

Graphene for batteries, supercapacitors and beyond

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Abstract | Graphene has recently enabled the dramatic improvement of portable electronics and electric vehicles by providing better means for storing electricity. In this Review, we discuss the current status of graphene in energy storage and highlight ongoing research activities, with specific emphasis placed on the processing of graphene into electrodes, which is an essential step in the production of devices. We calculate the maximum energy density of graphene supercapacitors and outline ways for future improvements. We also discuss the synthesis and assembly of graphene into macrostructures, ranging from 0D quantum dots, 1D wires, 2D sheets and 3D frameworks, to potentially 4D self-folding materials that allow the design of batteries and supercapacitors with many new features that do not exist in current technology.

Since its discovery a decade ago, dozens of potential uses for graphene have been proposed, from faster computer chips and flexible touchscreens to hyper-efficient solar cells and desalination membranes. One exciting property that has sparked significant interest is its ability to store electrical charge. A single sheet of graphene sufficient in size to cover an entire American football field would weigh just a fraction of a gram. This huge surface area associated with this small amount of graphene can be squeezed inside an AA battery, enabling the design of new energy-storage devices with the ability to store massive amounts of charge. In this Review, we discuss the inherent properties of graphene and what it has to offer for energy storage. Much of the Review covers the synthesis and assembly of graphene into macrostructures that exploit the unique features of individual graphene sheets to build new materials for various applications. Particular attention is paid to the processing of graphene into electrodes, which is an essential step in the production of devices. Graphene can be useful by itself, but it is also promising — as we discuss — for composites with superior performance compared with existing materials.

Currently, graphene is the most studied material for charge storage and the results from many laboratories confirm its potential to change today's energy-storage landscape. Specifically, graphene could present several new features for energy-storage devices, such as smaller capacitors, completely flexible and even rollable energy-storage devices, transparent batteries, and high-capacity and fast-charging devices. These and other features are explored in this Review. Despite notable progress, the future of graphene in the energy-storage market is uncertain because of several challenges. We

discuss and propose solutions to these challenges and also briefly discuss the potential of other emerging 2D materials for energy-storage applications.

Graphene for energy storage

The fundamental properties of graphene make it promising for a multitude of applications. In particular, graphene has attracted great interest for supercapacitors because of its extraordinarily high surface area of up to $2,630 \text{ m}^2 \text{ g}^{-1}$. Recently, the intrinsic capacitance of single-layer graphene was reported to be $\sim 21 \mu\text{F cm}^{-2}$; this value sets the upper limit for electric double-layer (EDL) capacitance for all carbon-based materials¹. Thus, supercapacitors based on graphene could, in principle, achieve an EDL capacitance as high as $\sim 550 \text{ F g}^{-1}$ if the entire surface area can be fully utilized. However, to understand the limits of graphene in supercapacitors, it is important to know the energy density of a fully packaged cell and not just the capacitance of the active material. In addition to the capacitance of graphene, the maximum energy density of graphene-based supercapacitors depends on several other parameters, such as the thickness and density of the graphene film and other cell components, including the current collector and the separator, the nature and density of the electrolyte, the operating voltage window of the cell and the packaging efficiency.

As illustrated in FIG. 1, when using a standard current collector, separator and acetonitrile-based electrolyte, the two key parameters that control the energy density of graphene supercapacitors are the density of the graphene film and the voltage of the cell. For an electrochemical cell using 200- μm -thick graphene electrodes with a density of 1.5 g cm^{-3} and an operating voltage of 4 V, the maximum theoretical energy density is $\sim 169 \text{ Wh kg}^{-1}$

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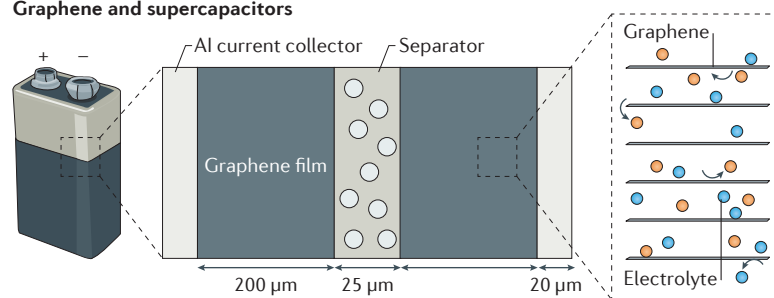
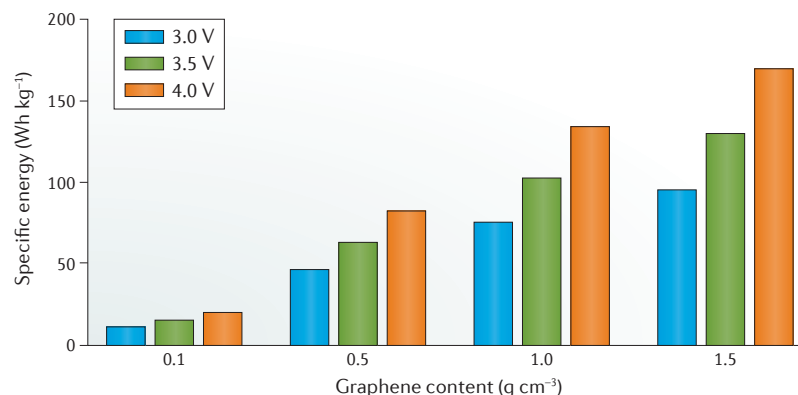
a Graphene and supercapacitors

b Theoretical specific energy of graphene


Figure 1 | Graphene and supercapacitors. Owing to its remarkable quantum capacitance and excellent electrical and mechanical properties, calculations show that graphene has the potential to help realize supercapacitors with the energy density of batteries that can be recharged in seconds. **a** | Representation of the structure of graphene supercapacitors with increasingly magnified views. **b** | Maximum theoretical energy density of a fully packaged graphene supercapacitor for different densities of the graphene film and voltage windows of the cell.

on a gravimetric basis and $\sim 303 \text{ Wh l}^{-1}$ on a volumetric basis. If achieved, these values could put graphene supercapacitors on par with nickel metal hydride and lithium-ion batteries (LIBs) with the additional advantages of higher power density and longer cycle life. In practice, the energy density of graphene supercapacitors achieved so far is between 15 and 35 Wh kg^{-1} , and less than 60 Wh l^{-1} — far below the theoretical values.

Graphene is also very useful in a wide range of batteries including redox flow, metal–air, lithium–sulfur and, more importantly, LIBs. For example, first-principles calculations indicate that lithium ions can be stored on both sides of graphene, forming C_3Li (REF. 2). Accordingly, graphene can deliver a theoretical capacity of 744 mAh g^{-1} , which is about twice the capacity of conventional graphite electrodes. While these calculations were carried out on perfect and crystalline graphene, real graphene electrodes use chemically modified and defective forms of graphene. The performance of these graphene electrodes varies between 100 and $1,000 \text{ mAh g}^{-1}$ depending on the properties of graphene, electrode processing, mass loading, structural defects and surface area. A few reports show that specially designed graphene electrodes can exceed $1,000 \text{ mAh g}^{-1}$, mainly when tested in a half cell, but normally, smaller values are obtained in full-cell measurements. Graphene can be chemically processed into various forms suitable for both the positive and negative electrodes, enabling

the fabrication of an all-graphene battery with an ultra-high energy density³. Graphene is a great substrate for anchoring LIB anode and cathode materials to create high-energy-density, flexible, stretchable, fast-charging and longer-lasting batteries. In addition to LIBs, graphene hybrids have also been shown to achieve excellent performance in a range of other batteries: for example, serving as electrodes in Na^+ and Al^{3+} batteries, and as a high-efficiency catalyst in metal–air batteries. Although graphite is an excellent anode in LIBs, it cannot be utilized in Na^+ and Al^{3+} batteries because these ions are too large to effectively intercalate into graphite under ambient conditions, so alternative anode materials are required, such as porous graphene composites, to achieve high energy-storage performance.

Graphene synthesis and assembly

Since it was first isolated in 2004, researchers have developed a plethora of methods to synthesize graphene, which can be classified as either ‘bottom-up’ strategies, including SiC epitaxial growth, chemical vapour deposition and chemical synthesis, or ‘top-down’ methods, including micromechanical cleavage, liquid-phase exfoliation and the reduction of graphene oxide⁴. However, extending the excellent properties of individual graphene sheets to a macroscopic scale is the most important issue for realizing its practical applications. Sheet assembly is a thermodynamic process in which the interactions between single sheets, such as van der Waals forces, π – π stacking, electrostatic interactions, hydrogen bonding and hydrophobic interactions, have decisive roles. Various unique macroscopic assemblies of graphene can be prepared that cover all ‘four’ dimensions, in the form of quantum dots (0D), wires (1D), films (2D), monoliths (3D), and potentially 4D self-healing and/or self-folding structures, as illustrated in FIG. 2. We now discuss how each of these forms affects the properties and applications of graphene.

Dimensionality is an important parameter and defines, to a large extent, the properties of a material. In fact, graphene can exhibit different properties in different dimensions. For example, interfacial self-assembly of graphene oxide at the water/air interface is an interesting strategy for the design of 0D graphene materials, such as nanospheres, hollow capsules and even crumpled balls. In contrast to 2D graphene sheets, which readily aggregate during electrode fabrication, these structures have proven to be very useful in preventing the restacking of graphene, thereby leading to supercapacitors with larger specific capacitances and higher rate capabilities⁵. Graphene can also be made into smaller fragments — less than 30 nm — called graphene quantum dots⁶. Their high surface area and biocompatibility make them promising for biosensors, bioimaging and drug delivery. They also have large open surfaces and free edges that allow the design of supercapacitors with high specific capacitances⁷ and micro-supercapacitors with extremely fast response times (with a time constant of approximately $100 \mu\text{s}$)⁸. Moreover, doping graphene oxide quantum dots with nitrogen results in a photocatalyst with both p- and n-type conduction that can drive overall water splitting spontaneously⁹.

| Dimension | | | | Preparation methods | Applications |
|----------------------------|--|---|---|--|---|
| 0D dots |  |  |  | <ul style="list-style-type: none"> • Templated reduction of GO (REF. 89) • Cage opening of fullerene C₆₀ (REF. 6) • Spray-assisted deep frying (REFS 5,93) | <ul style="list-style-type: none"> • Energy storage • Fluorescent QDs • Electrochemical biosensors • Drug delivery • Bioimaging • Photovoltaics • Composites • Water splitting |
| 1D linear structures |  |  |  | <ul style="list-style-type: none"> • Molecular assembly⁹⁴ • Unzipping of CNT⁹⁵ • Wet spinning⁹⁶ • CVD using Cu nanowire template¹³ • Hydrothermal using Cu wire template⁹⁷ • CVD using AAO template¹⁴ | <ul style="list-style-type: none"> • Microscale energy storage devices • Wearable electronics • Bioimaging • Transparent conducting electrodes • Thermal energy storage |
| 2D films |  |  |  | <ul style="list-style-type: none"> • Micromechanical cleavage⁴ • Photoexfoliation⁴ • Liquid-phase exfoliation⁴ • Growth on SiC⁴ • CVD⁴ • Molecular beam epitaxy⁴ • Chemical synthesis⁴ • Chemical exfoliation^{19,98} • Chemical under gaseous flow⁹⁹ • Chemical activation¹⁰⁰ • Block copolymer lithography¹⁰¹ • Wet spinning¹⁰² • CVD with metal mesh¹⁰³ • Induced edge nucleation¹⁰⁴ | <ul style="list-style-type: none"> • Photonic and optoelectronic devices • Energy storage and conversion • Photovoltaics • Sensors • Lubricants • Catalysts • Thermal management • Drug delivery |
| 3D monoliths |  |  |  | <ul style="list-style-type: none"> • Templated synthesis^{105,106} • Self-assembly¹⁰⁷ • Laser scribing^{55,56} • Thermal¹⁰⁹ • Microwave and chemical activation¹⁰⁰ • Vacuum filtration⁶⁰ • Freeze-drying¹¹⁰ • Crosslinking¹¹¹ • Chemical assembly¹¹²⁻¹¹⁴ • 3D printing¹⁶ | <ul style="list-style-type: none"> • Absorber for environmental remediation • Energy storage • Sensors • Biosensors • Catalysis • Electrochemistry • Fuel cells • Gas absorption • Hydrogen storage • Water splitting • Scaffold for electronic and biomedical applications • Tissue engineering and regeneration |
| 4D self-folding structures |  <p data-bbox="164 1686 228 1707">Before</p> <p data-bbox="360 1686 408 1707">After</p> <p data-bbox="185 1728 371 1749">Self-healing batteries</p> | | | <ul style="list-style-type: none"> • 4D printing? • Other methods? | <ul style="list-style-type: none"> • Self-healing batteries • Self-folding materials • Materials with on-demand shape transformations from one state to another |

Figure 2 | **Synthesis and assembly of graphene.** Graphene sheets can be manipulated to form macroscopic structures that take advantage of the unique features of the individual graphene sheets to enable the construction of new graphene architectures that are useful for many different applications. 2D graphene sheets can be assembled into macroscopic structures of all dimensionalities: 0D dots, 1D linear structures, 2D films, 3D monoliths and potentially 4D self-folding structures. Methods for the preparation of these structures and how they affect the properties and applications of graphene are described. AAO, anodic aluminium oxide; CNT, carbon nanotube; CVD, chemical vapour deposition; GO, graphene oxide; QDs, quantum dots.

One-dimensional graphene fibres are attractive because of their ability to integrate the fascinating properties of individual graphene sheets into macroscopic assemblies with mechanical and electrical properties beyond those of conventional carbon fibres¹⁰. Graphene fibres can reach an electrical conductivity of up to 10^4 S m^{-1} and a tensile strength of 400 MPa; these values are comparable to those of carbon nanotube (CNT) fibres and far exceed those of the carbon fibres widely used today in the aircraft and automotive industries. Compared with films and bulk structures, graphene fibres are favourable for the construction of flexible and wearable supercapacitors because they can be directly shaped into fabrics and textiles¹¹. In addition, graphene fibres can be tailored to yield batteries and supercapacitors with unconventional architectures¹². Another form of 1D graphene — nanowires — shows promise for flexible transparent conducting electrodes with excellent optical and electrical properties and high durability¹³. By contrast, graphene nanotubes exhibit extremely low sheet resistance down to $0.11 \Omega \text{ sq}^{-1}$ and a thermal conductivity of $8.28 \text{ W m}^{-1} \text{ K}^{-1}$, which allow the design of efficient reservoirs for thermal energy storage¹⁴.

Graphene film is one of the most applicable macroscopic forms of graphene because of the high aspect ratio along its lateral direction. Lamellar graphene sheets readily assemble into 2D macroscopic structures, such as thin films, membranes and paper, with orderly packed lamellar sheets. Graphene films are particularly promising in electrochemical energy-storage devices that already use film electrodes. Graphene batteries and supercapacitors can become viable if graphene films can equal or surpass current carbon electrodes in terms of cost, ease of processing and performance. The unique properties of graphene sheets provide graphene films with excellent electrical conductivity, mechanical strength, thermal conductivity and optical transparency, depending on the quality of the individual graphene layers and the thickness of the resulting film. In addition, graphene sheets are highly flexible and can be readily functionalized to create new materials with unique properties. They can also be processed into a library of other 2D structures that may find use in different applications (FIG. 2).

Perhaps one of the most effective ways to apply the unique features of 2D graphene sheets in practical applications is to assemble them into 3D structures, as shown in FIG. 2. Various 3D structures have been reported that include aerogels, hydrogels, sponges, foams, frameworks with periodic structures, honeycomb-like structures and 3D-printed graphene. These structures possess unique features, such as exceptionally high specific surface area, hierarchically interconnected pore structure and excellent electrical conductivity. They can support fast electron transfer in 3D and provide accessible surfaces for the adsorption and desorption of ions, leading to batteries and supercapacitors with very high energy densities. Not only does 3D graphene offer exceptionally high surface areas that are required for effective charge storage, but it also has large internal pores that are suitable for anchoring specific materials

for fuel cells, catalysis and sensing applications. These characteristics give graphene sponges the properties needed for cleaning oil spills. Experiments have shown that graphene sponges are capable of absorbing petroleum products up to 86 times their own weight, which is much higher than other common absorbents¹⁵. They also exhibit excellent electrical conductivity and biocompatibility, enabling their use as scaffolds for tissue engineering and regeneration¹⁶. Tremendous research efforts are ongoing to control the morphology and the properties of 3D graphene for integration into practical devices¹⁷ (FIG. 2).

The future of the field lies in the development of responsive graphene structures that can adapt to their surroundings. Normally, real-world objects do not change shape or properties once produced; however, a material that can transform and change shape when subjected to a change in its environment would be incredibly useful. This may lead to batteries that can self-heal in case of an accident or smart windows that can change colour to block out sunlight. These 3D objects that change structure over time are termed '4D materials'. It was recently shown that 4D printing of a 'smart object' may, one day, lead to the development of such devices¹⁸.

Processing of graphene

To realize the commercial potential of graphene, it is necessary to develop reliable, cost-effective and facile processes for the industry-scale fabrication of graphene electrodes with good performance. Solution processing offers a simple yet effective strategy for the fabrication of graphene electrodes and is compatible with the current production protocols adopted by industry for the preparation of battery electrodes. There are two requirements for solution-processing graphene-based dispersions in scalable devices: first, a homogeneous dispersion of high-quality graphene must be formed in a suitable solvent; second, a scalable technique for the continuous fabrication of graphene-based films must be used. Liquid-phase exfoliation of graphene in organic solvents is an efficient and low-cost method to produce graphene dispersions. However, the drawbacks of this process are the high boiling points and toxicity of the organic solvents required. Thus, aqueous dispersions of high-quality graphene sheets are highly desirable. In 2008, a facile method was developed to make chemically converted graphene sheets to form stable aqueous dispersions¹⁹, which has proven to be an excellent candidate method for fabricating graphene films.

Graphene dispersions can be processed into electrodes using various coating techniques, including dip coating, rod coating, spray coating, inkjet printing, spin coating, screen printing, gravure printing, blade coating, electrospinning, electrodeposition, vacuum filtration, drop casting, interfacial deposition, Langmuir–Blodgett deposition and layer-by-layer assembly^{20,21}. The most appropriate coating technique depends on the desired properties and size of the final electrodes, and the desired film thickness and amount of graphene in the dispersion. Another important parameter is the design of the device (that

is, whether a traditional sandwich structure or a planar energy storage device is needed). The setups used in the techniques listed above are evaluated in TABLE 1. Because many of these techniques involve similar mechanisms or properties, we focus on just a few of them.

Vacuum filtration is one of the most commonly used methods for preparing graphene and graphene-based composite films because of its general applicability and easy manipulation. One advantage of this process is that it affords convenient control of the density and thickness

Table 1 | Characteristics of graphene processing techniques

| Graphene coating technique | Common uses | Advantages | Disadvantages | Film quality | Film thickness (μm)* | Scale | Cost |
|--|---------------------------------------|--|--|--------------|-----------------------------------|--------|----------|
| Dip coating ⁴⁷ | Textile coating | <ul style="list-style-type: none"> • Can coat substrates of any geometry • Roll-to-roll processing | <ul style="list-style-type: none"> • Limited to thin films • Uses large amounts of material • Film jitters are possible | Medium | <10 | Large | Low |
| Rod coating ²⁴ | Adhesive coating | <ul style="list-style-type: none"> • Easy to use at different scales • Roll-to-roll processing | <ul style="list-style-type: none"> • Rods of different sizes and shapes have to be used • Easy clogging of the rod | Medium | 10–300 | Large | Low |
| Spray coating ¹¹⁴ | Painting and corrosion protection | <ul style="list-style-type: none"> • Independent of substrate topology | <ul style="list-style-type: none"> • Can lead to non-uniform coating | Medium | <10 | Medium | Low |
| Inkjet printing ³¹ | Printing papers | <ul style="list-style-type: none"> • Roll-to-roll processing • High-quality patterns | <ul style="list-style-type: none"> • Inkjet nozzles are prone to clogging | Medium | <1 | Large | Low |
| Spin coating ¹¹⁵ | Photolithography and microfabrication | <ul style="list-style-type: none"> • Uniform films • Rapid coating and drying | <ul style="list-style-type: none"> • High waste | Medium | <1 | Small | Medium |
| Screen printing ³² | Coloured designs on clothes | <ul style="list-style-type: none"> • Fine patterning • No limitations on the substrate to be coated | <ul style="list-style-type: none"> • Long preparation time • Screens can warp and readily damage | Medium | <10 | Small | Low |
| Gravure printing ³³ | Printing magazines and newspapers | <ul style="list-style-type: none"> • Uniformity • Patterning • High line speed • Roll-to-roll processing | <ul style="list-style-type: none"> • Long lead time on the preparation of the gravure cylinder | Good | <1 | Large | Low |
| Roll coating ¹¹⁶ | Batteries and supercapacitors | <ul style="list-style-type: none"> • High speed • Large-volume production | <ul style="list-style-type: none"> • Potential for clogging and roller damage | Medium | 10–500 | Large | Very low |
| Doctor blade ¹¹⁷ | Films of various materials | <ul style="list-style-type: none"> • Minimal ink waste • Roll-to-roll processing | <ul style="list-style-type: none"> • Tendency to aggregate at high solution concentrations | Medium | 10–500 | Large | Low |
| Electrospinning ¹¹⁸ | Research | <ul style="list-style-type: none"> • Porous films made up of 1D nanofibres | <ul style="list-style-type: none"> • Very high voltage required | Good | 0.1–100 | Medium | Medium |
| Electrodeposition ³⁶ | Metal finishing and jewellery | <ul style="list-style-type: none"> • Single-step coating and deoxygenation of GO • Substrates of any geometry can be used | <ul style="list-style-type: none"> • Substrate must be conductive | Good | <10 | Small | Medium |
| Vacuum filtration ⁶⁰ | Research | <ul style="list-style-type: none"> • No need for binders • Good control over density of film | <ul style="list-style-type: none"> • May lead to films with wrinkles • Slow processing | Low | 1–100 | Small | Low |
| Drop casting ¹¹⁹ | Research | <ul style="list-style-type: none"> • Very simple • No waste of materials | <ul style="list-style-type: none"> • Uneven coating • Slow drying | Low | 0.1–100 | Small | Low |
| Interfacial deposition ¹²⁰ | Research | <ul style="list-style-type: none"> • Morphological homogeneity at the nanoscale • Solutions can be recycled | <ul style="list-style-type: none"> • Requires vigorous mixing of water • Requires a dense oil • Produces polymer nanofibres | Good | Monolayer | Small | Low |
| Langmuir–Blodgett films ¹²¹ | Research | <ul style="list-style-type: none"> • An ideal monolayer can be grown | <ul style="list-style-type: none"> • Only amphiphilic molecules can be deposited • Time consuming | Good | Monolayer | Small | Medium |
| Layer-by-layer assembly ¹²² | Research | <ul style="list-style-type: none"> • Simple • High degree of control over thickness | <ul style="list-style-type: none"> • Requires charged substrates • Deposition is based solely on electrostatic attraction | Good | <1 | Small | Medium |

*The thickness of the film is a crucial parameter for energy-storage devices; higher thickness means the ability to store more charge per unit area. GO, graphene oxide.

of the as-filtered film simply by adjusting the filtration time, concentration and/or volume of the graphene dispersion. The filtered graphene film can be transferred onto essentially any substrate. Alternatively, a freestanding graphene film can be produced by peeling off or dissolving the filter membrane. For example, by using such a method, the properties of graphene-based LIB anodes can be controlled, which allows the rapid transport of both electrons and ions throughout the electrode, resulting in a high material tap density (1.3 g cm^{-3})²². However, there are drawbacks of the filtration method. Most importantly, the practical size of the filtered graphene film is limited by the filtration apparatus, which means it is difficult to continuously fabricate graphene films by filtration processing on a large scale.

Doctor blading, also known as knife coating, is an established method for processing large-area films over rigid or flexible substrates. This technique is widely used in research laboratories to produce graphene films for battery and supercapacitor applications. In a typical experiment, the slurry is transferred to the current collector by moving the blade over a flat substrate. Variable film thicknesses can be obtained by controlling the size of the gap between the blade and the substrate. Recently, this technique was used for the direct preparation and processing of graphene composite electrodes with ultrahigh specific capacitances in excess of $1,100 \text{ F g}^{-1}$ (REF. 23).

Mayer-rod coating is one of the most popular coating techniques. In this method, a stainless steel wire of varying diameter is tightly wound around a metal rod. The grooves made by the wire allow the right amount of the slurry to pass through, thereby controlling the coating thickness. This technique was used to produce large-area graphene electrodes with excellent optical properties, with potential for use in flexible devices²⁴. A Mayer rod was also shown to be effective for fabricating flexible energy-storage devices by integrating electrodes and separators into a single sheet of paper²⁵.

Spray coating may be the simplest method to realize the scalable fabrication of graphene films from graphene dispersions. In general, spray coating involves the atomization of a dispersion and deposition of the formed droplets onto a heated substrate, which evaporates the solvent to form a film. The spray-coating process usually results in a more uniform deposition than other methods, such as drop casting or dip coating. The quantity and density of the film can be controlled by adjusting the dispersion concentration and spray time. Low-temperature spray coating can be used to fabricate high-performance LIBs²⁶. The cycling stability of lithium-sulfur batteries was also improved by coating a thin layer of graphene oxide-oxidized CNTs on the separator²⁷. In addition, some extended approaches, including supersonic kinetic spraying²⁸ and electrospray deposition²⁹, have been developed to improve the quality of the final films.

Roll coating is the standard technology used today in the battery and supercapacitor industries, whereby a slurry is continuously coated onto the substrate of choice at high speed using a coating roll. This is the technique of choice in these industries because it offers several advantages, including large-volume production, high line

speeds and lower manufacturing costs. Unfortunately, this technique is rarely used in academic institutions to make graphene electrodes, although it would be beneficial because the equipment required is already commercially available, which would lead to decreased capital investment and time-to-market for new products.

With the continuous shrinking of electronic devices, research on microbatteries and micro-supercapacitors has recently flourished³⁰. In these cases, the most important requirement for the processing method is the ability to print patterned microelectrodes with large storage capacity. Techniques such as inkjet printing³¹, screen printing³², gravure printing³³ and electrodeposition³⁴ have successfully been used in the fabrication of miniaturized energy-storage devices.

Energy-storage devices with new features

Now that smartphones and other portable electronic devices have become ubiquitous, one major problem remains: battery technology has not kept up with the demands placed on them. In addition, the lack of a reliable battery still holds back electric vehicles from being readily adopted over vehicles using an internal combustion engine. Soon, graphene could establish a new generation of energy-storage devices with 12 new features not possible with current technology, as summarized in TABLE 2 and discussed in the following 12 subsections.

Supercapacitors with AC line filtering. Capacitors are essential components in almost all electronic devices. They are primarily used as electronic filters to smooth out the ripples from power supplies because they have a very fast response time — on the submillisecond timescale. However, unlike transistors and other electronic components that are constantly shrinking over time, capacitors are still bulky and often limit the miniaturization of the entire system. Commercial-grade carbon-based supercapacitors charge and discharge in seconds, which is much faster than batteries but not quite fast enough to be used as electronic filters.

In 2010, it was reported that an EDL capacitor based on vertically oriented graphene sheets could be charged and discharged in less than a millisecond, which is similar to the performance of capacitors but with a capacitance per volume at least ten times higher³⁵. This ultrafast supercapacitor could replace the large electrolytic capacitors used in today's electronics and may someday help make electronic devices smaller and lighter. The key to achieving ultrafast charging and discharging is to vertically orient graphene electrodes with external rather than internal surface area. This leads to a high-frequency response and eliminates the slow diffusion of ions, which has so far limited the speed of carbon-based supercapacitors. This work has inspired several research efforts to design new electrodes with ultrahigh power density by controlling pore size and distribution. Various materials, including electrochemically reduced graphene oxide³⁶, graphene quantum dots⁸, a graphene-CNT carpet³⁷, graphene-PEDOT:PSS³⁸ and conducting polymers³⁹, have been developed and tested for alternating current (AC) line filtering.

Flexible, rollable and twistable energy-storage devices.

The market for flexible and printed electronics is rapidly growing, with products now ranging from flexible solar-cell arrays to flexible displays and wearable electronics⁴⁰. The rise of this technology is mainly due to rapid progress in the production of flexible electronic devices over large areas at a fraction of the cost of traditional semiconductor technology⁴¹. In the field of energy storage, various devices, such as flexible supercapacitors and thin LIBs with variable sizes, shapes and mechanical properties, are being developed.

Current batteries and supercapacitors come in several sizes and shapes but are all rigid; therefore, bending them may cause cell damage and electrolyte leakage. In brief, this is because the current technology relies on particulate-like energy-storage materials, which lose their mechanical integrity upon bending. With its

2D one-atom-thick structure, graphene can adapt to mechanical stress by deforming in the direction normal to its surface. This inherent mechanical flexibility together with exceptional electrical properties and large surface area makes graphene attractive for flexible energy-storage devices. Interesting research activities in this area are discussed in detail in recent reviews^{42,43}.

Stretchable batteries and supercapacitors. Stretchable electronics is an emerging field featuring materials and devices that can sustain large deformations while maintaining normal function and reliability⁴⁴. Stretchable devices will help monitor body functions, make portable electronics more comfortable and perhaps even wearable. Inspired by human skin, crumpled graphene was used to develop supercapacitors that can be stretched up to eight times their length. This was accomplished

Table 2 | New features of energy-storage devices afforded by graphene

| Features | Materials | Performance | Refs |
|--|--|---|--------|
| Supercapacitors with AC line filtering | Vertically oriented graphene | RC time: ~0.2 ms; C_s ~0.087 mF cm ⁻² | 35 |
| | Electrochemically reduced graphene oxide | RC time: ~1.35 ms, C_s ~0.283 mF cm ⁻² | 36 |
| | Graphene–CNT carpets | RC time: ~0.195 ms, C_s ~0.230 mF cm ⁻² | 36, 37 |
| | Graphene–PEDOT:PSS hybrid film | RC time: ~0.644 ms, C_s ~0.179 mF cm ⁻² | 36, 38 |
| Flexible energy-storage devices | 3D graphene foam | 170 mAh g ⁻¹ at 145 mA g ⁻¹ , $r = 5$ mm | 42 |
| | V ₂ O ₅ –graphene paper | 300 mAh g ⁻¹ at 186 mA g ⁻¹ (rolled up or twisted) | 54 |
| | rGO–cellulose paper | 120 F g ⁻¹ at 1 mV s ⁻¹ , 1,000 bending cycles: $r = 4$ mm | 43 |
| | 3D graphene network fibre | 1.7 mF cm ⁻² at 30 mV s ⁻¹ , 500 bending cycles: $r = 2$ mm | 48 |
| Stretchable batteries and supercapacitors | Wrinkled CVD graphene | 5.8 μ F cm ⁻² , stretchable, up to 40% strain | 45 |
| Energy-storage devices for wearable electronics | Graphene–MnO ₂ coated textile | 315 F g ⁻¹ at 2 mV s ⁻¹ | 47 |
| | Graphene–CNT core–sheath fibre | 177 mF cm ⁻² at 0.1 mA cm ⁻² | 11 |
| Transparent batteries and capacitors | Wrinkled CVD graphene | 5.8 μ F cm ⁻² , stretchable, 57% transmittance | 45 |
| | Li ₄ Ti ₅ O ₁₂ and LiMn ₂ O ₄ | 10 Wh l ⁻¹ at a transparency of 60% | 50 |
| Fast-charging batteries | Li ₄ Ti ₅ O ₁₂ –graphene foam | 86 mAh g ⁻¹ at 200C, full discharging time ~18 s | 51 |
| | CVD graphene foam Al battery | 60 mAh g ⁻¹ at 75C, charge–discharge time <1 min | 52 |
| Lightweight batteries for ultrathin electronics | 3D graphene or few-layer graphene | 770 mAh g ⁻¹ at 100 mA g ⁻¹ , 388 Wh kg ⁻¹ | 53 |
| | V ₂ O ₅ –graphene paper | 807 mAh g ⁻¹ at 186 mA g ⁻¹ | 54 |
| Graphene oxide as solid electrolyte and separator | Graphene oxide nanosheets | Proton conductivities of 10 ⁻⁴ –10 ⁻² S cm ⁻¹ | 57, 58 |
| | rGO–GO–rGO microsupercapacitors | 3.1 F cm ⁻³ , 4.3 \times 10 ⁻⁴ Wh cm ⁻³ | 56 |
| | rGO–GO–rGO supercapacitors | 0.86 mF cm ⁻² | 59 |
| Supercapacitors with the energy density of batteries | Liquid-mediated graphene film | 60 Wh l ⁻¹ | 60 |
| | Holey graphene frameworks | 35 Wh kg ⁻¹ and 49 Wh l ⁻¹ | 61 |
| | 3D MnO ₂ –graphene hybrid film | 42 Wh l ⁻¹ | 62 |
| Permselective membranes for safe batteries | Permselective GO Membrane | Coulombic efficiency of 95–98% for 100 cycles at 0.1C | 64 |
| Longer lasting energy-storage devices | Photothermally reduced graphene | 61 mAh g ⁻¹ at 150C for 6,000 cycles | 69 |
| | Solvated graphene framework | 472 mAh g ⁻¹ at 5 A g ⁻¹ for 500 cycles (93% retention) | 70 |
| Binder and additive-free electrodes | Laser-scribed 3D graphene | 265 F g ⁻¹ and 4.82 mF cm ⁻² | 55 |
| | Holey graphene frameworks | 298 F g ⁻¹ and 212 F cm ⁻³ | 61 |
| | Liquid-mediated graphene film | 203 F g ⁻¹ and 261 F cm ⁻³ | 60 |

AC, alternating current; CNT, carbon nanotube; C_s , areal capacitance; CVD, chemical vapour deposition; GO, graphene oxide; r , bending radius; rGO, reduced graphene oxide; RC time, time constant of a resistor–capacitor circuit.

by attaching graphene paper to an elastomer that had been pre-stretched up to five times its original dimensions. When the pre-stretched parts were released, the lateral dimensions of the graphene paper were reduced by the same ratio. An alternative approach was adopted in another study, in which a wrinkled graphene film was first synthesized by chemical vapour deposition. Transfer of the graphene film to a polydimethylsiloxane substrate resulted in supercapacitors that were both stretchable and transparent⁴⁵.

Energy-storage devices for wearable electronics.

Portable electronics have revolutionized our everyday lives and have driven the development of other future electronic devices (for example, wearable electronics that can be incorporated into clothing and accessories, and worn comfortably on the body). These smart garments are expected to need to communicate with the user to give them access to information in real time⁴⁶. In 2011, the first textile-based batteries and supercapacitors were obtained by coating graphene and CNTs onto cotton fabrics⁴⁷. Recently, research efforts have been directed towards the development of coaxial and core–sheath electrodes that combine the current collector and electrode material in a single yarn, which can be knitted or woven directly into textiles. Graphene is a great candidate as it can be readily tailored and assembled into multifunctional microfibres and woven into fabrics. For example, graphene core–sheath microfibres were used to demonstrate spring-like supercapacitors that are flexible, stretchable, all solid-state and can be incorporated into textiles using conventional weaving technology⁴⁸. Similarly, a coaxial wet-spinning strategy was used to produce polyelectrolyte-wrapped graphene/CNT core–sheath yarns, but unlike most yarn electrodes that suffer from low areal capacitance, this one produced up to 269 mF cm⁻² (REF. 11).

Transparent batteries and supercapacitors. Imagine an electronic display nearly as clear as a window or a flexible smartphone that you can see through. This may not be too far off owing to recent advances in transparent electronics that have focused on the use of wide-bandgap semiconductors for the realization of invisible electronic circuits⁴⁹. Although researchers have shown that transistors, organic light-emitting diodes and other electronic components can be made transparent, the development of a transparent power source remains a challenge. This is because of the traditional multilayer structure of a battery comprising two electrodes, a separator, an electrolyte and packaging to hold these layers together. This means that each of these layers will have to be clear for the battery to be transparent. Unfortunately, only the electrolyte is inherently transparent, whereas the other components are opaque, with the electrodes being the most difficult component to make transparent. One way to make a transparent electrode is to make it very thin — on the nanometre scale⁴⁵. But thin electrodes do not store much charge. Another approach is to make patterned electrodes with design features smaller than the detection limit of the human eye⁵⁰. In either case, graphene can have a

key role in making transparent batteries more efficient because of its high conductivity and good transparency (up to 97.7% transmittance). These characteristics make graphene an ideal electrode material not only for transparent energy-storage devices, but also for solar cells, smart windows and other optoelectronic devices.

Fast-charging lithium-ion batteries. First commercialized by Sony in 1991, LIBs represent a major technological advancement from lead–acid batteries, which have been dominant since the late 1850s. Owing to their low weight and high energy density, LIBs have become the technology of choice for consumer electronics. However, they suffer from long recharge times (typically hours), whereas battery users are looking for a battery that recharges in minutes or even seconds.

The use of graphene allows faster electron and ion transport in the electrodes, which controls the speed over which the battery can be charged and discharged. For example, a fast-charging LIB was developed by loading nanoscale Li₄Ti₅O₁₂ anode and LiFePO₄ cathode materials on flexible graphene foam without the use of conducting additives or binders⁵¹. The excellent electrical conductivity and the open pore structure of the hybrid electrodes allowed the battery to become fully charged in only 18 s. Pure graphene can also be used as the anode for LIBs with an improved capacity, and ultrafast charge and discharge rate.

Few-layered graphene may have an important role in the progress of other battery chemistries. For example, an aluminium-ion battery was recently reported that can be fully charged in under one minute because of the ultrafast ion intercalation into 3D graphene foams⁵².

Ultrathin current collectors for lightweight devices. The continuing demand for lighter and smaller mobile electronics, especially notebook personal computers and cell phones, has driven the development of higher-capacity LIBs. Current efforts focus mainly on developing new battery materials with higher capacities; however, reducing the weight of the existing battery components is also very useful. Existing battery technology uses metal foil current collectors, such as aluminium, copper or nickel, with thicknesses between 20 and 80 μm to allow for the transfer of electrons between electrodes and external circuits. This accounts for at least 30% of the weight of the battery, and because it does not store any charge, it reduces the overall energy density. In addition, these metal foils often suffer from corrosion during operation, which has a negative effect on the internal resistance of the cell and the lifetime of the battery.

Graphene has been proposed as an alternative current collector because of its low density, high electrical conductivity and chemical stability under harsh operating conditions. Graphene can be processed into films with wrinkles and ripples on the surface, resulting in better electrical contact with the active materials and thus may further reduce the equivalent series resistance of the cell⁵³. Interestingly, it was found that a LIB with a graphene paper current collector exhibits a better cycle life than a battery with a traditional metal current

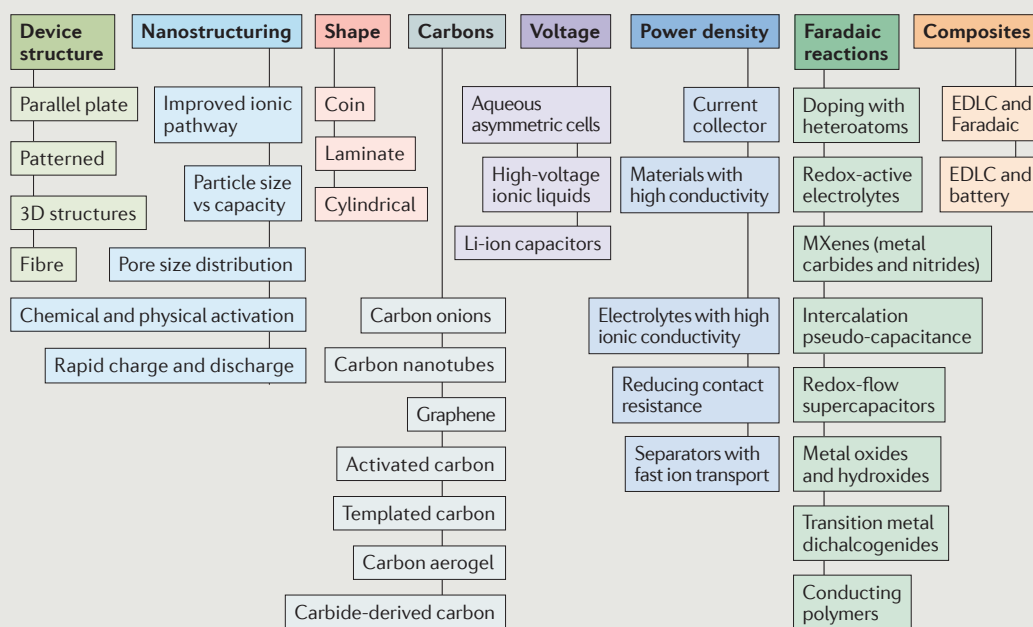
collector⁵⁴. Owing to its good electrical conductivity and high surface area, graphene can be used as both the active material and the current collector, leading to lightweight, flexible supercapacitors⁵⁵.

Graphene oxide as solid electrolyte and separator.

Batteries are generally treated as hazardous waste because of the potential leakage of the liquid electrolyte. Therefore, there is the need to develop alternative, solid-type electrolytes. Graphene oxide is an excellent electronic insulator; however, when a

substantial amount of moisture is entrapped in the layered graphene oxide structure, it becomes an ion conductor with ion-transport features similar to those observed in the Nafion membranes used in fuel cells⁵⁶. The hydrophilic sites on the surface of graphene oxide, such as $-OH$, $-O^-$ and $-COOH$ functional groups, attract protons that are propagated on the graphene oxide surface by the adsorbed water molecules. This contributes to the ionic connection between the positive and negative electrodes and enables the use of graphene oxide as both a viable solid electrolyte and

Box 1 | Strategies for improving the energy density of supercapacitors



Supercapacitors have several useful features, such as high power density, excellent performance at low temperatures and essentially an unlimited number of charge and discharge cycles. Supercapacitors exist in different shapes and structures, as detailed in the diagram. However, the low energy density of current supercapacitors is the main impediment to realizing the full commercial potential of this technology. Since they were introduced into the market in the 1970s, the majority of supercapacitor electrodes rely on activated carbons for charge storage. Over the past two decades, various carbon allotropes have been used, such as 0D carbon onions, 1D carbon nanotubes, 2D graphene, 3D templated carbons, 3D carbon aerogels and 3D carbide-derived carbons. Charge storage in these materials is limited to the surfaces and is thus controlled by their respective specific surface area, average pore size and pore size distribution. The continuous need to improve the energy density of supercapacitors has led to the development of a new class of charge-storage materials, known as redox or Faradaic materials. In Faradaic supercapacitors, the charge is stored through fast and reversible redox reactions at or near the surface of the electrode. Although metal oxides and conducting polymers are classic examples in this category, a number of new Faradaic systems have been recently discovered with great potential for high-capacity charge-storage devices (see the diagram). Recently, the prospects of generating hybrid materials, in which the fascinating properties of carbons are combined with those of Faradaic materials, have generated considerable interest.

Progress in the field of supercapacitors has benefited from tremendous advancements in synthesis at the nanoscale. Nanostructuring has become a general strategy for improving the energy density of electrode materials because of the improved electrochemical properties of nanomaterials. Because the energy density is directly proportional to the square of the voltage, great effort has been devoted to improving supercapacitor cell voltages. This can be achieved through various strategies, including the design of ionic-liquid mixtures with large operating voltage windows, building asymmetric cells, such as lithium-ion capacitors or aqueous asymmetric supercapacitors that contain a metal oxide positive electrode and a carbon negative electrode. Further improvements in the power density of a supercapacitor may be attained by reducing the internal resistance of the cell, which is affected by the intrinsic resistance of all cell components. Future supercapacitors may include new structures, multifunctional electrode materials and electrolytes, enabling unprecedented energy and power densities.

electrode separator simultaneously. This has led to the development of in-plane and sandwich supercapacitors with many rGO–GO–rGO (GO, graphene oxide; rGO, reduced graphene oxide) configurations without the use of any external electrolyte⁵⁶. In one experiment, the proton conductivity of three different forms of graphene oxide was measured: graphene oxide nanosheets, bulk graphite oxide and a graphene-oxide/proton hybrid. Surprisingly, it was found that the in-plane conductivity of graphene oxide nanosheets is two to three orders of magnitude higher than that of bulk graphene oxide⁵⁷. Further investigation of the proton conductivity of individual graphene oxide sheets led to the development of multilayered graphene oxide films with high proton conductivity that may be useful for energy storage and fuel cells⁵⁸.

In another study, it was found that a rGO–GO–rGO sandwich structure, in which a graphite oxide film acts as a solid electrolyte, shows a capacitance (up to 0.86 mF cm⁻²) comparable to that of electrochemical capacitors but with undetectable ionic diffusion similar to dielectric capacitors, indicating a new ‘third’ category of electrical capacitor⁵⁹. These interesting results may lead to the development of lightweight, energy-dense and ultrafast solid-state capacitors that do not suffer from ion diffusion, which limits the kinetics of traditional electrochemical capacitors, or the hazards associated with electrolyte leakage.

Supercapacitors with the energy density of batteries.

Most currently available supercapacitors feature activated-carbon electrodes and an organic electrolyte that operates at voltages between 2.3 and 2.8 V. Although they offer higher power density and exceptional cycling stability compared with batteries, their energy density (5–7 Wh kg⁻¹) is one order of magnitude lower. As described earlier, graphene has the potential to produce EDL capacitors with similar energy density to batteries without compromising the high power density and cycling stability. However, in most cases, graphene sheets tend to agglomerate during the processing of electrodes, resulting in devices that provide little performance advantage over traditional activated-carbon supercapacitors. To solve this problem, a colloidal approach was adopted for the assembly of graphene using a mixture of a volatile and a non-volatile solvent⁶⁰. In this case, the non-volatile solvent prevents the sheets from touching by acting as a nanospacer. This makes it possible to control the density of the graphene electrodes and thus improve the volumetric performance. These supercapacitors demonstrated ultrahigh energy densities of up to 60 Wh l⁻¹, which is comparable to lead–acid batteries. In a different approach, porous and dense graphene foams were developed for efficient capacitive energy storage by digging nanoholes in the basal planes of graphene and using a hydraulic press to control the density of the foam⁶¹. Recently, graphene-based hybrid supercapacitors capable of providing up to 42 Wh l⁻¹ have been reported⁶². The advantage of these hybrid supercapacitors is that they work with aqueous electrolytes and can be produced in air without the need

for expensive ‘dry room’ assembly. An overview of the different strategies used to improve the energy density of supercapacitors is provided in BOX 1.

Permselective graphene oxide membranes. The separator is an essential component of electrochemical energy-storage devices. According to classic battery textbooks, a separator is a permeable membrane placed between the anode and cathode of a battery⁶³. The main function of a separator is to provide a physical barrier between the two electrodes to prevent electrical short circuits, while also allowing the transport of ions during charge and discharge cycles. Separators are normally porous polymer membranes, which physically keep the two electrodes apart without affecting the transport of ions through the membrane. This nonselective nature of the separator can, in some cases, have a large influence on the cycling stability and rate capability of the battery. For example, in lithium–sulfur batteries, the polysulfide species generated at the sulfur cathode can diffuse freely through the membrane and react with the lithium-metal anode, which induces rapid capacity degradation and poor cycling stability. An ideal battery separator should, thus, be permselective; that is, it should allow specific species to be transported while restricting the passage of other species that can reduce the reversibility of the battery.

Graphene oxide membranes exhibit great mechanical strength and are electrically insulating. Owing to their negative charge, graphene oxide membranes are expected to be permeable for lithium ions but reject anions. This electrostatic repulsion has been shown to largely inhibit the diffusion of polysulfides through graphene oxide membranes in lithium–sulfur batteries, which leads to a stable electrochemical response with greatly improved self-discharge rates⁶⁴. Graphene oxide membranes consist of micrometre-sized graphene oxide crystallites that form an interlocked layered structure. These characteristics can also be very useful in LIBs, in which the pore size and the non-uniform permeability across the separator may result in the growth of metallic lithium dendrites that can eventually lead to short circuiting between the anode and cathode. We note that graphene oxide membranes exhibit a wide range of unique barrier properties. It was shown that graphene oxide membranes, in the dry state, are impermeable to everything except water vapour⁶⁵. When immersed in water, graphene oxide membranes act as molecular sieves, allowing transport of small ions while blocking large ones⁶⁶. These features offer opportunities for the design of a new generation of ion-selective membranes for batteries, supercapacitors and fuel cells⁶⁷.

Longer-lasting energy-storage devices. One of the main reasons why consumers choose one smartphone over another is not the processor speed or data storage; it is how long the smartphone will last on a single charge. Although the next big breakthrough may still be a few years away, recent advances in graphene research are bringing us closer to arguably the most important feature of all: longer-lasting batteries. Researchers have

shown that it is possible to fabricate such batteries by replacing the graphite anodes used in today's LIBs with graphene electrodes in the form of folded graphene paper⁶⁸, porous graphene films⁶⁹ and solvated graphene frameworks⁷⁰. This has led to LIB anodes with specific capacities of more than $1,000 \text{ mAh g}^{-1}$ — more than three times the capacity of standard graphite electrodes — which promises longer run times for portable electronics and a longer range for electric vehicles. It has also been discovered that nitrogen and boron doping are crucial in improving the capacity and power density of graphene anodes⁷¹.

In addition, graphene can serve as a support for metal oxide active materials, while providing high electrical conductivity, mechanical strength and greater surface area. For example, with a reduced graphene oxide wrapping, an Fe_2O_3 composite anode exhibited a specific capacity three times higher than that of a pure Fe_2O_3 electrode⁷². Graphene can effectively increase the capacity of LIB cathodes as well. For example, LiFePO_4 is widely used in LIB cathodes because of its long cycle life and low cost. In this case, graphene can act as a structural backbone on which LiFePO_4 can be attached, creating a hybrid material with improved conductivity and better cycling durability. Because this hybrid allows for the maximum utilization of LiFePO_4 in charge storage, it stores twice as much charge as commercially available LiFePO_4 (REF. 73).

Binder and additive-free electrodes. In both batteries and supercapacitors, the electrodes are generally made by mixing particulate active materials with carbon additives and polymeric binders (such as polyvinylidene fluoride and polytetrafluoroethylene) with the help of an appropriate solvent. The resulting slurry is coated on the current collector of choice, dried and then exposed to a mechanical press to control the pore volume and density of the electrodes. The binder is used to glue the materials together with the current collector, whereas the conductive agent improves the electrical properties of the laminate. Although this process is widely used in industry, the use of insulating polymer binders increases the contact resistance between particles, which increases the equivalent series resistance of the cell⁷⁴. The binder and additive together makes up 20–40% of the mass of the electrode. This is called 'dead mass' because it does not contribute to charge storage, but instead decreases the energy density of the electrodes. In addition, the diffusion pathways of ions and electrons are unclear because of the inhomogeneous nature of the blend, which causes low power density and slow rate capability.

Recent studies have demonstrated that graphene can be fabricated into electrodes directly without the need for binders and conductive agents, as is the case for conventional particulate materials⁵⁵. This is possible because of the ability to assemble graphene into self-standing 2D and 3D structures with excellent electrical conductivity. Compared with other battery and supercapacitor electrodes, graphene-based materials exhibit additional advantages, such as low weight, diverse macroscopic structures, controllable pore size and distribution, and mechanical flexibility⁷⁵.

Other 2D materials for charge storage

The discovery of graphene has led to a new class of materials known as '2D crystals' (REF. 76). In addition to graphene, the family of 2D materials includes many transition metal dichalcogenides (such as MoS_2 , TiS_2 and WS_2), layered metal oxides (such as Nb_2O_5 , MnO_2 and TiO_2), hydroxides, nitrides and carbides, and several other compounds (for example, BN and Bi_2Te_3). Although graphene has unveiled a set of fascinating properties, the other 2D materials cover a wide variety of properties as well; for example, they range from electrically insulating to superconducting and from transparent to optically active⁷⁷. By combining graphene with other 2D materials, researchers hope to create 'heterostructures' with functionalities capable of delivering a new generation of superconductors, metallic materials, semimetals, semiconductors and insulators⁷⁸. These materials have the potential for use in a wide range of applications, such as high-performance electronics, sensors, solar cells, gas separation, catalysis and energy storage.

Because of the reduced dimensionality of these 2D crystals, they exhibit electrochemical properties that are distinct from their bulk counterparts⁷⁹. Two-dimensional transition metal dichalcogenides and oxides can support the ultrafast ion transport of lithium, hydrogen and sodium ions — a characteristic that makes them ideal for ultrafast battery and capacitor electrodes⁸⁰. These materials are promising alternatives to currently used 3D bulk materials with slow ion diffusion that have so far limited the power density of traditional battery electrodes. In addition, MoS_2 nanosheets show excellent capacitive behaviour by storing charge via intersheet and intrasheet double layers over individual MoS_2 layers and through Faradaic reactions on the Mo centre because of its multiple oxidation states. Combining MoS_2 with graphene results in supercapacitors with higher capacitance and better cycling stability⁸¹. These hybrid electrodes can also be used as LIB anodes, offering stable cycling performance and a high specific capacity of up to $\sim 1,100 \text{ mAh g}^{-1}$ at a current density of 100 mA g^{-1} (REF. 82).

Recently, a new class of 2D transition metal carbides or carbonitrides, known as MXenes, was synthesized by selective etching of the so-called MAX phases⁸³. These materials offer an unusual combination of metallic conductivity and hydrophilicity, and are attractive for electrochemical energy storage. They can be shaped like clay and processed into films achieving an ultrahigh volumetric capacitance of 900 F cm^{-3} (REF. 84). Exfoliated layers can be suspended in water and filtered into flexible MXene papers that can be used in LIBs to achieve a high capacity at high charging rates⁸⁵.

Limitations of graphene and possible solutions

Graphene batteries and supercapacitors have witnessed rapid developments and substantial achievements during the past few years, but there are still many challenges to be addressed to realize their practical applications. Although researchers have demonstrated graphene-based batteries and supercapacitors with performance characteristics

far exceeding those of commercially available ones, the lack of feasible techniques for the mass production of high-quality graphene limits their potential. Estimates for the cost of production of graphene vary depending on the quality of the material from tens to thousands of dollars per kilogram⁸⁶, but it is still not competitive with state-of-the-art materials. For example, the very low cost of activated carbon currently used in supercapacitors (US\$15 per kilogram) presents a difficult barrier to the entry of other materials⁸⁷.

Most techniques that have shown potential for large-scale production depend on the exfoliation of expanded graphite or the reduction of graphite oxide. The former often results in multilayered graphene platelets with limited surface area, which is a critical parameter for supercapacitors⁸⁸, and the latter form of graphene has relatively low electronic conductivity caused by residual oxygen and structural defects. In addition, reduction of graphite oxide is still challenging as it involves complicated procedures and purification methods, and often employs toxic and corrosive chemicals leading to environmental concerns. The conductivity of reduced graphene oxide needs to be further enhanced with more efficient reduction methods.

Ultrathin graphene flakes, when processed, result in electrodes with low densities and large pore volumes. The addition of an electrolyte causes huge 'dead mass' that adds weight and volume, but does not contribute to charge storage; this kills the performance of graphene electrodes on the device level. It is necessary to find simple methods for making graphene electrodes with large packing densities without affecting their accessible surface area. Some recent studies have addressed this issue, but the solutions are not yet practical.

The processing of electrodes is another important parameter that defines the viability of new technologies. Current battery and supercapacitor technologies use roll coating for manufacturing electrodes. This process is inexpensive, efficient and fast, producing up to several metres of electrodes per minute. Most devices made out of graphene use techniques that are limited to research laboratories and difficult to scale up. Future studies on graphene should focus on competitive processing techniques and not just laboratory-feasible preparation methods.

Finally, the properties of graphene electrodes are determined by their microstructure; however, precise control of the pore size and porosity of graphene is a big technical challenge. Most of the 3D graphene electrodes reported thus far feature pores that vary in size between hundreds of nanometres and several micrometres. To address this issue and to increase the capacity of graphene electrodes, it would be interesting to introduce micropores into the structure of graphene through assembly from porous graphene sheets or by using a chemical activation process of the type that is widely used nowadays for the preparation of activated carbon.

Graphene is widely used in batteries either as the active component or inactive conductive additive. In the latter case, graphene forms a 3D electron conducting network offering electron 'superhighways' that promote

the charge transfer exchange rate of active materials. This increases electron conductivity and therefore rate capability of the electrode under investigation. Graphene can also buffer the volume changes during charge and discharge, and therefore increase the cycling stability of the active materials. However, in most cases, large amounts of graphene (10–20% w/w) are normally used in these hybrid electrodes. It should be noted that too much graphene does not help because of its low packing density, which can reduce the energy density of the battery. It is thus advisable to reduce the amount of graphene in the hybrid electrodes while maintaining good electrochemical performance. The low electrical conductivity of chemically derived graphene — which is almost always lower than carbon black — is another challenge. Improving the conductivity of graphene for conductive additive applications should be a priority at this stage. Solution processing of graphene oxide offers a great opportunity for large-scale production of chemically derived graphene, although stronger reducing agents are needed. Graphitization of the produced graphene through chemical and thermal methods holds great promise too.

There are several methods in which graphene can be hybridized with battery materials to produce composites with improved electrochemical performance. Specifically, the battery materials can be anchored to the graphene surface, wrapped by graphene sheets, encapsulated in a graphene shell or sandwiched between two graphene monolayers. In addition, graphene can be assembled with 2D battery materials forming layered heterogeneous structures⁹⁰. However, it is not clear which of these structures produces graphene composites with the best electrochemical performance. More efforts are needed to gain a fundamental understanding of the molecular interaction between graphene and other battery components in both the bulk and at the electrode/electrolyte interface. This will allow the design of novel materials and composites with custom properties and could enable the practical use of graphene-based materials in energy-storage devices.

Another issue to be considered in graphene composites is the accessibility of the active materials to the electrolyte. Although ion diffusion may occur through surface defects and grain boundaries, the diffusion through the basal plane is rather limited. A small amount of graphene may thus provide a good balance between improved electron transport and fast ion diffusion, whereas too much graphene may isolate the active material from reaching the electrolyte because of complete wrapping⁹¹. This also depends on the structure of the graphene; for example, the narrow width of graphene nanoribbons provides more grain boundaries and therefore faster ion diffusion than normal graphene sheets. Another strategy to combat this problem is to open nanopores in the basal plane of graphene through chemical activation.

Although graphene is attractive as an anode for LIBs with a capacity of more than 1,000 mAh g⁻¹ already achieved, it suffers from low first-cycle Coulombic efficiency⁹². This is mainly attributed to the high surface area of graphene and structural defects associated with

the different synthetic routes. The storage of lithium ions at defects causes very high initial irreversible capacity, which results in poor energy efficiency. Unless a solution is found, this problem may hinder the practical application of graphene anodes. One possible solution is to carefully design the structure of graphene to lower the surface area contacting the electrolyte and reduce the defects on graphene to avoid side reactions. Knowing that reduced graphene oxide is the most common form of graphene currently explored in LIBs, the progressive reduction of oxygenated functional groups should produce fewer defects and may help improve the Coulombic efficiency of graphene anodes. Another strategy is to make hybrid electrodes from graphene and other battery materials to reduce or dilute the negative effect of graphene on the Coulombic efficiency.

There is no doubt that graphene has changed the landscape of energy storage because of its outstanding electrochemical properties and unique combination

of large surface area, high electronic conductivity and excellent mechanical properties. Innovative techniques have been demonstrated for the fabrication of energy-storage devices with new features not possible with current state-of-the-art technology. However, the full potential of energy-storage devices built from graphene has yet to be realized. Many challenges remain, particularly with regard to feasible techniques for the low-cost mass production of graphene with controlled microstructure and low residual oxygen content. More research efforts should be made for resolving the existing challenges using theoretical calculations together with experimental investigations. Further understanding of the interaction of graphene sheets at the nanoscale to form self-assembled structures of different shapes and dimensionalities will drive more potential applications for graphene. Graphene research is expected to continue to expand rapidly during the next decade with the promise that it will make a real impact on our lives.

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Competing interests statement

The authors declare no competing interests.