Carbon nanotubes and graphene in context

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Carbon nanotubes, also called buckytubes, are nanoscale hollow tubes composed of carbon atoms. The cylindrical carbon molecules feature high aspect ratios (length-to-diameter values) typically above 10^3, with diameters from about one nanometer up to tens of nanometers and lengths up to millimeters. This unique one-dimensional structure and concomitant properties endow carbon nanotubes with special natures, rendering them with unlimited potential in nanotechnology-associated applications. Carbon nanotubes are members of the fullerene family. Although the first fullerene molecules were discovered in 1985 [1], it was not until Sumio Iijima reported his findings in 1991 about needlelike carbon tubes in *Nature* that carbon nanotubes came to public awareness [2]. Since then, carbon nanotubes with various structures have been discovered. According to the number of graphic shells, they are mainly categorized as single-walled carbon nanotubes and multi-walled carbon nanotubes. The carbon nanotubes reported by Sumio Iijima were multi-walled carbon nanotubes synthesized by arc discharge methods. Two years later, two sets of researchers working independently, Sumio Iijima and Toshinari Ichihashi [3], along with Donald Stimson Bethune and his colleagues at *International Business Machines Corporation* [4], synthesized single-walled carbon nanotubes, using transition-metal catalyzed arc discharge.

A single-walled carbon nanotube can be described as a long tube formed by wrapping a single graphene sheet into a cylinder with diameter of about one nanometer, the ends of which are capped by fullerene cages [5]. The fullerene structures, with alternating structures of five hexagons adjacent to one pentagon, form the surface with desired curvature to enclose the volume. The sidewalls of carbon nanotubes are made of graphene sheets consisting of neighboring hexagonal cells. Other polygon structures, such as pentagons and heptagons, constitute defects of sidewalls. The cylindrical sidewalls can be produced from different rolling directions to make single-walled carbon nanotubes with distinct structures and properties. Due to cylindrical symmetry, there are only a handful of methods that are effective in making seamless cylinders, and they are characterized by the chiral vectors with integer indices (n, m). To establish the chiral vector, two atoms in the graphene sheet are selected, with one serving as the origin of the vector pointing toward the other atom. The graphene sheet is then rolled in a way that allows the two atoms to coincide. Under these circumstances, the chiral vectors form a plane perpendicular to the longitude direction of nanotubes and the lengths of the chiral vectors are equal to the circumference. Three different types of single-walled carbon nanotubes are distinctly characterized, named "zigzag", "armchair", and "chiral" [5]. These structural variations result in differences in

electrical conductivity and mechanical strength.

Multi-walled carbon nanotubes are concentrically aligned single-walled carbon nanotube assemblies with different diameters [5]. The distance between adjacent shells is about 0.34 nanometer. Multi-walled carbon nanotubes differ from single-walled carbon nanotubes not only in their dimensions, but also in their corresponding properties. Various techniques have been developed to produce carbon nanotubes in sizable quantity, high yield, and purity, while maintaining a reasonable cost. Well-developed techniques include arc discharge, laser ablation, and chemical vapor deposition, and most processes involve costly vacuum conditions. Arc discharge was initially used for the synthesis of fullerenes. In a typical experimental setup, a chamber filled with low-pressure (50 to 700 millibars) inert gas (helium, argon) is where the reaction takes place. Two carbon rods are placed end-to-end as the electrodes, separated by a few millimeters, and a direct current of 50 to 100 amperes (driven by a potential difference of 20 volts) generates a high discharge temperature to sublime the negative electrode, leaving soot where carbon nanotubes are found. This method is the most common way to synthesize carbon nanotubes and perhaps the easiest way. The quality of carbon nanotubes depends on the uniformity of plasma arc, catalysts, and the selection of filling gases [5]. A mixture of carbon nanotubes is usually produced; thus, purification processes are needed to remove the fullerenes, amorphous carbon, and catalysts.

Laser ablation was first employed to produce carbon nanotubes in 1995 [5]. A pulsed or continuous laser is used to vaporize a graphite (or graphite metal mixture) target in an oven with a temperature of 1,200 °C filled with inert gas at a pressure of 500 torr. Carbon vapors cool down rapidly during expansion, and carbon atoms quickly condense to form tubular structures with the help of catalyst particles. Multi-walled carbon nanotubes can be synthesized when pure graphite is vaporized, and single-walled carbon nanotubes are grown from graphite-transition metal (cobalt, nickel, and the like) mixtures. The method is primarily used to synthesize single-walled carbon nanotubes with high selectivity and in a diameter-controllable way by tailoring reaction temperatures. The resulting products are usually in the form of bundles. Laser ablation is the most-costly technique due to the involvement of expensive lasers and high-power input. Chemical vapor deposition is the most promising way to produce carbon nanotubes on an industrial scale. This process utilizes high energy (temperatures of 600-900 °C) to atomize gaseous carbon sources, such as methane, carbon monoxide, and acetylene. The resulting reactive carbon atoms diffuse toward a catalyst-coated substrate and condense to form carbon nanotubes [5]. Well-aligned carbon nanotubes can be synthesized with precisely controlled morphology, provided that proper reaction conditions are maintained, including preparation of substrates, selection of catalysts, and the like.

Novel chemical, electrical, and mechanical properties absent in other materials have been discovered in carbon nanotubes [5]. Pristine carbon nanotubes are inert to most chemicals and need to be grafted with surface functional groups to increase their chemical reactivity and add new properties. For single-walled carbon nanotubes, electrical conductivity is dependent on the chiral vector and independent of the length as determined by quantum mechanics. Considering a chiral vector with indices (n, m), carbon nanotubes are metallic in some cases and semiconducting in other cases. Along the longitude

directions, carbon nanotubes show superior mechanical strength, with the highest known tensile strength and elastic modulus among known materials. As for thermal properties, carbon nanotubes outperform diamond as the best thermal conductor. Applications of carbon nanotubes are aimed to make use of their unique properties to solve problems at the nanoscale. Their high surface area, together with the unique ability to carry any chemical compounds after surface modification, offers carbon nanotubes the potential to be used as nanoscale catalyst supports with high catalytic reactivity and chemical sensors. They are known to be the best field emitters due to their sharp tips, which can concentrate electric field easily, enabling them to emit electrons at low voltages. This property has special applications in field emission flat-panel displays and cold-cathode electron guns used in microscopes. In nanoelectronics, single-walled carbon nanotubes have been used to fabricate transistors that can function at room temperature and are potential candidates for devices operating at terahertz frequencies [5]. Engineering materials using carbon nanotubes as additives have exhibited capability to make plastic composites with enhanced electrical conductivity and mechanical strength.

Graphene is a two-dimensional form of crystalline carbon, either a single layer of carbon atoms forming a honeycomb (hexagonal) lattice or several coupled layers of this honeycomb structure [6]. The word graphene, when used without specifying the form (for example, bilayer graphene, multilayer graphene), usually refers to single-layer graphene [6]. Graphene is a parent form of all graphitic structures of carbon: graphite, which is a three-dimensional crystal consisting of relatively weakly coupled graphene layers; nanotubes, which may be represented as scrolls of graphene; and buckyballs, spherical molecules made from graphene with some hexagonal rings replaced by pentagonal rings.

The theoretical study of graphene was started in 1947 by physicist Philip Russell Wallace as a first step to understanding the electronic structure of graphite [6]. The term graphene was introduced by chemists Hanns-Peter Boehm, Ralph Setton, and Eberhard Stumpp in 1986 as a combination of the word graphite, referring to carbon in its ordered crystalline form, and the suffix -ene, referring to polycyclic aromatic hydrocarbons in which the carbon atoms form hexagonal, or six-sided, ring structures [6]. In 2004 University of Manchester physicists Konstantin Novoselov and Andre Geim and colleagues isolated single-layer graphene using an extremely simple method of exfoliation from graphite [7]. Their "scotch-tape method" used adhesive tape to remove the top layers from a sample of graphite and then apply the layers to a substrate material. When the tape was removed, some graphene remained on the substrate in single-layer form. In fact, derivation of graphene is not a difficult task by itself; each time someone draws with a pencil on paper, the pencil trace contains a small fraction of single-layer and multilayer graphene. The achievement of the Manchester group was not only to isolate graphene flakes but also to study their physical properties. In particular, they demonstrated that electrons in graphene have a very high mobility, which means that graphene could possibly be used in electronic applications. In 2010 Geim and Novoselov were awarded the Nobel Prize for Physics for their work [6]. In these first experiments, the substrate for graphene was silicon naturally covered by a thin transparent layer of silicon dioxide. It turned out that single-layer graphene created an optical contrast with the silicon dioxide that was strong enough to make the graphene visible under a standard optical microscope. This visibility has two

causes. First, electrons in graphene interact very strongly with photons in the visible light frequencies, absorbing about 2.3 percent of the light's intensity per atomic layer. Second, the optical contrast is strongly enhanced by interference phenomena in the silicon dioxide layer; these are the same phenomena that create rainbow colors in thin films.

The basic electronic structure of graphene and, as a consequence, its electric properties are very peculiar [6]. By applying a gate voltage or using chemical doping by adsorbed atoms and molecules, one can create either electron or hole (a region where an electron is missing that acts as a positive electric charge) conductivity in graphene that is similar to the electrical conductivity created in semiconductors. However, in most semiconductors there are certain energy levels where electrons and holes do not have allowed quantum states, and, because electrons and holes cannot occupy these levels, for certain gate voltages and types of chemical doping, the semiconductor acts as an insulator. Graphene, on the other hand, does not have an insulator state, and the electrical conductivity remains finite at any doping, including zero doping. Existence of this minimal electrical conductivity for the undoped case is a striking difference between graphene and conventional semiconductors [6]. Electron and hole states in graphene relevant for charge-carrier transport are similar to the states of ultra-relativistic quantum particles, that is, quantum particles moving at the speed of light (the ultimate velocity in nature, according to the theory of relativity).

The honeycomb lattice of graphene actually consists of two sublattices, designated A and B, such that each atom in sublattice A is surrounded by three atoms of sublattice B and vice versa [6]. This simple geometrical arrangement leads to the appearance that the electrons and holes in graphene have an unusual degree of internal freedom, usually called pseudospin [6]. In fact, making the analogy more complete, pseudospin mimics the spin, or internal angular momentum, of subatomic particles [6]. Within this analogy, electrons and holes in graphene play the same role as particles and antiparticles (for example, electrons and positrons) in quantum electrodynamics [6]. At the same time, however, the velocity of the electrons and holes is only about one three-hundredth the speed of light. This makes graphene a test bed for high-energy physics. More specifically, some quantum relativistic effects that are hardly reachable in experiments with subatomic particles using particle accelerators have clear analogs in the physics of electrons and holes in graphene, which can be measured and studied more easily because of their lower velocity [6]. An example is the Klein paradox, in which ultra-relativistic quantum particles, contrary to intuition, penetrate easily through very high and broad energy barriers [6]. Consequently, graphene provides a bridge between materials science and some areas of fundamental physics, for example, relativistic quantum mechanics.

There is another reason why graphene is of special interest to fundamental science: it is the first and simplest example of a two-dimensional crystal, that is, a solid material that contains just a single layer of atoms arranged in an ordered pattern [6]. Two-dimensional systems (surfaces, membranes, and interfaces) are of huge interest not only for physics but also for chemistry and other natural sciences. In many respects, two-dimensional systems are fundamentally different from three-dimensional systems. In particular, due to very strong thermal fluctuations of atomic positions that remain correlated at large distances, long-range crystalline order cannot exist in two dimensions. Instead, only short-range order exists, and it does so only on some finite scale of characteristic length, a caveat that should

be noted when graphene is called a two-dimensional "crystal". For this reason, two-dimensional systems are inherently "flexural", manifesting strong bending fluctuations, so that they cannot be flat and are always rippled or corrugated. Graphene, because of its relative simplicity, can be considered as a model system for studying two-dimensional physics and chemistry in general [6]. Other two-dimensional crystals besides graphene can be derived by exfoliation from other multilayer crystals (for example, hexagonal boron nitride, molybdenum disulfide, or tungsten disulfide) or by chemical modification of graphene (for example, graphane, hydrogenated graphene, or fluorinated graphene).

Modern electronics (for example, integrated circuits in computer chips) are basically two-dimensional in that they use mainly the surface of semiconducting materials [6]. Therefore, graphene and other two-dimensional materials are considered very promising for many such applications. Using graphene, for example, it should be possible to make transistors and other electronic devices that are much thinner than devices made of traditional materials. Many other applications have been proposed. For example, graphene, being electrically conducting, transparent, strong, and flexible, may be a prospective material for use in touch screens [6]. Graphene also has very high thermal conductivity and, therefore, could be used to remove heat from electronic circuits.

The field of graphene science and technology is relatively new, having emerged since Geim and Novoselov's work in 2004 [6]. In the decades that followed, it remained difficult to say which applications would prove to be the most popular. Progress depends not only on the basic science but also on the development of new ways to produce graphene on an industrial scale. For example, obtaining graphene by exfoliation is too expensive for mass production. Methods proposed include the formation of graphene layers by burning silicon carbide or by chemical vapor deposition of carbon on the surface of some metals such as copper or nickel. These methods would allow the production of samples of graphene that were macroscopically large in two dimensions (for example, up to tens of centimeters) but still atomically thin. From unique physical properties to mechanical properties, graphene offers tremendous opportunities for the development of fundamentally new material systems [8]. In particular, the exceptional physical and mechanical properties offer scope for the development of graphene-reinforced polymer matrix composite materials.

Declaration of competing interest

The author declares that there is no conflict of interest.

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