SIO GRAFEN

Graphene Research and Advances

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Introduction

The family of two-dimensional (2D) materials contains a wide range of materials exhibiting numerous properties, allowing them to cover a broad spectrum of possible applications. Theoretically, there are over 2000 2D materials, most of which have not be synthetized yet and of the ones that have been produced, several were used before their 2D nature was revealed.

Graphene, a 2D layer of carbon arranged in a hexagonal fashion, is the most well-known compound of the family. It is of particular interest because it possesses high heat and electrical conductivities, is transparent, flexible and incredibly strong. It was first isolated in 2004 by Nobel Prize winners Andre Geim and Konstantin Novoselov, from Manchester University. Since then, several methods of productions of graphene have been developed, each opening the way to utilisation in different markets and tens of thousands of people have joined the quest to develop products where graphene plays a role.

The true strength of graphene is revealed by the numerous systems it can be integrated in. If dispersed in a solvent, it can be used as long-lasting protection against corrosion. When combined with other compounds in a composite material, it can be used for example in the transport industry, sporting goods or as an electromagnetic shield. It could play an important role to help mitigate the effects of human activities. For example, graphene-based membranes can be used to filter water or harmful isotopes of hydrogen. Graphene can be functionalized, which makes it sensitive to a specific molecules or atoms, is flexible and biocompatible, making it an attractive material for sensors and wearable electronics. Its large surface to volume ratio is also making it an interesting material for energy storage applications, in particular in supercapacitors, where the area of the electrodes correlates directly to the storage capacity.

Interest in graphene has also spread in the last few years to other 2D materials, for example hexagonal boron nitride. There have already been several demonstrations of heterostructures where graphene and other 2D materials are used together to give extraordinary properties.

Research on the topic is certainly fuelling the imagination of academics and industrials, and the possibilities seem endless. In the coming years, this will result in more and more products based on graphene and other 2D materials entering the market.

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Content

Graphene Production

Graphene, a two-dimensional material made of carbon atoms arranged in a hexagonal crystal structure, was first isolated using household scotch tape to cleave a piece of graphite. Graphite consists of randomly stacked layers of graphene, connected through weak van der Waals bonds, enabling easy cleavage. Even though this technique yields high quality graphene flakes, it is not suitable for industrial applications. Consequently, several techniques to produce graphene have been developed, all with their advantages and disadvantages.

Liquid phase exfoliation is a technique where graphite is exfoliated in a liquid solvent, which, with the help of ultrasonication, breaks the van der Waals bonds between the graphene sheets. This is a scalable method with high yield, but that produces a mixture of single and multi-layer graphene of various sizes, so the product may need to be filtered. The flakes can be used for example in composites, conductive inks and sensor applications.

Graphene oxide is obtained by treating graphite with strong oxidizing agents, which facilitates the exfoliation of the flakes. The graphene oxide can then be reduced to recover graphene-like properties. This technique is scalable but the properties of pristine graphene are not completely recovered. It is also used in conductive inks, paints, composites and even for energy applications, such as battery electrodes and supercapacitors.

Epitaxial growth of graphene on silicon carbide (SiC) is done 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 very high quality and can be used in electronic applications. However, it is expensive and the strong bonds to the substrate limits the possibility of transfer, making it incompatible for example with silicon technologies.

Graphene can also be deposited on a metallic substrate (generally copper) using **chemical vapour deposition (CVD)**. In a hot furnace with a controlled partial pressure of a carbon-based gas mixture, the metallic substrate catalyses the reaction of carbon gases on its surface forming a graphene layer. After the growth, the graphene can be transferred from the metallic substrate to any suitable substrate. CVD graphene is of good quality and can be produced in relatively large scale, but it is polycrystalline. It consists of small single crystal grains with a typical grain size of a few tens of micrometres and thus contains a high density of grain boundaries. CVD graphene can be used in touch screens, smart windows and flexible LCDs.

High Quality CVD Graphene

The current mechanical, electrical and thermal properties of CVD graphene are limited by the size of these grains prompting researchers to develop techniques to obtain large area single crystal of graphene. Recently, a Chinese group developed a technique to grow large single crystals of graphene in a short time (3cm in 2.5h). The researchers explored the metallic catalysts for graphene and noted that while copper is the default choice for monolayer graphene synthesis, its catalytic power decreases during the growth. Nickel, another common substrate for the CVD growth of graphene, has a superior catalytic power, but yields randomly stacked non-uniform graphene multilayers. The advantages of both catalysts can be exploited by using a copper/nickel alloy: $Cu_{85}Ni_{15}$. By using this substrate and local precursor feeding, which insures that the nucleation occurs only at a designed location, they were able to grow large single crystals at a very high growth rate (roughly an order of magnitude higher than conventional techniques) with mobilities as high as 20 000cm^2/(Vs) at room temperature.

T. Wu *et al. Nat. Materials* **15**, 43 (2016)

Making the single crystal of graphene as large as possible is not the only way to obtain high quality CVD graphene. Recently, a group in Korea developed a technique to heal various types of defects commonly created during CVD synthesis and transfer, such as grain boundaries, pinholes, wrinkles and cracks. Their method works by selective electrochemical deposition of silver on graphene defects. Graphene defects are zones where the mechanical and electrical properties are the weakest. Depositing silver on these zones physically bridges the gaps between good graphene areas and dramatically improves the mechanical and electrical properties, effectively healing the graphene.

T. Yoon *et al*. *ACS Nano* **10**, 1539 (2016)

Polymer Free CVD Graphene Transfer

The transfer process is the critical step to use CVD graphene onto any target substrate, which poses drawbacks. In the most commonly used technique, the deposited graphene is covered with a polymer, followed by an etching of the metal catalyst and a transfer to a planar surface. The final chemical removal of the polymer is usually incomplete and leaves contaminations. Furthermore, the polymer induces stiffness, making a transfer of the graphene sheet on a coarse or 3D structure challenging or even impossible. To solve these issues, researchers in the United Kingdom recently develop a biphasic method for CVD graphene transfer. After the growth, the metal/graphene sheet is put on the water-based metal etchant, the graphene-side facing up. Subsequently, a layer of hexane is introduced on top of the graphene and etchant in a way that enables the two layers to stay unmixed. After the metal is completely etched, the graphene is trapped at the interface between the etchant and the hexane. The key is that the surface tension for the hexane-water interface is lower than that of the air-water interface, which prevents the water layer from pulling the graphene sheet apart. Using a silicon substrate, the graphene can be extracted from the liquids interface and deposited in another bilayer bath of water/hexane for cleaning before being transferred on the substrate of interest. In their report, the researchers show that this method can be used to transfer continuous films of graphene onto 3D surfaces, such as grids and AFM tips, paving the way to transfer to a wide variety of substrates.

Zhang, G. *et al. ACS Appl. Mater. Interfaces* (2016)

Surface protection

Graphene is strong, chemically inert, impermeable to gas and stable in ambient conditions up to 400°C. It holds great promises to provide long-lasting protection against corrosion and friction.

Anticorrosion

Graphene can be incorporated with paints and protect metals form corrosion in a brine environment and last a few times longer than the normal coating. Transferred CVD graphene could also be used to prevent corrosion. Unfortunately, transferring CVD graphene onto any shape is challenging. Its anticorrosion properties are also significantly lower than the ones of as-grown graphene, mainly due to poor adhesion to the surface to protect. Until recently, technical difficulties, high process temperature (around 1050°C) and low catalytic activity, prevented the direct growth of graphene on steel, the commonly used metal. At the end of last year, researchers have, using a special multiheating-zone furnace, developed a technique to grow CVD graphene at low temperatures (400-450°C). Graphene grown using this technique not only show that it has anticorrosion ability, decreasing the corrosion of steel by a factor 9 compared to bare steel, but that it can be a long-lasting anticorrosion coating. The growth technique can also be generalized to a variety of substrates, from bulk materials (metal or alloy) to nanofibers, opening potential applications for all kinds of materials used in harsh environment, such as boats.

M. Zhu *et al. ACS Appl. Mater. Interfaces* **8**, 502 (2016)

Friction and wear reduction

Ultrafine particles can be added to conventional oil lubricant to increase their performance in the so called boundary regime, such as start-up and low velocity regime, where the thickness of the oil is too thin to prevent direct metal-metal contact. Unfortunately, the effective dispersion of these particles is a challenge, and is usually done by surface functionalizing, which can degrade with time, yielding unstable tribological properties. To solve this issue, a group of researcher from South Korea used graphene crumpled balls. Crumpled balls have a rough surface texture, which reduces the area of contact when placed on top of a flat surface. Also, not only the multiple folding also make the balls strain-hardened, thus stiffer, under mechanical stress, but the interparticle interaction is also very weak, making their dispersion in a solvent easy and stable over time. In their work, researchers compared the friction properties of oil lubricant with different carbon-based additives and showed that crumpled graphene balls give the lowest friction coefficient, even with only 0.01wt% concentration. The oil modified with crumbled graphene balls even outperforms commercial lubricants, making these particles an attractive additive for tribological applications.

X. Dou *et al. Proc. Natl. Acad. Sci.* **113**, 1528 (2016)

Making the World Safer with Composites Materials

Combining several materials together 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 low filling factor, can significantly affect the properties of the compounds, making it an attractive additive for all sorts of applications.

Flame Retardancy

Commonly used flame retardant materials often show poor tolerance to chemicals and toxicity problems. Graphene, being very stable and able to form lightweight conducting foams, is natural choice to develop a flame retardant material. A group of researchers working in China and in the United States have developed a material by mixing graphene oxide (GO) solution with hexachlorocyclotriphosphazene (HCTP: $P_3N_3Cl_6$), forming a GO-HCTP foam that once thermally treated, gives a highly fire-retardant ultralight GPO foam. The obtained composite is not only lightweight, compressible and easy to produce in large quantity, but its flame-retardant properties are outperforming those of traditionally used materials. It also present good microwave-absorbing properties, a quality currently in high demand, both for commercial and defence purpose. Conventionally used material are bulky and heavy, which limits their use in for example aircrafts; the use of a lightweight GPO foam provides a promising candidate for the development of new types of microwave absorbing materials.

C. Hu *et al. ACS Nano* **10**, 1325 (2016)

Wing Deicing

Graphene can also be added to insulating polymers to form conducting composites. One possible application has been recently demonstrated by researchers in the United States, which created a conducting composite of graphene nanoribbons (GNR) stacks in an epoxy matrix used for wing deicing via Joule heating. Ice accumulation on surfaces of helicopter rotor blades or aircraft wings is a common problem that degrades their performances. Several methods have been explored to solve this issue, most of which can only be used on the ground. Joule heating, however, a technique where heat is generated by applying a voltage to a conducting material, is a versatile deicing method that can be use even while flying. By adding 5wt% of GNR to an epoxy, the researchers created a conducting composite that can perform voltage-induced heating: a 1cm-thick piece of ice was removed from a part of a rotor blade in a -20C environment to demonstrate the efficiency of the method. GNR are an interesting additive because of their good thermal and electrical conductivity, but notably because of their large aspect ratio, which allows them to form percolative networks even at small filling ratio. Such composites could have widespread applications in the aircraft industries.

A.-R. O. Raji *et al. ACS Appl. Mater. Interfaces* **8**, 3551 (2016).

Green Membranes

The impacts of human activity on the environment are undeniable: the world population is growing, the agricultural and industrial activities are intensifying and pollution increasingly contaminates air, soils and water supplies. These issues are becoming an important focus of political and scientific efforts, increasing the demand for new technologies to mitigate the effects of human activities. Thanks to its extraordinary properties, graphene is anticipated play an important role toward this goal.

Membranes for water treatment

In recent years, membranes have attracted 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 a dense separation films that acts 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 form to form a separation film. 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 vapor can pass. Unfortunately, the direct preparation of GO membrane on a porous material is still a challenge because of the big pore size of the supporting layer. In a recent paper, a Chinese group has developed a GO membrane using a simple vacuum suction method, relying also on their previous work that enabled them to obtain large platelets of GO. Their membrane shows an increased water flow and is efficiently sieving pollutant with relatively large sizes. They also show it can be used, but less effectively to remove different types of salts (Na_2SO_4 and NaCl).

J. Wang *et al. ACS Appl. Mater. Interfaces* **8**, 6211 (2016)

Another group of scientist from Australia developed a controlled way to make large scale (up to 13x14cm^2) membranes by shear-induced alignment of liquid crystal. Their technique was made possible by developing an innovative method to quickly produce nematic GO dispersions. In this nematic phase, present when the GO solution is highly concentrated, the GO flakes tend to point in the same general direction on a local scale. By applying shear pressure on the viscous GO nematic liquid, the researchers obtained a highly aligned GO nanosheets forming a films. This alignment is giving better control on the size of the pores of the membrane, consequently achieving a better control of the sieving properties. The best membranes, which are roughly 150 nm thick, enabled the best compromise between flux and retention: they possess a permeability of $71 lm^{-2}hr^{-1}bar^{-1}$, several times better than other type of membranes. Their results show a retention of 30-40% of monovalent and divalent salts, a clear improvement when compared to other membranes, establishing this kind of membrane as an ideal candidate for low-pressure and high performance filtration applications.

A. Akbari *et al. Nat.Commun.* **7**, 10891 (2016)

Sieving Hydrogen Isotopes

In a paper recently published in Science, a team of researchers in Manchester lead by one of the two graphene Nobel Prize winner, showed that graphene can be used to separate different isotopes of hydrogen, in particular deuterium (a hydrogen atom with one neutron and one proton in its nucleus) from common hydrogen (containing only one proton it its nucleus). This is of great interest, as deuterium is in high demand to create heavy water, a special coolant necessary in nuclear power plants, which is currently produced using high energy and expensive techniques. The sieving property of single layer graphene can be explained by noting that hydrogen has a thermal energy barrier to overcome while passing through it, which is slightly different for each of its isotope. Using this property to their advantage, the researchers were also able to show the same sieving effect on centimetre sized CVD graphene sheet presenting cracks and grain boundaries. The technique could also be used to separate tritium (a hydrogen atom with 2 neutrons and one proton in its nucleus), a waste product in several nuclear reactions, which is damaging for the environment.

M. Lozada-Hidalgo *et al. Science* **351**, 6268 (2016)

From Life Science to Wearable Sensors

The “Internet of Things” is here, and it is growing fast: already in 2008, every person on earth had on average access internet through more than one device. Monitoring people and their environment is generally desired for industrial, environmental and personal applications. There is therefore a necessity to develop better, more accurate sensors, which are not only cheap but also easy to interact with. Graphene clearly has a role to play in this new branch of application, since it offers a large surface to volume ratio, making it an ideal material for sensors. Moreover, it can be functionalized and is biocompatible.

Graphene Nanodots

In 2014, it was estimated that roughly 164 million metric tons of rice husks biomass (a byproduct of rice milling) was generated. There is currently no clear utilization strategy of this waste and most of it ends up in open-field burning or land filling, which results in air pollution, wasted energy and occupancy of landfill space. Most common approaches of valorisation of the rice husks take advantages of its high concentration of silica (between 15-28wt%) to prepare silicon-based materials, such as silica, silicon or zeolite. However, the organic components of the rice husks (72-85wt%) is typically completely wasted. Last year, researchers in China developed a technique enabling a comprehensive utilization of rice rusk: it produces mesoporous silica nanoparticles as a byproduct during the fabrication of graphene nanodots (tiny graphene platelets with a typical radius of a few nanometres). The graphene nanodots obtained with their technique are water-dispersible, possess intense photoluminescence with a tunable response wavelength and excellent biocompability which could enable them to be used as fluorescent bioprobes.

Z. Wang *et al. ACS Appl. Mater. Interfaces* **8**, 1434 (2015)

DNA Sequencing

Graphene can also be used as a new method of DNA sensing. Current DNA sequencing technology relies on a 40 years old method, which involves separating copying, labelling and reassembling pieces of DNA to read the genetic information. Various alternative methods have been put forward to improve the speed and decrease the cost, one of which is to pass the DNA strand in a nanopore and detect the local chemical composition. Graphene, being a one atom thick layer material, is the perfect candidate to enable the kind of spatial resolution required. However, practical implementation has proved to be challenging, due to high count errors and noise levels. A team of researchers at NIST, in the Unites States, recently proposed a new theoretical sensing method relying on the functionalization of the inside of a nanopore, as well as graphene's capacity for converting anisotropic lattice strain to changes in electrical current. What makes this technique special is the functionalization of the pore with selected nucleobase. When the DNA strand passes through the pore, a temporary bond is formed when the functionalized group and the DNA pair are complementary: this creates a deformation of the graphene sheet, which should create an easily measurable current. This accurate sensing method should enable high-speed DNA sequencing (66 million nucleobases per second) at ambient condition and in aqueous environments. If implemented experimentally, this technique would hold great promises for realistic DNA sensing using graphene.

E. Paulechka *et al. Nanoscale* **8**, 1861 (2015)

In Vivo Electrodes

In addition to being used as an imaging and sequencing tool, the fact that graphene is biocompatible will help it play an important role in the development of prosthetic applications. Developments in modern medicine have enabled the direct interfacing with the brain via the implantation of electrodes, that can be used for examples to control robotic limbs and motor disorders (epilepsy or Parkinson's), or even to recover sensory function. The technology currently in use suffers from some drawbacks since the conventional electrodes are made from inorganic, rigid material (tungsten or silicon). When implanted, their long-term performance is also affected by the formation of a scar tissue, which results in the loss of the signal over time. Previous work showed that it is possible to use treated graphene to interface with neurons. However, the signal generated in such a structure was low, possibly because of the high resistance of the contact between the neurons and the graphene. Carbon nanotubes were also used, but studies showed that they interfere with the synaptic network. Recently, a European multidisciplinary team of researchers showed that bare graphene-based conducting substrate supports neuronal functional development without any perturbation of the neuronal network synaptic performance. This shows that graphene could be use in a variety of biological applications where flexible, biocompatible electrodes are needed for example in neural interfaces.

A. Fabro *et al. ACS Nano* **10**, 615 (2016)

Pressure Sensors

Health-monitoring can also be performed using pressure sensors, which can be designed to be very sensitive to contact pressure, for clinical applications. A group of international researchers recently showed that a polymer infused with carbon nanotubes and graphene can be used in such a sensor up to 10mbar. The main advantages of this sensor are twofold: on the one hand, the resistance changes as a function of the pressure is very pronounced, 1 000 000Ω for 10mbar, enabling the detection of very small pressure signals, such as those from biological tissue. On the other hand, the active region of the sensor is very thin (few micrometers), making it insensitive to bending and wrinkling. The latter is even more important when sensing soft tissue, as separating pressure and mechanical stress is a challenge when using a soft pressure sensor on a soft object. Several sensors can also be integrated in an active matrix, each pixel being a pressure sensor, allowing a mapping of the pressure as a function of the position. This type of sensors paves the way to health-monitoring applications, such as *in situ* digital monitoring of palpation for breast cancer or blood flow monitoring.

S. Lee *et al. Nat. Nanotechnol.* (2016)

Pressure sensors are also the most widespread membrane-based mechanical sensors (MEMS) and presents in phones, cars and several medical devices. The sensitivity of MEMS increases when the thickness of the membrane decreases: thick membranes are less sensitives. Graphene is flexible, stretchable and thin, and hence a natural choice to replace conventional MEMS, which are several hundreds of nanometres thick, for highly sensitive devices. Previous studies showed that pressure changes can be measured using graphene to seal a reference cavity, where the pressure change is then calculated by a measurement of the deflection of the graphene sheet. However, graphene sealed cavities were showed to slowly leak over time, preventing long term usage of such sensors. In a recent study, researchers from the Netherlands showed graphene-based squeeze-film pressure sensors. The sensor is formed by a dumbbell cavity, carved in a silicon substrate, which is half covered by graphene: because the cavity if open, the average pressure inside is equal to the ambient pressure. The pressure is measured via the graphene’s sheet frequency, which is pressure dependent: the viscous forces (which depend on the pressure) present in the gas increase the stiffness, changing its resonance frequency. This sensor shows reproducible measurements between 8 and 1000mbar and a responsivity up to 45 times higher than state-of-the-art MEMS based sensors, due to the small thickness of the graphene membrane. It is also several times smaller than the conventional MEMS squeeze sensors and thus provide a promising route toward miniaturized, highly sensitive pressure sensors.

R. J. Dolleman *et al. Nano Letters* **16**, 568 (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, the possibilities limitless. Graphene and graphene oxide (GO) inks, consisting of dispersed flakes in a solution, are particularly interesting for all sorts of applications.

Printed Touch Sensors

In a recent paper, a Spanish team showed a new way for printing GO, that enables simple and fast patterning, without the use of optimizing the ink or the substrate treatment using a wax stencil to define the pattern. The inverse of the desired patterned is printed using a wax printer on a membrane: the wax clogs the pores of the membrane wherever it is printed. Then, the membrane is set on a filtering system and a solution containing dispersed GO is filtered through it, leaving a mesh of GO in the gaps of the wax. The GO mesh dries and is water activated: the hydrophobic nature of the GO enables an easy detachment of the GO mesh from the membrane. By applying pressure, the GO pattern can finally be transferred to the desired target substrate: adhesive film, PET, textile... As a proof of the potential usages of this technique, the researchers printed a GO touch sensor with an interdigitated geometry. They calibrated the changes in the capacitive and resistive properties of their touch sensitive device upon interaction with a human finger and used it as an on/off switch for a LED. This easy, versatile and cost effective technique of patterning GO could be used to pattern all sorts of devices.

L. Baptista-Pires *et al. ACS Nano* **10**, 853 (2016)

3D Printed Supercapacitors

Recent interest in portable and wearable devices creates a high demand for high performance and rechargeable energy storage. Supercapacitors are electrochemical capacitors with extremely high capacitance, thanks 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. Graphene-based materials hold promises 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. Several papers reported 3D graphene-based devices, which could in principle overcome these limitations. Unfortunately, the usual methods are not scalable and the obtained material is generally brittle under low compression. A group in the United States decided to print a 3D graphene aerogel designed with periodic pores. One of the important steps was to develop a special compound containing graphene oxide and graphene nanoplatelets: when using only graphene oxide, the resistivity of the structure is too high, while using only graphene nanoplatelets decreases significantly the surface area of the composite. The researchers also adapted the 3D printing process to prevent premature drying of the printed structure. To show a how their technique can be useful, they assembled a supercapacitor, using 2 identical aerogels, which showed great charge retention (95.5% after 10 000 cycles) and power and energy densities comparable to other electrical double-layer capacitors. The real advantage of the technique is to allow the production of unique, irregularly shaped electrodes and even supercapacitors with geometries that are inaccessible with conventional techniques.

C. Zhu *et al. Nano Letters* (2016)

Rechargeable Lithium-ion Batteries

While supercapacitors charge and discharge cycle 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, complementing the supercapacitors.

Graphene Covered Silicon Particles

There have been tremendous efforts to optimize the material of the electrodes in commercial lithium-ion batteries (LIB), in particular the anode, which is generally made of activated carbon. Silicon (Si) is an attractive material for high density LIB, promising more than 10 times the capacity of commercial graphite anodes. However, it suffers from 2 problems. First, during a battery cycle, the silicon expands by 300%, which causes strong mechanical stress, resulting in poor cycling performance, mechanical cracks and loss of signal over time. Second, due to interaction with the electrolyte, an insulating layer forms in an uncontrollable way at the surface of the Si, decreasing the efficiency of the battery. The first problem is generally tackled by nanostructuring the Si. The small size of the nanostructures helps to accommodate the mechanical stress, but the synthesis of these structures is complex and do not solve the second problem. Researchers in the United States recently showed that both problems can be solved by using graphene covered Si microparticles. Starting from Si microparticles, they developed a way to grow graphene so it encapsulates the microparticles while leaving a built-in and tunable void space around them. During a cycling of the battery, the graphene cage holds the fractured silicon pieces together, maintains the electrical contact between them and prevents the growth of the insulating layer directly on the Si. Controlling the growth of the insulating layer on the graphene is easier, thanks to several years of work on similar material (graphite). This work opens up the utilization of Si in LIB.

Y. Li *et al. Nat. Energy* **1**, 15029 (2016)

Safeguarding Batteries

Even if in the last decades, we saw a steady improvement of energy and power densities of conventional LIBs, there has not been a corresponding boost in safety: when the temperature of the battery increase, for examples due to shorting, a series of exothermic reactions rapidly propagates inside the battery, leading to risks of fire and explosion. Commercial batteries are equipped with external sensors that can release the pressure, but the reactions inside occur so rapidly that an integrated solution would be advantageous. Researchers at Stanford University recently demonstrated the use of a thermoresponsive polymer, applied directly on the electrodes of the battery, to regulate the internal temperature of rechargeable lithium-ion batteries. The polymer consists of nickel nanoparticles with spikes on their surface, coated with graphene. The nano-spikes allow a high electrical conductivity as well as high thermal sensitivity, the graphene coating chemically stabilize the metal particle. When the temperature is low, the polymer conducts very well and the reaction inside of the battery is unaffected. On the contrary, when the temperature increase, the resistivity of the polymer increases by several order of magnitudes, stopping the reaction inside of the battery. These batteries not only have comparable performances to normal ones, but the action of the polymer is reversible: when the temperature decrease, normal operation restarts. It is therefore a great safety strategy for future battery applications.

Z. Chen *et al. Nat. Energy* **1**, 15009 (2016)

Heat Management with Functionalized Graphene Oxide

Heat management is one of the most important bottlenecks in the quest for the next-generation integrated circuits. With miniaturization and the increase of the number of devices per surface area, the power density increases. This also increasing the heat density, elevating the operating temperature, which increase the failure rate and slows down the operating speed of devices of the circuits. Consequently, there is a need to find a solution for heat dissipation. Free-standing, or suspended graphene possess a very high thermal conductivity in-plane, making it an attractive prospect for heat management. Unfortunately, the thermal conductivity decreases dramatically when the graphene is supported by a substrate, limiting the use of graphene in real applications. As a result, there is a need to decrease the scattering from the substrate, which limits the in-plane heat conductivity and increases the thermal resistance of the substrate/graphene interface, thereby promoting the out-of-plane heat conductivity. Recently, several European research groups, including one in Chalmers University of Technology in Sweden, published a collaborative article, where they show an efficient way of cooling electronics by using functionalized graphene oxide (FGO). In their experiments, the researchers show that the heat conduction of graphene-based films bound to GO can be increased by 75% by introducing a functionalization layer. This lowers the thermal contact resistance between the GO substrate and the graphene layer. The researchers tested the heat dissipation by heating the graphene locally and measuring the change in temperature as a function of the heating power and time. They compared results obtained on bare substrate, graphene layer on substrate, graphene layer on GO and graphene on FGO and explored different molecules for the functionalization of the GO. Their best result, obtained with the molecule 3-Amino-propyltriethoxysilane (APTES), yields a temperature decrease of the heated spot of 28°C at 1300Wcm^{-2} when compared to graphene on the bare substrate, 9°C more than the largest effect previously reported. Their comprehensive study suggests great potential for graphene in heat management solutions for electronic devices.

H. Han *et al. Nat. Commun.* **7**, 11281 (2016)

Hexagonal Boron Nitride

Boron nitride is a heat and chemically resistant compound of boron and nitrogen, which exists in several crystalline forms. One of these forms, hexagonal boron nitride (h-BN) is very similar to graphene. The crystal lattice of h-BN is made of a layered structure; inside a layer, alternating boron and nitrogen atoms are organized in a hexagonal fashion with a lattice mismatch of only 1.7% when compared to graphene. It possesses a large band gap (almost 6eV), has a white colour (hence its nickname: white graphene) and is the most stable and softest form of boron nitride. It is already used in several commercial applications such as lubricant, high temperature ceramics, corrosion/oxidation resistance as well as cosmetics.

M. Engler *et al. CFI. Ceramic forum international* **84**, 49 (2007)

h-BN: Insulator and Thermal Conductor

In the past few years, interest in h-BN has been revived because of its potential use in electronic devices, in particular in combination with graphene. h-BN can be produced by the same methods than graphene: mechanical or liquid exfoliation, as well as by CVD growth.

CVD grown h-BN can also be transferred with the same technology developed for graphene. It has a large band gap, which makes it a good insulator and an atomically flat surface, making it an ideal candidate for high quality substrate supported graphene devices. In 2010, researchers showed that graphene devices prepared on a h-BN substrate present a record carrier mobility due to a decreased scattering rate coming from the substrate.

A. R. Dean *et al. Nat. Nanotechnol.* **5**, 722 (2010)

In a recent paper, an international group of researchers from China and Sweden reviewed the potential usages of h-BN for electronic applications. Their survey show that not only the insulating properties of h-BN are interesting for such applications, but also its high thermal conductivity: the thermal conductivity of h-BN is orders or magnitude larger than other commonly used insulators. It can also act as a defect-free dielectric, with high breakdown field, which holds great promises for applications in tunnel devices. These properties can be used in van der Waals heterostructures with other layered 2D materials, including graphene.

J. Bao *et al. Electron. Mater. Lett.* **12**, 1 (2016)

Recently, researchers in Chalmers University of Technology in Sweden used h-BN as an insulating tunnel barrier in van der Waals heterostructures in combination with graphene. It was previously shown that spin injection into a material from a magnetic contact is more efficient when using tunnel contacts. In their paper, the researchers study the use of h-BN as a tunnel barrier, as it is an atomically flat insulator and very similar to graphene. For thin (1-2 layers) h-BN, they observed the expected spin valve effect. However, while measuring using ferromagnetic contacts through a thicker h-BN barrier, they observed an inversion of the spin signal in a non-local graphene spin valve with an effective spin polarization higher than that of the ferromagnetic contact. This indicated that h-BN can be use beyond its insulating capability, offering different spin dependent interface conditions, depending on its thickness, and spin filtering capabilities.

M. V. Kalamakar *et al. Sci. Rep.* **6**, 21168, (2016)