CHAPTER 12.13

Graphene

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STRUCTURE AND PROPERTIES

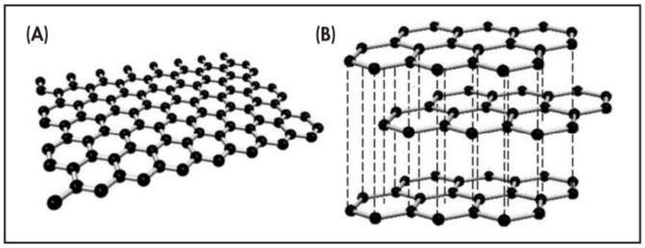
Graphene is a synthetic nano-allotrope of carbon, related in structure to carbon nanotubes and other fullerenes. By its strictest definition, graphene is a single-atom-thick lattice of covalently bonded carbon atoms in a hexagonal, honeycomb-like arrangement. In reality, many products marketed as graphene have multiple layers, and these additional layers typically detract from the idealized properties of single-layer *pristine* graphene.

A single-atom-thick, pristine graphene qualifies as a two-dimensional crystal and was the first of this type of crystal to be isolated and studied. Figure 1 illustrates the close relationship between the crystal structure of graphene and that of the naturally occurring carbon allotrope graphite. Graphite is made up of many layers of graphene stacked one on the other. The individual layers are connected not by chemical bonding but by much weaker van der Waals forces. This allows the planes of graphene within graphite to slide across one another with relative ease, and even to be pried apart. The latter method was used in the first isolation of graphene in 2004 (Novoselov et al. 2004).

Each carbon in the lattice of graphene shares three sp^2-hybridized covalent bonds with adjacent carbons. The remaining p_z orbital of each carbon contributes to pi-bonding in an aromatic network that extends throughout the whole of the crystal. This system allows unparalleled electrical conductivity through the material, with pristine graphene demonstrating a charge mobility of 10,000 $cm^2V^{-1}s^{-1}$ (Novoselov et al. 2004) and a high thermal conductivity of 5,000 $W \cdot m^{-1}K^{-1}$ (Balandin et al. 2008).

Pristine graphene is also physically very strong, with a Young's modulus of 1 TPa, and a tensile strength of 130 GPa (Lee et al. 2008). It is highly optically transparent (97.7%) (Nair et al. 2008), possesses a high theoretical specific surface area (2,630 $m^2\ g^{-1}$) (Stoller et al. 2008), and is impermeable to gases as small as helium (Bunch et al. 2008).

Graphene's allure as a material is perhaps best summed up by Novoselov (2011), one of the two scientists who originally isolated it: "In graphene, we have a unique combination of properties which are not seen together anywhere else: conductivity and transparency, mechanical strength and elasticity." Although the physical properties of graphene are indeed characterized by impressively large numbers, graphene is really a fundamentally new and different kind of material, and little can be said with certainty about its ultimate potential.



Source: Kumar and Lee 2013

Figure 1 Structural relationship between (A) graphene and (B) graphite

Characterization

Producing defect-free, single-atom-thick graphene in macroscopic quantities is still very difficult. Depending on the method of production used, the resulting graphene may have extra layers, structural deformities, or chemical impurities. Graphene cannot be called pristine if it contains defects like these. The presence of any such defects alters the properties of the material, and typically these changes will be for the worse. The grain size of the individual crystals of graphene also affects the material's properties because the grain boundaries will not be as strong or conductive as the pristine portions of the material. Methods have been developed to characterize graphene to demonstrate the quality of material produced using different techniques.

Graphene quality can be demonstrated in terms of the material's electrical properties. The ratio of charge mobility to electrical resistance is inversely proportional to the number of layers present in the graphene (Nezich et al. 2012). Reporting the sheet resistance by itself is common, as it gives

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a qualitative indication of graphene quality. Lower resistance implies that the material in question more closely resembles pristine graphene (Bae et al. 2010).

Ultraviolet-visible (UV-vis) spectroscopy can be used to determine the number of graphene layers present in the material by reading the transmittance of a certain frequency. Pristine graphene has an optical transmittance of 97.1% at 550-nm wavelength. At this same wavelength, two-layer graphene allows 94.3% transmittance and six-layer allows only 83% (Sun et al. 2010). UV-vis can also be used to distinguish between graphene and the related material graphene oxide. The first absorbs at 262 nm and the second at 232 nm. Graphene oxide is discussed in greater detail later in this chapter.

The step height between individual layers of graphene is 0.34 nm, well within the detection limits of atomic force microscopy (Allen et al. 2010). Complications in reading the height profile can arise because of differential attraction between the substrate and graphene which itself is semimetallic. Difficulties can also be attributed to the fact that water can adsorb onto the graphene in a thin layer. These factors result in increased readings between 0.6 and 1.0 nm for single-layer graphene (Novoselov et al. 2004). Therefore, even though they are themselves undesirable features, folds in the graphene structure are often relied upon to calculate the number of layers in the graphene because the step height of 0.34 nm remains consistent for each layer (Allen et al. 2010).

Raman spectroscopy can be used to characterize graphene as well. Defects in the network of sp^2 bonds result in a band (the D band) around 1,350 cm^{-1} that does not present itself in pristine graphene (Allen et al. 2010). Increasing the number of layers of graphene decreases the intensity of a band at ~1,580 cm^{-1} (the G band) and decreases the intensity of a band at ~2,700 cm^{-1} (the 2D band, also called the G' band), thereby allowing the quantification of the number of layers present in the graphene (Allen et al. 2010; Wang et al. 2008).

MARKETS

In 2009, worldwide production of graphene was about 15 tons per year (Segal 2009). By 2015, annual graphene *nanoplatelet* production capacity alone increased to more than 900 tons, although it is not known how much of this capacity is actually utilized (Peplow 2015). About 27% of this production is in the Americas, 68% in Asia, and the rest in Europe, Africa, and the Middle East. A study from the same year noted that there were more than 200 companies producing graphene or graphene applications worldwide (Future Markets 2015).

China is the leading producer of graphene today. The majority of graphene produced is in the form of either nanoplatelets or thin films. The former is applied in nanocomposite materials, conductive inks and coatings, and energy storage; the latter is mainly geared toward transparent electrodes. Millipore Sigma sells graphene nanoplatelets with a variety of particle sizes and surface areas for as low at $115 per 250 mg (Millipore Sigma 2018a). They package their nanoplatelets in glass bottles as a dry powder or as a dispersion in either N,N-dimethylformamide (DMF) or N-methyl-2-pyrrolidone (NMP). For comparison, Millipore Sigma also sells monolayer thin films of graphene at $375 for a sheet about 10 cm in diameter (Millipore Sigma 2018b). Note that these films are not monocrystals; rather, they have a grain size near 10 μm. The thin film is embedded on a layer of copper foil and can be purchased coated with poly-methyl-methacrylate (PMMA) to prevent contamination.

Graphene currently sees use in many commercial products. Several companies that produce sports equipment have incorporated graphene nanocomposites into their equipment. These include Vittoria's line of graphene-enhanced bike wheels (Vittoria 2018), Head's Graphene-XT tennis rackets (Lammer 2013), and Victor's Meteor X JJS badminton racket (Victor 2018). Applications of graphene in electronics are plentiful as well. Vorbeck uses graphene in their conductive inks and coatings (Crain et al. 2012). Zap&Go produces graphene supercapacitors for quick charging of consumer electronics (Voller et al. 2017). Graphene Lighting PLC produces energy-efficient graphene-enabled lightbulbs (Lai 2017).

SOURCES

Graphene only exists naturally in the form of graphite, from which it must be isolated to take advantage of its properties. The original isolation of graphene used highly oriented pyrolytic graphite, an expensive, manufactured form of graphite used for calibrating certain instrumentation. Despite this costly parent material, the isolation was simple and effective, involving repeated peeling apart of the graphite crystals with adhesive tape (Novoselov et al. 2004), a process commonly referred to as the Scotch-tape method. Although this is an effective way to acquire high-quality graphene for laboratory testing, this method is time consuming and lacks scalability, so other methods of producing graphene have since been found.

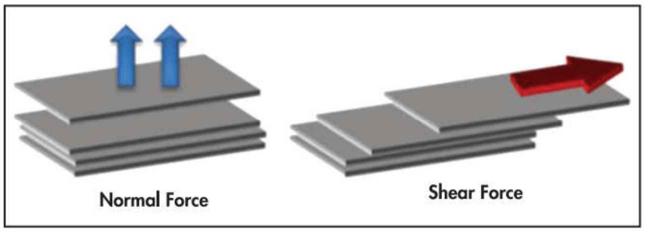
Graphene production methods generally fall into one of two categories: top-down or bottom-up. Top-down processes utilize either naturally occurring or synthetic graphite and involve physical or chemical separation to isolate sheets of single- to multilayer graphene. The strength of top-down processes is that they more easily produce high-quality graphene, can be done at relatively low temperatures, and require less energy. The main weakness of industrial-scale top-down methods is that they do not produce very large sheets of graphene.

Bottom-up methods of graphene production necessarily involve a starting material other than elemental carbon, such as methane or ethanol. Chemical and/or physical techniques are then used to *build* graphene from these ingredients. Bottom-up methods vary in their effectiveness, but can produce arbitrarily large sheets of graphene. These sheets are not necessarily monocrystalline, and in fact, bottom-up techniques are more likely than top-down to produce defects in the resulting graphene. In this regard, however, the gap between top-down and bottom-up may be closing.

TOP-DOWN PRODUCTION TECHNIQUES

Mechanical exfoliation methods involve applying physical forces to graphite to free individual layers of graphene. These layers are connected not by chemical bonds, but by comparatively weak van der Waals forces. As shown in Figure 2, the forces applied to separate graphene layers can be either normal to the lattice plane (as when prying the layers apart with adhesive tape) or within the lattice plane as a shear force (Yi and Shen 2015). Many top-down methods utilize both forces.

A very common way to apply the normal force is by liquid-phase intercalation. In this case, van der Waals forces are overcome chemically using either an organic solvent (Hernandez et al. 2010) or water combined with surfactants (Lotya et al. 2009). For organic solvents, NMP is the most common. Solvents and water/surfactant systems used must have a similar surface tension to that of graphene to be energetically favorable (Hernandez et al. 2008), allowing liquid to



Source: Yi and Shen 2015
Figure 2 Mechanical exfoliation

enter between individual layers and force them apart. Van der Waals forces approach zero and become negligible at a separation distance of ~5 angstroms (Spanu et al. 2009).

It is common to combine this method with sonication to enhance the rate and extent of exfoliation. Sonication has, however, been shown to cause defects in the graphene produced (Bracamonte et al. 2014). Another way of enhancing exfoliation is by applying shear forces via ball milling, which can be done dry or wet and in the absence or presence of sonication (Zhao et al. 2010; Knieke et al. 2010). Dry milling is typically assisted by the presence of water-soluble salts, and the liquid used in wet milling is the intercalating solvent or water/surfactant mixture (Lv et al. 2014; Varrla et al. 2014).

Collisions during milling may as easily impart a normal force as a shear force. Normal force collisions result in some exfoliation along the graphite planes, but also fracture graphite into smaller particles, resulting in smaller diameters of graphene platelets. A way of imparting shear force that seeks to avoid fracturing does so by blending the graphene-liquid mixture to separate the layers (Varrla et al. 2014). Interestingly enough, a patent has been acquired for a graphene-producing process that quite literally uses a kitchen blender, although a precise balance of surfactant concentration and blending speed are required (Coleman and Paton 2014).

Another top-down method of graphene production involves creating the graphite oxide intermediate. This method is highly related to other forms of mechanical exfoliation, but the normal force used to push the layers of graphene apart is supplied primarily by a chemical method. Graphite is submerged in a strong acid that reacts with the graphite on the surface and in between the layers, adding carboxyl groups, hydroxyl groups, and even epoxides to the graphene. A maximum of about 40% of the carbon atoms, previously sp^2 hybridized, become sp^3 hybridized (Mkhoyan et al. 2009). The change in hybridization increases the spacing between each layer from 0.34 nm to about 0.65–0.75 nm in a period of about 96 hours (Schniepp et al. 2006).

The chemically transformed graphite, now called *graphite oxide*, is made of up of layers of graphene oxide. The graphene oxide layers are easily separated by intercalation with a polar solvent and can then be reduced to graphene by the introduction of hydrazine. The resulting graphene is of fairly low quality and is referred to as *reduced graphene oxide* rather than just graphene. This process is arguably the least-expensive scalable method of producing something that can be called graphene. Although too poor quality for electronic applications, reduced graphene oxide is suitable for use in strength-based composite materials.

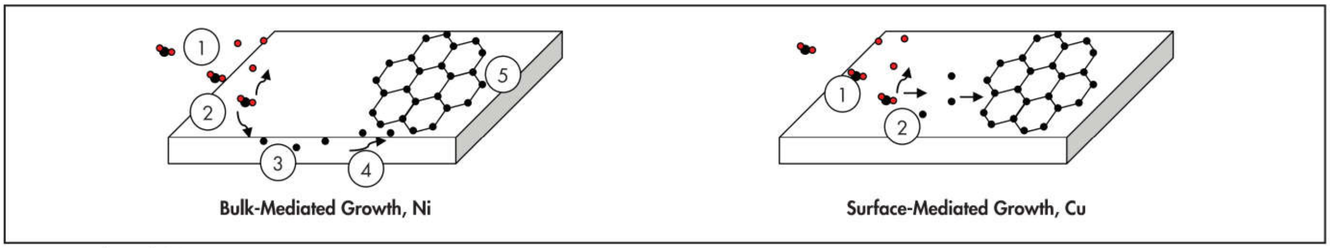
BOTTOM-UP PRODUCTION TECHNIQUES

Chemical vapor deposition (CVD) begins with a carbon precursor as feed, typically a short-chain hydrocarbon such as methane or ethane (Seah et al. 2014). Unsaturated short-chain hydrocarbons, such as acetylene and ethylene, have been shown to be more effective at graphene production, allowing for lower production temperatures (Nandamuri et al. 2010). These highly flammable gases are more difficult to handle safely though, and CVD is a high-temperature process (typically 800°–1,000°C) (Seah et al. 2014). Industrially, short-chain aliphatic alcohols may be preferred, as they are much less flammable and are still capable of producing high-quality graphene (Guermoune et al. 2011).

The carbon precursor is fed, typically in a gaseous state, to the chamber with the transition metal substrate. Transition metals were originally favored because the vacancies in their *d* shells can act as an electron acceptor to facilitate chemisorption of the carbon precursor onto the surface. Copper, however, is widely used despite having a filled 3*d* shell, and has a slightly different mechanism of graphene growth from that of another common transition metal substrate, nickel (Figure 3) (Seah et al. 2014).

On a nickel substrate, the carbon precursor (1) adsorbs onto the surface, then (2) dissociates by hydrogenation to generate hydrogen gas and carbon adatoms (adsorbed atoms). The carbon adatoms (3) diffuse into the nickel foil at high temperature, and then the temperature is lowered to decrease the solubility of the carbon adatoms in the foil. In a step called *segregation*, the carbon adatoms are (4) expelled to the surface, where they (5) self-organize into graphene.

Graphene formation on a copper foil acts by a similar process, but the solubility of carbon in copper is very low, so the segregation step (2) is thought to immediately follow dehydrogenation (1) in a completely surface-mediated process. An important consequence of the difference between these two processes is that, on nickel, the segregation step will continue until the carbon dissolved in the bulk material reaches equilibrium with the carbon that is expelled to the surface, even if the feed of carbon precursor has been shut off (Seah et al. 2014). This makes it potentially more difficult to control the



Source: Seah et al. 2014
Figure 3 Growth by chemical vapor deposition on nickel and copper

Table 1 Qualitative comparison of graphene produced by different methods

Method	Maximum Grain Size	Minimum Thickness	Crystal Quality	Cost	Applicability
Scotch tape	Large	Monolayer	Pristine	Not applicable	Laboratory
Ball milling	Small	Multilayer	High	Low	Conductive inks, composites
Blending	Small	Few-layer	High	Low	Conductive inks, composites
Reduced graphene oxide	Small	Multilayer	Low	Very low	Composites
Chemical vapor deposition (CVD)	Large	Monolayer	Pristine	High	Electronics, energy storage
Plasma-enhanced CVD	Large	Monolayer	Pristine or less	Medium high	Electronics, energy storage

number of layers of graphene produced as compared to the purely surface-mediated growth on copper, where segregation stops as soon as the feed of carbon precursor stops.

Temperature is a major parameter influencing the size and quality of graphene produced by CVD. Lower temperatures are desired both to save energy and to allow for applications in electronics, which would be damaged by higher temperatures, but a certain amount of heat is necessary to decompose the carbon precursor. However, the low solubility of C in Cu films requires *higher* temperatures (Memon et al. 2013), and these higher temperatures increase the quality and quantity of monolayer graphene produced. At temperatures above 1,050°C, however, the low melting point of Cu begins to interfere with graphene formation (Fan et al. 2011). Ni foils also require high temperatures (though not as high as Cu) because graphene formation competes with nickel carbide (Ni_2C) formation at low temperatures (Lahiri et al. 2011).

One variation of CVD that has succeeded in lowering processing temperatures is plasma-enhanced chemical vapor deposition (PECVD). A growth temperature as low at 240°C has been reported (Kalita et al. 2012). In PECVD, a plasma is produced through radio frequencies (Qi et al. 2011), magnetically enhanced arc discharges (Levchenko et al. 2010), or microwaves (Kalita et al. 2012). The plasma couples with the substrate, causing localized rapid heating and potentially removing the metal's native oxide layer, allowing for more uniform nucleation of graphene (Kumar et al. 2012). Continuous plasma bombardment can produce defects as well, and apparently, the quality of graphene produced by PECVD is still better when performed at higher temperatures (Woo et al. 2013).

Large sheets of graphene, on the order of meters, are currently produced by CVD but are ridden with defects. As of 2015, the largest monolayer single-crystal grains of graphene grown were about 1 cm in diameter (Hao et al. 2013). An important downside to CVD is the substrate. Graphene attached to a transition metal foil is usually not a useful form of the material. The substrate must be dissolved (typically in an acid) and the graphene layer transferred to the more useful substrate (Reina et al. 2008). The transfer process likely produces defects in the graphene as well.

The various features of graphene produced by each of the production methods discussed in this chapter are summarized in Table 1.

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