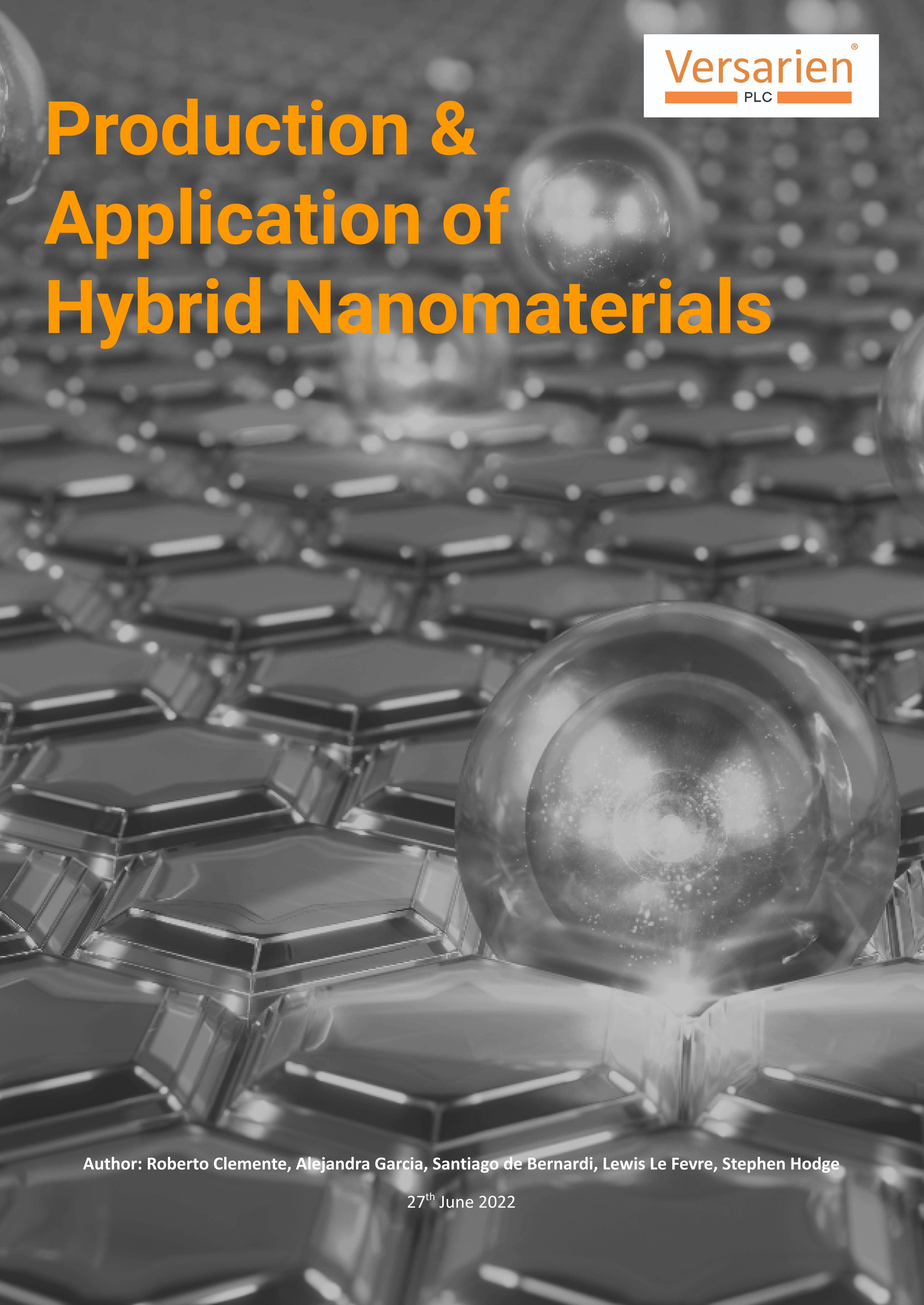

Production & Application of Hybrid Nanomaterials

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27th June 2022

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Glossary

AGV	Automated Guided Vehicle
BPR	Biocidal Products Regulation
BMS	Battery Management System
CDI	Capacitive Deionisation
CNTs	Carbon Nanotubes
CAGR	Compound Annual Growth Rate
DfT	Department for Transport
ECHA	European Chemicals Agency
EMI	Electromagnetic Interference
EPA	Environmental Protection Agency
ES	Energy Storage
EV	Electric Vehicle
FIFRA	Federal Insecticide, Fungicide, and Rodenticide Act
KERS	Kinetic Energy Recovery System
LIBs	Lithium Ion Batteries
MABs	Metal-Air Batteries
MRI	Magnetic Resonance Imaging
OER	Oxygen Evolution Reaction
OITB	Open Innovation Test Bed
ORR	Oxygen Reduction Reaction
PC	Polycarbonate
RGV	Rail Guided Vehicle

Introduction

Developments in graphene technologies have opened new possibilities in areas such as structural materials, textiles, coatings, and energy storage [1]. Although graphene brings a remarkable array of properties and functionalities to conventional materials, on its own, graphene does not have magnetic properties, is not a broadband antimicrobial material, nor is a catalytically active material.

Graphene-supported metal (oxide) nanoparticles form a very large family of materials whereby graphene provides a high surface area substrate that makes (oxide) nanoparticles accessible to the environment, allowing them to better perform their functions [2]. Graphene adds electrical conductivity to oxides, which are usually poor conductors; electron injection from graphene into oxides increases the concentration of holes in graphene and may increase the conductivity of the entire hybrid material. Synergistic benefits are observed in a number of applications such as battery and supercapacitor electrodes, as well as in electrocatalysis.

Gnanomat S.L. (Madrid, Spain), a subsidiary of Versarien plc, has developed a technological platform to design, manufacture and test hybrid materials that combine graphene/carbon materials with metal (oxide) nanoparticles using industrial procedures. With this approach it is possible to impart new or improved properties to the graphene affording a higher variety of products and applications and, hence could also enable better opportunities to address industrial applications (Fig. 1).

Table 1 shows a selection of graphene-metal oxide hybrid nanomaterials reported in the scientific literature; the possibility to manufacture so many different hybrid materials results in the creation of novel materials with a unique physicochemical profile that offer use for a variety of applications. Gnanomat has synthesised many of these materials (examples are shown in Fig. 2), and tested key candidates in a wide variety of applications that are reviewed in this white paper. Gnanomat's materials are designed and manufactured following industrial processes in order to demonstrate scalability and demonstrate that they can be part of real technological solutions for our customers as a key differential factor.

Table 1 Examples of graphene-supported metal (oxide) nanoparticles and their applications.

Metal (oxide)	Chemical Symbol	Example Applications	Refs.
Iron oxide	**Fe_3O_4, Fe_2O_3**	Biomedical applications including magnetic resonance imaging (MRI) and drug delivery, electromagnetic interference (EMI) shielding, energy storage applications, capacitive deionisation (CDI), CO_2 capture	[3–8]
Copper oxide	**Cu_2O, CuO**	Sensitive detection of glucose, removal of pharmaceuticals, degradation of organic dyes, antifouling paints, fungicide	[9–13]
Manganese oxide	**MnO_x**	Cathode of fuel cells and oxygen generation systems, electrocatalyst for metal-air batteries, electrode for energy storage devices, wastewater treatment, CDI	[14–19]
Zinc oxide	**ZnO**	Photocatalytic water treatment, catalyst to remove organic contaminants, biomedical applications, UV protection in personal healthcare, antimicrobial, gas sensors	[20–25]
Titanium oxide	**TiO_2**	Antimicrobial, self-cleaning surfaces, super-hydrophobic surfaces	[26,27]
Silver	**Ag**	Biomedical applications, catalysis, biofouling membranes, nanofiltration, fuel cells, solar cells, organic dye degradation	[28–37]
Niobium oxide	**Nb_2O_5**	Supercapacitor (aqueous- and organic-based electrolytes), anode for batteries, hydrogen storage/generation, solar hydrogen production	[38–41]
Ruthenium oxide	**RuO_2**	Nanocatalysts for lithium-oxygen batteries, hydrogen evolution reaction (HER) catalyst, hydrogen production, supercapacitor applications, redox flow batteries	[42–46]
Tungsten oxide	**WO_3**	Gas sensing, NIR absorber, photocatalysis	[47–52]
Vanadium oxide	**V_2O_5**	Supercapacitors, lithium ion batteries (LIBs)	[53–55]
Cerium oxide	**CeO_2**	Electrochemical sensors, LIBs, heavy metal removal from water, EMI shielding	[56–59]

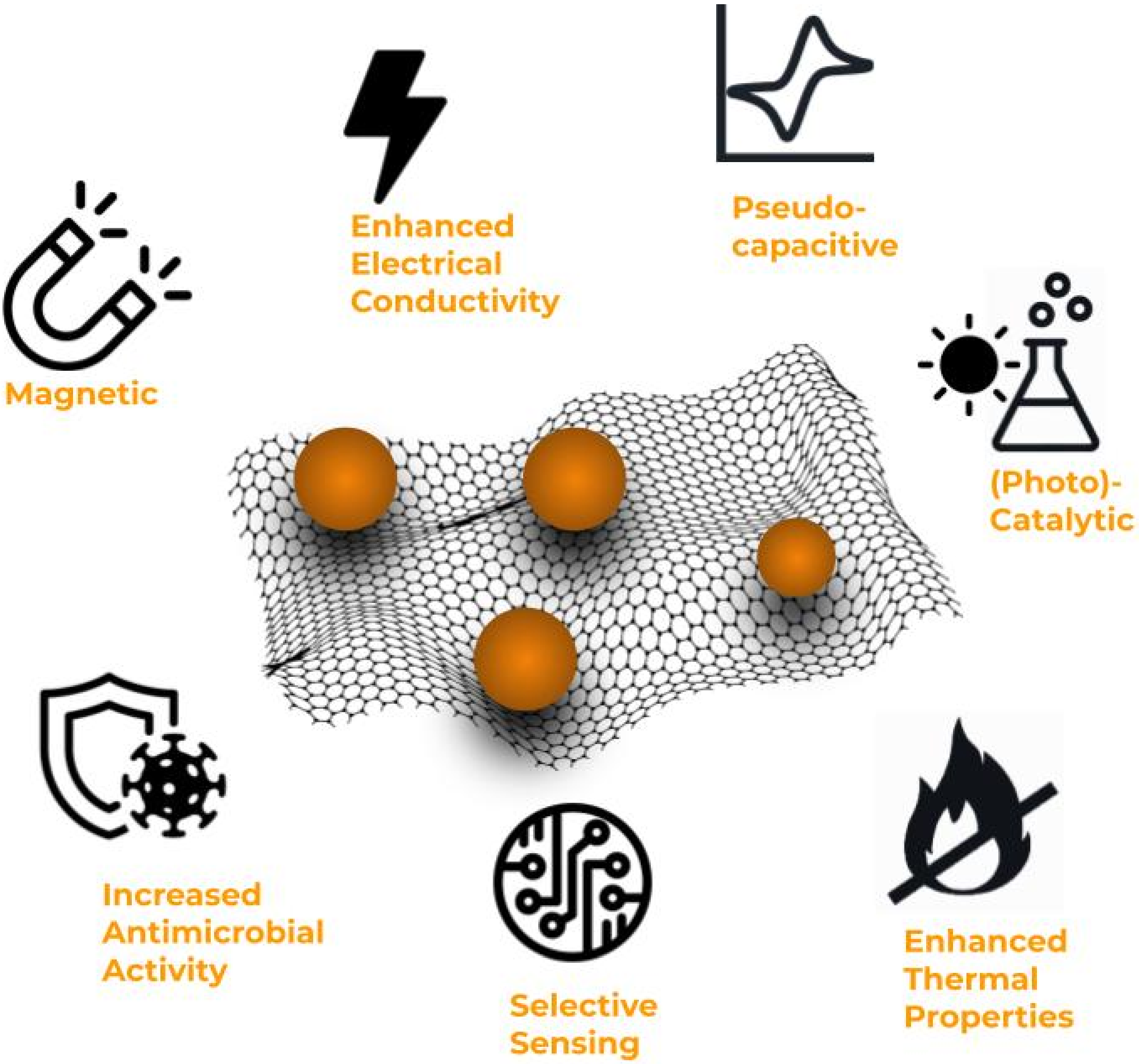


Fig. 1 Dual/multi-functional properties and applications that can be realised following surface functionalisation of graphene with metal (oxide) nanoparticles.

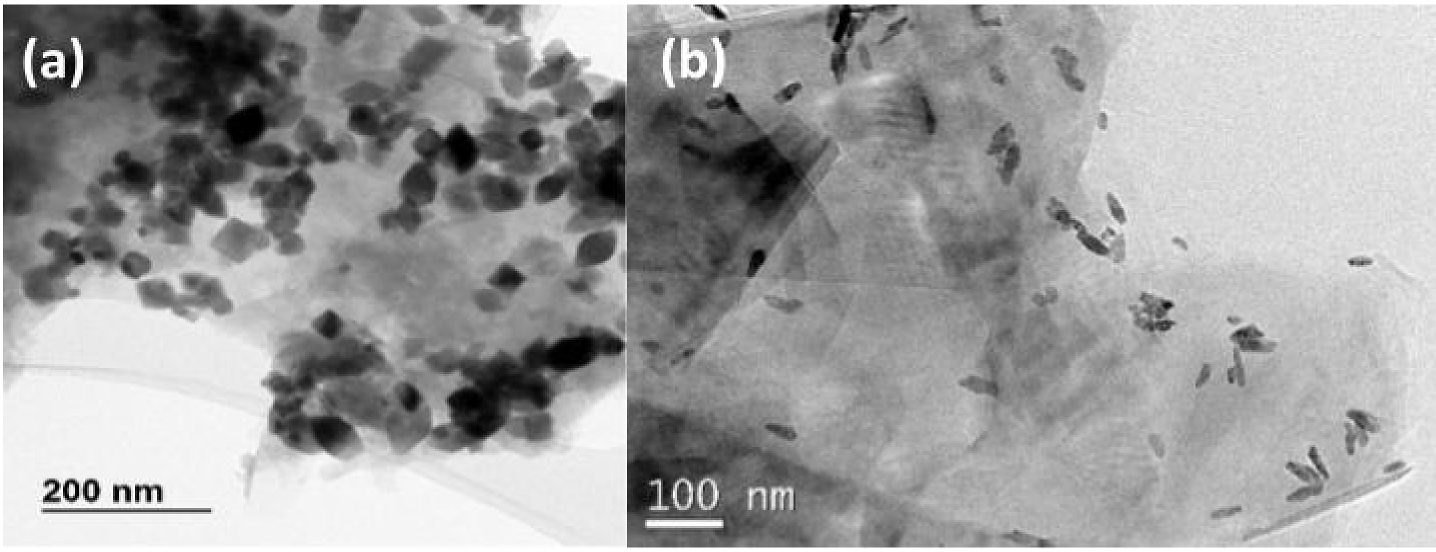


Fig. 2 TEM micrographs of Gnanomat's (a) graphene/manganese oxide hybrid nanomaterial and (b) graphene/copper oxide hybrid nanomaterial.

Hybrid Nanomaterials Manufacturing

The current methods for production of graphene-based hybrid materials require multi reactor chemical transformations, making their industrial production challenging and expensive. Gnanomat has patented [60] an environmentally friendly, safe (no need for hazardous or toxic chemical reagents or solvents) and straightforward method for the production of hybrid materials in a one-pot synthesis procedure, which lends itself to low cost industrial production. Thanks to the unique features of our technology, it has the potential to become the gold-standard method for industrial production of hybrid nanomaterials, offering a solution to overcome the critical barriers in actually exploiting the benefits of these materials in energy storage devices and beyond.

The hybrid nanomaterials manufacturing process follows a bottom-up strategy, where the metal (oxide) nanoparticles are synthesised on the graphenic surface by a controlled precipitation process (Fig. 3). Firstly, the metallic component is dissolved in a reactor vessel. Once a homogeneous solution is obtained, graphene is added to the reactor and dispersed. The following precipitation step requires extraordinary control as it is critical in determining the correct nanoparticle formation in terms of particle size, crystallographic properties and, hence, functionality of the final product. Following the reaction, the reactor vessel contents are transferred and the product filtered, dried and analysed. The hybrid nanomaterial synthesis process is protected by a family of patents [60] and company know-how.

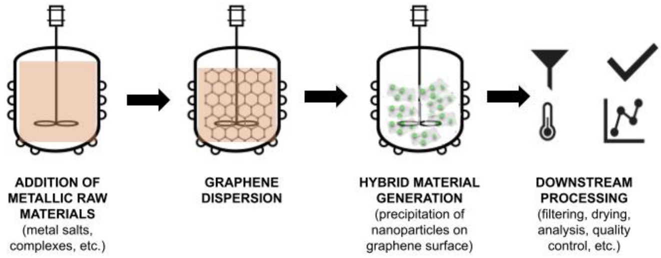


Fig. 3 Schematic of the bottom-up hybrid manufacturing process of the hybrid materials.

Our pilot scale production has been developed through two Horizon 2020 projects: GRAPHEEN (Green and straightforward process for the synthesis of Graphene-based nanomaterials) and INNPRESSME (open INNovation ecosystem for sustainable Plant-based nano-enabled biomateRials deploymEnt for packaging, tranSport and conSuMEr goods) [61]. Figure 4 shows a photograph of Gnanomat's current hybrid nanomaterials manufacturing pilot plant.

The process is also compatible with the manufacturing of other derivative support materials. For instance, it is possible to manufacture hybrid materials where the graphene is substituted by other carbonaceous materials such as carbon nanotubes (CNTs), activated carbons, etc. Moreover, other opportunities exist in manufacturing the metal (oxide) nanoparticles on their own without a nanocarbon support.

Fig. 4 Gnanomat's pilot plant for hybrid nanomaterial production.

GRAPHEEN INNPRESSME Open Innovation Test Bed

Hybrid Nanomaterials Portfolio

To date, Gnanomat has synthesised hundreds of different hybrid nanomaterials. The technological platform is highly versatile and offers several degrees of freedom: different ratios of graphene:nanoparticle, nanoparticles derived from different raw materials (typically metal salts/complexes), integration of two or more nanoparticles in the same hybrid material, the crystal structure of the nanoparticles, etc.

Thus far, Gnanomat has developed a preliminary list of materials that are available for academic and small scale purposes with different formulations (Table 2, Fig. 5). These materials were reported to have differential activity in energy storage, biocide, molecular biology, EMI shielding, sensing, CO_2 capture, etc. Some of these markets and applications are being explored with final customers and integrators that provide notorious market-fit information for commercial exploitation.

Table 2 Gnanomat's graphene-supported metal (oxide) nanoparticle hybrid nanomaterial portfolio and their applications.

Product Name	Composition	Applications
Graphene – MnOx	**Graphene-Manganese Oxide**	Electrical energy storage systems as active material in supercapacitor electrodes and as a LIB anode material. Catalysis, water purification and chemical sensing
Graphene – ZnO	**Graphene-Zinc Oxide**	Electrical energy storage systems as active material in supercapacitor electrodes and as a LIB anode material. (Photo)catalysis, photocurrent generation and antibacterial applications
Graphene – CuO	**Graphene-Copper Oxide**	Catalysis, sensors, energy storage and antimicrobial applications.
Graphene – Ag	**Graphene-Silver**	Inks on textiles for highly conductive wearable electronics, electrochemical sensors, detection of heavy metal ions, catalysis and antibacterial applications
Superparamagnetic Graphene	**Graphene-Iron/Manganese Oxide**	Graphene with superparamagnetic properties - the nanomaterial has shown interesting features for biomedical applications such as magnetofection and hyperthermia applications, EMI shielding and wastewater remediation

Fig. 5 Gnanomat's portfolio of hybrid nanomaterial products.

Energy Storage Applications

There is a great dependency of LIB technology at the moment, that correlates with a remarkable dependency on lithium as a raw material and their providers. Furthermore, most assemblers of LIBs are located in Asia with a very minor contribution from Europe. The UK and EU are making great efforts to react to this situation supporting the internal development of competitive technologies to supply raw materials from their sources and the construction of gigafactories to assemble and distribute to local markets. However, it is of key relevance that the industry discovers environmentally friendly alternatives to lithium and other critical materials. With surging demands from Electric Vehicle (EV) constructors, a large opportunity for technologies that can provide viable alternatives in this area exists.

The Ragone plot (Fig. 6), which charts ES technologies according to their Energy vs Power performance highlights a massive opportunity for solutions that improves both Energy and Power, together with other requirements such as cost reduction, avoiding critical materials (Li, Co, etc.), and improving the safety of the devices, etc.

Graphene is incorporated into ES devices in various structural elements of the devices, with particular relevance as electrode materials due to its high surface area and electrical conductivity. Gnanomat has undergone significant R&D into **supercapacitors** utilising graphene and graphene-supported metal oxide hybrid nanomaterials in the development of electric double layer capacitor (EDLC) and electrochemical pseudocapacitor type devices.

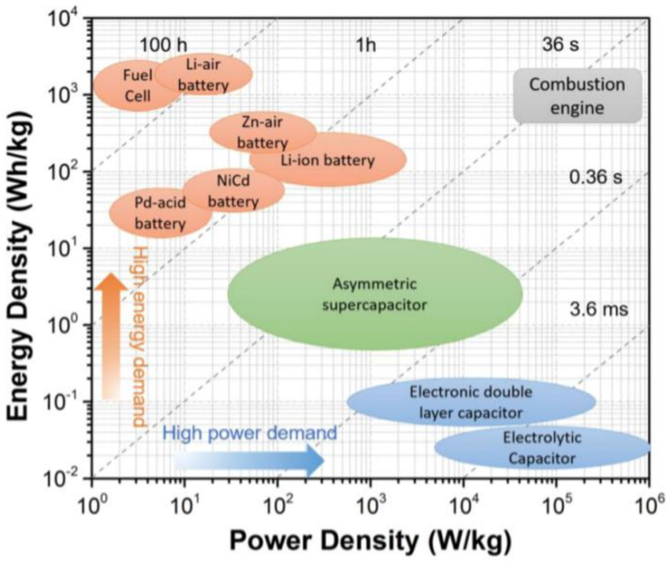


Fig. 6 Ragone plot illustrating the performances of specific power vs specific energy for different electrical energy-storage technologies. Times shown in the plot are the discharge time, obtained by dividing the energy density by the power density. Reprinted with permission from ref. [62]. Copyright © 2018, American Chemical Society.

Today, supercapacitors are found in Micro-Smart Grids, covering peaks of Energy demands, elevators or cranes, where energy is required in a short space of time (great alternative for power demands), and in Automated Guided Vehicle (AGV)/Rail Guided Vehicle (RGV) among some industrial applications. Kinetic energy recovery systems (KERS) or start-and-stop solutions are also an ideal application for supercapacitors in EVs. The penetration of pseudocapacitors could help to improve the current state of the art devices in the Ragone plot offering better energy vs power profiles. The supercapacitor market, according to forecasts, will grow with a CAGR over 20% in the following years to reach a market size of $28 bn in 2028 [63,64].

In an EDLC, energy is stored at the surface of the electrode either through fast reversible redox reactions or accumulation of ions on the electrode surface. These processes can occur in the order of seconds meaning that supercapacitors have higher power capabilities than batteries. Therefore, this makes supercapacitors more suitable for applications requiring rapid energy delivery and recharging.

Among Ganomat's hybrid nanomaterials portfolio, pseudocapacitive behaviour is typically observed. Briefly, this property is the additional capacitance generated as a result of electrochemical reduction and oxidation (redox) reactions related to the metal (oxide) nanoparticles. This can be observed during cyclic voltammetry measurements (Fig. 7). This technology offers a great innovation opportunity by the implementation of novel electrodes with enhanced performance.

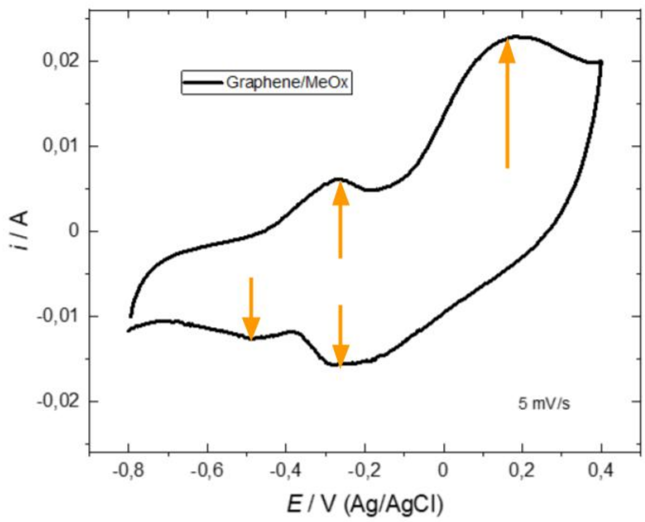


Fig. 7 Cyclic voltammetry of a typical graphene/metal oxide electrode during a three-electrode measurement. Orange arrows indicate the increased pseudocapacitive contribution arising from redox reactions of the metal oxide nanoparticles.

Production & Application of Hybrid Nanomaterials

Gnanomat has designed a family of hybrid nanomaterials that have shown a remarkable capacitance performance versus current market standard electrode materials (Fig. 8) due to the pseudocapacitance contribution by the metal (oxide) nanoparticles in combination with graphene. To demonstrate the use of these materials as electrode materials in ES devices, we designed and developed asymmetric pouch cell devices in collaboration with CIDETEC (Spain), an independent development centre. Asymmetric devices are built with one electrode bearing Gnanomat's hybrid nanomaterials and the other electrode with activated carbon, a market standard material. Results shown in Fig. 9 confirmed that Gnanomat's hybrid nanomaterials can provide enhanced performance of whole devices and paved the way to perform further developments by improving electrode slurries, cell design, electrolytes, etc.

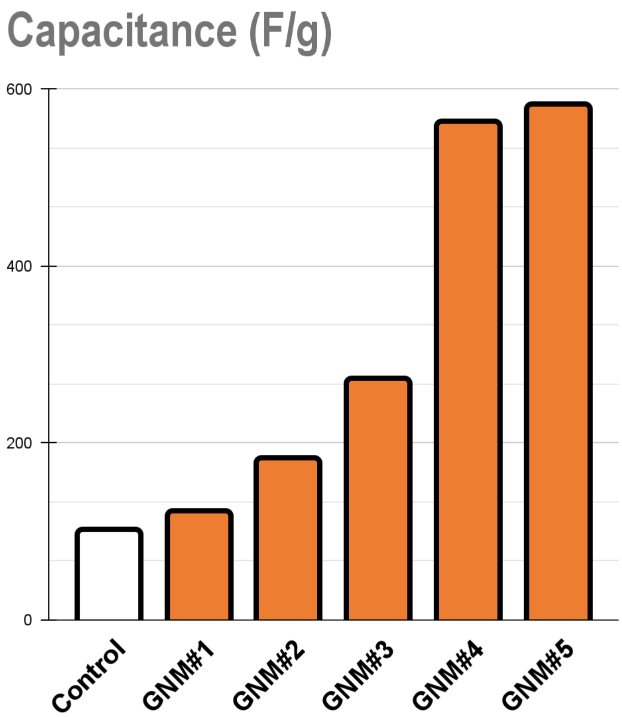


Fig. 8 Capacitance of different hybrid nanomaterials compared to a market standard activated carbon electrode.

Gnanomat's hybrid nanomaterials platform is being utilised in the INNPRESSME project in work package 5 "Demo Case 2: Transport and Energy", where Gnanomat will design and manufacture hybrid bio-based materials for supercapacitor electrodes in collaboration with other partners.

Gnanomat is also upgrading the pilot plant to become an EU nanomaterials Open Innovation Test Bed

INN PRESSME Open Innovation Test Bed

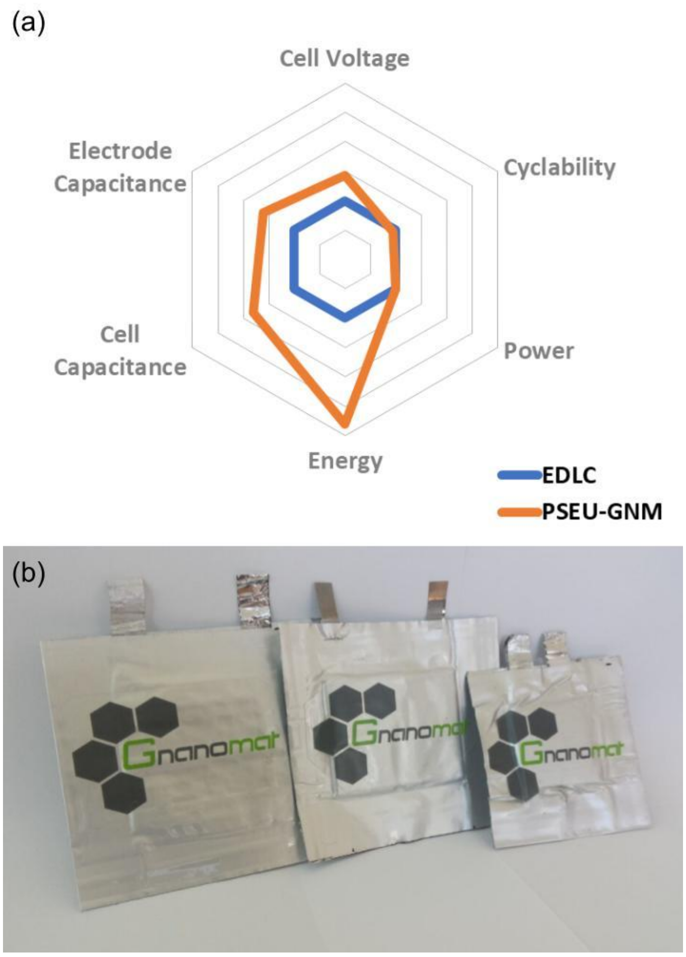


Fig. 9 (a) Improvement of Gnanomat asymmetric pseudocapacitor (PSEU-GNM) cells compared to a standard EDLC cell. (b) Photograph of manufactured pouch cells.

Versarien subsidiaries **2-DTech** (UK) and **Gnanomat** have worked together closely to develop and scale promising supercapacitor cells for commercial exploitation. Two types of cell have been scaled with impressive performance - **GMX (Asymmetric)** and **GWISE (Symmetric)** with datasheets available on request.

These cells were developed in project **SUPPORTIVE** (SUPercapacitors for zero emission PORT-sIde VEhicles), grant funded by the UK Department for Transport (DfT) in partnership with Innovate UK, part of UK Research and Innovation. **SUPPORTIVE** aims to convert a former diesel-powered shipping container tug vehicle to electric; talks are ongoing with several port authorities in Europe who are looking to transition to Net Zero emissions by the end of the decade and for whom replacing the current diesel vehicles is a particular challenge. Outside of this use case there is immediate application at airports and in EVs more generally where the cells will facilitate greater levels of regenerative braking and greater acceleration [65]. We are currently looking to enter into discussions with prospective UK cell manufacturing partners.

Catalytic Applications in Energy Storage

Catalysis is a process by which a reaction rate is enhanced by a small amount of the so-called catalyst, which supposedly does not undergo any change during the reaction. Metal oxides became prominent in the mid-1950s when they were found to effectively catalyse a wide variety of reactions, in particular oxidation and acid-base reactions [66]. The combination of graphene as a structural support for metal (oxide) nanoparticles has shown a good profile for the ORR (Oxygen Reduction Reaction) and OER (Oxygen Evolution Reaction) (Fig. 10) in laboratory scale tests, which allows potential exploitation in two key applications: metal-air batteries (MABs) and fuel cells.

Metal-air batteries (MABs) are an ES technology that can store large amounts of energy with a reduced weight since one of the electrodes is atmospheric oxygen. The MAB technology provides a clean, safe and reliable source of energy (theoretically up to four times that of LIBs), with a modest profile of power and a very limited weight and cost. Some of the applications of this ES technology range from back-up power solutions, to parking metres or feeding electric fences [67]. There is a major drawback to this technology, however, in its limited cyclability. In fact, there are only primary (non-rechargeable) batteries in the market due to the absence of alternatives that combine both ORR and OER reactions in the cathode of the battery in order to make secondary (rechargeable) batteries commercially viable. Gnanomat has conducted developments in collaboration with an independent institution to bring some of the materials with good profiles for ORR and OER to prototypes of secondary MAB. In these tests, secondary MAB electrodes containing Gnanomat catalyst optimised materials showed a satisfactory cyclability and confirmed viability to become a suitable alternative to state of the art devices. Also, the formulation of the hybrid nanomaterials tested exhibited very good safety and toxicity profiles, in contrast to some of the alternatives under development in this field where critical and toxic materials are typically used. These findings are part of a patent application that is already under review [68]. These results have allowed us to collaborate with MAB developers to bring these materials to commercial products. At the moment, we have tested our materials in the primary zinc-air battery, (current highest maturity MAB technology) with an industrial player with promising results with as yet un-optimised hybrid nanomaterials, suggesting a remarkable development opportunity towards bringing rechargeable MAB devices to market in the near future.

Fuel cells are considered to be an ideal source of energy due to their high efficiency, mild operation process, zero emission and most importantly, unlimited renewable source of reactants [56]. Recently, transition metal oxide based electrocatalysts have attracted tremendous attention suitable for the sluggish ORR and OER reactions due to their high activity. Other factors that promote their utilisation include low cost, high availability and the presence of variable oxidation states, attractive in replacing precious and low abundant platinum-based catalysts. The stability of metal oxide catalysts is still relatively poorly understood. Manganese oxide allotropes are commonly used but their degradation has been reported to be related to the production of hydrogen peroxide species on manganese oxides during ORR [70]. Some of Gnanomat's hybrid nanomaterials have been tested with alkaline fuel cell developers confirming suitability for use. This development is already ongoing but is also a very good example of how our materials are being tested in different applications, involving key commercial customers that can provide significant and relevant feedback.

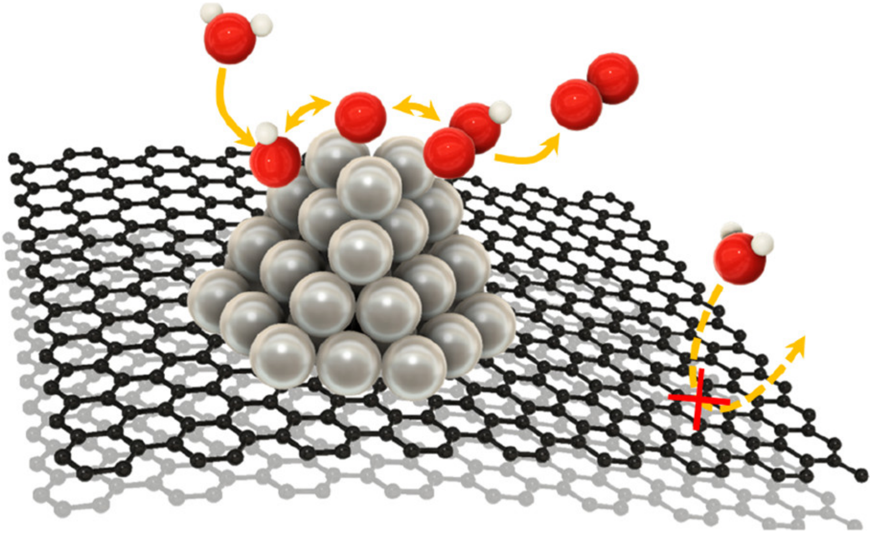


Fig. 10 Oxygen evolution reaction (OER) taking place on a metal oxide electrocatalyst surface. Reprinted with permission from Ref. [71]. Copyright © 2019 American Chemical Society.

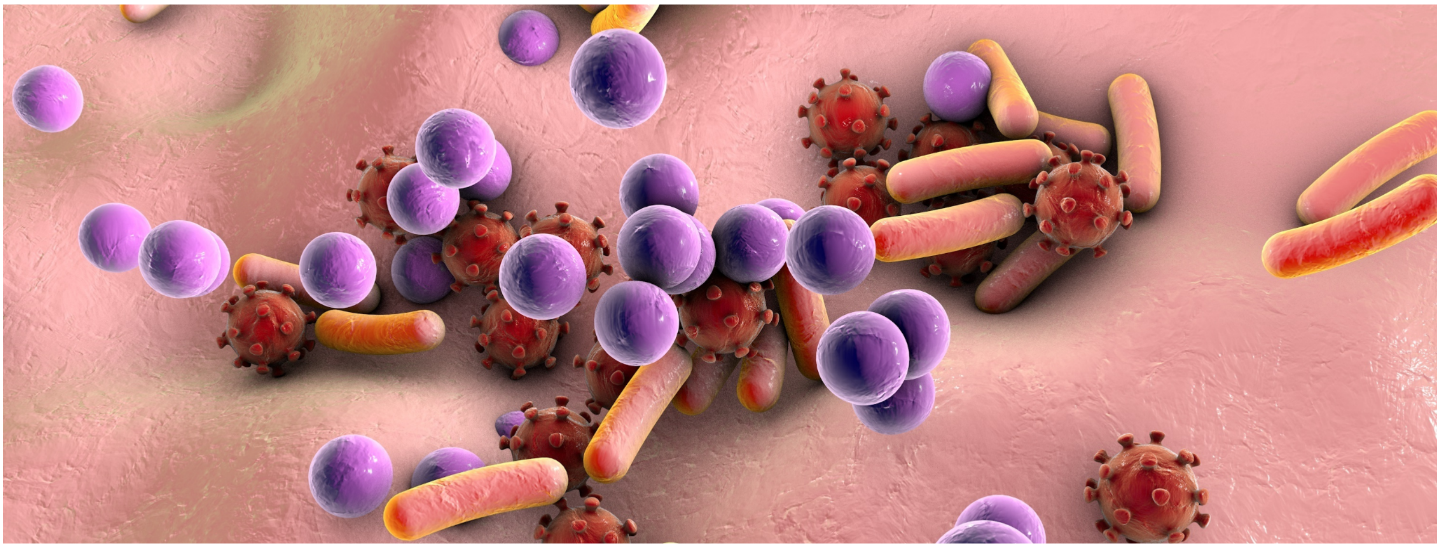
Antimicrobials

Over the last few years, and due to the massive impact of the COVID-19 pandemic at both health and economic levels, a new demand for biocide products and solutions has arisen. In addition, there are other trends that boost the identification and commercialization of new biocides solutions including the antibiotic resistance strains of different bacteria, which is pushing the innovation of alternative tools to fight these microorganisms. Another trend is the high cost of healthcare by creating safer spaces incorporating biocidal surfaces. All together, there is a developing market opportunity from coatings to textiles or polymers integrating biocidal materials. There is a global antimicrobial surface market estimated at $4.0 bn in 2019 and a CAGR of 13.3% which is expected to reach a market size of $11.6 bn in 2027 [72].

The ability of metal (oxide) nanoparticles to exhibit antimicrobial effects is well known. In addition, the biocidal effect of graphene on its own against different pathogens has been reported, which has led to reported synergistic effects of both types of material when combined in a hybrid material [73].

Within Versarien, the behaviour of hybrid materials was explored initially for severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2). Tests, performed in collaboration with Ankara University, showed a specific and strong effect in the deactivation of SARS-CoV-2, by reducing from 2-4 levels of magnitude (99% and 99.99% of viral replication reduction). These tests confirm the effect not only in an enveloped virus but more importantly in the virus that caused the recent COVID-19 pandemic, in contrast with other tests where the viral model is a surrogate of this virus due to the difficulties to handle a pathogen under research environments. This study confirmed the antiviral properties of our hybrid nanomaterials materials and opened the opportunity to apply these properties to other viral pathogens and into materials or formats that could be marketed as inks, coatings, or other products such as air filters [74].

Through conducting these assays we obtained a great demonstration of the potential of the hybrid nanomaterials platform. We discovered two candidates - one material with a very strong effect towards SARS-CoV-2 and another with a milder effect but with reduced cytotoxicity. This affords alternative downstream products, for example, the hybrid nanomaterial profile with mild effect/low cytotoxicity for applications with restricted safety and regulatory requirements, whereas in applications that require the strongest antiviral effect or because human exposure requires lower regulatory restrictions the strong effect hybrid nanomaterial could fit better. Again, the possibility to have a tunable platform favours the fitting of these products into real solutions [75].



Production & Application of Hybrid Nanomaterials

During the COVID-19 pandemic, 2-DTech also developed an antimicrobial coating for Airway Medical's Suction Unit (AMSU^{TM}), a portable suction device for clearing blocked airways in emergency and chronic conditions. The protective coating was required to offer a back-up line of defence to reduce pathogen loading in countries around the world where sterilisation facilities are likely to be sub-optimal. The active ingredient of the coating is based on Gnanomat's graphene/metal (oxide) hybrid nanomaterials. The hybrid nanomaterial was dispersed into a polymeric coating that could be deposited onto the exterior of AMSU bottles (Fig. 11) by dip or spray coating. The bottles were made of polycarbonate (PC) plastic, and so hybrid nanomaterials were first deposited on PC discs to perform biological assays. The biocidal effect of these surfaces was evaluated against pathogens from bacteria sources (gram positive and negative models) and a viral model (escherichia coli, staphylococcus aureus and bacteriophage MS2) following the BS EN ISO22196 testing protocol. In these tests the biocide effect was also observed either with long (24 hours of pathogen exposure to treated surface) and short (1 hour of exposure) with a reduction of up to three levels of magnitude (99.9% pathogen inactivation).

In this study, not only was the biocide functionality confirmed, but more importantly, wide biocidal pathogen scope was demonstrated.

The above works illustrate how our materials are not only functional but also industrially viable, since they can be produced through industrial manufacturing processes, in contrast to other alternatives. However, before we can introduce these hybrid nanomaterials products to the market, we need to address various regulatory concerns. Depending on the sort of application and usage of these products a different regulation will apply for example if the product is a medical device or is a biocidal product. For biocidal applications, registration of a new "active substance", regulated by the Biocidal Products Regulation (BPR) in the EU enforced by the European Chemicals Agency (ECHA), or by the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), enforced by the Environmental Protection Agency (EPA) in the US.

Fig. 11 Optically transparent antimicrobial coatings developed using Gnanomat's hybrid nanomaterials.

Magnetism

Of all the properties hybrid nanomaterials can possess, magnetism is probably the most interesting, since graphene is typically non-magnetic. Based on the alignment and response of magnetic dipoles, materials are classified as diamagnetic, paramagnetic, ferromagnetic, ferrimagnetic, antiferromagnetic as shown in Figure 12 [76].

Diamagnetism is a very weak form of magnetism that is induced by a change in the orbital motion of electrons due to an applied magnetic field. This magnetism is nonpermanent and persists only in the presence of an external field.

Paramagnetism is a form of magnetism whereby some materials are weakly attracted by an externally applied magnetic field, and form internal, induced magnetic fields in the direction of the applied magnetic field.

Ferromagnetism comes from the term 'ferrous' meaning iron, the first type of metal discovered to exhibit attraction to magnetic fields. Ferromagnetism is the basic method in which a compound forms a permanent magnet or is attracted to a magnetic field. It arises from the spontaneous lining up of permanent dipoles parallel to each other within a compound.

Antiferromagnetic materials are like ferromagnets but their magnetic moments align antiparallel to the neighbouring moments. This alignment occurs spontaneously below a critical temperature known as the Néel temperature. Antiferromagnets are less common compared to the other types of magnetic behaviours, and are mostly observed at low temperatures.

Ferrimagnetism can be defined as a kind of magnetism where magnetic moments have opposing moments similar to that of antiferromagnetism; however, the antiparallel moments do not cancel each other out, and a spontaneous magnetization occurs in absence of coercivity below the Néel temperature.

Superparamagnetism is a form of magnetism which appears in small ferromagnetic or ferrimagnetic nanoparticles. In sufficiently small nanoparticles, magnetization can randomly flip direction under the influence of temperature. The typical time between two flips is called the Néel relaxation time. In the absence of an external magnetic field, when the time used to measure the magnetization of the nanoparticles is much longer than the Néel relaxation time, their magnetization appears to be in average zero; they are said to be in the superparamagnetic state. Their magnetic susceptibility (the degree to which a material can be magnetised in an external magnetic field) is much larger than that of paramagnets.

Figure 13 shows a typical magnetization curve for ferromagnetic/ferrimagnetic nanoparticles showing the characteristic positions on the curve associated with saturation magnetization (Ms, maximum induced magnetization), remanent magnetization (Mr, induced magnetization remaining after an applied field is removed), and coercivity (Hc, the intensity of an external coercive field needed to force the magnetization to zero). Ferromagnetic particles show a hysteresis whereas the response of superparamagnetic nanoparticles to an external field follows a similar sigmoidal curve but with no hysteresis.

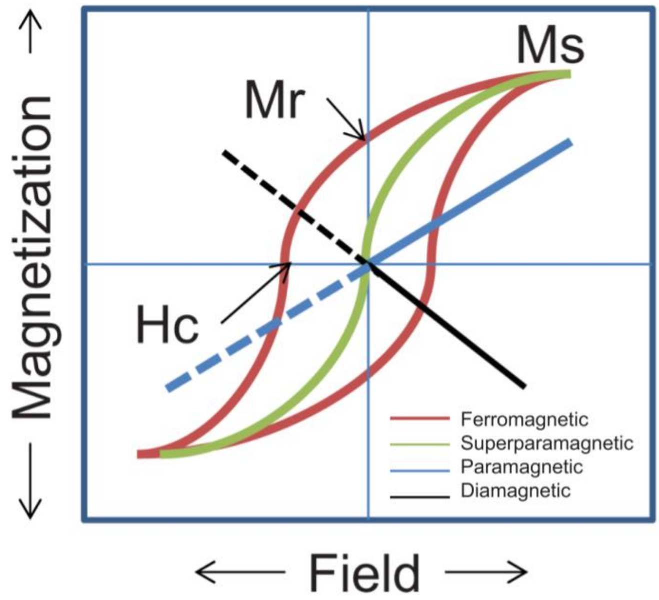


Fig. 13 Magnetic behaviour under the influence of an applied field. The x-axis is the applied field (Oe, oersted), and the y-axis is the magnetization of the sample as a function of field exposure (emu/g). Ms (saturation magnetization), Mr (remanent magnetization), Hc (coercivity).

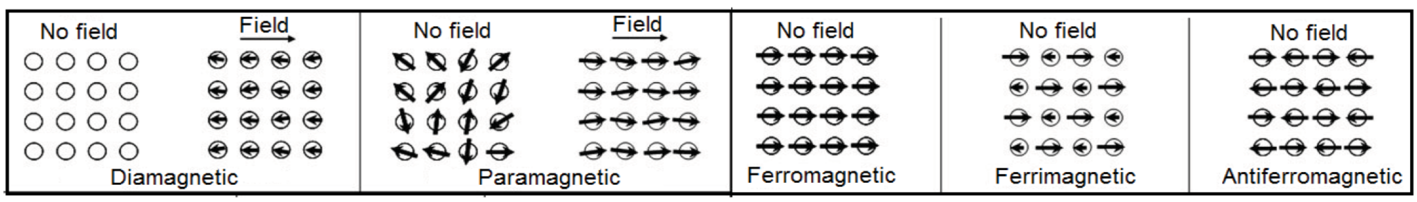


Fig. 12 Magnetic dipoles and behaviour in the presence and absence of an external magnetic field.

Production & Application of Hybrid Nanomaterials

New to Gnanomat's hybrid nanomaterials portfolio is a graphene-based material that exhibits superparamagnetic properties which offers a whole new frontier to generate new products for a variety of applications (Figs. 14, 15). The combination of magnetic nanoparticles and graphene creates a very interesting tool to be exploited in biotechnology, nanobiotechnology and biomedicine applications, in processes such as magnetofection, drug delivery and others. The possibility to localise these nanostructures in specific body areas can be very useful as Drug Delivery Nanocarriers or in cancer therapies [77]. Due to the regulatory concerns, *in vitro* applications show less restraints to adopt these kinds of tools, however, Gnanomat's hybrid nanomaterial toxicity has already been tested to some extent by the Toxicology Research Group of ICCRAM-Universidad de Burgos in the project NANOCOMP [78], concluding that materials analysed can be considered as non-irritant nanomaterials according to the EU and United Nations' Globally Harmonised System of Classification and Labelling Chemicals [79].

Fig. 14 Gnanomat's Superparamagnetic Graphene hybrid powder reacting to a magnetic field.

Beyond biomedical applications, one of the most interesting applications of the magnetic hybrid nanomaterials is EMI shielding, an ever increasing problem over the last decades due to an increase of the exposure of high-power electromagnetic pollution in both civil and military situations. Hence, there is an existing and growing demand for industrial solutions designed to quench and absorb the electromagnetic footprint. Another application of these magnetic nanomaterials is in wastewater remediation. The adsorption and removal of contaminants such as dyes and heavy metals can be achieved since graphene provides a high surface area to adsorb contaminants. The magnetic manipulation afforded by the metal oxide nanoparticles, demonstrated in Figure 14, could be used to recover and recycle these hybrid nanomaterials so that they can be reused a number of times.

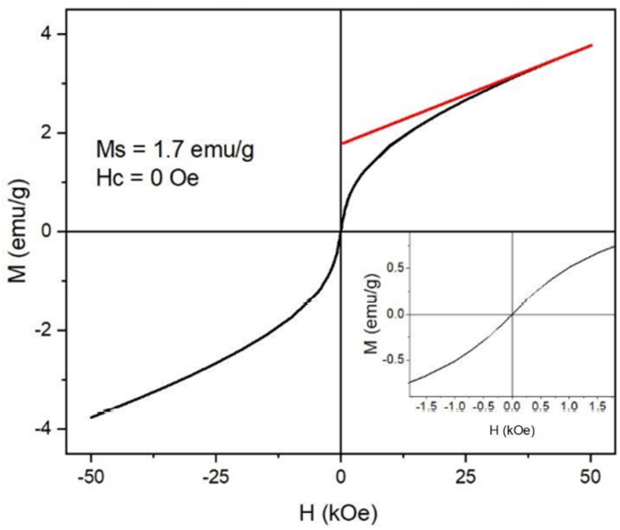


Fig. 15 Magnetic behaviour of Gnanomat's Superparamagnetic Graphene hybrid nanomaterial powder (null coercive field).

Our magnetic hybrid materials are an excellent alternative to develop fine solutions to develop downstream materials (coatings, textiles, etc.). All the properties of these materials need to be tested in products as masterbatches, inks or polymers as vehicles to bring the benefits of this material to the final applications.

Summary & Future Outlook

In this white paper, we have described the progress achieved with our hybrid nanomaterial platform. In the area of energy storage systems, Gnanomat is developing pseudocapacitor technology with an enhanced profile to conventional products. We have explored our material as electrodes in metal-air batteries achieving a strong proof of concept to bring this technology to the market with the absence of contaminant materials and great cyclability. We have also accumulated promising results in the area of alkaline fuel cells where our products could also be used. To exploit these opportunities, Gnanomat is one of the partners of the Open Innovation Test Bed of INNPRESSME that will give us access to collaborate with innovative industrial players. Gnanomat is also a member of the European Batteries Alliance (EBA250), Batteries Europe, BatteryPlat, Materplat and is an associate member of WP12 (Energy Storage) of the EC's Graphene Flagship project.

Although Gnanomat was born with the idea to develop novel materials to provide solutions to energy storage systems, it is apparent how hybrid nanomaterials are beginning to pave the way for opportunities in many more diverse sectors. Materials have been developed with enhanced antimicrobial properties and magnetic properties; not only have we synthesised a wide array of key candidates for different applications, our know-how of the whole synthesis process has increased significantly. A major part of this learning has been in tailoring the nanoparticle size and crystallographic properties to make them suitable for such diverse applications.

The exploration and exploitation of these alternative industrial pathways is aligned with the strategy of diversification to create more success opportunities, but also to speed up the time-to-market involving from the first steps of development the technology integrators and customers. Our strategy is to generate a wide portfolio, not of formulations, but of innovative products, protected by means of patents and other Intellectual property assets, to deliver solutions at large scale. We also aim to expand our actions in the value-chain to be more than a raw materials supplier to a technology and innovation partner for our customers. To do so, we seek to confirm market-fit of developments with industrial players from a very early stage. The next step is to analyse the business opportunities and identify the best partners in order to create the right collaborations to move each development forward.

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