Graphene Research and Advances

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Introduction

Thanks to its long list of interesting properties, graphene can be integrated in numerous systems. High quality single layer graphene can be used for electronics and sensor applications. New techniques have also been developed for large scale production of high quality graphene flakes that can be printed and used in flexible circuits and for energy storage, or be combined with other compounds in a composite material, which for example can be used as an electromagnetic shield.

Graphene flakes can be incorporated in paints and in other types of coatings, be used for anti- and de-icing of airplane wings and in antimicrobial coatings. It could play an important role to help mitigate the effects of human activities. For example, graphene-based membranes can effectively be used in the next generation of food packaging and to filter water. Graphene is biocompatible, making it an attractive material for bioscaffolds and other life science applications.

This report is included in the SIO Grafen Research Intelligence Report Series, published twice a year. The aim with the report is to highlight the most interesting new research papers, selected to match Swedish interest areas.

Content:

Graphene Production

More than ten years after its discovery, scalable and cost-effective production of high quality graphene remains critical for its incorporation in commercial products and for realising its full potential. Over the years, several techniques to produce graphene have been developed, targeting different applications.

Graphene oxide is obtained by treating graphite with strong oxidizing agents, which facilitates the exfoliation of the flakes. After exfoliation, the graphene oxide (GO) flakes are not conducting and need to be reduced (i.e. the oxygen functional groups attached to the graphene plane need to be removed) to recover graphene-like properties. This technique is scalable, but the properties of the flakes obtained after reduction, are not as good as the ones of pristine graphene; previous studies routinely reported electronic mobility values on the order of 1 cm^3/V·s, orders of magnitudes lower than values reported for pristine graphene. Graphene flakes produced with this method are used in inks, paints, composites and even for energy applications, such as battery electrodes and supercapacitors.

The low values of electron mobility recorded, prevent the use of GO in applications where highly conducting graphene is necessary. To solve this problem, a group of researchers from the United States recently developed a technique to reduce GO very efficiently, using a conventional microwave. The GO flakes are first slightly reduced by thermal annealing, leading to slightly conducting GO that could then absorb microwaves. The GO flakes were further reduced by exposing them to short pulses of microwave (one to two seconds), which rapidly heat the GO flakes, causing desorption of the oxygen functional groups and reordering the graphene basal plane. The electron mobility of the reduced GO (rGO) flakes produced using this method, ~ 1000 cm^3/V·s, is significantly higher than the ones previously reported. These results pave the way to an even broader range of applications accessible with rGO.

D. Voiry *et al. Science* **353**, 1413 (2016)

Epitaxial growth of graphene on silicon carbide (SiC) is made using a controlled annealing process, which yield a sublimation of carbon at the surface of the insulating SiC substrate, leaving behind a layer of graphene. Graphene obtained with this method has a very high quality on a wafer scale and can be used in electronic applications. However, it is expensive and the strong bonds to the substrate limit the possibility of transfer, making it incompatible for example with silicon technologies.

As SiC is insulating, graphene devices can be fabricated directly without the need to transfer the graphene layer, as it is the case for CVD graphene. A review of the different applications possible for epitaxial graphene on SiC has recently been published by a collaborative work from teams in Sweden and in Bulgaria. In their work, they review how graphene on SiC can be used to fabricate FET transistors for post Si CMOS applications, RF-transistors and amplifiers and even wafer-scale graphene integrated circuits. Graphene on SiC is also suitable for gas sensing and magnetic field detection, where the high values of mobility recorded for graphene on SiC are enabling the fabrication of very sensitive devices.

M. Beshkova *et al. Vacuum* **128**, 186 (2016)

Graphene Devices and Sensors

The properties of graphene make it an attractive material for electronics and sensor applications. The high mobility, high conductivity and low noise measured in graphene make it a suitable material for high-speed electronics. Besides, graphene possesses a highly sensitive surface, which can also be further functionalised to enable the very sensitive detection of a variety of molecules, making it a great choice for gas- and bio-sensors.

A New Resistance Standard

The very high quality of the epitaxial graphene grown on SiC can be used to define the resistance standard. In the past, the most accurate resistance standards were based on the quantum Hall effect, a physical phenomenon that can be measured and characterised in fabricated samples of a two dimensional (2D) semiconductor at very low temperatures (below 1 K) and high magnetic fields (around 10 T). These constraints, which are strongly dependent on the mobility of the carriers in the 2D electron gas, make the measurement of the resistance standard complicated and only accessible in expensive systems. Earlier this year, researchers from Sergey Kubatkin's team at Chalmers University of Technology and Rositsa Yakimova's team at Linköping University collaborated with researchers in the United Kingdom, to demonstrate the potential of devices fabricated with graphene on SiC to define the resistance standard. Using graphene instead of 2D semiconductors to measure the resistance standard has several advantages. The measurements can be performed with a very high degree of accuracy at 4 K and 5 T; these conditions can easily be reached in a much simpler and cheaper system. Additionally, the resistance plateau, which is used to define the resistance standard, is stable over a wide range of magnetic fields and the critical currents are high, making it easier to define the standard with high accuracy. The researchers are also developing a technique to get rid of intrinsic doping and identify regions of the samples with bilayer graphene, as these can decrease the accuracy of the measurement, but they successfully are developing a technique to simply and cheaply define the resistance standard using graphene devices.

H. He *et al. CPEM 2016, published in IEEE* Art. No. 7540516 (2016)

High Frequency Integrated Mixer

Terahertz radiation lies between microwaves and infrared light waves in a range of the electromagnetic spectrum known as the terahertz gap, where technology to generate, detect and interact with the radiation is still in its infancy. This frequency range is predicted to have applications in for example high-speed wireless communications links and security imaging. The first step in developing possible high-speed applications by using graphene is to develop a graphene field-effect transistor (GFET)-based integrated circuit. Previous experimental reports showed that GFET-based circuits are limited to the microwave range, with a maximum reported frequency of 30 GHz. Researchers from Jan Stake’s team at Chalmers University of Technology recently developed a GFET mixer circuit fabricated on CVD graphene, transferred beforehand on a silicon wafer. The device is operating at 185-215 GHz, the highest frequency range reported for any graphene integrated circuit. The performances of such devices are currently not reaching the performances of current CMOS technology, but could be enhanced by optimising the material growth, transfer process and fabrication process. It also represents an important step towards the potential utilisations of CVD graphene in terahertz components. The process could even be adapted to a flexible substrate.

M. A. Andersson *et al. IEEE Trans. Microw. Theory Techn.* (2016).

A Step Towards Integrated Flexible Electronics

Jan Stake’s research team at Chalmers University of Technology also investigated the use of Al_2O_3 as a gate dielectric in the fabrication of GFETs on a flexible substrate. To ensure the high performance of GFETs, the presence of a uniform and efficient dielectric film is needed for charge injection into the graphene channel. Al_2O_3 is a widely used insulating material for such purposes, due to its excellent dielectric properties, strong adhesion to a variety of materials and thermal and chemical stability. However, its widespread use in graphene-based devices have been prevented because its properties are very sensitive to growth conditions. The Swedish research team characterised the quality of the Al_2O_3 used in GFET devices fabricated, using CVD graphene, transferred beforehand on a flexible PET substrate. They confirmed the high quality of the gate dielectric, promoting the use of Al_2O_3 as a gate dielectric in GFETs on a flexible substrate.

X. Yang *et al. GSMM 2016, published in IEEE* Art. No. 16107723 (2016)

Flexible gas sensors

Every year, wearables are getting a more useful and accurate and an increasing interest in the connected world, the “Internet of Things”. For such applications, flexible and stretchable devices that can adapt to different shapes are necessary. Graphene clearly has a role to play in this new branch application, since it offers good conductivity, transparency, flexibility and sensitivity. A team of researchers in Korea recently developed a gas sensor using a highly stretchable and transparent film made of metal nanowires and graphene. The advantage of using such a hybrid structure is that the metal nanowires and the graphene complement the weaknesses of each other. The gas sensor is based on a GFET device, where the electrodes are made of this hybrid film. The active part of the GFET is made of functionalised graphene enabling the detection of different types of gas molecules, such as methanol and acetone etcetera. The detector is very sensitive and could in principle be used to detect harmful gases, such as nerve gases. The researchers also demonstrated that their detector is working even after mechanical deformations and can be read by being integrated with a Bluetooth system, enabling wireless sensing, which makes it an important milestone in the quest to wireless and wearable sensors.

J. Park *et al. Nanoscale* **8**, 10591 (2016)

Printed Electronics

Printed electronics pave 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 and graphene oxide (GO) inks, consisting of dispersed flakes in a solution, are particularly interesting for all sorts of applications.

Flexible Circuits

In a recent paper, a Chinese research team reported an effective way to improve the conductivity of printed GO patterns. GO flakes are generally larger and they can be dispersed in water (contrary to graphene flakes). It is, however, a problem to recover a high electrical conductivity of the patterns, even after the reduction of the GO. The researchers used a direct printed ink method to define the patterns. This allows them to use very large flakes, while having a good resolution. Their findings show that these very large GO flakes (having an aspect ratio of roughly 20 000) can be aligned during the printing process, enabling a better conduction after the chemical reduction. The value they recorded for the electrical conductivity, 4.5×10^4 S/m, is among the highest ever recorded in printed graphene electronics and could possibly be increased by optimising the size of the flakes and the reduction process. By taking advantage of the high conductivity and flexibility of the printed rGO patterns, the researchers also showed that an rGO circuit maintained its performance during repeated bending tests, demonstrating that the method is suitable for producing highly conducting, flexible circuits.

W. Li *et al. ACS Appl. Mat. Interfaces* **8**, 12369 (2016)

Micro-Supercapacitors

The interest in portable and wearable devices increases also the demand for high performance, compact and rechargeable energy storage. Supercapacitors are electrochemical capacitors with extremely high capacitance, owing to the large surface area of the electrodes. They are of particular interest for their high power density, fast charging/discharging and long cycle lifetime. Micro-supercapacitors, also called ultra-compact supercapacitors, could be used to power implantable medical devices or could be integrated directly on-chip. Graphene-based materials hold promises in this application area because of their large specific surface area, elasticity, chemical stability and high electrical conductivity. However, several technical challenges, such as the tendency of graphene to aggregate and restack, have prevented its widespread usage. Researchers in Mikael Östling's team at the KTH Royal Institute of Technology recently demonstrated that it is possible to fabricate an all-solid-state micro-supercapacitor based on printed graphene electrodes and drop-cast polymer electrolyte (polyvinyl alcohol/H3PO4). The printed graphene electrodes exhibit a porous morphology with vertically oriented graphene flakes, increasing the surface area and making it particularly attractive for supercapacitor applications. The devices presented in the paper show areal capacitances of about 0.1 mF/cm^2 and long cycle life of over 1000 cycles, comparable to other graphene-based micro-supercapacitor. This technique is particularly interesting because it allows the facile and scalable fabrication of on-chip energy storage component for emerging electronics.

J. Li *et al. Appl. Phys. Lett.* **109**, 123901 (2016)

Composites

Combining several materials together in order to form composites gives rise to unexpected characteristics that are more than the sum of the individual properties of the combined materials. Composite materials can be lighter, stronger, more flexible and more transparent than their individual buildings blocks. They are already widely used for example in the transport industry and in sporting goods. Adding graphene, even with a low filling factor, can significantly affect the properties of the compounds, making it an attractive additive for all sorts of applications.

Hydrogen Storage

Hydrogen is a very attractive fuel because it is very energy efficient and environmentally clean. Its widespread usage as a clean fuel is hindered by the difficulty to store it efficiently and safely. The U.S. Department of Energy has set energy density and gravimetric capacity goals for such a storage, which so far have not been reached. Nanostructured graphene has been identified as a good candidate to reach this target as it is lightweight, possesses a large surface area, chemical stability and reversibility. Earlier this year, researchers based in Canada reported on a simple method to produce palladium/graphene nanocomposites for the storage of hydrogen. The nanostructured graphene acts as a highly porous structure where the metallic particles can attach itself. These particles then catalyses the capture of hydrogen by helping its dissociation and by anchoring the hydrogen ions. Their research shows that the palladium/graphene composites have a high hydrogen uptake under pressure and ambient temperature. The hydrogen is stored without any significant release until the temperature is increased between 60ºC and 100ºC, where it rapidly discharges hydrogen, with a complete release within 200ºC. By using a loading pressure of 60bar, the researchers were able to meet the criteria set by the U.S. Department of Energy, making this graphene-based composite an interesting material for high density storage of hydrogen.

C. Zhou *et al. ACS Appl. Mater Interfaces* **8**, 25940 (2016)

Electromagnetic Interference Shielding

Adding dispersed graphene sheets to an insulating matrix can enable high electrical conductivity, necessary to build an electromagnetic interference (EMI) shield. In general, when developing conducting composites for EMI shielding, one has to compromise between its shielding effectiveness, ductility and toughness. Research efforts have, hence, been put forward to balance mechanical robustness and shielding properties. This balance can be reached using three-dimensional aerogels and foams. This kind of porous structure not only has a low density, but the electrical network can be created in the polymer matrix at lower loading, thus affecting the mechanical properties to a smaller extent. For EMI shielding, the porous structure is also an advantage as it attenuates the incident electromagnetic waves by enhancing the multi-reflection of the incident waves. A recent paper showed how one can use the anisotropy in the properties of the porous structure to maximise the shielding effectiveness in a graphene-based composite aerogel. The researchers developed an anisotropic graphene/epoxy aerogel by using a directional-freezing technique. This allows them to tune the density, shapes and direction of the pores in the aerogel, leading to significantly improved electrical and EMI shielding performances. The performance of such a composite is comparable to the best reported for graphene based polymer composites, using lower graphene loadings.

X.-H. Li *et al. ACS Appl. Mater. Interfaces* **8**, 33230 (2016)

Coatings

Graphene can also be added to paints and to other types of coatings and enables a variety of functional coatings for several applications. Graphene is strong, chemically inert, impermeable to gas and stable in ambient conditions up to 400°C. It holds great promises for example in long-lasting protection against corrosion and friction.

Anti- and De-icing

Earlier this year, researchers in the United States developed a super-hydrophobic coating using specially designed films made of conducting perfluorododecylated graphene nanoribbons (FDO-GNR) with anti- and de-icing properties. Down to -14ºC, the super-hydrophobicity prevents passively the freezing of incoming water. At lower temperatures, the conducting properties can be used to remove the ice using Joule heating. The de-icing action can be enhanced by adding a lubricant to the surface, resulting in a slippery surface where the ice can easily be removed by gravity. Adding this lubricant is also more energy efficient than only using Joule heating. Once the surface is heated to sufficiently high temperatures, the anti-icing properties are recovered. This hybrid film clearly shows promising results for use in extreme environments and is the first report where a coating is used with this double functionality.

T. Wang *et al. ACS Appl. Mater. Interfaces* **8**, 14169 (2016)

Fighting Against Microbes

Another area of applications where graphene coatings can be used is in the medical domain. In the recent years, there has been a growing interest in exploiting nanomaterials with antimicrobial properties. The aim is to develop new tools and strategies to fight against the growing resistant bacterial strains. Carbon-based materials like graphene are of particular interest because of their high surface area and the ease of chemical and physical modifications that can allow the tuning of antimicrobial properties depending on the targeted applications. Researchers in Italy developed a graphene-layered nanoparticle which prevents the growth of *Staphylococcus aureus*, one of the most important bacteria causing diseases in humans. The graphene-like layers were prepared by oxidation of carbon-black, then chemically reduced and coated on cells, before they were exposed to the bacteria. These graphene-like layers are in an oxidation state between fully oxygenated GO and pristine graphene: the presence of oxygen-containing functional groups stabilises the dispersion in water, but can activate unwanted biological processes. However, its low enough concentration does not allow it to become a concern for biomedical applications.

M. Olivi *et al. J. Nanopart. Res.* **18**, 358 (2016)

Membranes

Graphene is the perfect membrane: it has been shown that a thin and a continuous layer is impermeable to everything (except protons), including the smallest gas molecules: hydrogen. This makes it ideal as an environmental barrier. By stacking flakes of graphene, it is also possible to create and engineer membranes that can be used to filter for example saline water.

Membranes for water treatment

In recent years, membranes have attracted a growing interest in water treatment applications due to their high efficiency, low energy consumption and the fact that they are environmentally friendly. The challenge is to find a good balance between a good filter selectivity/retention and a good flow. Filtration membranes generally have dense separation films that act as a sieve, supported by a porous and more permeable support that also gives mechanical strength to the membrane. Graphene based membranes are not only interesting because graphene is inert, but also because it can be dispersed in a solution and deposited in a thin film to form a separation layer. Attention has been particularly drawn to graphene oxide (GO) nanosheets, due to their unique physical and chemical properties: dispersed GO nanosheets can be tightly packed after drying and the spacing between them can be engineered so that only water vapour can pass. In a recent paper, a Chinese team has developed an rGO membrane, using a simple vacuum suction method. The key to their technique is the chemical reduction of the GO, which is done by using a solution of dopamine-hydrochloride. When compared to GO membranes prepared in the same way (but without the reduction), the membranes using this reduction method are 4-5 times more effective. At the same time, the water permeation (the flux of water through the membrane in pressurised conditions) is 12 times superior, resulting in a very efficient desalination and making these graphene-based membranes promising materials for water treatment.

J. Pei *et al. RSC Advances.* **6**, 101948 (2016)

Food packaging films

Biodegradable food packaging promises a more sustainable future. The most likely candidate to be used for this purpose, PLA, is 100% derived from renewable sources, possesses good mechanical and physical properties and can easily be manufactured in large quantities. However, it suffers from poor water and oxygen barrier properties when compared to conventional petroleum-derived packaging materials. The lamellar structure of graphene membranes and films is expected to have an impact in this area of application. A recent paper reported efforts to enhance both the water and oxygen barrier properties of the PLA food packaging using a sandwich structure, where an rGO impermeable film is clamped between two films of PLA. The GO film is fabricated via a pressure-assisted filtration process and is then chemically reduced with hydroiodic acid. Embedding the rGO film between two films of PLA not only allows more design freedom compared to bulk composites, but it also prevents the exposure of rGO to the food (increasing the food safety). However, the resulting packaging films are not transparent, since rGO is black, contrary to pristine graphene. Compared to PLA, rGO enhanced membranes decrease the water vapour permeability by 87.6% and the oxygen permeability by two orders of magnitude. The study also presents a comparison between sandwiches prepared with GO and rGO membranes. Although rGO and GO offer similar oxygen barrier properties, the water permeability of the rGO membrane is clearly lower. Further studies will concentrate on improving the transparency and leveraging the electrical conductivity of rGO to realise intelligent food packaging.

K. Goh, *et al. ACS Appl. Mater. Interfaces* **8**, 9994 (2016)

Life Science

Graphene is projected to have an impact also in life science. It could be used for example to facilitate drug/gene delivery, in biological sensing and imaging and as a biocompatible scaffold for cell culture.

Bioscaffold

Graphene has unique properties that may have a great potential as a bioscaffold for neuronal regeneration after spinal cord injury as they might physically support, electrically stimulate, positionally inform and organize the 3D cell architecture, required for the regeneration of nerve fibres

The conventional process to treat acutely severed spinal cords is based on the use of polyethylene glycol (PEG), a substance that restores the integrity of cutely transected nerve fibres and reseals the membranes of the injured neurons. An article published in 2016 showed how the addition of a small quantity of conducting graphene nanoribbons (GNR) can improve the efficiency of the PEG. The GNR is believed to first act as an electrical conduit, then as an electrically active scaffold on which the neurons will grow, directing in this way the process across the gap. The study of the conductive GNR-PEG shows great promises to rapidly be able to restore the neurophysiologic sensory transmission after spinal cord injuries.

C.-Y. Kim *et al. Surg. Neurol. Int.* **7, Supp. 24**, S632 (2016)

Another approach to treat this kind of injury is the direct use of graphene scaffold to allow the growth of different types of cells. Previous studies showed that 2D graphene films can be used for studying neuronal growth *in vitro*[1], but they do not translate to any *in vivo* applications. Research efforts have focused on the production of 3D rGO scaffolds by reducing GO, using a variety of methods. Recently, a study showed, for the first time, their use in an *in vivo*[2] model of a spinal cord injury. The graphene scaffolds were produced by the reduction of GO and the porous structure was formed by cross-linked rGO sheets. The study compared the cell growth on spinal injuries treated using a hydrogel matrix with and without the presence of the rGO scaffold. It showed that the presence of this 3D rGO scaffold allowed the growth of blood vessels, neurofilaments and cells in the peripheral nervous system on its surface, an important step towards the use of rGO in the treatment of spinal cord injuries. The study also suggests a low level of toxicity of the rGO scaffold when compared with other nanomaterials.

[1]D. Sahni *et al. J. Neurosurg. Pediatr.* **11**, 575 (2013)

[2]A. H. Palejwala *et al. Surg. Neurol. Int.* **7**, 75 (2016)

Cancer detection

Graphene also possess properties that can be used favourably for early cancer detection. Cancer is one of the leading causes of death worldwide and its successful treatment relies on early detection at high sensitivity and specificity. Graphene was recently used to detect the presence of cancer on a single cell level by a team of researchers in the United States. In their study, the researchers took advantage of the link between the doping level in graphene and Raman peak frequency. Raman scattering is a characterisation technique where light is shined on a sample and the emitted light is collected and its energy spectrum is analysed. The difference in energy between the incident and emitted beam gives information about the sample. The graphene Raman spectrum presents characteristic peaks, whose position in energy gives information about the doping in the graphene. When a cell is attaching to a graphene layer, it influences its doping in different ways depending on if the cell is cancerous or not. The direct link between doping in graphene and its Raman peak frequency can then be used to detect the presence of a cancerous cell. By using this technique, the researchers were able to differentiate between a single normal and a cancerous Glioblastoma Multiform cell (a malignant brain tumour) attached on a graphene layer. This technique could potentially be extended to other types of cancer cells.

B. Keisham *et al. ACS Appl. Mater. Interfaces* **8**, 32717 (2016)

Other Two Dimensional Materials

The interest in graphene has in the last few years also spread to other two dimensional (2D) materials. From a few 2D materials only 10 years ago, the scientists have now discovered and engineered hundreds of materials. This family of 2D materials now includes transition metal dichalcogenides (TMDC), topological insulators (TI), Weyl materials, insulators (hexagonal boron nitride, h-BN), and many more. In itself, the group of TMDCs contains around 40 different compounds with properties ranging from metallic and half-metallic, to semiconducting and even superconducting. For TI and Weyl materials, a strong spin-orbit coupling yields special electronic properties, creating a dissipationless metallic surface, insulating bulk states and spin textures that can be of interest for electronic devices and quantum computing.

TMDC are formed by a single sheet of transition-metal atoms, such as molybdenum or tungsten, sandwiched between equally thin layers of chalcogen elements, such as sulphur and selenium. The canonical example of this group is molybdenum disulphide (MoS_2), which in its bulk form, has the appearance and the feel of graphite and is widely used as a solid lubricant. What is particularly interesting about MoS_2 is the fact that its band structure is very sensitive to the thickness of the material. From an indirect bang-gap (1.2 eV) semiconductor in its bulk form it changes into a direct band-gap (1.8 eV) semiconductor when it is exfoliated to become one layer thick. The presence of this band-gap gives MoS_2 an advantage when compared to graphene for uses in switchable transistors and photodetectors, as graphene devices suffer leakages in the “off” state, due to its gapless brand structure. It also possesses mechanical strength and electrical conductivity, which clearly makes it an interesting material for future flexible and optical circuits.

E. Gibney, *Nature* **522**, 274 (2015)

K.S. Novoselov *et al. Science* **353**, 461 (2016)