Graphene Research and Advances

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Johan Ek Weis, Aleksandra Kempinska

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Table of contents

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.

It has now been 10 years since the graphene Nobel Prize and 16 years since the publication that kicked off the whole field. SIO Grafen celebrated the 10-year anniversary with a webinar. This webinar and several more are available at http://www.gotostage.com/channel/siografen

The field started off as one dream material for physicists with all its extraordinary properties, including allowing studies of quantum physics. It did take a few years, but now we see a fast growing number of products containing graphene and companies focusing more and more on developing graphene technology. In this edition of the Research Intelligence series we will take a quick look at the market value of some of these international companies. Following the patent analyses of the previous editions we will also give an overview of the Swedish patent landscape, both patents with Swedish assignees and patents that are protected in Sweden.

Several studies by researchers based in Sweden are highlighted here. These cover a range of different topics from composites and textiles to sensors and thermal management.

The possibilities with graphene have led to the discovery of many other 2D materials. These have complementary properties to graphene and are interesting on their own. Some new findings are highlighted here. The development of these is in general a few years behind graphene and the production capacity is significantly lower than the 10 tonnes per annum of graphene in Sweden or up to 100 times higher of graphene globally. But they will lead to interesting new applications, with some already on the market.

The next step which is extensively researched, especially in electronics, is to combine these different 2D materials to form new devices. Looking further into the future in this direction is the field of twistronics where new phenomena occur in stacked 2D materials that have an angle between the different layers. Some of the early small-scale experiments have been described in earlier issues of this Research Intelligence. Now new findings pave the way to autonomous robotic control of manufacturing these structures, which leads to better control of the properties. The process is however still only for individual devices, which means that modelling in order to find the most interesting combinations is crucial. Both aspects will be discussed here.

2D material technology has come a long way from one academic dream material. Many new applications have been realised, but just like in the early days of electronics when no one could imagine what a smartphone can do today, the possibilities of 2D materials have expanded so much that the full potential of the technology can still only be found in dreams.

Market values

Just over a year ago the global market demand for graphene was estimated to US$ 15-50 million in 2015 and US$ 200-2 000 million in 2025 (T. Reiss *et al.*, Nature Nanotechnology 54, 904-910, October 2019). This referred to the revenue generated with the material itself and the market demand for products containing graphene was estimated to be a factor 100 higher.

There are more and more public graphene companies, that is corporations whose ownership is distributed amongst general public shareholders. The number of these companies is growing and some of them are growing larger. Below is a table with a number of these. However, not all graphene companies are publicly listed and therefore do not appear on this list even if they are large. The combined market cap of these ten graphene companies is thus about 1 billion euros as of November 2020.

Company	Country	Application areas	Market Cap in million euros in November 2020
Applied Graphene Materials	UK	Coatings, composites, polymers and functional fluids	19
Archer Materials	Australia	Graphene powder, nanocomposites and oxide. Biosensors.	72
Comet Resources	Australia	Graphite mining, graphene production	19
Directa Plus	Italy	Graphene nanoplatelets for textiles and composites	42
First Graphene	Australia	Graphene nanoplatelet products for composites, concrete, fire retardancy etc	52
Haydale Graphene Industries	UK	Solutions to raw material suppliers and product manufacturers. Polymer composite materials.	16
NanoXplore	Canada	GrapheneBlack™ Graphene powder, plastic products	316
Talga Resources	Australia	Graphene products on the polymer, battery and construction industries. Mines in Sweden. Facilities in Germany.	309
Versarien	UK	Multiple product categories (composite materials and thermal interface materials etc.)	59
ZEN Graphene Solutions	Canada	Graphene solutions for concrete and composite materials	87

Patent landscape

The following chapter provides a summary of an analysis of the graphene patent landscape, giving insights into the current state of this dynamic technology space. Both a general global overview of the area and a closer look at patenting trends in Sweden are presented. The patent search that this analysis is based on was done using the Orbit Intelligence, a global patent database comprising more than 50 million patent families. Please note that there are patents and patent applications which due to different reasons did not appear when this search was performed. 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-dimensional carbon sheet".[1] This search string was used for searches within the title, abstract and claims of the patents and patent applications. In addition, the Swedish country code (SE) was used for geography specific searches.[2]

The overall number of graphene related patents and patent applications found reached over 119300 globally with about 40% of them granted, 37% pending and the remaining 23% being revoked, lapsed or otherwise not in force.

The combination of this data with the number and trend of patent families on the timeline in Figure 1 yields that the graphene area is still trending in new inventions. The exponential growth of patent applications over time indicates that there is an ongoing race for patents in this sector.

[1] The following search string has been used: (graphen+ OR graphane OR graphyne OR graphdiyne OR graphone) OR ((single OR mono OR few OR "2"_D OR "2"_dimension?? OR two_dimension?? OR (two 2W dimension??) OR ("2" 2W dimension??) OR (one 2W atom)) 3W (layer? OR sheet? OR film? OR plate? OR ribbon? OR flake? OR flaky OR plane? OR nano_sheet? OR nano_plate? OR nano_ribbon? OR nano_flake?) 3W (carbon+ or graphit+)).
[2] The following fields were used for geographic specific searches: protection country, assignee country.

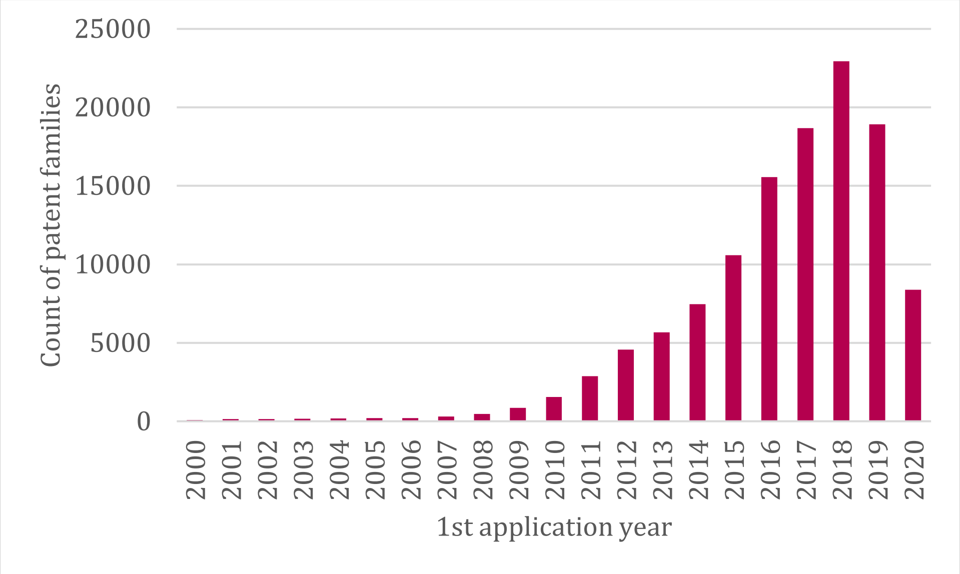

Figure 1 Graph showing the global patenting trend over the last 20 years. The numbers above each bar indicate the exact number of patent families found for that application year. The apparent decrease in 2019 and 2020 is due to that a patent application does not become public until 18 months after filling.

Chinese organisations have the highest number of pending or granted patents, no other country has more protected graphene patents than China, and it has 9 out of the top 10 most active players in the world. USA places 2nd after China and South Korea in 3rd (see Figure 2), also having the only company – Samsung Electronics in the top 10 most active players globally.

Europe placed 4th in the patent families count ranking with 6589 patent families being protected through the EPO procedure. Germany, United Kingdom and France also appeared in the top 10 placing respectively on the 6th, 9th and 10th positions.

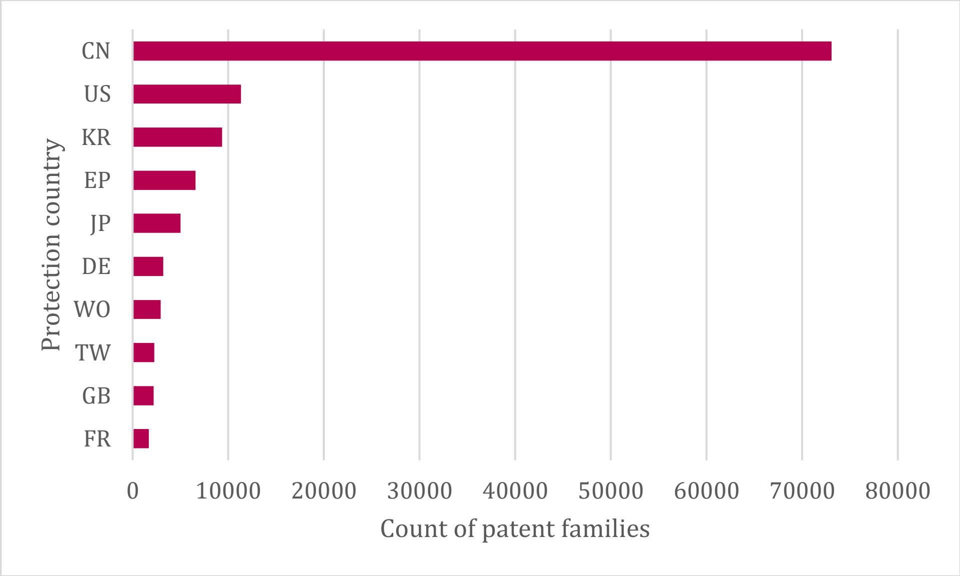

Figure 2 Top 10 protection countries by the count of patent families: CN – 72433, US – 11280, KR – 9252, EP – 6589, JP – 4982, DE – 3169, WO – 2921, TW – 2248, GB – 2157, FR – 1705. This representation illustrates the number of alive patents protected in the various national Offices. This graph includes extension countries for EP documents. For EP patents you will see both the EP authority itself as well as all of the countries which are currently covered by the EP patents being analyzed.

The search for Swedish assignees, that is for patent owners based in Sweden, revealed 88 patent families. Interesting enough the timeline of patented inventions shows two peaks (see Figure 3). One in the year 2011 and then in 2016-2018. The first peak could be explained by the growing interest around graphene material after the award of the Nobel Prize in 2010 to Andre Geim and Konstantin Novoselov. The second peak could be related to the advanced works within the Graphene Flagship consortium and the activity of the SIO Grafen community. However, the 2nd peak could also instead be the beginning of an advancing trend as patents filed in the last 18 months do not appear in the search.

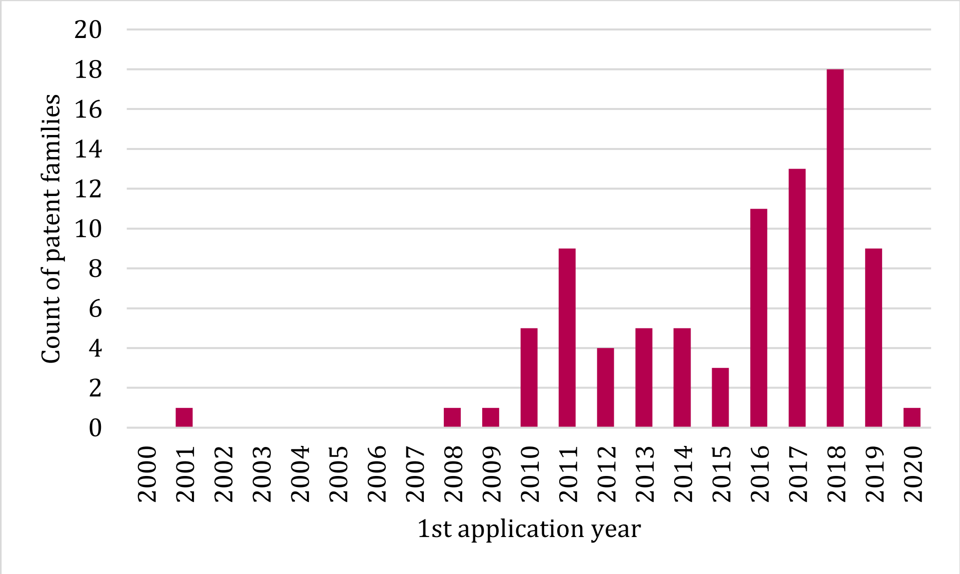

Figure 3 Graph showing patenting trend over the last 20 years from Swedish Assignees.

65 Swedish organisations were found that possess at least one graphene related patent or patent application, but only 16 of them had more than one. The rest thus only had one patent each. Among the top 10 assignees, only two are international companies (Sony, BASF) and the rest are companies of Swedish origin like Smart High Technology, Graphensic, and Ericsson, see Table 1. Swedish assignees are protecting their inventions mostly in Europe (61 patent families). The second most targeted market is the USA with 44 protected patents, and then China with 34 patents protected in this market, see Figure 4.

Table 1 Top 10 assignees and top 10 countries in which Swedish assignees have their patents published. The EP patent will only be shown under EP and not in each designated state.

	WO	EP	US	CN	SE	JP	KR	CA	AU	BR
SHT SMART HIGH TECH	6	0	2	2	0	0	0	0	0	0
GRAPHENSIC	4	3	3	4	2	1	0	0	0	0
ERICSSON	3	1	1	0	0	0	0	0	0	0
SAAB	3	3	3	0	0	0	0	1	0	1
SONY	3	3	3	2	0	0	0	0	0	0
ABB	2	1	1	1	0	0	0	0	0	0
APR TECHNOLOGY	2	1	0	0	1	0	0	0	0	0
BASF	2	2	2	2	0	2	2	2	1	1
CHALMERS VENTURES	2	0	0	0	2	0	0	0	0	0
CLIMATEWELL	2	2	2	2	2	2	2	1	2	2

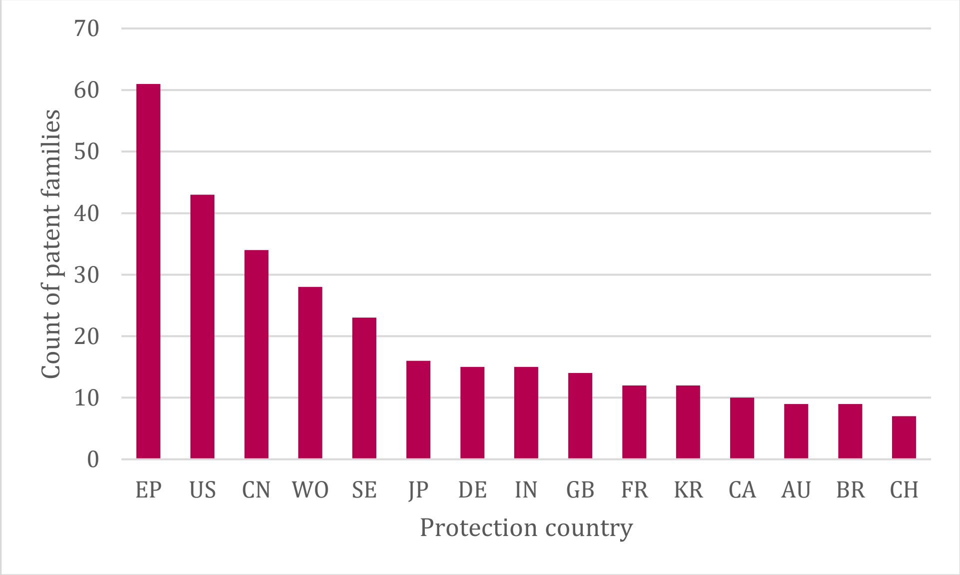

Figure 4 Top 15 protection countries of Swedish assignees. This representation illustrates the number of alive patents protected in the various national Offices. This graph includes extension countries for EP documents. For EP patents you will see both the EP authority itself as well as all of the countries which are currently covered by the EP patents being analyzed.

The global search revealed that there are 222 graphene patents protected in Sweden and 100% of them are in force (98,2% granted and 1,8% pending applications). Organisations protecting their inventions in Sweden have similar market spread as Swedish assignees. The largest number of inventions is protected through the European Patent Office, in the USA and through the PCT system, see Table 2.

Table 2 Top 20 assignees and top 10 countries in which patents protected in Sweden are published. The EP patent will only be shown under EP and not in each designated state.

	EP	US	WO	CN	JP	ES	CA	KR	IN	PL
CEA - COMMISSARIAT A L ENERGIE ATOMIQUE & AUX ENER...	8	8	7	2	4	4	4	2		
ARKEMA	4	4	4	4	4	1	3	4	1	2
DOW GLOBAL TECHNOLOGIES	4	4	4	4	4		4	3	1	1
PPG INDUSTRIES	4	3	4	4	2		2	4	4	4
SALTX TECHNOLOGY	1	1	3	1	1	1		1	1	
SEI	4	4	4	4	4	3	4	4	2	
BAE SYSTEMS	3	3	3			1			2	1
CONTEMPORARY AMPEREX TECHNOLOGY	3	3		3	1					1
DASSAULT SYSTEMES	3	3	1	3	3		3	3		
GRAPHENSIC	2	2	3	3	1					
HYDRO QUEBEC	3	3	3	3	3	2	3	3	3	
TATA CONSULTANCY SERVICES	3	3					1		3	
TATA STEEL	3	2	3	1	1	1		1	2	
BIO NANO CENTRE	2	2	2	1		2	1			
CHALMERS VENTURES			2							
CNRS - CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQU...	2	2	2	2	2		1	2		
CYTEC INDUSTRIES	2	2	2	2	2	2	2	2	2	
DEPUY SYNTHES	2	2	2	2	2	2	2	2	2	2
DIAMOND INNOVATIONS	2	2	2	2	2		1	2	1	
FRAUNHOFER	2	2	2			1	2			1

In conclusion the global patenting trend within the graphene area is still on the rise, showing that many companies are putting their hopes in graphene and research organisations are trying to deliver new ideas to the market. Although Sweden is not on the forefront of the most attractive markets, nor is it the most active player in the global arena, the national and European initiatives are starting to bear fruits and catalyse research and development of graphene.

Publications

There has now been a significant amount of research about graphene for over 10 years. Some researchers have moved on to even newer subjects, such as other 2D materials, and new researchers have entered the field as graphene has spread into new application areas. The total number of scientific publications about graphene thus continues to increase, see Figure 5. However, the rate of the increase appears to be decreasing. The amount of publications for 2020 appears lower as the database did not contain all the publications from 2020 when the search was made in December.

The amount of scientific publications including authors with a Swedish address, on the other hand, has been stagnant for a few years, see Figure 5. The numbers are still high with about 280 Swedish publications and around 35 000 global publications in 2020 (as found in Web of Science in the middle of December).

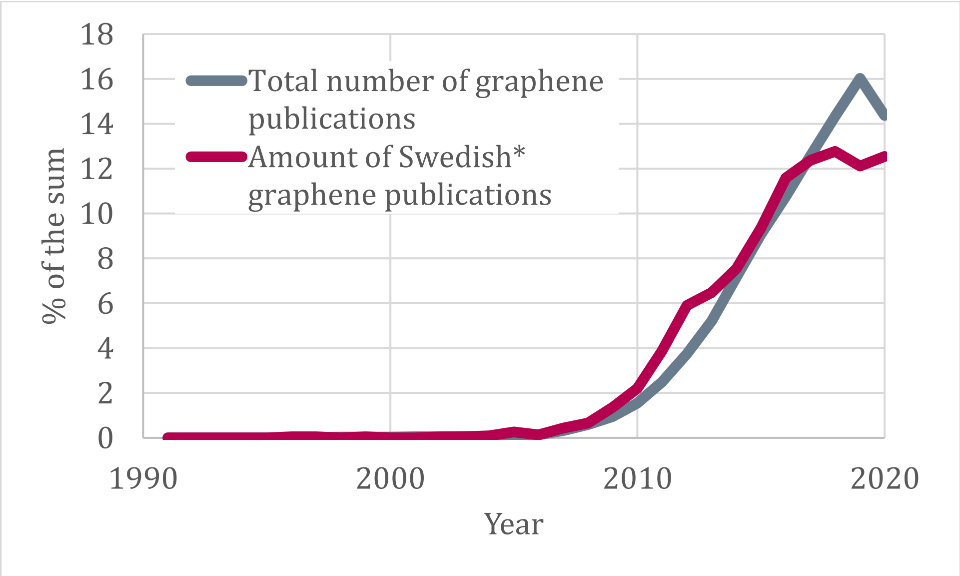

Figure 5 Trend of the number of scientific publications per year for graphene globally and for publications where at least one author stated a Swedish address. To facilitate the trend comparison, the curves were rescaled, and the different curves are expressed as a percentage of the total amount of publications for each. Data from Web of Science, December 2020. The word graphene was searched for in topic (that is in the title, abstract, author keywords, and Keywords Plus).

Manufacturing

One of the main routes to produce graphene is to exfoliate graphite. Other 2D materials can similarly be produced by exfoliation of their bulk counterparts. This has been demonstrated on many synthetic layered materials, such as hBN, $MoSe_2$ and WSe_2 to just name a few. The different 2D materials have complementary properties to graphene and to each other and are thus interesting for different applications or in combinations with each other.

A recent publication gives an overview over many naturally occurring van der Waals materials, which can be exfoliated to 2D materials. These materials belong to different mineral families such as sulphides, sulfosalts, oxides, silicates, phosphates, carbonates and natural elements. The authors discuss that most of the discussed minerals are easily available in mineral shops at reasonable prices. The cost of their synthetic counterparts is often significantly higher.

The authors believe this could lead to more work on exfoliation of new materials, forming 2D materials with interesting new properties and allow new applications.

R. Frisenda *et al.*, npj 2D Materials and Applications 38 (2020)

Electronics

When most people hear about electronics today, they think of digital electronics that is basically made up of the discrete signal values 0 and 1. However, analogue electronics, with a continuously variable signal, is still important in many devices and applications. These devices are typically made using silicon as the active material, but recently 2D materials have been investigated more and more. A new study demonstrates a basic building block of analogue electronics; the operational amplifier, made of two-dimensional MoS_2.

The performance of the operational amplifier is not yet as good as that of commercial silicon devices, but there are still improvements to be made in processing and development of CMOS technology in 2D materials. This is already an important milestone towards flexible and foldable electronics.

D. Polyushkin *et al.,* Nature Electronics 3, 486–491 (2020)

Another important milestone in electronics using 2D materials was recently demonstrated when a first neural network for artificial intelligence was made of MoS_2. An analogue optoelectronic processor inspired by biological vision was demonstrated, which could mimic two core functions of human vision. Like the eye and optic nerve chain it could capture and store an optical image into electrical data, and then, like the brain, it could recognize this electrical form of the captured image.

This was made by an integrated circuit containing more than 1000 transistors all based on 2D materials, and that could interact with light. The researchers made a machine vision processor that could capture, store and recognize more than 1000 images with 94% accuracy. This is already an advancement in the functional complexity of 2D electronics, but the authors are already working on scaling up the technology to even higher resolution systems.

H. Jang et al., Adv. Mater. 32, 2002431 (2020)

A recent collaboration between several researchers in Sweden (at Linköping University, Chalmers, University of Uppsala and at MAX IV in Lund) and in Spain have investigated chemical sensing by an atomically thin platinum layer.

The sensitivity of a sensor becomes greater the more the conductivity of the sensing layer is dominated by surface effects, in contrast to bulk effects. The limit is thus to produce a one-atom thin sensor. The researchers managed to produce a one-atom thin platinum layer by using a buffer layer of carbon on silicon carbide, similarly as for epitaxial graphene.

The sensor could detect part-per-billion contents of toxic gases, as demonstrated on benzene which is cancerogenic already at very low concentrations.

K. H. Kim *et al.*, Adv. Mater. Interfaces 7, 1902104 (2020)

A review article about nanoelectromechanical sensors based on suspended 2D materials was recently published by a consortium of researchers including from KTH. The review discusses the concept of 2D materials in pressure sensors, microphones, mass and gas sensors and also gives an overview of their properties, fabrication routes, and operation principles.

The authors show that the sensors based on 2D materials often have better performance and sometimes completely new functionalities as compared to conventional sensors. However, they also discuss that there is still a lot of work to be done before they can be used at a large scale. One of the main challenges is to establish high-yield manufacturing capabilities.

M. C. Lemme *et al.*, Research 1–25 (2020)

Twistronics

Many interesting new properties, such as superconductivity, appear when two graphene sheets are stacked and twisted at so-called magic angles. Similar effects can appear in other 2D materials and in combinations of these. There is consequently a huge amount of possible structures which can result in interesting properties. Many of these systems are investigated at many universities. However, it would be very time-consuming and difficult to manufacture and experimentally test all of these systems and combinations of rotations and materials. Modelling is thus very important.

Two recent articles lay the groundwork to this modelling and have designed a computational system to screen twisted multi-layers of 2D materials. The intention was “to develop an automated system that an experimentalist, engineer, or perhaps an algorithm, could use to quickly answer the question, is this layered configuration likely to be interesting or not.”

G. Tritsaris *et al.*, 2D Mater. 7, 035028 (2020)

G. Tritsaris *et al.*, J. Chem. Inf. Model. 60, 7, 3457–3462 (2020)

In addition to experimental studies of many specific configurations and their properties, there has also been progress in how to manufacture these structures more efficiently.

A recently developed technique can precisely and dynamically control the rotation and positioning of 2D materials by depositing a polymer resist patch on target 2D crystals and using a polymer gel manipulator. The method was demonstrated by achieving perfect alignment of graphene with respect to hBN layers with a much higher success rate as compared with conventional optical alignment of crystal edges during micromechanical transfer.

The technique could be further developed to allow autonomous robotic manipulation of two- dimensional crystals to build desired structures of twisted layers of 2D materials and thus facilitating the development of the whole new field of twistronics.

Y. Yang *et al.*, Sci. Adv. 6, eabd3655 (2020)

Composites

One challenge when utilizing graphene flakes in composites is to handle the graphene powder. The industry manufacturing plastic components is generally not used to handling powders and neither are their equipment. Importantly, the powder can also be a safety hazard. However, the industry is used to work with masterbatches where a filler, such as graphene, is dispersed in polymer pellets. These work perfectly in common equipment such as injection moulding and also minimizes the safety hazard.

There are now some masterbatches with graphene on the market. A new study by researchers at Luleå University of Technology, RISE SICOMP and Podcomp investigated two of these masterbatches based on HDPE and compared the performance with wood polymer composites. Graphene of two different thicknesses were compared and it was found that the thinner graphene resulted in better performance. A maximum of 140% and 79% for the tensile stiffness and yield stress, respectively, were found with 15 wt% graphene.

Z. Al-Maqdasi *et al.*, Materials 13, 2089 (2020)

A recent review article by authors from Sweden, India, China, New Zealand, Hungary and Iran have summarised the flammability properties of carbon-based polymeric composites. Carbon-based fillers, including graphene, actively reduce the flammability of polymer composites by the formation of a protective char layer and by absorbing free radicals. These fillers additionally improve the thermal stability, mechanical properties and the thermal conductivity of the polymers.

It was concluded that graphene as well as graphene oxide and reduced graphene oxide are potent fire retardants. They can be used individually in polymers or in combination with other conventional fire retardants or inorganic nanofillers. It was noted that in most cases when graphene is used in combination with intumescent flame retardants (that is materials that swell when heated), the concentration should be kept below 1 wt% as higher loadings have adverse effects.

K. Babu *et al.*, Polymers 12, 1518 (2020)

Textiles

Metals are often used in smart textiles to create electrically conductive materials. However, sweat oxidises the metals forming rust which limits the potential. Several new articles have investigated graphene in textiles, which avoids this problem. It is also desirable from a sustainability perspective to replace the metals with a carbon-based materials as graphene. All of the studies below used graphene oxide as it is water soluble, in contrast to pure graphene, which makes it easier for future large-scale production of graphene textiles.

One study from Chalmers focused on making a uniform coating of reduced graphene oxide on polyester textiles by a simple and energy efficient spray coating technique. In addition to making the textile electrically conductive, the tensile modulus was improved compared to the neat textiles.

A. Samanta *et al.*, RSC Adv., 10, 2396–2403 (2020)

Researchers at Smart Textiles in Borås have also investigated graphene. In one recent study they deposited graphene oxide and iron on polyester fabric using a coating technique and with PAMAM (hyperbranched poly(amidoamine)) dendrimer as binder. This resulted in a uniform coating of graphene oxide and iron on the polyester fabric. A sheet resistance of 0.74 ± 0.13 kΩ sq^{-1} was achieved and the textiles were found to be effective in the catalytic removal of toxic water pollutants (99% removal in one hour).

Morshed *et al.*, Dalton Trans., Advance Article (2020)

The same group has also investigated graphene enhanced polyamide (PA 6,6) yarns. The yarns were modified with chitosan to allow dip-coating of the graphene oxide. The process resulted in durable electrically conductive yarns (3×10^{-2} to 4×10^{-2} S m^{-1}) and thereby show a pathway to smart textiles, such as metal-free sensors. It was demonstrated that the yarns could supply power to a LED light using a 9 volt battery and a prototype of a wearable tactile sensor was designed and prepared.

M. Asadi Miankafshe *et al.*, New J. Chem., 44, 7591-7601 (2020)

Energy storage

Environmental pollution and energy issues are two of the main global challenges today. Better and more efficient energy storage technologies can help both these challenges. Graphene and other 2D materials are explored in multiple ways to enhance the current energy storage systems and allow for new technologies.

A recent review article by researchers at Uppsala University highlights the progress made on how battery anodes can be improved by defect chemistry on 2D materials. The basic principle is that the 2D materials can yield improved anodes with more active adsorption sites to more rapid metal-ions diffusion, and more metal-ions storage. It has specifically been found that by engineering defects on the 2D materials anode, a greater structural stability during the extraction/insertion of metal-ions can be achieved and thus improving the electrochemical reversibility.

The researchers highlight that although some challenges remain, strategies using defective 2D nanomaterials is an interesting field in order to develop superior rechargeable batteries.

N. Khossossi *et al.*, Chem Asian J. 15, 3390–3404 (2020)

Thermal management

Thermal management and thermal dissipation are important challenges in many industries, including on many different scales in electronics. Thermal management is for example one of the limiting factors in designing electronic chips for computers, in removing heat from the battery in smartphones and for example in keeping whole data centres cool.

Graphene has a very high thermal conductivity and can be a part of the solutions in many of these applications. Graphene has for example famously been used as a heat spreader in some mass-produced smartphones. A review article by many authors, including from Chalmers and SHT Smart High Tech, from about a year ago describes and summarizes a lot of the current knowledge about thermal management using graphene and a few other two-dimensional materials. The article states that one of the major hurdles for implementing graphene and other 2D materials has been the large-scale production of high-quality material, but that there now are methods for mass production that enable using 2D materials for industrial thermal management applications. The authors conclude with that they are sure that more scientific studies and commercial applications will be developed in this area.

Y. Fu *et al.,* 2D Mater. 7, 012001 (2020)

Some of the same authors have indeed already followed up the review with new studies. They show that graphene can be used to replace copper or aluminium in heat pipes. Heat pipes are typically used to transfer heat over large distances with minimal losses, for example in power electronics or data centres.

The developed graphene heat pipes have a heat dissipation capacity which is about 3.5 times that of copper-based commercial heat pipes. In addition to the enhanced thermal conductivity the graphene enables a lower weight and corrosion resistance. This allows the technology to also be used in portable devices.

Y. Liu *et al.*, Nano Select 1–9 (2020)

Health aspects

It is obviously important to know of and handle any hazards such as potential health risks and impacts on the environment when working with new materials. An update on the current knowledge about graphene will soon be published on SIO Grafen's webpage. The current knowledge of the toxicology of graphene is also summarized in a recent publication.

One of the main challenges in order to know of all hazards is that there are many different kinds of graphene that need to be analyzed and characterised. Different kinds of graphene can have different influences on human health and on the environment. The graphene materials thus have to be properly characterised, which is a challenge as standardised characterisation methods still are under development.

The authors additionally state that current biosafety assessments of nanomaterials cannot reach a comprehensive conclusion due to the lack of reliable experimental models, effective detection techniques and recognized evaluation standards.

F. Xiaoli *et al.*, Archives of Toxicology 94, 1915–1939(2020)