



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.

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