In 2016 the Graphene Flagship left the ramp-up phase and entered the main part of its voyage when the first Core Project was launched on April 1. The project is now quite well established, and most of our routines function well.

The Graphene Flagship represents a new way of doing research on the European scale. The implementation of a large, focused research activity as a flagship has been assessed by an interim evaluation panel led by the former Italian Minister for Education and Research, Maria Chiara Carrozza, who published their findings in January 2017. I am very happy to see that the panel endorses the flagship concept and finds it an efficient and effective way of organizing large research endeavors.

During 2016 the Flagship has continued to produce excellent scientific and technological results as described on the following pages and noted during the final review of the ramp-up phase and the interim evaluation. We have attracted many new Associated Members and several Partnering Projects, showing that the Flagship impact extends beyond the EC-funded Core Projects. Internationally, we are recognized as a key collaboration partner, as demonstrated by our workshops with US, Japan, Korea and China.

We have to continually re-assess our initial plans: is the technological promise still there in terms of improved performance, and is the technological uncertainty decreasing in the manner that justifies continued investment? In most areas we see that this is the case, as witnessed by the products and demonstrators emerging from our work, but in some cases we have to accept that we need to adjust our course. This continuous re-assessment is integral to the success of a long-term action such as the Flagship.

We must now concentrate on producing the results that enable the impacts that the Flagship aims to deliver. I see that many work packages are becoming more technology-oriented, ideas are evolving to concrete prototypes that have true promise in society outside the academic laboratories. This said, we must not forget that the Flagship’s origins lie in fundamental, curiosity-driven research: we would not be where we are now without ground-breaking basic research. The Flagship will continue to balance the fundamental and applied dimensions of its research portfolio, with a moderate increase of the more applied parts as time moves on.

I am looking forward to a new year of research and discovery as the Flagship’s voyage continues.

Jari Kinaret
Director of the Graphene Flagship
Enabling Research
The development and commercialisation of novel technologies that exploit the specific properties of graphene and related layered materials (GRMs) require detailed understanding of their fundamental properties and interactions, as a comprehensive toolbox.

The research performed in the Enabling Research Work Package includes studying the detailed interactions of GRMs, developing new device concepts for layered heterostructures with novel electronic and optoelectronic properties, giving the Graphene Flagship a strong foundation on which to build new technologies and devices.

Building on previous work form the Graphene Flagship [1], the University of Geneva and the École Polytechnique Fédérale de Lausanne (EPFL) determined the origin and magnitude of the spin-orbit coupling effect that occurs in graphene placed on semi-conducting transition metal dichalcogenides [2]. The spin-orbit coupling is due to modification of the electronic band structure in graphene, and has a very large effect. The electronic bands of the two spin states are split by 10 meV, approximately 1000 times larger than the intrinsic coupling in graphene. The large splitting is of great interest for spin transport devices, and research is continuing within the Spintronics Work Package.

This fundamental result opens up real possibilities for directly engineering the electrical properties for graphene-based devices, without chemical or structural modification of the graphene. Alberto Morpurgo, Deputy Leader of the Enabling Research Work Package, coordinated the work. “In the future, the ability to control the electronic properties of GRMs by forming appropriate interfaces will offer unprecedented technological opportunities. This work represents an important first step in our understanding,” he said.

As well as this significant achievement, in another collaboration between the University of Geneva and EPFL, researchers demonstrated that superconductivity can be induced in monolayer molybdenum disulphide – a wide band-gap transition metal dichalcogenide – by applying a gate voltage [3]. In bulk materials, electrostatic gating affects only the electronic properties of the surface. In layered materials, the geometry of the field can be tailored to control the properties of the whole material. “These results illustrate the impressive level of electrostatic control offered by GRMs, which would have been just unthinkable until a few years ago,” said Morpurgo.

WORK PACKAGE LEADER
Vladimir Falko, University of Manchester, United Kingdom

WORK PACKAGE DEPUTY
Alberto Morpurgo, University of Geneva, Switzerland

Spintronics
As well as charge, electrons possess the property of spin. Like charge currents, motion of electrons leads to spin currents, which can be manipulated in different ways in spintronic devices – ranging from novel circuits to data storage. The fundamental ingredients for spintronics are the efficient creation, manipulation and detection of spin currents.

Graphene’s long spin lifetime and high electron mobility make it appealing for spintronic applications, and researchers from the Graphene Flagship are working to develop new spintronics technologies using GRMs.

However, in order to bring spintronics applications to high technology readiness levels (TRLs), there are some important challenges to overcome. It is very difficult to maintain and direct spin currents as they propagate, which is essential for designing spin devices and circuits. In a breakthrough result, the University of Groningen have shown that it is possible to maintain spin currents over long distances of up to 90 µm using drift currents [1]. This work also demonstrated that it is possible to steer the spin currents using the drift fields with unprecedented high efficiency. These results show that the transport of spins can be tuned in a controllable way, essential for logic operations.

The spin Hall effect is a typical means by which pure spin currents can be generated and further controlled – but it is not observable in pristine graphene due to low spin-orbit coupling. Instead, a large spin Hall effect has been reported for graphene decorated with metal adatoms, but the origin of the measurements has been controversial and remains debated. Now, the effect is better understood thanks to research efforts from the Catalan Institute of Nanoscience and Nanotechnology (ICN2) [2]. In a theoretical study, researchers revealed that the observed SHE results from several contributions, some intrinsic to spin scattering mechanisms, while others results from background effects unrelated with spin physics.

Stephan Roche, Deputy Leader of the Spintronics Work Package, coordinated this work. “We have theoretically established that the interpretation of the giant spin Hall effect seen in adatom-decorated graphene using non-local resistance measurements must be revised, due to the multiple background contributions. Based on this analysis, we proposed a new device configuration to unambiguously estimate and further optimize the generation of pure spin currents in graphene devices,” he said. The proposed device geometry would suppress the background contributions, allowing direct observation of the intrinsic SHE in the adatom-decorated graphene and accessing its maximum efficiency. This knowledge milestone also represents a step towards the engineering of future efficient spin-torque technologies based on the SHE.

Enabling Materials
Underpinning the Graphene Flagship’s mission to develop commercialised graphene technologies is a strong foundation in fundamental materials science of GRMs.

The properties of GRMs depend strongly on their physical and chemical characteristics, while the latter depends on the synthetic method, so a detailed understanding of the materials science is essential. This helps researchers not only in selecting the best type of GRM for the application at hand, but also in developing new technologies that fully exploit GRM properties. “Enabling materials is at the forefront of the scalable synthesis of GRMs in the Graphene Flagship. Our success makes it possible to translate the promise of GRM platforms into real world devices and products,” said Mar Garcia-Hernandez, the Leader of the Enabling Materials Work Package.

A collaborative effort between Dresden University of Technology, the Swiss Federal Laboratories for Materials Science (EMPA), the Max Planck Institute for Polymer Research, and the University of Basel explored, via both experimental and computational means, the mechanisms of friction in graphene nanoribbons sliding across surfaces [1], unravelling the interplay between ribbon size, elasticity, and the surface. The ultra-low friction between graphene and a gold surface leads to a superlubric effect – almost perfect, frictionless movement. While this effect is known in graphene sliding on graphene – such as in graphite, which is used as an excellent dry lubricant – this study demonstrated that graphene slides with ultra-low friction on other surfaces as well. This important result opens up possibilities for the use of graphene in frictionless coatings and in nanomechanical devices.

Graphene is being explored for use in different types of composites, to make the multifunctional materials with enhanced mechanical, electrical, thermal and barrier properties. Understanding the behaviour of graphene within polymers is vital to optimise composite materials. In collaboration with the Polymer Composites Work Package, Trinity College Dublin found that adding graphene to a soft, viscoelastic polymer – the novelty material commonly known as Silly Putty – forms a composite with unexpected properties [2].

The composite graphene-putty is an excellent sensor material – sensitive enough to detect the footsteps of a small spider. Electrical resistance depends on deformation or impact, but the self-healing nature of the graphene network within the polymer slowly returns the resistance to the pre-strain level. These unexpectedly sensitive polymers could be ideal for low-cost devices for healthcare, since their sensitivity is high enough to measure pulse waveforms. Johnathan Coleman, Deputy Leader of the Enabling Materials Work Package said “While a common application has been to add graphene to plastics in order to improve the electrical, mechanical, thermal or barrier properties, the resultant composites have generally performed as expected without any great surprises. The behaviour we found with the G-putty has not been found in any other composite material. This unique discovery will open up major possibilities in sensor manufacturing.”

WORK PACKAGE LEADER
Mar Garcia-Hernandez, Spanish National Research Council (CSIC), Spain

WORK PACKAGE DEPUTY
Jonathan Coleman, Trinity College Dublin, Ireland

Identifying and controlling any possible safety and toxicity issues regarding the use of GRMs in humans, animals and the environment is of paramount importance, and cannot be separated from the development of new, GRM-based technologies. GRMs must be well characterised for the different applications, as the physical and chemical properties of the materials strongly affect their interactions with biological materials.

One important potential application of GRMs in nanomedicine is drug delivery, with GRMs acting as vehicles to carry and deliver therapeutic molecules to specific targets within the body. For this, it is very important that GRMs do not induce unwanted effects within the body, and that they can be safely excreted through the body’s normal functions. The University of Manchester and the National Centre for Scientific Research (CNRS) investigated the effect of graphene oxide (GO) sheets on the function of mouse kidneys when injected intravenously [1]. Importantly, they found that not only are the GO sheets readily excreted in urine, the excreted sheets are intact, confirming stability within the body.

Hexagonal boron nitride (hBN) is another layered material is promising for use alongside graphene in a wide range of areas. It is chemically inert and strongly resistant to oxidation, meaning that biopersistance could be a potential problem with its use. CNRS and Trinity College Dublin explored the degradation of hBN when exposed to peroxidases – enzymes produced by microorganisms and in the human immune system – and under a UV-assisted Fenton reaction [2]. Biodegradation of hBN is quite different to that of graphene and GO. It was found that hBN can be degraded by myeloperoxidase, an enzyme expressed in activated neutrophils, white blood cells present in the lungs. Significantly, the UV-assisted Fenton reaction is highly effective, suggesting a route to treating waste hBN on an industrial scale. Maurizio Prato, Leader of the Health and Environment Work Package, said “The Health and Environment Work Package is widening its research horizons – extending the studies to other GRMs that may be interesting for their chemical and physical properties. It is an important result that hBN, a very robust material, with increasing appeal for applications, is relatively easily degraded by specific enzymes. This may avoid the accumulation and persistence of hBN in the environment in the perspective use of this fascinating material.”

CNRS, the French Alternative Energies and Atomic Energy Commission (CEA) and the University of Castilla-LaMancha performed an investigation into the effect of various different types of carbon nanoparticles, including graphene, on the growth of larval *Xenopus laevis*, an aquatic organism. Their results show that it is the size of the carbon nanoparticle that affects the larval growth, rather than the morphology. This study is a step towards a realistic metric of assessing the dose of nanoparticles in the environment.

WORK PACKAGE LEADER
Maurizio Prato, University of Trieste, Italy

WORK PACKAGE DEPUTY
Alberto Bianco, National Centre for Scientific Research (CNRS), France

Graphene’s excellent combination of physical properties and the biocompatibility demonstrated so far make it ideal for a range of biomedical technologies. A new work package for the Core 1 phase of the Graphene Flagship, Biomedical Technologies explores graphene and related materials for novel drug delivery systems and for neural and retinal implants that can both record and stimulate activity.

In a collaborative effort with the Health and Environment Work Package, led by the University of Trieste and the University of Manchester, the effect of GO nanosheets of different sizes on neural activity was investigated [1]. In this first demonstration of the ability of GO to affect synaptic and glial function, neural cells were cultured in media containing dispersions of GO nanosheets and the efficiency of the cellular networks was investigated. GO flakes can downregulate synaptic activity in healthy neural cells. This is significant for safely designing neural therapies using GO, and forms the basis for ongoing research. For example, this effect could be exploited for treatment of neurodegenerative disorders that are characterised by hyperactivity in certain brain areas.

Previous work in the Ramp-Up phase from the University of Trieste showed that planar graphene has no effect neuronal function [2]. This opens up the possibility of using the excellent electrical properties of graphene in neural interfaces, to record and stimulate electrical activity with the brain. The Technical University of Munich, Institut d’Investigacions Biomèdiques August Pi i Sunyer (IDIBAPS) and ICN2 demonstrated highly sensitive, flexible neural probes based on graphene field-effect transistors [3] that have several benefits over contemporary state-of-the-art metal electrode probes. The high sensitivity gives excellent signal-to-noise ratio, meaning that pre-amplification near to the recording site is not necessary. This, combined with their excellent performance at small sizes, means that graphene-based neural probes could lead to neural interfaces with high resolution. Such devices could be used to develop understanding of diseases such as epilepsy and other disorders that affect brain function and motor control, and in neuroprosthetics for control of artificial limbs.

“High-resolution recording of neural activity using flexible, graphene-based devices and targeted electrophysiological interference of neuronal function using nanoscale 2D sheets are important targets of the Biomedical Technologies Work Package,” said Kostas Kostarelos, Leader of the Biomedical Technologies Work Package. “Alone or in combination, these two application areas can offer new options towards the much-needed management of neurological disease.”

In an important step to widen the clinical application of graphene-based neural probe systems, partner company Guger Technologies developed an integrated system for neural recording and stimulation devices based on graphene. This interface device acts as and an amplifier and control system for graphene-based neural probes, with a pre-amplifier, power source and CPU, and is USB-compatible.

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Sensing devices are rapidly gaining importance in our society, with applications across the Internet of Things with consumer market and industrial process monitoring, early diagnostics and health hacking, and food and environmental safety. The Sensors Work Package focuses on exploiting the strong surface responses of GRMs for selective sensing of gases, biomolecules, radiation and pressure.

A key requirement for chemical sensors based on GRMs is specificity, which is usually engendered by functionalisation of the material. The University of Tartu reported highly sensitive and selective sensing of NO₂ in air, by using graphene sheets functionalised by pulsed laser deposition of different targets [1]. Chalmers University of Technology has also shown a route towards chemically discriminant gas sensors, without functionalisation. Dipolar molecules shift optically dark exciton states in transition metal dichalcogenides to be optically accessible, producing a clearly defined molecular fingerprint that can be exploited in chemical sensors [2].

Using single-layer graphene sheets suspended over holes cut into silicon, Delft University of Technology developed an effective gas pressure sensor that can be used to characterise devices comprising suspended graphene membranes [3]. The non-invasive technique detects colour changes associated with deformation of the graphene membrane to determine relative pressure and identify defects in suspended devices. The colour change mechanism is promising for use in low-power interferometry modulation displays, for colour displays in e-readers and smart watches.

Plasmon resonances in graphene are strongly confined and long-lived, and have potential in many different applications including biosensing and photonic devices. However, exciting plasmons in single-layer graphene is difficult without strong doping, affecting graphene’s other properties. The Institute of Photonic Sciences (ICFO) showed that double-layer graphene significantly enhances the strength and tunability of plasmon resonances in graphene [4], which will lead to interesting opportunities in gas- and biosensing based on chemical fingerprints in the infrared range.

Specificity in biosensing typically relies on the use of biological antibodies or synthetic bioreceptors. VTT Technical Research Center of Finland have demonstrated proof-of-principle result for detecting mycotoxins – common food contaminants produced by several types of mould that can cause severe health issues. This in-situ diagnostic tool will be a powerful tool in increasing food safety, offering simple method of determining contamination levels. Another target in biosensor development is early diagnostics, requiring highly specific detection of small concentrations of disease markers that can identify the need for immediate medical care. “The high selectivity and sensitivity of graphene biosensors was demonstrated with several model cases. The next steps to industrialization require simplification and optimization of the functionalization procedures, as well as performance verification in relevant environments,” said Sanna Arpiainen, Deputy Leader of the Sensors Work Package.
Electronic Devices
Graphene’s exceptional electronic properties make it ideal for high performance electronic devices that can surpass the state-of-the-art. Such electronic devices will enable improvements and novel innovations in many areas, including wireless communication, data processing, low power electronics and sensor systems.

“Graphene-based integrated circuits are already operating at hundreds of GHz with promising performance. While this is in principle also possible with some established materials, the co-integration of graphene-based radio circuits on silicon CMOS devices provides a unique opportunity to really exploit these frequency bands for future communication systems and sensor devices,” said Daniel Neumaier, Leader of the Electronic Devices Work Package.

In a highly significant result for scalable device fabrication, the Technical University of Denmark have developed a versatile assembly technique for batch fabrication of high-quality graphene devices. Using a polymer stamp, hBN and graphene flakes are successively picked up and dropped down to produce stacked heterostructures. By performing the drop-down at temperatures of 110 °C, contaminants and defects are pushed out of the interface, giving near perfect contact between graphene and hBN. “It is essential for us to have the highest material quality available in order to exploit the ultimate performance of electronic devices based on GRMs. The hot pick-up technique is an important step in this direction, giving us access to the lab scale production of graphene devices with charge carrier mobilities approaching the intrinsic limits,” said Neumaier.

Mixers are key components of electronic circuits, combining two or more input signals into one or more outputs. The recent demonstration of an integrated subharmonic mixer using a graphene field effect transistor by Chalmers University of Technology [2] is an important step forward for high-frequency integrated circuits based on graphene. The mixer operates at 185–215 GHz – the highest reported frequency for graphene-based devices. This result paves the way for the use of high-quality graphene in millimetre-wave electronics, ubiquitous for communications and imaging systems. The method is also promising for flexible electronic devices.

The Electronic Devices Work Package is leading to new technologies relevant for the unprecedented expansion of connectivity and communications in the modern technological society. The Graphene Flagship’s research efforts in this direction will be concentrated on those areas that have direct commercial applications, as Neumaier explains: “The specific needs of wireless communication systems in 5G and beyond, as well as devices for the Internet of Things will define the future research activities in the Electronic Devices Work Package.”

Photonics and Optoelectronics
The combination of ultrahigh electron mobility and wide-band optical response make graphene an ideal choice for enabling high performance optoelectronic and photonic devices. Both photonic and optoelectronics are of increasing importance in our everyday, highly connected lifestyles as enabling technologies for a wide range of applications in communications, security, and energy generation.

“The mission of the Photonics and Optoelectronics Work Package is to provide key solutions for next generation data communications (5G) based on integrated photonics, as well as broadband sources and imaging systems for self-driving cars, medical imaging, food inspection and security. For IoT, graphene is an ideal solution because of its form factor - it is flexible and transparent - and because it can have many functions at the same time: e.g. sensors, photodetector, wireless receiver,” said Frank Koppens, Leader of the Photonics and Optoelectronics Work Package.

Optoelectronics – the control and manipulation of light by electrical means – provides an interface between optical communication and electronics devices, and is the backbone of modern communications technologies. In a landmark result, AMO and the Vienna University of Technology demonstrated ultra-high speed photodetectors based on graphene that are capable handling a record 100 Gbit/s data transmission [1]. Increasing the speed and capacity of next generation communication networks is important to support the large amounts of data generated by smart devices and the Internet of Things. As well as the ultra-fast data rates, the graphene-based detectors are also incredibly compact and are compatible with silicon-based technologies, making them easy to integrate in existing fibre-optic systems.

Graphene’s excellent electrical properties were also put to use in highly sensitive infrared (IR) thermal detectors from the University of Cambridge, Emberton, ICFO, Nokia R&D UK, and the University of Ioannina [2]. These detectors are opening up possibilities for spectral thermal imaging. Typical thermal cameras absorb a wide range of IR frequencies in order to generate an image, but the graphene-based thermal detectors are sensitive enough to produce a detection signal when trained to a narrow frequency band. This is ideal for security screening applications; for example, when looking for explosive chemicals, which often have characteristic IR emission or absorption spectra. With high spectral and spatial resolution, a camera based on an array of these graphene-based IR detector can give not only information about what materials are present, but also precisely where they are. “Graphene cameras, currently under development, can ‘see’ much more than we can see with our bare eye. These will be used for security and inspection, for night vision and to identify invisible objects and spurious chemical species,” said Koppens.

Flexible Electronics
Graphene’s two-dimensional nature makes it very attractive for flexible electronics, where both its excellent electrical and mechanical properties are relevant. The inherent flexibility of GRMs provides a toolbox for creating various electronics components in conformable and flexible formats without compromising on performance. Flexibility is a key driver for consumer electronics for connected devices and the Internet of Things.

The solution-processability of GRMs also enables low-cost fabrication by printing, for high volume applications such as smart packaging. For integrated flexible graphene-based circuits, materials and processing techniques have been developed to allow all-printed devices such as pressure sensitive touch screens.

Multiple different kinds of flexible electronic devices were demonstrated at the Graphene Experience Zone at Mobile World Congress 2017, the world’s largest exhibition fair for the mobile technology industry. Flexible sensors for physical and chemical detection, such as pressure, light, different ions, were a key attraction for visitors to the Graphene Experience Zone. RWTH Aachen University and AMO demonstrated the first flexible WiFi receiver in the Graphene Experience Zone. This breakthrough result paves the way for fully flexible, integrated communication devices for wearable technologies and the Internet of Things.

Also on display at Mobile World Congress 2017 was a flexible transistor device based on MoS2 with high charge carrier mobility (>120 cm²/Vs), from FlexEnable. These transistors have potential applications in readout electronics for flexible multi-analyte sensor devices. Henrik Sandberg, Leader of the Flexible Electronics Work Package said “Flexible transistor-based electronics utilizing layered materials such as MoS2 is a key development area for the Flexible Electronics Work Package. The electronic performance is far superior to organic semiconductors, the materials are compatible with a range of substrate materials and they are inherently flexible, which is not the case for traditional semiconductors used in electronics today. The possibility of monolithic integration of transistors in flexible electronics will change the way flexible devices are made in the future.”

In a significant step towards integrated radio-frequency flexible devices, CNRS demonstrated high frequency flexible graphene field effect transistors (FETs) with excellent mechanical stability [1]. The graphene FETs, constructed on a flexible Kapton substrate, show a record high cut-off frequency of 39 GHz. Importantly, the flexible graphene FETs were shown to have good stability on heating. Thermal management is a key consideration of flexible electronic devices, as flexible substrates tend to have worse thermal conductivity than rigid substrates.

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\text{Nanoscale 8, 14097 (2016)} \]
Graphene’s excellent electrical properties are very promising for a variety of applications, including for high frequency electronics, photonics and optoelectronics, and flexible electronics. These require high quality graphene, with high mobility and good reproducibility for industrial applications. The Wafer Scale Systems Integration Work Package focuses on developing scalable techniques for the use of graphene-based technologies in integrated electronics.

The development of graphene-based technologies that are compatible with the strict requirements of silicon electronics fabrication technologies paves the way for exploiting graphene’s benefits in real-world devices.

Chemical vapour deposition (CVD) has emerged as the most promising route for scalable production of high-quality graphene at industrial scales. Typical approaches result in randomly oriented multicrystalline graphene. As well as this, transfer from the growth substrate to the target can be tricky, often leading to degradation of the graphene, or only is viable for transfer of small areas of graphene up to tens of µm. In a breakthrough result, the Italian Institute of Technology (IIT) and CNIT overcame these issues in a collaborative effort with the Enabling Materials Work Package, demonstrating the controllable growth of large-scale, single crystals of graphene, up to 350 µm in size [1]. By nucleating the growth with chromium, single crystalline graphene can be deterministically grown in specified locations, including in arrays of periodicity up to 1 mm. The seeded growth technique is fast and flexible, resulting in hBN-encapsulated graphene with high mobility of up to 21,000 cm²/Vs and no chromium contamination.

This result paves the way for large-scale production of graphene-based electronic and photonic devices, as the arrays of single crystal graphene can be transferred all at once onto a patterned substrate. By designing the arrays of nucleated graphene to match with the patterns of the target, it becomes possible to produce electronic devices in large batches. The nucleated growth technique is scalable to the size of full wafers, so this method opens up possibilities for industrial production of graphene-based integrated electronics.

Marco Romagnoli, Leader of the Wafer Scale Systems Integration Work Package, commented “The impact of this result on the Wafer Scale Systems Integration Work Package is that we can plan future transfer processes based on the possibility to grow and transfer graphene and GRMs only in the locations in which they are needed. We expect this approach will simplify the wafer scale processing and improve yield.”

References:
Energy Generation
Technological growth is driving an unprecedented demand for electrical power. At the same time, environmental factors mean that new technologies for sustainable energy sources are urgently needed. The Energy Generation Work Package focuses on the development of building blocks based on GRMs for solar and fuel cells, and their integration into large area power generating demonstrators suitable for industrialisation.

Great progress has been made in using GRMs to boost performance of organic and perovskite solar cells. Exfoliated GRM nanosheets have high surface area and aspect ratio, comprising a combination of excellent electronic, mechanical and photophysical properties. Availability of the reactive groups on the nanosheets enables their functionalization with molecules, which can be used to manipulate their optoelectronic properties and energy levels.

The key aspects of the layered solar cell structure are the interfaces between each functional layer. The Energy Generation Work Package has demonstrated that these interfaces can be engineered to enhance charge transport and collection, through the utilization of GRMs. In particular, solution processable GRMs such as WSe₂ flakes with fine-tuned morphological characteristics, were successfully utilized as energy cascade materials in ternary organic solar cells [1], and a wide range of work-function tuned GRMs have been utilized as universal buffer layers in organic and perovskite solar cells for charge transport and collection between the layers [2,3,4]. These results from the Technological Educational Institute of Crete, IIT and University of Rome Tor Vergata demonstrate the advantage of GRMs over traditional materials in boosting both performance and stability.

Graphene interface engineering is also enabling the fabrication of large area perovskite solar cells [5]. The Energy Generation Work Package reported world record power conversion efficiency of 12.6% in printable solar modules with an active area of 50.6 cm². This result, a collaboration between University of Rome Tor Vergata, IIT and the Technological Educational Institute of Crete, paves the way for achieving the Graphene Flagships targets for commercial-scale solar generators. Emmanuel Kymakis, Deputy Leader of the Energy Generation Work Package, outlines the strategy for the future: “The Energy Generation Work Package will focus on GRM interfacial engineering in hybrid solar cells and modules to improve the triangle of efficiency, stability and cost, and on the industrialization of this technology through their integration in an industrial pilot line. Special attention will be paid to stability and lead removal strategies, to avoid the environmental problem posed by lead leaching and regulation restrictions. This approach, coupled with the prospective upscaling of GRM inks and deposition, will pave the way for a large demonstrator solar farm in Crete during the next stage of the Flagship.”

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Energy Storage
GRMs provide an opportunity in energy storage due to their excellent electrical conductivity, mechanical strength and high surface-to-weight ratio. While GRMs alone are not ideal solutions as active electrode materials [1], a major effort is focused on pairing GRMs with silicon nanoparticles to obtain Li-ion electrodes with superior performance. IIT, the University of Cambridge, CEA and CIC EnergiGUNE are systematically investigating different recipes showing promising results in terms of electrode capacities and cyclability. In particular, CIC EnergiGUNE produced binder-free electrodes for lithium ion batteries, using self-standing films and aerogels of silicon nanoparticles and reduced GO [2]. These electrodes are one example of a particularly promising and scalable material approach for high-capacity, Li-ion anodes.

GRMs can also be processed into foams and aerogels with high specific surface areas ideal for high-capacity supercapacitor electrodes and flexible designs. Research is targeting high-capacity electrodes capable of charging very quickly and delivering high power. Supercapacitors can also be made in a flexible form factor, which is ideal for making fully flexible devices, for example, for wearable electronics and health devices. Dresden University of Technology used hybrid inks containing nanosheets of graphene and titanium carbide – a layered transition metal carbide – to produce fully flexible, all-solid state supercapacitors ideal for on-chip power supplies [3].

Solution processing of hybrid graphene dispersions is an ideal method for producing electrodes for both batteries and supercapacitors on industrial scales. Thales has developed a new method for spray-gun deposition of graphene dispersions to produce large-area electrodes for supercapacitors and batteries. In a collaboration with M-Solv, a production-line machine based on this technology is under development.

“Graphene offers the way to finally exploit high-capacity nanomaterials such as silicon nanoparticles into a new generation of reliable batteries” said Vittorio Pellegrini, Leader of the Energy Storage Work Package, and chair of the Flagship Executive Committee. “We are developing processes able to prevent the degradation of silicon material during battery operation thanks to the combination of the mechanical and electrical properties of graphene.”

“We also aim at developing scalable technologies for large-area electrode deposition,” added Teófilo Rojo, Deputy Leader of the Energy Storage Work Package, “Such as the spray-gun process perfectly adaptable to solution processed GRMs developed by our industrial partners.”

Functional Foams and Coatings
Xinliang Feng, Leader of the Functional Foams and Coatings Work Package, stated that “The Functional Foams and Coatings Work Package targets chemical approaches to generate functional porous structures such as foams and membranes, coatings and thin films for applications in various technological realms.” Paolo Samorì, Deputy Leader of Functional Foams and Coatings, added “It’s all about how molecules, which by design are functional, interact with GRMs, opening broad prospects in terms of processability and functions that are conferred to the GRMs.” Significant progress was made in the chemical approaches to GRMs. A Special Issue in Advanced Materials was dedicated to showcasing developments in the chemical control of GRMs, and their technological relevance [1]. This Special Issue was co-edited by Paolo Samorì, Vincenzo Palermo, and Xinliang Feng, and featured several highlights from the Graphene Flagship.

Liquid-phase exfoliation methods are of great significance in the production and functionalisation of graphene for use in coatings. Molecule-assisted exfoliation with surfactants is an efficient way to boost yield and stabilise the resulting dispersion. Using light-sensitive alkoxyl-substituted azobenzene molecules, the University of Strasbourg, the National Research Council (CNR) and the University of Cambridge demonstrated scalable photo-assisted exfoliation and created functionalised GRM with light-switchable electronic properties [2]. Artur Ciesielski, a researcher at the University of Strasbourg, stated “The motivation was the need of conferring a new function to graphene, like the capacity to respond to an external stimulus such as light, to form an optically responsive ink, as a prototypical smart hybrid material.”

Electrochemical exfoliation of graphene is a promising route towards scalable and fast production of graphene dispersions. Dresden University of Technology and the Max Planck Institute for Polymer Research filed a patent application on an electrochemical exfoliation process, leading to high quality graphene with low defect concentrations [3]. Martin Lohe, co-inventor, said “Electrochemical exfoliation offers an expedited approach towards the preparation of high quality graphene at large scales. It is environmentally benign and can be adapted to natural carbon resources. The achieved graphene materials have already shown vast application capabilities such as batteries, supercapacitors, printable electronics, sensors, and more.”

Dresden University of Technology also focused on developing a platform for synthesizing mesoporous conductive polymer sheets with record high electrical conductivity. This result also demonstrated the first supramolecular self-assembly route for the bottom-up synthesis of polypyrrole nanosheets with a controlled mesoporous structure, paving the way for the development of low-cost, solution-based self-assembly techniques for sensors, electronics, and energy related applications [4].
Polymer Composites
The Graphene Flagship has had great success with its work on composite materials this year, with several products launched into commercial markets. In a collaboration with leading Italian design company MomoDesign, IIT developed a high-performance graphene-based coating for motorcycle helmets for the consumer market. The graphene coating improves heat management, protecting the helmet from damage and making it more comfortable to wear.

Making use of graphene’s conductivity, Avanzare collaborated with Ashland, a chemical manufacturing company, to produce a polymer resin for use in chemical storage tanks. Conductivity is important in chemical storage tanks to prevent the build-up of static charges that could cause explosions in volatile chemicals. This successful collaboration has led to Ashland replacing the metal tanks in their Spanish production plant with new graphene-based tanks, which are lighter and 30% cheaper to produce.

Commercial applications of GRM-based composites require exfoliation of GRMs on a large scale. The choice of solvents and additives for the exfoliation process an important consideration for the ultimate application of the material. CNR demonstrated exfoliation of graphene using perylene diimide as a surfactant, a widely-used polymer additive [1], in a new method that could greatly simplify the processing of graphene-polymer composites.

Talking about commercial application for graphene composites, Vincenzo Palermo, Leader of the Polymer Composites Work Package said “The use of graphene in composites has already led to products commercialized on a large scale. Industrial end-users are keen to better understand what can be achieved with graphene, and how it compares with more established technologies.”

A major challenge is the need to develop metrology and quality control for GRMs. To this aim, CNR reported a reliable method to follow the fragmentation of GRM nanosheets and determine their size distribution [2], based on an automatic image-processing, using a mathematical approach previously used to study the size distribution of galaxies. This quantitative analysis tool generates statistically representative data, essential in understanding the characteristics of graphene sheets used in composites. “This work was inspired by work done in the early 20th century, when chemists were challenged to find new techniques to produce, characterize and define polymers. One century after, we needed to invent new ways to characterize an additional class of materials, formed by repeating units in not one but two dimensions,” said Palermo.
Production
The Production Work Package targets industrial scale processing and production of GRMs, to develop cost-effective methods for commercial market applications. Specific targets are the automotive, aerospace and electronics industries, where GRMs’ multifunctional benefits are expected to make a significant difference.

The partners of the Production Work Package are an industrial equipment manufacturer (Aixtron), commercial producers of graphene (Avanzare, Graphenea and Grupo Antolin) and end users who would benefit from graphene in their products (Aernnova and Airbus). Our partners supply commercial-grade graphene to other partners within the Graphene Flagship to facilitate research across the Flagship. Ken Teo, Leader of the Production Work Package, stated “We play a vital role of bringing deposition technologies from the laboratory to industry. This enables graphene to be produced with high quality, consistency and significant quantities to be used in real world applications. One such example is in fire retardant materials, where graphene is in qualification by Avanzare to be used in automotive and building applications.”

Avanzare scaled up production of graphene materials for supply to companies in the automotive, building and chemical industries. By adding graphene into a polymer composite, a flame-retardant plastic was developed in a collaboration between Avanzare and the Institute of Chemical Technologies Emerging Rioja. This composite uses the excellent thermal properties of graphene to quickly dissipate heat. In contrast to composites that do not contain graphene, melting and burning are suppressed. These flame-retardant graphene plastics were presented at Composites Europe 2016, Dusseldorf and K 2016, Dusseldorf, the largest international trade show for plastics and rubber.

This flame-retardant plastic and other graphene-based functional composites could lead to developments within the building and automotive industries. By integrating fire protection and security in smart building materials, early and efficient fire-detection systems can be set up, improving building safety and saving lives. Flame retardant materials are important in the automotive industry, as road vehicle fires are a significant problem, with an estimated 70,000 occurring worldwide each year. To help counter this problem, demand for flame-retardant materials in the automotive industry has increased. The graphene-based fire-retardant plastics will be tested for the automotive industry, and their use in cars and other vehicles could significantly increase road safety.
The Graphene Flagship has partnered with a wide range of projects on the European and national levels that align with the aims of the Flagship’s diverse research program. The collaborations between the Core project and the Partnering Projects provide mutual benefits and foster a strong graphene community in Europe. Listed here are recent research highlights from several such projects.

**G-IMMUNOMICS:** The G-IMMUNOMICS project aims to assess the potential toxicological impacts of graphene and provide grounding for developing safe new medical technologies. G-IMMUNOMICS demonstrated that dispersions of few-layer graphene can play a key role in specific targeting of monocyte tumour cells in aggressive myelomonocytic leukaemia with no activity towards other immune cells [1], opening up new therapeutic possibilities beyond chemotherapies.


**PolyGraph:** The aim of the PolyGraph project is to develop processes for industrial-scale integration of graphene into thermoset resins, to make cost-effective composites for the aerospace and automotive industries. A recent highlight is the evaluation of the filtration effect that leads to non-uniform distribution of the graphene during processing [1], and the proposal of an innovative spray coating method to overcome this problem.


**GLADIATOR:** As part of the GLADIATOR project, which focuses on improving the size, quality and cost-effectiveness of chemical vapour deposition-grown graphene, the cytotoxic and genotoxic effects of GO and reduced GO on mouse lung cells were investigated [1]. Even at high doses of 200 µg /ml, exposure was found to be safe, with no significant cytotoxic or genotoxic effects observed.


**GRMH2TANK:** The GRMH2TANK project aims to use graphene develop high-performance and lightweight compressed hydrogen storage tank, for use in aerospace applications. The structural properties of individual tetrapods made of porous aerographite foams have been investigated, providing important guidance on the behaviour of close-packed networks of aerographite tetrapods that could be used as shock absorbers.


**GraNitE:** The GraNitE project focuses on using graphene in heterostructures with Group III-nitride semiconductors to make high-frequency electronic devices. Recent results include the investigation of atomic layer deposition of insulating Al₂O₃ onto graphene, demonstrating uniform, pin-hole-free films without inducing defects in the graphene [1], and a review of the state-of-the-art in graphene-nitride electronics [2].


**PHONAMP:** The PHONAMP project investigates the potential use of graphene nanostructures for applications in photonics and electronics. Under this project, the mechanical breakage of graphene studied [1], showing that CVD-grown graphene always breaks along wrinkles formed during growth, or transfer. As well as the mechanical breakage, this result has implications for the electrical properties, as the wrinkles affect graphene’s conductivity.


**GRIFONE:** The GRIFONE project studies the properties of graphitic films of semiconducting group III nitrides and group II oxides and applications in heterostructure devices. A recent highlight is the ab-initio investigation of the structure, interaction energy, and electronic properties of different stacking configurations of hexagonal AlN with graphene. Remarkably, a strong interface dipole is induced by the stacking which has implications for the adhesion and reactivity of the stacks.

In the Core 1 phase, the Graphene Flagship is reaching maturity in terms of internal organization and more defined innovation and technology aims, underpinned by a new technology and innovation roadmap to be released as an open access publication later in the year. Several companies have joined as Associate Members, and products developed by Flagship Partners and Associate Members are already reaching the markets.

We are present at major technology showcases, such as Mobile World Congress and Composites Europe. Tens of patents have been filed, and several spin-off companies created. We are beginning to see the realization of our initial mission to take graphene and related materials from the lab to the factory floor. The science and technology outlook is exciting and positive.

A lot of work is still needed and the close partnership and collaboration we developed in the Ramp-Up phase must now be channelled to reach the common goals. Several working groups and task forces have been created, which aim to bring us to a more project-managed structure, where all partners share the efforts (and the rewards) in reaching the key performance indicators set by close consultation with industry.

The new concept of Spearhead Projects was introduced at the Science and Technology Forum in February 2017. The first six projects will start in Core 2. These are ambitious, well-defined and application-oriented subprojects of the Graphene Flagship. They have clear objectives, motivated by future market opportunities and aim at significant breakthroughs. These will cover applications in high speed telecommunications, a new solar farm, a new pilot line for silicon-graphene batteries, new and smart RFID tags for the Internet of Things, new wearable sensors and smart textiles.

The second part of Core 1 will already see several Work Packages put down the basis for these new projects.

I am proud of what the Flagship has achieved. I am grateful to all the Partners and Associate Members for their passion and dedication and for their enthusiasm in responding to the increasing demands for development, innovation and market-driven research.

We are a strong, integrated, and open community and we are best equipped to face and overcome the challenges ahead, ensuring that Europe reaps the rewards of the Flagship investment.

Andrea C. Ferrari

Science and Technology Officer

Andrea C. Ferrari
The Graphene Flagship’s principal mission is to take technologies based on graphene and related materials from the laboratory to commercial applications. As such, innovation is a key focus of the Flagship. Bringing together research community and companies adding industry viewpoints to discussions has a great boosting effect on the innovation activities, which leads to new initiatives and paves the way for commercialization efforts.

In Core Project 1, the Graphene Flagship has participated in large conferences such as Composite Europe in Dusseldorf and Mobile World Congress in Barcelona, presenting focused Graphene Flagship exhibitions. As a trial, we also combined these exhibitions with Graphene Connect events, with great success. The interest in our technology demonstrators was evidenced in both the number of visitors and the vivid discussions.

The Graphene Connect events have proved to be very valuable tools in bringing together industry and Graphene Flagship partners and initiating future collaboration possibilities. The interplay between research and industry stakeholders is instrumental in order to find the right hot spots for innovations and it helps to aim the research efforts towards the most commercially promising application areas.

We have also started to witness the potential of graphene-based technologies to create market disruptions and transformational innovations. Graphene has the unique capability to enhance multiple product attributes concurrently, which is nicely demonstrated in the different applications for composite materials such as graphene-Derakane™, a resin developed by Avanzare in collaboration with Ashland, enabling production of pipes and tanks for potentially explosive atmospheres (ATEX) industrial areas; the enhanced motor cycle helmet by Italian Institute of Technology (IIT) in collaboration with Italian luxury design company Momodesign; and the world’s first car made with graphene in its bodywork, stemming out of joint efforts by University of Manchester and UK firms Haydale and Briggs Automotive Company.
Partners

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Guger Technologies OG
Varta Micro Innovation
Vienna University of Technology

BELARUS
Belarusian State University

BELGIUM
Catholic University of Louvain
University of Namur
Université libre de Bruxelles
IMEC

BULGARIA
Bulgarian Academy of Sciences, Institute of Mechanics
Nano Tech Lab Ltd.

CZECH REPUBLIC
J. Heyrovsky Institute of Physical Chemistry

DENMARK
Technical University of Denmark

ESTONIA
University of Tartu

FINLAND
Aalto University
Nokia Finland
University of Eastern Finland
VTT Technical Research Centre of Finland

FRANCE
Atherm*
CEA French Alternative Energies and Atomic Energy Commission
CNRS National Centre for Scientific Research
ESF European Science Foundation
Horiba scientific
Laboratoire national de métrologie et d’essais
Pixium Vision
Polymem
Thales
Université Montpellier
University of Lille 1
University of Strasbourg
UPMC Sorbonne Universités

GERMANY
Alcatel Lucent
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BASF SE
Bielefeld University
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Chemnitz University of Technology
CNM Technologies GmbH
Dresden University of Technology
EPCOS AG
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Hamburg University of Technology
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Max Planck Society
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Centro Ricerche Fiat S.C.p.A. (CRF)
CNT
CNR National Research Council
Delta-Tech S.p.A.
Dyesol Headquarters
FBK Bruno Kessler Foundation
Grimp S.r.l.
IIT Italian Institute of Technology
INFN - National Institute for Nuclear Physics
Italcementi Group
Leonardo
Libre S.r.l.
Nanesa
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Polytechnic University of Turin
Scuola Internazionale Superiore di Studi Avanzati
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University of Padova
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University of Salerno
University of Trieste
University of Tor Vergata

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University of Warsaw

PORTUGAL
University of Minho

SPAIN
Airbus
Autonomous University of Barcelona
Avanzare
The Biomedical Research Networking center in Bioengineering, Biomaterials and Nanomedicine (CIBER-BBN)
CIC BiomagUNE
CIC enerGUNE
CIC NanogUNE
CSIC Spanish National Research Council
Fundación IMDEA Nanociencia
Fundación para la Investigación, Desarrollo y Aplicación de Materiales Compuestos
Graphenea
Grupo Antolin
ICFO Institute of Photonic Sciences
ION2 Catalan Institute of Nanoscience and Nanotechnology
Institut d’Investigacions Biomèdiques August Pi i Sunyer (IDIBAPS)
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EMPA Swiss Federal Laboratories for Materials Science and Technology
ETH Swiss Federal Institute of Technology Zurich
University of Basel
University of Geneva
University of Zurich

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University of Antwerp
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CZECH REPUBLIC
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SIBERIA
Institute of Physics in Belgrade

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EMPA Swiss Federal Laboratories for Materials Science and Technology
ETH Swiss Federal Institute of Technology Zurich
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University of Geneva
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* Until 1 April 2016
The Graphene Flagship was launched by the European Union in 2013 as part of its largest research initiative ever. With a budget of €1 billion it represents a new form of joint, coordinated research initiative on an unprecedented scale. The overall goal of the Graphene Flagship is to take graphene from the realm of academic laboratories into European society, facilitating economic growth and creating new jobs, in the space of ten years. Through a combined academic-industrial consortium consisting of more than 150 partners in over 20 European countries, the research effort covers the entire value chain, from materials production to components and system integration, and targets a number of specific goals that exploit the unique properties of graphene.

Learn more at www.graphene-flagship.eu