# Graphene in A Nutshell

By Peter Marino

## Making Headlines

Physics students, techies, geeks, and lots of other curious minds may have read one, or more, of the numerous recently published articles or press releases about graphene. Graphene, an allotrope of carbon, has been making headlines since the 2010 Nobel Prize for Physics was awarded. Two Russian research physicists, working at the University of Manchester, located in Manchester, United Kingdom, received the prestigious award for their experimental research and findings concerning graphene.

Laboratories filled with thousands of dollars' worth of high-tech equipment and supplies at their disposal and all they really needed was a roll of tape and a "rock." Actually, there is a little more than that to the story. However, in 2004, Andre Geim and Konstantin Novoselov initiated a tremendous resurgence of interest in a revolutionary atomic substance called graphene; and, they did it with a roll of transparent adhesive tape and a chunk of graphite.

## A Few Facts

Carbon is one of the six most abundant elements in the world. The element plays many essential roles in the universe and in everyday human life. Carbon and its abundance of chemical compounds are among the most important elements for living and non-living things. Prior to the new millennium, amorphous, graphite, diamond, and fullerene were the four, recognized, basic allotropes of carbon. During recent years, researchers have discovered and developed new forms of carbon.

Carbon nanotubes have been used in various industries, including medical technology and electronic technology, for more than a decade. Carbon nanofibers, nanowires, nanoparticles, and graphite nanofibers have been integrated into many products. In 2004, physicists at the Australian National University in Canberra created magnetic carbon nanofoam. Also, in 2004, Andre Geim and Konstantin Novoselov successfully isolated individual graphene planes, or layers, for the first time.

Graphene is derived from graphite, an allotrope of carbon. It can be defined as an individual planar sheet, one atom thick, of sp2-bonded carbon atoms retaining a two dimensional, honeycomb pattern formation. A planar sheet of graphene resembles chicken wire or hexagonal lattice, in appearance. It can be considered the basic building block for all other dimensionalities of graphitic materials, such as zero dimension fullerenes, one dimension nanotubes, or 3D graphite.

Each atomic monolayer of graphene is extremely thin, nearly weightless, flexible, stretchable, and almost transparent. It would take three million sheets of stacked graphene to form a piece of graphite one millimeter thick. However, it is one of the strongest materials known to science. It is much stronger than structural steel and virtually impermeable. Graphene is an excellent conductor of electricity and heat, also.

## A Little History

Although graphene has been a hot topic recently, its existence was, actually, discovered a long time ago. In fact, numerous obscure references, papers, and notations concerning experimental research involving the properties of graphene and layers of graphite, dating back to the late 1800s, have been unearthed in recent years. An industry report, published by Highbeam Business, references early experimental work. Inarguably, graphene's existence has been recognized since X-ray crystallography was invented. Evidence suggests most early research was conducted with "few layer" samples and limited monolayer samples. Due to continued advancements and new discoveries during the 1990s and a major breakthrough in 2004, a renewed interest in graphene has emerged.

Washington H. Lawrence and Charles F. Brush began experimenting with carbon electrodes, in1877. In 1878, Charles Brush began manufacturing the first carbon electrodes. P. Haenni and V. Kohlschutter studied thermally reduced graphite oxide in 1918. They described the properties of graphite oxide paper in their research reports, also. In 1947, while attempting to gain insight regarding the electronic properties of graphite, P.R. Wallace first explored the theory of graphene. Hanns-Peter Boehm is credited for coining the term graphene. In 1962, he used the term to describe single layer carbon foils.

Epitaxial graphene has been produced since the 1970s. Often this type of graphene contains variations, which alter the electronic structure. In 1987, graphene was listed as a constituent of graphite intercalation compounds. Through the eighties and nineties a number of researchers explored numerous methods of producing structurally stable graphene in larger quantities.

In 2004, research physicist, Andre Geim and his assistant, Konstantin Novoselov were able to isolate an individual layer of graphite crystallites using transparent adhesive tape. The research team, based at the University of Manchester, applied tape to graphite and removed it to secure some layers of the material. Then, they used the tape to separate the layers, pressing the tape together and pulling it apart. They continued this process until a single layer, one atom thick, was obtained.

The Manchester research team, and many others, continued their endeavors to characterize the amazing properties of graphene. The ballistic conveyance of charges, the bipolar transistor effect, and the large quantum oscillations are a few of the interesting, intrinsic characteristics. In 2010, Andre Geim and Konstantin Novoselov received the Nobel Prize for Physics for their work involving graphene. Due to the special properties and the recognizable potential of graphene, many scientists have devoted their research and experimental efforts to developing the production of graphene and discovering new substances derived from graphene. Fluorographene, or 2D Teflon, introduced by Geim and Novoselov, is one example.

### Viability and Production Progress

Through the combined efforts of Geim's team and Philip Kim's group at Columbia University, in 2005, a demonstration proved that the quasiparticles of graphene were Dirac fermions without mass. Since then, interest in the substance has intensified. Hundreds of researchers have turned their attention to finding effective, efficient methods for producing useable sheets of graphene. Many are dedicated to discovering beneficial uses for the super strong, ultra-thin material, also. In 2010, Walter A. de Heer, Professor of Physics at Georgia Institute of Technology, received the Materials Research Society Medal for his experimental work with epitaxial graphene. According to an article by Absolute Astronomy, the surface science community has studied epitaxial graphene on a variety of surfaces, extensively. They wrote over three hundred articles and papers on the subject prior to 2004.

Obtaining viable amounts of the "wonder" material has been one of the main issues impeding progress and innovations involving graphene. Pure, exfoliated graphene was one of the most expensive materials in the world, in 2008. One square centimeter of graphene could be purchased for around $100,000,000. Fortunately, exfoliation techniques have improved reducing the price. Scientists and research groups have been working diligently to develop successful methods of producing larger quantities of graphene for practical purposes.

Most people have practiced a very common technique for exfoliating flakes, or crystals, of graphene. The technique involves writing or drawing with a pencil. With each line that is drawn, flakes of graphite are produced. Some of the flakes are monolayer graphene. The exfoliating technique used by the Nobel Prize winning physicists has been named the drawing method or the tape method. Although it is cleverly resourceful, the tape method would need some modification to produce sufficient quantities of the material.

Heating silicon carbide, or SiC, is another technique for creating graphene. The silicon carbide substrate is called a wafer. The SiC is heated to a temperature above 1100 degrees Celsius and reduced to form graphene. With this method the mobility and carrier density of the samples are affected by the silicon or carbon terminated face of the wafer. It was this technique that first revealed the Dirac cone structure represented in graphene. The material exhibits the anomalous quantum Hall effect and weak anti-location. MIT Lincoln Lab and Hughes Research Laboratories have successfully developed epitaxial graphene microchips, which support large volumes of transistors.

Epitaxial graphene can be grown on metal substrates, as well. Experimentation with iridium substrates has produced slightly rippled, weakly bonded, uniformly thick sheets of epitaxial graphene. Minigaps within the Dirac cone structure are visible in this material. Chemical vapor deposition has been used to produce very high quality, “few layer” sheets of graphene, grown on nickel films. The viability of the material for many electronic applications has been demonstrated by transferring the planes of graphene to a variety of substrates. Using extremely low pressure, monolayer sheets of graphene can be created on copper foil.

Graphite oxide reduction is another method of synthesizing graphene. Historically, this method may have been the first successful graphene synthesis technique. In 1962, P. Boehm documented the ability to obtain single layer flakes of graphene through graphite oxide reduction. With this technique, rapid heating and gradual cooling are used to exfoliate graphene films. Due to variations and residual impurities, the quality of the graphene produced through this method is lower.

Metal-carbon melts have proven successful for creating high quality, single layer graphene. This method involves melting metal in conjunction with a source of carbon. Basically, the carbon atoms are dissolved, blending with the metal. The melt is then allowed to cool. As the temperature decreases, the carbon precipitates out of the melt forming a floating layer of graphene. Nickel has been shown to be one of the best substrates for this process. Thermal management applications and thermal interfacing are two potential uses for this material.

Deconstructing nanotubes to create graphene ribbons, thermochemical decomposition, or pyrolysis, to produce gram amounts of graphene, and a ten minute process involving sucrose are some of the other techniques used for creating graphene. The results of a study published by Nature Nanotechnology showed that long carbon nanotubes produced the same reactions in lab mice as asbestos. Most experts concur that graphene is a safer option. Walt de Heer’s team at Georgia Tech has discovered a better way to create epitaxial graphene nanoribbons using a “templated” substrate. In 2011, Professor Jacek Baranowski and a team of Polish researchers, in Warsaw, announced the production of the highest quality of large sheets of graphene. Worldwide research continues.

## Characteristics and Properties

TEM, or transmission electron microscopy, was used to study monolayer graphene sheets. The use of electron diffraction patterns revealed the “chicken wire” atomic structure of the material. The ripples that appear in graphene may be due to the instability of 2D substances; or, they might originate from impurities or residues. Ripples in graphene samples on silicon dioxide may be caused by the substrate surface.

Graphene is a semi-metal. It is a conductor and a semi-conductor. Graphene has surprisingly high electron mobility at average temperatures ranging between 68 and 77 degrees Fahrenheit. GNRs, or graphene nanoribbons, with zig-zag oriented band structures are always metallic. GNRs with armchair oriented band structures can be metallic or semiconducting, according to width.

It is important to note the surprisingly high opacity produced by graphene’s electronic properties. An atomic plane of graphene absorbs 2.3 percent of white light. Pure graphene is virtually transparent. The unique structure of this material, which demonstrates electrochromic behavior, allows the band gap and the optical response to be tuned. Graphene’s ability to absorb light, or saturable absorption, is relevant to an unlimited number of potential high speed photonics applications.

The Hall effect, discovered by Edwin Hall in 1879, is the potential for a voltage difference within an electrical conductor, called a Hall bar. The voltage difference is produced when a magnetic field is perpendicular to the electric current crossing the conductor. The Hall effect is useful for obtaining accurate measurements of electrical quantities. The quantum Hall effect, which is applicable in 2D electron systems, is a quantum-mechanical adaptation of the Hall effect. SLG, or single layer graphene, exhibits an anomalous quantum Hall effect. Anomalous refers to deviations or abnormalities from the standard Hall effect. In the interest of getting to the point and avoiding a lengthy physics lesson, this information is used to explore the myriad of conductive possibilities for graphene.

Graphite, essentially 3D graphene, has basal plane thermal conductivity comparable to that of diamond. The thermal phonon dominated conductivity of graphene, at “near room temperature,” exceeds that of carbon nanotubes and diamond. Graphene’s ballistic thermal conductance is isotropic, or the same regardless of the direction of measurement. The “membrane effect” is evident in graphene at low temperatures where phonon frequencies increase, exactly as Soviet physicist Ilya Lifshitz theorized in 1952.

The spring constant range of a suspended sheet of graphene has been measured at 1-5N/m and the Young’s modulus at 0.5 TPa. These values are high, meaning the material is very stiff and very strong. It has a break-through point, or strength, two hundred times higher than structural steel. It has a tensile strength of 130 GPa, or 19,000,000 Psi. Recently, researchers at the University of Technology Sydney developed a new graphene paper. The paper is created by chemical purification and filtration of raw milled graphite which reforms into nano-structured configurations. This material is processed into thin sheets of graphene paper. According to researchers, the paper sheets are harder and stronger than steel. Yet, they are much lighter and more flexible than steel. The newly developed material is, also, reported to be recyclable and sustainable for manufacture, making it an eco-friendly and cost effective product.

Additional properties and characteristics of graphene include electrical spin current detection, electrical spin current injection, and spin polarized edge currents suggesting many possible useful applications in spintronics. In April 2011, the University of Manchester team, led by Professor Andre Geim, announced the ability to magnetize graphene using electric current. Magnetic graphene could lead to numerous innovations in the area of spintronics.

Monolayer graphene sheets are thin, electrically conductive planes capable of generating the Casimir effect, also. Graphite, graphite oxide, graphene, and graphene oxide exhibit a number of promising characteristics worthy of further research, as well. Partial, or one-sided, hydrogenation of graphene results in hydrogenated graphene. Complete hydrogenation from both sides of a graphene sheet creates graphane. Graphane is a 2D carbon-hydrogen polymer. The carbon bonds in graphane are arranged in sp3 configuration, indentifying it as a 2D version of cubic diamond.

### Back to the Future

Today, thousands of researchers around the world are working with graphene. This phenomenal "new" substance has an infinite number of possible future applications. If, and when, graphene becomes a viable commodity, it will revolutionize almost every industry. In addition to the ability to produce large quantities of quality graphene, viability would entail safe production and processing. Sustainability, low toxicity/non-hazardous materials, eco-friendly products, and affordability still need to be realized, as well.

A small number of companies produce graphene for experimental work and a variety of industrial purposes. The material is produced and marketed in various states, or forms, and quantities. Graphene wafers, graphene oxide, graphene flakes, nanopowder, and more are available for research experiments and manufacturing processes. Q-graphene, or carbon Q-dots, are multi-wall carbon nanospheres. They are closely related to fullerenes. Q-dots, also called nanoonions, are expected to have many practical applications in composite materials, film batteries, and supercapacitors.

At this time, prices are still relatively high and vary according to quality, form, and quantity. For example, five grams of 12 nanometer graphene nanopowder flakes cost about $50.00, while five grams of 8 nanometer flakes would be about $100.00. And, a 4 inch by 2 inch sheet of SLG on copper foil is priced around $450.00. The cost of one four inch wafer of graphene film on nickel is about $350.00. The inability to produce sufficient quantities of safe, structurally stable, single layer graphene sheets is one of the biggest hurdles impeding the progressive development of applications and manufacturing of graphene products. Researchers around the world are committed to solving this problem. Already, several promising techniques have been introduced. Considering the interest and enthusiasm fueled by graphene's prodigious potential, it will not be long before an effective, efficient method is developed.

### Speaking of Potential

Graphene is a promising "new" material that could revolutionize the worlds of electronics, technology, manufacturing, and more. Graphene's impressive properties and characteristics have opened the door to an infinite number of innovative opportunities. This amazing material is very thin, very lightweight, and virtually transparent. It is flexible and stretchable. It is extremely strong and durable. It can be magnetized. And, it is an excellent thermal and electrical conductor. Could anyone ask for more?

Almost every industry, and every area of everyday life, will be impacted by the successful production and integration of graphene. The electronics industry will be the first to experience the “graphene revolution.” The world of electronics is huge; and, graphene has the potential to reinvent, or redesign, it. Electronics are implemented, in one way or another, in nearly every industry.

Smaller, faster transistors, more powerful, high frequency electronics, compact high speed modulators, ultracapacitors, replacement transparent-electrodes for indium tin oxide, electromagnetic graphene-based switches, and better conductors and semiconductors are only a few of the soon to realized nanoelectronic “graphene inspired” concepts. Many experts view graphene as a replacement for silicon in most electronic applications. Although more research is needed, nanotechnology is progressing into the future.

What does this “electronics revolution” mean to the average consumer? It means things will be faster and more efficient. Of course, computers will operate faster and more efficiently. Everything that has any type of electronic function, from household appliances to factory machinery to air traffic control equipment will operate, or execute functions, at higher speeds, using less power. At room temperature, graphene has a much lower resistance than silicon or copper. Therefore, the higher speeds generated through graphene do not use more energy. Energy waste is significantly reduced, as well. In this continually evolving world, with its ever-increasing reliance on technology, graphene could be the solution to a wide variety of current issues and impending problems.

In addition to futuristic-like, miniature, hand-held PCs, there are many other “futuristic” products on the horizon. Graphene based nanoelectronics will provide tremendous opportunities for advancement in robotics. Robots, like C3PO in the movie “Star Wars,” may become a part of reality before too long. The exciting, and anxiously anticipated, conversational interface for operating systems could debut earlier than expected. Graphene based nanotechnology provides countless opportunities for advancement in the medical field, also. The ultra-small, ultra-lightweight, ultra-fast electronic technology can be used in millions of applications from touchscreens and prosthetics to solar chargers and defense missiles.

Graphene’s astounding strength and surprising flexibility allows for an endless number of possibilities and improvements in manufacturing. Graphene is much stronger than steel and virtually impenetrable. Plastics, metals, glasses, woods, and composite materials can be strengthened, or reinforced, with graphene. Manufactured products, such as sports equipment or toys, would be able to withstand much more abuse and neglect. Cars, airplanes, motorcycles, and boats can be fabricated from stronger, lighter materials. With more strength and less weight, transportation vehicles would be safer and more economical. Imagine this on a larger scale, at a military level. Military personnel, police officers, fire fighters, and other emergency personnel could benefit from protective, high-tech uniforms and equipment, also. Imagine the plethora of possible applications for this “super strength.”

Houses, hospitals, and office buildings could be constructed with stronger materials. Many lives could be saved and much destruction averted with graphene-strengthened building supplies and construction materials. Unbreakable glass would provide numerous advantages in the construction industry, the automotive industry, and many other areas. Highway overpasses, tunnels, and bridges would be built to last. Graphene’s flexibility would be a huge advantage in construction, as well. A bridge or building with a little “extra strength flexibility” would have a better chance of survival, during an earthquake or tsunami. Graphene could extend the "useful life expectancy" of most manufactured products.

Graphene's potential is virtually infinite and is only limited from our current inability to manufacture reliable, defect-free quantities of the material (note: there is great promise coming out of the University of Houston to overcome this barrier). This awesome "new" material may be the key to resolving a wide spectrum of present and future challenges. Graphene, an age-old substance, offers an exciting new future for all of humanities endeavors.

Reference Links:
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