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Graphene Research and Advances

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Introduction

SIO Grafen's *Research Intelligence Report Series* aims to highlight some of the most interesting research findings on graphene that have emerged during the last few months. In this issue, we are for example reporting on new production methods which include both new source materials and new techniques, as well as discussing electronic skin and contact lenses.

Graphene has been envisioned in many types of sensors, whereof some new results are being discussed. Battery technology is another area with many possible graphene applications, out of which some are highlighted here.

In the very early days of graphene technology it was sometimes imagined that graphene could replace the silicon technology. A more realistic and quicker view is to integrate graphene into the complementary metal-oxide–semiconductor (CMOS) technology of today. A few recent examples where graphene is monolithicially integrated with mature CMOS technology are presented here.

Part of the research on graphene and other 2D materials include the development of individual devices with fantastic properties, but often without consideration to large scale manufacturing. In this issue we will show that there are successful examples of larger electronic structures, such as complete circuits (i.e. a microprocessor) and large scale electronic devices (a 50 cm^2 solar cell). They might not be truly large scale yet, but it shows that the electronics field is well on its way. The microprocessor was made with 115 transistors based on MoS_2, highlighting that in addition to graphene, other 2D materials are developing from the single device stage.

Water-based inks of a range of different 2D materials (such as graphene, MoS_2, WS_2 and BN) have been developed, which further facilitates large scale applications of 2D materials.

It is not necessarily true that the highest quality of graphene is the best suited for all applications. Two examples are shown where defects are intentionally created in the structure in order to improve the performance.

Content:

Graphene Production

New high yield production method

There are several different methods for graphene production, which has been discussed in the previous editions. The most relevant production methods for use of graphene as a filler are in most applications based on exfoliation of graphite in solvents or in water/surfactant solutions. The graphite can be exfoliated by for example sonication or by shear forces from a mixer. These techniques typically result in concentrations of graphene in the order of 1 g/L. A new technique uses micro fluidisation to create a high shear rate ($\sim 10^8$/s) in a scalable process. The authors report a 100 % exfoliation yield, where 4 % of the flakes are thinner than 4 nm and 96 % between 4 and 70 nm. Other techniques often use centrifugation in order to remove the thickest flakes and to increase the concentration of graphene. This technique is reported to produce graphene inks with concentrations up to 100 g/L in carboxymethylcellulose sodium salt without any centrifugation. A sheet resistance of a blade coated film reached 2Ω/□ at a thickness of 25 µm after thermal annealing at 300°C.

P. Karagiannidis *et al. ACS Nano* **11**, 2742 (2017)

Graphene from renewable sources (seaweed and soybeans)

Techniques to produce graphene based on pyrolysis of biomass have started to get more attention in the last few years. A recent paper describes the synthesis of graphene by pyrolysis from a naturally abundant seaweed (*Sargassum tenerrimum*). The graphene was functionalised by Fe, Sn or Zn. The cytotoxicity of the graphene was tested on human lung carcinoma cells and was found to be non-toxic. The graphene was then used to remove fluoride from fluoride-rich natural drinking water. This is important as long-term exposure to fluoridated drinking water can cause deformation of bones and teeth. The concentration of fluoride was reduced by around 80 % and no significant contamination of metal ions was found in the water. The Fe-functionalised graphene was found to be more efficient at removing fluoride than the Sn- and Zn-functionalised graphene.

M. Sharma *et al. ACS Sustainable Chem. Eng.* **5**, 3488 (2017)

Another study also used a renewable carbon source to produce graphene. It was shown that graphene films can be grown from soybean oil. The chemical vapour deposition (CVD) technique did not require any vacuum or purified gases, but was a fast and simple technique. Copper foil is the most commonly used substrate for CVD growth of graphene due to its low carbon solubility, which limits the carbon deposition to one layer of graphene when methane is used as precursor. Nickel has a higher solubility of carbon which leads to the formation of more layers of graphene in a standard CVD process. In this study, it was found that nickel is a suitable substrate for growth of graphene films from soybean oil. The graphene film consisted of one to few layers on nickel substrates, whereas graphene did not form on copper substrates. The functionality of the graphene was demonstrated by an electrochemical sensor.

D.H Seo *et al. Nature Communications* **8**, 14217 (2017)

Graphene nanotube foam

Graphene foams with multi-walled carbon nanotubes (MWCNTs) as reinforcement has been produced. The structures were synthesized using a powder metallurgy technique with Ni particles as templates and sucrose as the carbon source. The Ni particles, sucrose and MWCNTs were mixed, dried and pressed in a die. Graphene was then grown using a chemical vapour deposition (CVD) technique after which the Ni was etched away. This results in a free-standing all-carbon structure where the shape is completely controlled by the shape of the die. The density of the foam was calculated to 0.16 ± 0.01 g cm^{-3} with a porosity of 90-96 %. The foam is compressible and retains its initial shape even after loading of more than 3000 times its own weight. A loading of 8500 times of the foams weight results in a 25 % height change. Tests without any MWCNTs showed that the foam could only support 150x its own weight, which shows the importance of the combination of graphene and nanotubes. TEM images show that the MWCNTs functions as rebar by partly bonding with the graphene and carbon shells formed during the synthesis. The foam also showed a promising performance as electrode in lithium ion capacitors with an energy density of 32 Wh kg^{-1}. The foam could consequently be used in applications requiring high mechanical and electrochemical properties.

J. Sha *et al. ACS Appl. Mater. Interfaces* **9**, 7376 (2017)

Intentional defects in epitaxial graphene

The quality and amount of defects in graphene are important factors in many applications. Recently researchers at Linköping University investigated the effect of the defect level on the ability to store electrical energy. They grew epitaxial graphene on SiC, which is a slow, high temperature process which results in high quality graphene. The defect level of the graphene was controlled using an anodization process, which simultaneously cleaned the surface. It was found that the defects were mainly created in the graphene monolayer and not in the bilayer areas. Similar effects have previously been found for functionalisation and other defect-inducing processes. The defect density was found to be 4–8 x 10^{13}cm^{-2}, which corresponds to approximately 2 % of the carbon atoms in the monolayer. The introduction of reactive defective sites together with the surface cleaning resulted in a significant increase of the reactivity of the graphene and a 21 fold increase in the charge storage capacity.

M. Y. Vagin *et al. Electrochimica Acta* **238**, 91 (2017)

Researchers from Linköping University collaborated with researchers from India in another recent study, which investigated the role of defects on the sensing ability of epitaxial graphene. The defects were created by irradiating the graphene with heavy ions. The irradiated graphene layers folded and formed hillocks and wrinkles. The amount and type of defects was controlled by varying the fluence of the bombarding ions. It was found that the sensitivity first increased, as more reactive sites were formed, and was then reduced at higher ion fluence as the monolayer was converted into multi-layered graphene.

P. D. Kaushik *et al. Applied Surface Science* **403**, 707 (2017)

Electronics

Microprocessor based on 2D MoS_2

Many individual electronic components based on graphene and other 2D materials have been demonstrated with great performance, but there have been relatively few studies on scaling up the technology. However, a microprocessor consisting of 115 transistors based on 2D MoS_2 was recently demonstrated. This proof of concept device had a field-effect mobility of 3 cm^2 V^{-1} s^{-1}, a threshold voltage of 0.65 V, an on/off ratio of 10^8 and a size of 0.6 mm^2. It could run simple programs, perform logical operations and communicate with its surroundings. The operation frequency was estimated to 2-20 kHz, which can be increased by for example doping, improved carrier mobility or reduced transistor channel lengths. The yield was low mainly due to the transfer process of the MoS_2 film from the growth to the target substrate, but could potentially be solved by directly growing the 2D film on the target substrate. This was the only potential roadblock the authors could see for taking this 1-bit device to larger designs.

S. Wachter *et al. Nature Communications* **8**, 14948 (2017)

The demand for high data rate wireless communication systems is quickly growing. Graphene's excellent electron transport properties make it a promising material for millimetre-wave electronics which could meet this demand. Researchers at Chalmers recently demonstrated monolithic integrated circuits (IC) based on graphene operating at unprecedented frequencies (80-100 GHz). High quality epitaxial graphene was used in a fabrication process of more than 30 steps which is scalable up to full wafers. The circuits were highly linear and could receive information at a rate of 4 Gbps and generate a modulated signal at up to 8 Gbps in the 90 GHz band. The researchers highlight that the operating frequency is about 20 times higher and the achieved data rate is more than 200 times better than the previously reported graphene based IC, which takes the graphene technology to a level where it starts to compete with existing mature technology.

O. Habibpour *et al. Scientific Reports* **7**, 41828 (2017)

Monolayer graphene does not have a bandgap. This prevents field-effect transistors based on graphene (GFETs) from being turned off, which is a fundamental issue when developing logic circuits. For most analog applications, however, a bandgap is not necessary. The lack of a bandgap then results in a poor saturation of the drain current, which prevents high-gain operation. Researchers from Italy, Spain, Sweden and USA recently managed to improve the saturation by utilizing a thin (4 nm) dielectric material (AlOx) with a good dielectric constant (6.4) to electrically insulate the top gate of the GFET. This improved the control of the charge carriers in the graphene channel which resulted in the highest gains (open-circuit voltage gain $A_v > 30$ dB and forward gain S21 = 12.5 dB) achieved in GFETs so far.

E. Guerriero *et al. Scientific Reports* **7**, 2419 (2017)

Electronic skin

More and better robots and prosthetics are constantly being developed. One interesting part is the development of tactile or electronic skin. This is an artificial skin which aims to provide a similar sense of touch as human skin. Some of the challenges in producing this skin include that it needs to be flexible, conductive and possible to manufacture in large scale with a reliable and repeatable performance. An extra dimension would be if the skin can be made transparent as it enables incorporation of for example photovoltaic energy harvesting devices, which would remove the need of batteries. This type of tactile skin, using graphene, was recently demonstrated. The graphene was grown by CVD and transferred to poly vinyl chloride (PVC) substrates using a lamination process. Interdigitated electrodes were shaped using a blade-cutting system without the need of optical lithography or laser cutting. The skin was flexible and sensitive to pressures in the range 0.11-80 kPa with a sensitivity of 4.3 Pa^{-1} as demonstrated on a bionic hand. The bionic hand could controllably grab soft objects with feedback from sensors in the artificial skin. Owing to the transparency of the skin and the low power consumption (20 nW cm^{-2}), it was demonstrated that the battery could be replaced with a solar cell in the back plane of the skin. This type of artificial skin could consequently lead to new energy-autonomous applications for robotics, prosthetics and wearable systems.

C. G. Núñez *et al. Adv. Funct. Mater.* **27**, 1606287 (2017)

Another recent study demonstrated a tactile pressure sensor based on integrated arrays of air-dielectric graphene transistors. These were sensitive at significantly higher pressures, 250Pa to 3 MPa.

S.-H. Shin *et al. Nature Communications* **8**, 14950 (2017)

Printed Electronics

Printed 2D transistors

The importance of printed electronics was highlighted in the previous edition of this Research Intelligence Report (no 2, 2016). Papers demonstrating micro-supercapacitors as well as showing good electrical conductivity of circuits on flexible substrates were discussed. Printed transistors consisting entirely of 2-dimensional nanomaterials have now been fabricated for the first time. The research demonstrate all-printed, vertically stacked transistors with source, drain, and gate electrodes made of graphene, a transition metal dichalcogenide channel, and a boron nitride (BN) separator, all formed from nanosheet networks. These nanosheet network channels display on-off ratios of up to 600, transconductances exceeding 5mS, and mobility of more than 0.1 cm^2/Vs. This discovery opens up a path to cheaply print a multitude of electronic devices with plenty of applications (for example solar cells, LEDs, labels, posters, packaging etcetera). The team behind the study discusses that the technology can for example be used to replace the barcodes on packaging and in the future send you text messages when the food is about to go bad.

A. Kelly *et al., Science* **356**, 69 (2017)

Water-based inks

Another recent paper demonstrates biocompatible water-based inks for a range of different 2D materials (graphene, MoS_2, WS_2 and BN). Many other inkjet printable inks are based on toxic and expensive solvents. The inks were printed onto flexible and stiff substrates, such as paper, glass and plastic. Printing multilayer stacks is typically a challenge, as the stack tends to re-disperse at the interface. These inks were used to fabricate a photodetector by printing a graphene/WS_2/graphene heterostructure and the first ink-jet printable read-only memory. This memory could for example be used in radio-frequency identification (RFID) tags, but many other designs can be imagined. The cytotoxicity was investigated and no significant responses were observed, showing the biocompatibility of the inks.

D. McManus *et al. Nature Nanotechnology* **12**, 343 (2017)

Water-based graphene inks were also reported recently by researchers at Uppsala University. The graphene was synthesised from graphite using the shear mixing technique with the aid of bromine intercalation and a water soluble cellulose stabiliser. A conductivity of 1400 S/m was achieved after annealing at 100 °C, most likely owing to the doping effect of remaining bromine in the film. This could be increased further by annealing at higher temperatures and/or by iodine doping, which resulted in a conductivity of 10^5 S/m.

S. Majee *et al. Carbon* **114**, 77 (2017)

Sensors

Dark state gas sensor

The fact that 2D materials have a maximum surface-to-volume ratio makes them very interesting in many sensor applications as it makes them very sensitive to their environment. Transition metal dichalcogenides also have a strong light-matter interaction which can be exploited for optical read-out. Typical sensing methods rely on small shifts in frequency or intensity, which can be difficult to detect. Researchers at Chalmers and TU Berlin have shown proof-of-principle of a sensor where molecules are identified by activating dark electronic states in the sensor material. The researchers believe the method is promising for fast, efficient and accurate sensors. The next step is to work with experimental physicists and chemists to demonstrate the proof-of-principle for this new class of chemical sensors.

M. Feierabend *et al. Nature Communications* **8**, 14776 (2017)

Nanopore sensor

In another recent paper, researchers at Uppsala University and in Brazil have reported on a sensor, based on a nanopore formed in a hybrid of graphene and h-BN. Molecules are detected as they pass through the nanopore. The geometry thus results in a sensing element as small as a single electrically conducting carbon chain forming one edge of the nanopore. When molecules move through the nanopore, the electric potential of the chain is modulated and the conductivity of the material is therefore affected. Molecules can consequently be identified through their characteristic dipole moment by measuring the electric current in the material. Computer simulations showed that the sensor can distinguish the DNA nucleotides (the building blocks of DNA). The technique is however not necessarily limited to applications for DNA sequencing.

F. de Souza *et al.Nanoscale* **9**, 2207 (2017)

Colour changing coating

It is well known that the colour of most materials depends on the frequency of light which is absorbed in its chemical pigments. However, materials can also get their colour from periodically arranged microscopic surface structures, where interference between reflected light waves amplifies specific wavelengths. The colour can then be changed by changing the periodicity of the structures. This is one of the methods animals use to change their colour or to get very vibrant colours. The same idea has now been used by tuning overlapping graphene nanoplatelets (GNPs). A composite of GNPs-glass fibre/epoxy was produced where the colour changed from red to orange and to green depending on the tensile strain. The authors envision that this kind of sensor could be used as a kind of traffic light system for the danger rating and warn of micro cracks appearing in the coated material.

Y. Deng *et al. Mater. Horiz.* **4**, 389 (2017)

Broad band optical sensor

Today most electronics and integrated circuits are based on CMOS technology. In the last 40 years, this technology has been developed enormously, which has resulted in for example an unmatched data processing power. However, one drawback with this technology is that it is difficult to combine semiconductors other than silicon with CMOS. Photodetectors are therefore largely limited to the properties of the silicon, which has very limited absorption in the infrared spectrum. There are for example InGaAs detectors which work very well in the infrared, but they also have problems such as that they do not work in the visible range, and they are very expensive due to difficult processing. Graphene was recently monolithically integrated with an off-the-shelf read-out CMOS integrated circuit and a broadband image sensor was demonstrated. PbS colloidal quantum dots were used to absorb light in the whole range from 300 to 2000 nm and photo generated charge carriers were transferred to the graphene. This signal is sensed as a change in the conductivity of the graphene, where the high charge mobility of graphene enables a high sensitivity of the device. The detector had over 100k pixels, a power consumption of 211 mW and a frame rate of 50 frames per second. The yield was high as 99.8 % of the pixels were functional. The detectivity was measured to be above 10^{12} cm $\sqrt{Hz}$ W^{-1}. This clearly shows that graphene can be integrated in CMOS technology using a simple process.

S. Goossens *et al. Nature Photonics* **11**, 366 (2017)

Membranes and Coatings

Water desalination

The availability of freshwater is a crucial topic globally. GO membranes have been used to separate nanoparticles, organic molecules and large salts, respectively. However, these membranes could not be used for sieving common salts as the membranes swell in water, which allows smaller salts to pass through. A strategy to avoid this swelling and precisely control the pore size in the membrane has now been developed. The sieve size could accurately be controlled from 0.68 nm to 0.98 nm. The permeation rates of the salts decrease exponentially within this regime, whereas the water transport is only weakly affected. The group believe that it is possible to scale up the production of these membranes and mass produce them with 97 % rejection for NaCl. The membranes can thus be used to desalinate seawater into drinkable freshwater.

J. Abraham *et al. Nature Nanotechnology* https://doi.org/10.1038/nnano.2017.21

It was found last year that graphene can separate protons from deuterons (one proton and one neutron). This isotope effect can be used to separate heavy water (where the hydrogen contains a neutron as well as a proton) from normal water. Heavy water is used in huge amounts in nuclear reactors as a coolant and neutron absorber. The methods currently used for producing heavy water require huge amounts of energy, but it was found that graphene has the potential to revolutionise the production. However, the effect was originally only tested using monocrystalline membranes of micron-sized graphene obtained by mechanical exfoliation. The authors have now developed the discovery and demonstrated recently a scalable prototype of a process to manufacture graphene membranes using CVD which can separate both deuterium and tritium (hydrogen with two neutrons) from normal hydrogen significantly more efficiently than the currently used technology. This technology can potentially be used at a large scale to separate heavy water from normal water significantly more energy efficiently than the methods currently used.

M. Lozada-Hidalgo *et al. Science* **351**, 68 (2016)

M. Lozada-Hidalgo *et al. Nature Communications* **8**, 15215 (2017)

Graphene for contact lenses

It has been found that graphene can absorb electromagnetic (EM) energy and dissipate the energy as heat. Scientists used this in combination with graphene's impermeability to water, to design a smart contact lens which protects the eye from electromagnetic radiation and simultaneously protects the eye from dehydration. The graphene was grown by CVD and transferred onto a contact lens. The EM wave-shielding properties of the coated lens were evaluated by placing it on egg whites, which were exposed to strong EM waves inside a microwave oven. Infrared cameras then detected a significantly larger temperature increase in graphene coated samples as compared to uncoated samples. The researchers now plan to integrate an active circuit with graphene-based sensors and electrodes for real-time wireless monitoring of glucose concentration in a tear, which could be important for people with diabetes.

S. Lee *et al. ACS Nano* DOI: 10.1021/acsnano.7b00370

Many attempts have already been made to monitor diabetes with contact lenses using other materials. The biggest drawback of these has been the poor wearability. The electrodes have not been adequately transparent and the lenses have been firm since the electronics have not been bendable. South Korean scientists have been collaborating to develop a sensor based on graphene and silver nanowires on a soft contact lens. The combination of graphene and silver nanowires were used as it lowers the sheet resistance. The sensor monitors glucose within tears and intraocular pressure simultaneously and independently, using the resistance and capacitance of the electronic device on the lens. The system uses a wireless antenna to read the sensor information without requiring any separate battery and it also allows real-time monitoring. The contact lens was successfully tested on both a rabbit and a bovine eyeball.

J. Kim *et al. Nature Communications* **8**, 14997 (2017)

Energy

Stretchable Na-ion battery

There is currently a large interest globally in wearable electronics, which leads to that wearable power sources need to be developed. The focus has been on storage devices with flexible characteristics, but the stretchable properties are also important for many applications. There are reports in the literature on stretchable Li-ion batteries, but very few are on stretchable Na-ion batteries. An all-stretchable-component Na-ion full battery was recently demonstrated by researchers in China and in the US. The battery is based on a graphene-modified poly(dimethylsiloxane), PDMS, sponge current collector, a sodium-ion conducting gel polymer separator, and elastic PDMS substrates. A PDMS sponge was first produced using a sugar cube as scaffolding. The sponge was then coated with graphene oxide (GO), after which the GO was reduced to reduced graphene oxide (rGO) in order to increase the conductivity. The battery exhibited excellent stretchability up to 60 % and was stable over hundreds of stretch-release cycles. A reversible capacity of 103 mA h g^{-1} was achieved at 0.1 C.

H. Li *et al. Adv. Mater.* **29**, 1700898 (2017)

Graphene perovskite solar cell

Many different types of solar cells are being studied and produced. One interesting area is the development of perovskite solar cells (PSCs). The power conversion efficiency of these has improved from 3.8 % to 22.1 % in just 7 years. These efficiencies are however only found on laboratory devices produced with methods which are difficult to scale up. Recently, graphene in large-area perovskite-based solar modules with an active area of 50 cm^2 were demonstrated, with a record high power conversion efficiency of 12.6 %. The graphene was used to limit charge losses at the interface between the perovskite and the underlying mesoporous TiO_2 layer. The addition of graphene also increased the lifetime of the solar cells with a factor three. The power conversion efficiency was more than 90 % of the initial value after 1630 hours.

A. Agresti *et al. ACS Energy Lett.* **2**, 279 (2017)

Life Science

Implantable energy storage

We have previously in this report seen that graphene can aid batteries in becoming stretchable and photovoltaics to be incorporated into transparent artificial skin. However, solar cells do not help when it comes to powering devices inside the body, such as for example pacemakers, and conventional batteries contain toxic materials and electrolytes which can be dangerous if leakage occurs. Researchers have now designed a new biological supercapacitor which is intended for implantable medical devices. The supercapacitor is based on rGO interlayered with chemically modified mammalian proteins, whereas biological fluids from the body itself can be used as electrolytes. The devices are 1 µm thick, fully flexible, and have high energy density, comparable to that of lithium thin film batteries. A capacitance of around 600 F cm^{-3} and an energy density of 1.8 mWh cm^{-3} was achieved without any signs of cell toxicity at concentrations 160 times higher than those used in the device. The device can provide long-term energy to devices in combination with an energy harvester, which converts heat and motion from the human body into electricity, without the need of any battery.

I. M. Mosa *et al. Adv. Energy Mater.* DOI: 10.1002/aenm.201700358 (2017)

Schwann cells promote regeneration of nerve cells, but are hard to get in useful numbers. There are chemical techniques to turn (or differentiate) readily available and non-controversial mesenchymal stem cells (MSCs) into Schwann cells. A new technique for this process was recently developed based on electrical stimulation instead of a chemical process. It has previously been found that graphene is very promising as neurointerfacial substrates as the material enables favorable adhesion, growth, proliferation, spreading, and migration of immobilized cells. Graphene circuits were inkjet printed and MSCs were seeded and grown on top. The cells were then exposed to small doses of electricity (100 mV for 10 minutes per day over 15 days) which turned the cells into Schwann-like cells. The researchers reported that this was the first time MSCs were differentiated into Schwann-like cells solely via electrical stimuli without additional chemical factors. The process was very effective and differentiated 85 % of the cells compared to 75 % by the standard chemical approach. The flexibility of graphene has the additional potential benefit that the electrodes can be made flexible and can conform to the injury site in future applications.

S. R. Das et al. Adv. Healthcare Mater. 6, 1601087 (2017)

Room temperature carbon magnets

Magnets that function at room temperature are typically metals, and many of these have been known for centuries. The development of room temperature carbon based magnets exclusively containing sp orbitals is a challenge across several scientific disciplines. This type of magnet has now been demonstrated using functionalized graphene. The magnets were made by first producing fluorographene from fluorinated graphite with a C:F ratio of 1:1 in a similar process as how graphene oxide can be synthesized from graphite oxide, using ultra sonication. The important following step was to substitute some of the fluorine atoms with hydroxyl groups, which was done using a combination of stirring, ultrasonication and centrifugation. With a suitable chemical composition (the F/OH ratio) and sp^3 coverage, these materials show a room temperature antiferromagnetic ordering for the first time for any sp-based material. The magnetic properties could be tuned by controlling the sp3 functiona-lisation. These magnets could for example be useful in biomedical technology or spintronics.

J. Tuček *et al. Nature Communications* **8**, 14525 (2017)