



Graphene synthesis



Keith E. Whitener Jr.^{a,*}, Paul E. Sheehan^b

^a NRC Postdoctoral Research Associate, Washington, DC 20375, USA

^b Chemistry Division, U. S. Naval Research Laboratory, Washington, DC 20375, USA

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ABSTRACT

The promise of graphene, a two-dimensional hexagonal form of elemental carbon, as a revolutionary material has sparked a flurry of research into its optical, electronic, thermal, and mechanical properties. The most famous method of isolating graphene sheets, introduced by Novoselov et al. in 2004 [1], uses adhesive tape to mechanically cleave graphite crystals into successively thinner platelets. This micromechanical cleavage is time-consuming and produces an abundance of few- and multilayer graphene along with single-layer material. In addition, the area of the graphene sheet obtained by this method is limited by the initial size of the graphite crystal. These limitations of micromechanical cleavage, along with the explosion of interest in graphene in general, have led researchers to devise a number of alternative methods for graphene synthesis. In this review, we discuss different synthetic methods for obtaining graphene along with their advantages and disadvantages and then introduce current avenues of research in this rapidly expanding field.

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1. Introduction

The current popularity of graphene in scientific research can be traced to the 2004 paper by the group of Nobel Laureates Andre Geim

* Corresponding author.

E-mail address: keith.whitener.ctr@nrl.navy.mil (K.E. Whitener).

and Konstantin Novoselov [1]. But the history of single-sheet graphene as an experimentally attainable material stretches back at least to 1962 [2], and the scientific study of multilayer ultrathin carbon is even older, with the first instance of graphene oxide as an applied material showing up in the literature as early as 1919 [3]. Even before that, the Braggs had used X-ray powder diffraction to measure the spacing between the cleavage planes of graphite, and Bernal resolved the full hexagonal layered structure of graphite in 1924 [4].

Graphene represents one member of an increasingly populated class of carbon allotropes. The recent interest in graphene was motivated in part by developments surrounding carbon nanotubes as rolled up sheets of graphene. The low dimensionality of these structures lent them new properties, and part of the excitement surrounding the work by Geim and Novoselov was the promise of experimental confirmation of intriguing effects that had been predicted theoretically. Graphene was first tackled theoretically in 1947 by Wallace, who used a tight binding model to describe conductivity in terms of electrons hopping from one lattice site to the next [5]. Wallace showed that the energy-momentum dispersion at the K point of the first Brillouin zone was approximately linear instead of the typical parabolic shape. However, it was not until 1984 that DiVincenzo and Mele realized that there was a connection between the linearity of the dispersion relation and quantum field theory [6]. They showed that Wallace's hopping conduction electrons could be recast as massless spin-1/2 particles in a Dirac-Weyl formalism, an equation typically used to model neutrinos. This meant that electrons behave as if they have an extra degree of freedom, known as pseudospin, based on where they are in the unit cell of the graphene. A further development occurred at the hands of Semenoff, who predicted anomalous behavior of graphene with respect to the quantum Hall effect [7]. It was the observation of this effect, reported by the group of Novoselov and Geim as well as the Kim group at Columbia that truly kicked off the race for graphene [8,9].

Beyond its electronic properties, graphene has many superlative physical properties and so has been employed in polymer composites [10], in corrosion inhibitors [11], in chemical and biological sensors [12], and in photovoltaic cells as a transparent conductor [13]. Its thermal conductivity exceeds that of diamond [14], and the strong sp^2 linkages that bind each sheet together confer upon graphene the highest known elastic modulus (~ 1.0 TPa) which it shares with carbon nanotubes [15,16]. The market for graphene enhanced devices has been poised to take off but, until now, has been stymied by the cost of graphene synthesis, which remains uneconomical for commercial applications. This situation is improving rapidly as more effective synthetic methods are being researched that promise to fuel the availability of graphene not only as a research material, but also as a product in everyday devices.

This review focuses on current research areas in graphene synthesis. The subject matter splits into two broad areas: graphene derived from graphite, and graphene derived from other sources such as epitaxial and CVD growth methods. Several aspects of each of those two areas will be addressed with emphasis on current research foci, merits, and drawbacks of the given method.

2. Graphene produced from graphite

As graphene is a subunit of graphite, it makes sense that the earliest and simplest approach to its synthesis would be direct extraction from bulk graphite. At the start, it should be noted that not all graphite is created equal. There are two important varieties of graphite: natural and synthetic. The highest quality natural graphite possesses single crystalline domains with in-plane dimensions exceeding 1 mm and, consequently, single-layer graphene sheets obtained from natural sources are of exceptional crystal quality [17]. In particular, the absence of in-plane grain boundaries in this graphene enhances performance in electronic devices. The difficulty is that while the crystal dimensions are roughly 1 mm in-plane, they are typically much less than 1 mm out-of-

plane; materials this thin can be difficult to work with. Thus, much of the work done on graphene has proceeded from large-area synthetic graphite, namely highly ordered pyrolytic graphite (HOPG) and Kish graphite.

HOPG is made from the thermal decomposition of hydrocarbons under pressure. This process yields graphite crystals which are much thicker than natural graphite. The larger dimensions make the material much easier to handle and exfoliate; however, the in-plane crystal domains tend to be much smaller than in natural graphite, on the order of 1 μm . Kish graphite is produced by the fractional crystallization of carbon from molten steel, and its crystallinity properties are intermediate between HOPG and natural graphite [17]. The in-plane grain boundaries in these two graphenes impair electronic and phononic transports. Therefore, devices built from this material are typically easier to fabricate, with the tradeoff being that they are usually of lower quality than devices made from natural graphite. This observation, that defects in the crystal domain directly degrade the superlative properties that theoreticians predict for graphene, is a major engineering challenge in the synthesis of graphene and graphene devices [18]. It is of importance not only in graphene produced from graphite, but also in graphene of non-graphitic origins. Much of the current research in graphene synthesis focuses on obtaining large-area single crystal graphene, or at least increasing crystal domain sizes and reducing the preponderance of grain boundaries, with the aim of producing graphene with material properties approaching the predictions of the theoreticians. Indeed, recent results show that CVD graphene growth has now surpassed natural graphite crystallinity with ~ 1 cm wide crystals [19].

2.1. Mechanical cleavage and exfoliation

2.1.1. Micromechanical cleavage, a.k.a., the scotch tape method

Once a high quality sample of graphite is obtained, one needs to extract graphene from it. In 2004, Novoselov et al. published a paper detailing electronic measurements made on single- and few-layer graphene [1]. They obtained this graphene by repeated use of a technique known as micromechanical cleavage or, more colloquially, the scotch tape method. Cleavage of graphite and other atomically flat crystals using adhesive tape was not unprecedented; researchers in the scanning probe community have been using the method to obtain suitable surfaces for atomic force microscopy and scanning tunneling microscopy for many years. The novel aspect of the technique developed by Novoselov et al. was in realizing that the thin flakes obtained by micromechanical cleavage could be further cleaved into successively thinner samples, all the way down to few-layer and even single-layer graphene. With this breakthrough, Novoselov et al. could perform experiments demonstrating the unique electronic structure of single-layer graphene, namely the observation of the anomalous quantum Hall effect, confirming the Dirac-fermionic behavior of the charge carriers in graphene.

The micromechanical method itself is straightforward and can be performed without specialized equipment. A piece of adhesive tape is placed onto and then peeled off the surface of a sample of graphite. The flakes of graphite that adhere to the tape are cleaved preferentially along the plane of the crystal, leaving the exposed atomically flat surfaces [17]. To obtain few- and single-layer graphene, clean tape is pressed against the graphite flakes adhering to the first piece of tape. Peeling apart these two pieces of tape further cleaves the graphite into even thinner flakes. This process is repeated as many times as desired, with each iteration producing thinner sheets of graphite. The graphite flakes are then pressed against a substrate such as SiO_2 on silicon, where further processing or device-building with the graphene sheets can be performed (Fig. 1). The time consuming step of micromechanical cleavage is identifying single or few-layer sheets. This is typically achieved using optical microscopy, exfoliation onto a 300 nm thick SiO_2 film to enhance the optical contrast [1], and considerable patience.

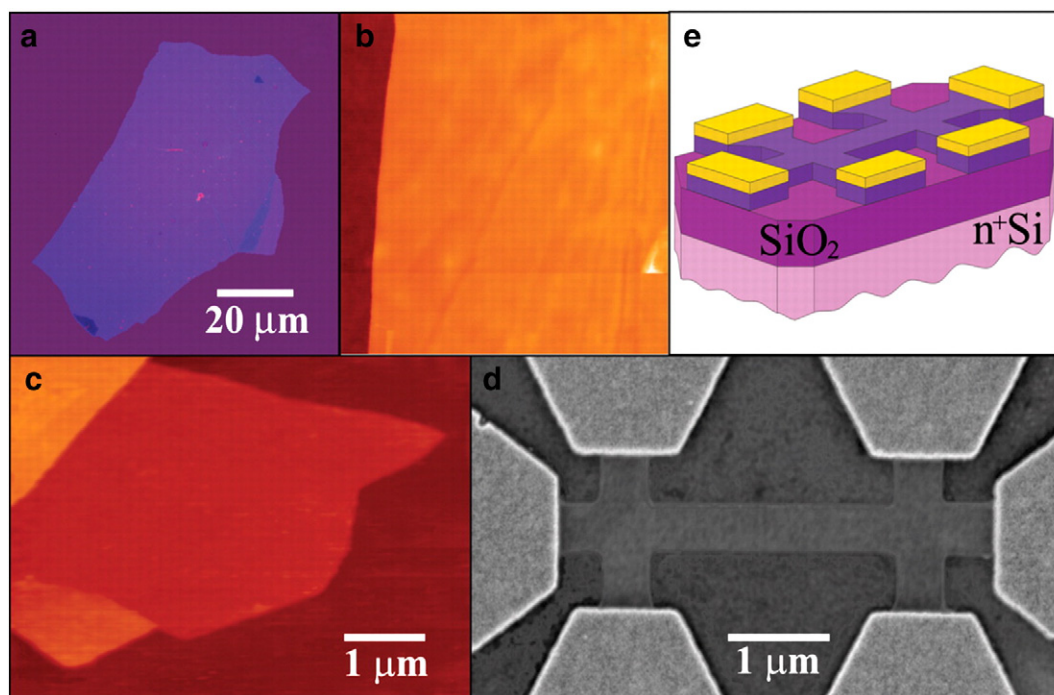


Fig. 1. a) Optical microscope image of multilayer graphene cleaved from bulk graphite using the “scotch tape method.” b) AFM image of an edge of the flake. c) AFM image of few-layer graphene. d) SEM of a device used by Geim and Novoselov for their studies of the electric field effect in graphene. e) Schematic of device in d. From Ref [1]. Reprinted with permission from AAAS.

Graphene is not the only substance that can be obtained via micromechanical cleavage. In fact, the method is generally useful for isolating sheets of two-dimensional layered materials where alternative methods of production are infeasible or have not yet been developed. Novoselov et al. showed that micromechanical cleavage can isolate few- and single-layer crystallites of hexagonal boron nitride, transition metal dichalcogenides, and the high-temperature superconductor $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ [20], and other groups have begun building various structures and devices from boron nitride, molybdenum disulfide, and bismuth telluride obtained in this fashion [21–23].

After the publication of the first graphene papers, many other groups began to use micromechanical cleavage to isolate graphene and to build devices out of it. As interest in—and demand for—graphene grew, and as the new material's potential as a game-changer in electronics became apparent, researchers realized that this simple production method was not sufficiently scalable to meet future demand. As a result, other methods of graphene production were sought out as described below. However, micromechanical cleavage remains a popular method for graphene production for demonstration and educational purposes, as well as for obtaining high quality samples whose surfaces are exceptionally clean.

2.1.2. Liquid-phase mechanical exfoliation

Most forms of elemental carbon—with the notable exception of the fullerenes—are completely insoluble under ordinary laboratory conditions. This observation has been a major stumbling block for researchers studying carbon nanotubes, as the tubes tend to bundle together and aggregate and do not solvate in any commonly available solvents. Various approaches have been used to circumvent this problem and isolate individual carbon nanotubes for use in electronic devices and other experiments without chemically altering the surface of the nanotube and thereby changing its electronic properties. These approaches generally pursue one of two strategies. In the first strategy, nanotubes are mixed with water and a surfactant and sonicated; the hydrophobic group of the surfactant interacts with the hydrophobic nanotube, while the

hydrophilic group of the surfactant stabilizes the individual nanotubes in solution. In the second strategy, the nanotubes are sonicated directly in a solvent which has a surface energy that closely matches that of the carbonaceous material. This decreases the energetic penalty to separate individual nanotubes from their bundles and enables a fraction of weakly solvated nanotubes to persist in solution.

Both of these liquid-phase approaches have been adopted by graphene researchers to exfoliate individual sheets of graphene from bulk graphite. In one study, scientists sonicated graphite powder in N-methylpyrrolidone and centrifuged the resultant dispersion to remove large unexfoliated graphite pieces. They produced suspensions of few-layer graphene with concentrations of up to 1 wt.% that showed remarkable stability toward aggregation over a period of weeks to months [24]. Surfactant-assisted graphene exfoliation is another well-established technique, with many surfactants being employed [25,26].

A somewhat less common method of graphene exfoliation is the intercalation of supercritical carbon dioxide (scCO_2) into the interstitial spaces in the graphite lattice, followed by rapid depressurization. The carbon dioxide intercalates quite easily between the layers of graphene at a pressure of roughly 100 atm. When the vessel is depressurized, the carbon dioxide becomes gaseous and exerts a large mechanical force on the layers, so that they explode apart and separate into few-layer graphene [27]. Using interstitial gases to blow apart layers of graphene had previously been explored in the context of graphene oxide. We will discuss the advantages and disadvantages of the graphite oxide route to graphene in the next section, but it suffices to mention now that intercalated supercritical carbon dioxide provides several distinct advantages. Namely, the graphite used as the initial material does not need to be chemically functionalized to be exfoliated. The supercritical CO_2 process involves one step, as opposed to chemical functionalization, which requires prior oxidation of the graphene, followed by exfoliation, which must further be followed by a reduction step if the graphene is to be used for any sort of electronics application. This method eliminates the chemical steps, and moreover, it avoids the major complication of a quasi-irreversible chemical functionalization step.

2.1.3. Advantages and disadvantages

The elegant simplicity of micromechanical cleavage has captured the public's imagination: in spite of the construction of massive multibillion dollar research facilities and the passing of global science policy initiatives, an experiment involving little more than adhesive tape and pencil lead can produce Nobel Prize-winning science [28]. However, it has been evident almost from the outset that the scotch tape method is far too inefficient to be useful in mass-producing graphene for practical applications. For this reason, solvent-aided and surfactant-aided sonication methods have been explored as ways to efficiently generate ultrathin carbon films with an eye toward device fabrication. But even using liquid-phase exfoliation, the highest concentration of few-layer graphene that one can reasonably achieve is less than 0.1 mg/mL of solvent.

The main advantage of mechanical exfoliation, be it solvent-mediated or adhesive-tape-mediated, is that large-area single-crystalline domains can be isolated with the technique. Using HOPG, single two-dimensional crystals of graphene with lengths on the order of micrometers can be isolated, and in-plane polycrystalline samples can be on the order of centimeters. With natural graphite, the single crystal domain can extend to millimeters. The purity of these crystals enables electronics with extremely high performance to be constructed. However, the spatial extent of the graphene sheet is limited to the crystal dimensions of the graphite starting material, i.e., a few centimeters of continuous polycrystalline graphene using HOPG as a starting material. Thus, synthesizing truly large-area graphene samples using mechanical exfoliation is out of the question. To compound the problem, the exfoliated sheets are often multilayer, and multilayer graphite with more than about 10 layers has roughly the same properties as bulk graphite, which is a fundamentally different physical system from graphene. Therefore, obtaining true control over graphene's properties requires a method of synthesis where the number of graphene layers can be anticipated with a high degree of reproducibility.

2.2. Chemical cleavage and exfoliation

2.2.1. Graphite oxide

In 1859, in an attempt to measure the atomic weight of carbon, Benjamin Brodie performed some of the first experiments on the chemical reactivity of graphite [29]. He noticed that graphite could be extensively oxidized by repeatedly exposing it to a mixture of nitric acid and potassium chlorate for several days. At the end of his experiments, he obtained "...a substance of a light yellow colour, consisting of minute transparent and brilliant plates." He went on to evaluate many properties of what he called "graphic acid," which we today call graphite oxide. Nearly a century later, Hummers and Offeman pioneered a significantly safer synthesis of graphite oxide using a mixture of graphite with sodium nitrate, sulfuric acid, and potassium permanganate [30]. The Hummers method is still the favored method for the production of graphite oxide in the lab.

Graphite oxide resembles graphite in that it has a lamellar structure and is mostly carbonaceous. However, the similarities end there. Oxidation riddles the graphite basal plane with different oxygen-bearing functional groups such as hydroxides and epoxides, while rimming the layers with carboxyl, carbonyl, and phenol functionalities. The material itself loses its gray-black metallic sheen as well as its conductivity and becomes a reddish orange insulator that is highly dispersible in water. The material is generally amorphous and inhomogeneous, and the various methods of preparation lead to graphite oxides that differ somewhat in their properties [31].

The two-step process to obtain graphene from graphite oxide requires first exfoliating the bulk material and then reducing the individual sheets back to graphene. Exfoliation is usually achieved by sonicating graphite oxide in water, followed by centrifugation. The supernatant from this procedure is colloidal and contains few- and single-layer sheets of graphene oxide. This liquid can be left as is or

drop-cast onto a substrate for further processing (Fig. 2). Another, older exfoliation procedure consists of heating the graphite oxide rapidly to several hundred degrees in an inert atmosphere. This causes explosive thermal reduction of the material, producing large amounts of CO₂ and H₂O in the interstitial spaces between the graphite layers [32]. Analogous to the depressurization of scCO₂-intercalated graphite mentioned above, the rapid expansion of the gases produced by this chemical reaction rends asunder the graphene sheets and produces few-layer weakly reduced graphene oxide. A more complete reduction of the material is achieved either by slow thermal annealing or by chemical means. Thermal annealing typically takes place in a reducing atmosphere, but can also be locally induced in air by scanning a heated AFM tip across the surface of the graphene oxide [33]. Chemical reduction proceeds using any number of reagents—from sodium borohydride to ascorbic acid to baker's yeast—with hydrazine hydrate being the most common reagent in use nowadays [31,34]. Both chemical and thermal reductions of GO give exfoliated material with a high BET surface area (466 m² g^{−1} for chemical reduction, 600–900 m² g^{−1} for thermal reduction; cf. 2620 m² g^{−1} theoretical limit for graphene) [31], which may prove useful in sensing applications as well as separations and gas storage.

Graphite oxide is an old compound and has been studied intensely for well over a century. It is surprising to see just how close many earlier works in the literature were to isolating graphene outright 50 or 100 years ago. The pioneers in this field were no doubt Ulrich Hoffman and Hans Boehm who, in 1962, obtained electron microscopy images of few-layer (and possibly even single-layer) reduced graphene oxide that bear a striking resemblance to images obtained with modern instruments [2]. In general, the long history of research on graphite oxide favors this material for further advancement and rapid commercialization.

Production from graphite oxide would seem an ideal route to graphene. The merits and drawbacks will be discussed in detail below, but it is important to mention one serious drawback before we proceed. Specifically, many defects are introduced into graphene during oxidation, and the subsequent reduction cannot remove them all, especially edge ethers [24]. The end material of this process differs sufficiently from pristine graphene that there is some confusion in the literature about how to name it. While many scientists still call these highly *sp*² carbon rich films "graphene", others find the term inaccurate and instead call it "reduced graphene oxide" (rGO) or "chemically converted graphene". We will use rGO in this review. Regardless of how it is named, rGO finds use in many applications where high carrier mobility is not critical.

2.2.2. Graphite intercalation compounds

Graphite intercalation compounds may predate even graphite oxide. Dresselhaus and Dresselhaus [17] cite an 1841 paper by Schaffäutl as the first to isolate a graphite intercalation compound. The variety of species that can be introduced into the interplanar regions of graphite is huge, and significant engineering of the material properties may be obtained by doing so [35]. For the purpose of producing graphene, however, the most important species are the alkali metals. Lithium, potassium, and cesium all readily intercalate into the graphene crystal lattice. The resulting charge transfer complex, formed when the metal donates an electron into the graphite lattice, yields negatively charged graphene sheets that are powerful reducing agents. Exfoliation proceeds spontaneously in this system and is expedited by two effects. First, the intercalated alkali ions increase the distance between the graphene sheets, thereby decreasing the van der Waals forces that hold the graphite crystal together. Second, the negatively charged sheets tend to repel one another, making it easier to exfoliate and separate them [36,37]. The material can be quenched with proton donors to form hydrogenated graphene, or other donors to form otherwise functionalized graphene. In the case of hydrogenated graphene, simple thermal annealing is enough to restore the graphene back to a quasi-pristine state [38].

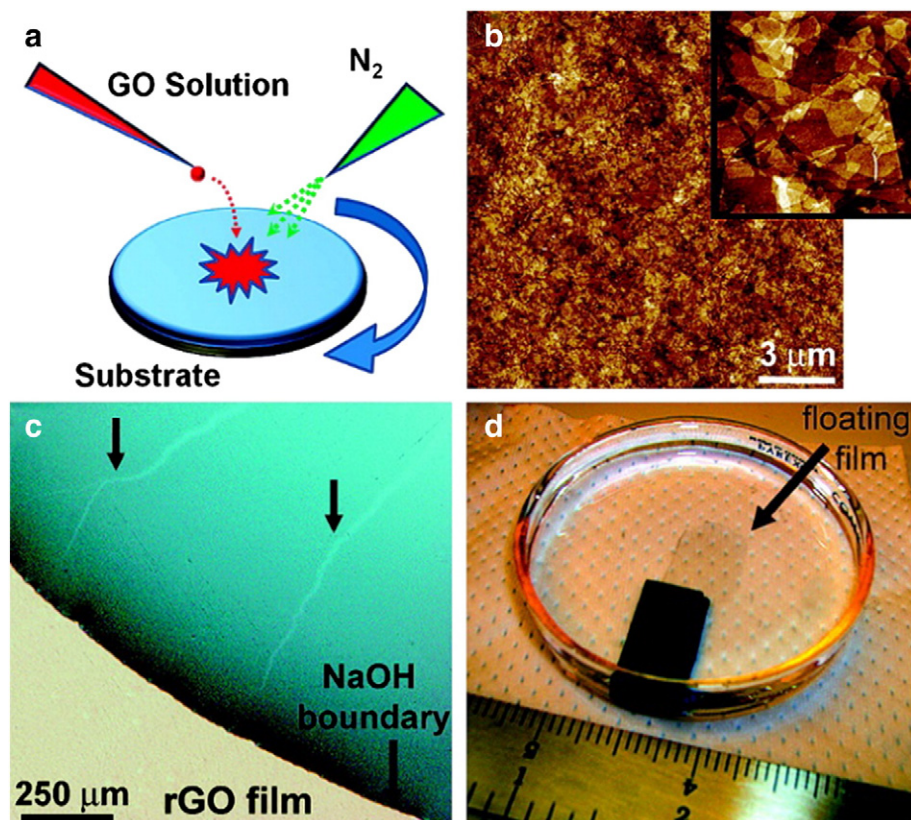


Fig. 2. (a) Spin-coating technique employed in the deposition of graphene oxide on a surface. (b) AFM image of thin film spin-coated graphene oxide. (c) Optical microscope image of the delamination of rGO film from its substrate. (d) Floating rGO film ready for transfer onto an arbitrary substrate.

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2.2.3. Graphite fluoride

Graphite can be fluorinated directly with fluorine gas at elevated temperatures. This material is used as a solid lubricant and as a highly efficient cathode in lithium batteries [39]. The introduction of covalently bound fluoride into the crystal lattice of graphite causes the interlayer spacing to increase from 0.335 nm to between 0.8 and 0.9 nm [40]. Bourlinos et al. have performed studies on the exfoliation and reduction of fluorinated graphite similar to those on graphite oxide [41]. The protocol for producing graphene-like sheets is a hybrid of liquid-phase graphene exfoliation and graphene oxide processing. Graphite fluoride is exfoliated in N-Methylpyrrolidone, and the resulting colloid is spin-coated onto a substrate and reduced using either a silane or a zinc-acid combination. The material obtained from reduction, like reduced graphite oxide, does not behave in the exact same way as pristine graphene that has never seen exposure to functionalization. However, as the starting material graphite fluoride has different properties from graphite oxide, so too does so-called “reduced graphene fluoride” differ from reduced graphene oxide. This material might therefore be useful someday as a complement to graphene oxide in similar applications [42].

2.2.4. Advantages and disadvantages

The oxidation of graphite is currently the most cost effective way to exfoliate bulk graphite to few- and single-layer species. Not only is the graphite itself inexpensive, but all of the reagents (sulfuric acid, permanganate, and nitrate salts) are available on an industrial scale. Furthermore, the oxidation and reduction can each be accomplished as one-pot reactions, simplifying manufacturing protocols. One distinct stumbling-block in scaling up the preparation of thin carbon films

from graphite oxide is exfoliation. Exfoliation via ultrasonication is unlikely to be cost-effective at an industrial scale, and so thermal exfoliation might be a more promising route to commercialization.

As mentioned above, the most significant disadvantage of using graphite oxide to make graphene for electronics applications is that the reduced material contains enough defects to degrade graphene's superlative electronic mobility. Given the amount of work already done on the restoration of graphene from graphene oxide, and the relative lack of progress therein, it might well be the case that another, perhaps more costly route to graphene is warranted when the material is intended for an electronic device that relies on the properties observed in pristine graphene. However, reduced graphene oxide remains a highly promising material for applications in materials composites where its mechanical strength and thermal properties can be leveraged to produce high performance materials. Indeed, in some mechanical applications such as resonators, rGO's stronger adhesion to a support and ability to be crosslinked enable it to outperform graphene resonators [43]. Another area of research where graphene oxide might outperform is that of water purification. The interstices of graphene oxide transport water preferentially over dissolved species, and filters made from graphene oxide are promising candidates for water desalinization and purification [44,45].

Preparation of graphene from graphite intercalation compounds is somewhat less damaging to the electronic structure of the graphene, but this material suffers from the one drawback that all graphite-derived materials suffer from: limited spatial extent of the crystal. The length scale of the pristine 2D crystal is always limited by the size of the starting crystal. Thus, in order to obtain large-area graphene for use in, e.g., flexible electronic displays, we must turn to methods where we are not limited by the intrinsic size of a graphite single crystal.

3. Graphene produced from non-graphitic sources

3.1. Epitaxial growth from silicon carbide

In 1893, Edward Goodrich Acheson patented a method for producing silicon carbide, or carborundum, by heating coke or other carbonaceous sources and silica or aluminum silicate to $\sim 2000^\circ\text{C}$ [46]. Building upon this work, Acheson discovered that when silicon carbide was heated even hotter to $>4000^\circ\text{C}$, the silicon preferentially sublimed, leaving behind pure crystalline graphite [47]. In the course of this process, the silicon sublimates from the outside in, producing a silicon carbide core with a graphite shell as an intermediate.

The discoveries in the late 1990s of new low-dimensional carbon species such as fullerenes and carbon nanotubes prompted a revisiting of the Acheson process as a potential method for producing quasi-2-dimensional carbon films. High quality single-crystal silicon carbide was commercially available, thanks to its utility as a semiconductor growth substrate, and several research groups began examining the surfaces of these crystals. Using techniques such as scanning tunneling microscopy (STM), low energy electron diffraction (LEED), and electron energy loss spectroscopy (EELS), the researchers saw graphite-like features appear when the SiC crystals were heated to only 1000°C , which they attributed to the formation of monolayer and few-layer graphene [48,49]. Forbeaux et al. showed that, under certain conditions, the ultra-thin graphite overlayer on SiC was essentially decoupled from the surface of the crystal, creating the possibility that a single layer of graphene could be electronically isolated [50,51].

This line of research was picked up by Berger et al. who published a paper pointing out the 2D electron gas properties of epitaxial graphene on SiC. Their paper included field effect and magnetoconductance measurements, and suggested several avenues forward, including studying the quantum Hall effect on graphene [52]. Unfortunately for this group, the *Science* paper by Novoselov et al. was published just six weeks prior. This would lead to no small degree of controversy when the Nobel Prize in Physics was awarded in 2010. The lead researcher on the Berger paper, Walter de Heer, wrote a letter to the Nobel Committee criticizing them for overstating the accomplishments of Geim and Novoselov and for overlooking the fundamental contributions to graphene science from other researchers. Other scientists also weighed in on the issue, and even Geim agreed that the Nobel Committee's document seemed to have been written in haste [53].

Controversies aside, the growth of graphene from silicon carbide is quite important technologically since it produces very high quality graphene. The films are continuous even over step edges and can be single crystal over distances of tens of microns or more. The principal limiting factor for crystal size is the morphology of the SiC surface. The surface of the SiC crystal is terraced due to an imperfect cleavage plane, and the terrace size determines the size of the single crystal graphene [54]. Significant effort to produce SiC with larger terraces is underway with the hope of improving the quality of graphene grown from this method. Other avenues of research in this area involve searching the parameter space of pressure and temperature for cleaner growth of single-layer graphene.

3.1.1. Advantages and disadvantages

As mentioned before, epitaxial graphene on silicon carbide is typically of very high quality and is suitable for the most demanding electronics applications. When properly passivated, the SiC substrate does not interact with the graphene layer, and it has a wide enough bandgap that it can be considered an insulator at room temperature. This feature makes it possible to create gated electronics directly on SiC-graphene. With advances in the synthetic parameters of this method, and as the surface quality of SiC crystals improves, this evaporative technique will progress and may eventually become the graphene synthesis method *par excellence*. The main drawback to the technique is that it requires highly specialized equipment and personnel as well as the daunting cost

of the single crystal SiC growth substrate. Therefore, this synthetic route tends to result in rather expensive material. However, if the technique can be refined and standardized, companies might find it profitable to produce graphene in this manner.

3.2. Chemical vapor deposition

The chemical vapor deposition (CVD) method is an excellent example of convergent evolution in research, where work on two seemingly unrelated problems led to a similar outcome. The first research problem was that of soot formation. Scientists in the 1950s were examining thin sooty films formed on porcelain and graphite, when a group led by Walker decided to survey soot formation on many different materials. They discovered that metal surfaces—in particular, nickel surfaces—form carbon films with single crystal sizes much larger than those on ceramics [55]. While this method saw some subsequent development, interest did not increase significantly until the late 1970s, in the course of experiments to determine the mechanism of high-temperature alkylation on catalytic surfaces. When hydrocarbons are exposed to a heated metal surface under vacuum, the metal catalyzes the loss of hydrogen and dissolves the remaining carbon, forming a layer of metal carbide. As the temperature drops, the metal carbide surface layers saturate and graphitic carbon precipitates from the carbide sol [56]. In the 1980s, scientists examined the thin carbon overlayer more rigorously, and likely made some of the first observations of graphene's electronic structure and phonon dispersion curves. Researchers in this area were aware that they were making single-layer graphene, a material that they called “monolayer graphite,” as is evidenced by the fact that this term appears extensively in the literature of thin graphitic films on metal surfaces during the 1980s and 1990s [57].

After the graphene frenzy began in 2004–2005, many researchers worked to refine the CVD method. A seminal breakthrough came in 2009 when CVD conditions were discovered where graphene growth on copper was self-limited to a single layer, such that very large sheets (side length $\approx 75\text{ cm}$) of single-layer graphene could be grown (Fig. 3) [58,59]. Single crystal grain size has increased steadily; as of January 2014, the largest reported single crystal of graphene is roughly 1 cm in diameter (Fig. 4) [19]. Other groups have focused on low-temperature graphene deposition on arbitrary substrates. In this direction, Kwak et al. have deposited single crystals of graphene on the micrometer scale onto arbitrary substrates by allowing carbon to diffuse through a thin overlayer of catalyst metal and graphitize at the metal–substrate interface [60].

CVD graphene growth is most commonly performed on copper and nickel surfaces via a thermal method. Plasma-enhanced CVD methods have been reported, but generally produce lower quality films than thermal methods [61,62]. Thermal growth procedures are quite similar on both metals. Typically, a preannealing run is performed by heating the substrate to around 1000°C under a continuous flow of a hydrogen–argon mixture in a 1:10 volumetric ratio. The growth itself is performed at between 800 and 1100°C (nickel growth tends to be somewhat cooler than copper growth), using methane as the carbon source with a small amount of hydrogen to maintain a reducing environment. Argon can be used as a carrier gas in order to fine-tune the pressure of the growth experiments [63]. One major feature to point out is that the grain boundaries of the graphene do not necessarily coincide with the grain boundaries of the polycrystalline substrate. Grain boundaries in graphene are formed when two separately nucleated and misaligned single crystals of graphene encounter each other on the surface of the substrate, not by interaction with the substrate itself [58]. That said, it has been found that graphene growth proceeds more rapidly on Cu(111) than on other surface facets [64].

Since the formation of grain boundaries in graphene is inversely dependent on the number of nucleation sites, strategies for CVD growth of single-crystal CVD graphene on copper generally involve suppressing the number of graphene nucleation sites. The most successful method

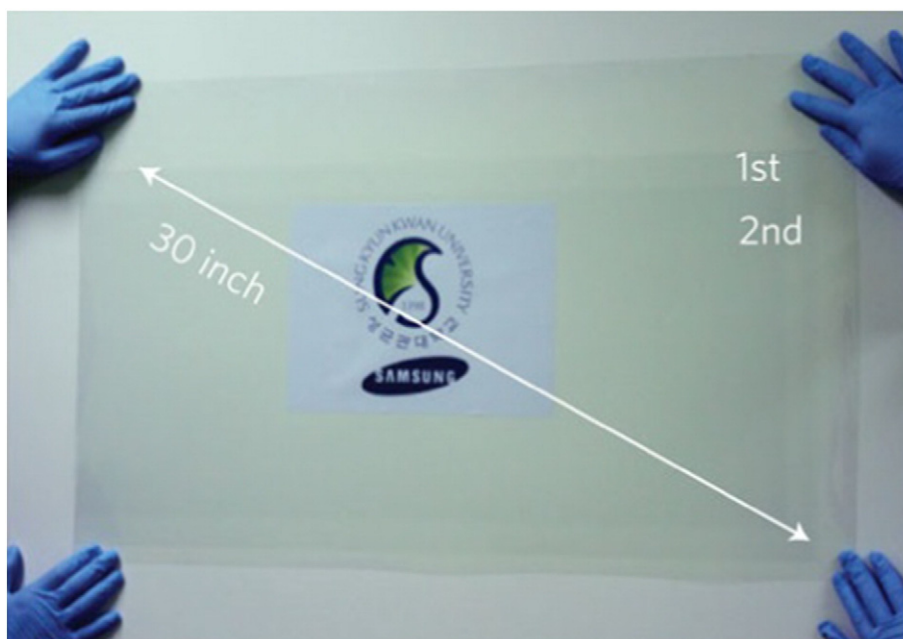


Fig. 3. Two roughly 30 inch (75 cm) sheets of CVD-grown graphene on a PET polymer support, showing the transparency of graphene. Adapted by permission from Macmillan Publishers Ltd: *Nature Nanotechnology*, Ref [59], copyright 2010.

for achieving this so far involves the introduction of oxygen impurities on the copper substrate before growth. These impurities dramatically reduce the nucleation density of graphene, which in turn allows single crystal domains to grow much larger than if the nucleation density were high [19,65,66]. Other methods of suppressing nucleation, including electrochemical polishing of the copper surface and using copper enclosures to limit the partial pressure of the carbon seed gas at the growth site, are also effective at promoting large single crystal growth [66].

Very recently, another avenue toward single crystal growth has been presented by Lee et al. [67]. This group used hydrogen-terminated germanium(110) as a growth substrate. Since the surface of this material has an anisotropic symmetry axis, the large number of nucleated graphene crystals all grow with the same orientation, and individual grains are therefore much more readily stitched together than CVD material grown on copper or nickel, where the orientation of the graphene crystals is random, leading to grain boundaries as the crystals grow into one another.

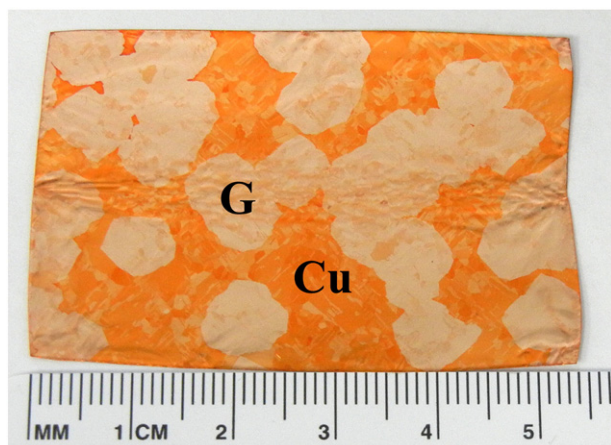


Fig. 4. Optical microscope image of 1 cm single crystal graphene. From Ref [19]. Reprinted with permission from AAAS. Adapted with permission from the author.

3.2.1. Advantages and disadvantages

CVD graphene synthesis has seen very rapid advancement in the last 5 years. Very high quality large-area single crystals of graphene are now attainable, and polycrystalline single-layer graphene can be made as large as the underlying substrate will allow. The quality of the graphene is sufficient for sensitive electronics applications, much like the case of silicon carbide-derived graphene. The areal size of graphene that can be obtained with CVD promises to open up applications in areas such as active displays as well as transparent organic electronics. One advantage that the CVD method has over the SiC method is that it is self-limiting while the growth of a single-layer on SiC is much more technically challenging. The lower cost of the copper substrate and the lower required processing temperature in the CVD process are both advantages of this process over SiC sublimation. Just the same, either source produces graphene that is readily transferred from the metal surface to an arbitrary substrate by supporting the graphene with a polymer and etching away the metal [68]. Notably, it has been found recently that graphene's electronic and chemical properties are strongly affected by its substrate. This substrate effect can be used to create patterned graphene functionalization [69] or modulate its global reactivity [70]. Another advantage that easy transfer confers is that novel heterostructures can be constructed. In the last two years, twisted bilayer and multilayer graphenes have attracted attention from research groups. While some polycrystalline misalignment can occur on SiC-grown graphene [71], easily transferrable CVD graphene makes the construction of bilayers with any angle of twist possible. Twisted bilayer graphene has intriguing optoelectronic properties that researchers are only just beginning to explore [72].

A few words should be said here about graphene transfer. Transfer from the growth substrate is essential for applications development, but the transfer process itself can be quite damaging to the graphene sheet. In fact, improving the quality of graphene transfer is an active area of research. Of course, it is possible to measure some of graphene's properties on the growth substrate without transferring the material. For instance, STM measurements, which require a conductive substrate, can be performed without transferring the graphene. However, most applications require the graphene to be isolated electronically, necessitating the transfer of graphene from the metallic growth substrate to an insulating surface such as SiO₂.

The principal method of graphene transfer involves, as mentioned previously, coating the graphene with a polymer support and etching the metal with an oxidizing solution such as ammonium persulfate or ferric chloride. Once the graphene-polymer sheet is free of metal, it is transferred to a substrate and the polymer is dissolved with acetone or another solvent [68]. However, it is very difficult to remove the polymer completely, and there is some evidence that the polymer actually binds covalently to damaged sections of the graphene during the annealing process [73]. As a result, many groups are currently researching dry transfers—that is, graphene transfer methods that do not require polymer support. These methods include heat- and pressure-mediated laminations [74], azide linkages [75], and electrostatic methods [76]. This proliferation of complicated transfer methods is necessitated by the fact that the adhesive force between graphene and copper is much stronger than the force between graphene and insulating substrates.

Another approach has been to use growth substrates with weak adhesive forces. This was recently demonstrated in a dramatic fashion by Lee et al. [67] with their growth of graphene on hydrogen-terminated germanium. The adhesive force between graphene and the growth substrate is much weaker than the gold-graphene adhesion, allowing the graphene to be coated with gold and peeled off the germanium surface mechanically. The germanium can then be reused for growth and the gold can be etched away with cyanide or another standard etchant. Continued progress in graphene transfer will eventually allow higher quality graphene to be transferred onto arbitrary substrates.

CVD-grown graphene is currently one of the best options that scientists have for electronics and optical applications. However, it is not the best technique for producing large amounts of bulk graphene platelets. Thus, CVD graphene is not well-suited for applications such as polymer composites that require a significant quantity of material.

3.3. Bottom-up synthesis of graphene nanoribbons

One of the most intriguing new methods of graphene synthesis involves using chemical techniques to polymerize and cyclodehydrogenate simple aromatic precursors and thereby obtain atomically precise graphene nanostructures (Fig. 5). This method was pioneered by the groups of Müllen and Fasel, who originally exposed anthracene and triphenylene derivatives to a hot gold surface to assemble graphene nanoribbons with rationally designed geometry [77]. Recent developments include building working devices from these nanoribbons [78], as well as synthesizing soluble and heteroatom-substituted nanoribbons [79]. This interdisciplinary effort between synthetic chemists and materials scientists holds a great deal of promise, in that the technique of bottom-up synthesis of nanomaterials allows for atom-by-atom control of the material. The major drawback to these synthetic techniques right now is that they are still in their infancy, but exciting progress in this direction is being made quickly.

4. Conclusions

In the decade since the science community's focus was brought to bear on graphene as a material with unique and desirable properties, many different methods of synthesis have been developed. As a happy accident, the strengths and weaknesses of one method often complement those of another method (see Table 1). For instance, silicon carbide grown graphene is sufficiently crystalline for sensitive electronics applications, but the method suffers a setback in its lack of scalability. On the other hand, reduced graphene oxide is easily and cheaply scalable for industrial production, but suffers from degraded electronic quality.

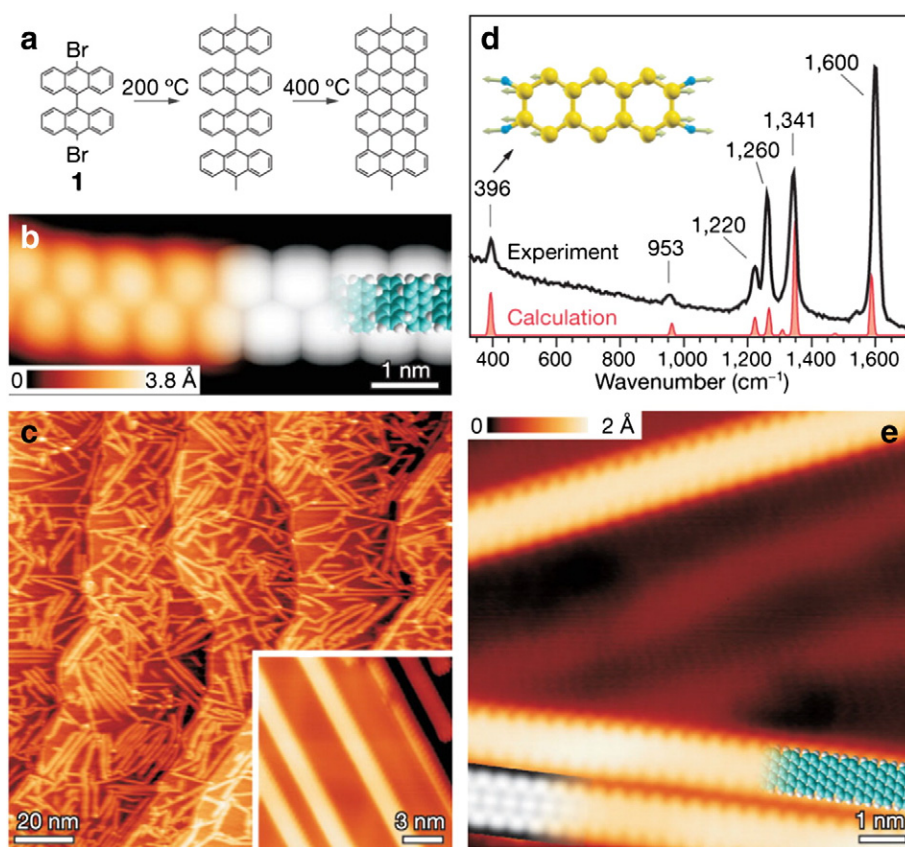


Fig. 5. (a) Scheme of bottom-up synthesis of graphene nanoribbons from simple aromatic precursors. (b) STM image of polymeric anthracene before full cyclodehydrogenation. (c and e) STM image of fully aromatic graphene nanoribbons after cyclodehydrogenation. (d) Raman spectrum of graphene nanoribbons, showing the radial breathing mode at 396 cm^{-1} . Reprinted by permission from Macmillan Publishers Ltd: Nature, Ref [77], copyright 2010.

Table 1
Comparison of different graphene production methods.

Production method		Advantages	Disadvantages
From graphite	Mechanical cleavage	<ul style="list-style-type: none"> Simple, inexpensive Usable with many different layered materials Suitable for demonstrations 	<ul style="list-style-type: none"> Too inefficient for mass production Yields mainly few-layer to many-layer graphene Dimensions constrained by size of initial crystal Dimensions constrained to size of initial crystal Not high-yielding
	Liquid-phase exfoliation	<ul style="list-style-type: none"> Simple and inexpensive Faster than mechanical cleavage Less damaging than chemical exfoliation 	
	Graphite oxide/fluoride reduction	<ul style="list-style-type: none"> Inexpensive Industrial-scale production Reducible to rGO/rGF Allows for expanded chemistry on graphene 	<ul style="list-style-type: none"> Processing degrades electronic properties Not completely reversible Dimensions constrained to size of initial crystal
	Intercalation compound exfoliation	<ul style="list-style-type: none"> Cleaner than GO production and reduction Exfoliation is very efficient 	<ul style="list-style-type: none"> Requires special processing techniques Dimensions constrained to size of initial crystal
Not from graphite	Epitaxial silicon carbide decomposition	<ul style="list-style-type: none"> Large-area single layer and few layer graphene Growth directly on insulating substrate Easily transferrable to arbitrary substrates 	<ul style="list-style-type: none"> Requires specialized equipment and apparatus Very expensive to produce Single crystal size limited to SiC terrace size Still somewhat expensive compared to GO
	CVD growth	<ul style="list-style-type: none"> Arbitrarily large area graphene Self-limiting to a single or few layers Large single-crystal growth Easily transferrable to arbitrary substrates 	<ul style="list-style-type: none"> Transfer can contaminate and damage graphene sheet
	Bottom-up chemical synthesis	<ul style="list-style-type: none"> Atomically precise Simple chemical process 	<ul style="list-style-type: none"> Very low yield Field is too new for confident predictions

While this fortuitous situation is a boon for researchers working on the various aspects of the graphene problem, it is often frustrating for those wishing to commercialize graphene in an economical manner. The dream of large-area, high-yield single crystal graphene suitable for all sorts of applications drives research in this field. But the ongoing refinement of synthetic protocols has brought down the price of graphene dramatically. In 2008, Geim and Kim estimated the price of scotch tape graphene at around \$1000 for a 50 μm^2 flake [80]. Nowadays, \$1000 will buy around 100 cm^2 of CVD graphene on copper, or roughly 1/200,000,000th the starting cost [81]. As production has ramped up, at least one company now claims a production capacity of up to 200 m^2 of graphene per day [82]. As more and larger companies become involved, the price of graphene should continue to drop precipitously.

In terms of commercial applications, the plethora of complementary synthetic methods will likely find some champions as companies diversify their uses of graphene. Because the material has superlative properties in so many different areas (electronic, thermal, mechanical, etc.) we are likely to see a wide range of chemical and materials manufacturers take an interest in the material, in addition to the interest it has already generated among electronics manufacturers. In the end, the advancement and refinement of the synthetic methods presented here, possibly along with new methods, will ultimately take graphene from a position as an advanced material suitable only for research applications to a position of ubiquity in our everyday lives.

Prime novelty statement

This manuscript is an invited thematic review of the state of the art of graphene synthesis. We describe all major methods of graphene synthesis currently in use and present their advantages and drawbacks, providing a straightforward introduction to graphene synthesis for scientists outside the field.

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References

- [1] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, et al., Electric field effect in atomically thin carbon films, *Science* 306 (5696) (2004) 666–669.
- [2] H.P. Boehm, A. Clauss, G.O. Fischer, U. Hofmann, Das Adsorptionsverhalten sehr dünner Kohlenstoff-Folien, *Z. Anorg. Allg. Chem.* 316 (3–4) (1962) 119–127.
- [3] V. Kohlschütter, P. Haenni, Zur Kenntnis des Graphitischen Kohlenstoffs und der Graphitsäure, *Z. Anorg. Allg. Chem.* 105 (1) (1919) 121–144.
- [4] J.D. Bernal, The structure of graphite, *Proc. R. Soc. Lond.* 106 (740) (1924) 749–773.
- [5] P.R. Wallace, The band theory of graphite, *Phys. Rev.* 71 (9) (1947) 622–634.
- [6] D.P. DiVincenzo, E.J. Mele, Self-consistent effective-mass theory for intralayer screening in graphite intercalation compounds, *Phys. Rev. B* 29 (4) (1984) 1685–1694.
- [7] G.W. Semenoff, Condensed-matter simulation of a three-dimensional anomaly, *Phys. Rev. Lett.* 53 (26) (1984) 2449–2452.
- [8] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, M.I. Katsnelson, I.V. Grigorieva, et al., Two-dimensional gas of massless Dirac fermions in graphene, *Nature* 438 (7065) (2005) 197–200.
- [9] Y. Zhang, Y.-W. Tan, H.L. Stormer, P. Kim, Experimental observation of the quantum Hall effect and Berry's phase in graphene, *Nature* 438 (7065) (2005) 201–204.
- [10] T. Kuilla, S. Bhadra, D. Yao, N.H. Kim, S. Bose, J.H. Lee, Recent advances in graphene based polymer composites, *Prog. Polym. Sci.* 35 (11) (2010) 1350–1375.
- [11] D. Prasai, J.C. Tuberquia, R.R. Harl, G.K. Jennings, K.I. Bolotin, Graphene: corrosion-inhibiting coating, *ACS Nano* 6 (2) (2012) 1102–1108.
- [12] T. Kuila, S. Bose, P. Khanra, A.K. Mishra, N.H. Kim, J.H. Lee, Recent advances in graphene-based biosensors, *Biosens. Bioelectron.* 26 (12) (2011) 4637–4648.
- [13] K. Wee Shing, G. Choon How, P. Wee Kee, Y.A. Akimov, B. Ping, The potential of graphene as an ITO replacement in organic solar cells: an optical perspective, *IEEE J. Sel. Top. Quantum Electron.* 20 (1) (2014) 36–42.
- [14] A.A. Balandin, S. Ghosh, W. Bao, I. Calizo, D. Teweldebrhan, F. Miao, et al., Superior thermal conductivity of single-layer graphene, *Nano Lett.* 8 (3) (2008) 902–907.
- [15] E.W. Wong, P.E. Sheehan, C.M. Lieber, Nanobeam mechanics: elasticity, strength, and toughness of nanorods and nanotubes, *Science* 277 (5334) (1997) 1971–1975.
- [16] C. Lee, X. Wei, J.W. Kysar, J. Hone, Measurement of the elastic properties and intrinsic strength of monolayer graphene, *Science* 321 (5887) (2008) 385–388.
- [17] M.S. Dresselhaus, G. Dresselhaus, Intercalation compounds of graphite, *Adv. Phys.* 51 (1) (2002) 1–186.
- [18] F. Banhart, J. Kotakoski, A.V. Krashennnikov, Structural defects in graphene, *ACS Nano* 5 (1) (2010) 26–41.
- [19] Y. Hao, M.S. Bharathi, L. Wang, Y. Liu, H. Chen, S. Nie, et al., The role of surface oxygen in the growth of large single-crystal graphene on copper, *Science* 342 (6159) (2013) 720–723.
- [20] K.S. Novoselov, D. Jiang, F. Schedin, T.J. Booth, V.V. Khotkevich, S.V. Morozov, et al., Two-dimensional atomic crystals, *Proc. Natl. Acad. Sci. U. S. A.* 102 (30) (2005) 10451–10453.
- [21] D. Pacilé, J.C. Meyer, Ç.Ö. Girit, A. Zettl, The two-dimensional phase of boron nitride: few-atomic-layer sheets and suspended membranes, *Appl. Phys. Lett.* 92 (13) (2008).
- [22] D. Teweldebrhan, V. Goyal, A.A. Balandin, Exfoliation and characterization of bis-muth telluride atomic quintuples and quasi-two-dimensional crystals, *Nano Lett.* 10 (4) (2010) 1209–1218.
- [23] B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, A. Kis, Single-layer MoS₂ transistors, *Nat. Nanotechnol.* 6 (3) (2011) 147–150.
- [24] Y. Hernandez, V. Nicolosi, M. Lotya, F.M. Blighe, Z. Sun, S. De, et al., High-yield production of graphene by liquid-phase exfoliation of graphite, *Nat. Nanotechnol.* 3 (9) (2008) 563–568.
- [25] M. Lotya, Y. Hernandez, P.J. King, R.J. Smith, V. Nicolosi, L.S. Karlsson, et al., Liquid phase production of graphene by exfoliation of graphite in surfactant/water solutions, *J. Am. Chem. Soc.* 131 (10) (2009) 3611–3620.
- [26] M. Lotya, P.J. King, U. Khan, S. De, J.N. Coleman, High-concentration, surfactant-stabilized graphene dispersions, *ACS Nano* 4 (6) (2010) 3155–3162.

- [27] N.-W. Pu, C.-A. Wang, Y. Sung, Y.-M. Liu, M.-D. Ger, Production of few-layer graphene by supercritical CO₂ exfoliation of graphite, *Mater. Lett.* 63 (23) (2009) 1987–1989.
- [28] D. Overbye, Physics Nobel Honors Work on Ultra-Thin Carbon, *New York Times*, 2010.
- [29] B.C. Brodie, On the atomic weight of graphite, *Phil. Trans. R. Soc. London* 149 (1859) 249–259.
- [30] W.S. Hummers, R.E. Offeman, Preparation of graphitic oxide, *J. Am. Chem. Soc.* 80 (6) (1958) 1339.
- [31] D.R. Dreyer, S. Park, C.W. Bielawski, R.S. Ruoff, The chemistry of graphene oxide, *Chem. Soc. Rev.* 39 (1) (2010) 228–240.
- [32] H.C. Schniepp, J.-L. Li, M.J. McAllister, H. Sai, M. Herrera-Alonso, D.H. Adamson, et al., Functionalized single graphene sheets derived from splitting graphite oxide, *J. Phys. Chem. B* 110 (17) (2006) 8535–8539.
- [33] Z. Wei, D. Wang, S. Kim, S.-Y. Kim, Y. Hu, M.K. Yakes, et al., Nanoscale tunable reduction of graphene oxide for graphene electronics, *Science* 328 (5984) (2010) 1373–1376.
- [34] C.K. Chua, M. Pumera, Chemical reduction of graphene oxide: a synthetic chemistry viewpoint, *Chem. Soc. Rev.* 43 (1) (2014) 291–312.
- [35] T. Enoki, M. Suzuki, M. Endo, *Graphite Intercalation Compounds and Applications*, Oxford University Press, New York, 2003.
- [36] C. Vallés, C. Drummond, H. Saadaoui, C.A. Furtado, M. He, O. Roubeau, et al., Solutions of negatively charged graphene sheets and ribbons, *J. Am. Chem. Soc.* 130 (47) (2008) 15802–15804.
- [37] S. Park, R.S. Ruoff, Chemical methods for the production of graphenes, *Nat. Nanotechnol.* 4 (4) (2009) 217–224.
- [38] K.E. Whitener Jr., W.K. Lee, P.M. Campbell, J.T. Robinson, P.E. Sheehan, Chemical hydrogenation of single-layer graphene enables completely reversible removal of electrical conductivity, *Carbon* 72 (2014) 348–353.
- [39] S. Koyama, T. Maeda, K. Okamura, Formation process and some properties of graphite fluoride, (C₂F)_n, *Z. Anorg. Allg. Chem.* 540 (9–10) (1986) 117–134.
- [40] H. Toghiani, K. Kadono, Y. Fujii, N. Watanabe, On the structure of graphite fluoride, *Z. Anorg. Allg. Chem.* 544 (1) (1987) 7–20.
- [41] A.B. Bourlino, K. Safarova, K. Siskova, R. Zbořil, The production of chemically converted graphenes from graphite fluoride, *Carbon* 50 (3) (2012) 1425–1428.
- [42] A.B. Bourlino, A. Bakandritsos, N. Liaros, S. Couris, K. Safarova, M. Otyepka, et al., Water dispersible functionalized graphene fluoride with significant nonlinear optical response, *Chem. Phys. Lett.* 543 (2012) 101–105.
- [43] M.K. Zhalutdinov, J.T. Robinson, C.E. Junkermeier, J.C. Culbertson, T.L. Reinecke, R. Stine, et al., Engineering graphene mechanical systems, *Nano Lett.* 12 (8) (2012) 4212–4218.
- [44] D. Cohen-Tanugi, J.C. Grossman, Water desalination across nanoporous graphene, *Nano Lett.* 12 (7) (2012) 3602–3608.
- [45] R.R. Nair, H.A. Wu, P.N. Jayaram, I.V. Grigorieva, A.K. Geim, Unimpeded permeation of water through helium-leak-tight graphene-based membranes, *Science* 335 (6067) (2012) 442–444.
- [46] Acheson EG, inventor. Production of Artificial Crystalline Materials. US patent 492767. 1893.
- [47] Acheson EG, inventor. Manufacture of Graphite. US patent 568323. 1896.
- [48] S. Tanaka, R.S. Kern, R.F. Davis, J.F. Wendelken, J. Xu, Vicinal and on-axis surfaces of 6H-SiC(0001) thin films observed by scanning tunneling microscopy, *Surf. Sci.* 350 (1–3) (1996) 247–253.
- [49] T. Tsukamoto, M. Hirai, M. Kusaka, M. Iwami, T. Ozawa, T. Nagamura, et al., Structural analysis of the heat-treated 4H(6H)-SiC(0001)Si surface, *Surf. Sci.* 371 (2–3) (1997) 316–320.
- [50] I. Forbeaux, J.M. Themlin, J.M. Debever, Heteroepitaxial graphite on 6H-SiC(0001): interface formation through conduction-band electronic structure, *Phys. Rev. B* 58 (24) (1998) 16396–16406.
- [51] A. Charrier, A. Coati, T. Argunova, F. Thibaudau, Y. Garreau, R. Pinchaux, et al., Solid-state decomposition of silicon carbide for growing ultra-thin heteroepitaxial graphite films, *J. Appl. Phys.* 92 (5) (2002) 2479.
- [52] C. Berger, Z. Song, T. Li, X. Li, A.Y. Ogbazghi, R. Feng, et al., Ultrathin epitaxial graphite: 2D electron gas properties and a route toward graphene-based nanoelectronics, *J. Phys. Chem. B* 108 (52) (2004) 19912–19916.
- [53] E.S. Reich, Nobel document triggers debate, *Nature* (2010) 486.
- [54] K.V. Emtsev, A. Bostwick, K. Horn, J. Jobst, G.L. Kellogg, L. Ley, et al., Towards wafer-size graphene layers by atmospheric pressure graphitization of silicon carbide, *Nat. Mater.* 8 (3) (2009) 203–207.
- [55] B.C. Banerjee, T.J. Hirt, P.L. Walker, Pyrolytic carbon formation from carbon suboxide, *Nature* 192 (4801) (1961) 450–451.
- [56] H. Marsh, A.P. Warburton, Catalysis of graphitisation, *J. Appl. Chem.* 20 (4) (1970) 133–142.
- [57] C. Oshima, N. Ayato, Ultra-thin epitaxial films of graphite and hexagonal boron nitride on solid surfaces, *J. Phys. Condens. Matter* 9 (1) (1997) 1.
- [58] X.S. Li, W.W. Cai, J.H. An, S. Kim, J. Nah, D.X. Yang, et al., Large-area synthesis of high-quality and uniform graphene films on copper foils, *Science* 324 (5932) (2009) 1312–1314.
- [59] S. Bae, H. Kim, Y. Lee, X. Xu, J.-S. Park, Y. Zheng, et al., Roll-to-roll production of 30-inch graphene films for transparent electrodes, *Nat. Nanotechnol.* 5 (8) (2010) 574–578.
- [60] J. Kwak, J.H. Chu, J.-K. Choi, S.-D. Park, H. Go, S.Y. Kim, et al., Near room-temperature synthesis of transfer-free graphene films, *Nat. Commun.* 3 (2012) 645.
- [61] Takatoshi Yamada, Jaeho Kim, Masatou Ishihara, H. Masataka, Low-temperature graphene synthesis using microwave plasma CVD, *J. Phys. D. Appl. Phys.* 46 (6) (2013) 063001.
- [62] T.-o. Terasawa, K. Saiki, Growth of graphene on Cu by plasma enhanced chemical vapor deposition, *Carbon* 50 (3) (2012) 869–874.
- [63] Y. Zhang, L. Zhang, C. Zhou, Review of chemical vapor deposition of graphene and related applications, *Acc. Chem. Res.* 46 (10) (2013) 2329–2339.
- [64] J.D. Wood, S.W. Schmucker, A.S. Lyons, E. Pop, J.W. Lyding, Effects of polycrystalline Cu substrate on graphene growth by chemical vapor deposition, *Nano Lett.* 11 (11) (2011) 4547–4554.
- [65] H. Zhou, W.J. Yu, L. Liu, R. Cheng, Y. Chen, X. Huang, et al., Chemical vapour deposition growth of large single crystals of monolayer and bilayer graphene, *Nat. Commun.* 4 (2013).
- [66] Z. Yan, Z. Peng, J.M. Tour, Chemical vapor deposition of graphene single crystals, *Acc. Chem. Res.* 47 (4) (2014) 1327–1337.
- [67] J.-H. Lee, E.K. Lee, W.-J. Joo, Y. Jang, B.-S. Kim, J.Y. Lim, et al., Wafer-scale growth of single-crystal monolayer graphene on reusable hydrogen-terminated germanium, *Science* 344 (6181) (2014) 286–289.
- [68] A. Reina, X. Jia, J. Ho, D. Nezich, H. Son, V. Bulovic, et al., Large area, few-layer graphene films on arbitrary substrates by chemical vapor deposition, *Nano Lett.* 9 (1) (2008) 30–35.
- [69] Q.H. Wang, Z. Jin, K.K. Kim, A.J. Hilmer, G.L.C. Paulus, C.-J. Shih, et al., Understanding and controlling the substrate effect on graphene electron-transfer chemistry via reactivity imprint lithography, *Nat. Chem.* 4 (9) (2012) 724–732.
- [70] R. Stine, W.-K. Lee, K.E. Whitener, J.T. Robinson, P.E. Sheehan, Chemical stability of graphene fluoride produced by exposure to XeF₂, *Nano Lett.* 13 (9) (2013) 4311–4316.
- [71] P. Hofmann, Bilayer graphene: a little twist with big consequences, *Nat. Mater.* 12 (10) (2013) 874–875.
- [72] J.T. Robinson, S.W. Schmucker, C.B. Diaconescu, J.P. Long, J.C. Culbertson, T. Ohta, et al., Electronic hybridization of large-area stacked graphene films, *ACS Nano* 7 (1) (2012) 637–644.
- [73] Y.-C. Lin, C.-C. Lu, C.-H. Yeh, C. Jin, K. Suenaga, P.-W. Chiu, Graphene annealing: how clean can it be? *Nano Lett.* 12 (1) (2011) 414–419.
- [74] L.G.P. Martins, Y. Song, T. Zeng, M.S. Dresselhaus, J. Kong, P.T. Araujo, Direct transfer of graphene onto flexible substrates, *Proc. Natl. Acad. Sci. U. S. A.* (2013), <http://dx.doi.org/10.1073/pnas.1306508110>.
- [75] E.H. Lock, M. Baraket, M. Laskoski, S.P. Mulvaney, W.K. Lee, P.E. Sheehan, et al., High-quality uniform dry transfer of graphene to polymers, *Nano Lett.* 12 (1) (2011) 102–107.
- [76] D.-Y. Wang, I.S. Huang, P.-H. Ho, S.-S. Li, Y.-C. Yeh, D.-W. Wang, et al., Clean-lifting transfer of large-area residual-free graphene films, *Adv. Mater.* 25 (32) (2013) 4521–4526.
- [77] J. Cai, P. Ruffieux, R. Jaafar, M. Bieri, T. Braun, S. Blankenburg, et al., Atomically precise bottom-up fabrication of graphene nanoribbons, *Nature* 466 (7305) (2010) 470–473.
- [78] P.B. Bennett, Z. Pedramrazi, A. Madani, Y.-C. Chen, D.G. de Oteyza, C. Chen, et al., Bottom-up graphene nanoribbon field-effect transistors, *Appl. Phys. Lett.* 103 (25) (2013).
- [79] T.H. Vo, M. Shekhiriev, D.A. Kunkel, M.D. Morton, E. Berglund, L. Kong, et al., Large-scale solution synthesis of narrow graphene nanoribbons, *Nat. Commun.* 5 (2014).
- [80] A.K. Geim, P. Kim, Carbon Wonderland, *Scientific American* 2008.
- [81] Graphene supermarket–CVD graphene–CVD graphene on metals–single layer graphene on copper foil: 4" × 4", [cited 18 February 2014]; Available from <https://graphene-supermarket.com/Single-Layer-Graphene-on-Copper-foil-4-x4-CVD-Cu.html>.
- [82] K.S. Novoselov, Technology: rapid progress in producing graphene, *Nature* 505 (7483) (2014) 291.
- [83] J.T. Robinson, M. Zhalutdinov, J.W. Baldwin, E.S. Snow, Z. Wei, P. Sheehan, et al., Wafer-scale reduced graphene oxide films for nanomechanical devices, *Nano Lett.* 8 (10) (2008) 3441–3445.