Advances in 2D Materials☆

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In this, the second of two special reports, science writers Vivienne Raper and Jon Evans provide their insights into the hottest research topics in 2D materials by looking through the publication data provided by Scopus and SciVal.

Introduction

Research into two-dimensional (2D) materials has exploded in recent years, thanks to the amazing physical and electrical properties of these atomic-scale materials. For example, graphene, the first 2D material to be isolated, is incredibly light and transparent, but also stronger than steel and highly electrically conductive.

Since Andre Geim and Kostya Novoselov performed their Nobel-prize-winning experiments on graphene in 2004, scientists have scrambled to characterize new 2D materials. They have been spurred by the realization that these wonder materials have the potential to revolutionize everything from solar cells to medical devices. Comprising individual sheets at most a few atoms thick, 2D materials often have dramatically different properties to their three-dimensional (3D) counterparts.

Although researchers are still actively searching for new 2D materials, they are also increasingly looking for applications for existing 2D materials. One active area of research is building ultrathin devices from layers of different 2D materials, such as combining a layer of molybdenum disulfide, a light-sensitive semiconductor, with graphene to create a light detector just a few atoms thick. Researchers are also actively developing new manufacturing techniques for mass producing these new materials and devices. Novoselov and Geim famously created graphene by peeling individual flakes from graphite, graphene's 3D form, with Scotch tape, but this method clearly isn't suitable for large-scale production.

This new report, *Advances in 2D Materials*, provides detailed insights into the current state and future prospects of this exciting and cutting-edge field, based on research data provided by Scopus and SciVal, part of Elsevier's research intelligence suite. Using the wealth of data provided by Scopus and SciVal, the authors of this report have been able to gain insight into the hottest research topics in 2D materials and the countries that are most active in this research, and how this has changed over the past few years. They have also been able to identify which countries are producing the most influential research, and which materials and applications are closest to being commercialized. To add expert analysis, they conducted interviews with the editors-in-chief of some of Elsevier's high-impact materials journals, who gave their personal views on the current state of research into 2D materials and its future development.

This report begins by describing the history, properties, applications, and synthesis processes for the main 2D materials, including graphene, transition metal dichalcogenides, and hexagonal boron nitride. The next chapter contains a detailed analysis of research data on 2D materials derived from Scopus and SciVal, and includes a host of informative tables and graphs. Finally, the last chapter examines the patent landscape for 2D materials and their commercialization prospects, and predicts how the field will develop over the next few years.

Report methodology

The information in this report was generated by conducting searches in Scopus and SciVal, primarily for the years 2012–2016. These years were chosen to highlight recent developments in 2D materials and also to ensure that comparisons were between comprehensive data sets comprising whole years.

☆ A summary of this report has been published as *The wonderful world of materials: Perspectives on the materials research landscape*. Mater. Today, Volume 22, January–February 2019, Pages 1-2.

To try to cover the field of 2D materials as comprehensively as possible, we searched SciVal using several search terms relating to 2D materials. These were: atom-thick materials; graphene; monolayers; nanosheets; thin films; and two-dimensional.

We used Scopus to determine the number of academic publications and patents referencing specific 2D materials. These were: borophene; germanene; graphene; hexagonal boron nitride; MXene; phosphorene; silicene; stanene; and transition metal dichalcogenides. In this case, we did extend the analysis into 2017, as some of the growth is so rapid that the extra data are required to present a more accurate reflection of current activity.

Throughout, this report refers to specialist terms and metrics used by Scopus and SciVal to collate and analyze the research data. These terms and metrics are defined below.

Scholarly output

A collective term for a range of academic publications, including journal articles, conference proceedings, and book chapters. A search in SciVal will reveal all the scholarly outputs relating to the specific search term produced over a set time period. Each scholarly output includes its title, abstract, authors, and their affiliated institutions, number of views and citations, and associated patent citations, allowing for a whole range of detailed analyses.

Keyphrases

Concepts that appear frequently in the titles and abstracts of the scholarly outputs, as determined by automated text mining. Keyphrases indicate active research topics within each search term and can be displayed as keyphrase maps. Here, the size of each keyphrase relates to its frequency, with larger keyphrases being more frequent, and the color of the keyphrase indicates whether its appearance in the scholarly outputs is increasing or decreasing, with red increasing and blue decreasing.

Field-weighted citation impact (FWCI)

The ratio of citations received relative to the expected world average for the subject field, publication type and publication year. Together with the percentage of scholarly outputs published in the top 5% of journals, it is used in this report as an indication of the overall impact of a country's research.

Patent-citations count

The total count of patents citing the scholarly output for each material class, based on patent information from the European Patent Office, the US Patent Office, the UK Intellectual Property Office, the Japan Patent Office and the World Intellectual Property Organization.

Rise of 2D materials

Two-dimensional (2D) materials are the superstars of the material world. With amazing physical and electronic properties, they have the potential to revolutionize everything from digital electronics to energy storage. Key to their incredible properties is their physical size. Comprising layers at most several atoms thick, these crystalline materials are effectively all surface. Not only does this give them a huge surface area for interacting with molecules and reacting to physical forces, but it means they're also influenced by quantum effects, conferring properties that can differ dramatically from their three-dimensional counterparts.

The ongoing revolution of 2D materials started with experiments on graphene, the first 2D material to be isolated. Made up of carbon atoms arranged in a hexagonal pattern, like honeycomb, graphene has exciting properties that differ from graphite, its bulk form. Despite being the thinnest-known material, at just one atom thick, graphene is the strongest material ever measured; it is also able to conduct electricity better than copper.

Although considered an advanced material, the origin of graphene actually dates to the last century. English chemist Benjamin Collins Brodie, in 1859, was the first to notice that graphite was layered, but it took until 1947 for Canadian theoretical physicist Philip Russell Wallace to coin the name graphene. He derived the electrical properties of graphite by stacking up layers of a theoretical two-dimensional material he called graphene. By the 1970s, chemists had found a way to deposit single layers of graphene onto other materials, but strong interactions between these materials made it difficult to determine graphene's physical properties.

This all changed in 2004 when two scientists at the University of Manchester, Andre Geim and Kostya Novoselov, were playing around in the lab one Friday evening, using Scotch (sticky) tape to tear flakes off a chunk of graphite. They removed smaller and smaller pieces until – after tens of rounds – they had produced Wallace's graphene in a way that allowed its physical properties to be examined.

This soon revealed that these properties are highly impressive: graphene is transparent and a very good conductor of electricity – properties rarely found in the same material – as well as being unbelievably strong, flexible, and light. Scientists have gone on to find a wide range of potential applications for this 'wonder' material, including as a physical support for growing cells, as an electrode material in batteries, as a conductor in electronic circuits, and as an additive for metals and alloys. The discovery of graphene also inspired scientists to look for similar layered materials made from other elements and, as a consequence, the field of 2D materials has expanded dramatically over the past decade or so.

Scientists are ideally looking for 2D materials with slightly different properties to graphene. They're particularly looking for semiconducting 2D materials that can form the basis for the next generation of atomic-scale electronic circuits. Unlike graphene, which conducts electricity all the time, semiconductors only conduct electricity when their electrons are given sufficient energy, usually via an applied voltage, causing them to 'jump' over a band gap to a higher energy level. Switching the conductivity of semiconductors 'on' and 'off' creates the ones and zeroes that carry digital information.

One approach to creating semiconducting 2D materials is to try producing versions of graphene made with atoms of other elements. This has produced a whole range of 2D materials collectively known as Xenes, because they are all given the characteristic '-ene' suffix. They include: silicene, based on silicon; phosphorene, based on phosphorus; stanene, based on tin; germanene, based on germanium; and borophene, based on boron.

These Xenes possess the same honeycomb, hexagonal structure as graphene, but their atoms don't bond together as neatly as carbon atoms, giving them a buckled surface. Only phosphorene and silicene possess bandgaps, making them natural semiconductors, although germanene can be given a bandgap by adding molecules such as hydrogen to its surface, as can also be done with graphene. Borophene is an efficient conductor, like graphene, whereas stanene is a topological insulator, meaning the middle of the material acts as an insulator while its edges are highly conductive. With this unusual property, stanene could help usher in a whole new form of computing known as spintronics, in which digital information is encoded in electron spins rather than the switching on and off of electrical current.

As well as research into single-element materials, researchers are also looking at 2D materials made from molecules. Retaining the '-ene' suffix is a family of potentially hundreds of different 2D materials termed MXenes, which combine properties of ceramics and metals. MXenes consist of carbon or nitrogen with an early transition metal, meaning a metal such as titanium that lies around the middle of the periodic table. MXenes were originally made by chemically stripping aluminum from a carbide called a MAX Phase, fragmenting it into 2D sheets. Like graphene, MXenes are strong with a high conductivity and are being explored for various potential applications, including as electrode materials in batteries and fuel cells.

Another example of a molecular 2D material is hexagonal boron nitride (h-BN, or 'white graphene'), which shares the hexagonal structure of graphene but comprises alternating boron and nitrogen atoms. Unlike graphene, h-BN is an insulator, making it a perfect complement for graphene and semiconducting 2D materials in electronic circuits. This 2D material is highly versatile and has many interesting properties, such as being fluorescent and resistant to oxidation. Scientists are exploring a range of applications, including as a nanofiller in electrical packaging and a laser emitter, as well as in oil spill remediation. An aerogel made from 2D h-BN nanosheets was found to absorb up to 33 times its own weight in oil and organic solvents, while also being water repellent.

Other 2D materials, such as transition metal dichalcogenides (TMDCs), are made up of several atomic layers. TMDCs consist of a layer of transition metal atoms, such as molybdenum or tungsten, sandwiched between layers of chalcogenide atoms, usually sulfur or selenium, which lie below oxygen in the periodic table. Different combinations of these basic elements can produce TMDCs with different properties, with many being natural semiconductors. TMDCs can also convert light into electricity, and vice versa, giving them the potential for use in solar cells and as light emitters in quantum cryptography.

Owing to the huge range of 2D materials now available, research has turned toward stacking different 2D materials together to form heterostructures. These are held together by weak Van der Waal forces, which limit the strain between layers. Stack multiple layers of graphene together and you get bulk graphene but stack different 2D materials together and you get a material that doesn't exist in nature and could well possess some interesting properties.

For example, graphene has been combined with tungsten disulfide, a TMDC, to create a highly efficient solar cell. When the semiconducting TMDC absorbs light, the excited electrons 'jump' into the graphene layers and are carried away as an electric current. The same arrangement has also been used, in reverse, to create a light-emitting diode: passing an electrical current through graphene stimulates a TMDC semiconductor to emit light, with different TMDCs producing different wavelengths.

Due to the promise of 2D materials, scientists are working on developing techniques for mass production. Although graphene was first isolated by manually peeling flakes from bulk graphite, a technique called mechanical exfoliation, this is not suitable for manufacturing at industrial scales. Instead, scientists are turning to techniques such as liquid exfoliation, and ion-intercalation and exfoliation.

Liquid exfoliation uses a solvent, such as water, to prevent the graphene layers from sticking together after they have been separated by physical vibrations. In ion-intercalation and exfoliation, ions are inserted between the layers to weaken the weak Van der Waal bonds, before they are broken apart with sound energy.

Both these techniques have problems, however: liquid exfoliation produces relatively low yields while intercalation has long reaction times. What is more, these exfoliation techniques clearly won't work with 2D materials that simply don't exist in bulk form, such as silicene, germanene and stanene.

The only way to synthesize these 2D materials, which also works with those such as graphene that can be produced via exfoliation, is from the bottom up, using a chemical reaction. The most popular method is chemical vapor deposition (CVD), in which one or more gases containing the molecules making up the 2D material are passed over a flat substrate, often covered in particles of a catalyst such as iron. The gases then react together to form the 2D material on the substrate. This method has been used to create large sheets of graphene, employing methane as the carbon source, but it has proved difficult to obtain a uniform coating and to separate the 2D material from the underlying substrate.

World of 2D materials

The SciVal data show that the field of 2D materials continues to grow rapidly, driven by the development of existing 2D materials and the discovery of new ones. Between 2012 and 2016, scholarly outputs increased for every 2D material search term, from 6% for two-dimensional to 200% for nanosheets (see Table 1).

TABLE 1

Scholarly output 2012–2016 for each search term.

Search term	Scholarly outputs	% increase 2012–2016
Graphene	67,912	101%
Thin film	57,690	7%
Two-dimensional	35,354	6%
Monolayer	25,447	25%
Nanosheet	14,312	200%
Atom-thick materials	12,061	13%

TABLE 2

Scholarly output 2012–2016 for specific 2D materials.

2D material	2012	2013	2014	2015	2016	Total	% increase '12–'16
Graphene	8,736	11,316	14,402	16,485	17,472	68,411	100%
Monolayer hexagonal boron nitride(h-BN)/white graphene	213	247	366	466	537	1,829	152%
Silicene	65	173	263	270	272	1,043	318%
Transition metal dichalcogenide monolayers	15	51	123	236	302	727	1913%
Phosphorene	–	–	62	201	265	528	327%
MXene	4	8	22	53	111	198	2675%
Germanene	9	25	56	64	92	246	922%
Stanene	–	–	8	25	53	86	563%
Borophene	–	–	4	3	38	45	850%

This growth in scholarly outputs was also seen for specific 2D materials between 2012 and 2016, from 100% for graphene to 2675% for MXene (see Table 2).

Despite a comparatively low rate of growth in scholarly outputs compared to other 2D materials, graphene remains by far the most important 2D material. Of all the search terms, it was responsible for the largest number of scholarly outputs between 2012 and 2016, at 67,912, even though all the other search terms encompassed outputs for several 2D materials, including graphene. Because these other search terms only encompassed certain aspects of graphene, however, none of them could match graphene itself in terms of scholarly output.

The dominance of graphene is demonstrated even more starkly in the scholarly outputs for specific 2D materials between 2012 and 2016. Graphene is on 68,411 (the slight difference between the output figures for Scopus and SciVal is due to differences in the way they collate the data), while the second highest output figure is 1829 for h-BN. Indeed, the comparatively low growth rate for graphene outputs is due to graphene already being a major research area in 2012, unlike all the other 2D materials.

The keyphrase analyses show the same picture. The keyphrase map for graphene is almost entirely red, showing that almost all the graphene keyphrases appeared in a growing number of scholarly outputs between 2012 and 2016 (see Figure 1).

The only other search term showing a similar dominance of red in its keyphrase map is nanosheets (see Figure 2), which saw the largest growth in scholarly output of all the search terms. Graphene also appears as a keyphrase in all the other search terms apart from thin films (see Figure 3, A–D); indeed, it is one of the top five most frequently used keyphrases in all these search terms, with growth in its frequency of use ranging from 26% for atom-thick materials to 149% for nanosheets.

Examining the keyphrases for graphene in more detail indicates that applications are becoming a major research topic. Application-related keyphrases are much more prevalent for graphene than for the other search terms, with the top four fastest-growing keyphrases all relating to applications: yarn (10,833%),

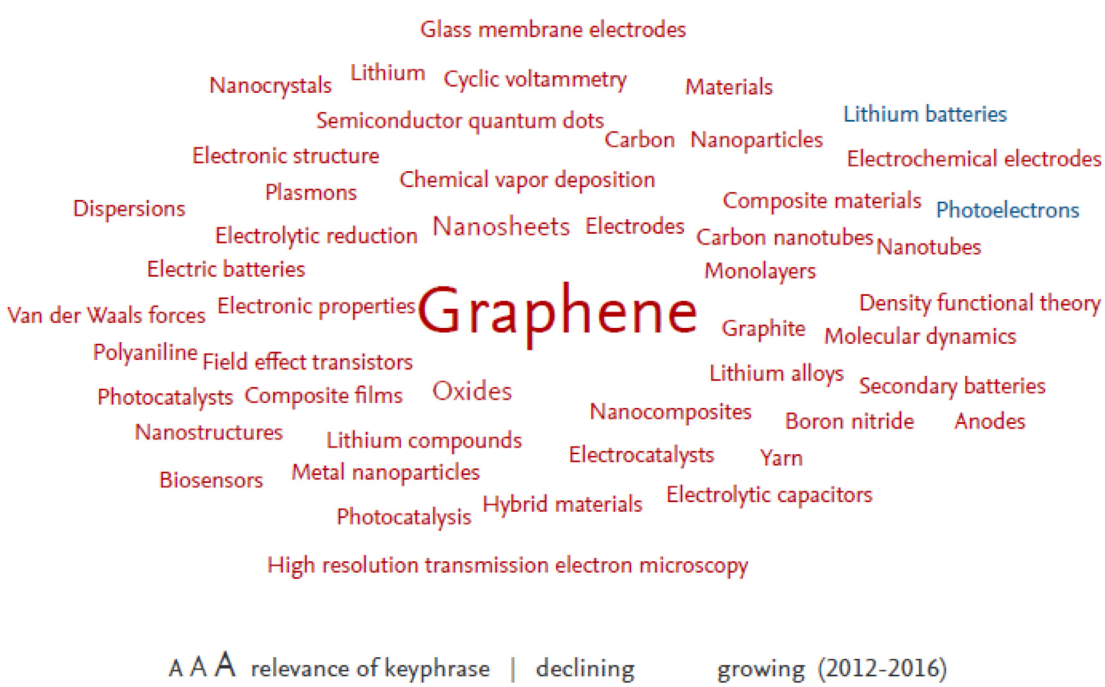

FIGURE 1

Keyphrase map for graphene.

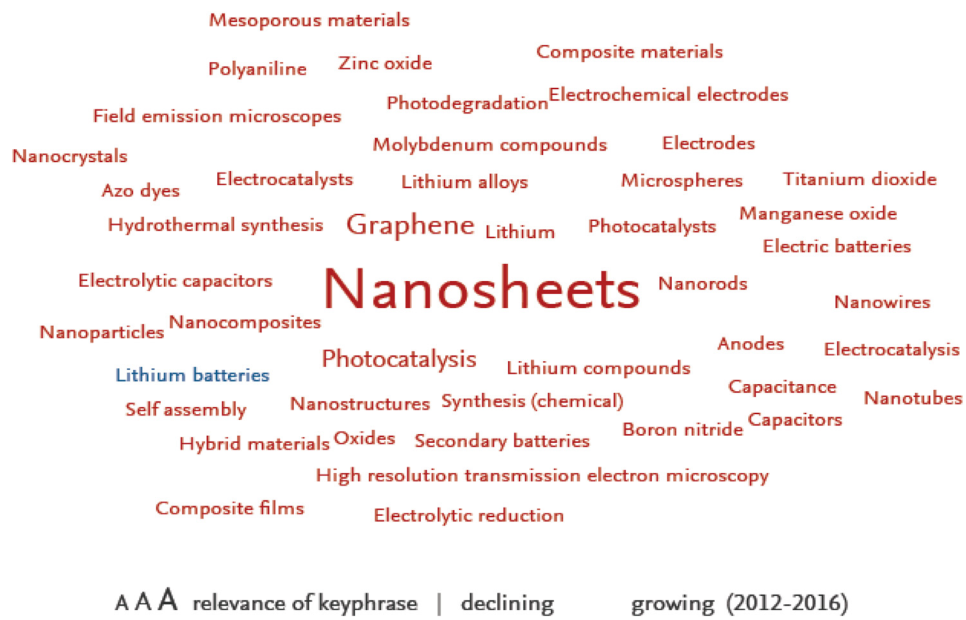

FIGURE 2

Keyphrase map for nanosheets.

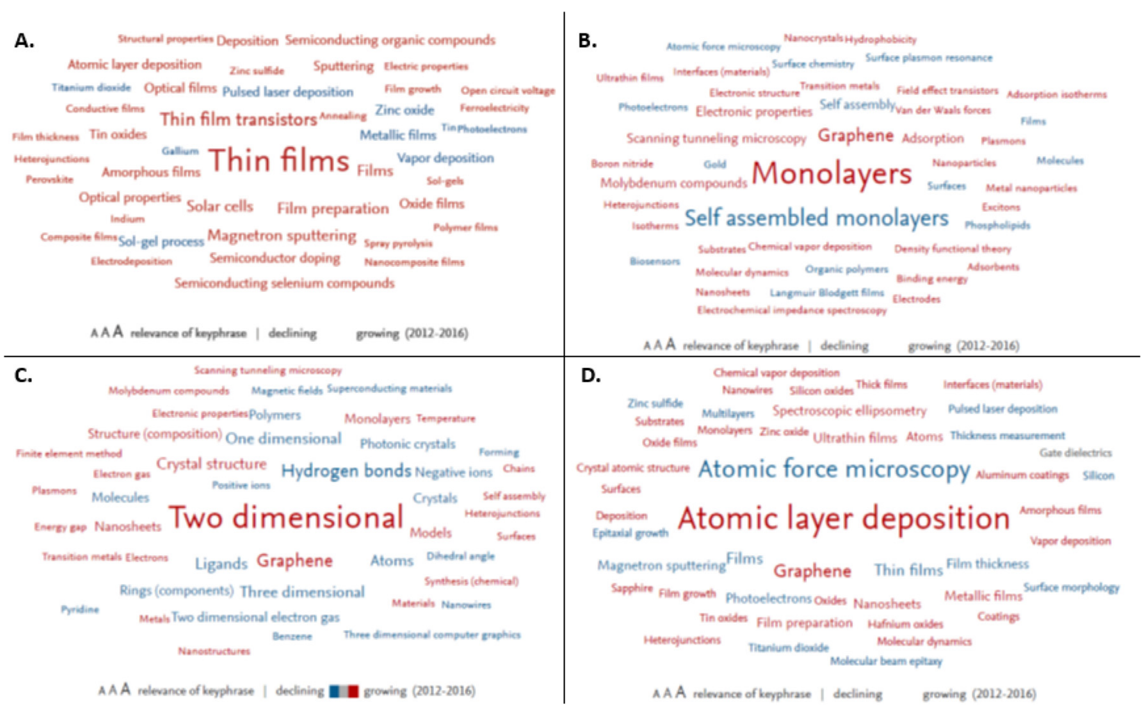

FIGURE 3

Keyphrase map of: A. thin films, B. monolayers, C. two-dimensional and D. atomic layer desposition.

electric batteries (5473%), secondary batteries (1979%) and lithium alloys (1493%). This reflects the fact that graphene is at a more advanced stage of development than other 2D materials.

"The biggest and most exciting topic is graphene applications and using graphene to make new materials," says Robert Hurt, professor of engineering at Brown University, US, and former editor-in-chief of *Carbon*. He highlights catalysis and electrocatalysis, hybrid materials, and energy storage, especially advanced batteries and supercapacitors, as the primary applications of graphene currently being investigated by researchers. "Carbon materials as components in electrodes for energy storage applications is a huge area."

This is supported by the keyphrases, which group into four main applications: energy, with keyphrases such as electrodes, electric batteries and lithium alloys; catalysis, with keyphrases such as electrocatalysts and photocatalysts; advanced materials, with keyphrases such as hybrid materials and nanocomposites; and electronics and sensors, with keyphrases such as field effect transistors and growth.

Of these, it is energy applications that seem to be receiving most interest, based on the number of different keyphrases, their frequency in scholarly outputs and their rate of growth. This also corresponds to growing research activity around energy materials in general.

"One of the areas that I think is becoming really interesting for researchers is energy materials, in terms of designing better energy storage and energy conversion systems," says Jun Lou, professor of materials science and nanoengineering at Rice University, US, and co-editor-in-chief of *Materials Today*.

Despite the rise of applications, synthesis and analysis techniques remain active areas of graphene research. Saying that, the only synthesis keyphrases for graphene are chemical vapor deposition (CVD) and dispersions, albeit CVD is one of the top five most frequent keyphrases in the scholarly output for graphene and its use grew by 53% between 2012 and 2016. This implies that scientists are primarily focusing on ways to improve CVD and exfoliation, rather than looking for alternative synthesis techniques. Several keyphrases relating to analyzing graphene and determining its basic properties showed growth between 2012 and 2016, including molecular dynamics (70%), cyclic voltammetry (171%) and high-resolution transmission electron microscopy (TEM; 1043%).

Many other 2D materials were not specifically mentioned in the keyphrases for any of the search terms. This was particularly the case for analogs of graphene containing other elements – borophene, germanene, phosphorene, silicene, and stanine – none of which were mentioned. The same was true of MXene. This is probably due to many of these materials being fairly new – borophene and stanene were first reported in 2014 – and only being mentioned in large numbers of publications in the past few years. Nevertheless, all these 2D materials are experiencing rapid year-on-year growth in scholarly output (see Table 2).

Unlike these Xenes, both h-BN and transition metal dichalcogenides (TMDCs) are referenced in the keyphrases for certain of the search terms. Boron nitride is mentioned directly in the keyphrases for graphene, monolayers and nanosheets, with growth in its frequency ranging from 103% to 256%. For TMDC, the relevant keyphrases are slightly more oblique, and include transition metals (in two-dimensional and monolayers) and molybdenum compounds (in two-dimensional, monolayers and nanosheets). In all cases, these keyphrases showed high rates of growth, with transition metals increasing by at least 569% and molybdenum compounds by at least 794%. Similar high rates of growth were seen in scholarly output for the specific materials, with h-BN output growing by 152% between 2012 and 2016 and TMDCs output growing by 1913% over the same period. This growth has continued in 2017 and shows no sign of slowing (see Table 3).

Application keyphrases are less prevalent in atom-thick materials, monolayers, thin films, nanosheets and two-dimensional than in graphene, whereas keyphrases relating to synthesis and analysis are generally more prevalent and more varied. This reflects the fact that 2D materials such as h-BN and TMDCs are at an earlier stage of development than graphene, so scientists are still actively analyzing these materials with a wide range of techniques and haven't yet alighted on the most effective synthesis methods.

Fabrication keyphrases found in multiple search terms include CVD (atom-thick materials, monolayers), self-assembly (2D, nanosheets), atomic-layer deposition (atom-thick materials, thin films) and film growth (atom-thick materials, thin films). Analysis keyphrases found in multiple search terms include high-resolution TEM (atom-thick materials, nanosheets), electronic properties and electronic structure (two-dimensional, monolayers), and energy gaps (2D, monolayer).

Many other analytical keyphrases, such as scanning tunneling microscopy and electrochemical properties, were only found in single search terms, with atom-thick materials containing the largest number of different analytical keyphrases. This suggests that different search terms are capturing different aspects of 2D materials.

Despite the focus on fabrication and analysis, the keyphrases also reveal that scientists are beginning to explore the applications of 2D materials other than graphene. Perhaps unsurprisingly, these applications are typically the same as for graphene: energy, electronics and biosensors, advanced materials and catalysts.

As with graphene, many of the energy keyphrases showing the highest frequency and rates of growth relate to energy storage, especially batteries and supercapacitors. These keyphrases include electrodes, anodes, secondary batteries, electric batteries and supercapacitors.

TABLE 3

Scholarly output for specific 2D materials in 2017. *Figures for 2017 collected in November 2017.

2D material	Total 2012–2016	2017*	Number of journal articles 2012–2017*	% growth in 2017
Graphene	68,411	17,858	86,269	26%
Monolayer hexagonal boron nitride(h-BN)/white graphene	1,829	563	2,392	31%
Silicene	1,043	253	1,296	24%
Transition metal dichalcogenide monolayers	727	376	1,103	52%
Phosphorene	528	293	821	55%
MXene	198	165	363	83%
Germanene	246	88	334	36%
Stanene	86	62	148	72%
Borophene	45	71	116	158%

"You need energy storage because the future lies in renewable energy to a large extent," says Gleb Yushin, a professor in the School of Materials and Engineering at the Georgia Institute of Technology, US, and co-editor-in-chief of *Materials Today*. "Energy has become more and more important because the world is changing, and the technology has become more commercially successful."

According to Yushin, there is also much research activity on developing "small flexible devices for consumer and medical applications," including wearable computer technology. Some of these are "what I would call materials for next-generation sensors. I think sensing is going to be a very important area as we move toward the internet of things," says Jun Lou.

This is reflected in those electronics and biosensors keyphrases that show the highest frequencies and rates of growth in the search terms other than graphene. These keyphrases include field effect transistors, thin film transistors, thin semiconducting selenium compounds and conductive films, all of which are being developed for use in flexible devices and next-generation sensors.

Taking advantage of the high strength of many 2D materials by combining them with other materials, such as polymers, is also the focus of much research. "There is also very active development of different nanocomposites," says Yushin. "These are materials that attain properties unachievable with their individual components." As a keyphrase, nanocomposite films showed high rates of growth between 2012 and 2016, as did other related advanced material keyphrases such as polymer films and composite films.

Finally, the keyphrases photocatalysis and photocatalysts showed high rates of growth in monolayers and nanosheets. Cheap and efficient catalysts made from 2D materials could offer a cost-effective way to produce hydrogen by splitting water, thereby connecting catalysis back to energy storage. "Catalysts are also an important field," says Yushin.

Interestingly, the applications keyphrases seemed to congregate in different search terms, again suggesting that different search terms are capturing different aspects of 2D materials. Keyphrases relating to batteries and supercapacitors were particularly common in nanosheets and monolayers, those relating to electronics, solar cells and advanced materials were particularly common in thin films, and those relating to catalysts were particularly common in nanosheets.

One application, however, was referenced in every search term apart from nanosheets, and always experienced high rates of growth, up to 354% in monolayers. This is heterostructures, the creation of new materials by stacking together layers of different 2D materials. "There's a lot of interest in heterostructures," says Hurt, with 2D heterostructures involving graphene being a particularly "up-and-coming" area. Several keyphrases related to heterostructures were found in the search terms, including heterojunctions (two-dimensional, monolayers, thin films, atom-thick materials), van der Waal forces (two-dimensional, monolayers, graphene) and interfaces (materials) (monolayers, atom-thick materials).

China and the US led the world in the number of scholarly outputs on 2D materials produced between 2012 and 2016, with China producing 66,080 and the US producing 39,688 (see Table 4).

China produced more scholarly outputs than the US for every search term except monolayers, while experiencing a larger growth in scholarly output for every search term. Now these figures are slightly misleading, because many of the scholarly outputs will appear in more than one search term, but they amply demonstrate the increasing dominance of China in 2D materials research. This reflects the large amount of investment the Chinese government is now putting into materials science in general and 2D materials in particular.

The results of this investment are seen most starkly in graphene, where China produced over twice as many scholarly outputs as the US between 2012 and 2016, at almost 27,000 (and over four times as many as South Korea, in third place). This reflects growth in scholarly outputs over this period of 145%, compared to just 24% for the US.

"Until recently, the USA dominated material science, but China has taken over because of significantly more investment," confirms Yushin.

When it comes to the impact of its research, however, China tends to fall behind the US. China had a lower FWCI and a lower percentage of its scholarly outputs appearing in the top 5% of journals than the US (see Table 5). It's scholarly output for nanosheets had the highest impact, with a FWCI of 2.88 and 41% of its output in the top 5% of journals, but the figures for the US were 4.16 and 60%. For graphene, China had a FWCI of 2.5 and 37% of its output in the top 5% of journals, compared with 3 and 49% for the US.

It was a similar story for India, whose government has also invested heavily in material science research. India was the fourth largest producer of scholarly outputs on graphene between 2012 and 2016, at 3955, but these outputs had an average FWCI of 1.75 and only 24% of them appeared in the top 5% of journals.

Other countries commonly in the top 5 producers of scholarly output for the 2D material search terms include South Korea, Japan, Germany, and the UK (see Tables 6–11). Germany and the UK also generally produce high impact research on 2D mate-

TABLE 4

Scholarly output 2012–2016 by China and US for each search term.

	Atom-thick materials	Graphene	Monolayers	Nanosheets	Thin films	Two-dimensional	Total
China	2,526	26,927	5,664	9,277	11,294	10,392	66,080
% increase 2012–2016	59%	145%	87%	224%	26%	32%	
US	2,518	12,024	5,946	1,359	10,350	7,491	39,688
% increase 2012–2016	14%	24%	19%	220%	-4%	9%	

TABLE 5

Impact of scholarly output 2012–2016 for China and US.

Search term	China		US	
	FWCI	% in top 5% of journals	FWCI	% in top 5% of journals
Graphene	2.5	37%	3	49%
Thin film	1.04	15%	1.78	33%
Two-dimensional	1.48	21%	2.36	30%
Monolayer	1.8	28%	2.57	43%
Nanosheet	2.88	41%	4.16	60%
Atom-thick materials	1.43	20%	2.07	31%

TABLE 6

Top 5 country producers of scholarly output for two-dimensional.

	Scholarly Output per year				
Country	2012	2013	2014	2015	2016
China	1764	1801	2115	2380	2332
France	394	350	336	358	273
Germany	591	562	554	623	457
Japan	554	537	576	566	453
United States	1366	1413	1526	1692	1494

TABLE 7

Top 5 country producers of scholarly output for graphene.

	Scholarly Output per year				
Country	2012	2013	2014	2015	2016
China	2937	4232	5790	6744	7217
India	336	550	813	1063	1195
Japan	555	627	665	664	734
South Korea	736	1002	1277	1515	1363
United States	2071	2267	2442	2689	2568

TABLE 8

Top 5 country producers of scholarly output for monolayers.

	Scholarly Output per year				
Country	2012	2013	2014	2015	2016
China	796	942	1120	1316	1490
France	282	285	279	279	332
Germany	486	513	467	544	514
Japan	416	403	406	399	405
United States	1058	1179	1183	1267	1259

TABLE 9

Top 5 country producers of scholarly output for nanosheets.

	Scholarly Output per year				
Country	2012	2013	2014	2015	2016
China	876	1245	1899	2415	2842
India	49	105	158	226	231
Japan	132	137	190	159	165
South Korea	108	137	181	234	238
United States	129	187	274	355	414

TABLE 10

Top 5 country producers of scholarly output for thin films.

	Scholarly Output per year				
Country	2012	2013	2014	2015	2016
China	1936	2207	2236	2483	2432
Germany	817	896	884	946	812
India	741	923	985	1039	1082
South Korea	1177	1199	1153	1182	1159
United States	1997	2005	2136	2295	1917

TABLE 11

Top 5 country producers of scholarly output for atom-thick materials.

	Scholarly Output per year				
Country	2012	2013	2014	2015	2016
China	377	446	526	576	601
Germany	179	235	193	193	211
Japan	191	229	196	179	181
South Korea	186	172	185	171	178
United States	471	512	496	500	539

rials, as do several countries outside the top 5, including Ireland, Switzerland, Australia, Singapore, and the Netherlands.

Collaborations between researchers in different countries increased for all search terms between 2012 and 2016, especially for nanosheets, monolayers and graphene. Researchers in the US collaborated much more than those in China; other countries with high levels of international collaboration included Germany, France, the UK, Saudi Arabia, Switzerland, Australia, and Singapore.

Outlook for 2D materials

Following on from the prevalence of applications-related keyphrases, an analysis of patents for 2D materials confirms that graphene is at a more advanced stage of development, including commercial development, than other 2D materials. Graphene has many more patent citations associated with its scholarly outputs, at 2885, than any other search term (see Table 12).

Admittedly, this is largely due to graphene simply having more scholarly outputs than any other search term, but graphene also has the highest number of patent-citations per 1000 scholarly outputs, which is independent of total number of scholarly outputs. This shows that patents are being generated at a higher rate for graphene than any other 2D material.

TABLE 12

Patents relating to scholarly outputs for search terms 2012–2016.

Search term	Patent-citation count	Patent-citations per 1000 scholarly outputs
Graphene	2,885	42.5
Thin film	1,688	29.3
Monolayer	816	32.1
Two-dimensional	668	18.9
Nanosheet	458	32
Atom-thick materials	359	29.8

Between 2012 and 2016, graphene was also the subject of more patents than all other 2D materials put together, at 39,003 (see Table 13).

Indeed, between January 2017 and November 2017, more patents were filed on graphene (9235) than on all the other 2D materials between 2012 and November 2017, bringing the total to 48,238. Whereas the patent citation figure measures the total number of patents citing the scholarly outputs for graphene as a search term, the patent figure for graphene as a material represents all the issued patents that mention graphene, which is why it's much larger. Nevertheless, both figures demonstrate that the patent activity for graphene is much greater than for any other 2D material.

Translating that patent activity into workable products is another challenge altogether, however, and at the moment there are few, if any, graphene-based products on the market. Nevertheless, quite a few companies are now producing graphene at commercial scales or developing graphene-based products.

In a study that appeared in the *Journal of Nanoparticle Research* in 2016, researchers at the University of Manchester in the UK identified 65 small and medium-size companies with graphene-based activities. Around half of these were based in North America, while the second largest number (10) were based in the UK, with 12 elsewhere in Western Europe and 11 in East Asia, including three in China. These companies were working on a variety of graphene-based products, which generally matched the applications highlighted in the keyphrases for graphene. They included electrodes for batteries and supercapacitors, field effect transistors and thin film transistors, and nanocomposites, as well as graphene-based inks and coatings.

TABLE 13

Patents collected in November 2017, mentioning specific 2D materials 2012–2017.

2D material	Patents
Graphene	48,238
Monolayer hexagonal boron nitride (h-BN)/white graphene	2,851
Silicene	235
Transition metal dichalcogenide monolayers	392
Phosphorene	279
MXene	55
Germanene	120
Stanene	64
Borophene	27

A recent report on the graphene market produced by the technology research company IDTechEx predicted that graphene inks would be some of the first graphene-based products to be commercialized, as they are comparatively easy to produce and have a ready market. But it also expected energy storage and composites to become the largest commercial applications, accounting for 25% and 40% of the graphene market respectively by 2027, when the global market should be worth $300 million.

Hurt is also confident that graphene-based materials show great scope for commercialization, suffering few of the challenges that have hampered the commercialization of carbon nanotubes. "Graphene-based materials are doing better," he says. "The safety issues aren't as important for them and they can be made in pretty high yields. They're in inks and coatings and that commercial field is developing pretty well."

Where graphene leads, other 2D materials will surely follow, especially as every major type of 2D material has patents associated with it, even stanene and borophene, which were only discovered in 2014. Many more 2D materials, with a whole range of other useful properties, are likely to be synthesized in the future. Indeed, hundreds of other 2D materials have already been predicted using computer modeling techniques such as density functional theory, which is also a keyphrase in graphene and monolayers.

Borophene is an example of a 2D material that was theoretically predicted before it was actually synthesized, whereas penta-graphene, in which the carbon atoms are bonded together as pentagons rather than hexagons, is an example of a 2D material that has been predicted but not yet synthesized. These theoretical predictions suggest that penta-graphene could be even stronger than normal graphene. TMDCs also offer a rich source of new potential materials, as there are many different transition metals and chalcogenides to explore.

With an ever-growing range of 2D materials to choose from, scientists can also potentially form a wide array of different heterostructures that could possess some very interesting properties. They are also beginning to find ways to fit 2D materials together horizontally, producing nanoscale tiled materials that could offer further scope for novel properties, especially at the interfaces between different 2D materials.

Another way to expand the range of properties is to chemically modify the surface of 2D materials with other elements and molecules, which is already an active area of research for graphene. "Now people realise they can exchange a carbon atom for something else – nitrogen, boron, phosphorus – and so atomically-designing carbon is a big science area," says Hurt. "Introducing these foreign elements into the carbon lattice and seeing what kind of changes and properties you get."

As soon as graphene was discovered, it was heralded as a 'wonder material' for its impressive properties, which are now beginning to find the first applications, but this is just the start. Graphene looks set to be joined by many other 'wonder materials' with a whole range of impressive properties, causing the field of 2D materials to expand in many different directions.

FEATURE COMMENT

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