Graphene Research and Advances

The Swedish strategic innovation program for graphene (SIO Grafen)

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André Dankert
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**Introduction**

This is the first research intelligence report written by Ph D André Dankert at Chalmers University of Technology, on behalf of SIO Graphene capturing important research results in the priorities areas of strength.

Two-dimensional layered materials offer a wide range of materials with different properties allowing for a broad spectrum of possible applications. Single or few layer flakes of such material can be grown or extracted from a larger bulk crystal. Graphene is the most famous and extensively studied member of the family of two-dimensional materials. It exhibits no bandgap giving it a metallic character with large charge carrier mobility. Beyond graphene, the properties of other two-dimensional materials include semiconductors and insulators, as well as superconductors.

In the recent years several scalable techniques have been developed to grow, transfer and chemically alter these layered materials, which make them highly interesting for the applicability on an industrial level. Even though large scale fabrication processes result so far in polycrystalline compounds which are commonly less attractive for electronic research, several studies still demonstrated their extraordinary properties in many applications.

This issue demonstrates the ongoing broad research field of graphene and graphene-based devices within the prioritised areas. Mechanically, graphene is interesting due to its robustness, durability and bio-compatibility. Large scale graphene has shown to be completely impermeable, but can be threatend or oxidized to create custom made membranes for filtration applications. It can also be combined to polymer compounds for light-weight applications or as scaffolding material for tissue growth. The electrical properties of graphene depend also on its state, which can be significantly affected by its environment or internal strain making it ideal for sensor applications. Graphene exhibits excellent properties for high frequency applications, such as amplifiers and mixers, even on wafer-scale fabricated devices. Furthermore, graphene can be utilised in printed electronics, where it is suspended in an ink solution. This unique combination of optical, mechanical, chemical and electrical properties make graphene also a promising candidate for a wide-spread application in the field of sustainable energy, for example in solar cells or high capacity storage devices.
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Fabrication of graphene

Graphene is a two-dimensional layered material made of carbon atoms arranged in a hexagonal crystal structure. Initially, it has been suggested that a single layer of graphene cannot exist at finite temperatures or in atmosphere. Nevertheless, since its first isolation in 2004, researchers explored several scalable techniques to produce wafer size layers of graphene for industrial compatible processes.

Exfoliation

Two-dimensional layered materials exhibit a bulk structure made of stacked and atomically thin sheets bound together by weak inter-layer van der Waals forces. In contrast, the intra-layer bonds are significantly stronger, which allows the cleavage of individual sheets from the bulk crystal. In the case of graphene, these properties lead to the first isolation of a single layer on an insulating substrate by Andre Geim and Konstantin Novoselov. The researchers simply used scotch tape to separate the layers from a bulk graphite crystal. This is to date the most reliable technique to produce graphene of a high mechanical and electrical quality – showing carrier mobilities of up to 100000 cm²/(Vs) - but also limits its applicability to small scale or for research purposes.


Epitaxial growth

Shortly after the synthesis of monolayer graphene by exfoliation, the search for alternative techniques to fabricate graphene in a large scale bottom-up technique grew rapidly. Silicon carbide (SiC) was found as ideal material to synthesis high quality graphene and as substrate for possible applications. Clean SiC, made of silicon and carbon atoms, is transparent and insulating, which is ideal for opto-electronic applications, but can also be doped to be metallic. Using a controlled annealing process, silicon atoms can be desorbed from its surface leaving a layer of carbon atoms behind, which form one or several layers of graphene. The final graphene sheet shows excellent electrical and mechanical properties with a particularly smooth surface and carrier mobilities above 11000 cm²/(Vs). Even though a large scale growth of high quality graphene is possible on SiC, strong bonds to the substrate limit the theoretically possible intrinsic properties and hamper a possible transfer to another substrate.

Virojanadara et al. PRB 78, 245403 (2008)
**Chemical vapour deposition**

The most promising scalable technique is the growth of thin layers of a 2D material on a metal catalyst by chemical vapour deposition (CVD). It has been shown that a high temperatures furnace with a partial pressure controlled gas mixture can grow graphene on a copper or nickel foil. The growth of graphene on copper by CVD is limited to one layer. The foil acts not only as a catalyst but also as a carrier substrate. Once deposited, the layers can be transferred to a desired substrate by etching out the metal foil. This process allows to grow high quality graphene – with mobilities up to 25000 cm²/(Vs) – and to transfer it on any substrate. In recent years this technique has been adapted for industrial-scale fabrication of up to 30inch in a roll-to-roll technique.


**Graphene oxidation**

Graphene oxide is a stable hexagonal compound of carbon, oxygen and hydrogen in variable ratios obtained by treating graphite with strong oxidizing agents. The flakes can be dispersed in water by sonication and sprayed or spin-coated to produce a multilayer membrane, which is stable without substrate at ambient conditions. A common technique to fabricate graphene oxide is the Hummers method. Graphene flakes are treated in a bath of oxidizing agents, before it is neutralized by rinsing with water. Subsequently, the water/graphene-oxide solution can be sprayed or spin coated onto a substrate to create a membrane. The final membrane is porous and possesses varying electrical and mechanical properties, depending on the degree of oxidation.

Membranes and coatings

It has been shown that ideal single layers of graphene or graphene oxide are completely impermeable to any gas or liquid, including the smallest gas molecule possible – helium. This property makes it ideal as environmental barrier. Recently it has been shown, that even commercially available graphene oxide reduces the permeation of mercury by 90%. A possible application would be to use graphene or graphene oxide coatings or to implement layers within the polymer of containers for dangerous goods, such as oil and fuel, which could significantly reduce the risk of leakage and additionally increase their mechanical strength.


In contrast, researchers around Nobel Prize winner Andre Geim at the University of Manchester studied multi-layer graphene oxide membranes with a selective permeability. Their membranes were only several hundred nanometer to micrometer thick, but able to withstand large pressure differences and showed no significant permeation of any gas and most liquids. Interestingly, only water showed permeation whereby the rate was similar to a straight diffusion without a barrier. Further research revealed nano-capillaries between the graphene oxide sheets, which were filled with water remaining from the fabrication process. A capillary effect wetted them permanently and allowed almost frictionless transport to the surface of the membrane. The researchers suggested, that controlling the size of the capillaries would allow engineering of tailor-made porous membranes for filtration and desalination.

Nair et al. Science 335, 442 (2012)
Joshi et al. Science 343, 752 (2014)

A similar approach, using graphene membranes, has been recently presented by researchers from the Massachusetts Institute of Technology (MIT). Since graphene is generally impermeable, the researchers developed a technique to create sub-nanometer pores with a controllable size. Currently, the porosity is less than 1%, but evaluations showed that membranes reaching a porosity of 10% would possess permeability two to three orders of magnitude higher than current reverse osmosis membranes. Such membranes could significantly decrease the power consumption in filtration and desalination facilities.

O’Hern et al. Nano Letters 14, 1234 (2014)
**Printed electronics**

The mechanical properties of graphene make it a promising candidate for printing circuits, in particular on flexible polymers. Graphene can be easily dispersed in a solution and exhibits remarkable and reproducible electric properties, which are unaffected when being scaled to industrial requirements.

It has been already shown in 2012, that graphene exfoliated in a solvent can be used for printing electronics. The collaboration between French and US scientists demonstrated the possibility to manufacture flexible Graphene Field-Effect Transistors (GFET) using single layer graphene produced by chemical exfoliation. Single layers could be separated from multilayer graphene using ultracentrifugation. The printed transistor showed comparable values to previously reported GFETs based on exfoliated graphene flakes. The intrinsic mobility was found to be around 100 cm²/(Vs), which is comparable to organic or silicon based transistors, but small compared to ordinary graphene. The transistors could withstand frequent flexing with a bending radius of 25 mm without significant change to the electrical properties. A smaller bending radius exhibited a permanently decreased performance possibly due to loosely clamped flakes. Even though the solution was deposited using dielectrophoresis, which is not suitable for large scale applications, the researchers insist that it can be replaced with state-of-the-art printing techniques.


An approach using a regular inkjet technique has been demonstrated recently, also using chemically exfoliated graphene in a solution. The printed graphene ink exhibited a low resistance in traces down to 160 nm thickness. The main difficulty lies in the size of the dispersed flakes: if too big, clogging of the nozzle can occur; too small flakes result in low connectivity and reduced performance. The researchers optimized the flakes to be made of four layers of graphene having a length of 173 nm. Furthermore, this process showed to be adaptable for other two-dimensional materials, which the scientists demonstrated by printing a photodetector made of graphene and molybdenum disulphide exhibiting a strong
photoresponse. This would also allow for the fabrication of transistor circuits using two-dimensional semiconductors.


More recently, researchers from the University of Illinois presented an alternative approach to produce p-n-junctions on flexible substrates in large scale CVD graphene. The doping of graphene is strongly affected by its environment. In this case, the researchers produced a hole doping in the graphene by applying a particular resist. Subsequently, they could controllably create electron doped areas through exposure to a laser. Furthermore, the doping was adjustable with different irradiation times and laser intensities. The laser source was a commercial available laser writer system, which means that the process can be arbitrarily scaled for practical applications.

Seo et al. *ACS Nano* 8, 8831 (2014)

**Energy applications**

The technological development over the last 30 years raises an increasing demand for more energy efficient and sustainable products. In particular, the increasing market of mobile devices demands high capacity energy storage solutions with high cycle rate and long lifetime. Graphene offers unique electrical and mechanical properties to super-charge developments in this field, since it offers new ways to efficiently transport, store and generate energy.

The increasing demand for printable electronics comes along with a higher need for printed energy storage solutions. Typical batteries are too rigid and bulky for the next generation of flexible and ultrathin electronic devices. In contrast, super-capacitors can hold a large electric charge and have been flexible fabricated by several large scale techniques, such as roll-to-roll, Meyer rod coating or spraying. An efficient super-capacitor requires a combination of large surface area and large pseudo-capacitance. So far, polyaniline (PANI) has been used in these processes due to its ease to manufacture and excellent pseudo-capacitance. However, PANI is exhibits weak mechanical and conductive properties making it unsuitable for flexible devices with repeated charge cycling. Recently, researchers from BASF in Germany developed an inkjet printable solution by combining nano graphene platelets (NGP) with PANI. The large
surface area of graphene and its excellent electrical and mechanical properties are very complementary to PANI resulting in a large specific surface of the final NGP/PANI ink. Furthermore, the scientists demonstrated the applicability by printing NGP/PANI electrodes to create a simple super-capacitor. This capacitor exhibited a large capacitance and high power storage ability, which remained unchanged for more than 1000 charging cycles. Further optimization of the ink solution could yield an industrial applicable alternative for printed, flexible super-capacitors.

Xu et al. Journal of Power Sources 248, 483 (2014)

A recent report from the researchers around Andre Geim in Manchester demonstrated that graphene allows protons to diffuse through a single layer of the material, even though it is impermeable to hydrogen. This would open up new possibilities for designing fuel cells, where different electrolytes have to be separated, but protons are allowed to pass to create a current. Using graphene would minimize the size of the membrane and allows combining membrane and electrode, as well as the ability to control the proton flow using a bias voltage. In contrast, the researchers also demonstrated the reverse process producing hydrogen from air. Placing the graphene membrane between normal air and a vacuum and applying a negative bias to the graphene, a flow of hydrogen could be measured on the vacuum-side of the membrane, which stems from the flow of protons through the membrane neutralized by electrons from the negatively charged graphene. This proof of concept suggests the possibility for hydrogen extraction from the air for use in hydrogen fuel cells and could allow for the development of an energy-source running on air.


Several application fields, such as military, medical and spatial exploration missions, require so-called primary batteries, which are portable voltaic cells that are not rechargeable, but which possess high energy and power densities. Li/CFx batteries exhibit the highest energy densities known in primary batteries combined with a long service life and wide operation temperature range. Unfortunately, Li/CFx batteries exhibit limited kinetics and low conductivities, which motivates research to increase their current-efficiency. In 2013, a research team collaborating between India and the U.S. reported the first solution to widely
increase the rate capabilities of Li/CFx batteries and to increase the energy density and power capability. They employed fluorinated graphene as cathode material, which was chemically treated similarly to the Hummers method. This means, this method can be easily scaled since the electrodes are manufactured is completely based on chemical exfoliation and functionalization. The scientists predict further enhancements of the performance of the battery by optimizing the fluorination content, which would make Li/CFx a viable alternative as a primary battery.

Damien et al. *RSC Advances* 3, 25702 (2013)

For mobile applications more reusable solutions are desirable. Over the last decade Li-air (Li-O₂) batteries have been discovered as a cheap and highly efficient secondary battery, which possess a very high capacity and are rechargeable. So far the main drawback of these batteries is the unstable electrolytes, a significant overpotential while charging and a low cyclability. Very recently a research team, collaborating between the University of Copenhagen and Uppsala, demonstrated how different stages of oxidized graphene can affect the performance of Li-air batteries. They prepared reduced graphene oxide chemically and thermally, whereas they also varied the oxidation times. These graphene oxide cathodes exhibit very different charging curves and cycling times, whereas thermally oxidized graphene showed the highest discharge capacity. These results are very promising to develop different types of batteries dependent on the degree of oxidation of the graphene which could yield high capacity Li-air batteries.


**Graphene-based composite materials**

Combining two or more materials with different properties creates composite materials with unique characteristics. Composite materials can be lighter, stronger, flexible, and transparent as well showing a higher degree of corrosion and heat resistance, compared to their individual building blocks. They are already used in many industries, such as automobile, boats, aerospace, sports equipment, wind turbines, body armour, building materials, bridges and medical utilities. Graphene composites have many potential applications, since it can be light,
fire and radiation resistant, as well as an improved electrical and heat transport, and can even possess opto-electronic or chemical active properties. Furthermore, graphene can significantly affect the properties of the composite whilst having an extremely low filling factor.

One possible application demonstrated by Indian researchers, which created a composite of graphene and silver nanoparticles as a catalyst to break down environmental pollutants. Some of these pollutants, so called endocrine disruptors, are particularly harmful for the health of animals, including humans, since they can affect the hormonal system and cause reproductive problems, such as cancer, miscarriage and infertility. Unfortunately, these compounds are used to make many household and industrial products, and can be already found in soil, water and even human breast milk. Even though several approaches exist to develop catalysts to break down these pollutants, their efficiency has been rather low due to the required ultraviolet light, which makes up only a small percentage of the sunlight. The scientists from Kolkata demonstrated that a composite of reduced graphene oxide and silver nanoparticles can act as an efficient catalyst powered by visible light, which makes up more than half of suns spectrum. The researchers tweaked already developed graphene composites which are used to degrade dyes. Additionally, they loaded them with silver nanoparticles, which act as an antenna for visible light. The final composite successfully degraded three different kinds of endocrine disruptors: phenol, biphenol A (BPA) and atrazine. Further engineering could yield other catalysts to breakdown different pollutants. The production is simple and scalable and provides a promising way to use visible light to break down these potentially harmful compounds and other organic pollutants. These composites could also be integrated into final products to reduce pollutants in everyday life before being consumed.

Bhunia and Jana ACS Applied Materials & Interfaces 6, 20085 (2014)

Another application has been recently presented integrating graphene oxide directly into a commonly used polymer. The researchers produced a homogeneous distribution of graphene oxide flakes in polyvinyl chloride (PVC) and studied its electromagnetic properties. PVC is the third largest polymer produced in the world. It is chemically resistant, cheap, light, fire resistant, insulating, and its softness and flexibility can be adjusted by plasticizers. By adding different concentrations of graphene oxide, the scientists significantly affected the electrical properties of the polymer. Depending on the concentration of the graphene oxide (0-3%) the
researchers were able to change the energy absorbance of the composite. Furthermore, the resonance frequency, that means the frequency with the highest absorbance, could be tuned between 30 MHz and 100 kHz. This is very promising, since tailor made electro-magnetic shields could be fabricated of light and recyclable PVC.

Joshi and Deshmukh Journal of Electronic Materials 43, 1161 (2014)

Sensors and life science

Entrance into the Internet of Things era is not possible without sensors. They can detect changes in their physical environment, for example light, heat, motion, moisture, pressure, gases, chemicals and many more. Their applications touch every industrial and research field and are particularly interesting for mobile devices and medical applications. Graphene is an promising choice as a sensor component, since it offers a large surface to volume ratio combined with unique arrangement of optical, electrical, mechanical and thermal properties. In the future, it could allow the creation of better, cheaper, smaller and lightering alternative to already existing sensors, but also offering completely new possibilities diagnostic devices with low detection limits, making it possible to measure ppm levels and lower.

A recent report by a Korean research team highlights the possible application of graphene as a mechanically stable wearable sensor. Such sensors require transparent electrodes with constant electrical and optical properties independent of their mechanical deformation. Even though graphene is mechanically robust on the nanoscale, it would not withstand mechanical distortions on a large scale. The researchers overcame this problem by reinforcing the graphene with a metal nanothrough. The final hybrid exhibits properties beyond either graphene or the nanothrough itself with a high uniformity and low sheet resistance, high transparency (91%) and excellent stretchability. Furthermore, the scientists demonstrated the applicability by fabricating functional transparent arrays of oxide semiconductor transistors on such a hybrid and attaching it to skin. This successful demonstration is extremely promising for the development of medical “tattoos” and other wearable sensors.

An et al. Nano Letters 14, 6322 (2014)
In parallel, an alternative approach has been presented by a group from the Trinity College in Dublin. The scientists infused liquid exfoliated graphene into natural rubber to create a conductive composite. They discovered that the electrical properties of the material became extremely sensitive to strain increasing its resistance about four orders of magnitude and operating at strains exceeding 800%. Furthermore, the sensors were able to track dynamic strain with vibration frequencies of at least 160 Hz. As a final proof of concept, the researchers used the rubber-graphene hybrids to track bodily motion, such as joint and muscle motion as well as breathing and pulse. This is promising for a simple, cheap and sensitive alternative for motion sensors for wearable technologies or medical applications.


Finally, graphene is an excellent tool to detect the chemical environment of a device. The electric conductivity combined with the large surface-to-volume ratio allows to custom engineer the surface properties so that changes in the exterior can be detected electrically. However, commonly used sensors for detecting environmental molecules suffer a slow intrinsic dynamic due to interface-trapped charges and defect-mediated charge transfer processes, which significantly limits the response time. For actual applications a fast and sensitive response is desired. Recently, a research team from the University of Michigan demonstrated a novel way to detect different molecules in a vapour. They used graphene field effect transistors to create a heterodyne sensor. Such sensors react to the proximity of a dipole moment and do not involve the slow dynamic of interface states and charge transfer processes. The scientists predict that the detection limit of the sensors can optimized to less than 100 molecules, which would allow fundamental studies of molecular interactions with high precision. Furthermore, the high mobility of the graphene provides an in situ intrinsic gain for the signal amplification. Since graphene can be easily scaled to wafer size and fabricated with commonly used top-down techniques, these sensors are well suited for practical applications.

Graphene logic circuits

Even though graphene exists only two-dimensional, as atomically thick material it exhibits an extraordinary conductance and a high mobility. Nevertheless, the initial hope of creating transparent transistors is hindered by the missing band gap in graphene, which is a main requirement for switching operations in logic devices. So far, all attempts to introduce a band gap, such as doping through ad-atoms or defects, resulted in reduced transport and transistor properties. Alternatively, hot-electron transistors (HET) emerged, which relied on quantum tunnelling and did not require a band gap, but the tunnelling effect drastically reduces the transmitted current.

Early HETs based on metal were typically limited due to carrier scattering and in-plane voltage drops. Graphene overcomes these problems due to its high conductivity and two-dimensional nature. Researchers from the Royal Institute of Technology in Sweden recently constructed such a HET device using CMOS compatible processes. They reported on/off current-ratios of over $10^3$ and $10^4$ and showed that their transistor has potential in high-speed low noise amplifiers and power amplifiers. Further reduction in the thickness of the insulators could improve the current transfer ratios which are typically small in tunnel-barrier devices.


Such a study has been presented by researchers from the University of California. The group characterized four different graphene-based HETs and demonstrated that the current transfer ratio can be optimized through choice of material and thickness of the insulators, which act as filtering- and tunnelling barriers. They achieved a large on/off current ratio of $10^3$ with a collector and emitter size optimized for high frequency applications. These values can be further optimized, which makes these devices are promising alternatives for the future of high-speed electronics based on graphene.


Another approach to overcome the shortcomings of HETs has been demonstrated by researchers from the HRL Labs in California. Instead of a horizontal structure, the scientists created a vertical sandwich structure made of graphene-fluorographene-graphene. They used epitaxial graphene as a conductive base and large bandgap fluorographene as an insulating
barrier. This heterostructures demonstrated an on/off ratio of about $10^5$ up to 100°C. Furthermore, the growth of epitaxial graphene allows an industrial scale fabrication, which makes these results promising for wafer-size logic devices made with graphene HETs.


Recently, a research group from the Royal Institute of Technology in Sweden presented a chip to wafer scale technique to fabricate graphene field effect transistors (GFETs) using chemical vapor deposited (CVD) graphene compatible with current CMOS processes. This means it could be combined with the back end of the line (BEOL) production of conventional semiconductor process flows. They present devices with a carrier mobility up to several hundred cm$^2$/Vs reaching current saturation regions comparable to average values in exfoliated graphene. This approach is a crucial step towards reliability, reproducibility and variability, and marks an important milestone for introducing graphene into wafer scale process lines.


Another alternative technique to perform logic operations is presented by spintronics, which employs the spin degree of freedom of the charge carriers as the element of logic. The high mobility as well as the low spin-orbit and hyperfine interaction of graphene make it highly interesting for spintronic applications. Nevertheless, the spin information possesses only a limited lifetime of up to 1ns, depending on the material and environment, which lessens the applicability. So far, theoretical predictions for graphene promised a long spin lifetime of up to 1µs and hence a long spin diffusion length, but these values were not observed experimentally yet. It has been proposed that the reduced parameters stem from environmental influences roughening and doping the graphene. Previous studies tried to overcome these problems by replacing the substrate or even encapsulating the graphene entirely.

Very recently, researchers from the Chalmers University in Sweden demonstrated a long distance spin transport of up to 16µm and spin lifetimes of about 1.2ns at room temperature in graphene on a silicon oxide substrate. These results belong to the highest spin parameters
observed in any graphene so far, but even more remarkable, since the scientists used chemical vapour deposited (CVD) graphene. This demonstrates that CVD graphene is finally comparable with exfoliated flakes and could allow for scalable wafer-size spintronic devices for future applications.