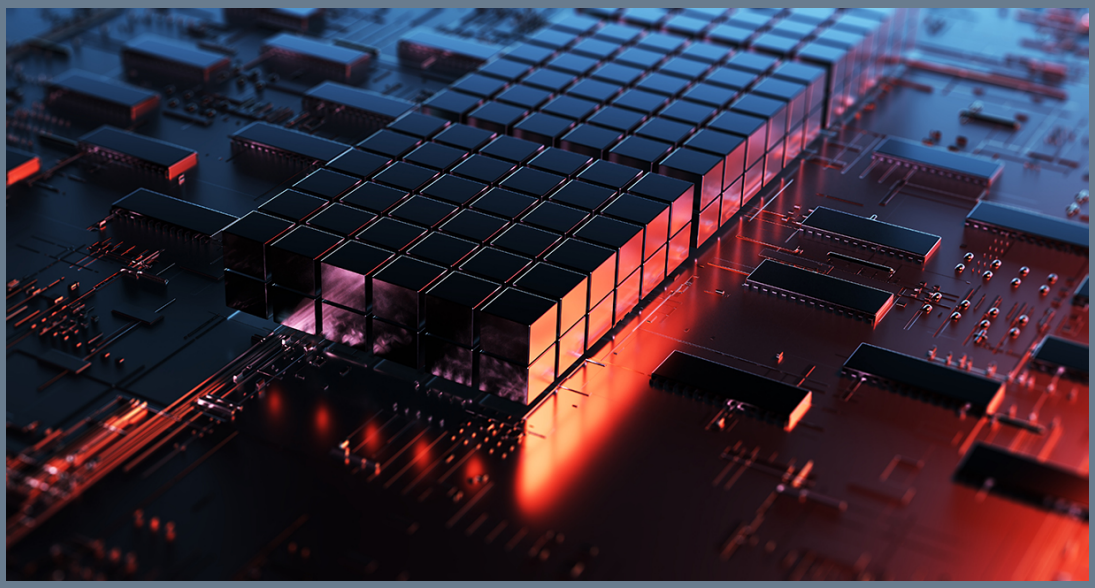
SIO GRAFEN



# Graphene Research and Advances

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Content

# Introduction

SIO Grafen's Research Intelligence Report Series, published twice a year, aims to highlight some of the most interesting research findings on graphene that have emerged during the last few months.

The graphene field started off as a dream material for physicists with all its extraordinary properties, including allowing studies of quantum physics. It did take a few years, but now we see a fast-growing number of products containing graphene and companies focusing more on developing graphene technology. This edition of the Research Intelligence series will take a quick look at some of the products that were brought to market in the last year: sensors and batteries, as well as composites and coatings.

Graphene is still an interesting material for researchers and the amount of published scientific papers is still large. Additionally, a significant amount of work is now focused on other 2D materials than graphene. A presentation of the latest state-of-art research in the six areas of strength within SIO Grafen (manufacturing, electronics, composites, coatings, biomedical technology and energy) will follow.

It has now been 10 years since the first 2D-material of the MXene class was produced. The development has been summarized in a few review articles.

In the electronic area, graphene can be used in fully recyclable electronics and thanks to its sensitivity, it can also be used in several types of sensors.

Graphene composites are used in several types of applications: noise dampening graphene aerogels could for example revolutionize the aeronautic industry.

Graphene membranes have for a long time been promising for water filtration. They can now also work at a large scale.

Another important topic for graphene research and development is how graphene can be used in biomedical technology. There it could be used as a novel mRNA delivery platform or as the active medium in sensor arrays to map brain activity.

Graphene can enhance and enable many new kinds of energy storage systems. Two of these (a sodium ion battery and a micro-supercapacitor) that are being developed in Sweden are highlighted here.

# Recent Graphene-Based Products

Many companies that are putting their hopes in graphene and research organisations are trying to deliver new ideas to the market. There are several tens of companies producing graphene and an even larger number of companies developing graphene-based products. The number of these companies is growing and some of them are growing more than others. This gives rise to an increasing number of graphene-enhanced products on the market. The following are just a few examples of products from the last year and more will inevitably soon follow.

A few companies have launched different types of sensors:

- Graphenea, a well-known Chemical Vapour Deposition (CVD) graphene supplier, started a few years ago to integrate vertically and offer different prepatterned substrates to its clients and has expanded its line of sensing platform.
- Paragraf, a spin-out of Cambridge University, launched a series of Hall sensors.
- Imagine Intelligent Materials used graphene sensors, imbedded in a floormat to detect if people are maintaining a safe distance while waiting in line.
- Graphensic in Sweden has previously also launched high performance Hall sensors.

Two new graphene-enhanced batteries were also brought to market:

- Real Graphene used their innovation in their G-Lite power banks.
- Xiaomi has integrated this new battery in its My 10 Ultra mobile phone (available only on the Chinese market).

In the composite area there have been many new products, such as:

- A new type of concrete with increased durability, water resistance and lower carbon footprint, was developed by Concrene.
- It is now possible to buy compostable carrier bags from Toraphene.
- Huvis is selling graphene-enhanced yarn with antibacterial, antifungal and antiviral function.
- The Korean sports equipment manufacturer Win&Win have produced bows and bicycles made of graphene. The Korean archer Kim Je-Deok used one of these bows when winning two gold medals at the Tokyo Olympics. The bicycles were used by 7 athletes at the Olympics.

Several new coating products also hit the market:

- Anker, Nokia and Creative all launched headphones with graphene drivers.
- GrapheneCA is now selling antimicrobial coatings and antibacterial paints.
- Infinity Wax developed a new long lasting car polish with high water beading/sheeting.

# State-Of-Art Research - Manufacturing

## 10-year anniversary of MXenes

MXenes is a class of 2D materials that were first synthesised about ten years ago. MXenes can be viewed as 2D carbides and nitrides of transition metals and are produced by selective etching of strongly bonded layered solids. MXenes are very good electrical conductors, have high strength and stiffness and can be synthesised in scalable processes in solutions without surfactants. MXenes can for example be used in energy storage, electrocatalysis, photocatalysis, sensors, antennas, photonic and optoelectronic devices. However, perhaps the most interesting prospects might be to combine the MXenes with other 2D materials in order to tailor-make completely new devices.

The 10-year anniversary since the first synthesis of MXenes has inspired a recent review article in Science and a virtual issue in ACS Nano with a new editorial which highlights many key findings from this first decade of research. The reports summarise the possibilities and main research challenges for the next decade. Another article from researchers at Linköping University reviews electron microscopy studies of MXenes.

A. Vahid Mohammadi *et al.*, Science **372**, eabf1581 (2021)

Y. Gogotsi and Q. Huang, ACS Nano **15**, 5775 (2021)

H. Alnoor *et al.*, Materials Today Advances **9** 100123 (2021)

## Quality control using TGA

A rapid, reliable and cost-effective method for quality control of graphene is needed. There are many different producers of graphene flakes who supply material with different sizes, thicknesses and oxygen content. Work developing and validating thermogravimetric analysis (TGA), as a simple analytical tool for characterization and quality control, was recently published. It was shown that few-layer graphene, graphene oxide and graphite powders have signatory distinctive peaks in the derivative TGA graphs with temperature of maximum mass decomposition rates in

specific ranges. This can be used to assess the mass concentration percentage of the different types of graphene. The next step is to standardise the measurement conditions in order to establish a reliable method for quality control.

F. Farivar *et al.*, Carbon **179,** 505 (2021)

### Large-Scale 2D Material Heterostructures

The transfer process is a critical and challenging step to use CVD graphene. In a recent collaborative article, researchers from Sweden (KTH) and Germany demonstrated the transfer of large-scale high-quality transfer of graphene and other 2D materials using an adhesive layer of thermosetting BCB (bisbenzocyclobutene), a standard dielectric material. A wafer covered with 2D material is pressed against a target wafer coated with BCB and then placed in a conventional wafer bonding equipment that heats the stack and applies pressure. The heat softens the BCB, creating a good contact to the 2D material wafer on the entire surface, which in turn ensures a good quality transfer without the introduction of wrinkles or excessive strain. The 2D material substrate is then removed, leaving the 2D material transferred on the target substrate coated with BCB. A contactless THz method was used to map the mobility of the graphene on an entire wafer, confirming the quality of the transferred film. Top-gated field-effect graphene devices were fabricated to demonstrate the fabrication of high-quality devices using a method which is compatible with large-scale device manufacturing.

A. Quellmalz *et al. Nat. Commun.* **12**, 917 (2021)

## State-Of-Art Research – Electronics

### Fully Recyclable Electronics

In a recent article, researchers reported the development of a crystalline nanocellulose ink that can be used as a dielectric in all-carbon recyclable electronics components. Thin film transistors were printed on paper using three kinds of carbon-based inks as presented in Figure 1.

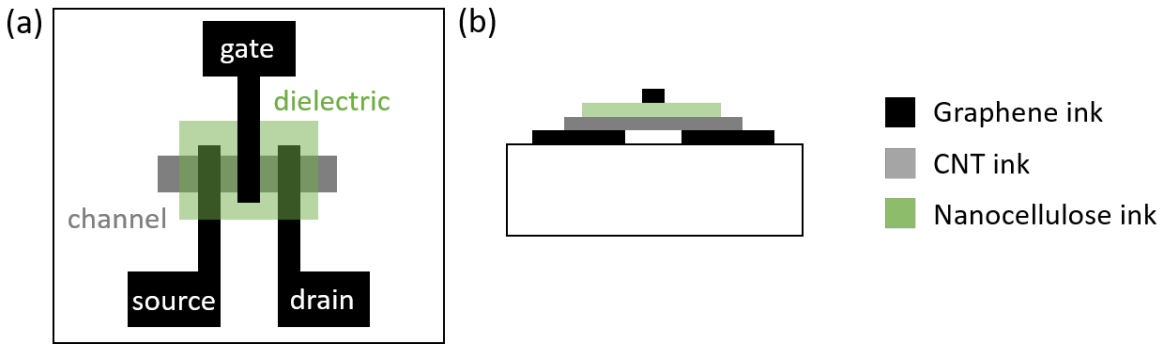


Figure 1 Top (a) and side (b) schematic view of an all-carbon printed transistor. Graphene ink (black) is used as a conductor for the source/drain/gate electrodes, carbon nanotubes (CNT, grey) ink is the semiconductor channel and insulating nanocellulose (green), the dielectric.

The researchers demonstrated the concepts by fabricating lactate bio sensors that were stable in ambient conditions over the course of 6 months. Both the graphene and carbon nanotubes inks could be controllably broken down and recycled for later reuse, demonstrating an environmentally friendly approach to printing custom electronic devices.

N. X. Williams *et al. Nat. Electron.* **4**, 261 (2021)

## Humidity Sensor for Intelligent Food Packaging

Graphene oxide (GO) is often used for gases and humidity sensing because it possesses 2D graphene sheets that have reactive oxygen groups. A recent study presented the fabrication of highly sensitive GO humidity sensors. The sensors were fabricated from GO nanoplatelets and plasticized Polyvinyl chloride (PPVC) matrix, improving the mechanical and thermal stability properties as well as the tensile properties when compared to previously fabricated sensors. The concentration of GO in the PPVC matrix was varied from 1 to 6%. The best results were obtained with a concentration of 3%. The sensors had high sensitivity, low hysteresis, ultrafast response and recovery times, making the nanocomposites promising for humidity sensing in intelligent food packaging.

H. Moustafa *et al. Sens. Actuator, A* **331**, 112918 (2021)

## Flexible Multi-Sensor for Harsh Environment Applications

Last year, a study showing the potential of graphene as a multi-sensor for harsh environment was published. Two types of sensors were produced, the first by patterning a chemical vapor deposition (CVD) graphene layer grown on copper, and the second by inducing a porous graphene film using laser irradiation on a polyimide paper. They were designed to function at high temperature (up to 650 °C), high salinity and chemically harsh environment (pH sensing). The sensors' resistance varies as a function of the physical parameter such as temperature, salinity and pH. The fabricated sensors showed a temperature sensitivity of 260% higher than a conventional platinum sensor.

S. F. Shaikh *et al. Appl. Phys. Lett.* **117**, 074101 (2020)

# State-Of-Art Research – Composites

## An Ultralight Aerogel

An ultralight graphene oxide (GO)/polyvinyl alcohol (PVA) aerogel was recently studied as a new acoustic material. The material was manufactured by ultra-high shear mixing blends of GO and PVA, in a process that allows the incorporation of air bubbles in a templated structure that leads to ultralight aerogels with hierarchical and tuneable porosity. The aerogels produced using this technique possessed an enhanced ability to dissipate sound energy, with average sound absorption coefficients as high as 0.79 over the 400-2500 Hz range and average sound transmission losses that could reach 15.8 dB. They have also an extremely low density, 2.10 kg $m^{-3}$, one of the lowest values ever reported for acoustic materials and a very interesting material for the aeronautical industry.

M. Rapisarda *et al. Sci. Rep.* **11**, 10572 (2021)

# State-Of-Art Research – Coatings

## Water filtration

Graphene membranes have for several years been promising for use in water filtration. However, it has been a major challenge to sustain high solute rejections at realistic concentrations. It has now been shown that a series of membranes based on graphene oxide bound to polycyclic π-conjugated cations work over a wide concentration range. The cations act as spacers between the graphene sheets. The membranes were succesfully tested under realistic conditions on rest products from wood pulping (345 K, pH of 12.6, flow rate of approximately 11 l/min, 10–50 bar pressure). The membranes were 1 $ft^2$ and showed >99% rejection of lignin with excellent chemical and mechanical stability over 1500 hours of continous operation.

Z. Wang *et al.*, Nature Sustainability **4**, 402 (2021)

## Ultra-high density hard disk drives

Solid state drives are popular for storing media on mobile devices, but when it comes to storing large amounts of data on stationary devices, hard disk drives (HDD) are still the best option. New research has found a way to increase the storage capacity of HDDs by up to a factor 10. This requires the thickness of the normally used carbon overcoats (COCs) to be <2 nm. However, friction, wear, corrosion, and thermal stability are critical concerns below 2 nm. The researchers instead used graphene, as the material excels in all of these areas, and found that it meets the requirements for 4–10 Tb/$in^2$ areal density HDDs, when using suitable recording technologies.

N. Dwivedi *et al.*, Nature Communications **12**, 2854 (2021)

# State-Of-Art Research – Biomedical Technology

## A Novel mRNA Delivery Platform

Due to their good dispersibility, biocompatibility, large surface area, colloidal stability and tuneable surface structure, graphene quantum dots (GQD) are an attractive platform for bio-applications, from biosensing and bio imaging to drug delivery. A recent study from a team of researchers based in Sweden and China showed how GQD can be functionalised to enable Messenger RNA (mRNA) delivery. mRNA-based medicines are especially interesting because they can go inside cells and direct protein production. However, mRNA molecules are, when alone, unstable and have poor cell penetration. These shortcomings can be overcome by creating composite particles, for example by attaching mRNA to functionalized GQDs. The efficiency of the method was demonstrated by using functionalized GQD to deliver intact and functional mRNA liver cells. This technique is the first step towards a novel preparation method for stable and effective mRNA delivery.

Y. Liu *et al. ChemistryOpen* **10**, 1 (2021)

## Sensor Arrays to Map Brain Activity

The biocompatibility of epicortical graphene chronic implants was recently demonstrated by a team of researchers. The performance of 64-channel graphene sensors arrays was evaluated in terms of homogeneity and sensitivity. The graphene-based devices were produced in a wafer-scale process using commercially available CVD graphene and is an important milestone towards the industrial scale production. Using the devices, researchers were able to detect cortical signals from a wide frequency band. The stability of the graphene sensors was demonstrated in vivo by characterizing their sensitivity over the course of several weeks using a freely behaving rodent with a headstage that transmitted the data wirelessly.

R. Garcia-Cortadella *et al. Nat. Commun.* **12**, 211 (2021)

# State-Of-Art Research – Energy

## Sodium ion batteries using graphene

Sodium is a cheaper and more abundant alternative to lithium in batteries. However, it is typically only possible to store about 10% as much sodium as lithium in the graphite anodes, which reduces the capacity of the batteries correspondingly. Now researchers from Sweden (Chalmers), Germany and Italy have managed to increase the loading of sodium to similar levels as lithium. This is done by instead of using graphite anodes, they stack individual sheets of graphene and functionalise each sheet on one side in order to form a spacer which allows intercalation between the

graphene sheets. The intercalation is reversible and provides a proof of concept for new sodium ion batteries.

J. Sun *et al.*, Sci. Adv. **7**, eabf0812 (2021)

## Micro-supercapacitors

More and more portable microelctronic devices are being developed, which leads to a growing interest in high performance and low-cost microscale energy storage. Researchers from Sweden (Chalmers and KTH) and Italy have developed new micro-supercapacitors with a high volumetric capacitance of 110 $F/cm^3$, broad operation potential range of 1.6 V and with a long cycle life showing a capacitance retention of 95.7% after 10 000 cycles.

The devices were created by inkjet-printing of graphene patterns as negative and positive electrodes, which were coated by mesoporous $Fe_2O_3$ and $MnO_2$ nanoflakes by electrodeposition. The low-cost technique is scalabe and thus feasible for large scale production.

Z. Xia *et al.*, Nanoscale, **13**, 3285 (2021)

Programmets vision är att Sverige är ett av världens tio främsta länder på att använda grafen för att säkerställa industriellt ledarskap år 2030.