**Graphene Bulk Materials** 



# Polymeric Graphene Bulk Materials with a 3D Cross-Linked Monolithic Graphene Network

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Although many great potential applications are proposed for graphene, till now none are yet realized as a stellar application. The most challenging issue for such practical applications is to figure out how to prepare graphene bulk materials while maintaining the unique two-dimensional (2D) structure and the many excellent properties of graphene sheets. Herein, such polymeric graphene bulk materials containing three-dimensional (3D) cross-linked networks with graphene sheets as the building unit are reviewed. The theoretical research on various proposed structures of graphene bulk materials is summarized first. Then, the synthesis or fabrication of these graphene materials is described, which comprises mainly two approaches: chemical vapor deposition and crosslinking using graphene oxide directly. Finally, some exotic and exciting potential applications of these graphene bulk materials are presented.

# 1. Introduction

As the rising star in last decade, graphene has received exceptional attention in both scientific and industry communities, mainly driven by its excellent/unique properties as well as various proposed potential applications.<sup>[1-48]</sup> Unfortunately, no any killer application has yet been materialized, at least in large scale. The main research needed to tackle such a challenging issue is how to prepare this material in bulk state while maintain the unique two dimensional (2D) structure and many excellent properties of graphene sheets. The main obstacle mainly stems from the intrinsic trend of the graphene sheets to restack, due to their strong  $\pi$ - $\pi$  interactions. Despite the existence of these intrinsic force, scientists are still curious about the possibility in fabricating one or few layers of graphene at a macroscopic scale (or even potentially up to an infinite size)

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either in free-standing state or on some certain substrates, and opening up the potential for their use in killer applications such as electronics,<sup>[2,5–7,10,14,35,38,43–46,49–59]</sup> optoelectronics,<sup>[12,38,43,52,54,60]</sup> etc.

The challenges to address in the abovementioned scenario are obvious, because: 1) the free standing graphene sheet is too fragile to be handled or used; and 2) a graphene sheet on substrate may result in unfavorable interactions between the sheet and the substrate, where a weak interaction may cause the graphene to fall from the substrate and a strong interaction will severely affect the properties of the graphene.<sup>[61]</sup> Thus, in order to preserve its 2D structure and unique properties of gra-

phene while in its bulk state material, the individual graphene sheets must be free of the normal  $\pi$ - $\pi$  interaction range in the direction, perpendicularly (c-axis, out of plane) to the graphene basal plane, and further be locked to overcome the intrinsic  $\pi$ - $\pi$ interaction force to achieve the required structural stability for applications. In this context, two types of materials can be made to achieve the goal of industrial scale applications: one is to use only graphene sheets (or other all-carbon based units such as carbon nanotubes (CNTs)) as the building units and link them together through bonded junctions to achieve monolithic three dimensional (3D) cross-linked graphene (3DGraphene) network;<sup>[62–64]</sup> the other one is to form some kind of composites or hybrid materials, where graphene sheets are separated by the additive (secondary) component molecule, and the interaction between graphene sheets and the secondary molecules are chemical bonding or van der Waals forces.<sup>[23,24,65-74]</sup> There are two types of strategies to approach these materials through a structural perspective: one is to introduce some ordered (crystalline) structure, which has been proven to be rather challenging and has not yet been achieved macroscopically; the other is to form random (amorphous) structures, as have been reported in graphene composite or hybrid materials (short named as graphene composite below). Clearly, the best approach would be the graphene sheets as the only building unit to form the ordered structure (ordered 3DGraphene), which will retain most properties of graphene. However, such a material has been proven to be extremely difficult to achieve.

One effective way is to construct a monolithic 3D network, but with some sacrifice, is by using graphene sheets as the building unit via C-X bonds (X = C, O, S, and even metal atoms, etc.) at the edges. This kind of monolithic polymeric



graphene-network material can be considered as 3D crosslinked polymers, such as most metal-based coordinated polymers and cross-linked thermoset polymers, where the linking units can be metal atoms or normally linear monomer molecules. In this context, graphene sheets are kept well-separated in the *c*-axis and locked for structural integrity stability.<sup>[20]</sup> In principal, such bulk materials should exhibit the intrinsic properties of graphene at macroscopic scale. Together with their structural integrity and stability due to the chemical bonding, these materials could be suitable for many applications such as optoelectronics, thermal, and mechanical devices (units), and other structural-related designs.

There are many reported graphene-based composite materials with the 3D label. However, it must be noted that most of these materials are just mixtures of graphene sheets with other components, and the graphene sheets in these composites are randomly distributed in the matrix (or second component) without any bonding between either the graphene sheets themselves or between the sheets and the second component. Such materials might be enough for certain applications with limited requirements to achieve some improved properties due to the existence of graphene. For example, in energy related applications, the additive graphene could efficiently enhance electrical conductivity or mechanical strength. However, to really present the huge potential of graphene and particularly its applications in high end microelectronics or optoelectronics, it is believed that the dominant units in the bulk state material should be comprised of graphene sheets, and also necessarily contain the formation of some kind of polymeric (monolithic) cross-linked networks of graphene sheets.

Here, we will focus on the 3D cross-linked graphene (3DGraphene) materials, where 2D graphene sheets act as dominant building blocks and are cross-linked together to form monolithic 3D networks of graphene. Such 3DGraphene materials should have the great potential to possess most of the intrinsic properties of graphene while in bulk state. Since many reviews related to the graphene-based composite or hybrid materials have been published,<sup>[41,66,75-80]</sup> it is not necessary to cover them in most cases. We must point out that in previous reports on such composite materials, the excellent properties of graphene have either been lost or severely weakened. Additionally, the graphene community does not seem to pay adequate attention to this type of 3DGraphene material. Thus, herein, the theoretical research on various proposed structures of graphene bulk materials will first be summarized. Then, the synthesis or fabrication of these graphene materials will be described, which mainly includes two approaches: chemical vapor deposition and cross-linking using graphene oxide directly. Finally, some exotic and exciting potential applications of these graphene bulk materials will be presented.

# 2. Theoretical Works

Even before the emergence of graphene, some models had been proposed to construct new 3D architectures consisting of graphite sheets as new carbon allotropes. For example, in 1991, Terrones and Mackay introduced the concept of triply periodic minimal surfaces, known as Schwatzites, to build





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1) carbon-based nanomaterials, including carbon nanotubes and graphene, 2) organic and polymeric functional materials, and 3) energy devices including organic photovoltaics and supercapacitors.

an all-carbon periodic structure with a negative curvature and all sp<sup>2</sup> carbons.<sup>[81]</sup> It was found that the introduction of a few eight-member rings within the sp<sup>2</sup> structure does not cause large strain to the framework. However, the synthesis of the desired structure is rather difficult, though several ordered graphite foams have been proposed. In 2002, Tomanek made a proposal named as "Carbon Foam," essentially a 3D cross-linked graphene joined together through sp<sup>3</sup> carbon (**Figure 1**).<sup>[82]</sup> The periodic 3D network could be further tuned by regulating the geometry of the building block of graphitic strips, leading to a varied structural phase space between diamond and graphite. The calculated results for this type of proposed material indicate that this material would not only be as



Figure 1. Left panel: perspective view of the unoptimized 3D foam lattice structure, based on the 64-atom unit cell. Right panel: use of the sp<sup>2</sup> and sp<sup>3</sup> carbon atoms in the carbon foam structure. Reproduced with permission.<sup>[82]</sup> Copyright 2002, Taylor & Francis.

stable as graphite and diamond, but more interestingly could have a higher density than graphite and exhibit high bulk modulus and possess metallic properties. Possible strategies for synthesizing this material have also proposed, which include directed assembly from nanographite and polymerizing aligned nanotubes.

In 2005, Kawai et al. proposed similar polymeric (monolithic) structures based on graphene sheets called "graphitic Y junction (GYJ)" (**Figure 2**A) and carried out the simulation for their properties.<sup>[83]</sup> Based on the intersectional collision model of graphene patches, GYJ could be formed through constructing fourfold 3D bonded junctions, where the lattice underwent a gradual distortion. Eventually, covalent bonds with sp<sup>2</sup>–sp<sup>3</sup> hybridized states could emerge between the edge and the surface. The results from density functional theory calculations indicate that the reaction barrier required for the formation of graphitic Y junctions is almost zero. The simulated results also show that the proposed structures are not only stable, but possess many similar properties to graphene.

In recent years, many other theoretical studies have been reported and various structures have been proposed (Figure 2B).<sup>[84]</sup> Although some of these 3D networks may have either four- or eight-membered carbon rings onto the Schwarz minimal surface, all 3D carbon allotropes with all sp<sup>2</sup> carbons are called a Mackay–Terrones crystals (MTCs) (Figure 2C).<sup>[85]</sup> Meanwhile, 3D architectures with sp<sup>2</sup>-sp<sup>3</sup> hybridized structures are referred to GYJ (Figure 2A).<sup>[83,86-88]</sup> In 2013, Jiang et al. proposed two classes of cross-linked 3DGraphene monoliths by using sp<sup>2</sup> zigzag and armchair graphene nanoribbons as building blocks and sp<sup>3</sup> carbon chains as junction nodes (Figure 3).<sup>[63]</sup> The covalently bonded 3D networks of graphene show the semiconducting properties with tunable band gaps, the intrinsic merits of graphene, and novel negative linear compressibility, which are due to their unique wine-rack-like structures and anisotropic mechanical strength. In 2006, Kuc and Seifert theoretically demonstrated hexagon-preserving carbon foams consisting of graphene planes interconnected rigidly with one another at 120°, forming a linear chain of sp<sup>3</sup>-bonded atoms along the junction (Figure 4).<sup>[87]</sup> According to the optimized geometry, the chain of sp<sup>3</sup>-hybridized atoms along the junction is covalently linked with the graphene sheets with either zigzag or armchair types of edges. It should be pointed that these graphene-based networks with all sp<sup>2</sup> or sp<sup>2</sup>-sp<sup>3</sup> hybridized structures are thought to have carbon foam structures with high stability at low mass density, a large surface area and unique electronic and mechanical properties.<sup>[86-88]</sup>

In the abovementioned theoretically proposed interpenetrating graphene networks, the jointed bonds are only formed by carbon atoms. It should be pointed out, understandably, the  $sp^2$  and  $sp^3$  carbon atoms in such junction bonds could also be replaced with other multiple valence atoms such as O, N,



**Figure 2.** Some proposed 3D carbon architectures. A) Total spin density isosurfaces of a new architecture with Y junctions formed by both sp<sup>2</sup> and sp<sup>3</sup> carbon atoms. Reproduced with permission.<sup>[83]</sup> Copyright 2005, American Physical Society. B) The top view of a 6-1-1-p MTC in a 2 × 2 supercell; the junctions are formed with non-six-membered rings but with all atoms exhibit sp<sup>2</sup> hybridization. Reproduced with permission.<sup>[84]</sup> Copyright 2015, American Physical Society. C) Molecular model of an extended periodic gyroid surface decorated with graphene; note the presence located at the saddles. Reproduced with permission.<sup>[85]</sup> Copyright 2018, Elsevier.

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**Figure 3.** Schematic illustration of the formation of the GMs. A) ZGM-28 with zigzag graphene nanoribbons as building blocks. B) AGM-28 with armchair graphene nanoribbons as building blocks. (a) Graphene nanoribbon building block with tunable width and direction, (b) view of sp<sup>3</sup> linking chain, and (c) structure of ZGM-28 and of AGM-28. Blue and red represent carbon atoms corresponding to the nanoribbon building blocks and linker chains, respectively. Reproduced with permission.<sup>[63]</sup> Copyright 2013, Wiley-VCH.

S, etc.<sup>[20,62]</sup> or even multiple linking molecules.<sup>[89]</sup> Both types of carbon junction units (e.g., with and without sp<sup>2</sup>/sp<sup>3</sup> carbon) may also widely exist in carbon-based materials including amorphous carbon materials, although this is difficult to prove currently.

With the improvement of computer-modeling abilities, the prediction of the unique properties for truly ordered 3D cross-linked graphene-based covalent networks has been achieved, and results indicate that these 3DGraphene materials exhibit many excellent and some even unprecedented properties.<sup>[63,81,83,85–87,90]</sup> Recently, a full atomic model of a 3DGraphene assembly has been demonstrated by Buehler and co-workers to show the outstanding properties of 3D networks based on triply periodic minimal surfaces (**Figure 5**).<sup>[91]</sup> Combing the bottom-up computational modeling with experiment results based on 3D-printed models, the authors presented the relationship between the mechanics of such 3DGraphene materials and their density. These results indicate that by changing the chemical synthesis process (especially the reacting conditions, including pressure and temperature), stable 3D porous bulk materials with novel architecture and decent density under control could be made for many engineering applications.

Our group has also theoretically investigated graphene networks with three-membered and four-membered rings and found that the four-membered ring systems and its derivatives are kinetically stable with a metallic nature.<sup>[92]</sup> More recently, Buehler and co-workers further investigated the thermal conductivity of materials with a 3D gyroid graphene structure as mentioned above by using full-atom molecular dynamics simulations, and found that although these materials could have high mechanical strength, their thermal conductivity decreases significantly and is insensitive to the bulk density due to shorter photo mean free path originating from the increased defects and curvatures of graphene.<sup>[93]</sup> In 2017, Chen and co-workers proposed a new metastable 3D carbon allotrope entirely composed of pentagon rings, named as "Pentagon Carbon."<sup>[94]</sup> This highly rare lattice motif demonstrates a fancy







**Figure 4.** Proposed zigzag carbon foams with different unit size. A–C) Zigzag carbon foams of sizes (1,5), (1,1), and (5,1), respectively; D,E) Armchair carbon foams (5,5) and (3,3), respectively. Reproduced with permission.<sup>[87]</sup> Copyright 2006, American Physical Society.



**Figure 5.** Different atomistic and 3D-printed models of gyroid geometry for mechanical tests. A) Simulation snapshots taken during the modeling of the atomic 3D graphene structure with gyroid geometry. B) Five models of gyroid graphene with different length constants of L = 3, 5, 10, 15, and 20 nm from left to right. Scale bar: 2.5 nm. C) The normalized Young's modulus (a), tensile strength (b), and compressive strength (c) of the 3D graphene assembly as a function of its mass density. Reproduced with permission.<sup>[91]</sup> Copyright 2017, American Association for the Advancement of Science.





uniaxial strain-induced transformation from isospin-1 triplet fermions to triply degenerate fermions and eventually to interconnected Hopf-link Weyl loops. Moreover, a possible reaction route for preparing the Pentagon Carbon was also suggested in this paper. Very recently, a new body-centered tetragonal carbon allotrope, has been proposed to be prepared by inserting a benzene ring into each C–C bond in bct-C<sub>4</sub> carbon lattice, or by a structural modification of the (5,5) CNT. Electronic band structure calculations indicate that the novel carbon allotrope bct-C<sub>40</sub> could have a topological semimetallic state.<sup>[95]</sup>

# 3. Synthesis and Fabrication

Note that we will not cover the conventional synthesis or fabrication of graphene or graphene oxide (GO). Also in last few years, there have been a tremendous number of works on graphene composites with/out 3D cross-linking, which have been reviewed in many places.<sup>[41,66,75-80,89,96]</sup> Although there have been some progress on the truly challenging ordered and cross-linked 3DGraphene materials, the synthesis and studies for such materials have lagged far behind conventional composite materials using graphene. Although there are many reports on methods to directly synthesize 3D cross-linked bulk polymeric graphene network materials,<sup>[90]</sup> most fit into two groups of approaches;<sup>[22,64,70,88,97–101]</sup> one is chemical vapor deposition (CVD) growth on some kind of 3D frameworks (templates) and then removing the templates afterward;<sup>[102-104]</sup> the other one is using GO sheets directly<sup>[105]</sup> and then cross-linking them together with either themselves or linking agents.[106-108]

## 3.1. 3DGraphene Materials with Graphene Only

In this section, we will cover the materials with 2D graphene sheets as the sole building units.<sup>[89]</sup> it is possible produce the materials in bulk state while still maintaining the intrinsic properties of graphene by linking the building units onto each other via chemical bonding at the edge along the 2D sheet plane or relatively weak  $\pi$ - $\pi$  interactions perpendicular to the plane (as over strong coupling along the  $\pi$ - $\pi$  direction would diminish or severely damage graphene's properties).

In 2010, Shi and co-workers reported a mechanically strong, electrically conductive, and thermally stable self-assembled hydrogel of graphene oxide only, prepared via a hydrothermal process.<sup>[109]</sup> However, it may be argued that the proposed holding force between the sheets for the increased stability and mechanical strength is the  $\pi$ - $\pi$  stacking interaction through the overlapping of the flexible graphene sheets.<sup>[96]</sup> Later on, this method has been widely used (see below) and further developed. For example, with the proper size of the graphene unit, a solvothermal method (for example, with ethanol as a solvent) has been developed. when concentration and solvents were controlled properly, a highly elastic graphene-only 3D cross-linked 3DGraphene was obtained (Figure 6).<sup>[20,110]</sup> Various analysis indicate that the condensation/cross-linking of the functional groups such as OH, COOH, and epoxy groups were mainly located on GO sheets edges, and covalently interconnected with



Graphene sponge

**Figure 6.** The synthesis and structure of graphene sponges. Illustration of the solvothermal conversion of ethanol-dispersed GO platelets into a graphene sponge. Reproduced with permission.<sup>[110]</sup> Copyright 2015, Nature Publishing Group.

other sheets to form a monolithic 3D chemically linked network, which has been proven to be thermoset 3D cross-linked polymers with the 2D graphene sheets as a building units.

Prefabricated 3D metal substrates, such as nickel foam, could be used as catalysts/templates to fabricate 3D graphene foams (GFs) with controlled morphologies and properties. Probably the earliest and most important work is from Cheng's group in 2011, where a monolith of a continuous and interconnected foam-like graphene 3D network was obtained using Ni foam template-directed CVD and CH<sub>4</sub> as the carbon source.<sup>[111]</sup> The GF inherits the interconnected 3D scaffold structure of the nickel foam template, and all the graphene sheets in the GF are in direct contact with each other and are also well separated as few-layer graphene sheets. Many ripples and wrinkles exist for the graphene sheets. The free-standing GF is extremely light and flexible and also exhibits high conductivity. The average number of graphene layers, specific surface area, and density of the GF can also be controlled. Similarly, attempts to use Cu foams for the preparation of such GF failed to obtain free-standing sample, probably due to the monolayer growth of graphene on Cu surface. Soon afterward, Ruoff and co-workers reported a similar approach by using Ni foam as the template to obtain 3D GF structures consisting of few-layer graphene and ultrathin graphite using CVD and methane as the carbon source.[112] Structural analysis indicates that the strut walls of the GF exhibit the characteristics of high-quality single- and fewlayer graphene sheets. Using a reverse CVD process starting from lithographically predefined 3D pyrolyzed photoresist films and after depositing Ni on the predefined 3D carbon structure, a well-defined 3D porous structure with few layered graphene sheets as the walls has been prepared (Figure 7).<sup>[113]</sup> Starting from an alloy Ni<sub>30</sub>Mn<sub>70</sub>, a free-standing complex 3D network comprised of interconnected graphene can be obtained by chemically etching out Mn and leaving nanoporous Ni foam film,<sup>[98]</sup> the network retains a 2D coherent electron system of massless Dirac fermions, which holds intrinsic 2D electronic properties and high electron mobility. A similar approach was also reported through using 3D microporous copper as catalysts and substrates.<sup>[102]</sup>

Using a metal ion-exchange resin as a carbon precursor, a 3D hierarchical porous graphene-like material can be prepared after direct graphitization and KOH activation.<sup>[114]</sup> The material exhibits high surface area and high supercapacitor performance when it was applied as the active material.







**Figure 7.** Schematic drawings illustrating the steps and mechanism for chemical conversion of amorphous porous carbon to 3D graphene: A) porous carbon, B) conformal Ni coating, C) diffusion of carbon into Ni top surface during thermal annealing, and D) hollow 3D graphene after Ni etching. Reproduced with permission.<sup>[113]</sup> Copyright 2012, American Chemical Society.

Using a zeolite template and CVD process (Figure 8), a cross-linked-fullerene-like framework has been obtained. The building unit of the carbon framework in each supercage of the zeolite Y has an average composition of  $C_{63}H_{4,9}O_{1,2}$ , very close

to that of fullerene  $C_{60}\ cross-linked-fullerene-like framework carbon Schwarzite.^{[115]}$ 

One interesting method for the fabrication of 3D cross-linked graphene was reported by Bando's group using a controlled



**Figure 8.** A) Synthetic scheme for conventional ZTC consisting of a cross-linked-buckybowl-like framework. B) Enlarged structural model of carbon/ zeolite composite, including two supercages; one supercage contains a  $C_{36}H_9$  unit. C)  $CO_2$  adsorption isotherm of carbon/zeolite composite. D) Example of hypothetical carbon structure, with a cross-linked tubular framework formed inside zeolite nanochannels. Reproduced with permission.<sup>[115]</sup> Copyright 2013, Elsevier.



**Figure 9.** Growth process and structural regulation of sugar-blowing production. Scanning electron microscopy (SEM) images of glucose (crystals marked in green) and NH<sub>4</sub>Cl (marked in blue), which were subsequently transformed to melanoidin bubbles (marked in brown) under a browning reaction; these were finally converted into the SG containing graphitic membranes and struts (marked in gray). Scale bar: 50 mm. Reproduced with permission.<sup>[100]</sup> Copyright 2013, Nature Publishing Group.

heating of glucose and NH<sub>4</sub>Cl (**Figure 9**).<sup>[100]</sup> In this process, the molten syrup was gradually heated and polymerization of the glucose unit occurred. The thermally decomposed gases from NH<sub>4</sub>Cl then gradually blew the glucose-derived polymers into large bubbles to form the 3D self-supported graphene product (graphene elastomeric foams), showing excellent supercapacitor performance. The walls are mainly comprised of large-area, ultrathin, high-quality mono-/few-layered graphene, and some multilayered graphite sheets.

Krainyukova and Zubarev have obtained a very stable honeycomb carbon allotrope via the deposition of vacuum-sublimated graphite.<sup>[90]</sup> High resolution transmission electron microscopy (TEM) analysis indicates that this material consists of both periodic and random Y-junction type repeating units with a honeycomb structure built exclusively from sp<sup>2</sup>-bonded carbon atoms, and is considered as a truly foaming 3DGraphene structure.

# 3.2. 3DGraphene Materials with Graphene Linked by Other Ions or Atoms/Molecules

In 2007, Rouff and co-workers<sup>[108]</sup> prepared a graphene paper prepared with a rather small amount (<1%) of  $Mg^{2+}/Ca^{2+}$  ions linked graphene sheets, and found that significant enhancement in the mechanical stiffness (10–200%) and fracture strength (50%) of GO paper can be achieved. Other ions such as  $Ca^{2+}$ , Ni<sup>2+</sup>, or Co<sup>2+</sup> have also been used to link the reduced GO (rGO) sheets into gel-like 3D architecture under hydrothermal conditions.<sup>[116]</sup> A similar work from the same group using polyallylamine as bridges for cross-linked GO sheets also showed excellent mechanical stiffness and strength.<sup>[117]</sup>

A controlled assembly of single-layered GO into 3D macrostructures promoted by a noble-metal nanocrystal (Au, Ag, Pd, Ir, Rh, or Pt, etc.) and glucose as the linker was reported in 2010 by Wang's group, and it was further used as fixed-bed catalysts for a Heck reaction resulting in both 100% selectivity and conversion.<sup>[118]</sup>

In 2011, Nguyen reported a borate-crosslinked GO thin film fabricated via the cofiltration of an aqueous dispersion containing 0.75 mg mL<sup>-1</sup> of GO and varying concentrations of sodium tetraborate.<sup>[119]</sup> The stiffness and strength increased by over 255% and 20%, respectively, compared with that in the absence of sodium tetraborate. The increased stiffness and

strength are primarily attributed to the presence of covalent borate orthoester bonds with the GO nanosheet (Figure 10) through hydroxyl moieties on the sheet.

Some polymer/graphene cross-linked materials have been made by grafting polymer units on the graphene sheets, and then using these units to perform the polymerization. Loh



**Figure 10.** Left: schematic illustration of the formation of the borate crosslinked network across two adjacent graphene oxide nanosheets in a thin film. A) Water molecules form hydrogen bonds with epoxide and hydroxyl groups to bridge nanosheets in an unmodified graphene oxide thin film. B) In addition to forming hydrogen bonds, borate anions react with surface-bound hydroxyl groups to give borate orthoester bonds, improving the mechanical properties beyond those of the unmodified film. C) Thermal annealing drives the formation of more covalent bonds within the intersheet gallery, affording an ultrastiff thin film. Right: mechanical properties of respective films, demonstrating that ultrastiff films are only obtained after annealing borate-modified films under a flow of dry N<sub>2</sub>. Reproduced with permission.<sup>[119]</sup> Copyright 2011, Wiley-VCH.



and co-workers used the methacrylate-functionalized GO sheets (GO-ac) as the building units, benzoyl peroxide as the initiator and dipentaerythritol penta-/hexa-acrylate as the crosslinker to prepare a cross-linked graphene material made by the polymerization of the C=C double bond on the attached methacrylate end group.<sup>[120]</sup> The mechanical properties of the GO film formed is much stronger compared to the film prepared by the Langmuir-Blodgett method without any covalent bonding. By grafting the surface of the GO sheets in GO films with 10,12-pentacosadiyn-1-ol monomer, then cross-linking through 1,4-addition polymerization of their diacetylenic units under UV irradiation, and then following with hydroiodic acid reduction, the resulting GO film exhibits significantly improved toughness and conductivity.<sup>[121]</sup> Many other organic/polymeric molecules have also been used for such cross-linking including phenol-formaldehyde<sup>[122]</sup> and glutaraldehyde.<sup>[123,124]</sup>

By soaking the hydrothermally produced graphene hydrogel (GH) in ammonia solution, followed by freeze drying, Yang reported a strengthened 3DGraphene aerogel, where covalent bonds between graphene sheets were created with N atoms (**Figure 11**).<sup>[125]</sup>

Using an amine-terminated randomly branched oligomer (HB-NH<sub>2</sub>) prepared from diethylene triamine, a self-healing elastic material has been made via the formation of cross-linking amide bonds between polymer and graphene, the numerous hydrogen bonding sites in the network renders its self-healing property.<sup>[126]</sup> Using various diamines as the linker, cross-linking GO membranes have also been prepared for separation purposes.<sup>[127–129]</sup> The cross-linking of graphene sheets can also be achieved using poly(oxypropylene) diamines (D<sub>400</sub>) promptly.<sup>[130]</sup>

One interesting all-carbon hybrid material made by linking graphene sheets with  $C_{60}$  was reported and has been found that

there is strong electronic coupling between the two units.<sup>[131]</sup> A hybrid material with 3D CNT/graphene sandwiched structures was prepared by Wei<sup>[132]</sup> and other groups,<sup>[107]</sup> using GO as the substrate to CVD-grown CNT as pillars between the graphene sheets, and the material was demonstrated to show excellent properties for supercapacitor application (**Figure 12**).

Additionally, Tour's group reported a CVD process for preparing a seamless covalent bonded graphene/CNT nanostructure (**Figure 13**),<sup>[101,104]</sup> where the covalent transformation of sp<sup>2</sup> carbon between the planar graphene and the single-walled carbon nanotubes was observed at the atomic resolution level by using aberration-corrected scanning transmission electron microscopy (STEM). In addition to the seamless connection between the CNT and graphene units, the material exhibits a large specific surface area (SSA) of 2000–2600 m<sup>2</sup> g<sup>-1</sup>.

## 4. Some Important Properties and Applications

There have been many reviews for the applications of graphene-based materials, including graphene composites, which will not be covered since many reviews regarding this research direction have been published.<sup>[79,80,133]</sup> But one point worthy of highlighting is that the essential point for almost all composite materials to achieve desired and better properties is to have graphene sheets dispersed in the matrix or secondary material at the individual sheet (molecular) level, as has been indicated a long time ago.<sup>[134]</sup> Thus, in this section, we will only focus on some unique/important properties or application offered by the 3DGraphene materials, where in most cases the graphene would be the single unit in the materials, and offer some unique or important applications.



**Figure 11.** Schematic process of the formation of GA via a classical hydrothermal method and its freeze drying before and after ammonia solution treatment. A) GO dispersed in water with a concentration of 2 mg mL<sup>-1</sup>. B) The formation of GH and the forming force including van der Waals force,  $\pi$ - $\pi$  stacking and hydrogen bonds in GH. C) GA, the abundant hydrogen bonds lost in GA, and the expansion of ice induced the destruction of the porous structure. D) GH was treated by ammonia solution, C–N formed between graphene sheets besides van der Waals force,  $\pi$ - $\pi$  stacking and hydrogen bonds. E) *a*-GA-N, porous structure of GH was preserved and there were some covalent bonds formed between graphene sheets. Reproduced with permission.<sup>[125]</sup> Copyright 2013, Royal Society of Chemistry.







**Figure 12.** Illustration of the formation of hybrid materials with CNTs grown in between graphene nanosheets, showing stacked layers of graphene oxide (left), catalyst particles adhered onto layer surface after deposition (middle), and CNTs in between graphene layers after growth (right). Reproduced with permission.<sup>[132]</sup> Copyright 2010, Wiley-VCH.

#### 4.1. Structural/Mechanical and Superelasticity

Truly 3D cross-linked graphene bulk materials have been demonstrated to show some unique and even unprecedented mechanical properties.<sup>[135]</sup> We have demonstrated that such materials could provide a combination of both cork-like and rubber-like properties and display near-zero Poisson's ratios in all directions that are almost strain-independent during reversible compression to huge strains.<sup>[110]</sup> Furthermore, they function as enthalpic rubbers, which can repeatedly recover up to 98% compression in air and 90% in liquids between -196 and 900 °C, which is not yet observed in any other material so far. Additionally, this material can absorb organic liquids over 1000 times its own weight, offering a great potential for cleaning applications. Such remarkable elastic properties, combined with the dually capable hydrophobic and hydrophilic surface treatments of the material offers an exciting and highly reversible and recyclable absorption/separation method with high capacity for both organic and aqueous liquids.<sup>[136]</sup> Furthermore, using a prebuckled hierarchical structure and synergistic reinforcement between graphene and carbon nanotubes, highly stretchable carbon aerogels with a retractable 200% elongation have been fabricated.<sup>[21]</sup>

Linking graphene sheets with multiple valence ions or functional molecules has been widely used to achieve better mechanical performance.<sup>[119]</sup> Artificial bone materials have been prepared by linking graphene sheets with inorganic materials.<sup>[137]</sup> The composition of graphene with other polymers can also improve the matrix's material mechanical properties.<sup>[121,138–140]</sup> Elastic hydrogels with diamine material<sup>[127,130]</sup> or with polyvinyl alcohol polyvinyl alcohol (PVA),<sup>[141]</sup> and self-healing graphene composites have also been reported by cross-linking graphene sheets with polyurethane,<sup>[142]</sup> poly(acrylic acid),<sup>[143]</sup> or C<sub>3</sub>N<sub>4</sub>,<sup>[144]</sup>

#### 4.2. Electromagnetic Wave Absorber

Graphene-only 3DGraphene foam materials also demonstrate a broadband and tunable high performance microwave absorption (MA) properties in the measured frequency ranges of 2–18, 26.5–40, and 75–110 GHz (a total bandwidth of 64.5 GHz), which are occupied for many critical applications, including radar detection, satellite communications, and remote sensing.<sup>[19]</sup> This excellent and broadband MA performance is attributed to both the intrinsic property of graphene sheets and the cell structure of the foam

(Figure 14), causing multiple absorption and reflection. Furthermore, the GF under 90% compressive strain even can achieve a qualified absorption bandwidth (reflection loss (RL)  $\leq$  -10 dB) of 60.5 GHz, about 70% wider than that of the best currently available MA material in open literature. A RL value of -34.0 dB as well as a 14.3 GHz qualified absorption bandwidth has been achieved for an ultralow bulk density GF.<sup>[145]</sup> 3D assemblies of CNT with graphene also exhibit excellent MA properties.<sup>[146]</sup>

Using the same material, an excellent terahertz absorption property at frequency ranging from 0.1 to 1.2 THz was achieved. More interestingly and importantly, the terahertz absorption performance increases when increasing the incidence angle while the majority of materials become invalid at oblique incidence. For example at the incidence of 45°, the maximum RL value increases 50% to 28.6 dB.<sup>[147]</sup>

#### 4.3. Photoinduced Electron Emission and Light Propulsion

One very unique property observed for 3DGraphene materials made with only graphene units is the direct light propulsion of these materials at the macroscopic scale up to submeter distances (**Figure 15**).<sup>[20]</sup> The mechanism behind such a remarkable phenomenon is due to the efficient hot electron emission following a light-induced ejected electron (LIEE) mechanism. The unique Dirac band structure of graphene, and the novel morphology of the bulk 3D cross-linked graphene material make it capable of not only absorbing light at various wavelengths, but also emitting energetic (hot) electrons efficiently enough to drive the bulk material following the principles of Newtonian mechanics. Thus, the unique photonic and electronic properties of individual graphene sheets are manifested in the translation to the bulk state. These unprecedented



**Figure 13.** Scheme for the synthesis of CNT carpets directly from graphene. A) Copper foil substrate. B) Graphene is formed on the copper foil by chemical vapor deposition (CVD) or solid carbon-source growth. C) Iron and alumina are deposited on the graphene-covered copper foil by using e-beam evaporation. D) A CNT carpet is directly grown from graphene surface. The iron catalyst and alumina protective layer are lifted up by the CNT carpet as it grows. Reproduced with permission.<sup>[101]</sup> Copyright 2012, Nature Publishing Group.





**Figure 14.** Schematic representation of the MA mechanism for the GF. Reproduced with permission.<sup>[19]</sup> Copyright 2015, Wiley-VCH.

results offer exciting opportunities to bring about bulk-scale light manipulation with the potential to realize long-sought applications in novel areas such as the solar sail and space transportation/travel driven directly by sunlight.<sup>[148]</sup> Thus, some exotic and unprecedented properties or phenomena could be achieved when these unique 2D materials are assembled in such a way that their intrinsic 2D properties are truly retained. Furthermore, due to the efficient hot electron emission, the material could also be used as a novel and convenient electron emission source and as a catalyst for some reactions required tough conditions. For example, unique catalytic systems for ambient condition ammonia synthesis and water splitting<sup>[149-151]</sup> have been developed based on the properties of the LIEE mechanism. Furthermore, strong plasmonic absorptions tunable from terahertz to mid-infrared ranges via controllable doping level and porosity have been observed for 3DGraphene grown using the Ni-foam CVD approach.[152]

Furthermore, the same material also demonstrates outstanding photoacoustic transduction properties with a linear and universal coupler between light and sound through a highly efficient photothermal effect independent of light wavelength in a broad spectral range from infrared to ultraviolet.<sup>[153]</sup> Also, due to the wide range and efficient light absorption of

this material, combined with its superelasticity, the material can be used directly as an extremely simple but reusable standalone solar energy converter without any other supporting components.<sup>[154]</sup> This simple solar energy converter could deliver a high specific water production rate of 2.6 kg m<sup>-2</sup> h<sup>-1</sup> g<sup>-1</sup> with a near similar rate of 87% under 1 sun intensity and >80% efficiency even under ambient sunlight (<1 sun), proving competitive for desalination and sewage treatment application.

#### 4.4. Energy Devices

There have been numerous reports and reviews about hybrids or composites with graphene some in the form of 3D crosslinked structures, for energy storage applications,<sup>[17,23,31,155–162]</sup> including supercapacitors<sup>[97]</sup> and all-solid<sup>[163,164]</sup> or flexible energy devices.<sup>[165–167]</sup> Indeed, as demonstrated in 2009,<sup>[168]</sup> if the high surface area and electrical conductivity could be maintained, graphene-only bulk materials for supercapacitors can exhibit rather high performance in terms of both capacity and cycling ability.<sup>[62,169,170]</sup>

The 3D cross-linked graphene structures prepared using CVD on Ni foam have been utilized in many areas, such as flexible conductors,<sup>[22]</sup> supercapacitors, fuel cells,<sup>[171]</sup> batteries,<sup>[155]</sup> and electrochemical detection.<sup>[172]</sup> The 3D crosslinked graphene aerogel (GA) prepared under the hydrothermal reaction from GO, if controlled properly, could achieve ultrahigh SSA (3523 m<sup>2</sup> g<sup>-1</sup>) and high conductivity together with structural stability with specific capacitance and energy density of 231 F g<sup>-1</sup> and 98 Wh kg<sup>-1</sup> and high cycling capability.<sup>[62]</sup> The effective surface area and pore size distribution could also be controlled in a wide range.<sup>[170,173]</sup> Müllen and co-workers<sup>[174]</sup> has prepared B/N-doped aerogel and used it for all-solid-state supercapacitors. The as-fabricated devices possess an electrodeseparator-electrolyte integrated structure. With a PVA/H<sub>2</sub>SO<sub>4</sub> gel as a solid-state electrolyte, the resulting BN-GAs shows high specific capacitance ( $\approx$ 62 F g<sup>-1</sup>), good rate capability, and enhanced energy density (≈8.65 Wh kg<sup>-1</sup>) and power density



Figure 15. Measurement apparatus and schematics of light-induced propulsion and rotation of graphene sponge. A) Schematic of the graphene sponge being propelled vertical upwardly with laser illumination from below. B) Apparatus for light-induced rotation of graphene sponge under laser illumination. Reproduced with permission.<sup>[20]</sup> Copyright 2015, Nature Publishing Group.





(≈1600 W kg<sup>-1</sup>). A flexible solid-state supercapacitor was also reported using the material as the electrode.<sup>[164]</sup> Using the 3D cross-linked graphene structure as the template to load Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> (LTO), a much improved Li<sup>+</sup> capacitor was developed with both high energy density and rate performance.<sup>[175]</sup> When further used as a template to load metal oxides such as Co<sub>3</sub>O<sub>4</sub>, the capacitor using the as-produced material exhibits outstanding specific capacitance (226 F g<sup>-1</sup>), high rate capability, and excellent cycling stability.<sup>[176]</sup> Loading Fe<sub>3</sub>O<sub>4</sub> onto graphene foam grown on Ni foam by CVD renders the material a high capacity of 785 mAh g<sup>-1</sup> for Li<sup>+</sup> batteries.<sup>[69]</sup> The 3D cross-linked graphene can also be used to load sulfur for Li-S batteries with high performance due to the improved conductivity, structural stability and the immobilization of the polysulfide intermediates.[155,177,178] Using such 3DGraphene structures, both high rate and capacity have been achieved for Al ion batteries.<sup>[179-181]</sup> An ultrahigh rate (20 mA cm<sup>-2</sup>) electrochemical energy storage obtained by a highly interconnected graphene network to support niobia (Nb<sub>2</sub>O<sub>5</sub>) has been reported.<sup>[68]</sup>

# 5. Conclusion and Outlook

Although polymeric graphene bulk materials with 3D crosslinked graphene networks have not been fully studied and are proved to be difficult to prepare, these materials demonstrate many excellent properties (some of which unprecedented), showing their potential in many possible applications.<sup>[63,81,83,87,90]</sup> Here, we have highlighted the theoretical works, fabrication strategies, and several important application directions of 3DGraphene materials. Although certain promising processes have been achieved, many challenges still remain before the realization of the controllable synthesis and practical application of these desired 3DGraphene materials.

In theoretical research, in-depth understanding of the 3DGraphene materials from integrated multiscales has seldom been realized. Currently, most theoretical works focus on the nanoscale level with a limited number of atoms (building blocks) in the modeling system or sufficiently large systems with relatively low precision in the accuracy of nanostructure. Ideal modeling systems should reflect the real environment in which the cross-linked graphene frameworks emerge. Therefore, the integration of quantum mechanical models, molecular dynamics models, nanoscale models, and macroscopic models might be addressed together to gain more reliable simulation results and to guide experimental studies. Furthermore, the effects of heteroatoms doping and their distribution on the band structure and optoelectronic properties of 3DGgraphene are also essential for targeted application.

Quantitative methods to characterize the covalent bonds between the building blocks also need to be strengthened; this is of vital significance. Except for some routine characterizations, such as X-ray photoelectron spectroscopy, NMR, IR, etc., it is still a great challenge to clearly detect the chemical bonds between graphene sheets through some straightforward techniques or collect sufficient and quantitative evidence. In this respect, Zhu et al.<sup>[101]</sup> demonstrated an enlightening work on the conjugated covalent bonds in the junction region of a 3D carbon nanotube/graphene hybrid material using an atomic

scale STEM, which may offer a reference for the characterization of chemical bonds in the junction points of building blocks in 3DGraphene materials. Additionally, perhaps the in situ TEM or atomic force microscope tension tests of the intermediates could reveal the marginal difference between chemically bonded graphene sheets and graphene sheets assembled by noncovalent interactions. However, there are still many factors that are likely to interfere with the experiments, including the chemical properties of graphene sheets and the morphology of twisted graphene sheets. Therefore, exquisite design for characterization techniques (for instance, advanced scanning probe microscopy) must be developed. Furthermore, the improved detection of the bonding type between building blocks largely relies on future advancements in instruments, such as improvements in the spatial resolution of spectroscopic techniques. We expect more essential and critical studies on these matters to be published in the future.

Currently, all as-obtained 3DGraphene materials have graphene units in random sizes. While tremendous efforts have been made on the part of many groups to achieve truly ordered 3D cross-linked (crystal) bulk material, the challenge remains to be addressed. These truly ordered materials are believed to possibly offer even more exciting opportunities and exotic properties not present in current materials. In addition, some fundamental physical effects (e.g., macroscopic ferromagnetism and quantum Hall effect) and unprecedented phenomena are expected to be discovered in certain 3DGraphene systems with well-designed building blocks and junction nodes. Compared to monolayer graphene, which possesses a relatively perfect lattice structure, the mechanical properties of 3DGraphene materials are always barely satisfactory, and problems remain for both theoretical and experimental works on how to achieve a considerable structure strength within 3DGraphene materials. On the other hand, 2D graphene sheets could be assembled with other novel 2D structure units,<sup>[106,182-185]</sup> such as hexagonal boron nitride (h-BN), tungsten disulfide (WS<sub>2</sub>), molybdenum disulfide (MoS<sub>2</sub>), and rhenium disulfide (ReS<sub>2</sub>), which also exhibit some novel physical-chemical properties. This together, if achieved, could revolutionize materials science in the future.

As a final note, currently most of the reported so-called 3DGraphene materials are mixtures of graphene with other components, where the excellent properties of graphene are only partially conserved, and thus only generate an incremental amount of improved performance. The truly killer applications that will materialize the huge potential of graphene properties are believed to not only use graphene as the main building unit but also manage to avoid the restacking of the sheets. Thus, materials with truly ordered 3D cross-linked networks formed with only graphene units or other nanocarbon units such as CNT should be the direction of further research, where much effort is required. In light of these developments, we envisage that there will be a brilliant future for 3DGraphene materials in many cutting-edge fields.

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## **Conflict of Interest**

The authors declare no conflict of interest.

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cross-linked materials, graphene, networks, synthesis, theory

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