Graphene aerogels for efficient energy storage and conversion

Jiajun Mao, James Iocozzia, Jianying Huang, Kai Meng, Yuekun Lai and Zhiqun Lin

Concerns over air quality reduction resulting from burning fossil fuels have driven the development of clean and renewable energy sources. Supercapacitors, batteries, and solar cells serve as eco-friendly energy storage and conversion systems vital for the sustainable development of human society. However, many diverse elements influence the performance of energy storage and conversion systems. The overall efficiency of systems depends on the specific structure and properties of incorporated functional materials. Carbon materials, such as graphene, are especially promising for materials development in the energy storage and conversion fields. Graphene, a two-dimensional (2D) carbon material only a single atom thick, has massless Dirac fermions (electron transport is governed by Dirac’s equation), displays outstanding electrical conductivity, superior thermal conductivity and excellent mechanical properties. 2D free-standing graphene films and powders have paved the way for promising energy applications. Recently, much effort has been spent trying to improve the number of active sites in electrode materials within 3D network/aerogel structures derived from graphene. This is because graphene aerogels are promising materials for energy systems due to their porous hierarchical structure which affords rapid electron/ion transport, superior chemical and physical stability, and good cycle performance. This review aims to summarize the synthetic methods, mechanistic aspects, and energy storage and conversion applications of novel 3D network graphene, graphene derivatives and graphene-based materials. Areas of application include supercapacitors, Li-batteries, H₂ and thermal energy storage, fuel cells and solar cells.

**Broader context**
Environmental pollution caused by the rapid consumption of fossil fuels has prompted investigation into alternative sources of efficient, cost-effective, and sustainable energy systems. Traditionally, noble metals and transition-metal oxides are the most widely used electrode materials. However, their high price and associated toxicity hinder further development. The combination of the chemical properties and 3D network morphology which ensure excellent electron transport performance make graphene aerogels (GAs) ideal candidates for various future energy storage and conversion systems, e.g., supercapacitors, Li-batteries, fuel cells and solar cells. Moreover, the ultralow density and flexibility of 3D aerogels are beneficial for portable equipment and roll-to-roll processing. This review will briefly outline and compare various fabrication methods of GAs and detail the roles of GAs in energy systems. In addition, we will look into some critical engineering strategies that give rise to the electrochemical properties of 3D GAs such as enlarged surface area, tailored porosity, efficient separation of carriers, and chemical/physical modification. The creative points and trends detailed in this review will offer promising development directions for aerogels and other porous network structures as well as metal-free materials in energy storage and conversion systems.

**1. Introduction**

The environmental pollution caused by the rapid consumption of fossil fuels in many developing countries has prompted necessary investigation into alternative sources of energy.

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green and renewable energy systems which have received various degrees of industrial success while also satisfying the energy requirements of modern life.\textsuperscript{10–14} However, there are many factors that influence the efficiency of these energy systems \textit{(i.e.} the amount of electricity generated for a given amount of incident energy input\textit{)}. Maximizing the efficiency is one of the most important challenges dictating the success of any renewable energy technology and it is largely dependent on the structure and properties of candidate materials.

Nanotechnology takes advantage of the significant relationship between properties and structure size that occurs on the nano-scale in materials from 0D to 3D complexity. In addition the properties of nanostructured materials are often vastly different from familiar bulk counterparts. Possessing a single carbon atom thickness and massless Dirac fermions, sheet-like \textit{(2D)} graphene derivatives have attracted great interest for energy applications due to their outstanding photoelectrochemical performance. With these in mind, the rational assembly of nano-sheets into macroscopic structures which afford large internal reactive areas and directed molecular transport are vital factors to realize the rapid development of energy storage and conversion. In contrast to 2D films, 3D network aerogel morphologies are a framework containing interconnected micro-/nanosheets while also possessing hierarchical pores on micro, meso, and macro scales. The micro and mesopores structures contribute to the high specific surface area and the macropores provide accessibility to the active surfaces. At the same time, the ultralow density and flexibility of 3D aerogels are beneficial for portable electronics affording excellent mechanical stability and high flexural strength. In addition to structure and morphology, the electronic and chemical properties are important in all applications. For example, graphene has a high specific surface area (\(~2800 \text{ m}^2 \text{ g}^{-1}\)), superior electrical conductivity (\(~10^6 \text{ S cm}^{-1}\)), excellent thermal conductivity (\(~6000 \text{ W m}^{-1} \text{ K}^{-1}\)), and ultra-low optical absorption (2.3\%). When combined with other nano and micron materials, the resulting composites can combine desirable bulk properties.
and processability with the unique nanoscale properties described above.

Owing to their numerous conductive interconnections between 2D sheets, graphene aerogels and their composites are promising for various energy systems. Among energy storage devices, supercapacitors typically have high power densities and low energy densities (i.e. a small water jug with a large spout). In contrast, batteries typically have high energy densities but low power densities (i.e. a large water jug with a small spout). Ideal storage devices should possess high power and energy densities as well as quick charging/recharging, and long cycle life. Superior conductivity and specific graphene aerogel morphologies contribute to a qualitative leap in performance and applicability because the hierarchical porosity and high contact area satisfy the requirement for a large number of stored charges as well as the rapid transport of ions/electrons during the reversible charge/discharge processes. The robust graphene aerogel 3D network provides physical and chemical stability during repeated ion intercalation and deintercalation enabling long cycle lifetimes for graphene aerogel-based devices. For fuel cells or metal-air batteries, water splitting, oxygen reduction reaction (ORR), oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) are crucial half-electrochemical processes that occur. Noble metals (Pd, Au, and Pt) and transition-metal oxides (TiO$_2$, RuO$_2$) are the most wildly used catalysts. However they are not ideal due to high costs as well as toxicity both of which greatly hinder their development. Owing to the large number of active sites, high conductivity and metal-free composition (i.e. low cost), graphene aerogel-based materials are attractive for electro-catalytic applications. In dye-sensitized solar cells (DSSCs), graphene aerogels can serve as a counter electrode, a modifier for TiO$_2$ inverse opal electrodes, and a solid state electrolyte possessing improved power conversion efficiencies due to its quick charge transfer capabilities.

This review will provide an in-depth understanding of graphene aerogel-based materials as they apply to energy systems (supercapacitors, Li-batteries, fuel cells, metal–air batteries, and solar cells). This work will briefly outline and compare various fabrication methods of graphene aerogels and detail the various advantages of graphene aerogels as they apply to each specific device area. In addition, we will look into some critical engineering strategies that give rise to the excellent properties of 3D graphene aerogels such as enlarged surface area, tailored porosity and efficient separation of carriers. Graphene aerogels represent a high performance, low-cost material for near future energy technologies.

2. Fabrication of graphene aerogels

The realization of high performance graphene materials immediately necessitates the nanoscale exfoliation of neighboring sheets into individual layers prior to incorporation into any macrostructure. This section details significant reports dealing with the improvement in the quantity and quality of graphene layers. Many techniques including mechanical stripping, chemical vapor deposition (CVD), and oxidation–reduction method, have been proposed to construct carbon-based nanomaterials. The latter two are the most widely used techniques. The oxidation-reduction method first converts graphite into graphitic/graphene oxide through the well-known Hummers’ method. After intermediate exfoliation or ultrasonication to produce graphene oxide (GO), it is then reduced by hydrazine hydrate, vitamin C, isocyanic acid or thermally to yield graphene. CVD harnesses a different carbon source to grow graphene on a variety of substrates such as metallic (Cu, Ni, Co, Fe) or planar nonmetallic surfaces (SiO$_2$, Si$_3$N$_4$, SrTiO$_3$, NaCl). During a typical CVD treatment, hydrocarbon precursors are pyrolyzed to carbon.
radicals when they pass through the hot zone and then deposited on the surface where self-limited growth occurs to form a single-layer or few-layer graphene on substrates. Compared to the oxidation–reduction technique, CVD growth has several including an ordered structure, and excellent electronic properties of the resulting graphene nanostructures. However, it requires an extra transfer process to put the graphene layer onto other desired substrates, often accompanied with lower yields and reduced quality.

2D materials manufactured using freestanding graphene nanosheets and modified graphene can be used in sensors, electrochemistry, photocatalysis and filtration. These materials have attracted great interest in recent years. However, there are few reviews related to graphene aerogels which have stable 3D networks and high pore volumes in contrast to conventional graphene films. Monte and coworkers summarized the synthesis and application of carbon nanotubes and graphene aerogels. Chen and coworkers investigated the synthesis, properties and application of 3D graphene networks. Building on this previous work, we summarize multiple fabrication techniques for the rational construction of 3D graphene aerogels.

Self-assembly strategies are a common “bottom-up” approach. Graphene nanosheets serve as the building blocks for self-assembly to obtain 3D porous networks. Shi et al. successfully fabricated mechanically strong, electrically conductive and thermally stable graphene aerogels by a hydrothermal process (Fig. 1a). This is a convenient one-step method. However, hydrothermal processes typically occur in a Teflon-lined autoclave requiring high pressures. This hinders large scale synthesis as it is a batch rather than continuous process. Yan et al. prepared graphene aerogels by the mild chemical reduction of GO with various reducing agents under atmospheric pressure in an open system. The resulting graphene aerogels showed good mechanical strength, low density and high electrical conductivity facilitating large scale fabrication (Fig. 1c). Self-assembly is possible because of the abundance of oxygen-containing functional groups on graphene oxide which enable interaction between various sheets. These groups enhance the presence of π–π stacking among the graphene layers and make the graphene nanosheets hydrophobic. Yu et al. reported graphene aerogels induced by Fe(II) ions at different pH values to obtain free-standing graphene/R-FeOOH and magnetic graphene/Fe₃O₄ aerogels with different

![Fig. 1](image-url)
functionalities for different applications (Fig. 1b). 3D graphene aerogels with embedded nanoparticles (NPs) endow additional functionalities in graphene aerogels. Feng et al. hydrothermally assembled GO dispersions and iron acetate to enable the nucleation and growth of Fe$_3$O$_4$ nanoparticles on the graphene surface to yield high surface area Fe$_3$O$_4$/graphene aerogel composites (Fig. 1d). Similarly, other materials have been decorated internally and externally onto graphene aerogels such as hierarchical porous MOFs@GA.

Self-assembly strategies offer a convenient and scalable process to manufacture graphene aerogels with good electrical conductivity, and thermal stability. Cross-linkers can also be used to link the graphene layers to form 3D aerogels via electrostatic interaction, hydrogen bonding, and covalent bonding. Cross-linkers provide a more convenient route than direct cryodesiccation from the aqueous state. Gao et al. constructed 3D graphene frameworks with carbon nanotubes (CNTs) using sol cryodesiccation and carbonization. The aerogel had very low density, excellent thermal stability and high absorption (Fig. 2a). Biopolymers coated with graphene are also beneficial due to their elasticity and fatigue resistance in resulting aerogels. Yu et al. synthesized lamellar chitosan–graphene oxide scaffolds (CS–GO) from a homogeneous mixture via bidirectional freezing and annealing. The resulting composite showed high compressibility, super-elasticity, and low density (Fig. 2b). Other cross-linkers, such as sodium dodecyl sulfate, cellulose, and resorcinol-formaldehyde (RF), have also been reported.

Normally, graphene aerogels prepared by self-assembly and cross-linking start with the reduction of graphene oxide. This typically leads to a large number of surface defects and unreduced oxygen-containing groups. CVD-growth is an alternative method that can produce more pristine graphene materials. Zhang et al. obtained high-quality 3D graphene networks using Ni foam templates by the ethanol-CVD method (Fig. 2c). Templated CVD-growth produces a decent interconnectivity, but the mechanical strength is poor because of the soft pristine graphene framework. Bando et al. developed a template-free strategy for producing 3D graphene aerogel. The frameworks are tightly connected and supported by robust graphitic microstructures (Fig. 2d). In both the templated and template-free strategies, it is possible to ensure that the carbon source converts into 3D graphene aerogel network structures. However, the process is difficult to scale-up. Recently, a 3D printing technique also known as direct ink writing has been applied in the construction of 3D cellular architectures. Worsley et al. constructed graphene aerogels by a graphene-based direct ink writing process. The as-prepared aerogels were lightweight, highly conductive and highly compressible (Fig. 2e).

3. Mechanisms and roles of graphene aerogels in energy storage

Energy storage technology is especially important for mobile applications. For example, cell phone batteries require high...
energy densities and quick-charging times. Remote controlled drones and electric vehicles also require high gravimetric energy densities and have developed significantly due to their shrinking costs and improved safety. Both supercapacitors and batteries are essential electrochemical energy storage devices that have attracted great attention due to the significant potential improvements that remain. Graphene aerogels and their derivatives functionalized with metal oxides and conductive polymers have been widely used in supercapacitors and batteries.

### 3.1 Supercapacitors

A supercapacitor is one kind of energy storage device filling the gap between batteries and conventional capacitors possessing higher energy densities than conventional capacitors and higher power densities than batteries. Early capacitor designs were composed of a glass insulating medium covered with foil. More recently, mica, ceramic and polystyrene have largely replaced glass as an insulating medium. Double-layer capacitors appeared in 1957 when General Electric filed the first patent followed by a SOHIO patent about fundamental varieties of supercapacitors in 1962. NEC fabricated market-oriented capacitors in the 1970s and Panasonic manufactured two different supercapacitors including button type and spiral type around the same time. ELIT packaged the first asymmetric capacitors with nickel–metal hydride as the cathode, KOH as the electrolyte, and activated carbon as the anode. Subsequently, multiple supercapacitor types have been optimized for highly specific capacitance and output voltages. Electrochemical adsorption/desorption and redox reactions contribute to the energy storage in supercapacitors. The two storage approaches are highly reversible even at high numbers of charge–discharge cycles on the order of hundreds of millions. They have higher power densities on the order of 300–5000 kW kg$^{-1}$ which are 5–10 times that of Li-ion batteries. Supercapacitors also have superior cycling stability with lifetimes 10–100 times that of batteries. To date, supercapacitors have been widely used in portable electronic devices, electric vehicles, aerospace, and national defense fields for their excellent cycle stability, safety, and rapid charge–discharge performance.

#### 3.1.1 Double-layer capacitors

Double-layer capacitors (DLCs) are energy storage devices with a double electric layer interface formed between the electrode-active materials and electrolyte for charge storage.$^{37,38}$ While an external electric field is applied, the positive and negative electrodes, which have stored the corresponding positive and negative charges, gather the opposite ions from the electrolyte to balance the electric field. The potential difference resulting from the migration of ions is the mechanism for energy storage. This is a classical physical model of supercapacitors. They are attractive because they possess excellent stability and circulation. The charging process of double-layer capacitors is described by the following equations and Scheme 1:

**Cathode:** $C_e + A^- \rightarrow C_e||A^- + e$

**Anode:** $C_e + B^+ + e \rightarrow B^+||C_e$

where $C_e$ is the surface of the electrodes, “||” is the double-layer cell between the electrodes and electrolyte, and $A^-$ and $B^+$ represent the anion and cation.

The primary theoretical model was put forward by Helmholtz with the capacitance dictated by the following equation:

$$C = \frac{\varepsilon_0 \times \varepsilon_r}{d} \times A$$

where $\varepsilon_0$ is the internal dielectric constant, $\varepsilon_r$ is the vacuum dielectric constant, $A$ is the surface area of the electrode, and $d$ is the effective diameter of the cell. This capacitance model was further perfected by dividing the interface of the electrode active materials and electrolyte into a close layer ($C_s$) which is the layer occurring on polarization at the electrode–electrolyte interface and diffusion layer ($C_{diff}$) which is the layer forming from the accumulation of ions close to the electrode surface. In this framework, a double-layer capacitor is essentially equal to a series connection of a close layer capacitor and diffusion layer capacitor as follows:

$$\frac{1}{C_{dl}} = \frac{1}{C_s} + \frac{1}{C_{diff}}$$

The cell voltage ($V$) plays a significant role both in the specific energy and the power of supercapacitors because the stored energy ($E$) and power ($P$) are related to the voltage by the following:

$$E = \frac{1}{2}CV^2, P = \frac{V^2}{4R}$$

Despite the fact that aqueous alkaline and acid solutions possess high ionic conductivity and low cost, organic electrolytes are still widely utilized because they can endure higher operation voltages and thus store more energy and have larger power (alkaline or acid electrolytes $\sim$ 1.23 V, organic electrolytes $\sim$ 2.7 V).

Electrode interfacial contact, electrode active material type, and their Brunauer–Emmett–Teller specific surface (BET) are key properties in capacitor research.$^{39,40}$ Graphene is a promising electrode material due to its high BET and conductivity.$^{41–44}$ Ruoff et al. developed symmetrical double-layer capacitors with modified hydrazine hydrate-reduced graphene. The graphene BET reached 705 m$^2$ g$^{-1}$ with a capacitance of 135 F g$^{-1}$. 

![Scheme 1 Schematic diagram of typical double layer capacitors (DLC).](image-url)
Such high performance measures are a testament to graphene’s applicability in supercapacitors.\textsuperscript{37}

However, graphene powders and films have a tendency to aggregate, often leading to lower BET values. Graphene aerogel, with its high pore volume, enhances the contact area between the network and electrolyte. Shi \textit{et al.} synthesized graphene hydrogels \textit{via} a hydrothermal method. Capacitance values reached as high as 160 F g\textsuperscript{-1} and were attributed to the macroporous 3D network structure of the graphene.\textsuperscript{24} Subsequently, the hydrogel was further reduced by hydrazine leading to an increased capacitance of 222 F g\textsuperscript{-1}.\textsuperscript{45} The performance enhancement is attributed to the reduction of oxygen-containing groups which enhance the conductivity from 0.005 S cm\textsuperscript{-1} to 0.032 S cm\textsuperscript{-1}. A higher conductivity represents a higher electronic mobility and higher output power potential.

Similarly, Lu and \textit{et al.} developed graphene aerogels with ethylenediamine (EDA) cross-links which when reduced achieved conductivities of 13.51 S cm\textsuperscript{-1} and specific capacitances of 231 F g\textsuperscript{-1}.\textsuperscript{46} In addition, recent work has shown that thermal treatment under inert gasses can yield highly-conductive graphene aerogels analogous to chemical reduction.\textsuperscript{57-49} Doping graphene with one or several elements such as S, N, B, and P can restructure the graphene crystal lattice and locally manipulate the electronic structures resulting in beneficial chemical and physical changes that can improve the performance of graphene.\textsuperscript{50-53} To date, nitrogen is the most popular dopant due to its abundance and ease of incorporation. There are a variety of nitrogen units that can form when graphene is treated with nitrogen plasma including pyridine, pyrrole and nitrogen-substituted graphene. Yu \textit{et al.} used organic amine as the nitrogen source to produce nitrogen-doped graphene aerogel (N-GA) by hydrothermal synthesis. Resulting devices had a high power density of 205.0 kW kg\textsuperscript{-1} at 185.0 A g\textsuperscript{-1} (Fig. 3d–h).\textsuperscript{54} Liu \textit{et al.} prepared hierarchical porous nitrogen-doped GA by carbonizing in the presence of chitosan (nitrogen-containing biopolymer derivative). The resulting supercapacitors had a specific capacitance of 197 F g\textsuperscript{-1}.\textsuperscript{53} Kang \textit{et al.} employed nitrogen plasma treatment to dope the graphene basal planes to yield capacitances of 280 F g\textsuperscript{-1} (Fig. 3a–c) with excellent cycle life (> 200 000 cycles).\textsuperscript{51}

High specific surface area can increase the effective contact area between the electrode materials and electrolyte to reduce the transfer distance for the electron charge and enhance the power density.\textsuperscript{56,57} When increasing the BET, activation of graphene aerogel was a great way to increase the porous structure. Since KOH has a strong etching effect on carbon materials, Ruffo \textit{et al.} activated graphene with KOH to increase the porosity. The BET of etched graphene reached 3100 m\textsuperscript{2} g\textsuperscript{-1}, which exceed the theoretical BET of graphene (2800 m\textsuperscript{2} g\textsuperscript{-1}).\textsuperscript{52} When incorporated into a modified graphene supercapacitor, energy densities as high as 70 W h kg\textsuperscript{-1} were observed.\textsuperscript{58} Lei \textit{et al.} reported the activation of graphene aerogel with phosphoric acid to realize a specific capacitance of 204 F g\textsuperscript{-1} (Fig. 4).\textsuperscript{59} CVD-growth could produce few-layer graphene with...
et al. (226 F g⁻¹) The resulting 3D graphene aerogel–SiO₂ had large capacitances (71.4 S m⁻¹) and a capacitance of 366 F at 2 A g⁻¹. Bando et al. reported the preparation of high-power/high-energy GA-based supercapacitors through a substrate-free reduction method. Zhang et al. deposited graphene aerogel on Ni foam with a BET of 463 m² g⁻¹ and conductivity of 71.4 S m⁻¹ affording a specific capacitance of 366 F at 2 A g⁻¹. Duan et al. reported the preparation of high-power/high-energy GA-based supercapacitors through a substrate-free sugar blowing process to significantly increase the BET of the electrode.

In addition to having a high BET, the size and distribution of pores in graphene aerogels are also key factors dictating overall performance. Pores in graphene aerogels are divided into three categories: macropores (greater than 50 nm), mesopores (2–50 nm), and micropores (less than 2 nm). Each pore size plays specific roles within the cycling supercapacitor device. Macropores store electrolyte ions, mesopores offer electrolyte ion transport, and micropores enable charge accommodation. During activation, macropores are formed by the corrugations of the closely packed graphene layers, while micro and mesopores are directly formed by activation (i.e., etching). Song et al. prepared well-developed porous structures by chemical activation using K₂CO₃ with excellent capacitance properties (300 F g⁻¹). Park et al. used CO₂ to activate graphene aerogels creating hierarchical trimodal porous graphene aerogels with a capacitance of 278.5 F g⁻¹ and good cycle stability. Feng et al. described another way to produce macro and mesopores by adding tetraethoxysilane silica source (TEOS) and annealing at 800 °C. The resulting 3D graphene aerogel-SiO₂ had large capacitances (226 F g⁻¹), high charging rates, and good cycle stability (Fig. 5 a–d).

Recently, Li et al. combined graphene oxide (GO) and graphene nanoplatelets in an ink for 3D printing of periodic macroporous graphene aerogels for supercapacitor applications. The supercapacitors using these GAs delivered a maximum power density of 4079.9 W kg⁻¹ at 0.26 W h kg⁻¹ (Fig. 5e–i).

### 3.1.2 Pseudo-capacitors

Although double-layer capacitors have excellent stability due to a largely physical process dominating the charge/discharge processes, their capacitance remains relatively low. Pseudo-capacitors rely on highly reversible electrochemical adsorption/desorption processes or oxidation–reduction reactions for storing energy. These reactions lead to deposition of materials onto the various surfaces and sub-surfaces. Pseudo-capacitors are usually asymmetric supercapacitors whose cathodes are typically carbon materials and anodes are metal oxides (MOs) or conducting polymers. The supercapacitor energy storage type can be classified into three groups: highly reversible chemical adsorption–desorption (such as oxygen adsorption onto Pt or Au), fast reversible redox reactions (such as transition metal oxides or hydroxides), and reversible electrochemical doping and de-doping (such as polyaniline or poly-pyrrole). The energy storage mechanism in metal oxide-based pseudo-capacitors in acidic (Scheme 2) or alkaline solution can be considered a rapid and reversible electron transfer process accompanied by an adsorption of protons onto the metal oxide surfaces according to the following equations:

**Acidic:**

\[
\text{MO} + H^+ + e^{-} \leftrightarrow \text{MOH}^{-}
\]

**Alkaline:**

\[
\text{MO} + OH^- + e^{-} \leftrightarrow \text{MO(OH)}
\]

When organic electrolytes are used to increase the operating voltage window, the charge storage mechanism is based on electrolyte cations (K⁺, Na⁺) and proton incorporation on the surface.

GAs composed of hexagonally bonded sp² C atoms have complementary electrochemical windows, a 3D network structure with high surface area, and large pores that prevent the aggregation of graphene layers while also facilitating ion diffusion for enhanced rate performance. Duan et al. successfully fabricated pseudo-capacitors with 3D graphene aerogel as the anode and aligned MnO₂ on nickel foam as the cathode. The device exhibited a broad potential window of 0–2.0 V and a high energy density of 23.2 W h kg⁻¹ with 83.4% retention after 5000 cycles (Fig. 6).

Li et al. also manufactured high energy density pseudo-capacitors with a nickel oxide cathode and a reduced graphene aerogel anode. The device had a capacitance of 248 mF cm⁻² and a high energy density of 39.9 W h kg⁻¹ at a current density of 1 mA cm⁻². These electrodes directly grew on metals (or metal oxides) without the need for polymer binders. This likely contributed to the good electrochemical performance because most polymer binders are electrochemically inactive.

Transitional metal oxides or hydroxides have intriguing electronic, electrochemical, and electrocatalytic properties which can be applied in pseudo-capacitor reversible redox reactions to enable higher theoretical specific capacitances. However, high costs, limited stock, low electrical conductivity and cycle stability restrict the development of metal oxide supercapacitors.
Incorporating metal oxides and hydroxides into conductive graphene aerogel networks can enhance the electrical conductivity, charge transfer, and structure stability.\textsuperscript{73–76} Chen et al. synthesized graphene aerogels via CVD growth and then incorporated cobalt oxide nanowires to form a composite for supercapacitors. The calculated specific capacitances were found to be 768, 618, 552, and 456 F g\(^{-1}\) at 10, 15, 20, and 30 A g\(^{-1}\), respectively.\textsuperscript{77} Jun et al. fabricated graphene/Co(OH)\(_2\) aerogels to improve the...
specific capacitances ($\sim 1139 \, \text{F g}^{-1}$) and deliver higher energy densities ($\sim 13.9 \, \text{W h kg}^{-1}$) and power densities ($\sim 18 \, \text{kW kg}^{-1}$) (Fig. 7a–e).\textsuperscript{78} Binary metal oxide electrodes perform better than single-component electrodes due to their more accessible oxidation states and higher electrical conductivity.\textsuperscript{79} Xu et al.\textsuperscript{79} combined CoMoO$_4$ and 3D graphene networks to produce superlong-life pseudo-capacitors providing a high specific capacitance of 2098 F g$^{-1}$ at 5 A g$^{-1}$ (Fig. 7f–j).\textsuperscript{80} The nano-honeycomb structure possesses a close-packed geometry that compliments lightweight and elastic materials.

Conducting polymers are important active materials for supercapacitors due to their synthetic flexibility and variety, low cost, stability and high redox pseudocapacitance.\textsuperscript{42,81–83} However, they also have several disadvantages such as mediocre conductivity and poor cycling stability due to swelling and shrinkage during the doping–dedoping process. Qu et al.\textsuperscript{84} fabricated polypyrrole/graphene aerogel composites to overcome these shortcomings. These highly compression-tolerant devices showed volumetric capacitances of 14 F cm$^{-3}$ for uncompressed polypyrrole/GA which doubled to 28 F cm$^{-3}$ when compressed by 50% (Fig. 8).\textsuperscript{84} This indicated no performance loss as a function of compression. These devices display high specific capacitances without obvious variation while compressive loads are applied and removed. The development of strain-tolerant polymer/GA network composites for supercapacitors such as these will enable the development of next generation advanced supercapacitors that are tough. Polyaniline hybrids are an alternative storage material amenable to large energy capture. Xiao et al.\textsuperscript{85} produced GA/polyaniline flexible all-solid-state supercapacitor hybrids that provided fast ionic conducting channels with a gravimetric energy density of 24.02 W h kg$^{-1}$ at a power density of 400.33 W kg$^{-1}$.\textsuperscript{85} The protonated nitrogen atoms of polyaniline could bind to metal ions forming binary metal oxide/polymer complexes. These binary nano-hybrid structures have good electrochemical properties that can effectively increase the total capacitance.\textsuperscript{75,86} Lu et al.\textsuperscript{87} fabricated GA/polyaniline/Co$_3$O$_4$ composites by hydrothermal synthesis. These ternary composites possessed large specific capacitances of 1247 F g$^{-1}$ at 1 A g$^{-1}$ and high cycle stability.\textsuperscript{87} The specific capacitance, cycling, and voltage window of several GA compounds used in supercapacitors are summarized in Table 1.

### 3.2 Lithium batteries

Batteries are an essential energy storage technology which has seen a significant increase in energy density requirements as more powerful mobile devices and electric cars have developed. In contrast to other battery types (Ni–Cd, lead–acid, Ni–MH), lithium ion batteries possess high energy densities, long cycle life, no memory effect, and no self-discharge. Studies of lithium ion batteries began in the 1960s when the lithium anode was being developed. However, lithium ion batteries generated dendritic arms which can lead to shorts over time. To address this major safety concern, Armond et al. fabricated “rocking-chair batteries” that employed lithium-ion intercalated compounds,
Li$_x$A$_y$B$_z$, as the anode and octahedral TiS$_2$ as the cathode in 1980. Next, SONY introduced commercial Li-batteries with carbonaceous anode materials and LiCoO$_2$ as the cathode. Lithium batteries have since found widespread use in phones, laptops, cameras, and electric vehicles due to their high power and energy densities. They are generally composed of a cathode, anode and electrolyte. Differing from pseudo-capacitors whose faradaic reaction occurs on the surface, the lithium ions in batteries can insert and diffuse into the solid phase of the electrode contributing to higher energy densities. Specifically, the lithium ions reversibly embed into and out of the positive and negative electrodes during charging and discharging. Lithium ions migrate out of the cathode lattice material and embed in the anode material forming lithium compounds. The lithium ions migrate from one electrode to the other through an electrolyte (lithium salt dissolved in an organic solvent). Consider a battery setup with a graphite anode, LiCoO$_2$ cathode, and LiPF$_6$ (1.0 mol L$^{-1}$) dissolved in ethylene carbonate (EC), ethylmethyl carbonate (EMC), and diethyl carbonate (DEC) (1:1:1 volume ratio) electrolyte (Scheme 3):

\[
\text{Arrangement: } (-) \text{ GA|LiPF}_6\text{-EC + EMC + DEC|LiCoO}_2 \text{ (+)}
\]

**Cathode reaction:** LiCoO$_2$ $\leftrightarrow$ Li$_{1-x}$CoO$_2$ + xLi$^+$ + xe$^-$

**Anode reaction:** C$_n$ + xLi$^+$ + xe$^-$ $\leftrightarrow$ Li$_x$C$_n$

**Battery reaction:** LiCoO$_2$ + C$_n$ $\leftrightarrow$ Li$_{1-x}$CoO$_2$ + Li$_x$C$_n$

When charging, lithium ions are removed (deintercalated) from the crystal lattice of LiCoO$_2$ together with a change in Li oxidation state. The deintercalated lithium ions are transported by the non-aqueous electrolyte to the negative electrode (graphite) with electron capture and transfer to the external circuit through the anode. Lastly, the lithium ions are reduced to metallic lithium and held in between the graphite layers. The process is reversed during the discharge process.

### 3.2.1 Graphene aerogel-modified cathodes in lithium ion batteries

Cathode materials are an essential component contributing to the energy storage capacity of lithium ion batteries. There are several common cathode materials. The first group consists of layered oxide structures. First, layered oxides of the form LiMO$_2$ (M = Co, Ni, Mn) are composed of MO$_2$ layers with octahedral MO$_6$ edge lines providing 2D diffusion paths for lithium ions. Another typical layered oxide

<table>
<thead>
<tr>
<th>Materials</th>
<th>Specific capacitance (F g$^{-1}$)</th>
<th>Cycle retention</th>
<th>Voltage window (V)</th>
<th>Current load or scan rate (A g$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Macro-/mesoporous GA</td>
<td>226</td>
<td>100% after 5000 cycles</td>
<td>0–0.8</td>
<td>N.A.</td>
<td>66</td>
</tr>
<tr>
<td>N-doped GA</td>
<td>113.8</td>
<td>91% after 4000 cycles</td>
<td>0–1.0</td>
<td>185</td>
<td>54</td>
</tr>
<tr>
<td>GA/carbon bulk</td>
<td>231</td>
<td>99% after 5000 cycles</td>
<td>0–3.5</td>
<td>248</td>
<td></td>
</tr>
<tr>
<td>GA anode &amp; MnO$_2$–Ni cathode</td>
<td>157.7</td>
<td>83% after 5000 cycles</td>
<td>0–2.0</td>
<td>1.0</td>
<td>71</td>
</tr>
<tr>
<td>GA anode &amp; NiO cathode</td>
<td>210</td>
<td>95% after 3000 cycles</td>
<td>−1.2 to 0.5</td>
<td>3.1</td>
<td>72</td>
</tr>
<tr>
<td>GA/Co$_2$O$_4$</td>
<td>768</td>
<td>143% after 500 cycles</td>
<td>0–0.5</td>
<td>10</td>
<td>77</td>
</tr>
<tr>
<td>GA/NiO</td>
<td>745</td>
<td>100% after 2000 cycles</td>
<td>0–0.5</td>
<td>1.4</td>
<td>34</td>
</tr>
<tr>
<td>GA/MnO$_2$</td>
<td>175</td>
<td>81% after 5000 cycles</td>
<td>0–1.0</td>
<td>N.A.</td>
<td>249</td>
</tr>
<tr>
<td>GA/Ni(OH)$_2$</td>
<td>119</td>
<td>63.2% after 10 000 cycles</td>
<td>0–0.5</td>
<td>1.0</td>
<td>250</td>
</tr>
<tr>
<td>GA/Co$_2$Mo$_4$</td>
<td>274</td>
<td>96.36% after 10 000 cycles</td>
<td>0–0.9</td>
<td>1.43</td>
<td>80</td>
</tr>
<tr>
<td>GA/TiO$_2$</td>
<td>206.7</td>
<td>96.4% after 150 cycles</td>
<td>−0.2 to 0.8</td>
<td>0.5</td>
<td>251</td>
</tr>
<tr>
<td>GA/ZnO</td>
<td>316</td>
<td>99% after 1000 cycles</td>
<td>0–0.5</td>
<td>6.7</td>
<td>252</td>
</tr>
<tr>
<td>N-GA/CNTs</td>
<td>180</td>
<td>96% after 3000 cycles</td>
<td>−1.0 to 0</td>
<td>0.5</td>
<td>253</td>
</tr>
<tr>
<td>GA/MWNT</td>
<td>286</td>
<td>99.34% after 85 000 cycles</td>
<td>N.A.</td>
<td>N.A.</td>
<td>254</td>
</tr>
<tr>
<td>GA/Ag nanowire/carbon</td>
<td>213</td>
<td>&gt;90% after 10 000 cycles</td>
<td>0–1.0</td>
<td>N.A.</td>
<td>255</td>
</tr>
<tr>
<td>GA/polyaniline</td>
<td>463</td>
<td>90.6% after 500 cycles</td>
<td>0–0.4</td>
<td>1.0</td>
<td>85</td>
</tr>
<tr>
<td>GA/Co(OH)$_2$</td>
<td>1139</td>
<td>N.A.</td>
<td>0–1.2</td>
<td>10</td>
<td>77</td>
</tr>
<tr>
<td>GA/polyaniline/Co$_3$O$_4$</td>
<td>1247</td>
<td>80% after 6000 cycles</td>
<td>0–0.4</td>
<td>1.0</td>
<td>87</td>
</tr>
<tr>
<td>GA/polypyrrole</td>
<td>350</td>
<td>N.A.</td>
<td>0–1.0</td>
<td>1.5</td>
<td>84</td>
</tr>
</tbody>
</table>

When charging, lithium ions are removed (deintercalated) from the crystal lattice of LiCoO$_2$ together with a change in Li oxidation state. The deintercalated lithium ions are transported by the non-aqueous electrolyte to the negative electrode (graphite) with electron capture and transfer to the external circuit through the anode. Lastly, the lithium ions are reduced to metallic lithium and held in between the graphite layers. The process is reversed during the discharge process.
has the form Li–Ni–Co–Mn–O (such as LiNi1/3Co1/3Mn1/3O2). These ternary layered structures combine the rate capability of LiCoO2, the high power capacity of LiNiO2, and the structural stability of Mn4+88. Another example is xLiMnO3(1 – x)Li2MnO3. This lithium-rich layered oxide has two different metal oxide structures: LiMnO2 (R3m) and Li2MO3 (C2/m). The residual lithium ions occupy transition metal layers with higher power capacity at initial charge.89 The second group consists of spinel oxide structures. LiMn2O4 has a 3D framework for lithium ions to easily diffuse in and out of the structure. This material also has better safety performance. LiNi0.5Mn1.5O4 is a Ni-doped spinel structure with Ni partially replacing Mn. This material has a higher rate capability and cycle stability than LiMn2O4.90 The third group consists of poly-anionic compounds. LiFePO4 (LFP) has a periodic structure that is thermodynamically stable, environmentally friendly and inexpensive. The strong covalent O–P and O–Fe bonds afford a highly stable and safe battery material.91

LFP has attracted increasing interest as a cathode material due to its several attractive properties including relatively high capacity, good stability, low cost, and environmental friendliness.92,93 However, poor electrical conductivity and low Li-ion diffusivity have plagued its development. Designing 3D porous networks for the electrode material is an efficient way to create ion pathways throughout the electrode and improve electrical conductivity.94 Zhao et al.36 combined N-doped graphene aerogels with LFP. This shortens the lithium ion diffusion length in LFP crystals and provides new and rapid pathways for lithium ion transport (Fig. 9a–c). A cathode composed of LFP modified by 3D graphene displayed high capacities (78 mA h g−1 at 100 °C) and excellent cycle stability.95 Due to a theoretical storage 5–10 times that of lithium batteries, lithium–oxygen (Li–O2) batteries are another promising lithium battery technology relying on porous carbon materials covered with gaseous O2 as the cathode and lithium metal as the anode.96,97 However, O2 can easily oxidize Li+ to form insoluble Li2O or Li2O2 during the charge–discharge process. This can lead to blocked oxygen pathways and reduced performance.98 The large pore volume of the added graphene aerogel is key to reducing the formation of pathway-blocking insoluble lithium peroxide and lithium oxide thus enabling prolonged battery life.99 Zhang et al.36 prepared porous graphene aerogel/O2 cathodes for Li–O2 batteries. The batteries reached capacities of 11 060 mA h g−1 at 0.2 mA cm−2 (280 mA g−1) and 20 mA h g−1 at 2 mA cm−2 (Fig. 9d).100 Owing to their multi-electron chemical reactions, lithium–sulphur (Li–S) based batteries have attracted much attention due to theoretical specific capacities five times larger and energy densities two to three times larger than that of commercial lithium ion batteries.101,102 However, the applicability of Li–S batteries remains limited due to poor conductivity and structural damage incurred during the charge–discharge process.103,104 Capitalizing on the conductivity and porosity of the graphene aerogel 3D network, Ren et al.36 constructed Li–S batteries with high sulphur loading (14.36 mg cm−2 and total sulphur content of 89.4 wt%) on GA. The device had a capacitance of 1000 mA h g−1 (Fig. 9e).105 Selenium, another chalcogen element, has also been considered for use in lithium ion batteries, but it is limited by low conductivity and high volume expansion.106,107 He et al.36 fabricated tellurium nanowire/3D rGO for free-standing and binder-free Li–Te battery cathodes that showed a high initial capacitance of 2611 mA h cm−2 with 88% retention after 200 cycles.108

### 3.2.2 Modified anodes

Despite the varied work in cathode materials design, more effort has been devoted to designing anode materials with large reversible specific capacities. There are several promising anode materials currently being investigated. The first is carbon-based anode materials with graphite being the most popular due to its low potential, long cycle stability, high conductivity and low cost.110,111 The second group is transition metal oxides grouped based on how lithium is incorporated into their structure. The first group includes MoO2, WO3, Fe2O3, TiO2 and Nb2O5. In these metal oxides the lithium ion directly embeds within the structure. Another group of metal oxides have the form M2O3 (M = Co, Ni, Cu, Fe). In these structures, Li2O is produced when the ions are incorporated.112–114 The third group is metal alloy anode materials. Representative materials include Si, Ge, and Sn which undergo alloying and deallloying with lithium during charging and discharging.115,116

Nanoscale metal oxides (nano-MOs) are ideal anode materials for lithium ion batteries due to several advantages.117 However, most nano-MOs are semiconductors with inherently poor electric conductivity restricting their performance in lithium ion storage.118 One approach to address the limitations of nanoscale metal oxides is to wrap them with conducting graphene sheets to produce a 3D network material with improved overall conductivity and improved accommodation to volume changes during charging and discharging.119–121 Feng et al.36 fabricated an interconnected macroporous 3D Fe2O3/graphene aerogel. The device showed a high reversible capacity of 372 mA h g−1 at a rate of 5000 mA g−1 and 995 mA h g−1 after 50 cycles at 100 mA g−1.122 Similarly, a TiO2/graphene aerogel displayed an excellent capacity of 200 mA h g−1 at 0.59C after 50 cycles and a capacity of 99 mA h g−1 at 5000 mA g−1 (Fig. 11a–e).123 Lastly a wrapped Bi2O3/graphene aerogel produced a large capacitance of 417 mA h g−1 over 100 cycles at 200 mA h g−1 and 273 mA h g−1 at 10 000 mA g−1.124

Other MOs (M2O3; M = Co, Ni, Cu, Fe) have also been incorporated into graphene aerogels for anode applications.
Kim et al. demonstrated enhanced electron and ion transport for improved cycle stability in a Co$_3$O$_4$/graphene aerogel anode showing corresponding specific capacities of 1001, 900 and 798 mA h g$^{-1}$ at 0.2, 0.5 and 1.0 A g$^{-1}$ (Fig. 11f). Fe$_3$O$_4$/GA fabricated by Müllen et al. exhibited a capacity of 63 mA h g$^{-1}$ at 4800 mA g$^{-1}$ and cycling performance of 1059 mA h g$^{-1}$ over 150 cycles at 93 mA g$^{-1}$. The range of performance values for batteries are also being pushed to higher levels. In general, lithium ion batteries tend to have high energy densities and low power densities. Recently, Duan et al. designed a 3D holey-graphene oxide/Nb$_2$O$_5$ anode (Fig. 10) with both a high energy density and power density at higher mass loadings. They systematically tailored the graphene aerogel porosity to facilitate rapid ion transport and minimize diffusion limitations throughout the structure.

Earth abundant alloys of Si, Sn, Ge and relevant oxides possess high reversible capacities ranging from 783 mA h g$^{-1}$ (SnO$_2$) to 4200 mA h g$^{-1}$ (Si) have attracted much attention for use in lithium ion batteries. Researchers have investigated the working mechanism of such materials for anode applications. For example, it was found that lithium ions can break Si–Si bonds to form isolated Si clusters. The lithium ions then embed in the clusters to locally form Li–Si alloys (Li$_x$Sn$_{1-x}$). However, the migration of a large number of lithium ions into and out of the structure leads to large volume changes and subsequent pulverization of the anode material ultimately shortening the battery lifetime. Graphene, owing to its excellent electrical conductivity, flexibility and high BET, makes it a suitable reinforcement material for enhancing the coulombic efficiency and rate capability of various incorporated alloys. Similarly, 3D networks maintain structural stability and transport electrons and ions between the GA walls and alloy. Zheng et al. synthesized amorphous SiO$_2$/graphene aerogel anodes that showed reversible capacities of 300 mA h g$^{-1}$ at 500 mA g$^{-1}$ and stable cycling performance. He et al. prepared Sn/3D network graphene which showed a capacitance of 1022 mA h g$^{-1}$ at 200 mA g$^{-1}$, and 459 mA h g$^{-1}$ at 5000 mA h g$^{-1}$ with 96.3% performance retention after 1000 cycles (Fig. 11g). The role, cyclability, and rate capability of various GA compound materials for lithium batteries are listed in Table 2.

### 3.2.3 Other batteries.

Lithium ion batteries have been successfully commercialized into a global portable energy storage system over the past several decades. However, the increasing demand for lithium ion batteries is met with increasingly scarce natural availability of lithium sources and consequently higher costs ($5000 per ton of lithium). In anticipation of limited supply and increasing costs of lithium-based energy storage, the development of other battery types based on sodium, aluminium, and magnesium have attracted more attention due to their natural abundance and significantly lower costs. Specifically, Na, Mg and Al based materials have been developed for use in cathodes. Whereas carbon materials, with chemical
stability, low environmental impact, low cost, and high conductivity, are promising anode materials. The porous morphology and pore diameter of carbon-based anodes accounts for the high electrochemical performance and large ion storage potential. Dai et al. prepared 3D N-GA with a high nitrogen (6.8 at%) content and capacitance of 1057.1 mA h g\(^{-1}\) at 200 mA g\(^{-1}\) and 244.7 mA h g\(^{-1}\) at 4000 mA g\(^{-1}\) (Fig. 12a–f).

3D porous carbon networks and defects induced by heteroatom-doping were promising for anode materials. Yao et al. synthesized V\(_2\)O\(_5\)/GA for magnesium battery cathodes showing a 330 mA h g\(^{-1}\) (1000 mA g\(^{-1}\)) capacity over a wide working temperature range from \(-30.1\) °C to 55 °C with long-cycle-life (80% retention after 200 cycles, Fig. 12g–k).

Hydrogen has been investigated as an alternative fuel source due to its low environmental impact, high efficiency, and abundance. Compared to other hydrogen storage materials like metal alloys, COFs and MOFs, graphene-based materials can function over a wide range of conditions with excellent structural stability. Froudakis et al. fabricated new 3D network pillar graphene with tunable pore sizes. They utilized a multiscale theoretical approach to measure the \(H_2\) storage (41 g L\(^{-1}\)) under ambient conditions (Fig. 13a and b). Jhi et al. developed a porous 3D graphene with dispersed Ca atoms anchored to the...
carbon centers of graphene forming chain-like structures. The total hydrogen storage capacity of this 3D Ca–graphene composite reached 5–6 wt% and hydrogen adsorption at the vertices of Ca chains exhibits the multipole Coulomb and Kubas interactions. In particular, high specific surface area and pores with diameters around 0.7 nm possess higher hydrogen adsorption. Zhu et al. synthesized graphene aerogels with acetone and trifluoroacetic acid to carbonize multifunctional aerogels to produce a high specific surface area and small pore diameters. Such structures with pore sizes of 0.72 nm showed unexpectedly high hydrogen adsorption.

Thermal management has been a significant concern dictating progress in the electronics industry. Phase change materials (PCMs) have been widely applied in thermal management and energy storage for transition-edge sensors (TES). In addition to its superior electrical conductivity, graphene also possesses excellent thermal conductivity \( (\approx 5000 \text{ W m}^{-1} \text{ K}^{-1}) \) which makes it especially appropriate for thermal storage. Thus 3D interconnected graphene aerogel networks can greatly reduce or eliminate thermal resistance in energy capture/storage devices. Huang et al. combined graphene sheets and octadeca-noic acid (OA) into a GA/OA hybrid material. The thermal energy generated \( (181.8 \text{ J g}^{-1}) \) was stored in the GA/OA hybrid. They further deposited porous graphene by CVD growth onto aluminium oxide with ceramic which has a latent heat of 186 J g\(^{-1}\).

**Table 2** Performance characteristics of graphene aerogel composite materials for lithium-based batteries

<table>
<thead>
<tr>
<th>Materials</th>
<th>Type</th>
<th>Capacity</th>
<th>Cycling</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiFePO(_4)/GA</td>
<td>Cathode of Li-ion battery</td>
<td>78 mA h g(^{-1})@100C</td>
<td>89% after 1000 cycles@10C</td>
<td>95</td>
</tr>
<tr>
<td>O(_2)/GA</td>
<td>Cathode of Li-O(_2) battery</td>
<td>11 060 mA h g(^{-1})@20 mA g(^{-1})</td>
<td>N.A.</td>
<td>100</td>
</tr>
<tr>
<td>S/GA</td>
<td>Cathode of Li-S battery</td>
<td>10.3 mA h cm(^{-2})@0.2C</td>
<td>63.8% after 350 cycles</td>
<td>105</td>
</tr>
<tr>
<td>Te/GA</td>
<td>Cathode of Li–Te battery</td>
<td>2611 mA h cm(^{-2})@0.2C</td>
<td>88% after 250 cycles</td>
<td>108</td>
</tr>
<tr>
<td>Fe(_3)O(_4)/GA</td>
<td>Anode of Li-ion battery</td>
<td>1060 mA h g(^{-1})@93 mA g(^{-1})</td>
<td>1059 mA h g(^{-1}) after 150 cycle</td>
<td>126</td>
</tr>
<tr>
<td>TiO(_2)/GA</td>
<td>Anode of Li-ion battery</td>
<td>605 mA h g(^{-1})@100 mA g(^{-1})</td>
<td>80% after 50 cycles</td>
<td>123</td>
</tr>
<tr>
<td>Mg(_2)O(_3)/GA</td>
<td>Anode of Li-ion battery</td>
<td>995 mA h g(^{-1})@100 mA g(^{-1})</td>
<td>995 mA h g(^{-1}) after 50 cycles</td>
<td>122</td>
</tr>
<tr>
<td>Co(_3)O(_4)/GA</td>
<td>Anode of Li-ion battery</td>
<td>1012 mA h g(^{-1})@100 mA g(^{-1})</td>
<td>1012 mA h g(^{-1}) after 100 cycles</td>
<td>125</td>
</tr>
<tr>
<td>CuO/GA/CNTs</td>
<td>Anode of Li-ion battery</td>
<td>753 mA h g(^{-1})@0.1C</td>
<td>639 mA h g(^{-1}) after 80 cycles</td>
<td>256</td>
</tr>
<tr>
<td>Bi(_2)O(_3)/GA</td>
<td>Anode of Li-ion battery</td>
<td>273 mA h g(^{-1})@10,000 mA g(^{-1})</td>
<td>417 mA h g(^{-1}) after 100 cycle@200C</td>
<td>124</td>
</tr>
<tr>
<td>C/MoS(_2)/N-GA</td>
<td>Anode of Li-ion battery</td>
<td>1600 mA h g(^{-1})@200 mA g(^{-1})</td>
<td>900 mA h g(^{-1}) after 500 cycle</td>
<td>257</td>
</tr>
<tr>
<td>ZnO/GA</td>
<td>Anode of Li-ion battery</td>
<td>415 mA h g(^{-1})@1000 mA g(^{-1})</td>
<td>490 mA h g(^{-1}) after 100 cycle@100C</td>
<td>258</td>
</tr>
<tr>
<td>Mo(_2)O(_3)/GA</td>
<td>Anode of Li-ion battery</td>
<td>1235 mA h g(^{-1})@200 mA g(^{-1})</td>
<td>85.8% after 60 cycle@80C</td>
<td>259</td>
</tr>
<tr>
<td>Si/GA</td>
<td>Anode of Li-ion battery</td>
<td>963 mA h g(^{-1})@1.5 mg cm(^{-2})</td>
<td>370 mA h g(^{-1}) after 100 cycle</td>
<td>260</td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>Anode of Li-ion battery</td>
<td>300 mA h g(^{-1})@500 mA g(^{-1})</td>
<td>96.3% after 1000 cycles</td>
<td>138</td>
</tr>
<tr>
<td>Sn/GA</td>
<td>Anode of Li-ion battery</td>
<td>1022 mA h g(^{-1})@200 mA g(^{-1})</td>
<td>148% after 450 cycle</td>
<td>261</td>
</tr>
<tr>
<td>SnO(_2)/GA</td>
<td>Anode of Li-ion battery</td>
<td>1299 mA h g(^{-1})@100 mA g(^{-1})</td>
<td>148% after 450 cycle</td>
<td>261</td>
</tr>
</tbody>
</table>

![Fig. 12](image-url) (a) SEM image, (b) nitrogen adsorption–desorption isotherm and pore size distribution curve, (c) initial charge–discharge curves at 0.2C, (d) rate performance from 0.2C to 10C, (e) capacity retention, and (f) cycling performance of N-doped 3D graphene foam anode in a Na-ion battery. (g) Schematic illustration of the V\(_2\)O\(_5\)--nH\(_2\)O/GA fabrication process, (h) rate performance, (i) charge–discharge profiles, (j) cycling performance of samples annealed at different temperatures, and (k) the effect of crystal water content on the capacity of GA/V\(_2\)O\(_5\)-nH\(_2\)O.
Feng et al. constructed core–shell GA for shape-stable PCMs showing a high encapsulation ratio of paraffin, excellent cycling performance and a latent heat of 213 J g⁻¹ (Fig. 13c and d). 160

4. Mechanisms and roles of graphene aerogels in energy conversion

Fuel cells and solar cells that directly convert chemical or solar energy into electrical power are a significant technology for harnessing renewable energy. The oxygen reduction reaction (ORR), oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) are three electrochemical processes (Scheme 4b) that take place in metal–air batteries, regenerative fuel cells, and water splitting cells respectively. 161

Fuel cells offer a convenient way to generate electricity with high efficiency, stability, and longevity; all three of which are essential for applications in portable electronic devices and electric cars. 162,163 Fuel cell systems directly transform chemical energy from fuel gas (such as hydrogen or methane) into electrical energy. Fuel cells can be classified into five different types according to the electrolyte used with each having specific ranges of operating temperature. The types include: (1) proton-exchange membrane fuel cells (PEMFC, 50–100 °C), solid oxide fuel cells (SOFC, 500–1000 °C), molten carbonate fuel cells (MCFC, 650–800 °C), phosphoric acid fuel cells (PAFC, 160–210 °C), and alkaline fuel cells (AFC, 60–100 °C). 164–167 The simplified mechanism behind proton exchange membrane fuel cells is highlighted in Scheme 4a. First, gaseous H₂ is broken into two protons (H⁺) by the anode catalyst. After passing through the proton exchange membrane the protons react with oxygen at the cathode to produce water. When an acidic electrolyte is utilized; the anode, cathode and overall reaction can be written as follows:

\[ \text{Anode: } 2\text{H}_2 \rightarrow 4\text{H}^+ + 4e^-; \]

\[ \text{Cathode: } \text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O}; \]

\[ \text{Overall reaction: } 2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O} \]

4.1 The oxygen reduction reaction (ORR) and oxygen evolution reaction (OER)

In the ORR oxygen reacts with both electrons and protons to form H₂O [4 electrons absorbed] or H₂O₂ [2 electrons absorbed]. This reactions is essentially what occurs at the cathode of fuel cells and metal–air batteries. It is in many ways the biggest advantage of PEMFC as the only by-product is water. Platinum (Pt) and its alloys remain the most popular ORR catalysts. However, due to its scarcity and oftentimes prohibitive cost, the use of Pt has contributed to hindered large-scale development and commercialization of fuel cell systems. 168,169 Consequently, low-cost alternative catalysts such as earth-abundant metals (Fe, Co, etc.), metal oxides (Fe₂O₃, Fe₃O₄, Co₃O₄, MnO₂, etc.), and metal-free carbon-based materials have attracted much interest. 170–173 Graphene aerogels or 3D network graphene have high BETs, fast electron-transfer kinetics, excellent mechanical strength, and porous structures providing sufficient contact and high stability for the ORR. Carbon materials doped by N, B, and P have shown improved ORR performance. 174,175 Chen et al. prepared N-doped graphene metal-free catalysts with an ORR peak centred at −0.31 V with a current density of −2.9 mA cm⁻². 176 Meanwhile He et al. fabricated N and B-doped graphene which had a current density of 6.2 mA cm⁻² and H₂O₂ yield less than 10% (Fig. 14i and j). 177 Chen et al. created holey surface
structures on N-GA to create more exposed active edge sites to further improve the catalytic performance of the metal-free catalyst for ORR. Yi et al. incorporated carbon nanotubes (CNT) into a CNT/N-GA composite with a nano leaf-like network, and N-doped CNT containing 85% graphene aerogel (N-CNT@GNRs85-A) as a metal-free catalyst for ORR had a current density of 31.8 mA cm$^{-2}$ and H$_2$O$_2$ yield below 5.5%. Bagheri et al. developed a Co/N-doped GA glassy carbon electrode (Fig. 14a–d) that showed excellent catalytic activity and stability for ORR in acid. Muller et al. prepared N-GA/Fe$_3$O$_4$ by a hydrothermal self-assembly process. This material displayed a more positive onset potential (−0.19 V) for ORR and a high current density (−2.56 mA cm$^{-2}$). Linear sweep voltammograms (LSV) measured at 10 mV s$^{-1}$ in 0.1 M KOH showed a direct four-electron transfer pathway from −0.19 to −1.2 V for producing OH$^-$ ions and an 11% H$_2$O$_2$ yield at a potential of −0.4 V. In addition, various metals and metal chalcogenide particles have been incorporated into 3D porous graphene including Pt/GA, Cds-P25/GA, Co/N-GA, and Fe-nitride/N-GA (Fig. 14e–h). As always, the graphene aerogel provides a high surface area and porosity while the nanoparticles offer more active sites for considerably enhanced ORR activity.

Fuel cells and metal–air batteries systems are both attractive energy storage technologies. The former requires optimization of the OER whereas the latter requires an understanding of both OER and ORR which occur during charging and discharging respectively. Most carbon catalysts reported are combined with noble metals (such as Pt) and metal oxides for OER and ORR. The incorporation of polymers into such catalysts was relatively new and unexplored until recently. Dai et al. designed a N,P co-doped polyaniline aerogel with graphene edges for bifunctional electrocatalysis (Fig. 15a). As always, the graphene aerogel provides a high surface area and porosity while the nanoparticles offer more active sites for considerably enhanced ORR activity.

Fuel cells and metal–air batteries systems are both attractive energy storage technologies. The former requires optimization of the OER whereas the latter requires an understanding of both OER and ORR which occur during charging and discharging respectively. Most carbon catalysts reported are combined with noble metals (such as Pt) and metal oxides for OER and ORR. The incorporation of polymers into such catalysts was relatively new and unexplored until recently. Dai et al. designed a N,P co-doped polyaniline aerogel with graphene edges for bifunctional electrocatalysis (Fig. 15a). As always, the graphene aerogel provides a high surface area and porosity while the nanoparticles offer more active sites for considerably enhanced ORR activity.

Fig. 14 (a) Schematic illustration of ORR in graphene network composites. (b) SEM image of a metal and nonmetal co-doped graphene aerogel. (c) Rotating disk electrode (RDE) polarization curves. (d) Electron-transfer number and H$_2$O$_2$ yield of Co–N-GA for ORR. Muller et al. prepared N-GA/Fe$_3$O$_4$ by a hydrothermal self-assembly process. This material displayed a more positive onset potential (−0.19 V) for ORR and a high current density (−2.56 mA cm$^{-2}$). Linear sweep voltammograms (LSV) measured at 10 mV s$^{-1}$ in 0.1 M KOH showed a direct four-electron transfer pathway from −0.19 to −1.2 V for producing OH$^-$ ions and an 11% H$_2$O$_2$ yield at a potential of −0.4 V. In addition, various metals and metal chalcogenide particles have been incorporated into 3D porous graphene including Pt/GA, Cds-P25/GA, Co/N-GA, and Fe-nitride/N-GA (Fig. 14e–h). As always, the graphene aerogel provides a high surface area and porosity while the nanoparticles offer more active sites for considerably enhanced ORR activity.

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4.2 The hydrogen evolution reaction (HER) and CO₂ reduction

Hydrogen is considered an ideal clean energy alternative to replace fossil fuels. The hydrogen evolution reaction (HER), in which hydrogen is generated from water splitting in fuel cells, is one of the most important methods for making hydrogen. Noble metal platinum is the most effective HER catalysts owing to the high current densities possible. Again, due to the relative scarcity and high cost of such noble metals, it is of great importance that new and inexpensive catalysts are developed for electrocatalytic HER. Owing to their high electrical conductivity, versatility, and stability, graphene aerogels are promising for HER catalysis. Qu et al. assembled graphene sheets containing graphitic carbon nitride (g-C₃N₄) and Wang et al. electrocatalysis in HER with a lower overpotential, higher catalytic activity, and improved stability.199,200 Zhang et al. further

Zhang et al. functionalized GA/O-MWCNT with p-phenylenediamine-supported MoS₂ which has also shown excellent catalytic performance and stability.201 Transition-metal phosphides (TMPs), such as CoP and Ni₃P, have attracted much attention as non-noble-metal catalysts for HER with high activity. Dong et al. prepared CoP/GA showing an overpotential of 121 mV at 10 mA cm⁻² and an exchange current density of 0.105 mA cm⁻² (Fig. 16e–h).202 Interested in expanding the understanding of the effects of pH on electrocatalysis, Du et al. designed a material composed of crystalline nickel phosphide embedded within a graphene/nickel foam. In extremely acidic environments (pH = 0), there was a 30 mV overpotential (Fig. 16j). Whereas in extremely basic environments (pH = 14), there was a 7 mV overpotential (Fig. 16l).203

The future of alternative fuel sources can take on several forms. In the case of HER, one is generating a high energy fuel (H₂) and using it to generate electricity through fuel cells and metal–air batteries. In contrast, one can also take an abundant waste product and convert it into useful products as is the case in CO₂ reduction. Electrolytic preparation of fuel from CO₂ reduction is a carbon-neutral energy cycle.204–206 Noble metals generally have good selectivity for CO₂ reduction. However, they have poor durability and are more scarce thus limiting their application.207 It remains a challenge to directly convert CO₂ into multi-carbon hydrocarbons or oxygenates due to the absence of powerful, low cost catalysts.208 Graphene aerogels are a natural catalytic candidate for CO₂ reduction due to their 3D network structure, ease of fabrication, and high BET which enhances the interfacial contact with the electrolyte and adsorbed CO₂. Further doping with nitrogen generates active sites with a low overpotential, good selectivity, and high durability toward CO₂ catalysis. Ajayan et al. manufactured N-GAs with an onset overpotential of −0.19 V for CO₂ production, and at a lower overpotential (~0.47 V) than Au with a similar maximum Faradaic efficiency of CO formation (~85%) and higher stability (Fig. 17).209

4.3 Alcohol and microbial fuel cells

Electro-oxidation of alcohol has also attracted interest due to the high energy conversion rate, low work temperature, easy storage and handling, low pollutant emission, and cost. Typically, Pt and Pd are the most commonly used catalysts in alcohol oxidation because of their excellent electrocatalytic performance.210–212 Zhang et al. synthesized graphene oxide aerogel-supported Pt which facilitates reaction and avoids the detrimental effect of reduced platinum active surface area. Furthermore, it was found that the electro-catalytic properties of GA/Pt were five times that of Pt/rGO (reduced graphene oxide) and 40% higher than that of commercial Pt/C (Fig. 13).213 Hui et al. prepared binder-free Pd/graphene aerogel/Ni foam (Pd/GA/NF) electrodes that exhibited good electrocatalytic activity and an outstanding stability for alcohol electro-oxidation.214 Fuel cells for direct alcohol conversion (such as ethanol, methanol, propanol, and butanol) have garnered much attention due to their operational safety, excellent energy density, low toxicity, and large-scale production potential.215,216 However, the absence of appropriate anode materials, easy catalyst deactivation, and
sluggish oxidation kinetics have greatly hindered their development. Liu et al. developed N-doped GA decorated with PtRu nanoparticles as a freestanding anode. The resulting power density and current density were 93 mW cm\(^{-2}\) and 426 mA cm\(^{-2}\) respectively (Fig. 18).\(^{217}\) This device indeed performs well, but the cost of intermetallic PtRu nanoparticles remains high. Hui et al. developed a similar 3D free-standing anode material composed of graphene aerogel decorated with nickel. Their devices recorded a lower current density of 6 mA cm\(^{-2}\) in 0.1 M ethanol and 0.1 M NaOH solution.\(^{218}\) Clearly there remains an immense performance disparity between the noble metal and non-noble metal systems.

Microbial fuel cells (MFCs) are another type of fuel cell that relies on certain bacteria to convert organic waste into hydrogen for electricity generation.\(^{219,220}\) From a theoretical standpoint, microbial fuel cells are ideal as they are using waste to generate electricity. However, poor energy conversion efficiency and low power densities limit their practical application. The key component that is missing from microbial electrolysis cells (MECs) is a cost-effective catalyst for hydrogen production and bacterial adhesion.\(^{221,222}\) Graphene is already being applied in conventional fuel cells due to its chemical inertness, excellent electrical conductivity and biocompatibility.\(^{223}\) The 3D network structure of graphene aerogels provides a large BET for bacterial adsorption and directed pathways for extracellular electron transfer and proton diffusion. Chen et al. prepared 3D MoS\(_2\)/N-GAs as a microbial electro-catalyst in which organic waste was oxidized by bacteria with generated electrons transferred to the cathode to reduce protons and generate hydrogen (Fig. 19a–d), which achieved a high hydrogen production rate of 0.19 m\(^3\) H\(_2\) m\(^{-3}\) d\(^{-1}\).\(^{224}\) Chen et al. developed a polyaniline/graphene 3D network hybrid as a MFC anode. The cell had a power density of 190 mW m\(^{-2}\) at 24 h with a maximum power density of 768 mW m\(^{-2}\).\(^{225}\) Qiao et al. synthesized a graphene aerogel by direct reduction of cysteine for a microbial fuel cell anode. The biocompatible, porous, and 3D structure of the graphene aerogel afforded a maximum power density to 679.7 mW m\(^{-2}\) and increased the loading of bacterial cells on the GA.\(^{217}\) The large open pore structure and good biocompatibility are ideal for the effective immobilization, growth and cultivation.
of living microorganisms. The excellent conductivity promotes efficient current collection. When coupled with the high stability, these graphene aerogels may contribute to improved longevity toward the practical application of MFCs. Liu et al. reported 3D graphene aerogels homogenously decorated with Pt nanoparticles for an MFC anode (Fig. 19e–h). The MFC generated a maximum power density of 1460 mW m$^{-2}$; enough to successfully power a kitchen timer (Fig. 19h).226

4.4 Photocatalytic water splitting

In addition to bacterial-mediated generation of hydrogen, an obvious source of abundant hydrogen is water. Sunlight-driven photocatalytic and photoelectrochemical water splitting can produce hydrogen and oxygen in an environmentally friendly fashion.225,227 Due to the large energy requirements to electrochemically split water, it is essential to develop novel and efficient photocatalysts with low-cost and high-stability.228 The key requirements for effective photoanodes include efficient light-trapping, excellent separation, fast OER kinetics, and fast transportation of photogenerated charge carriers.229,230 For these reasons, 3D network graphene materials are an ideal candidate for photoanode research. Chen et al. reported a graphene aerogel-based hybrid containing N-deficient g-C$_3$N$_4$/N-GA/Ni-Fe layered double hydroxide (DPCN/N-GA/Ni-Fe-LDH). This photoanode lead to effective separation and transport of photogenerated charge carriers with electrons/holes moving between the g-C$_3$N$_4$ and NiFe layers.

The device showed photocurrent densities of 162.3 µA cm$^{-2}$ at 1.4 V with an incident photon-to-current efficiency (IPCE) of 2.5% at 350 nm during photo-electrocatalytic water splitting (Fig. 20).231

4.5 Dye-sensitized and perovskite solar cells

The direct conversion of solar energy into electricity is another promising area for renewable energy generation.232,233 There are several different solar cell types being developed along these lines. An established type is the dye-sensitized solar cell (DSSC). DSSCs are composed of a working electrode, electrolyte, and counter electrode. DSSCs offer several advantages including large material availability and low cost.234,235 The first solar cell was actually manufactured by Fritts in 1883 by making use of the photovoltaic effect. Bell Labs fabricated the first monocrystalline silicon solar cells in 1954 promoting the development of a variety of solar cells. Over the past 30 years, dye-sensitized solar cells have been development with efficiencies up to 12% and excellent stability. The general operating...
mechanism of DSSCs is as follows: first, the adsorbed dye in the anode absorbs photons to generate electrons which are transported to the counter electrode leaving the dye in an oxidized state. Second, a redox couple reduces the oxidized dye with an electron thus refreshing the dye and leaving an oxidized redox couple. Lastly, the redox couple migrates to the counter electrode where it is reduced. The theory of dye-sensitized solar cells is shown in Scheme 5.

The counter electrode (cathode) performs a crucial role in the DSSC system by catalyzing the reduction of the redox couple (typically an iodide–triiodide system) which serves as a mediator for refreshing the sensitizer dye. To improve the electrochemical performance of DSSCs, an ideal counter electrode must quickly transfer charges while also possessing high reducing strength. 3D graphene aerogel networks are a natural material for counter electrode development. Hu et al. developed a 3D honeycomb graphene structure by reaction between Li₂O and CO. The resulting 3D graphene aerogel counter electrode exhibited an energy conversion efficiency of 7.8%. Dai, Jang et al. fabricated N-doped graphene aerogel (Fig. 21a and b) and P-doped graphene aerogel as metal-free counter electrodes for DSSCs with a power conversion efficiency up to 7.07% and 8.46%, respectively. Conventional DSSCs typically use a liquid electrolyte with a power conversion efficiency around 12.3%. The leakage of liquid electrolyte and evaporation of the organic solvent often limits the lifetime and can lead to reduced performance over time. For these reasons, solid electrolytes have also been investigated. Polymer gels are one class of solid electrolytes, but they suffer from relatively low charge transfer. To address this issue, researchers have begun doping solid electrolytes with conductive materials. Tang et al. modified poly(acrylic acid)–cetyltrimethylammonium bromide (PAA–CTAB) gel electrolytes with graphene to create a quasi-solid-state DSSCs (Fig. 21e–i, right panel). This technique combines the stability of the solid electrolytes with the rapid charge transfer of graphene to yield a high power conversion efficiency of 7.06% as compared to 6.07% for pure PAA–CTAB.

Perovskites are a recent rediscovery in the photovoltaics community that has attracted frenzied attention for solar cell applications due to their low cost, sizable absorption across the visible spectrum, narrow and widely tunable photoluminescence, and high photostability. As a result of these properties, theoretical conversion efficiencies as high as 28% may be possible. Organic–inorganic halide perovskite materials are suitable alternatives to conventional solar cells due to their high light absorption capability and long diffusion lengths. The development of graded bandgap materials is a promising approach to further increase solar spectrum utilization. Despite the considerable enhancement in electron–hole collection efficiency, satisfactory open-circuit output voltage and superior output current proved elusive. This is likely due to excessive cation mixing, which eliminates the graded bandgap. Many strategies have been implemented such as replacing the metal cations, varying the composition of halide ions, and altering the moisture content. Zettl et al. fabricated double perovskite layers (layer 1: CH₃NH₃SnI₃ and layer 2: CH₃NH₃PbI₃₋ₓBrₓ) incorporating GaN, hexagonal boron nitride (h-BN), and graphene aerogel (Fig. 22). The cells reliably produce very high current densities up to 45 mA cm⁻² with average power conversion efficiencies of 18.41%. The graphene aerogel also serves as a barrier to moisture penetration and improves the perovskite film morphology (continuous films rather than perovskite islands).
5. Conclusions and outlook

A number of nanomaterials have been investigated for extensive applications in energy capture and energy storage. However, there are few nanomaterials that exhibit the performance, processability and abundance of graphene. Graphene has rapidly developed over the previous decade into a diverse assortment of types, composites and mixtures for countless applications. With the ever-present threat associated with depleted resources and environmental pollution, much attention has centred on developing various 3D nano-porous materials possessing large internal spaces, and high surface area. It is only natural then that combining 2D graphene with 3D porous networks as well as the direct formation of 3D graphene aerogels has attracted much attention. With endless material recipes currently being investigated, it is important to organize them into useful groups based on their different end uses.

In this review, we summarized the recent developments in the synthesis of 3D graphene networks and graphene aerogel compounds, and elaborated on their applications in energy capture, storage, and conversion. Graphene aerogels are especially attractive due to the large number of synthesis techniques including self-assembly (reducing, hydrothermal, metal ions), cross-linkers (organic and inorganic), CVD-growth (with or without template), and 3D printing. In double-layer capacitors, graphene aerogels can be directly substituted for or incorporated with other carbon materials (CNTs, porous carbon, carbon bulk) as electrode materials to enable high power densities and large cycle lifetimes. The electrochemical performance of graphene aerogel electrodes could also be enhanced by increasing the specific surface area, increasing the electrical conductivity, increasing the porosity, and doping/co-doping with various non-metals including N, P, S, and B. In pseudo-capacitors, graphene aerogel was employed as an anode. Subsequent modification with metal compounds (single/binary metal oxides, metal hydroxides), and conducting polymers (polypyrrole, polyaniline) lead to enhanced energy density compared to double layer capacitors. Unlike ion migration in pseudo-capacitors in which reactions largely occur on the
surface of the electrodes, in graphene aerogel electrodes ions can insert and diffuse into the solid phase of the electrode leading to higher energy densities. For fuel cells, GAs can serve as catalysts for electrolysise cells promoting the generation of fuel from water (HER), organic waste (MFCs), and alcohol. GAs can also function as a cathode for fuel cell systems (hydrogen, alcohol, microbial fuel cells) by catalyzing reduction reactions. For solar cells, GAs can be used as a counter electrode, a component in electrolyte gels for quasi-solid-state DSSCs, as a moisture barrier, and scaffold material for HTMs in perovskite solar cells to improve performance and stability.

It is clear that graphene aerogels and graphene aerogel-modified materials show much promise and application in energy capture, storage, and conversion technologies. Despite this, there remain some developmental hurdles to be overcome in transitioning from the lab to real world applications. First, synthetic methods and post-treatments need to be optimized to improve the surface area of graphene aerogels and increase the porosity. Fortunately, the material cost of graphene-based materials is substantially lower than that of traditional noble metal catalysts. It is the development and/or repurposing of new and existing industrial scale technology that will limit the time it takes to see graphene-based materials make the jump into energy capture, conversion and storage technologies.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors thank the National Natural Science Foundation of China (21501127 and 51502185), the Natural Science Foundation of Jiangsu Province of China (BK20140400). We also acknowledge the funds from the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD), and the Jiangsu Scientific and Technological Innovation Team (2013).

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