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Sector Review

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The Mining Investment Experts

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The Investors' Guide to Graphene

"Disruptive Technology that is Opening the Door to a New Age in Industry"



Possible applications for graphene

DNA sequencing: A super-thin membrane that can quickly read the DNA molecule one chemical letter at a time

◆ E-paper: Electronic display devices made with thin, flexible graphene may someday allow them to be folded

◆ **Batteries:** Electrical conductivity offers electrode material for high-performing capacity lithium batteries

 Futuristic cars: Composite materials strong enough to build high-pressure natural-gas tanks

 Deicing wings: Graphene embedded in resin to form heating circuits in a plane's wing

 Water desalination: Graphene's strength and permeability can block salt ions from seawater while simultaneously allowing water molecules to pass through rapidly

The Wall Street Journal

Source: Royal Swedish Academy of Sciences (images); Bluestone Global Tech (applications) **Investment Perspective**: Graphene has been talked about in glowing terms with scientists suggesting confidently that it is the key to the future of almost all materials. So revolutionary are its qualities that they even talk of the "graphene age". The most common reaction of investors is that it is "too good to be true", but beware of cynicism that may blind you to the opportunities

Its disruptive qualities are one consideration, but investors want to know what the path to commercialisation looks like, and how they are going to make money out of this new material. There is no road map, but some parallels can be drawn with the path taken by the internet with graphene being to materials what the internet has been to communications.

To start with the internet was about emails. A major breakthrough occurred with the release of the first web browser in 1994, which turned the web into a user friendly graphical interface communications environment. As computing power increased and technology convergence accelerated we have experienced the development of smart phones and wireless-based applications offeringing flexibility and commercial opportunity and massive productivity gains well beyond what was first contemplated.

Commercialisation of graphene is poised to follow a similar trajectory. Initially it is all about strength and flexibility, and enhancing the materials to which it is added. Improved performance will lead to generational changes and new opportunities as industry starts to appreciate what is possible and consumers demand their insatiable expectations for more, better, faster ... to be met.

On a higher level, the order of magnitude increase in conductivity that graphene promises will lead to continual advancements that will impact information transportation and communications, power storage, solar energy capture and many other applications that will be developed.

The graphene technologies are only just starting to leave the laboratory. Supply has been the constraining factor, but not the cost. While it is expensive, a tiny amount goes a long way, so that the benefits already outweigh the cost factor.

To date all the graphene in use is "made" via expensive laboratory processes. There is one exception though. Talga Resources has a very high-grade graphite orebody that enables direct production of graphene in a simple one step process, at nominal cost. This company could hold the key to rapid development of more graphene applications by solving the supply issue. Confirmation of this will depend upon pilot study results planned for 2015.

There are very few vehicles by which investors can participate in this new industry. It is too early to be dogmatic about which will be most successful, but it is not too early to be dipping your toe in the water. The advantages will lie with those who grow with the sector.

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Figure 1: Graphene-based nanocarbons. Source: A.K.Geim, K.S. Novoselov, Nature Materials, 6, (2007) 183-190

Introduction

There has never been a material talked about with more hyperbole than graphene. There has never been anything promoted with more potential to change our industrial world than graphene, so the understandable reaction of anyone being introduced to graphene is one of scepticism. This is not surprising. What is different with graphene is that it is being promoted by the scientific community more consistently and more vocally than by the entrepreneurial businessman.

In Australia, we are familiar with promoters of mining projects and opportunities. We are familiar with bioscience and technology promoters, and our experiences have given us reason to be sceptical about the promises being made for graphene. How can something be so revolutionary, so disruptive, and yet be tangible? That is the hurdle in perception facing the investor.

Graphene presents us with a generational change in technology, taking the field of nano-science one step further. Nano-science that has given us the capability of identifying and separating a material than can be combined with many other materials to achieve performance levels not otherwise considered possible. Graphene is that facilitator.

Graphene is not about mining and mining stocks, though some mining companies may have a window of opportunity to participate at the front end of the supply chain. It is not about technology and bioscience. Rather, it is a precursor to these fields. It empowers these fields ab initio, to aim for new horizons. It is an enabler.

How do stock market investors profit from this new horizon? How tangible is this horizon, today? Is the money to be made in the business of supplying graphene, in the development of new processes and compound materials, or in the value adding gains from employing graphene in the manufacturing process? Ultimately the gains will be made in the manufacturing sector but suppliers of the raw materials and the processes need to be proactive in encouraging manufacturers to take the adventurous steps. Those that can see the vision will seek to profit from each step in the value chain. They will realise the greatest success stories.

Australian investors who restrict themselves to ASX-listed companies will have limited access to opportunities given that the momentum is building overseas situations initially. Nevertheless, a few opportunities emerge. On the supply side, Talga Resources Limited (TLG) appears to be uniquely positioned to supply bulk graphene to the market. On the deployment of graphene products into applications, a new and highly motivated private company, NanoCarbon Pty Ltd, is working closely with the University of Wollongong (and other research groups) and with potential end users. Others will be out there flying under the radar, and even more haven't even been conceptualised yet.

This introductory paper on graphene has drawn information from many published articles and what limited reference material that is available. The intention is to communicate as simply as possible the many aspects of graphene and its possibilities so that investors may better understand the issues that come with the opportunities. The timeframe for effective commercialisation of graphene is uncertain, but each month brings re-enforcing news of significant developments in the graphene space.

Title	Link
Graphene on the One Show	https://www.youtube.com/embed/WFacA6OwCjA
Graphene Science - Mikael Fogelstrom - TEDx	https://www.youtube.com/watch?v=eh3dA8xnZ4
Graphene Supercapacitor	http://vimeo.com/51873011

Useful Links Describing Graphene and its Potential

1. The Amazing Properties of Graphene

Graphene is a natural material that is the basic building block of graphite, achieved when the thickness is reduced to less than 10 atoms. Though it was "discovered" in the 1940s, it took until 2004, before scientists figured out how to isolate it from graphite particles, using the simple "scotch tape" exfoliation method. Since then there has been tremendous interest in graphene with research scientists demonstrating its suitability for combination with a vast range of materials, to greatly enhance the performance of those materials. There has also been an explosion in the number of patents being taken out as industry has been preparing for the start of the new and deeply disruptive "graphene age". The table below lists the key properties of graphene that industry is seeking to employ.

Thinnest material	It is only one carbon atom in thickness i.e. only ~0.345 nm thick				
Stronger than steel	It is one of the hardest materials in the world, being harder than diamonds and 200x stronger than steel $(1,100\text{TPa}/125\text{ GPa})$ of the same thickness but it is very flexible and will not break. As an example, a graphene sheet 1 m ² in size could support a 4 kg cat, but that sheet would weigh only as much as the cat's whiskers (1).				
Optical properties	One atom thick layer sheets absorb ~2.3% visible light, making it transparent.				
Light and stretchable	It weighs only 0.77 milligrams per square meter and is stretchable up to 20% of its initial length. It has the largest volume to surface area ratio of any material.				
Impermeable	It is completely impermeable. Even helium atoms cannot pass through it.				
Thermal conductivity	It is a perfect thermal conductor (over 5,000 W/mK), being 5x the conductivity of graphite. It conducts heat in all directions i.e. it is an isotropic conductor.				
Electronic properties	It has the highest electrical current density (one million times that of copper) and the highest intrinsic mobility (100x that of silicon). It has a lower resistivity than any other know material, at room temperature.				
Chemical properties	It is an inert material and does not readily react with other atoms. However, it can "absorb" different atoms and molecules, leading to changes in its properties. It can be functionalised by several different chemical groups, resulting in different materials such as graphene oxide and fluorinated graphene.				
Other qualities	Self repairing - graphene can self-repair holes in its sheets when exposed to molecules containing carbon. Reactive - it is the most reactive form of carbon.				

2. Making Graphene Useable

One of the most challenging features of graphene is its size. Handling anything as small as a few atoms in thickness requires a new generation of material handling expertise. Further, graphene must be in a format that enables its application i.e. it needs to be functionalised.

Graphene Functionalisation

Functionalising a material also involves adding functional groups on the surface of the material to achieve desired surface properties (such as water repellant coating or changing the colour). In effect graphene is 'slippery' and cannot impart it's properties to surrounding materials unless functionalised with additional bonds.

Functionalising graphene makes it useable in a wide range of applications. It also enables the dispersion of graphene in solutions and enables solution-based production processes.

Functionalising can be achieved in two ways. The simplest way is the covalent bonding of organic functional groups. In the case of polymers, referred to below, the polymers provide the basic mechanical and morphological characteristics, while the graphene addends electrical conductivity and chemical reactivity to optimise the end material.

A second functionalising method is the non-covalent type. This enables the dispersion of graphite in solvents and creates monolayer graphene sheets, avoiding stacking of the graphene.

Graphene Composites

One method of functionalising graphene is to combine it with other materials to create composites, or hybrid materials, thereby capturing its benefits in a material that can be further processed and utilised. Graphene can be an active "passenger" when combined with metals, polymers and ceramics. An example of a composite material is a silicongraphene lithium-ion battery anode. This reportedly increases energy density by 3x and anode capacity by 4x. It is being commercialised by CalBattery.

In another example, a graphene sheet on top of a molybdenum disulphide sheet is said to offer photovoltaic cells that are 1,000x more efficient than silicon-based panels.

Graphene Doping

Doping is a process whereby you introduce "impurities" into a pure material, usually to change the electric properties. While the introduction of impurities may seem unusual, in the case of graphene, it is necessary to introduce a bandgap so that graphene can be used for transistors. While having no bandgap is one of the reasons why graphene is an excellent conductor, modern electronic componentry is based on semiconductors that use bandgaps. In effect graphene has to be "dumbed down" to meet the current standards.

Graphene Substrates

Graphene can be laid on a substrate to overcome the problem with handling the ultra-thin material. You know how difficult it can be in handling cling-wrap. Well, the same issues apply to the handling of a sheet of graphene.

Graphene sheets can be made on substrates such as silicon, copper, nickel and flexible polymers, to name some examples. This graphene can be lifted from the substrate in the final application stage. However the use of substrates can induce defects in the graphene, via impurities or tears, and these are substantial problems for some methods of graphene to overcome, particularly CVD.



Figure 2: Functionalisation of Graphene: Covalent and Non-Covalent Approaches, Derivatives and Applications. Source: R. White. Towards the Commercialisation of Sensors Based on Functionalised Inks. Paper presented at Manchester Conference 2014.

3. Potential Applications of Graphene

Graphene is of interest not because of what it can do on its own, but because of what it can do when combined with other materials. Industry is on a steep learning curve as research is finding more and more applications for graphene. The following applications provide examples as opposed to an exhaustive list.

Screens and displays

An early application of graphene will be in the field of conductive wires and transparent touch screens. Most smart phone and tablet touch screens use indium tin oxide (ITO), but ITO is in scarce supply and is brittle. A graphene-based product offers the perfect solution to supply and flexibility.

Graphene could also be used to produce a display backplane, the driver used to control which pixels are on and off in a display.



Figure 3. Flexible screen using graphene

Conductive inks

One of the applications with the biggest potential for graphene use is conductive printing and packaging. Using graphene based conductive inks means that the printed item can be rubbed, flexed, creased, or dropped without damage, and will be stable against temperature, humidity, and corrosion. This also means that they will not oxidise and can withstand handling without flaking off.

Most conductive inks today are made from either silver or carbon-based materials. Current applications include RFID tags, heating elements (in car windscreens), biosensors, computer keyboards and touch screens.

Vorbeck Materials is marketing a range of graphenebased conductive inks. Using this ink, in 2012, MWT Packing announced the Siren Technology security smart packaging, used to identify items in retail stores (electronic article surveillance). Each tag has a fully integrated conductive circuit made from graphene. These tags offer 10x the conductivity of silver inks and are totally flexible even when crumpled. A second company to offer graphene-based inks was Haydale, in the UK.

In 2012, the 3D printing market was valued at around US\$2bn. Analysts at Credit Suisse have estimated that this could grow to US\$20bn by 2020, representing annual growth rates in the order of 20-30% p.a. Adding graphene to the polymers used in 3D printing improves mechanical strength, electrical and thermal conductivities.

Composite materials

Graphene can enhance the mechanical, thermal and electrical properties of a vast range of composite materials. As examples, graphene can be added to rubber and plastics to make them lighter, stronger, more flexible and conductive. A UK project (called NanoSynth) aims to make graphene-filled epoxy resins that offer better strength, stiffness, toughness, electrical conductivity and thermal performance. The world market for resins is estimated at \$15bn p.a.

Coatings and paints

Graphene is impermeable and hydrophobic, making it suitable for coatings that protect surfaces from oxygen, moisture, gases and other environmental hazards. It can be applied to metals to prevent corrosion, thereby substituting for zinc. It can provide for much lighter gas tanks. It has been applied to anti-fogging coating systems for glass.

Monash University has demonstrated graphene's potential as an anti-corrosive coating material. A thin graphene film can make copper 100x more resistant to corrosion than uncoated copper.

Researchers at the Shenyang National Laboratory for Material Sciences and the Rensselaer Polytechnic Institute have shown that graphene can be used to create a superhydrophobic coating material.

Electronics

As the world's most conductive material it has potential uses in the electronics business. Some people say it will be the next "silicon". Modifications will be needed to overcome the lack of natural bandgap but that seems to be just a matter of time. Negative resistance is being researched as an alternative to a bandgap, focusing on the counterintuitive phenomenon in which a current entering a material causes voltage across it to drop.

A new flash memory cell is being designed in Switzerland, made of graphene and molybdenum. An ultra-fast bi-stable graphene transistor is being researched in the UK for application in medical imaging and security devices. Combination of graphene with silicon-based electronics provides a heat dissipation ability that can reduce hotspot temperatures by 25%.

Korean researchers have produced a transparent, lightweight graphene-based audio speaker made of PVDF film sandwiched between two graphene electrodes. The University of California has developed speakers with multi-layer graphene diaphragm with excellent performance measures

Energy generation

As graphene is highly efficient in converting light to energy, and it is conductive, it is being tested in a new range of solar cells. Researchers claim that they can be 1,000x more efficient, for the same weight, than silicon products. This opens the path to its application in coatings of solar cells as well as in the panels.

Energy storage and lithium ion batteries

Graphene could be used in Li-Ion battery electrodes, leading to faster and more dense charging properties ⁽³⁾. Already XG Sciences has launched a new graphene nanoplatelet anode material that has 4x the capacity of conventional anodes. Battery manufacturers are doing follow-up tests.

California Lithium Battery claims to have made a silicon-graphene composite anode material (called GEN₃) that shows unrivalled performance characteristics. SiNode has developed its own version in a layered structure that it claims offers 10x higher battery capacity and a tenfold decrease in charging time when compared with current technology. Numerous other parties are conducting research.

Fuel cells

Graphene could be used as a catalyst in fuels cells, replacing the much more expensive platinum. Researchers at the UD DOE Brookhaven National Laboratory have made a new catalyst from graphene, molybdenum and soybeans. Brown University has made one from cobalt and graphene that outperforms platinum, reducing oxygen faster and degrading more slowly.

In addition, graphene being impermeable and strong, would suit manufacture of the tasks required for hydrogen to be carried for fuel cell powered vehicles. Thus it can play a role in both major technologies for next generation low emission vehicles and not be stranded by a technology fork in the road.

Membranes

Graphene's advantage in membranes is that it is strong, flexible and impermeable. By cutting holes in graphene sheets you can create a purpose specific selective barrier membrane. Lockheed Martin has created *Perforene* for water desalination, allowing water but not salt to pass through. As graphene is 500x thinner than current water desalination membranes, the energy required to push water through is very low, requiring only 1% of energy currently needed. American Water Recycling is working on a membrane to separate grease from water. Firmus SAM is another company conducting research into membranes.

High performance sensors

Graphene has shown its suitability for a wide range of sensors, detecting gases, environmental contaminants, for water quality, temperature, humidity and light. It can facilitate much smaller, more sensitive and more flexible sensors than those currently available.

For example it can be used in diagnostics for detection of glucose, cholesterol, haemoglobin and cancer cells. It can be used as a pH sensor for detection of contaminants, detection of pharmaceutical compounds and as a gas sensor.

Photonics/optics

Research by Nokia has shown graphene-based photodetectors will outperform CMOS detectors in low light conditions, as well as being thinner and cheaper to produce. The University of Exeter has developed metal-free detectors only a few atoms in size that can be woven into textures. Nanyang Technology University has developed a new camera sensor that is 1,000x more sensitive than current sensors, using less than 10% of the energy now needed. French and UK researchers have demonstrated laser devices that emit light over the entire spectrum of visible light.

A graphene optical switch (modulator) has been developed in the UK which is 100x faster than existing switches (measuring in picoseconds) which can lead to faster communications.

Medicine and biomedical devices

Graphene can be used in fighting bacteria. It can slice bacteria like a knife. It can be used for photo-thermal antibacterial therapy and can be used to build bacterial sensors.

Graphene can be used in artificial muscles, drug delivery, neural stem cell research, neural protheses, cholesterol removal, MRI agents and more. It can be used for DNA sequencing.

A joint venture has been formed between Grafoid and ProScan Rx Pharma to develop a graphene-based platform for precise targeting and thermal eradication of solid cancer tumours.

Its ability to conduct electrical signals in the harsh ionic solutions found in the human body mean that it can interface with neutrons and other cells that communicate by nerve impulse. Graphene can provide the pathways for electrical impulses that control artificial muscle, made out of polymers, in artificial limbs. The flexibility of graphene enables it to be wrapped around delicate tissues like no other alternative. Research is continuing to demonstrate potential for a new generation of neural devices.

Lubricants

Graphene mechanical properties make it an excellent steel lubricant, dramatically reducing the amount of wear and friction in sliding steel surfaces. It prevents oxidation of steel surfaces at these contact interfaces and it lasts longer than current lubricants. Graphene NanoChem in the UK is developing lubricants for the oil and gas sector.

Body armour

Researchers at the University of Massachusetts have shown that graphene may be extremely efficient in preventing bullet penetration. Firing a micron-sized glass bullet into 10-100 sheets of graphene at 3,000m per second (3x the speed of an M16 bullet), it performed twice as well as kevlar and endured 10x the kinetic energy that steel can.

Keeping glass ice-free

Rice University scientists have demonstrated that atom-thick graphene nanotubes sprayed or painted on sensitive military radar domes will keep the glass icefree through the transmission of heat and electricity. This is more efficient and cost effective than a bulky and energy-hungry metal oxide framework. Consistency of the layer is important and it needs to be kept between 50 and 200 nanometers thick to avoid hot spots that may absorb the radar signal and develop holes in the film. This application can be extended to automotive glass applications as an invisible de-icer and on windows of skyscrapers, whilst being transparent to radio frequencies and WiFi signals. Metal films in windows currently obstruct signals.

Oilfield chemicals and enhanced recovery

Graphene nanomaterials could be used as emulsion stabilisers, wellbore strength improvers, drag reduction agents and barriers to fluid permeation for drilling and completion fluids. They could form the basis for "smart fluids" for drilling operations that actively;

- · reduce formation damage,
- produce thinner filter cakes,
- · reduce fluid loss into rock formation pores,
- preserve original rock formation pressure,
- · reduce wear on drilling tools and
- reduce the likelihood of drill stem hydraulic adhesion or stuck pipe.

Enhanced oil recovery research using graphene materials and single walled nanocarbon materials has shown potential to react with and modify the oil properties to increase oil mobilisation, and therefore encourage higher production of oil, particularly from more mature fields.

UK company Graphene Nanochem already has a substantial business supplying graphene-liquids to the drilling market, and has sales to major petro-conglomerates such as Shell.



Figure 4: Graphene Ink. Source: Antonio Pàez Duenas. Benchmarking the Effects of Substrates Upon Graphene Properties. Paper presented at Manchester Graphene Conference, June 2014.



4. Methods of Making Graphene

There are two approaches to making graphene, being top-down and bottom-up. Top-down involves starting with graphite or other materials and using exfoliation (peeling) or reduction methods from graphene oxide. Bottom-up involves synthesis of carbon in some form to produce graphene atom by atom.

There are dozens of possible methods of making graphene, but there is yet to be one that has proved itself suitable to mass production, particularly of graphene sheets.

Methods of Making Graphene

Graphene can be manufactured from many different carbon sources, not just from graphite, be it natural or synthetic. The method employed has implications for quality and levels of defects, which in turn influences the applications to which the graphene is suited. The currently recognised methods include;

- · carbon vapour deposition (CVD)
- carbon dioxide reduction
- epitaxial growth on silicon carbides and metal substrates
- · graphite oxide reduction
- · graphite sonication
- CNT
- mechanical exfoliation

Carbon Vapour Deposition

CVD does not process graphite ore, but it uses various gases to achieve a coating of graphene on a substrate (usually copper) through a reduction process. It is currently the most popular method of producing graphene. While the quality is imperfect, with uniformity being an issue, it can provide large area graphene. This is an example of bottom-up production but it is not scaleable.

Exfoliation Methods

1) Micro-Mechanical Exfoliation

This involves splitting single layers from multi-layered graphite. Achieving single layers typically involves multiple exfoliation steps, each producing a slice with a few layers until only one remains. The "scotch tape" method is an example.

2) Direct Exfoliation in Organosilanes

This process involves the separation and collection of graphene particles via exfoliation, directly into a colloidal suspension within a media for commercial use, without having to produce graphene in a solid state. Thereby it avoids the possibility of the graphene re-aggregating. Graphene produced through this method could be used for a wide range of applications including spray coating, vacuum filtration or mixing with polymers.

Selection of the appropriate dispersion media (organosilanes) is a key consideration here, affecting the level of concentration that can be achieved and usability of the graphene product. Test work has shown that production of multi-layer graphene (2-5 layers) is readily achievable.



Figure 5: TopDown/BottomUp. Source: Kitty Cha, "Standardisation of Supply", paper presented at Manchester Graphene Conference, June 2014.

3) Chemical Exfoliation - Graphite Oxide Reduction

Chemical exfoliation, based on the Hummer's Method, oxidises graphite to produce thin layers of graphite oxide (GO), which can be chemically or thermally reduced to produce potentially low cost graphene. However, the oxidation process severely damages the honeycomb lattices of graphene.

4) Liquid Phase Exfoliation

This method uses sonication methods (sound energy) which results in small graphene sheets. Transparent conducting film made from this graphene suffers from large amounts of intersheet junctions, reducing transparency to below 90% with high resistance of 5,000 to 8,000 Ω /sq.

5) Electrochemical Exfoliation

This can produce larger sheets, up to $\mu \text{m},$ with fewer intersheet junctions.

Molecular Bean Epitaxy (MBE)

This refers to the deposition of a crystalline overlay on a crystalline substrate. It is similar to CVD in that you heat elements in a high vacuum chamber until they slowly begin to sublime. The gaseous elements condense on the substrate. It operates at half the temperature of CVD, at around 300 degrees C. Examples are;

- a) Sonication applying a layer of graphite oxide film to a DVD and burning it in a DVD writer produced a thin graphene film
- b) Silicon carbide epitaxy heating silicon carbide to high temperatures under low pressure reduces it to graphene
- c) Metal substrate epitaxy single layer graphene can grow on a copper substrate.

Keeping graphene disaggregated is desirable

Having gone to great lengths to take carbonaceous feedstock down to the sub-nano particle size, a practical challenge is to keep it at this size long enough to enable it to be combined with the end use material with maximum efficiency. The very quality that makes it so applicable to many materials - the urge to combine and create stable connections - means that it will seek to recombine with itself and clump together prematurely, thereby limiting the qualities needed for commercial benefit.

One method of keeping the graphene particles in a dispersed state is to store it in surfactants (detergents) that inhibit premature clumping. However, this can coat particles and result in less effective utilisation rates

Figure 6: Steps to Graphene. Source: Talga Resources

Talga's one step process

Having listed the various methods of making graphene in the laboratory, and perhaps confusing some of you with complicated science, there appears to be a refreshingly simple alternative offered by Talga Resource due to unique mineralogy and metallurgy. This could result in bulk tonnages at a fraction of the cost of all other known methods. The merits of this process will be discussed in a separate. Talga specific research note, but for the time being, this diagram below demonstrates its simplicity.





5. Not All Graphene is Equal



Graphite Expanded Graphite Graphite Nanoplatelet Few-layer Graphene Graphene-Like

Figure 8: Images of Graphite and Graphene Types. Source: Kitty Cha, "Standardisation of Supply", paper presented at Manchester Graphene Conference, June 2014.

Sources of Differences

Just as the TV advertisement ran a few years ago said, "Oils Ain't Oils", "Graphene Ain't Graphene". Differences in quality will arise from;

- the method of production,
- the source of the feedstock and
- the method used to stabilise the product.

The theoretically perfect graphene is an hexagonal, honeycomb carbon lattice with not a single atom out of place. In practice the carbon lattice will be strained by defects, it will be polluted by 5 or 7 member rings, its edges will be raged and it will be associated with a surfactant or a substrate that could interfere with its properties. The extent to which these imperfections matter depend upon the application for which it is required. The fewer steps and chemicals involved in making the graphene, the more pristine the end product is likely to be.

Different Types of Graphene

Graphene comes in a number of different forms, from different processes, with a variety of uses. Basic types of graphene include;

- Single sheet graphene. This is the purest form for uses in high frequency electronics and similar applications. It is a single-atom-thick sheet of hexagonally arranged, bonded carbon atoms either freely suspended or adhered to a substrate. Different qualities are observed when extended to two or three layers and the cost of production becomes progressively cheaper
- Few-layer (FLG) & multi-layer graphene (MLG). This is a 2D, sheet-like material either free-standing or a substrate-bound coating of between two and ten layers used for composite materials and mechanical reinforcement.
- Graphene flakes (GNFs). Production of graphene flakes, usually in solution, is easier than making graphene sheets. They can be made from single layer flakes that are stacked and can be made in different shapes, providing a degree of engineering freedom not available with sheets. However, the randomness with which they are made possess issues with the engineering.

 Graphene nanoplatelets (GODs) A nanoplatelet is a small round diskissues found with GNF

Investors' G

BASE

 Graphene oxide (G graphite, hydrogen a graphene that has t oxidation and exfoliation applications as a bulk can be reduced to m



graphene from rGo contains chemical and structural defects. Nevertheless, it can be suitable for transparent conductive films and composite paper-like materials.

 Reduced graphene oxide (rGO). This is GO that has been reductively processed by chemical, thermal or microbial methods to reduce its oxygen content, for uses such as in conductive inks.

Surfactant-Free Graphene

The University of Wollongong has developed a patented process whereby it can use synthetic graphite to produce graphene in dispersion without surfactants. This is believed to involve fewer manufacturing steps than competing processes and it involves less complexity when integrating into manufacturing processes. The primary benefits are described as:

- less exposure to supply chain risk from third party chemical suppliers,
- potentially fewer issues with disposal,
- less dependency on processes requiring toxic chemicals and
- better suitability for coatings and composite materials where there is a high need for purity.

6. Considering Graphene Supply

Industries emerge and grow over time to meet a need or a demand. Supply responds when there is an expectation that there is a profit to be made, but that supply must respond to the requirements of the buyers, both in terms of quantity and quality, at a price that enables the buyers to make a profit. That is the reason why co-ordination and co-operation with buyers should be one of the most important focuses of existing and prospective suppliers, with the objective of converting science into products.

The Size of the Market

Reliable information on the market size is not easy to obtain. One authority has suggested that the market was worth \$10m in 2012. Conservative estimates suggest the market might only be \$100-200m by 2018. Optimists suggest it will be \$1bn by 2023. Pick a number.

The flaw with talking about a market value is that it depends upon your pricing assumptions. A more useful number would be tonnes produced. On this front the production for 2013 has been estimated at 250 tonnes with an expectation of increasing to 800-1,000 tonnes by 2015, but this seems to be based on purported capacity without verifiable data on actual production and sales.

The largest planned capacity over the period under review is that of Ningo Morsh, with target capacity of 300 tpa. XG Sciences has disclosed a capacity of 80 tpa of graphene nanoplatelets and graphene sheets, supplying up to 600 customers.

In what looks like the elephant in the room, Talga Resources (TLG) has released a scoping study (October 2014) that targets graphene production of 1,000 tpa from it Vittangi Project in Sweden. Significantly, this is intended to be produced as a coproduct from a single step whole-of-ore treatment process, from an ultra high-grade graphite orebody. While this may seem an overwhelming figure on consumption levels today, it places the Company in a dominating, highly competitive supply position for a growing market. It expects low cost of production could facilitate more rapid commercialisation of graphene through the supply of a range of products at lower prices than currently being experienced.

Scale is Still an Issue

So far the challenge has been to manufacture graphene in the first instance. The high price of graphene is a function of the processes by which it is currently manufactured. Whilst some suppliers insist that scalability is not a restrictive issue, we are yet to see volumes come onto the markets to evidence this opinion. Each process will have its own scalability issues that relate to material handling, costs and qualities.

There is one exception, that of Talga Resources. Talga presents a potentially game changing source of bulk supply of graphene, one that could enable a real advancement of graphene applications. Research test work has shown that it can supply high quality natural graphene from a graphitic orebody, without prohibitive capital expenditure. The simplicity of the process, with the resultant low cost of production, could be the gateway for the supply of bulk graphene for industry.

Bulk Supply Considerations

Notwithstanding the possibilities for bulk supply of graphene from Talga Resources, thought still needs to be given to the optimum business model for that company and other suppliers of graphene, particularly in the early stages of commercialisation where bulk supply might not needed.

We need to consider whether bulk supply necessarily means diminished quality and whether this will have a significant impact on pricing. Perhaps pristine quality is not required in bulk markets, and consumers may be happy with a tradeoff between quality, cost, and ease of handling.

Whatever the answer to these questions, the demand for bulk supply is not immediately apparent. It will develop overtime.



Figure 9: Graphite ore sample from which graphene can be produced in bulk. Source: Talga Resources Ltd paper presented at Manchester Graphene Conference, June 2014.

Just in Time delivery

A reasonable business model for today may be "just in time supply", with small, modular graphene plants that can be installed near to, or on sites of consumers. These could be containerised units capable of supplying up to 5 tpa of graphene within an optimised supply chain, using a variety of production methods.

Vertical Integration Models

Graphene is a new material coming into a market that is also new. The graphene industry needs to be populated from top to bottom, with suppliers, product refiners, marketers, distributers and end users. What section of the chain will be most profitable for participant? Is it all about supplying, trading it or using the material? What opportunity exists for suppliers to promote the end demand? How long will it take to commoditise the supply, if that is possible with the variety of quality types that may be available?

Being such an embryonic market the opportunity exists for parties from either end of the chain to be expansive in their ambitions, before players are pigeon-holed in any particular strata of the value chain.

Measuring Graphene Quality

Three basic methods are used to view and analyse graphene material.

 Scanning Electron Microscopy (SEM). The microscope sends a focused beam of electrons to interact with the sample, creating signals that can be detected. Resolution better than one nanometer can be achieved.

- Transmission Electron Microscopy (TEM). This also uses a beam of electrons, but these are passed through the sample.
- Atomic Force Microscopy (AFM). A mechanical probe touches the sample to gather information. It can also gather electrical information. It can measure contact force, chemical bonding, electrostatic forces and magnetic forces.

Another method that assesses quality, Raman spectroscopy, uses a laser light to interact with molecular vibrations in a sample to gather vibrational modes. It takes advantage of Raman scattering (the inelastic scattering of photon) to detect low-frequency modes to identify molecules and changes in chemical bonding. Raman spectroscopy is accepted as a good measure of graphene quality, being complementary to infrared absorption spectroscopy.

Standards Regime is Required

One of the first steps that the graphene industry needs to undertake is the establishment of a standards regime so that customers can have confidence in what they are buying. This could come from;

- an industry leader defining quality standards and applying brand names that guarantee the quality, or
- it may come from an industry body that proscribes standards that are acceptable, and are universally adopted or
- the consumers may demand certain standards that supplier agrees to conform with.



Figure 10: Example of a Raman spectrography chart.

7. Graphene Pricing

Extraordinarily expensive today

Getting a firm handle on the price of graphene today is not easy due to the small volumes available to the market. Indicative pricing from one supplier is \$300/gm for single layer graphene oxide. Another one has quoted 99 Euro for 250 mL of graphene oxide, but neither of these have implications for volume.

Expect movements in prices - downwards

The first point to note is that whatever price you are seeing quoted today, it will not be the price at which commercial quantities will be made available for commercial applications. Almost all graphene production to date has been from small facilities that have been supplying product for research and testing purposes. Calculating the cost of production has not been on the agenda up until now. The discussion has been about what graphene can do as opposed to what it costs. That will have to change.

What is the appropriate pricing model?

New commercial scale producers will need to carefully consider what pricing model is most appropriate for the type of graphene they will be supplying. It is unlikely to be a "cost plus" calculation in the first instance as that would eliminate any cost advantage that individual companies may possess in an opaque market.

The other end of the pricing spectrum is what the buyers are willing pay. To maximise profits the new producers will need to have an intimate understanding of the cost profiles of customers. They will need to negotiate a price that enables the buyer to capture an improvement in its production economics. They will need to meet stringent quality specifications, consistently, to maintain the price, and they will need to ensure regular and timely supply.

Demand is a short term constraint

Any new producer that is supplying the market with graphene as its primary product will be constrained by the depth of demand in the early stages of the commercialisation of graphene-enhanced products. That could compromise economies of scale on the supply side, assuming that this is a relevant concept with graphene. This will be of particular concern to producers of more capital intensive sources of graphene.

On the other hand, where graphene is a co-product of an operation, such as from the proposed graphite mine of Talga Resources, economics of graphene production and scale are only collateral considerations.

Likelihood of commoditisation

While scarcity factors dominate graphene pricing today, the further down the commercialisation path the industry travels the more likely it is that graphene pricing will be commoditised. There will be a number of preconditions though.

- there will need to be a number of commercial suppliers that result in a competitive market
- there will need to be a credible authentication and standards regime in force that facilitates comparison of specifications and quality of graphene products

In the absence of these parameters we are likely to see a fragmented and secretive market, as it is now, where transactions between buyers and sellers will be highly confidential as to pricing and quality. There will be a significant first mover advantage where that gives access to market information that would not be readily available to new entrants into the supply chain.

The industry is open to disruption from sources of low cost graphene where these could shift the cost curve and make it difficult for pre-existing suppliers. A candidate for this possibility is Talga Resources with its one-step production process direct from the ore. It is possible that this opportunity could give Talga a dominant market position as it could employ predatory pricing strategies.



Figure 11: Qualities and Prices from Different Methods. Source: Antonio Pàez Dueñas, "Benchmarking the Effects of Substrates Upon Graphene Propertied", paper presented at Manchester Graphene Conference, June 2014.

8. The Road to Commercialisation

Graphene is a new material that promises to be as innovative in the field of materials as the internet has been to communications. The commentary has been so enthusiastic that is has inevitably led to many people saying it is too good to be true. The sceptics say "come back in 10 years".

Looking back at the growth of the internet

If you go back to the early stages of the internet, say in the mid 1990s, we were all arranging to get online for emails and surfing the internet. Now we can't imagine life without it.

We saw the enthusiasm for web technology explode around the turn of the century with many businesses embracing internet-based commercial solutions. In the decade since then we have seen the emergence of wireless technology and the rise of smart phones as the next generation of devices making commerce much more efficient.

What was the best entry point over the last 20 years? There is no single answer as all along there have been many opportunities. The earlier you became involved the more opportunities you would have seen, and the better you will understand the technology. It is this understanding that keeps opening the doors along the evolutionary path.

Graphene is building on graphite research

Graphene was first mentioned as a theoretical substance in 1947, but physicists thought it would be impossible to isolate such thin, unstable crystalline sheets. The problem was solved in 2004, by two scientists in Manchester.

Since its discovery in 2004, improved understanding of graphene's mechanical, thermal, optical and conductive properties have broadened the scope for commercial applications. This is in turn leading to improvements in the graphene production processes as suppliers seek to provide quality suitable to the new applications. Research into graphene applications is the logical extension of research into fullerines and carbon nanotubes, which has been ongoing since the 1980s and 1990s. Each step is leading to superior products.

Commercialisation issues for graphene

The advancement of new nanomaterials for commercial products relies on the evolution of a new paradigm known as "*molecular precision manufacturing*" (MPM). It requires new tools, new standards, new protocols and new processes (TSPPs) to foster the commercialisation of nanomaterials and enable us to take advantage of the extraordinary properties of nanomaterials.

The objective of the TSPPs is to ensure that the mechanical properties of the new products can be predictable and reliable. Repeatability is essential to commercialisation.

The discovery and development of processes for graphene production are only the initial steps. The graphene needs to be purified and made free of catalysts used in the production process. Functionalising of graphene requires its dispersion, and this can involve the use of acids that involve higher costs, vicious waste streams and structural degradation. Optimisation of the functionalising step is priority.

Characterisation of graphene and other nanomaterials is essential for quality control and the development of standards. It involves the use of sophisticated metrology tools that aid the identification of the material being worked, as the human eye is not capable of precise identification at the nano-scale. The scanning probe microscope (SPM) is a useful tool but it has limited powers of penetration. Ultrasonic force microscope (UFM) is a variation of the atomic force microscope (AFM), that can overcome limitations of the SPM.

The term graphene covers a family of different materials, including several-layer flakes, powders, liquid dispersions and graphene oxide. Properties and potential applications will differ depending upon the material being used, and that material will have to be correctly identified.

The functionalising process, which is essential for commercialisation, involves the consistent and uniform dispersion of graphene in another material in order to realise the improved properties of the material graphemes being bonded with. Again, care must be taken that the functionalising method does not damage the graphene particles. Functionalising must be tailored to meet the needs of the customer.

The key to successful commercialisation is close collaboration amongst suppliers and producers. Just *"having the goods"* is not enough on its own.

Approval processes need to be overcome

Having a great idea or a superior product is only the start of the journey. Depending on what it is, and where it is proposed to be employed, there could be a myriad of approval processes and regulatory requirements to be overcome.

The most rapid commercialisation will occur in consumer products where there is a constant search for better materials, and where the life of those products can be measured in less than three years so there is constant refreshment of demand. Coatings, paints and conductive inks can be rapidly commercialised compared with the applications that require collateral engineering breakthroughs. Bulk uses in building products that require greater certification, industry and government approvals will take the longest time frames.

Graphene patents

Analysis of inventions involving the manufacture or application of graphene shows dramatic growth over the last decade from just 33 inventions described in published patents in 2004 to over 5,000 inventions last year



Figure 11: Graph of patent applications identified by county and application. Source: Reuters.

In a presentation given by MTI Ventures at the Manchester Graphene Conference in 2014, Dr Mark Rahn said that he was tracking 145 companies, globally, that had public disclosed interests in graphene. He cautioned that the list was not exhaustive, but it is representative of the spread of interest. Figure 12 provides a breakdown by activity.



9. Companies in the Graphene Space - A Sample

Company	Listing Location	Mkt Cap	Main Focus
Angstrom Materials	Unilsted Ohio	n/a	 produces nano graphene platelets working with customers to design graphene solutions www.angstronmaterials.com
Applied Graphene Materials plc (AGM)	AIM	£34m	 £11m in IPO, November 2014 spun out of Durham University, based in Cleveland claims it can mass produce graphene powder using carbon atoms sourced from ethanol www.appliedgraphenematerials.com
Aixtron SE	NASDAQ Germany	E800m	 involved in semiconductors, lighting, photovoltaics working with graphene, CNTs and CNWs in fields of transistors, electronic, energy storage and sensors www.aixtron.com
CVD Equipment Corp (CVV)	NASDAQ	U\$61m	 produces specialised equipment for graphene production supplies coatings of graphene products by CVD process
Graphenea SA	Unlisted Spain	n/a	 exports graphene materials to 40 countries www.graphenea.com
Graphene Square Inc.	South Korea	n/a	 provides CVD-grown graphene products and CVD systems aims to be the leading company in the production of graphene film based touch screen panel (TSP) for electronics founded with Seoul National University www.graphenesq.com
Graphensic AB	Sweden	n/a	 produces epitaxial graphene on silicon carbide also supplies monolayer and bilayer graphene www.graphensic.com
Grafoid Inc.	Private	n/a	 promoting its brand name product, MesoGraf which is exfoliated graphene said to come from raw graphite ore where grade exceeds 15%. Closer analysis suggests that the ore, sourced from Focus Metals' Lac Knife deposit, needs to pre-concentrated to form a slurry first. It is then treated in a chemically complex electrolyte with temperature and gas impositions, prior to the electrochemical exfoliation step. Thus it is more than a one step process. privately held company
Graftech International (GTI.NYSE)	NY	US\$1bn	 manufactures graphite related products and holds >200 patents relating to graphed www.graphtech.com
Graphene 3D Lab Inc (GGG.TSXV)	Toronto New York	C\$52m	 working with graphene and 3D printing of batteries www.graphene3dlab.com
Graphene Nanochem (GRPH.AIM)	AIM	£43m	 raised \$50m to develop graphene enhanced products for the oil services field. Also dealing with nano fluids, polymers and inks www.graphenenanochem.com
Lomiko Metals Inc. (LMR.V)	TSX-Venture	C\$12m	 option to buy 49% of Graphene Labs, which has a pilot scale graphene production facility www.lomiko.com
Talga Resources Ltd	ASX	A\$40m	 can produce bulk graphene at nominal cost from the highest grade, JORC compliant graphite ore (25%), using non-mechanical exfoliation method www.talgaresources.com

Footnotes and References

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