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.

The development within the graphene community is growing and more and more products are entering the market. There are many different techniques to produce the graphene required for the diverse applications. A few different methods enabling the upscaling of graphene and its products are discussed here.

Graphene can be used to improve coatings for various applications. A recent report utilizing graphene in order to create a hard self-healing coating, which is a combination that is difficult to achieve, is discussed. Another study used the coating properties of graphene, along with the fact that many layers of graphene is black, to prepare graphene-based hair dye.

Many other two-dimensional materials in addition to graphene are being studied extensively, although graphene has received the greatest attention. One study using graphene in cement and another using hexagonal boron nitride, h-BN, ultimately for concrete applications are highlighted.

Printed electronics is an interesting area where graphene could decrease cost while maintaining high quality. An example of inkjet printed graphene composite is given.

Graphene is all surface and all its atoms are exposed to the surrounding environment. This makes graphene an ideal material for building sensors as it can sense changes in its surroundings with high sensitivity. Different perspectives and applications are discussed here, such as the use of graphene for radiation detection and glucose monitoring.

Graphene is projected to have an impact also in the health sector. When prepared using certain parameters, it has a clear antibacterial effect, which could be exploited in coatings for medical equipment or in a novel type of bandage for infected wounds.

Graphene could also have an important impact in the energy sector, thanks to its high areal density. Even though graphene flakes have a tendency to restack and agglomerate, decreasing this density, researchers are coming up with new creative ways to increase the surface to volume ratio of graphene-based systems.

Content:

Manufacturing

High concentration graphene slurries

Most commercial graphene producers are substantially increasing their production volumes. However, one remaining challenge is that the concentration of graphene flakes in solvents and dispersions is very low. The concentration of graphene is typically around 1 g/L. Transporting graphene dispersions is consequently very expensive and environmentally unfriendly as 1 kg of graphene would require around one tonne of liquid. One common way around this is that most producers offer to ship their graphene as a powder. However, this increases the risk of agglomeration leading to a thicker material which might require varying levels and efforts of redispersion.

A recent study shows that by producing and storing graphene as a flocculated aqueous slurry, the concentration can be increased by a factor of 50. The graphene was produced from partially oxidized graphite by high shear rate exfoliation in a highly alkaline aqueous solution (pH=14). The restacking of graphene flakes was limited by repulsive electrostatic forces from adsorbed ions on the flakes. Flakes of graphene oxide (GO), in contrast to pure graphene, typically have many functional groups and negative charges from the synthesis process and can be dispersed at higher concentrations without this flocculation technique.

The graphene flakes formed a loosely stacked 3D microstructure which easily could be re-dispersed or stored for months as a slurry. The slurry could also directly be used to 3D-print graphene aerogels and conductive polymer materials without any additional dispersion.

L. Dong *et al. Nature Communications* **9**, 76 (2018)

Laser induced graphene on multiple substrates

Graphene can be made by several different methods and form many different kinds of graphene. One of the less common ones is called laser induced graphene. The technique relies on heating a precursor (typically polyimide, but it can also be other natural lignin containing materials) in an inert atmosphere with a laser to such high temperatures that the precursor transforms into graphene. This has been used to make for example supercapacitors, biosensors and photodetectors.

A new development has now shown that the process can take place without the need for an inert atmosphere by using multiple lasing. A defocused laser is first used to turn the precursor into amorphous carbon, while a second CO_2 laser turns the amorphous carbon into graphene. It was found that the wavelength of the laser is an important factor. The method thus works on any material that can be converted into amorphous carbon and was demonstrated on a wide range of substrates such as cloth, paper, potato skin, coconut shell and cork and a range of polymers. The important ingredient in all the natural materials is the lignin. The method is envisioned to be able to put tiny RFID tags on a wide range of materials, including directly on food.

Y. Chyan *et al. ACS Nano* **12**, 2176−2183 (2018)

Large-scale CVD graphene for membranes

Chemical vapour deposition (CVD) of graphene on polycrystalline copper foil is the most common method to produce monolayer graphene of high quality. Although most of the research on these has been performed on small samples of a few square centimetres, some studies have shown roll-to-roll synthesis of large scale CVD graphene. However, the focus of these has typically been on electronic properties and not for membranes and have therefore had different quality requirements. A pinhole of sub-nanometre to nanometre size might be unnoticed in a micrometre-sized electronic device, but could severely influence a membrane where the flow through such a pinhole could be larger than through the selective pores.

A scalable manufacturing process of roll-to-roll CVD graphene with casting of a porous polymer support, polyether sulfone (PES), optimised for membranes was recently reported. The graphene had a uniform high quality (Raman $I_D/I_G < 0.065$) and was produced at speeds above 5 cm/min. Nanopores were created in the membrane by pulsed oxygen plasma etching, which resulted in a membrane with size-selective molecular transport. The performance of the membrane was comparable to other recently reported membranes based on CVD graphene, which were synthesised in a much smaller batch scale. This shows that it is possible to synthesise continuous CVD graphene of high-quality at a large scale. During their longest experiment, the researchers produced about 10 metres of continuous graphene but this could be extended to a continuous process.

P. Kidambi *et al. ACS Appl. Mater. Interfaces* **10**, 10369−10378 (2018)

Coatings

Hard and self-healing coating

Coatings are often applied on the surface of objects as a protective layer. These can work in many different ways with different functions. Comparing with nature, which often has found very good and interesting solutions, the pulp and dentin in our teeth are protected by tooth enamel, which is the hardest substance in the human body. The drawback with this coating is that it cannot self-heal after it's been damaged. Skin, on the other hand, is comprised of several layers which are significantly softer than our teeth, but this allows self-healing by migration between the layers. It is very difficult to achieve a high hardness in a material that can self-heal, as the healing process most often relies on migration in softer materials. This is not only true for natural biological material, but also for artificial self-healing systems, which most often are made of polymers.

A recent study shows that it is possible to create a hard (2.3 GPa) and stiff (31 GPa) material which can repair itself. The researchers used a layer-by-layer assembly technique, where the bottom layers contain a mixture of tannic acid (TA) and polyvinylalcohol (PVA), whereas the top layers have a similar structure but with graphene oxide (GO) added. The GO in the top layers provide the mechanical reinforcement while there is a constant supply of TA and PVA from the bottom layers to the top layers enabling the self-healing mechanism. The structure is rather similar to the enamel in teeth, but with a similar self-healing system as the skin. Additionally, the coating was found to have excellent antibacterial properties. The researchers discuss that this coating could be used for smart coatings for applications in for example healthcare, construction or consumer electronics.

X. Qi *et al. ACS Nano* **12**, 1062−1073 (2018)

Wearable e-textiles

Wearable e-textiles is a rapidly growing field with a forecasted market of USD 5 billion by 2027. Graphene with its exceptional properties fits perfectly into this as the idea is to create new functionality to common textiles and garments by integrating lightweight and flexible electronics. A recent study has shown a scalable and cost-effective method to manufacture graphene-based wearable e-textiles on an industrial scale. GO is typically used in similar studies as the interaction with the functional groups of the textile is better than for pure graphene.

Previous techniques first coated the textiles with GO and afterwards reduced the GO to reduced graphene oxide (rGO). The new method has reversed this and first reduces the GO and coats the textile as the final step. This allows a padding technique to be used for the coating, which is a very common method to apply functional finishes to textiles in the industry today. The technique can be used at speeds of 150 m/s.

The GO was uniformly coated around the cotton fibres, which resulted in good electrical conductivity, tensile strength, flexibility and also remained electrically conductive after several washing cycles. The researchers demonstrated a sensor with the material, which could be used to record mechanical movements such as bending or stretching. The technique could also potentially be used to incorporate heating elements or supercapacitors.

N. Karim *et al. ACS Nano*, **11**, 12266−12275 (2017)

Graphene hair dye

Many hair dyes function by first damaging the hair and then allowing dye molecules to faster penetrate the hair. These can result in permanently coloured hair, but they often contain toxic or sometimes even carcinogenic compounds. Weaker compounds can also be used, but this results in insufficient colouring or leads to coloration that is removed after a few washes. An alternative method, which doesn’t need to damage the hair, is to coat it with colorants instead of inserting the dye inside the hair. The clear drawback of the coating method is that it tends to wash away quickly.

It has recently been found that graphene can be used to coat and colour hair and keep it that way for at least 30 washes. Water-based suspensions of GO was used for brown colouring, whereas rGO was used for black. The shade of the colouring could be controlled by the concentration of the graphene (0.0025-0.025 wt %). As the main function of the graphene in this case is its colour, thicker and cheaper qualities could be used. A polymer binder (chitosan) was used to improve the adhesion to the hair. As the graphene is bound in a polymer matrix, the researchers discuss that any potential adverse health effects due to the graphene is minimal.

The graphene could be applied to the hair by spraying or brushing. This allowed a very quick dyeing process of less than 10 minutes. The electrical conductivity of the graphene was high enough (10^4 – 10^5 Ω/□) to dissipate electrostatic charges, which otherwise would leave the hair standing in all directions.

C. Luo *et al. Chem* **4**, 784–794 (2018)

Composites

Graphene in cement

As discussed in the manufacturing section of this report, there is a lot of progress in the upscaling of the graphene production. However, the amount used in applications today is still relatively low, but this might be about to change. A recent study found that the addition of graphene to cement gives the most widely used construction material – concrete – significantly improved properties. Other studies have used GO to reinforce cement, but the team here chose to work with graphene as several challenges with GO were identified. One example is that the hydrophilicity of GO affects the hydration of the cement, which makes the dispersion difficult. The mechanical properties were substantially improved (for example an increase of compressive strength by 146 %), the thermal and electrical performance was enhanced and the water permeability was decreased by nearly 400 %. The cost to incorporate graphene in concrete is still high, but the study shows that the addition could reduce the required concrete material in today's constructions by 50 %, while still fulfilling the specifications for the loading of buildings. Cement production causes approximately 5 % of the global carbon dioxide emissions, the addition of graphene in the structure would have a real measurable impact on the global scale.

D. Dimov *et al. Adv. Funct. Mater.* 1705183 (2018)

h-BN in ceramics

There are many more 2D materials than the most commonly discussed graphene. One of the more studied alternatives is hexagonal boron nitride, h-BN. The structure of h-BN is similar to graphene but with alternating boron and nitrogen atoms in the lattice. Similarly to graphene, h-BN has remarkable properties; chemical stability, excellent mechanical strength and great thermal conductivity, but also some differences to graphene; stable in air up to 1000 °C and electrically insulating.

A recent study used density functional theory (DFT) calculations to investigate the addition of h-BN to ceramics. Tobermorite, which is a layered calcium-silicate mineral, was used as model ceramic system. The mineral can be dried to form cement and simultaneously self-assemble into layers of calcium and oxygen held together by silicate chains.

Graphene is typically distributed rather randomly (but sometimes aligned) when incorporated into composites. Here, however, the h-BN could be intercalated in between the layers in the tobermorite structure. This results in a structure where the h-BN forms an integral part of the structure in contrast to many other fillers that are loosely connected to the matrix.

The toughness of a material is often reduced when the strength is increased. In this system, however, it was found that the addition of h-BN increased the yield strength from 10 GPa to 25 GPa and simultaneously the yield strain from 7 % to 20 %. The thermal and radiational properties were also enhanced, resulting in a multifunctional cement composite.

R. Shahsavari, *ACS Appl. Mater. Interfaces* **10**, 2203−2209 (2018)

Stretchable carbon aerogels

Carbon aerogels can be used in many applications due to their ultralow density, porosity, high conductivity and stability. However, they are typically brittle under tensile deformation, which limits their use for example in the growing field of wearable electronics. A new approach have solved this by assembling graphene and carbon nanotubes in hierarchical structures ranging from the nanometre to the centimetre scale. The structures were formed by 3D printing, followed by freeze-drying and a pre-bucked reduction. In contrast to previous studies, small amounts of calcium ions were added as gelators in order to facilitate the printing process.

The prepared aerogel had a stretchability up to 200 % elongation with a density of 5.7 mg/cm^{-3}. The plastic deformation was very small (1 %), the energy dissipation low (~0.1) and the conductivity high (up to 1 000 S/m), the stability very good (from -180 to 500 °C) and the fatigue resistance excellent (up to 10^6 cycles). Additionally, the aerogel was demonstrated to allow a new type of sensor which could enable logical identification of shape changes of a snake-like robot.

The excellent properties could be achieved due to the combination of the hierarchical structures (which could reproducibly deform under large tensile strains) and the strong bonding between the graphene and carbon nanotubes which both could prevent crack propagation and also allow the high conductivity.

F. Guo *et al. Nature Communications* **9**, 881 (2018)

Electronics

Inkjet Printed Composites

Printed electronics are paving the way to a new, low cost type of technology that allows a wide variety of substrates to be used to build electrical devices. The designs are flexible and the possibilities are limitless. Graphene inks are interesting as they occupy the conductivity gap between metallic inks, which are very conducting but expensive, and carbon paste, not very conducting but cheap.

Researchers at Uppsala University, have in a collaborative work with researchers in China, recently demonstrated the potential of combining both metallic particles, in this case silver, with graphene to allow high conducting inkjet printed patterns. Starting from an aqueous ink formulation using a reactive silver solution and graphene nanoplatelets, they inkjet printed the desired design and annealed it at 100 °C, much lower than the usual sintering temperature used for silver (150 °C). This lower annealing temperature makes the process more versatile for applications requiring a variety of substrates, such as polymeric substrates that do not tolerate annealing at 150 °C. The printed composite films exhibit high electrical conductivity $<10^6$ S/m. This value is almost as high as the one obtained with a more expensive silver-only ink, but more than an order of magnitude more conductive than graphene nanoplatelets based ink.

J. Zhao *et al. J. Micromech. Microeng.* **28**, 035006 (2018)

Radiation Detector

Amongst the list of interesting properties of graphene is its strong and tuneable thermoelectric effects, which can be leveraged to detect incoming radiation. In a recent article, researchers from August Yurgens’s team at Chalmers University of Technology developed a radiation detector using these effects in a device based on mechanically exfoliated graphene. The graphene is completely encapsulated in Parylene, a dielectric polymer, which not only keeps the graphene clean and protects it during processing but allows the device to stay stable over time and protect it against parasitic doping.

The detector is based on the fact that when radiation hits the device, it heats part of it, generating a voltage bias across the device, which can be measured to infer the amount of incoming radiation. The antenna is capacitively coupled to the graphene. This simplified design, where the antenna can be used as the top electrode, maximize also the efficiency of the signal detection.

Contrary to previous studies, which reported devices working only at cryogenic temperature, the detector has a temperature independent response below 100 K and works up to 200 K. The optical responsivity reached 700 V/W using 94 GHz radiation and noise equivalent power of less than 200 $mW/Hz^{0.5}$ at 50 K. Currently, the design only functioned at 94 GHz, but the design could be optimized to widen the range. In the future, the researchers also want to develop a large-scale compatible process using Chemical Vapor Deposition (CVD) graphene.

G. Skoblin *et al. Appl. Phys. Lett.* **112**, 063501 (2018)

Sensor for Fire Alarm Wallpaper

As discussed in previous editions of this Research Intelligence Report (no. 1 and 2, 2016), one of the popular methods to produce graphene is to treat graphite with strong oxidizing agents, facilitating the exfoliation of the flakes. However, contrary to pristine graphene, the graphene obtained using this method, graphene oxide (GO), is not a good conductor. One can then use chemical or thermal treatments to reduce the graphene (i.e. the oxygen functional groups attached to the graphene plane need to be removed) to partially recover graphene-like properties.

Researchers in China recently published a study where they took advantage of this process and used GO as a fire sensor in a novel wallpaper. In their study, GO sensors are integrated on a special fire-resistant hydroxyapatite nanowire inorganic paper. In normal condition, the GO present in the sensor is not conducting, but the presence of heat reduces it, making it conducting and triggering a visual/auditory alarm. This trigger is observed at roughly 230 °C after only 5 seconds of exposure. However, the alarm time is only 3 seconds because the GO sensor is easily burned out. This property of the GO sensor and the trigger temperature can be improved by capping it with polydopamine. This compound will shield the sensor, preventing it from burning out too quickly and promote the reduction of GO. This improves the response time to 2 seconds at 127° C and increases the alarm time to more than five minutes.

F. Chen *et al. ACS Nano.***12**, 3159 (2018)

Biotechnology

Antibacterial Coating

Even though the interaction of graphene with bacterial cells has been extensively studied, some controversy remains in this field. While the majority of reports are describing bactericidal effects of graphene flakes, there is no consensus on the mechanism of killing the bacteria. Some studies even show that graphene and GO are not harmful to bacteria and can even promote bacterial growth.

In a recent study, a multidisciplinary team of researchers at Chalmers University of Technology showed that the relative orientation of graphene with respect to bacteria is a key parameter in defining the outcome of their interaction. Their study showed that while a continuous uniform horizontal graphene coating has no harmful effect toward bacteria, graphene flakes perpendicular to the substrate act as little stabbing knives toward the bacteria, killing them by penetrating the bacterial membrane and draining the cytosolic content. The bacteria are not able to develop a resistance to this killing mechanism. By keeping the height of the graphene flakes between 60 and 100 nm, the coating has an effect on bacteria but not on mammalian cells. This was the first study clarifying the mechanism of bactericidal effect of graphene coatings.

S. Pandit *et al. ACS Sustainable Chem. Eng.* **5**, 1701331 (2018)

Antibacterial Bandage

In a recent study, the antibacterial property of graphene was also a key element in the development of a novel bandage material. In this study, the researchers developed a type of cotton patch coated with chitosan-based hydrogel, which can easily be loaded with different chemicals or drugs. They explored how graphene GO not only provides the antimicrobial property but also improves the mechanical strength of the patches. The results showed that the maximum tensile strength can be increased from 6MPa to 10MPa with a loading of 1 wt % of GO (using a concentration of 22 % chitosan). The antibacterial properties of the bandage were tested not only using GO, but also curcumin, a well-known natural antimicrobial agent. Patches with no loading, with GO, with curcumin and with both GO and curcumin were tested to treat wounds infected with *Staphylococcus aureus* and *Escherichia coli.* Loading both compounds in the patch gave the best results, with only minimal or no growth of bacterial colonies observed. Next, the researchers want to try to control how the drug is released over time.

A. Konwar *et al. Adv. Mater. Interfaces* **6**, 5806wea (2018)

Flexible Glucose Sensors

Graphene is an attractive material for wearable applications, since it offers good conductivity, transparency, flexibility and sensitivity. Its highly sensitive surface can also be functionalized to detect a variety of molecules. A recent paper showed how a graphene-based glucose sensor can be integrated in flexible contact lenses to continuously detect metabolites in tears to monitor glucose in diabetic patients.

The developed contact lenses allowed real time monitoring and eliminated the need for additional measurement equipment: there is also an integrated wireless display enabling the wearer to monitor his glucose level live. To detect glucose, glucose oxidase (GOD) is immobilized on CVD graphene and when glucose passes next to the graphene channel, it oxidizes the GOD, creating a chemical reaction that creates a charge imbalance and alters the resistance of the graphene channel. The relative change of resistance can then be directly linked to the glucose level. The relative change of resistance is tailored to trigger a LED display: when glucose levels get too high, the LED light turns on and alerts the wearer of their elevated blood sugar level. In the future, multiple sensors could be integrated to monitor other types of chronic diseases.

J. Park *et al. Sci. Adv.* **4**, eaap9841 (2018)

Liquid Strain Sensors

Other types of sensors can also be prepared using graphene. In a recent article, researchers from University of Sussex in England used exfoliated graphene in a very sensitive liquid strain sensor. They noticed that the surface tension of graphene is between those of water and many water-immiscible liquids (such as oils) and used it to stabilize a water-in-oil emulsion.

Graphite was added to an oil and water mixture and exfoliated/dispersed using ultrasonication and high shear mixing. The presence of graphene had 2 functions. On the one hand, it stabilizes the emulsion, creating a shell around the water droplets. On the other hand, the emulsion containing graphene is conducting. As the conduction is created from electron tunnelling from particles to particles, it is very sensitive to strain. The reported sensitivity, would allow the sensor to measure respiration rates, pulse rates of people wearing the devices and they have the potential to improve sleep apnoea diagnosis and monitoring, for example.

M. J. Large *et al. Nanoscale* **10**, 1582 (2018)

Energy

Bioinspired Supercapacitors

The interest in portable and wearable devices increases also the demand for high performance, compact and rechargeable energy storage. Supercapacitors are of particular interest for their high power density, fast charging/discharging and long cycle lifetime. Recently, a group of international researchers fabricated supercapacitors electrodes with a carbon-based structure inspired by nature.

Starting from carbon fibres, they grew carbon nanotubes (CNTs) using microwave plasma chemical vapor deposition (MPCVD) and carefully chose the parameters in order to create a hollow structure, with an outer diameter of 30 to 40 µm. Then, the parameters of the growth are changed and graphene petals (GPs) with a width of about 100 nm are grown, attached to the CNTs along the axial direction to the micro-conduit surfaces. The micro-conduit can be seen as a branchlet where the GP attached like leaves.

On a structural level, the presence of GPs stabilizes the CNT conduits, making them more stable. The hollow structure increases the accessible electrode surface area to the electrolyte and facilitate the diffusion of ions during the charge/discharge, enabling high rate capability and power delivery. Moreover, a simulation showed that the sharp edges of the GPs can facilitate rapid access of electrolyte ions to the surfaces electrodes with short ion diffusion length, giving rise to superior electrochemical performances. The results presented in the study showed that the areal capacitance of the CNT/GP micro-conduit electrode is 2.35 F/cm^2 at a current density of 2 mA/cm^2, 10 to 1000 times higher than those of the state-of-the-art carbon nanostructure-based electrodes. The structures also possess a cyclic stability of 95 % capacitance retention over 10 000 cycles.

G. Xiong *et al. Nat. Commun.* **9**, 790 (2018)

High Areal Energy Storage

While supercapacitors charge and discharge cycles are extremely quick, their energy density is unfortunately not optimal as they deliver a high amount of energy but over a very short period of time. Batteries are giving a lower flow of energy, but over a long period of time, their properties therefore complement the supercapacitors well.

In a recent paper, researchers from North Korea produced an anode using folded graphene film. The produced anode has an areal capacity of more than 4 mAh/cm^2, above that of commercial graphite anodes (between 2.5 and 3.5 mAh/cm^2) and is stable over 500 cycles of battery charging and discharging. The advantage of folding the graphene paper, when compared to having a block of graphene composite is an increased areal energy storage and increased electron/ion transport kinetics. It is a good way to increase the thickness/volume of the electrode, while maintaining the electron transport efficiency, giving high real and volumetric energy density. This technique could also be used in other types of batteries, not only Li-ion ones.

B. Wang *et al. ACS Nano* **12**, 1739 (2018)