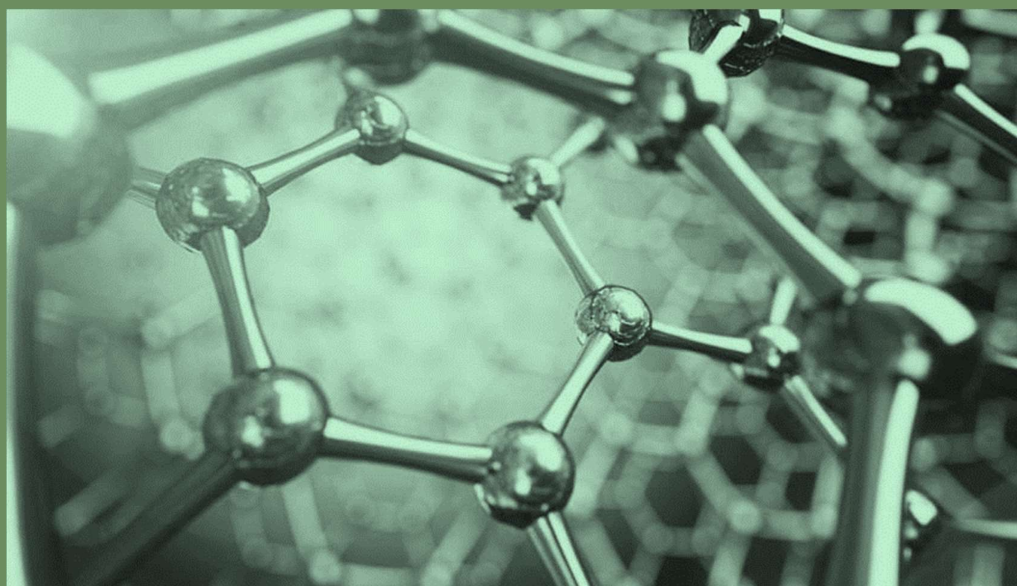
Research Intelligence and Advances



Graphene Research and Advances

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Summary

The need for graphene materials will increase in the coming years especially in fields related to energy storage, composites and coatings, electronics, and biomedical applications. Although, graphene product penetration into the market in various applications is anticipated to be beneficial, there are many factors affecting a full success such as **cost, product availability, sustainability, and consistent quality.**

In this report, SIO Grafen aims to summarize graphene-based applications at different development and maturity stages. The report includes examples from research phase applications to early prototype technologies and finally to graphene applications where industrial validation stage have been reached.

From recent publications data, it was found that the main grades (types) of materials implemented in applications areas are **graphene nano-platelets (GNP), graphene oxide (GO), and reduced graphene oxide (rGO).** Whereas sheets of graphene (predominantly produced by chemical vapor deposition, CVD) are being used in fewer of the applications on the market. Most of the available reports focus on GNP and GO, pointing towards them as the largest market shareholders. GNP demand is driven by a need for lightweight composite materials in the aerospace and automotive industries. Whereas GO and derivatives (rGO) are implemented in energy storage and electronics due to better properties in terms of electrical, mechanical, and surface area.

In the last part, reports on the graphene-related material availability with some considerations of the most common graphene market barriers will be highlighted considering their significant performance in future technologies.

1. Introduction

SIO Grafen releases, on a regular basis, reports with market analysis and the latest applications based on graphene and other 2D materials available on the SIO Grafen homepage and other social media. Already, graphene-related 2D materials (GR2M) have been an object of research for more than 15 years. Consequently, nowadays there are commercial applications in several fields including electronics, composites, and membranes, to mention just a few of them.

Applications based on graphene materials are expected to grow and consequently also the graphene market and sales, considering the increasing demand from companies for graphene-based products production and institutes for research and development purposes.

As it is largely reported in literature, scientific publications and in previous **SIO Grafen research intelligence reports**, GR2M have excellent properties in terms of thermal, electrical, and mechanical performance etc. It is important to underline that the use of graphene in each application has a significant impact on the performance even at very low concentration (less than 1%).

Moreover, the performance depends on factors related to the material such as surface chemistry, defects, functionalization and morphology. Finally, rising product penetration into the market in various applications including coatings, composites and electronics, is anticipated to benefit the market.

However, there are many factors affecting a full success such as **price, product availability** and in particular **health and quality (standards)**.

Graphene produced today is not one single material but includes a group of different materials which differ in number of layers (thickness), morphology, defects, functional groups ect.

These characteristics and the type of graphene material produced depends on the manufacturing process. As the classes of the graphene family increases (functionalization to tune the material), it has become mandatory for a successful application to adopt standardization procedures. The lack of standards in graphene manufacturing represents today one of the major obstacles for end users to integrate graphene in a target application. With a growth in the number of applications, standardization and other quality characterizations are addressed more closely from different entities with more graphene producers involved in the process.

In this report, SIO Grafen aims to summarize graphene-based applications at different development and maturity stages.

At first, we will describe examples of energy storage devices such as supercapacitors in their research phase. Afterwards, early prototype technologies will be reported based on stretchable supercapacitors. Finally, we have a look at recently reported graphene-based membranes for water filtration as this technology has reached an industrial validation stage.

Before going into the details of research or ready to be commercialized applications, an overview of the market analysis and patent applications will be updated since the last report of this series.

In the last part, reports on the graphene related material availability with some considerations of the most common graphene market barriers will be highlighted considering the environmental impact of the graphene-based materials and their significant performance in future technologies.

In this report the following examples will be highlighted:

1. Market and Patent Trends and Growth
2. Graphene based materials: Research phase application (Supercapacitors)
3. Early Phase applications: Stretchable Supercapacitors
4. Commercialization Graphene based Applications: Membranes for Water Treatment
5. Summary Graphene based materials availability.

2. Market and Patents: Trends and Growth

All reports agree that the demand on graphene will increase in the coming years especially in fields related to energy storage, composites and coatings, electronics and biomedical applications.

SIO Grafen has investigated graphene materials patent trends and material growth for several years now. In this report, we will focus on the top applications by filed patents and price for graphene related materials.

In accordance with the past articles, **energy storage and electronics** have had a significant progress, in particular **semiconductors** where we see a general interest by large international companies. In relation to **composites and biomedical**, we can see a steady development although a general decrease in filed patent applications is estimated.

So far graphene demand is mostly driven by research organizations (universities and research institutes) and global companies such as AIXTRON, IBM, Airbus, and Samsung. These large companies at the same time set a target cost of graphene which remains still relatively high especially when the materials are implemented in very inexpensive polymers or if compared to other carbonaceous materials such as carbon black.

On the other hand, when we have a look to patents related to graphene production there is a general decrease in number of patents in the manufacturing area. This could indicate that the production capacity has met the markets demand to reduce the cost by enhancing production.

When we compare the **cost of graphene**, in 2017 the price for graphene powder ranged between USD 50,000-200,000/t, depending on quality and volume of purchase. After 3 years, the commercial cost of graphene was estimated between ca USD 67,000 - 200,000/t slightly higher if compared to previous price.

Today US based graphene manufacturer - CIT Materials, sells industrial-quality graphene nano-platelets (GNP)for USD 50-75/kg for commercial volumes and USD 15/g for small quantities. Research quality GNPs' is sold for USD 65-90/kg for large volumes and USD 35-40/g for small quantities. In Europe, graphene oxide manufacturers sell dispersion for USD 186 per 1000 mL (0.4 wt%).

The status of graphene materials suppliers has overcome the capacity problem as mentioned earlier, therefore the focus is shifted towards the implementation of such materials into the end application.

When we have a look to graphene applications developed, we see a different segmentation in the graphene market. The main grades (types) of materials mentioned in publications are **graphene nano-platelets, graphene oxide, and reduced graphene oxide (rGO).** Most of the available reports focus on GNP and GO, pointing towards them as the largest market shareholders. GNP demand is driven by a need for lightweight composite materials in the aerospace and automotive industries. At the same time GNP is used in different areas such as biomedical, conductive inks, composites, and coatings.

GO on the other hand can be exfoliated to single sheet or thin transparent film and modified to reduced graphene oxide. Therefore, both GO/rGO are implemented in supercapacitors, flexible electronics, and optoelectronic devices. Reduced graphene oxide is mostly implemented in energy storage and electronics due to better properties in terms of electrical, mechanical, and surface area.

To compare with last year SIO graphene reports, we see the same trend as the past years where graphene is the domain China and North America. Nevertheless, in the past years, Asia-Pacific with China (APAC) reportedly had the highest market revenue and volume share in 2019-2021. Northern America and Europe regions are also active producers and developers, characterized by the presence of many SME manufacturers, whereas China invests in graphene to support its position as a global manufacturing force supplier. Asia-Pacific is also considered to hold the title of the fastest-growing end consumer of graphene products in the next few years. The rising electronics and automotive consumption, and favorable government policies are driving this growth. SIO grafen will continue to monitor the Market and Patents trend as an indication of growing activities within graphene technologies and manufacturing capacities.

3. Graphene Based Materials Research Phase (Supercapacitors)

Graphene used in Energy storage systems have been an object of study for several years due to its excellent properties such as mechanical, electrical and high surface area. Because of the extraordinary properties graphene materials represents an ideal candidate for next generation energy systems such as **supercapacitors.** If compared to batteries, supercapacitors have many advantages including **faster charging and longer life span** which makes them highly attractive in electrically powered systems. A major drawback of supercapacitors over batteries is the relatively **low power performance** which makes their use still limited in energy field applications. Supercapacitors (SCs) store energy on the surface of the material, unlike batteries, which involve chemical reactions. SCs are characterized by electrodes coated with a porous material, generally activated carbon, a separator in the middle, and an electrolyte which can be of a different nature (liquid or solid state). In general, the stability of supercapacitors highly depends on the structure of the electrode material.

Activated carbons are currently used as electrode materials, but they lack in temperature and cycling stability when applied to electric vehicles systems which require high temperature operation and voltage.

The potential of graphene and derivatives as materials for electrodes relies in their:

- excellent mechanical properties, which is beneficial in maintaining a high capacitance retention.
- high electrical conductivity enabling fast transfer of electrons and ions through the different device interfaces (electrodes and collectors).
- Improved surface area for the functional interaction between ions and electrons.

Although many efforts have been made toward new materials for the electrode, alternative solutions to activated carbons remains a challenge.

As mentioned earlier, supercapacitors lack in energy density if compared to batteries and currently lithium accumulators reach an energy density up to 265 Kilowatt hours (KW/h), supercapacitors indeed have reached only a tenth of it. To improve this, graphene with excellent properties (high surface area and electrical conductivity), opens new opportunities for energy storage applications.

Recently researchers from Technical University of Munich published a work which describes an asymmetric supercapacitor using a graphene hybrid material (positive electrode) with an improved capacitance **up to 651 F g^{-1}** and Mxene as opposite electrode (Figure 1). In this work it was shown that the large surface area, essential for supercapacitors, was achieved by covalent bonding of conductive graphene with microporous MOF materials. The improved surface area facilitates a fast charge transportation which translate in enhanced overall capacitance.

The strong bond between the two structures allows at the same time cycle stability (more charging and discharging cycles) retaining **ca 90%** capacity after **10,000** cycles. The cell **power density** (up to 16kW kg^{-1}) and energy density (up to 73Wh kg^{-1}) **are comparable to commercial energy storage devices**, confirming the industrial viability of the energy storage devices.

To conclude this early-stage research, summarize a promising graphene application in a hybrid supercapacitor which uses graphene and 2D MXene to enhance devices useful life cycles if compared to lithium accumulators (5000 cycles).

This improvement in life cycle on supercapacitors and other reported progress in a more advanced research phase, have shown the great potential of graphene and 2D materials in energy storage applications in a novel and sustainable way.

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4. Graphene Based Materials Flexible Electronics

4.1 Energy (Mxene-rGO Stretchable Supercapacitors)

In the past years, we have witnessed a continuous and fast growth of micro-electronics such as smart wearable and flexible sensors, electronics, stretchable displays, and other implantable devices.

The increasing demand in such electronics, has motivated the research towards power sources that can bend or be implemented with different flexibility into stretchable displays and other devices.

Thus, batteries and supercapacitors (SCs) with superior battery storage represents excellent candidates in achieving high performing power systems for different flexible wearables and other applications. Existing power sources available today are in different sizes and forms but they are rigid and upon bending they tend to break due to lack of flexibility.

For this reason, **graphene materials, together with other 2D materials (Mxene) with superior mechanical flexibility**, high surface area and elevated electrical performances are very attractive in **flexible supercapacitors and batteries.**

SIO Grafen reported last year an example of a micro-supercapacitor device fabricated by **inkjet-printing** of **graphene patterns**. The technique is low-cost thus feasible for large scale production.

Indeed, this time, we focus on recent work reported by Cao, Glass, and others, using hybrid graphene derivatives **(rGO)** and **M-Xene** materials (similar system presented above) but for **Stretchable Supercapacitors.**

In the paper, the performance of a hybrid electrode based on 2D titanium carbide MXene and rGO (reduced graphene oxide) used in a stretchable supercapacitor is reported.

The effect of using **MXene /rGO composite** in the electrode results in **enhanced mechanical and electrochemical properties** fabricating a robust printed energy storage device (supercapacitor). Moreover, it was found that the composite electrodes with 50% rGO incorporated exhibit a large capacitance of (49 mF/cm^2) and good mechanical flexibility when subjected to cyclic strains (stretching up to 250% strain for over 1000 stretching-relaxation cycles).

Mxene/rGO composite films were obtained using a vacuum assisted filtration. Further *Cao et al* discussed the coated film electrode was pressed into an acrylic elastomer and the filter membrane is peeled off to transfer the composite (MXene/rGO) into the substrate stretched to a specific strain. Due to better adhesion force, the composite film was finally transferred to the elastomeric substrate, followed by slow release along the pre-strained direction, allowing in this way to restore its original length.

Stretchable supercapacitor electrodes can be fabricated using different scalable techniques, such as **screen printing or drop casting**. In addition, **laser writing and inkjet printing** have shown advantages for fast production, making possible transfer to almost any target substrate. This flexibility is crucial for their integration into the growing industry of wearable micro-electronics such as smart wearable and flexible sensors, electronics, stretchable displays, and other implantable devices, where SCs are expected to play an important role in the future.

Although stretchable supercapacitors have great potential in flexible electronics, most of them lack in efficient fabrication methods and are limited by low stretchability, performance, and robustness. An efficient process method to improve flexibility is reported by the same group *Cao et al*. As a development in the technology, in this article an easy and scalable approach is reported to produce stretchable supercapacitors combining 4D printing technique with self-organized origami patterns with the aim to control simultaneously the shape of such power devices. In this case the printed electrode is composed by electrodes made of rGO, CNT, and conducting polymer which have shown very good performance and mechanical flexibility.

Finally, as the researchers suggest in the paper, 4D printing methodology can be extended to next generation energy storage devices, offering a promising solution to the **scalable manufacturing of stretchable SCs.**

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5. Toward Commercialization Graphene-Based Applications

5.1 Membranes for Water Treatment

As mentioned earlier, graphene is a high-tech, 2D nanomaterial which, owing to its unique properties, has many applications to both enable and enhance the performance in several applications.

One of the areas where graphene has been used to improve micro- and ultrafiltration is water purification. Due to the potable water scarcity worldwide and increasing contaminants and pollutants in water, it has become clear that efficient and sustainable technology to provide water purification is not only of high demand but also necessary (UN Sustainable Development and EU Directive in drinking water). Therefore, with the aim to improve the removal of contaminants, the development of efficient systems for water filtration using nanomaterials has been studied for many years.

In general, there are different polymeric membranes used at industrial scale for filtration using size exclusion mechanisms and in recent years graphene materials have been implemented in such polymers for water treatment technologies due to their excellent performances as absorbents towards different contaminants present in water. Graphene oxide (GO) and reduced graphene oxide (rGO) represent optimal candidates in terms of versatility, enabling access to multifunctional materials with selective absorption capacity against different pollutants/contaminants present in water.

Substantial efforts have been made towards membrane technology development and herein we focus on the latest works and progress of graphene-based membrane upscaling and commercialization.

The optimal performance of GO based membranes is due to a combination of factors as reported by recent publications from Bologna University, Medica Company and others.

Together with Industrial partners (Medica Italy, UK, France), in this work has been demonstrated that GO/rGO 2D-nanosheets imbedded with commercial hollow fibers can be used for adsorption of contaminants from water and easily removed by combining an innovative two-step method consisting of adsorption in batch and microfiltration on hollow fiber modules.

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Compared to other structure, the hollow fiber is characterized by a larger membrane area per unit volume of membrane module, resulting thus in higher productivity. This technology is developed in the company MEDICA (phase inversion extrusion by a customized semi-industrial plan).

The optimized procedure was then applied using both with GO and rGO materials, for an efficient and selective removal of:

- Mixture of perfluoroalkyl substances (**PFASs)** from tap water at µg/L levels
- Mixture of different **heavy metal** (Lead, Chromium, Arsenic, Copper etc)
- **Different drugs**: antibiotics/anti-inflammatory present in water
- **Plastic Additives**

In the development of the graphene-based filters, the researchers have investigated the lifetime which is scaled up to 100 L volume and the next step will be to 5000 L volume of water. The same authors have reported scaling up **sustainable membranes** generated with **recycled material** from the hollow fibers and graphene oxide which has been demonstrated to have comparable results in terms of efficiency and selectivity to the filters coated with GO material. Studies towards safety in using graphene materials, released from the filters, have been carried out demonstrating with advance techniques that **no release of graphene oxide in water** was observed. Moreover, chemical potability tests have been performed confirming the removal of any contaminants in the filtered water, in agreement with existing legal limits.

In these works, it has been demonstrated that graphene-based membrane products are in **industrial phase validation** and ready to be **commercialized** for water purification applications. In addition, enhanced separation performances toward new emerging organic pollutants and high selectivity for heavy metals have been reported. Finally, the filters for water purification are currently installed at Chalmers (Gothenburg) showers to validate the membrane graphene product.

6. Graphene Based materials (GBM) Availability and Growth

The forementioned examples in graphene-based technologies and the road to commercialization of graphene-based materials are possible if the supply chain is secured with required standards and quality assurance. For this reason, we will focus on recent work and roadmaps summarizing the availability of GBM and prospective in applications and recent technologies requires. As mentioned in the introduction, graphene product penetration into the market in various applications is anticipated to benefit the market, although there are many factors affecting a full success such as **cost, product availability, sustainability, and quality.**
Gradual but limited increase of production volume (graphene availability) translates into high material costs. This represents not only a critical barrier for graphene-based product commercialization but also indicates a general lack of maturity of the supply chain as reported in an extended graphene roadmap **by *Döscher et al*.**

In general, in this publication it is reported that graphene pricing and production is strictly connected to the demand and maturity of the graphene applications. Successful commercial products will increase production capacity and decrease therefore the cost related to GBM.

Beside these two important factors (cost and capacity) there are other aspects to be addressed namely, **standardization, health concerns** using GBM and chemical **registration (REACH),** a necessary regulation when scaling up chemical products up to 1 Ton per year.

In relation to this SIO Grafen has also reported internal reports on graphene safety and regulations.

As reported in the forementioned work, it is challenging for industrial users today to find the right graphene material available in the market and often tailored products are developed directly with the customer. Because of the uncertainty in the graphene supply chain the industrial implementation of graphene material is rather slow and the commercial applications available today does not necessarily translate into capacity expansion and cost reduction.

As mentioned in the introduction graphene does not exist as one material but rather a family of materials.

Therefore, for a successful integration of graphene in applications, as we have discussed above, standardization procedures must be in place. In other words, customers must receive reliable graphene materials ensuring in this case that performance will not be impacted by purchasing from different suppliers.

As mentioned, the chemical and physical composition of graphene greatly impacts application performances therefore standards to ensure quality are highly demanded for a successful penetration into the market.

Despite the reported considerations and forecasts, graphene production has been expanded in some sections (applications) in the last four years and graphene-based technologies have been consequently growing in view also of the development of sustainable materials for *e.g* energy storage.

In addition, in recent publication (**J. Munuera *et al***) data from 34 different graphene suppliers last year report **a production capacity of ca 9.7 kT** with different prices for several volumes and materials whereas the **estimated demand is ~900 tonnes**. An example is reported in the graphic below where graphene materials such as graphene nanoplatelets (GNP), monolayer graphene (MLG) and few layers graphene (FLG), differ in prices with volume increase.

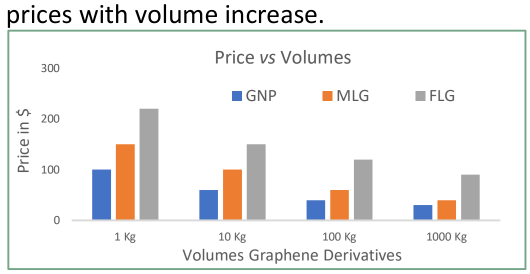

Figure 1. Price Graphene materials *vs* Volume

In addition, is reported that composites (275 tonnes) and batteries additives (160 tonnes) make up *ca* 50% of the orders graphene-based composites. Other applications such as electronics, automotive, paints and coatings contribute to ca. 75% of the demand which nevertheless is still below the current capacity worldwide, as described in the review.

It is worth to mention Companies in North America and China have announced a significant increase in the production capacity contributing to a cost decrease and a further push for commercialization of graphene-based products, as confirmed also by SIO Grafen previous research where most patents were from China and North America.

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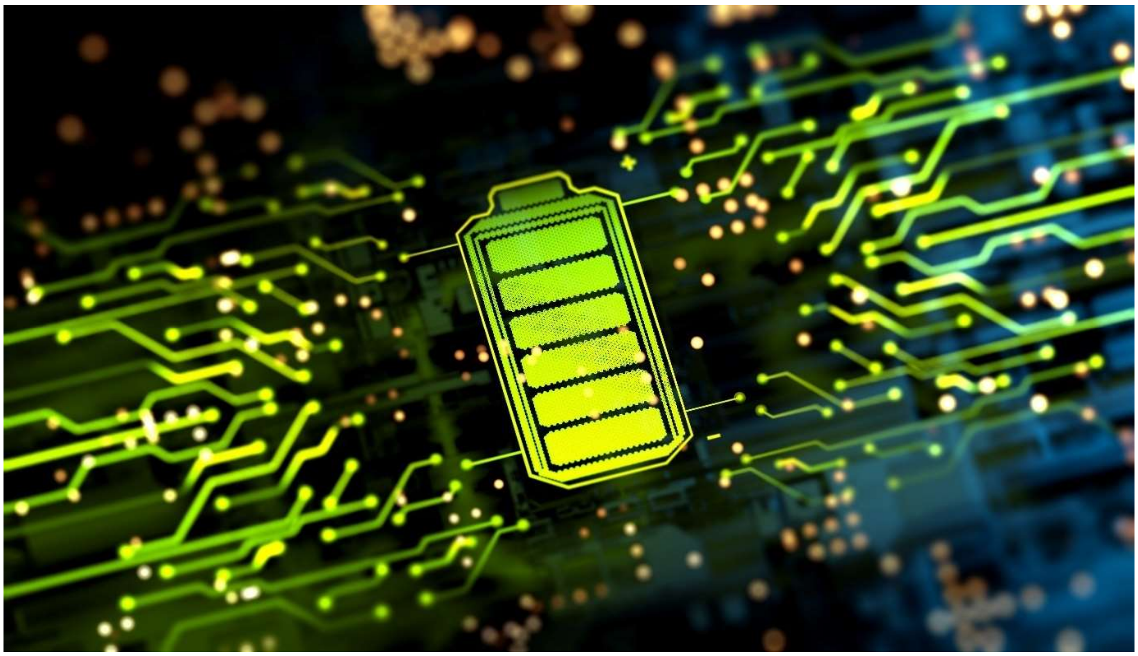
To summarize, based on production costs and application field, not all graphene materials are developed and produced at the same pace. Experts in the field anticipates that by 2030 we will have a more general picture of whether graphene and other 2-D materials will have an impact in high tech applications, or the market will be dictated by material availability, quality, costs, and safety making the use of graphene limited to niche applications.



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