Roadblocks faced by graphene in replacing graphite in large-scale applications

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ABSTRACT

Since its isolation by Geim and coworkers, graphene has received a lot of attention from the research community as well as industry. Interesting and groundbreaking research has been published on graphene showing excellent properties and a wide range of applications. It was thought that graphene could replace well-established applications currently being controlled by graphite. In this perspective, we review large-scale applications of graphite that we think graphene can replace. We also discuss niche applications that we think graphene can make inroads for large-scale applications.

Key Words: graphene; graphite; lubrication; composite; batteries; refractories.

INTRODUCTION

Carbon is known to form many allotropes with the well-known forms being graphite and diamond [1]. In recent years, a lot more allotropes have been discovered such as ball-shaped buckminsterfullerene [2], tube-like structures carbon nanotubes (CNTs) [3, 4] and sheets like graphene [5–7]. More than 500 hypothetical allotropes have been proposed based on the Samara Carbon Allotrope Database [8]. Selected few of these allotropes are shown in Fig. 1. In terms of industrial application, graphene has been the most widely used allotrope of carbon.

Graphite

Named by Abraham Gottlob Werner in 1789, graphite is the most abundant carbon allotrope. The lamellar structure of graphite is mainly credited to Bragg, who reported it in 1928 by X-ray diffraction [9]. The lamellar structure consists of parallel layers of sp² carbon bonded in a hexagonal array, as shown in Fig. 2a and b [10]. The sp² bonding configuration leads to a stable local chemical environment for each carbon atom where the carbon–carbon bond length is 1.42 Å [11]. Weak van der Waals forces hold basal planes together. The weak van der Waals forces are responsible for allowing individual layers to easily
slide past each other [9]. This leads to the low shear strength that is inherent in bulk graphite and promotes its use in applications requiring low friction. Graphite is also a good conductor of electricity. The conductivity is only possible in layers direction [5–7, 12, 13] and achieved as a result of the existing delocalization of the pi bond electrons that are above and below the planes of the carbon (Fig. 2c). Unlike in diamond, graphite uses only three of its four outer energy level electrons to form covalent bonding to three other carbon atoms (Fig. 2d). Furthermore, graphite is the most stable allotrope of carbon; high-purity graphite does not readily burn, even at elevated temperatures [14]. This stability at high-temperature makes it an indispensable material for nuclear reactors and high-temperature crucibles for metal casting industries [15]. Graphite is slightly more reactive than diamond due to reactant tendency to penetrate between the hexagonal layers of carbon atoms in graphite.

Graphene
The isolation of graphene by Geim et al. [5, 13] was a momentous occasion that spurs huge research in graphene as well as a Nobel Prize. There was excitement about how graphene will lead to better materials and applications. The excitement emanated from the superior properties of graphene as demonstrated later by other researchers [5, 16–23]. Considered the thinnest, hardest and most conductive nanometer carbon material graphene has been praised as ‘king of new materials’ in the industry. Graphene has excellent electrical mobility of up to 200 000 cm 2/ Vs at room temperature [24, 25]. It is a lightweight material with a thermal conductivity of 5000 W/mK [26]. Very large surface area of 2630 m 2/g has been reported with a Young Modulus of 1100 GPa and rupture strength of 125 GPa [5, 27]. Some of these properties are shown in Fig. 3a [28, 29]. Many uses of graphene have been proposed (see Fig. 3b). Graphene has been studied for suitability in battery electrode materials, solar battery electrode materials, sensors, semiconductor devices, thin-film transistors, supercapacitors, etc. [30–33]. Graphene has been combined with polymers, ceramics, metals to make nanocomposites [34–36]. Also, when graphene is combined with fibers has led to special applications such as anti-mite, anti-heat, anti-static, antibacterial, anti-ultraviolet, etc. [37].

Figure 1: Common allotropes of carbon (a) diamond, (b) graphite, (c) lonsdaleite, (d) C60 buckminsterfullerene, (e) C460, fullerite (f) C70, (g) amorphous carbon, (h) zigzag single-walled carbon nanotube. Image printed from Wikipedia.
It is worth noting here that the isolation of graphene led to a ‘new subfield’ in physics in what is referred to as two-dimensional (2D) materials where a large suite of materials have been discovered with promising properties [38–42]. In this review, we limit ourselves to areas that we think graphene can be used on a large scale.

Production of graphene.
Graphene production methods that have gained a lot of traction are liquid exfoliation, modified Hummers–Offeman method for production of graphene oxide (GO), chemical vapor deposition (CVD) and microwave synthesis. The aim of the above-mentioned methods is to produce graphene sheets or graphene nanoplatelets. Production of GO begins by oxidizing graphite into graphite oxide by strong oxidants and acids. The sheets are separated by sonication in GO resulting in discontinuous graphene sheets that are later transformed (thermal annealing) to graphene (Fig. 4a [43–45]). Another method that has gained traction is the liquid phase exfoliation directly from graphite by shear force in a solvent or presence of ozone. The choice of solvent is an important parameter to consider for better yield and produce graphene with fewer defects (Fig. 4b and c). As shown by Hernandez et al. [46], liquid exfoliation can be achieved in different solvents. They used N,N-dimethylacetamide, 1,3-dimethyl-2-imidazolidinone and g-butylrolactone. They showed that this method can be scaled up and has the advantage of producing unoxidized graphene flakes from graphite powder. Besides, the produced graphene can be dispersed in a solvent to up to 0.01 mg ml\(^{-1}\) that can be used in various methods such as drop-casting, vacuum filtration, spray coating, etc.

Chemical vapor method (CVD) a bottom-up method can result in graphene with fewer defects. A lot of research is focusing on making the CVD process a continuous method where graphene can be produced and rolled up into sheets (see Fig. 4d). CVD has also been used to grow centimeters size graphene films with less than 5% multiple layers [47]. This was achieved on copper foil due to the low solubility of carbon in copper resulting in self-limiting growth. The same study developed graphene film transfer to different substrates.

An interesting large-scale production of layered materials including graphene has been proposed by Castillo et al. [48] using the wet-jet milling process. They report high-quality 2D crystals of not only graphene but also MoS\(_2\) and tungsten disulfide (WS\(_2\)). The process takes advantage of high pressure
quickly expanded following the Industrial Revolution of the 1800s to include friction materials, crucibles, pencils and many other products that benefit from graphite’s extraordinary versatility. Nowadays the world produces around 1000 MT/year of natural graphite [49] which is consumed in applications as diverse as refractories, steel refining, foundry facings, brake linings, lubricants, batteries and fuel cells [50, 51]. Also, growing amounts of synthetic graphite (about 150 MT/year in the USA alone [49] have been dramatically expanding the technical applications of graphite toward energy, metallurgical, transportation, aeronautics and environmental markets. This section highlights major industrial markets that involve the use of large quantities of graphite materials. A visual illustration of rough graphite consumption estimates per major market segment is provided in Fig. 5. Selected applications in a niche and emerging graphite markets with clear potential for graphene utilization (as a product of, or replacement for, graphite) are discussed in later sections.

Refractories
The major application of graphite is in refractory (or heat-resistant) materials. The division between refractory and metallurgical applications of graphite is not clear-cut since both applications rely heavily on the high-temperature stability of graphite. Graphite materials provide the thermal shock and corrosion resistance that is needed for electrodes in electric arc furnaces (which are widely used for steel manufacture), for composite bricks used as furnace linings, for steel ladles and for glass or cement kilns, to name a few. Flake graphite is preferred for these applications because it can add strength to the refractory parts through preferential graphite structure orientation. Iso-graphite (made by pressing of graphite with a binder in all directions), though more expensive, can also provide uniform thermal expansion and mechanical properties in every direction. The lifespan of inorganic refractory firebricks can be further enhanced through the incorporation of graphite flakes [52]. In these applications, the high thermal conductivity of the graphite is critical and justifies the lining of furnaces with continuous high-purity monoliths instead of refractory bricks. These applications consume large amounts of natural graphite, mostly in flake forms.

Metallurgy
Graphite is typically incorporated into foundry molds, dies and bricks that are used in continuous casting processes and ladles. Crucibles used for handling molten metals and alloys in foundries are generally made of mixtures of graphite and clay as their primary components. Both flake and amorphous graphite types are used for these applications, although other graphite forms can provide specific technical improvements. Graphite is also processed with metal powders to produce metal–graphite components via powder metallurgy processes [53]. On the contrary, graphite recarburizers are generally added to molten steel to control its carbon content during its manufacture.

Lubricants
Graphite lubricants are unique in their ability to perform well at both high and low temperatures. Natural graphite finds widespread use in friction materials such as brake or clutch linings. Blending the natural graphite with synthetic graphite can be used to reduce the wear rates of components subjected to friction forces during tribological processes. As a solid lubricant, low-grit graphite provides the required patina generation in...
carbon brushes for electrical motors and generators. Graphite is also used as gear lubricants for mining machinery, to lubricate locks and as an anti-seize agent in railways and steel mills.

Batteries
Electrical applications of graphite materials rely upon the high electrical conductivity of high purity graphite. In particular, the rising demand for both portable batteries (for laptops, tablets, smartphones, etc.) and stationary batteries (e.g. for electric vehicle charging stations) continues to increase the demand for graphite materials. Current hybrid and electric car designs contain roughly between 10 and 40 kg of graphite, respectively. Nowadays both natural and synthetic graphite is used as anode materials to construct electrodes for commercial batteries. Indeed, both flake and amorphous graphite are employed in alkaline/manganese batteries. Amorphous graphite is extensively used in commercial dry cell zinc-based batteries. On the contrary, graphite foil made from expanded graphite is used in bipolar plates of fuel cells. Graphite foil is also used as low-weight heat sinks in portable electronic devices. Perhaps more importantly, it should be noted that the ability of graphite to intercalate lithium ions without experiencing significant damage from swelling is what gives graphite its dominant role as anode material in commercial lithium-ion batteries (LIBs). Since current Li-ion batteries often use around 30–40 g of graphite per gram of Li, the demand for graphite for this market is expected to rise significantly in the coming years.

Other applications
Technical or specialty applications of graphite materials place more emphasis on properties other than the refractory, electrical or lubricating qualities of graphite. For example, natural graphite is also used to make expanded graphite (expanded by acid intercalation to effect graphene layer separation and exfoliation) for insulation applications and is incorporated into polymer foams to improve their flame retardancy. Exfoliated graphite can in turn be used for the manufacture of gaskets and seals in cars. The more economical amorphous graphite is also

Figure 4: Synthesis of graphene. (a) Modified Hummers–Offeman method printed from Ref. [43] under Creative Commons license. (b) An example of large-scale sonication equipment image from Altrasonic Company. (c) Liquid exfoliation of graphite to graphene with aid of ozone, printed from Ref. [44] under Creative Commons license. (d) Large-scale CVD method. Reprinted from Ref. [45] under Creative Commons license.
used as an additive to increase the mechanical properties and yield of plastics and resins in composite materials. Graphite-based materials such as carbon fiber composites provide unrivalled performance in applications where superior mechanical properties and lightweight are essential (such as in aerospace fuselage or sports equipment). Applications in construction and packaging industries have already been extended to include graphene-based material improvements [53]. Graphite has also been used for radar absorption and electromagnetic interference shielding applications. Specialty graphite finds use as moderators in nuclear reactors and as coatings for uranium pellets. More traditional applications of graphite include the manufacture of pencils, which are consumed at rates in the billions/year worldwide. Pencil cores are made using mixtures of vein or amorphous graphite with clay and an organic binder. Paints, inks and conductive coatings for antistatic control or protection in metal bearings. Graphite intercalation compounds plus metallic additives have also been found to provide conducting properties of interest to high-speed transport applications for example as an electric collector or ‘pantograph’. It is important to mention that if the cost targets are not met product commercialization viability is a huge challenge. However, if the target is a specialty application cost could be tolerated but the product must result in high margins in a competitive environment. On the contrary, cost sensitivity is high and tolerances are very low for high volume products, where it becomes more stringent to develop simple methods of production. This applies more strictly to graphene and that’s why have limited graphene’s applications to date.

**Market projections**

Besides the well-established graphite markets mentioned above, the advent of electric vehicle and energy needs are expected to increase the demand for graphite to supply growing battery, nuclear and consumer electronic market applications. The high purity and superior property requirements of these applications can drive the prices of specialty graphite up and thus ease the introduction of graphene alternatives into these markets.

**NICHE APPLICATIONS WHERE GRAPHENE CAN REPLACE GRAPHITE**

**Graphene in energy storage**

LIBs play a pivotal role in our everyday life thanks to their better power density, outstanding energy density and excellent rechargeability [54–60]. The success of LIBs is greatly tied to the anode that acts as a lithium-ion host that is made of graphite. There is a general agreement in the battery community that graphite may have reached its peak in terms of performance. Graphite anode suffers from the following major issues; insufficient capacity, side reactions and lower purity, poor stability of the layered structure that can easily collapse during cycling, very low charging and discharging voltage [61–63]. With a future that millions of fossil-fuel-powered cars will be displaced from roadways by plug-in electric vehicles, this will present a significant challenge to greatly increase the specific energy of current...
Graphene anode has a specific capacity of 350 mAh/g that is considered poor compared to other proposed anode materials (see Table 1), however, from the table it is the only one that is stable and used widely. The anode can constitute around 10%–15% of the total cost of battery. It is estimated the global anode market could reach $10 billion by 2025. Compared to the market capitalization of graphene right now, this could be a great area where graphene can gain market share. Unlike graphite especially natural ones, it has been shown that impurities can play a role in lowering the theoretical capacity of graphite. With graphene, this problem could be eliminated due to fewer impurities found in graphene compared to graphite that has to go through extreme temperature (above 2500 °C) to purify. Also, graphene can be tailored to eliminate some hurdles associated with graphite. We review a few types of research that have shown the potential of graphene as an energy storage material. Two major methods of using graphene as anode pursued by many researchers and companies involve the use of graphene as an additive in graphite or coating on the surfaces of anodes as demonstrated by Samsung with their ‘graphene balls’ in electrode coating [64]. graphene can be also be used in a cathode as a composite hybrid containing metallic material. Graphene has been used as a support material to keep metallic ions in the required order that can help with electrode efficiency [65, 66]. When used as a composite in electrodes, graphene facilitates fast charging as a result of its high conductivity and well-ordered structure [62, 67, 68].

**Graphene–metal oxide hybrids electrodes**

When graphite is employed as the primary cathode material, the lithium ions move into the structured holes or empty spaces between layers [69–71]. Graphene lacks this ability of graphite however it stores lithium ions via surface adsorption and occasionally through induced bonding as a result of large surface area [72–76]. Induced bonding is possible only with graphene derivatives such as functionalized graphene, GOs [19, 77, 78], reduced CO, fluorinated graphene [79], etc. The high conductivity of graphene is also an important characteristic compared to conventional metal oxides that have low conductivity, lower volumetric energy density and suffer from loss of contact points [21, 72, 80]. Hybridizing the graphene with metal oxide matrix, therefore, eliminates a majority of the abovementioned problems due to improvement in the interaction between interstitial ions and the matrix [77, 78, 81–83]. One of the proposed methods of synthesizing these hybrid metal oxide-graphene is to use graphene as a template that results in an evenly distributed matrix because of the regular repeating structure of graphene [28]. The use of graphene as a template eliminates the aggregation problem leading to the large surface area during charge and discharge cycles of lithium [28, 84] leading to an improvement in specific capacity and cycling performance compared to pristine metal oxide electrode. graphene-metal oxide electrode has been shown to exhibit up to 1100 mAh g⁻¹ for initial 10 cycles and maintains the specific energy density at 1000 mAh g⁻¹ after 130 cycles. Many technologies in this area can give good performance but cost is the major limiter.

**Graphene lithium–sulfur batteries**

Lithium–sulfur batteries are another area where we think graphene can play a major role. Lithium–sulfur batteries have a huge potential to replace LIBs in commercial applications especially standalone energy storage systems. Lithium–sulfur batteries are low cost, less toxic and possess an energy density of approximately 2567 W h kg⁻¹, which is more than 5 times that of LIBs [22]. They have received a lot of interest from industry as well as research institutes. Despite their favorable advantages compared to LIBs, they still suffer from significant shortcomings chiefly among them; inorganic salt deposit at the cathode due to highly soluble reactants in the cell [85]. The deposition of salts to the cathode leads to loss of active material, low coulombic efficiency, degradation of cycle life and low utilization of sulfur cathode [86]. Another shortcoming is the low conductivity of sulfur. graphene’s large surface area, high chemical, and thermal stability, high electrical conductivity has been shown to prevent problems associated with lithium–sulfur when used as support for sulfur ions [67]. Furthermore, the high surface area of graphene provides a favorable dispersion of sulfur thereby controlling the mobility of sulfur ions leading to a lower build-up of sulfur ions on the cathode [86]. The concentration of sulfur contributes greatly to the performance of the battery. For electrodes produced to-date, 63 wt% sulfur exhibits a capacity of 731 mAh g⁻¹, with a potential to reach up to 1160 mAh g⁻¹ [67, 85, 86]. Such high sulfur content leads to stability of the battery under high rate cycling. There is degradation of the electrodes but this is much lower compared to nongraphene-based sulfur electrodes [22, 28, 56, 85, 86]. The sulfur batteries perhaps present an important area that graphene can make significant inroads as a large application material. A further possible advantage here is that graphene can be mixed with sulfur powder in a typical powder metallurgy process with no need for sophisticated production equipment.

**Table 1: Properties of various anode materials**

| Anode material | Specific capacity, (mAh)/g | Volume change, % | Benefits | Challenges |
|----------------|---------------------------|-----------------|----------|------------|
| Lithium        | 3862                      | None            | Highest density, light | Unstable; slow charge rate |
| Silicon        | 3600                      | 320             | High energy density   | Capacity fade from expansion/contraction |
| Aluminum       | 2235                      | 604             | Better energy density graphite | Worse energy density and expansion than silicon |
| Tin            | 990                       | 252             | Stable than silicon   | Worse energy density than silicon |

The study of tribology is of paramount practical importance, as the function of many mechanical, electromechanical, and biological systems depends on the appropriate value of the coefficient of friction and wear data [53]. Recently, tribology has received increasing attention globally due to energy consumption on friction and wear, cost and CO₂ emissions as well as...
huge potential savings by implementing advanced tribological solutions. According to a recent study [53], these potential savings offered by improved tribological knowledge are immense (Fig. 6 [87]).

Designing longer-lasting mechanical systems have always been a great challenge for scientists and engineers. In the last few decades, researchers are continuously looking for new lubricant materials to overcome or reduce frictional barriers. Oil and grease-based liquid lubrication systems or solid lubricants in the form of surface coatings or as fillers in self-lubricating composites are the most common types of lubrication. Both types of lubrication systems are selected for unique engineering applications, such as from automotive engine parts and gear assembly to a very harsh, corrosive and high-temperature conditions [87]. However, there is a third category called gas or vapor phase lubrication system and a typical example of such a system is a roller bearing application. Likewise, in solid lubricants, vapor phase lubrication is advantageous in environments where parts operate usually at a high temperature which limits the usage of liquid oil lubrication. On the contrary, vapor phase lubrication is especially beneficial in microelectromechanical systems where the capillary effect of liquid lubrication causes a big problem [88].

Due to environmental and chemical limitations, graphene has proven to be an excellent candidate over conventional lubricants such as graphite, hexagonal boron nitride (hBN), molybdenum disulfide (MoS2), diamond-like carbon (DLC) thin films coatings, calcium fluoride (CaF2) and boric acid (H3BO3) [89–93]. For instance, graphite has been used as a lubricant for over 40 years, but it seldom works in dry conditions. Graphite is good in humid conditions only. Scientists in Argonne National Lab [94] have shown that a single atomic layer of graphene can last more than 6500 cycles in a ball on disk wear test where two sliding surfaces were coated with graphene. Their findings indicate extraordinary wear-resistant behavior of graphene at macroscale as compared to other solid lubricants (see Fig. 7a and b [95]). Due to its 2D atomically smooth structure, graphene has proven to be an excellent material for such application as it can easily make a bond with the surface and coating can be smoother and more homogenous. One of the practical examples of this application is graphene as a lubricant on silver (Ag) for electrical contact applications. Mao et al. [94] coated flake graphene by evaporating the graphene solution on a highly polished Ag plate and performed the tribology using a pin on disk test at 1 N. It was found that the addition of graphene reduced the friction coefficient to a factor of ~10 in an Ag/Ag contact and lubrication behavior was maintained for more than 150 000 cycles. Jinjin et al. [94] achieved super-lubricity of graphite by creating multiple transferred graphene nanoflakes on the asperities of silica surfaces through the frictional sliding on the graphite. The friction coefficient reduced to 0.0003 and remains very stable at a contact pressure of up to 700 MPa. Kim et al. [96] demonstrated that graphene due to an atomically thin nature and with low surface energy is an excellent candidate for reducing adhesion and friction when coated on various surfaces. It has been found in literature [95] that friction coefficient with rGO coated 440C stainless steel (SS) ball on 440C SS plate in water lubrication was comparable to the value obtained with the uncoated ball in oil lubrication. In addition, with water lubrication, the wear rate of the SS plate slid against the rGO coated ball was 3 times lower than that of the SS plate slid against the uncoated ball with oil lubrication (see Fig. 7a–e).

**Graphene as additive in liquid lubricants and composites**

Graphene can be used as a solid or a colloidal additive in conventional lubricants, such as oils, solvents and other types of fluids. It has been revealed by the experimental studies that even a minimal amount of graphene platelets added to oil [91, 97] has resulted in a remarkable reduction in coefficient of friction and wear of steel. The addition of chemically modified graphene platelets in base oil [97] resulted in better load-carrying capacity than a base oil or oil with graphite flake additive. Both the friction coefficient and wear reduced with the addition of graphene platelets. Lin [97] studied the lubrication performance of graphite, GO and graphene-based semisolid greases. It has been found from the friction test results that friction coefficients of graphite, GO and graphene are 0.105, 0.075 (30% lower than graphite-based) and 0.04–0.06 (40%–60% lower than graphite-based), respectively. Lin et al. [97] found the friction-induced transformation from graphite dispersed in esterified bio-oil to graphene at high loads and low sliding velocities which facilitate the formation of high-quality single-layer graphene during sliding, and high loads and low sliding velocities also contributed to obtaining excellent tribological performance for friction pairs. In another study, tribological applications of silver nanoparticle-decorated graphene in engine oil nanofluid have been investigated by Meng et al. [98]. The silver nanoparticles (of size ~2–16 nm) were uniformly distributed and firmly attached to graphene nanosheets. A four-ball tribometer was used to evaluate the tribological properties of the as-synthesized nanocomposites as lubricant additives in engine oil. Results show that lubricating performance of engine oil

![Graphene as additive in liquid lubricants and composites](https://academic.oup.com/ooms/article-abstract/1/1/itab004/6162175)

**Figure 6:** (a) Energy consumption, cost and CO2 emissions due to friction and wear globally. (b) Calculated potential savings over the current state of the art by the reduction of advanced tribology solutions in four case studies and their time scale of implementation reprinted from Ref. [87] under Creative Commons license.
was improved with the single nanomaterial of GOs, nano-Ag particles and zinc dialkyl dithiophosphate. However, engine oil containing 0.06–0.10 wt% Sc-Ag/GN nanocomposites show remarkable performance as compared to pure engine oil and all other additives (see Fig. 8a and b [98, 99]). Similar kind of study was conducted by Gupta et al. [99], where reduced graphene oxide (rGO) concentrations in polyethylene glycol (PEG) were optimized for effective lubrication and antiwear properties. It has been found that lower and higher concentrations of rGO nanosheets in PEG are ineffective due to less activity and

Figure 7: (a) Schematic of the reciprocating type of a tribometer with fluid injector attached to provide continuous supply of water or oil lubricant to the sliding system. Schematic indicated with blue dotted line shows the magnified image of the test region. The schematic was drawn by H.-J. Kim using conventional 3D modeling software. (b) Friction coefficient under different lubricant conditions with respect to the number of sliding cycles. Inset red graph shows the friction coefficient of rGO-water lubrication condition for the first 3000 cycles. (c) Steady-state friction coefficients with respect to different experimental conditions. Each bar is represented by an average value with standard deviation for three tests. (d) Friction coefficient of rGO-water lubrication condition with respect to different normal loads. (e) Friction coefficient of oil lubrication condition with respect to different normal loads. Each data point is represented by an average value with standard deviation of three tests. Reprinted from Ref. [95] under Creative Commons license.
agglomeration effects, respectively. However, at optimum concentration, friction coefficient and wear are remarkably reduced to 70% and 50%, respectively, as compared to base oil (see Fig. 8c and d).

**EMERGING APPLICATIONS OF GRAPHENE**

**Graphene in flexible electronics**

Flexible electronics promise an entirely new design tool such as flexible displays that can fold out to the size of a television, smartphones that wrap around wrists, flexible implants that can be used to treat cancer, etc. [100–102]. The interest in flexible electronics arises from the fact that they cost less to make compared to conventional semiconductors needing complex processes. The hope is that these electronics can be printed on plastic films similar to the way newspapers are printed. Large flexible sensors can be used to monitor vibrations on bridges, windmills blades, airplanes fuselage, etc. for a quick repair. We believe this is an emerging area and graphene can make a huge contribution and may help in pushing it into large industrial applications. This area has exploded in the last few years based on publications coming out yearly (see Fig. 9a) [103, 104].

There are countless synthesis techniques to utilize graphene in flexible electronics, here we focus on methods that we think have a better odd of leading to large-scale industrial application. One such method is graphene printing. Graphene has been shown it can be made into printable inks [104–106]. The main obstacle for large-scale use of graphene remains the initial production before it can be turned into ink. Solvent exfoliation of graphene from graphite is still the preferred method to get bulk graphene however it involves the use of sometimes very toxic solvents and further purification may be needed [107]. Other methods such as microwave synthesis and CVD are still being used to produce graphene for purpose of synthesizing inks. Benign solvents to exfoliate graphite may offer a reasonable route to produce graphene to be used in making inks. An encouraging step in graphene printing is the ink production that appears to head into a standardized model. A typical method to synthesize the ink involves dispersing graphene into a solvent blend. The mixing can be done on bath sonication, filtered in a requirement filter size and heating the mixture to remove ethanol leading to an ink with required graphene content [108]. Research has demonstrated that inkjet printing of graphene can be used to fabricate flexible devices such as thin film transistors [103, 109], acoustic actuators [31], thermal and chemical sensors [110, 111], dipole antennas [103], etc. The inkjet printing is however still limited to rapid prototyping in research laboratories and for graphene to be used on large-scale better techniques are needed.
Secor et al. [108] have proposed a throughput printing called ‘Gravure’. They claim this method can lead to large-area flexible electronics that can be used in various applications. Graphene is obtained from graphite by the typical tip sonication, separated, purified and mixed with a blend of solvent to make the ink. The solvent blend used here was ethanol and terpineol, ethanol is later removed leading to a polymer-stabilized graphene-terpineol. The gravure process is illustrated in Fig. 9b. Gravure printing is characterized by a tradeoff between the ink viscosity and ink transferring. Less viscous ink allows better filling of cells but with less transferring in the pressing stage. Decreased ink flow during doctor blading causes unreliable ink filling and to overcome this problem, the flooding step is introduced before the doctoring process to ensure better filling of the gravure cells (see Fig. 9). The key idea is to use the flooding-doctoring printing technique. The method separates filling gravure cells with ink, removing excess ink from the surface by a doctor blade, and finally transferring requirement patterns to the substrate. The decoupling of all these processes allows easy parameters optimization from the individual processes. All three processes of gravure printing depend highly on the physical properties of the ink especially surface tension and viscosity.

Figure 9: (a) Research publications per year obtained for the term ‘Flexible Electronics’ on Web of science. Printed from Ref. [103] under Creative Commons License. (b and c) Gravure printing. (I) Formulated ink. (I–IV) Illustration of the gravure printing method: (II) flooding; (III) doctor blading; (IV) printing. Printed from Ref. [104] under Creative Commons license.
Viscosity is the most parameter to control to achieve inks with required properties.

We further propose for graphene to truly take over as flexible electronic materials, it must overcome its intrinsic limitations such as the absence of a bandgap, high sheet resistance and lower work-function [24]. Doping (charge transfer, substitutional doping) can be an excellent method to improve the electronic properties. A finite bandgap in pristine graphene can be demonstrated for a broad range of emerging applications, the real challenge of graphene relies on to make it ideal for engineering applications [112–118]. When it is attempted to use graphene structure in engineering applications, the layers of graphene tend to restack and lose their outstanding properties and performances far below the theoretical values [118–120]. To overcome this challenge, 2D-layers of graphene need to be interconnected so that they can be organized as 3D interconnected nanostructured networks with tunable characteristics and thus prevent from restacking [40, 118] (Fig. 10). To date, various approaches such as freeze-drying [121], CVD [122], interface chemistry [123], hydrothermal reaction [124], spark-plasma welding [125] and recently 3D printing have been used for the fabrication of graphene-based 3D-building blocks [126], which is a porous 3D monolith by integrated or interconnected few-layer graphene sheets. The methods for creating such building blocks can be classified as (i) self-assembled structures with noncovalent interactions such as van der Waals forces and π-π interactions, (ii) interconnection graphene layers by covalent bonding. Compared to these two classes of 3D-graphene building blocks, the integrated 3D-graphene structures with covalent bonding show higher integrity with superior properties.

The first 3D-graphene structure was a foil made by Hofman and Claus [127]. Later Rodney S. Ruoff’s group made a free-standing GO buckypaper using vacuum filtration [128]. With this work, they have shown that the unique layered structure of GO sheets is integrated into a parallel manner. The interaction between graphene layers, their integration at the nanoscale and wrinkly morphology allow for good load distribution and thus make this material more resilient than traditional carbon-based buckypapers. After the first report, the concept of 3D engineering of graphene becomes attractive. One of the most promising methods to create 3D-graphene building blocks using individual honeycomb graphene sheets is the self-assembly strategy [129]. GO is the main precursor for the fabrication of a self-assembled 3D-structure of graphene. Here, the self-assembly relies on physical interactions between the chemical functionalities on the surface of GO and additives with improved noncovalent interface interactions [130, 131]. Generally, GO is reduced during or after the self-assembly process by several methods, which is the key step to determine the final structures and properties of 3D-graphene structures called 3D-reduced GO (rGO). The reduction process eliminates the oxygen-containing functional groups on the GO surface and restores the graphene structure [132]. Various approaches have been used successively to reduce GO to rGO [132]. The most commonly used methods are thermal reduction with annealing the structure at >550 °C under inert atmosphere and chemical reduction that includes several reducing agents such as hydrazine, sodium borohydride (NaBH₄), ascorbic acid (AAO) and hydrohalic acid, etc. [132–138]. The unique structure of the 3D-macroscopic self-assemblies of graphene could provide excellent opportunities to integrate their properties into a broad range of engineering applications [139]. Vacuum filtration is the most commonly used method to create GO-based buckypaper and the thickness can be controlled by the concentration of GO [128]. Here, the formation of GO-buckypaper forms at the surface of the filter membrane (polyvinyl difluoride, AAO, cellulose, etc.), while the solvent pass through the pores of the filter membrane [128]. Besides the vacuum filtration method, several other techniques such as spray, electrochemical and roll to roll have been used to create 3D-graphene papers [102, 140, 141]. Among all these demonstrated techniques, a large area of free-standing paper has been fabricated using electrospray integrated roll-to-roll process and followed by water exfoliation to peel off from the aluminum substrate [102].

The other form of the 3D-graphene is porous building block architectures that are named aerogels, foam, and sponge [142]. One of the most commonly used methods to fabricate 3D-graphene building block by self-assembly approach is a freeze-drying method, in a typical process, GO and composite additives (polymers, nanoparticles, organic molecules, etc.) are dispersing in an appropriate solvent, followed by a freezing and lyophilization process for removing solvents trapped in the pore structures [143–145]. Thus, the interconnected porous building block of GO sheets can be obtained. Usually, there are two crucial factors for the self-assembly of 3D-graphene sheets and their 3D-building block stabilization. The first parameter is the good dispersion of GO and additives in suspensions and the second factor is strong interface interactions between GO sheets and additives so that they self-assemble into 3D-building block during and after removal of the solvent. Alternatively, the self-assemble behavior of 3D-graphene macrostructures can be created by chemical surface functionalization of GO-sheets and thus improve the interface interactions between individual GO-sheets such as hydrogen bonding, Van der Waals interactions, hydrophobic interactions [40].

The other approach to create 3D-graphene building block structures is creating an atomic-scale junction between individual graphene sheets so that the graphene sheets can be organized as covalently bonded 3D-solid networks with control-over properties [123, 146]. The interconnection between individual graphene sheets can be formed by several methods such as the CVD method using various templates, surface chemistry and welding techniques [122, 123, 125]. CVD method is one of the exceptional approaches to create 3D-graphene building blocks using various templates such as metallic foams [e.g. Nickel (Ni), Cu Foams] followed by etching templates and obtain free-standing 3D-graphene building blocks. To the best of our knowledge, the first 3D-graphene foam using Ni-foam as a template obtained by Cheng et al. with the micrometer pore size, 850 m²/g specific surface area and 5 mg/cm³ density [147]. Graphene films were grown on Ni foam by pyrolyzing methane (CH₄) at 1000 °C under ambient pressure. Before etching the Ni-foam, a thin layer of poly(methyl methacrylate) (PMMA) was deposited on the surface of the graphene as support that prevents the
graphene network from collapsing during etching, and then the Ni-foam was etched by hot HCl and iron chloride (FeCl₃) solution. After the Ni-foam etched, the coated PMMA was removed by hot acetone and thus they obtain free-standing 3D-graphene building block [147].

The other promising and commonly used method is creating covalent interconnection between individual graphene sheets using surface chemistry. Various molecules such as metal ions, biomolecules, organic molecules and polymers have been used as cross-linkers to fabricate 3D-building blocks of graphene [130, 146, 148, 149]. For example, Sudeep et al. [123] used glutaraldehyde that contains aldehyde functional groups to interconnect GO sheets. After the controlled reduction of GO, a highly porous interconnected structure and 3D-conductive graphene were obtained [123].

Recently, 3D-printing technologies have been used to manufacture more complicated architecture of 3D-graphene-based building blocks. Although, currently the extrusion-based 3D-printing method is the most commonly used technique for the manufacturing of 3D-graphene-based building blocks, novel 3D-printing techniques such as laser and ultraviolet-curing has been established for tuning the structure down to micrometer scales [126, 150-154].

**Figure 10:** (a) Diagram of the relationships between graphite, graphene, 3D-graphene building block. (b) Illustration of self-assembled and chemically interconnected 3D-graphene building block.

**Polymer reinforcement composite of 3D-graphene building blocks.**

The development of graphene reinforced polymer composites has revealed promising functional and structural characteristics for the use of a broad range of engineering applications. There has been much interest in the production of multiscale high-performance, lightweight and robust, multifunctional graphene-enhanced polymer composites [155, 156]. However, challenges such as the restacking of graphene sheets, poor dispersion and interfacial interaction between graphene and polymer matrix have hindered the reinforcement efficiency of graphene from its full potentials [119, 157]. Therefore, 3D-graphene building blocks offer great advantages to overcome these challenges because the interconnection and spacer
between graphene sheets make them continuous reinforcement [158–160].

Various processing such as dip-coating, casting, vacuum filtration, in situ polymerization and melting of polymers are commonly used methods to manufacture the polymer composite of 3D-graphene building blocks [34, 161–163]. Dip-coating technique is a more suitable method for liquid polymer or polymer solutions. This method typically involves the immersion of a 3D-graphene building block in the polymer solution. The properties of the composite can be tailored by polymer type, polymer concentration and dipping time. Casting is another technique to manufacture polymer composite of 3D-graphene building block by infiltration of polymer into the porous graphene building block. The vacuum infiltration method can also be employed to fabricate polymer composites of 3D-graphene building block [129, 164]. This technique involves simply an infusion of the polymer into porous 3D-graphene or graphene Buckypapers using a vacuum chamber.

In situ polymerization approach is another commonly used method for manufacturing 3D-graphene nanocomposites [163]. Usually, in situ polymerization for 3D-graphene nanocomposites is started with suitable monomers. For a typical process, a 3D-graphene building block is immersed in the monomer with an appropriate initiator. For example, Gao et al. reported a 3D-Graphene building block with a small pore size by a CVD method using nickel nanoparticles as a template. Then, the 3D-graphene/polyaniline (PANI) building block was placed in a PANI solution with ammonium peroxydisulfate as an initiator and in situ polymerization was conducted [162]. In another example, anodic electropolymerization has been used to polymerize aniline onto 3D-graphene buckypapers by directly applying a voltage in an aniline solution with the graphene papers as an electrode [165]. This method has been used to manufacture various 3D-graphene-based polymer nanocomposites [166, 167]. It has been shown that the size of graphene nanoplatelets in a polymer matrix system plays a major role in its mechanical properties [168]. In a study, Cataldi et al. [168] fabricated two types of composites using biopolymers as matrix systems by making hard and soft matrix and reinforce with graphene nanoplatelets (GnP). They used the solvent casting method to make the nanocomposites that did not show any marked improvement of mechanical properties by the addition of graphene nanoplatelets compared to other nano-reinforcement additives. However, after hot-pressing large (>300 nm) multilayer GnP (>3 layers) doubled the elastic modulus of the soft biopolyester matrix. Optimized alignment of the large 2D crystals of GnP flakes leads to such high mechanical improvement. Alignment of 2D crystals in a polymer matrix may be challenging to achieve especially at high volume loading. Jin et al. [169] proposed stacking and folding to synthesize an aligned polycarbonate/graphene composites with more than 320 parallel layers (0.032–0.11 mm) in thickness. The resulting nanocomposites showed high strength and elastic modulus at very low graphene loading (0.082 wt%). Spiral fibers generated the nanocomposite results in telescoping elongation at a break of 110% that is 30 times greater than Kevlar. Lago et al. [170] also showed improved mechanical properties in the nanocomposite of polycarbonate and graphene. They claim their method is simple and scalable. They used a solvent-exchange process utilizing environmentally friendly solvent such as 1,3-dioxolane that is used to dissolve the polycarbonate pellets thus aiding mixing with graphene. An improvement of elastic modulus to the tune of +26% was recorded with a loading of 1 wt% loading. It was proposed such nanocomposites can be turned into filaments for 3D printing. The effect of the lateral dimensions of the graphene affects the physical properties of PMMA nanocomposites matrix [171]. Electrochemically exfoliated few-layer graphene with average diameters of 5 µm (5-FLG) and 20 µm (20-FLG) was added into a PMMA matrix with loadings from 0.5 to 20 wt%. Melt mixing with a help of a twin-screw compounder was used as dispersing aid. Smaller size flakes did not show any change in the viscosity of PMMA, unlike large size flakes that increased the viscosity of PMMA. Similar to the above discussion on the effect of graphene size, large flakes improved mechanical properties behaving like short fibers [171].

Applications.

The outstanding properties of graphene such as high transmit- tance, low sheet resistance, mechanical properties make it potential to be used in a broad range of applications including next-generation conducting materials, optoelectronic devices, flexible electronics, thin-film photovoltaics, sensors, energy storage and conversion [172]. However, the restacking of graphene sheets tend to lose its unique properties and thus limits the application areas [119, 157].

The 3D graphene architectures strategically eliminate the risk of face-to-face restacking and expand the utilization of gra phene in a wider range of fields [129, 164, 173]. They hold great promise for electrochemical applications such as supercapacitors, batteries, solar cells, fuel cells, electrochemical sensors and flexible electronics [174–178]. Also, 3D graphene building blocks are promising materials for the next generation aerospace vehicles and automotive industry, sporting goods, packaging and boat hulls because of their ultralightweight, flexibility, radiation-resistance and outstanding mechanical properties [129]. The high surface area, hydrophobicity, high thermal and electrical conductivity, and tunability of their properties by surface functionalization make the 3D-graphene building blocks an excellent material for environmental applications such as oil absorbent, water purification, CO2 storage [179, 180]. Light weighting of structural materials and composites is another opportunity, where graphene can impart not one but many functions such as strength, impact, aesthetics, etc.

Challenges and outlook for composite of graphene.

A variety of methods such as template-assisted CVD method and self-assembly methods including surface functionalization have been developed for the fabrication of 3D-graphene building blocks. Although the 3D-graphene building blocks are growing with an increasing number of novel structures and properties, still both challenges and opportunities exist. The biggest challenge that prevents commercialization of 3D-graphene building blocks and their polymer composites is mass-production with control-over properties for desirable applications. To overcome this challenge new manufacturing methods, need to be developed and graphene needs to be integrated into the current scalable manufacturing systems including methods that can tweak their properties such as tunable surface functionalization, doping and defects. Furthermore, the role of different defects and functional groups on the properties of the micro- and macro-structures for specific applications has not been understood well. 3D-graphene building blocks shows a diverse property that relies on the unique architecture and sheet qualities. Although the 3D structures are shown by microscopic characterization, their pore distributions are examined by Brunauer-Emmett-Teller (BET) surface analyzer, which can not reveal the information about the large pore channels (>100 nm). To overcome this issue, novel techniques need to be developed to fully
understand the intrinsic morphologies of the 3D-graphene building blocks. The other challenge is a correlation between microscopic and macroscopic properties such as mechanical, electrical, optical and thermal conductivity of the graphene-based building blocks. A systematic analysis of different 3D-graphene building blocks needs to be done by comparing and the correlating between micro-, macrostructure properties and performances in different engineering applications.

RECOMMENDATIONS AND FUTURE PROSPECTS OF GRAPHENE TO LARGE-SCALE APPLICATION

Graphene still faces many hurdles before it can be fully utilized in large-scale applications. For instance, flexible electronics require large graphene sheets with few defects. This has been a challenge with current methods. Current large-scale production of graphene is heavily reliant on graphene nanoplatelets produced from the modified Hammers method. The process may lead to large graphene production, but it is a non-friendly procedure due to the chemicals used. Another problem associated with graphene is standardization. There is a huge variation in synthesized graphene run-to-run in terms of quality, thickness, doping or even defects. As we move toward scalable approaches and applications, academic world must collaborate with industry to also develop lean six sigma techniques in this area that reduce waste and increases output within desired tolerances. However, how this impacts the cost will be an empirical exercise and remains elusive. The variation in graphene quality may occur even in the same lab. The variations are widely spread from different vendors and some may not even be optimal for graphene applications envisioned. There is a need to standardize the production method of graphene from different vendors as well as research laboratories. Related to the variation of graphene production, there is a need to narrow the properties of synthesized graphene to pristine graphene. Graphene derivatives such as GO, reduced graphene, etc. have shown values much less than what is predicted in graphene. Also, graphene used in batteries has not met predicted values. Making graphene industry-friendly, significant efforts are needed in synthesis, storage, reduction in cost and close collaboration between industry and research laboratories.

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CONFLICT OF INTERESTS

The authors declare no conflict of interests.

AUTHORS’ CONTRIBUTIONS

P.S.O., A.K., C.L.L. and S.O. all drafted and compiled sections of the manuscripts. R.D.P., C.B.A., N.C. and C.S.T edited, proofread and finalized the manuscript. Some discussions in this work also originated from prior collaboration between SABIC and Rice University (Houston, TX) in early 2016 led by C.S.T (as a part of Prof. Pulickel M. Ajayan) and N.C. (SABIC).

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