Promising applications of graphene and graphene-based nanostructures

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Review

Promising applications of graphene and graphene-based nanostructures

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Abstract

The present article is a review of research works on promising applications of graphene and graphene-based nanostructures. It contains five main scientific subjects. The first one is the research on graphene-based transparent and flexible conductive films for displays and electrodes: efficient method ensuring uniform and controllable deposition of reduced graphene oxide thin films over large areas, large-scale pattern growth of graphene films for stretchble transparent electrodes, utilization of graphene-based transparent conducting films and graphene oxide-based ones in many photonic and optoelectronic devices and equipments such as the window electrodes of inorganic, organic and dye-sensitized solar cells, organic light-emitting diodes, light-emitting electrochemical cells, touch screens, flexible smart windows, graphene-based saturated absorbers in laser cavities for ultrafast generations, graphene-based flexible, transparent heaters in automobile defogging/deicing systems, heatable smart windows, graphene electrodes for high-performance organic field-effect transistors, flexible and transparent acoustic actuators and nanogenerators etc. The second scientific subject is the research on conductive inks for printed electronics to revolutionize the electronic industry by producing cost-effective electronic circuits and sensors in very large quantities: preparing high mobility printable semiconductors, low sintering temperature conducting inks, graphene-based ink by liquid phase exfoliation of graphite in organic solutions, and developing inkjet printing technique for mass production of high-quality graphene patterns with high resolution and for fabricating a variety of good-performance electronic devices, including transparent conductors, embedded resistors, thin-film transistors and micro supercapacitors. The third scientific subject is the research on graphene-based separation membranes: molecular dynamics simulation study on the mechanisms of the transport of molecules, vapors and gases through nanopores in graphene membranes, experimental works investigating selective transport of different molecules through nanopores in single-layer graphene and graphene-based membranes toward the water desalination, chemical mixture separation and gas control. Various applications of graphene in bio-medicine are the contents of the fourth scientific subject of the review. They include the DNA translocations through nanopores in graphene membranes toward the fabrication of devices for genomic screening, in particular DNA sequencing; subnanometre trans-electrode membranes with

potential applications to the fabrication of very high resolution, high throughput nanopore-based single-molecule detectors; antibacterial activity of graphene, graphite oxide, graphene oxide and reduced graphene oxide; nanopore sensors for nucleic acid analysis; utilization of graphene multilayers as the gates for sequential release of proteins from surface; utilization of graphene-based electroresponsive scaffolds as implants for on-demand drug delivery etc. The fifth scientific subject of the review is the research on the utilization of graphene in energy storage devices: ternary self-assembly of ordered metal oxide-graphene nanocomposites for electrochemical energy storage; self-assembled graphene/carbon nanotube hybrid films for supercapacitors; carbon-based supercapacitors fabricated by activation of graphene; functionalized graphene sheet-sulfure nanocomposite for using as cathode material in rechargeable lithium batteries; tunable three-dimensional pillared carbon nanotube-graphene networks for high-performance capacitance; fabrications of electrochemical micro-capacitors using thin films of carbon nanotubes and chemically reduced graphenes; laser scribing of high-performance and flexible graphene-based electrochemical capacitors; emergence of next-generation safe batteries featuring graphene-supported Li metal anode with exceptionally high energy or power densities; fabrication of anodes for lithium ion batteries from crumpled graphene-encapsulated Si nanoparticles; liquid-mediated dense integration of graphene materials for compact capacitive energy storage; scalable fabrication of high-power graphene micro-supercapacitors for flexible and on-chip energy storage; superior micro-supercapacitors based on graphene quantum dots; all-graphene core-sheat microfibres for all-solid-state, stretchable fibriform supercapacitors and wearable electronic textiles; micro-supercapacitors with high electrochemical performance based on three-dimensional graphene-carbon nanotube carpets; macroscopic nitrogen-doped graphene hydrogels for ultrafast capacitors; manufacture of scalable ultra-thin and high power density graphene electrochemical capacitor electrodes by aqueous exfoliation and spray deposition; scalable synthesis of hierarchically structured carbon nanotube-graphene fibers for capacitive energy storage; phosphorene-graphene hybrid material as a high-capacity anode material for sodium-ion batteries. Beside above-presented promising applications of graphene and graphene-based nanostructures, other less widespread, but perhaps not less important, applications of graphene and graphene-based nanomaterials, are also briefly discussed.

1. Introduction

The discovery of graphene by Novoselov *et al* [1] has opened a new and very promising scicentific area which has emerged like '*a rapidly rising star on the horizon of materials science and condensed-matter physics*', and revealed '*a cornucopia of new physics and potential applications*' [2]. Since that time several reviews on the basic research as well as on the efficient applications of graphene and graphene-based nanostructures were published [3–7]. Recent advances in experimental basic research on graphene and graphene-based nanomaterials were reported in our previous review [8]. The purpose of present work is to review promising applications of graphene and graphene-based nanostructures.

In section 2 we summarize the results of the study on graphene-based transparent and flexible conductive films for displays and electrodes. The content of section 3 includes conductive inks for printed electronics. Section 4 is a review of the research on graphene-based separation membranes. A review on the utilization of graphene in bio-medicine is presented in section 5. In section 6 we summarize the result of a large number of research works on the efficient utilization of graphene in energy storage devices. Section 7 contains the conclusion and discussions.

2. Graphene-based transparent and flexible conductive films for displays and electrodes

Development of transfer printing and solution-based methods allowed to incorporate graphene into large area electronics. In [9] Chhowalla *et al* proposed an efficient method ensuring uniform and controllable deposition of reduced graphene oxide (RGO) thin films with thickness ranging from a single monolayer to several layers over large areas. The opto-electronic properties can thus be tuned over several orders of magnitude, making them potentially useful for flexible and transparent semiconductors or semi-metals. The thinnest films exhibit graphene-like ambipolar transistor characteristics, whereas thicker films behave as graphite-like semi-metals. On the whole, the proposed deposition method represented a route for translating the fundamental properties of graphene into technologically viable devices.

The large-scale pattern growth of transparent electrodes was successfully performed by Hong *et al* [10]. The authors used the chemical vapor deposition (CVD) on thin nickel layers and applied two methods for patterning the films and transferring them to arbitrary substrates.

The transferred graphene films showed very low sheet resistance and very high optical transparency. At low

temperatures the graphene monolayer transferred to SiO$_2$ substrates showed high electron mobility and exhibited the half-integer quantum Hall effect. Thus the quality of graphene grown by CVD is as high as mechanically cleaved graphene. Having employed the outstanding mechanical properties of graphene, the authors also demonstrated the macroscopic use of these highly conducting and transparent electrodes in flexible, stretchable and foldable electronics.

In [11] Colombo *et al* demonstrated the large-area synthesis of high-quality and uniform graphene films of copper foils. The authors grew large-area graphene films of the order of centimeters on copper substrates by CVD using methane. The films were predominantly single-layer graphene, with a small percentage (less than 5%) of the area having few layers and are continuous across copper surface steps and grain boundaries. The low solubility of carbon in copper appeared to make this growth process self-limiting. The authors also developed the graphene film transfer process to arbitrary substrates. The dual-gated field-effect transistor fabricated on silicon/silicon dioxide showed electron mobilities as high as $4050 \, \text{cm}^2$ per volt per second at room temperature.

With the excellent optical and electronic properties of graphene such as high mobility and optical transparency as well as flexibility, robustness and environmental stability, it is a promising material for the application to photonics and optoelectronics. A comprehensive review on graphene photonics and optoelectronics was presented by Ferrari *et al* [12]. From the rich scientific contents of this review it can be clearly seen that graphene-based transparent conducting films as well as graphene oxide (GO)-based transparent conducting films were efficiently used in the fabrications of many photonic and optoelectronic devices and equipments such as the window electrodes of inorganic, organic and dye-sensitized solar cells, organic light-emitting diodes, light-emitting electrochemical cells; the touch screens; the flexible smart windows; the graphene-based saturated absorbers in laser cavities for ultrafast generation etc.

The high-performance, flexible, transparent heaters based on large-scale graphene films were synthesized by Hong *et al* [13]. The authors applied the CVD on Cu foils and fabricated graphene films with low sheet resistance and very high (~89%) optical transmittance, which are ideal low-voltage transparent heaters. Time-dependent temperature profiles and heat distribution analyzes showed that the performance of graphene-based heaters is superior to that of conventional transparent heaters based on indium tin oxide (ITO). These graphene-based, flexible, transparent heaters are expected to be widely applied, particularly in automobile defogging/deicing systems and heatable smart windows.

In [14] De and Coleman used published transmittance and sheet resistance data to calculate a figure of merit for transparent conducting graphene films, the DC to optical conductivity ratio, $\sigma_{\text{DC}}/\sigma_{\text{op}} = 0.7, 4.5$ and 11. The authors showed that these results represented fundamental limiting values for networks of graphene flakes, undoped graphene stacks and graphite films, respectively. The limiting value for graphene flake networks was much too low for transparent-

electrode applications. For graphite, a conductivity ratio of 11 gave a resistance too low compared to the minimum requirement for transparent conductors in current driven applications. However, the authors suggested that substrate-induced doping can potentially increase the two-dimensional (2D) DC conductivity enough to make graphene a viable transparent conductor.

In [15] Choi and Hong demonstrated high-performance, flexible, transparent heaters based on large-scale graphene films synthesized by CVD on Cu foils. After multiple transfers and chemical doping processes, the graphene films showed sheet resistance as low as $\sim 43 \, \Omega/\text{sq}$ with 89% transmittance, which are ideal as low-voltage transparent heaters. Time-dependent temperature profiles and heat distribution analyzes showed that the performance of graphene-based heaters is superior to that of conventional transparent heaters based on ITO. In addition, the authors confirmed that mechanical strain as high as ~4% did not substantialy affect heater performance. Therefore, graphene-based, flexible, transparent heaters are expected to find uses in a broad range of applications, including automobile defogging/deicing systems and heatable smart windows.

The graphene electrodes for high-performance organic field-effect transistors were fabricated by Kim *et al* [16]. In order to optimize the performance of these devices the authors controlled the work-function of graphene electrodes by functionalizing the surfaces of SiO$_2$ substrates (SAMs). The electron-donating NH$_2$-terminated SAMs induced strong n-doping in graphene, whereas the CH$_3$-terminated SAMs neutralized p-doping was induced by SiO$_2$ substrates. As the result, work-functions of graphene electrodes considerably changed. The SAMs were patternable and robust. The result of this work can be applied also to the fabrication of many other graphene-based electronic and optoelectronic devices.

In a subsequent work [17] Lee *et al* reported the fabrication of flexible organic light-emitting diodes by engineering the graphene electrodes to have high work-functions and low sheet resistances for achieving extremely high luminous efficiencies.

By using poly(vinylidence fluoride-trifluoroethylene), briefly denoted P(VPF-TrFE), as an effective doping layer between two graphene layers for significantly decreasing the sheet resistance of graphene, Ahn *et al* [18] fabricated flexible, transparent acoustic actuator and nanogenerator based on graphene/P(VPF-TrFE)/graphene multilayer film. The prepared acoustic actuator showed good preformance and sensitivity over a broad range of frequency. The output voltage and the current density of the prepared nanogenerator were comparable to those of ZnO- and PZT-based nanogenerators. The authors demonstrated also the possibility of rollable devices based on graphene/P(VDF-TrFE)/graphene multilayer under a dynamical mechanical loading condition.

In the important experimental work [19] of Cho *et al* the authors elaborated an efficient method for fast synthesis of high-performance graphene films by hydrogene-free rapid thermal chemical vapor deposition (RT-CVD) and roll-to-roll etching towards its industrial development for the mass-production of graphene films with the size, uniformity and

reliability satisfying the industrial standards. The graphene film transfer methods were also elaborated.

The physical properties of RT-CVD graphene have been carefully characterized by transmission electron microscopy, Raman spectroscopy, chemical grain boundary analysis and various electrical device measurements, showing excellent uniformity and stability. Moreover, the actual application of the RT-CVD films to capacitive multi-touch devices installed in the most sophisticated mobile phone was demonstrated.

Beside many superior mechanical and optical properties of graphene films compared to other transparent thin films frequently used in photonics and optoelectronics, their conductivity is inferior to that of conventional ITO electrodes of comparable transparency, resulting in the lower performance of the devices using graphene transparent thin films. To overcome this inconvenience Ahn et al [20] applied an efficient method to improve the performance of graphene films by electrostatically doping them via a ferroelectric polymer. These graphene films with ferroelectric polarization were used to fabricate ultrathin organic solar cells (OSCs). Such graphene-based OSCs exhibited an efficiency of 2.07% with a superior stability compared to chemically doped graphene-based OSCs. Furthermore, OSCs constructed on ultrathin ferroelectric film as a substrate of only a few micrometers showed extremely good mechanical flexibility and durability. Moreover, they can be rolled up into a cylinder with 7 mm diameter.

Another method to enhance the performance of the flexible graphene-based OSCs was elaborated by Gradečak et al [21]. These authors showed that the high efficiency can be achieved via thermal treatment of MoO_3 electron blocking layer and direct deposition of ZnO electron transporting layer on graphene. The authors also demonstrated graphene-based flexible OSCs on polyethylene naphthalate substrate. The fabricated flexible OSCs with graphene anode and cathode achieved record-high power conversion efficiencies of 6.1% and 7.1%, respectively. Thus this work paved a way to fully graphene electrodes based flexible OSCs using a simple a reproducible process.

In a short review of above-mentioned experimental works Ahn and Hong [22] concluded that graphene has emerged as a promising material for transparent and flexible electrodes. The use of graphene-based transparent electrodes has been already demonstrated in various photonic and optoelectronic devices. Ahn and Hong anticipated that applications of graphene to flat and simple structures such as touch screens, smart windows, electromagnetic interference shields, lighting and transparent heater will be the first to be realized, whereas applications to flexible displays and microelectronic devices will follow some years later.

3. Conductive inks for printed electronics

Having noted that for at least past ten years printed electronics has promised to revolutionize the electronic industry by producing cost-effective electronic circuits and sensors in very large quantities, Noh et al [23] indicated also the need to find suitable functional inks, mainly high-mobility printable semiconductors and low sintering temperature conducting inks as well as to develop printing tools capable of higher resolution and uniformity compared to the conventional ones. In fact this need was responded in some previous works.

In [24] Jang et al fabricated patterned graphene sheets by an inkjet printing technique. High line resolution and sustained electrical conductivity were achieved, tuning of the sheet resistance was dependent on the concentration of GO ink and the number of print layers. The patterned graphene-based thin film was also applied as a practical wideband dipole antenna.

Subsequently Ferrari et al [25] demonstrated inkjet printing as a viable method for large-area fabrication of graphene devices. The authors produced the graphene-based ink by liquid phase exfoliation of graphite in N-methylpyrrolidone. The prepared ink was used to print thin-film transistors with mobilities up to $\sim95\ cm^2\ V^{-1}\ s^{-1}$ as well as transparent and conductive patterns with $\sim80\%$ transmittance and $\sim30\ k\Omega\ cm^{-2}$ sheet resistance. These result paved the way to all-printed, flexible and transparent graphene devices on arbitrary substrates.

In [26] Östling et al demonstrated an efficient and mature inkjet printing technology for mass production of high-quality graphene patterns with a high resolution. Typically, several passes of printing and a simple baking allowed fabricating a variety of good-performance electronic devices, including transparent conductors, embedded resistors, thin-film transistors and micro-supercapacitors.

Recently Torrisi and Coleman [27] described how graphene can be produced and then used in conductive inks for inkjet printing. First, a large quantity of pristine graphene nanosheets, typically hundreds of nanometers across and ~1 nm thick, can be produced quickly and easily by liquid-phase exfoliation in readily printable liquids such as water and organic solvents. The resulting ink is stable, processable in ambient conditions, and has high batch-to-batch reproducibility as well as good rheological properties for printing and coating.

Some heterostructures were fabricated by using nanosheet-based inks in the experimental work of Casiraghi et al [28]. The authors noted that the possibility of combining layers of different 2D materials in one stack can allow unprecedented control over the electronic and optical properties of the resulting material. These 2D materials might be graphene, hexagonal boron nitride (hBN) and tungsten disulphide (MoS_2). The authors demonstrated that such heterostructures can be assembled from chemically exfoliated 2D crystals, allowing for low-cost and scalable methods to be used in device fabrication.

For developing the large-area flexible electronics Hersam et al [29] demonstrated the gravure printing of graphene to rapidly produce conductive patterns on flexible substrates. The authors prepared suitable inks and chose printing parameters enabling the fabrication of patterns with a resolution down to 30 μm. A mild annealing step yielded conductive lines with high reliability and uniformity, providing an

efficient method for the integration of graphene into large-area printed and flexible electronics.

In [30] Coleman *et al* demonstrated inkjet printing of nanosheet of both graphene and MoS_2 prepared by liquid exfoliation. The authors described a procedure for preparing inks from nanosheets with well-defined size distribution and concentration up to 6 mg ml^{-1}. Graphene traces were printed at low temperature ($<70\,^\circ$C) without subsequent thermal or chemical treatment. Thin traces displayed percolation effects while traces with thickness above 160 nm displayed thickness-independent conductivity 3000 S m^{-1}. The authors also demonstrated the printing of semiconducting traces using solvent-exfoliated, size-selected MoS_2 nanosheets. Such traces can be combined with inkjet-printer graphene interdigitated array electrodes to produce all-printed photodetectors.

A review on recent developments of the study on conductive nanomaterials and their applications in printed electronics was presented by Magdasi and Kamyshny [31]. The authors particularly emphasized on inkjet printing of ink formulations based on metal nanoparticles, carbon nanotubes and graphene sheets. The review described the basic properties of conductive nanomaterials suitable for printed electronics, their stabilization in dispersions, formulations of conductive inks and various sintering methods to obtain conductive patterns. Applications of conductive nanomaterials for electronic devices (transparent electrodes, metallization of solar cells, RFID antennas, light emitting devices etc) were also briefly reviewed.

In a recent work [32] Hersam *et al* demonstrated the intense pulsed light annealing of graphene inks for rapid post-processing of inkjet-printed patterns on various substrates. A conductivity of ~25 000 S m^{-1} was achieved following a simple printing pass using a concentrated ink containing 20 mg ml^{-1} graphene, establishing this strategy as a practical and effective approach for the versatile and high-performance integration of graphene in printed and flexible electronics.

In another recent work [33] Park *et al* performed the direct printing of RGO on planar or highly curved surface with a high resolution using electrodynamic technology. The authors demonstrated the electrodynamic inkjet printing of RGO to form complex geometric devices with a high resolution. Both planar and highly curved surfaces (with the radius of curvature ~60 mm) can be used as substrates. Demonstration of counterfeit coin recognition using RGO patterns and all-printed RGO transistors suggested substantial promise for application in security and electronics.

4. Graphene-based separation membranes

The idea to use graphene sheets containing nanopores as the separation membranes was emerged since long time from the theoretical simulation studies. Král *et al* [34] designed functionalized nanopores in graphene monolayers and showed by molecular dynamics simulations that they provide highly selective passage of hydrated ions. Only ions that can be partly stripped of their hydration shells can pass through these ultrasmall pores with diameter ~5 Å. For example, a fluorine-nitrogen-terminated pore allows the passage of Li$^+$, Na$^+$ and K$^+$ cations with the ratio 9:14:33, but it blocks the passage of anion. The hydrogen-terminated pore allows the passage of F$^-$, Cl$^-$, Br$^-$ anions with the ratio 0:17:33 but it blocks the passage of cations. These nanopores could have potential applications in molecular separation, desalination, and energy storage systems.

Subsequently Jiang *et al* [35] investigated the permeability and selectivity of graphene sheets with designed sub-nanometer pores using first principles density functional calculations. The authors found high selectivity on the order of 10^5 for H_2/CH_4 with a high performance of H_2 for a nitrogen-functionalized pore. Moreover, the authors found extremely high selectivity on the order of 10^{23} for H_2/CH_4 at an all-hydrogen passivated pore whose small width (at 2.5 Å) presents a formidable barrier (1.6 eV) for CH_4 but easily surmountable for H_2 (0.22 eV). These results suggested that these pores are far superior to traditional polymer and silica membranes, where bulk solubility and diffusivity dominate the transport of gas molecules through the material. The authors proposed to use porous graphene sheets as one-atom-thin, highly efficient, and highly selective membranes for gas separation. Such the pores could have widespread impact on numerous energy and technological applications.

In [36] Strano *et al* studied the mechanisms of gas permeation through single layer graphene membranes. The authors derived analytical expressions for gas permeation through atomically thin membranes in various limit of gas diffusion, surface adsorption, or pore translocation. Gas permeation can proceed via direct gas-phase interaction with the pore, or interaction via the adsorbed phase on the membrane exterior surface. A series of van der Waals force fields allowed for the estimation of the energy barriers in various types of graphene nanopores.

Using molecular dynamics simulations Xue *et al* [37] investigated the separation of CO_2 from a mixture of CO_2 and N_2 by means of porous graphene membranes. The effects of chemical functionalization of the graphene sheet and pore rim on the gas separation performance of porous graphene membranes were examined. The authors found that chemical functionalization of the graphene sheet can increase the absorption ability of CO_2, while chemical functionalization of the pore rim can significantly improve the selectivity of CO_2 over N_2. Obtained results demonstrated the potential use of functionalized porous graphene as single-atom-thick membrane for CO_2 and N_2 separation. Thus the authors proposed an effective way to improve the gas separation performance of porous graphene membranes.

The utilization of nanoporous graphene (NPG) for water desalination was proposed by Grossman and Cohen-Tanugi [38]. Using classical molecular dynamics, the authors showed that nanometer-scale pores in single-layer freestanding graphene can effectively filter NaCl from water. Moreover, the authors studied the desalination performance of such membranes as a function of pore size, chemical functionalization and applied pressure. Obtained results indicated that the membrane's ability to prevent the salt passage depends

critically on pore diameter with adequately sized pores allowing for water flow while blocking ions. Further, an investigation on the role of chemical functional groups bonded to the edge of graphene pores suggested that commonly occurring hydroxyl groups can roughly double the water thanks to their hydrophylic character. However, the increase in water flux takes place at the expense of less consistent salt rejection performance, which can be attributed to the ability of hydroxyl functional group to substitute for water molecules in the hydration shell of the ions. Overall, obtained results indicated that the water permeability of this material is several orders of magnitude higher than conventional reverse osmosis (RO) membranes, and that NPG may have a valuable role to play for water purification.

At the same time Karnik *et al* [39] studied the selective transport of molecules through intrinsic defects in single layers of CVD graphene with nominal areas more than $25 \, mm^2$ which were then transferred onto porous polycarbonate substrates. A combination of pressure-driven and diffusive transport measurements provided evidence of size-selective transport of molecules through the membranes, which was attributed to the low-frequency occurrence of 1–15 nm diameter pores in CVD graphene. Thus the authors demonstrated the first step toward the realization of graphene-based selection membrane.

By applying molecular dynamics simulations Jiang *et al* [40] demonstrated that porous graphene of a certain pore size can efficiently separate CO_2 from N_2 with a high performance, in the agreement with the recent experimental finding [41]. The high selectivity was reflected in the much higher number of CO_2 passing-through events than that of N_2 from the trajectory. The simulated CO_2 permeance was on the order of magnitude of 10^5 GPU (gas permeation unit). The selective trend was further corrobolated by the free energy barrier of permeation. The predicted CO_2/N_2 selectivity was around 300. Overall, the combination of high CO_2 flux and high CO_2/N_2 selectivity makes NPG a promising membrane for post-combustion separation.

Subsequently to the suggestion of Grossman [38] the simulation study of graphene-based water desalination membranes was carried out again by Striolo *et al* [42]. The authors applied the molecular dynamics simulations to investigate the transport of water and ions through the pores created on the basal plane of the graphene sheet. Graphene pore diameters ranged from 7.5 to 14.5 Å. Different pore functionalities obtained by tethering various functional groups to the terminal carbon atom were considered. The ease of ion and water translocation was monitored by calculating the potential of mean force along the direction perpendicular to the graphene sheet. The results indicated that effective ion exclusion can be achieved only when nonfunctionalized (pristine) pores have diameters ~7.5 Å, whereas the ions can easily penetrate pristine pores of diameters ~10.5 and 14.5 Å. Carboxyl functional groups can enhance ion exclusion to all pores considered, but the effect becomes less pronounced as both the ion concentration and the pore diameter increase. Obtained results suggested that narrow graphene-pores functionalized with hydroxyl groups remained effective at

excluding Cl^- ions even at moderate solution ionic strength. These results are useful for the design of water desalination membranes.

In a recent work [43] Grossman and Cohen-Tanugi suggested to reconsider the water permeability of NPG at realistic pressure for RO desalination. The problem is as follows: NPG shows tremendous promise as an ultra-permeable membrane for water desalination thanks to its atomic thickness and precise sieving properties. However, a significant gap exists between the ideal conditions assumed for NPG desalination and the physical environment inherent to RO system. In particular, the water permeability of NPG has been calculated previously based on very high pressures (1000–2000 bars). Does NPG maintain its ultrahigh water permeability under realworld RO pressures (<100 bars)? The authors answered this question by drawing results from molecular dynamics simulations and indicating that NPG maintains its ultrahigh permeability even at low pressures, allowing a permeated water flux of $6.0 \, l \, h^{-1}$ bar per pore, or equivalently $1041 \pm 201 \, m^{-2} \, h$ bar assuming a nanopore density of $1.7 \times 10^{13} \, cm^2$.

Implications of permeation through intrinsic defects in graphene on the design of defect-tolerant membranes for gas separation were investigated by Karnik *et al* [44]. The authors demonstrated that independent stacking of graphene layers on a porous support exponentially decreases the flow through defects. On the basis of experimental data the authors developed a gas transport model that elucidated separate contributions of tears and intrinsic defects on gas leakage through these membranes. The model showed that the pore size of the porous support and its permeance critically affected the separation behavior, and revealed the parameter space where gas separation can be achieved regardless of the presence of nonselective defects, even for single-layer membranes. Obtained results provided a framework for understanding gas transport in graphene membranes and guided the design of practical, selectively permeable graphene membranes for gas separation.

In another work of Karnik *et al* [45] the selective transport of ions through tunable subnanometer pores in single-layer graphene membranes was investigated. Isolated, reactive defects were introduced into the graphene lattice through ion bombardment and subsequently enlarged by oxidative etching into permeable pores with diameters of 0.40 ± 0.24 nm and densities exceeding $10^{12} \, cm^{-2}$, while retaining structural integrity of graphene. Transport measurements revealed that the created pores were cation-selective at short oxidation times, consistent with electrostatic repulsion from negatively charged functional groups terminating the pore edges. At longer oxidative times, the pores allowed transport of salt but prevented transport of larger organic molecules, indicative of steric size exclusion. The ability to tune the selectivity of graphene through controlled generation of subnanometer pores promised the development of advanced NPG membranes for nanofiltration, desalination, gas separation and similar applications.

The mechanisms of molecular permeation through NPG membranes were studied by Hadjiconstantinou *et al* [46]. By

applying molecular dynamics simulations the authors investigated four different gases: helium, hydrogen, nitrogen and methane. They showed that in addition to the direct (gas-kinetic) flux of molecules crossing from the bulk phase on one side of the graphene to the bulk phase on the other side, for gases that adsorb onto the graphene, significant contribution to the flux across the membrane was obtained from a surface mechanism by which molecules cross after being adsorbed onto the graphene surface.

The authors quantified the relative contributions of the bulk and surface mechanisms and showed that the direct flux can be described reasonably and accurately by kinetic theory, provided the later is appropriately modified assuming steric molecule-pore interactions, with gas molecules behaving as hard spheres of known kinetic diameters. The surface flux is negligible for gases that do not adsorb onto graphene (e.g. He and H_2), while for gases that adsorb (e.g. CH_4 and N_2) it can be on the order of the direct flux or larger. The authors identified the nanopore geometry that is permeable to H_2 and He, significantly less permeable to N_2, and essentially impermeable to CH_4, thus validated previous suggestions that NPG membrane can be used for gas separation. The authors also showed that molecular permeation is strongly affected by pore functionalization. This observation may be sufficient to explain the large discrepancy between simulated and experimentally measured transport rates through NPG membranes.

In the search of graphene-based materials for filtration and separation techniques Geim *et al* [47] found that sub-micrometer-thick membranes made from GO can be completely impermeable to liquids, vapors and gases, including helium, but these membranes allowed unimpeded permeation of water (H_2O permeates through graphene-based membranes at least 10^{10} times faster than He). The authors attributed these seemingly incompatible observations to a low-friction flow of a monolayer of water through 2D capillaries formed by closely spaced graphene sheets. Diffusion of other molecules was blocked by reversible narrowing of the capillaires in low humidity and/or by their cloggings with water.

Almost at the same time Bunch *et al* [41] investigated selective molecular sieving through porous graphene. The authors noted that membranes act as selective barrier and play an important role in processes such as cellular compartmentalization and industrial-scale chemical and gas purification. The membranes should be as thin as possible to maximize flux, mechanically robust to prevent fracture, and have well-defined pore sizes to increase selectivity. Graphene is an excellent starting point for developing size-selective membranes because of its atomic thickness, high mechanical strength, relative inertness and impermeability to all standard gases. However, pores that can exclude larger molecules but allow smaller molecules to pass through would have to be introduced into the material. The authors showed that ultra-violet-induced oxidative etching can create pores in micro-meter-sized graphene membranes, and the resulting membranes can be used as molecular sieves. A pressurized blister test and mechanical resonance were used to measure the transport of a range of gases (H_2, CO_2, Ar, N_2, CH_4 and SF_6) through the pores. The experimentally measured leak

rate, separation factors and Raman spectrum agree well with models based on effusion through a small number of ångström -sized pores.

Subsequently Choi *et al* [48] investigated the selective gas transport through few-layered graphene and GO membranes. The authors demonstrated that few-and several-layered graphene and GO sheets can be engineered to exhibit the desired gas separation characteristics. Selective gas diffusion was achieved by controlling gas flow channels and pores via different stacking methods. For layered (3–10 nm) GO membranes tunable gas transport behavior was strongly dependent on the degree of interlocking within the GO stacking structure. High carbon dioxide/nitrogen selectivity was achieved by well-interlocked GO membranes in relative high humidity, which was most suitable for post combustion carbon dioxide capture processes.

At the same time the ultrathin molecular-sieving GO membranes for selective hydrogen separation were investigated also by Yu *et al* [49]. The authors noted that ultrathin, molecular-sieving have great potential to realize high-flux, high-selectivity mixture separation at low energy cost. However, current microporous membranes with the pore size <1 nm are usually relatively thick. Therefore, with the use of current membrane materials and techniques, it is difficult to prepare microporous membranes thinner than 20 nm without introducing extra defects. The authors have succeeded in preparing ultrathin GO membranes with the thickness approaching 1.8 nm by a facile filtration process. These membranes showed mixture separation selectivities as high as 3400 and 900 for H_2/CO_2 and H_2/N_2 mixtures, respectively, through selective structural defects on GO.

Recently precise and ultrafast molecular sieving through GO membranes was performed by Geim *et al* [50]. Having noted that graphene-based materials can have well-defined nanopores as well as can exhibit low frictional water flow inside them, making their properties of interest for filtration and separation, the authors investigated the permeation through micrometer-thick laminates prepared by means of vacuum filtration of GO suspensions. The laminates are vacuum-tight in the dry state but, if immersed in water, they act as molecular sieves, blocking all solutes with hydrated radii larger than 4.5 Å. Smaller ions permeat through the membranes at rates of thousands times faster than what is expected for simple diffusion. The authors believed that this behavior is caused by a network of nanocapillaries that open up in the hydrated state and accept only species that fit in. The anomalously fast permeation was attributed to capillary-like pressure acting on ions inside graphene capillaries.

Soon after Park *et al* [51] observed the ultimate permeation across atomically thin porous graphene. Having had in mind the ability of 2D porous layer to make the ideal membrane for separation of chemical mixtures because its infinitesimal thickness promises ultimate permeation, the authors believed that graphene, with great mechanical strength, chemical stability and inherent impermeability, offers a unique 2D system with which to realize this membrane, and studied the mass transport. The authors demonstrated the highly efficient mass transfer across physically

perforated double-layer graphene, having up to a few million pores with narrowly distributed diameters between less than 10 nm and 1 μm. The measured transport rates were in agreement with predictions of 2D transport theory. Attributed to their atomic thickness, these porous graphene membranes showed permeance of gas, liquid and water vapor far in excess of those shown by finite-thickness membranes, having highlighted the ultimate permeation these 2D membranes can provide.

Subsequently to the previous work [50] Geim *et al* [52] continued to study the proton transport through one-atom-thick crystals. The authors performed transport and mass spectroscopy measurements which demonstrated that monolayer of graphene and hexagonal boron nitride (hBN) are highly permeable to thermal protons under ambient conditions, whereas no proton transport was detected for thicker crystal such as monolayer molybdenum disulphide, bilayer graphene or multilayer hBN. Protons present an intermediate case between electrons (which can tunnel easily through atomically thin barriers) and atoms, yet the measured transport rates were unexpectedly high and raised fundamental question about the details of the transport process. The authors observed the highest room-temperature proton conductivity with monolayer hBN, for which the authors measured a resistivity to proton flow of about $10\,\Omega\,cm^2$ and a low activation energy of about 0.3 eV. At higher temperature hBN was outperformed by graphene, the resistivity of which was estimated to fall below $10\,\Omega\,cm^2$ above 250 °C. Moreover, proton transport was further enhanced by decorating the graphene and hBN membranes with catalytic metal nanoparticles. The high, selective proton conductivity and stability make one-atom-thick crystals promising candidates for use in many hydrogen-based technologies.

Very recently, after a short review of the research on water desalination, Koh and Lively [53] concluded that water desalination membranes can be created by etching nanometer-sized pores in a single layer of graphene. In particular, the authors highly evaluated the promising results of the research of Mahurin *et al* related to the water permeability of single-layer graphene membranes toward the application to water desalination. Indeed, a comprehensive experimental research work on water desalination using nanoporous single-layer graphene has been performed by Mahurin *et al* [54]. The authors have experimentally examined the transport of ions and water across a suspended, single-layer graphene membrane with stable nanometer-sized pores generated by oxygen plasma etching in order to validate the effectiveness of graphene-based desalination of water. These membranes exhibited both high salt rejection and exceptionally rapid water transport properties. Using aberration-corrected scanning transmission electron microscopy imaging, the authors correlated the porosity of graphene membrane with transport properties and determined the optimum pore size for effective desalination. The mechanism of water transport was explored, suggesting that graphene may be suitable both for membrane distillation and RO. The content of the research consisted of three parts: preparation and characterization of graphene membranes, water transport and salt rejection measurements,

and analysis of transport mechanisms. Following conclusions were attained:

The potential utility of NPG as a selective membrane that can be used for water desalination was demonstrated. It was shown that oxygen plasma can be used as a very convenient method for fabricating tailored nanopores of desired dimension (and probably altered chemical properties) in suspended single-layer graphene, with high precision. The resulting nanopores showed tremendous water molecule selectivity over dissolved ions (K^+, Na^+, Li^+, Cl^-). The selectivity exceeded five orders of magnitude for low porosities, but precipitously decreased at higher porosities, most probably due to enlargement of the nanopores. Based on the estimated nanopore density ($0.01\,nm^{-2}$), the estimated water flux through a single nanopore can reach the tremendously high value of 3 molecules per picosecond. At the same time, the water flux in a conventional geometry with an osmotic pressure gradient and liquid water on both sides of the porous graphene membrane showed smaller water flux values of 200 molecules per microsecond. Although scaling up these membranes for use in industrial and commercial processes remains a significant challenge, the present work represented a proof-of-concept of the effectiveness and potential of NPG for desalination applications.

As the continuation of the previous work [41] on selective molecular sieving through porous graphene Bunch *et al* [55] fabricated molecular valves for controlling gas phase transport by using graphene with discrete ångström-sized pores. The authors demonstrated that gas flux through discrete ångström-sized pores in monolayer graphene can be detected and then controlled using nanometer-sized gold clusters, which are formed on the surface of the graphene and can migrate and partially block a pore. In samples without gold clusters the authors observed stochastic switching of the magnitude of the gas permeance attributed to molecular rearrangement of the pore. The fabricated molecular valves could be used, for example, to develop unique approaches to molecular synthesis that are based on the controllable switching of molecular gas flux.

5. Graphene applications in bio-medicine

The efficient applications of graphene in bio-medicine were simultaneously developed by three independent research groups with the leaderships of Drndíc, Dekker and Golovchenko. In [56] Drndíc *et al* demonstrated the DNA translocations through nanopores created in graphene membranes. The devices consisted of 1–5 nm thick graphene membranes with electron-beam sculpted nanopores from 5 to 10 nm in diameter. Due to the thin nature of the graphene membranes, the authors observed larger blocked currents than for traditional solid-state nanopores. However, ionic current noise levels were several order of magnitude larger than those for silicon nitride nanopores. These fluctuations were reduced with the atomic-layer deposition of 5 nm of TiO_2 over the device. Unlike traditional solid-state nanopore materials that are insulating, graphene is an excellent electrical conductor.

The use of graphene as a membrane material opened the door to a new class of nanopore devices in which electronic sensing and control are performed directly at the pore.

In another work on DNA translocation through graphene nanopores [57] Dekker *et al* also noted that nanopores-nanosized holes that can transport ions and molecules-are very promising devices for genomic screening, in particular DNA sequencing. Solid-state nanopores currently suffer from the drawback, however, that the channel constituting the pore is long, ∼100 times the distance between two bases of DNA molecules (0.5 nm for single-stranded DNA). The authors provided the proof-of-concept that was possible to realize and use ultrathin nanopores fabricated in graphene monolayers for single-molecule DNA translocation. The pores were obtained by placing a graphene flake over a microsize hole in a silicon nitride membrane and drilling a nanosize hole in the graphene using an electron beam. As individual DNA molecules translocated through the pore, characteristic temporary conductance changes were observed in the ionic current through the nanopore, setting the stage for future single-molecule genomic screening devices.

The utilization of graphene as a subnanometre trans-electrode membrane was realized by Golovchenko *et al* [58]. The authors noted that a graphene membrane separating two ionic solutions in electrical contact is strongly ionically insulating despite being atomically thin, and has in-plane electronic properties dependent on the interfacial environment. The atomic thinness, stability and electrical sensitivity of graphene motivated the authors to investigate the potential use of graphene membranes and graphene nanopores to characterize single molecules of DNA in ionic solution. The authors showed that when immersed in an ionic solution, a layer of graphene becomes a new electrochemical structure called a trans-electrode. The trans-electrode's unique properties are the consequence of the atomic-scale proximity of its two opposing liquid-solid interfaces together with graphene's well-known in-plane conductivity. The authors showed that several trans-electrode properties were revealed by ionic conductance measurements on a graphene membrane that separated two aqueous ionic solutions. Although the used membranes were only one to two atomic layers thick, the authors found that they were remarkable ionic insulators with a very small stable conductance that depended on the ion species in solution. Electrical measurements on graphene membranes, in which a single nanopore has been drilled, showed that the membrane's effective insulating thickness was less than one nanometer. This small effective thickness makes graphene an ideal substrate for very high resolution, high through put nanopore-based single-molecule detectors. The sensitivity of graphene's in-plane electronic conductivity to its immediate surface environment and trans-membrane solution potentials offered new insights into atomic surface processes and sensor development opportunities.

The antibacterial activity of graphite, graphite oxide, GO and RGO was investigated by Chen *et al* [59]. The authors noted that graphene has strong cytotoxicity toward bacteria. To better understand its antimicrobial mechanism the authors compared the antibacterial activity of four types of graphene-based materials: graphite (Gt), graphite oxide (GtO), rGO and RGO toward a bacteria model—*Escherichia coli*. Under similar concentration and incubation conditions, GO showed the highest antibacterial activity, sequentially followed by rGO, Gt, and GtO. Scanning electron microscopy (SEM) and dynamic light scattering analyzes showed that GO aggregates have the smallest average size among four types of materials. SEM images displayed that the direct contacts with graphene nanosheets disrupt cell membrane. No superoxide anion (O_2^-) induced reactive oxygen species production was detected. However, four types of materials can oxidize glutathione, which serves as redox state mediator in bacteria. Conductive rGO and Gt have higher oxidation capacities than insulating GO and GtO. The authors envisioned that physicochemical properties of graphene-based materials, such as density of functional groups, size and conductivity can be precisely tailored to either reducing their health and environmental risks or increasing their application potentials.

In [60] Ruiz *et al* performed the characterization of antimicrobial properties of GO and its biocompatibility with mammalian cells. Authors showed that when GO was added to a bacterial culture at 25 μg ml^{-1}, bacteria grew faster. SEM images indicated that bacteria formed dense biofilms in the presence of GO. On filters coated with 25 and 75 μg of GO bacteria grew two and three times better than on filters without GO. Closer analysis showed that bacteria were able to attach and proliferate preferentially in areas containing GO at highest levels. Furthermore, GO acts as a general enhancer of cellular growth by increasing cell attachement and proliferation.

The applications of nanopore technology in DNA sequencing, genetics and medical diagnostics were presented in the review on nanopore sensors for nucleic acid analysis of Venkatesan and Bashir [61]. The authors indicated that nanopore analysis is an emerging technique that involves using a voltage to drive molecules through a nanoscale pore in a membrane between two electrolytes, and monitoring how the ionic current through the nanopore changes as single molecules pass through it. This approach allowed charged polymers (including single-stranded DNA, double-strainded DNA and RNA) to be analyzed with subnanometre resolution and without the need for labels or amplification. Recent advances suggested that nanopore-based sensors could be competitive with other third-generation DNA sequencing technologies, and might be able to rapidly and reliably sequence the human genome.

The utilization of graphene multilayers as the gates for sequential release of proteins from surfaces was performed by Hammond *et al* [62]. Protein-loaded polyelectrolyte multilayer films were fabricated using layer-by-layer assembly incorporating a hydrolytically degradable cationic poly(β-amino ester) (Poly 1) with a model protein antigen, ovabumin (ova), in a bilayer architecture along with positively and negatively functionalized GO capping layers for the degradable protein films. Ova release without the GO layers takes place in less than 1h but can be tuned to release from 30 to 90 days by varying the number of bilayers of functionalized GO in the multilayer architecture. The authors demonstrated that

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proteins can be released in sequence with multi-day gaps between the release of each species by incorporating GO layers between protein-loaded layers. This approach provided a new route for storage of therapeutics in a solid-state thin film for subsequent delivery in a time-controlled and sequential fashion.

Singular phase nano-optics in plasmonic metamaterials for label-free single-molecule detection was investigated by Kabashin, Grigorenko *et al* [63]. The authors showed that properly designed plasmonic metamaterials exhibit topologically protected zero reflection yielding to sharp phase changes nearly, which can be employed to radically improve the sensitivity of detectors based on plasmon resonance. By using reversible hydrogenation of graphene and binding of streptavidin-biotin, the authors demonstrated an areal mass sensitivity at a level of fg mm^{-2} and detection of individual biomolecules. The proof-of-concept results of the authors offered a router towards simple and scalable single-molecule label-free biosensing technologies.

With the intention to explore the interface between the research on graphene and the bioscience, Kostarelos and Novoselov [64] outlined three issues of complexity that are interconnected and need to be considered carefully in the development of graphene for use in biomedical applications: material characteristics; interactions of graphene with biological components (tissues, cells, proteins etc) and biological activity outcomes. Concerning the first issue the authors noted that graphene is highly conductive, flexible, and has controllable permittivity and hydrophilicity among its other distinctive properties. These properties could enable the development of multifunctional biomedical devices. Concerning the interactions of graphene with biological components the authors emphasized that the determination of the possible interactions is a key issue to reveal the opportunities offered and the limitations posed. As with any other nanomaterial, biological studies of graphene should be performed with very specific, well-designed, and well-characterized types of materials with definite exposure.

The utilization of graphene-based electroresponsive scaffolds as implants for on-demand drug delivery was proposed by Kostarelov *et al* [65]. The authors fabricated graphene hydrogel hybrid electro-active scaffolds capable of controlled small molecule release. Pristine ball-milled graphene sheets were incorporated into a three-dimensional (3D) macroporous hydrogel matrix to obtain hybrid gels with enhanced mechanical, electrical and thermal properties. These electroactive scaffolds demonstrated controlled drug release in a pulsatile fashion upon the ON/OFF application of low electrical voltages, at low concentrations of graphene (0.2 mg ml^{-1}) and by maintaining their structural integrity. Moreover, the *in vitro* performance of these electroactive scaffolds to release drug molecules without any 'resistive heating' was demonstrated.

Although there was the study of sequencing with graphene nanopores [61], at the present time there still exists the question: whether nanopores created in graphene could fulfill all of the requirements needed for sequencing, as this was asked by Drndic' [66]. Indeed, in all experiments with DNA

detection, the DNA passed through the nanopore too quickly for individual bases to be resolved, and achieving single-base resolution with graphene nanopores remains an unresolved challenge. For any solid-state nanopores-be it graphene, silicon nitride or something else-there is still a variety of fundamental issues that need to be resolved before DNA sequencing with ionic currents could become a reality. For example, should single-or double-stranded DNA be used? Is a specific range of nanopore diameters required, and how precisely will they have to be manufactured? Improvements in the nanopore devices will also be required. In particular, current noise needs to be lowered and signal-to-noise ratios increased at high bandwidths, or the translocation of the DNA needs to be slowed down without more noise being introduced into the signal. There are also more prosaic but crucial details that need to be dealt with: enough devices have to be tested and reproduced by independent labs to draw firm conclusion, a task that requires skill, time and effort.

Simultaneously with above-mentioned careful attitude of Drndic', Kostarelo and Novoselov [67] presented an optimistic point of view on the potential of graphene in biomedical applications. Graphene materials (GMs; a family of materials including pristine graphene sheets, few-layer graphene flakes, GO and many others) offer a range of unique, versatile and tunable proprieties that can be creatively used for biomedical purposes. Graphene applications in biomedicine, even though still in their infancy, can be divided into several main areas: transport (delivery) systems, sensors, tissue engineering and biological agents (for example antimicrobials). The unique properties of graphene to be used in biomedicine are: 2D flat shape, large available area, flexibility, excellent electrical conductivity, absence of a bandgap, aqueous solubility (in the case of GO), versatility of chemical functionlization. The feasible biomedical applications include: highly sensitive biosensors, molecular transporters, coatings/substrates for tissue engineering and implants. The opportunities are: responsive to a wide range of parameters, high sensitivity, multiple read-out routes, ease and speed of degradation. However, there exist also the challenges: unknown cytotoxic limitations, controllable dimensions, determination of *in vivo* biodegradability kinetics.

6. Graphene in energy storage devices

During last five years the research on utilization of graphene in energy storage devices achieved significant progress. The ternary self-assembly of ordered metal oxide-graphene nanocomposites for electrochemical energy storage was demonstrated by Liu *et al* [68]. Previously surfactant or polymer directed self-assembly was widely used to prepare nanostructured metal oxides, semiconductors and polymers, but this approach was mostly limited to two-phase materials, organic/inorganic hybrids, and nanoparticle or polymer-based nanocomposites. In the present work the authors demonstrated a ternary self-assembly approach using graphene as fundamental building blocks to construct ordered

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metal oxide-graphene nanocomposites. A new class of layered nanocomposites was formed containing stable, ordered alternating layers of nanocrystalline metal oxides with graphene or graphene stacks. Alternatively, the graphene or graphene stacks can be incorporated into liquid-crystal-templated nanoporous structures to form high surface area, conductive networks. The self-assembly method can also be used to fabricate free-standing, flexible metal oxide-graphene nanocomposite films and electrodes. The authors investigated the Li-ion insertion properties of the self-assembled electrodes for energy storage and showed that SnO_2-graphene nanocomposite films can achieve near theoretical specific energy density without significant charge/discharge degradation.

The self-assembled graphene/carbon nanotube hybrid films for supercapacitors were fabricated by Dai *et al* [69]. In this work stable aqueous dispersions of polymer-modified graphene sheets were prepared via *in situ* reduction of exfoliated graphite oxides in the presence of cationic poly(ethyleneimine) (PEI). The resultant water-soluble PEI-modified graphene sheets were then used for sequential self-assembly with acid-oxidized multiwalled carbon nanotubes, forming hybrid carbon films. These hybrid films were demonstrated to possess an interconnected network of carbon structures with well-defined nanopores to be promising for supercapacitor electrodes, exhibiting a nearly rectangular cyclic voltammogram even at an exceedingly high scan rate of $1\,V\,s^{-1}$ with an average specific capacitance of $120\,F\,g^{-1}$.

In [70] Ruoff *et al* demonstrated the carbon-based supercapacitors fabricated by activation of graphene. The supercapacitors store electrical charge on high-surface-area conducting materials. Their widespread use is limited by their low energy storage density and relatively high effective series resistance. Using chemical activation of exfoliated graphite oxide, the authors synthesized a porous carbon with a Brunauer–Emmett–Teller surface area up o $3100\,m^2\,g^{-1}$, a high electrical conductivity, and a low oxygen and hydrogen content. This sp^2-bonded carbon has a continuous three-dimensional network of highly curved, atom-thick walls that form primarily 0.6- to 5-nanometer-width pores. Two-electrode supercapacitor cells constructed with this carbon yielded high values of gravimetric capacitance and energy density with organic and ionic liquid electrolytes. The processes used to make this carbon are readily scalable to industrial levels.

The functionalized graphene sheet-sulfure (FGSS) nanocomposite for using as cathode material in rechargeable lithium batteries was synthesized by Liu *et al* [71]. The structure has a layer of functionalized graphene sheets/stacks and a layer of sulfure nanoparticles creating a 3D sandwich-type architecture. This unique FGSS nanoscale layered composite has a high loading (70 wt%) of active material (S), a high tap density of $\sim 92\,g\,cm^{-3}$, and a reversible capacity of $\sim 505\,mA\,h\,g^{-1}$ ($\sim 464\,mA\,g^{-3}$) at a current density of $1680\,mA\,g^{-1}$. When coated with a thin layer of cation exchange Nafion film, the migration of dissolved polysulfide anions from the FGSS nanocomposit was effectively reduced, leading to a good cycling stability of 75% capacity retention over 100 cycles. This sandwich-structured composite

conceptually provided a new strategy to design electrodes for energy storage applications.

In [72] Cui *et al* synthesized graphene-sulfure composite material by wrapping poly(ethylene glycol) (PEG)-coated submicrometer sulfur particles with mildly oxidized GO sheets decorated by carbon black nanoparticles. The PEG and graphene coating layers are important to accommodating volume expansion of the coated sulfur particles during discharge, trapping soluble polysulfide intermediates, and rendering the sulfur particle electrically conducting. The resulting graphene-sulfure composite showed high and stable specific capacities up to $\sim 600\,mA\,h\,g^{-1}$ over more than 100 cycles, representing a promising cathode material for rechargeable lithium batteries with high energy density.

Hierarchically porous graphene was used as lithium-air battery electrode by Zhang *et al* [73]. The authors demonstrated that a novel air electrode consisting of an unsual hierarchical arrangement of functionalized graphene sheets (without catalyst) delivered an exceptionally high capacity of $15\,000\,mA\,h\,g^{-1}$ in lithium-O_2 batteries which was the highest value ever reported. This excellent performance was attributed to the unique biomodal porous structure of the electrode consisting of microporous channels facilitating rapid O_2 diffusion while the highly density of reactive sites for Li$-O_2$ reactions. Further, the authors showed that the defects and functional groups on graphene favored the formation of isolated nanosized Li_2O_2 particles and helped to prevent air blocking in the air electrode. The hierarchically ordered porous structure in bulk graphene enabled its practical applications by promoting accessibility to most graphene sheets in this structure.

In [74] Liu *et al* performed the reversible sodium ion insertion in single crystalline manganese oxide nanowires with long cycle life. The authors prepared single crystalline $Na_4Mn_9O_{18}$ nanowires by a polymer-pyrolysis method. This material showed a high, reversible sodium ion insertion/extraction capacity, excellent cycling ability, and promising rate capability for sodium-ion battery applications.

The tunable 3D pillared carbon nanotube-graphene networks for high-performance capacitance were fabricated and investigated by Dai *et al* [75]. The authors have developed a rational strategy for creating the 3D pillared vertically aligned carbon nanotube (VACNT)-graphene architecture by intercalated growth of VACNT into thermally expanded highly ordered pyrolytic graphite. By controlling the fabrication process, the length of VACNT pillars can be tuned. In conjunction with the electrodeposition of nickel hydroxide to introduce the pseudocapacitance, these 3D pillared VACNT-graphene architectures with a controllable nanotube length were demonstrated to show a high specific capacitance and remarkable rate capability, and they significantly outperformed many electrode materials currently used in the state of the art supercapacitors.

The thin films of carbon nanotubes and chemically reduced graphenes were used for fabricating electrochemical micro-capacitors by Hammond, Shao-Horn *et al* [76]. The authors prepared the structure consisting of chemically reduced graphene (CRG) sheets separated by layer-by-layer-

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assembled multi-walled carbon nanotubes (MWCNTs) for electrochemical micro-capacitor applications. Submicron thin films of amine-functionalized MWCNTs (MWCNT$-$NH$_2$) and CRG were shown to be cross-linked with amide bonds having high packing density of ~70%. These carbon-only electrodes were found to have large volumetric capacitance of ~160 F cm^3 in an acidic electrolyte (0.5 M H$_2$SO$_4$). The electrode capacitance in a neutral electrolyte (1 M KCl) was found much lower, which supported the hypothesis that the observed high capacitances in the acidic electrolyte can be attributed primarily to redox reactions between protons and surface oxygen-containing groups on carbon.

Kaner *et al* [77] performed laser scribing of high-performance and flexible graphene-based electrochemical capacitors (ECs). Although ECs charge and discharge faster than batteries they are limited by low energy densities and slow rate capabilities. The authors used a standard LightScribe DVD optical drive to do the direct laser reduction of graphite oxide films to graphene. The fabricated films were mechanically robust, showed high electrical conductivity (1738 S m^{-1}) and specific surface area (1520 m^2 g^{-1}), and could thus be used directly as EC electrodes without the need for binders or current collectors, as is the case for conventional EC. Devices fabricated with these electrodes exhibited ultrahigh energy density values in different electrolytes while maintaining the high power density and excellent cycle stability of ECs. Moreover, these ECs maintained excellent electrochemical stress and thus held the promise for high-power, flexible electronics.

In [78] Jang *et al* proposed a fundamentally new strategy for reviving rechargeable lithium (Li) metal batteries and enabling the emergence of next-generation safe batteries featuring a graphene-supported Li metal anode, including the highly promising Li–sulfur, Li–air and Li–graphene cells with exceptionally high energy or power densities. All the Li metal anode-based batteries suffer from a high propensity to form dendrites (tree-like structures) at the anode upon repeated discharge/charge. A dendrite could eventually penetrate through the separator to reach the cathode, causing internal short-circuiting and even explosion, the main reason for the battery industry to abandon rechargeable lithium metal batteries in the early 1990s. By implementing graphene sheets to increase the anode surface areas, one could significantly reduce the anode current density, thereby dramatically prolonging the dendrite initiation time and decreasing the growth rate of a dendrite, if ever initiated, possibly by a factor of up to 10^{10} and 10^5, respectively.

The fabrication of anodes for lithium ion batteries from crumpled graphene-encapsulated Si nanoparticles was demonstrated by Huang *et al* [79]. Aqueous dispersion of micrometer-sized GO sheets and Si nanoparticles were nebulized to form aerosol droplets, which were passed through a preheated tube furnace. Evaporation-induced capillary force wrapped GO sheets around Si nanoparti-cles and heavily crumpled the shell. Thus the submicrometer-sized capsules containing Si nanoparticles were wrapped with crumpled graphene shells by a rapid, one-step capillary-driven assembly route in aerosol droplets. The folds and wrinkles in the crumpled graphene coating can accommodate the volume expansion of Si upon lithiation without fracture, and thus help to protect Si nanoparticles from excessive deposition of the insulating solid electrolyte interphase. Compared to the native Si particles, the composite capsules have greatly improved performance as lithium ion battery anodes in terms of capacity, cycling stability, and Coulombic efficiency.

The liquid-mediated dense integration of GMs for compact capacitive energy storage was performed by Li *et al* [80]. Porous yet densely packed carbon electrodes with high ion-accessible surface area and low ion transport resistance are crucial to the realization of high-density electrochemical capacitive energy storage but have proved to be very challenging to produce. Taking advantage of chemically converted graphene's intrinsic micro-corrugated 2D configuration and self-assembly behavior, the authors showed that such materials can be readily formed by capillary compression of adaptive graphene gel films in the presence of a nonvolatile liquid electrolyte. This simple soft approach enabled sub-nanometer scale integration of graphene sheets with electrolytes to form highly compact carbon electrodes with a continuous ion transport network. ECs based on the resulting films can obtain volumetric energy densities approaching 60 W h l^{-1}.

The scalable fabrication of high-power graphene micro-supercapacitors for flexible and on-chip energy storage was performed by Kaner and El-Kady [81]. The rapid development of miniaturized electronic devices has increased the demand for compact on-chip energy storage. Microscale supercapacitors have great potential to complement or replace batteries and electrolyte capacitors in a variety of applications. However, conventional micro-fabrication techniques have proven to be cumbersome in building cost-effective micro-devices, thus limiting their widespread application. The authors demonstrated a scalable fabrication of graphene micro-supercapacitors over large areas by direct laser writing on graphite oxide films using a standard LightScribe DVD burner. More than 100 micro-supercapacitors can be produced on a single disc in 30 min or less. The devices were built on flexible substrates for flexible electronics and on-chip uses that can be integrated with MEMS or CMOS in a single chip. Remarkably, miniaturizing the devices to the microscale resulted in enhanced charge-storage capacity and rate capability. These micro-supercapacitors demonstrated a power density of ~200 W cm^{-3}, which was among the highest values achieved for any supercapacitor.

Porous graphene networks as high-performance anode materials for lithium ion batteries were fabricated by Wei *et al* [82]. The authors obtained porous graphene by CVD using porous MgO sheets as template and demonstrated a high reversible capacity (1732 mA h g^{-1}), excellent high-rate capability and cycling stability for Li-ion batteries. The simple CVD approach offered a new way for large-scale production of porous GMs for energy storage.

Superior micro-supercapacitors based on graphene quantum dots (GQDs) were fabricated by Yan *et al* [83]. The authors demonstrated a new application of GQDs as ideal electrode materials for supercapacitors. To this end, a

GQDs//GQDs symmetric micro-supercapacitors was prepared using a simple electro-deposition approach, and its electrochemical properties in aqueous electrolyte and ionic liquid electrolyte were systematically investigated. Obtained results showed that the as-prepared GQDs micro-supercapacitors had superior rate capability up to $1000\,V\,s^{-1}$, excellent power response with very short relaxation time constant ($\tau_0 = 103.6\,\mu s$ in aqueous electrolyte and $\tau_0 = 53.8\,\mu s$ in ionic liquid electrolyte), and excellent cycle stability. Additionally, another GQDs//MnO$_2$ asymmetric supercapacitor was also built using MnO$_2$ nanoneedles as the positive electrode and GQDs as the negative electrode in aqueous electrolyte. Its specific capacitance and energy density were both two times higher than those of GQDs//GQDs symmetric micro-supercapacitor in the same electrolyte. Obtained results might pave the way for a new promising application of GQDs in micropower suppliers and micro-energy storage devices.

All-graphene core-sheath microfibers for all-solid-state, stretchable fibriform supercapacitors and wearable electronic textiles were prepared by Meng *et al* [84]. The authors developed unique all-graphene core-sheath fibers composed of a graphene fiber core with a sheath for using to prepare flexible electrodes. All-solid-state fiber supercapacitors were fabricated, which can be managed to highly compressible and stretchable spring supercapacitors and can also be woven into a textile for wearable electronics.

Microsupercapacitors (MCs) with high electrochemical performance based on 3D graphene-carbon nanotube carpets (G/CNTCs) were investigated by Natelson, Tour *et al* [85]. The G/CNTCs-based microcapacitors (G/CNTCs-MCs) were fabricated *in situ* on nickel electrodes. The G/CNTCs-MCs showed impedance phase angle of $-81.5°$ at a frequency of $120\,Hz$, comparable to commercial aluminum electrolytic capacitors (AECs) for alternating current (ac) line filtering applications. In addition, G/CNTCs-MCs delivered a high volumetric energy density of $2.42\,mW\,h\,cm^{-3}$ in the ionic liquid, more than 2 orders of magnitude higher than that of AECs. The ultrahigh rate capability of $400\,V\,s^{-1}$ enable the microdevices to demonstrate a maximum power density of $115\,W\,cm^{-3}$ in aqueous electrolyte. The high-performance electrochemical properties of G/CNTCs-MCs can provide more compact ac filtering units and discrete power sources in future electronic devices. These elevated electrical features are likely enabled by the seamless nanotube/graphene junctions at the interface of different carbon allotropic forms.

Macroscopic nitrogen-doped graphene hydrogels for ultrafast supercapacitors were synthesized by Chen *et al* [86]. The authors demonstrated a convenient hydrothermal process for controlled synthesis and structural adjustment of the nitrogen-doped graphene hydrogel (GN-GH), which can be readily scaled-up for mass production, using organic amine and GO as precursors. The organic amine was used not only as a nitrogen source to obtain the nitrogen-doped graphene. The use of organic amine was an important modification to control the assembly of graphene sheets in the 3D structure. The inner structure of GN-GHs and the content of nitrogen in graphene were easily adjusted by organic amine, and the

supercapacitor performance of the typical product could be remarkably enhanced. Even at an ultrafast charge/discharge rate of $180\,A\,g^{-1}$, a high power density of $205\,kW\,kg^{-1}$ can be obtained. In addition, at a current density of $100\,A\,g^{-1}$, 95.2% of its capacitance was retained for 4000 cycles. Thus the present nitrogen-doped graphene hydrogels may have potential applications as ultrahigh power density capacitors in the vehicle, lift, and also other devices at high rates.

In [87] Mendoza-Sánchez *et al* demonstrated the manufacture of scalable ultra-thin and high power density graphene EC electrodes by aqueous exfoliation and spray deposition. Cyclic volt-ammetry and galvanostatic charge-discharge experiments revealed a combination of electric double layer and pseudocapacitive behavior that, unlike many graphene-oxide derived electrodes, was maintained to unusually high scan rates of $10\,000\,mV\,s^{-1}$, reaching a maximum capacitance of $543\,\mu F\,cm^{-2}$ and with a capacitive retention of 57% at $10\,000\,mV\,s^{-1}$. The performance of graphene electrodes was contrasted with carboxylated single walled nanotubes that showed a sharp decrease in capacitance above $200\,mV\,s^{-1}$. Electrochemical impedance spectroscopy analysis showed a fast capacitor response of $17.4\,ms$ for as manufactured electrodes which was further improved to $2.4\,ms$ for surfactant-free 40 nm thick electrodes. A maximum energy density of $75\,nW\,h\,cm^{-2}$ gradually decreased as power density increased up to $2.6\,mW\,cm^{-2}$. Graphene electrodes showed 100% capacitance retention for 5000 cycles at the high power scan rate of $10\,000\,mV\,s^{-1}$.

Recently Dai *et al* [88] performed a comprehensive study on scalable synthesis of hierarchically structured carbon nanotube-graphene fibers for capacitive energy storage with following contents: synthesis of carbon hybrid microfibers, structural characterization of carbon hybrid microfibres, electrochemical characterization of fiber electrodes, testing of all-solid-state micro-supercapacitors, and utilization of multiple micro-supercapacitors to power nanosystems. The results of this work can be summarized as follows:

The authors have developed a scalable method to continuously produce carbon nanofibers with hierarchical structures comprising nitrogen-doped RGO and acid-oxidized single-walled carbon nanotube. Directed assembly of these two carbon components within the microfibre confinement in the presence of ethylenediamine led to the formation of 3D pillared assemblies along the fiber exhibited high packing density and large ion-accessible surface area, as is desirable for high-volumetric-performance micro-supercapacitors. An all-solid-state micro-supercapacitor exhibited a long cycle life (93% device capacitance retention over 10 000 cycle) and an ultraghigh volumetric energy density of $\sim6.3\,mW\,h\,cm^{-3}$, about tenfold higher than those of state-of-the-art commercial supercapacitors and even comparable to the $4\,V/500\,\mu A$ h thin-film lithium battery. The micro-supercapacitors delivered a maximum power density of up to $1085\,mW\,cm^{-3}$, a value comparable to that of typical commercially available supercapacitors and more than two orders higher than the power density of lithium thin film batteries. Fabricated micro-supercapacitors can be integrated either in series or in parallel to meet the energy and power needs in various potential

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applications, including portable flexible optoelectronics, multifunctional textiles, sensors and energy devices.

Very recently Cui *et al* [89] prepared phosphorene-graphene hybrid material as a high-capacity anode for sodium-ion batteries owing to following motive: Sodium-ion batteries are attracting significant attention as an alternative to lithium-ion batteries because sodium source do not present the geo-political issues that lithium sources might. Although recent reports on cathode materials for sodium-ion batteries have demonstrated performances comparable to their lithium-ion counterparts, the major scientific challenge for a competitive sodium-ion battery technology is to develop viable anode materials. The content of present work includes the research on mechanisms of solidation in black phosphorus, fabrication of phosphorene-graphene hybrids and electrochemical testing of phosphorene-graphene hybrids. The results of present work can be summarized as follows:

The authors have developed a sandwiched phosphorene-graphene hybrid material that shows high specific capacity, rate capability and cycle life as an anode material in sodium-ion batteries. The graphene layers provide an elastic buffer layer to accommodate the expansion of phosphorene layers along the y and z axial directions during the alloy reaction to Na$_3$P. The phosphorene nanosheets, with increased interlayer distance, offer a short and effective diffusion distance for sodium ions. Moreover, the graphene both enhances the electrical conductivity of the material and provides a preferential path way to the electrons generated by the redox reaction of phosphorene. The facile synthesis and superior electrochemical properties of prepared sandwiched phosphorene-graphene hybrid could render it a suitable anode material for sodium-ion batteries.

7. Conclusion and discussion

In the present review we have summarized the results of a large number of research works on promising applications of graphene and graphene-based nanostructures. The main results can be classified according to five scientific subjects: graphene-based transparent and flexible conductive films for displays and electrodes; conductive inks for printed electronics; graphene-based separation membranes; graphene applications in bio-medicine; graphene in energy storage devices.

Beside above-mentioned widespread applications of graphene and graphene-based nanostructures, there exist also other less widespread, but perhaps not less important applications of graphene and graphene-based nanomaterials, such as: utilization of graphene in anticorrosion technology [90]; production of thermally insulating and fire-retardant light-weigh anisotropic foams based on nanocellulose and GO [91]; aerospace applications of graphene [92] etc.

Thus, graphene science and technology field was firmly proven to be a '*cornucopia of potential applications*', as this was predicted by Novoselov and Geim [2].

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