric NPs.***
- ✓ These have been used recently to produce organic nanomaterials for nanomedicine and electronic applications. This kind of methodologies offers more control over the size, shape, cargo, and composition of the NPs.

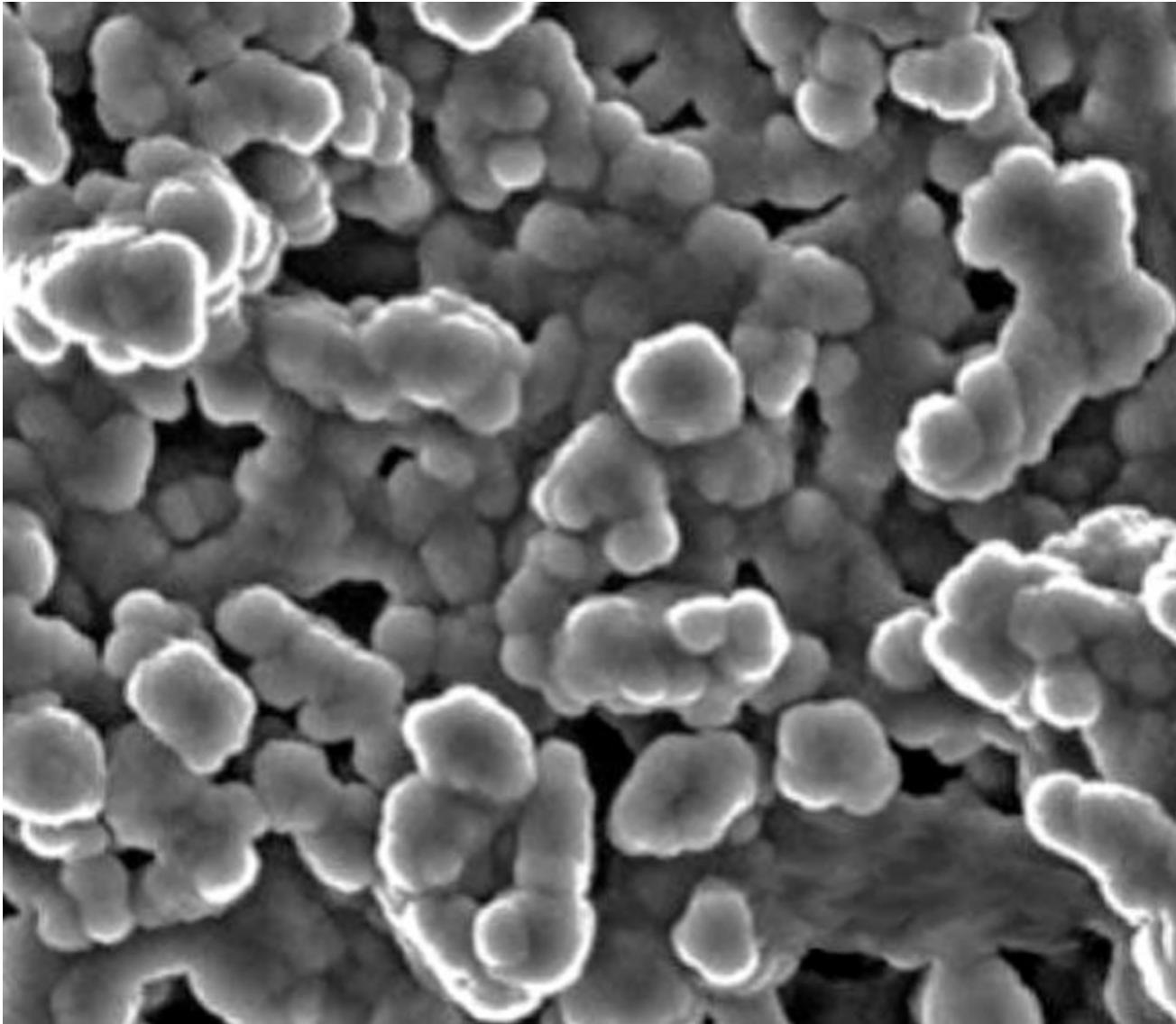


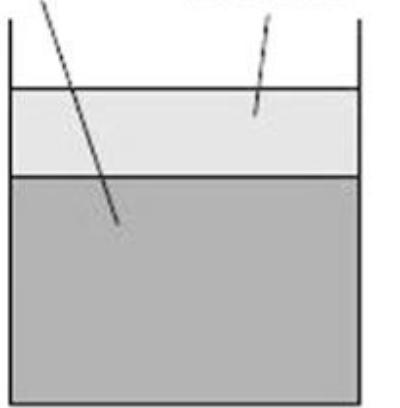
FIGURE 9.3 SEM image of perylene particles synthesized by the **reprecipitation method**.

Synthesis of Nanoparticles in Water–Oil Emulsion

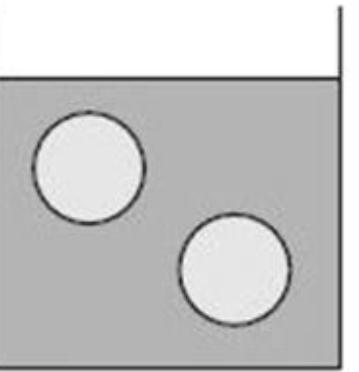
- ❑ Nanoparticles were synthesized in water–oil emulsions containing a solute in a volatile solvent.
- ❑ Evaporation of the solvent affords nanoparticles with sizes comparable with the emulsion drops.
- ❑ Emulsification required the use of special equipment to achieve the needed drop size.
- ❑ Nanodrops were prepared by high-pressure homogenization and sonication.
- ❑ From microemulsions containing sodium dodecyl sulfate as the surfactant, nanoparticles of propylparaben with the sizes of 40–70 nm were obtained.
- ❑ A version of producing nanoparticles in a stabilizer-free emulsion of the oil-in-water type was proposed. Figure 9.4 illustrates a possible mechanism of the organic nanocrystal fabrication, using the emulsion method. First, an emulsion of the target substance in an organic solvent was prepared at elevated temperature. Its subsequent cooling to room temperature brings about nucleation and the crystal growth inside the emulsion. The formed nanoparticles are transferred into the water phase and dispersed by a mechanical method, e.g. by sonication. Thus, nanoparticles of tetracene measuring 85 nm and anthracene measuring 75 nm were prepared.

at high temperature

hot water
hot organic solvent



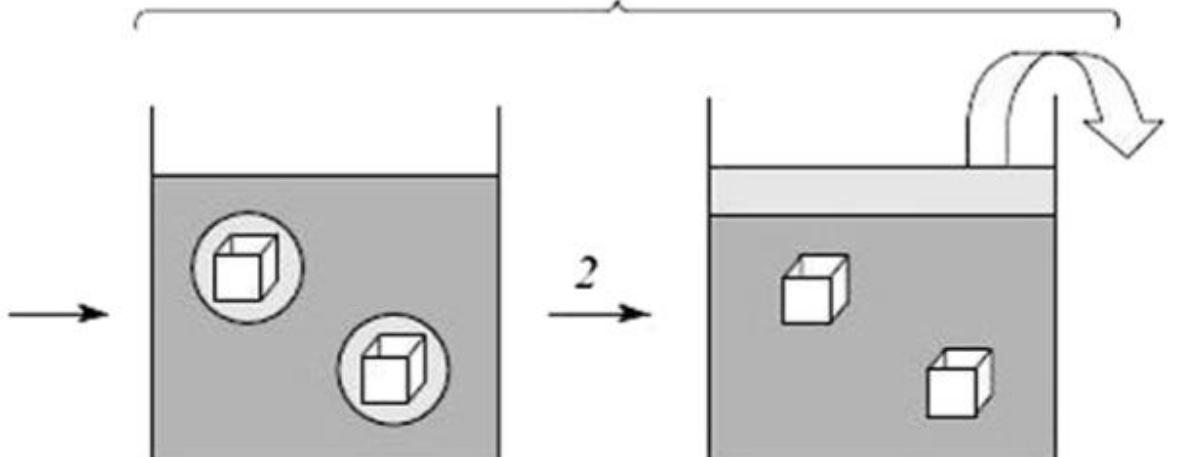
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cooling
nucleation and crystal growth

formation of water–oil emulsion

at room temperature



breaking of emulsion

FIGURE 9.4 Schematic model of the organic nanocrystal fabrication by the emulsion method of nanoparticles:

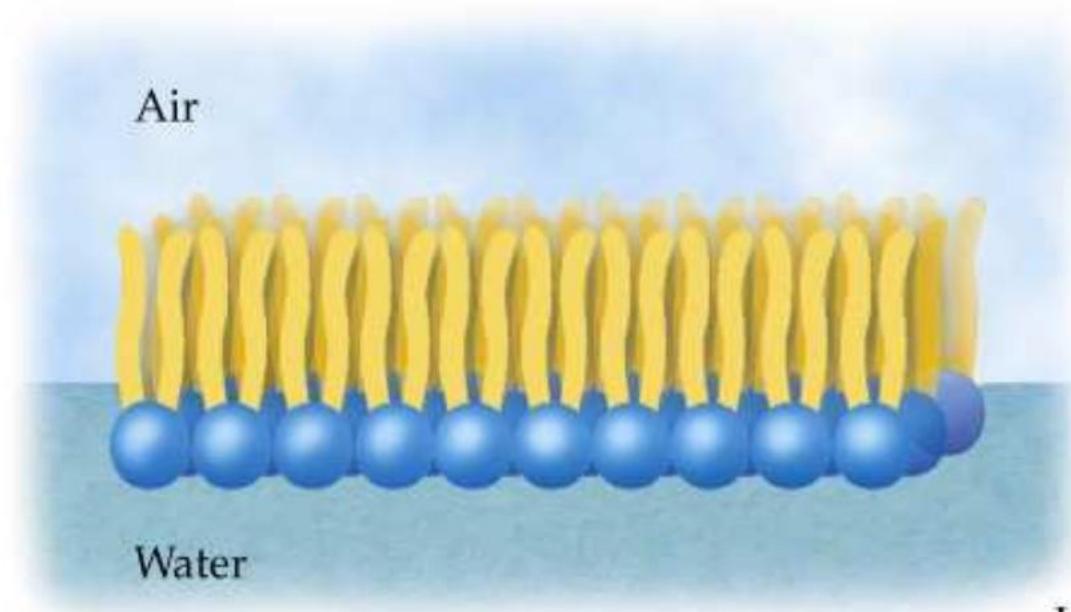
- (1) preparation of the oil-in-water emulsion by stirring;
- (2) transfer of nanoparticles into the water phase, for example, by sonication.

Micelles, Vesicles, and Liposomes

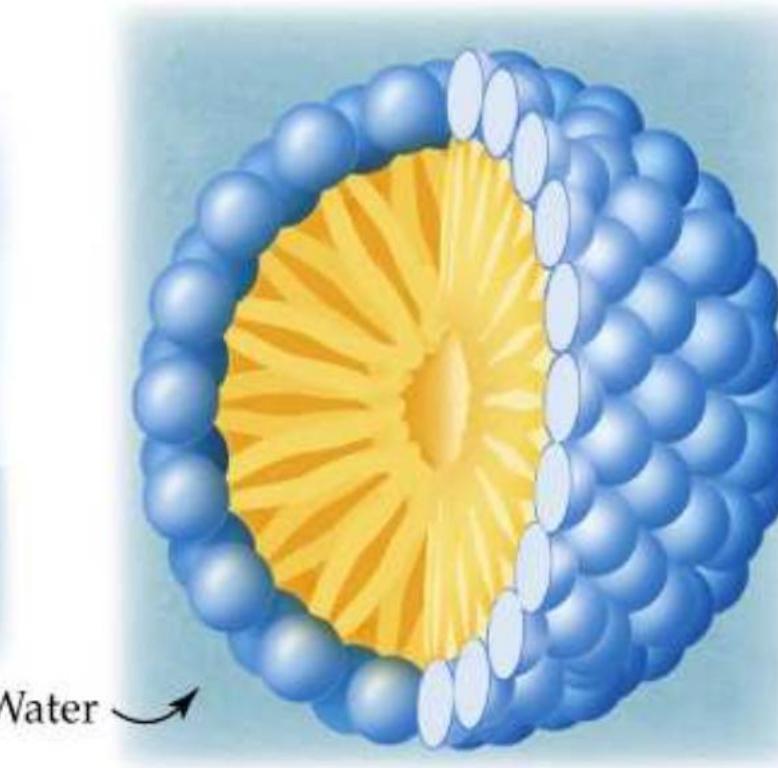
Liposomes, vesicles, and micelles are NPs formed by supramolecular self-assembly of surfactants and lipids. The driving force of the assembly is the low water solubility of the amphiphilic molecules.

- **Micelles** (1.5 to 2.0 nm diameter).
- ✓ The term “micelles” was introduced by McBain in 1913 to describe the colloidal particles formed by detergents and soaps. Basically, micelles are colloidal aggregates of amphiphilic molecules surfactants and polymers. When amphiphilic molecules are added to water, the nonpolar chain “tail” of the molecule aggregates, letting the polar side “head” in direct contact with the solvent molecules and a spherical or cylindrical structure that protects the hydrophobic tails in the center.
- **Inverse micelles** are obtained when the amphiphilic molecule is added to a nonpolar solvent. In this case, the particle formed has the head group in the center and the tail chains on the outside.
- The shape and size of the micelles can be controlled by the nature of the amphiphilic molecule and the solution conditions such as concentration, temperature, pH, and ionic strength. The concentration of the amphiphilic molecule (amphiphile) probably plays the most important role in micelle formation.

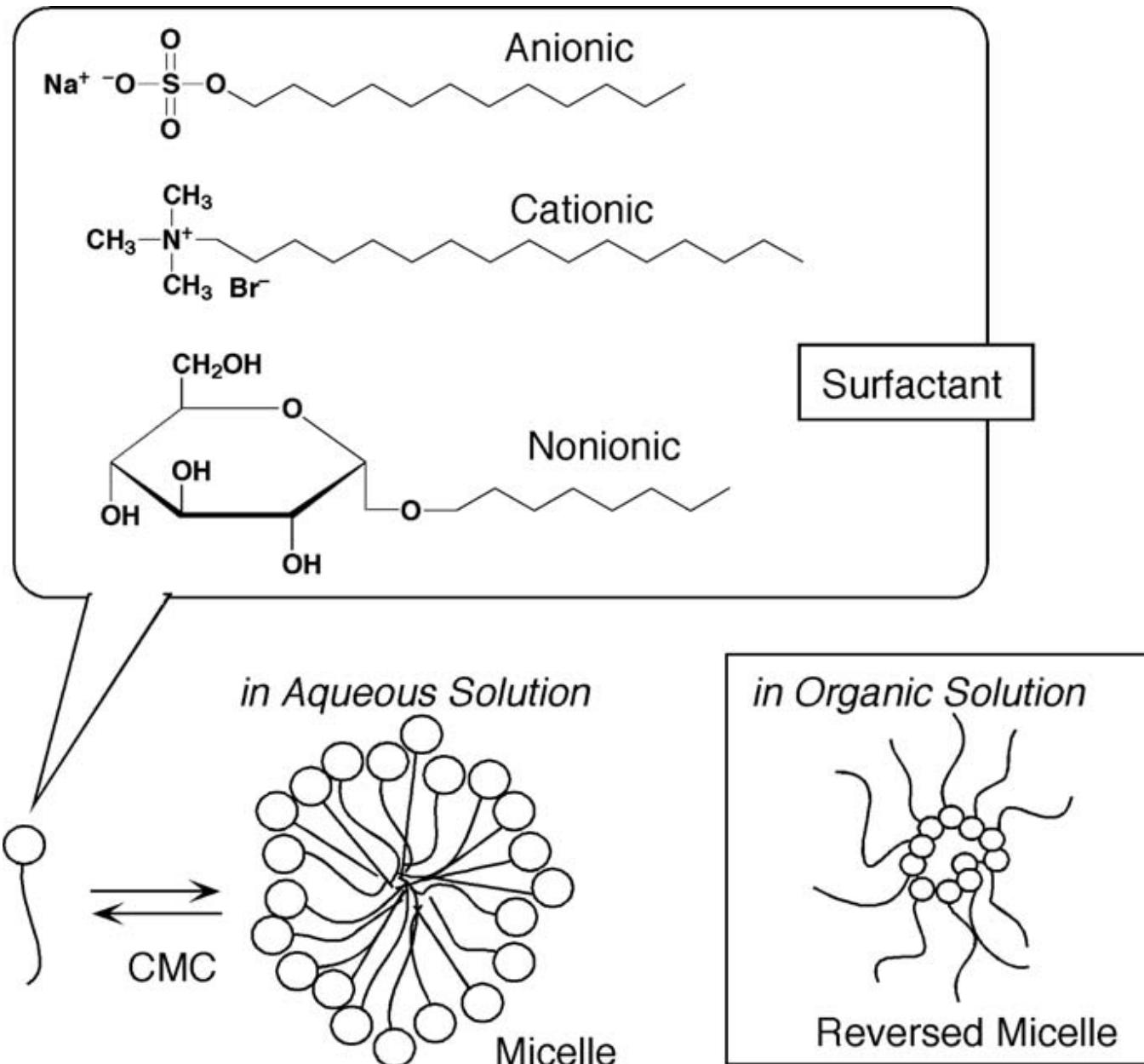
- Micelles are truly dynamic systems. Normally, micelle formation does not take place below a certain concentration of surfactant, called the **CMC**.
- Initially, micelles display spherical shapes, and their size increases with the addition of more surfactant, up to a point where they change shape and start to grow as cylinders.
- Typical surfactants forming micelles are sodium dodecyl sulfate and cetyltrimethylammonium bromide, just to give an example.
- These molecules are formed by a hydrophobic chain with a length of 10–20 carbons and sulfate and ammonium hydrophilic head, respectively.
- Some proteins and lipids, as well, can aggregate in micelles such as lipoxygenase 3 that, by inducing heat, form soluble spherical aggregates of around 26 nm in carbonate buffer pH 8.



Soap film on surface of water



Micelle surrounded by water



- ❑ In a micellar structure, the hydrophilic part of the component molecule is located on the outer surface of the micelle, in contact with the aqueous phase, which minimizes the unfavorable contact of the hydrophobic part with water. Micelles can trap organic materials like oils in the inner hydrophobic core, so micelle formation is used in many cleaning agents.

Figure 4.19. Micelle and reversed micelle

Shapes of micelles and vesicles:



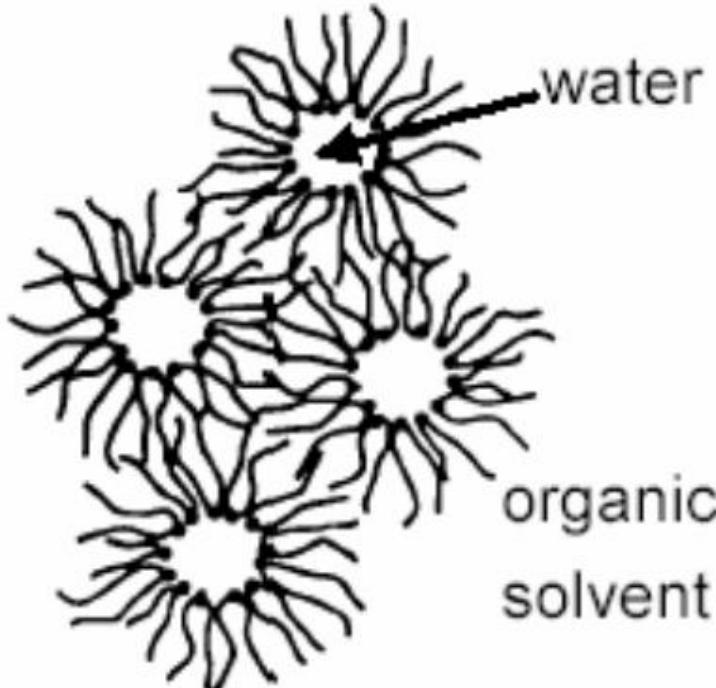
sphere



ellipsoid



cylinder



inverted micelle



unilamellar vesicle



planar structure

- **Vesicles**, unlike micelles, *are hollow spheres enclosed by a bilayer made of different amphiphilic molecules*.
- When the hollow sphere presents only **one amphiphilic bilayer**, they are called **unilamellar** vesicles (UVs), and if it is composed by **more than one amphiphilic bilayer**, the vesicles are known as **multilamellar** vesicles (MLVs) ([Figure 4.1](#)).

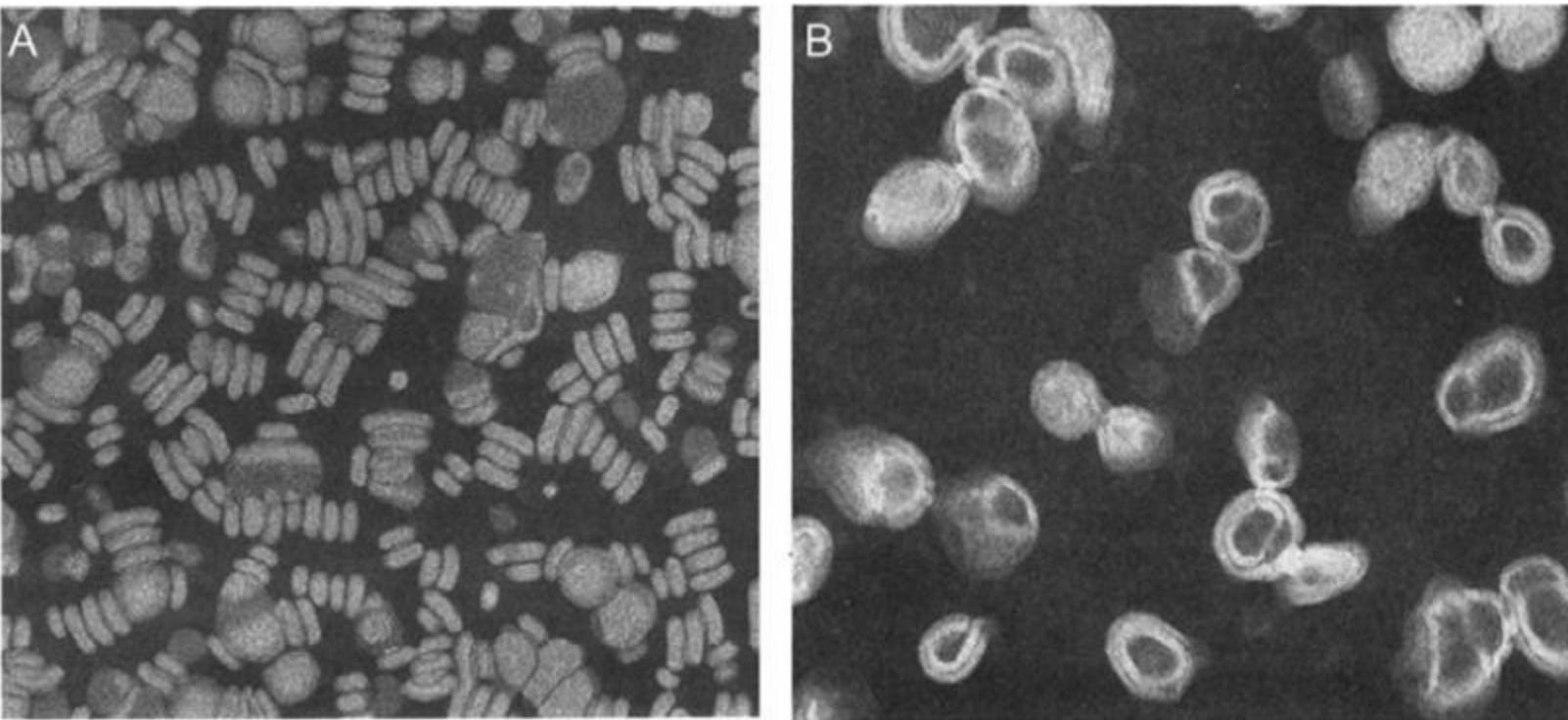


FIGURE 4.1 Examples of electron microscope images of unilamellar (A) and multilamellar (B) liposomes made of egg phosphatidyl choline containing 45 mol% cholesterol and fabricated with French pressure cell.

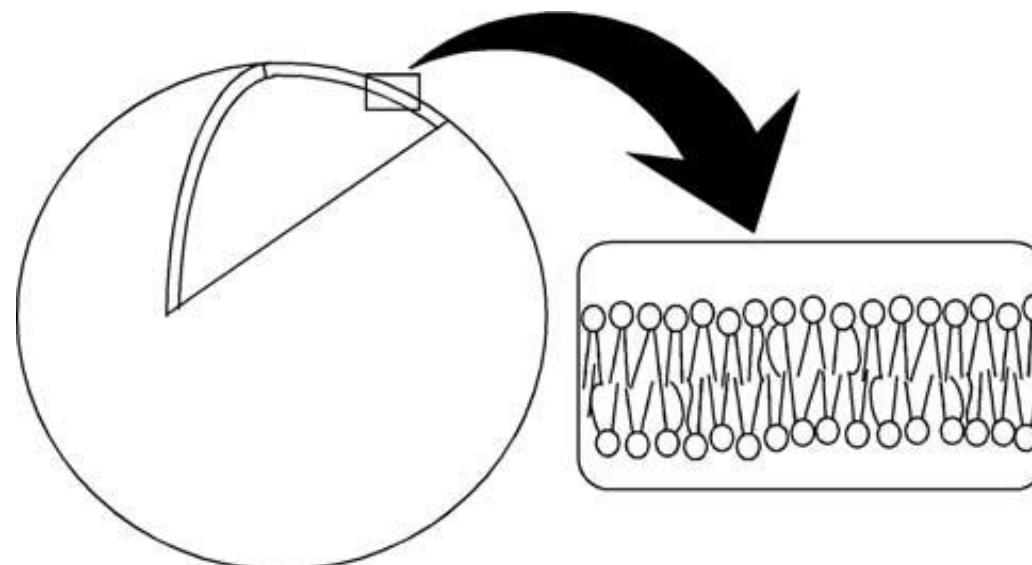
- Depending on their composition, **two kinds of vesicles** can be distinguished: first, **vesicles composed of *glycolipids***, either natural or synthetic, which are very important because the cell membrane is highly composed of glycolipids and can be formed naturally or can be prepared, and second, vesicles made of ***phospholipids*** and their mixtures, discovered by Bangham 1961, also called “**liposomes**” or “**lipid vesicles**.”
- Vesicle properties such as size and polydispersity, surface potential, degree of ionization, phase behavior, permeability, and physical stability depend on the method employed for their preparation as well as on the nature of the component molecules.
- The methods for vesicle formation can be classified into two groups.
 - The first one is the spontaneous formation of vesicles, in which it is just necessary to apply certain stress in order to homogenize the system, but no external energy is required for the vesicle formation.
 - The second method of vesicle fabrication is the induced vesicle formation by shearing, and this shearing can be via sonication, extrusion, and other methods; all of those techniques require the input of external energy, the reason for why vesicles are not thermodynamically stable though they can have high kinetic stability.

- For the formation of **MLVs**, usually lipids are dissolved in an organic solvent. Later, the solvent is eliminated via vacuum evaporation or convection to form a dry lipid film; this step is followed by the hydration of the film with an aqueous buffer and finally gentle agitation to form a MLV mixture. The size and the distribution of the MLVs depend on the lipid concentration and composition and on the input energy during agitation. Indeed, vigorous shaking will form vesicles with better size distribution.
- If phospholipids are dispersed in aqueous solution, they form large multilamellar structures as we discussed above.
- Nevertheless, several methods have been developed to form UVs from multilamellar structures. Sonication is the most common method to produce UVs from MLVs. The ultrasound applied during sonication induces collisions between vesicles, which, in turn, disrupt the lipid multilamellars. This results in the formation of lipid bilayer fragments and other small aggregates, which rearrange into vesicles. There are several drawbacks of this technique such as the nonuniform size distribution of the formed vesicles and the lack of stability of the formed vesicles that tend to aggregate over time.

□ Another way to prepare UVs from MLVs is by the French press technique. This consists in passing the MLV suspension through a small outlet orifice under extreme pressure to form UVs. Finally, the extrusion method described above can be used to produce UVs from MLVs through the sequential extrusion of the MLVs generating small and large UVs. There are different methods, not based on MLVs, to produce UVs such as the dry lipid hydration methods. This method consists in the creation of a thin film via evaporation of the amphiphile in chloroform, when the thin film in contact with water is dissolved and forms large UVs. Another way to produce UVs is by injection methods that mainly consist of injecting a lipid organic solution into water. The speed of the injection will determine the stability of the system over time. There are other methods of vesicle preparations available.

- Some lipids possess a phosphate moiety and are therefore called **phospholipids**.
- **Glycolipids** (which have heads carrying sugar moieties) and cholesterol are two other important components of the cell membrane. Most of these lipids have two alkyl chains.
- In these lipid structures, the ratios between the sizes of the hydrophilic heads and the hydrophobic tails are different to those for micelle-forming surfactants. **Amphiphiles that form bilayer structures tend to have larger tails than heads**. When these amphiphiles are dispersed in water, they assemble in order to avoid unfavorable contact of the hydrophobic parts with the water. However, **they cannot form micelle-like small assemblies because of their large hydrophobic tails**. Therefore, the phospholipid-like amphiphiles form double-layer structures (lipid bilayers) by contacting the hydrophobic faces of two leaf-like monolayer amphiphile assemblies. This lipid bilayer structure extends two-dimensionally and forms the “skin” of a closed sphere that has a water pool inside (Fig. 4.23).
- This capsule-like structure can be thought of as a simplified model of a cell. This capsule-like structure is called a *liposome*.

Figure 4.23. Liposome (or vesicle) with a lipid bilayer membrane.



Examples of artificially designed amphiphiles are shown in Fig. 4.24. Cationic, anionic, nonionic and zwitterionic groups are used in the polar heads. A dialkyl structure is often used for the tail, but trialkyl structures, tetraalkyl structures and azobenzene-type rigid structures are also available. Instead of hydrocarbon structures, a fluorocarbon structure that is highly immiscible with water has also been used as a hydrophobic tail. It was reported that introducing an amino acid residue between the hydrophilic head and hydrophobic tail increases bilayer stability. Hydrogen bonding associated with the amino acid part helps to improve the structural stability of the bilayer structure. Liposome-like structures formed from various kinds of amphiphiles are sometimes called “**vesicles**”, while the term “**liposome**” is sometimes limited to assemblies from phospholipids.

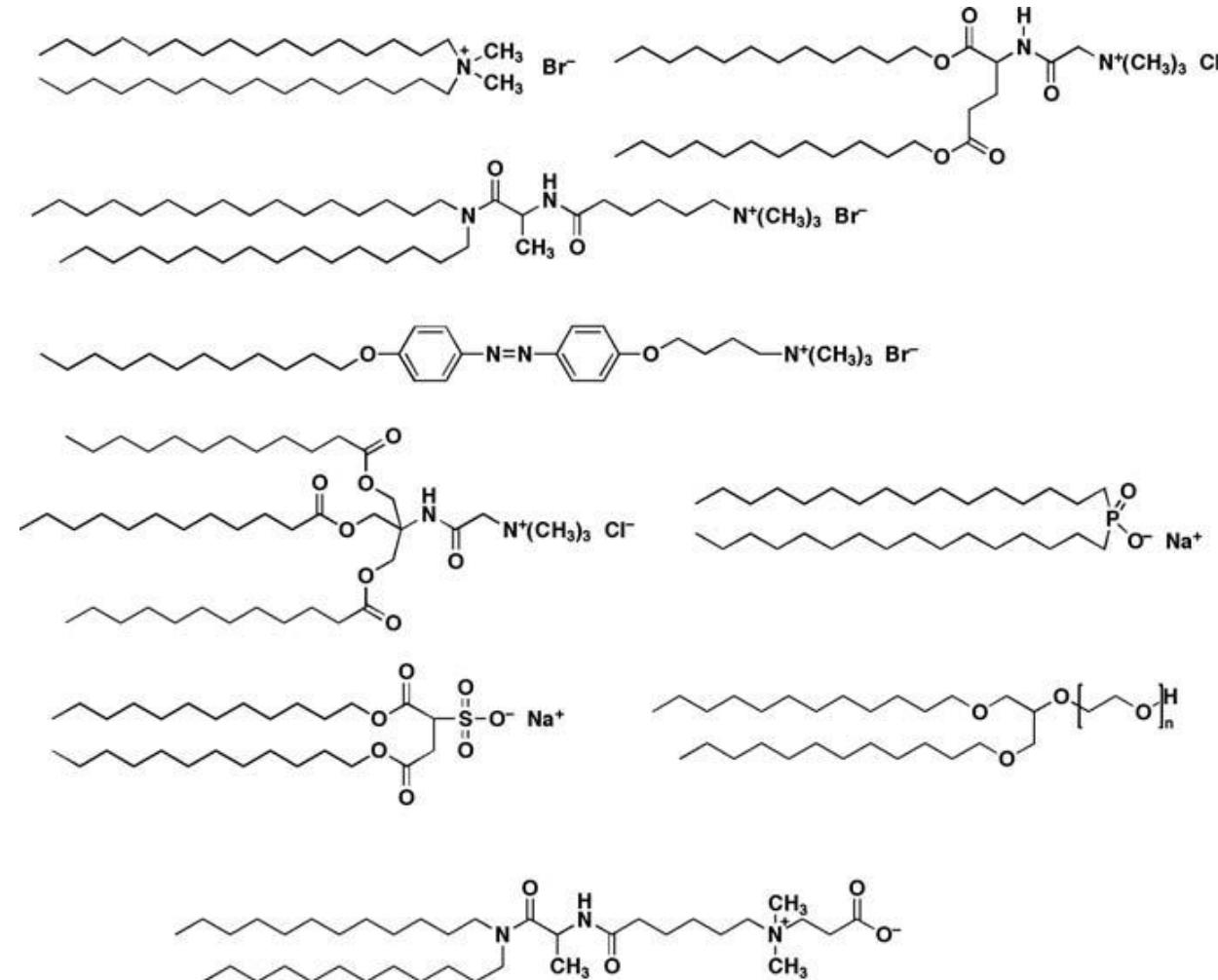
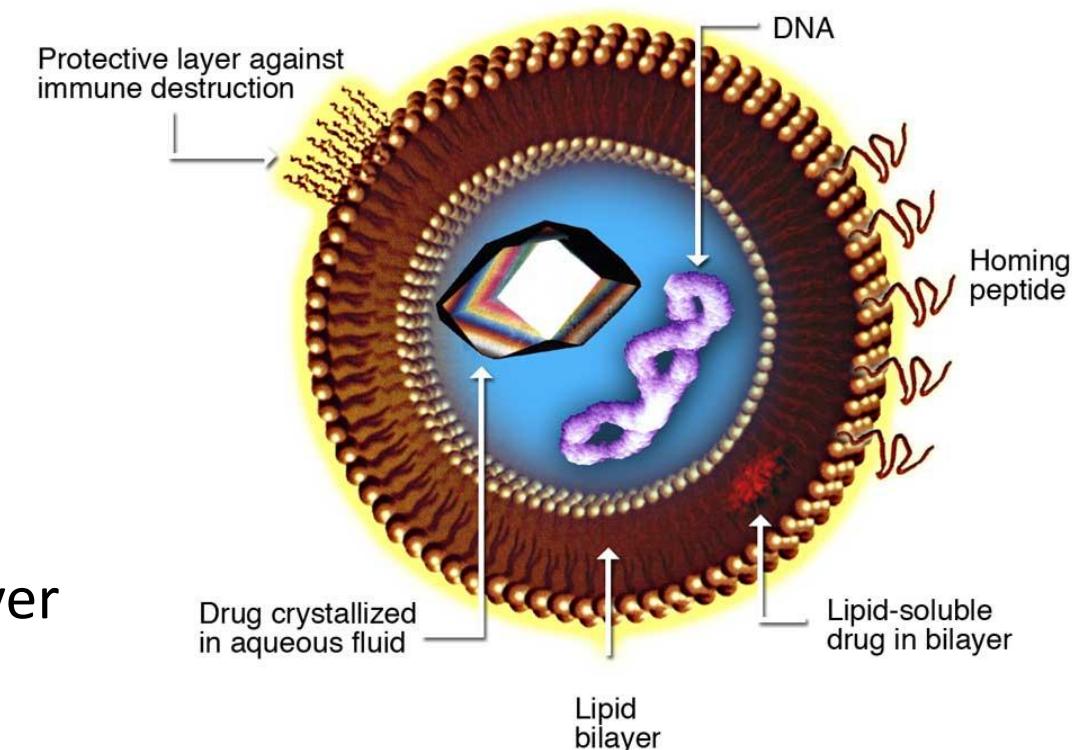


Figure 4.24. Examples of artificial lipids that form vesicles

Liposomes

- Liposomes are composite structures made of phospholipids and may contain small amounts of other molecules. Though liposomes can vary in size from low micrometer range to tens of micrometers, unilamellar liposomes, as pictured here, are typically in the lower size range with various targeting ligands attached to their surface allowing for their surface attachment and accumulation in pathological areas for the treatment of disease.
- **Liposomes** are artificially prepared *vesicles* made of the lipid bilayer.
- Liposomes can be prepared by disrupting biological membranes, such as sonication.
- Liposomes can be composed of naturally derived phospholipids with mixed lipid chains (like egg phosphatidylethanolamine) or other surfactants.
- Liposomes should not be confused with micelles and reverse micelles composed of monolayers.
- Liposomes can be filled with drugs and used to deliver drugs for cancer and other diseases.

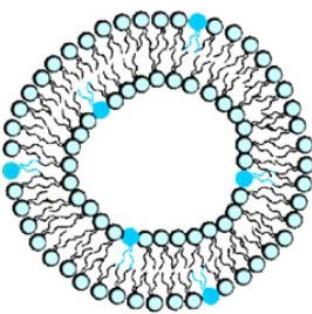
Liposome for Drug Delivery



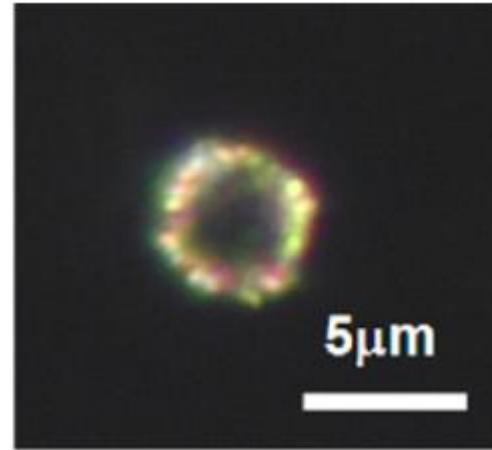
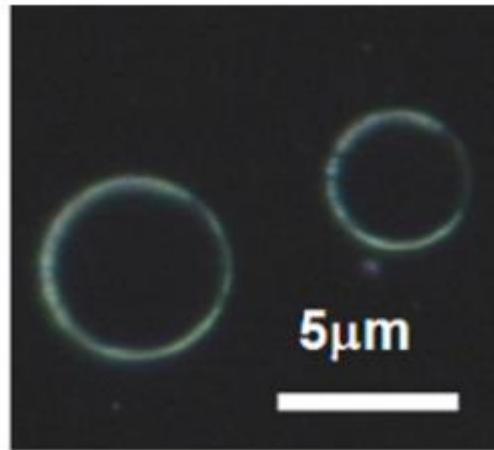
Applications

- Today, vesicles and liposomes play an important role in research as model systems for permeable biological membranes.
- They also have significance for the industry, especially in pharmaceutical, cosmetics, and food, as it is known that vesicles can entrap poor water-soluble materials with the possibility to control the action of the embedded molecules.
- In the pharmaceutical field, significant research is focused on trying to mimic different permeable membranes for drug delivery using vesicles and liposomes. Some liposome-based delivery systems are already in the market such as Doxil[®], Daunoxome[®], and AmBisome[®].
- In food industry, vesicles are normally used for encapsulation and controlled release of flavors and nutrients in order to protect them against degradation or contamination and to enhance bioavailability, stability, and shelf-life of sensitive materials. For example, the encapsulation of enzymes in liposomes protects them from degradation. It is also a means to control the release of the enzyme, like for cheese fabrication that encapsulation of enzyme in vesicles is carried out to decelerate cheese ripening.

- In the cosmetic industry, **vesicles are commercially used since 1987 when hydration creams made of liposomes were introduced by C. Dior (Capture) and L’Ore’al (Niosomes)**. Nowadays, we can find several cosmetic formulations of liposomes with encapsulated antibiotics, moisturizers, and different extracts and proteins, such as creams, sunscreens, perfumes, hair conditioners, aftershaves, and shampoos.
- The **phase transition behavior of an artificial bilayer membrane is easily controlled through appropriate design of the structure of the amphiphile, especially the lengths of the alkyl chains**. The transport of materials through the bilayer membrane significantly depends upon the state of the bilayer. **The release of drugs trapped in the inner water phase of the vesicle can be controlled via thermal stimuli with knowledge of the bilayer’s phase transition temperature**. This controlled release is an important concept in the development of drug delivery systems.



Bilayer Structure of vesicle



dark-field micrographs of the GUVs (left) and gold nanoparticle-loaded (right) GUV.

- ❖ Au nanoparticles can be heated by NIR laser to heat up the surrounding lipid layer and control the phase transition of the lipid layer and the openings in it.

Polymer Micelles, Polymersomes, and Polymer Conjugates

- Analogous to amphiphilic molecules, diblock copolymers with a hydrophilic and a hydrophobic block form micelles in certain solvents. When a solvent is thermodynamically good for one of the blocks and generates precipitation in the other block—in other words, when one of the blocks of the copolymers is soluble in the solvent and the other block is insoluble—the copolymer chains associate and form micellar aggregates with a core formed of insoluble copolymer blocks and a shell composed by the soluble copolymer blocks.
- The micelles of block copolymers have a wide practical interest because they can be used as dispersants, emulsifiers, wetting agents, foam stabilizers, flocculants, demulsifiers, viscosity modifiers, and among other applications in different industrial and pharmaceutical areas such as nanocarriers for drug delivery systems.
- A very good example of the use of block copolymers micelles as targeted nanocarriers is shown in Figure 4.2. Here 146 nm in diameter micelles were formed by folate-conjugated amphiphilic star-shaped block copolymers of poly(L-lactide), methoxy poly (ethylene glycol), and folate-poly(ethylene glycol). These polymeric micelles were loaded with the anti-inflammatory drug indomethacin via dialysis, and from the release studies, a sustained release time of 40 h was found. In a demonstration of specific targeting in HeLa cells, the micelles were taken up by the cells via receptor-mediated endocytosis.

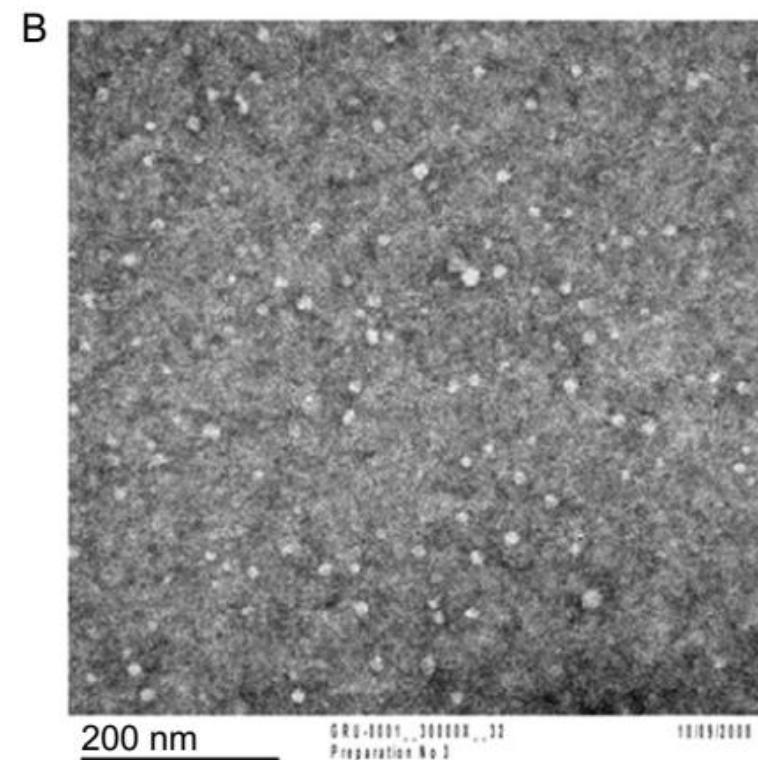
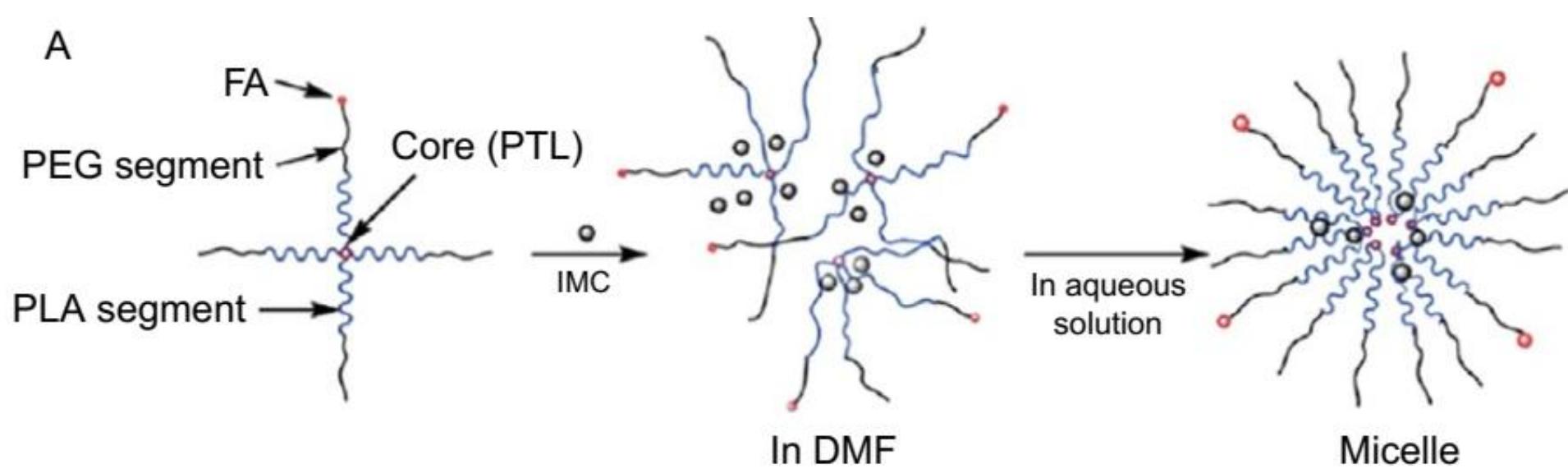


FIGURE 4.2 Diagram of the formation of a star-shaped polymeric micelle (A) and TEM image of polymeric micelles (B).

□ **Polymersomes** are polymer-based artificial vesicles that are formed during hydration of high-molecular-weight amphiphilic block copolymers. A block copolymer without presence of solvent displays a wide range of ordered morphologies including lamellar phase; the hydration of this lamellae by aqueous solution form a stable dispersion of block copolymer aggregates or polymersomes. The difference between the amphiphilic character of a lipid and the one in a block copolymer is that, in the last hydrophobic polymer, chains are covalently linked as a series of two or more hydrophilic blocks ([Figure 4.3](#)).

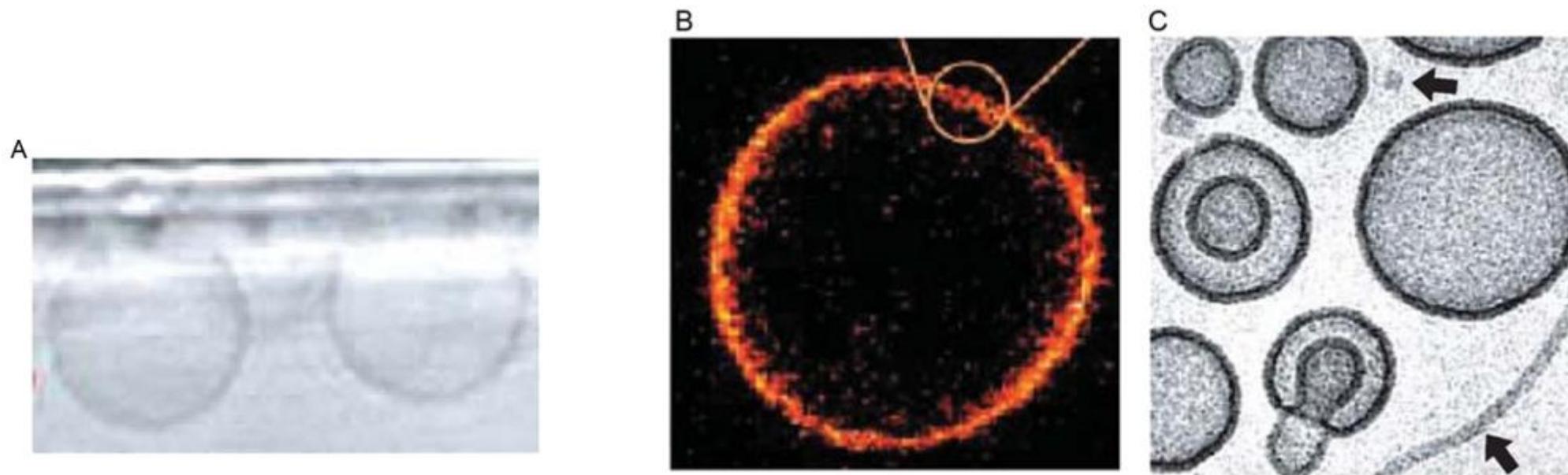


FIGURE 4.3 Illustration of self-directed assembly of polymersomes from hydrated films (A), fluoro-polymersome (B), and cryogenic transmission electron microscopy of 100 nm polymersomes (C).

□ **Polymersomes** can be prepared by the same methods used for vesicles and liposomes. Basically, the preparation methods can be summarized in two groups: solvent-free techniques and solvent displacement techniques. The solvent-free techniques broadly consist of hydrating the block copolymer in the dry state to form vesicles, such as film rehydration or electroformation. The last method consists in the rehydration of the polymers spread on a pair of electrodes; once the solvent is added, an electric field is applied to facilitate hydration and vesicle formation. Solvent displacement techniques are those methods which require first to dissolve the block copolymer in an organic solvent before mixing with water. After the mixture, the organic solvent is removed by different procedures. The injection method, reverse-phase evaporation, and detergent depletion are examples of solvent displacement techniques used for polymers. All of them described for the vesicle formation.

- **Polymersomes** are very attractive models to mimic biological membranes, and as *advantage over vesicles and liposomes*, polymersomes have the *ability to form versatile structures with high mechanical stability and resistance to external stimulus*.
- **Polymersomes can encapsulate either hydrophobic or hydrophilic molecules**, and this is the principal reason of their application in medical, pharmaceutical, and environmental fields. In the case of the medical and pharmaceutical field, polymersomes are used as carriers for drug delivery to encapsulate highly toxic therapeutic agents, and they can specifically tune their pharmacokinetics. An example is shown where polymersomes of poly(ethylene oxide)-b-polycaprolactone were loaded with doxorubicin (a drug for cancer treatment). The release profiles in vivo was probed in tumor-bearing mice and a retard in the tumor growth was successfully shown.
- In addition to applications in drug delivery, polymersomes have also been used in diagnosis for ex vivo cellular labeling and in vivo cellular tracking. Researchers have probed the ex vivo efficiency for labeling dendritic cells with polymersomes loaded with a porphyrin-based near-infrared agent. Finally, in the environmental area, polymersomes are commonly used to entrap toxic molecules, like to selectively entrap metal ion species in aqueous solutions.

Other types of polymer-based NPs are the polymer conjugates. Polymer conjugates are water-soluble hybrid structures formed by polymer chains covalently linked to a molecule such as a drug or a protein. The concept of polymer conjugate was proposed by Ringsdorf in 1975 with a polymer–drug conjugate model based on synthetic polymers. He proposed that certain number of drug molecules or bioactive molecules can be bounded to a macromolecule through a spacer molecule (linker), which can incorporate a breaking point to ensure the release of the drug at the site of interested; the polymer conjugate can additionally contain specific recognition functions (targeted molecules) or other molecules to enhance bioavailability ([Figure 4.4](#)).

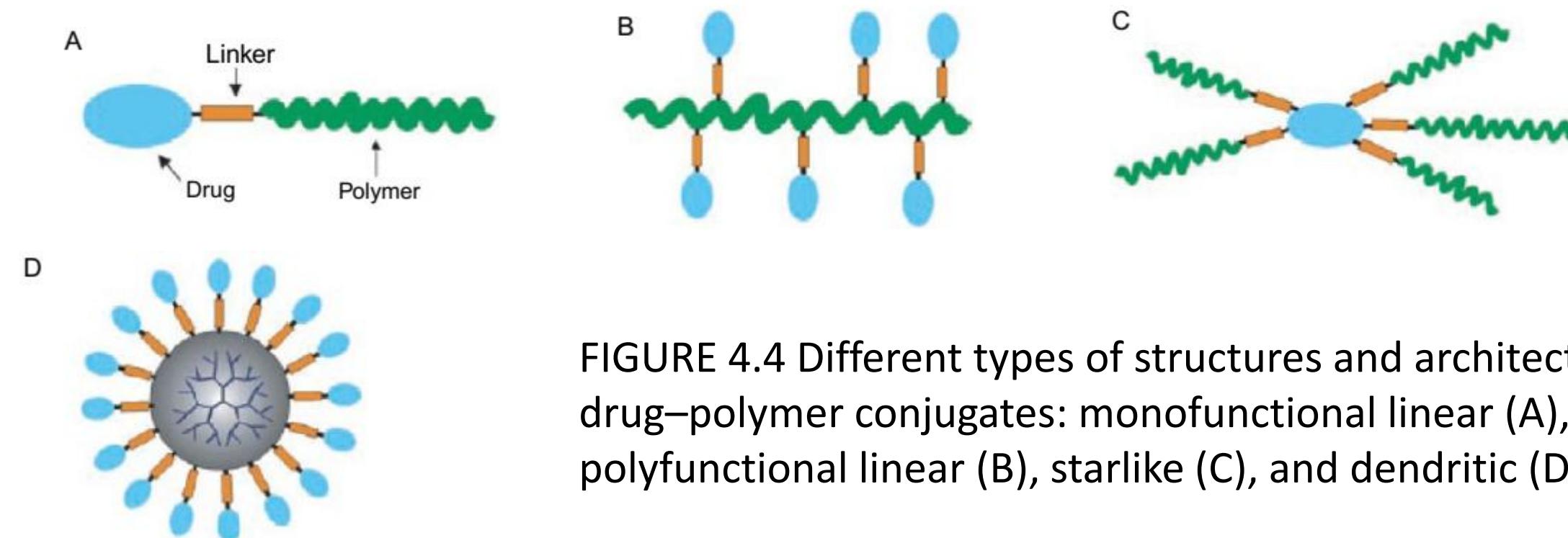


FIGURE 4.4 Different types of structures and architectures of drug–polymer conjugates: monofunctional linear (A), polyfunctional linear (B), starlike (C), and dendritic (D).

- The chemical synthesis of polymer conjugates via controlled radical polymerization methods has followed three different strategies: grafting to, grafting from, and grafting through.
- In the “grafting to,” the most typical strategy for the fabrication of polymer conjugates, the ends of the polymer chain are modified after the polymerization to form reactive groups for covalent linking of drugs or proteins.
- The “grafting from” consists in the functionalization of the drug or protein with a monomer, which is used as an initiator for the polymer synthesis. In the “grafting through,” the drug or protein to conjugate is employed as monomer for the polymerization. The majority of the applications of polymer conjugates are in the pharmaceutical and nanomedical field.
- In the clinical area, there are already some **polymer–protein conjugates in the market** such as **Zinostatin Stimalmer® (SMANCS)** for hepatocellular carcinoma treatment; **Oncaspar® PEG-Lasparaginase** for leukemia treatment; **PEG-intron™** to treat hepatitis C, multiple sclerosis, and HIV/AIDS; **Neulasta™** against neutropenia associated with cancer chemotherapy; and others.
- Regarding polymer–drug conjugates, most of the successful formulations are under clinical approval evaluations such as **CT-2103 XYOTAX™** for treating lung and ovarian cancer, **HPMA copolymer–doxorubicin** to treat hepatocellular carcinoma, **PROTHECAN™** for cancer therapies, etc.

Dendrimers

- Dendrimers ('dendri' means tree, 'mer' means branch) are a novel class of 3D nanoscale, core–shell structures that can be precisely synthesized for a wide range of applications.
- Dendrimers are one kind of polymeric nanoparticles constructed by the successive addition of layers of branching groups.
- Specialized chemistry techniques allow for precise control over the physical and chemical properties of the dendrimers.
- They are constructed generation by generation in a series of controlled steps that increase the number of small branching molecules around a central core molecule. Up to 10 generations can be incorporated into a single dendrimer molecule. The final generation of molecules added to the growing structure makes up the polyvalent surface of the dendrimer. The core, branching, and surface molecules are chosen to give desired properties and functions.

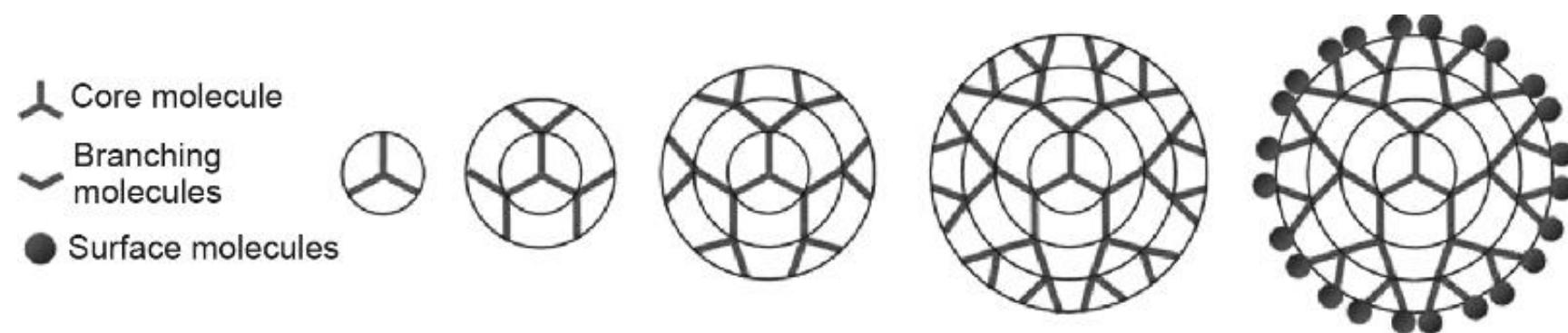


Fig.The core, branching, and surface molecules of dendrimers

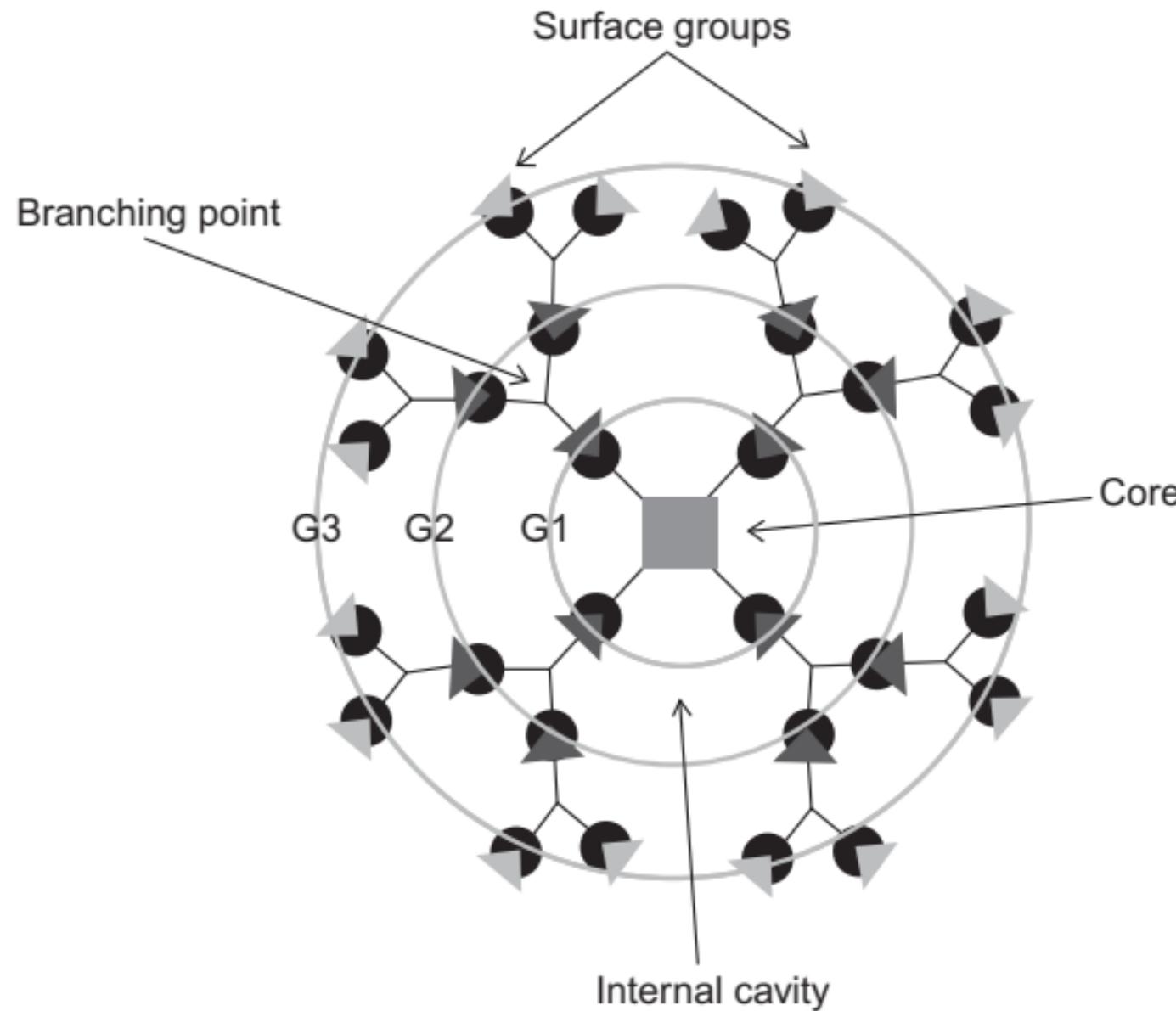


FIGURE 5.1 Domains of a general dendrimer structure.

Dendrimers

- **Precise architecture, size, and shape control**—Dendrimers branch out in a highly predictable fashion to form amplified 3D structures with highly ordered architectures.
- **High uniformity and purity**—The proprietary stepwise synthetic process used produces dendrimers with highly uniform sizes (monodispersity) possessing precisely defined surface functionality and very low impurity levels.
- Dendrimers can be synthesized by ***divergent*** and ***convergent*** methods.
- *In the divergent methods*, the dendrimer grows outward from the core molecule. The monomer that contains one reactive group and two dormant groups reacts first with the core forming the first-generation dendrimer, and successively the new periphery of the molecule is activated and reacts with more monomers until forming a big macromolecular structure. This method has the inconveniences that secondary products are formed which are not easy to purify.
- *In the convergent methods*, the dendrimer is synthesized stepwise from the end groups to the inward. When the branched molecules are big enough, they are attached to a core molecule. Dendrimers generated by these methods are easy to purify and have a controlled structure. On the other hand, it is not appropriate to form high-generation dendrimers because of steric impediments of the reaction.

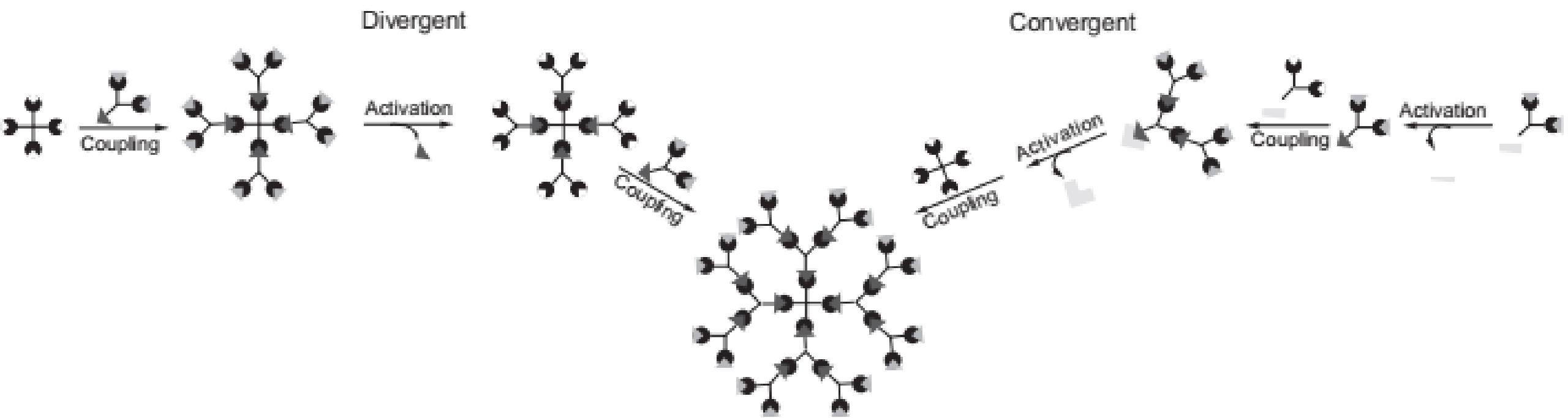


FIGURE 5.2 Schematic representation of the divergent and convergent synthetic strategies.

Properties

- Dendrimers are highly perfectly branched monodispersed macromolecules that emanate radially from a central core. This high branching of the polymer molecules gives to the dendrimers chemical and physical properties different from linear polymer molecules that are of enormous interest for biomedical and industrial applications. As a result of their unique architecture and construction, dendrimers possess inherently valuable physical, chemical, and biological properties. These are as follows:
 - *Transfection*—Dendrimers are able to move through cell boundaries and transport genetic materials into cell interiors.
 - *High loading capacity*—Internal cavities intrinsic to dendrimer structures can be used to carry and store a wide range of metals, organic, or inorganic molecules.
 - *High shear resistance*—Through their 3D structure dendrimers have a high resistance to shear forces and solution conditions.
 - *Low toxicity*—Most dendrimer systems display very low cytotoxicity levels.
 - *Low immunogenicity when injected or used topically*.

- The surface properties of dendrimers may be manipulated by the use of appropriate “capping” reagents on the outermost generation. In this way dendrimers can be readily decorated to yield a novel range of functional properties. These are as follows:
 - ✓ *Polyvalency*—The outer shell of each dendrimer can be manipulated to contain a large number of reactive groups. Each of these reactive sites has the potential to interact with a target entity, often resulting in polyvalent interactions.
 - ✓ *Flexible charge and solubility properties*—Through use of appropriate capping groups on the dendrimer exterior, the charge and solubility of dendrimers can be readily manipulated.
 - ✓ *Flexible binding properties*—By using appropriate capping groups on the dendrimer exterior, dendrimers can be designed to exhibit a strong affinity for specific targets.

Applications

Dendrimers, with their highly customizable properties, are basic building blocks with the promise of enabling specific nanostructures to be built to meet existing needs and solve evolving problems. Dendrimer research and development is currently making an impact on a broad range of fields as shown by exponential growth in the number of dendrimer-based publications.

Advances in understanding of the role of molecular weight and architecture on the *in vivo* behavior of dendrimers, together with recent progress in the design of biodegradable chemistries, have enabled the application of dendrimers as antiviral drugs, tissue repair scaffolds, targeted carriers of chemotherapeutics, and optical oxygen sensors.

Diagnostics: Sensors; Imaging contrast agents

Drug delivery: Improved delivery of existing drugs, Improved solubility of existing drugs

Drug development: Polyvalent dendrimers interacting simultaneously with multiple drug targets; Development of new pharmaceuticals with novel activities; Improving pharmacological activity of existing drugs; Improving bioavailability of existing drugs

Medicine and surgery: Prevention of scar tissue formation after surgery

Because of their unique properties and the easiness to tailor their surface and core with different molecules, dendrimers are suitable for many biomedical and industrial applications. In the biomedical area, dendrimers had been used for *in vitro* diagnosis in cardiac testing, as contrast agents for magnetic resonance imaging, as drug delivery systems, as therapeutic agents for boron neutron capture therapy, for example, in gene therapy as vectors to transfer genes through the cell membrane, and in regenerative medicine. Moreover, dendrimers have been used to improve many industrial processes such as nanocatalysis or in purification processes to entrap insoluble materials.

Nanocapsules

- Nanocapsules are hollow polymer shells with an internal cavity where a desired substance can be placed. The best examples of natural nanocapsules are the viral capsids in which the shell is composed of identical protein subunits. Capsids are responsible for the protection of the genetic material of the virus and also play an important role in the infection of the host cell.
- Inspired by virus capsids, scientists have developed synthetic polymer nanocapsules that offer many interesting applications for encapsulation, delivery, imaging, and catalysis.
- Nanocapsules can be obtained by ***interfacial polymerization or by direct deposition of a preformed polymer.***
- The interfacial polymerization reactions roughly consist in the interfacial reaction between two monomers. First, ***an emulsion of two immiscible phases is formed.*** Each phase contains a monomer able to react within each other to form an initial wall. After formation of this initial wall, the polymerization is diffusion controlled, leading the formation of capsules with size dependent on the initial emulsion.

□ Redox-responsive nanocapsules for protein delivery were recently reported. The protein caspase 3 was encapsulated via *in situ* interfacial polymerization into a positively charged polymeric shell of polyacrylamide and polymethacrylamide. The described nanocapsules were internalized into cells and the protein was released in the reducing cytosol, proving an effective intracellular delivery strategy for therapeutic, diagnosis, and reprogramming applications. *Some advantages* of the interfacial polymerization methods are the high efficiency in encapsulation and the possibility of *in situ* formation of the polymer that allows the formation of nanocapsules without using a template. The *main disadvantage* of this process is the elimination of the organic solvents used to form the emulsions.

- Several methods such as nanoprecipitation, emulsion–diffusion, double emulsification, emulsion–coacervation, and ***layer-by-layer (LbL) technique*** have been proposed up to now for the preparation of nanocapsules by direct deposition of a preformed polymer.
- The LbL process to fabricate capsules was introduced in 1998. This process is based on the alternative assembly of oppositely charged polyelectrolytes on colloidal substrates that can be later destroyed.
- The assembly results in a thin polymer film of a few nanometers thick. In the LBL method, polyelectrolyte assembly is triggered by the electrostatic attraction between the subsequent polymer layers. After polymer assembly, the colloidal sacrificial template can be removed by dissolution, leading to the formation of polyelectrolyte hollow nanocapsules. The capsules can be later loaded with different materials.
- Besides loading the capsules, this technique offers the possibility to assemble some delivery materials like proteins or DNA between the layers that will be eventually peeled off and liberated.
- The thickness of the *polyelectrolyte multilayers* (PEMs) can be controlled by the number of layers deposited, while the shape and size of the nanocapsules can be engineered by choosing the appropriated template. Then, the stability and surface functionality of the capsules can be controlled by the nature of the polyelectrolytes.

Different combinations of polymers for PEMs and colloids as templates have been used to fabricate nanocapsules via LbL technique. For example, [Figure 4.5 shows](#) a fabrication of capsules via PEMs employing *polystyrene sulfonate* (PSS) and *polyallylamine hydrochloride* (PAH) on human red blood cells and melamine formaldehyde followed by the template removal by dissolving in hypochlorite solution.

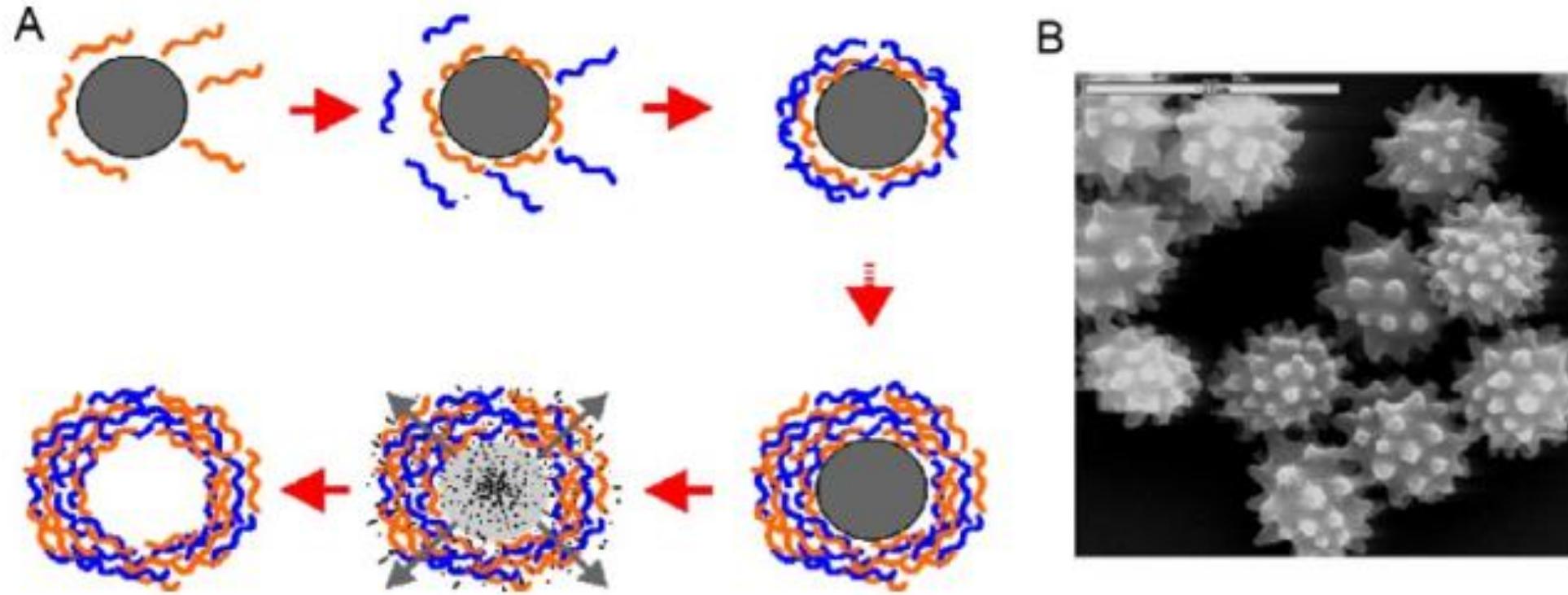


FIGURE 4.5 Scheme of the preparation of hollow polyelectrolyte capsules from spherical particles (A) and SEM micrographs of polyelectrolyte capsules templated on echinocytes (B).

- Typical colloids used as templates in this technique are particles made of polystyrene, silica, calcium carbonate, cadmium carbonate, or gold. Recently, the use of surfactant vesicles as template has also been reported.
- For each type of particle used as a template, the route to remove it without dissembling the polyelectrolyte layer is different.
- Silica particles require relative harsh conditions, employing hydrofluoric acid.
- Carbonate particles are dissolved by an increase of pH toward basic values that hydrolyze the carbonates.
- Both for silica and carbonate, the core is dissolved into an inorganic salt, that is, ions are released into solution in a progressive way.
- Melamine particles, prepared from weakly polymerized melamine monomers, are dissolved by a pH reduction, which breaks the ether linkages between the monomers. For the melamine particles, the depolymerization of the melamine core generates melamine oligomers of variable size that have to permeate through the capsule wall. The oligomers can be retained in the capsule, soaking up water and causing the capsule to swell osmotically. When the oligomers have been released, the capsule retains its original size. For the *melamine particles*, the process of swelling can induce the formation of holes and imperfections in the polymer structure. Besides, it is reported that melamine rests are normally retained in the capsule walls

- In the case of the inorganic cores, the polyelectrolyte layers have been reported to be almost not affected by the dissolution process. *The use of cells for capsule templating* with hypochlorite oxidation deserves a special consideration. The hypochlorite degrades the cell proteins through the oxidation of their amine groups. Typical polyelectrolytes employed for the capsule fabrication like PAH and PSS are oxidized by the hypochlorite. Indeed, capsules fabricated with this polymer no longer show amine groups, which are probably cross-linked. The amount of PSS in the capsule walls is also significantly diminished. Cell template capsules show mechanical and structural properties quite different from other LBL template capsules. In general, we can say that the methodology of core dissolution will have a strong impact on the fabricated capsules.
- Once the capsule template is removed, it can be loaded with both small- and high-molecular-weight molecules. Different procedures have been reported for the loading of the nanocapsules depending on the size and nature of the molecules to load and the physicochemical properties of the PEMs. If the PEMs are formed by materials responsive to salt concentration or pH, the material can be loaded via diffusion by opening the pores within the shell.

- When the desired cargo forms crystals, like drugs or proteins, the PEMs can be directly assembled using the crystals as template, providing capsules with high concentration of the encapsulated molecule. For high loading efficiency, the encapsulation can be done by the incorporation of the cargo within the sacrificial porous template (e.g., in porous silica particles) followed by the LbL assembly and core removal.
- Finally, in the specific case of high-molecular-weight molecules, that is, RNA, plasmids, or proteins, these can also be encapsulated within the PEMs.
- LbL capsules can also be surface modified to achieve specific targeting within the cells by coating the surface of the capsules with specific recognition molecules via electrostatic interactions or by covalent binding, such as polyethylene glycol (PEG) that has unfolding properties and improve the circulation time of the capsules, or lipids that have been proved to protect the capsules from nonspecific interactions. Moreover, to decrease toxicity, biocompatible polyelectrolytes are used to fabricate capsules such as chitosan/alginate, dextran sulfate/protamine, chondroitin sulfate/poly(L-arginine), and poly(L-lysine)/poly(glutamic acid).

- LbL capsules can be designed to release the cargo either for burst or for sustained release. Burst release can be achieved by capsule degradation due to an external stimulus, where near-infrared laser pulses are applied on capsules that have metallic NPs incorporated in the PEM wall, promoting burst intracellular release. Additionally, capsule degradation inside the cell can take place when hydrogen-bonded PEMs are cross-linked with disulfide; this linker is retained in the blood stream promoting disruption and burst release of the content in the capsules.
- In contrast, sustained release can be achieved by slow diffusion of the cargo through the PEM wall or by slow degradation of the PEM wall; in both cases, the release can be environmental stimuli with pH, ionic strength, or temperature changes.
- LbL capsules are promising and versatile nanocarriers for drug delivery that allow the specific design of carriers by tuning the surface chemistry, size, permeability, and degradability of the capsules. Different and multiple cargos can be incorporated inside the capsules or within the PEMs, and the release of the cargo and the degradation of the capsules can be easily controlled by different mechanisms.

Polymeric NPs

Polymeric NPs, also known as polymeric nanospheres, are usually defined as submicron-sized solid polymer particles with matrix type structure, in which a cargo can be encapsulated within the polymer matrix or absorbed in the surface.

Like polymer capsules, polymeric NPs can also be prepared via in situ polymerization techniques or directly by formed polymers. The most common reaction used to prepare NPs by polymerization is the emulsion polymerization either o/w or w/o.

Most of the organic NPs involve several organic or polymeric molecules. Polymer conjugates and dendrimers constitute special cases for organic NPs and have the particularity to be formed on singlemolecule basis. The fact that organic NPs are formed by several molecules imposes sometimes limitations to control size below a certain value. This is not the case for polymer conjugates or dendrimers, whose size can be controlled below 10 nm.

A remarkable issue about organic NPs is their capacity to load molecules either by conjugation on the surface or in the core or by physical encapsulation. This property makes them appealing systems for the delivery of molecules and more specifically for drug delivery and biomedical applications.

Polymeric nanoparticles (PNPs)

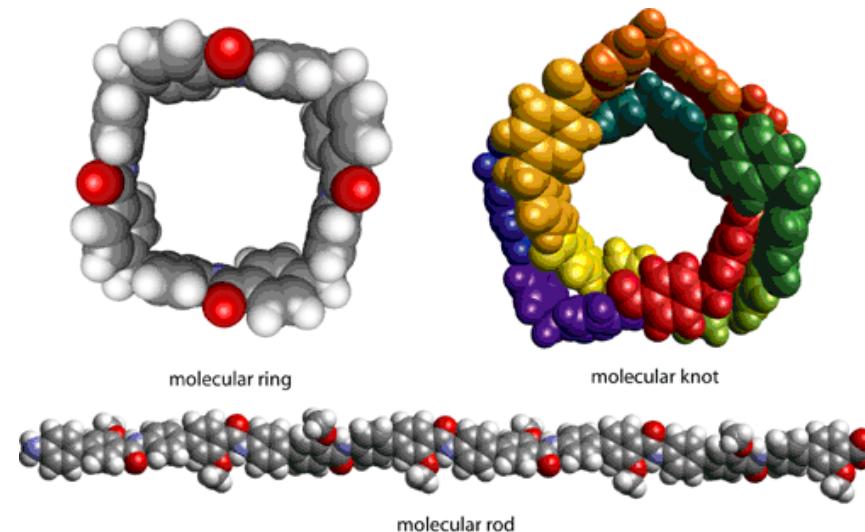
Polymeric nanoparticles (PNPs) have attracted considerable interest over the last few years due to their unique properties and behaviors resulting from their small size.

These nanoparticulate materials show potential for a wide range of applications such as diagnostics and drug delivery.

Advantages of PNPs as carriers include controlled release, the ability to combine both, therapy and imaging (theranostics), protection of drug molecules and its specific targeting, facilitating improvements in the therapeutic index.

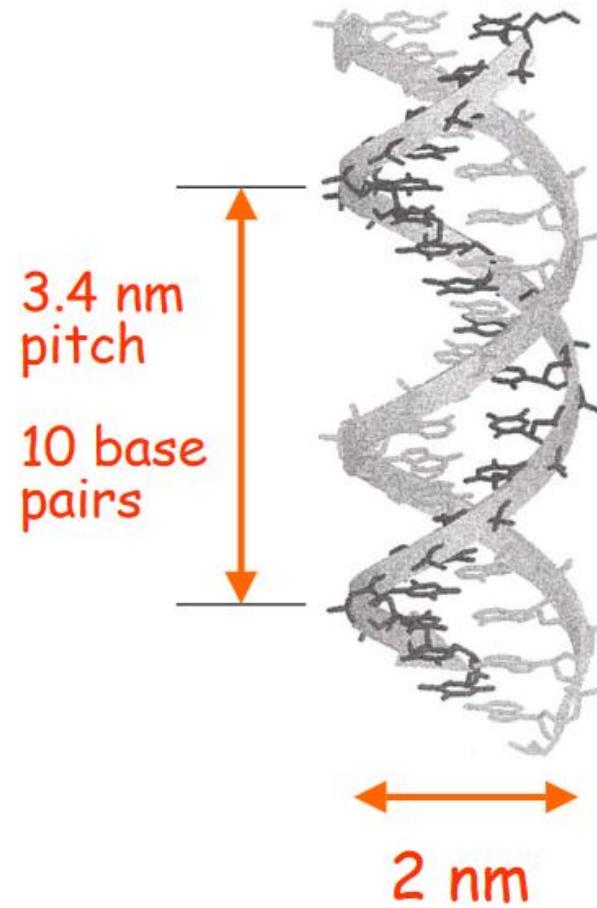
Biomolecular Nanotechnology

- Chaperone structures
- DNA templating
- Synthetic biology
- Synthetic proteins
- Liposomes and novel cellular structures



Biological Length Scales

DNA



Virus (TMV)

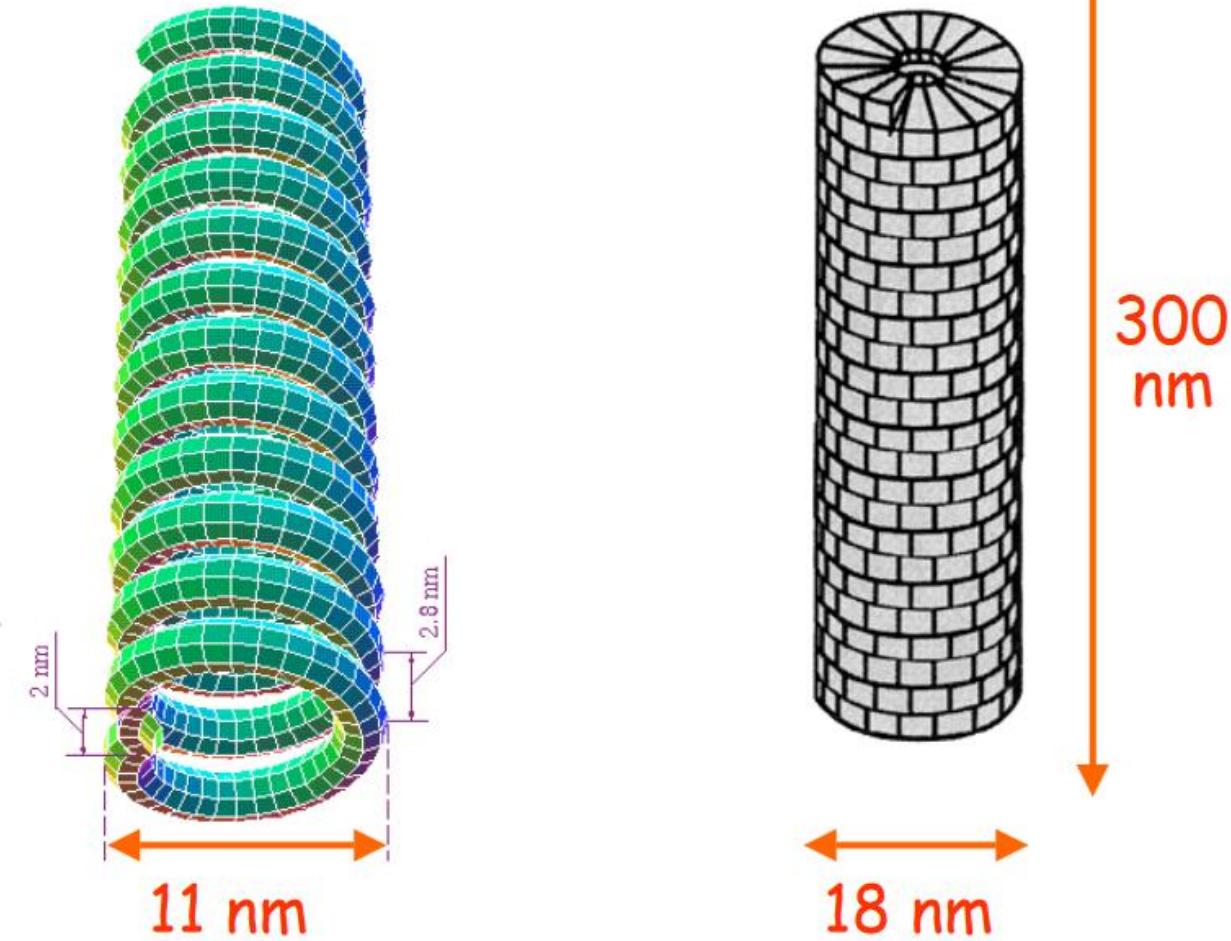


TABLE 4.1 Summary of the Organic NPs Fabricated via “Bottom-Up” Techniques

Nanoparticle Type	Composition	Size	Fabrication Techniques	Applications
Micelles	Amphiphilic molecules	Since 15–20 Å	Self-assembly	Drug delivery
Vesicles and liposomes	Natural and synthetic glycolipids and phospholipids	30–400 nm	Self-assembly, solvent-free techniques and solvent displacement techniques	Nanocarriers for drug delivery, food industry, and cosmetics
Polymersomes	Amphiphilic block copolymers	50–200 nm	Self-assembly, solvent-free techniques and solvent displacement techniques	Nanocarriers for drug delivery, labeling, and tracking and in environmental field to entrap selective toxic molecules
Polymer conjugates	Polymers, proteins, and drugs	5–20 nm	“Grafting to,” “grafting from,” and “grafting through” using ATRP and RAFT	Pharmaceutics as polymer therapeutics
Dendrimers	Polymers	From 10 nm	Divergent and convergent methods	In the biomedical field for <i>in vitro</i> diagnosis, as contrast agents, as drug delivery systems, as therapeutic agents, in gene therapy, and in regenerative medicine. In the industry to improve processes like nanocatalysis or in purification
Nanocapsules	Polymers	From 20 nm	Interfacial polymerization and by direct deposition of preformed polymers	Nanocarriers for drug delivery
Polymeric nanoparticles	Polymers	From 20 nm	Interfacial polymerization and by direct deposition of preformed polymers	Nanocarriers for drug delivery

Organic Versus Inorganic

- Organic NPs differ conceptually from inorganic NPs in terms of the principles of fabrication.
- Inorganic NPs are normally formed by the precipitation of inorganic salts, which are linked in a matrix. The nature of the binding among atoms can be different: covalent, metallic, etc., but in any case, the inorganic structure forms a three-dimensional arrangement with linked atoms.
- In this regard, the closest organic NPs to an inorganic one would be a dendrimer, which is a single-molecule NP.
- However, most of the organic NPs are formed by several organic molecules which are driven together by self-organization or chemical binding.
- For the synthesis of organic NPs, with the exception of dendrimers and some other polymer NPs, we first need organic molecules that can arrange themselves three-dimensionally.
- Interactions among the molecules are sometimes not strong like for micelles and vesicles. Self-assembly and the presence of zwitterionic molecules, with polar and nonpolar regions, as the main components of NPs or the means to encapsulate other organic molecules are key elements for the fabrication of many of the organic NPs.

- Also, another important difference from inorganic NPs is that many of the organic NPs, due to the week nature of the interactions holding them together, have a dynamic character. Micelles and vesicles can fuse and generate larger particles. The continuous addition of surfactant to a micellar solution can indeed increase the size of the micelles and even force it to change shape from spherical to cylindrical over the second critical micellar concentration (CMC).
- The formation of inorganic NPs sometimes needs only the clustering of a few atoms. *In the case of the organic NPs, the size and geometry of the organic molecules impose in many cases the limits to going nano.*
- In micelles, which are among the smallest organic NPs, size is controlled by the length of the surfactant and the smallest sizes to be achieved are that of a sphere with a radius equal to the length of the surfactant in the micellar phase, typically around 15–20 Å°. The lipids forming a vesicle assemble into bilayers because of the relation of their hydrophilic and hydrophobic volume. The bilayers must close in on themselves to make the vesicle, which not only results in an internal volume that can be used for encapsulation but also establishes limits for the smallest reachable size.
- For organic NPs such as polymer latexes, it is even more difficult to get below a certain size threshold. For latexes, the polymeric core is stabilized by a surfactant. The size of the NP is then that of the core and the stabilizing surfactant. Again, dendrimers, as single-molecule NPs, are an exception and can have a controllable size below 10 nm.

- Inorganic and organic nanoparticles are both similar and dissimilar.
- The similarity is expressed in the size dependence of physicochemical (especially, spectral) properties.
 - ✓ For nanoparticles of metals and inorganic semiconductors, the size effects are most strongly pronounced in the size range <10 nm.
 - ✓ For organic compounds, the size effects were discovered in studying the spectral properties of particles with the sizes from several tens to several hundreds of nanometers.
 - ✓ In metals, the size effect is associated with *collective electrons that can hold within the nanobulk*.
 - ✓ In organic molecules, the *electrons “pertain” to chemical bonds*, the mobility of these electrons is limited, and hence, the interactions that result in spontaneous formation of ensembles and favor the transfer of electrons and charge are weak.
 - ✓ So far, the proneness for self-assembling that can be employed in designing devices for opto- and nanoelectronics has been observed only for the systems that comprise several cyclic and aromatic molecules.
 - ✓ The structure and the interaction of these molecules favor the charge transfer and give rise to stacking—the appearance of excitons and shared electrons.