Graphene Research and Advances

Report December 2019

Johan Ek Weis, Sophie Charpentier, Aleksandra Kempinska

11 December 2019

Med stöd från

VINNOVA Sveriges innovationsmyndighet

Energimyndigheten

FORMAS

Strategiska innovations-program

Introduction

SIO Grafen's Research Intelligence Report Series, published twice a year, aims to highlight some of the most interesting research findings on graphene that have emerged during the last few months. This report focuses on two of the six areas of strength within SIO Grafen; energy and composites. In addition to the presentation of the latest state-of-art research, the report also includes a discussion of the patent landscape within these areas and the graphene field in general.

In the last few years, there has been a strong interest from the Swedish industry to incorporate graphene in a variety of applications, specifically in the area of composites, but also energy, resulting in a large number of innovation projects funded through SIO Grafen, with 28 projects on composites and 19 on energy applications. In total 89 innovations projects have been started within SIO Grafen since its creation in 2014. A complete list of these can be found on the SIO Grafen homepage.

Content:

State-Of-Art Research - Energy

Energy is one of the areas where graphene is expected to have a very large impact. There is a tremendous amount of research on for example different types of batteries, supercapacitors, photovoltaics and other new energy generation systems enabled by graphene.

In batteries, graphene is mainly used to improve the performance and life cycle due to its large surface area, high conductivity, high chemical and thermal stability and good mechanical strength.

Batteries

Li-ion batteries (LiBs) are the most commonly used batteries today. There are other types of batteries under development that for example have significantly higher energy density or can charge considerably faster. There are however challenges that still need to be solved with these batteries before they can replace LiBs and graphene might be the key to solve some of them.

Lithium-Sulphur Battery - Li-S

One of these new types of batteries that is widely studied is lithium-sulphur batteries. The sulphur theoretically enables a high specific energy density, which is about five times higher than in traditional LiBs. However, the Li-S batteries also suffer from dissolution of the active material by the electrolyte, which ultimately results in a short life cycle of Li-S cells.

A recent study[1] by researchers at Chalmers have investigated an interesting solution to this. They combined the electrolyte and the cathode into a "catholyte" and used a graphene aerogel (or sponge) in order to form a conductive and highly porous support. The graphene sponge was produced from graphene oxide (GO) and reduced in order to increase the electrical conductivity.

The new structure was stable for more than 350 cycles and demonstrated a high capacity of 3.4 mAh cm^{-2}. The Li-S cell was furthermore produced without any toxic fluorine in the catholyte, which is in contrast to many alternative structures.

Lithium-Silicon Battery

Another alternative to increase the energy storage density of LiBs is to add silicon into the anode. These anodes have a specific capacity which is approximately 10 times higher than for the commonly used graphite anodes. However, the volume of the silicon anodes expands and shrinks significantly (around 4 times difference in volume) during charging and operation. This mechanical stress leads to problems with for example a decreased electrical conductivity and short life cycle.

Many different alternatives and material combinations have been studied and now researchers at the Mid Sweden University might have solved the challenge using a simple, cost-efficient and scalable method.[2] They formed a hydrogel of silicon and nanographite (a mixture of graphene, multilayer graphene and graphite nano platelets). These hydrogels were freeze dried and thereafter heated at 800 °C to form a porous Si-nanographite aerogel.

The electrodes were estimated to contain 6.2% silicon and showed a stable and high specific capacity of 455 mAh g^{-1} for the 200th cycle, which corresponds to 341 Wh kg^{-1}. The coulombic efficiency was 97% at a current density of 100 mA g^{-1}.

Supercapacitors

A supercapacitor is basically a combination between common batteries and capacitors. They can typically store more energy than capacitors as well as both charge and deliver charge faster than batteries.

Structural supercapacitor

The batteries and supercapacitors used in electrical vehicles today are very heavy. There is a lot of research on reducing the weight by improving their energy density. A different approach is to store energy within the structural parts of the vehicle. This requires developing batteries or supercapacitors that are mechanically similar to the structural body panels used today. The idea is neither to make the best energy storage nor the best construction material, but a combination that can reduce the total weight. Structural batteries have been researched for over ten years. In Sweden, for example, Volvo, Chalmers and KTH have been investigating structural batteries based on glass fibres and carbon fibres for years.

A recent study[3] investigated structural supercapacitors based on graphene. In it the researchers functionalised reduced graphene oxide (rGO) using poly(dopamine) and combined them with high-tensile-strength Kevlar aramid nanofibers. This increased the Young's modulus and the tensile strength with over 200% as compared with the pure rGO.

The potential of structural energy storage units can be described by the multifunctional efficiency. This is a measure of the sum of the improvement of the mechanical properties (Young's modulus) and the improvement of the energy storage (specific energy) of the composite as compared to conventional materials. The authors compared their material with epoxy and carbon aerogels and found a high multifunctional efficiency of 5-13.

Smart textiles

Many kinds of wearables are being developed. These should ideally be self-powered, which means the inclusion of both a device for producing energy, such as a photovoltaic cell or a piezoelectric generator, and energy storage in a battery or supercapacitor. In some of these new wearables a traditional battery is sewn or glued into smart fabrics, which can be cumbersome, whereas new technologies using e-fibres often suffer from a low energy storage capacity.

A proof-of-concept smart textile based on graphene supercapacitors was recently developed.[4] The supercapacitor was made by coating a thick layer (3 μm) of graphene oxide flakes on nylon. In order to increase the electrical conductivity and form a porous layer, as required for a supercapacitor, the graphene oxide was reduced and patterned using a combination of lasers from continuous wave to femtosecond pulses. A gel electrolyte based on polyvinylalcohol and sulphuric acid was then added, and the devices were encapsulated.

The whole fabrication process could be made in 3 minutes, and resulted in supercapacitors with good stability, areal capacitance of 49 mF cm^{-2}, energy density of 6.73 mWh/cm^{-2}, power density of 2.5 mW/cm^{-2}, and stretchability up to 200%. The authors thus believe that these devices can become an important part of future self-powered smart textiles.

State-Of-Art Research - Composites

In recent years, graphene has gained attention as possible additive for nanocomposites due to its unique thermal, electrical and mechanical properties. The benefits of using graphene as an additive are already present at relatively low loading. Also, the type of graphene used for composites applications (graphene flakes) is relatively easy to produce, making it readily available and cheap. Composites is therefore one of the application areas where graphene is the most mature, with several products already on the market.

Filament for 3D Printing

As the pressure for reducing our usage of fossil fuels increases, so does the demand for energy consumption, both of which increase the need for finding innovative ways of manufacturing energy storage devices. Although the focus has traditionally been on the utilisation of two-dimensional printing methods (for example, blade coating), research has recently shifted toward the utilisation of 3D printing, especially in the field of energy storage where large surface area structures, such as those created using 3D printing, are beneficial.

Graphene can be used as an additive in polylactic acid (PLA) and acrylonitrile-butadiene-styrene (ABS) conductive filaments for 3D printing. In a recent study[5], researchers developed a new technique to produce filaments with a range of graphene-loaded PLA. The optimized filament was tested by 3D printing Li-ion batteries with a specific capacity of 500 mAh/g (at a current density of 40 mA/g). Filaments were produced with loadings ranging from 1 to 40 wt.%. graphene nanoplatelets, much higher than what had previously been reported (5.6 wt. %). These results are therefore an important step in the field of additive manufacturing for 3D printing.

Ultra-strong Graphene-based Films

Graphene's amazing properties in its pristine form are not translating completely when used as an additive in a composite. For example, the Young's modulus, a measure of the ability of a material to withstand changes in length when under lengthwise tension or compression, decreases by a factor of a hundred when going from a perfect graphene sheet to a graphene composite.

In a recent article[6], researchers showed that by carefully controlling the production process, one can optimize the chemical bonding between rGO nanosheets, creating an ultrastrong, supertough, and highly conductive graphene film with a tensile strength of 1054 MPa, a toughness of 36 mJ/m^3 and an electrical conductivity of 1192 S/cm. The film also presented electromagnetic interference (EMI) shielding capability and is highly fatigue resistant to repeated mechanical deformations.

Strong Paper from Weak Flakes

In another recent study[7], researchers used a different approach to obtain strong paper-like films. They produced 3 kinds of films, using porous GO flakes, solid flakes and a mix of the 2. Films made from only weak, porous GO flakes were also weaker than paper made from solid flakes. However, using both kinds of flakes gave better results than with either of them used separately: the addition of 10 or 25 percent of the weakest flakes strengthened the films by about 95 and 70 percent, respectively. The much softer and porous GO flakes effectively serve as a binder, increasing the effective connection between the solid flakes and distributing the stress in the film better. The insights gathered from these experiments should also be applicable to other materials.

Air Pollution Remediation

In urban areas, atmospheric pollution caused by vehicles' exhausts and industry is a growing health problem. Photocatalysts such as titania (TiO_2) can be used to mitigate this problem: when exposed to sunlight it degrades nitrogen oxides and volatile organic compounds present at the surface, oxidising them into inert or harmless products.

In a recent study[8], researchers produced graphene/TiO_2 composites with enhanced photocatalytic efficiency. The composite was produced using a one-step process by liquid-phase exfoliation of graphite in the presence of TiO_2 nanoparticles. The resulting composite was used as a coating and showed enhanced photocatalytic activity, degrading up to 40% more pollutants with respect to a coating with just TiO_2, and up to 70% more pollutants in the case of nitrogen oxides. The process developed is both simple and cost efficient and could therefore be scaled up for large scale trials.

Large Scale Initiatives

As mentioned previously, batteries and composites are quite mature application areas for graphene. This not only translates to the commercial availability of graphene-based products, but also in several large-scale initiatives, dedicated both to tests of new solutions on a large scale and to accelerate the commercialization.

A few years ago, the PolyGraph project (financed by the European Commission) was completed. This project was dedicated to up scaling the production of graphene thermosetting polymers for composite, coating and adhesive applications.

In May 2019, the BATTERY 2030+ initiative (financed by the European Commission) was launched. The goal is to help Europe take the lead in battery science and technologies by developing sustainable batteries with ultrahigh performance and smart functionalities. Graphene is not the focus of this initiative, but although it only started recently, a collaboration between the initiative representants and the graphene community has already been established.

In Manchester (United Kingdom), several centres have been created to boost the technology transfer between the academics and the industry. The National Graphene Institute (NGI), which enables academics and their industrial partners to work side-by-side on new and exciting applications. The Graphene Engineering Innovation Centre (GEIC) aims to accelerate the development and commercialisation of new graphene technologies. These centres cover several application areas, including energy and composites.

In Gothenburg (Sweden), a new competence centre for research on two-dimensional materials, 2D-Tech, will start in January 2020. It will focus on emerging materials, multi-functional composites, high-frequency electronics and energy applications. Several companies are involved, with the goal to create a collaboration platform for long term projects.

In Uppsala (Sweden), another competence centre on batteries, SweBAL, is starting. Graphene is not the focus of this centre, but it could be included for example in the development of new electrodes.

Late last year, Ford announced it would integrate graphene-enhanced parts in different types of covers on its cars to reduce noise. Earlier this year, a part of a highway in the United Kingdom was paved using a graphene-enhanced asphalt and the authorities are now considering extending the tests to a second one.

In august, Samsung made the news with rumours of a new phone model with a graphene-based battery that can charge in only 30 minutes, coming already in 2021.

These are just a few examples of large-scale initiatives, and there is no doubt more will soon follow.

Statistics of Scientific Publications

A trend analysis of scientific publications was conducted using Web of Science. The analysis performed on the data shows that the number of scientific publications on graphene continues to increase, as shown on Figure 1. The figure also shows that this trend holds true for the two specific application areas analysed, composites and energy. As was the case in the last report with electronics, a significant amount of the publications on energy applications using graphene do not explicitly mention the word "energy" in the abstract or as one of the topics. On the other hand, the word energy can also refer to topics that are not within the energy area of strength, such as for example energy levels. It is therefore not the best keyword and a search for battery and supercapacitors (and derivatives, such as supercaps etc.) is therefore also included here.

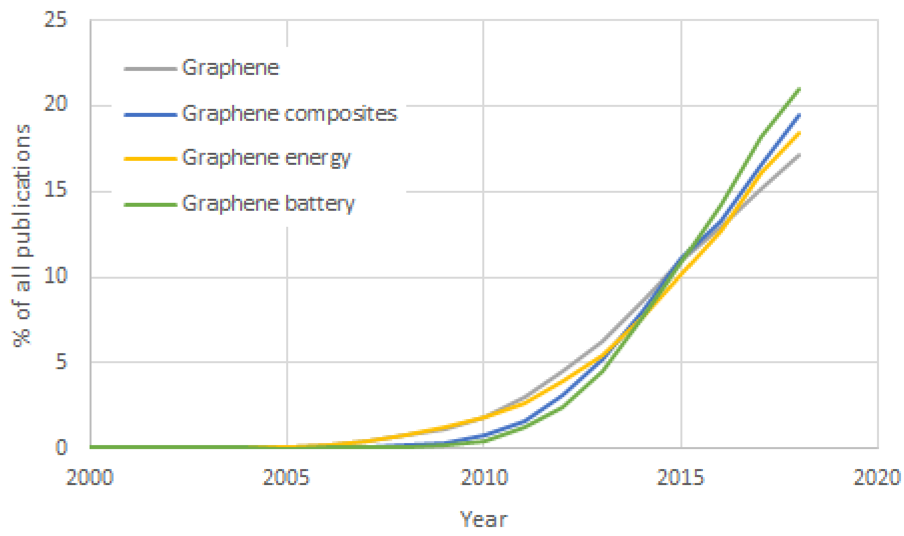

Figure 1 Total number of scientific publications per year for graphene, graphene and composites, energy and battery. To facilitate the trend comparison, the curves were rescaled, and expressed as a percentage of the total amount of publications for each application area. Data from Web of Science, November 2019. Keyword searches for topic were employed, including also derivatives such as nanocomposites.

There is a similar amount of publications on graphene and batteries as for graphene and supercapacitors, approximately 20 000 vs 16 000. There are significantly more on graphene and energy, almost 60 000 which is about 30% of all graphene publications, but this could be due to other aspects, as discussed above. Research on battery is a huge field, where graphene only takes a small part; the proportion of battery publications including graphene is increasing, reaching approximately 15 % last year. Graphene is however a significantly more important material for supercapacitors: last year, almost half of the supercapacitor publications included graphene.

Chinese organisations are dominating, with almost half of the publications on graphene and energy, and an even larger share in graphene batteries and supercapacitors. Other prominent countries are especially USA (with around 15% of the publications on graphene) but also South Korea (almost 10%).

None of the top 50 organisations with the most publications on graphene batteries or supercapacitors are European.

The field of composites is very important, with almost 42% of the graphene publications mentioning composites. This can probably be explained (at least partly) since composites are used in all types of applications, such as batteries, for example. Conversely, roughly 7% of all composite publications mention graphene. Publications on graphene-based polymers count for almost a quarter of all graphene composites.

Authors from China have published significantly more than any other country, with almost 60% of the publications on graphene composites. It is followed by the United States of America (10%), India (9%) and South Korea (8%). Only one of the top 50 organisations with the most publications are European (CNRS – Centre national de la recherche Scientifique).

When looking closer at statistics of publications of Swedish organisations both on graphene composites and graphene energy the following observations can be made:

- Sweden comes in 20-25th position when looking at the number of publications with roughly 0.5% of the total number of publications.
- Swedish organisations mainly collaborate with Chinese, American and German organisations.
- Chalmers University of Technology and the Royal Institute of Technology stand out when comparing the number of published articles by Swedish organisations both within composites and energy. Uppsala University have published the most within the energy field.

Patents

A patent landscape is an analysis of patent data that reveals business, scientific and technological trend. It can show if areas of applications are growing or saturating and by comparing different searches with each other, one can get a feeling of the importance of a certain application area.

The patent searches presented below were performed using the patent database Orbit Intelligence, a global patent database comprising more than 50 million patent families (itself comprising more than 100 million patent and patent applications). Please note that there are patents and patent applications which due to different reasons do not appear when performing this search. For example, this may be due to that a patent application does not become public until 18 months after filling, or due to mistakes which have been made when translating a patent or a patent application.

In order to find patents related to graphene, the search string included not only the word "graphene" but other expressions such as "two dimension".[a] This search string was used for searches within the full text of the patents and patent applications. In addition, specific keyword searches of titles, abstracts and claims were used for area specific searches.[b]

The trends for the number of patent families which have been filed every year are very similar to the trends for scientific publications, c.f. Figure 2 (see next page). The trends for the investigated application areas of graphene (composites, energy, batteries and supercapacitors) are almost identical to each other and to the one found for graphene in general (also shown in the same figure).

The distribution of legal statuses is very similar for graphene in general and within the subfields of composites and energy (including both batteries and supercapacitors). Approximately 40% of the filed and published applications have been granted and 40% are still pending. The fact that as many as 40% of the patent applications are pending is a sign that the area is still growing. This number could be higher as patent applications filed in the last 18

---

[a] The following search string has been used: (graphene) OR ((two 2W dimension+) 5W (carbon OR material)).

[b] The following keywords were used for searches within titles, abstracts and claims: (batter+), (supercap+) and (composit+).

months don't need to be public yet. The remaining 20% are dead patents, which include patents that have not been renewed etc.

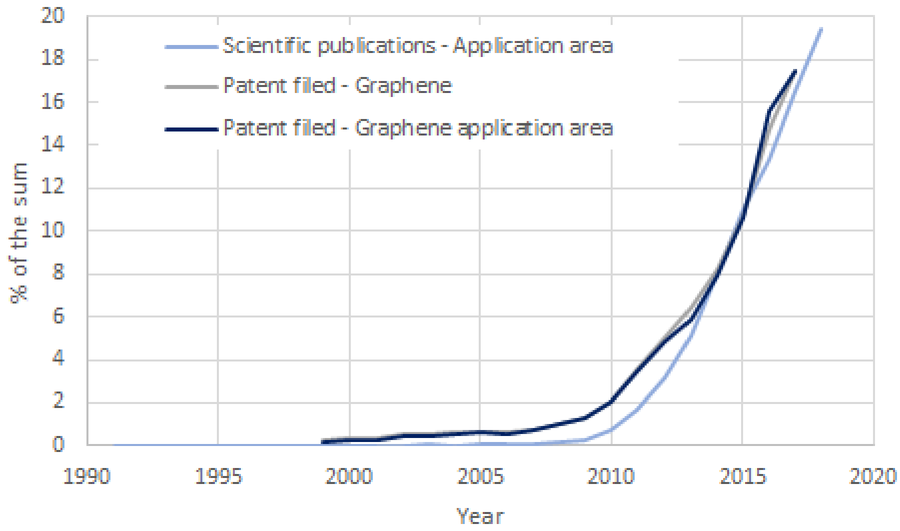

Figure 2 % of all patent families filed as a function of the priority year for graphene and one of the graphene application areas, as well as the % of all scientific publications per year for the same application area.

Approximately 40% of all patent families has one member which has been filed in China. This is significantly more than the second largest, USA with around 10%. China and USA thus, together hold half of all the graphene patents. Both these numbers are very similar for all graphene patents and for the individual subcategories of composites, energy, batteries and supercapacitors.

There is also a significant number of patent and patent applications published at the South Korean and Japanese patent offices, typically a few percent less than in USA. Consequently, almost 70% of all graphene patents and applications are published in these four countries. It should also be noted that a significant number of patents are filed from China and only there, as 56% of all patents are first filed in China.

Approximately 6% of the investigated patents and patent applications are published at the European patent office, a similar percentage to the one for graphene patents in general. In addition to these, almost 10% of all graphene patent applications are worldwide PCT[c] applications. This is again very similar for graphene composites, energy, battery and supercapacitors.

Swedish organisations have mainly been filing patent applications (which have been published) in Europe (12.5%), USA (9%) and China (7%). Swedish companies here include global organisations where the Swedish branch is listed as an assignee.

[c] A PCT-application is an international patent application which makes it possible to seek patent protection for an invention simultaneously in a large number of countries by filing a single application instead of filing several separate national or regional applications. The granting of patents remains under the control of the national or regional patent Offices in what is called the "national phase".

Summary

Composites and energy are two important application areas for graphene. There is a big potential for graphene to both supplement and improve the existing technologies, and to enable new devices.

Graphene has the potential to enable new types of batteries or even new kinds of energy storage devices. It is often a combination of the material's large surface area, high conductivity, high chemical and thermal stability and good mechanical strength that is utilized. Recent advances of lithium-sulphur and lithium-silicon batteries were discussed in this report together with structural and textile supercapacitors.

Graphene can be an important enabler within batteries with approximately one of seven research publications on batteries covering graphene. Graphene appear to be an even more important material for supercapacitors as almost half of the supercapacitor publications relate to graphene.

Applications where graphene is used as an additive, for example in composites, are in general closer to the market, as it relies mostly on graphene flakes produced by "low cost" methods and can be introduced in already existing production lines. For most applications, the benefits of using graphene as an additive is already present at relatively low loadings, so the cost of using graphene is not a big issue. As this report highlights, there is also possibilities to combine graphene with other additives, often with emerging properties.

This report highlights a few of the potential usages of graphene in this area, where graphene can be used either in ultra-strong films or for air pollution remediation. More applications are of interest, particularly in Sweden, for example graphene-based lightweight composites for bulletproof products and as an additive in concrete.

The patent trends for all investigated graphene application areas are quite similar. This include the composite and energy fields discussed here as well as the coatings, electronics and general graphene areas in the previous report. Roughly 40% of the patent applications are still pending, a clear sign that all graphene areas are growing, indicating that graphene is promising for many applications.

Bibliography

1. Cavallo, C., Agostini, M., Genders, J. P., Abdelhamid, M. E. & Matic, A. A free-standing reduced graphene oxide aerogel as supporting electrode in a fluorine-free Li2S8 catholyte Li-S battery. *J. Power Sources* **416**, 111–117 (2019).

2. Phadatare, M. *et al.* Silicon-Nanographite Aerogel-Based Anodes for High Performance Lithium Ion Batteries. *Sci. Rep.* **9**, 14621 (2019).

3. Flouda, P. *et al.* Highly Multifunctional Dopamine-Functionalized Reduced Graphene Oxide Supercapacitors. *Matter* **1**, 1–15 (2019).

4. Thekkekara, L. V & Gu, M. Large-scale waterproof and stretchable textile-integrated laser-printed graphene energy storages. *Sci. Rep.* **9**, 11822 (2019).

5. Foster, C. W. *et al.* Next-Generation Additive Manufacturing: Tailorable Graphene/Polylactic(acid) Filaments Allow the Fabrication of 3D Printable Porous Anodes for Utilisation within Lithium-Ion Batteries. *Batter. Supercaps* **2**, 396 (2019).

6. Wan, S. *et al.* Ultrastrong Graphene Films via Long-Chain π-Bridging. *Matter* **1**, 389 (2019).

7. Mao, L. *et al.* Stiffening of graphene oxide films by soft porous sheets. *Nat. Commun.* **10**, 3677 (2019).

8. Guidetti, G. *et al.* Photocatalytic activity of exfoliated graphite-TiO2 nanoparticle composites. *Nanoscale* **11**, 19301–19314 (2019).