

# From Conception to Realization: An Historial Account of Graphene and Some Perspectives for Its Future

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carbon · graphene · graphite · history of chemistry

*There has been an intense surge in interest in graphene during recent years. However, graphene-like materials derived from graphite oxide were reported in 1962, and related chemical modifications of graphite were described as early as 1840. In this detailed account of the fascinating development of the synthesis and characterization of graphene, we hope to demonstrate that the rich history of graphene chemistry laid the foundation for the exciting research that continues to this day. Important challenges remain, however; many with great technological relevance.*

## 1. Graphene Defined

Graphite—a term derived from the Greek word “graphein” (to write)<sup>[1]</sup>—has a long and interesting history in many areas of chemistry, physics, and engineering.<sup>[2–4]</sup> Its lamellar structure bestows unique electronic and mechanical properties, particularly when the individual layers of graphite (held together by van der Waals forces) are considered as independent entities. As early as the 1940s,<sup>[5]</sup> a series of theoretical analyses suggested that these layers—if isolated—might exhibit extraordinary electronic characteristics (e.g., 100 times greater conductivity within a plane than between planes). About 60 years later, these predictions were not only proven correct, but the isolated layers of graphite were also found to display other favorable properties, such as high carrier mobilities ( $> 200\,000\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$  at electron densities of  $2 \times 10^{11}\text{ cm}^{-2}$ ),<sup>[6–9]</sup> exceptional Young modulus values ( $> 0.5\text{--}1\text{ TPa}$ ), and large spring constants ( $1\text{--}5\text{ Nm}^{-1}$ ).<sup>[10–12]</sup> On the basis of their structure, one might further surmise that these materials exhibit unique morphological properties, such

as high specific surface areas. Indeed, the theoretically predicted ( $> 2500\text{ m}^2\text{ g}^{-1}$ )<sup>[13]</sup> and experimentally measured surface areas ( $400\text{--}700\text{ m}^2\text{ g}^{-1}$ )<sup>[14–16]</sup> of such materials have also made them attractive for many commercial applications, including gas<sup>[17–26]</sup> and energy<sup>[16]</sup> storage, as well as micro- and optoelectronics.<sup>[27–31]</sup>

Layers of carbon atoms that have been isolated from graphite are commonly referred to as “graphene”. Although the term “graphene” is often used to refer to a variety of compositions, a precise definition of this material has been available since 1986, when Boehm et al. recommended standardizing the term: “the ending *-ene* is used for fused polycyclic aromatic hydrocarbons, even when the root of the name is of trivial origin, for example, naphthalene, anthracene, tetracene, coronene, ovalene. A single carbon layer of the graphitic structure would be the final member of infinite size of this series. The term *graphene* layer should be used for such a single carbon layer.”<sup>[32–34]</sup> Nearly 11 years later, in 1997, IUPAC formalized these recommendations by incorporating them into their Compendium of Chemical Technology, which states: “previously, descriptions such as graphite layers, carbon layers or carbon sheets have been used for the term graphene. Because graphite designates that modification of the chemical element carbon, in which planar sheets of carbon atoms, each atom bound to three neighbours in a honeycomb-like structure, are stacked in a three-dimensional regular order, it is not correct to use for a single layer a term which includes the term graphite, which would imply a three-dimensional structure. *The term graphene should be used only when the reactions, structural relations or other properties of individual layers are discussed* [emphasis added].”<sup>[35]</sup>

With this definition in mind, and in an effort to provide researchers in this field with a broader appreciation of the

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foundations of graphene science, we first examine the history of graphene and chemically modified graphenes (CMGs), some of which predate IUPAC recognition (Figure 1).

## 2. History of Graphene

A discussion of the history of graphene would be incomplete without a brief mention of graphite oxide (GO), graphene oxide (i.e., exfoliated GO), and graphite intercalation compounds (GICs), as currently graphene and a related material called “reduced graphene oxide (r-GO)” (see below) are frequently prepared by the manipulation of GO and graphene oxide, which, remarkably, have been studied extensively for more than 170 years.<sup>[36–40]</sup>

The earliest reports of GO and GICs can be traced back to the 1840s, when the German scientist Schafhaeutl reported the intercalation (that is, insertion of a small-molecule species, such as an acid or alkali metal, in between the carbon lamellae) and exfoliation of graphite with sulfuric and nitric acids.<sup>[36–38]</sup> A wide range of intercalants and exfoliants have been used since that time, including potassium (as well as other alkali metals), fluoride salts of various types, transition metals (iron, nickel, and many others),<sup>[41–44]</sup> and various organic species.<sup>[45]</sup> The stacked structure of graphite is retained in GICs, but the interlayer spacing is widened, often by several angstroms or more, which results in electronic decoupling of the individual layers. This electronic decoupling leads, in some cases, to intriguing superconductivity effects:<sup>[46]</sup> a harbinger of the extraordinary electronic properties later demonstrated in freestanding graphene. In fact, the term “graphene” grew out of the chemistry of GICs as the need for language to describe the decoupled layers became apparent.<sup>[31,32]</sup> (To the best of our knowledge, the term graphene was first coined by Boehm et al. in 1986.<sup>[32]</sup>) It was later reasoned that if the interlayer spacing of GICs could be extended throughout the entire structure, and the small-molecule spacers removed, pristine graphene may be obtained.<sup>[47]</sup>

In 1859, the British chemist Brodie used what may be recognized as modifications of the methods described by



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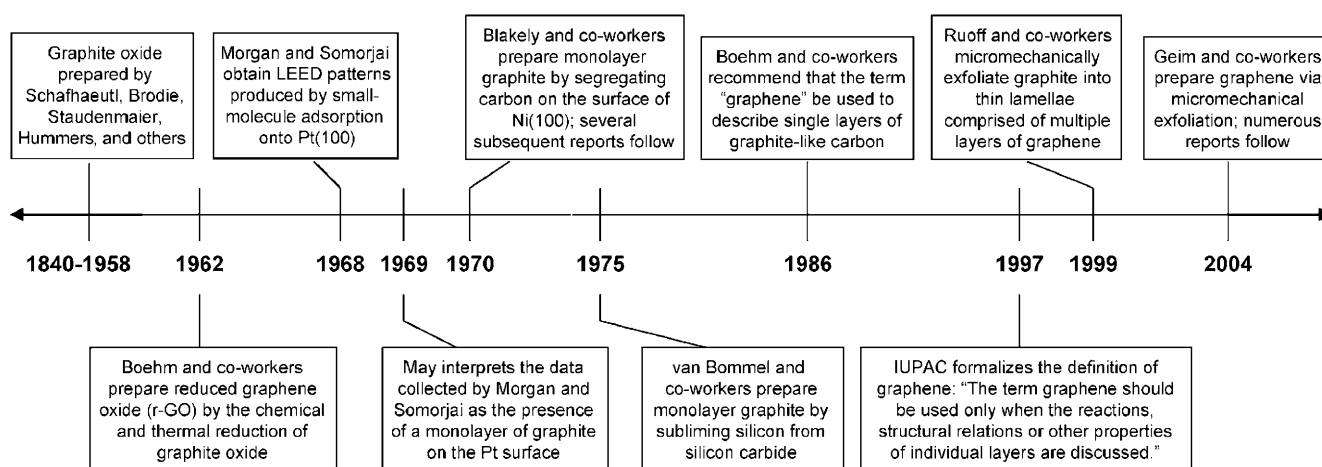


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Schafhaeutl in an effort to characterize the molecular weight of graphite by using strong acids (sulfuric and nitric), as well as oxidants, such as  $\text{KClO}_3$ .<sup>[48,49]</sup> The use of these conditions



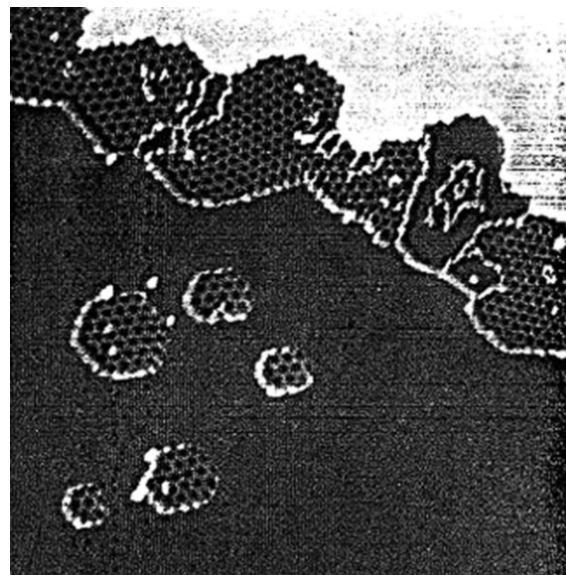
**Figure 1.** Timeline of selected events in the history of the preparation, isolation, and characterization of graphene.

resulted not only in the intercalation of the layers of graphite, but also in chemical oxidation of its surface, and ultimately in the formation of GO. Chemical modification of the surface of graphite in this manner has proven to be a valuable method for a variety of purposes, including the preparation of GICs, GO, and other similar materials; the preparation of single-layer r-GO; and the use of GO or graphene oxide as chemical oxidants in synthetic reactions.<sup>[39,50,51]</sup> Functionalization of the surface of graphite in this manner lessens the interplanar forces that cause lamellar stacking; thus, these oxidized layers can be readily exfoliated under ultrasonic, thermal, or other energetic conditions. Nearly 40 years later, Staudenmaier reported a slightly different version of the oxidation method used by Brodie for the preparation of GO by adding the chlorate salt in multiple aliquots over the course of the reaction instead of in a single portion.<sup>[52]</sup> These intercalation and oxidation experiments are the first examples of the delamination of graphite into its constituent lamellae. Moreover, as described below, many of these methods, or modifications thereof, are still used today for the preparation of r-GO and other CMGs.

Nearly a century after the studies reported by Brodie, in 1962, Boehm et al. found that the chemical reduction of dispersions of GO in dilute alkaline media with hydrazine, hydrogen sulfide, or iron(II) salts produced thin, lamellar carbon that contained only small amounts of hydrogen and oxygen.<sup>[53–55]</sup> The crucial task of determining the number of layers present in the lamellae was accomplished by densitometry against a set of standardized films of known thicknesses by using transmission electron microscopy (TEM). The carbon material was found to exhibit a minimum thickness of 4.6 Å, which deviates slightly from the thickness observed in recent studies (ca. 4.0 Å).<sup>[56–58]</sup> However, the aforementioned electron-micrograph densitometry measurements suffered from a relatively high degree of experimental error associated with variations in the thickness of the calibration standards used as well as unevenness in the photographic emulsions.<sup>[53]</sup> Regardless, Boehm concluded, “this observation confirms the assumption that the thinnest of the lamellae really consisted of single carbon layers”.<sup>[55]</sup>

In the same 1962 study, similar products were obtained by the thermal deflagration (i.e., exfoliation) of GO.<sup>[59]</sup> On the basis of the aforementioned IUPAC definition, one may conclude that Boehm et al. isolated r-GO, rather than “pristine” graphene (i.e., without heteroatomic contamination).<sup>[35,60]</sup> Nevertheless, similar methods are still widely used for the thermal reduction of GO, as is discussed in greater detail in Section 3. In a separate study, Morgan and Somorjai used low-energy electron diffraction (LEED) to investigate the adsorption of various gaseous organic molecules (e.g., CO, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>) onto a platinum (100) surface at high temperature.<sup>[61]</sup> After analyzing these LEED data, May postulated in 1969 that single, as well as multiple, layers of a material that features a graphitic structure were present as a result of these adsorption processes.<sup>[62]</sup> He also deduced that “the first monolayer of graphite minimizes its energy of placement on each of the studied faces of platinum”, which effectively met the IUPAC definition of graphene, although that definition had not yet been established. Soon thereafter,

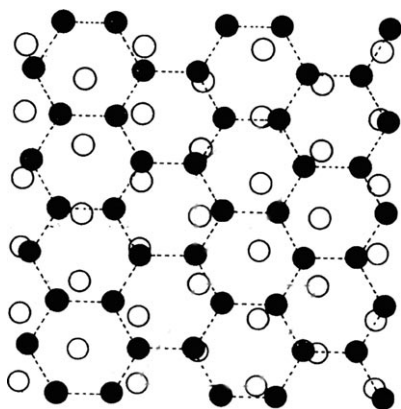
Blakely and co-workers reported an extensive series of studies on the surface segregation of mono- and multilayers of carbon from various crystalline faces of transition-metal substrates, including Ni (100) and (111), Pt (111), Pd (100), and Co (0001).<sup>[63–69]</sup> When exposed to high temperature, the carbon dissolved in these metal alloys was found to phase separate and form single or multiple layers of carbon on the metal surface, as determined by LEED and Auger electron spectroscopy, and later by scanning tunneling microscopy (STM; Figure 2).<sup>[70]</sup>



**Figure 2.** STM image (1000×1000 Å<sup>2</sup>) showing the formation of a graphitic structure on a metal surface; the image was obtained at room temperature after annealing ethylene over Pt (111) at 1230 K (adapted from reference [70]).

In 1975, van Bommel et al. described the epitaxial sublimation of silicon from single crystals of silicon carbide (0001). At elevated temperatures under ultrahigh vacuum (UHV; < 10<sup>−10</sup> Torr), monolayered flakes of carbon consistent with the structure of graphene were obtained, as determined by LEED and Auger electron spectroscopy.<sup>[71]</sup> Multilayered carbon materials were also found, with the number of layers formed dependent on the experimental conditions employed: at temperatures below 800°C, the SiC largely retained its native structure, whereas an increase in the temperature resulted in the appearance of “graphite rings” in the LEED pattern.<sup>[71]</sup> Moreover, the disappearance of the carbide peak in the Auger spectrum was reported to be coupled to the appearance of a graphite peak. The authors highlighted a graphitization mechanism proposed by Badami in which three layers of residual carbon collapse onto one another upon sublimation of the silicon to effectively form graphitic sheets (Figure 3).<sup>[72]</sup> In the studies that supported this model, Badami determined by X-ray diffraction analysis that when only one or two layers of carbon collapsed, the C–C distance was approximately 1.85 Å. However, upon the collapse of the third layer, the C–C distance decreased to 1.42 Å. This process is consistent with both the predicted and





**Figure 3.** Model of a silicon carbide structure in which three carbon layers of SiC have collapsed upon the evaporation of Si to form a single layer; ○ C atoms resulting from the collapse of three carbon layers of SiC; ● C atoms of the monocrystalline graphite top layer (adapted from reference [71]).

experimentally determined bond lengths in graphene (ca. 1.41–1.43 Å).<sup>[32]</sup> Recent results have shown that it is possible to perform the aforementioned sublimation experiments under much higher pressures than the ultrahigh-vacuum conditions used by van Bommel et al.<sup>[73,74]</sup> Under higher pressures, layers of graphene with dimensions of 3–50 μm may be obtained, as opposed to dimensions of tens of nanometers when the experiments are carried out under high vacuum.

Aside from epitaxial growth and the chemical/thermal reduction of GO, a unique, recently described method for the isolation of graphene, reduced graphene oxide, or CMGs is micromechanical exfoliation. There are several carbon sources available for this method, including natural graphite, kish graphite (precipitated from molten iron<sup>[75]</sup>), and highly ordered pyrolytic graphite (HOPG). HOPG is often chosen because of its high atomic purity and smooth surface, which enables the facile delamination of carbon layers as a result of the weak van der Waals forces that hold the layers together.<sup>[76]</sup>

In 1999, a micromechanical approach was used to obtain thin lamellae comprising multiple graphene layers, although these lamellae were not fully exfoliated into their respective monolayers.<sup>[77,78]</sup> In this method, lithographic patterning of HOPG was combined with oxygen-plasma etching to create pillars, which were converted into the thin lamellae by rubbing. Geim, Novoselov, and co-workers fulfilled the potential of this mechanical approach by showing in 2004 that when an HOPG surface was pressed against a silicon-wafer surface (i.e., silicon dioxide on silicon) and then removed, thin flakes of graphene could be located by optical microscopy and their electric-field effects characterized.<sup>[79]</sup> In addition, layers of about 0.8 nm thick were observed by AFM; such layers are consistent with the formation of carbon monolayers.<sup>[80]</sup> The carbon samples produced by micromechanical exfoliation were largely free from the significant presence of functional groups, as determined by X-ray photoelectron spectroscopy (XPS), elemental analysis, and other spectroscopic techniques. Platelets have also been

prepared micromechanically and are typically deposited onto an insulating layer, such as silicon dioxide on silicon, which enables the detailed study of the transport properties of graphene.<sup>[81]</sup> Thus, micromechanical exfoliation remains an important method for producing “pristine” graphene for electronic studies or other fundamental measurements.<sup>[60]</sup>

A persistent issue surrounding the micromechanical preparation of graphene or CMGs is its scalability. For the preparation of these materials in relatively large quantities (e.g., on a gram or higher scale), methods similar to those described by Boehm and co-workers have been particularly useful.<sup>[60]</sup> In addition, recent studies have shown that graphite can be exfoliated in liquid media into few-layer or even monolayer graphene,<sup>[82–84]</sup> and with further development, this method may be scalable. Despite these achievements, preparation of “pristine” graphene that is free of defects and has lateral dimensions larger than approximately 10–100 μm (a rough upper limit to the lateral size of graphene from graphitic sources<sup>[60]</sup>) remains challenging.<sup>[85,86]</sup>

### 3. Modern Preparation Methods: An Overview of the Last Decade

The majority of studies on graphene have not involved “pristine” graphene, but rather carbon materials produced by the reduction of GO or graphene oxide because of the proven scalability and ease of these methods. However, because of heteroatomic contamination and/or topographical defects, it is misleading to refer to such materials as graphene. As noted in Section 2, pristine graphene has been prepared by other approaches, such as vapor deposition, epitaxy/sublimation, and mechanical exfoliation. In this section, we provide a brief overview of how the methods discussed in Section 2 have evolved since their initial disclosure. We also direct interested readers to several excellent, recent reviews that cover these topics in greater detail.<sup>[15,56,87,88]</sup>

Remarkably, little has changed in the synthetic procedures used to access r-GO<sup>[87,88]</sup> since Boehm et al. first reported the reduction of dispersions of GO with a variety of chemical reductants<sup>[53,54]</sup> as well as by thermal reduction.<sup>[59]</sup> A modification to these original procedures is that a sonication period is now commonly included to exfoliate the oxidized graphite layers into isolated, single sheets dispersed in the aqueous or polar organic media in which these experiments are performed. The resulting dispersions are typically indefinitely stable in water at concentrations up to 3–4 mg mL<sup>−1</sup>,<sup>[89]</sup> primarily as a result of the strong polarity of the oxide functional groups present on the surface of the material formed. Upon reduction with hydrazine hydrate,<sup>[51]</sup> the carbon material agglomerates and precipitates from solution, although methods have been developed to stabilize the dispersion through the use of strong  $\pi$ – $\pi$  or ionic interactions.<sup>[90]</sup> The precipitated carbon materials produced by this method typically have high surface areas (ca. 470 m<sup>2</sup> g<sup>−1</sup>), high C/O ratios (ca. 12:1, versus 2:1 in GO), and high electrical conductivities (2420 ± 200 S m<sup>−1</sup>); these properties are consistent with a highly exfoliated, highly reduced material.<sup>[51]</sup> Similar transformations have also been demonstrated with

$\text{NaBH}_4$ ,<sup>[91]</sup> hydroquinone,<sup>[92]</sup> anhydrous hydrazine,<sup>[93,94]</sup> hydrogen plasma,<sup>[95]</sup> ascorbic acid,<sup>[96]</sup> various alcohols,<sup>[97]</sup> and bulk electrochemical reduction.<sup>[98–100]</sup> However, these chemical methods often introduce heteroatomic species, as shown by elemental analyses, XPS, and other spectroscopic techniques.<sup>[39,51]</sup>

Whereas the chemical or electrochemical reduction of graphene oxide probably proceeds through established reductive mechanisms,<sup>[101,102]</sup> the thermal reduction of graphite oxide is unique. Rapid heating of GO to approximately 1000 °C (heating rate  $>2000^\circ\text{Cmin}^{-1}$ ) splits the graphite oxide, or makes it burst like popcorn, to form a reduced product.<sup>[103,104]</sup> The expansion and reduction of the material is believed to be driven by the forceful (calculated to be as high as 130 mPa) release of small, gaseous molecules (principally carbon monoxide and carbon dioxide, although water may be a by-product as well).<sup>[104]</sup> A distinctive aspect of the thermal reduction process is that it avoids the potential for the introduction of heteroatomic impurities by a chemical reductant, although it does introduce topological defects/vacancies as carbon from the basal planes is released as gaseous species.<sup>[105]</sup> The measured surface areas, C/O ratios, and conductivities of the materials produced by thermal reduction are often similar to those of the materials obtained by the aforementioned chemical approaches.

Contemporary micromechanical, sublimation/epitaxial, and chemical vapor deposition (CVD) approaches to graphene synthesis are very similar to those mentioned in Section 2 on the whole, although variations on these themes have been developed. The recently demonstrated large-area growth of graphene on copper foils (from methane or other small organic molecules)<sup>[106]</sup> has also been used directly in roll-to-roll manufacturing processes,<sup>[107]</sup> and the production of graphene powders (rather than substrate-supported lamellae) by thermal or plasma-enhanced CVD (PE-CVD) could ultimately result in the production of these materials on large scale,<sup>[108]</sup> in analogy to the current large-scale production of carbon nanotubes. Additionally, routes toward liquid-phase micromechanical exfoliation through the ultrasonication of graphite are being explored as alternatives to solid-phase micromechanical approaches.<sup>[82,109]</sup> In these systems, solvent-graphene interactions lower the energy barrier to exfoliation by providing a better match of surface energies between the two components. Likewise, the exfoliation of GICs and the “unrolling” or “unzipping” of multiwalled carbon nanotubes (MWCNTs) that have not been chemically functionalized have been explored as methods for graphene and CMG production; these techniques may also be well-suited to scale-up.<sup>[47,110]</sup>

Each of the aforementioned preparation methods has its own advantages and disadvantages. For example, methods based on vapor deposition, sublimation/epitaxy, and mechanical exfoliation tend to produce monolayer carbon materials of high purity, but the scalability of these methods is only recently beginning to be demonstrated, and only under certain conditions. In contrast, the thermal or chemical reduction of graphite/graphene oxide is a time-tested and scalable method; however, the materials often exhibit significant heteroatomic impurities and/or structural defects.

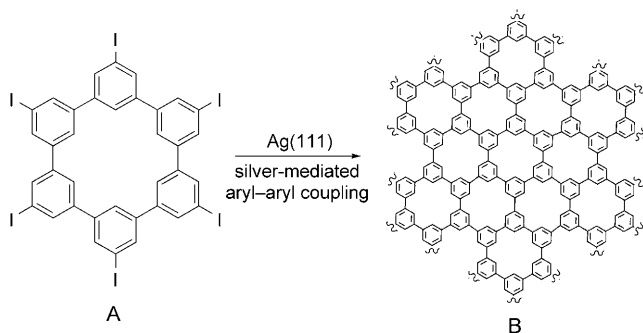
Thus, the choice of method must depend heavily on the intended use. When a way is found to combine different aspects of these methods (or develop new methods) to create a reliable, broadly applicable synthesis that results in high-purity materials on a large scale, graphene will become readily accessible, and it will be possible to realize the many proposed applications that are thus hindered by an inability to prepare material in both high quantity and high quality.

With all of the methods highlighted herein, the production of graphene of reproducible size and composition remains an outstanding challenge. Materials of inconsistent dimensions and/or atomic makeup often show variance in the measured properties (electronic, mechanical, etc.), as is widely observed for polymeric materials.<sup>[111,112]</sup> Therefore, access to atomically pristine, rather than simply macroscopically pristine, monolayers of carbon of reproducible and controllable size would be of great value. Such a goal is likely to be achieved by using more sophisticated bottom-up synthetic routes, in which control over composition, structure, and potentially function is enabled chemically, particularly through the proper selection of “monomers” or building blocks, as well as reaction conditions, as discussed below.

#### 4. Potential Preparation Methods: Imagining New Bottom-Up Routes to Graphene

An emerging realm of inquiry in this field is the rational synthesis of graphene, akin to that of  $\text{C}_{60}$ .<sup>[113–115]</sup> In a process conceptually similar to vapor deposition or epitaxial growth, a bottom-up synthetic approach may involve the use of small-molecule aromatic hydrocarbons in various coupling reactions for the synthesis of larger polycyclic aromatic hydrocarbons (PAHs), and ultimately small-area graphenes, which should function effectively as monomers in a two-dimensional polymerization.<sup>[30]</sup> These reactions are intended to be controlled processes that retain the majority of the connectivity of the units, unlike CVD/PE-CVD, in which entirely new bonding arrangements are formed. As a method for producing graphene, the  $n$ th-order product of the coupling of small, aromatic molecules is pristine graphene itself. Practically, however, the diminished solubility of large, polycyclic systems makes solution-based methodologies challenging. In this regard, solid-state synthesis may have much to offer, although it has not yet been widely applied toward the synthesis of graphene. Since 1995, defined-shape PAHs have been successfully deposited on gold substrates or at liquid–solid interfaces under STM control, which enabled the visualization of single monolayers, albeit of significantly smaller size than that of graphene prepared by other methods;<sup>[116,117]</sup> other bottom-up self-assembly techniques and gaseous vapor-deposition techniques have been used for the preparation of similar materials.<sup>[29,118–120]</sup>

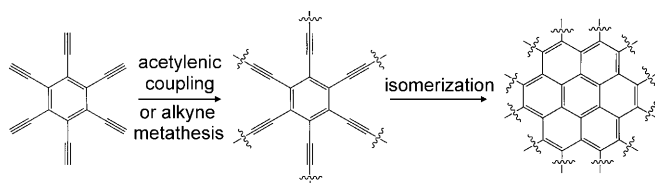
In a demonstration of the facile preparation of such large-area, two-dimensional, graphene-like materials, it was shown recently that materials referred to as “porous graphene”<sup>[121]</sup> may be formed through the coupling of multifunctional, polycyclic aryl halides onto a silver(0) surface (Scheme 1). In one possible mechanism, abstraction of the halide by  $\text{Ag}^0$



**Scheme 1.** Formation of "porous graphene". A) Hexafunctional polyphenylene core structure used as the monomer; B) structure of a fraction of the polyphenylene superhoneycomb network (adapted from reference [120]).

affords an aryl radical and silver iodide; the radical recombines with another aryl radical species to form covalent linkages between various monomers. Such constructs, with their large pores, the size of which could perhaps be controlled, are predicted to exhibit remarkably selective separation properties for gases or other small molecules.<sup>[122]</sup> An alternate approach to "porous graphenes" may be found in the synthesis of theoretically predicted graphyne, whose  $sp^2$ -hybridized carbon atoms are interspersed with regions of linearly connected,  $sp$ -hybridized carbon atoms.<sup>[123–125]</sup>

Acetylenic coupling<sup>[126]</sup> or alkyne metathesis<sup>[127,128]</sup> paired with isomerization may be a feasible de novo synthesis of pristine graphene (Scheme 2), although many other routes to



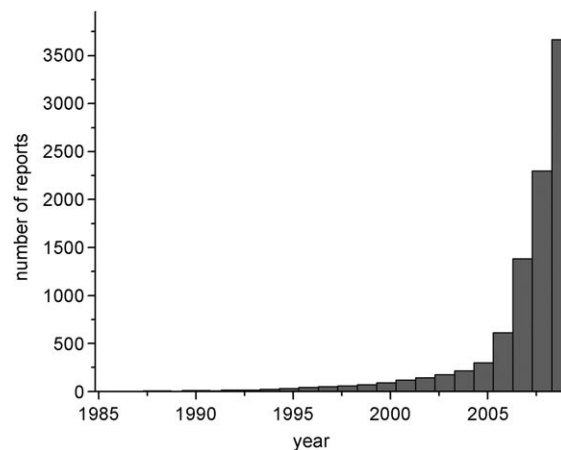
**Scheme 2.** A possible de novo synthetic route to graphene: acetylenic coupling or alkyne metathesis, followed by isomerization, to give an extensive aromatic network.

complex carbon networks have been proposed or demonstrated experimentally over the years.<sup>[115,129,130]</sup> Metal-mediated aryl coupling reactions have been used similarly in the preparation of graphene nanoribbons (semiconducting materials useful for their bandgap properties<sup>[131]</sup>) up to 12 nm in length from PAH precursors.<sup>[132]</sup>

Throughout their development, the synthesis of the aforementioned types of carbon networks has been guided by a set of criteria outlined by Diederich and Rubin: "1) The network structures should neither be highly strained nor easily interconverted into graphite or diamond, 2) the new compounds should have the potential to exhibit interesting material properties such as electrical conductivity, and 3) promising synthetic routes should be available."<sup>[115]</sup> A de novo synthesis of graphene is likely to abide by these criteria as well, and much potential remains in this vein.

## 5. Summary and Outlook

Although graphene has enjoyed widespread attention in the last several years (see Figure 4), its roots go back decades earlier to research beginning in the 1960s that demonstrated that it was possible to chemically and/or thermally reduce



**Figure 4.** Number of reports containing the search term "graphene" by year (determined by searching for "graphene" in the SciFinder Scholar database).

graphite oxide; these reactions probably involved intercalation/exfoliation processes that date back to the 1840s. As materials resulting from the reduction of graphene oxide were found to retain a portion of their oxygen impurities, they have more recently been termed "reduced graphene oxide", rather than pristine graphene. These efforts were followed shortly thereafter by CVD methods, as well as sublimation/epitaxial techniques, which demonstrated the ability to form pure, heteroatom-free graphene monolayers. Most recently, it has been demonstrated that it is possible to directly exfoliate layers of graphite mechanically, and to promote the large-area growth of monolayer graphene under non-UHV conditions. All of these methods continue to be optimized, and graphene or graphene-like materials are still formed by similar techniques or variations thereof. Likewise, one can envision a variety of more sophisticated routes to graphene. A bottom-up, rational design of this carbon macromolecule will be of considerable value, as will methods that enable precise control of its structural, electronic, mechanical, and thermal properties.

In light of the extraordinary range of carbon materials that have been prepared over the years, and the similarly expansive array of terms that have been used to describe those materials, we believe it worthwhile to summarize the terms that have been discussed herein, and either reiterate accepted definitions (in quotations) or propose definitions based on IUPAC terminology in its proper context as well as common usage in the literature. Although the list given is not comprehensive or authoritative, we hope that it will provide guidelines and foster discussion within the community on how best to use these terms:

Graphite: “An allotropic form of the element carbon consisting of layers of hexagonally arranged carbon atoms in a planar condensed ring system [of] graphene layers. The layers are stacked parallel to each other in a three-dimensional crystalline long-range order. There are two allotropic forms with different stacking arrangements, hexagonal and rhombohedral. The chemical bonds within the layers are covalent with  $sp^2$  hybridization and with a C–C distance of 141.7 pm. The weak bonds between the layers are metallic with a strength comparable to van der Waals bonding only.”<sup>[35]</sup>

Graphite oxide: A berthollide layered material prepared by treating graphite with strong oxidants, whereby the graphite surface and edges undergo covalent chemical oxidation. The degree of oxidation may vary, though strongly oxidized graphite oxide typically exhibits a C/O ratio of approximately 2:1.<sup>[48–50, 52, 133, 134]</sup>

Graphene: “A single carbon layer of the graphite structure”, the nature of which can be described “by analogy to a polycyclic aromatic hydrocarbon of quasi infinite size.”<sup>[35]</sup>

Graphene oxide: A single layer of graphite oxide, often obtained by exfoliating graphite oxide.<sup>[39, 135–138]</sup>

Reduced graphene oxide: A material (often of monolayer form) obtained by the chemical or thermal reduction of graphite oxide or graphene oxide. Reduced graphene oxide can be distinguished from graphene by the presence of heteroatomic contamination and/or topographical defects.<sup>[17, 40, 51, 91, 95–98, 100, 139, 140]</sup>

Chemically modified graphene: A material that bears functional groups covalently bound to the surface of the individual layers of graphitic carbon. Graphite oxide, graphene oxide, and reduced graphene oxide may all be considered chemically modified graphenes.<sup>[102, 104, 141–146]</sup>

Intercalation compounds (note that this IUPAC definition is not specific to graphite): “Compounds resulting from reversible inclusion, without covalent bonding, of one kind of molecule in a solid matrix of another compound, which has a laminar structure. The host compound, a solid, may be macromolecular, crystalline or amorphous.”<sup>[35]</sup>

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