# Path towards graphene commercialization from lab to market

Wei Kong<sup>1</sup>, Hyun Kum<sup>1</sup>, Sang-Hoon Bae<sup>1</sup>, Jaewoo Shim<sup>1</sup>, Hyunseok Kim<sup>1</sup>, Lingping Kong<sup>1</sup>, Yuan Meng<sup>1</sup>, Kejia Wang<sup>1</sup>, Chansoo Kim<sup>1</sup> and Jeehwan Kim<sup>1</sup>,<sup>2,3\*</sup>

The ground-breaking demonstration of the electric field effect in graphene reported more than a decade ago prompted the strong push towards the commercialization of graphene as evidenced by a wealth of graphene research, patents and applications. Graphene flake production capability has reached thousands of tonnes per year, while continuous graphene sheets of tens of metres in length have become available. Various graphene technologies developed in laboratories have now transformed into commercial products, with the very first demonstrations in sports goods, automotive coatings, conductive inks and touch screens, to name a few. Although challenges related to quality control in graphene materials remain to be addressed, the advancement in the understandings of graphene will propel the commercial success of graphene as a compelling technology. This Review discusses the progress towards commercialization of graphene for the past decade and future perspectives.

ver a decade ago, monolayer graphene became a heated topic of research, and its celebrated physical properties were measured and reported<sup>1-5</sup>. At the time, this atomically thin two-dimensional (2D) material with surprising electrical conductivity, and its mechanical strength, optical transparency and impermeability, promised many applications, and it has captivated the attention of the scientific community for the past decade. Since then, interests in graphene have increased rapidly, triggering the steady progress in graphene commercialization. Production of graphene has increased from 14 tonnes in 2009 to nearly 120 tonnes in 2015<sup>6-8</sup>, and is estimated to reach nearly 1,200 tonnes in 2019<sup>6-8</sup>. It also led to the rediscovery of entire categories of 2D materials and allotropes that have kept scientists and engineers busy for over a decade.

To harness the unprecedented properties of graphene, small companies were made to attempt commercialized applications of this revolutionary material. Presently, there are large consortiums such as the Graphene Flagship (https://graphene-flagship.eu), which provide long-term funding and support for putting graphene products out in the market<sup>9</sup>. Graphene has initially gained commercial success in sports goods and anti-corrosion coatings, functioning as passive additives. Over the years, the deepening understanding of graphene's electrical and optical properties in terms of an atomically thin material has led to the heavy pursuit of graphene in commercial electronics and optoelectronics (Fig. 1).

With such broad market categories that can potentially be revolutionized or significantly improved by utilizing graphene and related materials, there has been steady growth of the graphenebased device market. Top market analysis groups (IDTechEx) estimate an inflection point sometime in the very near future (around 2021) after which the volume of sales related to graphene and related materials will reach US\$100 million<sup>10</sup>.

Graphene research is at a stage where most of the outstanding physical properties have been studied, but the development of technology that bridges academic to industrial manufacturing still needs focus. Here we look back the past decade and have an overview of the development history of graphene, commercial opportunities and the recent progress of graphene commercialization.

### Availability of graphene

Although various research activities on graphene have been ongoing since the last century<sup>5,11,12</sup>, a monolayer of graphene was isolated by mechanical cleavage of bulk graphite a decade ago<sup>1</sup>. The technique comprises repeatedly peeling adhesive tape from the bulk until a monolayer of graphene remains. The so called Scotch tape method does not involve sophisticated lab equipment, yet historically it has provided the highest quality graphene flakes and has fuelled numerous scientific discoveries in the laboratory.

However, the flakes of monolayer graphene have been limited to hundreds of micrometres in size<sup>13</sup>, and require exhaustive identification under the microscope. Such a low-throughput procedure naturally fails to meet the requirements of industrial production. In time, a plethora of processes was invented for the synthesis of graphene and its derivatives. The graphene commonly available can be classified into two main categories, with one being discontinuous graphene flakes of up to hundreds of micrometres and the other being continuous graphene sheets. The synthesis, properties and product implementations of these two types of graphene and their respective applications differ significantly due to their different forms<sup>14</sup>.

#### Graphene nanoplatelets

Graphene nanoplatelets (GNPs), also called 'nanosheets' or 'nanoflakes', here refer to a multitude of graphene materials produced through exfoliation of graphite, the procedure of which generates graphene of arbitrary shapes and lateral dimensions on the order of hundreds of nanometres up to tens of micrometres. Graphene oxide is a form of GNP functionalized by oxygen-containing groups. The initial manufacturing process is based on the oxidation of graphite<sup>15–17</sup>. The process begins with oxidizing graphite into graphite oxides in the presence of strong acids and oxidants<sup>18</sup>. Then, the sheets in the graphite oxides are separated through sonication to form graphene oxide, which forms a discontinuous nanoplatelet dispersion in aqueous solutions. Given the abundance of graphite and the high exfoliation efficiency, this process has been proven suitable for mass production.

The access to discontinuous nanoplatelets dispersed in liquid permits graphene processing that would otherwise be difficult or

<sup>&</sup>lt;sup>1</sup>Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA, USA. <sup>2</sup>Research Laboratory of Electronics, Massachusetts Institute of Technology, Cambridge, MA, USA. <sup>3</sup>Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA, USA. \*e-mail: jeehwan@mit.edu

## **NATURE NANOTECHNOLOGY**



**Fig. 1** | A timeline of landmarks for graphene synthesis and commercialization in the past decade. The graphene-related products depicted include a tennis racket<sup>169</sup>, a touch screen<sup>43</sup>, a 3D printing cable<sup>170</sup>, a bio-sensor<sup>171</sup>, and electronic and optoelectronic microchips<sup>114</sup>. Images reproduced with the permission from refs. <sup>6,172,2728,43</sup>, Springer Nature Ltd. and ref. <sup>173</sup>, American Chemical Society.

costly. For example, dispersed GNPs in liquid allow processing to form freestanding thin films or coatings on arbitrary surfaces, and facilitate mixing with other materials to form composites<sup>19–21</sup>. However, graphene oxides in the primitive form differ significantly from crystalline graphene and possess excessive defects decorated with carbonyl and hydroxyl functional groups, although the graphitic backbone is largely preserved<sup>22,23</sup>. To restore the graphene lattice, graphene oxide is reduced through thermal annealing or chemical treatment to form reduced graphene oxides<sup>24,25</sup>. While the oxygen groups can be partially eliminated by reduction, the damages in the carbon networks remain with the presence of structural defects<sup>26</sup>.

Further developments, such as liquid phase exfoliation (LPE), involved disintegration of graphite directly into graphene by shear stress in solvent (Figs. 2a and 2b)<sup>27,28</sup>. The choice of a solvent with optimized surface tension is critical for efficient exfoliation and a stabilized dispersion of graphene. LPE produces GNPs with significantly reduced structural defects in comparison to graphene oxides or reduced graphene oxides due to the direct mechanical exfoliation<sup>27</sup>. Also, the production rate analysis shows promise in scaling up for industrial production (Fig. 2c)<sup>28</sup>. However, similar to graphene oxides and reduced graphene oxides, the lateral dimension of GNPs produced by LPE is limited to a few micrometres, and the thickness of GNPs varies from monolayer to more than ten layers due to the statistical nature of the process. Producing graphene sheets with large average diameter while maintaining structural integrity and uniformity in monolayer thickness has remained a challenge. Today, vendors are producing GNPs in the form of a powder, dispersion, or composite master batch. Recent reports show increasing commercial availability of graphene GNPs, with companies claiming production capabilities of thousands of tonnes per annum, while the specifications of graphene vary significantly in terms of lateral dimension, thickness and impurity content<sup>14,29</sup>.

#### **Continuous graphene sheets**

Continuous sheets of graphene can be synthesized from bottomup routes by sublimation of SiC or by chemical vapour deposition (CVD) with hydrocarbon precursors. Fabrication of graphene sheets directly on SiC, so called epitaxial graphene<sup>30</sup>, is done by sublimation of the top-most Si on single-crystalline SiC wafers at high temperature, which triggers the reconfiguration of the remaining carbon atoms into epitaxially aligned graphene. Since epitaxial graphene is formed on the atomically flat wafer surface free of wrinkles and contaminations, it is readily compatible with high-value microelectronic processing although at the expense of costly semiconductor substrates. The CVD process has evolved over the years and is currently the choice process for scalable graphene sheet production<sup>11,31-34</sup>. CVD of graphene involves the activation of gaseous carbon hydrate and subsequent chemical reaction to form a sheet of graphene, which was initially over a Ni foil<sup>11</sup>. It was found later that Cu is a better candidate as a substrate, leading to improved thickness uniformity over a large area. Coverage of up to 95% monolayer graphene can be achieved on Cu foils<sup>35</sup>. Despite the significant progress in the past decade, the majority of CVD graphene is polycrystalline with a domain size in the micrometre to millimetre range. Nevertheless, the room-temperature carrier mobility of CVD graphene can reach up to 70,000 m<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> (ref. <sup>36,37</sup>), close to that of pristine graphene and a significant improvement over GNPs<sup>38</sup>.

However, the synthesis of continuous CVD graphene of high quality requires tight process control, and its prices are still orders of magnitude higher than those of GNPs. Over the past decade, significant efforts have been made to scale up the production of highquality CVD graphene. Multiple research groups demonstrated roll-to-roll CVD processes for graphene synthesis<sup>39-42</sup>, realizing high-quality CVD graphene with a Raman peak intensity ratio of the D and G bands  $(I_D/I_G)$  as low as 0.065 and a growth rate up to 5 cm min<sup>-1</sup> (Fig. 2d). It has also been shown that the roll-to-roll process can be applied for graphene transferred to a flexible substrate of up to 30 inches<sup>43,44</sup>. These results pointed out the potential routes towards industrial production and handling of large-area electronic-grade graphene. Although CVD has been shown as a relatively scalable process, further production up-scaling is fundamentally limited by the efficiency in the phase change of carbon, as well as the complexity of infrastructures. Innovations to enable high-quality graphene synthesis without the need of a vacuum, high temperature or catalytic metal will be beneficial to accommodate the bulk consumptions in the market as well as to create extra market opportunities. Currently, CVD graphene of a few inches on various substrates including metal foils and SiO<sub>2</sub> is widely available for sale to support the research communities or pilot development, while leading vendors are supplying CVD graphene on the scale of tens of metres through the roll-to-roll process. Large-scale CVD





**Fig. 2 | Mass production of graphene as raw materials. a**, GNP dispersion in multiple bottles produced by LPE<sup>28</sup>. **b**, Lab scale GNP synthesis using a shear mixer<sup>28</sup>. **c**, GNP production on the scale of 100 L<sup>28</sup>. **d**, Roll-to-roll CVD of graphene at lab scale<sup>40</sup>.

graphene production with better quality control in terms of defects, uniformity and electrical properties is under development with leading vendors.

### Applications in the industry

With the fast development of graphene production techniques, intensive efforts have also been made to incorporate graphene into real commercial products. Based on graphene's unique properties, many applications spaces such as structural, environmental, electrical and optoelectronic technologies have been identified and there has been substantial progress, close to production levels. This section summarizes the current progress towards commercialization of graphene products in different technological sectors.

#### Graphene derivatives and composites

Due to the outstanding mechanical strength and electrical/thermal conductivity, graphene has been applied as scaffold or filler materials in composites. By filtering the dispersed GNPs followed by drying, GNPs can be assembled into free-standing foil-like materials, so called graphene paper (Figs. 3a and 3b)<sup>45</sup>. GNPs in graphene paper form a unique layer structure interlocked together in parallel, allowing effective load distribution. The Young's modulus and fracture strength of graphene paper reaches 42 GPa and 120 MPa<sup>45</sup>, respectively, superior to those of other paper-like materials, for example buckypaper or graphite foil<sup>46,47</sup>.

GNPs can also be fabricated as fibres by spinning, a similar process to the production of conventional synthetic fibres (Fig. 3c,d)<sup>48,49</sup>. Similar to graphene paper, graphene fibre forms the interconnected networks but in the form of a fibre. The Young's modulus and tensile strength of graphene fibre can reach more than 120 GPa and 1.2 GPa, respectively<sup>49-51</sup>. Although the reported modulus and tensile strength of graphene fibre are not comparable to those of carbon fibre, which are 380 GPa and 4.5 GPa, respectively<sup>52</sup>. Graphene fibre is flexible and possesses a five-times higher failure strain of 10%<sup>52,53</sup>, suggesting graphene fibre can sustain higher elongation before failure. Coupled with the high temperature stability and the outstanding electrical (>10<sup>5</sup> S m<sup>-1</sup>)<sup>48,51,54,55</sup> and thermal (>1,400 W m<sup>-1</sup> K<sup>-1</sup>)<sup>51,56</sup> conductivity, graphene papers and fibres can provide the structurally robust platforms for various applications in light-weight reinforcement, heat spreaders, conductive textiles and so on.

Additionally, GNPs are proposed to be the alternative filling agent in composite materials to replace conventional filler materials such as carbon black and carbon fibres<sup>21</sup>. The specifications of graphene are outstanding owing to its high surface area, tensile strength, thermal and electrical conductivity. Mixing a small amount of GNPs in the matrix of polymers, metals or ceramics can achieve significant enhancement in the mechanical, electrical and thermal properties of the composites. As an example, 0.5 wt.% of GNPs in epoxy resin achieves fracture toughness enhancement by 40%57. Electrical conductivity is enhanced by 8 orders of magnitude from 10<sup>-8</sup> S m<sup>-1</sup> to 1 S m<sup>-1</sup> (ref. <sup>58</sup>), and thermal conductivity is enhanced by 167 times to ~33 W m<sup>-1</sup> K<sup>-1</sup> with GNP filler<sup>59,60</sup>. Commercial applications under development include light-weight sports goods, electromagnetic shields for aircraft, flame retardant plastics and 3D printing filaments and inks promising for printed flexible electronics (Fig. 3e). For example, tennis racquets with a graphene-based composite were first commercialized (Table 1)61. Following this success, ski equipment, bicycles, helmets and shoes with graphene reinforcement are in production (Table 1). The chemical inertness and the special layered structure of graphene have also been utilized for anti-corrosion purposes<sup>62</sup>. The incorporation of GNPs into coatings creates a corrugated path for the permeation of oxidants, delaying the oxidation process. Graphene-based coatings have been demonstrated to outperform conventional zinc phosphate-based materials (Fig. 3g)<sup>63</sup>, and is commercially available (Table 1).

### **Energy and environment**

Energy is a major industry that requires the consumption of graphene in bulk quantity. The integration of graphene in batteries, supercapacitors and devices for hydrogen generation and storage offers opportunities to meet the challenge of ever-increasing global energy consumption<sup>64</sup>. The atomically thin graphene provides an extremely large surface-to-mass ratio of 2630 m<sup>2</sup> g<sup>-1</sup>, coupled with chemical stability and excellent electrical and thermal conductivity<sup>65</sup>, which is an ideal platform for energy applications, such as storage of electrical charges, ions and hydrogen atoms. Indeed, the amount of charge, ions, or hydrogen stored per unit mass is directly proportional to the surface available.

Graphene can be used as an active material for electrodes of Li-ion batteries. It has been considered that a monolayer graphene with two surfaces being used for Li adsorption enables a theoretical specific capacity of 744 mAh  $g^{-1}$ , doubling that of current graphite electrodes<sup>66,67</sup>. With further surface modification, graphene oxide electrodes have been demonstrated to achieve more than 2,000 mAh  $g^{-1}$  for the first discharge, surpassing the theoretical value of pristine monolayer graphene because of solid electrolyte interphase formation<sup>68</sup>.

So far, graphene is mostly used as a conductive agent in electrodes to improve rate capability and cyclability because of its thermal conductivity and electrical conductivity. For example, graphene is used in a combination of common cathode materials such as  $LiCoO_2$ ,  $LiMn_2O_4$  and  $LiFePO_4$ . Owing to the improved electrical and thermal conductivity of graphene in comparison to conventional additives such as carbon black, the path for the transport of charge and heat is much shortened. Improvement of up to 160% of the discharge capacity is observed with electrodes enhanced with graphene<sup>69</sup>. Also, graphene can form a matrix or skeleton to encapsulate active components to resolve the issues associated with

## **NATURE NANOTECHNOLOGY**



**Fig. 3** | **Selective applications of graphene in composites, energy and environment. a**, Macroscale graphene paper<sup>45</sup>. **b**, Microstructure of graphene paper<sup>45</sup>. **c**, Graphene fibres woven in textiles<sup>48</sup>. **d**, Microstructure of a knotted graphene fibre<sup>49</sup>. **e**, Printed electronics with graphene inks<sup>174</sup>. **f**, Testing of water filtration with a graphene membrane<sup>175</sup>. **g**, Salt spray testing after 2,000 hours showing the comparison between the zinc-based anti-corrosion coatings with (bottom) and without (top) graphene oxide additives<sup>63</sup>.

fast capacity decay, poor rate performance and low Coulombic efficiency<sup>70-72</sup>. The high-energy lithium-ion batteries with graphite anodes and transition metal oxide cathodes are still unable to achieve fast charging without negatively affecting electrochemical performance and safety<sup>73</sup>. Commercial batteries with graphene and graphene–Si composite electrodes are currently under development. Battery manufacturers have been developing graphene battery technology with 'graphene ball' materials that enables five times faster charging speeds than standard lithium-ion batteries<sup>74</sup>, and the technology is expected to be adopted in mobile phone products in the near future.

On the other hand, the large surface-to-mass ratio and theoretical capacitance of 550 F g<sup>-1</sup> of graphene are advantageous for supercapacitor implementation<sup>66,75</sup>. The key to success for graphene is to make full utilization of the intrinsic surface capacitance and specific surface area. Supercapacitors with graphene-based electrodes and a mesoporous structure exhibited a specific energy density of 85.6 Wh kg<sup>-1</sup> at room temperature and 136 Wh kg<sup>-1</sup> at 80 °C, with a current density of 1 A  $g^{-1}$  (ref.  $^{76}\!).$  Laser-scribed graphene films that have been used directly as electrodes without binder, conductive additives or metal current collectors, have shown energy densities of up to 1.36 mWh cm<sup>-3</sup> and power densities of 20 W cm<sup>-3</sup> in an ionic liquid electrolyte77. Further, graphene can be combined with pseudocapacitive materials maintaining high energy density and power performance to bridge the gap between batteries and electric double-layer capacitors<sup>78</sup>. In fact, the supercapacitor market is one of the first to have adopted graphene technology commercially. Graphene ultracapacitors have been reported to reduce elevator energy consumption by half and are currently in use throughout Europe79.

An emerging environmental application of graphene is in molecule or ion filtration. A GNP membrane can act as a selective barrier for permeation of molecules or ions<sup>80-82</sup>. GNPs are stacked in a layer by layer fashion, creating a corrugated nanochannel between the layers. The selectivity is based on the size exclusion. It was found that a 1µm-thick GNP membrane with interlayer distance of less than 9 Å rejects all solute with a hydrated radius more than 4.5 Å (ref. <sup>83</sup>), while the flow rate of water permeation can reach 0.2 l m<sup>-2</sup> h<sup>-1</sup>. Water filtration can also be achieved with monolayer graphene sheets, while the water permeates through well-defined nanopores<sup>84</sup>. The selectivity is based on pore diameter as well as the functional groups at the pores. The flow rate of filtration depends on the porous density and the upper bound permeance for water filtration is estimated to exceed 1,000 l m<sup>-2</sup> h<sup>-1</sup> bar<sup>-1</sup> (ref. <sup>85</sup>). The high selectivity and permeance of graphene membranes can be applied for energy efficient water desalination and gas filtration (Fig. 3f).

### Electronics

Driven by the challenge of further scaling Si transistors, searching for a replacement has become imminent in the past decades. Fabricating field-effect transistors using graphene has been the first motivation following the discovery of its outstanding carrier mobility. In addition, the high field velocity of graphene shows great promise over traditional semiconductors including Si. Although the performance of graphene-based transistors as logic switches has been rather restricted owing to the zero bandgap, leading to the dreadful on-off ratio<sup>86</sup>. Rapid progress has been made in the past decade for graphene-based radio frequency field effect transistors (FETs), which quickly broke the record set by the Si equivalent, achieving a cut-off frequency ( $f_T$ ) of 100 GHz given the same gate length<sup>87</sup>. Shortly after, a new record was set with  $f_{\rm T}$  of 427 GHz by aggressive gate length scaling (Fig. 4a)88. The impressive cut-off frequency owes to the high mobility in the channel. On the other hand, the maximum oscillation frequency  $(f_{max})$  of graphene FETs had been historically below 30 GHz due to a high contact resistant

### **NATURE NANOTECHNOLOGY**

## FOCUS | REVIEW ARTICLE

Graphene properties utilized	Company	Product (model)	Features
Thermal	Huawei	Smartphone (Mate 20 X)	Graphene film as a heat sink for cooling <sup>177</sup>
Thermal	TeamGroup	Solid-state drives (Cardea Zero M.2 PCIe SSD)	Graphene heat spreader for efficient SSD cooling $^{\ensuremath{^{178}}}$
Thermal, mechanical	Momodesign	Helmet (FGTR Graphene 1.0)	Graphene film for efficient heat dissipation <sup>179</sup>
Thermal, mechanical	Directa Plus/Colmar	Apparel (G+ series)	Graphene-assisted heat management and heat distribution <sup>180</sup>
Mechanical	HEAD	Tennis racquet, Ski (GrapheneXT)	Graphene for light weight, flexibility and robustness <sup>61,181</sup>
Mechanical	Dassi	Bicycle (Interceptor)	Graphene in frameset for light weight and stiffness $^{\mbox{\tiny 182}}$
Mechanical	inov-8	Shoes (G-series)	Graphene for improved elasticity, strength and durability $^{\mbox{\tiny 183}}$
Mechanical	ZOLO	Earphone (Liberty series)	Graphene-enhanced audio drivers for improved sound quality <sup>184</sup>
Mechanical	Richard Mille	Watch (RM 50-03)	Graphene for extremely light-weight chronograph <sup>185</sup>
Electrical	Nanomedical diagnostics	Biosensor (Agile)	Graphene FET as a biochemical sensor <sup>186</sup>
Electrical	Graphenea	Transistor array (GFET-S10)	FETs on SiO <sub>2</sub> with CVD graphene and 1,000 cm <sup>2</sup> V s <sup>-1</sup> mobility (https://www.graphenea. com)
Optical, electrical, mechanical	Chongqing Graphene Technology	Smartphone	Flexible touch screen for mobile phone <sup>187</sup>
Optical	Emberion	Photodetector	Prototype of graphene-based broadband photodetector <sup>188</sup>
Optical, electrical	Graphene Flagship	Communication link (modulator and detector)	All-graphene optical communication link at 25 Gb s $^{-1}$ (ref. $^{127}$ )
Optical, electrical	Galapad	Smartphone (Galapad Settler)	Graphene-based touch screen enabling better light transmission <sup>189</sup>
Chemical	Applied Graphene Materials	Additives for painting/coating (Genable series)	Graphene for anti-corrosion and for blocking moisture penetration <sup>190</sup>
Chemical	CalBattery	Lithium battery electrode	Silicon-graphene composite anode <sup>191</sup>

associated with organic residues<sup>87–89</sup>. Very recently,  $f_{max}$  exceeding 200 GHz has been achieved after optimizing contact resistant with a residue-free process<sup>90,91</sup>. Continuous efforts are ongoing to create graphene-based radio frequency electronic circuitry (Fig. 4b)<sup>92</sup>. So far, vendors have been supplying graphene-based field-effect transistors mainly for research and development purposes (Table 1).

Increasingly, instead of challenging the established role of Si, graphene attracts more attentions in the area where conventional electronic materials do not excel. For example, graphene interconnects can support a current density of  $10^8$  A cm<sup>-2</sup> and possess thermal conductivity of 5,000 W m<sup>-1</sup> K<sup>-1</sup>, 100 times and 4 times greater than those of copper, respectively<sup>93,94</sup>. These outstanding properties of graphene have led to its promising applications as current or heat spreaders in the back end of silicon integrated circuits. Graphene-based thermal management was successfully commercialized, especially in thermal cooling for solid state drives and memory where it allows normal operation without bulky heat sinks (Table 1).

Additionally, the 2D nature of graphene and its strong  $sp^2$  bonding enables opportunities in flexible and stretchable electronics<sup>19,95</sup>. The theoretical fracture strain of graphene has been estimated to be ~20%–25%<sup>96,97</sup>. Impressive uniaxial tensile strain of up to 450% is achievable when coupled with a pre-stretched substrate<sup>98</sup>. As a demonstration, graphene has been fabricated as active transistors on rubber and a high mobility of graphene is retained under 5% strain<sup>99</sup>. Coupled with its transparency, graphene is particularly attractive for transparent electrodes (Fig. 4c)<sup>100</sup>, as an alternative to indium tin oxide. Monolayer graphene has a transparency of 97.7%<sup>101</sup>, compared to indium tin oxides that have a value of 90.5%. It has been shown that a stack of four monolayers of graphene is enough to achieve the same sheet resistance of 10  $\Omega$  square<sup>-1</sup> with a transparency of 90%<sup>102</sup>, the standard in the industry currently set by indium tin oxides. The flexibility of graphene-based transparent electrodes is an extra benefit that can find applications in advanced electronics such as solar cells, display panels, radio frequency identification and wearables. Graphene has been incorporated in commercial electronics as transparent electrodes in mobile phone touch screens (Table 1).

A recent exotic application of graphene involves utilization of the special van der Waals feature on the surface of graphene. Semiconductor thin films deposited on graphene have been mechanically separated from substrates due to their weak van der Waals bonding with graphene<sup>103</sup>. It was further discovered that the crystallinity of a deposited semiconductor thin film can be significantly improved with atomically thin graphene, due to the reduced distance to its substrate<sup>104</sup>. Such new functionality of graphene potentially enables significant cost reduction in high-value nonsilicon electronics.

Overall, the implementation of graphene into commercial products must be compatible with existing technology in terms of fabrication and functionality. Especially for large-scale applications, graphene transferred from its host onto a target substrate has been a crucial step so far. The key is to avoid generating damages or residues

## **NATURE NANOTECHNOLOGY**



**Fig. 4** | **Selective applications of graphene in electronics and optoelectronics. a**, Graphene FET with aggressively scaled gate length demonstrating record cut-off frequency *f*<sub>max</sub>. Scale bar, 30 nm<sup>89</sup>. **b**, Integrated circuit demonstration with graphene transistors, functioning as a radio frequency receiver. Scale bar, 100µm<sup>92</sup>. **c**, Stretchable transparent electrodes using CVD graphene (MGGs) in comparison to those with carbon nanotubes (CNTs)<sup>176</sup>. **d**, A microscopic image of a graphene on Si phase modulator operating at communication wavelength of 1550 nm<sup>113</sup>. **e**, Image of a pixelated surface with 14 cells, individually addressable to radio frequency reflection<sup>125</sup>. **f**, A tree leaf imaged at 0.3 THz by a graphene-based terahertz detector revealing leaf veins<sup>123</sup>.

either to the graphene or the target substrate. Thus, a major focus is the development of contamination-free processes of graphene transfer. Starting from graphene grown on the wafers can alleviate such concerns. However, the requirements for low temperature synthesis processes while maintaining the quality and uniformity of graphene have been challenging, and successful development will be extremely valuable. An alternative is to scale up the residue-free transfer processes, for example the dry transfer or semi-dry transfer, with which graphene is not in direct contact with the polymer<sup>105,106</sup>.

### Optoelectronics

The exceptional properties of graphene have also found attractive applications in optoelectronics<sup>107</sup>. Due to its unique linear energymomentum dispersion relation, electrons in graphene interact strongly with photons across a wide range of the spectrum, theoretically covering the frequency from ultraviolet to infrared, and extending into terahertz or even radio frequency. The broadband responsivity is an outstanding feature found in graphene-based photonic devices<sup>108-110</sup>. Remarkably, such broadband responsivity can be effectively controlled by the Fermi level of graphene through either electrostatic gating or optical pumping<sup>111,112</sup>. Graphene has been implemented as a variety of photonic components with outstanding performance<sup>113</sup>, including optical sensors<sup>114</sup>, polarizers<sup>110,115</sup>, saturable absorbers<sup>116</sup> and so on, potentially to be integrated in photonic circuits for next generation communication systems<sup>117</sup>. The real and imaginary parts of the effective mode index are reconfigurable by electrical biasing, facilitating broadband optical amplitude, or phase modulation<sup>113</sup> (see Fig. 4d). The strong polarization-dependent optical absorption in graphene-laminated waveguides can be leveraged to realize integrated polarizers, while the broadband absorption

property facilitates photodetection across all optical communication bands<sup>118,119</sup>. For example, the state-of-the-art graphene-based photonic devices on wafers have demonstrated photodetection with a bandwidth of 128 GHz<sup>120</sup>, and optical modulation with a bandwidth of 30 GHz<sup>121</sup>, a modulation depth exceeding 15 dB<sup>121</sup> and energy consumption less than 350 fJ bit<sup>-1</sup> (ref. <sup>122</sup>). Additionally, due to the nature of van der Waals bonding of the graphene surface, the heterointegration of graphene with silicon-based photonic platforms is not limited to lattice matching, unlike other conventional semiconductor materials. The success could propel the advancement of on-chip optical interconnects and wireless data transmission with visible light (light fidelity).

So far, the performance of graphene-based photonic devices is on par with, or even better than, the best Si-based photonic devices at communication frequency. However, graphene optical components distinguish themselves in the infrared or terahertz wavelengths (Fig. 4e)<sup>123</sup>, where conventional optical materials are limited by their individual bandgap and the best solution has not been clear. As a demonstration, a broadband terahertz transmittance modulator was created by graphene gated via ionic liquid<sup>124</sup>. Modulation over frequencies ranging from 0.1 THz to 2.5THz have been achieved with a modulation depth of 20 dB. In addition, the modulation has even been extended to the microwave frequency range, around 10.5 GHz (Fig. 4f)<sup>125</sup>, where the reflection and transmission of the microwave were modulated with graphene integrated surfaces. Further multifunctional applications include compact terahertz imaging for airport security screening, microwave radar cloaking and so on.

The graphene-based integrated photonic devices reported so far are mainly small scale<sup>108-110</sup>, while system level integration still requires further development. Up-scaling of graphene-based

### **NATURE NANOTECHNOLOGY**

photonics is currently limited by the relatively low yield of the mechanical transfer process. High-quality monolayer graphene directly grown on fabricated photonic structures is ideal, although remains very challenging due to the lack of metallic catalysts. Additionally, the technological relevance of graphene-based optical components will also rely on compatibility with existing large-scale photonic fabrication processes<sup>126</sup>, for example complementary metal–oxide–semiconductor compatibility in foundries. Corresponding manufacturing technology is also needed to be optimized to realize device mass production with distinctive performances and robustness. Recently, the prototype of an all-graphene optical communication link has been demonstrated with an impressive data rate of 25 Gb s<sup>-1</sup> per channel<sup>127</sup>, and the increasing number of reports on product development indicates the ramping up of graphene commercialization for optical communications (Table 1).

#### Challenges for commercialization

Here we discuss the outstanding challenges for graphene production and standardization, along with the state-of-the-art solutions reported in literature.

Narrowing the gap to pristine graphene. As we have learned from the silicon industry, moderate performance enhancement is not enough to justify the replacement of an established technology that has been heavily invested in over time. New solutions should provide drastic improvements or be able to create new market opportunities. However, the graphene currently on the market differs significantly from pristine graphene<sup>29</sup>. Ideally, graphene is an atomic plane of carbon bonded with pure sp<sup>2</sup> bonds. Realistically, graphene varies in lateral size, thickness and density of structural defects, which are tied to the production methods. Such deviation causes changes in electronic or structural properties. For instance, thermal or electrical conductivity of graphene is reduced with increasing thickness and number of structural defects such as dangling bonds and grain boundaries<sup>128-131</sup>. The stiffness of graphene also increases with thickness, with bilayer graphene about 10 times stiffer than monolayer graphene. Structural defects such as grain boundaries and vacancies significantly weaken the mechanical strength of graphene<sup>132,133</sup>. For example, graphene oxides or reduced graphene oxides represent the defective state of graphene, the Young's modulus of which drops to the order of 250 GPa<sup>134</sup>, in comparison to the 1 TPa of pristine graphene. For CVD-synthesized polycrystalline graphene, although mechanical properties within the defect-free grains are outstanding, breakage tends to occur along the grain boundaries<sup>132</sup>. The reduction from the outstanding specifications of pristine graphene usually leads to the dissatisfactory performance in existing products and prevents applications where the intrinsic properties of graphene are critical. For example, graphene-based lithium ion battery electrodes so far have demonstrated performance far below expectations — the initial high capacity of the graphene-based electrode is not retained after the first charge<sup>135</sup>. The gap is partially because the defective graphene used in the electrode falls short in specific surface area, and defects decorated with oxygen and hydrogen containing groups become irreversible binding sites for lithium ions, leading to a low coulombic efficiency. Bridging the gap between commercially

available graphene and pristine graphene is essential to reach the initial expectations for graphene technology.

Progress has been made to reduce the inherent defects in graphene nanoplatelets and continuous sheets. Nanoplatelets with improved graphitic quality can be obtained by microwave heating or by increasing the annealing temperature up to 3,100 K<sup>136-138</sup>, in comparison to the typical annealing temperature of less than 1,500 K<sup>139</sup>. The structural defects on carbon backbones are further repaired, indicated by the strong 2D peak and the nearly disappearing D peak in Raman spectroscopy (Fig. 5a)137. Chemical impurities such as oxygen and hydrogen are largely removed to the level close to that of CVD graphene or graphite<sup>138</sup>. As a result, significant increases in the Young's modulus, and the electrical and thermal conductivity of graphene nanoplatelets are observed<sup>136,137</sup>. On the other hand, nonuniformity of continuous sheet graphene in terms of thickness variation and grain boundaries has been mitigated by using well-defined metal substrates. It was found that single crystalline (111) Cu provides a better surface for graphene nucleation than polycrystalline or (100) Cu due to the symmetry matching, yielding highly oriented graphene with improved thickness uniformity across the surface<sup>140-142</sup>. Additionally, single-crystalline graphene with grain size of up 1.5 inches in diameter can be produced by local precursor feeding (Fig. 5b)<sup>143</sup>. Wafer-scale monolayer single-crystal graphene has also been demonstrated on (110) Ge substrates<sup>144</sup>. Evolutionary selective growth or self-collimation growth are potentially more scalable for grain boundary reduction (Fig. 5c)<sup>145,146</sup>. Additionally, by separating synthesis and post-processing, the synthesis time and restrictions due to uniformity can be significantly reduced. A recent development showed that by the control of crack propagation at van der Waals interfaces, monolayer 2D material can be extracted layer-bylayer at the wafer-scale from a multilayer CVD 2D material stack, providing a potential solution for scalable uniformity control<sup>147</sup>. Further efforts should be made to incorporate these new understandings into cost-effective industrial-scale graphene production.

Standardization. One of the fundamental challenges of graphene production is run-to-run variations in terms of graphene quality, defects, thickness and doping. There is a large variation of graphene properties sold by various vendors, and a recent study have found that products from most vendors are not optimal for most graphene applications<sup>29</sup>. This large statistical variation in the quality of graphene and lack of standards is another detriment to its commercialization. To this end, a plethora of characterization methods has been developed and published in academia, allowing meticulous characterization of grown or transferred graphene on foreign substrates. However, most techniques developed in academia are limited in terms of inspection area and throughput, which is a must for industrial adoption. Some key parameters that require quality control are thickness uniformity, macroscopic defects such as tears and wrinkles, and microscopic defects such as grain boundaries, contamination, doping etc. and require assessment in a non-destructive manner. Here, we give an overview of past and recent inspection methods of various graphene parameters reported to date, consisting of spectroscopic methods, microscopic methods and chemical methods (Fig. 5d-e)148-160.

**Fig. 5** | **Progress towards defect minimization and standardization of graphene. a.** SEM showing the high temperature annealed graphene oxides (MWrGOs) with a lateral dimension of -50 μm (top), and Raman spectroscopy comparison of graphene from different sources, with high temperature annealed graphene oxides shown in red (bottom)<sup>138</sup>. HOPG, Highly oriented pyrolytic graphite; rGO, reduced graphene oxide. b, Single-crystalline graphene of up to 1.5 inches was demonstrated (bottom), by local feeding of carbon precursor (top)<sup>143</sup>. **c**, SEM images of growth evolution of hBN film on liquid metal. Random grain distribution was initially observed during growth (top), and grains alignment was achieved later through electrostatic attraction between grains upon coalescence (bottom)<sup>145</sup>. **d**, Characterization techniques using optical methods to visualize defects such as cracks, wrinkles, tears and grain boundaries over a large area and with high throughput<sup>153-155</sup>. T, transmission; I, incident beam; R, reflection; *n*, refractive index; *d*, thickness; BS, beam splitter; BP, band-pass filter; FD, field diaphragm; AOI, angle of incidence; PD, photodiode; IRM, interference reflection microscopy; SNR, signal-to-noise ratio; TAMPs, tuned amplifiers. **e**, Methods to characterize electrical properties of graphene layers<sup>152,155</sup>. IR, infrared; TDS, time-domain spectroscopy.

When graphene was first discovered, single point measurements such as Raman spectroscopy were predominantly used to detect and characterize the thickness, orientation and defects of the harvested graphene flakes. Raman spectroscopy has been one of the first breakthrough characterization methods for in-depth inspection of graphene flakes, first reported in 2006 on graphene flakes, and is still



the most widely used technique to characterize graphene<sup>148,161,162</sup>. It is highly sensitive to any disorders in the *sp*<sup>2</sup>-hybridized carbon bonds and can convey not only the structural properties but electrical as well. Despite its universality, robustness and simplicity, due to its single point nature, it is an open question if this technique can truly be applicable for large-area detection with the high throughput required for industrial needs. Thus, immediate efforts were made to use simple processes, such as optical microscopy, to detect graphene quality. Interference reflection microscopy was developed to visualize voids, cracks, wrinkles and the number of layers of graphene transferred on transparent substrates. It utilizes a collimated light that is reflected off of the interface between the substrate and graphene, resulting in reflection interference that allows visualization of the number of graphene layers with unprecedented contrast ratios<sup>153</sup>. With this technique, it is possible to directly visualize graphene on transparent substrates at 30-40% image contrast per graphene layer, also allowing identification of nanoscale structural defects such as wrinkles and cracks over a large area with a high throughput of about a thousand times faster than using scanning electron microscopy. Ellipsometric contrast microscopy was specifically designed for large area contactless visualization of graphene defects<sup>155</sup>. It was demonstrated on a monolayer of graphene transferred onto an oxide-free 4 inch silicon wafer and was able to resolve micrometre scale defects and contamination with an imaging speed of 1.7 cm<sup>2</sup> min<sup>-1</sup>. It is also applicable to graphene on Cu foils, potentially allowing inspection for a roll-to-roll process. Transient absorption microscopy allows detection of graphene grain boundaries where the graphene is produced by a roll-to-roll process<sup>154</sup>. It uses the decrease in pump beam intensity when carriers in graphene fill the conduction band in response to absorption of a light source. By using a line scan and an array of photodiodes, nearly six orders of magnitude increase in detection throughput was demonstrated compared to conventional Raman spectroscopy. Lock-in thermography was also introduced recently, whereby Joule heating was imaged by applying an a.c. voltage across a large area polycrystalline and single crystalline graphene film and capturing the thermal radiation resulting from the voltage bias<sup>159</sup>. A clear heat signature contrast was observed in the areas with microscopic defects such as cracks and holes. Last but not least, although the above techniques can directly visualize the structural integrity of graphene, its electrical characteristics cannot be quantified. There are a few methods developed that allow characterization of electrical performance of large area graphene films. One of the more promising technique is terahertz time-domain spectroscopy<sup>156</sup>, which is a non-contact and non-destructive method of measuring the sheet conductivity of a material. In this method, the attenuation of a femtosecond terahertz laser pulse is measured (either reflected or transmitted) which can be scanned over a large area within minutes.

#### **Outlook and conclusion**

To make graphene an industry-friendly material, significant efforts must be made in perfecting graphene as a basic building block at a much-reduced cost, including synthesis, storage and processing of graphene. Fortunately, we have seen a steady trend showing the steep slope of price reduction, for example, the price of GNP graphene decreases by an order of magnitude from US\$250 kg<sup>-1</sup> to US\$20 kg<sup>-1</sup> within four years after 2011<sup>163</sup>. On the other hand, there have been many variations of graphene in the form of films and composites, and they vary in dimensions and physical properties due to the inherent thermodynamic randomness of graphene synthesis. Specific graphene materials will be synthesized for a specific application from the beginning, and companies of graphene production need to work closely with the companies implementing graphene-based products. Like any other new material to be commercialized, graphene must first be compatible with existing technology in terms of fabrication and functionality to facilitate its penetration into the markets. Most established industries will be hesitant to invest in new materials, which have a high risk of failure, thus it will also require the efforts from small companies as well as from scientific communities to demonstrate convincing concepts for scalable products at this point.

Together with the efforts for graphene perfection, it is crucial to identify the markets that can utilize the special properties of graphene for successful commercialization. Being a material with one layer of atoms, graphene has shown its unique mechanical, chemical, thermal, electrical and optical properties. Mechanically, graphene's strong sp<sup>2</sup> bonding offers reinforcement for its surrounding matrix. Chemically, the anisotropic layered structure and stability of graphene provide barriers to penetration. For example, graphene has been considered as a replacement for metal diffusion barriers for logic and memory technologies in industry<sup>164</sup>. Thermally, the high thermal conductivity of graphene is immediately beneficial to fulfill the requirements for thermal management in macrostructures or microelectronics<sup>164</sup>. Thus, industry has been heavily pursuing graphene as a cooling mechanism for consumer electronics. Needless to say, the high carrier mobility of graphene allows numerous possibilities to outperform the established electronics, which will be the focus of development from this stage forward. While the justification for transistors has been weakened over time due to challenges in generating a sizable bandgap, the low sheet resistance of graphene at its atomic thickness has compelling applications as transparent electrodes for upcoming flexible electronics, the growth of which is imminent for internet-ofthings applications. Along with graphene's broadband light-matter interaction, reinforced absorption by coupling with 0D materials can accelerate the application of graphene in optoelectronics<sup>165</sup>. The weak van der Waals bonding of graphene to adjacent layers also enables graphene as a debonding laver for electronic devices. Single-crystalline devices can be grown on graphene and subsequently released from the surface allowing the reuse of expensive substrates, leading to wafer cost reduction for advanced non-Si electronics<sup>103</sup>.

The listed features above will certainly strengthen graphene's market value as a real commercial product in the foreseeable future, while the investigation of graphene at the fundamental level is still ongoing. For example, graphene-based superconducting circuits have been recently achieved<sup>166</sup> and twisted bilayer graphene stacking has been found to be tunable from superconductor to insulator<sup>167,168</sup>. The deeper understanding of graphene and the new discoveries in labs today will surely create new markets for graphene-based commercial products in the far future.

Received: 15 August 2019; Accepted: 6 September 2019; Published online: 3 October 2019

#### References

- Novoselov, K. S. et al. Two-dimensional atomic crystals. Proc. Natl Acad. Sci. USA 102, 10451–10453 (2005).
- Novoselov, K. S. et al. Electric field effect in atomically thin carbon films. Science 306, 666–669 (2004).
- Novoselov, K. S. et al. Two-dimensional gas of massless Dirac fermions in graphene. *Nature* 438, 197–200 (2005).
- Zhang, Y., Tan, Y. W., Stormer, H. L. & Kim, P. Experimental observation of the quantum Hall effect and Berry's phase in graphene. *Nature* 438, 201–204 (2005).
- Ruoff, R. S. Personal perspectives on graphene: new graphene-related materials on the horizon. MRS Bull. 37, 1314–1318 (2012).
- 6. Segal, M. Selling graphene by the ton. Nat. Nanotechnol. 4, 612–614 (2009).
- Ren, W. & Cheng, H. M. The global growth of graphene. *Nat. Nanotechnol.* 9, 726–730 (2014).
- 8. Zurutuza, A. & Marinelli, C. Challenges and opportunities in graphene commercialization. *Nat. Nanotechnol.* **9**, 730–734 (2014).
- Ferrari, A. C. et al. Science and technology roadmap for graphene, related two-dimensional crystals, and hybrid systems. *Nanoscale* 7, 4598–4810 (2015).
- Ghaffarzadeh, K. IDTechEx forecasts a \$100 million graphene market in 2018. *IDTechEx* https://www.idtechex.com/en/research-article/idtechexforecasts-a-100-million-graphene-market-in-2018/4721 (2012).

- Shelton, J. C., Patil, H. R. & Blakely, J. M. Equilibrium segregation of carbon to a nickel (111) surface: a surface phase transition. *Surf. Sci.* 43, 493–520 (1974).
- Berger, C. et al. Ultrathin epitaxial graphite: 2D electron gas properties and a route toward graphene-based nanoelectronics. *J. Phys. Chem. B* 108, 19912–19916 (2004).
- Huang, Y. et al. Reliable exfoliation of large-area high-quality flakes of graphene and other two-dimensional materials. ACS Nano 9, 10612–10620 (2015).
- 14. Zhu, Y., Ji, H., Cheng, H. M. & Ruoff, R. S. Mass production and industrial applications of graphene materials. *Natl Sci. Rev.* **5**, 90–101 (2018).
- Brodie, B. C. Sur le poids atomique du graphite. Ann. Chim. Phys. 59, 466–472 (1860).
- Kohmchutter, V. & Haenni, P. Zur kenntnis des graphitischen kohlenstoffs und der graphitsaure. Anorg. Allg. Chem. 105, 121 (1918).
- Hummers, W. S. & Offeman, R. E. Preparation of graphitic oxide. J. Am. Chem. Soc. 80, 1339 (1958).
- 18. Marcano, D. C. et al. Improved synthesis of graphene oxide. ACS Nano 4, 4806-4814 (2010).
- Eda, G., Fanchini, G. & Chhowalla, M. Large-area ultrathin films of reduced graphene oxide as a transparent and flexible electronic material. *Nat. Nanotechnol.* 3, 270–274 (2008).
- Li, D., Müller, M. B., Gilje, S., Kaner, R. B. & Wallace, G. G. Processable aqueous dispersions of graphene nanosheets. *Nat. Nanotechnol.* 3, 101–105 (2008).
- 21. Stankovich, S. et al. Graphene-based composite materials. *Nature* 442, 282–286 (2006).
- 22. Dreyer, D. R., Park, S., Bielawski, C. W. & Ruof, R. S. The chemistry of graphene oxide. *Chem. Soc. Rev.* **39**, 228–240 (2015).
- Su, C. Y. et al. Electrical and spectroscopic characterizations of ultra-large reduced graphene oxide monolayers. *Chem. Mater.* 21, 5674–5680 (2009).
- Hofmann, U. & Frenzel, A. The reduction of graphite oxide with hydrogen sulphide. *Kolloid-Z.* 68, 149–151 (1934).
- Moon, I. K., Lee, J., Ruoff, R. S. & Lee, H. Reduced graphene oxide by chemical graphitization. *Nat. Commun.* 1, 73 (2010).
- Pei, S. & Cheng, H.-M. The reduction of graphene oxide. *Carbon* 50, 3210–3228 (2012).
- 27. Hernandez, Y. et al. High-yield production of graphene by liquid-phase exfoliation of graphite. *Nat. Nanotechnol.* **3**, 563–568 (2008).
- Paton, K. R. et al. Scalable production of large quantities of defect-free few-layer graphene by shear exfoliation in liquids. *Nat. Mater.* 13, 624–630 (2014).
- Kauling, A. P. et al. The worldwide graphene flake production. *Adv. Mater.* 30, 1–6 (2018).
- Berger, C., Conrad, E. H. & de Heer, W. A. in *Physics of Solid Surfaces* Vol. 45B (eds Chiarotti, G. & Chiaradia, P.) Ch. 166 (Springer Materials, 2018).
- Batzill, M. The surface science of graphene: metal interfaces, CVD synthesis, nanoribbons, chemical modifications, and defects. *Surf. Sci. Rep.* 67, 83–115 (2012).
- Rosei, R. et al. Structure of graphitic carbon on Ni(111): a surface extended-energy-loss fine-structure study. *Phys. Rev. B* 28, 1161–1164 (1983).
- 33. Reina, A. et al. Large area, few-layer graphene films on arbitrary substrates by chemical vapor deposition. *Nano Lett.* **9**, 30–35 (2009).
- Muñoz, R. & Gómez-Aleixandre, C. Review of CVD synthesis of graphene. Chem. Vap. Depos. 19, 297–322 (2013).
- 35. Xuesong Li. et al. Large-area synthesis of high-quality and uniform graphene films on copper foils. *Science* **324**, 1312–1314 (2009).
- 36. Stampfer, C. et al. Ultrahigh-mobility graphene devices from chemical vapor deposition on reusable copper. *Sci. Adv.* **1**, e1500222 (2015).
- De Fazio, D. et al. High-mobility, wet-transferred graphene grown by chemical vapor deposition. ACS Nano 13, 8926–8935 (2019).
- Wang, L. et al. One-dimensional electrical contact to a two-dimensional material. *Science* 342, 614–617 (2013).
- Kidambi, P. R. et al. A scalable route to nanoporous large-area atomically thin graphene membranes by roll-to-roll chemical vapor deposition and polymer support casting. ACS Appl. Mater. Interfaces 10, 10369–10378 (2018).
- Polsen, E. S., McNerny, D. Q., Viswanath, B., Pattinson, S. W. & John Hart, A. High-speed roll-to-roll manufacturing of graphene using a concentric tube CVD reactor. *Sci. Rep.* 5, 1–12 (2015).
- 41. Kobayashi, T. et al. Production of a 100-m-long high-quality graphene transparent conductive film by roll-to-roll chemical vapor deposition and transfer process. *Appl. Phys. Lett.* **102**, 1–5 (2013).
- Yamada, T., Ishihara, M., Kim, J., Hasegawa, M. & Iijima, S. A roll-to-roll microwave plasma chemical vapor deposition process for the production of 294 mm width graphene films at low temperature. *Carbon N. Y.* 50, 2615–2619 (2012).
- 43. Bae, S. et al. Roll-to-roll production of 30-inch graphene films for transparent electrodes. *Nat. Nanotechnol.* **5**, 574–578 (2010).

- Chandrashekar, B. N. et al. Roll-to-roll green transfer of cvd graphene onto plastic for a transparent and flexible triboelectric nanogenerator. *Adv. Mater.* 27, 5210–5216 (2015).
- Dikin, D. A. et al. Preparation and characterization of graphene oxide paper. *Nature* 448, 457–460 (2007).
- Zhang, X., Sreekumar, T. V., Liu, T. & Kumar, S. Properties and structure of nitric acid oxidized single wall carbon nanotube films. *J. Phys. Chem. B* 108, 16435–16440 (2004).
- Dowell, M. B. & Howard, R. A. Tensile and compressive properties of flexible graphite foils. *Carbon N. Y.* 24, 311–323 (1986).
- 48. Xu, Z. & Gao, C. Graphene chiral liquid crystals and macroscopic assembled fibres. *Nat. Commun.* **2**, 571 (2011).
- Xiang, C. et al. Large flake graphene oxide fibers with unconventional 100% knot efficiency and highly aligned small flake graphene oxide fibers. *Adv. Mater.* 25, 4592–4597 (2013).
- 50. Hu, X., Xu, Z., Liu, Z. & Gao, C. Liquid crystal self-templating approach to ultrastrong and tough biomimic composites. *Sci. Rep.* **3**, 1–8 (2013).
- 51. Xin, G. et al. Highly thermally conductive and mechanically strong graphene fibers. *Science* **349**, 1083–1087 (2015).
- Soutis, C. Carbon fiber-reinforced plastics in aircraft construction. *Mater. Sci. Eng. A* 412, 171–176 (2005).
- Xu, Z., Liu, Z., Sun, H. & Gao, C. Highly electrically conductive Ag-doped graphene fibers as stretchable conductors. *Adv. Mater.* 25, 3249–3253 (2013).
- Vallés, C., David Núñez, J., Benito, A. M. & Maser, W. K. Flexible conductive graphene paper obtained by direct and gentle annealing of graphene oxide paper. *Carbon N. Y.* 50, 835–844 (2012).
- Lin, X. et al. Fabrication of highly-aligned, conductive, and strong graphene papers using ultralarge graphene oxide sheets. ACS Nano 6, 10708–10719 (2012).
- 56. Xin, G. et al. Large-area freestanding graphene paper for superior thermal management. *Adv. Mater.* **26**, 4521–4526 (2014).
- Chandrasekaran, S. et al. Fracture toughness and failure mechanism of graphene based epoxy composites. *Compos. Sci. Technol.* 97, 90–99 (2014).
- 58. Liang, J. et al. Electromagnetic interference shielding of graphene/epoxy composites. *Carbon* 47, 922–925 (2009).
- Lee, J. et al. Wafer-Scale Growth of Single-Crystal Monolayer Graphene on Reusable Hydrogen-Terminated Germanium. *Science* 344, 286–290 (2014).
- 60. Li, Q. et al. Ultrahigh thermal conductivity of assembled aligned multilayer graphene/epoxy composite. *Chem. Mater.* **26**, 4459–4465 (2014).
- 61. Discover a new era of graphene. *HEAD* https://www.head.com/us-US/ sports/tennis/technology/graphene-xt/ (2019).
- Ding, R. et al. A brief review of corrosion protective films and coatings based on graphene and graphene oxide. J. Alloy. Compd. 764, 1039–1055 (2018).
- Ramezanzadeh, B., Mohamadzadeh Moghadam, M. H., Shohani, N. & Mahdavian, M. Effects of highly crystalline and conductive polyaniline/ graphene oxide composites on the corrosion protection performance of a zinc-rich epoxy coating. *Chem. Eng. J.* **320**, 363–375 (2017).
- 64. Bonaccorso, F. et al. Graphene, related two-dimensional crystals, and hybrid systems for energy conversion and storage. *Science* **347**, 1246501 (2015).
- 65. Ivanovskii, A. L. Graphene-based and graphene-like materials. *Russ. Chem. Rev.* 81, 571–605 (2012).
- Dahn, J. R., Zheng, T., Liu, Y. & Xue, J. S. Mechanisms for lithium insertion in carbonaceous materials. *Science* 270, 590–593 (1995).
- Liu, Y., Xue, J. S., Zheng, T. & Dahn, J. R. Mechanism of lithium insertion in hard carbons prepared by pyrolysis of epoxy resins. *Carbon N. Y.* 34, 193–200 (1996).
- Vargas C, O. A., Caballero, Á. & Morales, J. Can the performance of graphene nanosheets for lithium storage in Li-ion batteries be predicted?. *Nanoscale* 4, 2083–2092 (2012).
- 69. Kucinskis, G., Bajars, G. & Kleperis, J. Graphene in lithium ion battery cathode materials: A review. *J. Power Sources* **240**, 66–79 (2013).
- Zhao, J. et al. Air-stable and freestanding lithium alloy/graphene foil as an alternative to lithium metal anodes. *Nat. Nanotechnol.* 12, 993–999 (2017).
- Fang, R. et al. Toward More Reliable Lithium-Sulfur Batteries: An All-Graphene Cathode Structure. ACS Nano 10, 8676–8682 (2016).
- 72. Zhu, J., Yang, D., Yin, Z., Yan, Q. & Zhang, H. Graphene and graphenebased materials for energy storage applications. *Small* **10**, 3480–3498 (2014).
- 73. Liu, Y., Zhu, Y. & Cui, Y. Challenges and opportunities towards fastcharging battery materials. *Nat. Energy* **4**, 540–550 (2019).
- 74. Son, I. H. et al. Graphene balls for lithium rechargeable batteries with fast charging and high volumetric energy densities. *Nat. Commun.* **8**, 1561 (2017).
- Xia, J., Chen, F., Li, J. & Tao, N. Measurement of the quantum capacitance of graphene. *Nat. Nanotechnol.* 4, 505–509 (2009).
- Liu, C., Yu, Z., Neff, D., Zhamu, A. & Jang, B. Z. Graphene-based supercapacitor with an ultrahigh energy density. *Nano Lett.* 10, 4863–4868 (2010).
- 77. Liberato, S. De et al. Laser scribing of high-performance. *Science* **335**, 1326–1330 (2012).

## **NATURE NANOTECHNOLOGY**

- Kong, L. et al. Free-standing T-Nb<sub>2</sub>O<sub>5</sub>/graphene composite papers with ultrahigh gravimetric/volumetric capacitance for Li-ion intercalation pseudocapacitor. ACS Nano 9, 11200–11208 (2015).
- Pikkarainen, J. Graphene cuts elevator energy consumption in half. Skeleton Technologies https://www.skeletontech.com/news/press-release-graphenecuts-elevator-energy-consumption-in-half (2019).
- 80. Tight, T. H. Unimpeded permeation of water. Science 335, 442-444 (2012).
- Sun, P. et al. Selective ion penetration of graphene oxide membranes. ACS Nano 7, 428–437 (2013).
- Boukhvalov, D. W., Katsnelson, M. I. & Son, Y. W. Origin of anomalous water permeation through graphene oxide membrane. *Nano Lett.* 13, 3930–3935 (2013).
- 83. Joshi, R. K. et al. Precise and ultrafast molecular sieving through graphene oxide membranes. *Science* **343**, 752–754 (2014).
- Surwade, S. P. et al. Water desalination using nanoporous single-layer graphene. Nat. Nanotechnol. 10, 459-464 (2015).
- Wang, L. et al. Fundamental transport mechanisms, fabrication and potential applications of nanoporous atomically thin membranes. *Nat. Nanotechnol.* 12, 509–522 (2017).
- Meric, I. et al. Current saturation in zero-bandgap, top-gated graphene field-effect transistors. *Nat. Nanotechnol.* 3, 654–659 (2008).
- 87. Lin, Y. M. et al. 100-GHz transistors from wafer-scale epitaxial graphene. *Science* **327**, 662 (2010).
- Cheng, R. et al. High-frequency self-aligned graphene transistors with transferred gate stacks. Proc. Natl Acad. Sci. USA 109, 11588–11592 (2012).
- Wu, Y. et al. High-frequency, scaled graphene transistors on diamond-like carbon. *Nature* 472, 74–78 (2011).
- Wu, Y. et al. 200 GHz Maximum Oscillation Frequency in CVD Graphene Radio Frequency Transistors. ACS Appl. Mater. Interfaces 8, 25645–25649 (2016).
- Yu, C. et al. High-frequency flexible graphene field-effect transistors with short gate length of 50 nm and record extrinsic cut-off frequency. *Phys. Status Solidi Rapid Res. Lett.* **12**, 10–13 (2018).
- Shalaev, V. et al. Wafer-scale graphene integrated circuits. Science 332, 1294–1297 (2011).
- Moser, J., Barreiro, A. & Bachtold, A. Current-induced cleaning of graphene. *Appl. Phys. Lett.* **91**, 1–4 (2007).
- Balandin, A. A. et al. Superior thermal conductivity of single-layer graphene. Nano Lett. 8, 902–907 (2008).
- 95. Han, T. H. et al. Extremely efficient flexible organic light-emitting diodes with modified graphene anode. *Nat. Photon.* **6**, 105–110 (2012).
- Lee, C., Wei, X., Kysar, J. W. & Hone, J. Measurement of the Elastic Properties and Intrinsic Strength of Monolayer Graphene. *Science* 321, 385–388 (2008).
- Zhao, H., Min, K. & Aluru, N. R. Size and chirality dependent elastic properties of graphene nanoribbons under uniaxial tension. *Nano Lett.* 9, 3012–3015 (2009).
- 98. Zang, J. et al. Multifunctionality and control of the crumpling and unfolding of large-area graphene. *Nat. Mater.* **12**, 321–325 (2013).
- Lee, S. K. et al. Stretchable graphene transistors with printed dielectrics and gate electrodes. *Nano Lett.* 11, 4642–4646 (2011).
- Kim, K. S. et al. Large-scale pattern growth of graphene films for stretchable transparent electrodes. *Nature* 457, 706–710 (2009).
- Nair, R. R. et al. Fine structure constant defines visual transparency of graphene. *Science* 320, 1308 (2008).
- Coleman, J. N. & De, S. Are there fundamental limitations on the sheet resistance and transmittance of thin graphene films. ACS Nano 4, 2713–2720 (2010).
- Kim, Y. et al. Remote epitaxy through graphene enables two-dimensional material-based layer transfer. *Nature* 544, 340–343 (2017).
- Kong, W. et al. Polarity governs atomic interaction through twodimensional materials. *Nat. Mater.* 17, 999–1004 (2018).
- 105. Shim, J. et al. Controlled crack propagation for atomic precision handling of wafer-scale two-dimensional materials. *Science* **362**, 665–670 (2018).
- Kim, J. et al. Layer-resolved graphene transfer via engineered strain layers. Science 342, 833–836 (2013).
- Bonaccorso, F., Sun, Z., Hasan, T. & Ferrari, A. C. Graphene photonics and optoelectronics. *Nat. Photon.* 4, 611–622 (2010).
- 108. Liu, M. et al. A graphene-based broadband optical modulator. *Nature* 474, 64–67 (2011).
- Liu, C. H., Chang, Y. C., Norris, T. B. & Zhong, Z. Graphene photodetectors with ultra-broadband and high responsivity at room temperature. *Nat. Nanotechnol.* 9, 273–278 (2014).
- 110. Bao, Q. et al. Broadband graphene polarizer. Nat. Photon. 5, 411-415 (2011).
- 111. Yu, S., Wu, X., Wang, Y., Guo, X. & Tong, L. 2D materials for optical modulation: challenges and opportunities. *Adv. Mater.* **29**, (2017).
- Higuchi, T., Heide, C., Ullmann, K., Weber, H. B. & Hommelhoff, P. Light-field-driven currents in graphene. *Nature* 550, 224–228 (2017).
- 113. Sorianello, V. et al. Graphene-silicon phase modulators with gigahertz bandwidth. *Nat. Photon.* **12**, 40–44 (2018).

- 114. Goossens, S. et al. Broadband image sensor array based on graphene-CMOS integration. *Nat. Photon.* **11**, 366–371 (2017).
- Lin, H. et al. Chalcogenide glass-on-graphene photonics. Nat. Photon. 11, 798–805 (2017).
- 116. Bao, Q. et al. Atomic-layer craphene as a saturable absorber for ultrafast pulsed lasers. *Adv. Funct. Mater.* **19**, 3077–3083 (2009).
- 117. Romagnoli, M. et al. Graphene-based integrated photonics for nextgeneration datacom and telecom. *Nat. Rev. Mater.* **3**, 392–414 (2018).
- Pospischil, A. et al. CMOS-compatible graphene photodetector covering all optical communication bands. *Nat. Photon.* 7, 892–896 (2013).
- Koppens, F. H. L. et al. Photodetectors based on graphene, other two-dimensional materials and hybrid systems. *Nat. Nanotechnol.* 9, 780–793 (2014).
- Schall, D. et al. Record high bandwidth integrated graphene photodetectors for communication beyond 180 Gb/s. In *Proc. Optical Fiber Communication Conference* (Ed. McEuen, P. L.) M2I.4 (OSA, 2018).
- Phare, C. T., Daniel Lee, Y. H., Cardenas, J. & Lipson, M. Graphene electro-optic modulator with 30 GHz bandwidth. *Nat. Photon.* 9, 511–514 (2015).
- 122. Gan, X. et al. High-contrast electrooptic modulation of a photonic crystal nanocavity by electrical gating of graphene. *Nano Lett.* **13**, 691–696 (2013).
- 123. Vicarelli, L. et al. Graphene field-effect transistors as room-temperature terahertz detectors. *Nat. Mater.* **11**, 865–871 (2012).
- 124. Wu, Y. et al. Graphene Terahertz Modulators by Ionic Liquid Gating. Adv. Mater. 27, 1874–1879 (2015).
- Balci, O., Polat, E. O., Kakenov, N. & Kocabas, C. Graphene-enabled electrically switchable radar-absorbing surfaces. *Nat. Commun.* 6, 6628 (2015).
- Kim, K., Choi, J. Y., Kim, T., Cho, S. H. & Chung, H. J. A role for graphene in silicon-based semiconductor devices. *Nature* 479, 338–344 (2011).
- 127. Fogden, S. Ultra-fast graphene photonics for next generation datacomms at the Graphene Pavilion at the Mobile World Congress. *Graphene Flagship* https://graphene-flagship.eu/ultra-fast-graphene-photonics (2018).
- Ghosh, S. et al. Dimensional crossover of thermal transport in few-layer graphene. Nat. Mater. 9, 555–558 (2010).
- 129. Serov, A. Y., Ong, Z. Y. & Pop, E. Effect of grain boundaries on thermal transport in graphene. *Appl. Phys. Lett.* **102**, (2013).
- Lindsay, L., Broido, D. A. & Mingo, N. Flexural phonons and thermal transport in graphene. *Phys. Rev. B Condens. Matter Mater. Phys.* 82, 2–7 (2010).
- Yu, Q. et al. Control and characterization of individual grains and grain boundaries in graphene grown by chemical vapour deposition. *Nat. Mater.* 10, 443–449 (2011).
- 132. Huang, P. Y. et al. Grains and grain boundaries in single-layer graphene atomic patchwork quilts. *Nature* **469**, 389–392 (2011).
- 133. Zandiatashbar, A. et al. Effect of defects on the intrinsic strength and stiffness of graphene. *Nat. Commun.* **5**, 3186 (2014).
- Gómez-navarro, C., Burghard, M. & Kern, K. Elastic properties of chemically derived single graphene sheets. *Nano Lett.* 8, 2045–2049 (2008).
- 135. Xiang, H. F. et al. Graphene sheets as anode materials for Li-ion batteries: Preparation, structure, electrochemical properties and mechanism for lithium storage. *RSC Adv.* 2, 6792–6799 (2012).
- 136. Chen, Y. et al. Reduced graphene oxide films with ultrahigh conductivity as Li-ion battery current collectors. *Nano Lett.* **16**, 3616–3623 (2016).
- 137. Xin, G. et al. Highly thermally conductive and mechanically strong graphene fibers. *Science* **349**, 1083–1087 (2015).
- Voiry, D. et al. High-quality graphene via microwave reduction of solution-exfoliated graphene oxide. *Science* 353, 1413–1416 (2016).
- Bagri, A. et al. Structural evolution during the reduction of chemically derived graphene oxide. *Nat. Chem.* 2, 581–587 (2010).
- Nguyen, V. L. et al. Seamless stitching of graphene domains on polished copper (111) foil. *Adv. Mater.* 27, 1376–1382 (2015).
- 141. Reddy, K. M., Gledhill, A. D., Chen, C. H., Drexler, J. M. & Padture, N. P. High quality, transferrable graphene grown on single crystal Cu(111) thin films on basal-plane sapphire. *Appl. Phys. Lett.* **98**, 1–4 (2011).
- 142. Zhao, L. et al. Influence of copper crystal surface on the CVD growth of large area monolayer graphene. *Solid State Commun.* **151**, 509–513 (2011).
- 143. Wu, T. et al. Fast growth of inch-sized single-crystalline graphene from a controlled single nucleus on Cu-Ni alloys. *Nat. Mater.* **15**, 43–47 (2016).
- 144. Lee, J. et al. Wafer-scale growth of single-crystal. Science 344, 286-290 (2014).
- 145. Lee, J. S. et al. Wafer-scale single-crystal hexagonal boron nitride film via self-collimated grain formation. *Science* **362**, 817–821 (2018).
- Vlassiouk, I. V. et al. Evolutionary selection growth of two-dimensional materials on polycrystalline substrates. *Nat. Mater.* 17, 318–322 (2018).
   Shim, J. et al. Controlled crack propagation for atomic precision handling
- of wafer-scale two-dimensional materials. *Science* **362**, 665–670 (2018).
- 148. Nolen, C. M., Denina, G., Teweldebrhan, D., Bhanu, B. & Balandin, A. A. High-throughput large-area automated identification and quality control of graphene and few-layer graphene films. ACS Nano 5, 914–922 (2011).

# FOCUS | REVIEW ARTICLE

## **NATURE NANOTECHNOLOGY**

- Qi, Z. et al. Rapid identification of the layer number of large-area graphene on copper. *Chem. Mater.* 30, 2067–2073 (2018).
- Banhart, F., Kotakoski, J. & Krasheninnikov, A. V. Structural defects in graphene RID A-3473-2009. ACS Nano 5, 26–41 (2011).
- 151. Dresselhaus, M. S., Jorio, A., Souza Filho, A. G. & Saito, R. Defect characterization in graphene and carbon nanotubes using Raman spectroscopy. *Philos. Trans. R. Soc. A Math. Phys. Eng. Sci.* 368, 5355–5377 (2010).
- Lee, T., Mas Ud, F. A., Kim, M. J. & Rho, H. Spatially resolved Raman spectroscopy of defects, strains, and strain fluctuations in domain structures of monolayer graphene. *Sci. Rep.* 7, 1–8 (2017).
- Li, W., Moon, S., Wojcik, M. & Xu, K. Direct Optical Visualization of Graphene and Its Nanoscale Defects on Transparent Substrates. *Nano Lett.* 16, 5027–5031 (2016).
- 154. Huang, K. C. et al. High-speed spectroscopic transient absorption imaging of defects in graphene. *Nano Lett.* **18**, 1489–1497 (2018).
- Braeuninger-Weimer, P. et al. Fast, noncontact, wafer-scale, atomic layer resolved imaging of two-dimensional materials by ellipsometric contrast micrography. ACS Nano 12, 8555–8563 (2018).
- 156. Jepsen, P. U. et al. Mapping the electrical properties of large-area graphene. 2D Mater. 4, 042003 (2017).
- Altan, A. I. & Chen, J. In situ chemical probing of hole defects and cracks in graphene at room temperature. *Nanoscale* 10, 11052–11063 (2018).
- Dong, X. et al. Microscale spectroscopic mapping of 2D optical materials. Adv. Opt. Mater. 1900324 (2019).
- Nakajima, H. et al. Imaging of local structures affecting electrical transport properties of large graphene sheets by lock-in thermography. *Sci. Adv.* 5, eaau3407 (2019).
- 160. Eckmann, A. et al. Probing the nature of defects in graphene by Raman spectroscopy. *Nano Lett.* **12**, 3925–3930 (2012).
- Ferrari, A. C. et al. Raman spectrum of graphene and graphene layers. *Phys. Rev. Lett.* 97, 1–4 (2006).
- Ferrari, A. C. & Basko, D. M. Raman spectroscopy as a versatile tool for studying the properties of graphene. *Nat. Nanotechnol.* 8, 235–246 (2013).
- 163. Shinohara, H. & Tiwari, A. Graphene: an introduction to the fundamentals and industrial applications (John Wiley & Sons, 2015).
- 164. Morrow, W. K., Pearton, S. J. & Ren, F. Review of graphene as a solid state diffusion barrier. *Small* 12, 120-134 (2016).
- 165. Konstantatos, G. et al. Hybrid graphene quantum dot phototransistors with ultrahigh gain. *Nat. Nanotechnol.* **7**, 363–368 (2012).
- 166. Wang, J. I. J. et al. Coherent control of a hybrid superconducting circuit made with graphene-based van der Waals heterostructures. *Nat. Nanotechnol.* 14, 120–125 (2019).
- Cao, Y. et al. Correlated insulator behaviour at half-filling in magic-angle graphene superlattices. *Nature* 556, 80–84 (2018).
- 168. Cao, Y. et al. Unconventional superconductivity in magic-angle graphene superlattices. *Nature* 556, 43–50 (2018).
- Young, R. J. & Liu, M. The microstructure of a graphene-reinforced tennis racquet. J. Mater. Sci. 51, 3861–3867 (2016).
- 170. Foster, C. W. et al. 3D printed graphene based energy storage devices. *Sci. Rep.* 7, 1–11 (2017).
- 171. Goldsmith, B. R. et al. Digital biosensing by foundry-fabricated graphene sensors. *Sci. Rep.* 9, 1–10 (2019).

- 172. Van Noorden, R. Beyond sticky tape. Nature 483, S32-S33 (2012).
- 173. Li, X. et al. Large-area graphene single crystals grown by low-pressure chemical vapor deposition of methane on copper. J. Am. Chem. Soc. 133, 2816–2819 (2011).
- 174. Secor, E. B., Ahn, B. Y., Gao, T. Z., Lewis, J. A. & Hersam, M. C. Rapid and Versatile Photonic Annealing of Graphene Inks for Flexible Printed Electronics. *Adv. Mater.* 27, 6683–6688 (2015).
- 175. Yang, Y. et al. Large-area graphene-nanomesh/carbon-nanotube hybrid membranes for ionic and molecular nanofiltration. *Science* 364, 1057–1062 (2019).
- Liu, N. et al. Ultratransparent and stretchable graphene electrodes. *Sci. Adv.* 3, e1700159 (2017).
- A higher intelligence: Huawei unveils HUAWEI Mate 20 series. *Huawei* https://www.huawei.com/en/press-events/news/2018/10/huawei-mate20series (2018).
- 178. CARDEA ZERO PCIe M.2 SSD. *TeamGroup* https://www.teamgroupinc. com/en/product/cardea-zero (2017).
- FGTR Graphene 1.0. Momodesign https://en.momodesign.com/products/ fgtr-graphene-1-0 (2016).
- REBORN Colmar https://www.colmar.it/en-gb/cms/index/stories/ colmar-sport-reborn (2017).
- Featuring graphene technology. HEAD https://www.head.com/us-US/sports/ ski/technology/graphene/ (2019).
- Free your ride. Interceptor. Dassi https://dassi.com/product-range/ interceptor-graphene (2018).
- 183. G-Series. inov-8 https://www.inov-8.com/us/g-series (2018).
- Audio Liberation. ZOLO https://zoloaudio.com/pages/liberty\_series#features (2019).
- RM 50-03. Richard Mille https://www.richardmille.com/collections/ rm-50-03-tourbillon-chronograph-mclaren-f1 (2019).
- 186. Agile. Nanomed https://nanomedical.com/agile/ (2019).
- Chongqing Science and Technology Co. Graphene flexible mobile phone. *Chongqing Graphene Technology Co.* http://www.cqmxi.com/archives1201. html (2019).
- Emberion to present graphene photonics developments at LASER. Optics.org https://optics.org/news/10/6/18 (2019).
- Ceraso, D. L. Galapad Settler, the first smartphone made with Grafene, is coming from China *GizChina.it* https://en.gizchina.it/2015/03/arrivo-dallacina-il-galapad-settler-primo-smartphone-realizzato-con-il-grafene/ (2015).
- Paint and coatings. Applied Graphene Materials https://www. appliedgraphenematerials.com/applications/paints-and-coatings/ (2019).
- 191. California Lithium Battery (CLB) addresses this fundamental challenge with a new disruptive technology: a silicon-graphene (SiGr) composite anode material. *California Lithium Battery* https://clbattery.com/thecalbattery-solution/ (2014).

### Additional information

Correspondence should be addressed to J.K.

Reprints and permissions information is available at www.nature.com/reprints.

**Publisher's note** Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

© Springer Nature Limited 2019