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Graphene Technology: The Nanomaterials Road Ahead

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A new paradigm is emerging for advanced nanomaterials and their use in commercial products. We call it "molecular precision manufacturing" (MPM), and it is evolving as a consequence of the need to develop new tools, new standards, new protocols, and new processes (TSPPs) to foster the commercialization of nanomaterials.

Nanomaterials possess extraordinary properties, but harnessing these properties for use in commercial products is challenging. The emerging MPM paradigm is required in order to realize the tremendous commercial potential of advanced nanomaterials – both 2D and 3D – discovered over the past 25 years.

The TSPPs associated with MPM have been in development for several decades. They combine activities that are critical to the use of advanced nanomaterials in products and applications: 2D materials, such as graphene, molybdenum disulfide, and boron nitride; and 3D nanomaterials, such as single-wall and multi-wall carbon nanotubes (CNTs). Additionally, technologies have been developed to functionalize these advanced 2D and 3D nanomaterials to enhance their properties for use in commercial products. We are at an early stage in the evolution of functionalized advanced 2D and 3D nanomaterials, but the research done thus far is encouraging.

1.1

Newly Discovered 2D Materials

The past decade has witnessed the discovery of several 2D nanomaterials, all of which possess unique properties suited to various applications. These discoveries include the following:

Graphene: Single layer of carbon atoms only 1 molecule thick packed in a hexagonal lattice.

Molybdenum disulfide (MoS_2): When stacked, MoS_2 looks and feels like graphite. However, it is very different from graphene at the 2D level. While graphene is a flat layer of carbon atoms, MoS_2 is composed of molybdenum atoms sandwiched between two sulfur atoms. Unlike graphene, in its natural

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form it can serve as a semiconductor in transistors, making it appealing for use in electronics and solar cells. Scientists have been experimenting with combining the two materials to allow graphene to have transistor-friendly properties, but are now looking at using MoS_2 on its own. It has properties similar to silicon, but requires the use of much less material and consumes less energy.

Silicene: When silicon is reduced to a 1-atom-thick layer, it takes on a slightly squished-looking honeycomb structure similar to graphene. Like molybdenum disulfide, it can be used as a transistor in its natural form. Silicene also shares one of graphene's especially interesting properties: electrons move through it at a very fast pace, as if they were massless. This means that silicene conducts electricity faster than any commercially available semiconductor. Because silicon is so ubiquitous in current electronics, silicene could be much easier to adopt than other 2D materials. It was only recently synthesized for the first time last year, so the research will take some time to mature. It also could turn out to be more difficult to make than graphene.

Germanane: The element germanium has already been used as a semiconductor, and actually formed the very first transistors in the 1940s. When reduced to a single layer of atoms, it forms a material known as germanane. Germanane conducts electrons 5 times faster than germanium and 10 times faster than silicon, which makes it ideal for creating faster computer chips. It is more stable than silicon and a better absorber and emitter of light. Manufacturers may also be able to produce it on existing equipment in large quantities, which would give it an advantage over emerging graphene manufacturing techniques.

Our experience of working with 2D nanomaterials is limited, given their relatively recent discovery – in the case of graphene, as recent as 2004. Working with 2D materials presents a set of learning curves that require scaling even before the potential of such promising materials can be realized. The TSPPs associated with the emerging MPM paradigm are critical to the commercialization of products and applications using 2D nanomaterials and their 3D counterparts.

Commercialization demands that one has a consistent and repeatable product available at a rational price, given the performance impact and value proposition. Creating the strongest composite in the world is of no value if its mechanical properties cannot be predicted or relied upon because of inconsistent materials or testing. Without these TSPPs, we are not likely to see the fruits anticipated with nanotechnology that many analysts have envisioned, given its vast potential in commercial applications.

In the following text, we offer an overview of MPM and shed light on the promises and challenges associated with the emerging MPM paradigm.

1.2
Wonder Materials

The ascent of MPM is associated with the discovery of "bulk" nanomaterials possessing remarkable properties. We make the distinction between bulk materials and nanoscale elements of electronic and semiconductor devices, for example, which are created as sub-micron architectures using processes such as chemical vapor deposition and epitaxial growth, but which are not "freestanding" materials.

One of the early nanomaterial discoveries came from Rice University in the mid 1980s, with the synthesis of fullerenes, commonly referred to as *bucky-balls* – hollow, spherical carbon structures that became an early impetus to research in novel carbon allotropes. The discovery led to more investigation in Japan on hollow tubes of carbon in the early 1990s and ignited great interest in single- and multi-wall CNTs. CNTs were seen to have a host of remarkable properties that stimulated the interest of nanotechnology researchers all over the world, and it was not long before patent filings on CNT-based applications began to skyrocket.

In 2004, researchers Andre Geim and Kostantin Novoselov from the University of Manchester discovered graphene – another nanomaterial possessing truly extraordinary properties. In 2010, Geim and Novoselov were awarded the Nobel Prize in Physics for their discovery of this "wonder material," which comprises a single layer of carbon atoms only 1 molecule thick (hence its 2D classification) and packed in a hexagonal lattice. It is the thinnest material known to man, with an exceptionally high theoretical surface area ($2630\,\mathrm{m}^2\,\mathrm{g}^{-1}$). Atomically, it is the strongest material ever measured, is extremely elastic (stretchable), and has exceptional thermal and electrical conductivity, making it the substance a design engineer's dreams.

Understandably, graphene-related patent filings have risen significantly around the world over the past several years. The United Kingdom is currently a hotbed of activity in graphene, with the University of Manchester acting as a magnet for millions of dollars of research funding. In 2013, the European Union created a Flagship to promote the development of graphene, committing 1 billion Euros in funding over a 10-year time frame. Entrepreneurial activity and investment associated with graphene has increased significantly. Technology stalwarts Samsung and IBM have been extremely active in patenting graphene-based applications. The Far East has been massively active not only in patent applications, but also in investment. Singapore, for example, boasts the highest level of graphene research funding as a percentage of GDP in the world.

With the discovery of graphene in 2004, we have entered a new age of materials and materials science. Since then, several other 1-atom or 1-molecule-thick crystals have been isolated and tentatively studied. These materials range from semiconducting monolayers to wide-gap insulators to metals. This growing library of 2D materials opens the potential to construct various 3D structures with on-demand properties that do not occur naturally, but can be assembled "Lego-style" by stacking individual atomic planes on top of one another in a desired sequence (see Section 1.1).

The discovery of new advanced nanomaterials – both 2D and 3D – over the past 25 years has generated much excitement and hype, which is understandable in light of their remarkable properties. Today, the range of potential applications for graphene and other 2D materials is limited only by one's imagination. Yet, this potential needs to be tempered by the kind of level-headedness that comes from experience working with advanced nanomaterials.

In May 2013, Bayer Material Science (BMS) exited the CNT business and shuttered its production plant, after many years of work and millions' worth of investment. BMS CEO Patrick Thomas noted that while the company remains convinced that CNTs have huge potential (they initially talked of over 3000 tons of output), their experience suggests that potential areas of application that once seemed promising from a technical standpoint are currently either extremely fragmented or do not overlap with the company's core products and spectrum of applications.

At the time of exiting the business, it was reported that BMS had invested some $30 million to produce multi-walled CNTs with a facility that had a capacity of producing over 200 tons per year. Mitsubishi Corp. had a similar experience in the 1990s when it attempted to scale and commercialize fullerenes. While no public information has been made available, insiders indicated that as much as $60 million was invested and, to date, no commercial products realized.

While sobering, the BMS experience holds many valuable lessons for those seeking to commercialize advanced nanomaterials. The commercialization of advanced nanomaterials, and nanotechnology in general, is unlike anything ever undertaken before. Successful commercialization of these advanced nanomaterials requires new approaches, tools, and processes, and a great deal of what seems to be in short supply these days with investors: patience. Often, to satisfy the demands of investors, substantial claims are made on production volumes and estimated sales prior to evaluating the market and without exercising caution.

Arriving at a pure material virtually free from the catalysts used in the production process was not as easy as expected. The challenge was compounded by the need to functionalize these materials; to aid dispersion, acids were often used (as that was all that was available then). High levels of functionalization required a vicious circle of excessive acid treatment, with higher resultant costs, waste streams, and structural degradation.

Crucially, the effect of nanomaterials on the target medium is often not known or precisely predicted until it is attempted. Experience shows that taking a process from the lab (micro) level to the commercialization (macro) level is not easy, and in scaling up, the results can often be different from the lab-based results. This will affect commercial outcomes, possibly rendering a positive projected return to an uneconomic position. It is here that we encounter the classic case of over-promising and under-delivery, effectively stunting the market.

Having to learn these important lessons the hard way is common in business – through failed multimillion-dollar investments, layoffs, plant sales, and closure. Yet, it would be foolhardy to extrapolate failures associated with the development of CNTs into the future, for the very success with advanced nanomaterials lies in these failures. Thomas Edison, Nikola Tesla, and Steve Jobs are just a few famous examples of innovators whose failures led to successes beyond their wildest dreams. Fostering a culture of acceptance of failure as a learning process that moves one closer to success is crucial. How often is a failure seen as unacceptable, resulting in management changes that may not be justified?

Failure is instructive, and a large part of the innovation process. That said, it is important to respect the meme that insanity is doing the same thing over and over and expecting different results, as Einstein once observed. What we learn from the failures of working with advanced nanomaterials is that traditional approaches and processes do not work, and something else is required. This is where MPM comes in.

1.3
The Rise of MPM

Humans have been figuring out how to turn various materials into useful products since the Stone Age. While some of this knowledge scales into the commercialization of nanomaterials today, new learning curves are clearly required to bring advanced nanomaterials to the market in the form of new products and applications.

The BMS experience over the past decade with CNTs is a clear example. Nobody disputes the theoretical properties of advanced nanomaterials such as CNTs and graphene. These are well known. As Andrew Geim recently put it: Graphene is dead. Long live graphene! Hundreds of peer-reviewed scientific papers have been published on the properties of graphene and other nanomaterials. The major issue associated with these materials is not theory and properties, but practice and application. How do we turn their fantastic properties into useful and, in some cases, game-changing products?

It is clear from the experience of BMS and others that traditional approaches to commercializing these materials are not effective. The emergence of MPM is due to the shortcomings of these traditional approaches. We know that growth is a function of learning. After all, the cave man had access to all of the materials we have today. What the cave man did not have was the propensity for learning that comes from having experienced failure and success. MPM embraces the learning curves associated with bringing advanced nanomaterials to the market through the development of new processes, standards, tools, and technologies.

There is no reason a priori to expect the earlier-described TSPPs associated with the successful commercialization of non-nanomaterials to be the same for nanomaterials. It is natural to want to apply the same tried-and-true TSPPs to commercialize advanced nanomaterials. At the heart of MPM is the development of new TSPPs necessary for the proper characterization and functionalization of advanced 2D and 3D nanomaterials, together with its effect on the target matrix and down-stream processing.

“Characterization” of nanomaterials is critical. Characterization involves the use of sophisticated metrology tools and information technology that peer down into the nano world and generate data that help us identify the type of nanomaterial being developed for commercialization. Manufacturers today might believe they are working with graphene because their supplier told them it was graphene, when in truth, characterization identifies the material as akin to "soot." And there is a world of difference between graphene and soot. Knowing the kind of material one is using is paramount to the commercialization process. The way to know what type of material is being used is via characterization analysis. Characterization analysis enables material comparison and is a key component – and the foundation – of the MPM paradigm.

A great deal of work is being done today by researchers at the National Physical Laboratory (NPL) in the United Kingdom and elsewhere that is pushing the envelope of characterization analysis. NPL and others are pioneering new techniques that allow for more accurate assessment of nanomaterials, and even tools to enable real-time characterization of graphene. New types of metrology tools are being developed to foster characterization analysis of newly discovered 2D nanomaterials.

Researchers at Lancaster University (LU) note that scanning probe microscopy (SPM) represents a powerful tool which, in the past three decades, has allowed researchers to investigate material surfaces in unprecedented ways at the nanoscale level. However, SPM has shown very little power of penetration, whereas several nanotechnology applications would require it. The LU researchers are using other tools, such as ultrasonic force microscopy (UFM), in work with graphene and other 2D materials, including MoS_2. UFM is a variation of the atomic force microscope (AFM) that overcomes the limitations of SPM in characterizing advanced nanomaterials such as graphene and other 2D materials.

These new tools and techniques in development will give manufacturers the important data necessary to ensure that the correct material is being used in the manufacturing process. They also promise to foster quality control in a manner that has not existed previously. As producers in any industry know, quality control is paramount to successful commercialization. Additionally, the creation of sophisticated models to assist in the development, design, and integration of these materials into devices and products relies heavily on the completeness and reliability of property data for these nanomaterials.

Characterization work also facilitates the development of standards that are critical to the evolution of advanced nanomaterials. The term graphene today covers a family of different materials, including several-layer flakes, powders, liquid dispersions, and graphene oxide. Importantly, the corresponding properties and potential applications will vary depending on the type of material used.

The other critical part of MPM is dispersion. The ability to consistently and uniformly disperse graphene in another material is important to realizing the outstanding properties of the material. Functionalizing graphene properly can enhance the strength, stiffness, and conductivity of the resulting composites, depending on the requirements and applications being targeted.

1.4
Addressing the Environment, Health, and Safety

Another important component of the emerging MPM paradigm relates to the environmental, health, and safety (EH&S) procedures and protocols for advanced nanomaterials. There have been a number of "scare stories" in the media about the potential toxicity of various nanomaterials. Most of these fail to consider the final product form that nanomaterials actually take when introduced to the market, as well as the potential, or lack thereof, of their release into the environment as nano-sized particles.

Without a clear understanding of the full manufacturing cycle, product form, and disposal considerations, the limited information generated by current studies is of little relevance. Additionally, lacking test standards and precise definitions, it is impossible to conduct credible, repeatable, and scientifically valid studies. All of the characterization work that is going on behind the scenes with graphene and other 2D materials today is important to future EH&S studies.

It is incumbent upon all in the nanomaterials community to collaborate on EH&S-related issues. The new characterization tools and techniques that have been developed and are being developed will help facilitate toxicity studies. There are groups of researchers today, such as the Arkansas Research Alliance, that are intent on doing credible nontoxicity research on graphene and other nanomaterials that can be of benefit to all who wish to promote the responsible development of such materials.

One way to minimize the EH&S effect and aid commercialization is to add the nanomaterials to a carrier in the form of a loaded masterbatch, which is then let down (diluted) by a processor with the raw, untreated carrier material. This offers controllability; and once in a masterbatch, it can be handled without the need for expensive nano-handling environments.

1.5
The Nanomaterials Road Ahead

We are still at an early stage with the new MPM paradigm. The promise of nanomaterials such as graphene and CNTs is great, but so, too, are the challenges associated with successful commercialization. Several of the key challenges associated with commercializing nanomaterials-enabled products are being addressed through the development of the MPM paradigm. Again, considerable progress has been made, but there is much more work to be done in terms of testing and data analysis.

Companies seeking to work with graphene and other nanomaterials need to know the type of materials they are using. Characterization analysis provides this information and also helps to facilitate standards that are necessary for industry maturity and EH&S-related research. Additionally, companies need ways of reliably producing materials to achieve their desired properties. Functionalization assists greatly in this area, for without it, the inert carbon-based material will not want to disperse readily into a target medium. With respect to functionalization, it is also early days, but we see a great deal of potential as functionalization becomes commonplace among those commercializing advanced nanomaterials. It is clear from the lack of progress with CNTs thus far that there is a need for a paradigm such as MPM if we are going to realize the promise and potential of graphene and other nanomaterials.

The excitement over these newly discovered nanomaterials is warranted, but again, those seeking to invest and innovate in this promising area need be mindful of the challenges associated with commercializing these materials. Key to progress on the commercialization front is close collaboration among suppliers and producers and a good deal of patience among all participants involved: the history of materials tells us that it can take years, and sometimes decades, before a new "wonder material" fulfills its promise and potential.

Consider the evolution of materials such as aluminum and advanced ceramics. Aluminum was discovered in a lab in the 1820s. Like CNTs and graphene, the material was hailed as a wonder substance, with qualities never seen before in a metal. However, it proved expensive to make, and it was not until many decades later that it took off in the marketplace, when a new process using electricity was invented.

Similarly, many of us remember the excitement surrounding advanced ceramics in the early 1980s, and the fever that developed with the discovery of high-temperature ceramic superconductors. The promise of ceramic engines, loss-free electrical transmission lines, and many other products that these material advances were expected to enable has remained unfulfilled. That said, the impact that these materials have had on our lives is nearly impossible to list – ranging from the mundane to the exotic and impacting transportation, communications, electronics, consumer goods, medical devices, and energy in ways that may be hidden but are enabling nonetheless.

The road ahead for the development of applications and products using 2D and 3D nanomaterials is filled with tremendous opportunities and key challenges. There is also always a great deal of hype surrounding the discovery of new materials, and experience teaches that hype often turns to disappointment before a wonder material's potential is eventually fulfilled. In the main, those who earlier tried CNTs and failed remain willing to experiment with the likes of graphene and other nano materials as the desire to get a competitive advantage remains a key economic driver in a very competitive world.

The emerging MPM paradigm discussed in this paper seeks to foster the acceleration of the commercialization process of advanced nanomaterials and promote their responsible development. The TSPPs are designed to avoid corporations from being tempted to reach for instant volume in a desire for market dominance, growth, and profit. The investor community needs to be wary of those who claim volumes that are in the many tons, or hundreds of tons, without proving scale-up as well as process controls to ensure consistent quality production. For those who seek instant "glory," the bear trap of failure through nonrepeatability looms large.

Despite the great deal of work ahead to realize the potential of these exciting materials, and despite some of the setbacks encountered over the past decade, we are encouraged by the progress we are making to bring these next-generation "wonder materials" to the market.

1.6
Can Graphene Survive the "Disillusionment" Downturn?

Even if you are not familiar with the life cycle of emerging technologies, you have certainly heard about technologies that generated lots of interest at an early stage but a few years later are gone, having never really entered the marketplace. Many of these technologies showed outstanding results in the lab but were unsuccessful in moving out of the lab into the real world. Most tech companies must pass through the ups and downs of their industry's life cycle, but how they understand and react to these cycles can make a big difference.

1.6.1
Gartner's Hype Cycle

The Hype Cycle is a branded graphical tool developed by the research and advisory firm Gartner (www.gartner.com) for analyzing the maturity and adoption of emerging technologies.

Technology X (a shiny, life changing, and innovative tech) is introduced as the next big thing (Technology Trigger) and everyone is talking about how it will change our life (Peak of Inflated Expectations)! Then, as reality sets in, people realize that everything has not magically changed and disappointment sets in (Trough of Disillusionment). The shiny, new technology starts to look dull. As time goes by, smart people look at the real opportunities for the shiny new technology (Slope of Enlightenment) and learn how to build solid businesses with the not-so-shiny-and-new thing (Plateau of Productivity). This is how technology X goes from the lab to the real market (Figure 1.1).

The period of time from discovery to maturity is variable and depends on the type of technology; for instance, it takes around 25–30 years for a new advanced material to move through the cycle. The best recent example is CNT, graphene's sister material, discovered in 1991. Today, after 23 years, the CNT industry is slowly moving up the "Slope of Enlightenment." Graphene will pass through a very similar cycle, although the cycle time may be slightly faster since many graphene players have learned from CNTs' hurdles.

Graphene was discovered in 2004, and the first generation of graphene producers, such as XG Science, Angstron Materials, and Vorbeck Materials, had launched and introduced their first generation of products by 2008. During early 2010, large corporations such as BASF (early adopters) showed interest in graphene and began to test first-generation products. Results were often disappointing due to problems with graphene dispersion, lack of batch-to-batch consistency, and the lack of clear graphene standards.

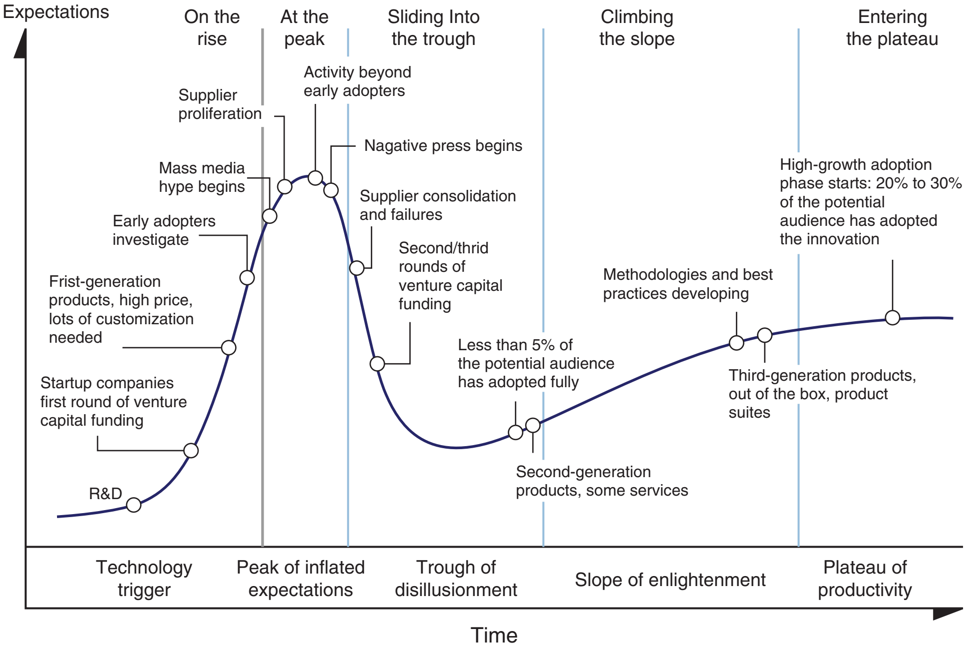

Figure 1.1 Gartner's hype cycle.

In September 2010, Konstantin Novoselov and Andre Geim were delighted to receive the Nobel Prize in Physics for the discovery of graphene. This award resulted in broad media coverage, building up to mass media hype by early 2011. Media hype continues today as governments launch and build support for large science to industry programs. After few years of excitement and buildup, graphene is now "At the Peak" of Gartner's Hype Cycle and sliding into the "Trough of Disillusionment" is happening.

1.6.2
Surviving the Trough of Disillusionment

As scary as the "Trough of Disillusionment" appears, there are a few key strategies that graphene companies can employ to safely move through this stage:

1) **Maintain low overheads**. Growing too fast and burning cash at the "Peak of Inflated Expectations" stage has killed a lot of businesses. Access to capital becomes much harder as an industry moves into the "Trough of Disillusionment."
2) **Concentrate**. Graphene companies need to focus on one target market in which their products provide the maximum value to their customers. Trying to chase all opportunities, across multiple industries, increases the burn and reduces the chances of success dramatically.

3) **Be revenue-driven**, **rather than value-driven**. Many potential markets (e.g., bio/health, aerospace) have a huge upside in terms of value, but time-to-market is long and regulatory hurdles exhausting; lots of cash will be burned before significant revenues are made. Unless graphene companies have a strong partner with deep pockets, short-term revenue opportunities must trump long-term, value-driven markets.

Investors on the other hand, need to understand that the development of an advanced material business is a long process and depends heavily on management strategy. Companies that can ignore the hype, and grow and generate revenues during the initial industry phases, will have the opportunity to create lasting, valuable businesses. Reviewing the life cycles of other high-tech markets, such as those of solar cells and plastics, may help provide investors with key insights.

1.6.3
Graphene and Batteries

Researchers note that graphene can improve battery attributes like energy density and form in various ways. Conventional battery electrode materials, as well as prospective ones, can be significantly improved when enhanced with graphene. Graphene’s unique traits, such as mechanical strength, electrical conductivity, large surface area, and lightness of weight can make batteries lighter and more durable and suitable for high-capacity energy storage. Additionally, graphene can shorten charging times – a highly desirable feature for electric vehicles (EVs) and consumer electronics products. A battery’s lifetime is negatively linked to the amount of carbon that is coated on the material or added to electrodes to achieve conductivity (Figure 1.2). Graphene adds conductivity without requiring the amounts of carbon that are used in conventional batteries.1)

Graphene, and in particular graphene oxide, has shown to be a valuable material for overcoming the hardest challenges presented in lithium–sulfur batteries. In summer 2014, researchers from Samsung’s Advanced Institute of Technology (SAIT) announced a novel way to extend the life of a lithium-ion battery (LIB) using a combination of silicon and graphene. SAIT fabricated anode material by growing graphene on the surface of silicon without forming silicon carbide. The new material has four times the capacity of commercial graphite. Researchers at SAIT note that the approach has the potential to increase the volumetric energy density of LIBs by 1.8×. Key to the commercialization of this advanced graphene-enabled battery technology is the ability to manufacture carbide-free graphene in mass quantities. The biggest obstacle to realizing the full application of graphene technology today is the relatively high cost and low reliability for large-scale production and manufacturing. There is a great deal of work being done in South Korea by Samsung as well as by other researchers inside and outside large established corporations around the world to address this critical issue.

1) For more, see Roni Peleg and Ron Mertens, *Graphene Batteries Market Report*, 2015.

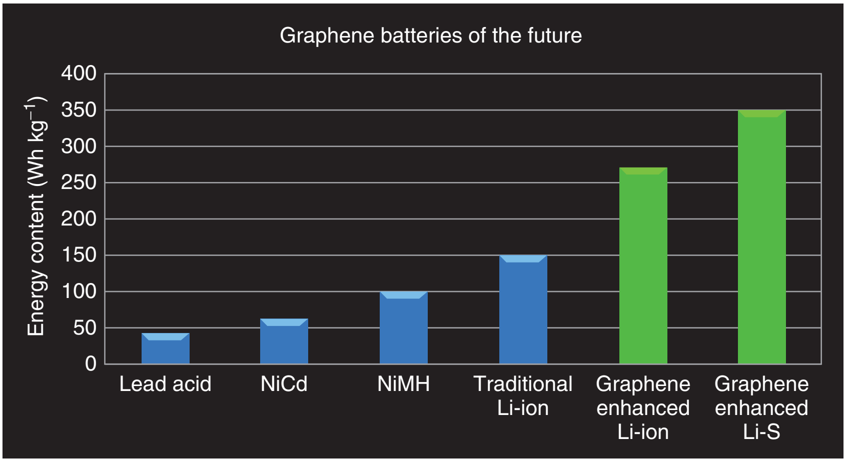

Figure 1.2 2-D nanomaterials enable more powerful batteries. (Peleg and Mertens, *The Graphene Batteries Market Report*, 2015.)

LIB is the most important type of rechargeable batteries. In such types of batteries, lithium moves back and forth between two electrodes, called cathode and anode, for charging and discharging. LIBs are common in many consumer electronics and electric cars due to their relatively high energy density (the amount of energy stored in a unit of battery), low hysteresis (after charging and discharging, there is little loss of energy capacity), and a very slow loss of energy when not in used. LIBs consist of a lithium compound as cathode, spherical graphite as anode, and lithium salt as an electrolyte to allow lithium ion movement between the cathode and anode. Increasing the capacity of LIB is dependent upon better materials for cathode and anode. It should be noted that the combination of cathode, anode, and electrolyte is one cell; several connected cells are called a *module and multiple modules* go together to make up a battery.

Recently, news regarding the proposed Tesla battery Gigafactory has had an impact on the industries involved in the LIB supply chain, notably on natural flake graphite junior miners. A large component of today's LIBs is graphite and, for the proposed Tesla factory only, more than 300k metric tons/year graphite would be needed. The news of the proposed Gigafactory has resulted in a boost in the graphite market, but graphite-based anodes are not at all adequate for the battery performance that is required for EVs by 2030. By that date, most hybrid electric cars will have been converted to full electric cars running completely on battery power and without any fossil fuel consumption. The replacement material has to radically improve the performance of existing batteries to provide longer run times (a larger storage of energy), faster charge times, all with the smallest possible weight and at the lowest possible added cost. Furthermore, the new batteries need to be long lasting (over 1000 cycles) and thermally stable (should not be over-heated during charging). Graphene is a leading candidate for the replacement material.

There are many studies and technical papers showing how graphene can improve batteries. Its outstanding electrical and thermal conductivity enhances the activity of cathodes and prevents over-heating of the batteries. Recent findings by researchers from Lawrence Berkley lab introduced lithium–sulphur graphene compounds that generated twice the energy of current batteries and were stable over 1500 cycles. Such batteries could enable EVs with an efficiency of more than 500 miles on a single charge, which is what future electric cars need. Newer technologies such as Li–air batteries or supercapacitors could replace LIBs as well.

The future of the energy industry is largely dependent upon improved batteries. Such batteries will change our life drastically. In a matter of few years, gas stations will be replaced by electric car charging stations and typical auto mechanics will require new certification to repair electric cars. Further investigation on graphene-enhanced batteries is absolutely crucial as graphene–silicon compounds have proved to be a potential replacement for spherical graphite as anode in LIBs and graphene oxide–sulphur compounds as cathode in lithium sulphur batteries.

1.6.4
Heat Management with Graphene

Miniaturization of electronic systems and circuits is heavily restricted with heat dissipation challenges. Heat buildup reduces the efficiency of the electric motors, performance of CPUs, and lifetime of consumer products and batteries. Heat dissipation becomes even more challenging when flexibility and bendability of the final product is important. Metals are not a suitable candidate anymore and plastics are rapidly replacing them as they are cheaper and easier to shape and are weightless. However, plastics severely suffer from lack of thermal conductivity. The possibility of enhancing thermal conductivity of plastics (preferably by keeping them electrically insulating) is game changing. Graphene is proved to have the highest thermal conductivity among all materials. Small loading of well-dispersed graphene into plastics can enhance their ability to dissipate the heat tremendously. If such a loading level is lower than the percolation threshold, plastics stay insulating. Percolation in plastics starts by 0.2–0.5 wt% of graphene addition. Lower concentration of graphene is likely to be ineffective to change electrical conductivity. Table 1.1 represents the impact of graphene addition upon the thermal conductivity of thermoplastics and thermosets.

Having said this, selection of the optimized graphene loading is crucial. Concentration of graphene has to be finely tuned to an optimal value in order to achieve the best results. For instance, in case of poly(lactic acid) (PLA), the optimal concentration of graphene was found to be 0.075% (Figure 1.3).

Table 1.1 NanoXplore graphene improves polymer thermal conductivity and effusivity.

Material	Thermal conductivity at 21–25 °C ($W m^{-1} K^{-1}$)	Improved thermal conductivity	Thermal effusivity ($Ws^{0.5} m^{-2} K^{-1}$)	Improved thermal effusivity
PLA[a]	0.36	245%	714	112%
PLA + 0.075 wt% graphene	1.23		1517	
PE[b]	0.74	44%	888	55%
PE + 0.1 wt% graphene	1.06		1377	
ABS[c]	0.29	339%	643	142%
ABS + 0.05 wt% graphene	1.28		1555	
Silicone rubber	0.23	446%	572	166%
Silicone rubber + 0.2 wt% graphene	1.24		1522	
2-Part epoxy potting compound	0.38	45%	771	17%
2-Part epoxy potting compound + 0.075 wt% graphene	0.55		905	
Silicone heat transfer compound	0.66	54%	1190	15%
Silicone heat transfer compound + 0.1 wt% graphene	1.02		1367	
Polyurethane	0.21	80%	550	33%
Polyurethane + 0.13 wt% graphene	0.37		730	

a) PLA stands for Poly(lactic acid).
b) PE stands for Polyethylene.
c) ABS stands for Acrylonitrile butadiene styrene.

1.6.5
How Graphene Could Revolutionize 3D Printing

Last year at the International Manufacturing Technology Show (IMTS) in Chicago, one of the largest industrial trade shows in the world with more than 100 000 visitors, 1900 exhibitors gathered in Chicago to showcase recent developments in machines, tools, and manufacturing systems. Arizona-based automobile manufacturer "Local Motors" stole the show by printing and assembling an entire automobile, called the *Strati*, from scratch and live in front of spectators. On the other side of the world, a Chinese company "WinSun Decoration Design Engineering" recently constructed a set of 10 single story, 3D-printed homes produced in under 24 h. These homes, based upon cement-based prefabricated panels printed on a custom-built 10 x 6.6 m 3D printer, were assembled on site

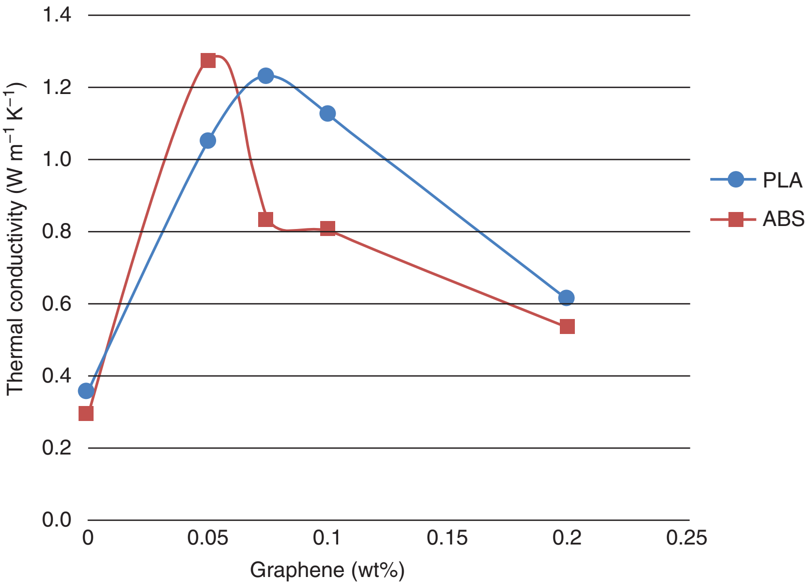

Figure 1.3 Thermal conductivity of thermoplastic/graphene in different loading of graphene.

and cost just $5000 to build. These are just two concrete examples of the recent rapid progress in the 3D printing industry.

Three-dimensional printing, also known as *additive manufacturing*, is the process of using successive layers of printed material to form solid 3D objects of virtually any shape from a digital model. Specially formulated materials, such as plastics or powdered metals, are used to build up successive layers to create components with complex shapes. The final characteristics of the 3D printed piece can be modified depending upon the additives used in the printed material and the printing techniques. Plastics are the most versatile printing material, but they are not mechanically strong and lack thermal and electrical conductivity, which is a requisite for many applications in the electronic and aerospace industries. In 2014, sales of industrial-grade 3D printers in the United States had risen to a level equivalent to one-third the volume of industrial automation and robotic sales. Sales of such printers are expected to continue to increase measurably in the years ahead due to advances in 3D printing software and the development of new printable materials such as graphene, CNTs, and other advanced nanomaterials.

Graphene, for example, has recently been explored for the printing of 3D structures of various dimensions having controlled properties. Example applications include printed electronics, biosensors, strain sensors, battery electrodes and separators, or filtration wherein the electrical, physical, chemical, or mechanical properties of the structures are controlled to provide targeted functionality by design. Utilizing processes such as inkjet or nanoimprint lithography, structures have been realized for printed electronics and sensors. More recently, a 3D printing strategy has been demonstrated for the fabrication of 3D graphene aerogels with designed macroscopic architectures, enabling a method to further control the mechanical and surface area properties of complex macroscale structures.

One of the main technical challenges to adding graphene to plastics is graphene's limited dispersibility, or its relatively poor ability to mix with other materials. Dispersibility of graphene in polymers requires special attention to the graphene's edge structure. Depending on the type of plastic, the graphene edge must be functionalized by adding specific molecules, which enables effective bonding between graphene and plastic. The severity of mixing problems of CNTs, a sister material to graphene, eventually nearly killed its market and forced many CNT producers to abandon their businesses. Graphene performs much better than CNTs in terms of dispersion; yet, ironically, the best quality graphene, with high purity and excellent crystalline structure (low defects), has the poorest mixing performance. Oxidized graphene, with lots of oxygen molecules available for bonding, provides better mixing with plastics, but large-scale production of graphene oxide is very challenging. Production of graphene oxide by the Hummer's method, the industry standard, is expensive and complex as it needs to guard against explosions and manage the use of large volumes of acids and harsh materials. The future of graphene additives for 3D printing requires either new approaches to managing the graphene edge structure or a new approach to manufacturing graphene oxide.

The value proposition for additive manufacturing is compelling today and likely to get more attractive in the months and years ahead. A significant part of the advantage of 3D printing is related to being able to manufacture single parts in one run, which can dramatically cut the cost of production. GE's Aviation division is 3D printing a fuel nozzle that previously involved assembly from 20 separately cast parts. GE found that the new additive process reduced the cost of manufacturing by a whopping 75%. Ducati is using 3D printing to substantially reduce product development time and to increase efficiency.

Additive manufacturing methods can be used to combine parts and foster greater detailing. They can also use multiple printer jets to lay down various materials simultaneously. There is also the ability to functionalize materials and create an array of innovative, customized products with unique features. Researchers today are using 3D printing to create customized body parts that can be used to replace human organs and limbs. With additive manufacturing, science fiction is becoming science fact. One envisions companies all over the planet having to redesign and reengineer their manufacturing processes around additive manufacturing and the processes associated with it. 3D printing with advanced nanomaterials such as graphene hugely enables technological innovation inspired by nature (i.e., biomimicry). The convergence of atoms (nanomaterials and hardware) and bits (3D printing software) represents a vast frontier of transformative deep science-enabled innovation attractive to companies and venture investors alike. When it comes to 3D printing, new breakthroughs and new achievements are being realized almost on a daily basis. Graphene is a great additive material and has significant potential to revolutionizing the range of possible products that can be manufactured with 3D printing. However, adding a complicated

Table 1.2 NanoXplore graphene improves polymer mechanical properties.

Material	Ultimate tensile strength (MPa)	Tensile strain at break (%)
Base rubber compound	11.70	540.56
Base rubber compound + 0.1 wt% graphene	12.99	663.18
Acrylated monomers	19.5	0.71
Acrylated monomers + 0.5 wt% graphene	30.6	1.23

Additive manufacturing is a game changer for industry.

material such as graphene will require significant effort and patience to perfect the technology and achieve its promise.

An example of such improvements are enhancing the mechanical properties of rubber-based filaments and UV curable filaments. Table 1.2 represents some of the improvements.

As we can see, there are many exciting opportunities that have arisen along with the discovery of graphene and other 2D nanomaterials in the past decade. This book provides an overview of some of the important ongoing research with graphene and also highlights some of the commercial trends and related issues associated with financing companies innovating with 2D materials. The past decade has been one of intense research in 2D nanomaterials. As we have seen with CNTs and other advanced materials, the commercialization cycle extends out over a decade. Experience informs us that where there is great opportunity for commercialization with 2D nanomaterials, there are also challenges and risks associated with creating sustainable business models and successful companies. Based on their remarkable properties and ongoing research and development trends highlighted in this book, we are optimistic about the commercialization prospects of graphene and other 2D nanomaterials-enabled products in the years ahead.