J. Mat. Chem. A

ARTICLE

Graphene: The Multipurpose Material for Protective Coatings

Md J. Nine, Martin A. Cole, Diana N. H. Tran, and Dusan Losic*

Graphene based materials have attracted a great interest for the development of new and advanced protective coatings due to their excellent chemical resistance, gaseous impermeability, adsorption capacity, anti-bacterial properties, mechanical strength, lubricity and thermal stability. This review presents current progress and discusses the major challenges and future potential of graphene in the field of protective coatings. This review specifically focuses on the most recent advances in the application of graphene for corrosion resistant coatings, flame retardant coatings, wear/scratch resistant coatings, anti-fouling coatings, pollutant adsorption coatings and anti-septic coatings.

The School of Chemical Engineering, University of Adelaide, Adelaide 5005, Australia. Email: dusan.losic@adelaide.edu.au, Fax: 0 8313 4373

1. Introduction

Graphene (Gr), the most recently discovered allotrope of carbon, has unique properties principally attributed to its 2D hexagonal lattice structure.[1] As an atomically thin material, Gr simultaneously exhibits an extremely high level of thermal conductivity (above $3,000 \text{WmK}^{-1}$),[2] electrical conductivity ($2.5 \times 10^5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$),[3] along with superb mechanical strength (Young's modulus of 1 TPa and intrinsic strength of 130GPa),[4] which makes this material exceptionally suitable for versatile applications. This material also possesses many other distinctive properties including gaseous impermeability,[5] chemical (acid/base/salt) resistance,[6, 7] antibacterial potential,[8] thermal stability,[9, 10] eco-friendliness,[11]

and most importantly having high specific surface area.[12] In addition, the flexible surface chemistry of Gr,[13, 14] with the above mentioned useful properties provide a fertile research ground to achieve advanced performance in protective surface-coatings.

A coating can be defined as a layer of material that covers the surface of a bulk material to achieve specific properties. Synthetic or modern engineered coatings are typically applied for decorative or functional purposes or a combination of both. Surface and bulk material protection purposes are the major goal of functional coatings in the combat against corrosion, fouling, mechanical wear, microorganisms, and environmental damage. Similarly, there are extensive uses of coating materials in military applications, marine industries, medical instruments, electronics and everyday household appliances.[15]

Md J Nine is currently a Ph.D. candidate at School of Chemical Engineering in the University of Adelaide, Australia. He obtained his "Masters of Engineering" degree at Gyeongsang National University, South Korea, in 2012 and granted for dean award for the excellence in research as young pioneer researcher. He received his B.Sc.in Mechanical Engineering from Khulna University of Engineering and Technology, Bangladesh, in 2009. His current research interest involves synthesis of graphene based composite nanomaterials for the application in protective coating to combat against corrosion, fouling, wear/scratch, icing and fire/irradiation.

Martin A. Cole, PhD, is currently a postdoctoral research fellow at the University of Adelaide, School of Chemical Engineering, Australia. He received his BSc (Honours) in Nanotechnology from Flinders University, Australia and his doctorate in Applied Science from the University of South Australia (in collaboration with Flinders University and The Commonwealth Scientific and Industrial Research Organisation). His interests range from surface modification and surface characterization methods to materials engineering, biomaterials and biological surface interactions.

Aside from aforementioned protective applications, functional coatings have also been designed for adsorption of chemical contaminants and hazardous gases (NO_x, SO_x, CO, H_2S, NH_3, or sulfur-containing compounds (e.g. organothiols)) from various environments.[16] Thus, the field of protective coating is not only limited to corrosion, fouling and mechanical wear, but also extends to adsorbing toxicants, resisting frost/fire/irradiation, and killing bacteria. Next generation coatings could protect against biological and chemical weapons as protective shield.[15]

Although, coatings commonly serve to protect materials, a number of conventional metal coating technologies are associated with negative environmental impact. The use of hexavalent chromium (Cr (VI)) and tributyltin (TBT) in the metal protective coating industry has recently been fully restricted because of their carcinogenic risk and biocidal properties. The amount of Cr(VI) in corrosion preventive coatings is limited to 0.1 wt % from July 1, 2007.[17] Identically, the legal prohibition on the use of TBT in antifouling coatings was imposed on January 1, 2003 to protect the marine eco-system, followed by a total ban since January 1, 2008.[18] Other powerful coating constituents such as cadmium (Cd), cobalt (Co) and copper (Cu) have also been classified as toxic for the eco-system and carcinogenic to humans.[19-21] Among them, cadmium plating for electronics and electrical equipment has already been restricted since July 1, 2006 due to its hazardous effects on the environment.[22] Therefore, a key goal in the coating industry is to find ecologically friendly substitutes for these commercial but hazardous coating constituents.

In this feature article, we review and discuss the recent progress in the development of multi-purpose Gr based coatings that are focused on prevention of corrosion, mechanical wear/abrasion, fouling, thermal/radiation damage, contamination and bacterial infection. The combination of unique physical structure (2D) and chemical and thermal properties of Gr (**Figure 1**) provides an excellent platform for these applications which will be described in details. As a general overview, the merits of Gr, graphene oxide (GrO) and/or reduced graphene oxide (rGrO) as protective materials are highlighted by introducing the intrinsic protective mechanisms before discussing the potential applications.

Finally, the challenges and the prospects of using Gr based materials for protective coatings are discussed and highlighted.

2. Modified graphene and graphene coating techniques

Tailoring of the Gr structure and corresponding surface properties are considered as the key parameters of Gr based functional coatings.[13, 23] The structural and chemical modification of Gr surface is necessary for not only the tunable surface properties but also to ensure the desired contact deposition, and film formation on the targeted substrate. Many approaches have been explored for the structural and the chemical modifications of Gr based materials in the last ten years which are mostly inherited from carbon nanotubes (CNTs) research.[24-26] These methods are classified into several categories including covalent and non-covalent functionalization, nanoparticle immobilization, and substitutional doping that are discussed in the available literatures.[14, 27-29]

The simplest functionalization approach is to control the oxidation of graphite flakes to generate hydrophilic GrO, which contains carbonyl, carboxyl, hydroxyl and epoxy functional groups on its basal plane and edges.[23, 30-32] In addition, stepwise and selective reduction of GrO using chemical and thermal methods can reduce and remove oxygen functionalities to transform hydrophilic GrO into hydrophobic rGrO.[33, 34] The oxygen containing functional groups (carboxyl, hydroxyl and epoxy) on the basal plane and edges of GrO are especially useful to form covalent bonds with organic molecules such as chromophores, diazonium compounds and polymers.[14, 35] Covalent attachment of highly reactive halogen groups to GrO can also provide enhanced useful properties, such as electrochemical sensing, energy storage, heat spreading.[36] This improved functionalization of Gr and GrO plays an important role to perform further modification with nanoarchitectonics by immobilizing the inorganic nanostructures (nanoparticles, nanocrystals, and quantum dots) for multifunctional applications.[36, 37] Furthermore, doping of Gr structure with nitrogen (N), boron (B), phosphorous (P), oxygen (O) and sulphur (S) has provided improved catalytic performance.[28]

Ngoc-Hoa Diana Tran is currently a postdoctoral research fellow with Professor Dusan Losic at the School of Chemical Engineering, The University of Adelaide working on the development of new technologies for processing graphite and preparation of graphene and graphene oxide nanomaterials for emerging applications. She obtained her PhD degree in Engineering (Minerals and Materials) from The Ian Wark Research Institute, University of South Australia in 2010.

Prof. Dusan Losic is an Australian Future Fellow and Research Professor at the School of Chemical Engineering, The University of Adelaide, where he is leading the NanoResearch Group. He completed his PhD in Nanoscience and Nanotechnology at Flinders University (2003), His multidisciplinary based research involves fundamental, engineering and applied aspects across several disciplines, including chemistry, materials science, engineering, biology and medicine. His major research interests are on engineering nanoscale materials, graphene, and their application for molecular separations, biosensing, drug delivery and agriculture.

Beyond these modification routes of Gr surfaces, non-covalent interaction involving the Gr π-system with other anionic, cationic molecules and hydrogen bond exhibits significant effect on the structure and properties of the Gr surface.[14, 29] These diverse functionalization methods for Gr provide exciting opportunities to develop coatings with improved protective properties that can prevent or protect surfaces from corrosion, fouling, toxic compounds, fire/irradiation and bacterial infection. These topics **(Figure 1)** will be discussed in depth in the dedicated sections below.
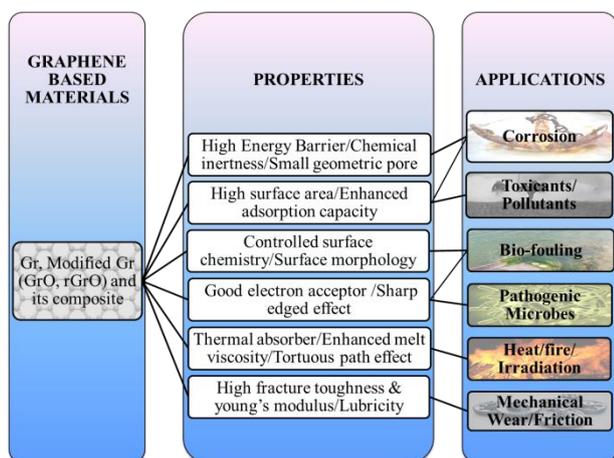

Fig. 1 Protective applications for graphene based materials

A large number of methods for preparation of Gr based protective coatings have been explored. These methods include chemical vapour deposition (CVD),[38-41] high temperature pyrolysis of organic molecules,[42, 43] rapid thermal annealing (RTA),[44] electrophoretic deposition (EPD),[45-47] powder spray (electro static powder coating and plasma spray coating),[48]

solution spray,[49, 50] dip coating,[51, 52] spin coating,[45, 53] drop casting,[54] vacuum filtration,[55] and brushing.[56, 57] In principle, they can be categorised into two basic approaches, dry and wet processing. **Table 1** shows some of the many possible methods reported for the fabrication of Gr based protective coatings to inhibit corrosion, flame/irradiation, fouling, bacterial growth, and scratch/wear. Both the dry and the wet processing techniques have different degrees of usefulness depending on the sensitivity of the environment and application.

The CVD-grown Gr is well adherent with the metal substrate as reported in early investigations,[38, 58] but this method is not suitable for extended duration corrosion resistance applications. In this case CVD-grown Gr has innumerable grain boundaries, folds, wrinkles, point defects on the coated surface that render the underlying metal material susceptible to corrosion damage.[59] Similarly, other coating applicators have some disadvantages for specific applications depending on the film formation mechanism and curing parameters. Whether Gr or Gr based composite coatings are used the coating strength depends on the interaction between the coating layer and substrate which is typically physisorption or chemisorption with the substrate. The fundamental interactions between the coating and the substrate do not depend on the application technique however the ability for the coating to be in intimate contact with the substrate obviously has an effect on the adhesion strength. There is no unique coating technique that is effective for all applications but several coating techniques may have similar film formation mechanisms. These mechanisms include physical deposition and subsequent curing,[60] self-assembly,[52, 61, 62] layer-by-layer (LBL) deposition,[63-66] and the sol-gel method[67, 68] as shown in **Figure 2.**
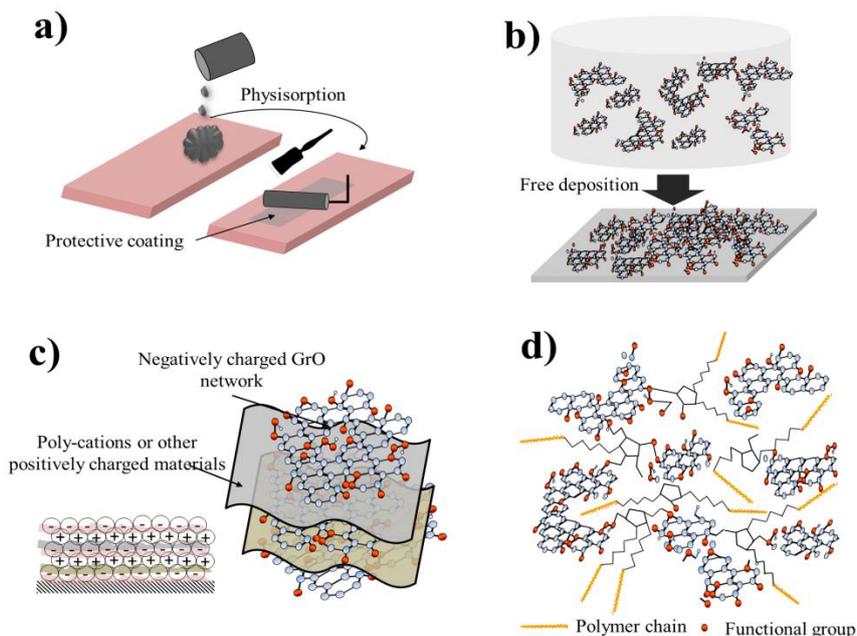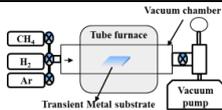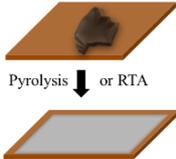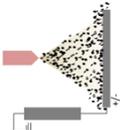

Fig. 2 Film formation mechanism of Gr and GrO, **a)** Physical deposition and subsequent curing, **b)** Self-assembly, **c)** Layer by layer deposition and **d)** Sol-gel process

Table 1 Dry and wet coating techniques for preparation of Gr based protective films

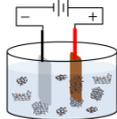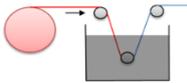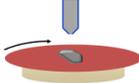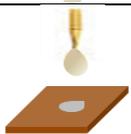| Coating Method		General Schematic	Concepts	References
Dry processing	CVD		Methane (CH_4) or acetylene (C_2H_2) gases are the precursors with argon (Ar) and hydrogen (H_2) gases injected to a CVD reactor at high temperature (around 1000 ℃) to synthesis corrosion resistant Gr coating.	38-41
	Rapid thermal processing		Organic material such as naphthalene, coronene, anthracene polyacrylonitrile, are applied over the metal substrate, which is converted into multi-layer Gr like coating by means of a pyrolysis process at 1000 ℃.	42, 43
			Corrosion resistant Gr coating can be achieved with acetone on a pre-annealed Cu- foil at 1000 ℃ by rapid thermal annealing (RTA).	44
	Powder spray		Gr/Ceramic composite powder is fed with a plasma forming gas at high temperature deposited at high velocity. Gr based polymer composite is mixed with binder and pigments in powder form and typically applied electrostatically and cured under heat. This powder may be a thermoplastic or a thermoset polymer.	48
Wet processing	EPD		Electrophoretic deposition (EPD). Negatively charged GrO is attracted to, and deposited at, an electrode of opposite charge by the influence of an electric field. A compact film remains after drying.	45-47
	Solution spray		GrO or GrO with other materials is dispersed in a suitable solvent before spraying over the substrate followed by a curing process under heat.	49, 50
	Dip coating		Substrate is dipped/immersed into a dispersion of GrO and subsequently dried after withdrawal.	51, 52
	Spin coating		Dispersed GrO solution is applied to a substrate that rotates at high speed. Centrifugal force spreads the coating material by to form a thin film.	45, 53
	Drop casting		Droplets of GrO solution is dropped on a cationic surfactant-treated surface for generating uniform films and then dried in air or placed in a drying oven.	54
	Vacuum filtration		Dispersions of Gr or GrO are vacuum filtered using a membrane support to deposit the Gr/GrO sheets. GrO based antibacterial paper and anti-fouling membranes are fabricated by this method.	55
	Brushing		Gr ink and GrO based paints have been used for coatings prepared by brush to form corrosion resistant thin films on metal and metal alloys.	56, 57

Application of Gr dispersions and subsequent curing is perhaps the simplest productive process for fabrication of Gr based films as shown in **Figure 2 (a)**. This approach has the flexibility to use substrates with different sizes and shapes that does not require any complex coating applicator. Other formation processes include solution spray,[49, 50] doctor blade,[69] brushing,[56, 57] and printing.[70] For such coatings, the strength depends on the adhesive, solvents and the curing condition. The self-concentration of the well dispersed GrO sheets with its negatively charged functional groups is the influential parameter of the self-assembly of GrO at the liquid-solid interfaces. Additionally, Gr/GrO itself can bond with π–π interaction that acts as bridges to link the sheets together to form a macroscopic film as shown in **Figure 2 (b)**. The macroscopic building blocks are often self-propelled or externally propelled (electrophoretic deposition) and can be induced by evaporative action[71] or the Langmuir–Blodgett.[72]

This simple film formation process of GrO and its subsequent reduction has been employed in different areas of protective coating.[52, 61, 62] When a self-assembly or a simple coating layer of such negatively charged GrO is overlapped by an oppositely charged material to form a bilayer thin film called layer by layer (LBL) deposition as shown in **Figure 2 (c)**. These bilayer formations can be performed in many different ways including dip coating, spin-coating, spray-coating and other flow based techniques. Strong interfacial interactions of negatively charged GrO and poly-cation or other positively charged materials are being proposed to extend the use of GrO properties in the coating industry.[63-66] Another strategy to develop GrO based functional polymer nanocomposite coatings is the sol-gel process.[67] In this process, different kinds of coupling agents (e.g. silane) are grafted onto the GrO nanosheets through free radicals to produce covalent bridges between the GrO and monomer by a sol-gel reaction as shown in **Figure 2 (d)**.[67, 68] Such covalent functionalization of Gr materials provides better compatibility and interfacial interactions in polymerization for the multi-functional protective applications.

3. Graphene based protective coatings: applications and recent progress

3.1 Graphene for corrosion barrier coatings

Corrosion is one of the biggest industrial problems with the immense annual cost about ~$2.2 trillion US, or about 3 % of the world's annual GDP.[73] The recent ban on the use of toxic corrosion resistant materials, such as chromium, cobalt, cadmium, demands urgent new alternative materials for advanced corrosion protection.[17, 19-22]

3.1.1 Barrier properties of graphene

The most recent studies suggest Gr for the control of corrosion by its uniquely impermeable 2D structure which simultaneously exhibits an exceptional barrier to reactive gases, liquids, salts and acids.[7] These barrier properties of Gr are principally attributed to its physical structure, as shown in **Figure 3 (a)**. The hexagonal pore diameter of the Gr lattice is 0.246 nm considering the nuclei of the carbon atoms with a measured C-C bond length of 0.14 nm.[74] The pore diameter reduces to 0.064 nm if the Van der Waals radii (0.11nm) of the carbon atoms are considered. Such a small geometric pore in the Gr lattice ensures minimal permeability even for smaller atoms such as helium.[5] Furthermore, the dense and delocalized electron cloud of π-conjugated carbon network in Gr[75] blocks the gap within its close packed aromatic rings and poses a repelling field to the reactive atom or molecule, thus providing a physical separation between the refined metal surface and environmental reactants. This energy barrier for a single layer coating of Gr is high enough to block the diffusion of oxygen to the underlying metal interface. The magnitude of this energy barrier varies with the path of the atomic and molecular permission through the Gr lattice as shown in **Figure 3 (b)**,[6] suggesting that Gr can be the thinnest ever known corrosion barrier.
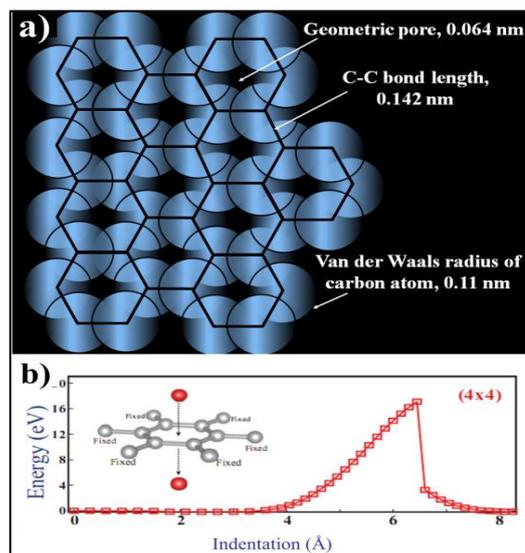

Fig. 3 (a) Close packed atomic structure of single layer Gr sheet, **(b)** Energy barriers singlet (nonmagnetic) O_2, which are forced to pass from the top to the bottom side of Gr.[6] (Reprinted with permission from ref. 6. Copyright (2012) American Physical Society)

3.1.2 CVD-grown graphene coatings as corrosion barriers

In 2011, Chen et al.[38] reported a process for CVD grown-Gr to protect metals for the first time. Here, a single layer Gr film was demonstrated to protect the metal surfaces (Copper (Cu) and Copper/Nickel (Cu/Ni) alloy) underneath from air-oxidation and liquid etchant. Only slight visible change of the coated metal was observed as opposed to the uncoated metals when exposed to air at an elevated temperature of 200 °C for 4 hours, followed by a surface treatment with 30 % hydrogen peroxide (H_2O_2) as shown in **Figure 4 (a) and (b)**. Later the reproduction of this work showed improved protection of Ni substrate even at 500 °C annealed for 3 hours.[76] Despite the coating being a good short term corrosion barrier, the wrinkles and point defects arisen in the synthesis and transfer process of the CVD-grown Gr film still allows oxidation on some places. However, multilayer-Gr solved the problem by reducing the grain boundaries and defects that appeared in the single layer-Gr, thus providing better protection over longer time period of exposure to corrosive environments.[39, 40, 77-79] A further application of CVD-grown Gr as a corrosion inhibitor was undertaken by Prasai et al.[39] where both the CVD-grown Gr and mechanically transferred CVD-grown Gr were shown to work effectively to prevent short term corrosion. Nickel with four layers of mechanically transferred Gr was found to have a corrosion rate 5 times faster than directly grown multilayer-Gr as shown in **Figure 4 (c)**. Overlapping of the transferred Gr layer was proposed to build a thicker and more robust corrosion barrier for the metal surface. However, the work did not elucidate the details of adhesion of the mechanically transferred Gr to the targeted substrate. In general, CVD-grown Gr on transient metals are weakly adhered which may result intercalation and allow lateral diffusion of oxygen atom to promote corrosion of metal substrates. To clarify this problem, Schriver et al.[59] provided an excellent report on the potential

pitfalls of CVD-grown Gr on Cu when exposed to extended oxidative environments. The diffusion of oxygen (O_2) and water (H_2O) through the defects of Gr layer oxidizes the underlying substrate and promotes wet corrosion in specific defect areas and leads to crack formation as shown in **Figure 4 (d)**. In fact the corrosion of Gr coated metal substrate was found to be more severe than the bare metal substrate when exposed to air oxidation due to the electrochemical reactions across the surface. These initial studies on CVD-grown Gr coatings or mechanically transferred Gr introduced the potential for Gr to be used against corrosion, hence providing opportunities for further advancement in this field of research through the use of commercially more feasible coating technologies.
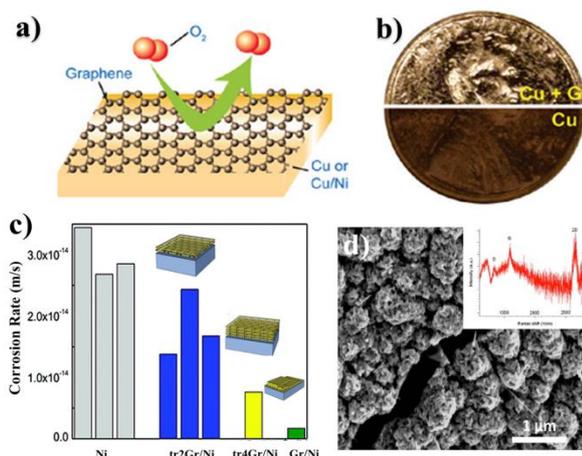

Fig. 4 (a) Illustration depicting a Gr sheet as a chemically inert diffusion barrier; **(b)** Photograph showing Gr coated (upper) and uncoated (lower) penny after H_2O_2 treatment (30 %, 2 min);.[38] **(c)** Corrosion rates of bare Ni samples and the samples where Gr was mechanically transferred onto Ni substrate and Gr grown on Ni;[39] **(d)** Complete surface oxidation of Cu foil covered with monolayer CVD-grown Gr at 250 °C for 17 hours.[59] (Reprinted with permission from ref. 38, 39, 59. Copyright (2011, 2012, 2013 respectively) American Chemical Society)
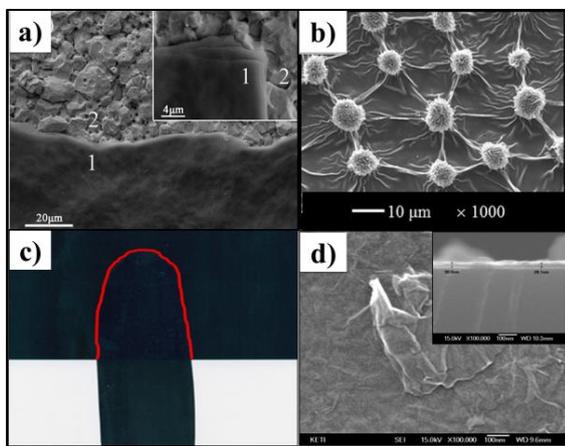

Fig. 5 Different approaches of Gr based corrosion protective coating; a) Electrophoretic deposition of GrO;[45] b) Templated epoxy/Gr based hydrophobic coating;[60] c) GrO nanopaint;[57] d) Layer-by-layer deposition of GrO and poly(ethylenimine).[61] (Reprinted with permission from ref. 45, 60, 57, and 61. Copyright (2013, 2014, 2014, 2012 respectively) Elsevier.)

3.1.3 Other graphene based coatings for corrosion barriers

Beyond the pioneering corrosion resistant reports based on Gr grown by CVD, few other facile routes have been reported to coat Gr on metal substrates to justify the anti-corrosion effect as an alternative to the CVD-grown Gr coating as shown in **Figure 5**. A thin film of GrO/poly-(hexamethylene diisocyanate) composite was coated by electrochemical deposition (ECD) on Cu and its subsequent reduction by sodium borohydrate ($NaBH_4$) (0.1 M) shows robust resistance to corrosion in a saline environment with inhibition efficiency above 94.3%.[80] Such reduction of GrO after electrophoretic deposition (EPD), shown in **Figure 5 (a)**, performs better than spin coated-GrO film due to their improved compactness in the coating layer. The degree of reduction affects the corrosion inhibitory efficiency due to dispatch of the compactness attributed to the hydrophilic nature of GrO in the aqueous environment.[45] Another simple route to fabricate Gr protective layer is rapid thermal annealing (RTA) of Cu with a drop of acetone on it. This monolayer Gr coating derived from acetone exhibit 37.5 times higher corrosion resistance in seawater in comparison to that of bare Cu. The efficiency is enhanced to 97.4 % by protecting the underlying Cu against the penetration of both the dissolved oxygen and chlorine ions. This acetone derived monolayer Gr performs even better than CVD-grown Gr due to having negligible defects on the coated Gr surface.[44]
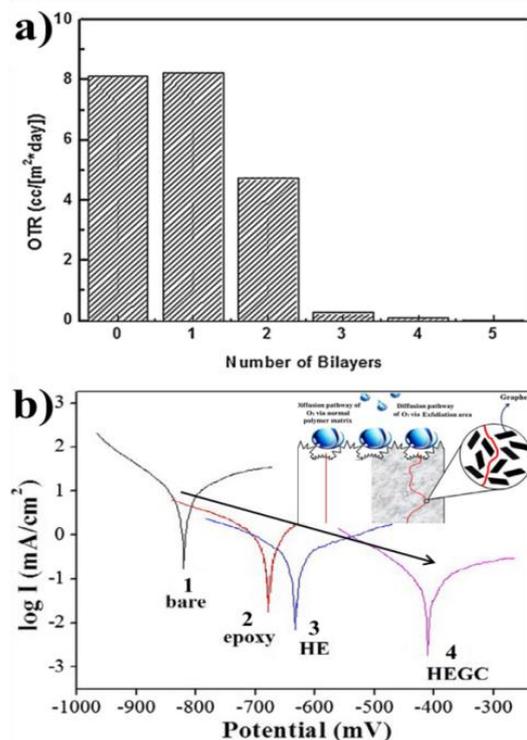

Fig. 6 (a) OTR of the oxygen barrier film as a function of the number of GrO/PEI deposition layers,[61] **(b)** Tafel plots for (1) bare, (2) epoxy-coated, (3) HE-coated, and (4) HEGC-coated cold-rolled steel electrodes measured at 25 ± 0.5 °C.[60] (Reprinted with permission from ref. 61 and 60. Copyright (2012, 2014 respectively) Elsevier)

Recently high temperature pyrolysis of organic compounds was performed to synthesize Gr coating on Ni foil. This time aromatic compounds such as naphthalene, coronene, and anthracene, are used as the precursor to achieve such corrosion protective coating,[43] which showed significant resistance against aerated oxidation at elevated temperature and acidic media.

Layer by layer deposition of GrO and poly-ethylenimine (PEI) has been investigated to improve the barrier properties of PEI deposited on polyethylene-terephthalate (PET) films (**Figure 5 (d)**). Oxygen transmittance rate (OTR) was found to decrease with increasing number of deposition layers as shown in **Figure 6 (a).** The investigation shows that PEI alone is not a good barrier to oxygen transmittance in comparison to the GrO/PEI on PET.[61] However, rGrO as a molecular and ionic barrier in an aqueous environment is proven to work superior to GrO. It is revealed that molecular permeation through GrO laminates occurs via the network of Gr capillaries into GrO coating. The capillaries of GrO have a width of 0.7 to 1.3 nm which decreases to ≈ 0.36 nm after reduction.[7] Hence reduction of GrO produces a more compact film to work as a better protective layer than non-reduced GrO.

Nanostructured roughness of epoxy/Gr composites (EGCs) was introduced to evaluate the ability for hydrophobic surfaces to resist corrosion (**Figure 5 (b)**). Interestingly epoxy alone, nanostructured hydrophobic epoxy (HE), and nanostructured hydrophobic epoxy/Gr composite (HEGC) showed successive improvement in corrosion resistance.[60] **Figure 6 (b)** shows the degree of reduction in the corrosion current (i_{corr}) improved by the approach of nanocasting and inclusion of Gr into the epoxy (**Figure 6 (b) inset**) with respect to the bare Cu substrate (down arrow). Gr in the epoxy was found to reduce the oxygen transmission rate creating a "tortuous path" effect providing an enhanced protection efficiency of 99.3 % whereas, epoxy alone showed 88.45%. Future efforts in anti-corrosive, anti-fouling and chemical shielding with graphene based coatings may draw inspiration from structured non-woven materials that have achieved superomniphobicity. Here, virtually all liquids including acid, base and wide range of Newtonian and non-Newtonian liquids are repelled from the surface.[81] Deposition of Gr ink using the solution process method can be another easy way to protect metallic surfaces from aggressive environments for shorter periods of time.[56] Recently, it has been proposed to use GrO as pigments in commercial paints to upgrade the intrinsic corrosion resistant properties of protective paints as shown in **Figure 5 (c)**.[57] It can be predicted that Gr and GrO paint additives will become commercially available in the near future.

3.1.4 Results of potentiodynamic polarization study

Potentiodynamic polarization studies in NaCl solution of several Gr and GrO based coatings (as discussed above) show different degrees of resistance to electrochemical degradation as illustrated in **Figure 7 and 8**. In general, the anodic dissolution rate of a metal substrate at a given potential is estimated by the anodic current densities, while the rate of oxygen reduction

reaction determines the cathodic current densities.[82] Hence, lower anodic current densities of the Gr coated specimens in -
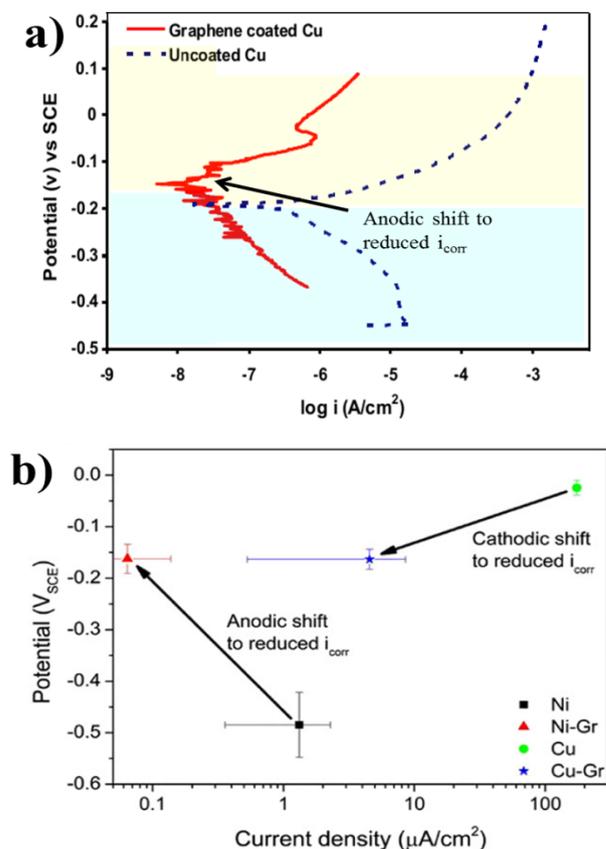
Fig. 7 Result of potentiodynamic polarization of the Gr and GrO based coating by different coating applicator (NaCl solution); **(a)** CVD grown Gr on Cu-Positive Shift of I_{corr} (0.1 M NaCl);[83] **(b)** CVD grown Gr on Ni-Positive shift of I_{corr} and Cu- negative shift of I_{corr};[77] (Reprinted with permission from ref. 83 and 77. Copyright (2012, 2012 respectively) Elsevier)

comparison to the uncoated specimens (**Figure 7 (a)**) suggests that the Gr coating acts to decrease Cu dissolution.[83]

Kirkland et al.[77] observed an anodic shift for Ni and a cathodic shift for Cu substrate when coated with CVD-grown Gr in his polarization study as shown in **Figure 7 (b)**. Other studies[45-47, 57, 83] are in contrast to the current densities demonstrated on Cu substrate reported by Kirkland et al.[77] where the i_{corr} was reduced insignificantly with an associated negative shift in the corrosion potential (E_{corr}) of approximately -0.15 V. On the other hand, studies on Gr, GrO with and without polymer,[46] or GrO as a pigment of paint,[57] showed positive shift in the E_{corr} with significant decrease in i_{corr}, which indicated good corrosion resistant of the Gr based coating. However, CVD-grown Gr on Cu reported by Raman et al.[83] acetone derived monolayer Gr on Cu,[44] and EPD of rGrO/Polymer composite,[80] results nearly two degree of reduction in i_{corr} with significant difference in E_{corr} as shown in **Figure 8 (a)** and **(b)**. This consistent resistance to electrochemical degradation of metal by different coating methods of Gr materials manifests protective potential of Gr.

However, different degrees of protection by different types of Gr based coatings are attributed to the variation of defects and thickness of coating reported by the different authors.
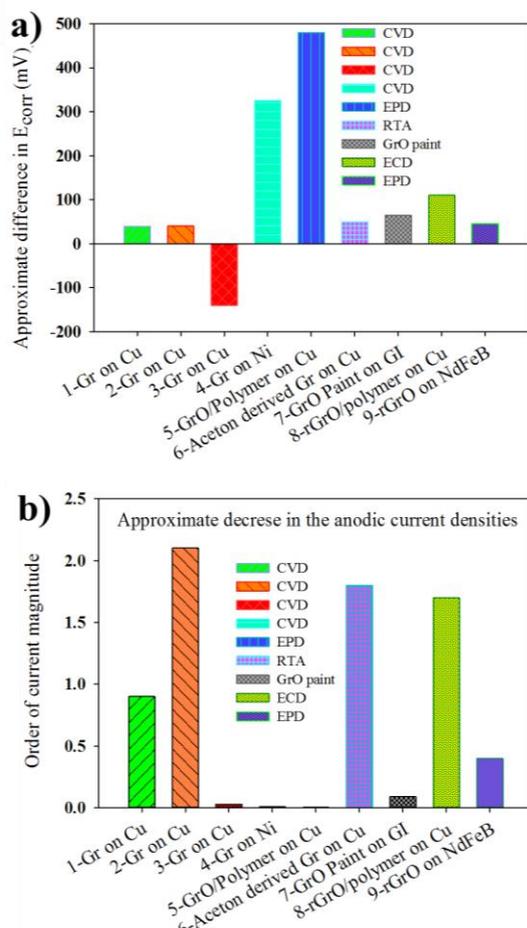

Fig. 8 a) and **(b)** Approximate difference in E_{corr} and decrease in I_{corr} for different works reported by 1-Prasai et al.,[39] 2-Raman et al.,[83] 3- & 4-Kirkland et al.,[77] 5-Singh et al.,[46] 6-Huh et al.,[44] 7-Krishnamoorthy et al.,[57] 8-Sahu et al.,[80] 9-He et al. [45]

3.2 Graphene for flame retardant coatings

A group of additive materials based on halogens (bromine and chlorine), as well as phosphorus, inorganic, and melamine compounds, have been used with polymer to improve flame retardant properties. Most of these additives, except inorganic compound, are toxic to human and environment. In addition, the high loading of these conventional flame retardant materials can cause deterioration of other effective properties of polymer and serious loss of effectiveness due to elutriation. However, the use of conventional additives can be reduced in amount by addition of Gr like new materials which withstand extreme temperatures for an extended time with mechanical stability.

3.2.1 Fire/flame retardant properties of graphene

Up to date, the use of Gr as filler materials is expected to increase the operating temperature of its composites, reduce moisture uptake, induce antistatic behaviour, give lightning strike protection by improving composite compressive strength.[1] The motivation to exploit Gr in high temperature applications is possibly due to its incredible thermal stability even at an elevated temperature of ≈2126°C (2400 K), though it encounters extensive vibrational motion and remains buckled at such high temperature as shown in **Figure 9 (a).**[84] In this regard, multilayer-Gr shows better thermal stability than the single layer at high temperature. Multilayer Gr prepared by mechanically cleavage (MC) is again more stable than CVD-grown multilayer Gr because of the relatively strong interlayer π-π interaction than that of the CVD-grown Gr.[85] However, progressive annihilation of lattice defects at the edge of CVD-grown Gr structure was identified when annealed at an elevated temperature of 2800 °C. In this process, single and multiple loop formation occurs on the ribbons edges that eventually become defect-free through graphitization and edge loop at 1500 °C as shown in **Figure 9 (b).**[9] Such graphitization and loop formation phenomena were believed to facilitate the tailoring of the Gr-structure with other molecules to strengthen the materials during high temperature operation. Moreover, owing to its high thermal conductivity (2000 to 5000 W/mK), heat dissipating capability, and gaseous impermeability incorporated with superb mechanical strength definitely makes Gr and GrO based materials ideal for high temperature applications.[2, 4, 5] Graphene materials incorporated with polymer are proposed to improve fire retardant properties such as thermal stability,[86] smoke suppression,[87] limiting oxygen index (LOI) value,[88] melt viscosity (MFI),[89] increase in char yield,[90] decrease in peak heat release rate (PHRR),[66] and anti-dripping[89] properties that motivates the exploitation of this material in fire resistant coating. However, high loading of rGrO into polymer can sometimes reduce mechanical strength of host materials despite increases in thermal stability.[91]

3.2.2 Fire retardant graphene/polymer composite coatings

One of the pioneering works on Gr as flame retardant additives was reported by Wang et al.,[89] where the presence of a Gr barrier in polymer matrix was shown to delay the oxidation of the materials. Coatings of Gr have exhibited improvement over expanded graphite, graphite oxide and functionalised graphite oxide in reducing PHRR (max^m 43.9%) at 5wt% of loading into epoxy.[92] GrO as a filler material in polyurethane acrylate resulted in a slight increase in the glass transition temperature of the composite hence, increasing the degradation temperature of the host polymer that ensured thermal stability.[86] Previously other carbon materials such as expanded graphite,[93] CNTs,[94] have also been used as nanofillers in the polymer matrix to perform as thermal absorber and to decrease the PHRR and delay time to ignition. In this case, Gr is structurally different and its synergistic effect with other fire retardant additives (cuprous oxide (CuO), 9, 10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO), intumescent flame retardant (IFR), multi-walled carbon nanotubes (MWCNTs), molybdenum di-sulfide (MoS_2), zinc sulphide (ZnS)) in the polymer matrix showed 2nd degree improvement in the major fire retardant properties listed in **Table 2**. Gr as nanocomposite filler in a polymer matrix can easily improve smoke

suppression properties of composites via the so-called "tortuous path" effect of the layered impermeable Gr structures (**Figure 10 (a)**). This hinders the escape of volatile degradation products especially carbon monoxide, thus reducing a major fire hazard.[87] This physical barrier can also significantly slow the combustion process of the polymer matrix and provide better flame retardant effects by the reduction of PHRR and LOI value. Another investigation found Gr and MWCNTs work together to improve the suppression of volatile degradation products generated during the combustion of epoxy polymer. The pore size and penetrative network of the composite dominates the flame retardancy of the host polymer.[88] The presence of 1D nanotube and 2D Gr creates an efficient impermeable structural network to resist the decomposed gas release (**Figure 10 (b)**).
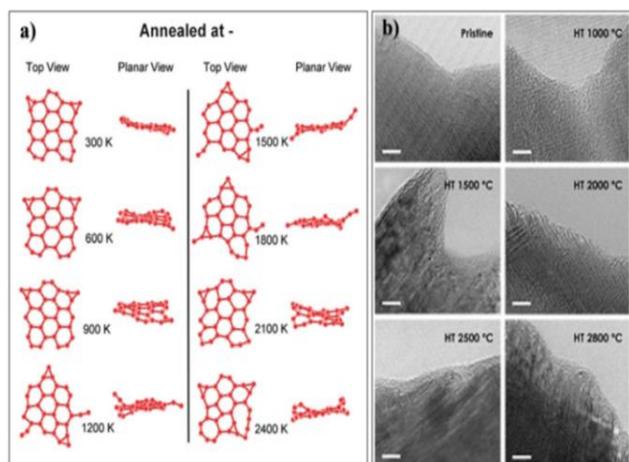

Fig. 9 (a) The top and planar views of the structure of asymmetric C32 flake annealed at various temperatures;[84] (b) Transmission electron micrographs of Gr- nanoribbons heat treated at various temperatures focusing especially on the structural changes of the edges as annealing temperature is increased (scale bar = 5 nm).[9] (Reprinted with permission from ref. 84 and 9. Copyright (2008 and 2009) AIP publishing LLC and Elsevier respectively)

Recently, ZnS incorporated with Gr-flakes into epoxy polymer was found to provide another mechanism to reduce the hazards of fire. Here, it was found that densification of the char layer lowered the efficiency of heat and volatile transfer.[95] In this regard, ZnS is expected to catalyze the carbonization of

degradation products while Gr can function as a physical barrier to adsorb degradation products and extend its contact time with the ZnS as shown in **Figure 10 (c)**. Microchar formation from the degradation products is intensified by ZnS on Gr and works as a template for another char layer. These degradation products are also converted into char by the combination of the physical barrier effect of the Gr flakes and the catalytic effect of ZnS.
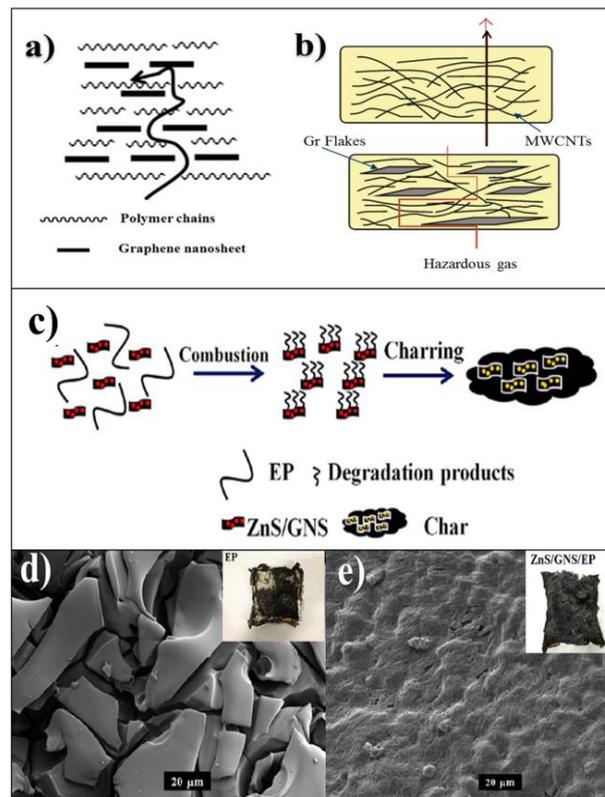
Fig. 10 Mechanisms of reducing fire hazard; a) Gr into polymer shows tortuous path effect to improve smoke suppression,[87] b) Synergy of Gr and MWCNTs in polymer for superior barrier effect,[88] c) Synergy of Gr and ZnS in Polymer for dense char formation ,[95] d) SEM surface morphology of epoxy char residue, [95] and e) Char residue of ZnS/Gr/Epoxy.[95] (Reprinted with permission from ref. 87, 95 Copyright (2013 and 2014 respectively) American Chemical Society.)

Table 2: Graphene based materials in fire retardant coating

Materials	Wt % of Gr or GrO	% increase in fire hazard properties			
		LOI value	Reducing % of PHRR	Char yields-%	Smoke suppression %
GrO/IFR- poly-acrylamide[66]	--	---	50%		---
Silane treated-Gr- Epoxy [68]	--	27		90 % at 800 °C	
Gr/MWCNT- Epoxy[88]	7.5		35 %		
Gr/CuO-Polypropylene [87]	< 1				47.2
Gr/IFR-Poly(butylene succinate)[89]	2	33			
DOPO/rGO-Epoxy[90]	<10	26		81 wt% at 700 °C	
MoS$_2$/Gr – Epoxy [96]	2		45.8 %		
ZnS/Gr- Epoxy[95]	<2		47%		high
SnO$_2$/Gr and Co$_3$O$_4$/Gr - Epoxy[97]	2				Medium

Figure 10 (d) and **(e)** shows the micro structure of the char formation of epoxy alone and composite of ZnS/Gr/epoxy, respectively. The composite results in a dense char layer formation that can protect the underlying surface in contrast to the rough and dissociated surface with a mass of cracks and holes in the epoxy char. Continuity in the char layer with good compactness and degree of graphitization are important factors for efficient thermal and mass loss insulation that dominate flame retardant properties.[96] Furthermore, the synergy of Gr and IFR into poly-butylene succinate composites is proven to increase the molten viscosity during the burning process by resulting enhanced restrain of melt dripping and improving the LOI value, MFI, and char yield.[89] The char layer constitutes a two-way barrier, for hindering the passage of combustible gases and molten polymer to the flame. This also provides shielding of the polymer from the heat of the flame.

Fire-retardant properties for cotton-fabrics that are normally fire sensitive have been developed by coating with Gr-IFR/polyacrylamide using LBL deposition.[66] Increasing the number of coating bi-layers significantly decreases PHRR, increases char residue, and delays ignition time of cotton fabrics. Tensile and tear strength of cotton fabrics are also improved by the incorporation of Gr in the polymer composite coating. In addition, David et al.[50] revealed that the potential for CNTs to protect against thermal damage is multiplied when CNTs are incorporated with rGrO as a composite coating exposed to laser irradiation, which can endure at least 2 kW.cm^{-2} for 10 seconds without significant damage. In this case, CNTs act as an efficient absorber of laser light while the much larger rGO sheets dissipate the heat over a wider area in order to minimise the thermal load and subsequent damage. Recently dispersed Gr in both heavy-atom solvents and polymer film matrix is reported to show excellent capability for broadband nonlinear optical absorption at fluences with a strong matrix effect. Such optical limiting materials are useful for the protection of sensitive sensors and devices from laser damage, and for optical circuits.[98] Overall, the research on Gr as a fire retardant additive shows great potential and has inspired work to protect many other fire and radiation sensitive structures (foam, aerogel, fabrics) from thermal damage caused by both fire and laser irradiation.[99]

3.3 Graphene for wear, scratch and fatigue resistant coatings

Wear and scratch resistant coating have been widely used in many industrial applications to reduce friction between dynamic interfaces. Solid surfaces subjected to cyclic load experience severe surface fatigue leading to reduced efficiency or failure. Basic engineering seeks to improve surfaces in order to increase performance, efficiency or working lifetime of devices. Vehicles, aeroplanes and ships need to be light weight, strong and smooth in order to minimize friction under the shear forces.

3.3.1 Wear and scratch resistant properties of graphene

Unlike previously described corrosion resistant and fire retardant coatings, Gr has also demonstrated to be a potential and promising candidate for wear and scratch resistant coatings

because it is the thinnest,[100, 101] lightest,[101] and strongest known nanomaterial.[4] In this case the ability for a mono-layer Gr film to withstand high pressure differences (6 atm) indicates its mechanical robustness.[5] The mechanical strength is quantified by measuring elastic modulus of chemically exfoliated GrO determined to be about 0.25 TPa,[102] whereas a defect-free Gr monolayer shows elastic modulus of 1 TPa with an intrinsic breaking strength of 42 N/m, (**Figure 11 (a)**).[4] This incredible mechanical strength of Gr is attributed to the strong covalent bond between the C-C atoms formed by sp^2 hybridization in the hexagonal closed packed crystal structure with a bond length of 0.142 nm.
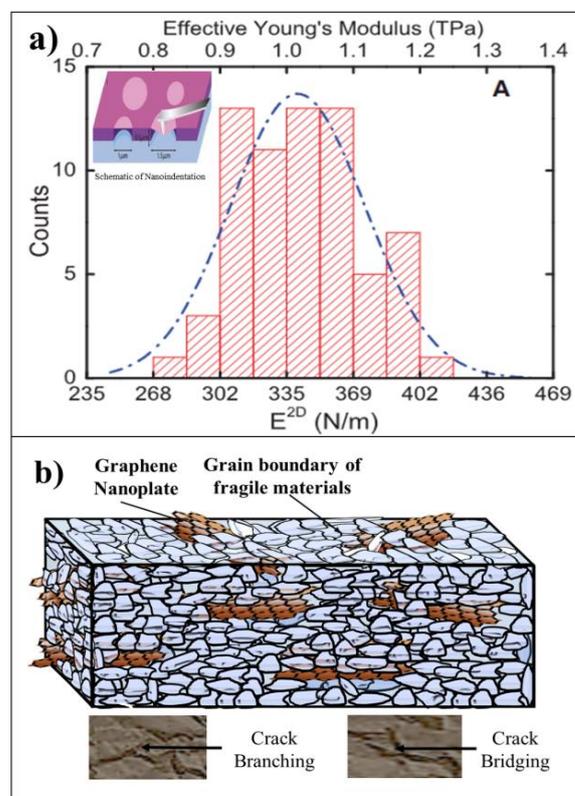
Fig. 11 (a) Histogram of elastic stiffness of Gr.[4] **(b)** Strengthening mechanism of fragile materials by Gr. (Reprinted with permission from ref. 4. Copyright (2008) AAAS)

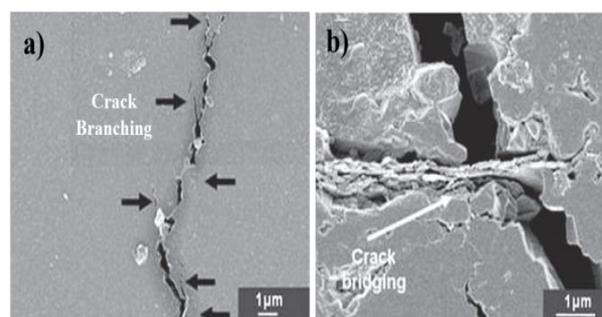**Fig. 12** (a) Crack branching at platelets with lower dimension characteristic for the systems; b) Crack bridging by platelet with the plane orientated nearly perpendicularly to the plane of the section.[103] (Reprinted with permission from ref. 103. Copyright (2012) Elsevier)

Gr can effectively prevent or reduce mechanical failure by strengthening and toughening the loaded surface as well as by transferring the stress throughout the structure.[104, 105] In fact, Gr can bridge grain boundaries of fragile and brittle surfaces in order to reinforce ceramic materials as shown in **Figure 11 (b)**. Crack branching, crack bridging, resistance to crack tip propagation, crack deflection are the results which are observed during crack formation of the samples, reinforced by Gr nanofillers as shown in **Figure 12 (a)** and **(b)**.[106] Gr hinders the ceramic grain growth and assists to generate crack deflection, bridging and branching while crack propagates under severe load. In addition, other mechanical properties, such as cold modulus of rupture, flexural modulus, force displacement, of the ceramics matrix can be significantly improved by this 2D strongest filler material.[107] Mechanical properties of host materials are enhanced by the addition of Gr material such that they can resist structural collapse, mechanical fatigue, and permanent deformation by distributing the operating stress and increasing the elasticity. This improvement in structural integrity of material surface improves wear resistance of the sliding interfaces.

3.3.2 Tribological outcome of graphene reinforced coatings

The positive tribological outcomes of Gr reinforced material under various dynamic loads revealed the potential of Gr based coatings in macro and micro tribology. Indeed, both Gr reinforced coatings and Gr lubricants are capable in reducing the wear/mechanical failure of sliding surfaces. Firstly, Gr has been reported to function as nanofiller to form a bridging network in the coating materials and secondly, to use as solid lubricant to reduce abrasive wear. Sometimes Gr coating on other weak structure enhances structural strength against mechanical fatigue For example, an aerogel-like, lightweight, inelastic and fragile structure can become super-elastic and mechanically strengthened to resist against mechanical fatigue when coated with a few layers of Gr.[42] This Gr-coated aerogel can be derived from polyacrylo-nitrile polymer prepared by pyrolysis which retains similar mechanical strength after being subjected to more than 1×10^6 compressive cycles. Its original shape can be quickly recovered after the compression release as shown in **Figure 13 (a)** and **(b)**. The coating is also found to increase Young's modulus and energy storage modulus by a factor of ~6, and the loss modulus by a factor of ~3. The load transfer from Gr to CNTs is favoured by the tight covering of CNTs, providing a super-elasticity for the entire aerogel structure as shown in **Figure 13 (c)**.[108]

Reduced GrO has been studied as an anti-friction and anti-wear coating material to ensure the steady-state operation of titanium (Ti) based micro and nano electro-mechanical systems (MEMS/NEMS) devices.[52] The self-assembly of GrO deposited on the Ti substrate and its hydrothermal reduction shows significant decrease in the adhesion and friction force which provides less affinity to the humid environment. The coating also improves the anti-wear properties as determined by measuring the wear depth under 500 nN applied force. In macroscale tribology, the addition of small fraction (2.0 wt.%)

of functionalized-Gr to a polyurethane nanocomposite coating on polytetrafluoroethylene (PTFE) exhibits 71 % increase in the tensile strength and a 86 % improvement of Young's modulus of coated surface.[67]

Another study on polymer based Gr composite coating shows significant improvement in the wear life by loading a small amount of Gr into the Polyamide11 composite coating. As little as 0.4 wt % of Gr into Polyamide11 composite deposited by spray coating on 45 steel (ASTM steel 1045) substrate provided 460% –880 % improvement in the wear resistant under 150 N force after plasticisation. Interestingly, Gr is able to suppress wear 10-30 times better than the polymer composite made with graphite microparticles.[49] Higher fraction of Gr loading (10 wt%) into PTFE has also been reported to reduce the wear rate from $0.4 \times 10^{-3} mm^3/Nm$ to ~$10^{-7} mm^3/Nm$.[109] which is 10-30 times wear rates achieved by micro size graphite at the same loading.
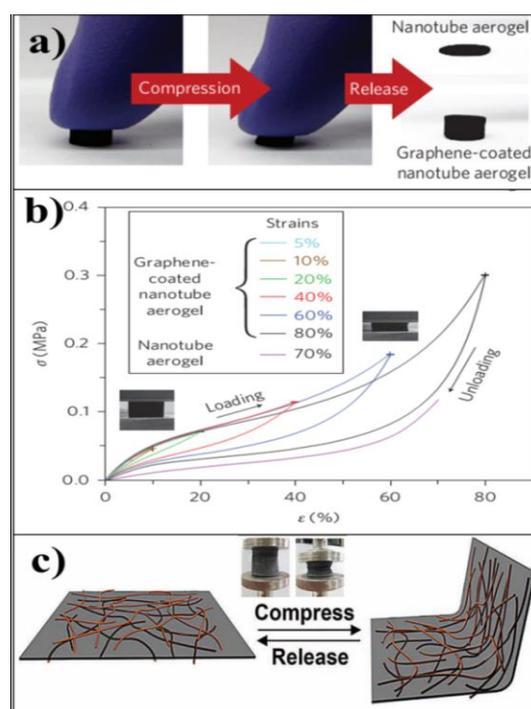
Fig. 13 (a) Macroscopic visualization, showing that nanotube aerogels collapse and Gr-coated aerogels recover their original shape after compression by $\geq 90\%$, **(b)** Stress (σ) versus strain (ε) curves for nanotube aerogels along the loading direction and for Gr-coated aerogels during loading–unloading cycles;[42] **(c)** Elastic mechanism of Gr and CNTs composite aerogel.[108] (Reprinted with permission from ref. 42 and 108. Copyright (2012 and 2013) Nature publishing group [Nat. nanotechnol.] and John Wiley and Sons respectively)

Potential increased biocompatibility of GrO leads scientists to explore the use of GrO in bio-tribological applications where the wear resistant properties of biomaterials are a key area for improvement. For example improvement of the tribological strength of implant bearings for joint implants is a required. In this case, GrO incorporated with ultrahigh molecular weight polyethylene (UHMWPE) shows transformation of fatigue wear to abrasive wear that is associated with the generation of a transfer layer on the contact surface, which efficiently reduces

the wear rate of UHMWPE.[110] The loading effect of GrO into UHMWPE on the wear rate and hardness is shown in **Figure 14**. Gr reinforced coatings have also been investigated with other biomaterials such as calcium silicate, and alumina and have provided improved anti-wear and anti-friction properties.[48, 111] Calcium silicate based Gr composite coatings were found to increase the number of adherent particles on the surface at higher Gr contents. The improved wear performance is due to the increase in the wetting behaviors (cell adhesion) of the ceramic matrix in biological environment influenced by Gr with below 4 wt % of loading.[48] Similarly, the insertion of Gr platelets into Silicon nitride (Si_3N_4) matrix as nanofillers increases the tribological performance by creating an adhered protective tribofilm formed by the exfoliation of the nanoplatelets under high contact pressure between the sliding surfaces.[112] This is how Gr reinforced ceramic coating plays a significant role to reduce delamination under bearing load.
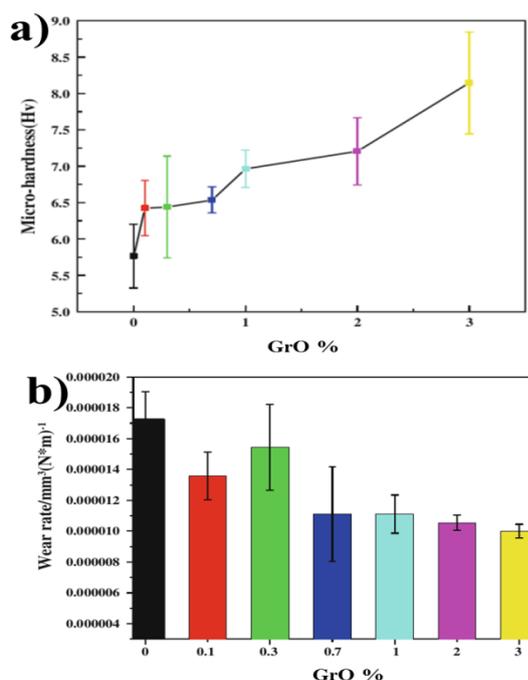

Fig. 14 (a) The microhardness of GrO/UHMWPE composites with the different GrO contents; (b) Variation of wear rate of the GrO/UHMWPE composites as a function of GrO content after the wear tests.[110] (Reprinted with permission from ref. 14. Copyright (2012) Springer)

3.3.3 Graphene based lubricants to protect surface

Gr thin films are also found to provide a protective layer while working as solid lubricants to reduce surface wear. More than a decade ago, it was proposed that solid lubricants in the form of thin films would perform better than powder or bulk forms at temperatures ranging from -270 to > 1,000 °C.[113] Gr nanoflakes have made this proposition true and provide even more efficient lubricity than graphite particles. Accordingly Gr has been reported as a new emerging lubricant.[114] Recently Gr and GrO are reported to be effective as solid lubricants,[115, 116]

and as an additive for base lubricants.[117-119] Multilayer Gr has minimizes the puckering effect caused by interlayer shear of themselves on a dynamic surface and acts as a passivation film to reduce adhesion and friction force as shown in **Figure 15**. Such layered Gr structure under dynamic load resists tribo-corrosion by forming a thin tribofilm and preventing direct contact of the sliding interface. [120, 121]
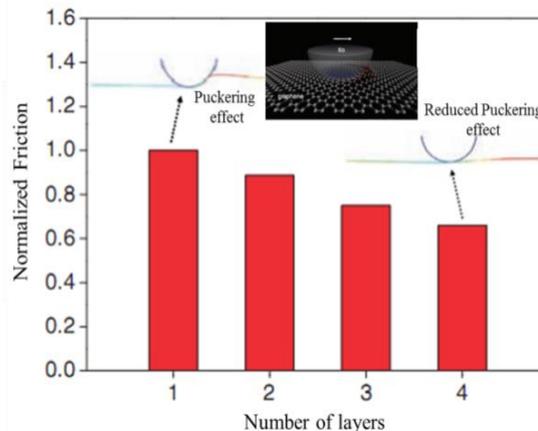

Fig. 15 Mechanism of reducing puckering effect by multi-layer Gr;[120] (Reprinted with permission from ref. 120. Copyright (2010) AAAS)

Superior lubricity of Gr is attributed to the sliding of Gr on neighbouring Gr flakes driven by temperature sensitive transitional and rotational motion between initial and final states.[122] Few layer Gr shows promising results to decrease friction coefficients by a factor of 6 on sliding steel interfaces both in air[123] and in dry nitrogen.[124] Gr based materials in ethanol,[123] water,[117] and oil[118] as additives works greater than base lubricants in reducing wear rate. GrO in water has been reported to be adsorbed by the frictional surface to form a thin film that behaves as a protective coating. This protective coating surprisingly generates no appreciable surface wear which was demonstrated after 60,000 cycles of friction testing under 1.88 N with a tungsten carbide ball on stainless steel flat plate.[125] Another study showed that the inclusion of multilayer GrO in water even has superior wear reduction performance in comparison to MWCNTs in water.[117] Modification of Gr by oleic acid also shows 14 % reduction in the diameter of scar which implies significant improvement in resisting direct contact of the sliding point.[119] In summary Gr, GrO and other forms of modified Gr as filler materials in polymer and ceramic based surface coatings and as additives to conventional lubricants present further promising applications of Gr in protective coatings.

3.4 Graphene enhanced antifouling coatings

The most practical and widespread fouling problem is deposition of organic and inorganic materials on marine vessels and structures including, cargo ships, military and leisure vessels, heat exchangers, oceanographic sensors, oil rigs, desalination system and other aquaculture system. The cost associated with such particulate, precipitation, and

solidification on ship hulls is estimated at \$180 to\$260 million per annum for only the entire US navy fleet that includes maintenance, powering penalty and fuel consumption.[126] In addition, the total ban on the use of TBT in antifouling coatings since January 1, 2008 demands new materials in this sector to save billions of dollars in the world.[18]

3.4.1 Properties of graphene to resist fouling

Several strategies have been developed to fight against both the organic and inorganic foulants and to resist successive surface fouling. These strategies include self-cleaning surfaces, biomimetic nanostructure, biocidal and newly developed amphiphilic surfaces.[126-128] Graphene is a good candidate for use as an anti-sticking coating agent. Surface tailoring of Gr structure facilitates design of antifouling coating with desired surface polarity and wettability.[33, 34] Super hydrophobic and super hydrophilic Gr based coatings have been proposed to prevent particulate fouling.[53, 129] Furthermore, due to its impermeable structure, Gr can increase salt rejection when coated on membranes.[130] The inclusion of carbon materials (graphite, CNTs, diamond-like-carbon (DLC), fullerene, carbon blacks) in antifouling coatings is not new and has already been extensively studied because of their known antibacterial, anti-settlement and salt rejection properties.[131-136] The success of these pioneering studies using other carbon allotropes in antifouling applications inspires work to integrate the newest member "graphene" due to its superb antibacterial properties,[137] flexible surface chemistry,[27] controlled protein adhesion,[138] and the ability to covalently bind with polymers when functionalized.[139]

3.4.2 Use of graphene in fabrication of antifouling coating

The use of Gr as an anti-settlement coating material has been investigated for application in waste water treatment, desalination systems, bioreactors and marine structures. This material is demonstrated to resist the deposition of dust, marine salts, microorganisms, proteins and cells on the useful surfaces. Graphene has been explored in the development of surfaces that facilitate cleaning via super-hydrophilic and super-hydrophobic action for dust deposited on indoor or outdoor engineered surfaces.

Titanium dioxide (TiO_2) loaded with Gr as a coating has been investigated to improve photo-induced self-cleaning properties. The composite coating functioned with enhanced hydrophilicity and even functions under extremely low UV intensity making it useful for indoor light apparatus.[53] Another study exploited Gr to fabricate a bi-functional, conductive and super hydrophobic coating combining with polyhedral oligomeric silsesquioxane (POSS) and CNTs showing a water contact angle about 155°. This Gr-based nanostructured hybrid coating have good potential use to prevent adhesion of water and snow to windows or antenna sand as self-cleaning, coating films for electronic devices.[129] Controlled fluorosilanization treatment on graphene coated cotton fabric may provide a new routes of fabrication of superoleophobic foulant resistant coating.[140]

One of the simplest ways of exploiting Gr based materials as antifouling additives is to use them as pigments in commercial paint formulations. Krishnamoorthy et al.[57] found that with GrO pigment in alkyd resin enhances the ability for the coated surface to resist the colonization of microorganisms, hence preventing/reducing the biofilm formation in the aqueous environment. The mechanism of the antifouling behaviour was not clearly discussed, but referred to a general antibacterial effect induced by GrO.[141] The change in surface morphology and surface energy due to addition of GrO in Alkyd resin might be a possible reason to change the adhesion mechanism.

Cell adhesion was found to be affected by GrO induced wettability when GrO was introduced into a gallium nitride (GaN) nanowires film. The cell-repellent property was reported to be controlled by the nanostructure and surface wettability of the film influenced by GrO.[142] In biofouling studies, it has been shown that GrO is less effective than nano-carbon black on the settlement of Amphibalanus amphitrite cypris larva but more active in altering the survival and inhibiting the swimming behaviour of the nauplii larva. The variation in results may have significant effect on the use of different particle size of both structurally different carbon materials.[136]

Research in the waste water treatment system has found that small inclusions of GrO (1 wt%) in polysulfone can result in large impact on reducing the formation of bio-film on membranes as shown in **Figure 16**.[143] The presence of GrO increases the negative zeta potential value due to the negatively charged, oxygen containing, functional groups. It is thought that these groups cause electrostatic repulsion between the microorganism and the membrane surface and thereby impede intimate contact and subsequent surface attachment of the microorganism.[143] It is also expected that the GrO-containing thin films can effectively deter fouling of membranes with precursors (bio-products, molecules, lipids) to microbe adhesion. Interestingly, polyester filter cloth coated with Gr and polyaniline-doped-phytic acid (PA) has been found to have enhanced antifouling properties for membrane bio-reactors. Membrane with higher conductivity was attributed to the addition of Gr had better antifouling property under the applied electric field.[144] The modified highly conductive membrane with applied electric field could suppress the deposition of particles to avoid internal pore clogging of the membrane. So it can further resist follow-up fouling mainly caused by the filtration cake layer.

Graphene oxide and oxidised-MWCNTs in 5:5 ratio are reported to work in synergy to reduce fouling of polyvinylidene fluoride (PVDF) ultrafiltration membranes. Improved hydrophilicity and change in membrane morphology of PVDF has been identified to reduce foulant cake formation. Enhanced hydrophilicity of GrO/Oxidised-MWCNTs also lowers the interaction of model foulant bovine serum albumin (BSA).[145] Currently, boron doped-Gr electrodes,[146] Gr or GrO/polypyrrole,[147] Polyvinylidene fluoride/GrO,[148-150] and polyethersulfone/GrO,[151] have been shown to reduce bio-fouling significantly.
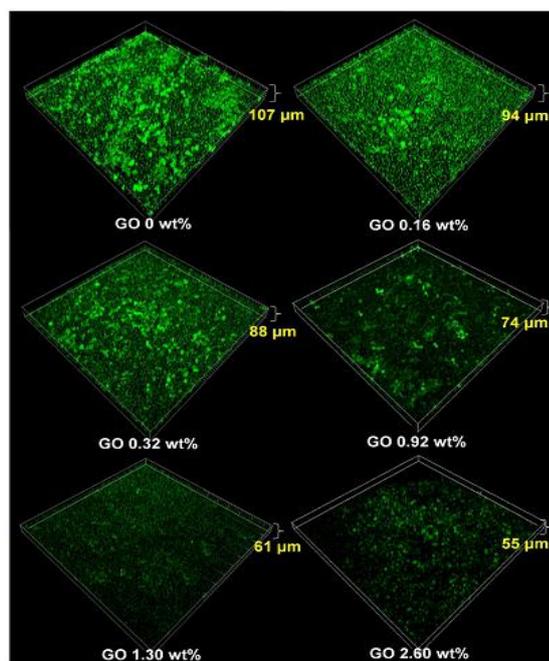
Fig. 16 Biofilm formed on surface of membrane containing various GrO contents. CLSM images of biofilm formed by attached microorganism (P. aeruginosa,PAO1) on membrane surface.[143] (Reprinted with permission from ref. 143. Copyright (2013) Elsevier)

In the desalination system, deposition of marine salt is considered as a major inorganic foulant. The deposition of salt can be significantly reduced by introducing GrO into polysulfone (PSf). The membrane loaded with 2000 ppm GrO exhibited a maximum of 72 % Na_2SO_4 rejection at an applied pressure of 4 bar whereas about 55% NaCl rejection was recorded under the same working condition.[130] Latter, rGrO/polyaniline composite dispersed in PSf showed improved salt rejection properties with enhanced porosity and water flux in comparison to the work reported by Ganesh et al.[130, 152] The rGO/polyaniline-modified membrane exhibited a maximum of 82% NaCl rejection at an applied pressure of 10 bar. The incorporation of rGO into the membrane matrix led to hydrophobic membrane surface with the enhanced macro-voids whereas partly hydrophilic zone is identified influenced by polyaniline fibers.[152]
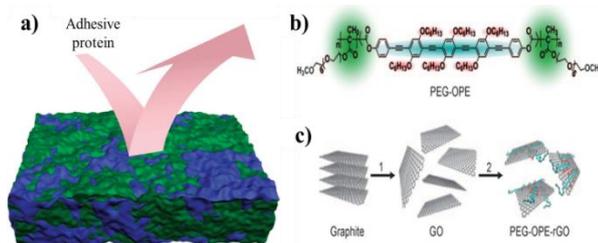

Fig. 17 a) The concept of a chemically heterogeneous or 'mosaic-like' surface that repels proteins,[126] **b)** Chemical structure of PEG-OPE co-polymer, **c)** The synthesis of amphiphilic PEG-OPE-rGrO structure in H_2O. **Step 1**: Oxidation of graphite yields single-layer GrO sheets. **Step 2**: Chemical reduction of GrO with hydrazine in the presence of PEG-OPE produces a stable aqueous suspension of PEG-OPE-rGrO.[153] (Reprinted with permission from ref. 126, 153. Copyright (2011, 2010) Nature Publishing Group and John & Wiley Sons respectively)

Recently Gr and GrO materials have been attracting great attention for use in oil/water adsorption/separation, however fouling is still a practical problem for the structure used during the operation (on the surface or underwater).[154] Li et al.[155] revealed that tuning of GrO coatings on porous membranes with ultraviolet (UV) irradiation before use in underwater operation modify the chemistry and morphology of GrO flakes via oxidative etching Cyclic oil/water separation tests of the UV-treated superoleophobic GrO coatings exhibited excellent antifouling and ease-of-cleaning performance.

The synthesis of amphiphilic Gr nanoplatelets[156] motivates the exploitation of Gr in the design of non-biocidal advanced nanostructured coatings that combats against a diverse range of foulants with an effective adhesion resistant mechanism as shown in (**Figure 17 (a)**).[126] Gr composite using an amphiphilic coil-rod-coil conjugated triblock copolymer (PEG-OPE; chemical structure shown in **Figure 16 (b)**) gave rise to a new green approach that incorporates Gr based polymer structures for the application in an anti-biofouling coating.[153]

3.5 Graphene coatings for pollutant adsorption

The application for Gr and Gr containing coatings to adsorb and sense substances is receiving increased attention while we predominantly focus on adsorption of pollutants here. The field has broader relevance to nanocarriers, delivery vessels, and sensors. Coatings of Gr have high affinity for particular matter and can be applied to trace the presence of specific substances dissolved in the aqueous or soil environment.

3.5.1 Adsorptive properties of graphene

Surface area and controlled surface chemistry are the major attributes of Gr materials that lend themselves to adsorption tasks since contaminants exhibit variable affinities for different surface functional groups and pore sizes.[157] Gr is a good candidate because of its high specific surface area (theoretically, 2700 m^2/g),[12] and flexibility for surface tailoring for selective adsorption and desorption applications.[14] Furthermore, Gr and GrO-based porous structures (~700 m^2/g to 1019 m^2/g) provide more active sites relative to the other materials (nanowire membranes, micro-porous polymers, carbon nanotubes, chitosan monoliths) applied in this area.[158-160] Therefore, Gr and GrO along with these materials are intensely studied for the adsorption of heavy metal ions (i.e. Cr, Co, As, Pb, Cd), dye and organic pollutants dissolved in water. Different degrees of adsorption for Gr and GrO based structure are reported for different type of pollutants required for recovery, and sensing.[161, 162] Graphene typically exhibits hydrophobic and oleophilic properties while GrO is hydrophilic and halogenation with fluorine makes GrO oleophobic.[154, 163] These chemically functionalized Gr based materials have recently become a highly studied area in pollution management. In this regard, it has been found that the oleophobicity/hydrophilicity of GrO coated membranes can be tuned with UV light source to conduct the etching treatment of the GrO dispersion for different times. The UV treated GrO

resist underwater bio-adhesion thus increasing separation efficiency.[155]

3.5.2 Synergy with other carbonaceous materials

Studies in this area is intensified by introducing a synergy of Gr-CNTs monolithic structure showing super hydrophobic and super-oleophilic properties for selective removal of organic pollutants from the water surface.[164] Their reduced oxide (GrO sheet with acid treated CNTs) can form in a robust aerogel with increased porosity and oleophilic properties. Such 3D structure can recover petroleum products, fats and organic solvents especially under continuous vacuum regime showing adsorption capacity of 28 L of oil per gram of aerogel.[165] Further development of such Gr based structures have resulted in the continuous adsorption and expulsion of oil from the water up to 35000 times its own weight with an oil purity >99.97 wt %.[154] Nano-Gr flakes as a simple adsorptive material in microfiltration membrane coating has been reported to function better than MWCNTs for contaminant removal while causing minimal flux reduction. Superfine activated carbon powder showed fastest removal of model contaminants amongst three carbonaceous adsorptive coating materials tested (superfine activated carbon, MWCNTs, Nano-Gr flakes). The variation in adsorption and removal capacity among these carbonaceous materials was due to the different external adsorption surface areas which is often influenced by applied coating approach.[157]
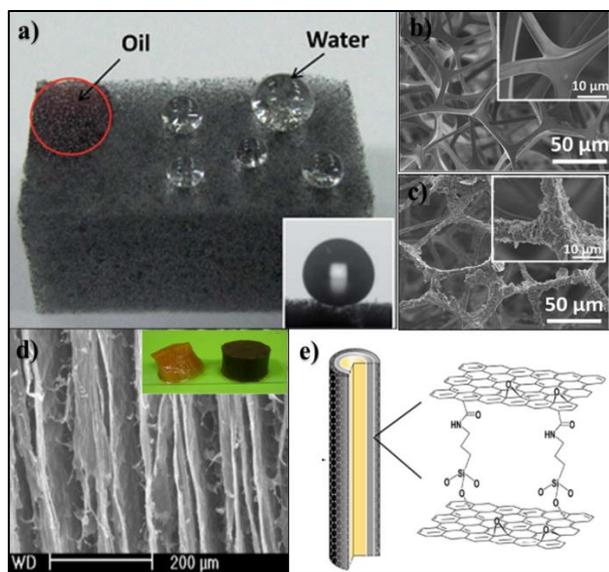

Fig. 18 a) Water droplets as quasi-spheres and motor oil trace on the surface of the Gr coated sponge,[166] **(b)** Typical FESEM images of the pure sponge,[166] **c)** The Gr-coated sponge at a loading of 7.3%,[166] (d) GrO (3 wt%) coated gelatin-Chitosan monoliths,[167] **(e)** Gr-coated Solid-phase microextraction (SPME) fibre.[65] (Reprinted with permission from ref. 167 and 65. Copyright (2011 and 2011) Elsevier and American Chemical Society respectively) (Ref. 166, RSC publisher)

3.5.3 Graphene coated porous structures for adsorption

GrO has been identified to be used for coating porous sponge like structures to change its absorption capability,

compressive strength and active surface area (**Figure 18 (c)**).[166, 167] Graphene was coated on a commercially available melamine sponge as shown in **Figure 18 (a)**, which had the absorption capacity of both water and oils or organic solvents before Gr coating.[166] However, this Gr coating regulates the sponge's characteristic from superhydrophilic (water CA of 0) to superhydrophobic (water CA of 162) and absorbs a broad variety of oils and organic solvents with high selectivity, good recyclability, and excellent absorption capacities approaching 165 times its own weight.[166] Similar research showed that the Gr/gelatin-coated chitosan monolith porous structures provide maximum porosity of 97% with an extremely high adsorbing ability for metal ions as shown in **Figure 18 (d)**. This change appears to be due to the large number of functional groups possessed by the GrO coated structure, which results in the variation of the surface area and absorption capacity.[159, 167, 168] In fact, GrO has the highest adsorption capacities of today's nanomaterials showing 1850 mg g^{-1} at 333 K for Pb (II) ion adsorption from aqueous solution.[169]

Another application of adsorptive coating is in solid-phase microextraction (SPME), SPME fibers have been developed by rGrO coating on the fused-silica substrate (**Figure 18 (e)**). The rGrO-coated fibres exhibited higher enrichment factors (EFs) as compared to the commercial polydimethylsioxane (PDMS) fibres. This repeatable and precise method was applied to simultaneous analysis of eight polycyclic aromatic hydrocarbons (PAHs) with satisfactory recoveries (84-102% for water and 72-95% for soil samples). The dominant role of π-π stacking interaction and hydrophobicity is believed to cause the strong adsorption affinity to PAHs.[65] It is likely that Gr-coating of commercial sensors and sensing equipment will enhance adsorbing and sensing applications in the future. In the laboratory, GrO/Silica composite coatings have been successfully applied for the detection of heavy metals (Mn, Co, Ni, Cu, Cd and Pb) in environmental water samples with recoveries ranging from 85 to 119 %.[170] Similarly, electrodes coated with Nafion/Gr composite was introduced for detection of metal ions (lead (Pb^{2+}) and cadmium (Cd^{2+})) in water sample.[171] The detection limits were estimated to be around 0.02 µgL−1 for Pb^{2+} and Cd^{2+}. The synergy of Gr and Nafion has been reported to enhance sensitivity compared with that of Nafion coated electrodes which was attributed to the strong adsorptive capability and huge specific surface area, good conductivity of Gr nano-sheets. This composite coating also provided better protecting coating to alleviate the fouling effect of surfactants.

3.6 Antiseptic coatings incorporating graphene

Antiseptic coatings are an important developing application area with the potential to protect against harmful and life-threatening bacteria and pathogens. Patient infection and medical devices intersect at the interface between wounds and synthetic surfaces. Here, antiseptic coatings can assist in prevention of post-surgical complexity (infection) to accelerate healing. There is also significant demand for antiseptic coatings in the food and beverage industry for antifungal/antibacterial

packaging used for food storage and marketing.[172, 173] Graphene is one of the latest biocompatible and antibacterial materials,[137, 141, 174, 175] which, thus far, has not shown significant toxic effects on many human cells lines or the eco-system.[176-178] (**Discussed elaborately in section 4**)

3.6.1 Anti-bacterial properties of graphene

Antibacterial mechanisms of Gr and GrO have been linked with oxidative stress,[141, 179] and physical disruption of the bacterial membrane.[8] This effect is explained by a few distinctive mechanisms such as, charge transfer between Gr and the bacteria,[180, 181] insertion of the sharp edges of Gr through the bacterial membrane,[8] and intertwining of the membrane pore that causes perturbation on the bacterial membrane.[137] Most of the studies[8, 137, 174, 175] have confirmed that the active mechanism is directly connected to the physical disruption of the cell membrane by direct contact of the sharp edged Gr or GrO, whereas no superoxide anion ($O_2^{\cdot -}$) induced reactive oxygen species (ROS) production is detected.[141]

In general, destructive lipid extraction reduces the density of the surface phospholipids and destroys the membrane's integrity. This phenomenon is observed at different stages of the physical disruption including partial and complete damage of the cell membrane with insertion of the sharp edges of Gr as shown in **Figure 19 (a)**[8]
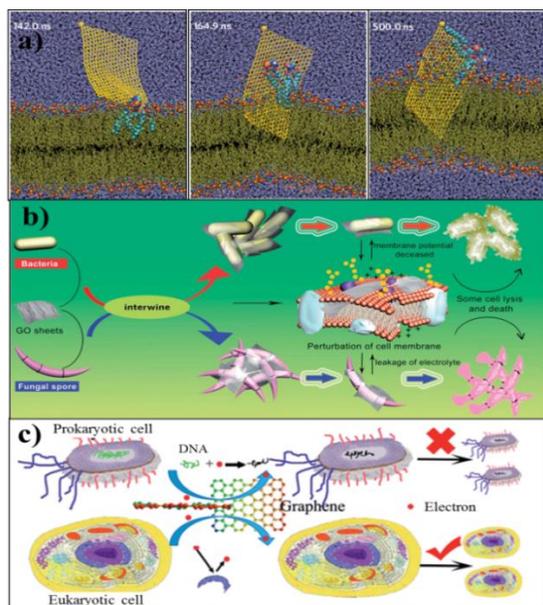

Fig. 19 Proposed antibacterial mechanisms of graphene; **(a)** Gr nanosheet insertion and lipid extraction (Simulated trajectory where-Water is shown in violet and the phospholipids in tan lines with hydrophilic charged atoms (hydrogen, white; oxygen, red; nitrogen, dark blue; carbon, cyan; phosphorus, orange).[8] **(b)** Schematic of interaction between GrO and pathogens, the bacterial cells and fungal spores were intertwined with a wide range of aggregated GrO sheets resulting in a local perturbation of the cell membrane;[137] **(c)** Possible mechanism for Gr as an antibacterial material based on DNA damage by electron transportation.[181] (Reprinted with permission from ref. 8. Copyright (2013) Nature Publishing group [Nat. Nanotechnol.) (Ref. 137 and 181, RSC publisher)

Intertwining the pores of the pathogens with a wide range of aggregated GrO sheets is also reported to be a reason for the perturbation of the cell membrane (**Figure 19 (b)**). This induces loss of bacterial membrane potential, leakage of electrolytes of fungal spores, and causes the lysis and death of pathogens.[137] Another possible antibacterial mechanisms is based the charge transfer between a Gr or GrO sheet and a bacterium. As GrO contains negative charges at the edges of its surface, it can work as a good electron acceptor to influence the damage of the cell membrane.[175] It was shown that prokaryotic cells are more vulnerable to Gr than eukaryotic cells as shown in **Figure 19 (c)**. Damaging the DNA structure by electron released from Gr to the prokaryotic cell relatively simple as it does not have a nuclear membrane.[181]

Krishnamoorthy et al.[174] revealed that the performance of Gr as an antibacterial agent is even greater than the standard drug, kanamycin (aminoglycoside antibiotic), against bacterial proliferation which has received significant attention from the research community. The minimum inhibitory concentration (MIC) of Gr nanosheets for both Gram-negative and Gram-positive pathogenic bacteria is found to be 64 and 32 times lower than the standard drug kanamycin, respectively.

3.6.2 Graphene coating for antiseptic applications

Important studies that involve Gr as a coating in clinical applications motivated by its antibacterial and biocompatible properties include Gr-coated bandages with other biocompatible materials, such as Chitosan–PVA nanofibers,[181] silver,[182] are reported to be beneficial for wound healing in mouse (C57/BL) and in rabbit (Van Beveren). **Figure 20** shows the healing effect of Gr on the skin wounds of mice where CS-PVA nanofibers without and with a Gr membrane were applied to the skin wounds of group 1 (CS without Gr), group 2 (CS with Gr), and with a control as group 3.[181] Ag/Gr based polymer hydrogel is demonstrated as another efficient wound healing material to apply in wound dressing. Gr inclusion in the dressing material is found to accelerate the healing rate of artificial wounds in rats, and successfully reconstruct and thicken the epidermis in impaired wounds.[182]

Moreover, Gr coated on metal implants has been introduced to reduce the immune response to metal surfaces in a clinical setting by inhibiting metal ion release to the biological environment.[41] The addition of thiol derivatives on the Gr coated Cu surface provides further improvement in durability of Gr protection. This work[41] lead to the use of Gr coating on other metal based implant materials such as Ti and Ti based alloys, stainless steel, chromium and cobalt based alloys used in joint replacements, stents, and dental prosthesis to reduce unwanted immune response.

For application relevant to the blood and vascular system, Gr based porous coatings with antibacterial and antithrombogenic function have been reported.[64] Here, GrO flakes were introduced into the porous structure of the polyelectrolyte based coatings.
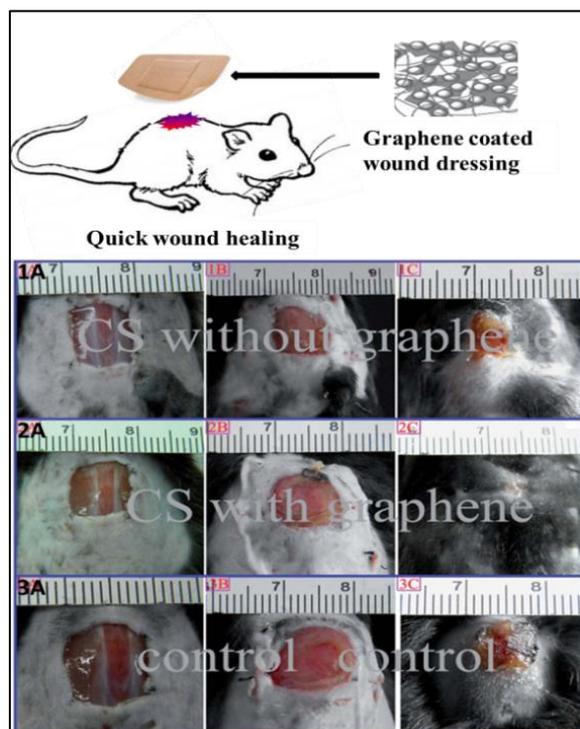
Fig. 20 Images of mice wound healing under: **1)** pure chitosan-PVA nanofibers, **2)** chitosan-PVA nanofibers contain G, and **3)** Control.[181] (Ref. 181, RSC publisher)

Results from bacteriological analysis showed that the presence of GrO flakes reduced the presence of bacteria on the coated surface and dynamic blood analysis showed high activation of coagulation (inhibiting blood coagulation), strong platelets consumption and a strong immune response. The antibacterial effect was attributed to the sharp edge of the single plane of the GrO flakes and subsequent physical disruption of the model bacteria used in the system Whereas the role of Gr to inhibit blood coagulation was not clearly described However, such Gr/polymer based composite coating with advance antibacterial effect was firstly introduce by Santos et al. [183] for use in the biomedical and industrial fields. This poly-N-vinyl carbazole (PVK) and GrO composite film is 90% more effective in preventing bacterial colonization relative to the unmodified surface. In addition to the work discussed above, GrO based antibacterial paper has been demonstrated to significantly inhibit the growth of E. coli bacteria which can be applied both in environmental and clinical applications.[55] The aforementioned studies show that Gr and GrO in particular have significant potential for applications in antimicrobial and medical devices. Further application in food packaging (extend storage) and shoes/socks (personal hygiene) have been identified.

4. Toxicity and ecotoxicity of graphene materials

The exposure of Gr based products and nanomaterials to humans and the environment are likely to increase in the future due to the ever expanding applications that have shown such great potential. Therefore, studies associated with the potential risk of Gr manufacture and use in different environments is essential to assure safe application.[184] There exists some controversy over the toxic potential of Gr with reports alluding to the potential safety and/or danger of the new technologies.

Toxicity assessment of Gr based materials against bacteria, mammalian cells, and animal models are found to affect adversely whereas surface modifications can significantly reduce their toxic interactions with living systems. The findings suggested for a further investigation in designing Gr based product with minimal toxicity for biomedical applications.[185] On the other hand, current progress of the use of Gr as nano-carriers in drug delivery, gene delivery, cancer therapy, and as scaffolds for cell culture has been identified.[186] So far, Gr and GrO have not shown significant *in vitro*-toxicity to many a number of human cell lines, including Raji, HCT-116, OVCAR-3, U87MG, MDA-MB-435 and MCF-7, even at high doses up to 100 mg/l of GrO.[176-178] In vitro toxicity evaluation of GrO on A549 cells also reports this material as a safe for the use at a cellular level as no obvious cytotoxicity is observed during the incubation of A549 cell. However, the dose and size of GrO materials should be considered in the development of bio-applications. as a dose-dependent oxidative stress inside the cell could induce a slight loss of cell viability at high concentration.[187]

Model marine organisms have been studied to evaluate the eco-toxicity of Gr materials. Studies on the settlement, survival and swimming behaviour of amphibalanus amphitrite larvae is shown to be influenced by a single layer of GrO.[136] In comparison with nano-carbon black, GrO exhibits lower anti-settlement effects with strong influence to alter the survival and inhibit the swimming behaviour of the nauplii. Similarly, single layer pristine Gr was reported as moderately toxic which can influence inhibition of the bioluminescent bacterium Vibrio fischeri and growth of the unicellular alga Dunaliella tertiolecta. However, no acute ecotoxicity were demonstrated with respect to the crustacean artemia salina. Results showed that the toxicity is particle size dependent, where relatively small (lateral size of 550 nm, with 0.35 nm thickness) size single layer-Gr had increased toxicity than the bulk graphite powder (>150 μm) and micron sized Gr powder (lateral size of 5-25 μm, with 5-30 nm thickness).[188] At this stage more research is required as some results indicated that the release of Gr flakes particularly in the nanoscopic range might be transported deep within the lungs similar to asbestos fibres and coal dust.[189] Therefore, careful management is required during production, distribution and uses of such tiny Gr nanoflakes. The biological response of Gr will vary across the material family depending on layer number, lateral size, stiffness, hydrophobicity, surface functionalization, and dose.[189]

One potentially positive discovery is that the green decomposition (or reduction) of GrO to Gr, which then expected to restack itself into harmless graphite as shown in **Figure 21**. The π–π stacking and Van der Waals interactions causes restacking of the Gr sheets to form graphite.[29]
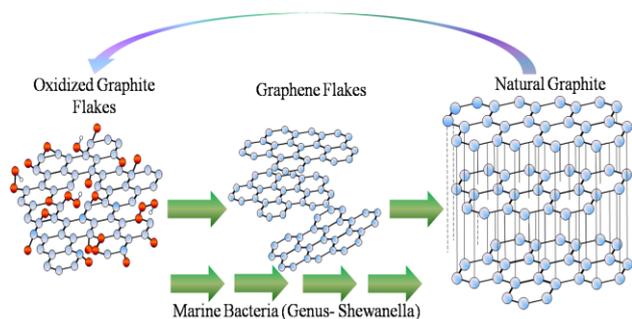
Fig. 21 Green decomposition of GrO in the environment

Such conversion of GrO into an environmentally benign mineral was demonstrated by bacteria from the genus "Shewanella" which can be found in lakes, ocean floors, rivers and even in oil brines.[11] If indeed Gr based materials can be extracted with minimal impact and can also decompose in nature without appreciable side effects to the eco-system. They certainly will have a meritorious property to add to the list of superlative properties already attributed. The biocompatible Gr can be a good alternative to the conventional anti-corrosion and anti-fouling coating constituents such as Cr, Co, Cd, Cu, TBT which have been identified to be toxic to the eco-system and carcinogenic to humans.[17-22]

5. Conclusion and future perspective

As can be seen from the scope and quality of the discussed research, Gr based materials have enormous potential for application in the field of protective coatings. The outstanding physical and chemical properties of Gr along with intense research have promoted unprecedented research progress in the pursuit of advanced protective coating technologies. Broad application areas stand to benefit and serve to show the immense depth of this multipurpose material. While specific applications may benefit from pure Gr coatings, Gr-like coatings or Gr enhanced composite coatings, the favourable properties of Gr can provide enhanced protective characteristics with very few disadvantages. The literature suggests that tuning the Gr structure as well as the microstructure of the nanomaterials at the bulk material interface and within the coatings is key to Gr based enhanced protection. The selection of the most appropriate coating methods are also being carefully scrutinized at research level for commercial use in the near future.

Polymer based composites featuring Gr nanomaterials are amongst a few Gr technologies that are expected to be realized soon. The relative ease by which Gr can be combined with existing polymers and manufacturing in relatively low amounts will allow economic performance enhancement with what is currently an expensive material. These Gr composites including paints and other surface coatings will provide iterative advancements on current technology as well as possibilities for novel products across the protective coating field.

There exists some discrepancy in the literature regarding the potential for Gr to protect against corrosion. Despite posing a good corrosion barrier for short periods, CVD-grown Gr coatings have been found to promote more extensive wet corrosion than uncoated metal surfaces. It is thought that O_2 and H_2O can bleed through Gr defects and diffuse through the protective layer to oxidise the underlying metal.[59] Exposure of the vulnerable surface via coating discontinuities or lifting of the Gr layers is also a problem.[58]

The literature clearly shows there is potential for Gr in corrosion protection but also there is a need for improved coating technology and methodology. Some discoveries for anti-corrosive Gr or GrO coatings have been surprising. Anti-corrosion barriers made of Gr were previously counterintuitive since graphite in contact with metals increases metallic corrosion.[83]

The use of Gr based materials as additives in fire retardant coatings has achieved new levels of protection. Gr dispersed into thermoset polymers provides enhanced thermal and barrier properties. In addition, the gaseous impermeability and high surface area in combination with intumescent flame retardant (IFR) additives enhances the ability for Gr composites to resist the transfer of toxic and flammable gases during a fire. Graphene has the capacity to reinforce and maintain surface integrity at high temperature, thus reduces molten dripping and delays structural collapse. More development is expected in the future with optimized formulations and combination with existing flame retardant materials and coating technologies.

Both polymers and ceramics have been successfully combined with Gr to fabricate improved wear and scratch resistant coatings. Possible transformation of thin Gr layers to amorphous carbon under dry sliding contact has been identified as of concern.[190] Subsequent third body abrasive wear of metal surface is the problem faced here yet other reports show positive improvement in wear and scratch resistance properties via addition of Gr. Further attention regarding delamination processes, tribo-corrosion and surface transformation of Gr based wear and scratch resistant coatings will provide better understanding to enable rational design of these protective coatings. Studies of extended cyclic loads will help to understand dynamic wear resistant properties of Gr enhanced coatings.

Dry Gr based materials are also capable of reducing puckering effects caused by inter-layer sliding and can resist tribo-corrosion by forming a passivation film. Before Gr is successfully applied as a solid lubricant the boundary limits of the working conditions require investigation. GrO in water and oil as lubricant additives have proven effective in tribological applications with sliding, rolling, or rotating contact interfaces.

Versatility in surface chemistry and wettability of modified Gr and GrO provides an interface that can alter the physisorption of different molecules and therefore provide passive control over adsorption and desorption of material for applications such as anti-fouling coatings, carriers and adsorbents. Modified Gr as an antifouling agent in surface coatings is applicable to both dry and aquatic environments and

includes applications such as household and building surfaces, desalination systems, bioreactors and marine structures. For many applications in the antifouling area large amounts of Gr are required and thus cost and scalability of coating technology are the most serious issues that need to be addressed. Bioinspired or biomimetic application of Gr may prove useful for antifouling applications providing that economic coating approaches can be developed. Graphene surfaces with amphiphillic behaviour can be exploited to deter biofilm formation and hence reduce surface colonization by microorganisms. However more research is required to understand this process and optimize coatings to better address the antifouling problems affecting specific industries.

The high surface area and tunable surface chemistry of Gr are key properties that can afford the adsorption of large quantities of pollutants with chemical selectivity. Substances including hydrocarbons, heavy metal ions and dyes can be targeted. Graphene and GrO have been used in combination with MWCNTs to fabricate porous aerogel structures and to coat other porous structures (melamine sponge, chitosan monoliths). These Gr-based materials can exhibit adsorption and expulsion performance of up to 35000 times their own weight. The use of Gr with Silica and Nafion in solid phase microextraction extends the surface area available to detect pollutants in water samples for enhanced sensing capability.

The use of Gr in antiseptic coatings, including combination with silver and chitosan has shown promise for wound healing and wound dressing agents. Graphene based antiseptic coatings have been investigated for use in cardiovascular devices with identified potential. The antibacterial mechanism of Gr or GrO is generally thought to arise from structural disruption of the bacterial membrane by the sharp edges of the nanosheets. Reports show potential for application of Gr in the medical area yet further research is required to better understand the effect of nanosheets on mammalian cells and ultimately human health.

Though significant advancement in the understanding of the applications of Gr has been made through applied research, fundamental understanding of Gr toxicity is less advanced. For the most part Gr has shown non-toxic properties and is also often applied in a manner where it is not exposed to the environment. Some reports have highlighted the need for further careful studies of potential adverse health/ecological effects arising from Gr nano-toxicity. Two areas that require considerable attention for future studies include cell toxicity/genotoxicity for humans and also ecotoxicity for the environment. The latter area in particular must identify the pathways of Gr and nanomaterials in general within water resources, the food chain, soil, flora and fauna.

Most of the research to date can be split into two generalized fabrication methodologies; the bottom up approaches involve carbon containing precursor gases, and top down graphite exfoliation approaches break apart layers of Gr from natural or synthetic graphite. CVD-grown Gr requires that Gr is deposited on a model surface whilst exfoliated Gr requires extensive modification and or preparation of Gr flakes/sheets/particles and subsequent coating methodologies

using neat or composite material blends. A multitude of techniques to deposit Gr have been explored and both top down and bottom up approaches are expected to find commercial application. The critical part to the widespread success of Gr based protective coatings will be the ease of manufacture and application. Focused research on coating adhesion working lifetime in addition to performance enhancement will be vital for each newly developed Gr based protective coating.

The global research effort is intensifying as applied research draws nearer to commercial application yet significant hurdles, particularly related to scalable and low cost Gr manufacture and Gr handling, must be overcome before Gr products are commonplace. In depth, studies are required for medical and environmental applications of Gr in order to prove that Gr materials are not hazardous to humans or the environment. Overall, the resounding consensus amongst the research community is that *when* graphene is realized it will bring a new technological revolution and whether as a stand-alone, or additive material, Gr will be readily adopted to improve the performance of a multitude of coating technologies as a true multipurpose tool of the 21st century

Notes and references

1. K. S. Novoselov, V. I. Falko, L. Colombo, P. R. Gellert, M. G. Schwab and K. Kim, *Nature*, 2012, 490, 192-200.
2. A. A. Balandin, *Nat Mater*, 2011, 10, 569-581.
3. A. S. Mayorov, R. V. Gorbachev, S. V. Morozov, L. Britnell, R. Jalil, L. A. Ponomarenko, P. Blake, K. S. Novoselov, K. Watanabe, T. Taniguchi and A. K. Geim, *Nano Letters*, 2011, 11, 2396-2399.
4. C. Lee, X. Wei, J. W. Kysar and J. Hone, *Science*, 2008, 321, 385-388.
5. J. S. Bunch, S. S. Verbridge, J. S. Alden, A. M. van der Zande, J. M. Parpia, H. G. Craighead and P. L. McEuen, *Nano Letters*, 2008, 8, 2458-2462.
6. M. Topsakal, H. Şahin and S. Ciraci, *Physical Review B*, 2012, 85, 155445.
7. Y. Su, V. G. Kravets, S. L. Wong, J. Waters, A. K. Geim and R. R. Nair, *Nat Commun*, 2014, 5.
8. Y. Tu, M. Lv, P. Xiu, T. Huynh, M. Zhang, M. Castelli, Z. Liu, Q. Huang, C. Fan, H. Fang and R. Zhou, *Nat Nano*, 2013, 8, 594-601.
9. J. Campos-Delgado, Y. A. Kim, T. Hayashi, A. Morelos-Gómez, M. Hofmann, H. Muramatsu, M. Endo, H. Terrones, R. D. Shull, M. S. Dresselhaus and M. Terrones, *Chemical Physics Letters*, 2009, 469, 177-182.
10. K. Yung Ho, L. Sangchul, P. Woojin, J. Gunho, C. Minhyeok, L. Jong-Hoon, Y. Hyunung, L. Takhee and L. Kwanghee, *Nanotechnology*, 2012, 23, 075702.
11. E. C. Salas, Z. Sun, A. Lüttge and J. M. Tour, *ACS Nano*, 2010, 4, 4852-4856.
12. G. Chen, W. Weng, D. Wu, C. Wu, J. Lu, P. Wang and X. Chen, *Carbon*, 2004, 42, 753-759.
13. J. Pu, S. Wan, Z. Lu, G.-a. Zhang, L. Wang, X. Zhang and Q. Xue, *Journal of Materials Chemistry A*, 2013, 1, 1254-1260.

14. V. Georgakilas, M. Otyepka, A. B. Bourlinos, V. Chandra, N. Kim, K. C. Kemp, P. Hobza, R. Zboril and K. S. Kim, *Chemical Reviews*, 2012, 112, 6156-6214.
15. J. Bohannon, *Science*, 2005, 309, 376-377.
16. E. Barea, C. Montoro and J. A. R. Navarro, *Chemical Society Reviews*, 2014, DOI: 10.1039/c3cs60475f.
17. *Official Journal of the European Communities*, 2002, L170, 81-84.
18. I. M. O. T. International Maritime Organization, 2001.
19. D. M. Templeton and Y. Liu, *Chemico-Biological Interactions*, 2010, 188, 267-275.
20. B. L'Azou, I. Passagne, S. Mounicou, M. Treguer-Delapierre, I. Puljalte, J. Szpunar, R. Lobinski and C. Ohayon-Courtes, *Toxicology Research*, 2014, 3, 32-41.
21. W. Bal and K. S. Kasprzak, *Toxicology Letters*, 2002, 127, 55-62.
22. *Official Journal of the European Communities*, 2003, L37, 19-37.
23. Y. J. Shin, Y. Wang, H. Huang, G. Kalon, A. T. S. Wee, Z. Shen, C. S. Bhatia and H. Yang, *Langmuir*, 2010, 26, 3798-3802.
24. A. Hirsch, *Angewandte Chemie International Edition*, 2002, 41, 1853-1859.
25. S. Banerjee, T. Hemraj-Benny and S. S. Wong, *Advanced Materials*, 2005, 17, 17-29.
26. K. Balasubramanian and M. Burghard, *Small*, 2005, 1, 180-192.
27. Y. Gogotsi, *The Journal of Physical Chemistry Letters*, 2011, 2, 2509-2510.
28. Y. Jiao, Y. Zheng, M. Jaroniec and S. Z. Qiao, *Journal of the American Chemical Society*, 2014, 136, 4394-4403.
29. T. Kuila, S. Bose, A. K. Mishra, P. Khanra, N. H. Kim and J. H. Lee, *Progress in Materials Science*, 2012, 57, 1061-1105.
30. S. Wang, Y. Zhang, N. Abidi and L. Cabrales, *Langmuir*, 2009, 25, 11078-11081.
31. H. Wang and Y. H. Hu, *Industrial & Engineering Chemistry Research*, 2011, 50, 6132-6137.
32. D. R. Dreyer, S. Park, C. W. Bielawski and R. S. Ruoff, *Chemical Society Reviews*, 2010, 39, 228-240.
33. C. Xu, R.-s. Yuan and X. Wang, *New Carbon Materials*, 2014, 29, 61-66.
34. A. Mathkar, D. Tozier, P. Cox, P. Ong, C. Galande, K. Balakrishnan, A. Leela Mohana Reddy and P. M. Ajayan, *The Journal of Physical Chemistry Letters*, 2012, 3, 986-991.
35. C. Peng, Y. Xiong, Z. Liu, F. Zhang, E. Ou, J. Qian, Y. Xiong and W. Xu, *Applied Surface Science*, 2013, 280, 914-919.
36. H. L. Poh, P. Šimek, Z. Sofer and M. Pumera, *Chemistry – A European Journal*, 2013, 19, 2655-2662.
37. K. Ariga, Q. Ji, M. J. McShane, Y. M. Lvov, A. Vinu and J. P. Hill, *Chemistry of Materials*, 2011, 24, 728-737.
38. S. Chen, L. Brown, M. Levendorf, W. Cai, S.-Y. Ju, J. Edgeworth, X. Li, C. W. Magnuson, A. Velamakanni, R. D. Piner, J. Kang, J. Park and R. S. Ruoff, *ACS Nano*, 2011, 5, 1321-1327.
39. D. Prasai, J. C. Tuberquia, R. R. Harl, G. K. Jennings and K. I. Bolotin, *ACS Nano*, 2012, 6, 1102-1108.
40. A. Krishnamurthy, V. Gadhamshetty, R. Mukherjee, Z. Chen, W. Ren, H. M. Cheng and N. Koratkar, *Carbon*, 2013, 56, 45-49.
41. W. Zhang, S. Lee, K. L. McNear, T. F. Chung, S. Lee, K. Lee, S. A. Crist, T. L. Ratliff, Z. Zhong, Y. P. Chen and C. Yang, *Sci. Rep.*, 2014, 4.
42. K. H. Kim, Y. Oh and M. F. Islam, *Nat Nano*, 2012, 7, 562-566.
43. U. Mogera, N. Kurra, D. Radhakrishnan, C. Narayana and G. U. Kulkarni, *Carbon*, 2014, 78, 384-391.
44. J.-H. Huh, S. H. Kim, J. H. Chu, S. Y. Kim, J. H. Kim and S.-Y. Kwon, *Nanoscale*, 2014, 6, 4379-4386.
45. W. He, L. Zhu, H. Chen, H. Nan, W. Li, H. Liu and Y. Wang, *Applied Surface Science*, 2013, 279, 416-423.
46. B. P. Singh, B. K. Jena, S. Bhattacharjee and L. Besra, *Surface and Coatings Technology*, 2013, 232, 475-481.
47. B. P. Singh, S. Nayak, K. K. Nanda, B. K. Jena, S. Bhattacharjee and L. Besra, *Carbon*, 2013, 61, 47-56.
48. X. Youtao, L. Hongqing, Z. Chi, G. Xin, Z. Xuebin and H. Liping, *Biomedical Materials*, 2014, 9, 025009.
49. B. Pan, G. Xu, B. Zhang, X. Ma, H. Li and Y. Zhang, *Polymer-Plastics Technology and Engineering*, 2012, 51, 1163-1166.
50. L. David, A. Feldman, E. Mansfield, J. Lehman and G. Singh, *Sci. Rep.*, 2014, 4.
51. M. Shateri-Khalilabad and M. Yazdanshenas, *Cellulose*, 2013, 20, 963-972.
52. P. F. Li, H. Zhou and X. Cheng, *Surface and Coatings Technology*, 2014, 254, 298-304.
53. S. Anandan, T. Narasinga Rao, M. Sathish, D. Rangappa, I. Honma and M. Miyauchi, *ACS Applied Materials & Interfaces*, 2012, 5, 207-212.
54. F. Guo, G. Silverberg, S. Bowers, S.-P. Kim, D. Datta, V. Shenoy and R. H. Hurt, *Environmental Science & Technology*, 2012, 46, 7717-7724.
55. W. Hu, C. Peng, W. Luo, M. Lv, X. Li, D. Li, Q. Huang and C. Fan, *ACS Nano*, 2010, 4, 4317-4323.
56. S. Mayavan, T. Siva and S. Sathiyanarayanan, *RSC Advances*, 2013, 3, 24868-24871.
57. K. Krishnamoorthy, K. Jeyasubramanian, M. Premanathan, G. Subbiah, H. S. Shin and S. J. Kim, *Carbon*, 2014, 72, 328-337.
58. L. Nilsson, M. Andersen, R. Balog, E. Laegsgaard, P. Hofmann, F. Besenbacher, B. Hammer, I. Stensgaard and L. Hornekaer, *ACS Nano*, 2012, 6, 10258-10266.
59. M. Schriver, W. Regan, W. J. Gannett, A. M. Zaniewski, M. F. Crommie and A. Zettl, *ACS Nano*, 2013, 7, 5763-5768.
60. K.-C. Chang, M.-H. Hsu, H.-I. Lu, M.-C. Lai, P.-J. Liu, C.-H. Hsu, W.-F. Ji, T.-L. Chuang, Y. Wei, J.-M. Yeh and W.-R. Liu, *Carbon*, 2014, 66, 144-153.
61. L. Yu, Y.-S. Lim, J. H. Han, K. Kim, J. Y. Kim, S.-Y. Choi and K. Shin, *Synthetic Metals*, 2012, 162, 710-714.
62. P. F. Li, H. Zhou and X. Cheng, *Surface and Coatings Technology*, 2014, 254, 298–304.
63. D. Kang, J. Y. Kwon, H. Cho, J.-H. Sim, H. S. Hwang, C. S. Kim, Y. J. Kim, R. S. Ruoff and H. S. Shin, *ACS Nano*, 2012, 6, 7763-7769.
64. R. Major, M. Sanak, A. Mzyk, L. Lipinska, M. Kot, P. Lacki, F. Bruckert and B. Major, *Archives of Civil and Mechanical Engineering*, 2014, 14, 540–549.
65. S. Zhang, Z. Du and G. Li, *Analytical Chemistry*, 2011, 83, 7531-7541.
66. G. Huang, J. Yang, J. Gao and X. Wang, *Industrial & Engineering Chemistry Research*, 2012, 51, 12355-12366.
67. X. Wang, W. Xing, L. Song, H. Yang, Y. Hu and G. H. Yeoh, *Surface and Coatings Technology*, 2012, 206, 4778-4784.
68. M.-Y. Shen, C.-F. Kuan, H.-C. Kuan, C.-H. Chen, J.-H. Wang, M.-C. Yip and C.-L. Chiang, *Journal of Nanomaterials*, 2013, 2013, 10.
69. F. S. Omar, H. Nay Ming, S. M. Hafiz and L. H. Ngee, *International Journal of Photoenergy*, 2014, 2014, 8.
70. J. Li, F. Ye, S. Vaziri, M. Muhammed, M. C. Lemme and M. Östling, *Advanced Materials*, 2013, 25, 3985-3992.
71. E. Ou, X. Zhang, Z. Chen, Y. Zhan, Y. Du, G. Zhang, Y. Xiang, Y. Xiong and W. Xu, *Chemistry – A European Journal*, 2011, 17, 8789-8793.
72. J.-J. Shao, W. Lv and Q.-H. Yang, *Advanced Materials*, 2014, 26, 5586-5612.
73. G. F. Hays, *Advanced Materials Research*, 2010, G. F. Hays, Adv. Mater. Res. 2010 , 95 , 2, 1–2
74. M. H. Gass, U. Bangert, A. L. Bleloch, P. Wang, R. R. Nair and A. K. Geim, *Nat Nano*, 2008, 3, 676-681.
75. T. S. Sreeprasad and V. Berry, *Small*, 2013, 9, 341-350.
76. P. K. Nayak, C.-J. Hsu, S.-C. Wang, J. C. Sung and J.-L. Huang, *Thin Solid Films*, 2013, 529, 312-316.
77. N. T. Kirkland, T. Schiller, N. Medhekar and N. Birbilis, *Corrosion Science*, 2012, 56, 1-4.

78. A. S. Kousalya, A. Kumar, R. Paul, D. Zemlyanov and T. S. Fisher, *Corrosion Science*, 2013, 69, 5-10.
79. B. Dlubak, M.-B. Martin, R. S. Weatherup, H. Yang, C. Deranlot, R. Blume, R. Schloegl, A. Fert, A. Anane, S. Hofmann, P. Seneor and J. Robertson, *ACS Nano*, 2012, 6, 10930-10934.
80. S. C. Sahu, A. K. Samantara, M. Seth, S. Parwaiz, B. P. Singh, P. C. Rath and B. K. Jena, *Electrochemistry Communications*, 2013, 32, 22-26.
81. S. Pan, A. K. Kota, J. M. Mabry and A. Tuteja, *Journal of the American Chemical Society*, 2013, 135, 578-581.
82. G. Kear, B. D. Barker and F. C. Walsh, *Corrosion Science*, 2004, 46, 109-135.
83. R. K. Singh Raman, P. Chakraborty Banerjee, D. E. Lobo, H. Gullapalli, M. Sumandasa, A. Kumar, L. Choudhary, R. Tkacz, P. M. Ajayan and M. Majumder, *Carbon*, 2012, 50, 4040-4045.
84. A. S. Barnard and I. K. Snook, *J Chem Phys*, 2008, 128, 094707.
85. H. Y. Nan, Z. H. Ni, J. Wang, Z. Zafar, Z. X. Shi and Y. Y. Wang, *Journal of Raman Spectroscopy*, 2013, 44, 1018-1021.
86. B. Yu, X. Wang, W. Xing, H. Yang, L. Song and Y. Hu, *Industrial & Engineering Chemistry Research*, 2012, 51, 14629-14636.
87. Y. Shi, X. Qian, K. Zhou, Q. Tang, S. Jiang, B. Wang, B. Wang, B. Yu, Y. Hu and R. K. K. Yuen, *Industrial & Engineering Chemistry Research*, 2013, 52, 13654-13660.
88. D. Zhuo, R. Wang, L. Wu, Y. Guo, L. Ma, Z. Weng and J. Qi, *Journal of Nanomaterials*, 2013, 2013, 7.
89. X. Wang, L. Song, H. Yang, H. Lu and Y. Hu, *Industrial & Engineering Chemistry Research*, 2011, 50, 5376-5383.
90. S.-H. Liao, P.-L. Liu, M.-C. Hsiao, C.-C. Teng, C.-A. Wang, M.-D. Ger and C.-L. Chiang, *Industrial & Engineering Chemistry Research*, 2012, 51, 4573-4581.
91. Y. Xiong, Y. Xie, F. Zhang, E. Ou, Z. Jiang, L. Ke, D. Hu and W. Xu, *Materials Science and Engineering: B*, 2012, 177, 1163-1169.
92. Y. Guo, C. Bao, L. Song, B. Yuan and Y. Hu, *Industrial & Engineering Chemistry Research*, 2011, 50, 7772-7783.
93. M. Murariu, A. L. Dechief, L. Bonnaud, Y. Paint, A. Gallos, G. Fontaine, S. Bourbigot and P. Dubois, *Polymer Degradation and Stability*, 2010, 95, 889-900.
94. S. Peeterbroeck, F. Laoutid, J. M. Taulemesse, F. Monteverde, J. M. Lopez-Cuesta, J. B. Nagy, M. Alexandre and P. Dubois, *Advanced Functional Materials*, 2007, 17, 2787-2791.
95. S.-D. Jiang, Z.-M. Bai, G. Tang, Y. Hu and L. Song, *Industrial & Engineering Chemistry Research*, 2014, 53, 6708-6717.
96. D. Wang, K. Zhou, W. Yang, W. Xing, Y. Hu and X. Gong, *Industrial & Engineering Chemistry Research*, 2013, 52, 17882-17890.
97. X. Wang, W. Xing, X. Feng, B. Yu, H. Lu, L. Song and Y. Hu, *Chemical Engineering Journal*, 2014, 250, 214-221.
98. R. A. K. Rao, S. Singh, B. R. Singh, W. Khan and A. H. Naqvi, *Journal of Environmental Chemical Engineering*, 2014, 2, 199-210.
99. J. Li, J. Li, H. Meng, S. Xie, B. Zhang, L. Li, H. Ma, J. Zhang and M. Yu, *Journal of Materials Chemistry A*, 2014, 2, 2934-2941.
100. A. K. Geim and K. S. Novoselov, *Nat Mater*, 2007, 6, 183-191.
101. B. Wen, X. X. Wang, W. Q. Cao, H. L. Shi, M. M. Lu, G. Wang, H. B. Jin, W. Z. Wang, J. Yuan and M. S. Cao, *Nanoscale*, 2014, DOI: 10.1039/c3nr06717c.
102. C. Gómez-Navarro, M. Burghard and K. Kern, *Nano Letters*, 2008, 8, 2045-2049.
103. J. Dusza, J. Morgiel, A. Duszová, L. Kvetková, M. Nosko, P. Kun and C. Balázsi, *Journal of the European Ceramic Society*, 2012, 32, 3389-3397.
104. L. Gong, I. A. Kinloch, R. J. Young, I. Riaz, R. Jalil and K. S. Novoselov, *Advanced Materials*, 2010, 22, 2694-2697.
105. R. J. Young, I. A. Kinloch, L. Gong and K. S. Novoselov, *Composites Science and Technology*, 2012, 72, 1459-1476.
106. C. Gao, T. Liu, C. Shuai and S. Peng, *Sci. Rep.*, 2014, 4.
107. Q. Wang, Y. Li, M. Luo, S. Sang, T. Zhu and L. Zhao, *Ceramics International*, 2014, 40, 163-172.
108. H. Sun, Z. Xu and C. Gao, *Advanced Materials*, 2013, 25, 2554-2560.
109. S. S. Kandanur, M. A. Rafiee, F. Yavari, M. Schrameyer, Z.-Z. Yu, T. A. Blanchet and N. Koratkar, *Carbon*, 2012, 50, 3178-3183.
110. Z. Tai, Y. Chen, Y. An, X. Yan and Q. Xue, *Tribol Lett*, 2012, 46, 55-63.
111. H. J. Kim, S.-M. Lee, Y.-S. Oh, Y.-H. Yang, Y. S. Lim, D. H. Yoon, C. Lee, J.-Y. Kim and R. S. Ruoff, *Sci. Rep.*, 2014, 4.
112. M. Belmonte, C. Ramírez, J. González-Julián, J. Schneider, P. Miranzo and M. I. Osendi, *Carbon*, 2013, 61, 431-435.
113. D.-Y. Wang, C.-L. Chang, Z.-Y. Chen and W.-Y. Ho, *Surface and Coatings Technology*, 1999, 120–121, 629-635.
114. K.-S. Kim, H.-J. Lee, C. Lee, S.-K. Lee, H. Jang, J.-H. Ahn, J.-H. Kim and H.-J. Lee, *ACS Nano*, 2011, 5, 5107-5114.
115. L. Hyunsoo, L. Naesung, S. Yongho, E. Jonghwa and L. SangWook, *Nanotechnology*, 2009, 20, 325701.
116. L.-Y. Lin, D.-E. Kim, W.-K. Kim and S.-C. Jun, *Surface and Coatings Technology*, 2011, 205, 4864-4869.
117. H.-J. Song and N. Li, *Appl. Phys. A*, 2011, 105, 827-832.
118. J. Lin, L. Wang and G. Chen, *Tribol Lett*, 2011, 41, 209-215.
119. Z. Wei, Z. Ming, Z. Hongwei, T. Yu, W. Kunlin, W. Jinquan, J. Fei, L. Xiao, L. Zhen, Z. Peng and W. Dehai, *Journal of Physics D: Applied Physics*, 2011, 44, 205303.
120. C. Lee, Q. Li, W. Kalb, X.-Z. Liu, H. Berger, R. W. Carpick and J. Hone, *Science*, 2010, 328, 76-80.
121. D. Berman, A. Erdemir and A. V. Sumant, *Materials Today*, 2014, 17, 31-42.
122. X. Feng, S. Kwon, J. Y. Park and M. Salmeron, *ACS Nano*, 2013, 7, 1718-1724.
123. D. Berman, A. Erdemir and A. V. Sumant, *Carbon*, 2013, 54, 454-459.
124. D. Berman, A. Erdemir and A. V. Sumant, *Carbon*, 2013, 59, 167-175.
125. H. Kinoshita, Y. Nishina, A. A. Alias and M. Fujii, *Carbon*, 2014, 66, 720-723.
126. J. A. Callow and M. E. Callow, *Nat Commun*, 2011, 2, 244.
127. I. Banerjee, R. C. Pangule and R. S. Kane, *Advanced Materials*, 2011, 23, 690-718.
128. S. Nishimoto and B. Bhushan, *RSC Advances*, 2013, 3, 671-690.
129. J. Jin, X. Wang and M. Song, *Journal of Nanoscience and Nanotechnology*, 2011, 11, 7715-7722.
130. B. M. Ganesh, A. M. Isloor and A. F. Ismail, *Desalination*, 2013, 313, 199-207.
131. G. Wang, L. Zhu, H. Liu and W. Li, *Materials Letters*, 2011, 65, 3095-3097.
132. D. R. Camp and S. R. Zawacky, Google Patents, 2006.
133. A. Beigbeder, P. Degee, S. L. Conlan, R. J. Mutton, A. S. Clare, M. E. Pettitt, M. E. Callow, J. A. Callow and P. Dubois, *Biofouling*, 2008, 24, 291-302.
134. D. Y. Lyon, D. Brown, E. R. Sundstrom and P. J. J. Alvarez, *International Biodeterioration & Biodegradation*, 2008, 62, 475-478.
135. X. J. Su, Q. Zhao, S. Wang and A. Bendavid, *Surface and Coatings Technology*, 2010, 204, 2454-2458.
136. T. Mesarič, K. Sepčič, V. Piazza, C. Gambardella, F. Garaventa, D. Drobne and M. Faimali, *Chemistry and Ecology*, 2013, 29, 643-652.
137. J. Chen, H. Peng, X. Wang, F. Shao, Z. Yuan and H. Han, *Nanoscale*, 2014, 6, 1879-1889.
138. C. J. Russo and L. A. Passmore, *Nat Meth*, 2014, 11, 649-652.
139. T. Kuilla, S. Bhadra, D. Yao, N. H. Kim, S. Bose and J. H. Lee, *Progress in Polymer Science*, 2010, 35, 1350-1375.
140. S. Pan, R. Guo and W. Xu, *AIChE Journal*, 2014, 60, 2752-2756.

141. S. Liu, T. H. Zeng, M. Hofmann, E. Burcombe, J. Wei, R. Jiang, J. Kong and Y. Chen, *ACS Nano*, 2011, 5, 6971-6980.
142. R. Yang, Y. Zhang, J. Li, Q. Han, W. Zhang, C. Lu, Y. Yang, H. Dong and C. Wang, *Nanoscale*, 2013, 5, 11019-11027.
143. J. Lee, H.-R. Chae, Y. J. Won, K. Lee, C.-H. Lee, H. H. Lee, I.-C. Kim and J.-m. Lee, *Journal of Membrane Science*, 2013, 448, 223-230.
144. N. Li, L. Liu and F. Yang, *Desalination*, 2014, 338, 10-16.
145. J. Zhang, Z. Xu, M. Shan, B. Zhou, Y. Li, B. Li, J. Niu and X. Qian, *Journal of Membrane Science*, 2013, 448, 81-92.
146. S. M. Tan, H. L. Poh, Z. Sofer and M. Pumera, *Analyst*, 2013, 138, 4885-4891.
147. L. Liu, F. Zhao, J. Liu and F. Yang, *Journal of Membrane Science*, 2013, 437, 99-107.
148. C. Zhao, X. Xu, J. Chen and F. Yang, *Journal of Environmental Chemical Engineering*, 2013, 1, 349-354.
149. C. Zhao, X. Xu, J. Chen, G. Wang and F. Yang, *Desalination*, 2014, 340, 59-66.
150. Z. Xu, J. Zhang, M. Shan, Y. Li, B. Li, J. Niu, B. Zhou and X. Qian, *Journal of Membrane Science*, 2014, 458, 1-13.
151. S. Zinadini, A. A. Zinatizadeh, M. Rahimi, V. Vatanpour and H. Zangeneh, *Journal of Membrane Science*, 2014, 453, 292-301.
152. I. Akin, E. Zor, H. Bingol and M. Ersoz, *The Journal of Physical Chemistry B*, 2014, 118, 5707-5716.
153. X. Qi, K.-Y. Pu, H. Li, X. Zhou, S. Wu, Q.-L. Fan, B. Liu, F. Boey, W. Huang and H. Zhang, *Angewandte Chemie International Edition*, 2010, 49, 9426-9429.
154. C.-F. Wang and S.-J. Lin, *ACS Applied Materials & Interfaces*, 2013, 5, 8861-8864.
155. H. Li, Y. Huang, Y. Mao, W. L. Xu, H. J. Ploehn and M. Yu, *Chemical Communications*, 2014, 50, 9849-9851.
156. J. Shen, Y. Hu, C. Li, C. Qin and M. Ye, *Small*, 2009, 5, 82-85.
157. J. R. Ellerie, O. G. Apul, T. Karanfil and D. A. Ladner, *Journal of Hazardous Materials*, 2013, 261, 91-98.
158. P. Montes-Navajas, N. G. Asenjo, R. Santamaría, R. Menéndez, A. Corma and H. García, *Langmuir*, 2013, 29, 13443-13448.
159. Y. Qian, I. M. Ismail and A. Stein, *Carbon*, 2014, 68, 221-231.
160. Y. He, Y. Liu, T. Wu, J. Ma, X. Wang, Q. Gong, W. Kong, F. Xing, Y. Liu and J. Gao, *Journal of Hazardous Materials*, 2013, 260, 796-805.
161. S. Chowdhury and R. Balasubramanian, *Advances in Colloid and Interface Science*, 2014, 204, 35-56.
162. S. Wang, H. Sun, H. M. Ang and M. O. Tadé, *Chemical Engineering Journal*, 2013, 226, 336-347.
163. C.-T. Hsieh and W.-Y. Chen, *Surface and Coatings Technology*, 2011, 205, 4554-4561.
164. X. Dong, J. Chen, Y. Ma, J. Wang, M. B. Chan-Park, X. Liu, L. Wang, W. Huang and P. Chen, *Chemical Communications*, 2012, 48, 10660-10662.
165. S. Kabiri, D. N. H. Tran, T. Altalhi and D. Losic, *Carbon*, 2014, 80, 523-533.
166. D. D. Nguyen, N.-H. Tai, S.-B. Lee and W.-S. Kuo, *Energy & Environmental Science*, 2012, 5, 7908-7912.
167. N. Zhang, H. Qiu, Y. Si, W. Wang and J. Gao, *Carbon*, 2011, 49, 827-837.
168. Y. Q. He, N. N. Zhang and X. D. Wang, *Chinese Chemical Letters*, 2011, 22, 859-862.
169. G. Zhao, X. Ren, X. Gao, X. Tan, J. Li, C. Chen, Y. Huang and X. Wang, *Dalton Transactions*, 2011, 40, 10945-10952.
170. S. Su, B. Chen, M. He and B. Hu, *Talanta*, 2014, 123, 1-9.
171. J. Li, S. Guo, Y. Zhai and E. Wang, *Analytica Chimica Acta*, 2009, 649, 196-201.
172. L. Guo, W. Yuan, Z. Lu and C. M. Li, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2013, 439, 69-83.
173. W. A. Ismail, Z. A. Ali and R. Puteh, *Journal of Nanomaterials*, 2013, 2013, 6.
174. K. Krishnamoorthy, M. Veerapandian, L.-H. Zhang, K. Yun and S. J. Kim, *The Journal of Physical Chemistry C*, 2012, 116, 17280-17287.
175. O. Akhavan and E. Ghaderi, *ACS Nano*, 2010, 4, 5731-5736.
176. X. Sun, Z. Liu, K. Welsher, J. Robinson, A. Goodwin, S. Zaric and H. Dai, *Nano Res.*, 2008, 1, 203-212.
177. Z. Liu, J. T. Robinson, X. Sun and H. Dai, *Journal of the American Chemical Society*, 2008, 130, 10876-10877.
178. L. Feng and Z. Liu, *Nanomedicine*, 2011, 6, 317+.
179. S. Gurunathan, J. W. Han, A. A. Dayem, V. Eppakayala and J.-H. Kim, *International Journal of Nanomedicine*, 2012, 7, 5901-5914.
180. J. Li, G. Wang, H. Zhu, M. Zhang, X. Zheng, Z. Di, X. Liu and X. Wang, *Sci. Rep.*, 2014, 4.
181. B. Lu, T. Li, H. Zhao, X. Li, C. Gao, S. Zhang and E. Xie, *Nanoscale*, 2012, 4, 2978-2982.
182. Z. Fan, B. Liu, J. Wang, S. Zhang, Q. Lin, P. Gong, L. Ma and S. Yang, *Advanced Functional Materials*, 2014, DOI: 10.1002/adfm.201304202, n/a-n/a.
183. C. M. Santos, M. C. R. Tria, R. A. M. V. Vergara, F. Ahmed, R. C. Advincula and D. F. Rodrigues, *Chemical Communications*, 2011, 47, 8892-8894.
184. A. B. Seabra, A. J. Paula, R. de Lima, O. L. Alves and N. Durán, *Chemical Research in Toxicology*, 2014, 27, 159-168.
185. X. Guo and N. Mei, *Journal of Food and Drug Analysis*, 2014, 22, 105-115.
186. Z. L. Shen H, Liu M, Zhang Z. , *Theranostics* 2012, 2, 283-294.
187. Y. Chang, S.-T. Yang, J.-H. Liu, E. Dong, Y. Wang, A. Cao, Y. Liu and H. Wang, *Toxicology Letters*, 2011, 200, 201-210.
188. C. Pretti, M. Oliva, R. D. Pietro, G. Monni, G. Cevasco, F. Chiellini, C. Pomelli and C. Chiappe, *Ecotoxicology and Environmental Safety*, 2014, 101, 138-145.
189. D. Bradley, *Materials Today*, 2012, 15, 230.
190. M.-S. Won, O. V. Penkov and D.-E. Kim, *Carbon*, 2013, 54, 472-481.

Table of contents

Color graphic:
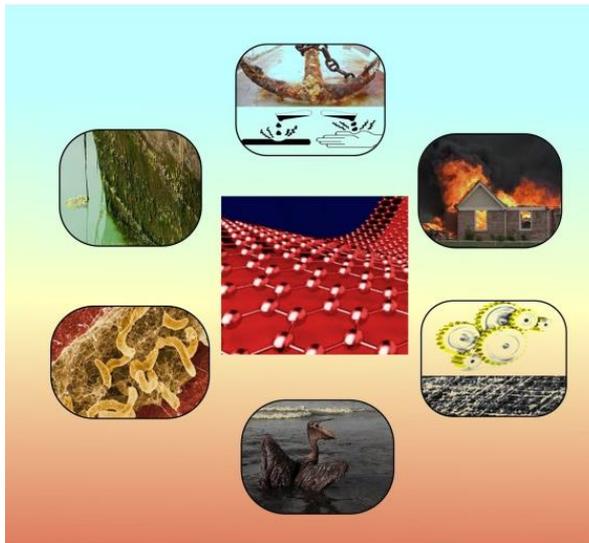
Highlight:

The article revewed and duscused potentialities, chanlenges and progress of the graphene for application in   multifuntional protective coatings