NANOTECHNOLOGY

1. Introduction

The properties of manufactured products depend on how the atoms are arranged. Contemporary manufacturing methods provide limited control over the position of specific atoms in the final product. For example, continuing improvements in lithography have resulted in line widths that are less than 100 nm (100×10^{-9}m). Although submicron lithography is very valuable, it is clear that current lithography will not lead to the building of semiconductor devices in which individual atoms are located at specific unit cell sites. A manufacturing capability able to assemble atoms precisely in patterns chosen to improve material properties would permit radical improvements in product performance and capabilities. Nanotechnology allows this.

When Eric Drexler (1) introduced the term nanotechnology in mid 1980s, he was discussing manufacturing machines on the scale of molecules, nanometer-size motors, robot arms, and complete computers. The meaning of nanotechnology has altered over the years from machines that have been deliberately built from nanoscale components to mean "anything in the range of 0.1 to 100 nm," such as powders and coatings, and other materials that are nanoscale. This altered version of the term is more accurately characterized as "nanoscale technology," while the initial meaning should be labeled as molecular nanotechnology, molecular mechanics, or nanoengineering. Recently, the Foresight Institute suggested a novel term to represent the initial meaning of nanotechnology: zettatechnology (2). Whatever the name, nanotechnology allows for the movement of an individual atom to a desired place and almost any structure that agrees with the laws of chemistry and physics can then be built. Nanotechnology offers not just better products, but a new way of production. This is the authentic meaning of the term nanotechnology, and that is why it is frequently regarded as "the next industrial revolution". In the 21st Century, the societal impact of nanotechnology is expected to be far superior to the combined influences that the silicon chip, medical imaging, computer-aided engineering, and synthetic polymers have had in the preceding century. Thus, nanotechnology will change the nature of almost every man-made object.

2. Properties at Nanoscale

Once the material sizes are reduced below 100 nm, they begin demonstrating an array of unique properties based on quantum mechanical effects, rather than the familiar Newtonian mechanics that operates in the macroscopic scale. The quantum effects may influence a variety of material properties such as conductivity, heat transfer, melting temperature, magnetization etc, without changing the chemical composition. That is, the same molecules are present, but their physical assembly is different. For example, colloidal structures immersed in liquid are subjected to constant attack from the liquid molecules, causing them to move about and bend in a random manner (Brownian motion). Although the combination of Brownian motion and strong surface forces is sometimes considered as a difficulty that nanoscience must overcome, these features at nanoscale converge to offer a remarkable opportunity to exploit new approaches to fabricating nanomachines. For example, some biological nanomachines such as molecular motors are not subject to these limitations because they actually depend in a profound way on Brownian motion. The Brownian motion can also lead to formation of rather complex nanoscale structures in liquid by self-assembly (3). The real power of nanoscience is the convergence of sciences that can be integrated on the molecular field and results in an area of research and development that is truly multidisciplinary (4,5).

3. Reductive vs. Synthetic Approaches

There are two fundamental strategies to produce very small machines or devices. First, there is a progressively precise "top-down" approach of taking a chunk of material and by physical methods carve out the desired nanostructure. Top-down researchers attempt to extend current technology to engineer devices with smaller design features. A typical example of modern top-down technology in use today is the manufacture of the semiconductor chip based on the lithography that tries to reach "down" as much as possible to atoms and molecules. However, the most promising strategy is offered by the "bottom-up" approach, where increasingly complex structures are intentionally assembled from nanoscale components to build larger scale devices. This is exactly how things are formed in Nature. From a chemist's perspective, a self-assembly technique is of greatest interest for developing nanoscale objects with complex compositions such as macromolecules and multicomponent systems. The macromolecules allow bottom-up creation of functionally designed devices economically. Although the future is in the bottom-up approach to nanotechnology, at present nanotechnology can be considered as a more primitive "top-down" stage.

4. Carbon Nanostructures

In 1980 only three forms of carbon; diamond, graphite and amorphous (noncrystalline carbon) were known. Today there is a whole family of other forms of carbon: spheres, cones, tubes, and even more complicated structures and shapes. For example, ultrasmall cylinders of carbon atoms called carbon nanotubes are one-sixth the weight of steel, but about 100 times stronger per unit weight. These nanotubes are the strongest fibers known to humankind. Carbon nanotubes could be used as building blocks for nanostructures, but they have other remarkable properties.

The lowest energy state of elemental carbon at ambient temperature and pressure is graphite. The graphite crystal lattice consists of stacks of parallel two-dimensional graphene sheets with sp^2 hybridized carbon atoms tightly bonded in hexagonal rings. In the sheet, the $2s$, $2p_x$ and $2p_y$ orbitals are superimposed in the x-y plane whereas the remaining $2p_z$ orbital is perpendicular (Fig. 1).

Because the $2p_z$ orbitals of the carbon atoms overlap most effectively if they are parallel, the graphene sheet has lowest energy when it is completely flat.

From a geometric perspective, many of carbon nanostructures such as fullerenes and carbon nanotubes can be related to the covalent graphene building units coiled in the third dimension.

Fullerenes were first discovered in 1985 when the roundest and most symmetrical bulky molecule containing carbon atoms only was synthesized (6). The sixty carbon atoms in C_{60} fullerene are arranged in a spherical shape consisting of 12 pentagons and 20 hexagons (Fig. 2**a**).

As already noted, the carbon atoms are sp^2 hybridized with 120° angles between the bonds in the hexagonal units, while pentagons have 108° internal angles. There is no ring strain on the carbon in the hexagons since sp^2 hybridized carbon has planar bonds. However, an isolated sp^2 hybridized carbon in the pentagon has 12° of angle strain per carbon atom. Two pentagons together will produce 24° of angle strain per atom. Therefore the most stable fullerene structures allow pentagons to be isolated from each other (7). There is no restriction on the number of hexagon units present so that additional structures with extra hexagons can be subsequently synthesized with similar cage-like structures incorporating up to 240 carbon atoms (7–9). Recently the synthesis of the smallest possible fullerene (C_{20}) consisting of 12 pentagonal faces and no hexagonal faces has been demonstrated, but not surprisingly, is less stable than C_{60} (Fig. 2**b**) (10–13). Fullerenes smaller than C_{20} would need to contain cylobutane rings, which are highly unstable.

Carbon nanotubes (CNT) discovered in 1991 by Sumio Iijima (14) resemble a coiled-up graphene sheet. The single-wall carbon nanotube (SWCNT) can be constructed by the rolling of a graphene sheet into a hollow cylinder and then adding two end caps consisting of pentagons, and each pentagon is surrounded by five hexagons. The combination of pentagons and hexagons produces the desired curvature of surface to close the end of the nanotube. Therefore CNT end caps resemble half fullerene balls and these can differ depending on the CNT's diameter. The dimensions are variable (from 0.4 to 3 nm in diameter) and can be extremely long (several hundreds of micrometers plus) (15). There are different SWCNTs because the graphene sheet can be "cut" and "coiled up" in more than one way. Three types of SWCNTs are identified: armchair, zig-zag, and chiral (twisted) nanotubes (Fig. 3).

The conventional way to describe this is by looking at the unrolled sheet and expressing the rolling process by vectors ($\mathbf{a_1}$, $\mathbf{a_2}$), where n and m are integers, corresponding to the number of hexagons in the respective direction, of the vector equation $\mathbf{C_h}=n\mathbf{a}_1+m\mathbf{a}_2$. The vector $\mathbf{C_h}$ quantifies the direction that the tubes appear to have been rolled. The designation is, armchair for tubes with $n=m$, zigzag tubes for $m=0$ according to the pattern of the chain of carbon atoms along the direction of the vector $C_\mathbf{h}$ in the graphite sheet along the circumference. For any other values of n and m, the tubes are called chiral because the chains of carbon atoms spiral around the tube axis rather than closing around the circumference. (See Fig. 3). One vector, $\mathbf{a_1}$, is placed horizontally on the graphite sheet along the zigzag bonds. The other vector, $\mathbf{a_2}$, is placed in any other location. The armchair line (**AC**) travels across each hexagon, separating them into two equal halves. If the tube is rolled directly over this line, the resultant nanotube is an armchair nanotube. In this case, to ensure the vector sum lies over the armchair line, the second vector, $m\mathbf{a_2}$ is placed at an angle such that the armchair line bisects the angle made with the first vector, $n\mathbf{a_1}$. That is, the sum of the vectors $\mathbf{C_h}$ equates to rolling over the armchair line and $n\mathbf{a_1} = m\mathbf{a_2}$. Armchair nanotubes thus have configurations (5,5; 6,6; 7,7 etc) because the vectors must be the same to bring $\mathbf{C_h}$ over the armchair line. The numbers 5,5; 6,6 etc reflect the diameter of the nanotube and the pairing of numbers in its stereochemistry. If the second vector, $m\mathbf{a_2}$, is zero, then $\mathbf{C_h}$ lies along $n\mathbf{a_1}$, and the tube rolls along this line. Zigzag nanotubes have configurations 9,0; 10,0; 11,0 etc, since one vector must be zero. Other possibilities, where $n\mathbf{a_1}$ and $m\mathbf{a_2}$ are not zero or equal, result in a chiral nanotube that has left- and right-handed forms. A coaxial assembly of several SWCNTs with different diameters is called a multiwall carbon nanotube (MWCNT). The separation between the coaxial tubes is approximately equal to that between the layers in natural graphite (0.3 nm). MWCNTs are possible in an even more complex array of forms because each concentric SWCNT can have different structures (armchair, zigzag, chiral). Thus, there are a variety of sequential arrangements. The simplest sequence is when the concentric layers are identical but different in diameter. However, mixed variants are possible consisting of two or more types of nanotubes arranged in different orders.

4.1. Properties and Applications of Carbon Nanotubes and Fullerenes.

The chemical and physical properties of the fullerenes and nanotubes are related to (*1*) the strength of the covalent carbon-carbon bond, (*2*) the geometry of the hexagonal building units and (*3*) to the delocalized p_z orbital and its mismatch caused by the curvature that gives a limited sp^3 character to the C−C bond (16,17). Thus, the chemical and physical properties of the CNTs depend to large extent on the diameter of the nanotube. Those with diameters smaller than 0.7 nm are less stable because of the energy increase during the bending of the C−C bond (10). In wider diameter CNTs, the curvature generally becomes less important and the energy value approaches that of the planar graphene sheet.

Mechanical Properties. The fullerenes and the nanotubes are among the strongest and most durable and flexible materials known to humankind because of the giant delocalized electron system and the strength of the C−C bond (18,19). Fullerenes can endure enormous pressure and can recover their original shape after being pressurized to over 3,000 atmospheres (20,21). In an experiment where a discrete MWCNT was bent by an atomic force microscope (AFM) tip, a Young's modulus of 1.28±0.56 TPa was obtained (19). Krishnan and coworkers (22) reported an average Young's modulus of 1.3 −0.4/+0.6 TPa for 27 individual SWCNT measurements. Comparable results for MWCNT with a diameter of 12 nm were also reported (23).

Unlike carbon fibers that break easily under compression, carbon nanotubes are much more flexible and can be compressed without fracture (24–26). The exceptional strength of the CNTs indicates that they may provide reinforcing elements in high performance composite materials replacing standard carbon fibers, Kevlar, and glass fiber. Incorporation of CNTs in plastics may provide structural materials with a vastly increased modulus that can endure great strain before mechanical failure. The creation of a good contact between nanotube and the polymeric matrix for effective load transfer is a major difficulty because the nanotubes are very smooth and have a small diameter that is almost the same as that of a polymer chain (27–32). The high aspect ratio (length/diameter) of SWCNTs (more than 1000) and their strength make them ideal atomic force microscopy (AFM) probes. Their aspect ratio provides accurate imaging of deep ditches, while superior resolution is maintained because of their nanometer-scale diameter (33). They are electrically conductive, which allows their use in scanning tunneling (STM) and electric force microscopy (EFM). Their tips can be modified with specific chemical or biological groups for high resolution functional imaging (33–36).

Electrical Properties. Despite structural similarity to graphite, the electronic properties of pristine nanotubes are different and depend on how the graphene sheet has been coiled up to form the tube. Armchair-type CNTs are metallic, zigzag-type semiconductive, or metallic depending upon the chirality and tube diameter although the chemical properties are the same (34,37–40). The narrower the diameter, the more CNT's electronic properties depends on the chiral vector ($\mathbf{C_h}$). The wider the diameter of the nanotube, the less is the p_z orbital mismatch, and the behavior is more like graphite. Simple electronic devices have been produced employing the CNTs semiconducting properties including field-effect transistors, single-electron transistors, rectifying diodes (41) and logic circuits (41,42). IBM was the first to produce arrays of NT transistors. They are valuable for future nanocomputer design (43–47). Superconductivity in SWCNTs has also been observed, but only at low temperatures with transition temperatures of about 0.55 K for 1.4 nm SWCNT (40,48–50). The electronic properties of ideal MWCNTs are quite similar to those of ideal SWCNTs because coupling between the cylinders in MWCNTs is weak. The first large-scale commercial application of MWCNTs is as an electrical conducting phase in polymer composites. Depending on the polymer matrix, conductivities of 0.01 to 0.1 S/cm have been reported for 5% loading, whereas a much lower loading is sufficient for dispersing electrostatic charge (51–53).

Field Emission Devices. Most current research activity on electronic devices has focused on using SWCNT and MWCNT as electron sources for flat-panel displays (54), lamps, X-ray (55), and microwave generators. For industrial applications, the electron emitter should have a low threshold emission field and great stability at high current densities. Electron field emission is a quantum process, where, under external electric field, electrons can leave a metal surface by tunneling (56). The characteristic external field thresholds for extremely sharp metallic electron sources are on the order of 10 to 100 V/μm for current density of 10 mA/cm^2. For CNTs 1−2 V/μm for 1 μA per tube current density is sufficient (57). The nanometer-scale diameter, the high aspect ratio of $>$1000, the high conductivity and chemical stability make CNTs ideal candidates as electron-emitters (58–61). In recent times, major companies, eg, Samsung produced prototypes of field-emission flat-panel displays with CNTs electron sources. With advances in technology, this could be the first major commercial application of CNTs.

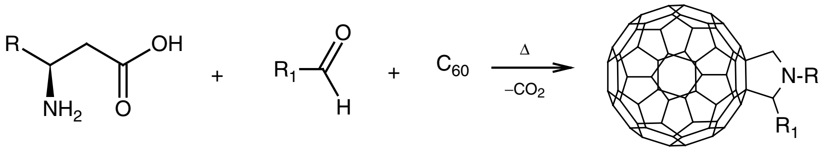
Energy Storage. The two commonly used means to store hydrogen are gas phase and electrochemical absorption. Graphite and other carbonaceous materials are typically used in hydrogen fuel cells, and in electrochemical devices as batteries and super capacitors. Because of the high electrochemically accessible area of CNTs combined with their high electric conductivity, they are attractive as electrodes for devices that use electrochemical double-layer charge injection. The maximum reported reversible capacity is 1000 mAh/g for lithium ion storage and the large irreversible capacity is 2500 mAh/g for SWCNT (62–65). Super capacitors with CNT electrodes can be used in applications that require much higher power capabilities than batteries and much higher storage capabilities than ordinary capacitors (66–70).

The U.S. Department of Energy (DOE) has set two goals for economical hydrogen storage capacity for automotive applications. DOE requires a ratio of *hydrogen mass/ tank mass* that is at least 6.5% weight and a hydrogen volumetric density higher than 62 kg/m^3 (15,71). Hydrogen fuel cells seem to have a feasible role with fullerenes since the C_{60} molecule can absorb a large quantity of hydrogen atoms without disrupting the structure (21,72). It is anticipated that up to 60 hydrogen atoms can be attached to inside (endohedrally) and outside (exohedrally) of the fullerene surface, which allows a storage of maximum 7.7 wt% H_2 (73,74). Since many of the fullerene reactions seem to be reversible, if a 100% conversion of $C_{60}H_{60}$ can be achieved, 30 moles of H_2 gas would be liberated from each mole of fullerene hydride. However, these are optimistic estimates, valid at very low temperatures and under idealized conditions. Since Dillon and co-workers (75) reported that SWCNTs had the potential of accumulating up to 5−10% wt hydrogen at moderate pressures and temperatures, there has been tremendous research activity aimed at a better understanding of the hydrogen storage mechanism in CNTs (15,76–78). Theoretical estimations showed the maximum number of hydrogen atoms covalently bound in carbon nanotubes corresponds to a storage capacity of 14 wt% (78). It was reported that storage capacity can reach 8 wt% below 77 K. However, it should be noted that the value reported for storage capacity at room temperature and moderate pressure varies significantly among the research groups (76,78–81). Therefore, it is less likely that at moderate pressures and at room temperature, carbon nanostructures would be able to meet hydrogen storage specifications required for automotive applications.

4.2. Functionalization of Nanotubes and Fullerenes. The strength and unique properties of the fullerenes and the CNTs seem to offer potential in advanced materials, however, they are very inert and do not bond to other molecules easily. In order to tailor and exploit the unique properties of the fullerenes and nanotubes, they should be modified *via* process known as functionalization.

Fullerene Functionalization. Bulk or thin films of pure C_{60} are semiconducting. However, the electrical resistivity can be decreased by many orders of magnitude by adding alkali metals as salts. When a fullerene molecule is “doped” by inserting just the right amount of alkali into the voids in between the C_{60} molecules in the polycrystalline fullerenes, the material becomes the best organic superconductor known (82,83). The structure is then $M_x{}^+C_{60}{}^{n-}$, where M^+ is an alkali cation and x is the number to balance the charge on the fullerene. As x in $M_x{}^+C_{60}{}^{n-}$ increases, the resistivity decreases, reaching a minimum for $x = 3$ stoichiometry. The $x = 3$ state is superconducting, with a transition temperature of approximately −243°C for M = Rb, (Rubidium). By further increasing the alkali metal stoichiometry, the resistivity increases again until an insulator is produced for $x = 6$. Recently, the addition of some simple organic compounds such as bromoform, $CHBr_3$, to the ball has been shown to increase conductivity.

Despite their extensive conjugation, which should lead to high electron delocalization and aromaticity, the fullerenes are good electron acceptors and react as strained, electron deficient components in many reactions (7,84,85). Thus, the chemistry of C_{60} and higher fullerenes is more similar to that of alkenes rather than to the chemistry of electron-rich aromatic systems as benzene and naphthalene (86–89). Addition and cyclo-addition reactions are the usual synthetic methods used to functionalize fullerenes (90–92). Among them, Prato (93–95), Bingel (96,97), and Bingel−Hirsch (98–101) reactions have been the most widely used to produce numerous C_{60} derivatives. In the majority of the these reactions, a nucleophile attacks one of the fullerene C−C bonds at the linkage between two hexagons (6,6-ring junction). Additions at the linkage between a hexagon and pentagon (5,6-ring junction) have also been reported as reorganizations that follow a 6,6 junction attack (93,102). Several organofullerene donor-acceptor hybrid systems have been synthesized mainly *via* 1,3 dipolar cyclo-addition reactions of azomethine ylides (102–106). Azomethine ylides can be readily produced upon decarboxylation of immonium salts derived from condensation of variety of α-amino acids and aldehydes or ketones (105). A fulleropyrrolidine mono adduct is formed, in which the pyrrolydine ring is fused to the junction between two hexagons (eq. 1).



(1)

Structurally different fullerene derivatives can be obtained by either properly functionalized azomethine ylide precursors or by further functionalization of the fullerene pyrrolydine product (105,107). The additional chemical functionalization of fullerene pyrrolydine provides an opportunity to combine the excellent electron acceptor properties of the pristine fullerene with those of photosensitive molecular units such as porphyrines (108,109), phthalocyanines (110), ferrocene (111,112), tetrathiafulvalene (113), or ruthenium complexes (114–116). These fullerene derivatives demonstrate strong absorption bands in uv region and considerable absorption in the visual region, which makes them very good building blocks of more complex devices for conversion of light into electricity (Fig. 4).

So far, there are only two areas where functionalized fullerenes have had an impact: plastic solar cells with lesser applications in polymeric materials and fullerene-modified traditional materials. Several other possible applications include energy storage devices, molecular switches, and materials imitating for hotosynthesis (111,112,117).

CNTs functionalization. Like graphene, carbon nanotubes demonstrate quite high chemical stability and resistance to wetting by relatively polar solvents. They usually exist as ropes or bundles 10−30 nm in diameter because of the weak π-π interactions between the individual tubes (118). This has caused application difficulties during processing and manipulation due to CNTs insolubility and poor dispersion in regular solvents and polymeric matrixes. For various applications, it is necessary to attach chemical functional groups to the CNTs. For example, it is believed that chemical functionalization may provide the "velcro effect" needed for incorporating CNTs in a host matrix for developing composites. Accordingly, much effort has been made on targeted chemical functionalization of sidewalls and the end-caps of CNTs because this is a potential way to improve their solubility and to ease their manipulation. The chemical modification and the connection to other molecules will eventually lead to new physical and chemical properties for specific applications.

Because of the curvature and structural differences at the end-caps and at the sidewall of CNTs, two separate areas with different physical properties and chemical reactivity have been observed (14,119–123). The hemispherical fullerene-like end-caps possess higher curvature, and therefore, are more reactive than the cylindrical sidewalls of the CNTs. The chemical reactivity of the perfect CNT is essentially related to the reactivity of the parent graphene sheet enhanced by the p_z-orbital mismatch caused by the curvature and therefore bond strain is increased (17). The release of this strain as a result of a chemical reaction controls the chemical properties of the CNTs' sidewalls. In general, the CNTs functionalization strategies include: (*1*) noncovalent functionalization of the tube walls with detergents and polymers, (*2*) creation of defect sites at the tube end-caps and sidewalls by oxidation followed by further functionalization and (*3*) direct covalent bonding at the conjugated double bonds at CNT's sidewalls using addition reactions.

Noncovalent Functionalization. The formation of noncovalent van der Waals, or electrostatic bonds with detergents, or polymer covering results in noncovalent functionalization of various molecules to CNTs (124–126). The polymer molecules attach rigidly and uniformly to the cylindrical body of the nanotube, disrupting the hydrophobic interface with water and enhancing the CNTs solubility (Fig. 5**A**) (118).

When the hydrophobic part of an amphiphilic molecule has planar π-moiety, a strong π-π interaction between the nanotube sidewalls will take place (126–128). This effect has been successfully demonstrated in the agglomeration with *N*-succinimidyl pyrenebutanoate (Fig. 5**B**) (129). In fact, the interaction was found to be so strong that the aromatic moiety was permanently attached to the CNTs' surface. This approach could be used to append biologically active molecules such as DNA on the CNTs sidewalls with the mediation of 1-pyrenebutanoic acid (128–131). One of the main advantages of the noncovalent functionalization is that the nanotube sp^2 arrangement and conjugation is preserved.

Covalent Functionalization. *Role of Defects* During the synthesis or chemical treatment of CNTs various types of defects can occur caused by vacancies, dislocations, heteroatom incorporation, topological defects on the nanotube sidewall (inclusion of pentagons and heptagons instead of hexagons) (132). The increased reactivity of these "hotspots" provides a means for functionalization of the nanotubes. However, a CNT can bear only a limited quantity of defects before it changes its electronic and mechanical properties (133–136). Early works on CNTs chemistry showed that oxidation at 700°C in air opens the end-caps indicating that the ends are more reactive than the sidewalls (137,138). The treatment of CNTs in solution of strong mineral acids such as nitric acid, or other strong oxidizing agents such as $KMnO_4/H_2SO_4$, $K_2Cr_2O_7/H_2SO_4$, has proven to be more efficient for functionalization of the CNTs than thermal oxidation in air (137,139). The chemical treatment opens not only the end-caps of CNTs, but leaves holes on the sidewalls that could be functionalized with carboxylic groups and other weakly acidic groups (140–142). The introduction of these acidic functional groups is seen as a handle to introduce many other different functional groups by well-established procedures. For example, long chains of alkyl- or aryl- amines were joined to carboxylic groups by an amidation reaction in presence of $SOCl_2$ (Fig. 6) (143).

Direct Covalent Functionalization. Several direct functionalization methodologies without preliminary oxidation exist. They have one thing in common; a highly reactive species is necessary to attack the nanotubes. Although carbon nanotubes are rather inert towards fluorine at ambient temperature, chemical attack by fluorine gas can occur at temperatures 150−400°C (144–146). The fluorination of the CNTs significantly enhances their chemical reactivity, which makes fluorinated nanotubes suitable precursors for a number of functionalization reactions. Alkylated nanotubes can be produced by treatment of the fluorinated nanotube with alkyl-lithium or Grignard reagent (Fig. 7) (65, 147–149). Amines and diamines have been reported to displace fluorine from the sidewall to form amino alkyl nanotubes (144,150,151). Sidewall fluorinated CNTs have been reacted with diols in presence of alkali metal or metal hydroxides to produce hydroxyl terminated molecular fragments (150).

Direct sidewall functionalization to the π-electron system of CNT's is possible if very reactive species are employed (Fig. 7) (152–155). Sidewall nanotube functionalization of CNTs have been achieved by generation of alkyl (147) and aryl (156,157) radicals, azomethine ylides (152,158), and carbenes (154). Recently, a novel solvent-free protocol for sidewall nanotube functionalization involving reaction with aryl diazonium species in the formation of heavily functionalized nanotubes has been reported (159). Similar to the fullerene chemistry, the functionalization based on cyclo-addition of highly reactive azomethine ylide species generated *in situ* has been used to improve the solubility of nanotube derivatives (158,160). The degree of functionalization is very high and the nanotubes are soluble in many organic solvents (152). Other cyclo-addition methods that have been developed for fullerene functionalization include the Bingel reaction (cyclopropane addition) (161,162) and nitrene decomposition (aziridene addition) (163). Further functionalization by photoactive electron donors such as ferrocene, porphyrine, pyrene or other photosensitive moieties affords CNTs building blocks that can be used in solar cell devices (63,164–167).

Covalent sidewall functionalization also overcomes the issues of poor interfacial bonding in host polymeric matrixes paving the way to ultrahigh performance materials. However, the significance of direct functionalization is in that the applicability to the sidewalls by means of synthetic organic chemistry has been highlighted.

4.3. Preparation of Thin Films. Scientists and manufacturers have been searching for methods for organizing fullerenes and nanotubes into highly ordered thin films. These thin films containing fullerenes and nanotubes are the source of high expectations for valuable components in many useful applications such as detectors, sensors, displays, and electronic circuit components. In this respect, two techniques may be used: Langmuir-Blodgett (LB) and self-assembly (168). These methods are frequently referred to in the articles on nanotechnology as, the bottom-up approaches to assemble nanoscale objects into hierarchical macroscopic structures.

Langmuir-Blodgett. One of the most broadly implemented methods for preparation of structurally ordered films has been the formation of Langmuir monolayers at the air−water interface and the following transfer of these films onto a solid substrate (Langmuir-Blodgett technique, LB technique). A Langmuir monolayer is formed by spreading of an amphiphilic compound (surfactant) on the surface of a liquid. Surfactants are a class of molecules that have hydrophilic and hydrophobic moieties. The hydrophobic moiety generally consists of a nonpolar hydrocarbon chain, while the hydrophilic moiety consists of a polar group (−OH, −COOH, etc). Many of these amphiphilic chemicals can be spread on water to form an insoluble monolayer at the air-water interface. The amphiphilic character of the surfactant determines the orientation of the molecules at the interface (air−water or oil−water) so that the hydrophilic head group is immersed in the water and the hydrophobic hydrocarbon chain is oriented towards the gas or oil phase (Fig. 8**a**).

The surfactant monolayers represent an ultimate situation when all amphiphilic molecules are concentrated at the surface (Langmuir monolayer). When a monolayer is transferred to a solid substrate, it is then referred to as a Langmuir-Blodgett (LB) film (168). If a solid substrate is dipped up and down in a solution containing amphiphilic molecules, the floating monolayer can be deposited onto its surface. The film forms on the substrate as the triple line (solid−liquid−gas) progresses downwards. The deposition process is schematically shown in Fig. 8**b**.

Several research groups have explored its suitability in the preparation of Langmuir monolayers and Langmuir-Blodgett films based on functionalized C_{60} (84,169–171). The hydrophobic fullerene has been made amphiphilic by two step functionalization. Cyclo-addition of azomethine ylides to fullerene has proven to provide access to a variety of fullerene pyrrolidine derivatives (eq. 1). Further functionalization of the fullerene pyrrolidine with carboxylic acid affords a highly hydrophilic fullerene pyrrolidine dicarboxylic acid (FDA) suitable for monolayer formation at the water surface (Fig. 8**c**) (172). FDA can form a stable monolayer at the air−water interface, and this monolayer can be easily transferred onto quartz or glass substrates (160). The attachment of photosensitive moieties to C_{60} creates an attractive synergism for the manufacture of effective ordered electrodes for solar energy conversion (84,100). This is an excellent example of how fullerenes, when chemically modified with the appropriate functionalities, can be organized into useful materials.

Self-Assembly. Manufacturing of complex nanoscale devices requires designing systems that self-assemble into more complex structures that sequentially self-assemble into others. This is Nature's preferred way of manufacturing complex structures. Recent progress in molecular self-organization chemistry has shown the viability of the method to nanotechnology and bottom-up material fabrication (168,173–175). Self-assembled monolayers are deposited when a substrate is immersed in solution of organic molecules, which then spontaneously align themselves with respect to substrate (168). Additional layers can be then added, leading to laminates where each layer is just a molecule thick. Since it is necessary that the ultimate structures be the most thermodynamically stable, the technique is inclined to create superstructures that are generally defect-free and self-repairing (168).

The development of two-and three-dimensional superstructures integrating prefunctionalized fullerenes or nanotubes has recently become achievable assisted by the spontaneous self-assembly nanotubes on treated substrates (171,176–183). Similarly to the LB technique, the CNTs or the fullerenes are first made hydrophilic and then they are dispersed in suitable solvent producing a stable suspension. Often molecules such as alkyl-thiols are used because they can act as delivery agents of the CNT and/or fullerene to gold surfaces. Alkyl-thiols are compounds that have a 1–4 nm long hydrocarbon tail group and a thiol group (-SH group). These form a monolayer in which the thiol head groups form relatively strong bonds to the gold, and the alkane chains extend roughly perpendicular to the surface (183–185). For example, Plank and co-workers (183) have prepared aligned carboxyl group terminated SWCNTs by self-assembly through thiol amide linkage onto gold substrate (Fig. 9**A**).

Many oxidized substrates can also be used because the end-cap carboxylic acid functionalized CNTs can be deprotonated by a range of metal oxides. The deportonation at the oxide surface leads to sticking of aligned nanotubes on the oxide surface through their, carboxylic end groups (Fig. 9**B**). CNTs can be also directly sidewall functionalized. The approach affords the opportunity to derive sidewall aligned nanotubes on variety of substrates (30,106). The essential benefit of the stepwise multilayer self-assembly via alternate adsorption of the structure-forming components makes it possible to control the composition, structure, and properties of individual layers within the film. Thus, effective design of novel supramolecular and composite nanostructured thin films and coatings is achieved. Self assembly and LB techniques are perhaps, technologically and commercially viable solutions for constructing hierarchical superstructures in which the advantages of conventional microelectronic technologies such as lithography and new nontraditional approaches can be merged effectively.

In summary, the development of superstructures in the nanometer level has become possible because of spontaneous self-assembly. Numerous novel materials derived from the functionalized fullerene and nanotubes can be synthesized, with a wide variety of properties associated with the attached functional group.

5. Molecular Nanotechnology

There are a large number of other possible ways to build complex nanostructures as molecular nanotechnology (MNT). This technology does not yet exist but when realized should allow for the control of the organization of matter. The capacity to build commercial products may yet be several decades away but theoretical and computational models indicate that molecular manufacturing systems are feasible that do not violate existing physical laws (186). These models also give us a sense for what a molecular manufacturing line might look like. At the most basic technical level, MNT is building, with intent and design, and molecule by molecule (*1*) incredibly advanced and extremely capable nano-scale and micro-scale machines and computers, and (*2*) ordinary size objects, using other incredibly small machines called assemblers or fabricators.

During the last twenty years, the advance in supramolecular chemistry has allowed the creation of simple molecular devices that are essential for the growing field of nanotechnology (187–190). At present, attempts are being made to construct molecular level devices by bottom-up approach following the supramolecular chemistry requirements (191). Thus, from the perspective of a nanotechnologist, the objective of supramolecular chemistry is drifting from structure to function (192). Many research groups are working on development and realization of devices at nanoscale for molecular electronics (193–195), molecular motors (196,197), and artificial photosynthesis (111). In general, the machines and devices are assemblies of components designed to achieve a specific function. A molecular level machine can be described as an assembly of a distinct number of molecular components that are designed to perform machine-like movements as a result of some input (198). Each component of the assembly performs a simple operation while the whole assembly performs more intricate functions characteristic of a machine (192). Such machines would be much smaller than those made by current technologies and ultimately present the smallest machines theoretically possible.

5.1. Molecular Rotors. Bulky groups on crowded molecules have similar morphology to propellers. A molecule comprized of two bulky aromatic rings attached to a focal atom can be regarded as the molecular equivalent of a macroscopic two-bladed propeller (191). The structure shown in the top area of Figure 10 incorporates two identical aromatic rings linked to the same atom. Rotation of one ring in one direction about the single bond linking it to the focal carbon group in the middle forces the other ring to rotate in the opposite direction. Thus, when one ring rotates clockwise, the other must rotate anticlockwise. This arrangement can be used in a traditional macroscopic manner as paddles.

There are other examples in which molecules resemble everyday macroscopic rotors. The coupled motions of two structures have been used in the design of molecular gears incorporating 9-triptycyl ring systems. For example, the gear shown in the middle area of Figure 10 incorporates two 9-triptycyl ring systems bridged by a methylene group. The aryl rings of the two triptycyl ring systems interdigitate in a manner reminiscent of the notches of a pair of meshed gears, much like those in models for carbon-based nanotube gears. As a result, the rotations of the two 9-triptycyl ring systems about a single bond linked to a common group are coupled. When one 9-triptycyl ring system rotates clockwise, the other rotates anticlockwise and vice versa. In Figure 10, the bottom area depicts a rotor in a framework. Thus, electricity could be generated and passed down a conducting carbon nanotube wire a few nanometers thick.

Some useful molecular structures are joined bracelets linked through each other and called catenanes, and their polymers, polycatenanes, which consist of catenanes chained together. The naming of these compounds is quite simple; a number is placed in the front to describe the number of rings. Thus, a [2] catenane has two rings and a [3] polycatenane has three rings. Two-bracelet catenanes ([2] catenanes) are useful because each bracelet can be rotated around the other (Figure 11**a**).

Another useful molecular structure which can be modeled at the molecular level is the axle and collar. In this structure, a central rod holds the axle to the superstructure through a collar and dumbbell structures at each end to prevent the collar from falling off. The molecular equivalents of these structures are called rotaxanes (Fig. 11**a**). The rotaxanes and catenanes can be activated so that the components move in either linear way (rotaxanes) or a rotary way (catenanes) similarly to the moving parts of macroscopic machines (199). Rotaxanes are also of particular interest because the collar structure can often be moved by some external force and used as a molecular switch (198). The principle behind these molecular switches is the ability to move the collar under some external influence. If the collar can be switched back and forth (Fig. 11**b**) from each site "S", then it acts as a switch. The number of sites at which the collar can stop can be increased so that there are a number of stations where it could stop. These structures then become like molecular railway lines and the collar is, in effect, a train. It is possible to put more than one train on the line and also design trains that stop only at particular stations. The idea is to have collars that will stop only at certain sites depending on different environmental changes. The structures that can stop a train or collar, or make it move, are variable and depend on the nature of the collar or track. There are a number of desired phenomena for collar movement, however, one cannot always design a rotaxane for such purposes. Preferred train departure signals are biological materials, because these substances are sensitive detectors for cancer or biochemical imbalances, but the easiest responses are to electrons, light, or heat. A number of useful sensors can be generated in this way particularly if these switches can be made to function in tandem on a larger scale. If a large number of rotaxanes are aligned on a surface, then when all the collars move, they can influence macroscopic properties. Thus, a molecular change can be transmitted to a measuring device that can detect the change. This then becomes a nanomachine that is easy to observe at the level at which human beings can observe and control.

5.2. Rotaxanes and Molecular Computers.

Logic gates are the counting devices for computers. They are based on devices called silicon chips. It does not take much imagination to see that a row of rotaxanes could be used as an abacus and hence as a molecular-based logic gate. Indeed it has been shown that they can do exactly the same task as silicon (191,200,201). Rotaxane counting devices are called chemical computers. They do not suffer from the packing defects that exist in surface based technology. Unlike silicon technology, each molecule is a counting device. In a mole of rotaxane there are Avogadro's number of counting units; thus even a thousandth of a mole of rotaxane can undergo computations at a level undreamed of by conventional devices. To make one type of molecular computer, a set of wires is arranged in one direction above a layer of molecular switches, and a second set of wires is aligned in the opposite direction below. At the junction of the wires is a single layer of rotaxanes. Each rotaxane collar is moved by electrical input that is controlled by the wire circuits. The apparatus then operates as a logic circuit as in a conventional computer. Quantum computers are similar except they rely on single atom orientations to count and have the advantage that they can use the power of the quantum behavior of atoms and electrons to provide additional counting methodologies.

Molecular computers hold the promise of being far less expensive and much smaller and faster than today's silicon-based computers. In principle, it is possible that these machines will perform 100 billion times better than current old fashioned chip machines. While silicon based chips are not going to improve by much more than a factor of ten, with molecular computers the potential is there to get the computational power of 100 workstations on the size of a grain of sand. Power consumption would be mostly reduced with molecular electronic based computers. In addition, such computers would contain vast amounts of memory resources. This implies that all data could be securely hardwired into the machine, and that nothing would ever need to be erased, making such machines immune to disruptions such as those caused by computer viruses.

Today, scientists are inventing numerous tools and techniques that will be needed to transform nanotechnology from computer models into reality. In many instances the actual structures, devices and systems will be much larger, but they will be classified as products of nanotechnology since they will either be created at the nanoscale or nanotechnology will enable them to perform new and/or improved functions. With advances in nanotechnology, it is possible to bridge the gap between the contemporary lithography, and to control matter on every important length scale, enabling incredible new power in materials fabrication.

6. Tools

It was not until the 1980s that miniaturization of apparatus was developed, such as in scanning probe microscopy, includes several newly developed microscopy technologies. The most well-known are atomic force microscopy (AFM) and scanning tunneling microscopy (STM). In these techniques, images are obtained not by gathering reflected or refracted waves from a sample, as happens in conventional light or electron microcopy methods. These operate by employing a sharp tip (the probe) that scans across the surface at a distance of a few nanometers. In particular, the STM works by detecting small currents flows between the microscope probe and the sample being observed. When the probe is brought within about 1 nm of the sample, electrons from the sample begin to pass through the 1 nm gap into the tip or vice versa, depending upon the sign of the bias voltage. Just as per waves can pass over rocks without moving the rocks, so the electrons can pass over the energy barrier to the sample. In other words, this process invokes the wave properties of an electron to move across an energy barrier at lower energy than if it were a particle. The process is called tunneling. The resulting tunneling current varies with tip-to-sample spacing, and it is the signal used to create an STM image. For tunneling to take place, both the sample and the tip must be conductors or semiconductors. The STM was the first instrument to generate real-space images of surfaces with atomic scale resolution.

Several years after the invention of the STM, the atomic force microscope (AFM) was introduced. Instead of measuring the tunneling current, AFM detects the force between the probe and the sample surface. It has a very sharp tip on the end of a cantilever that moves over the surface of the sample. The variations of the surface topography cause bending of the cantilever which is detected by measuring the deflection of the laser beam. A schematic representation of an atomic force microscope is shown in Figure 12**a**.

The extension of a crystal (a piezo) is responsible for the movement of the tip across the surface. As the tip tracks the surface, the force between the tip and the surface causes the cantilever to bend. An optical lever measures the deflection of the cantilever. The optical lever of most machines consists of a laser beam reflected from the gold-coated back of the cantilever on to a positional sensitive diode. The positional sensitive diode can measure changes in position of the incident laser beam as small as 1 nm, thus, giving sub-nanometer resolution.

The AFM normally works in two modes: contact and noncontact modes. In contact mode the repulsive forces are measured as the sample cantilever pushes into the sample. These are interactions between the atoms in the tip and the atoms of the material's surface. Consequently the tip is in physical contact with the surface during the analysis and can cause physical damage to soft materials. However, a way around this is a variant of contact mode called 'tapping mode'. The cantilever is vibrated so that the tip contacts the surface intermittently (Figure 12**b**). This intermittent contact serves to reduce the lateral forces incident on the soft sample, reducing possible surface damage or tip contamination but maintaining resolution. In noncontact mode the attractive van der Waals forces are measured by oscillating the cantilever with small amplitude from 5 to 10 nm from the surface of the sample. Because noncontact mode measures the weaker attractive forces, the lateral resolution is often said to be less than that achieved with contact mode. This is not correct, since noncontact AFM is used to demonstrate true atomic resolution. Apart from imaging, AFM can be used for sample manipulation at atomic or nanometer scale, as well as for nano lithographic processes.

The invention of scanning probe microscopes and a number of more specialized variants is perhaps the single most important development in nanoscale science and technology as a new discipline. This linked family of techniques was not the first form of microscopy that could provide information at the atomic and molecular scale, but a number of factors combine to make the impact of these techniques on nanotechnology particularly important.

7. Conclusions and Outlook

Over the last twenty five years, microscale machines such as microelectromechanical systems (MEMS) have been developed, and their uses are growing rapidly. They currently represent the lowest size limits of commercially available machines. The nanotechnology equivalent of MEMS is nanoelectromechanical systems (NEMS) are in a very early stage of development in the laboratory and would involve using or mimicking naturally occurring biological motors, nanotubes, and related materials. In the development of nanodevices, problems start with localized nanoscale distortion or dislocation in materials at the atomic level, which may be a precursor to cracking and then total failure. Therefore, the role of nanosensors, eg, would be able to detect and send early warnings of these nanocracks, when repair or discard is easier and cost effective. These nanosensors may be active, ie, linked to an electrical or optical fiber circuit, or they may be passive and subject to external interrogation at periodic intervals using various types of radiation or by imaging which in turn will allow ‘health checks’ to be performed on all materials nondestructively. Repair at the local atomic level could be carried out with advanced laser and ion beam techniques, or atomic force nanoprobes, which can be used to supply energy locally to enable atoms to move back into correct, low energy positions. Although it will be a huge challenge to achieve localized repairs, the possibilities include apply, fill in, or “ion stitch” in, nanopatches, nanoparticles, or ions of the correct material. These are just a few of the potential nanotechnological applications. Much development is needed before any serious prospects emerge. Nanotechnology is very much at its infancy and as such it can be expected to give rise to a great deal of intellectually stimulating science before becoming a viable companion to the current silicon based technologies.

BIBLIOGRAPHY

“Nanotechnology”, in *ECT* 4th ed., Supplement Vol., pp. 397–437, by Rajesh Vaidya and Gabriel López, University of New Mexico, and José A. López, Baylor College of Medicine; “Nanotechnology” in *ECT* (online), posting date: December 4, 2000, by Rajesh Vaidya and Gabriel López, University of New Mexico, and José A. López, Baylor College of Medicine.

CITED PUBLICATIONS

1. E. Drexler, *Engines of Creation*, Fourth Estate, London, 1990, pp. 296.
2. E. Drexler, paper presented at the Royal Society’s Working Group on Nanotechnology, 2003.
3. S. Wood, A. Geldart, and R. Jones, *The Economic and Social Challenges of Nanotechnology* ESRC External Relations Division, Polaris House, Swindon, UK, 2003.
4. M. C. Roco, *Current Opinion in Biotechnology* **14**, 337 (2003).
5. T. E. Harper and C. V. Roman, *Abstracts of Papers, 229th ACS National Meeting, San Diego, CA, United States, March 13-17, 2005*, POLY, 2005.
6. H. W. Kroto, J. R. Heath, S. C. O’Brien, R. F. Curl, and R. E. Smalley, *Nature (London)* **318**, 162 (1985).
7. M. A. Wilson, L. S. K. Pang, G. D. Willett, K. J. Fisher, and I. G. Dance, *Carbon* **30**, 675 (1992).
8. A. M. Vassallo, A. J. Palmisano, L. S. K. Pang, and M. A. Wilson, *J. Chem. Soc. Chem. Communications*, 60 (1992).
9. G. A. Olah, I. Bucsi, R. Aniszfeld, and G. K. Surya Prakash, *Carbon* **30**, 1203 (1992).
10. H. Prinzbach and co-workers, *Nature* (*London*) **407**, 60 (2000).
11. Z. K. Tang, G. D. Li, Z. M. Li, N. Wang, and J. Wang, *AIP Conference Proceedings* **591**, 221 (2001).
12. M. Saito and Y. Miyamoto, *Physical Review Letters* **87**, 035503/1 (2001).
13. Z. Wang and co-workers, *Physics Letters A* **280**, 351 (2001).
14. S. Iijima, T. Ishihashi, and Y. Ando, *Nature* (*London*) **356**, 776 (1992).

15. R. G. Ding, G. Q. Lu, Z. F. Yan, and M. A. Wilson, *Journal of Nanoscience and Nanotechnology* **1**, 7 (2001).
16. F. Nunzi, F. Mercuri, and A. Sgamellotti, *Molecular Physics* **101**, 2047 (2003).
17. S. Niyogi and co-workers, *Accounts of Chemical Research* **35**, 1105 (2002).
18. R. S. Ruoff, D. Qian, and W. K. Liu, *Comptes Rendus Physique* **4**, 993 (2003).
19. E. W. Wong, P. E. Sheehan, and C. M. Lieber, *Science* (*Washington, D.C.*) **277**, 1971 (1997).
20. B. Sundqvist, *Advances in Physics* **48**, 1 (1999).
21. A. V. Talyzin and S. Klyamkin, *Chemical Physics Letters* **397**, 77 (2004).
22. A. Krishnan, E. Dujardin, T. W. Ebbesen, P. N. Yianilos, and M. M. J. Treacy, *Physical Review B: Condensed Matter and Materials Physics* **58**, 14013 (1998).
23. P. Poncharal, L. Wang, D. Ugarte, and W. A. de Heer, *Science* (*Washington, D.C.*) **283**, 1513 (1999).
24. D. Srivastava, M. Menon, and K. Cho, *Physical Review Letters* **83**, 2973 (1999).
25. C. F. Cornwell and L. T. Wille, *Solid State Communications* **101**, 555 (1997).
26. T. Ozaki, Y. Iwasa, and T. Mitani, *Physical Review Letters* **84**, 1712 (2000).
27. M. J. Biercuk and co-workers, *Applied Physics Letters* **80**, 2767 (2002).
28. R. Andrews and M. C. Weisenberger, *Current Opinion in Solid State & Materials Science* **8**, 31 (2004).
29. C. Wei, D. Srivastava, and K. Cho, *Nano Letters* **4**, 1949 (2004).
30. E. T. Thostenson and T.-W. Chou, *Carbon* **42**, 3015 (2004).
31. N. R. Raravikar and co-workers, *Chem. Mater.* **17**, 974 (2005).
32. K.-t. Lau, *Chem. Phys. Letters* **370**, 399 (2003).
33. L. Chen, C. L. Cheung, P. D. Ashby, and C. M. Lieber, *Nano Letters* **4**, 1725 (2004).
34. M. Ouyang, J.-L. Huang, and C. M. Lieber, *Accounts of Chemical Research* **35**, 1018 (2002).
35. J. H. Hafner, C. L. Cheung, A. T. Woolley, and C. M. Lieber, *Progress in Biophysics Molecular Biology* **77**, 73 (2001).
36. J. H. Hafner, C.-L. Cheung, T. H. Oosterkamp, and C. M. Lieber, *J. Phys. Chem. B* **105**, 743 (2001).
37. J. C. Charlier and P. Lambin, *Physical Review B: Condensed Matter and Materials Physics* **57**, R15037 (1998).
38. R. R. He, H. Z. Jin, J. Zhu, Y. J. Yan, and X. H. Chen, *Chem. Phys. Letters* **298**, 170 (1998).
39. L. Yang and J. Han, *Physical Review Letters* **85**, 154 (2000).
40. A. Sedeki, L. G. Caron, and C. Bourbonnais, *Physical Review B: Condensed Matter and Materials Physics* **65**, 140515/1 (2002).
41. A. Bachtold, P. Hadley, T. Nakanishi, and C. Dekker, *Science* **294**, 1317 (2001).
42. P. G. Collins, M. S. Arnold, and P. Avouris, *Science* **292**, 706 (2001).
43. J. Chen, C. Klinke, A. Afzali, and P. Avouris, *Appl. Phys. Letters* **86**, 123108/1 (2005).
44. C. Klinke, J. Chen, A. Afzali, and P. Avouris, *Nano Letters* **5**, 555 (2005).
45. U.S. Pat. Appl. (2004) P.-Y. Lo and co-workers (Industrial Technology Research Institute, Taiwan).
46. A. Javey and co-workers, *Nano Letters* **4**, 1319 (2004).
47. R. Seidel and co-workers, *Nano Letters* **4**, 831 (2004).
48. M. Kociak and co-workers, *Physical Review Letters* **86**, 2416 (2001).
49. M. Ferrier and co-workers, *Solid State Communications* **131**, 615 (2004).
50. J. Gonzalez, *Physical Review B: Condensed Matter and Materials Physics* **67**, 014528/1 (2003).

51. J. Wang, J. Dai, and T. Yarlagadda, *Langmuir* **21**, 9 (2005).
52. S. Li and co-workers, *Chemistry of Materials* **17**, 130 (2005).
53. J. Wang, J. Dai, and T. Yarlagadda, *Langmuir.* **21**, 9 (2005).
54. J.-M. Bonard and co-workers, *Carbon* **40**, 1715 (2002).
55. H. Sugie and co-workers, *Applied Physics Letters* **78**, 2578 (2001).
56. J. W. Gadzuk and E. W. Plummer, *Reviews of Modern Physics* **45**, 487 (1973).
57. O. Zhou and co-workers, *Accounts of Chemical Research* **35**, 1045 (2002).
58. Y. M. Wong and co-workers, *Diamond and Related Materials* **14**, 697 (2005).
59. W. P. Kang and co-workers, *Diamond and Related Materials* **14**, 685 (2005).
60. Y.-T. Jang, C.-H. Choi, B.-K. Ju, J.-H. Ahn, and Y.-H. Lee, *Thin Solid Films* **436**, 298 (2003).
61. S. Uemura, *Perspectives of Fullerene Nanotechnology*, 57 (2002).
62. S. Komiyama, H. Miyawaki, F. Okino, H. Kataura, and H. Touhara, *Tanso* **216**, 25 (2005).
63. R. P. Raffaelle, B. J. Landi, J. D. Harris, S. G. Bailey, and A. F. Hepp, *Materials Science & Engineering, B: Solid-State Materials for Advanced Technology* **B116**, 233 (2005).
64. R. S. Morris, B. G. Dixon, T. Gennett, R. Raffaelle, and M. J. Heben, *J. Power Sources* **138**, 277 (2004).
65. H.-C. Shin, M. Liu, B. Sadanadan, and A. M. Rao, *J. Solid State Electrochemistry* **8**, 908 (2004).
66. V. Khomenko, E. Frackowiak, and F. Beguin, *Electrochimica Acta* **50**, 2499 (2005).
67. G. Arabale and co-workers, *Chemical Physics Letters* **376**, 207 (2003).
68. C. Zhou, S. Kumar, C. D. Doyle, and J. M. Tour, *Chemistry of Materials* **17**, 1997 (2005).
69. C. Portet, P. L. Taberna, P. Simon, and E. Flahaut, *J. Power Sources* **139**, 371 (2005).
70. J. Y. Lee, K. H. An, J. K. Heo, and Y. H. Lee, *J. Phys. Chem. B* **107**, 8812 (2003).
71. S. Hynek, W. Fuller, and J. Bentley, *Intern. J. Hydrogen Energy* **22**, 601 (1997).
72. M. Carravetta and co-workers, *J. Amer. Chem. Soc.* **126**, 4092 (2004).
73. A. A. Peera, L. B. Alemany, and W. E. Billups, *Applied Physics A: Materials Science & Processing* **A78**, 995 (2004).
74. G. Seifert, *Solid State Ionics* **168**, 265 (2004).
75. A. C. Dillon and co-workers, *Nature* (*London*) **386**, 377 (1997).
76. M. Hirscher and co-workers, *J. Alloys and Compounds* **356–357**, 433 (2003).
77. F. Liu and co-workers, *Taiyangneng Xuebao* **24**, 116 (2003).
78. S. M. Lee, K. H. An, Y. H. Lee, G. Seifert, and T. Frauenheim, *J. Amer. Chem. Soc.* **123**, 5059 (2001).
79. M. S. Dresselhaus, K. A. Williams, and P. C. Eklund, *MRS Bulletin* **24**, 45 (1999).
80. C. C. Ahn and co-workers, *Applied Physics Letters* **73**, 3378 (1998).
81. M. Hirscher and M. Becher, *J. Nanoscience Nanotechnology* **3**, 3 (2003).
82. L. Piekara-Sady, W. Kempinski, B. Andrzejewski, and L. Duclaux, *Superconductor Science and Technology* **17**, 517 (2004).
83. R. Roding, P. Stenmark, T. Wagberg, D. Johnels, and B. Sundqvist, *Fullerenes Nanotubes and Carbon Nanostructures* **12**, 319 (2004).
84. J.-F. Nierengarten, *New Journal of Chemistry* **28**, 1177 (2004).
85. F. Diederich and C. Thilgen, *Science* (*Washington, D.C.*) **271**, 317 (1996).
86. R. Smith, K. Beardmore, and J. Belbruno, *J. Chem. Phys.* **111**, 9227 (1999).
87. J. Mattay and co-workers, *J. Physics and Chemistry of Solids* **58**, 1929 (1997).
88. P. W. Fowler, D. J. Collins, S. J. Austin, *J. Chem. Soc., Perkin Trans. 2: Physical Organic Chemistry* (1972–1999) 275 (1993).

89. J. Poater, M. Duran, and M. Sola, *Intern. J. Quantum Chem.* **98**, 361 (2004).
90. A. Hirsch, *Synthesis*, 895 (1995).
91. M. Cases, M. Duran, J. Mestres, N. Martin, and M. Sola, *J. Org. Chem.* **66**, 433 (2001).
92. Z. Xiao and co-workers, *J. Org. Chem.* **70**, 2060 (2005).
93. M. Prato, Q. Chan Li, L. V. F. Wudl, *J. Am. Chem. Soc.* **115**, 1148 (1993).
94. Y. Nakamura, K. Okawa, T. Nishimura, E. Yashima, and J. Nishimura, *J. Org. Chem.* **68**, 3251 (2003).
95. A. Alvarez and co-workers, *J. Org. Chem.* **70**, 3256 (2005).
96. R. Kessinger and co-workers, *J. Amer. Chem. Soc.* **120**, 8545 (1998).
97. C. Thilgen, N. N. P. Moonen, J.-L. Schmitt, R. Kessinger, and F. Diederich, *Proceedings-Electrochemical Society* **2000-11**, 85 (2000).
98. C. F. Richardson, D. I. Schuster, and S. R. Wilson, *Organic Letters* **2**, 1011 (2000).
99. S. R. Wilson and co-workers, *J. Amer. Chem. Soc.* **124**, 1977 (2002).
100. F. Wudl, *Journal of Materials Chemistry* **12**, 1959 (2002).
101. A. Bar-Shir, Y. Engel, and M. Gozin, *J. Org. Chem.* **70**, 2660 (2005).
102. F. Diederich, L. Isaacs, and D. Philp, *Chemical Society Reviews* **23**, 243 (1994).
103. U. Reuther and A. Hirsch, *Carbon* **38**, 1539 (2000).
104. J. Mattay and co-workers, *J. Physics Chem. Solids* **58**, 1929 (1997).
105. M. Maggini, G. Scorrano, and M. Prato, *J. Amer. Chem. Soc.* **115**, 9798 (1993).
106. M. Prato and M. Maggini, *Accounts of Chemical Research* **31**, 519 (1998).
107. G. Torres-Garcia, and J. Mattay, *Tetrahedron* **52**, 5421 (1996).
108. N. Martin, L. Sanchez, B. Illescas, and I. Perez, *Chemical Reviews (Washington, D.C.)* **98**, 2527 (1998).
109. H. Maruyama, M. Fujiwara, and K. Tanaka, *Chemistry Letters*, 805 (1998).
110. D. Godovsky, L. Chen, L. Petterson, and O. Inganas, *AIP Conference Proceedings* **544**, 512 (2000).
111. D. M. Guldi, M. Maggini, G. Scorrano, and M. Prato, *J. Amer. Chem. Soc.* **119**, 974 (1997).
112. D. M. Guldi and M. Prato, *Accounts of Chemical Research* **33**, 695 (2000).
113. N. Martin, I. Perez, L. Sanchez, and C. Seoane, *J. Org. Chem.* **62**, 5690 (1997).
114. D. M. Guldi, T. Da Ros, P. Braiuca, and M. Prato, *Photochemical Photobiological Sciences* **2**, 1067 (2003).
115. S. Bosi and co-workers, *MCLC S&T, Section B: Nonlinear Optics* **27**, 367 (2001).
116. D. Armspach, E. C. Constable, F. Diederich, C. E. Housecroft, and J.-F. Nierengarten, *Chemistry–A European Journal* **4**, 723 (1998).
117. M. Prato, *J. Materials Chem.* **7**, 1097 (1997).
118. M. J. O'Connell and co-workers, *Chemical Physics Letters* **342**, 265 (2001).
119. E. Joselevich, *Angewandte Chemie, Internat. Ed.* **43**, 2992 (2004).
120. M. Zhao, Y. Xia, J. P. Lewis, and L. Mei, *J. Physical Chem. B* **108**, 9599 (2004).
121. E. Joselevich, *Chem Phys Chem* **5**, 619 (2004).
122. P. M. Ajayan and F. Banhart, *Nature Materials* **3**, 135 (2004).
123. S. Park, D. Srivastava, and K. Cho, *Nano Letters* **3**, 1273 (2003).
124. J. Hilding, E. A. Grulke, Z. G. Zhang, and F. Lockwood, *J. Dispersion Sci. Technol.* **24**, 1 (2003).
125. A. Hirsch, *Angewandte Chemie, Intern. Ed.* **41**, 1853 (2002).
126. M. Grujicic, G. Cao, and W. N. Roy, *Applied Surface Science* **227**, 349 (2004).
127. R. Ramasubramaniam, J. Chen, and H. Liu, *Applied Physics Letters* **83**, 2928 (2003).
128. X. Lou and co-workers, *Chemistry of Materials* **16**, 4005 (2004).
129. R. J. Chen, Y. Zhang, D. Wang, and H. Dai, *J. Amer. Chem. Soc.* **123**, 3838 (2001).

130. J. Chen, R. Ramasubramaniam, and H. Liu, *Abstracts of Papers, 227th ACS National Meeting, Anaheim, CA, United States, March 28–April 1, 2004*, IEC 2004.
131. K. Kelley and W. Zhao, *Abstracts of Papers, 227th ACS National Meeting, Anaheim, CA, United States, March 28–April 1, 2004*, IEC 2004
132. J.-C. Charlier, *Accounts of Chemical Research* **35**, 1063 (2002).
133. N. Chandra, S. Namilae, and C. Shet, *Physical Review B* (*Condensed Matter and Materials Physics*) **69**, 094101 (2004).
134. H. F. Bettinger, *Abstracts of Papers, 228th ACS National Meeting, Philadelphia, PA, United States, August 22–26, 2004*, COMP, 2004.
135. M. T. Martinez and co-workers, *Carbon* **41**, 2247 (2003).
136. L. G. Zhou, S.-Q. Shi, *Applied Physics Letters* **83**, 1222 (2003).
137. P. M. Ajayan and co-workers, *Nature* (*London*) **362**, 522 (1993).
138. S.-P. Chan, G. Chen, X. G. Gong, and Z.-F. Liu, *Physical Review Letters* **90**, 086403/1 (2003).
139. J. Liu and co-workers, *Science* (*Washington, D.C.*) **280**, 1253 (1998).
140. S. Chen, W. Shen, G. Wu, D. Chen, and M. Jiang, *Chem. Phys. Letters* **402**, 312 (2005).
141. H. Peng and co-workers, *Abstracts of Papers, 226th ACS National Meeting, New York, NY, United States, September 7–11, 2003*, INOR, 2003.
142. H. Peng, L. B. Alemany, J. L. Margrave, and V. N. Khabashesku, *J. Amer. Chem. Soc.* **125**, 15174 (2003).
143. B. Zhou and co-workers, *J. Phys. Chem. B* **107**, 13588 (2003).
144. Y. Liu, Z. Gu, J. L. Margrave, and V. N. Khabashesku, *Chemistry of Materials* **16**, 3924 (2004).
145. V. N. Khabashesku and J. L. Margrave, *Encyclopedia of Nanoscience and Nanotechnology* Vol. **1**, 2004, p. 849.
146. V. N. Khabashesku, W. E. Billups, J. L. Margrave, *Accounts of Chemical Research* **35**, 1087 (2002).
147. F. Liang and co-workers, *Nano Letters* **4**, 1257 (2004).
148. P. J. Boul and co-workers, *Chemical Physics Letters* **310**, 367 (1999).
149. R. K. Saini and co-workers, *J. Amer. Chem. Soc.* **125**, 3617 (2003).
150. L. Zhang and co-workers, *Chemistry of Materials* **16**, 2055 (2004).
151. L. Valentini, D. Puglia, I. Armentano, and J. M. Kenny, *Chemical Physics Letters* **403**, 385 (2005).
152. V. Georgakilas and co-workers, *J. Amer. Chem. Soc.* **124**, 760 (2002).
153. M. Holzinger and co-workers, *J. Amer. Chem. Soc.* **125**, 8566 (2003).
154. H. Hu and co-workers, *J. Amer. Chem. Soc.* **125**, 14893 (2003).
155. M. Holzinger and co-workers, *Angewandte Chemie, International Edition* **40**, 4002 (2001).
156. C. A. Dyke and J. M. Tour, *J. Amer. Chem. Soc.* **125**, 1156 (2003).
157. J. L. Bahr and co-workers, *J. Amer. Chem. Soc.* **123**, 6536 (2001).
158. N. Tagmatarchis and M. Prato, *J. Materials Chem.* **14**, 437 (2004).
159. C. A. Dyke and J. M. Tour, *Chemistry–A European Journal* **10**, 812 (2004).
160. D. Tasis and co-workers, *Comptes Rendus Chimie* **6**, 597 (2003).
161. K. S. Coleman, S. R. Bailey, S. Fogden, and M. L. H. Green, *J. Amer. Chem. Soc.* **125**, 8722 (2003).
162. K. A. Worsley, K. R. Moonoosawmy, and P. Kruse, *Nano Letters* **4**, 1541 (2004).
163. M. Holzinger and co-workers, *AIP Conference Proceedings* **685**, 87 (2003).
164. S.-R. Jang, R. Vittal, and K.-J. Kim, *Langmuir* **20**, 9807 (2004).
165. H. Murakami, T. Nomura, and N. Nakashima, *Chemical Physics Letters* **378**, 481 (2003).

166. R. B. Martin and co-workers, *J. Phys. Chem. B* **108**, 11447 (2004).
167. H. Li, R. Martin, B. Harruff, Y.-P. Sun, *Abstracts, 55th Southeast Regional Meeting of the American Chemical Society, Atlanta, GA, United States, November 16–19, 2003*, p. 502 2003.
168. A. Ullman, *An Introduction to Ultrathin Organic Films-From Langmuir-Blodgett to Self Assembly*, Academic Press, San Diego, 1991.
169. D. M. Guldi, Y. Tian, J. H. Fendler, H. Hungerbuehler, and K.-D. Asmus, *J. Phys. Chem.* **99**, 17673 (1995).
170. D. Zhu and co-workers, *Thin Solid Films* **284–285**, 102 (1996).
171. R. Marczak, K. Noworyta, W. Kutner, S. Gadde, and F. D'Souza, *AIP Conference Proceedings* **685**, 3 (2003).
172. Y. Huang, Y. Zhao, L. Gan, C.-H. Huang, and N. Wu, *Journal of Colloid and Interface Science* **204**, 277 (1998).
173. J.-M. Lehn, *Science* (*Washington, D.C.*) **295**, 2400 (2002).
174. A. D. Bokare and A. Patnaik, *J. Phys. Chem. B* **107**, 6079 (2003).
175. L. Huang and co-workers, *Carbon* **43**, 654 (2005).
176. H. Lee and I. C. Jeon, *Synthetic Metals* **86**, 2297 (1997).
177. Z. Shi and co-workers, *New Journal of Chemistry* **25**, 670 (2001).
178. K. Porfyrakis and co-workers, *AIP Conference Proceedings* **723**, 255 (2004).
179. H. Fenniri, M. Packiarajan, A. E. Ribbe, and K. L. Vidale, *Polymer Preprints* (*American Chemical Society, Division of Polymer Chemistry*) **42**, 569 (2001).
180. H. Shimoda, L. Fleming, K. Horton, and O. Zhou, *Physica B: Condensed Matter* (*Amsterdam, Netherlands*) **323**, 135 (2002).
181. Z. J. Zhang, B. Q. Wei, and P. M. Ajayan, *Surface Engineering: Science and Technology II, Proceedings of a Symposium held during the TMS Annual Meeting, Seattle, WA, United States, Feb. 17–21, 2002*, p. 99, 2002.
182. M. S. Arnold, S. I. Stupp, and M. C. Hersam, *Proceedings of SPIE-The International Society for Optical Engineering* **4999**, 238 (2003).
183. N. O. V. Plank, R. Cheung, and R. J. Andrews, *Applied Physics Letters* **85**, 3229 (2004).
184. J. C. Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo, and G. M. Whitesides, *Chemical Reviews* (*Washington, D.C.*) **105**, 1103 (2005).
185. Z. Konya and co-workers, *Chemical Physics Letters* **360**, 429 (2002).
186. Anon, *Nanosystems, Molecular Machinery, Manufacturing and Computation, by K. E. Drexler*, Coordination Chemistry Reviews, 1996, pp. 598−599.
187. M. C. T. Fyfe and J. F. Stoddart, *Accounts of Chemical Research* **30**, 393 (1997).
188. P. A. Gale, *Annual Reports on the Progress of Chemistry, Section B: Organic Chemistry* **100**, 207 (2004).
189. D. Bethell and D. J. Schiffrin, *Nature* **382**, 581 (1996).
190. D. N. Reinhoudt and M. Crego-Calama, *Science* **295**, 2403 (2002).
191. V. Balzani, A. Credi, F. M. Raymo, and J. F. Stoddart, *Angewandte Chemie, International Edition* **39**, 3348 (2000).
192. V. Balzani, A. Credi, and M. Venturi, *Chemistry–A European Journal* **8**, 5524 (2002).
193. N. O. V. Plank and R. Cheung, *Microelectronic Engineering* **73-74**, 578 (2004).
194. A. Credi, B. Ferrer Ribera, and M. Venturi, *Electrochimica Acta* **49**, 3865 (2004).
195. G. Cuniberti and co-workers, *Physica E: Low-Dimensional Systems & Nanostructures* (*Amsterdam, Netherlands*) **12**, 749 (2002).
196. B. L. Feringa, *Nature* (*London*) **408**, 151 (2000).
197. C. A. Schalley, *Journal of Physical Organic Chemistry* **17**, 967 (2004).

198. D. B. Amabilino, J. F. Stoddart, *Chemical Reviews* (*Washington, D.C.*) **95**, 2725 (1995).
199. A. H. Flood and co-workers, *Australian J. Chem.* **57**, 301 (2004).
200. V. Balzani and co-workers, *J. Org. Chem.* **65**, 1924 (2000).
201. V. Balzani, *Small* **1**, 278 (2005).

Adriyan S. Milev
G. S. Kamali Kannangara
Michael A. Wilson
College of Science, Technology and Environment,
University of Western Sydney

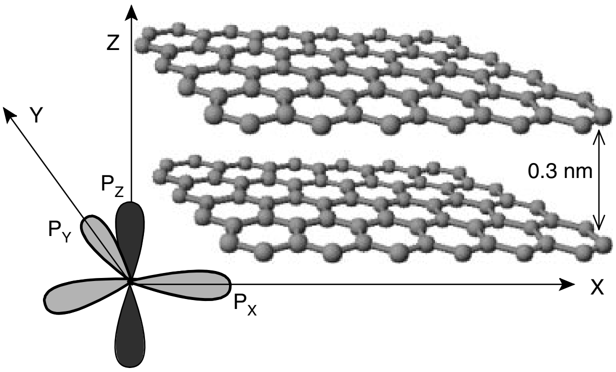


Fig. 1. Graphene.

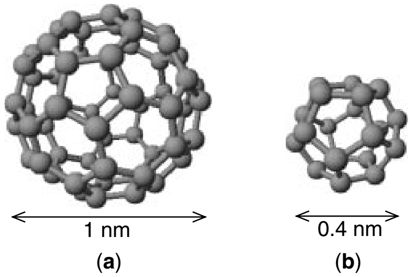


Fig. 2. Fullerenes. (**a**) The well known C60 is composed of 20 hexagons and 12 pentagons. (**b**) The smallest fullerene C_{20} composed of 12 pentagons only.

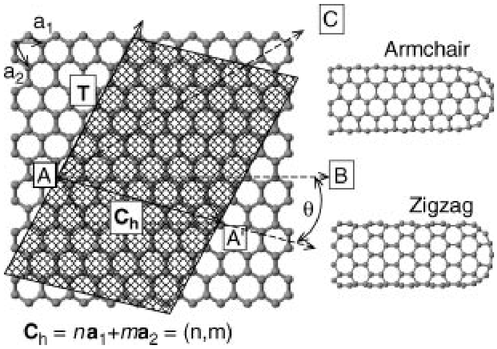


Fig. 3. Nanotubes nomenclature. The two basis vectors $\mathbf{a_1}$ and $\mathbf{a_2}$ and examples of the lattice vectors are shown. **AA′** defines the chiral vector $\mathbf{C_h} = n\mathbf{a_1} + m\mathbf{a_2}$. The (m, n) indices determine the diameter and the chirality of the nanotube. The chiral angle, θ, is defined by the angle between $\mathbf{C_h}$ and (**AB**) zigzag direction. Translation vector **T**, is along the nanotube axis and perpendicular to $\mathbf{C_h}$. The shaded area is the unit cell formed by **T** and $\mathbf{C_h}$ where the graphene sheet is rolled up to create the tube.

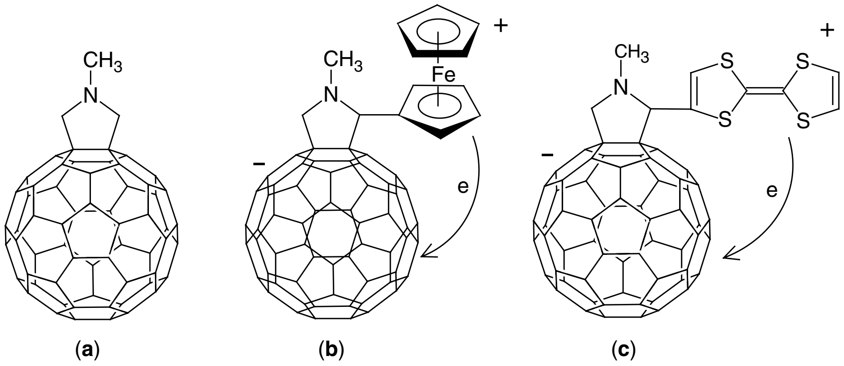


Fig. 4. Fullerene derivatives. (**a**) Fulleropyrrolidine, (**b**) ferrocene–fulleropyrrolidine and (**c**) tetrathiafulvalene–fulleropyrrolidine. A probable electron transfer by light radiation is shown.

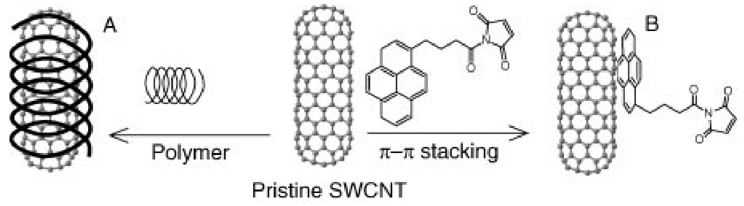


Fig. 5. Noncovalent functionalization of the sidewall of SWCNT. **A**, Functionalization with a polymer molecule. **B**, π-π stacking of 1-pyrene-butanoic acid succinimidyl ester. Adapted from Ref. 129.

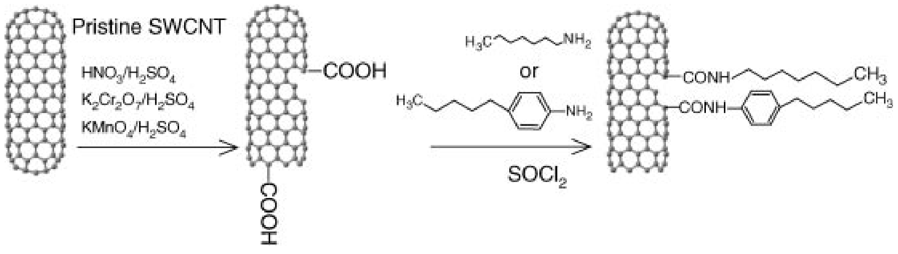


Fig. 6. Examples of covalent chemistry at open ends and defects of CNTs. The treatment under strong oxidative condition creates defects in the sidewall and opens the nanotube ends producing carboxylic groups.

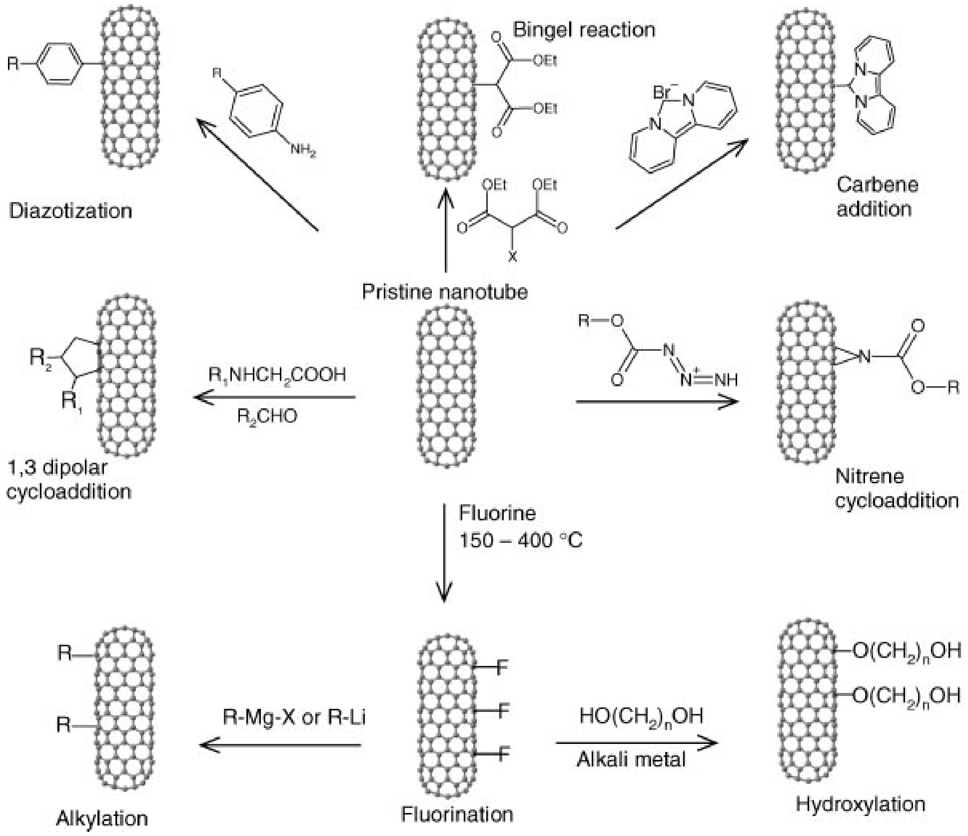


Fig. 7. Strategies of direct nanotube functionalization. These do not require preliminary oxidation or defect creation.

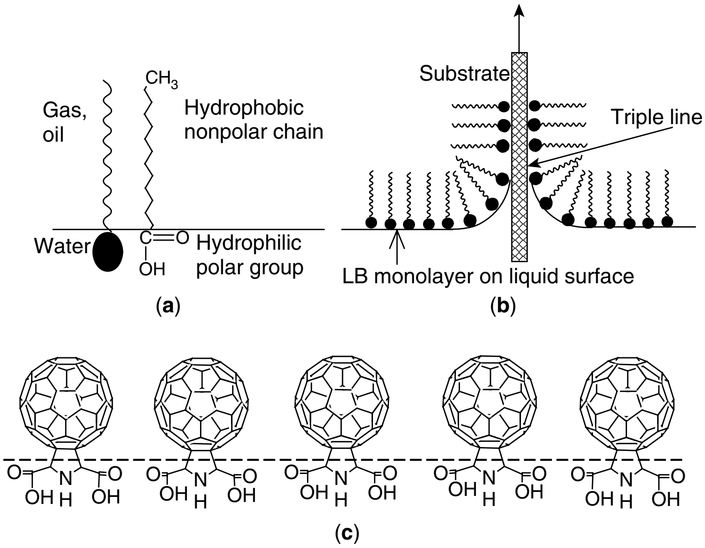


Fig. 8. (**a**) Orientation of amphiphilic molecule. (**b**) LB monolayer deposition. (**c**) LB film deposition of fullerenepyrrolidine dicarboxylic acid (FDA) molecules on water surface. Adapted from Ref. 172.

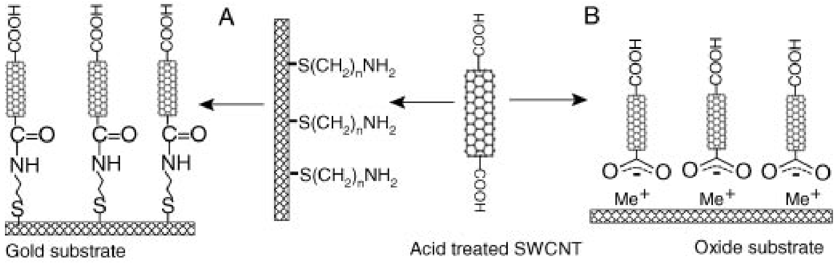


Fig. 9. Schematic representation of the self-assembly process. **A**, SWCNT containing organized thin film prepared via thiol amide linkage onto a pretreated gold substrate. **B**, SWCNT deposition on metal oxide surface.

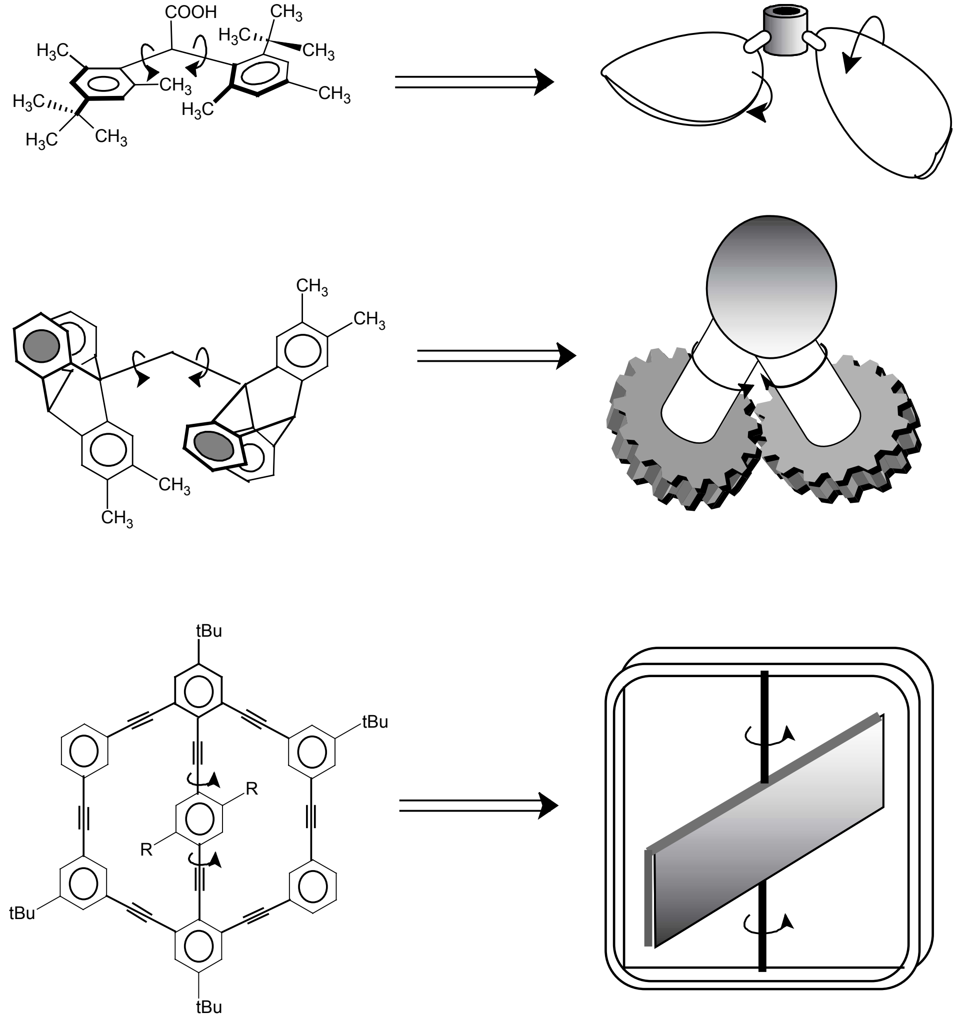


Fig. 10. Parts of molecular machines: top trace, paddle; middle trace, gears; and bottom trace, an armature. Adapted from Ref. 191.

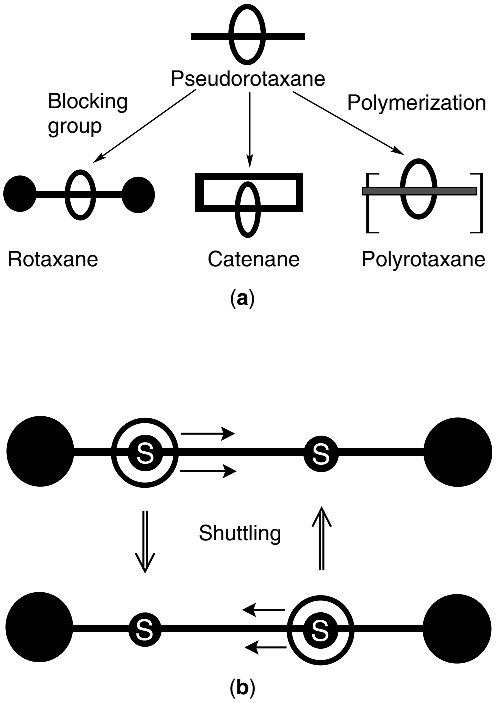
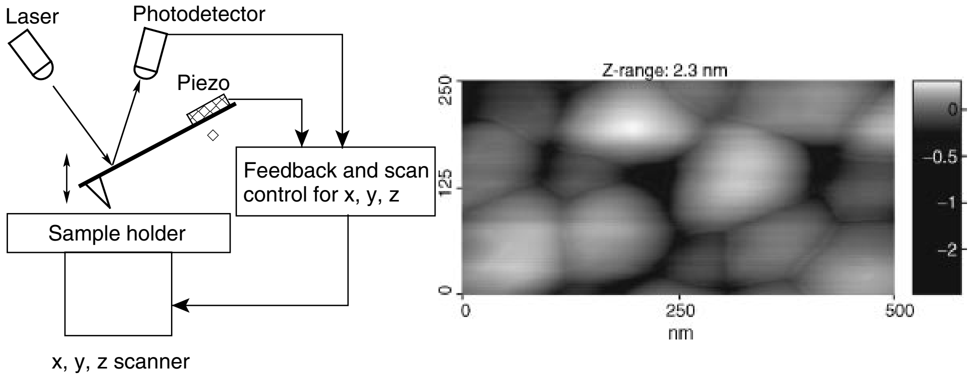


Fig. 11. (**a**) The structure of rotaxanes, and catenanes. (**b**) The mechanism of rotaxane shuttling.



(**a**) (**b**)

Fig. 12. (**a**) Diagram of AFM. (**b**) Tapping mode AFM image of coating on ceramic substrate.