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Reviews of Science for Science Librarians: Graphene

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Reviews of Science for Science Librarians: Graphene

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Graphene is, in many ways, a simple substance. Made of a single atomic layer of graphite, graphene has emerged as a material providing many surprises and having immense scientific and industrial potential. In 2010, scientists Andre K. Geim and Konstantin S. Novoselov received the Nobel Prize in Physics for their isolation of graphene and for their research pertaining to the ultrathin material. In his presentation speech, Professor Per Delsing described how we all have made graphene each time we write with a pencil: microscopic bits of graphite and graphene flake away as the pencil moves across the paper (Delsing 2010). It was Geim and Novoselov's ability to point and say "there," however, that has gained them fame. Since graphene's isolation, scientists have been discovering its surprising properties including its strength, flexibility, and high mobility of its charge carriers, properties that will undoubtedly lead to many industrial applications. This article will give an introduction to the importance of graphene and an analysis of when and where graphene has appeared in scholarly literature.

KEYWORDS carbon, Andre K. Geim, graphene, graphite, monoatomic material, Nobel Prize in Physics, Konstantin S. Novoselov

WHAT IS GRAPHENE?

Graphene is a two-dimensional, or single layer, of graphite, which is made of carbon atoms (Huang et al. 2011). Carbon, the base for all life on Earth,

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also makes up precious diamonds and common pencil graphite; graphene is another carbon material. For many years, as early as the 1930s, graphene was considered a theoretical material only good for academic consideration. It was theorized that two-dimensional crystals would be thermodynamically unstable (Geim and Novoselov 2007). Scientists believed that the atoms' movements at any given temperature would be greater than distance between the atoms themselves, making the material unstable. Single atomic layers of crystalline materials could only be grown on the top of three-dimensional bases of substances with a similar lattice structure or grown between layers of other atoms or molecules, which would provide the needed stability. Then in 2004, monoatomic carbon, graphene, was isolated by scientists Andre K. Geim and Konstantin S. Novoselov, both of the Manchester Centre for Mesoscience and Nanotechnology at the University of Manchester in the United Kingdom (Geim and Novoselov 2007). Contrary to what scientists thought would happen, graphene's and other monoatomic materials' stability comes in part from the strong bonds between the atoms. The material's hexagonal shape makes it look like familiar honeycomb or chicken wire. Graphene is not completely flat but has waves because of thermal energy at any temperature above absolute zero (Day 2010). Carbonto-carbon bonds keep the graphene from completely buckling or folding, which is what theorists had formerly predicted would happen. Scientists may also refer to double-layer graphene, which has been found to have many properties similar to single-layer graphene. Few-layer graphene, which is material with anywhere between three and nine layers, has increasingly divergent properties from single- and double-layer graphene (Geim and Novoselov 2007). Once the material reaches ten layers, scientists consider it thin-layer graphite.

Looking at graphene on a "large" scale, scientists have called it a patchwork quilt (Huang et al. 2011). Areas of crystals are created and oriented in different directions, potentially due to impurities or other small variations that influence the crystals' growth and initial orientation. The meetings of these areas of differently oriented crystals, or grains, are called grain boundaries. Future directions for study will include learning more about how these grain boundaries, other defects, and impurities might affect the properties of the graphene (Chen and Yu 2010). Certainly of interest, too, will be how to gain greater control on the growth of the crystals.

WHY IS GRAPHENE IMPORTANT?

Because of its unique and exciting properties, graphene has been a highly popular research topic. For a material to be useful in electronics, its properties need to be reliably controlled by an externally applied voltage (Novoselov et al. 2004). In silicon, which is used for computer chips and

other electronic devices, electrons need added energy—heat or voltage to move freely and make the material behave as a conductor (Day 2010). The problem with using three-dimensional materials for electronic applications is that the influence of the internal electrons dominates the properties of the surface electrons. Because of this, graphene is more desirable than three-dimensional material, but also it is superior to other two-dimensional crystalline material because of its electronic properties. The electrons in graphene act similarly to Dirac fermions, meaning they act like massless particles but moving 300 times slower than the speed of light, which is still very fast (Castro Neto 2007). In the case of graphene, the electrons interact with phonons, which reside in the nucleus of carbon, rather than with photons, or light. This all means that graphene has high carrier mobility, which refers to the ease at which the charged particles can move within a material (Liao at al. 2010). Graphene's electrons move in a straight path, without scattering, for comparatively long distances, on the order of thousands of times the distances between the atoms themselves (Geim and Novoselov 2007; [Anon] 2007). This mobility is not significantly affected by either temperature or by chemical-doping (Geim and Novoselov 2007; Farmer et al. 2009). Producing high-frequency transistors, for use in the terahertz range, from graphene would be useful in technologies such as ultrahigh-speed radio frequency electronics (Liao et al. 2010; Lin et al. 2010, 662; Anonymous 2011). Past practices for producing these types of transistors, however, have damaged the graphene. Recent experiments have been developing new ways to create the transistors that will preserve the graphene and its desirable properties (Liao et al. 2010; Lin et al. 2010, 662; Anonymous 2011).

In addition to its desirable charge carrier properties, graphene is strong, stretchable, flexible, transparent, and has the potential for useful chemical modifications. Although it is transparent, graphene is so dense even the smallest atom—helium—cannot pass through (Shankland 2010). Also, graphene is one hundred times stronger than steel (Delsing 2010). The analogy given in the Nobel Prize presentation was that if a hammock were made of graphene, it would be strong enough to hold a cat and yet weigh only about as much as one of that cat's whiskers and, of course, be only one atom thick (Delsing 2010). Also, graphene conducts heat ten times better than silver. Although these properties have been discovered and tested in the lab, the future of graphene is in its mainstream applications. For example, graphene would be useful for touch-screens devices, display panels, solar cells, computer chips, conductive plastics, and lighter aircraft (Chen and Yu 2010; Shankland 2010). Indium tin oxide (ITO) is the material that is currently used in many applications for which graphene would be better in terms of being more flexible, less fragile, and having the potential of being cheaper than ITO. Graphene is able to withstand more strain than materials such as ITO while retaining its electrical properties (Bae et al. 2010). One study reported that while an ITO touch-screen broke under approximately 2-3-percent strain, a graphene touch-screen withstood up to approximately 6 percent and was limited by the electrodes on the screen rather than by the graphene itself (Bae et al. 2010). This same team used graphene electrodes in a fully-functional touch-screen panel. Another study reported that the electrical resistance of the graphene sheet showed little change up to a strain of approximately 6.5 percent and was fully restored after unbending (Kim et al. 2009). Even after straining the material up to approximately 18.7 percent, the original electric resistance was restored after being relaxed. In order for graphene to become the chosen material, industry needs to be able to quickly and reliably produce large quantities of high-quality graphene. As of mid-2010, one team had created graphene sheets with a diagonal length of thirty inches (Bae et al. 2010). The 2010 Nobel Prize announcement stated that sheets with a width of seventy centimeters had been produced "using near-industrial methods" (Class for Physics of the Royal Swedish Academy of Sciences 2010, 6). Truly large-scale production seems at hand.

HOW IS GRAPHENE CREATED AND FOUND?

Even though graphene was not isolated until 2004, the pursuit for singlelayer graphite started much earlier. A conference paper from 1962 reports on creating graphite only a few layers thick and even suggests that some areas of the material the authors created might be only a single layer (Boehm et al. 1962). As noted previously, scientists had been considering the properties of two-dimensional crystals even earlier in the century, although at the time it was merely theoretical contemplation. Free-standing graphene was first isolated using the graphite from unassuming pencils and adhesive tape (most popularly referred to as Scotch® tape) (Delsing 2010). Geim and Novoselov are credited with isolating graphene in 2004 by taking a small bit of graphite and repeatedly using adhesive tape to remove layers of the substance, a technique suggested by Oleg Shkliarevskii, a member of Geim's lab (Day 2010). Although other groups had tried this technique, the challenge was in identifying the flakes of truly single-layer graphene (Geim and Novoselov 2007). Graphene is so thin, it is optically invisible, and therefore difficult to find. By placing it on a silicon surface, however, an optical interference pattern is created so the graphene can be located. In 2010, Geim and Novoselov were awarded the Nobel Prize in Physics for their work with graphene. The scientists earned the award not because they were able to produce graphene but because they were able to find it and identify it for what it is and for the subsequent research they completed to discover graphene's fundamental properties (Class for Physics of the Royal Swedish Academy of Sciences 2010).

Since the successful 2004 isolation, significantly more complicated ways have been used to create and isolate graphene. The aim is to produce large

sheets of graphene in a reliable way, which will lead to industrial applications. Chemical vapor deposition (CVD) is a process of creating graphene by breaking down CH₄ (methane) at high temperatures and depositing the carbon onto a substrate such as copper (Chen and Yu 2010). In the similar process of dissolution-precipitation, graphene is created on a nickel film where the nickel and carbon are heated to around 1000°C. As they cool, the carbon settles on the nickel surface, crystallizing into graphene (Garaj, Hubbard, and Golovchenko 2010). The problem with these processes is the difficulty in controlling the graphene thickness and ensuring the creation of a single atomic layer since not all the available carbon creates the graphene. The process of producing graphene through ion implantation of polycrystalline nickel substrates (or other suitable substrates) with carbon atoms again at about 1000°C was reported in Applied Physics Letters in late 2010 (Garaj, Hubbard, and Golovchenko 2010). Ion implantation gives the scientists better control over how many layers of graphene are produced. By controlling the amount of carbon implanted into the substrate material, there is little excess since nearly all of the available carbon atoms crystalize into graphene once the samples cool.

One issue of growing graphene on a substrate is that the graphene is then confined to its host material (Bae et al. 2010). A roll-to-roll process was developed to transfer the graphene from the original host copper to another material. Copper substrate has been preferred because of its flexibility. Once the graphene has been created, a polymer is pressed on with rollers, and the copper is dissolved in a chemical solution before the graphene is transferred to a new substance (Bae et al. 2010). One can assume that as more time passes and more work is done, the production process will continue to improve.

WHEN AND WHERE DOES GRAPHENE APPEAR IN THE LITERATURE?

As the subject of the 2010 Nobel Prize in Physics, graphene clearly is an important material. Nobel Prize winners Geim and Novoselov published their seminal paper on graphene in 2004 in *Science* entitled "Electric Field Effect in Atomically Thin Carbon Films" along with colleagues (Novoselov et al. 2004). In order to develop a picture of the prevalence and impact of graphene on the scientific literature, this author used the Web of Science database hosted by Thomson Reuters's (formerly ISI) Web of Knowledge to analyze graphene publications. All figures and tables presented in this publication are based on the search results along with the citation report and the analyze results functions provided by Web of Knowledge. A search of "graphene" in the title field retrieved 6,103 publications. It is interesting to note that the *Science* article by Novoselov and Geim does not actually

have the term graphene in the title and is retrieved, instead, among the 9,655 results from a search of "graphene" in the topic field. Clearly, there is a significant amount of overlap in the two searches, and trends found in the results of one search are mirrored in the results of the other. Numbers and figures used for this analysis refer to the search with "graphene" in the topic field. In examining the results of the graphene-as-topic results, there is a steady increase in the number of articles produced each year. The earliest items found in this search are from 1991. Certainly, graphene had been considered much earlier than this, but other phrases, such as singlelayer carbon or monoatomic carbon, could have been assigned as subject terms, plus the limits inherent in any single database could easily account for the lack of older results. Early publications prior to graphene's isolation consider graphene in theory, in experiments as part of a layered material, or in structures such as carbon nanotubes. The substantial increase in the number of publications following graphene's 2004 isolation attests to the extreme popularity of graphene as an isolated two-dimensional crystal used for experimentation. See Figure 1 for the number of graphene-as-topic publications by year. In the twenty-year span from 1991 through 2010, the number exploded from five to 3,439. From 2005, the year following Novoselov and Geim's announcement of isolating graphene, to 2010 the jump was from 189 to 3,439 publications, a difference of 3,250 items/year in the span of six years. The articles published in 2010 alone account for about 35.5 percent of all the publication over the past twenty years.

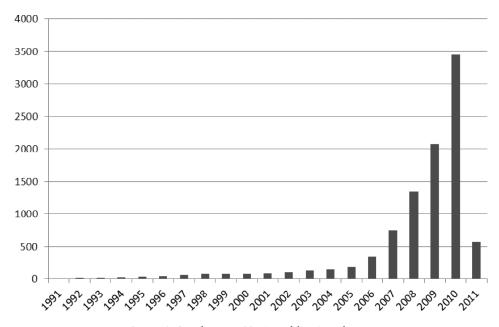


FIGURE 1 Graphene-as-Topic Publications by Year.

The number of citations for the 9,655 items has followed the same pattern as the number of publications. In 1991 the retrieved papers produced one citation; in 2010 the number of total citations was 67,752. See Figure 2 for the number of citations per year. The total number of citations from 1991 through 2010 is 169,801. The article that tops the list for greatest total number of citations is the 2004 paper from Novoselov and Geim. As of the date of the search, the paper had 3,903 total citations, which gives a per year average of 487.88 from the year in which it was published. Of the publications retrieved, only four have average citations of over 400 per year; Novoselov and Geim are listed as authors on all four. The article "The Rise of Graphene," published in Nature Materials in March 2007, has the highest average citation number at 540 per year. Of the four articles with the highest total citations, Novoselov and Geim are listed as authors on three of them. The one of which they were not a part, and the one with the second highest number of total citations, 3,231, is "Crystalline Ropes of Metallic Carbon Nanotubes" in Science (Thess et al. 1996). As the title suggests, this article focuses on carbon nanotubes and not on graphene as an isolated twodimensional sheet; it was written eight years prior to the successful isolation and identification of single-layer graphene.

A large number of journals have published articles on the topic of graphene. In fact, the search results include over 600 distinct titles. The top ten journals are the same whether the graphene search is conducted in the topic or title field, with only minor differences in the ranking. See Table 1 for the top ten journals based on the number of graphene-as-topic articles published. *Physical Review B* and *Physical Review Letters*, ranked first and third

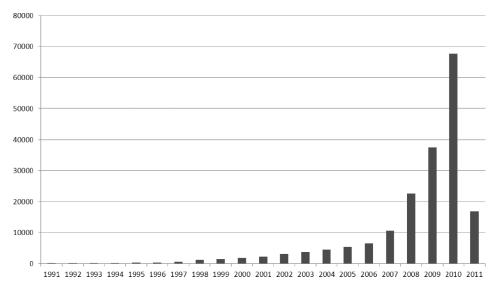


FIGURE 2 Citations of Graphene-as-Topic Publications by Year.

TABLE 1 Top Ten Journals

Source title	Number of retrieved articles	Percentage of retrieved articles
APS Physical Review B	1,700	17.6075%
Applied Physics Letters	569	5.8933%
APS Physical Review Letters	503	5.2097%
Carbon	386	3.9979%
Nano Letters	322	3.3351%
Journal of Physical Chemistry C	279	2.8897%
ACS Nano	235	2.4340%
Journal of Physics: Condensed Matter	186	1.9265%
Nanotechnology	181	1.8747%
Journal of Applied Physics	171	1.7711%

respectively, are both journals produced by the American Physical Society; whereas *Applied Physics Letters* was the second-ranked host journal. *Physical Review B* has an impact factor of 3.475 from 2009, and "is the largest and most comprehensive international journal specializing in condensed matter and materials physics" (American Physical Society). *Applied Physics Letters*'s impact factor for 2009 is 3.544, and is published by the American Institute of Physics (American Institute of Physics). *Physical Review Letters* has a 2009 impact factor of 7.328 (American Physical Society). The purpose of the *Letters* journals is to quickly disseminate important and new scientific findings in the field of physics.

The graphene publications are not just being produced from a localized group, but search results also show that the exploration and experimentation with graphene is spread across the world. See Table 2 for the top ten publishing countries based on the number of articles retrieved in this search. Percentages from the results analysis total more than 100 percent because of collaborating authors from different countries and institutions. The United States has the highest number of publications with 3,051, followed by the People's Republic of China with 1,655. The other top ten publishing countries are Japan, Germany, France, England, South Korea,

TABLE 2 Top Ten Publishing Countries

Country	Number of retrieved articles	Percentage of retrieved articles
United States of America	3051	31.6002%
People's Republic of China	1655	17.1414%
Japan	1062	10.9995%
Germany	796	8.2444%
France	546	5.6551%
England	514	5.3237%
South Korea	459	4.7540%
Spain	442	4.5779%
Russia	342	3.5422%
Singapore	315	3.2626%

TABLE 3 Top Ten Publishing Institutions

Institution name	Number of retrieved articles	Percentage of retrieved articles
Chinese Academy of Science	396	4.1015%
CSIC (Spanish National Research Council)	223	2.3097%
National University of Singapore	193	1.9990%
Russian Academy of Science	181	1.8747%
University of California Berkeley	174	1.8022%
Massachusetts Institute of Technology	169	1.7504%
CNRS (National Center for Scientific Research, France)	152	1.5743%
Tohoku University (Japan)	139	1.4397%
Tsinghua University (China)	139	1.4397%
Nanyang Technological University (Singapore)	134	1.3879%

Spain, Russia, and Singapore, which rounds out the top ten with 315 publications. Eighty-four countries/territories are listed with less than 3 percent of the records lacking this information. The top publishing institution is the Chinese Academy of Sciences with 396 publications, followed by the CISC (Spanish National Research Council) with 223 publications. See Table 3 for the top ten publishing institutions based on the number of articles retrieved in this search. The University of Manchester, the home of Novoselov and Geim, ranks seventeenth overall in number of graphene publications with 103. A total of 2,684 institutions are represented in the search results, with less than 3 percent of the publications lacking this field.

The top publishing individual researchers generally reflect the totals by country and institution. The top author, with 107 publications, is Min-Fa Lin, a researcher at the National Cheng Kung University in Taiwan; this institution ranks number 15, and Taiwan ranks number 13 in terms of retrieved articles. Also in the top ten individual researchers are F. Guinea, ranking third with eighty-three publications and Rodney S. Ruoff, seventh with sixty-eight. Both researchers are a part of the CISC, which ranks second in institutions, with Spain ranking eighth among countries/territories. It should be noted that the second-ranked spot for individual researchers is held by articles with no author listed, which accounts for eighty-five publications. These documents are seventy-four news items, nine editorial pieces, one article, and one correction. The Nobel Prize authors, Geim and Novoselov, rank sixth and eighth among individual authors, credited with seventy-one and sixty-seven publications, respectively. See Table 4 for the top ten individual publishing authors. Search analysis lists 15,765 authors for the retrieved publications.

SUMMARY

For a material whose existence in the 1930s was argued to not be possible, graphene has now inspired such phrases as "a rapidly rising star

Author	Number of retrieved articles	Percentage of retrieved articles
Lin, M. F.	107	1.1082%
Anonymous	85	0.8804%
Guinea, F.	83	0.8497%
Dresselhaus, M. S.	80	0.8286%
Katsnelson, M. I.	78	0.8079%
Geim, A. K.	71	0.7354%
Ruoff, R. S.	68	0.7043%
Novoselov, K. S.	67	0.6939%
Peeters, F. M.	65	0.6732%
Peres, N. M. R.	63	0.6525%

TABLE 4 Top Ten Publishing Individual Authors

on the horizon of materials science and condensed matter physics" and "a cornucopia of new physics" (Geim and Novoselov 2007, 183). The widespread research into the properties and applications of graphene attests to the growing interest in this enthralling two-dimensional material. Graphene's strength and flexibility, coupled with its fascinating charge carrier and other properties, point to the promising potential of this material to improve existing technologies and for the development of new ones that reach far beyond the hypothetical transparent cat hammock.

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