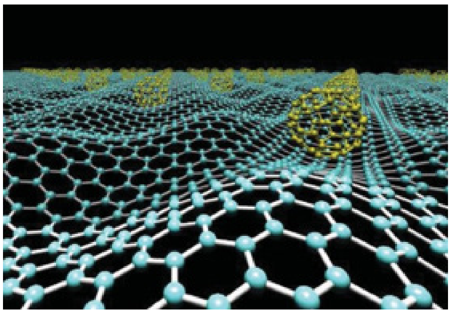
Graphene Technology and Commercialization



Graphene composites will change the way we live (ourtesy of Prof. Federico Rosei, small 2013, DOI: 10.1002/smll.201301982)

Introduction

"Graphene: The Magic of Flat Carbon" was the title of a series of lectures by pioneers of Graphene science, Prof. Andre K. Geim and Prof. Konstantin S. Novoselov from University of Manchester who were recognised by the Nobel Prize in Physics in 2010. Graphene is a single, one atomic thick layer of the common mineral graphite and is the first example of a truly two-dimensional material. There is no doubt that Graphene is a magic material. Graphene is transparent, extremely flexible yet still rigid, and is the best electrical and thermal conductor ever known. It could be used to create products that are lighter, more robust, transparent, flexible and stretchable such as electronic paper, bendable personal communication devices, and more energy-efficient airplanes. Graphene based batteries could enable electric cars to drive longer and smart phones to charge faster. It filters salt, heavy metals, and oil from water and enables more efficient solar energy conversion. Graphene coatings prevent steel and aluminium from rusting and, in the longer term, promise to give rise to new computational paradigms and revolutionary medical applications, including artificial retinas and brain electrodes. What sets Graphene apart is its remarkable combination of superior properties which will enable a multitude of applications in different fields and increasingly begin to impact our daily lives over the next 10 years.

Early Graphene results were limited to academic research but increasingly industry giants are in the running too. IBM has produced several electronic component prototypes, while Samsung has produced a flat screen (70cm in the diagonal) with Graphene electrodes. The tennis racket maker Head used tennis champions Novak Djokovic and Maria Sharapova to promote rackets made with Graphene. BASF and Daimler-Benz have designed a concept electric car called Smart Forvision incorporating Graphene in a conductive e-textile. In 2012, BASF produced a report on the future of Graphene, forecasting a market worth \$1.5bn in 2015 and growing to \$7.5bn in 2025; this outlook significantly exceeded previous Graphene market forecasts.

Challenges

In order for Graphene to fulfil its potential, three things are required:

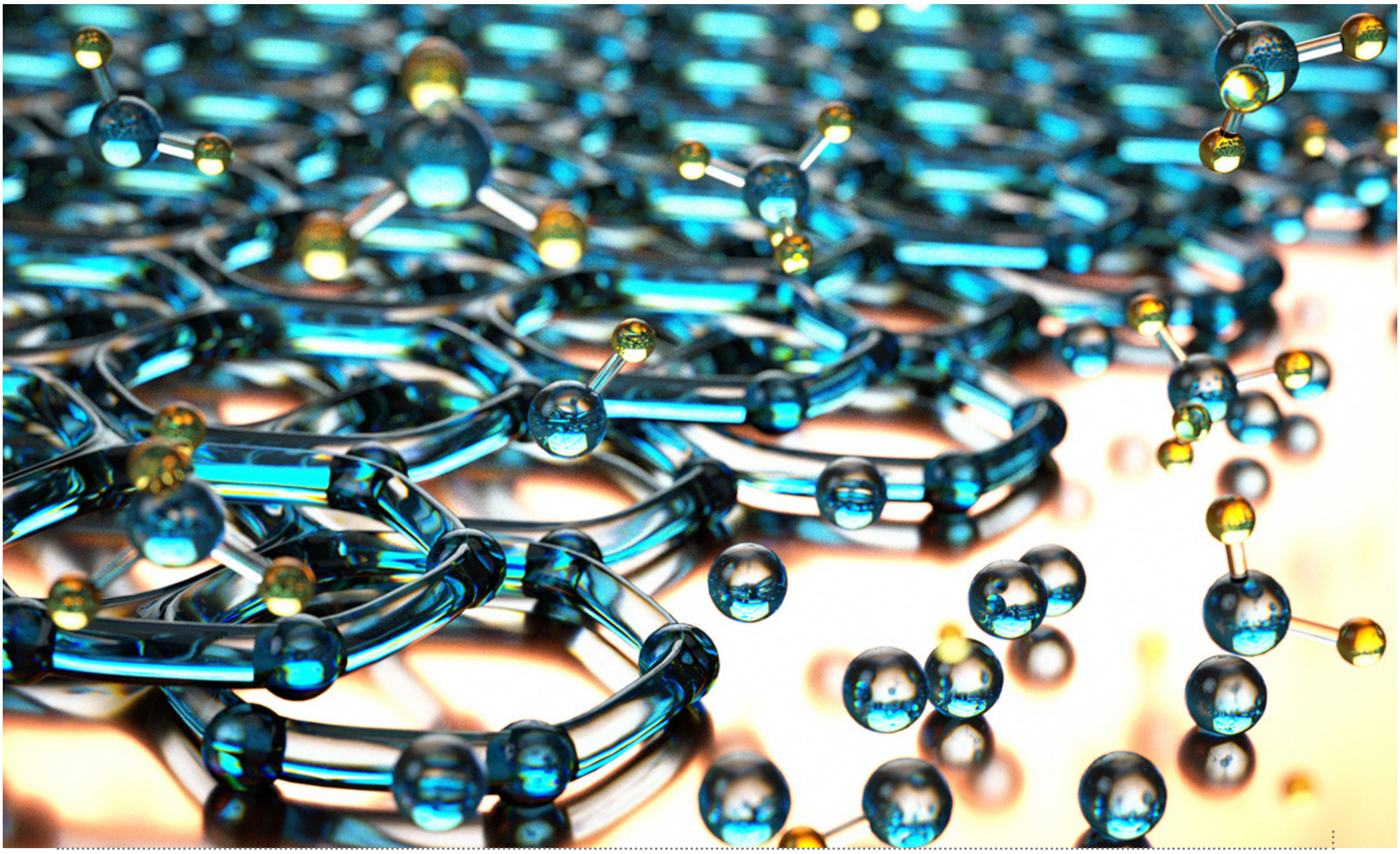
1. A clear path to low cost production;
2. Scalable production techniques compatible with a wide range of manufacturing processes and government regulations; and
3. Development of practical techniques to integrate Graphene, likely through mixing or dispersing, with other industrial materials.

Before discussing these challenges, a review of current production methods will be helpful.

Production Techniques

Graphene is derived from graphite ore or synthesized. There are a large number of synthesis processes, and these processes begin with an array of material sources such as graphite, carbon nanotube, carbon precursor, CO_2.

To obtain Graphene from graphite ore, one needs to perform another manufacturing step, for example liquid phase exfoliation or another chemical "exfoliation" procedure. "Exfoliation" is a term that describes the breaking of bulk graphite ore into its constituent Graphene layers. In recent years, various manufacturers have used Hummer's technique in which graphite is initially oxidized and converted to Graphene oxide. Graphene oxide is then reduced to Graphene using specific reducing agents. However, the initial oxidation process is highly exothermic resulting into explosion risks and toxic gas release that hinders the scalability of the conversion process. Most recently, novel exfoliation techniques have been developed in which graphite is directly exfoliate into Graphene without intermediate oxidation steps. Currently these techniques are the lowest cost production methods for Graphene, however optimization is needed to produce larger Graphene sheets. This optimisation is much easier when



when the input graphite has large flakes and higher purity. Canadian Graphene producers such as NanoXplore and Grafoid are leaders in these novel exfoliation techniques.

Another Graphene production technique is Chemical Vapour Deposition (CVD). CVD results in large-area Graphene with superb qualities but the production technique is expensive and therefore the technique is most suitable for electronic and photonic applications where Graphene coating (versus Graphene powder) is needed. Large consumer electronic producers such as Samsung and IBM are leaders in this segment, and several other companies involved include Graphenea, Graphene Frontiers, as well as CVD system producers such as CVD Equipment and Aixtron.

Another attractive production option is to utilize greenhouse pollutant gases and naturally occurring and recyclable minerals to produce high quality Graphene. One such process has been developed by Graphene Technologies (High Temperature Physics, LLC), USA. The company is planning to launch Graphene and intermediate products under the brand name GraphenX™. The most appealing feature of this process is that it utilizes low cost, widely available carbon dioxide gas or other carbon bearing feedstock materials. Such processes utilize a highly exothermic reaction occurring between magnesium and CO2, and thereby, substantially reduces the energy requirement for the production of Graphene. Another feature of this technology is that it recycles the important materials, including Mg feedstock and HCl employed in the separation and purification of reaction products.

The quality of Graphene produced by the various techniques described above can vary widely. For Graphene sheets, the presence of defects, impurities, grain boundaries, multiple domains, structural disorders, and wrinkles in the Graphene sheet can have an adverse effect on electronic and optical properties. Large, high quality Graphene sheets are currently only possible with CVD processes, but even these process struggle to produce high quality and single crystalline Graphene thin films possessing very high electrical and thermal conductivities along with excellent optical transparency, as well as clean etching and lithography of Graphene thin films. For applications that are less sensitive to high electrical conduction, where spray-coated Graphene from powder source is the solution, requirements are much less stringent. Hence exfoliation techniques from graphite that end up with Graphene in powder format are currently the most viable techniques to commercialize Graphene, but the Graphene produced is not suitable for all applications.

Production Cost and Scalability

Scalability and cost of production are currently the most important factors limiting the commercialization of Graphene. The cost of producing Graphene is falling dramatically as techniques improve. In 2008, it was estimated that it would cost $100M to produce a square centimetre. In 2012, price estimates ranged from $200K a square centimetre for ultra-high quality material, to $20 for a lower quality sample of the same size. A recent ParisTech Review article (September, 2013) estimated production costs for Graphene at $800/g, while many industry participants suggest that successful commercialization of Graphene requires a final price of about $10/g for high quality and pure Graphene in large sheets. The major hurdle in manufacturing Graphene on an industrial scale is process complexity and the associated high cost of its production, which results in an expensive product.

Production costs vary depending upon the cost of chemical consumables and process complexity. Chemical vapour deposition is a vacuum-based process with various gases used and at multiple stages of production.

The resulting safety precautions lead to a capital intensive cost structure that significantly hinders the scalability of this process. Other more conventional techniques, such as Hummers that results into reduced Graphene oxide, are explosive with high risk of toxic gas release. Such processes may be low cost however, scaling to large volumes is a significant challenge. Various other processes have been reported that use super-acids mixed with hydrogen peroxide to exfoliate graphite powders. These types of process are low cost with acceptable yield of production however, the process is extremely dangerous due to use of very strong acids and high risk of explosion. Government restriction severely restrict processes that use strong acids. Furthermore such processes are not green (there are several issues regarding consumables residue) and the resulting Graphene does not show a great degree of biocompatibility. An optimal production process for Graphene is a green one, with no acid or oxidizer involved, with no risk of explosion or toxic gas release, and with a high yield of production (scalable).

Exfoliation processes have the same challenges as above, but the challenges are minimized in part by the simplicity of the overall process. This is especially true for those processes that avoid the use of super acids. However, for exfoliation processes, another difficulty is the washing and purification process for graphite. Using centrifuges to remove large graphite particles from exfoliated ones hinders the scalability of the process and using sonicators to reduce the number of layers of Graphene dramatically reduces its sheet size. Developing techniques that do not require these post-processing steps definitely improves scalability.

Integration

Graphene has the potential to greatly improve future products, but the timing and path to these innovative products will depend upon the adaptability of Graphene and its compounds to end user production processes and the ability of Graphene producers to explain the value of Graphene to all the industrial and manufacturing players in the products' supply chain. In rough terms, Graphene is likely to enter the supply chain as either a compound - Graphene integrated with another material - or as a component - for example, a Graphene layer in a semiconductor structure.

Graphene-based compounds are mixtures of Graphene with, for example, polymers, metals, or ceramics. Mixture of Graphene with other materials brings distinctive characteristics however, mixing is a complex process. In the case of Graphene-polymer composites, dispersibility is the main disadvantage. The challenge is to find suitable solvents that have a high degree of solubility for both the Graphene and selected polymer. Graphene is not soluble in aqueous media and represents limited solubility in organic solvents in which polymers are soluble. Mixing Graphene with ceramics is much easier, but currently relatively limited applications are foreseen for resulting compounds. Graphene composites with metals and alloys suffer from weak bonding in the atomic interface. This results in weak thermal conduction after adding Graphene to say aluminium or titanium. Theoretically such compounds should demonstrate an enhanced thermal conduction however, in practise, tuning the mixing process has proved quite difficult.

Several companies focus on low cost production of such Graphene compounds and own patents on Graphene-related products. These companies typically aim to partner with larger companies closer to the end user, or manufacturers from other industries which could make use of Graphene and its compounds. The leading incumbents manufacturers in various industries have started to expand in this direction as well and are evaluating the feasibility of incorporating Graphene compounds into their products.

Graphene component companies include very large players such as IBM and Samsung, as well as smaller companies such as AMO GmbH Aachen and Bluestone Global Tech and others. Many of these are focused on electronic, electro-optical and semiconductor type applications. The challenge for these players is to bring the benefits of Graphene to existing, complex and multistage manufacturing processes. However, these manufacturing processes are stable and very well understood and so successful integration of Graphene is highly likely eventually.

Commercialization of Graphene requires a deep knowledge of various industries with strong grasp on how each industry produces the targeted product. Each product in each industry has its own unique production techniques and Graphene integration must adapt to such processes. An example is temperature. Graphene normally decomposes at high temperatures, severely limiting its integration in existing production process with high temperature steps. Unless Graphene can be modified to tolerate high temperature processes, it will be very difficult for it to enter into many sectors - such as casting and other heavy industries - where high temperature processes are common.

Conclusion

Graphene is poised to impact a wide range of industries and promises to make significant improvements to consumers' lives as it is incorporated into processes and products. In order for Graphene to meets its potential however, low cost production processes must be developed, these production processes must be both scalable and suitable for integration into existing manufacturing processes and regulations, and the challenges of integrating Graphene into products, either as Graphene compounds or Graphene components, must be met. Great strides have been made meeting all these goals over the last few years as a broad range of players have pushed ahead simultaneously on many different fronts. It is still difficult to predict the exact shape of the coming Graphene industry, but regardless of the details for the world at large the benefits of Graphene will soon be enjoyed widely.

About NanoXplore

NanoXplore produces Graphene, and derivative materials such as Graphene oxide and doped Graphene, directly from high quality flake graphite. Our Graphene products are produced using a proprietary, low cost and scalable technology, and are of remarkable high purity and quality. NanoXplore's team have experience in a wide range of industries and the process knowledge to enable customers to incorporate our Graphene material into their products. NanoXplore is currently working on solutions for customers in the energy, health, textile, sensor, and packaging industries.

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