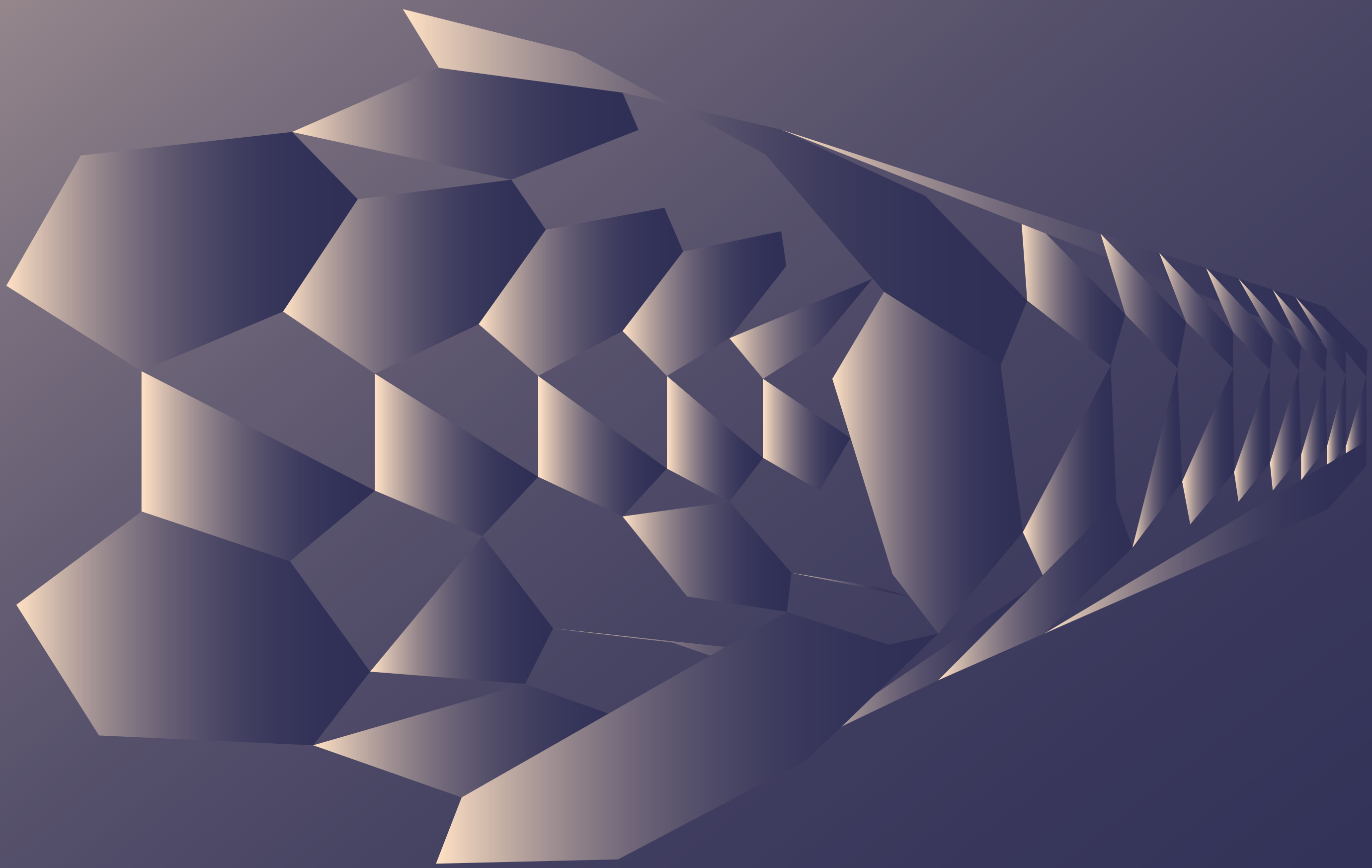
Graphene and Carbon NanoTubes



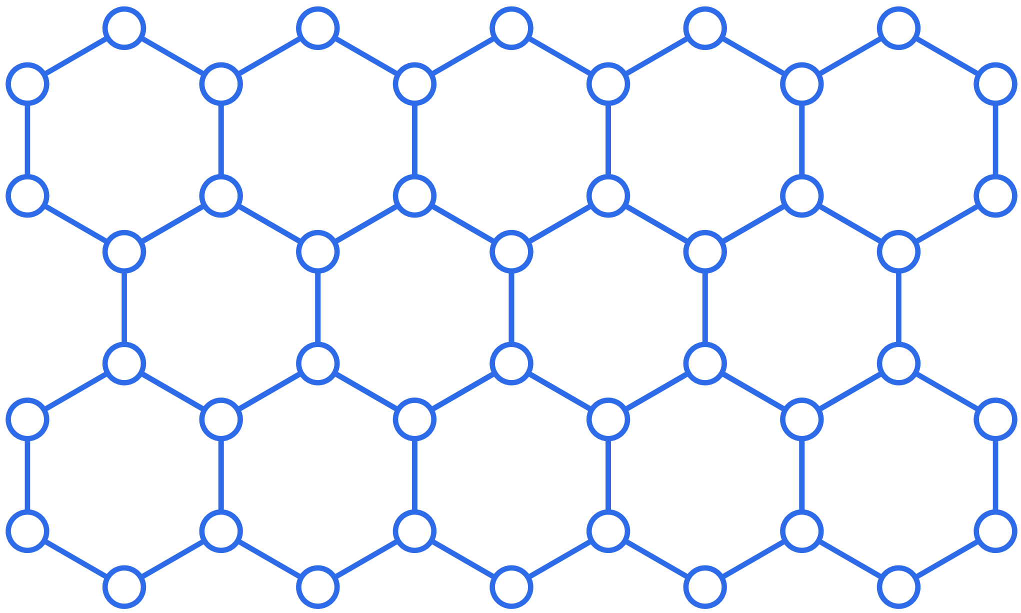
Prime Movers Lab
April 2020

Prime Movers Lab

What it is, and why it’s important

Graphene is a material that has one sole element: carbon. Carbon forms very strong bonds with itself to make chains (hydrocarbons), crystals (diamond), and spherical shapes known as fullerenes. In graphene these atoms of carbon are bonded to each other to form a flat sheet that is only one atom thick, with the carbon forming a hexagonal grid. Take a sheet of graphene and roll it back on itself into a cylinder, and you have a carbon nanotube. A sheet graphene arranged as the skin on a sphere is called a bucky-ball, named after the buckminsterfullerene, the first discovered fullerene.

Typically, graphene is arranged in a “honeycomb” pattern and is black in color. Below is an image of graphene to give you a visual idea of what this is about:



Graphene, even as a single layer of carbon atoms is very strong and extremely light weight. Carbon nanotubes (CNT) are even stronger, as the stresses are distributed around the walls of the tube, like a rolled piece of paper is stronger than the same paper as a flat sheet. In fact carbon nanotubes may have the highest tensile strength of any fibrous material known to man (if we are someday able to produce them at lengths greater than a couple of millimeters).

Both graphene and CNTs have incredible electrical and thermal conduction capabilities, even becoming superconducting in some conditions. Both are typically black colored, stretchable, and can be twisted and returned back to original shape an unlimited number of times. These qualities have led to the development of wearable electronics and flexible circuitry using graphene as a breakthrough material.

Graphene has a plethora of promising uses: anti-corrosion coatings and paints, efficient and accurate sensors, quicker and lighter electronics, flexible screens, economical solar panels, more rapid DNA sequencing, pharmaceutical delivery, and more. Graphene is such a simple building block that many industries can theoretically incorporate graphene into their products to make them better, stronger, lighter.

Graphene is beginning to be successfully integrated into cellphones (such as the Huawei Mate 20 X) to make foldable screens, higher capacity batteries, and displays that cool more efficiently. In this article we walk through current state of the art uses, progressive research concepts, five-year projections of the technology, startups working with graphene, and major players in the industry.

Why we aren't using it in everything

In short, because carbon in these forms is difficult to produce and to incorporate in real-world applications. A single layer of graphene is so thin that it cannot be seen by the human eye. In fact if you layered one million sheets of graphene on top of each other it would be the thickness of a human hair. With material this thin, it requires extremely careful handling. And so today it is still only used in high-value and specialized applications.

The first graphene was isolated in 2004 by peeling a piece of adhesive tape off of a block of graphite, yielding a single layer of carbon one atom thick across the surface of the tape. This is because graphite is essentially a three dimensional stack of graphene layers bonded together. Like a stack of paper that has been soaked in water or glue; where the pages are layers of graphene held together with crosslinked carbon-carbon bonds between the sheets.

Today graphene is made in special reactors purpose-built for that task. The vast majority of graphene is produced today by exfoliating common graphite in a liquid bath, either by mechanical exfoliation (literally using a diamond knife to peel off layers), or electrochemical exfoliation in which chemical reactions and electrostatic repulsion are induced between the layers to separate them. However, both of these processes are quite rough on the material, and yield only tiny flakes of low-quality multi-layer graphene (due to failure to peel a single layer at a time), or with extensive mechanical damage to the crystalline structure. These flakes are referred to as nano-platelets.

It can also be fabricated using chemical vapor deposition (CVD) in a large single sheet with a high surface area, this is a very difficult and expensive operation with the graphene layer being grown on a sheet of copper. It can also be produced by growing carbon nanotubes and then chemically de-bonded and flattening them to form microscopic strips of monolayer graphene.

As a result, graphene comes in various levels of quality ranging from from high quality monolayer graphene, down to tiny flecks of mechanically shredded powders.

Perfect monolayer graphene is the highest quality and is what we see depicted in illustrations and diagrams. It has a perfect hexagonal pattern with high purity of sp2 bonds, extremely low surface inconsistency, and arrives in a pristine single layer. Then there is lower quality “few-layer” graphene that has multiple layers of graphene clumped together like the pages of a wet book, often with a great many defects, snags, and tattered edges). Most of the world’s producers of graphene are producing this latter low quality type, which is sometimes even called counterfeit graphene, since it is really flakes of graphite, with inferior physical properties that make it unusable for most real applications. Imagine trying to make use of a fishing net with many breaks and tears, and other sections that have many layers stitched together in clumps, all with loose, tattered outer edges.

A paper published in Advanced Materials (“The Worldwide Graphene Flake Production”) studied graphene purchased from 60 producers around the world. This study concluded: *“that the quality of the graphene produced in the world today is rather poor, not optimal for most applications, and most companies are producing graphite microplatelets. This is possibly the main reason for the slow development of graphene applications, which usually require a customized solution in terms of graphene properties.” And further: “our extensive studies of graphene production worldwide indicate that there is almost no high quality graphene, as defined by the ISO (International Standards Organization), in the market yet.”*

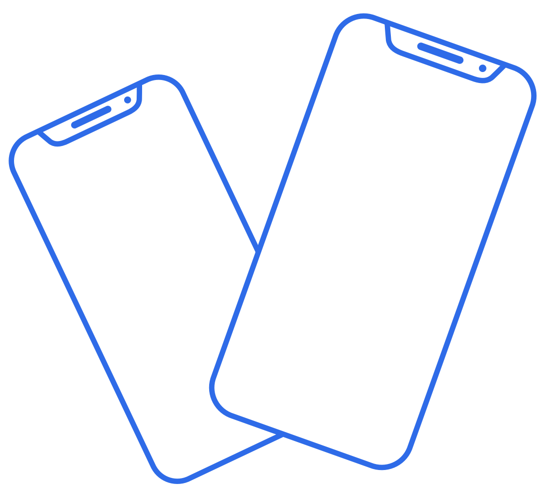
One way that sample quality is evaluated is by measuring the proportion of sp2 bonds in the material. The study found that “*crystalline graphene should have 100% sp2 bonds. However, we were not able to find, in any of the companies studied, a sample with more than 60% sp2 bonds.*” And an additional stumbling block is that most of what is sold as graphene is actually graphene oxide, with many oxygen atoms contaminating the mesh and weakening the Carbon-Carbon bonds.

Carbon nanotubes (CNTs) have faced similar challenges in the push to incorporate them into real-world products. The typical CNT is only a few microns (thousandths of a millimeter) in length, and thus has limited applications that can make use of a structure of this size. And while scientists have succeeded in making CNTs that are 50 centimeters long, these long CNTs were produced at great expense in laboratory conditions. Despite their amazing properties we simply do not have the production technology yet to reliably produce these materials at economic scales.

At Prime Movers Lab we see the greatest investment opportunities in the near-term to be technologies that enable cheaper and higher quality production of these materials. A key consideration will be the companies and processes that can scale to meet the massive demand that is expected to emerge once consistent supply is realized; at which point it will be possible to develop specialized equipment to handle more standardized and predictable input materials.

Current State of the Art

Pharmaceuticals, material science, nanotechnology, and cellphone technology are all current environments where graphene is presently used or being considered. Being highly biocompatible, graphene oxide is being used to deliver cancer drugs, antibiotics, poorly soluble drugs, peptides, antibodies, DNA, RNA and nucleic acids in biotech applications. On the electronics side graphene is used to make super strong, lightweight materials, especially for flexible circuits and wearable technologies. Companies are leveraging nanotech manufacturing methods to grow graphene for thin-film supercapacitors that can be used as alternatives to electrochemical batteries. In most of these applications graphene is still being evaluated for efficacy, so it is not yet clear where it will gain the most traction.



One area that is seeing more immediate growth is in paints and composites. By mixing flakes of graphene into resins, the mixture can serve as a cheaper alternative to carbon fiber composites with the same or higher strength rating. And for paints the graphene is converted to graphene oxide so the nanoplatelet powders can be mixed into a liquid dispersant system and then sprayed or otherwise applied onto surfaces. These hybrid graphene products provide improved strength and conductivity using today's application technologies, though have greatly reduced benefits as coatings or objects made with pure graphene.

Global Suppliers and Consumers

Graphene can be purchased online in bulk, but prices vary wildly with the quality level. But doing something meaningful with the samples once you receive them is a different story.

Pristine monolayer graphene is the highest quality product. For a single layer thickness, grown on a metallic substrate using CVD will cost $100–200 USD for a 1cm x 1cm square.

Few-layer graphene nanoplatelets are medium quality, consisting of tiny irregular flakes. These can be purchased in jars for approximately $10–20 USD per gram. Multi-layer graphene powder or graphene oxide powder are the lowest quality and can be purchased for $0.10–1.00 USD per gram.

As you can see, the price varies by many orders of magnitude based on quality. Thomasnet estimates that the world market size for graphene production is approximately $640 million today. The United States is the largest consumer of graphene followed by Italy, Australia, UK, Canada, and China. Thomasnet has provided the following tables to show the largest producers and what their sales look like:

Publicly-Traded Global Graphene Manufacturers

Graphene is a relatively new market and there are several active non-US manufacturers of graphene. Australia, Canada, China, Italy, and the United Kingdom are home to the most prominent of these companies. Many of the larger companies have graphene-oriented subsidiaries.

Table 2: Global Manufacturers of Graphene

Company Name	Location	Market Cap*
Directa Plus PLC	Italy	$ 242.0 million
Talga Resources Ltd.	Australia	$ 116.0 million
Versarien PLC	United Kingdom	$ 100.1 million
Saint Jean Carbon Inc.	Canada	$ 94.7 million
Haydale Graphene Industries	United Kingdom	$ 51.6 million
Group NanoXplore Inc.	Canada	$ 20.3 million
Graphene NanoChem LLC	United Kingdom	$ 7.1 million
First Graphene	Australia	$ 6.9 million
Elcora Advanced Materials	Canada	$ 5.9 million
China Carbon Graphite Group	China	$ 2.4 million

Table 1 -- Selected Graphene Manufacturers in the United States

Company Name	City, State
1st Graphene	Santa Ana, CA
Global Graphene Group	Dayton, OH
Graphene 3d Lab, Inc.	Ronkonkoma, NY
Graphene One LLC	Los Angeles, CA
Graphenea Inc.	Cambridge, MA
Graphite Central	Rockleigh, NJ
Grolltex	San Diego, CA
TCI America	Portland, OR
XG Sciences, Inc.	Lansing, MI

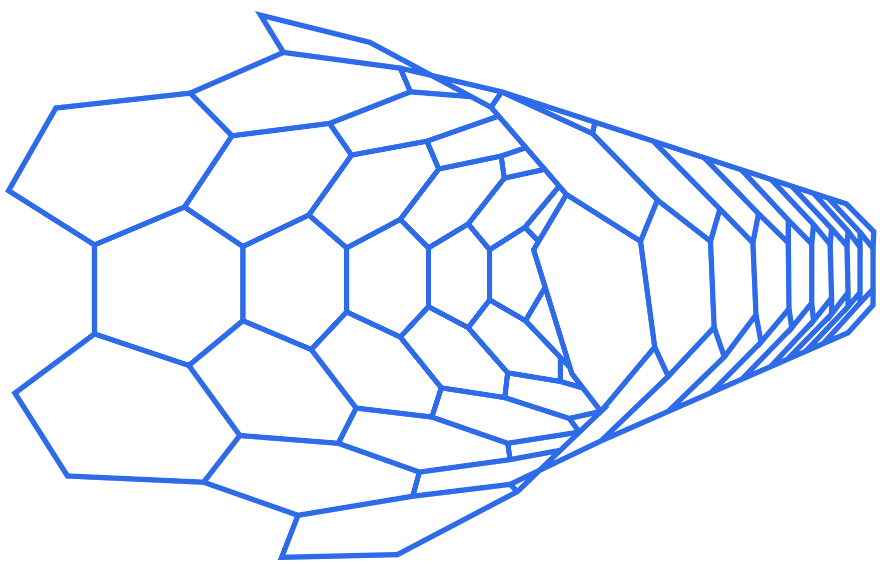
Production Costs

Perfectly formed monolayer graphene like we see in the news is difficult to make in large quantities with present technology. The very highest grades of graphene are grown one layer at a time on nickel or copper foil in chemical vapor deposition (CVD) chambers. This CVD-produced graphene can sell for USD $10 / cm2 ***per layer***, and then requires sophisticated techniques to remove the graphene layer from the metal foil and apply this tiny sheet to the surface of other devices.

Most graphene is produced via mechanical or chemical exfoliation of graphite. This process attempts to peel a 3 dimensional block of graphite down one atomic layer at a time to form 2 dimensional sheets of graphene. The graphene planes are spaced about 0.335nm apart in the graphite, so there are approximately three million layers of stacked graphene per millimeter of graphite. The most basic form of this is mechanical exfoliation using the “scotch tape method” in which an adhesive substrate is pressed onto a flat surface of graphite and the adhesive pulls up layers of carbon atoms. As you can imagine, this is an imperfect process leading to many defects in the material, especially when more than a single layer of carbon binds together during the exfoliation, leading to the lower quality few-layer graphene discussed earlier. There is also often difficulty removing the graphene layer from the adhesive backing. Further, the result is highly dependent on the quality of the input graphite material. Although this was how the first true monolayer graphene was isolated in 2004, it is quite impractical to scale for production.

To put the magnitude of this undertaking in perspective, a 1 centimeter cube of high-purity synthetic graphite costs around $0.20/cm^3. This 1 cm cube of graphite theoretically contains approximately 30 million layers of graphene. If you were to successfully exfoliate the entire cube of graphite into perfect single-layer squares of graphene, it would turn $0.20 worth of graphite into a pile of graphene sheets worth over $30,000,000 retail price. This is not possible with today's technology, but it highlights the magnitude of the difficulty in securing high-quality graphene samples.

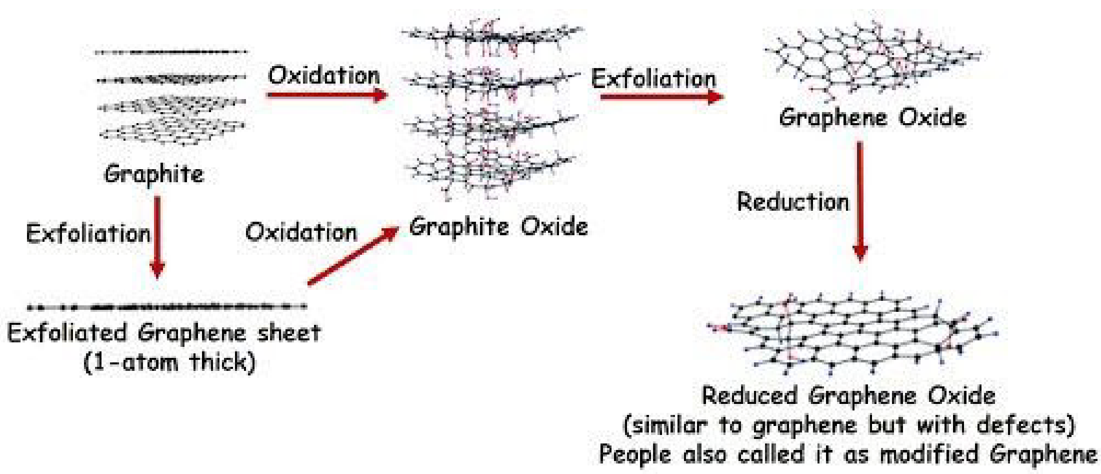
Thus these processing costs appear to be the key reason why the graphene market hasn't flourished yet. The apparent costs for setting up and producing graphene can be quite expensive. And all production methods used today require specialized equipment and production techniques, which in turn require extensive engineering skills to operate and maintain. So by the time the graphene production is completed, marketed, and shipped, the cost can be prohibitively high for mid-level consumers.



Additionally, there's the risk of buying "counterfeit" graphene, which is nothing more than thin graphite flakes or finely ground graphite powders. A flake with more than 10 layers of graphene still bonded together in its natural state is considered to still be graphite. Beyond this there is not yet a grading system for evaluating and enforcing quality standards on different tiers of graphene. So a bad shipment of "graphene" might be as much as 90% graphite, with the customer being unable to recoup the loss when the material that arrives is too irregular to meet their process needs. All these factors appear to be limiting graphene adoption in the world today, which is perhaps why it hasn't totally captivated consumers. Further, the production methods and customer use-cases can be difficult to explain to would-be investors; so despite the hype-cycle on graphene as a material, the economics of raising a startup in this space can be quite challenging.

At PML we see the biggest opportunities for carbon-materials investing to be in companies that are pioneering radically cheaper and more scalable methods to produce high quality graphene and carbon nanotubes. As a rule of thumb I am looking for technologies that enable 10x reductions in cost, or 10x increases in quality and throughput. Or even better, in companies that are enabling a class of graphene product that no other method can achieve.

Manufacturers are putting forth patient R&D efforts to improve production processes. Namely, we see the flourishing of academic and applied research efforts to learn more about the structural properties of graphene and how it might be used in real-world applications. Further, improved mechanical engineering and advanced component selection efforts have yielded increasingly simpler graphene reactors at reduced costs. And chemistry-based approaches are being used to optimize graphene production and quality, such as chemical exfoliation of graphite and the production of reduced graphene oxide. Graphene oxide is easier to produce and is thus a cheaper alternative to pure graphene. And although it typically has more defects and decreased performance properties, it is still adequate for many applications where graphene would be a valuable addition.



Research in Progress — Looking towards Tomorrow

Despite the high production costs, graphene has seen increasing demand in recent years originating from multiple sources. There have been new applications of graphene for optoelectronics, OLEDS, automotive composites, coolants, sensors, super-capacitors, cigarette filters, membrane technology, and next generation temperature-regulating fabrics. This last category is noteworthy, as there is always an interest in stronger, lighter and more effective military armors and sporting equipment, in addition to wearable electronics technologies for both athletes and defense systems. And there is always an insatiable worldwide demand for improved smartphone and laptop designs using the latest next-generation materials; so with graphene's second-to-none thermal and electrical conductivity properties it can be expected to find its way into more and more devices in the coming decade. Numerous manufacturers with strong R&D capabilities are looking to incorporate graphene and CNTs into their products, so we expect demand to continue to grow steadily despite the current production obstacles.

Two of the most promising near-term applications of graphene and carbon nanotubes are in super-capacitors and lithium ion batteries. Carbon-based super-capacitors could theoretically rival lithium batteries in terms of energy density, while simultaneously being able to charge and discharge about 100x faster, and being able to go through 10,000 or more charge/discharge cycles before needing to be replaced. These graphene and CNT-based super-capacitors could be used in place of batteries to power electric vehicles, charging up from empty in less than the time it takes to fill a conventional gas tank. The problem is that they are still at the proof-of-concept phase and will require more research and material advances before we will see them in action. Similarly, graphene can be used in lithium-ion batteries to improve the energy capacity and charge-discharge rates by providing an anode material with much greater surface area than the graphite anodes used today. Both of these technologies are worth tracking in the coming years for commercialization opportunities.

Graphene has gained a toehold in the world market as a driver of improved quality and performance in many products. There are over 100 start-ups producing or developing applications that leverage graphene as a key enabler. Many of these companies have been in operation for over a decade, which demonstrates the slow growth of the graphene economy that is finally showing signs of momentum.

Below are a few companies that caught our eye for further consideration:

Graphenea
A world-leading producer of CVD graphene films and graphene oxide, supplying to research institutions and major industry players worldwide. Their online store is an excellent source and reference for retail-price monolayer graphene.

Graphenest
Graphenest is a company focused on producing sprayable and paintable coatings made with graphene. Their products are being used in inks, paints, coatings, and resins as alternatives to carbon fiber, carbon black, and other carbon-based materials. They are tailoring their resins for creating strong but lightweight frames and panels.

"Graphenest announces the lightest surfski kayak in the world. The lightest* surfski kayak in the World with 5.75 m [meter] size that weighs just 9.3 kgs [kilograms] was achieved by a joint venture between Graphenest and Sipre."

CrayoNano
What makes CrayoNano interesting is the development of nanowires grown on graphene, with the graphene serving as a transparent electrode. They claim "Nanowires on graphene enables critical improved internal quantum efficiency, operating lifetime, and reliability, especially for ultraviolet UVC wavelength lightsources. The result is UV LEDs with higher efficiency at significantly lower cost, resulting in a reduced cost performance ratio of more than a factor of 10. The cost performance ratio is defined as the price paid per watt of UVC light output." For reference, UVC wavelength light can be used to sterilize medical equipment, or used in industrial processes such as semiconductor fabrication and stereolithography. A similar application of graphene as a transparent electrode could be used to make more efficient solar panels and other photonics devices.

GrapheneTech
GrapheneTech is another company working to produce economical industrial precursors using graphene dispersed into liquids and powders. They bring us "Graphene nanoplatelet powder…produced using a proprietary "top down" green process based on mechanical exfoliation, without the use of any chemical or solvent." In other words, they are producing powders that consist of few-layer graphene chunks for use as a replacement to carbon fiber or in a wide range of applications such as composites, resins, lubricant oils, or anticorrosive paintings. And they specialize in supplying customized dispersions of graphene into other solvents or materials, for use as feedstock materials in other application processes.

Thermavance
Thermavance was originally named “Promethient” and was founded in 2012 by Charles Cauchy. They are producing thermoelectric cooling (TEC) devices for use in clothing or seat fabrics to move heat away from the skin of the wearer. Graphene is incorporated into the design for efficient thermal conduction to and from the tiny TEC heat-pumps. This technology could be applicable to many different cooling and active heat-pump use-cases.

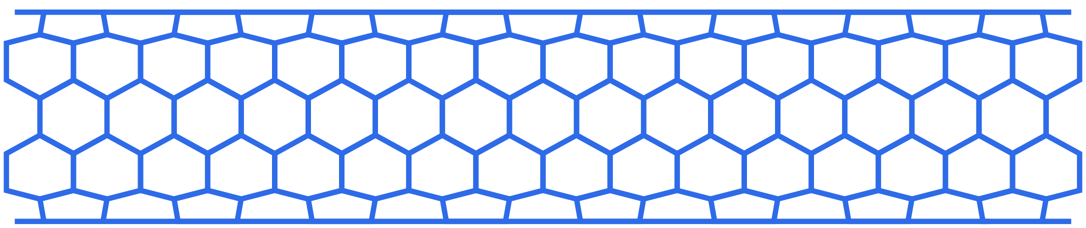
Log 9 Material
Log 9 Materials is a nanotechnology company specializing in incorporating Graphene to make practical products today. They have a number of existing offerings already: water and air filtration media, cigarette filters, and oil sorbent sheets for cleaning up petroleum spills. Their newest undertaking is using graphene membranes to improve upon an aluminum fuel cell technology developed by NASA in the 1990s. They see graphene as a powerful enabler for improving the mature products of yesterday for use in the world of tomorrow.

Long View — 5+ years away

Based on market forecasts, graphene and CNTs will be a growing market well into 2026 and beyond. Finding cheaper ways to produce and process graphene and finding more novel uses for the material will continue to drive growth in this market.

A material with such attractive physical properties will continue to inspire and attract research funding until it is fully commercialized. We can expect to see more wearable technology, advanced electronics using graphene rather than conventional conduction systems, and more flexible electronics technology (touchscreens, wearables, and circuits). For instance, wearable technologies (shirts, jackets, or other clothing with embedded circuitry) are likely to be a common and lucrative use of graphene in the future. Since graphene is conductive, flexible, and super strong for its size it is an ideal material for fabrics, or for wearable electronics that can be used within fabrics or flexible materials. It’s possible that our future clothing will be internet connected using this material, running on power harvested from the microwave energy that surround us 24/7 in the form of wifi and 5G broadcasts.

It has also been proposed to create incredibly strong rope or support cables from graphene or CNTs for such advanced constructions as balloon tethers. And a hallmark daydream for anyone excited about graphene or CNTs is the concept of the space elevator. A space elevator is a conceptual idea describing a cable attachment between the earth and an orbiting body with a lifting mechanism to shuttle people and supplies into space. Theoretically, carbon nanotubes or graphene being 100x stronger than steel could be strong enough to form such a cable. Or a wire of such high conductivity could theoretically be used for power generation or improved power transmission. However, to isolate, manipulate, and mass produce CNTs or graphene on this scale is outside the scope of current technology and would be far too expensive using today's techniques. We will need to see a huge deflation in the current price of production while also massively improving quality over anything we can create today. For now, these concepts remain enticing anchor points to a promising future.



Conclusion

Graphene and carbon nanotubes are undoubtedly the materials of the future. In their perfect form they are the strongest materials that are known to exist, with thermal conductivity among the highest of known materials, and even superconducting electrical properties. However, defects in the lattice structure cause significant decreases in these physical properties; and so quality and purity are of paramount importance. On top of this it is very difficult to make continuous sheets more than a couple of millimeters long, and even harder to wrangle this atomically thin layer into real-world applications. We recommend paying attention to companies that are developing methods to produce graphene and CNTs in larger sizes and for lower costs. And we will be tracking companies that show themselves to be successful at leveraging today's low-quality graphene flakes to improve existing products, or to develop new capabilities for applying this material in novel ways.