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Review Article

Graphene research and their outputs: Status and prospect

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ABSTRACT

Among various 2D materials, graphene has received extensive research attention in the last 2–3 decades due to its fascinating properties. The discovery of graphene provided an immense boost up and new dimension to materials research and nanotechnology. The multidisciplinary characteristics of graphene have a wide range of applications from health to aerospace. Modern graphene research has been directed towards the exploration of new graphene derivatives and their utilizations for fabrication of products and devices. The enhancement of graphene properties by functionalization or surface modification is another innovative approach. However, like other 2D materials, graphene research also needs amendments and up-gradation in the light of recent scientific output. In this contribution, we have reassessed the recent research output on graphene and graphene-based materials for applications in different fields. For the reader's comfort and to maintain lucidity, first, some fundamental aspects of graphene are discussed and then recent overviews in graphene research are explored in a systematic manner. Overall, this review article provides an outline of graphene in terms of fundamental properties, cutting-edge research and applications.

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1. Introduction

Our world is full of materials and these are the backbone of our modern society. Among these materials, carbon-based materials are popular and play a crucial role in human civilization. In the present situation, it is not an overstatement by saying that without carbon materials, our life is impossible on the planet earth. Since 2004, graphene is treated as one of the most wonderful achievements in the field of science and technology [1]. The hexagonal crystalline single layer of graphite (the simplest form and one of the most important crystalline allotropes of carbon atoms having a C–C bond distance of 0.142 nm) has received massive attention in the field of sensors, biomedical, composite materials and microelectronics [1–3]. A wide range of applications such as transparent conductive films, ultra sensitive chemical sensors, thin-film

transistors, quantum dot devices and anti-corrosion coverings has been tested and is well established [1–5]. However, industrial-scale production of graphene for these overwhelming applications strongly depends on the easypath of graphene production which was a bottleneck in the past and which, fortunately, has been improved recently.

Graphene is the only allotrope of carbon in which every carbon atom is tightly bonded to its neighbours by an unique electronic cloud that raises several exceptional questions to quantum physics [3,5]. Along with the unique quantum hall phenomenon, graphene itself exists in several forms like graphene nanoribbons, nanosheets, nanoplates and 3D graphene. Each of them displays amazing applications. As mentioned above, the electronic and quantum properties of graphene are still a matter of fundamental studies. Each carbon atom in graphene is sp^2 hybridised, having three bonds, related to different neighbour carbon atoms (Fig. 2). The sp^2 hybridisation is a combination of s, p_x , and p_y orbitals [1–3]. In the hexagonal phase, three distinct carbon atoms fortify covalently to each carbon atom and all of them are essentially sp^2 hybridised, resulting for each carbon atom in one free electron. The p_z orbital holds this free electron and this p-orbital lies above the plane and forms the pi bond [1–3]. Interestingly, the p_z orbital of

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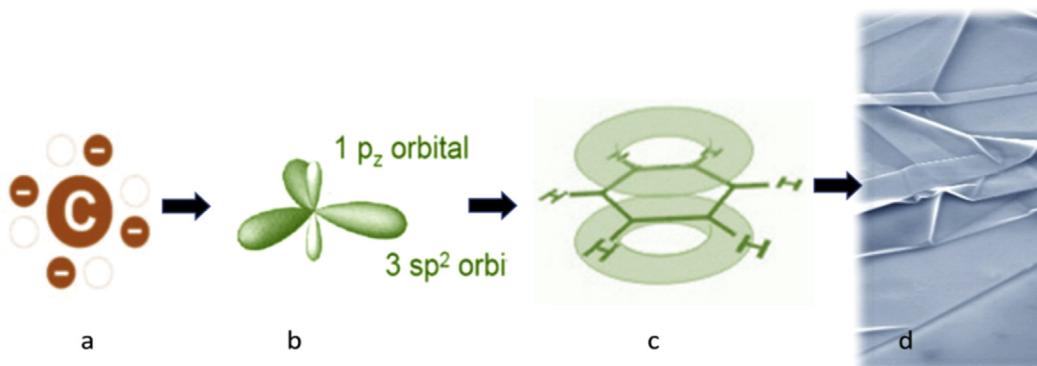


Fig. 1. (a–c) Fundamental aspect of graphene bonding properties and (d) SEM image of single-layer graphene.

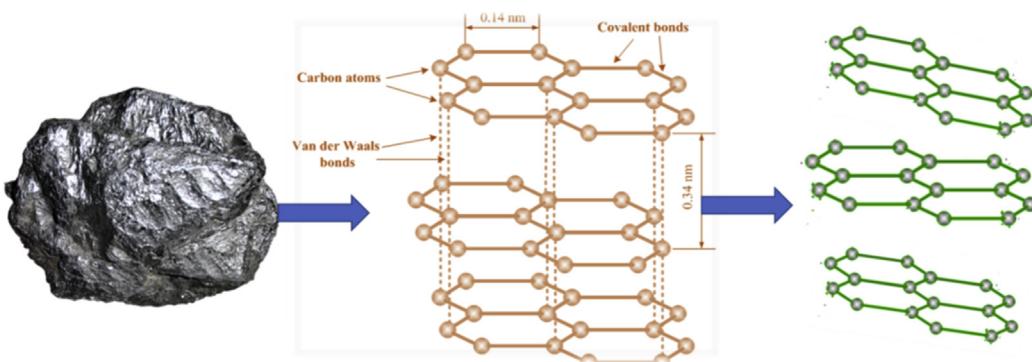


Fig. 2. Schematic depictions about the Origin (presenting the transformation) of graphene from graphite and peculiar structure of graphite and graphene.

graphene plays a vital role in the chemical and physical behaviour of this miraculous material [1–3]. The presence of a zero bandgap is a drawback and unique feature of graphene, which opens several new opportunities to develop artificial humanmade materials with tunable bandgaps that can be of use for the next-generation of computing.

The two pi-electrons that are present in every hexagon of the graphene sheets are responsible for the exceptional conductivity of graphene. Due to the tight packing of atoms in the crystal lattice of graphene, it is highly stable, but only in case its size is less than 20 nm, otherwise it is quite unstable thermodynamically except for some specific conditions [2,3]. Due to the gigantic reputation of graphene and its derivatives, several original research articles and reviews have been produced by researchers all over the world [1,4–6]. Now, a timely update on recent progress in graphene research is needed for the academic and industrial scientists. In this aspect, the current review article aims to serve the science community.

The current review article provides a brief research update on graphene/graphene-related materials and their engineering applications in different fields of science and technology. For the reader's comfort and to maintain lucidity, first, some fundamental aspects of graphene, graphene oxide, graphene quantum dots, graphene nanoribbon etc. are discussed in brief. Then, recent signs of progress in Materials Engineering concerning graphene covering materials fabrication, properties and applications are pointed out in detail. After a decade of graphene research, a huge number of review articles has already been published on graphene and related materials. In addition, each section of this review article has copious new bibliography associated with the graphene research around the globe, which permits further reading and assessment.

2. Structure and properties of graphene

The electronic structure of graphene's basic unit is presented below (Fig. 1) for a better understanding of the electronic properties of graphene and their derivatives.

It is interesting to note that structural holes permit the phonons to go unobstructed, which leads to a significant thermal conductivity in graphene. However, this property has not been observed in graphene oxide and other derivatives of graphene owing to the altered band structure [2,3]. The classification of graphene as metal, non-metal or semimetal is still a matter of debate and requires further research [3]. But, due to the presence of metallic layers with very low bandgaps, it can be treated as a semimetal with an exceptional theoretical background [2,3]. As a whole, it has numerous remarkable characteristics that are not observed for other non-metallic materials as well as for the exiting ideal semimetals. The properties of graphene solely depend on the number of layers and the defects present in the graphene layers. For example, the theoretical surface area of pristine graphene is ~2630 m²/g which is much higher than the surface area of carbon black (850–900 m²/g), carbon nanotubes (100–1000 m²/g), and many other analogues [1–3]. On the otherhand, the surface area of a few layers graphene, graphene oxide, and many other derivatives are much less in comparison to single-layer graphene [1–3]. Due to these exceptional properties, graphene acts as a perfect material for many modern technologies including electronic applications along with many other materials as substrate or template [3].

One of the significant properties of graphene is its unparalleled electrical conductivity, which is highly essential for next-generation technologies. As mentioned above, the zero band gap of graphene and its engineered analogue with little overlap

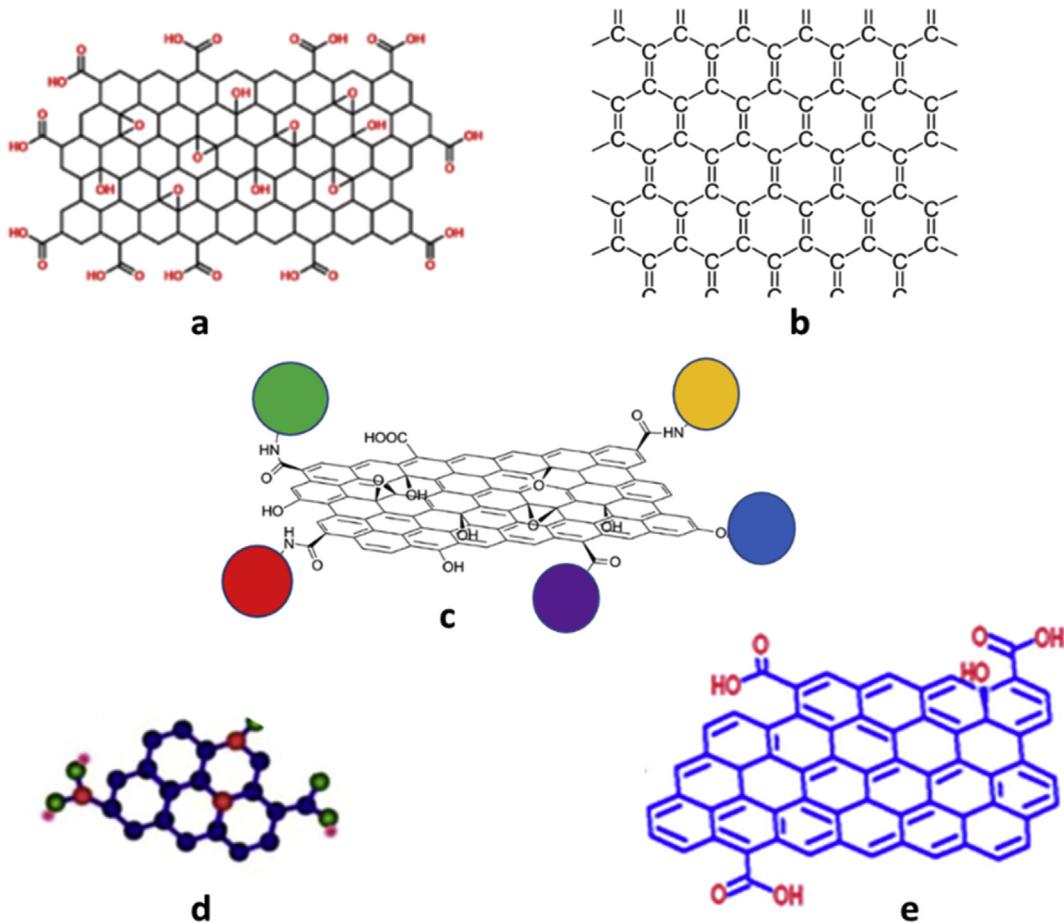


Fig. 3. Different forms of graphene: (a) graphene oxide (b) pristine graphene (c) functionalized graphene (d) graphene quantum dot, and (e) reduced graphene oxide.

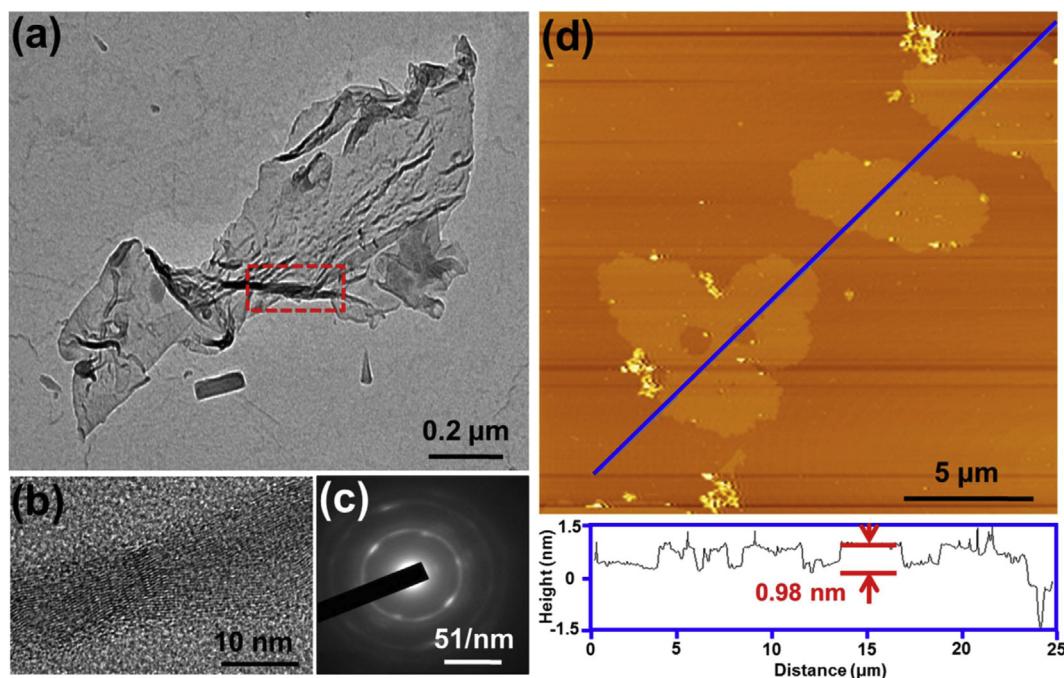


Fig. 4. (a) TEM image, (b) HRTEM image, (c) SAED image, and (d) AFM image of graphene from GS-2 after removal of the silica (Reproduced with permission from ref. [2]).

between valence and conduction band opened huge possibilities for the applied and fundamental research [1–3]. It is mainly due to electrons, which behave as massless relativistic particles. In recent times, many scientists around the globe are working in the same area for the development of next-generation 2D materials [1–3]. Many researchers reported that graphene could show several charge transporters and carriers up to 10^{13} cm^{-2} with a mobility of $1 \times 10^4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temperature and it could be tuned according to real-time applications [1–4]. It has also been explored that this mobility can increase up to $2 \times 10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at low temperature under certain boundary conditions [4]. Since the charge carriers in graphene behave as in semi-metals, commonly called massless Dirac Fermions, graphene shows a half-integer Quantum Hall Effect (QHE) [1]. In this way, the Quantum Hall Effect in graphene is unique and shows an exceptional relation between charge, thickness, and speed of the charge carriers. Owing to these properties of graphene, it has been found that the electrical resistance of a graphene sheet is much less than that of silver, which is highly favourable for electronic applications [5]. Such prototype devices and electronic gadgets are in the development process and are expected to be available in the market within the next 5 years [4,5]. It has also been investigated that when the magnetic field acts perpendicular to the conducting materials, especially to the 2D system's plane and along the axis, then the QHE takes place which strongly supports the exceptional Hall Effect in the case of graphene [1,2]. The electron reversion produces

discrete band levels due to the two-dimensional nature of graphene; Hence, these levels are called Landau levels (the charge carriers occupy these levels). However, it remains a matter of in-depth research for graphene and their analogous materials [1,2].

Further, graphene has excellent optical, thermal, and mechanical characteristics [6]. It has been found that up to 2.3% of white light is absorbed by each layer of graphene with a reflectance of less than 0.1%. Thus, the pure single graphene layer is highly transparent along with a high degree of flexibility [6]. There is a linear relationship between the absorbance and the number of layers of graphene; consequently, as the number of layers increases in graphene, the absorbance increases rapidly [6]. Theoretically, at room temperature, single-layer graphene can show a thermal conductivity of $3000\text{--}5000 \text{ W m}^{-1} \text{ K}^{-1}$. Scientists are still searching for the origin of such an exceptional property in graphene. Herein, it can be mentioned that depending on the nature of the substrate, this thermal conductivity can be reduced to $600 \text{ W m}^{-1} \text{ K}^{-1}$ even for single-layer graphene [1,2]. It has also been demonstrated that the mixture of ^{12}C and ^{13}C has a remarkable value of thermal conductivity of graphene [6]. Such a kind of dissimilar variation of thermal conductivity is due to the dissemination of phonons at the interface of the graphene gallery which blocks their movement. In single layer graphene the pathway of phonons is different [1–4]. Indeed, even at this lower conductivity, graphene performs much better as compared to copper (Cu). Thus, graphene is the strongest and best conductive material. In particular, a single layer of graphene can

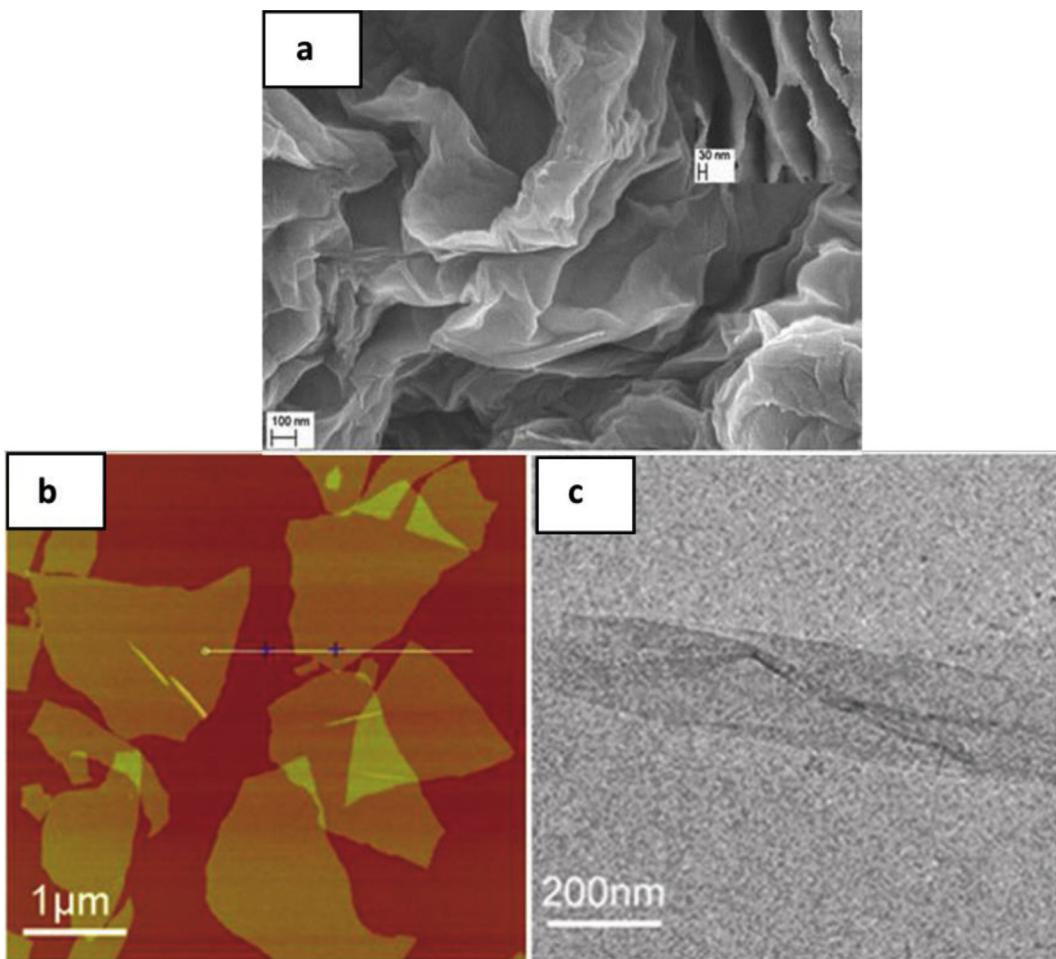


Fig. 5. The (a) SEM, (b) AFM, and (c) HRTEM micrographs of chemically produced graphene oxide showing the wrinkled morphology of few-layer graphene oxides (Reproduced with permission from ref. [12,13]).

withstand up to 42 N m^{-1} of stresses, with Young's modulus of 1.0 TPa [6].

3. Graphene-based nanostructures

Pure graphene contains a monolayer of carbon atoms as discussed in the previous section. These monolayer layers commonly exist as an ultrathin film, especially when these are pasted with the help of templates [2,3]. These graphitic layers can be utilized in their solitary form. Further, it can be skinned off and redeposited onto the substrate for electronic applications [1]. It is notable that including powder form of these nanosystems, graphene can also be seen in other forms as the derivatives of graphite. Different forms of graphene include GO (graphene oxide), GNPs (graphene nanoplatelets), GNRs (graphene nanoribbons), rGO (reduced graphene oxide), QDs (graphene quantum dots) and also graphene empowered items like graphene ink, graphene masterbatches etc. [7]. Since the inception of graphene, various methods have been developed for its synthesis. Among them, three synthetic approaches have been adopted frequently: (1) Chemical Vapor Deposition (CVD), (2) Mechanical cleavage from natural graphite, and (3) Chemical methods [7,8]. However, these methods haven't proven to be commercially viable yet [8]. The CVD method is very useful for pure and single-layer graphene production while the oxidation-reduction approach using graphite is one of the simplest and inexpensive approaches for the production of graphene and their derivatives [7,8]. However, the number of layers and defects in graphene can be controlled using the CVD approach, but the same is not possible in the case of Hummer's method (oxidation-reduction using graphite). The different forms of graphene are presented in Fig. 3.

3.1. Monolayer graphene film

Single-layer, pristine graphene production mainly in bulk amounts is a critical task. Yet, CVD is the most widely recognised strategy for single-layer graphene preparation when it is targeted for sensing flexible electronic and theoretical studies [2,3,8]. Additionally, various techniques have been adopted for graphene film preparation, including chemical reduction, mechanical exfoliation, thermal exfoliation, and epitaxial growth [4]. The CVD strategy proceeds in a reaction assembly in which substrate material is framed; volatile carbon atoms are consolidated and accumulated at the surface of the substrate and disused gases are directed out. The process has been discussed elsewhere, and in this

paper we will give an outlook of the same [8]. It is notable that temperature is an important factor that influences the reaction during the deposition process [3,4]. Though the chemical deposition strategy forms high-quality and pure graphene films, it cannot be used for commercial applications owing to the high cost and low production yield [3,4,8]. The CVD methodology for graphene development is a two-stage process [8,9]. Pyrolysis of precursor material is the initial step of this procedure which manages the development of carbon atoms on the surface of the substrate material (selection of substrate materials in the case of CVD is an important step) [8,9]. The second step is a heat-involving stage which manages the aggregation of separated carbon atoms on the substrate (with the help of an impetus), which forms a solitary layer structure [10]. In this technique, a metal impetus is required. In this procedure, a large amount of heat is required to break the carbon–carbon bonds (carbon–carbon single bond = 347 kJ mol^{-1} , carbon–carbon double bond = 614 kJ mol^{-1} , carbon–carbon triple bond = 839 kJ mol^{-1} , carbon–hydrogen bond = 413 kJ mol^{-1}). Graphene films framed by the CVD strategy have a wide range of characteristics depending on the layer thickness and the edge properties [11]. Among many substrates for graphene production using CVD, Copper is known to yield a high level of graphene [11,12]. Cu shows a dual nature as it acts as catalyst and as substrate. There is a solid affinity between the carbons and Cu that permits the simple growth of a single graphene layer at the surface. For easy removal of a single layer, CuO can be embedded in the middle of graphene layers [12]. Dealing with Cu substrate can likewise revise the surface morphology of the substrate–catalyst and is acknowledged to deliver graphene with fewer imperfections [12]. Recently Yang et al. produced a high-quality graphene silica substrate via a facile soft-hard template approach. A few results are presented in Fig. 4.

3.2. Graphene oxide (GO)

Graphite is a 3D material which is organised and built up by millions of graphene layers [13]. Through an oxidation process, oxygen-containing functional groups are attached to the surface of graphite and thus converting the graphite to graphite oxide [1,13]. After sonication of graphite oxide, a single or a few-layer graphene, called graphene oxide (GO), is produced (Fig. 5). What's more, it likewise functionalizes the graphene surface with various sorts of oxygenated functional moieties [1,13,14]. These diverse functional moieties on the surface of the graphene layers enable the partition of layers in segments and the hydrophilicity [13,14]. Because of this

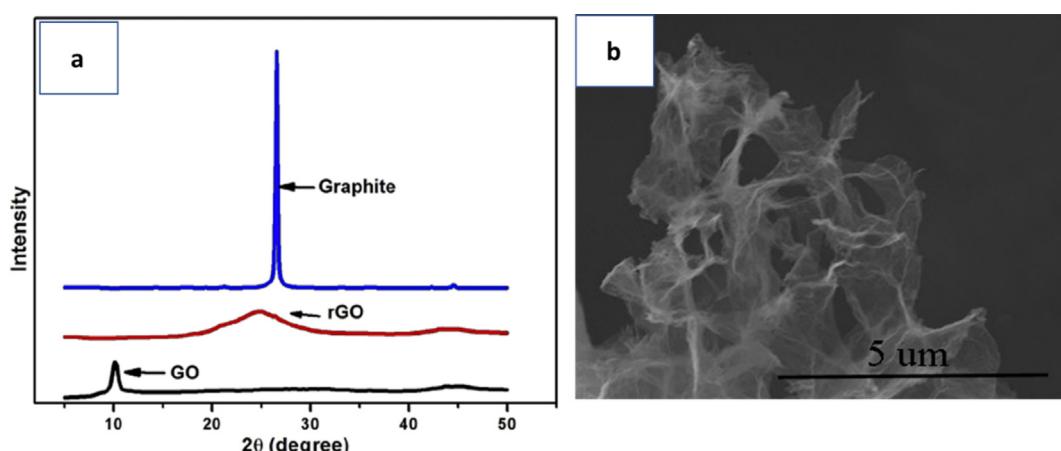


Fig. 6. (a) XRD spectra of graphite, reduced graphene oxide, and graphene oxide; (b) TEM image of reduced graphene oxide (Reproduced from ref. [24]).

GO hydrophilicity, an ultrasonic treatment yields a single or a few graphene layers which are exceedingly steady in deionised water and other solvents [15]. It is important to note that graphite oxide and graphene oxide are different from each other. While graphite oxide is a multilayered system, the graphene oxide is a few- or a single-layer system [1,14,15]. The graphite oxide interlayer separation is 6.35 Å. However, in liquid, it increases from 6.35 to 11.6 Å. The characteristics of graphene oxide can be altered by functionalization on the basis of the specific application. The existence of both the electron-rich oxygen species and the electron-rich graphene backbone are favourable for various applications from materials chemistry to quantum physics [1,16,17]. Due to the low electrical conductivity of GO, it offers a great applicability for drug delivery and also can be used as a nanofiller for polymer composites [1,17]. GO is equally dissolvable in numerous solvents, including both synthetic and natural fluids. However, it is vastly soluble in polar solvents along with some other solvents as well [1,18].

3.3. Reduced graphene oxide (rGO)

GO can be transformed into reduced graphene oxide (rGO) through a reduction process [18,19]. There are numerous techniques for the conversion of GO to rGO and each developed method has its own advantages and disadvantages [1,2]. All these methods can be divided into three classes: chemical reduction, thermal reduction, and electrochemical reduction [20]. The chemical reduction method is suitable to produce rGO with a high surface area and excellent electrical conductivity [19,20]. The chemical reduction using hydrazine is also a highly acceptable method, but it causes minimal N-doping on graphene sheets during reduction [21]. However, the production of rGO through a thermal reduction process yields rGO in bulk amounts within a short period of time [19,20]. Unfortunately, the heating effect can damage the graphene platelets' structure and can release CO₂. It has also been found that the mass of GO is reduced up to 25–30% [21]. Moreover, in this synthesis process, the incorporation of imperfections and vacancies also affects the mechanical strength of rGO. Apart from these processes, there are some other synthetic approaches that are also adopted such as a vapour treatment, toughening, laser and microwave reduction etc. Numerous commercial methods to produce nanoplates of reduced graphene oxides have also been developed [19–21].

The chemical reduction is a versatile synthetic approach. However, this approach can frequently result in a low yield and, as a profound shortcoming, uses toxic materials like hydrazine. In contrast, thermal reduction produces rGO with a high surface zone that is near the surface zone of pure graphene. But, the extreme

heating treatment creates a high-pressure of carbon dioxide which can destroy the well-organized graphene structure. The structural damage would include huge voids that block the mechanical toughness of the graphene sheets. The electrochemical reduction has been considered to be the best choice in terms of quality. The rGO produced via this route is comparable with that of pure graphene [22]. In the electrochemical procedure, the substrates (mainly ITO or glass) are covered with a layer of GO, and a current is passed through the material (by means of terminals at either end of the substrate). The rGO formed by this technique has appeared to have a high carbon to oxygen ratio and demonstrates similar conductivity as that of silver. Additionally, non-toxic materials are being used in this process [23]. This route does anyway experience some issues concerning the versatility of the technique [22,23]. Once the rGO is formed, it can be functionalized for the desired applications. The characteristic feature of rGO and GO are shown by the XRD and TEM analysis in Fig. 6.

3.4. Graphene nanoplatelets (GNPs)

Graphene nanoplatelets (GNPs) are a new form of carbon species which are formed from graphite under certain conditions. These nanoparticles are mostly found in the range of 1–15 nm in thickness and up to 100 μm in lateral size [2–5]. The synthesis of GNPs is performed with the assistance of micromechanical breaking of graphite and just offers the development of graphene nanocomposites with enhanced barrier properties [2–5]. GNPs have a percolation threshold for conductivity of 1.9 weight percent in a thermoplastic matrix. Conductivity within densities of 2–5 weight percent results in insufficient levels to give electromagnetic shielding [5]. GNPs can provide enough conductivity after mixing with glass fibres, polymers, or another matrix. Moreover, GNPs can also enhance the mechanical characteristics, including stiffness and tensile strength of different composites due to the strong interfacial interaction of nanoplates with the matrices [2–5]. GNP in bulk quantities can be synthesized by mechanical cleavage after chemical reduction of GO, but it needs vacuum conditions [2–5]. Plasma exfoliation is another methodology for the production of GNPs in bulk amounts for commercial applications. The preferred stand-point of plasma exfoliation is that it can shape and functionalize the GNPs according to the need of surface manipulation [25]. All these points of interest make the material reasonably useful for modern execution with a wide assortment of accessible, functional groups for example, –OH, –COOH, NH₂, N₂, and F [25]. Because of the low cost of input materials, plasma purging and easy functionalization, the GNPs can eventually be a cost-effective material as compared to

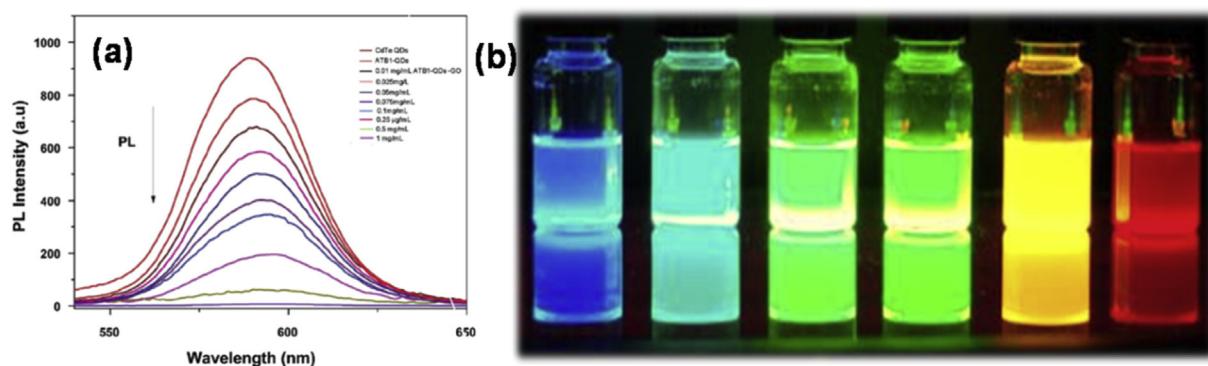


Fig. 7. Characterisation of graphene oxide quantum dots: (a) monitoring the fluorescence quenching of quantum dots at various graphene oxide ($0.01\text{--}1\text{ mg ml}^{-1}$) concentrations using PL spectroscopy, (b) Images of light-emitting of specific frequencies if electricity or light is applied to quantum dots (Reproduced with permission from ref. [24]).

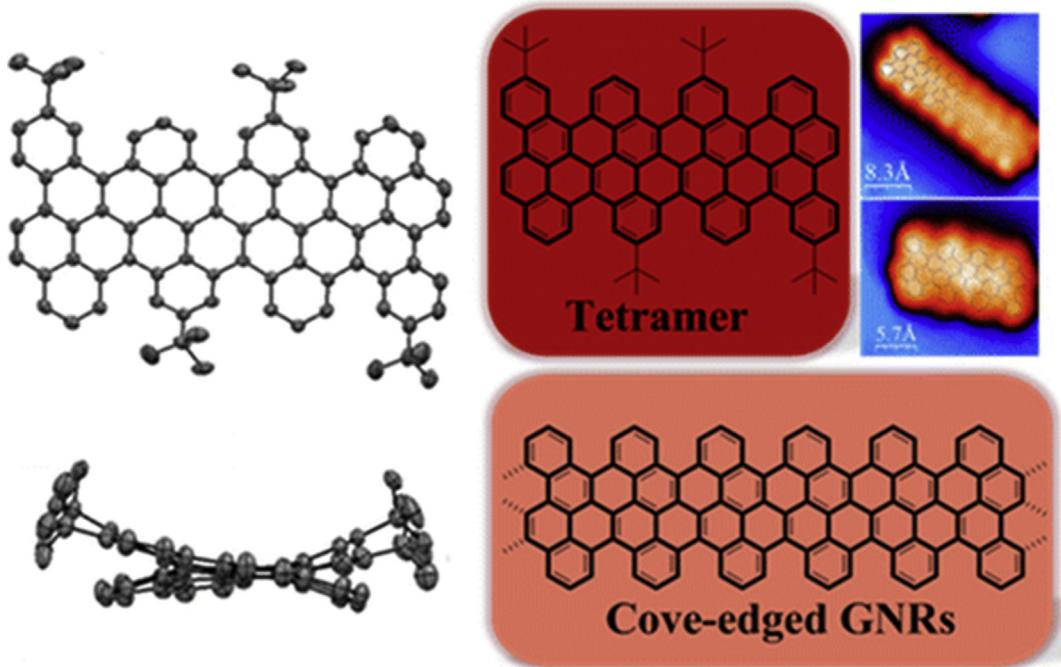


Fig. 8. Different forms of GNRs and their crystal lattices (Reproduced with permission from ref. [33]).

CNTs and single-layer graphene at large scale for similar applications with better performance [25].

3.5. Graphene and graphene oxide quantum dots

Graphene and graphene oxide quantum dots (GQDs) can be set up into a wide range of structures, from single-layer to many layers [26,27]. In the past few years, numerous methods have been introduced for GQDs preparation including electron beam lithography, chemical synthesis, electrochemical preparation, GO in-situ reduction, soft template processes, CVD and hydrothermal methods [26,27]. In general, GQDs possess desirable properties like low toxicity, stable photoluminescence, tunable physical properties and high chemical stability [26,27]. Additionally, GQDs demonstrate comparable characteristics to different kinds of quantum dots, especially in the case of inorganic quantum dots [26]. Similar to the other nanomaterials derived from graphene, GQDs display an enhanced surface area, great straight dispensability, and high charge bearer versatility [26]. GQDs likewise displays a proficient gap transporting capacity, forming them to productive materials for opening transport layers [26,27]. These materials are frequently applied to both electronic and optoelectronic applications [27]. Moreover, GQDs display significant characteristics in different applications such as bioimaging, cancer therapeutics, temperature sensing, drug delivery, surfactants, and LEDs light converters [26,27]. Various spectroscopic studies demonstrate that the GQDs are multi-layered graphene consisting of up to 10 layers of 10–60 nm size reduced graphene oxide. The desired dimension of GQDs can be created by a bottom-up strategy (because of the capacity to restrain the band gap). However, the product itself can be unpredictable, which needs stringent conditions. Top-down strategies have been considered as a substantially more straightforward and less expensive way. The breakdown of graphite oxide can create Single-layered GQDs. However, the yields are not up to the standard [26,27]. GQDs can likewise be prepared by the breakdown of carbon contour incorporated CNTs, fullerenes, and carbon fibres. Different strategies have been implemented including ultra-

sonication, microwave illumination, radical techniques and hydrothermal/solvothermal methods [27]. Even though GQDs have the capacity to be used in different applications, the creation of GQDs at an industrial level in a proficient way is the main problem of today's world [26,27]. The characterisation of graphene oxide quantum dots is depicted with the help of PL spectroscopy. A very important application of GQD is monitoring the fluorescence quenching of quantum dots for a specific application (Fig. 7).

GQDs can be utilized in different applications including light-emitting diode (LED) screen, lithium-ion batteries, super-capacitors, and solar cells [28]. Nowadays, GQDs-LEDs is a leading research field to save electricity and promote low light-weight electronic devices which can save 10–15% electricity [28]. GQDs-LEDs have been created by drawing CVD-developed graphene with copolymers, trailed by the manufacturer with graphite intercalation compounds [28]. The approach forms the low oxygenated functional group, low poisonous quality, and ecologically protected graphene flakes.

3.6. Graphene nanoribbons (GNRs)

At present, many forms of graphene have been developed and GNRs is one of them. It is a quasi 1D form of graphene having an ultra-thin width [28,29]. Graphene nanoribbons are also known as nano-graphite ribbons. These are the strips of graphene having a width of less than 2–5 nm [29]. GNRs were first extensively studied by Prof. Mitsutaka Fujita and his co-workers who investigated the effect of nano-scale size on the transport properties of graphene [29]. GNRs can be formed from graphite in bulk quantity through the anatomy process or by unzipping carbon nanotubes along with many other recently developed procedures. In the unzipping process, multi-walled carbon nanotubes were unzipped by the action of KMnO₄ and H₂SO₄ [29,30]. GNRs show tuneable electrical characteristics depending on the size of nanoribbons, edge morphology, edge defect, and type of functionalization on the GNR [29]. In zigzag edges, each progressive edge is inverse to the previous. Zigzag nanoribbons are semiconducting and exhibit spin-polarised edges

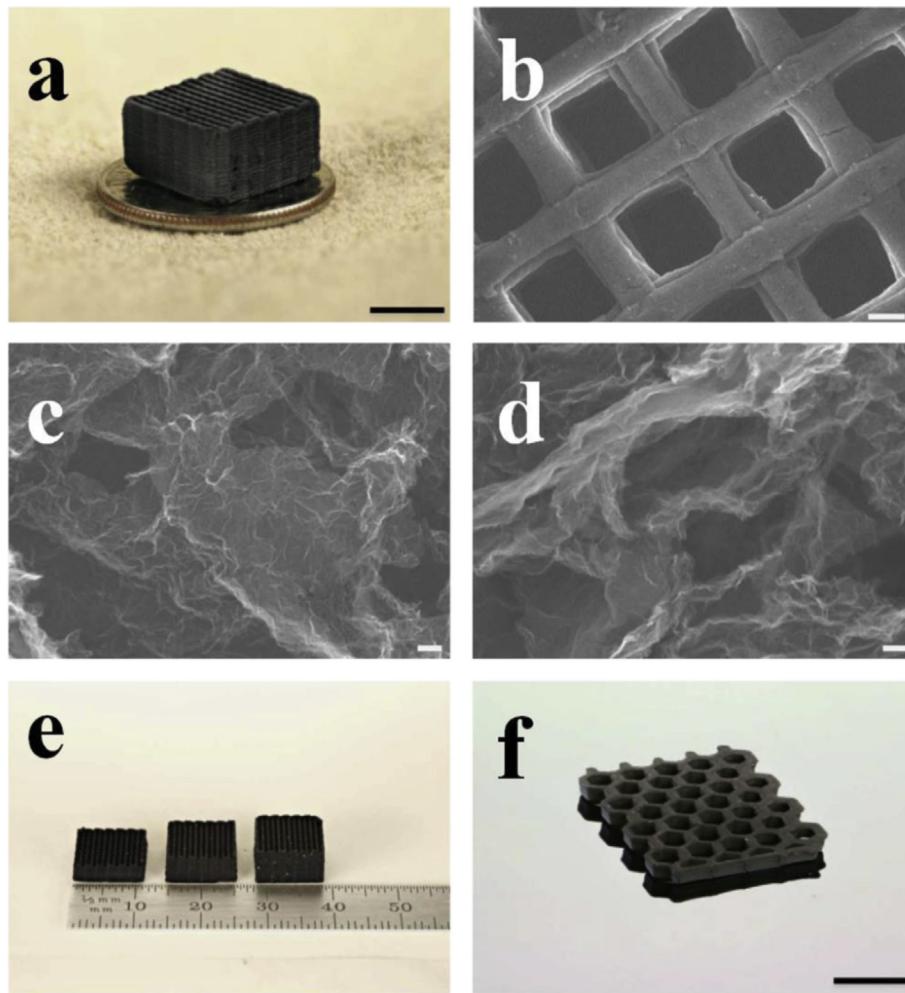


Fig. 9. Morphology and structure of graphene aerogels: (a) Optical image of a 3Dprinted graphene aerogel microlattice, (b–d) SEM images, (b) A 3D printed graphene aerogel micro lattice, (c) Graphene aerogel without R–F after etching, (d) Graphene aerogel with 4wt%R–F after etching. (e–f) Optical images, (e) 3D printed graphene aerogel micro lattices with varying thickness, and (f) A 3D printed graphene aerogel honeycomb. Scalebars, 5 mm (a), 200 nm (b), 100 nm (c,d), 1 cm (f) (Reproduced with permission from ref. [33]).

[29,30]. Due to the gap, there is an unusual antiferromagnetic coupling between the magnetic moments at the inverse edge carbon atom. This gap size is inversely related to the ribbon width. Its performance can be traced back to the spatial distribution characteristics of the edge-state wave functions and the mostly local character of the exchange interaction that arises from the spin polarisation [29,30]. Therefore, the quantum confinement, inter-edge super-exchange, and intra-edge direct exchange interactions in zigzag GNR are vital factors for its magnetism and bandgap [30]. The edge magnetic moment, bandgap, and magnetic moment of zigzag GNR are reversely related to the amount of electron/hole, which can be controlled by suitable modification [30]. These characteristics make the GNRs suitable for electronic purposes. GNRs anode exhibit a reversible capacity of 1130 mAh g^{-1} , with a coulombic efficiency of >98 %which makes it a unique material and quite distinct from graphene [30]. GNRs are produced by different synthetic strategies as discussed above. But the most frequently used technique includes the unfastening of the walls of MWCNTs using Na and K compounds followed by sonication and drying in vacuum [31]. Further, these GNRs can be synthesized by plasma scratching of nanotubes onto polymer films, by epitaxial development, through strengthening on silicon carbide and by CVD as well. The bandgap of graphene nanoribbons is inversely proportional to its width, which is reliant on its edge chirality [31]. Owing to the

edge chirality effect in case of GNR, the performance of lithium-ion batteries can be upgraded using the same. For electronic purposes, the edges of GNRs give the best outcomes when armchair and metallic edges are available because of their semi-conducting capacities [30,31]. For a specific width armchair edge, GNRs additionally reduce the bandgap energy. Therefore, GNRs edges energy depends on density [30,31]. Armchair edges are more firmly attached to the graphene interface so that the energy of the zigzag edges is lower [30]. These edges can be created on GNRs by using electron beam bombardment and electron beam lithography. A GNR with a high fixation and immaculateness of armchair edges has been found to display an exceptionally proficient p-n junction in electronic gadgets [3,30]. A deep study about GNRs was carried out by Liu et al.and types of GNRs are shown in Fig. 8. They predict several promising applications of GNRs mainly for the electronics and energy devices.

3.7. Graphene aerogels (GAs)

GAs act as suitable materials for energy-related applications because of their high mass-specific surface area, elevated electrical conductivity, superior environmental compatibility, lightweight, and their chemical inertness [32,33]. Because of their porous

nanoarchitecture, these materials have been considered as promising candidates for flexible supercapacitors and batteries [33].

Aerogels are an exceptional kind of open-cell nanomaterials that display numerous novel and gripping characteristics, for example, less weight density, persistent permeability and large surface area [32,33]. These characteristics are generated from the aerogel microstructure that comprises of 3D systems of linked nanoscale aerogels [33]. Aerogels, especially graphene derived aerogels, are normally synthesized by sol–gel strategies; a procedure that changes atomic precursors into exceedingly cross-connected inorganic or natural gels. For example, supercritical drying, solidifying drying processes are employed to synthesize flexible GA. For natural and carbon aerogels, the change includes the polymerization of multi-functional natural species into 3D polymer systems [32,33]. Notably, different precursors have been used for the synthesis of graphene aerogels, and they show different properties. The lightness of the graphene aerogel, SEM image and 3D printed graphene aerogel micro lattices of the same are presented in Fig. 9.

3.8. Graphene Master-batches

Graphene master-batches are characterized as materials comprising of polymer and graphene-based materials for several applications. Few of them are available in the market for real-time applications [33]. Graphene is utilised to modify the attributes of distinct types of polymer materials [34]. Low cost, less harmfulness, bio-similarity, and chemical resistance are the kinds of desirable qualities that appear in the distinct polymers. However, these polymers can be modified and largely improved with respect to their mechanical properties. Utilizing graphene and its derivatives as fillers results in an improved electrical conductivity of the polymer. However, few reports also demonstrate that the electric properties are reduced after the incorporation of graphene and its derivatives. In numerous graphene-based composites, graphene oxide acts as the scattering support for different particles and atoms [33]. In polymer masterbatches, this can prompt issues as graphene doesn't generally scatter well in polymer stages (particularly polyolefin) due to the lack of positive interactions at the graphene/polymer interface. However, this can be overwhelmed by the utilisation of a surfactant, or by fitting surface usefulness of the graphene surface. The surfactant expands the surface link between the polymer and graphene [33]. If functionalized, the functional groups enhance the interaction between themselves and the polymer chains [33,34].

4. Exceptional physical properties of graphene

Pristine graphene is considered as an unique zero bandgap semiconductor because its conduction band and valence bands encounter at the Dirac points [1,15,21–26]. Owing to the exceptional electronic characteristics, graphene, GO, rGO, GNRs and QDs all have different electronic properties. Graphene's exceptional optical properties yield an unexpectedly high opacity for a single atom in vacuum, absorbing $\pi\alpha \approx 2.3\%$ for red light, where α is the fine-structure constant for the graphene and similar nano-systems [21–26]. Graphene also shows an unique absorption which could become saturated when the input optical intensity is above the threshold point. However, this threshold point depends on the number of vertical and lateral lengths of graphene and their derivatives. Such graphene shows nonlinear optical behaviour, which is referred to the saturable absorption. The threshold point is named the saturation fluence. Thus, graphene can be saturated readily under strong excitation from the visible (UV) to the near-infrared region (NIR), owing to the universal optical absorption and unique bandgap structure [21–26]. It has a significant effect on the mode-locking of fibre lasers, wherever a graphene-based saturable absorber has accomplished full band mode-locking. Owing to this singular stuff, graphene has extensive applications in ultrafast photonics and supercomputers [1,15]. The thermal transport in graphene and its derivatives is a vigorous and demanding area for fundamental research which has fascinated attention because of its great potential for thermal management applications (especially for the development of high-quality supercomputers). Primary measurements of the thermal conductivity of single-layer graphene exhibit mammoth thermal conductivity of approximately $5300 \text{ W m}^{-1} \text{ K}^{-1}$ and this is much higher than graphite (pyrolytic). The exact C–C bond length in graphene is around 0.142 nm, which is quite shorter than the normal C–C single bond length and a graphene layer stack to form graphite with an interplanar arrangement of 0.335 nm [1]. These two parameters make graphene the strongest material ever tested in this universe with Young's modulus of 1 TPa (150,000,000 psi) and intrinsic tensile strength of 130.5 GPa. Recently large-angle-bent single-layer graphene on a template has been attained with insignificant strain, displaying great mechanical robustness of this 2D carbon nanostructure [21–26]. It has also been found that even with extreme deformation, excellent carrier mobility in pure and single-layer graphene can be well-maintained. Despite of its strength, graphene is relatively brittle, with a fracture toughness of

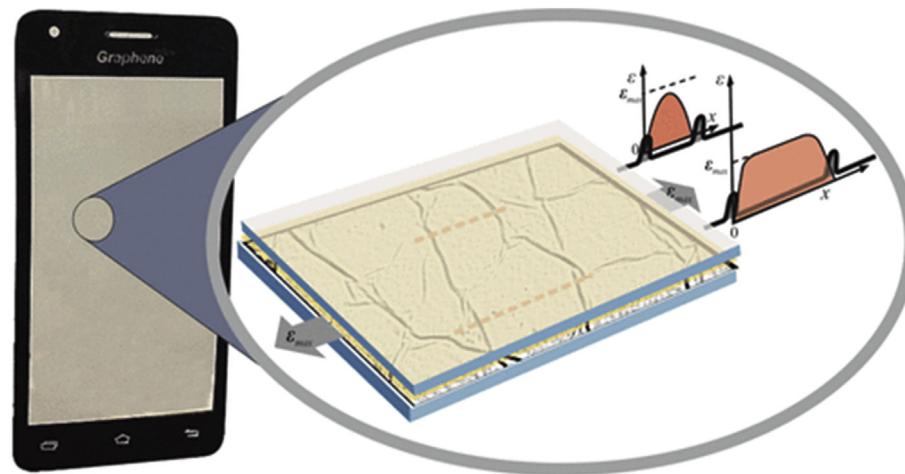


Fig. 10. Graphene-based highly efficient displays (Reproduced with permission from ref. [45]).

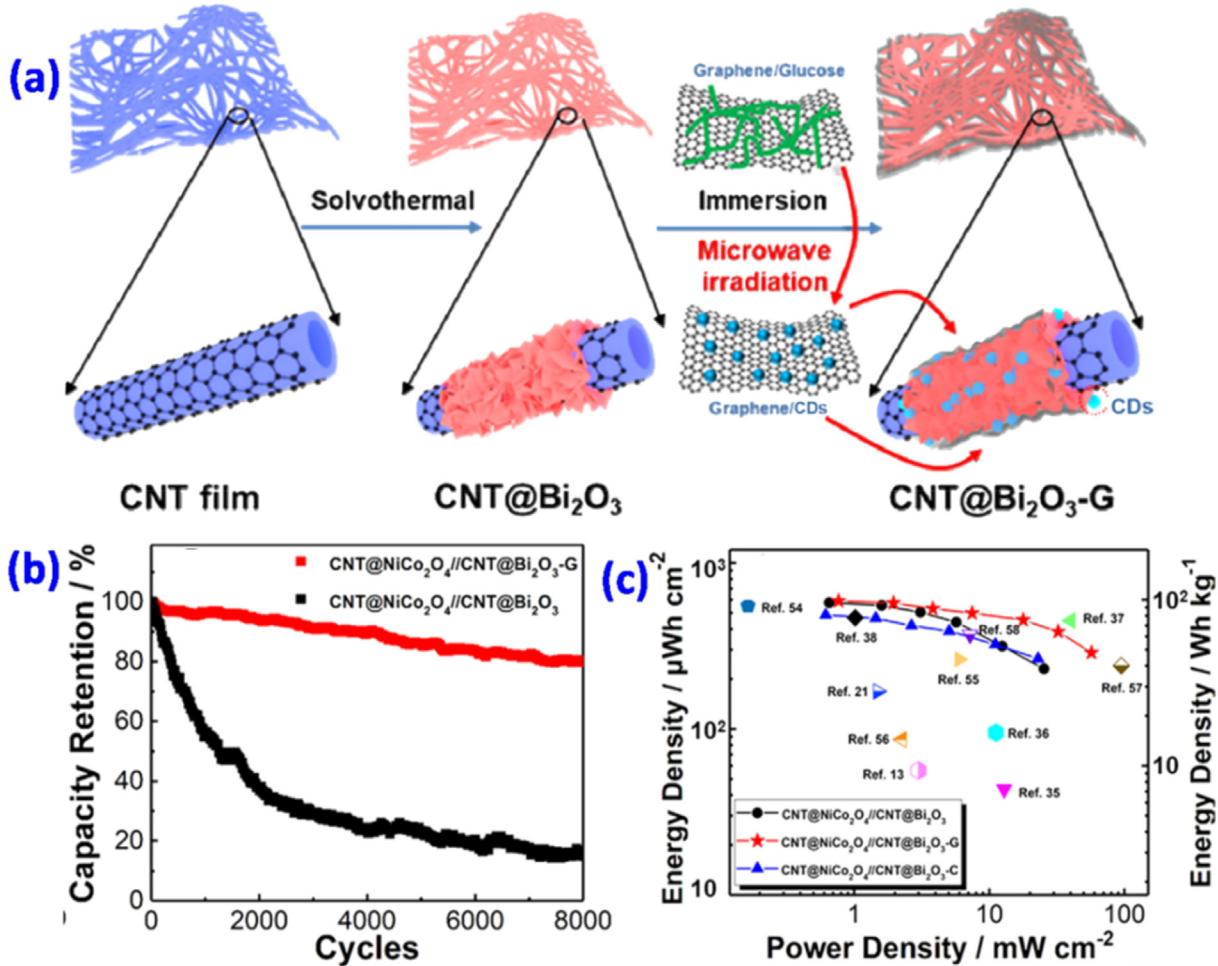


Fig. 11. (a) Schematic illustration of the formation process for CNT/Bi₂O₃/graphene (CNT@Bi₂O₃-G), (b) cycling stability curves and (c) Ragone plots of cycle stability curves of the asymmetric devices i.e. CNT/NiCo₂O₄//CNT@Bi₂O₃-G and CNT/NiCo₂O₄//CNT@Bi₂O₃ (Reproduced with permission from ref. [64]).

approximately 4 MPa \sqrt{m} [1,23,25]. This unique property of graphene indicates that defective graphene is likely to crack in a brittle manner like ceramic and metallic composites, as opposed to many metallic materials that have fracture toughnesses in the range of 15–50 MPa \sqrt{m} . Monolayer graphene also shows a superior ability to dispense force from an impact than any known material and it is about ten times that of steel per unit weight. Apart from these, many biological applications of graphene have also been reported due to its good compatibility with Biosystems.

5. Applications of graphene for real-time applications

Graphene is considered to be a revolutionary material. The applications of graphene are truly endless, and many are yet to be conceived of [35–40]. In this section, few key applications of graphene are discussed in brief.

5.1. Flexible graphene transistors

The graphene-based transistor is a single electron nanoscale device, which involves the crossing of only one electron through it at once [35]. Such a transistor has evoked huge attention since its inception, and now many of them are in the market for daily applications [35]. The main advantage of graphene-based transistors is that they can be operated easily at room temperature and also

have the capability to operate at low voltage with high sensitivity [35]. These qualities make graphene-based transistors better than silicon-based transistors and they also advance the microchip technology. Moreover, due to the intrinsic properties of graphene, such transistors are extremely flexible and foldable. The movement of electrons through graphene is 1000 to 10,000 times faster than in silicon. Therefore, it is much better than silicon in terms of electron mobility. However, pristine graphene cannot be used as an alternative of silicon due to the bandgap issue. The electrons in case of graphene behave like phonons which contrasts to their movement capabilities.

5.2. Graphene sensors

A sensor is a device that perceives actions that occur in the surroundings (like heat, motion, light, pressure, moisture, etc), and retorts with an output, usually with an optical, mechanical or electrical signal. The domestic mercury thermometer is a modest example of a daily used sensor. Graphene and sensors are natural combinations due to graphene's large surface-to-volume ratio, unique optical properties, excellent electrical conductivity, high carrier mobility and density, high thermal conductivity etc. [39–41]. The large surface area of graphene can enhance the surface loading of desired biomolecules. Its excellent conductivity and small bandgap can be beneficial for conducting electrons between

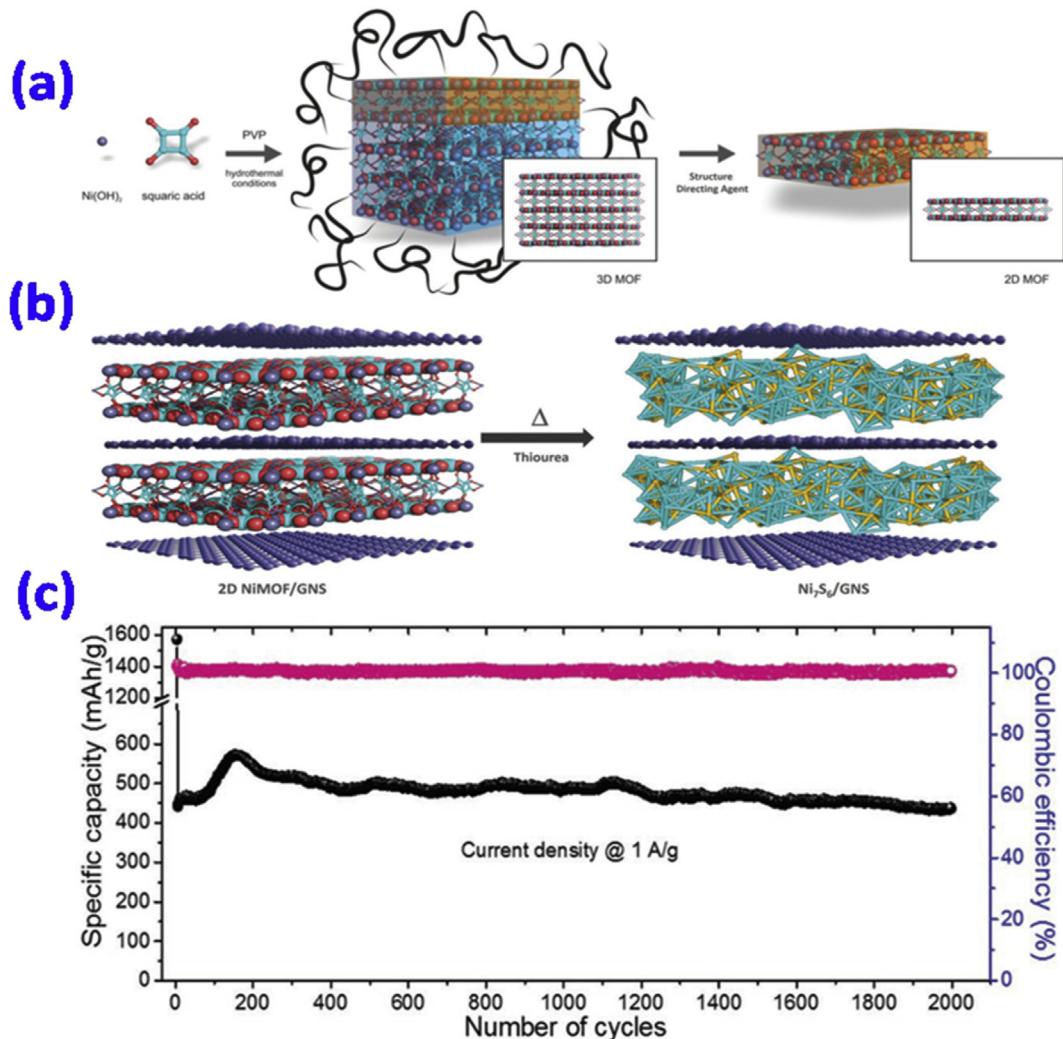


Fig. 12. (a) Schematic illustration of the formation of 2D NiMOF layers from 3D MOF, (b) In situ preparation of heterobilayer hybrids of 2D graphene with nickel sulfide from 2D Ni MOF using thiourea under solvothermal conditions, (c) Long-term cycle stability over 2000 cycles at 1 A/g for the anode material (Reproduced with permission from ref. [70]).

biomolecules and the electrode surface. A perfect sensor can distinguish minute changes in its encompassing condition because of the 2D, planar, and compatible settlement of particles in a graphene sheet. It is important to note that, each particle inside the sheet is presented to the encompassing condition [40,41]. This permits graphene to adequately recognize changes in its surroundings at micrometre measurements, giving a high level of affectability [40,41]. Graphene is likewise ready to distinguish singular perturbations on an atomic level [40]. A significant number of graphene characteristics are helpful in sensor applications. As a whole, graphene could be utilized as a part of sensors in distinct areas consisting of bio-sensors, diagnostics, field-effect transistors, DNA sensors, and gas sensors [40,41].

5.3. Graphene for lithium–sulfur (Li–S) battery

Different kinds of batteries including the lithium–sulfur battery, are fabricated since 1940 [42]. The demerits of the Li–S battery and others is that it is expensive and the life span is very short. Generally, in the lithium–sulphur battery, sulphur act as cathode and lithium act as an anode. During the discharge of the lithium–sulphur battery, lithium is oxidized and converted into a lithium-ion at the anode and at the cathode, sulfur is reduced and

converted into a sulfur ion [42,43]. Then, the lithium ion moves towards the cathode to react with the reduced sulfur and forms Li₂S. To solve all these issues, graphene can be consolidated into both the anode and cathode in different battery frameworks to build the effectiveness of the battery and enhance the charge/discharge cycle rate in many folds [42,43]. The superlative electrical conductivity, high aspect ratio, and dispersibility of graphene become much superior over the conventional inorganic-based cathode while mitigating the terminals of their constraints [42,43]. Because of its adaptable behaviour, graphene has been frequently utilized in lithium-ion batteries, Li–S batteries, supercapacitors and energy components. Li–S batteries give energies up to 500 Wh/kg and even more for the real-time utilisation [42,43].

5.4. Graphene displays

Graphene is a suitable material for utilising in EED (electron emission display) as it displays a high aspect ratio and the dangling bonds at either end of the sheet display proficient electron tunnelling [44]. It is noteworthy that the graphene interface gives massless Dirac Fermions. When it's subjected to an electric field, the field outflow releases electrons while avoiding all back-dissipating because its escape speed is not dependant on its

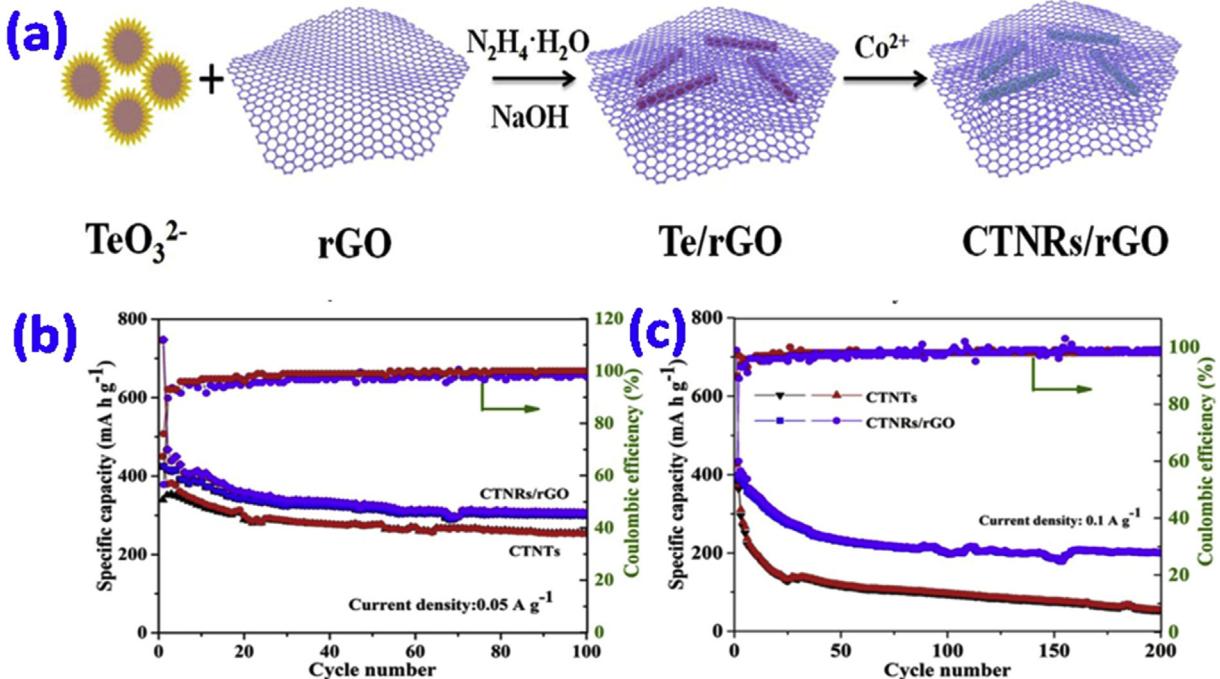


Fig. 13. (a) Scheme illustration of the formation process of CoTenanorods/rGO composites, (b) cycling performances at a current density of 0.05 A/g and (c) at 0.1 A/g of the CoTenanorods/rGO and the CoTe nanotubes (Reproduced with permission from ref. [78]).

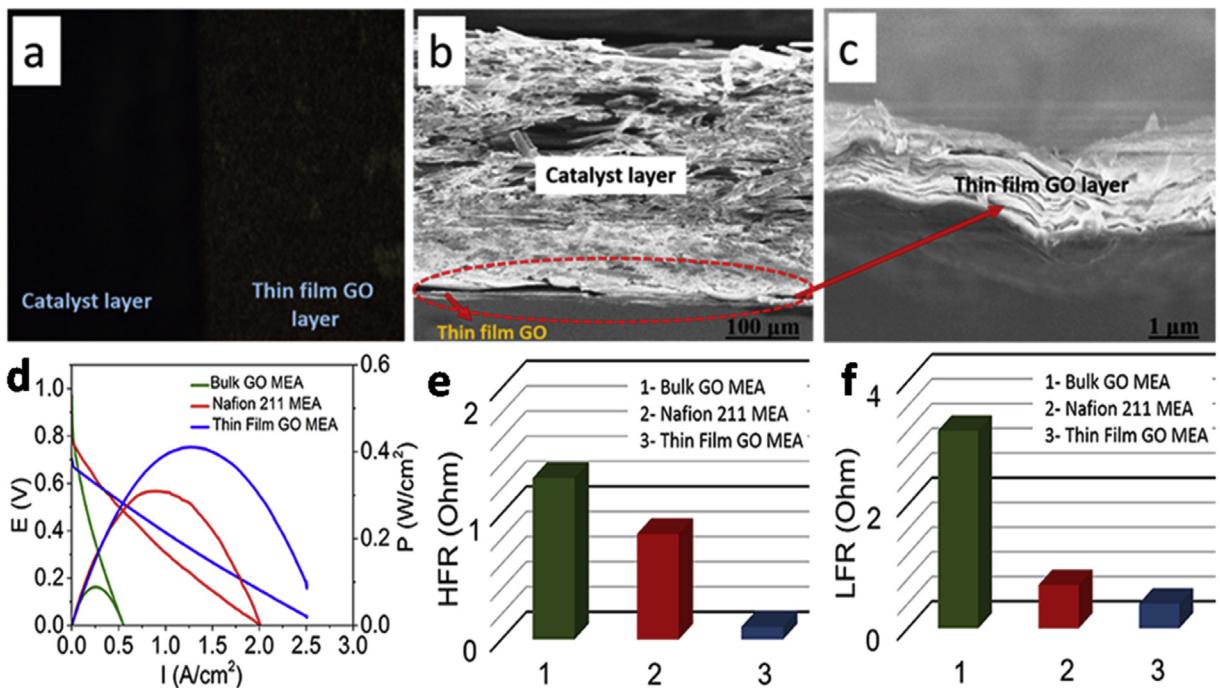


Fig. 14. (a) Optical surface image of spray-coated GO regions distinctly standing out from uncoated catalyst (platinum supported on carbon) regions, (b) SEM cross-sectional image of a thin-layer GO membrane electrode assembly (GO-MEA), (c) enlarged view of the thin-layer GO membrane region in Fig. 14b, room-temperature fuel cell performance with non-humidified H_2 and O_2 with (d) thin-film GO MEA (~ $3 \mu\text{m}$ thick), bulk GO MEA (~ $25 \mu\text{m}$ thick) and commercial Nafion 211 MEA (~ $24 \mu\text{m}$ thick), (e) high-frequency resistance (HFR) and (f) low-frequency resistance (LFR) extracted from the Nyquist plots at the open-circuit voltage (OCV) in the fuel cell configuration for GO and Nafion-based fuel cells (Reproduced with permission from ref. [82]).

energy [45]. Graphene can turn on an electric field at $0.1 \text{ V } \mu\text{m}^{-2}$, with a field improvement factor up to 3700. The graphene displays are now in the market and used for the various applications. In this contest, George et al. investigated the mechanical behavior of a

model touch panel display, which comprises of two layers of CVD grown pure graphene entrenched into PET films in tension and under contact-stress dynamic loading [45]. They investigated several properties of graphene-based prototype panel displays for

real-time applications in the cell phone. According to this study, graphene could be the ideal candidate for the next-generation flexible touch panel displays [45]. The graphene-based display is shown in Fig. 10 schematically.

5.5. Structural composites

Graphene is fused into different composites for applications where quality and weight are restricting components, for instance in aeronautics [46]. Graphene has been introduced to numerous materials to make them more strong, valuable, and light weight. For the aviation industry, a composite material that is substantially lighter than steel yet giving the vital quality will spare cash on fuel utilization, which is the reason graphene has begun to be fused into such materials [46,47]. Graphene-based basic composites have a gigantic potential to be more utilized as novel options to numerous materials utilized today [47].

5.6. Catalyst supports

Catalysis is an important class of fundamental study for the industrial revolution and research development. Due to the rich surface properties, flake morphology, elevated surface area and high electron mobility, graphene and its derivatives are proven to be very efficient as catalytic materials [48]. Traditionally, many catalytic reactions use a noble metal which behaves like a mechanical support and also as a moderator to enhance the rate of reaction and productivity [48]. For the same, graphene acts as a

chemically inert substance because in its purest form no bond is free [48]. However, the addition of functional groups changes the characteristics of graphene and makes it suitable to act as a catalytic support. Moreover, it has been found that the planar and uniform surface of graphene upsurge interfacial interactions between substrate and catalyst [48,49]. Due to 2D surface morphologies, metal catalysts can be located properly on the surface of graphene and could give the best possible performance. Similarly, efficient mechanical background and phenomenal charge bearer capacity of graphene help the charge exchange during the reactions through maximal catalyst–substrate participation [48]. Additionally, graphene is dormant and does not participate in the catalytic cycle and therefore, it can be used as the ideal support for the catalyst [48,49]. Likewise, graphene gives a dispersion of catalyst particles, so the catalyst substrate collision becomes maximal which again helps to achieve the best performance of that catalyst [48–50]. As a whole, graphene is best for catalytic support particularly in the emerging technology of non-covalently bonded support that offers low-cost technologies like fuel cells.

5.7. Polymer masterbatches

Another possible way to couple these properties for innovative applications is to incorporate graphene sheets in polymeric systems. This could enhance the electrical, thermal and mechanical properties of polymer composites [51,52]. The engineering of such polymeric materials requires homogeneous dispersion of graphene materials including GO and graphene derivatives into the polymer

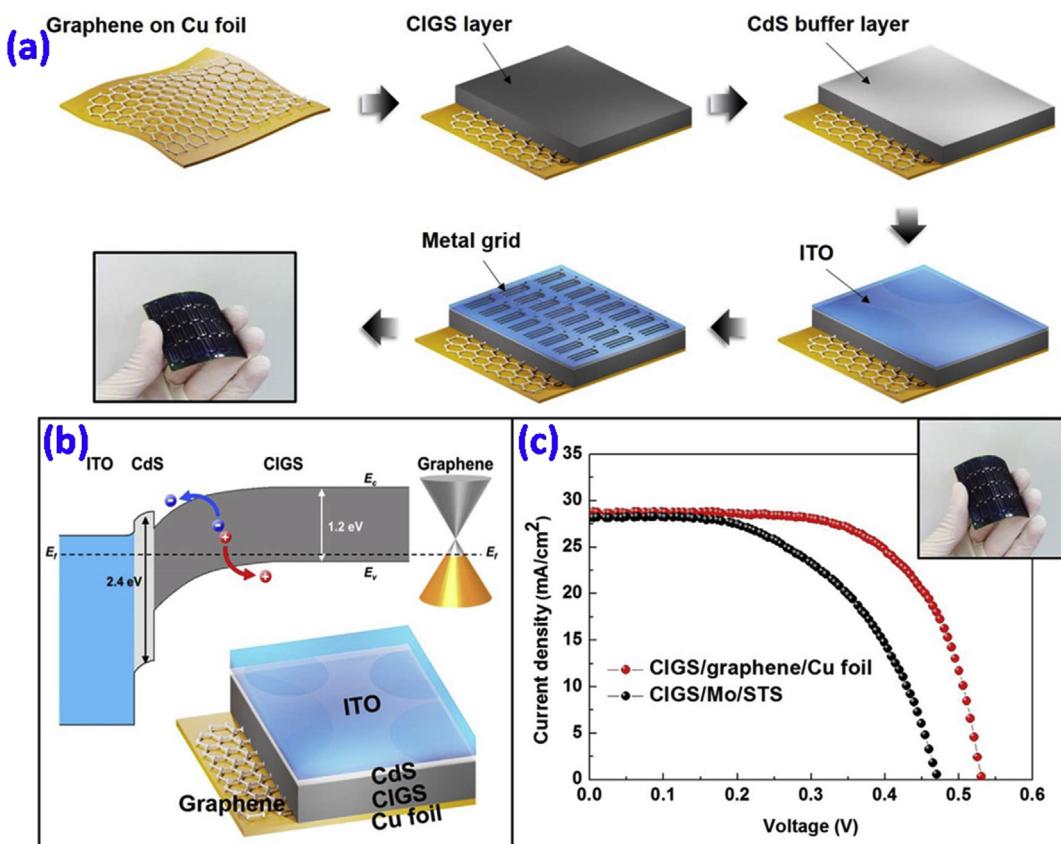


Fig. 15. (a) Schematic representation of the deposition and fabrication processes of flexible CIGS solar cells on a graphene/Cu foil electrode; (b) schematic band diagram of CIGS/graphene solar cells under zero-bias voltage condition displaying the generation and collection of charge carriers and (c) J-V characteristics of the CIGS solar cell fabricated on graphene/Cu foil compared with those of the reference cell fabricated on Mo/STS (inset shows optical image of the flexible device) (Reproduced with permission from ref. [88]).

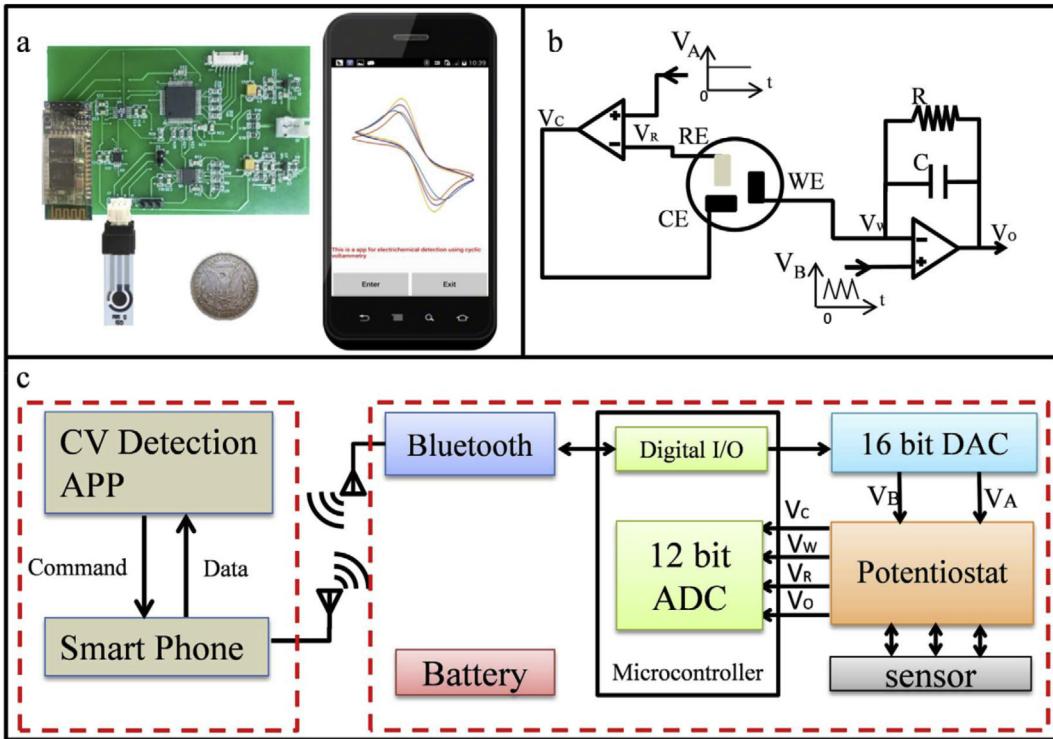


Fig. 16. The schematic and the design of the smartphone-based CV system: (a) The image of the hand-held detector connected with SPE and the welcome interface of the App on the smartphone, (b) the circuit design of the potentiostat based on a resistive feedback transimpedance amplifier, (c) a schematic diagram of the smartphone-based CV system (Reproduced with permission from ref. [95]).

matrices. It has been found that the involvement of graphene and its derivatives results in a significant increment in the tensile strength of the polymers (4–5 fold), along with an increase of the life span of polymeric composites for commercial purposes [51,53].

5.8. Functional inks

Graphene has been further used to produce functional inks for electronics, heat resistant and anti-corrosion purposes [56]. By incorporating graphene into ink formulations, the conductivity properties associated with graphene influence the ink, causing it to become conductive and workable. Compared to other conducting inks (even some newly developed nano inks), graphene ink is non-toxic, environmentally friendly, cheaper, and quite recyclable [54–57]. Additionally, graphene also has high thermal stability, making it ideal for heat resistant ink coating in electronic applications that produce large amounts of heat. It is also an ink of preferable choice when processing temperatures need to be high, as graphene would not break down during the manufacturing process. Graphene also exhibits excellent chemical stability and it is highly inert. These additional advantages make graphene an ideal candidate for functional ink applications [53–57]. Thus, for the applications where environmental factors are critical issues, graphene inks can provide a stable barrier to protect materials from chemicals and corrosion.

6. Recent progress on graphene research

In recent years, graphene-based materials have been extensively investigated for different applications. In this section, the most recent application of graphene-based materials will be discussed in brief.

Graphene has been extensively utilized for the development of electrode materials for supercapacitors. For example, graphene was combined with defect-induced 1T-MoS₂ to develop a supercapacitor electrode [58]. The hydrothermally synthesized hybrid electrode exhibited the specific capacitance of 442 F/g at the current density of 1 A/g and cycling stability of 90.3% up to 1000 cycles. In another study, Elessawy et al. synthesised N-doped graphene from the waste polyethyleneterephthalate (PET) bottles via a green synthetic approach using urea as the N-source [59]. The fabricated electrode achieved the capacitance of 405 F/g at 1 A/g current density and capacitance retention of 87.7% after 5000 cycles. Apart from N, other heteroatom-doped graphene-based supercapacitor electrodes have also been synthesized. Balaji et al. synthesized B-doped graphene through a supercritical fluid processing technique and a hydrothermal method [60]. The doping level was found to be higher in case of the hydrothermal process (9.5 atomic%) than by the supercritical fluid route (8.9 atomic%). The doped electrode displayed a maximum capacitance of 286 F/g and a cycling stability of 96% over 10,000 cycles. Further, the corresponding symmetric device achieved the energy density of 43.1 Wh/kg in the 1-ethyl-3-methyl imidazolium tetrafluoroborate (EMIMBF₄) electrolyte. In another article, Cheng et al. synthesised the N,P co-doped rGO by a supramolecular self-assembly strategy [61]. In this process, melamine and phytic acid supramolecular polymers were used as the precursors. The 3D structured electrode showed desirable electrochemical properties like a specific capacitance of 416 F/g and a capacitance retention of 94.63% after 10,000 cycles. Nevertheless, the assembled symmetric device displayed an energy density of 22.3 Wh/kg. In a recent article, Krishnamoorthy et al. demonstrated the application potential of oxygen-rich porous graphene for a supercapacitor Al-ion battery, and capacitive deionization [62]. The introduction of oxygen functionalities was performed with nitric acid by inducing natural solar radiation. As a supercapacitor

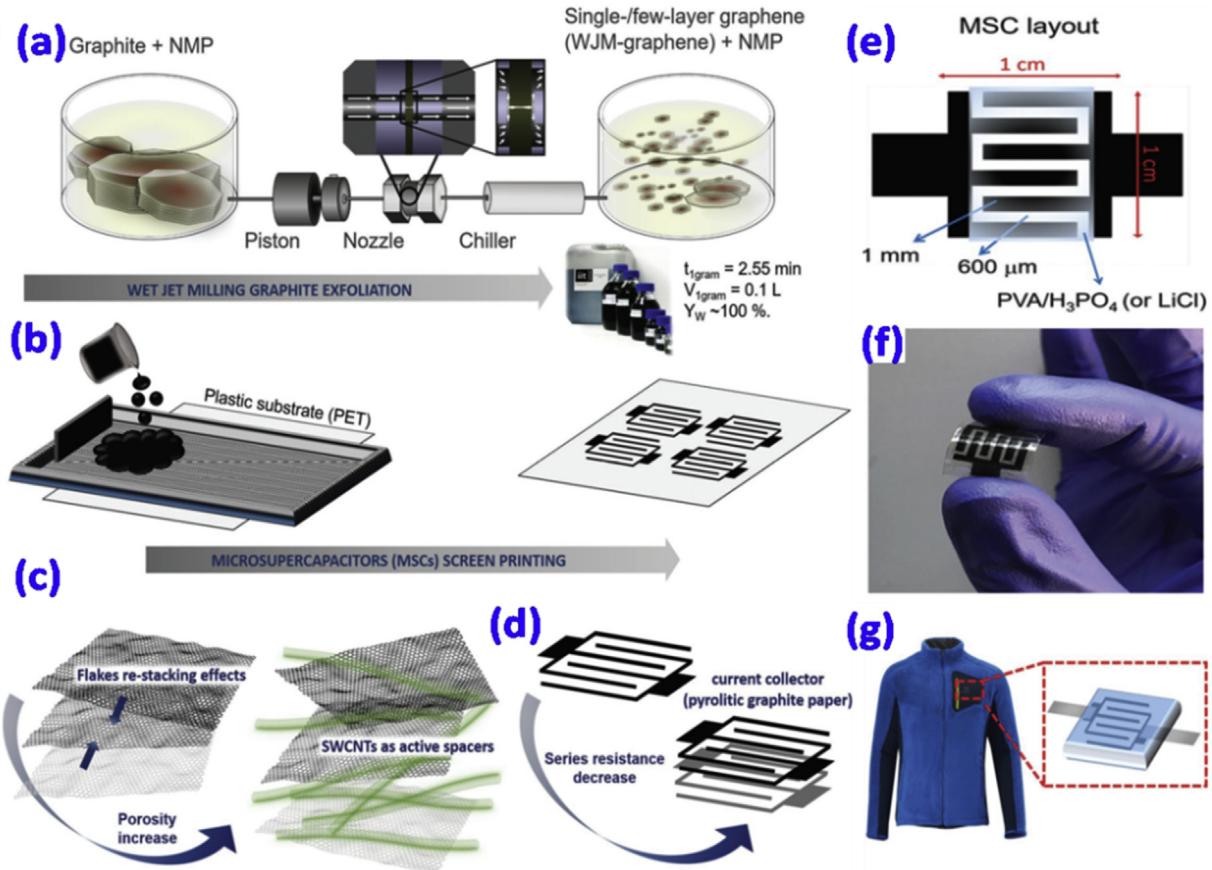


Fig. 17. (a) Schematic illustration of the production of single-/few-layer graphene by WJM exfoliation of graphite (WJM-graphene), (b) Screen printing of MSCs onto plastic substrate (PET), (c) Addition of SWCNTs as active spacers for avoiding the re-stacking of the flakes, (d) use of pyrolytic graphite (PG) paper in order to decrease the current collector resistance of MSCs for high-power density requirements, (e) layout adopted as interdigitated electrodes for screen-printing MSCs onto PET substrates, (f) digital photograph of a screen-printed MSC, (g) schematic illustration of the MSCs accommodation into microfleece garment simulating practical home-laundry conditions (Reproduced with permission from ref. [100]).

electrode, the functionalized graphene delivered a capacitance of 354 F/g and an energy density of 110.6 Wh/kg at a current density of 1 A/g. On the other hand, as Al-ion battery material it achieved the maximal capacity of 90 mAh/g and an exceptional stability up to 10,000 cycles. Further, it also displayed a decent salt removal capacity of 21.1 mg/g for 500 mg/L NaCl solution at 1.4 V. Manchala et al. used the Eucalyptus polyphenol solution to reduce graphene oxide for the synthesis of soluble graphene through a green route [63]. Owing to its porous architecture, this multi-layered graphene electrode displayed a capacitance of 239 F/g and an energy density of 71 Wh/kg at a current density of 2 A/g. For the enhancement of electrochemical properties, graphene has been integrated with other carbon materials and metal oxides. Wang et al. developed a supercapacitor-battery hybrid device based on graphene, CNT, and Bi₂O₃ through an in-situ nano-welded technique (Fig. 11) [64]. The synthesised anode material achieved a capacity of 1.90 mAh/g at a current density of 1 mA/cm². Moreover, the corresponding asymmetric device with NiCo₂O₄/CNT composite as cathode exhibited an energy density of 98.2 Wh/kg and a capacity retention of 80.1% after 8000 cycles. These studies clearly indicate that graphene can be considered as an efficient electrode material for supercapacitors.

Apart from the supercapacitor, graphene-based materials have been frequently used as the essential components for secondary batteries. Among various secondary batteries, Li-ion batteries (LiBs) are the most investigated ones. In this aspect, Lin et al. fabricated a LiB anode by synthesizing a binder-free nanocomposite based on graphene nanowall and Si [65]. Owing to its high surface area,

enhanced conductivity, elevated flexibility and high porosity, the hybrid electrode possess a specific capacity of 1116.2 mAh/g and a cycling stability of 79.1% after 200 cycles. In another work, Abdollahi et al. fabricated a free-standing paper-based electrode by combining vertically aligned CNT and rGO through the plasma-enhanced chemical vapour deposition process [66]. The flexible 3D structured anode material exhibited a reversible capacity of 958 mAh/g at a current density of 150 mA/g. Further, the electrode also displayed a capacity of 459 mAh/g after 100 cycles with 100% coulombic efficiency. Apart from anode material, graphene was also used as a coating agent for the development of an efficient current collector for LiB. The electrochemical performance of LiB was enhanced by integrating catalytically grown graphene with the current collector [67]. The improved battery performance was attributed to the enhancement in conductivity, reduction of internal resistance, and protection towards corrosion. Apart from anode material and current collector, graphene materials have also been utilized for the construction of LiB cathodes. Zeng et al. fabricated the cathode material by combining V₂O₅ nanoribbons with graphene through the hydrothermal method [68]. This hybrid electrode delivered an initial capacity of 225 mAh/g and a capacity retention of 92.8% after 600 cycles. In another report, Kuang et al. investigated the battery performance of a sandwich structured composite anode based on NiCo₂O₄, ZIF-67, and graphene [69]. This MOF (Metal–Organic Framework) based electrode exhibited a capacity of 1025 mAh/g after 80 cycles at a current density of 0.5 A/g. In recent work, Jayaramulu et al. first synthesised 2D Ni-based MOF

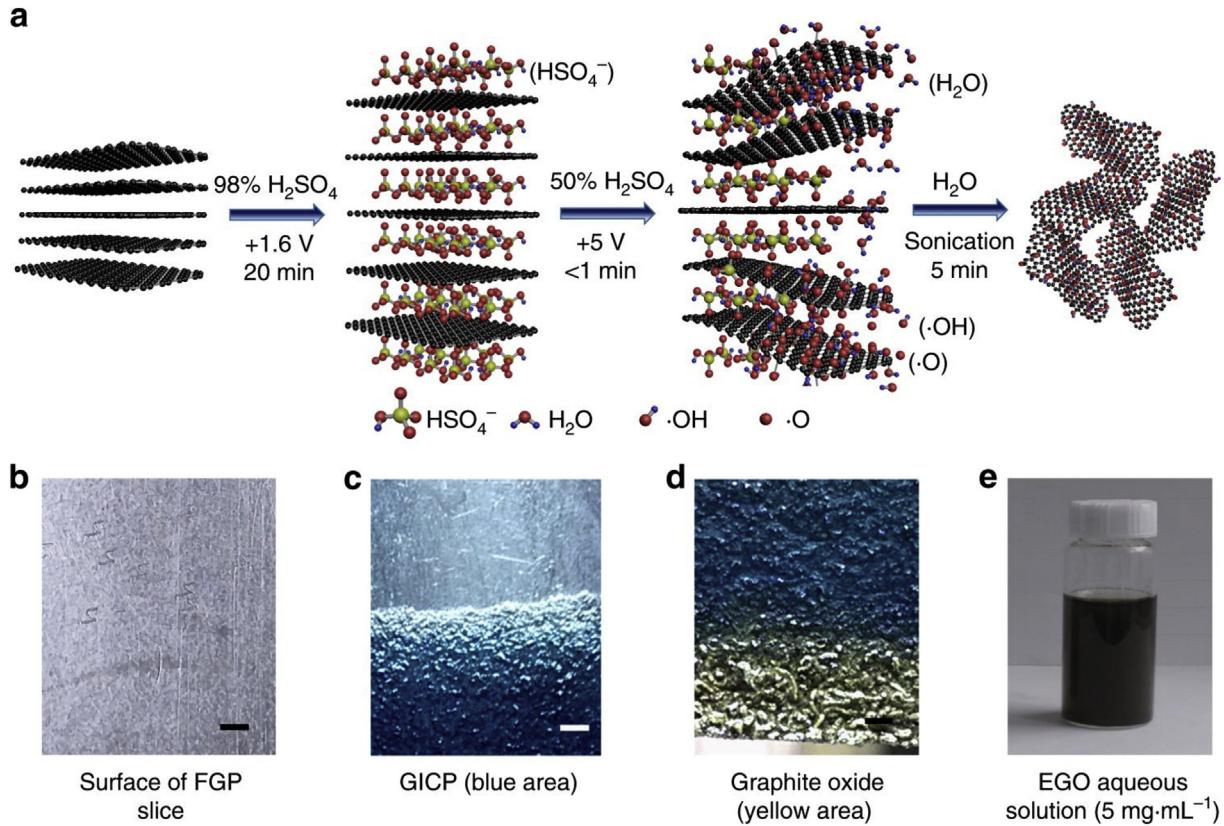


Fig. 18. Synthesis of electrochemically synthesised GO (EGO) by water electrolytic oxidation: (a) Schematic illustration of the synthesis process of EGO by water electrolytic oxidation. (b–e) Photos of the raw material and the products obtained at each step. (b) FGP. (c) GICP (blue area) obtained after EC intercalation of FGP in 98 wt.% H₂SO₄ at 1.6 V for 20 min. (d) Graphite oxide (yellow area) obtained by water electrolytic oxidation of the GICP in 50 wt.% H₂SO₄ at 5 V for 30 s. (e) Well-dispersed EGO aqueous solution (5 mg·mL⁻¹) obtained by sonication of the graphite oxide in water for 5 min. Scale bars in (b–d): 1 mm (Reproduced with permission from ref. [120]).

nanosheets by using Ni(OH)₂, squaric acid, and poly-vinylpyrrolidone as the precursors (Fig. 12) [70]. In the next step, the Ni-based MOF was converted to Ni₇S₆ in the presence of graphene by using thiourea as the sulfur-source. The Ni₇S₆/graphene hybrid anode displayed a reversible capacity of 1010 mAh/g at 0.12 A/g and a cycling stability of 95% after 2000 cycles. Graphene has also been combined with other 2D materials. Jiao et al. fabricated a LiB anode, which was based on red Phosphorous and crumpled N-doped graphene [71]. As the LiB anode, this 3D structured composite displayed a capacity of 2522.6 mAh/g at 130 mA/g. Further, the electrode also achieved a capacity of 1470.1 mAh/g at a current density of 1300 mA/g even after 300 cycles.

Apart From LiB, Na-ion batteries (SIBs) are other secondary batteries which have gained nowadays extensive research interest, because of the safety issue and the high natural abundance of Na [72–74]. Nanocomposites based on graphene metal oxides are frequently used as the electrode materials (mainly anode) for SIBs. In a recent article, Wang et al. theoretically demonstrated the double interstitial mechanism of energy storage for such kind of materials [75]. Through theoretical simulation and experimental data, they also displayed the diffusion kinetics and pseudo-capacity of these materials. Further, they claimed that the SIB battery performance could be enhanced by increasing the contact between 3D graphene and metal oxide as well as by hetero-atom doping of graphene. Following the current research trend, a flexible SIB electrode was fabricated by synthesizing rGO modified carbon foam supported TiO₂ (Fig. 13) [76]. This ternary hybrid electrode exhibits a specific capacity of 305 mAh/g at 0.5 C current and a 100% capacity retention over 70 cycles. As the LiB anode material, the

electrode also displayed significant electrochemical performance. Metal sulfide was also combined with graphene for developing the SIB electrodes. Jiang et al. synthesised a SnS₂/graphene/SnS₂ composite through the hydrothermal process, which exhibited the specific capacity of 844 and 765 mA/g at a current density of 10 A/g as the LiB anode and SIB anode, respectively [77]. The sandwich-structured electrode also displayed no significant change in morphology after 200 cycles, indicating an enhanced cycling stability. In another report, Ding et al. fabricated a SIB anode by integrating CoTe nanotubes and CoTe nanorods with rGO [78]. The CoTe-based electrode demonstrated the maximal specific capacity of 306 mAh/g at a current density of 50 mA/g after 100 charges/discharge cycles. The improved electrochemical performance of the electrode was attributed to the enhanced conductivity, elevated surface area, and high mechanical strength.

Owing to the tuneable catalytic activity, graphene materials have been used as efficient alternatives for the development of metal-free catalysts for the oxygen reduction reaction (ORR) in fuel cells. In this aspect, Larijani et al. explored the significant ORR activity of B, N co-doped graphene through a theoretical calculation using the density functional theory (DFT) [79]. The researchers explored the dominating role of pyridinic N towards the effective four-electron pathway reaction by reducing the activation energy. In a recent article, Xin et al. demonstrated that the Cu₂O nanoparticles decorated rGO displayed a better coulombic efficiency and a higher output voltage than the commercial Pt/C catalyst for microbial fuel cells [80]. Graphene materials were actively utilised to fabricate membranes for proton exchange membrane fuel cells. For example, Li et al. fabricated a conductive proton exchange

membrane by combining GO with sulfonated polysulfone [81]. The composite membrane displayed a higher proton conductivity and a better relative humidity than pristine sulfonated polysulfone. Moreover, the researchers also demonstrated that the fabricated fuel cell could exhibit improved fuel cell performance in hydrous as well as low relative humidity conditions. In another report, Thimmappa et al. explored that the proton-conductive GO exhibited better fuel cell performance than the commercial Nafion membrane at room temperature [82]. Specifically, the GO-based membrane displayed a peak power of $\sim 410 \text{ mW/cm}^2$ at a current density of $\sim 1300 \text{ mA/cm}^2$ (Fig. 14). In a recent article, Qin et al. synthesized an ORR catalyst by integrating hexagonal $\text{Bi}_2\text{O}_2\text{CO}_3$ nanoplates with N-doped graphene through a template-free synthetic route [83]. The doped graphene-based catalyst displayed a maximal onset potential of 1.179 V and a limiting current density of 7.38 mA/cm^2 in an 0.1 HClO_4 solution, indicating a desirable fuel cell performance in an acidic medium. These recent studies clearly indicate that graphene materials are significantly used as a vital component in different types of fuel cells.

Graphene materials have been explored for solar cell applications too because of their elevated optical transparency, superior mechanical strength, and high carrier mobility. In solar cell devices, graphene materials have been considerably utilized as the transparent electrode, buffer layer, as well as the electron/hole transport materials [84–87]. In a recent article, Sim et al. used a graphene film as the hole transport electrode for $\text{Cu}(\text{In}, \text{Ga})\text{Se}_2$ (CIGS)solar cells [88]. In this work, Cu foil was used as the substrate to deposit graphene through the chemical vapour deposition (CVD) technique. The fabricated graphene-based solar cell displayed a power conversion efficiency of $9.91 \pm 0.89\%$, which was better than the reference electrodes. The enhanced conversion efficiency was attributed to the elevated open-circuit voltage and large fill factor. The fabrication technique of the graphene/Cu flexible solar cell and the performance of the device is shown in Fig. 15. On the other hand, Ishikawa et al. fabricated a solar cell based on graphene and perovskite ($\text{CH}_3\text{NH}_3\text{PbBr}_3$), which did not require any hole-transport layer [89]. The vacuum lamination of graphene designed the device. In another recent article, Das et al. demonstrated the current state of the art in graphene research for solar photovoltaics [90]. The authors concluded that the conductivity of graphene increased with increasing the layers; however, the optical transparency is reduced. They also reviewed the utilisation of other 2D materials beyond graphene for solar cell applications. A graphene/Si Schottky junction solar cell was fabricated by Suhail et al., which exhibited a power conversion efficiency of 10% [91]. The chemical doping of graphene further enhanced the efficiency. Moreover, the device also displayed a efficiency retention of 84% after 9 days of storage in air. In this work, the authors introduced a deep UV treatment to enhance the performance in the solar cell.

Graphene-based screen-printed electrodes (GSPE) are being used for various applications. For example, Jampasa et al. fabricated the GSPE electrode for the electrochemical detection of c-reactive protein in human serum samples [92]. Mainly, the authors developed an electrochemical immunosensor based on graphene through an in house screen-printing technique. Further, a Glucose/Oxygen Enzymatic Fuel Cell was fabricated by employing Gold nanoparticles modified GSPE [93]. The fabricated bio-device displayed a significant performance when tested for human saliva samples. The GSPE was further assembled with the nano-molecularly imprinted polymer to develop a biomimetic sensor for the detection of acute myocardial infarction (a cardiovascular disease) [94]. Ji et al. fabricated a glucose sensor by developing a smartphone-based cyclic voltammetry system with GSPE (Fig. 16) [95]. The smartphone-based system displayed minimal test errors in comparison with the commercial electrochemical workstations

for the electrochemical detection of redox couples, indicating better applicability for electrochemical tests. GSPE was further used to develop an immunosensor for the level-free detection of Cortisol and Lactate [96]. These studies imply that GSPE has been considered as an essential tool for the development of biosensors.

With the rapid progress in graphene research, various kinds of graphene materials have been developed. Among those, graphene-based inks (GI) are significantly utilized for different applications. The printed 3D GI exhibited elevated compressive strength and better electrical conductivity ($> 4 \times 10^3 \text{ S/m}$) [97]. The GI was developed through a direct ink wetting process using a single surfactant. Conductive GI was further developed by Liu et al. [98]. The conductive ink was prepared by dispersing graphene and MWCNT through the use of polyvinylpyrrolidone in a mixture of ethanol and water. The ink displayed a low sheet resistance and a high optical transmittance of 90%. A facile strategy has been developed to print GI on inert 3D surfaces [99]. The water-insoluble conductive ink was produced by using commercial binders and was used to develop multilayered devices through a conformal printing process. GI based energy storage devices have drawn extensive research interest. Bellani et al. fabricated a micro-supercapacitor (MSC) with GI through a screen-printing technique (Fig. 17) [100]. The GI was produced through wet-jet milling exfoliation of graphene. The fabricated device exhibited a maximal areal capacitance of 1.324 mF/cm^2 and an energy density of $0.064 \mu\text{Wh/cm}^2$. In another work, He et al. fabricated supercapacitor devices through screen-printing of GI on plastic and paper substrates [101]. The printed device displayed a high conductivity of $8.81 \times 10^4 \text{ S/m}$ and a better rate capability up to a high scan rate of 200 mV/s. These works significantly demonstrated that the GIs could serve as the potential tool for the fabrication of flexible electronic devices.

Beyond these, graphene has shown a wide-range of application in different fields of science and technology. The properties and application of graphene materials have been discussed in a few previous and latest noted articles, which will be beneficial for the future progress in graphene research [102–124]. In this aspect, it is important to note the few latest findings of graphene research. For example, exceptional superconductivity has been found in graphene superlattices. In particular, the unconventional superconductivity was generated in the superlattice, which was formed by stacking two graphene sheets which were twisted relative to each other by a small angle (called as "Magic Angle") [107–109]. During the early stage of graphene research, graphene oxide (the precursor of graphene) has been synthesized through multi-step time-consuming synthetic routes using harsh chemicals including strong acids, strong oxidant etc. But, in a recent article, GO was synthesized within a few seconds through a green synthesis process [120]. Fig. 18 represents the schematic diagram of this synthesis process. In particular, the synthesis process was based on the water electrolytic oxidation of graphite. The adopted electrochemical process generated a high yield of GO. In another work, K.H. Thebo et al. reported the synthesis of GO membranes, which exhibited 10–1000 times higher water permeance properties than the commercial membranes [124]. The GO-based membranes also displayed high-quality separation efficiency towards organic dyes. The authors also reported the synthesis of rGO-based membranes using theanine amino acid as reducing agent and tannic acid as cross-linker. These studies clearly indicate the bright future of graphene research.

7. Conclusion and future prospects

At present, graphene and graphene-based hybrid nanostructures are appealing much consideration as the novel materials for nanotechnology, biomedical engineering, material science,

physics, and green chemistry due to their tunable physical properties, high surface area, elevated electronic, and thermal properties. That is why, within a very short period of time, graphene and its derivatives have shown wonderful commercial applications in the field of composites, nanoelectronics, bioimaging, and nanomedicines. For example, functionalized graphene nanosheets have revealed enhanced interfacial interaction and adhesive properties with mammalian cells, protein and microbial, which make graphene a valuable nanosystem for the next-generation multifunctional bioengineering applications. Similarly, many exceptional applications of graphene in pipelines will dominate our market very soon. However, the production of inexpensive and ultrapure pristine graphene layers are still a matter of deep research. So, an easy and adorable route for graphene production is an inordinate challenge and headache for the materials scientists. In the same line, time-dependent compatibility and interactions of graphene and its derivatives *in vivo* and *in vitro* conditions is one of the most challenging tasks for the researchers working on different aspects of graphene. Therefore, we can say, graphene has shown great proficiency in every branch of science and technology but a great support for further research is required from the governments and industries to harness the full potential of graphene and its derivatives for optoelectronics, bio-imaging, frequency multiplier, Hall effect sensors, conductive ink, Spintronics, ultraviolet lens, charge conductor, radio wave absorption, catalyst, sound transducers, waterproof coating, condenser coating, coolant additive, and piezoelectric applications.

Since graphene is an inspiration for other 2D materials, materials like hexagonal boron nitride, Germanene, Silicene, different transition metal chalcogenides, Phosphorene, Stanene, Borophene, and Boron nitride nanosheets are emerging as new and novel nanostructures for the next generation nanoscience and nanotechnology research. It is reported that in some cases, these 2D nanomaterials are quite better than graphene. Deep investigations on these new nanosystems are currently underway with increasing achievements for prototype applications. However, more intense research and funding are required for their industrial-scale applications. In this way, these 2D materials are new challenges for the materials scientists and a great opportunity for further research and development.

Declaration of Competing Interest

The authors declare no conflict of interest associated with this manuscript.

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