

The Rise of Carbon Nanoscience in South Carolina

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Our history has been defined by the materials we use, starting with the stone age up until the present day. While several kinds of materials such as copper, bronze and iron have been the predominant resources for technology development (tool making) in those eras, carbon is undoubtedly proving to be the copper and iron of the 21st century. This is largely due to carbon's unique ability to form covalently connected bulk and nanostructured materials with varying sp hybridized bonding states. While *graphite* and *diamond* represent the sp^2 and sp^3 hybridized bulk forms of carbon, *carbon nanotubes* and *fullerenes* represent nanostructured forms of carbon with intermediate hybridization sp^x , where $2 < x < 3$. *Graphene*, which is the most recent and widely studied form of nanostructured carbon, is a single sheet of carbon atoms that is isolated from the graphite bulk material. In other words, any of the shaded two-dimensional (2D) sheets that compose graphite, when isolated from the bulk, acquire a new form, known as graphene (Fig. 1).

Generation One: Fullerene

My journey in carbon science began with early studies of the fullerene C_{60} molecule during my tenure as a young research assistant professor in the department of physics and astronomy at the University of Kentucky, Lexington. A C_{60} molecule is a closed cage carbon structure in which 60 carbon atoms bond covalently to yield a molecule with a shape that resembles the all-familiar soccer ball. Like a soccer ball, a C_{60} molecule also has 12 pentagons and 20 hexagons, but the latter has a diameter of only 0.7 nm! Profs. Robert Curl, Harold Kroto and Richard Smalley discovered this new carbon allotrope in 1985 in the carbon soot they generated by impinging a focused laser beam on a rotating graphite target in an inert atmosphere. The trio shared the 1996 Nobel Prize in chemistry for discovering this new class of closed-caged carbon nanostructures.

An individual C_{60} molecule is so tiny that highly sophisticated research equipment is required for its analysis. Through such analyses it is now known that these caged molecules can self-assemble into a face-centered-cubic (fcc) structure when powders containing C_{60} are sublimed to form thin film coatings on substrates such as silicon or glass (Fig. 2a). Since all bonds in a C_{60} molecule are satisfied, the neighboring C_{60} molecules in the fcc structure have weak interactions between them. In other words, a C_{60} film (or a crystal) is a van der Waals bonded solid, and hence its spectroscopic fingerprints are similar to that of an individual C_{60} molecule. Interestingly, in my collaborative work with Prof. Peter Eklund who was then at the University of Kentucky, we discovered two novel photochemical processes in C_{60} films. First we found that a C_{60} film, upon irradiation with moderately intense visible light in the absence of oxygen,

undergoes a 2 + 2 cycloaddition reaction (top schematic in Fig. 2b) through which neighboring C_{60} molecules bond covalently to each other to yield a polymeric form of C_{60} . We named this covalently linked form of C_{60} molecules the *photo-polymerized* form of C_{60} since the transformation from a van der Waals bonded solid to a polymerized form was driven by light. This discovery spurred an intense search for other plausible forms of polymerized C_{60} , and through an international effort of researchers from the US, France, Austria and Japan, alternate methods for preparing the polymerized forms of C_{60} were created. Through this research, a simultaneous application of high pressure and temperature, or a beam of ions or electrons, or the presence of an alkali metal at the right concentration, was also found to transform a van der Waals bonded C_{60} solid into a covalently bonded solid to form either 1D orthorhombic chain-like, or 2D tetragonal or rhombohedral networks (Fig. 2c). These networks of covalently bonded C_{60} were then used as *molecular sieves* for gas separation in subsequent research.

A second light-assisted phenomenon we uncovered in C_{60} films involved the uptake of molecular oxygen. We investigated the interaction of molecular oxygen with thin C_{60} films using Rutherford backscattering spectroscopy to measure the concentration profile of oxygen in the fullerene films. A thin ($d \sim 20$ nm) layer containing oxygen was observed on the surface of C_{60} films ($d \sim 200$ nm) exposed to 1 atm. of O_2 for 1 h in the absence of light. In contrast, oxygen was uniformly distributed throughout the entire film when samples were irradiated for 1 h with either an Ar ion laser or a Xe lamp in the presence of 1 atm. of O_2 . Moreover, this light-assisted O_2 uptake was both power dependent and reversible, which caused the formation of the C_{60} epoxide (bottom schematic in Fig. 2b). While the presence of light is essential for creating both of these photochemical pathways, the presence or absence of oxygen is the dominating factor which dictates which pathway will proceed and what products will form: either the polymer or the epoxide phases. This marvelously compelling photochemistry is related to the so-called HOMO-LUMO energy gap in C_{60} that matches closely with the energy level difference between the singlet and triplet levels of oxygen. For further details the reader may refer to the bibliography at the end of this article.

Generation Two: Carbon Nanotube

A second method of synthesizing C_{60} was discovered in 1990. Here, fullerenes (e.g., C_{60} , C_{70}) were produced from the generation of carbon plasma in a simple electric arc discharge between two carbon electrodes in a helium atmosphere. Three years later, Dr. Sumio Iijima at NEC and Dr. Donald Bethune at the IBM Almaden Research Center found that small amounts of

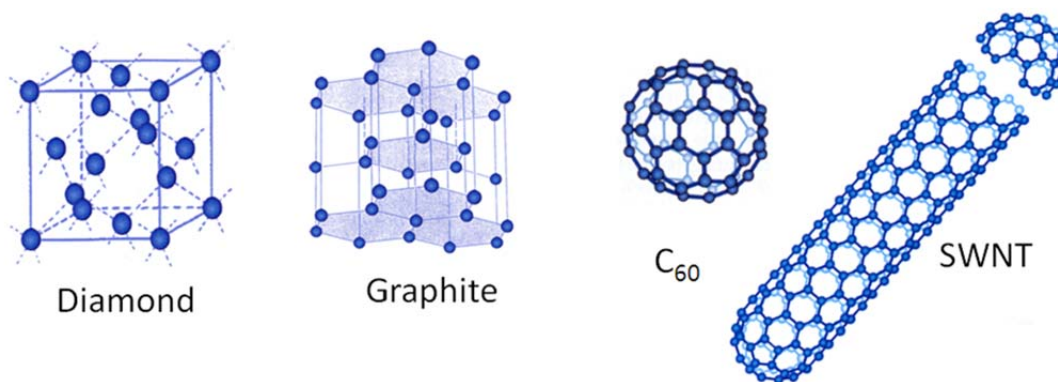


Figure 1. Schematic representations of allotropes of carbon. Allotropes are different arrangements of the same element, which in this case is the humble carbon atom represented by the blue dots. The diameter of a single walled carbon nanotube (SWNT) is ~1 nm, and its typical aspect ratio (length/diameter) is ~500.

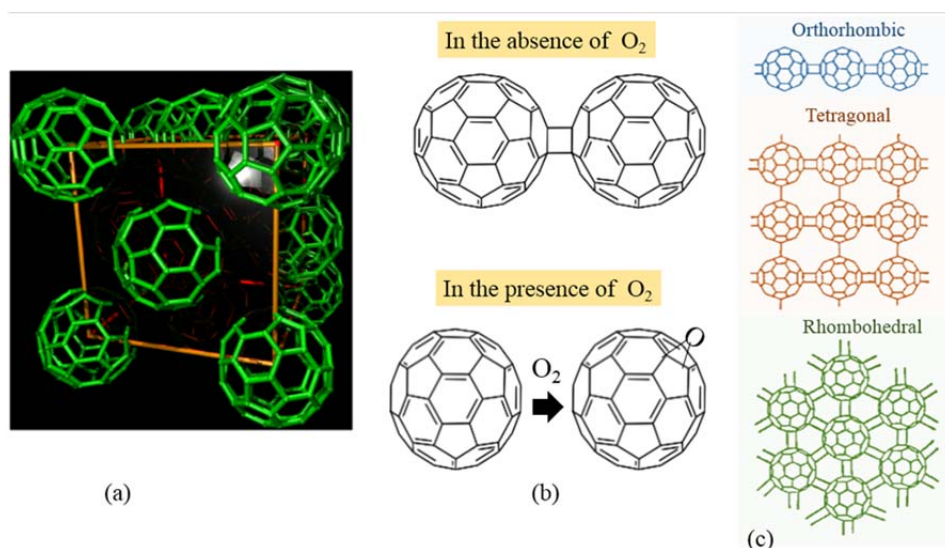


Figure 2. (a) The C_{60} molecules adopt a face-centered-cubic structure when a C_{60} containing powder is sublimed to form a thin film on quartz or silicon substrates; (b) A schematic of the end products derived from the two photochemical reactions described in the text; (c) Different bonding configurations that are possible in polymerized C_{60} .

transition metal catalysts, when added to one of the carbon electrodes, produced small diameter ($d \sim 1\text{-}2$ nm) seamless, isolated carbon tubes, now known as “single walled” carbon nanotubes (SWNT) (see Fig. 1). Although the typical aspect ratios (length/diameter) were ~ 500 , the SWNT yields were very low ($\sim 3\text{-}4\%$ yield). The majority of this carbonaceous material in the arc-generated soot was composed of carbon nanospheres, with small amounts of fullerenes also present. Subsequently, Richard Smalley at Rice University improved this yield twenty-folds by employing pulsed lasers to generate the carbon plasma, thus pioneering in-depth studies undertaken to elucidate the physical and chemical properties of these one-dimensional (1D) carbon tubes. Most strikingly, Smalley’s laser method produced bundles of SWNTs, with as many as several hundred packed inside a bundle parallel to one another to form a regular array (Fig. 3). Using transmission electron microscopy (TEM), we observed a very narrow diameter distribution of the tubes produced by the laser method. The parallel lines in the TEM image in Fig. 3 represent the tube walls, and the dark circular spots in the image represent the metal catalyst particles.

Since the 1970s, Raman scattering spectroscopy has been used with great success to study the physical properties of carbon-based materials. In collaboration with Prof. Mildred Dresselhaus of MIT, we used this spectroscopic technique extensively to study the bonding properties of pristine, metallic and superconducting phases of graphite intercalation compounds and fullerene-based solids. Given our success with Raman spectroscopy in this context, we again used it to elucidate the properties of these fascinating “quantum” wires. We found that the innate properties of these SWNTs were revealed through the light they scatter when subjected to laser illumination. From the analysis of the scattered light, we inferred the diameter and the electrical property of the SWNT – whether it had a metallic or semiconducting character – and the approximate size of the bundle in which the SWNT resided. We then designed Raman scattering experiments to investigate the possibility of using chemical doping to enhance the nanotube’s electrical conductivity. We concluded, from our studies, that dopant atoms or molecules reside in the channels between the nanotubes present in a bundle and exchange charge with the nanotubes.

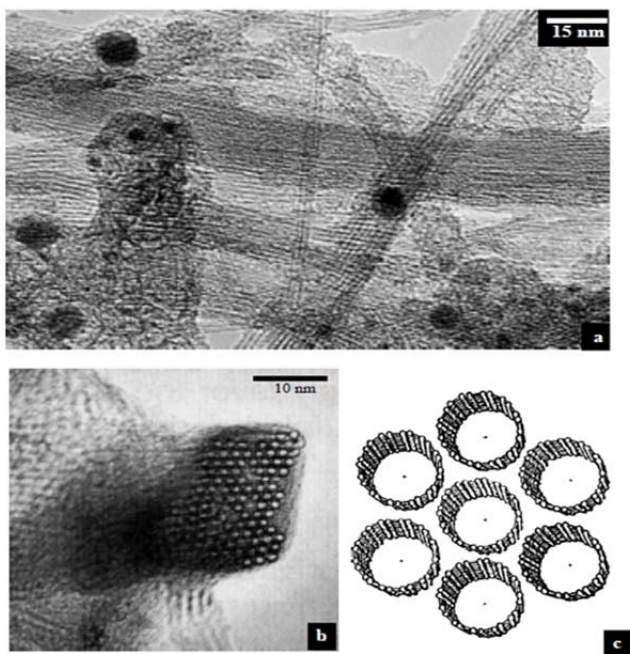


Figure 3. (a) A transmission electron microscope (TEM) image of a bundle of single-walled carbon nanotubes; (b) A TEM image of a bundle folded upon itself, revealing the self-assembly of the nanotubes into a triangular lattice, as shown schematically in panel (c).

Specifically, we demonstrated for the first time the amphoteric nature of the SWNTs and subsequently published these very novel and compelling findings. A material is “amphoteric” when it possesses the ability to accept (or donate) electrons from (to) dopant atoms or molecules. Again using Raman spectroscopy, we observed a series of doping-induced shifts in the high frequency vibrational modes while the electrical conductivity (under identical reaction conditions) increased by a factor of ten!

We also observed a downshift of Raman vibrational mode frequencies caused by donor atoms such as K or Rb, and an upshift in frequencies caused by the acceptor molecules (e.g., Br₂). A similar behavior in the Raman vibrational modes was observed during the doping of graphite in earlier studies, which resulted in the formation of graphite intercalation compounds. This behavior is associated with an expansion (donor doping) and contraction (acceptor doping) of the covalent bonds in the carbon hexagons. From a technological perspective, these bundles of SWNTs have high potential for use as inexpensive, light weight, highly conductive, high tensile strength “ultimate wires.” For their efforts to elucidate the fundamental properties of carbon nanotubes, both Prof. Iijima and Prof. Dresselhaus were awarded the Kavli Prize in 2008 and 2012, respectively. My team at Clemson University takes great pride in the fact that Prof. Dresselhaus has published over 30 joint publications with us in the past two decades.

Carbon nanotubes can also be grown in a Russian doll configuration, in which one nanotube resides concentrically inside a larger diameter nanotube, as shown in Fig. 4a. Such forms of carbon nanotubes are called multi-walled carbon nanotubes (MWNTs). Over a five-year period (2000–2005) my

team at Clemson developed several liquid precursor-based chemical vapor deposition methods for growing forests of straight, branched, or coiled MWNTs on silicon and quartz substrates (Fig. 4). We are presently growing MWNT forests on electrically conducting substrates such as aluminum foil to use as current electrodes in supercapacitors. In the menagerie of carbon nanotubes, some shapes are more equal than others. Indeed, one such example of particular merit is the Y-shaped carbon nanotube (Fig. 4b). In a Y-shaped carbon nanotube, the junction region can possess a charge due to the necessary presence of topological defects, or the presence of a catalyst particle that catalyzed the Y-shape. The induced charge and asymmetry is analogous to “gating” that can be harnessed for electrical modulation and switching, thus opening doors for *all-carbon* based logic devices as opposed to traditional SiO₂/Si based devices. Working with Prof. Prabhakar Bandaru at the University of California, San Diego, we fabricated nanoswitches and logic gates from Y-shaped MWNTs, which we expect will serve as the basis for a new type of logic device.

Just as the Y-shaped MWNTs are useful for logic circuits, we discovered that a forest of coiled MWNTs serve as an excellent mechanical shock absorber. In subsequent studies conducted in collaboration with UCSD, we concluded that a few-hundred-microns thick coating of coiled MWNTs, with the approximate thickness of a human hair, was sufficient for absorbing a large impact force, for example, equal to that experienced by a cell phone when accidentally dropped from a height of five feet. Through the use of the Y-shaped and coiled MWNTs, we demonstrated a new paradigm that *Function Follows Shape* at the nanoscale.

Generation Three: Graphene

Readers may be aware that the lead in our pencil is not true elemental lead, but amorphous graphite, a quasi-crystalline form of graphite. If one had a pencil sharpener so precise that it could peel off a shaving that is one atom thick, one would then have shavings of graphene! As explained in Fig. 1, graphene is a honeycomb carbon lattice that shares many of the equally amazing mechanical and electrical properties as the carbon nanotubes. However, it is infinitesimally thin! In 2010, Andre Geim and Konstantin Novoselov shared the Nobel Prize in physics for undertaking the very daunting task of peeling atomically thin layers of carbon off graphite, and demonstrating their innate superlative properties. We have demonstrated graphene as a protective wrapper for stents, the tube-like structures inserted into arteries or other bodily passageways to repair damage or improve fluid flow. Specifically, working with our colleague, Prof. Frank Alexis in the Clemson University department of bioengineering, we developed a method to mitigate thrombosis, or blood clots, that often result from the insertion of cardiac stents. The proteins in the human body interact with the stent material to create clots, which means the stent must be replaced via surgical procedure, often a mere five years after the first one was inserted. In our *in vitro* studies, however we

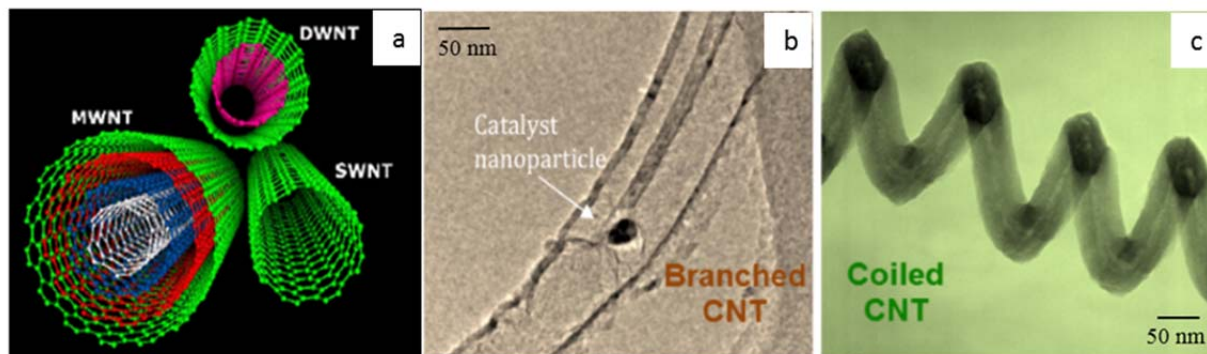


Figure 4. Schematics of single-walled, double-walled, and multi-walled carbon nanotubes (panel a); TEM images of a single Y shaped (panel b) and a coiled carbon nanotube (panel c).

doubled the lifetime of a stent, from five years to ten, by coating them with one to two layers of graphene.

In collaboration with Prof. Ramakrishna Podila in the department of physics and astronomy at Clemson, we resolved a scientific debate about the defects in graphene. From this recent research advance, we are now conducting research to create and control the energy band gap of graphene by folding, twisting and scrolling sheets of graphene. We also seek to determine what happens to the electrical properties of folded or scrolled graphene, and at what point does layered graphene begin to acquire similar properties as graphite. Through our studies, we are developing new materials and applications – the so-called novel “beyond-graphene” materials.

The continuing evolution to shrink the silicon transistors is now approaching a point of physical limitation. The increasingly small dimensions of these, now extending well into the realm of the nanoscale, will prohibit any gains in performance due to the nature of silicon and the fundamental laws of physics. Within a few more generations, classical scaling and shrinkage will no longer yield the sizable benefits of lower power, lower cost and higher speed processors to which industry has become accustomed. Carbon nanotubes (the Y-shaped nanotube described above) and graphene are both viable alternatives for replacing silicon in electronics applications. While current carbon nanotechnologies are well suited for configuration to the nanoscale, a concurrent increase in performance speed is also required, thus necessitating the need to develop all-carbon photonic devices. To this end, and in collaboration with Prof. Podila, we created the optical diode, which is the experimental realization of a key element that is needed for the development of an all-carbon based photonic device, viz., an optical diode. As the fundamental element in any photonic logic circuit, this diode allows the nonreciprocal transmission of light similar to the flow of charge in an electronic *p-n* junction diode. In our optical diode, light is transmitted in one direction only, which is not trivial to achieve and necessitates breaking the inherent time-reversal symmetry of electromagnetic waves. We disrupted this symmetry by fabricating a sandwich structure of thin-film of C_{60} ($d \sim 5$ nm) and graphene ($d \sim 2$ nm) to achieve a moderate optical non-reciprocity factor (ratio of forward to backward transmission) of ~ 4 . Unlike the traditional principles of physics (periodic variation of refractive index or dielectric constant) which present optical

diode technologies use, ours is based on an abrupt jump in the nonlinear absorption coefficient of the two carbon allotropes present in the sandwich structure, which breaks the time-reversal symmetry.

Because of this innovative approach, and because of our efforts to validate theories of many preeminent 20th century scientists in elucidating the quantum nature of fullerenes, nanotubes, and graphene, we have received over \$4 million from the National Science Foundation (NSF), besides funding from other federal agencies. Here, at the Clemson Nanomaterials Center, in addition to elucidating the fundamental properties of nanocarbons, we are developing methods to produce them, and beyond-graphene materials, on an industrial scale to make them economically viable for manufacturing devices. We expect to pioneer, in our SC based lab, the discovery of another carbon allotrope or two, such as penta-graphene which has recently been hypothesized to exist under ambient conditions, and to leverage our expertise in carbon science and technology to harness properties of other nanomaterials.

Notes

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