Creating Value from Non-carbon 2D Materials - beyond Graphene

A State of the Art Review

Table of contents

Executive Summary

The ability to isolate or grow two-dimensional (2D) materials has been a source of scientific fascination ever since it was shown to be possible with the isolation of graphene from graphite in 2004 at the University of Manchester in 2004. The increasing range of 2D materials extends far beyond graphene and its carbon analogues. It is believed that over 500 2D materials have been developed globally so far and these materials exhibit an exciting range of novel properties that open the door to a multitude of new potential applications.

Research in non-carbon 2D materials is accelerating at a rapid pace with significant contributions from UK research groups and materials producing SMEs. Clear progress has been made with the commercial availability of *hexagonal Boron Nitride, hBN,* and the growing industry interest in *transition-metal dichalcogenides (TMDCs)*, in particular semiconductor TMDCs such as molybdenum disulphide (MoS_2) which have direct gap and are attractive for optics and optoelectronic devices. There is also a particular excitement about the ability to custom stack thin layers of non-carbon 2D materials and in combination with graphene to create hetero-structured devices. These devices have a variety of different electronic and optical properties, which can be finely tuned by careful design of the stack. Ongoing research is showing great promise for new materials with specially designed electrical, magnetic, piezoelectric and optical functionalities.

Research in non-carbon 2D materials has benefited from the investments in developing graphene with complimentary developments that address graphene's major weakness in its lack of a band gap; a property that makes silicon and other semiconductors so useful for digital electronics. 2D semiconducting materials are likely to become an attractive choice for constructing digital circuits on flexible and transparent substrates for applications such as paper-like transparent displays, wearable electronics and photonic devices. A range of industries recognise the benefits they can derive from these new materials and have expressed the need to have greater understanding of the industrial challenges they will face.

This has led to the KTN undertaking a short project to bring together leading companies and academics working on 2D materials and devices from across UK and to meet with potential industry users and the wider supply chain to explore the challenges faced in bringing these 2D materials to market. This output from the project includes this state of the art report, which reviews the current innovation landscape and captures the views of senior academics and industrialists in terms of where the UK should be heading to create commercial value from developments in non-carbon 2D materials.

This KTN study has identified a body of work being undertaken globally to develop non-carbon 2D materials, mainly led by university research groups. Companies such as Samsung and IBM are active in this area and so are UK SMEs such as Thomas Swan. The discussions KTN have had with UK companies suggest that existing businesses with an interest in developing commercial applications for graphene are the ones most likely to look at exploiting other 2D materials. The following were noted as the priorities for the UK in our bid to create commercial value from current research and industry activities:

- More work needed to scale up the manufacturing and use of 2D materials;
- Funding is needed to improve manufacturing techniques for 2D materials, devices and products;
- UK industry needs to be more open about their trends and drivers with regards to 2D materials and to work closely with academic researchers to develop technology roadmaps for mass production and application of 2D materials.

Following considerable discussions with industry experts and academics, the following recommendations are made to both government and industry to drive forward the commercialisation of non-carbon 2D materials in the UK.

1. Create an Industry Challenge around hBN and MOS_2 to accelerate the development of supply chain and end user partnerships.
2. Provide 5-10 years long term funding for centres of excellence to carry out more work needed in scale-up of non-carbon 2D material production, device fabrication and end-user applications.
3. Consider the overall UK landscape and alignment with the EU Graphene Flagship project.
4. Invest in scaled-up demonstrators to show and exploit the game changing properties of non-carbon 2D materials, solely or in combination with graphene.

Glossary of Non-Carbon 2D Materials

CuO – Copper oxide

hBN - hexagonal Boron nitride

HfS2, - Hafnium disulfide

$LaNb_2O_7$ - Lanthanum niobate

MnO_2 – Manganese dioxide

MoO_3 - Molybdenum trioxide

MoS_2 - Molybdenum disulfide

$MoSe_2$ - Molybdenum diselenide

$MoTe_2$ - molybdenum ditelluride

NbS_2 - Niobium disulfide

$NbSe_2$ - Niobium diselenide

$Ni(OH)_2$ – Nickel hydroxide

ReS_2 – Rhenium disulfide

$ReSe_2$ – Rhenium diselenide

RuO_2 – Ruthenium dioxide

SnS_2 - Tin disulfide

$SnSe_2$ – Tin diselenide

TaS_2 – Tantalum disulfide

TiO_2 - Titanium dioxide

TiS_2 - Titanium disulfide

$TiSe_2$ - Titanium diselenide

TMDC - Transition-metal dichalcogenides

VS_2 - Vanadium disulfide

VSe_2 - Vanadium diselenide

WO_3 – Tungsten trioxide

WS_2 - Tungsten disulfide

WSe_2 - Tungsten diselenide

WTe_2 - Tungsten ditelluride

ZrS_2 - Zirconium disulfide

1. Introduction

Two-dimensional (2D) materials are new and expanding family of materials with exceptional properties. Graphene is currently the most famous of these 2D materials, which although one million times thinner than paper is the strongest material known to science. It is made up of carbon atoms arranged in a hexagonal lattice and has many superlative properties to its credit. The unique combination of superior electrical, optical and mechanical properties make graphene an incredible material for diverse applications across many sectors. The UK has been a global leader in research on graphene since its isolation from graphite crystal at the University of Manchester in 2004.

The ability to isolate or grow 2D materials has been a source of scientific fascination ever since it was shown to be possible, with the isolation of graphene leading to the discovery of a whole family of 2D materials, including large number of atomic layers derived from non-carbon 2D materials such as hexagonal boron nitride (hBN) and molybdenum disulphide (MoS_2). These can be combined with graphene to create exciting new devices and products. This field is accelerating at a rapid pace and significant contributions have been made by UK researchers, which includes the ability to build custom-made structures (hetero-structures) by stacking combinations of 2D materials on top of each other and constructing libraries of crystals to provide specific electrical, thermal, physical or mechanical properties and functionalities. A number of these non-carbon 2D materials address graphene's major weakness in its lack of a band gap, which is what makes silicon and other semiconductors so useful for digital electronics. 2D semiconducting materials are likely to become an attractive choice for constructing digital circuits on flexible and transparent substrates for applications such as paper-like transparent displays, wearable electronics and photonic devices. In addition, the mechanical properties of MoS_2 also appear to be very attractive. It is thought that there may be around 500 2D materials already developed, globally, including graphene.

Research in non-carbon 2D materials has benefited from the investments in developing graphene with activities in areas of material structure-property correlations, synthesis and nanofabrication, device integration and device characterisation studies. A range of industries recognise the benefits they could have from these new materials and have expressed the need to have greater understanding of the industrial challenges they will face.

This has led to the KTN undertaking a short project to bring together leading companies and academics working on 2D materials and devices from across UK and to meet with potential industry users and the wider supply chain to explore the challenges faced in bringing these 2D materials to market. The output from the project includes this state of the art report, which reviews the current innovation landscape and captures the views of senior academics and industrial community in terms of where the UK should be heading to create commercial value from developments in non-carbon 2D materials.

Definition of 2D Materials

An ISO terminology standard ISO/TS 80004-13:2017: 'Graphene and related two-dimensional (2D) materials' is in preparation to provide a common definition of 2D materials. The current draft defines 2D materials as "*one or several layers with the atoms in each layer strongly bonded to neighbouring atoms in the same layer, which has one dimension, its thickness, in the nanoscale or smaller, and the other two dimensions generally at larger scales".*

2. Family of Non-carbon 2D Materials

Some academics claim that non-carbon 2D materials can outperform graphene and pave the way to an exciting range of novel applications. They base their views on the fact that graphene has failed to deliver the required electrical and optical performance for applications such as photodetectors or digital electronics due to the lack of band gap. The band gap property/function is often found in other 2D materials, which in turn can be tuned through material processing, for instance, by changing the number of layers. A summary of the most known and researched non-carbon 2D material families is shown in Table 1. One example is the 2D *hexagon Boron Nitride, hBN*, also called "white graphene". hBN exhibits a natural band gap whilst providing good thermal conductivity. Another family of non-carbon 2D materials are the *transition-metal dichalcogenides (TMDC)* nanosheets. This family of layered materials, which include molybdenum disulphide (MoS_2), stabilise in a similar hexagonal structure and can exhibit a wide range of electronic properties ranging from semiconductor, metallic and even superconducting properties. This can be achieved by manipulating their composition, geometry, thickness and electronic density (Novoselov, 2016). Another family are the *2D oxides* such as layered CuO, MoO_3 and WO_3. These are known to exhibit lower dielectric constant but larger band gaps than their 3D equivalents. Other 3D oxides have been reported to have been successfully exfoliated down to monolayers to create 2D structures, e.g. TiO_2, MnO_2, RuO_2 and perovskite $LaNb_2O_7$, etc. More recently, a new group of semiconductor 2D materials have been synthesised. These are made up of single elements such as silicene, phosphorene and germanene nanosheets. This class of material tends to react with oxygen and thus highly unstable in ambient conditions.

Table 1 Non-carbon 2D materials [(Novoselov, 2016), (Geim, 2013)]

Hexagonal boron nitride, hBN

- Large band gap in the UV range of the spectrum.
- Resistant to mechanical and chemical interactions.
- High dielectric strength. For instance, it can sustain electric fields up to ⊕0.8V/nm.
- Application: substrate or encapsulation for 2D devices. For instance, combined with graphene, hBN greatly improves the mobility of graphene devices. Due to high dielectric strength, these have been characterised as gate dielectrics and tunnel barriers.

Transition-metal dichalcogenides, TMDCs

- Compositions include WSe_2, $MoSe_2$, MoS_2, $MoTe_2$, WTe_2, $NbSe_2$, NbS_2, TaS_2.
- Large optical absorption and band gap in the visible range of the spectrum.
- Wide range of electronic properties can be obtained, from insulating, semiconducting to metallic or semi-metallic. Properties can be tailored by changing composition, thickness, geometry and electronic density
- Thin, transparent and flexible materials.
- Applications include photovoltaic devices and photodetectors. For instance, a WS_2 300 nm film can absorb 95% of light. Moreover, semiconductor TMDCs with a direct gap like MoS_2 are attractive for optics and optoelectronics devices.

2D oxides

- Compositions include TiO_2, MnO_2, RuO_2, perovskite $LaNb_2O_7$, hydroxide $Ni(OH)_2$
- Large band gap.
- Low dielectric constant.
- Biocompatible and non-toxic.
- High surface to volume ratio and surface reaction.
- High adsorption and catalytic efficiencies.
- Applications include immobilisation of biomolecules, like enzymes and antibodies.

Single element

- Compositions include silicene, germanene and phosphorene.
- Exhibit natural band gap.
- Highly unstable (react with oxygen and water).
- Grown on metallic substrates.
- Mostly theoretical work.

3. Production of Non-carbon 2D Materials

Synthesis of 2D materials can be cost-effective and easy**.** This is due to the fact that the 3D compound counterparts tend to be bonded through weak bonds, i.e. Van der Waals bonds. Mechanical exfoliation is so far the most common method and uses the "Scotch tape" method as for graphene. It is less destructive compared with other methods and able to create large single layer flakes on different substrates. Examples of non-carbon 2D materials produced by this method include TMDCs and hBN. Although cost effective, it is rather limiting for large amounts of material. Alternative methods are available to synthesise single to few layer 2D materials and these depend on the desired structure of the materials and application. Examples are:

- *Chemical exfoliation* – the crystal is dispersed in a solvent, with compatible surface tension. TMDCs and hBN can be synthesised by this method.
- *Atom/molecule intercalation* – this method consists of inserting a molecule or atom into layered structured compounds. e.g. TMDCs or hBN
- *Surface growth* - this method entails the deposition of materials on substrates. Single element nanosheets, such as silicene are often synthesised by this method using metallic substrates.
- *Solution phase growth* - this method allows a straightforward production of grammes of 2D materials, with precise thickness. Examples of colloidal synthesised materials include TMDCs such as TiS_2, VS_2, ZrS_2, HfS_2, NbS_2, TaS_2, $TiSe_2$, VSe_2, and $NbSe_2$.
- *Vapour deposition* - most commonly used is chemical vapour deposition (CVD) which is a non-catalytic process for TMDCs.
- *Large area CVD - v*ery often to synthesise large areas of graphene and is similarly suitable for hBN.

The following summarises some the key developments taking place around the world to provide scalable volumes of non-carbon 2D materials. Appendix 1 provides further details.

Production of 2D Boron Nitride in the UK
Thomas Swan Ltd, UK
(Thomas Swan, 2016) Thomas Swan has launched a new range of 2D hBN materials which were synthesised by direct liquid exfoliation and exhibit high dielectric strength and thermal conductivity. Dielectric 2D hBN is available as few to many layers platelets powder and water/surfactant dispersion. These products are targeting applications as barrier additives, thermal interface materials and thermal conductivity enhancers for plastics, electronics and dielectric oils.

2D nanomaterials solutions
University College London, United Kingdom
(Cullen, 2017) Researchers have developed a scalable and stable production process of 2D materials solutions through their dissolution in polar solvents. According to this work, this process monolayers to be achieved by maintaining the 2D material morphology.

Large-scale growth of high-quality of $MoTe_2$ and WTe_2
Nanyang Technological University, Singapore
(Zhou, 2017) Researchers have developed a CVD method to able to synthesise high quality and large area (up to 300 µm lateral size) of atom thin $MoTe_2$ and WTe_2. Electric-transport characterization of the grown 2D materials indicate that semi metal and insulator properties in WTe_2 and superconductivity in $MoTe_2$. This was the first time that large-scale monolayer ditellurides have been synthesized.

Stacking of 2D Layers - Heterostructures

The stacking of different 2D crystals can result in a charge redistribution between neighbouring crystals and/or can cause structural changes. Both phenomena can lead to interesting properties. One may combine components made of different 2D materials or stack different 2D materials to make a component with finely tuned properties. The so called, 'Van der Waal heterostructures' properties can then be tailored by the stacking order, spacing and orientation of the materials. Examples found include graphene, MoS_2 and WSe_2 stacked together to make junctions for *solar cells* (Lee, 2014) and photodetectors (Zhang, 2014). There are examples of work carried out by UK researchers, including creating a sandwich of MoS_2 monolayers between graphene electrodes to make a light-emitting diode (LED) (Withers, 2015).

Van der Waals heterostructures for solar cells and photodetectors
Manchester University, UK
(Britnell, 2013) UK researchers have shown that a single-layer of WS_2 significantly enhances light-matter interactions, thus improving photon absorption and electron-hole creation. In this work, WS_2 was sandwiched between transparent graphene electrodes, through which photons were collected. The WS_2/Graphene heterostructure resulted in a photoresponsivity above 0.1 amperes per watt.

2D materials for biosensor devices
University of California, US
(Sarkar, 2014) A FET biosensor has been developed and demonstrated based on MoS_2 layered material which, according to the researchers, eases patternability and device fabrication. This research demonstrated an extremely high pH sensitivity (713 for a pH change by 1 unit), which surpassed graphene by more than 74-fold. Researchers have put this forward as a promising technology that will allow for the fabrication of flexible, transparent and low-cost biosensing.

4. The Innovation Landscape for Non-Carbon 2D Materials

As part this KTN study, innovations in non-carbon 2D materials were tracked through bibliometric and patent analysis and by benchmarking available commercial products and other relevant initiatives. The findings are presented below.

Scientific Publications

The last 6 years has seen an exponential growth in scientific publications on 2D materials. The increasing trend started in 2010, 6 years after the isolation of graphene and on the year of the Nobel prize for graphene (Figure 1). It is also the year, that Splendiani *et al,* from University of California, presented their work on the synthesis and photoluminescence properties of “low-dimensional” MoS_2. The most cited papers are shown in Table 2 below.

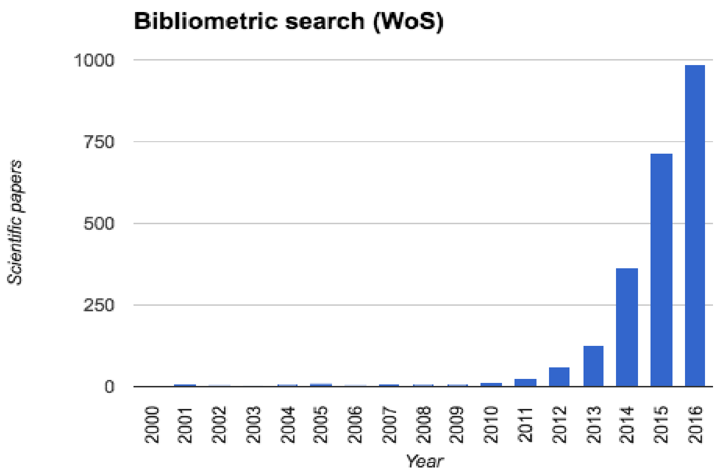

Figure 1 Number of scientific publications since 2000. Source: Web of Knowledge index. Keyword search: “2D materials”

Table 2 Top 5 most cited papers in the field of 2D materials. *Source: Thomson Reuters' Web of Science.*

Rank	Title and reference
1	**Experimental observation of the quantum Hall effect and Berry’s phase in graphene** By: Zhang, YB; Tan, YW; Stormer, HL; et al. NATURE Volume: 438 Issue: 7065 Pages: 201-204 Published: 10 Nov 2015
2	**Single-layer MoS_2 transistors** By: Radisavljevic, B; Radenovic, A; Brivio, J; Giacometti, V; Kis, A NATURE NANOTECHNOLOGY Volume: 6 Issue: 3 Pages: 147-150 Published: Mar 2011
3	**Electronics and optoelectronics of two-dimensional transition metal dichalcogenides** By: Wang, QH; Kalantar-Zadeh, K; Coleman, JN; et al. NATURE NANOTECHNOLOGY Volume: 7 Issue:11 Pages: 699-712 Published: Nov 2012
4	**Emerging photoluminescence in monolayer MoS2** By: Splendiani, A; Sun, L; Zhang, Y; Li, T; Kim, J; Chim, CY; et al. NANO LETTERS Volume: 10 Issue: 4 Pages:1271-1275 Published: Apr 2010
5	**Black phosphorus field-effect transistors** By: Li, L; Yu, Y; Ye, GJ; Ge, Q; Ou, Z; Wu, H; Feng, D; et al. NATURE NANOTECHNOLOGY Volume: 9 Issue: 5 Pages:372-377 Published: May 2014

Synthesis and application of non-carbon 2D materials research are among the most cited. Table 2 shows that 3 out of 5 most cited papers focus on the synthesis and application of TMDC materials, e.g. MoS_2. These were papers written by research groups from University of California, MIT, Fudan University (China) and EPFL.

Our analysis found that around 71.3% of scientific papers were published by institutions in the USA and China, as shown in Table 3, with a large gap between them and Germany (3rd in the ranking).

Table 3 Top 10 countries contributing to 2D materials innovation. *Source: Thomson Reuters' Web of Science.*

Rank	Country	%
1	USA	41.3%
2	China	30.0%
3	Germany	7.4%
4	South Korea	6.9%
5	Singapore	6.5%
6	Japan	5.4%
7	England (UK)	5.2%
8	France	4.3%
9	Italy	3.3%
10	Spain	3.1%

Table 4 Top 20 organisations contributing to 2D materials innovation based on the bibliometric analysis. *Source: Thomson Reuters' Web of Science.*

Rank	Organisation	%
1	Chinese Academy of Sciences	5.9%
2	MIT	3.0%
3	National University of Singapore	3.0%
4	Nanyang Technology University	2.9%
5	Rice University	2.9%
6	Peking University	2.7%
7	University of California Berkeley	2.6%
8	Oak Ridge National Laboratory	2.3%
9	Stanford University	1.9%
10	University of Science and Technology China	1.8%
11	Penn State University	1.8%
12	Ecole Polytechnique Fédérale de Lausanne	1.7%
13	University of Texas Austin	1.7%
14	Columbia University	1.5%
15	Tsinghua University	1.5%
16	Cornell University	1.4%
17	University of Manchester	1.4%
18	National Institute of Materials Science	1.3%
19	Sungkyunkwan University	1.3%
20	Northwestern University	1.2%

UK is ranked as the 7th country contributor to scientific publications on 2D materials. University of Manchester leads this ranking in the UK, responsible for 1.4% of the UK's 5.2% of scientific papers on 2D materials produced worldwide.

Patents

South Korea leads the patent ranking with the top ranking company being Samsung Electronics and SJE Steel Corporation fifth ranking. IBM, in the USA, ranks second.

Table 4. Top 5 organisations contributing to the 2D materials patent landscape. Source: Google scholar, Date: 24/03/17.

Top 5 organisations	Country	%
1. Samsung Electronics Co. Ltd 2. International Business Machines Corporation (IBM) 3. Hitachi Chemical Co. 4. Taiwan Semiconductor Manufacturing Company Ltd 5. SJE Steel Corporation	South Korean USA Japan Taiwan South Korean	4.6% 2.8% 2% 1.8% 1.6%

Although large corporations such as Samsung Electronics, IBM, Hitachi, are leading the number of patents on non-carbon 2D materials in the world, the trend is different in the UK, with Universities (e.g. University of Manchester) and SMEs (e.g. Thomas Swan) patenting the most (Table 5).

Table 5. Examples of UK patents. Google patent database was used to search for patented technologies. Advanced search of keyword "2D materials" was conducted and 486 hits were obtained.

Two-dimensional materials, Thomas Swan & Co. Ltd **(WO, 2014).** This patent describes a method of synthesise a 2D material, like graphene or boron nitride.
Functionalised material, **Imperial Innovations Ltd (GB, 2014, Pending).**
Photovoltaic cells, **University of Manchester (US, 2012, Pending)**. Patent describes a photovoltaic cell based on graphene and TMDC heterostructure.
Method for producing dispersions of nanosheets, **UCL Business Plc (WO, 2014).** Patent describes a method to produce 2D material solutions.
Methods for the production of 2-d materials, **2-Dtech Limited and Innovation Ulster Limited (WO, 2014)**. Patent describes a production process of graphene and other 2D materials.
Exfoliation, The University Of Manchester **(WO, 2014).** Patent describes a method to synthesise 2D materials by exfoliating layered materials in aqueous media.

Volume Production of Non-carbon 2D Materials

SMEs in the UK and the USA are producing non-carbon 2D materials for the research market. Table 6 provides examples of companies and commercially available materials, which that hBN and MoS_2 are the most commercially developed of the family of non-carbon 2D materials.

Table 6: Examples of companies and commercially available non-carbon 2D materials products.

Companies	Products	Country
Thomas Swan Ltd	hBN powder and dispersion	UK
Graphene Supermarket https://graphene-supermarket.com/	hBN, MoS_2, WS_2	US
Manchester Nanomaterials http://mos2crystals.com/	hBN, MoS_2, $MoSe_2$, WS_2, WSe_2, WTe_2	UK
2DSemiconductors http://www.2dsemiconductors.com/	CVD monolayers of MoS_2, WS_2, $MoSe_2$, WSe_2, WS_2, SnS_2, $SnSe_2$, ReS_2 and $ReSe_2$ on sapphire, quartz, SiO_2/Si, PET substrates.	US
Ossila https://www.ossila.com/	MoS_2 and WS_2 monolayers and multilayers.	UK

Centres of Excellence

Earlier we saw, in Table 4, the worldwide institutions that most contributed to scientific publications in 2D materials. In the UK, other centres of excellence are working closely with industry to support the development of 2D material manufacturing, scaling up and application. The following centres are active in pursuing activities that are aimed at helping industry to exploit the exciting properties of 2D materials:

National Graphene Institute	Synthesis, manufacturing, application
Cambridge Graphene Centre	Synthesis, manufacturing, application
High Value Manufacturing Catapult (CPI)	Manufacturing, application
National Physical Laboratory	Characterization, standards

Availability of Roadmaps

Our study has found that only a few roadmaps and market reports mention non-carbon 2D materials**.** These reports highlight R&D trends for both graphene and other 2D materials as well as industrial opportunities (see Table 7).

Table 7: Technology roadmaps and market reports for non-carbon 2D materials.

Technology roadmaps
Science and technology roadmap for graphene, related two-dimensional crystals, and hybrid systems (RSC, 2014)
Bulk Nanostructured Materials Based on Two-Dimensional Building Blocks: A Roadmap (ACSNano, 2015)
Opportunities for 2D Materials in Semiconductor Industry. Frost&Sullivan, 2016
2D Nanomaterials in Industrial Applications. Frost&Sullivan, 2017
Graphene, 2D Materials and Carbon Nanotubes: Markets, Technologies and Opportunities 2016-2026 (IDTechEx Research report, 2017)

Knowledge Sharing Initiatives

A number of graphene-community activities have expanded their scope to non-carbon 2D materials. These involve joint initiatives (e.g. consortium, conferences), which transfer knowledge and experience from graphene to non-carbon 2D materials (Table 8).

Table 8 2D materials initiatives.

Initiative	**Type of activity**
innoLAE2017, 31 Jan- 1 Feb 2017, Cambridge, UK	Conference
From Datacom to IoT, Enabled by Graphene, 2 March 2017, Barcelona, Spain	Conference
Graphene 2017, 27-28 March 2017, Barcelona, Spain	Conference
IDTEchex: Graphene and 2D materials, 10-11th May 2017, Germany	Conference
UK semiconductors, 12-13 July, Warwick, UK	Conference
Graphene & 2-D Materials Conference: From Research to Applications, NPL, UK	Conference
Graphene and 2D Materials USA 2017	Conference
EU Graphene Flagship	Consortium of over 150 academic and industrial research groups from 23 countries.
Recent Progress in Graphene & 2D Materials Research, September 2017 in Singapore	Conference and Graphene Technology Transfer Fair
EUREKA Cluster “Graphene and 2D Materials”	Eureka cluster proposal focused on industrial collaboration. TRL>5. Currently opened for expressions of interest.

Analysis of publicly funded projects found very few businesses leading non-carbon 2D materials. Table 9 shows examples of the types of projects receiving grant funding.

Table 9: Ongoing UK and European R&D projects. Sources: Gateway to Research (http://gtr.rcuk.ac.uk/), Innovate UK Funded Projecst Database (https://www.gov.uk/government/publications/innovate-uk-funded-projects) and Cordis database (http://cordis.europa.eu/)

Innovate UK
Two-Dimensional graphene-related Transition metal dichalcogenides for ultracapacitor Energy-storage Devices (2D TREND), DZP Technologies Limited, NPL, Set 16 – Aug' 17
EPSRC
Engineering van der Waals heterostructures: from atomic level layer-by-layer assembly to printable innovative devices, Lead organization: University of Manchester, Mar 16- Mar 21
Investigation of the Radiation Damage Mechanisms in Two-Dimensional Materials under Gamma and Ion Irradiation, Lead organization: Manchester University, Sep 16 - Mar 20
A systematic investigation of plasmonics in the non-classical regime with two-dimensional materials, Lead organization: Queen's University of Belfast, Oct 16 - Mar 18
Two-dimensional III-VI semiconductors and graphene-hybrid heterostructures, Lead organization: Nottingham University, Apr 15 - Jun 18
Horizon2020/ERC funded projects
Atomic layer deposition of two-dimensional transition metal dichalcogenide nanolayers, Coordinator Organisation: Technische Universiteit Eindhoven, Aug 15 - Jul 2020
Layered functional materials - beyond 'graphene', Coordinator Organisation: Univerzita Karlova, Aug 16 - Jul 21

Toxicity of Non-carbon 2D Materials

Research has been carried out to assess the toxicological impact of 2D materials. For example, MoS_2 and $MoSe_2$ have been found to present low toxicity to lung cancer cells compared to WSe_2. However, the later still shows lower toxicity than the already proven biocompatible graphene and graphene oxide. It has been increasingly accepted by the scientific community that cytotoxicology is strongly affected not only by the chemical composition and defect density, but also by parameters associated with the production process. For instance, it has been found that exfoliated MoS_2 nanosheet in vitro cytotoxicity depends on the intercalating agent used for the exfoliation and that as more layers exfoliated the stronger the impact of toxicity. This has been associated with the increase of surface area and the number of active edge sites (Chang, 2014).

5. Strategic Insights for the UK

To make sense of the trends in the innovation landscape of non-carbon 2D materials and how these should shape the UK's industrial approach to this family of 2D materials, KTN consulted with industry and academia to look at opportunities and challenges. Table 10 sums up a wide range of potential applications with significant export opportunities for the

UK. KTN asked the industry experts for their views on the timings of these opportunities. The outcome is shown as Figure 2, with sensors and structural composites seen as the applications with short to medium term opportunities for commercialisation.

Table 10: Applications for non-carbon 2D materials identified by the UK industrial and academic community during stakeholder and strategy workshops and one-to-one interviews.

Energy generation, harvesting and storage - High power density batteries. Nanosheets as battery electrodes. - Fuel Cells - Energy storage - Hydrogen storage
Health - Surface functionalization - Bio sensors - Smart wearables
Electronics and semiconductors - Flexible electronics - Display backplanes - Novel and integrated optoelectronics (e.g. lasers, switches, transistors) - Tunnelling devices. Insulating or semiconductor 2D material combined with graphene to create a tunnel junction - Optoelectronic devices - Thermal cooling fluids for electronics (oil/water based) - Semiconductor heterostructure devices for power saving - Microelectronics
Quantum technologies - Single photon sources
Composites - Nanocomposites (in thermoset and thermoplastic polymers) for electrical insulating applications like power cables and distribution components. - Structural composites - Multifunctional composites
Ambient barriers - Packaging. Barrier material for food/electronics and no additives for electronics. - Water vapour and gas barriers. - Anti-corrosion barriers.
Lubrication for other materials
Environmental - Membranes for water treatment

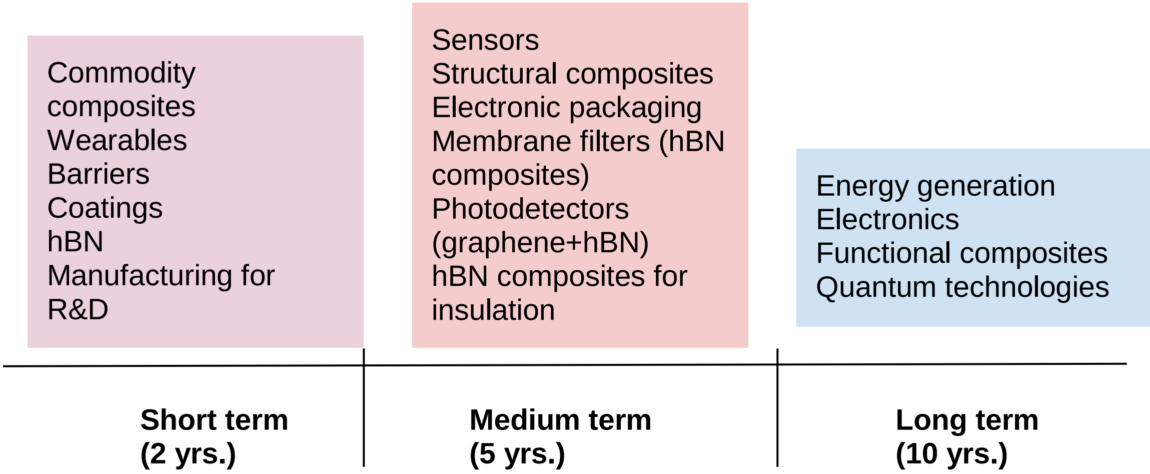

Figure 2**:** Commercialisation timescale for non-carbon 2D materials applications.

Challenges

High quality and large-scale synthesis are key barriers to the commercialisation and application of non-carbon 2D materials. In the case of hBN this is due to the lack of large scale demand from industry. A number of other technical challenges were identified in the KTN study. These are summarised in Table 11.

Table 11**:** Technical challenges of non-carbon 2D materials. Input from KTN stakeholder and strategy workshops (2016/17).

Technical challenges
Cost and time effective production. Sticky tape is time-consuming to scale up • Scale up of heterostructures • Lack of reliable measurements and data • Lack of characterisation methods • Lack of in-line characterization tools for quality control • Lack of standards • Reproducibility of 2D materials • Lack of large scale synthesis and high-quality materials (lack of large scale industry demand in the case of hBN) • Environmental stability of some non-carbon 2D materials • Long development path. Most are more complex than graphene • Lack of commercially-viable, transfer/contamination free, catalyst-free production method • Post production handling of materials not clear • Environmental and regulations. Toxicity, regulatory, end of life issues must be addressed. • Achieving good dispersion using industry relevant mixing equipment but without damaging the platelets; Materials dispersion and stability. • Clear demonstration of improvement in properties

Other challenges, of non-technical nature, were also identified as likely barriers to industry take up of non-carbon 2D materials. These include the need to develop and equip supply chains, reduction in the costs of materials and access to both public and private equity to de-risk non-carbon 2D materials. Table 12 provides a summary of the non-technical challenges discussed in the KTN workshops.

Table 12**:** Non-technical challenges of non-carbon 2D materials. Input from KTN stakeholder and strategy workshops.

Barriers to commercialisation
● Lack of relevant skills ● Lack of funding for translational journey ● Poor engagement with potential end users and customers ● Misaligned supply chain landscape – need to bring supply and value chain together ● Funding too focused on applications, need to improve manufacturing techniques ● Lack of technology roadmap for mass production and application ● Nott clear what the industrial drivers are ● High cost of raw materials and low yield ● Early stages of development for most of the materials ● Need consistent reliable sources of supply. Reliable, pure, reproducible materials source. ● Academia and industry progress at different speeds. ● Raw materials still expensive for large scale testing ● Lack of access to finance to complete concept and R&D tasks to generate, for example demonstration materials and hence prove applications ● Investors are sceptical that graphene and 2D materials will ever achieve their highly speculated potential

UK Strengths

The UK has credible strengths to help overcome these key challenges. According to the industry experts consulted, the UK can leverage learning from graphene and benefit from the common process technologies graphene has with non-carbon 2D materials. There are UK companies active in the synthesis and production of graphene, hBN, graphene heterostructures and TMDCs such as MoS_2. UK's approach to open innovation and knowledge sharing is also seen as a key strength by industry and experts are willing to collaborate to accelerate the commercialisation of non-carbon 2D materials. Many other UK strengths were identified and these are summarised in Table 13.

Table 13: UK strengths in non-carbon 2D materials. Input from the KTN strategy workshops.

UK strengths
- Growing capacity for manufacturing 2D materials - Strong academic research leadership and knowledge base. Knowledge base of multi-disciplinary R&D. - Key OEMs and End-users located in the UK (automotive, aerospace, oil and gas, wearables) - Characterisation and deposition capacity in the UK (measurement and metrology) - Modelling and simulation capability available - Good academic and industry relationship - Existing graphene infrastructure (e.g. CPI, NGI, Cambridge, Henry Royce) - Track record of applications development - Niche companies in raw materials - Standard bodies with international reputation (BSI, NPL, etc) - Willingness and ability to learn from other sectors, e.g. pharma and electronics

6. Conclusions

The KTN study has identified a body of work being undertaken globally to develop non-carbon 2D materials, mainly led by university research groups. Companies such as Samsung and IBM are active in this area and so are UK SMEs such as Thomas Swan. The discussions KTN have had with UK companies suggest that existing businesses with an interest in developing commercial applications for graphene are the ones most likely to look at exploiting other 2D materials. The following were seen as the priorities for the UK in our bid to create commercial value from current research and industry activities:

Clear progress has been made with the commercial availability of *hexagonal Boron Nitride,* hBN, and there is growing industry interest in *transition-metal dichalcogenides (TMDCs)*, in particular semiconductor TMDCs such as MoS_2 which have direct gap and are attractive for optics and optoelectronic devices.

There is also a particular excitement about the ability to custom stack thin layers of non-carbon 2D materials and in combination with graphene to create hetero-structured devices. These devices have a variety of different electronic and optical properties, which can be finely tuned by careful design of the stack. Ongoing research is showing great promise for new materials with specially designed electrical, magnetic, piezoelectric and optical functionalities.

7. Priorities and recommendations

The following were seen as the priorities for the UK, by those engaged with the KTN at the stakeholder workshops:

- More work needed to scale up the manufacturing and use of 2D materials
- Funding is needed to improve manufacturing techniques for 2D materials, devices and products
- UK industry needs to be more open about their trends and drivers with regards to 2D materials and to work closely with academic researchers to develop technology roadmaps for mass production and application of 2D materials

Following considerable discussions with industry and UK academics, the following recommendations are made to both government and industry to drive forward the commercialisation of non-carbon 2D materials in the UK.

1. Create an Industry Challenge around hBN and MOS_2 to accelerate the development of supply chain and end user partnerships
2. Provide 5-10 years long term funding for centres of excellence to carry out more work needed in scale-up of non-carbon 2D material production, device fabrication and end-user applications
3. Consider the overall UK landscape and alignment with the EU Graphene Flagship project

4. Provide funding for scaled demonstrators to show and exploit the game changing properties of non-carbon 2D materials, solely or in combination with graphene.

Acknowledgements

KTN would like to express sincere thanks to the many individual experts and organisations that have contributed to this review and analysis. In particular, we would like to thank the many contributors who attended the stakeholder and strategy workshops and also those who spoke to us during visits and completed the online questionnaire.

References

Britnell L. , R. M. Ribeiro, A. Eckmann, R. Jalil, B. D. Belle, A. Mishchenko, Y.-J. Kim, R. V. Gorbachev, T. Georgiou, S. V. Morozov, A. N. Grigorenko, A. K. Geim, C. Casiraghi, A. H. Castro Neto, K. S. Novoselov, Strong Light-Matter Interactions in Heterostructures of Atomically Thin Films, SCIENCE VOL 3, 1311-1314 (2013)

Chang E. L. K., Soferb Z., Pumer M., MoS2 exhibits stronger toxicity with increased exfoliation, Nanoscale,6(23),14412-8 (2014)

Cullen P., Cox K. M., Subhan M. K. B., Picco L., Payton O.D., Buckley D. J., Miller T. S., Hodge S. A., Skipper N. T., Tileli V., Howard C., Ionic solutions of two-dimensional materials, Nature Chemistry **9**, 244–249 (2017)

Sarkar D., Liu W., Xie X., Anselmo A. C., Mitragotri S., Banerjee K., MoS2 Field-Effect Transistor for Next-Generation Label-Free Biosensors, ACS Nano, 8 (4), 3992–4003 (2014)

Zhou J., Liu F., Huang X., Xia J., Zhang B., Zeng Q., Wang H., Zhu C., Niu L., Wang X., Fu W., Yu P., Chang T. R., Hsu C. H., Wu D., Jeng H. T., Huang Y., Lin H., Shen Z., Yang C., Lu L., Suenaga K., Zhou W., Pantelides S. T., Liu G., Liu Z., Large-area and high-quality 2D transition metal telluride, Adv. Mater. 29, 1603471 (2017)

Kalantar-zadeh K., Ou J. Z., Daeneke T., Strano M. S., Pumera M., Gras S. L., Two-Dimensional Transition Metal Dichalcogenides in Biosystems, Advanced Functional Materials, 25, Issue 32, 5086–5099 (2015)

ISO terminology standard – ISO/TS 80004-13:2017: ‘Graphene and related two-dimensional (2D) materials’

(2017). 2D Nanomaterials in Industrial Applications. TechVision Opportunity Engines. Retrieved from Frost & Sullivan database. [No authors listed]

(2016). Opportunities for 2D Materials in Semiconductor Industry (TechVision). TechVision Analysis. Retrieved from Frost & Sullivan database [No authors listed]

“2D Boron Nitride Products”, 2016. Retrieved from: http://www.thomas-swan.co.uk/sites/pdf/Boron_Nitride_Products_FINAL_March2016.pdf

Appendix 1: Examples of R&D and Innovations

Table A1: Examples of other innovations developed by the UK and non-UK organisations.

R&D work	Organization	Innovation
Light-emitting diodes by band-structure engineering in van der Waals heterostructures	University of Manchester	Application
Molecular Beam Epitaxy of 2D Materials	University of Sheffield (Presentation)	Manufacturing
2D Materials beyond Graphene for Electrical and Optical Device Applications	City University (Presentation)	Application
Ionic solutions of 2-dimensional materials	UCL (Presentation	Synthesis
Electronic properties of graphene-boron nitride tunnel transistors	University of Nottingham & Manchester	Application
Van der Waals epitaxy of monolayer hexagonal boron nitride on copper	Imperial College	Synthesis
CVD technology for 2D materials: transition metal dichalcogenides	University of Southampton	Synthesis
Standards for graphene and 2D materials. Terminology	NPL	Standard
Metrology for 2D materials	NPL	Characterization
CVD-based 2D film technology	Cambridge (Presentation)	Synthesis
MoS2 for friction and wear reduction	University of Leeds (Presentation)	Application
Single quantum emitters in monolayer semiconductors	University of Science and Technology of China	Synthesis
Modelling and simulation of silicene	Aix-Marseille University	Materials
Atomically thin p-n junctions with van der Waals heterointerfaces	Columbia University	Application
The valley Hall effect in MoS2 transistors	Cornell University	Application
Germanene on gold substrate	Instituto de Ciencia de Materiales de Madrid-ICMM-CSIC	Synthesis
Photoluminescence in Monolayer MoS2	University of California	Application
Van der Waals stacked 2D layered materials for optoelectronics	Shenzhen University	Application
Synthesis of Two-Dimensional Materials for Capacitive Energy Storage	University François Rabelais of Tours	Application

Appendix 2: Patent analysis

Google patent database was used to search for patented technologies. Advanced search of keyword "2D materials" was conducted and 486 hits were obtained.

Non-UK Patents

Two-dimensional materials and methods for ultra-high density data storage and retrieval, **Hewlett-Packard Development Co LP**
Memory devices including two-dimensional material, methods of manufacturing the same, and methods of operating the same, **Samsung Electronics Co Ltd**
Mems, **Infineon Technologies AG**
Method of manufacturing a junction electronic device having a 2-dimensional material as a channel, **Electronics and Telecommunications Research Institute**
Local doping of two-dimensional materials, **University of California**
Electronics device having two-dimensional (2d) material layer and method of manufacturing the electronic device by inkjet printing, **Samsung Electronics Co Ltd**
3D UTB transistor using 2D material channels, **Taiwan Semiconductor Manufacturing Co**
Electromechanical switching device with 2d layered material surfaces, **GlobalFoundries Inc**
Inverter including two-dimensional material, method of manufacturing the same and logic device including inverter, **Samsung Electronics Co**
Growth of Crystalline Materials on Two-Dimensional Inert Materials, **US Secretary of Navy**