University of Birmingham
Research at Birmingham

Producing graphene at scale

Stafford, Jason; Matar, Omar; Petit, Camille

License:
None: All rights reserved

Document Version
Peer reviewed version

Citation for published version (Harvard):
Stafford, J, Matar, O & Petit, C 2019, 'Producing graphene at scale' *The Chemical Engineer*, vol. 930, no. 31.
<https://www.thechemicalengineer.com/features/producing-graphene-at-scale/>

Link to publication on Research at Birmingham portal

General rights
Unless a licence is specified above, all rights (including copyright and moral rights) in this document are retained by the authors and/or the copyright holders. The express permission of the copyright holder must be obtained for any use of this material other than for purposes permitted by law.

•Users may freely distribute the URL that is used to identify this publication.
•Users may download and/or print one copy of the publication from the University of Birmingham research portal for the purpose of private study or non-commercial research.
•User may use extracts from the document in line with the concept of 'fair dealing' under the Copyright, Designs and Patents Act 1988 (?)
•Users may not further distribute the material nor use it for the purposes of commercial gain.

Where a licence is displayed above, please note the terms and conditions of the licence govern your use of this document.

When citing, please reference the published version.

Take down policy
While the University of Birmingham exercises care and attention in making items available there are rare occasions when an item has been uploaded in error or has been deemed to be commercially or otherwise sensitive.

If you believe that this is the case for this document, please contact UBIRA@lists.bham.ac.uk providing details and we will remove access to the work immediately and investigate.

Download date: 27. Apr. 2024

Reference: Stafford, J., Matar, O.K. and Petit, C., 2018, *The Chemical Engineer*, 930/31: 24-28.

Producing Graphene at Scale

Just over a decade ago, the isolation of graphene created a major stir in the scientific community. At the time, it was a material that many believed could not be stable enough to exist. It was found not only to be stable, but to possess a range of properties so extraordinary that it is regularly labelled as a "wonder material"; a material that will revolutionise every aspect of our technological world. Such promise and attention has put graphene into the spotlight. So, when we look around at our emerging technologies, why has it apparently not delivered? In this article, we discuss one of the biggest challenges that is blocking graphene's widespread adoption: how do we make high quality material on a large scale? It is the first step before it can be used in any technology, and a challenge, which is particularly suited to the chemical engineering discipline.

What is graphene?

Graphene is in a category that's known as a two-dimensional (2D) material. It is a flake made from carbon and is just one atom thick. This monolayer of carbon atoms is arranged in a 2D honeycomb lattice, illustrated in Figure 1 amongst other graphene-based materials. Graphene's unique properties are what make it such an exciting prospect, which, if realised on a large scale, could have far reaching benefits to society. Its electronic properties, such as carrier mobility and current density, exceed many other conductors in use today. It is also an effective conductor of heat, with a thermal conductivity that is several times greater than copper. In two-dimensional form, it is the strongest material known. All this, and more, from a material which is 98% transparent.

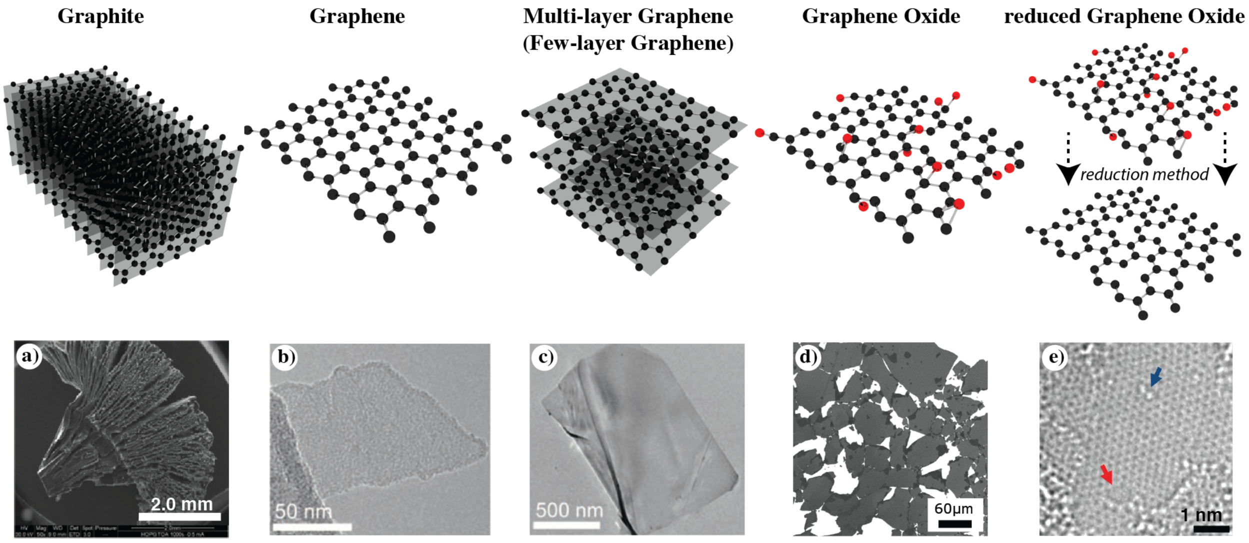

Figure 1: Illustrations and micrographs of Graphite, Graphene, and the other forms of graphene-based materials [1]. Although graphene is a monolayer, the name has been used somewhat ambiguously to describe other useful forms of the layered material. These include few-layer graphene, graphene oxide, and reduced graphene oxide.

Beyond ten atomic layers, the electronic properties of the material are no longer distinct from the bulk 3D graphite crystal [2].

Why all the attention?

Graphene's exceptional properties are central to why it is a special case. This is not, however, the only reason why it has reached rapid fame. The simplicity with which it was first isolated is so relatable, irrespective of whether or not you have a scientific or engineering background, that it was quick to gain traction in the media. Here is a single atomic layer material, touted to change the technological landscape that can be made using some sticky tape and graphite from our pencils. A Nobel Prize followed, six years after this ground-breaking research on graphene was published [3], making it one of the fastest times between discovery and award in the physics category. In terms of a science outreach story, it began with the perfect script and quickly achieved stardom on a global stage thereafter.

Now, the dust has settled, and we are past the hype. For some, the frequent attention that graphene receives, combined with its lack of visibility in our everyday lives, has given the impression that it has not delivered on what was expected. For others, particularly those of us working in this field of research, the outlook is positive and developments are happening faster than ever. Graphene has continued to serve as an excellent platform in academic and industrial research. Figure 2 shows this through the year-on-year increase in the number of scientific articles that have been published [1]. This covers topics from fundamental condensed matter physics to the development of novel graphene-based devices across a range of fields including: photonics, optoelectronics, energy storage and conversion, flexible electronics, sensors, composites and coatings, and biomedical applications [4].

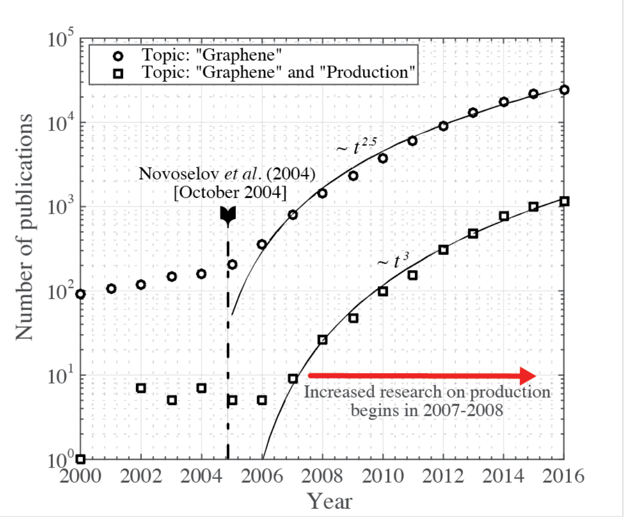

Figure 2: Growth in number of publications on Graphene and Graphene Production topics [1].

Why then, has the introduction of graphene been limited to only a handful of commercial products? The broad applicability and potential of graphene has not gone unnoticed by national and international funding bodies. Large scale consortia and research centres have been formed across the globe, all with the aim of translating graphene research from the lab to real-world solutions. In 2013, Europe started its biggest ever research initiative, creating a Graphene Flagship that brings academia and industry together to perform coordinated research with a budget of €1bn over 10 years. This example of long-term investment suggests a clear intent to accomplish real benefits to society. It simultaneously highlights, however, that the challenges are far from trivial if graphene is to successfully penetrate all technological areas. Among these challenges, large-scale sustainable production of high-quality material is near the top of the list.

Challenge and Opportunity

The attractive simplicity in the story of graphene's isolation has not translated to large-scale production. In order to produce large quantities of graphene for industrial applications, we've had to put away the sticky tape and consider new processing methods with the potential for high quality and high-throughput. These methods are categorised under two different production routes, summarised in Figure 3. Whether or not you choose bottom-up or top-down, depends on a number of factors, including your intended application and quality requirements. What about graphene quality? Not all 'graphenes' are the same and in fact a number of production routes lead to 'low-quality graphene'. This is a broad expression to cover: graphene containing more than one-layer, graphene with 'holes' in the structure due to missing atoms or graphene flakes with low aspect ratio. These 'defects' are often the result of the production route. While they can be an issue in some applications (e.g. photovoltaic cells, microelectronic devices), their effect is less of a concern in others (e.g. composites, inks). For now at least, one size does not fit all. What's common, however, is that there are process engineering challenges across both production routes.

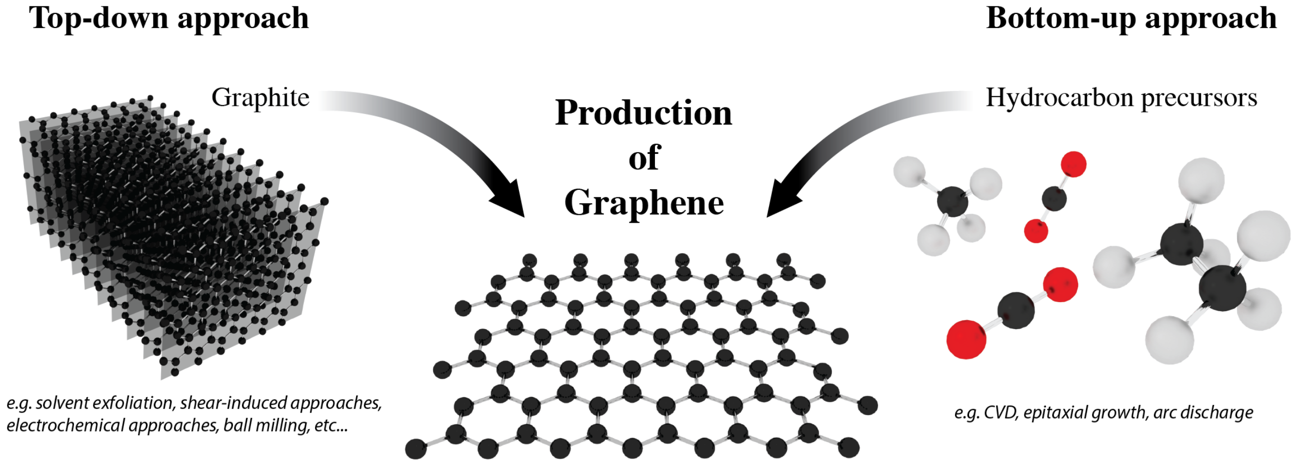

Figure 3: The two production routes for graphene [1].

Bottom-up production

Bottom-up production approaches start with hydrocarbon precursors and grow graphene. The most common of these methods is chemical vapor deposition (CVD) [5]. Large, millimeter-scale sheets can be grown and there is fine control of the number of atomic layers. This type of product is beneficial for applications requiring high quality, large area sheets, such as flexible transparent conductors for photovoltaic cells. A disadvantage is that the material, although high in quality, is produced in small quantities and typically requires a sometimes complex post-production transfer steps. This additional step takes graphene off the substrate from which it was grown, and moves it into the intended application.

The bottom-up approach has potential to incorporate graphene into microelectronic devices also. CVD is already in use in silicon fabs, and an obvious path is to integrate graphene into existing complementary-metal-oxide-semiconductor (CMOS) processing techniques in this way. This also leverages significant advancements previously made by the semiconductor industry. Aside from low-throughput, the major challenges here include differences in processing parameters (temperature, chemicals, catalysts) coupled with the current need to grow graphene on substrates such as copper, which is not compatible with contemporary silicon fabs.

Top-down production

Top-down production approaches use a graphite precursor, and exfoliate monolayer and few-layer graphene from this 3D crystal. The aim is to overcome the weak van der Waals attractive force holding layers together, and prevent them from restacking through dispersion in a suitable solvent. This is done through either mechanical, chemical, or electrochemical methods that fall under a domain known as *liquid-phase exfoliation* [1]. In general, top-down liquid-phase exfoliation offers the highest graphene production rates (lab scale devices have reached ~ 10 g/hr). These graphene dispersions have a distribution in both size and thickness. Due to these process characteristics, the material produced from top-down methods has already infiltrated many ‘low-hanging fruit’ applications. This includes composites and inks, where large quantities are important and size variability is acceptable. In particular, non-oxidising mechanical and electrochemical methods produce a material with sufficient quality for most application areas. This broad applicability means top-down production is a favourable route for scale-up. We will discuss in what follows a broad selection of methods that have emerged.

Reference: Stafford, J., Matar, O.K. and Petit, C., 2018, *The Chemical Engineer*, 930/31: 24-28.

Mechanical exfoliation of graphene is achieved by applying mechanical force to the layers of a graphitic crystal. Normally, this is done by dispersing graphite particles in a suitable solvent, and generating sufficient fluid stresses to separate layers of graphene within the dispersion. Ways to do this include sonication, high-shear mixing, supercritical fluids, microfluidisation, jet cavitation and many others. Some do not scale well beyond the lab (i.e. sonication) whereas other processes (i.e. high-shear mixing) have been shown to scale-up in batch operation. A lack of green solvents is a drawback, particularly if we are to develop sustainable and environmentally friendly solutions. The most suitable solvents include N-Methyl-Pyrrolidone (NMP) and Dimethylformamide (DMF). These solvents have high boiling points, making it difficult to remove from applications afterwards. Aqueous-surfactant dispersions work, and overcome these problems, however, production yields are substantially lower. It also impacts quality, as it is difficult to remove the surfactant from the product.

Chemical exfoliation relies on the conversion of graphite into graphite oxide using strong oxidants. Then, with an additional hydrolysis step, the graphite oxide is split into graphene oxide (see Figure 1). With attached oxygen groups and irreversible basal plane defects, the electronic properties of graphene oxide are poor compared to graphene. Thermal and chemical post-process steps can be used to reduce these adverse effects, however, the resultant product (known as reduced graphene oxide, Figure 1) is usually of lower quality than that produced by non-oxidising mechanical and electrochemical processes. The production steps are generally performed in batch operation, and the formation of toxic gases (i.e. NO_2 / N_2O_4) is a limiting characteristic.

Electrochemical processes implement a graphite electrode and a potential difference to promote the intercalation of molecules between the graphene layers. The layers are forced apart, separate from the bulk graphite electrode and disperse into an electrolyte solution. This method avoids the use of harsh solvents or oxidants as in chemical exfoliation, and can achieve some of the highest yields (up to 80%). When the graphite electrode is used as a cathode (cathodic exfoliation), the electrochemical exfoliation potential is lower than the oxidative potential and the product quality does not suffer from the attachment of oxidative species (unlike in the case of anodic exfoliation). A disadvantage of the current electrochemical methods is in the replenishment of the graphite electrode once spent, and unfavourable graphite breakup as this leads to a loss of electrical contact between the graphite and applied voltage potential.

Up to now, we have focused on methods for graphene production. There are many more aspects of the entire process that require consideration if industrial scale-up is to be realised. These are outlined in Figure 4. Out of all the components in the end-to-end process, quality assessments of the precursor and product, high-throughput separation, material recycling, and storage and handling are particularly underdeveloped.

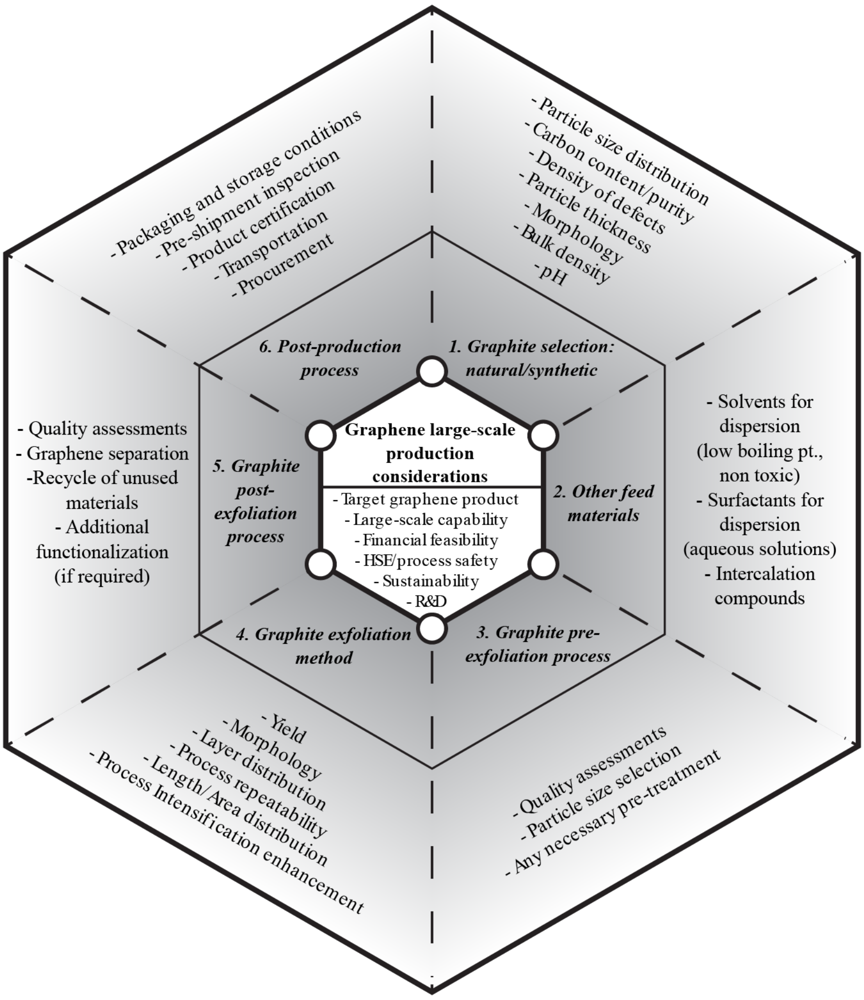

Figure 4: Process considerations for top-down graphene production [1].

One of Many

Graphene is unique in the breadth of its exceptional properties, but it’s not alone. Since its discovery, an entire field of research on layered materials and heterostructures (a combination of dissimilar layered materials) has emerged. Other layered materials with impressive properties include hexagonal boron nitride (insulator), molybdenum disulphide, and black phosphorous (semiconductors). These are only three examples from a larger set of a few dozen that have been investigated so far. In fact, it has been predicted that there may be up to 2000 exfoliable materials [6], with the possibility of them each having useful material properties. Advancements made in large-scale production techniques for graphene will no doubt be a benefit here.

When will it deliver?

In a recent roadmap from the Graphene Flagship [4], estimations of developmental timelines range from 2020 for composites to beyond 2024 for areas such as graphene photonics, integration with CMOS and silicon photonics, high frequency electronics, and printed heterostructures. This suggests approximately 20 years from breakthrough to widespread adoption, and based on historical evidence for other technological breakthroughs, that would be a reasonably fast outcome. The future for graphene and other layered materials is promising, however, a focused effort from multiple disciplines must continue if we are to achieve this. Many challenges remain. Production methods will have to be continuous, scalable, reliable, adaptable, and evolve in parallel with the developmental timelines for graphene technologies noted above. Environmental and sustainability issues must also be solved when moving from lab to industrial-scale volumes. The best solvents for liquid phase exfoliation of graphite are toxic, and the low process yields that many approaches deliver (typically less than 10%) do not help. High-fidelity measurement techniques that are used in the lab to characterise graphene materials do not scale-up, and alternate quality control solutions and metrics that work in an industrial environment are needed. One thing is certain, to succeed in making high-quality graphene at scale, process engineering will have a central role to play.

References

1. Stafford, J., Patapas, A., Uzo, N., Matar, O.K. and Petit, C., 2018, Towards scale-up of graphene production via nonoxidizing liquid exfoliation methods, AIChE Journal, 64(9): 3246-3276.

2. ISO/TS 80004-13:2017, 2017, Nanotechnologies -- Vocabulary -- Part 13: Graphene and related two-dimensional (2D) materials.

3. Novoselov, K.S., Geim, A.K., Morozov, S.V., Jiang, D., Zhang, Y., Dubonos, S.V., Grigorieva, I.V. and Firsov, A.A., 2004, Electric field effect in atomically thin carbon films, Science, 306(5696):666-669.

4. Ferrari, A.C., et al., 2015, Science and technology roadmap for graphene, related two-dimensional crystals, and hybrid systems, Nanoscale, 7(11):4598-4810.

5. Zhang, Y., Zhang, L. and Zhou, C., 2013, Review of chemical vapor deposition of graphene and related applications, Acc. Chem. Res., 46(10):2329-2339.

6. Mounet, N., et al., 2018, Two-dimensional materials from high-throughput computational exfoliation of experimentally known compounds, Nature Nano., 13:246-252.