Edited by Soroush Nazarpour and Stephen R. Waite

Graphene Technology

From Laboratory to Fabrication
Contents

List of Contributors  IX

1 Graphene Technology: The Nanomaterials Road Ahead  1
Stephen R. Waite and Soroush Nazarpour
1.1 Newly Discovered 2D Materials  1
1.2 Wonder Materials  2
1.3 The Rise of MPM  5
1.4 Addressing the Environment, Health, and Safety  7
1.5 The Nanomaterials Road Ahead  7
1.6 Can Graphene Survive the “Disillusionment” Downturn?  9
1.6.1 Gartner’s Hype Cycle  9
1.6.2 Surviving the Trough of Disillusionment  10
1.6.3 Graphene and Batteries  11
1.6.4 Heat Management with Graphene  13
1.6.5 How Graphene Could Revolutionize 3D Printing  14

2 Graphene Synthesis  19
Siegfried Eigler
2.1 Introduction  19
2.2 Definitions  20
2.2.1 Nomenclature and Structure  20
2.2.2 Polydispersity of Graphene  20
2.3 Characterization of Graphene by Raman Spectroscopy  22
2.4 Epitaxial Growth of Graphene from SiC  26
2.5 Graphene by Chemical-Vapor-Deposition  27
2.6 Delamination of Graphene from Graphite  31
2.6.1 Mechanical Cleavage of Graphite  32
2.6.2 Liquid Phase Exfoliation of Graphite – Stirred Media Mills  33
2.6.3 Liquid Phase Exfoliation of Graphite – Sonication  35
2.6.4 Liquid Phase Exfoliation of Graphite – Shear Mixing  36
2.6.5 Liquid Phase Exfoliation of Graphite Using Smart Surfactants  38
2.6.6 Electrochemical Exfoliation of Graphite  38
2.7 Wet-Chemical Functionalization and Defunctionalization  40
3 Graphene Composites 63
Suman Chhetri, Tapas Kuila, and Naresh Chandra Murmu

3.1 Introduction 63
3.2 Preparation and Properties of Graphene 65
3.3 Functionalization of Graphene 66
3.3.1 Covalent Modification 67
3.3.2 Non-Covalent Modification 70
3.4 Preparation of Graphene Polymer Composites 71
3.4.1 In Situ Polymerization 71
3.4.2 Solution Mixing 72
3.4.3 Melt Mixing 72
3.4.4 Other Preparative Technique 73
3.5 Characterization of Graphene-Polymer Composites 74
3.6 Properties of Graphene/Polymer Composites 77
3.6.1 Mechanical Properties 77
3.6.2 Thermal Properties 84
3.6.3 Electrical Properties 88
3.6.4 Dynamic Mechanical Properties 93
3.7 Application of Graphene Based Polymer Composites 94
3.7.1 Gas Barrier 95
3.7.2 Sensor 97
3.7.3 EMI Shielding 97
3.7.4 Flammability Reduction 99
3.7.5 Automotive and Aircrafts 99
3.7.6 Turbine Blades 100
3.7.7 Others 100
3.8 Conclusions and Outlook 101
References 102

4 Graphene in Lithium-ion Batteries 113
Cyrus Zamani

4.1 Introduction 113
4.2 Renewable Energies 114
4.3 Batteries, What are They? 115
4.4 Lithium-ion Batteries 116
4.5 Anodes, Cathodes, and Electrolytes 117
Contents

4.6 Carbon Materials 118
4.7 Graphite 119
4.8 Graphene 120
4.9 Graphene in Lithium-Ion Batteries 121
4.10 Graphene in Anodes 122
4.11 Graphene in Cathodes 126
4.12 Graphene in Other Types of Lithium Batteries 127
Summary 127
References 128

5 Graphene-Based Membranes for Separation Engineering 133
Luisa M. Pastrana-Martínez, Sergio Morales-Torres, José L. Figueiredo, and Adrián M.T. Silva
5.1 Introduction 133
5.2 Preparation of Graphene-Based Membranes 134
5.3 Graphene-based Membranes for Separation Applications 140
5.3.1 Gas Separation 140
5.3.2 Water Treatment 142
5.4 Conclusions 149
Acknowledgments 150
References 150

6 Graphene Coatings for the Corrosion Protection of Base Metals 155
Robert V. Dennis, Nathan A. Fleer, Rachel D. Davidson, and Sarbajit Banerjee
6.1 Introduction to Corrosion 155
6.2 Bare Graphene as a Protective Barrier 159
6.2.1 Some Electronic Structure Considerations at Graphene/Metal Interfaces 159
6.2.2 Graphene as a Standalone Corrosion-Resistant Coating and Some Mechanistic Considerations 162
6.3 Graphene Nanocomposites for Corrosion Inhibition 164
6.4 Graphene/Metal Nanocomposites for Corrosion Inhibition 168
6.5 Graphene/Ceramic Nanocomposites for Corrosion Inhibition 171
6.6 Summary and Future Outlook 172
Acknowledgments 173
References 174

7 Graphene Market Review 177
Marko Spasenovic
7.1 Introduction 177
7.2 Graphene Market: Past and Present 178
7.3 Co-ordinated Market Initiatives 184
7.4 Market and Application Projections 185
7.5 Conclusion 186
References 187
List of Contributors

*Sarbajit Banerjee*
Texas A&M University
Department of Chemistry
College Station
TX 77842-3012
USA

and

Texas A&M University
Department of Materials Science
and Engineering
575 Ross Street
College Station
TX 77843-3003
USA

*Suman Chhetri*
Surface Engineering & Tribology Division
Council of Scientific and Industrial Research-Central Mechanical Engineering Research Institute
Durgapur 713209
India

*Rachel D. Davidson*
Texas A&M University
Department of Chemistry
580 Ross Street
College Station
TX 77842-3012
USA

and

Texas A&M University
Department of Materials Science
and Engineering
575 Ross Street
College Station
TX 77843-3003
USA

and

Academy of Scientific and Innovative Research (AcSIR)
CSIR-CMERI, Campus
Durgapur 713209
India
Robert V. Dennis
Texas A&M University
Department of Chemistry
580 Ross Street
College Station
TX 77842-3012
USA

and

Texas A&M University
Department of Materials Science and Engineering
575 Ross Street
College Station
TX 77843-3003
USA

Siegfried Eigler
Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU)
Central Institute of Materials and Processes and
Department of Chemistry and Pharmacy
Dr.-Mack-Str. 81
D-90762 Fürth
Germany

and

Chalmers University of Technology
Department of Chemistry and Chemical Engineering
Kemivägen 10
SE-412 96 Göteborg
Sweden

José L. Figueiredo
Laboratory of Separation and Reaction Engineering
Laboratory of Catalysis and Materials (LSRE-LCM)
Chemical Engineering Department
Faculdade de Engenharia
Universidade do Porto
Rua Dr. Roberto Frias
4200-465 Porto
Portugal

Nathan A. Fleer
Texas A&M University
Department of Chemistry
580 Ross Street
College Station
TX 77842-3012
USA

and

Texas A&M University
Department of Materials Science and Engineering
575 Ross Street
College Station
TX 77843-3003
USA
Tapas Kuila  
Surface Engineering & Tribology Division  
Council of Scientific and Industrial Research-Central  
Mechanical Engineering Research Institute  
Durgapur 713209  
India

and

Academy of Scientific and Innovative Research (AcSIR)  
CSIR-CMERI, Campus  
Durgapur 713209  
India

Sergio Morales-Torres  
Laboratory of Separation and Reaction Engineering  
Laboratory of Catalysis and Materials (LSRE-LCM)  
Chemical Engineering Department  
Faculdade de Engenharia  
Universidade do Porto  
Rua Dr. Roberto Frias  
4200-465 Porto  
Portugal

Naresh Chandra Murmu  
Surface Engineering & Tribology Division  
Council of Scientific and Industrial Research-Central  
Mechanical Engineering Research Institute  
Durgapur 713209  
India

and

Academy of Scientific and Innovative Research (AcSIR)  
CSIR-CMERI, Campus  
Durgapur 713209  
India

Soroush Nazarpour  
Group NanoXplore Inc.  
25 Montpellier Blvd  
Montreal  
QC H4N 3K7  
Canada

Luisa M. Pastrana-Martínez  
Laboratory of Separation and Reaction Engineering  
Laboratory of Catalysis and Materials (LSRE-LCM)  
Chemical Engineering Department  
Faculdade de Engenharia  
Universidade do Porto  
Rua Dr. Roberto Frias  
4200-465 Porto  
Portugal

Adrián M.T. Silva  
Laboratory of Separation and Reaction Engineering  
Laboratory of Catalysis and Materials (LSRE-LCM)  
Chemical Engineering Department  
Faculdade de Engenharia  
Universidade do Porto  
Rua Dr. Roberto Frias  
4200-465 Porto  
Portugal
List of Contributors

Marko Spasenovic
Graphene Tracker
Center for Solid State Physics and New Materials
Institute of Physics
Pregrevica 118
11030 Belgrad
Serbia

Stephen R. Waite
Graphene Stakeholders Association
640 Ellicott Street, Suite 499
Buffalo
New York 14203
USA

Cyrus Zamani
University of Tehran
School of Metallurgy and Materials Engineering
College of Engineering
University of Tehran
North Kargar Street
P. O. Box 14395-515
Tehran
Iran
1

Graphene Technology: The Nanomaterials Road Ahead

Stephen R. Waite and Soroush Nazarpour

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 (MoS₂): When stacked, MoS₂ 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, MoS₂ is composed of molybdenum atoms sandwiched between two sulfur atoms. Unlike graphene, in its natural
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 buckyballs – 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 m² 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
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.
Graphene Technology: The Nanomaterials Road Ahead

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.

---

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.