Graphene Research and Advances

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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.

There are now many commercial graphene suppliers and products on the market. The properties of these different graphene products can vary significantly between different suppliers, as can be seen in SIO Grafen's suppliers guide. That guide is based on information provided by the suppliers themselves. A research team recently characterised graphene from many of the commercial suppliers and found that a lot of the material actually is graphite rather than graphene. The selection of specific graphene products is therefore crucial as the performance of any graphene-based application depends on the quality of the graphene. In order to facilitate the quality control of commercial graphene, SIO Graphene has launched Characterisation Checks, where funding is available for characterising graphene.

Graphene can be used to improve coatings for various applications. For examples, a recent report presents how it can be used as an active component in a lightweight and versatile camouflage screen.

Smart textile is another area of research where graphene, thanks to its electrical and flexible properties can play an important role. Recently, researchers also demonstrated that it is possible to integrate graphene-based touch-sensors and light-emitting devices directly into the fabric.

The flexibility and strength of graphene can also be used in display applications. In a recent study, researchers present how they used graphene in a low power, high resolution, high refresh rate display for virtual reality applications.

One very important topic within the graphene community is how graphene affects the human body and the environment. The risks need to be better understood so that countermeasures can be applied to reduce any potential hazards, just as is done with many other materials today. A couple of recent studies showing how the human body responds to exposure to graphene are discussed.

Individual graphene flakes have a very high thermal conductivity. However, it has been a challenge to preserve this conductivity on a large scale. Researchers have now found a method to produce large graphene films which conserves the high thermal conductivity.

Content:

Manufacturing

The quality of commercial graphene flakes

An ISO standard on the vocabulary of different graphene materials was published last year, which is a first step to facilitate comparisons of different products. This standard defines the nomenclature *graphene* as a single layer of carbon atoms, while materials with 2-10 atomic layers are to be named *few-layer graphene*. Anything thicker than ten atomic layers should not be labelled as graphene.

A research group at the University of Singapore have analysed the quality of graphene flakes from 60 producers (no graphene oxide, GO, nor any films of graphene were included). It was found that almost all of the analysed materials were in fact graphite powder rather than graphene.

A. P. Kauling *et al. Adv. Mater.* **30**, 1803784 (2018)

It is well-known that the properties and quality of graphene varies depending on the production method and the supplier. However, the report does not mention any specific suppliers or products. This raises the question how the products were selected. Most of the suppliers produce several products with varying thickness and quality. As the production methods constantly are developed, improvements are expected since these measurements were performed. There could consequently be high-quality graphene products available on the market, but these might have been missed in the study. Nonetheless, this report highlights the importance of choosing the right supplier and product.

Computational database over 2D materials

As graphene was the first among the two-dimensional (2D) materials to be manufactured, the research and development of graphene is typically a few years ahead of other types of 2D materials. Consequently, researchers have developed techniques to grow graphene with high quality at reasonable scales (for example by CVD), but more development is needed with the other 2D materials.

Several thousands of 2D materials have been predicted, but only around 50 have been synthesised until today. However, a lot is already known about these materials and a computational database has recently been developed. This database collects information on the structural, thermodynamic, elastic, electronic, magnetic, and optical properties of around

2000 two-dimensional materials. This data is fully open, published online and can be used to model and design new structures of 2D materials.

S. Haastrup *et al. 2D Mater*. **5,** 042002 (2018)

Wafer-scale production of new 2D materials

Another new study demonstrates a technique with which several 2D materials can be produced by a quick method. A nickel film is deposited on a stack of several layers of 2D materials. As the adhesion between the nickel and the stack is greater than that between the individual layers in the stack, individual layers of the 2D materials can be peeled off from the stack. The researchers developed a method such that a perfect monolayer is left on the nickel film after the peeling. The process can then be repeated by depositing a new nickel film on top of the stack and peeling off another layer. The monolayers were then deposited onto a SiO_2/Si substrate and the nickel was etched away.

The process was used to separate monolayers of MoS_2, $MoSe_2$, WS_2, WSe_2 and h-BN on a 2-inch scale. The method can also be used to build heterostructures or stacks of monolayers of separate 2D materials in order to combine the properties of these. New devices can therefore be manufactured in a process similar to stacking pieces of LEGO. It is thus a high throughput technique which allows production of largescale heterostructures. The authors are now planning to use the technique to build a range of devices.

J. Shim *et al. Science* DOI: 10.1126/science.aat8126 (2018)

Controlled deposition of nanomaterials

The liquid phase exfoliation process was developed 10 years ago for graphene. The method produces 2D materials from their bulk counterparts in a liquid with the aid of shear forces, and can today be applied to a large range of 2D materials. In order to integrate these flakes in semiconductor process technology, it is necessary to be able to controllably place them at pre-defined locations with sub-micron precision and without contamination. This is a major challenge in semiconductor manufacturing.

A new method uses an electric-field-assisted process for the deposition of nanomaterials. Electrodes are positioned on the substrate where the nanomaterial should be placed. By controlling the voltage between the electrodes, nanomaterials can selectively be deposited at the predefined locations. Similar processes have been reported previously for the deposition of several nanomaterials. The new study used graphene as electrode material as it enables wafer-scale integration with nanometer precision. Additionally, and perhaps most importantly, the graphene can in contrast to most other electrode materials (often copper) be removed almost without any residuals in a standard process without impacting the performance of the deposited material.

The researchers demonstrated the versatility of the method by depositing CdSeS/ZnS quantum dots, semiconducting carbon nanotubes and few-layer MoS_2. It was discussed that this method could enable large-scale integration of quantum electronics and optoelectronics devices.

M. Engel *et al. Nat. Commun.* **9**, 4095 (2018)

Coatings

Active camouflage coating

Inspired by nature, humans have been able to develop artificial systems with adaptative coloration to match the visual appearance of an object to its surrounding. Thermal camouflage, which requires the ability to control the emitted thermal radiation from a surface is still, however, a challenge. Devices exists, but have limitations that limit their applicability in the field: limited tunability, long response time, rigid substrate etc.

A recent study shows that it is possible to use graphene in a flexible, light ($30g/m^2$) paper-like device enabling real-time control of thermal emission over the full IR spectrum. The researchers used a membrane of polyethylene (PE) containing an ionic liquid, with a thin electrode of gold on one side and multilayer graphene on the other, the active part of the device.

The optical absorption of the graphene electrode is controlled electrically; when a voltage ($V < 4V$) is applied across the device, the ionic liquid intercalates into the graphene layer doping it, which supresses its IR absorption/emissivity. The device has a response time of less than a second and works to camouflage warm into cold and vice versa.

O. Salihoglu *et al. Nano Lett.* **18**, 4541 (2018)

Impermeable coating

A perfect layer of graphene is totally impermeable. In practice, large areas of monolayer graphene always have defects and coatings made of flakes include grain boundaries, point defects, etc where gases and liquids can pass by. Previous studies have explored how graphene can be used as an additive in different types of matrix (polyetherimide, polyethylene etc.) to alter their permeability to gases. However, there has been no publications on their efficiency for the high-pressure gases, used in for example the oil and gas industry. Today, a polyamide 11 (PA11) coating is generally used to prevent corrosive fluids like CO_2 and H_2S to get in contact with and corrode the pipe.

A recent study evaluated the potential of graphene as a barrier for this type of application. The best results were obtained for a sandwich structure where a graphene nanoplatelets paper was placed between two PA11 laminate. This structure decreases the permeation of CO_2 by over an order of magnitude and reduce the H_2S permeability to an undetectable level, for all pressures up to 40MPa.

T. P. Raine *et al. Adv. Mater. Interfaces* **5**, 1800304 (2018)

Gas separation

A team of researchers recently developed a scalable method to fabricate graphene-based membranes which outperform standard gas sieving material. A substrate is coated of alternated layers of graphene oxide (GO) flakes and poly(ethyleneimine) (PEI). Several (10 to 25) cycles of dipping are required to optimize the separation properties of the membrane. The GO layer acts as a physical sieve; the gas molecules are forced to diffuse across a tortuous path. The PEI layer acts as a spacer that allows significant gas transport, giving also high selectivity for smaller molecules. The obtained membranes give particularly good results for He/CO_2 and H_2/CO_2 gas mixtures.

Pierleoni, D. *et al. ACS Appl. Mater. Interfaces* **10**, 11242 (2018)

Membranes with controllable flow

The potential of using graphene to filter different types of salt from water was discussed in the previous editions of this Research Intelligence Report (no 1&2, 2017). A new study reports on a different type of application, where a GO-based membrane is used to control the flow of water. This GO-based membrane, is placed between two metal electrodes and before its first use, a high voltage is applied though the membrane. The voltage is increased until the first signs of electrical breakdowns. This creates thin electrical filaments imbedded in the insulting GO membrane. The presence of these filaments creates, when lower voltages are subsequently applied, electrical fields large enough to ionise the water, allowing control of the water transport through the membrane.

This technique can control the flow through the membrane over a wide range, from ultrafast permeation to completely blocking it. Possible applications include smart membrane technologies for artificial biological as well as system tissue engineering and filtration.

K.-G. Zhou *et al. Nature* **559**, 236 (2018)

Composites

3D printed aerogels

Maintaining the properties of individual graphene layers in 3D structure applications has been challenging. In 3D structures containing graphene, the flakes are randomly interconnected with no control on the orientation or position of individual flakes or grains, resulting in a reduction of the mechanical properties.

Recently, a group of researchers designed and synthetized photocurable graphene oxide resins that can be sequentially patterned through a light-based 3D printing technique. The 3D printing of the structure is followed by drying and pyrolysis to the final micro-architected graphene (MAG). The feature size is 10µm and the pore size, 60nm, an order-of-magnitude finer than previous reports. It also possesses higher elastic modulus (an order of magnitude higher) then other 3D printed structures having similar density.

These enhanced mechanical properties at low density, are especially desirable for electrode materials which can experience severe mechanical stress during energy storage cycling. Potential applications include energy storage and conversion, catalysis, sorbents and desalination.

R. M. Hensleigh, *et al. Mater. Horiz.* **5**, 1035 (2018)

Smart textile

Wearable e-textiles is a rapidly growing field with a forecasted market of USD 5 billion by 2027. Graphene fits perfectly into this as the idea is to create new functionality to common textiles and garments by integrating lightweight and flexible electronics. The potential of using graphene for cotton based smart textile was discussed in a previous edition of this Research Intelligence Report (no 1, 2018).

A new study explored the possibilities with a polypropylene-based (PP) textile. PP is a type of fibres widely used due to its properties (light weight, low thermal conductivity, high stain resistance and extreme mechanical flexibility at low temperature, resistance to bacteria, recyclable and eco-friendly). The objective of the study is to widen the scope of PP fibres without compromising on its current properties.

Liquid exfoliated flakes of graphene were filtered through a membrane to produce a conducting paper-like structure, which was detached and transferred by applying pressure to PP fabric. The researchers demonstrated the production of transparent, flexible and durable graphene-enabled touch-sensors and light-emitting devices, completely integrated on PP fibres. Their process is also compatible with roll-to-roll printing and could therefore be used in large-scale applications.

Torres Alonso, E. *et al. npj Flexible Electronics* **2**, 25 (2018)

Electronics

5G

The next generation of cellular mobile communications, 5G, requires an increase in bandwidth of 3 orders of magnitude to allow each person/object to be connected on the web. There is therefore a need for a technology that can meet requirements in terms of bandwidth and power consumption: information and communications technology already generate 2-2,5% of the greenhouse gas emission and is predicted to reach 4% in 5-year time.

Photonic components are projected to play an important role in 5G networks since it allows the possibility to realize high capacity, low cost and low energy consumption in transport infrastructure.

A recent review presents the key arguments supporting the development of graphene-based integrated photonics for high-speed datacom and telecom. It presents the main functions of graphene photonics and compares it with established technologies: modulators, detectors and switches and concludes that graphene photonics offers a combination of advantages in terms of both performance and manufacturing. The review envisions a future where integrated photonics takes advantage of the ultra-wide bandwidth communications and low power consumption enabled by graphene properties, which would radically change the way data is transmitted across the optical communications systems.

Romagnoli, M. *et al.* *Nat. Rev. Mater*. **3**, 393 (2018)

Ultrafast mechanical pixels

Virtual Reality (VR) is a relatively new and cutting-edge branch of technology in rapid expansion. Originally reserved for the gaming industry, VR is now used for all sorts of applications. To allow the technology to become mainstream, the development of new displays with higher resolution (more realistic), higher frame rates (to reduce motion sickness) and power efficiency is needed. Reflective displays, such as the one used for electronic paper, are good contenders to maximize power efficiency. However, commercial reflective displays have low frame rates and resolutions today.

In a new study, researchers developed mechanical pixels based on graphene with outstanding properties. Their device consists in a double layer of graphene, deposited on a Si/SiO_2 wafer with prefabricated circular trenches. The obtained graphene membranes are actuated electrostatically by applying a bias between a back gate and the graphene membrane.

By changing the applied voltage, the frequency is changes continuously from 580nm (orange) to 510nm (green). The graphene pixels are 5µm in diameter, at least 5 times smaller than commercial competitors), which results in a reflective-type display of 2500 pixels per inch (ppi) with high image refresh rates (at least 400 Hz).

Cartamil-Bueno, S. J. *et al. Nat. Commun.* **9**, 4837 (2018)

Emergent spin phenomena

The potential of using graphene in spin-based devices was discussed in previous editions of this Research Intelligence Report (no 1, 2015 and no 1, 2016). Researchers at Chalmers University of technology, have in a collaborative work with researchers in Spain, recently studied hybrid graphene/topological insulator (TI) devices which present electronic spin functionality that are not present in the individual materials.

Graphene is a material with intrinsically low spin-orbit coupling. On the one hand, this leads to long spin coherence lengths (even at room temperature), making it an interesting material for spin transport. On the other hand, it limits the degree to which one can manipulate spins. TI have strong spin-orbit coupling and spin-momentum locking.

Graphene/TI heterostructures are interesting because graphene still supports long distance spin transport, but at the same time acquires an induced strong spin-orbit coupling. The study shows a strong tunability and even suppression of the spin signal and spin lifetime due to the proximity of graphene to a TI. A careful analysis of the results revealed important information about the nature of the coupling and on the nature of the spin relaxation, which could be the base for future spin-based data storage and information processing technologies.

Khokhriakov, D. *et al. Sci. Adv.* **4**, eaat9349 (2018)

Biotechnology

Safety assessment of graphene-based materials

Several of the leading European researchers working on safety assessment of graphene (including Bengt Fadeel from Karolinska Institutet) recently published a comprehensive review article covering the status of graphene. They analysed what is known about the main exposure routes for graphene-based materials and the effect on key organs in the human body, but also a wide range of organisms in the ecosystem.

The researchers highlight that there are many different kinds of graphene, and that these may affect the body and environment differently. It is discussed that the most important properties of graphene are the thickness (number of layers), lateral dimensions and oxygen content, which influences the water solubility. As the performed analysis only use one or very few types of graphene and only within a specific investigated human or environmental model system it is not possible to draw conclusions regarding the effect of all graphene-based materials on the whole human body and our environment. A lot more data is needed before the risks are completely understood and predictive models can be made.

The researchers compare the situation with that of carbon nanotubes 10 years ago, where a study comparing them to asbestos drew a lot of attention. This study was detrimental to the field, even though it is today known that whereas some carbon nanotubes indeed are carcinogenic, others are nontoxic, can biodegrade and even hold great promise in nanomedicine.

The knowledge and awareness around graphene-based materials is growing quickly, but more information is required before it is known exactly which type of material in the graphene family that is most suitable for different applications and at what risks.

B. Fadeel *et al. ACS Nano* **12**, 10582 (2018)

Human immune system can break down graphene

There are many interesting ongoing studies where graphene is used to develop flexible biomedical electronic devices which are designed to be interfaced with the human body. In order to be used in such applications, the graphene needs to be biodegradable and thus expelled from the body. A previous study showed that graphene oxide can be broken down by myeloperoxidase (MPO), which is an enzyme found in the lungs which the body uses to eliminate any foreign bodies or bacteria.

Although this was a very interesting result, it was still unknown how pristine graphene would react, as it generally is more stable than graphene oxide which has more defects and functional groups. A team of researchers (including Bengt Fadeel from Karolinska Institutet) therefore recently investigated single- and few-layer pristine graphene. The graphene was exposed to MPO and investigated by Raman spectroscopy and transmission electron microscopy (TEM). It was found that the graphene is broken down, but at a slower rate than the graphene oxide.

Future large-scale production and use of graphene could lead to many more people getting exposed to the material. These results are therefore important indicating that our immune system has strategies to degrade graphene materials.

R. Kurapati *et al. Angew. Chem. Int. Ed.* **57**, 1 – 7 (2018)

Graphene based sensor for diagnostics

An increasing elderly population is a challenge for the healthcare industry and has made it more important to increase the knowledge about diseases of old age. Previous studies have provided proof-of-principle that systemic proteins have broad age-specific effects on tissue health and repair. However, the methods used to analyse the proteins include many steps and take a long time to complete. Therefore, a new sensor is required for diagnostics.

A new study show how graphene can be utilised to build a lab-on-a-chip detector for these proteins. The sensor is made by a graphene-based field effect transistor. The graphene is functionalised in order to only react to specifically labelled proteins. When these attaches to the sensor, the electrical conductivity of the graphene changes, which is detected.

The technology (which is termed Click-A+Chip) significantly reduces the sample size, complexity, cost and time associated with the measurements as compared to the optical and mass spectrometry methods typically used. Additionally, it can be used as a multiplex biosensor, simultaneously detecting numerous analytes. The authors believe that the method can be used both for diagnostics and for development of vaccines.

C. Sadlowski *et al. Lab Chip* **18**, 3230-3238 (2018)

Energy

High thermal conductivity of graphene film

One challenge in electronics today is that the reliability and the ever-increasing performance, which has been made possible with miniaturization, is threatened by the high temperatures that are also generated. It is therefore crucial to dissipate and to reduce this heat. Different materials with a high thermal conductivity are typically used, such as copper, aluminium or graphite films. However, the complex structures and the emergence of flexible electronics, which put high demands on the mechanical properties together with a high thermal conductivity, leads to that new materials need to be developed.

Graphene is an excellent candidate material to solve these issues as it is flexible, robust and has a very high thermal conductivity. Values as high as 5000 W/mK have been reached, but this has been measured on small pieces of single layer graphene. In order to dissipate large amounts of heat over macroscopic distances, many of these small flakes need to be put together.

Researchers at Chalmers have developed a method to produce a graphene film with a thermal conductivity of up to 3200 W/mK, which can be compared to almost 2000 W/mK of graphite films. They use a combination of high temperature and pressure to form the film from graphene oxide. The resulting film has large grains size, good alignment of the layers and low interlayer binding energy, which all improves the thermal conductivity. The graphene film additionally has a three times higher mechanical tensile strength (70 MPa) than graphite films.

N. Wang *et al. Small* **14**, 1801346 (2018)

3D-printed graphene supercapacitor

Supercapacitors bridge the gap between ordinary capacitors and batteries. They can store significantly more energy than capacitors, although not as much as batteries, but they can charge and discharge significantly faster than batteries and have a very long lifetime.

However, it has been difficult to achieve high loading levels without reducing the performance.

A new study show how graphene can be used to increase the loading and performance of supercapacitors. A scaffold of graphene oxide was 3D-printed for supporting pseudocapacitive MnO_2. The GO was then annealed to form a graphene aerogel with increased conductivity. Graphene aerogels have previously been studied as supercapacitors, but the 3D-printing in this study allowed a more uniform coverage of MnO_2 and an efficient ion diffusion also at high loading of MnO_2.

The performance per mass or volume of similar devices is typically significantly reduced when the thickness is increased. This new study nonetheless demonstrated a 4-mm-thick graphene aerogel loaded with 180 mg/cm^2 MnO_2 and achieved a capacitance of 44 F/cm^2, which according to the researchers is the highest ever recorded for any supercapacitor, and a very high energy density of 1.5 mWh/cm^2. The graphene aerogel can be 3D-printed in any shape which enables massive flexibility in the design of future supercapacitors.

B. Yao *et al. Joule* DOI : 10.1016/J.JOULE.2018.09.020 (2018)