

Faraday Discussions

Volume: 173

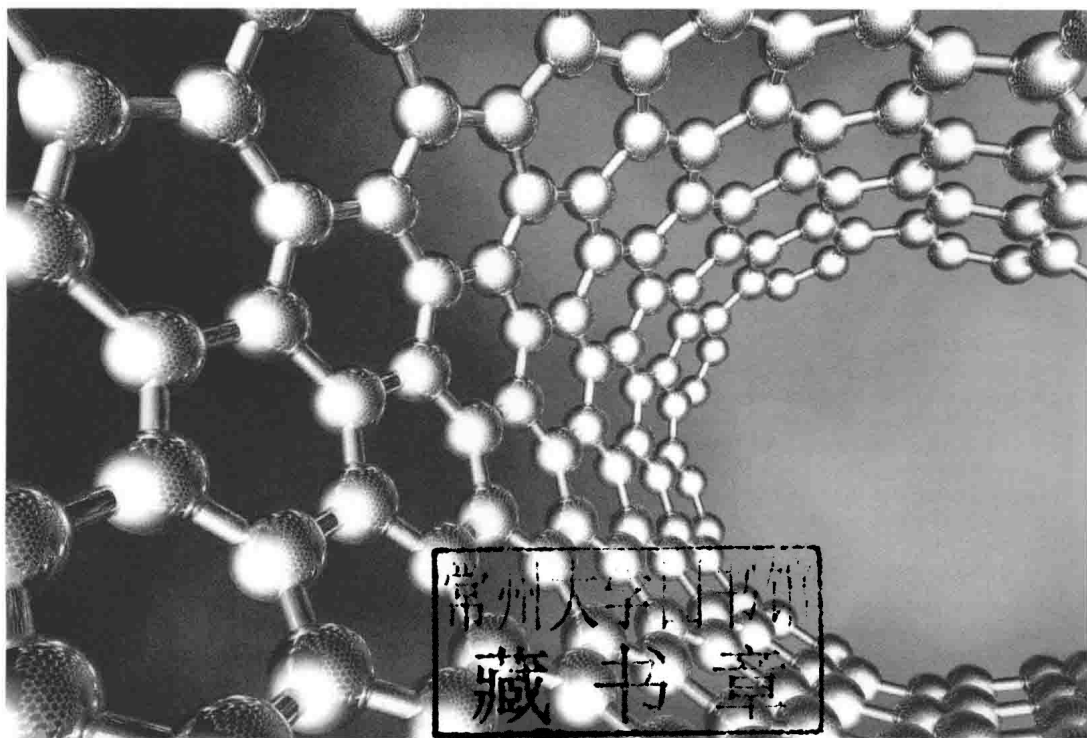
New Advances in Carbon Nanomaterials



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New Advances in Carbon Nanomaterials

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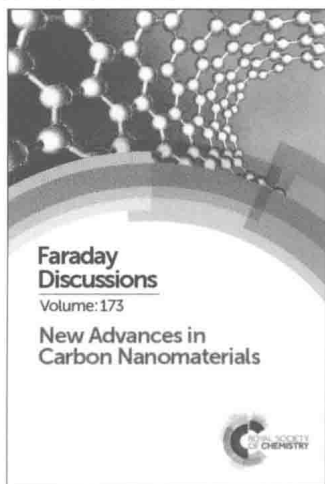
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PAPER

Spiers Memorial Lecture

Advances of carbon nanomaterials

Lulu Ma, Amelia H. C. Hart, Sehmus Ozden, Robert Vajtai
and Pulickel M. Ajayan*

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During the last two decades the exciting properties of carbon nanomaterials, *i.e.* fullerene, carbon nanotubes and graphene, have drawn pronounced attention. This brief review will discuss the recent advances in the science and applications of nanocarbons, mainly of nanotubes and graphene, and the opportunities and challenges that exist in future technologies based on these emerging materials. The review will discuss the growth and selection, chemical modifications, substitutional doping, and engineering three-dimensional structures, and demonstrations of possible applications. This is a perspective on how the advent of nanocarbons will enable the development of the next generation of carbon materials and technologies relevant for a broad range of applications.

1 Introduction

Carbon, an abundant element in nature, has long been known to exist in three forms: graphite, diamond, and amorphous carbon, in the form of soot and charcoal.¹ It is the discovery of fullerenes in 1985 that ignited a revolution for carbon materials.² Tremendous interest in this new material spawned further exploration, resulting in the synthesis of a series of larger carbon molecules, such as C₇₀, *etc.*³ The subsequent discovery of carbon nanotubes (CNTs) attracted significantly pronounced attention to nano-scale science and technology and accelerated the development of materials science and nanotechnology.^{4–10} The term nanocarbon emerged to specify these newly developed carbon materials whose structure and size are controlled at the nanometer scale.¹¹ Graphene, a one-atom-thick planar sheet of carbon, is the most recent member of the nanocarbon family.¹² As a building block for carbon nanotubes, fullerenes, and other carbon materials (see Fig. 1), the discovery of graphene has led to an explosion of interest in the central issues of nanoscience and nanotechnology in physics, chemistry, and materials science, producing a wide array of potential applications.^{13–25} Due

Department of Materials Science and NanoEngineering, Rice University, Houston, TX 77005, USA. E-mail: ajayan@rice.edu; Fax: +1 7133485423; Tel: +1 7133485904

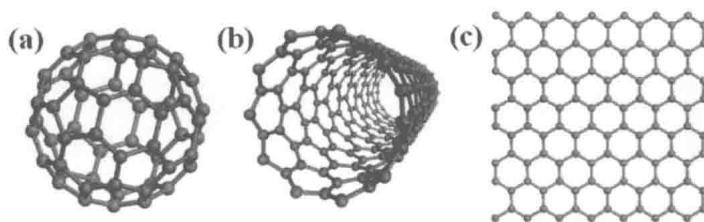


Fig. 1 Graphene is the building block for fullerenes and carbon nanotubes: (a) fullerene; (b) carbon nanotube; (c) graphene. (Courtesy, M. Liu).

to the large interest in nanocarbons over the last thirty years, the focus of this paper will be on the recent progress made in the areas of carbon nanotubes and graphene. Also to be discussed: advances in nanotube and graphene growth and selection, substitutional doping, chemical modification, three-dimensional (3D) structures, as well as their uses and potential applications.

2 Growth and selection

2.1 Carbon nanotubes

CNTs are cylindrically rolled graphene sheets with fullerene capped ends. These tubes are either single-walled carbon nanotubes (SWNTs), consisting of one rolled graphene sheet, or multi-walled carbon nanotubes (MWNTs), consisting of multiple concentric layers of varying diameter SWNTs. The first CNTs to be discovered were MWNTs found in carbon soot on graphite anodes made by arc discharging,^{4,26} then years later SWNTs were synthesized.^{5,27–29} SWNTs possess uniform diameters (0.8–2 nm), while MWNTs form in a large range of diameters, typically from 2 to 25 nm but can exceed 100 nm,^{30,31} and all CNTs can range in lengths from less than 100 nm to several centimeters.

Though there are many methods to synthesize CNTs, [electric arc charge, laser ablation and chemical vapor deposition (CVD)] CVD is currently the most dominant method. CVD can be used with either liquid, solid, or gas carbon sources; combined either by using thin catalyst layers pre-deposited on substrates,^{7,32–36} or through vapor-phase catalyst delivery,^{37–42} and is practical for large-scale production of high-purity SWNTs,^{7,43,44} double-walled CNTs (DWNTs)⁴⁵ and MWNTs.⁴⁶ DWNTs with heights of up to 2.2 mm were achieved with selectivity of 85% by precisely controlling the catalyst iron thickness.⁴⁵ The capacity for MWNT production worldwide in 2006 was estimated at approximately 200 tons per year. A variety of aligned CNT structures have been synthesized predominately on nonconducting substrates, posing limitations on applications where conductive substrates/contacts are required.^{7,33,34,38,47} To circumvent this problem, aligned MWNTs can be directly grown on a metallic alloy, Inconel 600, using vapor-phase catalyst delivery (see Fig. 2).⁴⁸

The growth mechanisms of CNTs have been explored since their discovery, and with each new discovery researchers are closer to enabling specific tailoring of CNT growth to very specialized applications. The latest news in CNT growth is the ability to control chiralities, or orientations of the lattice with respect to an arbitrary tube axis resulting from the way the graphene sheet is rolled during

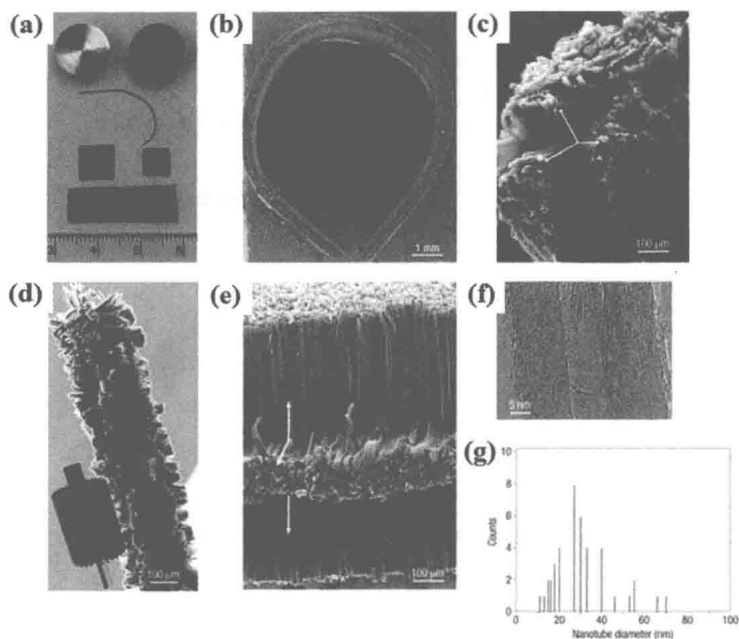


Fig. 2 Aligned MWNTs grown on different shapes of Inconel substrates. (a) Optical image showing various Inconel substrates used for CNT growth. Scale is in cm. (a and b) Scanning electron microscope (SEM) images of CNTs grown on a mechanically deformed Inconel sheet (b) and the corner of a CNT-grown Inconel sheet (c). (d) SEM image of CNTs grown on an Inconel wire (e) SEM image of one side of an Inconel sheet. (f) High resolution transmission electron microscope (HRTEM) image of a typical as-grown nanotube. (g) Typical diameter distribution of CNTs measured from the TEM data. Reproduced with permission from ref. 48. Copyright© 2006 Nature Publishing Group.

synthesis; by understanding the mechanisms of CNT growth, their chiralities can be more precisely controlled.

There are three possible CNT chiralities: zigzag, armchair, and chiral. These three different chiralities are defined by their chiral angle and wrapping integers (n, m), illustrated in Fig. 3, where $m \leq n$ at all times. By changing chiralities, the CNT's band gap and electrical conductivity changes between metallic and semiconducting. The bandgap of semiconducting SWNTs is inversely proportional to the tube diameter. MWNTs are typically metallic, due to wall numbers and the differing chiralities of each wall, and can carry currents of up to 109 A cm^{-2} .⁴⁹ SWNTs can exhibit metallic or semiconducting behaviors depending on the orientation of the graphene lattice with respect to the tube axis, indicating chirality.^{4,5} Since their discovery, a large problem faced when producing CNTs is the inability to produce a specific chirality; recently, this problem has been solved using various types of catalyst and growth methods.^{50,51}

With the CVD method, using a solid iron catalyst and gaseous carbon source, the mechanism of growth involves the deposited iron layer heating and separating to become iron nanoclusters. By diffusion and dissolution, the carbon atoms bond to the surface of the Fe nanocluster, and after having supersaturated the Fe nanocluster, the carbon atoms segregate and form carbonaceous structures from the catalyst surface. The controlled number of CNT walls can be achieved by varying the catalyst thickness.⁵²

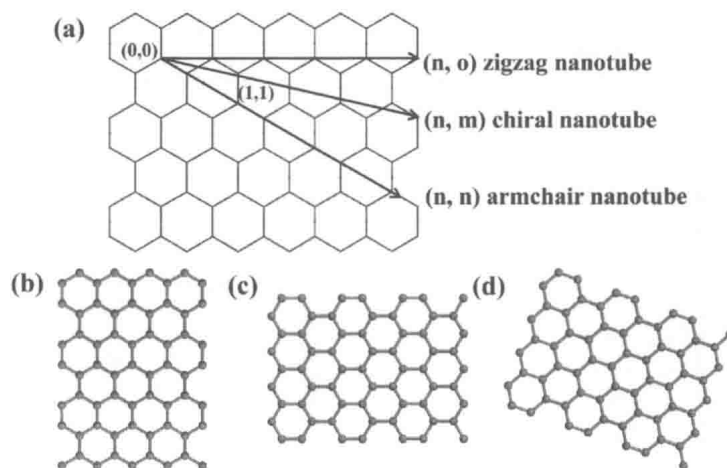


Fig. 3 (a) Schematic representation of how a graphene sheet is rolled to form three chiralities of nanotubes (b) zigzag, (c) armchair and (d) chiral nanotubes. (Courtesy, M. Liu).

Controlled synthesis has endowed SWNTs with narrow distributions of tube diameter and a large fraction of a predetermined tube type through composition and shape engineering of catalysts,^{53,54} end-cap engineering⁵⁵ or cloning strategies,^{56,57} and also tube sorting based on chromatography,^{58–60} density-gradient centrifugation,^{61–65} or electrophoresis.^{64,52} Nanotube separation, based on the chromatography technique, for biological applications includes dispersing bundled SWNTs in water by sonication in the presence of single stranded DNA.⁵⁹ The density gradient ultracentrifugation technique is also widely used. During this process, surfactant-suspended metallic and semiconducting SWNTs, which have different mass densities, are dispersed in an aqueous suspension to travel through a mass density gradient *via* ultracentrifugation. The CNTs are driven by density differences to positions in the centrifuge tube where their buoyant density is equal to that of the surrounding fluid.^{63,66,67}

The other, newly developed, method of easily obtaining a large amount of a required CNT chirality is through direct growth. Molecular precursors have been converted into ultrashort singly capped (6, 6) ‘armchair’ nanotube seeds using surface-catalyzed cyclodehydrogenation on a Pt (111) surface to produce single-chirality and essentially defect-free SWNTs with lengths up to a few hundred nanometers.⁵⁰ Similarly, (12, 6) chiral SWNTs were directly grown at >96% yield using a tungsten-based bimetallic catalyst system.⁵¹ The high melting point of catalysts was anticipated to be crucial in chirality control of SWNTs.

Though these new developments have been a significant step forward on the path to be able to consistently control chirality during CNT synthesis, without the theory of the exact mechanisms of this growth this cannot be a practice that is very common. A few months ago, the exact formation mechanism of each type of chirality during CNT growth was found. It was postulated that during nucleation, as carbon nanotubes attach to a nascent CNT nucleus, adding new hexagonal and pentagonal rings, the chirality of a CNT becomes permanently ‘locked in’ when the final 6th pentagon is added to the hemispherical cap. Each CNT ‘grows’ by adding only hexagons, in a periodic fashion. It was also found that the catalyst and growth temperatures will yield different chiralities of CNTs: lower

temperatures and solid catalysts yield near armchair nanotubes, whereas higher temperatures and liquid catalysts yield several types of chiralities but the abundance is nearly proportional to the chiral angle.⁶⁸

Besides their electrical conductive properties, carbon nanotubes are known for a large variety of other outstanding properties such as: high specific surface area, $1314 \text{ m}^2 \text{ g}^{-1}$ for SWNTs;¹⁰ ultrahigh elastic modulus of $\sim 1 \text{ TPa}$ and a tensile strength of 100 GPa for MWNTs.⁶⁹ SWNTs can possess an extraordinary thermal conductivity of $\sim 3500 \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature.⁷⁰

In addition to organized CNT structures, a variety of tailored structures have been synthesized for special applications with enhanced properties such as: one-dimensional (1D) yarns, fibers, ropes, brushes, 2D sheets, buckypapers, and 3D foams and sponges. CNT brushes have been synthesized using silicon carbide fiber partially masked by a 15 nm Au layer and grown in a ferrocene-xylene CVD to produce $\sim 60 \text{ }\mu\text{m}$ aligned CNTs to form a radial brush.⁴³ For electrical contacts, CNT brushes were also created using MWNT forests mounted on flexible brass cantilevers. These brushes produced more steady and regular voltage and less noise than traditional carbon-copper brushes.⁵⁶ Spun fibers and ribbons of CNTs were synthesized directly by CVD using a liquid source of carbon and iron catalyst. In this method, the key requirement for continuous spinning is the rapid growth of high-purity nanotubes to form an aerogel in the furnace hot zone and the forcible withdrawal of the product from reaction by continuous wind up.⁷¹ In 2007, CNT fiber was synthesized using the method of spun aerogel directly from CVD using mostly DWNTs and compared to the techniques of spinning from a lyotropic liquid crystalline suspension of nanotubes and spinning from MWNTs previously grown on a substrate as aligned carpets. It was found that the undensified direct spinning from aerogel is more mechanically advantageous.⁷² However, in 2013, it was found that wet spinning $\sim 5 \text{ }\mu\text{m}$ "short" CNTs into high-performance multifunctional fibers produced a fiber possessing a higher modulus than previous wet spinning methods and comparable to solid state spun fibers while enabling an easier scale-up ability.⁷³ CNT yarns were created up to 30 cm in length by drawing out CNTs from super aligned $100 \text{ }\mu\text{m}$ arrays.⁵⁰ The introduction of a twist during spinning is essential to create multi-ply, torque-stabilized yarns that have achieved yarn strengths of greater than 460 MPa .⁵¹ In 1996, crystalline ropes of metallic carbon nanotubes were synthesized from a mat of randomly oriented SWNTs $10\text{--}20 \text{ nm}$ in diameter.⁷⁴ CNT sheets have been synthesized using track patterns of exposed silica created in CNT films to grow longer CNT stripes.⁴¹ In 2005, buckypaper, a paper-like material consisting of hexagonally packed bundles of coaxial DWNTs with very small diameter was created.⁷⁵ Monolayered and multilayered colloidal silica templates were used to fabricate porous 3D architectures of CNTs *via* CVD. Mechanically and thermally stable porous CNT membranes and three dimensional CNT foams were obtained after the removal of silica with hydrofluoric acid.⁵⁸ Macroscopic, monolithic CNT sponges were made using CVD where ferrocene dissolved in dichlorobenzene was injected at $860 \text{ }^\circ\text{C}$ for 4 hours, yielding CNTs self-assembled into porous interconnected 3D frameworks.⁵⁹ Densely packed SWNTs were fabricated for use in supercapacitor electrodes using the zipping effect of liquids to draw tubes together.⁷⁶ Ultralong SWNTs, over 18.5 cm long, were synthesized⁷⁷ for mass production and very recently, half-meter long CNTs were reported.⁷⁸ With the demand of well-defined architectures for integrated systems, predetermined

orientations of CNT assemblies were synthesized, including: vertically aligned CNT pillars on selective areas, and flower-like patterns of multi-oriented, organized nanotube structures (see Fig. 4).³⁹

2.2 Graphene

As the mother of CNTs, graphene has many similarities to CNTs, in structure and properties, including: a large measured surface area of $2630 \text{ m}^2 \text{ g}^{-1}$,⁷⁹ a Young's modulus of 1 TPa and intrinsic strength of 130 GPa,⁸⁰ a high thermal conductivity of above 3000 W m K^{-1} ,²² and room-temperature electron mobility of $2.5 \times 10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.²³ Graphene's superior properties have stimulated a great amount of research over the last decade, and currently there are several methods for producing graphene in terms of specific size, shape, and quality.

Single-layer graphene samples were first isolated by the mechanical exfoliation technique.¹² This approach can produce the highest quality of samples but yield a minute amount of graphene only useful for fundamental study. A number of alternative approaches to mechanical exfoliation have been explored, including liquid and thermal exfoliation, CVD growth and epitaxial growth.^{12,81–96}

The liquid exfoliation method is based on immersing bulk graphite in solvents to yield single- and few-layer graphene sheets.^{84,97} A similar method is to chemically modify graphite to produce water dispersible graphite oxide using the Hummers' method.⁸¹ This is followed by thermal annealing or chemical reduction to produce reduced single- and few-layer graphene sheets,^{83,98–100} and can be used to fabricate macroscopic structures.^{101–107} This approach is cost effective and massively scalable, but the quality yielded is not appropriate for devices since a number of defects and impurities still remain in the graphene.

Graphene has also been synthesized from the high temperature reduction of silicon carbide by the epitaxial method,^{82,87,108} which produces few-layer graphene sheets behaving like graphene. The epitaxial growth of graphene on transition metals has been also reported,⁸⁶ but the ability to achieve graphene domains with uniform thickness remains a challenge.

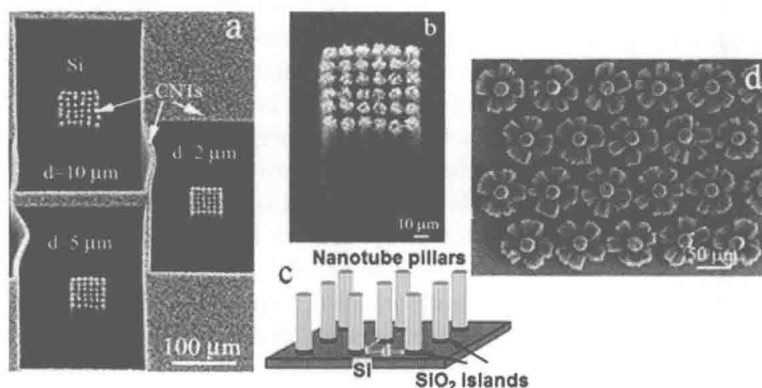


Fig. 4 (a) SEM image of three blocks of cylindrical pillars ($\sim 10 \mu\text{m}$ diameter) of vertically aligned CNT arrays. (b) CNTs were only grown on the silica islands. (c) Schematic of pillars shown in (b). (d) Growth in both vertical and horizontal directions from the top and the sides of silica, respectively. Figure adapted with permission from ref. 39. Copyright© 2002 Nature Publishing Group.

The CVD method can produce large-area uniform graphene films of single to few-layer graphene grown on different metal substrates using gas, solid and liquid precursors.^{89,91,92,94,103} The production of tens of square meters of graphene film has been developed by an industrial-scale roll-to-roll CVD method, allowing for the possibilities of the commercial production of large-scale transparent electrodes. Besides 2D graphene, the CVD synthesis of 3D graphene with interconnected networks was reported recently.¹⁰⁹

Since CVD-grown graphene is typically polycrystalline with many grain boundaries, which impede electron transport,^{110–112} the greatest challenge is to be able to gain control of the early stages of nucleation and growth of graphene and to ultimately create large single crystalline graphene domains. The solution could be to create nucleation sites situated far enough from each other and to grow the single crystalline domains appropriately fast, so that no additional nucleation sites can emerge.¹¹⁰

Recently, it has emerged as an intense interest for materials scientists to grow large-size single crystalline graphene using CVD.^{110–118} Electrochemical polishing and high-pressure annealing can be used to improve the quality of the copper foil and accordingly suppress graphene nucleation site density. Large single-crystal hexagonal single-layer graphene domains ($\sim 4.5 \text{ mm}^2$) were achieved (see Fig. 5),¹¹⁸ and show a mobility of positive charge carriers of $\sim 11\,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temperature. Also, a wafer-scale ($\sim 5 \text{ cm}$ in diameter) wrinkle-free single crystalline single-layer graphene grown on silicon wafer using a hydrogen-terminated germanium buffer layer was reported.¹¹⁹

Other shapes of single crystalline graphene domains have also been grown such as hexagonal,^{112–116,118,120} rectangular,^{117,121} triangular,¹²² and dendritic shapes.^{113,123} Theoretical work explains that hexagonal graphene domains form under kinetic control conditions because the zigzag edges grow slowest on Cu substrates under vacuum.¹²⁴ Under etching, the kinetically controlled island shape is determined by the fastest-moving edges, producing peculiar dodecagonal crystals.¹²² Lower-symmetry shapes of graphene islands, such as triangular or elongated, can also arise due to symmetry relations between graphene and the underlying metal surface.¹²⁵ Recent experimental and theoretical work discovered that oxygen on the copper surface was able to accelerate growth of large-size single crystalline graphene domains as well as shift the graphene domain shape from hexagonal to dendritic.¹²⁶

Another challenge for the CVD growth of graphene is its transfer from the preferred metal substrates to a desired substrate,¹⁰³ which causes unexpected cracks, folds and ridges which decreases the graphene quality. Toward this end, a

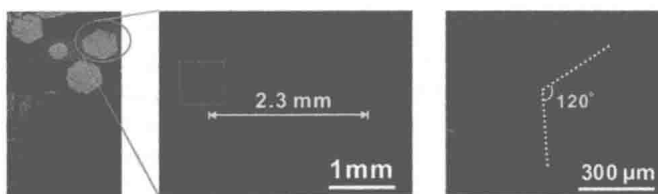


Fig. 5 Typical optical and SEM images of large-size ($\sim 2.3 \text{ mm}$) single crystalline graphene domains on Cu. Adapted with permission from ref. 118. Copyright 2013 American Chemical Society.

face-to-face transfer method for wafer-scale graphene films was reported, which could take advantage of nascent gas bubbles to form capillary bridges, so that graphene stays attached to the substrate while the copper is removed.¹²⁷

Though considerable effort has been made to grow large-size graphene, there is growing interest in breaking the atomic structures within the graphitic materials to create graphene components with special shapes, sizes and edge structures.^{128,129} For example, controlled nanocutting of graphene into pieces with specific edge configuration, using nickel nanoparticles as a knife which was driven by catalytic hydrogenation of graphene lattice, was reported.¹³⁰ Besides metal nanoparticles, nonmetal SiO_x nanoparticles were also used to tailor graphene into regular pieces with smooth edges.¹³¹

The graphene nanoribbon (GNR) is an ultra-narrow strip of graphene. It has been predicted that GNRs with zigzag edges are metallic, whereas armchair edges can make GNRs either metallic or semiconducting depending on their width. The bulk production of high-quality GNRs with the length of <20–30 μm and widths of 20–300 nm using the CVD method has been reported.¹³² GNRs could be also produced by unzipping CNTs by solution-based oxidative processes and plasma etching,^{133,134} which gives better control over the chemical functionalization and quality of the edges. A mechanical sonication of gas-phase oxidized MWNTs in organic solvent has also been reported to be able to make high-quality GNRs.¹³⁵ Recently, the unzipping of CNTs was reported using spherically shaped CNT pellets as bullets to shoot at an aluminum target at a velocity of 5.9 km s⁻¹. A large number of defects were generated in the nanotubes, as well as rapid atom evaporation, which led to the nanotubes unzipping along the axis.¹³⁶ In addition to the methods mentioned above, an exciting bottom-up method has been reported for producing high-quality GNRs of different geometries and widths using surface-assisted coupling of molecular precursors into linear polyphenylenes with subsequent cyclodehydrogenation.^{137,138}

Graphene quantum dots (GQDs) with nanometer sizes have been fabricated from a variety of graphitic materials including graphite,¹³⁹ fullerene,¹⁴⁰ CNTs,¹⁴¹ graphene,¹⁴² carbon fibers,¹⁴³ and even coal, containing crystalline carbon within its structure,¹⁴⁴ based on acid treatment and chemical exfoliation. GQDs were produced by oxidation cutting of carbon fiber in the size range of 1–4 nm with zigzag edge structure dominance, showing the tailored photoluminescence through changing the size of the GQDs (see Fig. 6).¹⁴³

Recently, graphene sheets were patterned into nanodisk and nanoring arrays using electron-beam lithography and oxygen plasma etching,¹⁴⁵ and gated tenability and hybridization of localized plasmons were observed in these nanostructured graphene pieces down to 3.7 μm light wavelengths.

Despite considerable efforts to explore the horizontal morphologies of graphene, there is increasing interest in the vertical features of graphene including stacking configuration and thickness, such as single- and bi-layer graphene.^{91,95,146–151} Graphene is known to have a zero band gap, but bi- and tri-layer graphene have tunable band gaps depending on their interlayer stacking configurations, allowing for broad applications in electronic devices. For example, bilayer graphene sheets can be AB-(Bernal) or AA-stacked and trilayer can be mostly stacked in ABA and ABC configurations. The CVD growths of large-area uniform Bernal-stacked bi-, tri- and tetra-layer polycrystalline graphene films were produced through a precisely tuned total pressure and methane/hydrogen

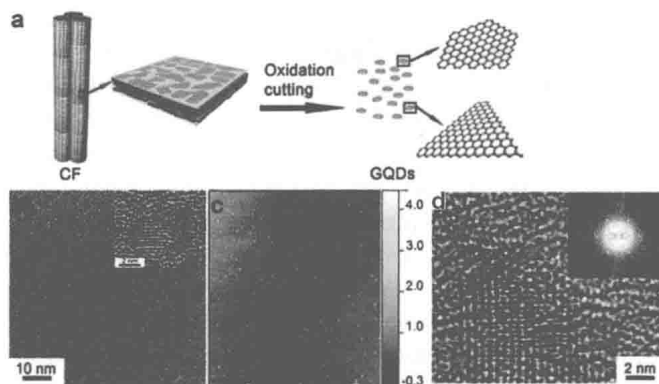


Fig. 6 (a) Schematic of oxidation cutting of carbon fiber into GQDs. (b) TEM images of GQDs, inset of (b) is the HRTEM of GQDs. (c) Atomic force microscopy (AFM) image of GQDs. (d) HRTEM image of the edge of a GQD, inset is the 2D fast Fourier transform of the edge in (d). Reproduced with permission from ref. 143. Copyright 2012 American Chemical Society.

gas ratio.¹⁴⁹ Recently, the synthesis of large hexagonal bi- and tri-layer graphene single crystals with 0° (Bernal stacked) or 30° interlayer rotations was reported.¹⁵²

Additionally, it is critical to confirm the graphene thicknesses before any further study. Raman spectroscopy emerged as an unambiguous, high-throughput, nondestructive technique to determine the quality and thickness of graphene samples.¹⁵³ The major features, a D peak at $\sim 1350\text{ cm}^{-1}$, G peak at $\sim 1580\text{ cm}^{-1}$, and G' peak at $\sim 2700\text{ cm}^{-1}$ recorded in the Raman spectra, reflect the changes in the electronic structure and electron-phonon interactions for single-, bi- and few-layer graphene, which are used to determine the number of graphene layers.

3 Chemical modification

When the intrinsic properties of CNTs and graphene alone do not meet the requirement of various applications, chemical modification creates a new interest area that involves altering the surface chemical properties and electronic properties of CNTs and graphene. The chemical modification of CNTs and graphene can be realized through both non-covalent and covalent modifications.

3.1 Carbon nanotubes

Although CNTs have outstanding properties, there are some challenges that bring limitations for their applications: they are not soluble, have limited dispersion in common solvents because of their surface energy, and their seamless surface does not provide good physical interactions with common chemical media. Because of these limitations, surface modifications of CNTs are desirable for their processability and specific applications. After their initial discovery, different surface modifications of CNTs were investigated and functionalization was found to be a unique method for these alterations. Functionalization has become one of the most important key routes to manipulate the properties of CNTs for desirable applications. For this reason, understanding the functionalization of CNTs is a

crucial step for exploiting their application potential. Some effective methods for the surface functionalization of CNTs can be classified into two major categories: covalent and non-covalent functionalization (see Fig. 7).¹⁵⁴ In covalent functionalization, CNTs are functionalized by non-reversible attachment onto the surface of CNTs. Since CNTs are chemically inert materials, there are a few reactive chemicals, such as fluorine, which is able to link up a conjugated π - π system (see Fig. 7). One of the most common processes to functionalize CNTs is the creation of defects on the surface of CNTs *via* acid treatment, mainly generating surface attached carboxyl groups.^{155,156} In this method, acid generated carboxyl groups are converted to acid chloride, and so can easily be functionalized with amine functional organic molecules.¹⁵⁷ Recently, CNTs were modified using the Suzuki cross-coupling reaction after carboxyl groups were converted to acyl chloride (see Fig. 8).¹⁵⁸

Other methods of covalent functionalization of CNTs that have been reported include fluorination followed by substitution of alkyl groups,¹⁵⁹ diazonium functionalization,^{160,161} and organic radicals.¹⁶² In diazonium functionalization,¹⁶⁰ functional groups were directly connected to the side-wall of CNTs. The mechanism of this process includes the reduction of aryl diazonium yielding aryl radicals that covalently attach to the carbon surface. While the acid treatment method reduces the physicochemical and mechanical properties of CNTs, these properties are not as affected by the diazonium functionalization. CNTs can be functionalized by generating free radicals *via* decomposition of benzoyl peroxide in the presence of alkyl iodides.¹⁶²

The second type of functionalization is non-covalent functionalization, which is an alternative way to modify CNTs without disturbing their straight tubular structures. This method relies on weak interactions such as: van der Waals,

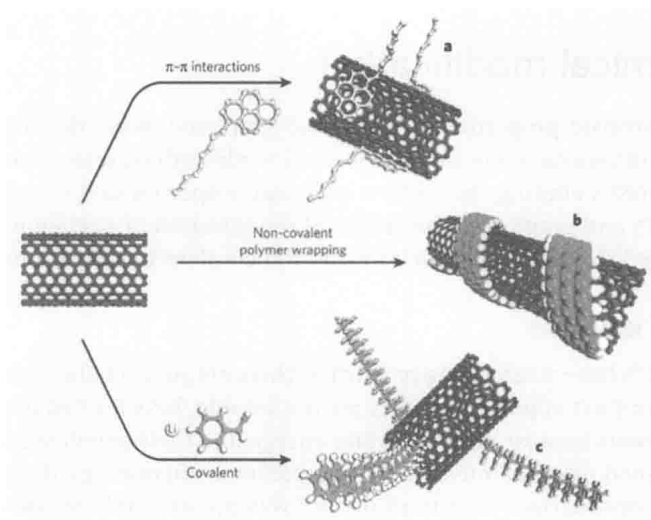


Fig. 7 Schematic of the three methods how CNTs can be made more soluble. (a) Aromatic molecules can be adsorbed to side-walls using certain non-covalent interactions. (b) Non-covalent interactions can be used to wrap polymers around nanotubes. (c) Chemical groups can be covalently attached to nanotubes. Reproduced with permission from ref. 154. Copyright© 2007 Nature Publishing Group.