How graphene is set to change the world

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1. Abstract

Graphene has attracted great interest for its excellent mechanical, electrical, thermal and optical properties. It can be produced by micro-mechanical exfoliation of highly ordered pyrolytic graphite, epitaxial growth, chemical vapor deposition, and the reduction of graphene oxide.

2. Introduction

Graphene is the name for an atom-thick honeycomb sheet of carbon atoms. It is the building block for other graphitic materials (since a typical carbon atom has a diameter of about 0.33 nanometers, there are about 3 million layers of graphene in 1 mm of graphite).

The single layers of carbon atoms tightly packed into a two-dimensional (2D) honeycomb crystal lattice is called graphene. This name was introduced by Boehm, Setton, and Stumpp in 1994 . Graphite exhibits a remarkable anisotropic behavior with respect to thermal and electrical conductivity.

3. Graphene Description

Units of graphene are known as nanographene; these are tailored to specific functions and as such their fabrication process is more complicated than that of generic graphene. Nanographene is made by selectively removing hydrogen atoms from organic molecules of carbon and hydrogen, a process called dehydrogenation.

Harder than diamond yet more elastic than rubber; tougher than steel yet lighter than aluminum. Graphene is the strongest known material.

To put this in perspective: if a sheet of cling film (like kitchen wrap film) had the same strength as a pristine monolayer of graphene, it would require the force exerted by a mass of 2000 kg, or a large car, to puncture it with a pencil.

Graphene possesses other amazing characteristics: Its high electron mobility is 100x faster than silicon; it conducts heat 2x better than diamond; its electrical conductivity is 13x better than copper; it absorbs only 2.3% of reflecting light; it is impervious so that even the smallest atom (helium) can't pass through a defect-free monolayer graphene sheet; and its high surface area of 2630 square meters per gram means that with less than 3 grams you could cover an entire soccer field (well, practically speaking you would need 6 grams, since 2630 m2/g is the surface area for both sides of a graphene sheet).

Graphene is the basic building block for other graphitic materials; it also represents a conceptually new class of materials that are only one atom thick, so-called two-dimensional (2D) materials (they are called 2D because they extends in only two dimensions: length and width; as the material is only one atom thick, the third dimension, height, is considered to be zero).

Graphene is also very attractive for the fabrication of mixed-dimensional van der Waals heterostructures that could be carried out through hybridizing graphene with 0D quantum dots or nanoparticles, 1D nanostructures such as nanowires or carbon nanotubes, or 3D bulk materials. The extraordinary characteristics of graphene originate from the 2p orbitals, which form the π state bands that delocalize over the sheet of carbons that constitute graphene.

Graphene has emerged as one of the most promising nanomaterial's because of its unique combination of superb properties: it is not only one of the thinnest but also strongest materials; it conducts heat better than all other materials; it is a great conductor of electricity; it is optically transparent, yet so dense that it is impermeable to gases – not even helium, the smallest gas atom, can pass through it.

These amazing properties, and its multifunctionality, make graphene suitable for a wide spectrum of applications ranging from electronics to optics, sensors, and bio devices.

Graphene research has evolved into a vast field with approximately 10,000 scientific papers now being published every year on a wide range of topics.

4. Graphene discovery

Carbon comes in many different forms (so-called *allotropes*), from the graphite found in pencils to the world's most expensive diamonds. In 1980, we knew of only three basic forms of carbon, namely diamond, graphite, and amorphous carbon. Then, fullerenes and carbon nanotubes were discovered and, in 2004, graphene joined the club.

Before graphene was first demonstrated by Andre Geim and Konstantin Novoselov, two physicists from the University of Manchester, in 2004 (for which they received the Nobel Prize in 2010) scientists argued that strictly 2D crystalline materials were thermodynamically unstable and could not exist.

Graphene had already been studied theoretically in 1947 by P.R. Wallace as a text book example for calculations in solid state physics. He predicted the electronic structure and noted the linear dispersion relation. The wave equation for excitations was written down by J.W. McClure already in 1956, and the similarity to the Dirac equation was discussed by G.W. Semenoff in 1984.

In their initial experiments, Geim and Novoselov extracted graphene from a piece of graphite such as is found in ordinary pencils. Using regular adhesive tape they managed to obtain a flake of carbon with a thickness of just one atom. This mechanical exfoliation is the simplest of the preparation methods and surprisingly is the method that made stand-alone graphene a reality.

5. How graphene is made

The quality of graphene plays a crucial role as the presence of defects, impurities, grain boundaries, multiple domains, structural disorders, wrinkles in the graphene sheet can have an adverse effect on its electronic and optical properties.

In electronic applications, the major bottleneck is the requirement of large size samples, which is possible only in the case of CVD process, but it is difficult to produce high quality and single crystalline graphene thin films possessing very high electrical and thermal conductivities along with excellent optical transparency.

Another issue of concern in the synthesis of graphene by conventional methods involves the use of toxic chemicals and these methods usually result in the generation hazardous waste and poisonous gases. Therefore, there is a need to develop green methods to produce graphene by following environmentally friendly approaches.

The preparation methods for graphene should also allow for *in situ* fabrication and integration of graphene-based devices with complex architecture that would enable eliminating the multi step and laborious fabrication methods at a lower production cost.

Currently, the most common techniques available for the production of graphene are shown schematically below, which includes micromechanical cleavage, chemical vapor deposition, epitaxial growth on SiC substrates, chemical reduction of exfoliated graphene oxide, liquid phase exfoliation (LPE) of graphite and unzipping of carbon nanotubes.

However, each of these methods can have its own advantages as well as limitations depending on its target application(s). In order to surmount these barriers in commercializing graphene, concerted efforts are being made by researchers at various R&D institutes, universities and companies from all over the globe to develop new methods for large scale production of low-cost and high quality graphene via simple and eco-friendly approaches.

Already, researchers have managed to produce large, single-crystal-like graphene films more than a foot long on virtually any flat surface – a step towards commercialization.

However – a big word of caution here: The global graphene production appears to suffer from serious quality issues and it appears that there is almost no high quality graphene, as defined by ISO, in the market yet.

6. Graphene properties

- *Electronic properties*

One of the reasons nanotechnology researchers working towards molecular electronics are so excited about graphene is its electronic properties – it is one of the best electrical conductors on Earth. The unique atomic arrangement of the carbon atoms in graphene allows its electrons to easily travel at extremely high velocity without the significant chance of scattering, saving precious energy typically lost in other conductors.

Scientists have found that graphene remains capable of conducting electricity even at the limit of nominally zero carrier concentration because the electrons don't seem to slow down or localize. The electrons moving around carbon atoms interact with the periodic potential of graphene's honeycomb lattice, which gives rise to new quasiparticles that have lost their mass, or *rest mass* (so-called *massless Dirac fermions*). That means that graphene never stops conducting. It was also found that they travel far faster than electrons in other semiconductors.

- *Mechanical properties*

The impressive intrinsic mechanical properties of graphene, its stiffness, strength and toughness, are one of the reasons that make graphene stand out both as an individual material and as a reinforcing agent in composites. They are caused by the stability of the sp2 bonds that form the hexagonal lattice and oppose a variety of in-plane deformations.

A detailed discussion of the mechanical properties of graphene and graphene-based Nano composites can be found in this review paper.

- *Stiffness*

The breaking force obtained experimentally and from simulation was almost identical and the experimental value of the second order elastic stiffness was equal to 340 ± 50 N m-1. This value corresponds to a Young's modulus of 1.0 ± 0.1 TPa, assuming an effective thickness of 0.335 nm.

- *Strength*

Defect-free, monolayer graphene is considered to be the strongest material ever tested with a strength of 42 N m-1, which equates to an intrinsic strength of 130 GPa.

- *Toughness*

Fracture toughness, which is a property very relevant to engineering applications, is one of the most important mechanical properties of graphene and was measured as a critical stress intensity factor of 4.0 ±0.6 MPa.

Research groups worldwide are working on the development of industrially manufacturable graphene sheets that have high strength and toughness in all sheet directions for diverse applications as graphene-based composites for vehicles, optoelectronics and neural implants.

A recent consumer product example that exploits graphene's mechanical properties is the Momo Evo Graphene motorcycle helmet, developed by Italy's Mom design and the Istituto Italiano di Tecnologia (IIT).

It is the first-ever graphene-infused carbon fiber helmet that capitalizes on the material's thin, strong and conductive, flexible and light characteristics to create a helmet that absorbs and dissipates impact better than your average helmet. It also disperses heat more efficiently, so it’s cooler.

Another example is the Dassi Interceptor Graphene bike – the world's first graphene bicycle. Enhancing carbon fiber with graphene allows to make lighter, thinner tubes, that are stronger than regular carbon. That means an aero-shaped frame with none of the usual weight sacrifice. Thanks to its graphene reinforced frame, this bike is 30% lighter yet twice as strong and super stiff.

7. Graphene uses and applications

- *Energy storage and solar cells*

Graphene-based nanomaterials have many promising applications in energy-related areas. Just some recent examples: Graphene improves both energy capacity and charge rate in rechargeable batteries; activated graphene makes superior super capacitors for energy storage; graphene electrodes may lead to a promising approach for making solar cells that are inexpensive, lightweight and flexible; and multifunctional graphene mats are promising substrates for catalytic systems.

Researchers also have discovered a critical and unexpected relationship between the graphene's chemical/structural defectiveness as a host material for electrodes and its ability to suppress the growth of dendrites – branch-like filament deposits on the electrodes that can penetrate the barrier between the two halves of the battery and potentially cause electrical shorts, overheating and fires ("Defect-free graphene might solve lithium-metal batteries' dendrite problem").

These examples highlight the four major energy-related areas where graphene will have an impact: solar cells, super capacitors, graphene batteries, and catalysis for fuel cells.

Due to their excellent electron-transport properties and extremely high carrier mobility, graphene and other other direct band gap monolayer materials such as transition-metal dichalcogenides (TMDCs) and black phosphorus show great potential to be used for low-cost, flexible, and highly efficient photovoltaic devices. They are the most promising materials for advanced solar cells.

An excellent review paper ("Chemical Approaches toward Graphene-Based Nanomaterials and their Applications in Energy-Related Areas") gives a brief overview of the recent research concerning chemical and thermal approaches toward the production of well-defined graphene-based nanomaterials and their applications in energy-related areas.

The authors note, however, that before graphene-based nanomaterials and devices find widespread commercial use, two important problems have to be solved: one is the preparation of graphene-based nanomaterials with well-defined structures, and the other is the controllable fabrication of these materials into functional devices.

- *Sensor applications*

Functionalized graphene holds exceptional promise for biological and chemical sensors. Already, researchers have shown that the distinctive 2D structure of graphene oxide (GO), combined with its super permeability to water molecules, leads to sensing devices with an unprecedented speed ("Ultrafast graphene sensor monitors your breath while you speak").

Scientists have found that chemical vapors change the noise spectra of graphene transistors, allowing them to perform selective gas sensing for many vapors with a single device made of pristine graphene – no functionalization of the graphene surface required ("Selective gas sensing with pristine graphene").

Quite a cool approach is to interface passive, wireless graphene Nano sensors onto biomaterials via silk bioresorption as demonstrated by a graphene Nano sensor tattoo on teeth monitors bacteria in your mouth.

Researchers also have begun to work with graphene foams – three-dimensional structures of interconnected graphene sheets with extremely high conductivity. These structures are very promising as gas sensors ("Graphene foam detects explosives, emissions better than today's gas sensors") and as biosensors to detect diseases (see for instance: "Nanotechnology biosensor to detect biomarkers for Parkinson's disease").

- *Graphene ink*

Graphene has a unique combination of properties that is ideal for next-generation electronics, including mechanical flexibility, high electrical conductivity, and chemical stability. Numerous research efforts already have demonstrated the feasibility of fabricating graphene-based electronics through high-throughput ink printing strategies. Formulating inkjet-printable graphene ink leads to an inexpensive and scalable path for exploiting graphene's properties in real-world technologies.

- *Transistors and memory*

Some of the most promising applications of graphene are in electronics (as transistors and interconnects), detectors (as sensor elements) and thermal management (as lateral heat spreaders). The first graphene field-effect transistors (FETs) – with both bottom and top gates – have already been demonstrated. At the same time, for any transistor to be useful for analog communication or digital applications, the level of the electronic low-frequency noise has to be decreased to an acceptable level ("Graphene transistors can work without much noise").

Transistors on the basis of graphene are considered to be potential successors for the some silicon components currently in use. Due to the fact that an electron can move faster through graphene than through silicon, the material shows potential to enable terahertz computing.

In the ultimate nanoscale transistor – dubbed a ballistic transistor – the electrons avoid collisions, i.e. there is a virtually unimpeded flow of current. Ballistic conduction would enable incredibly fast switching devices. Graphene has the potential to enable ballistic transistors at room temperature.

While graphene has the potential to revolutionize electronics and replace the currently used silicon materials ("High-performance graphene transistor with high room-temperature mobility"), it does have an Achilles heel: pristine graphene is semi-metallic and lacks the necessary band gap to serve as a transistor. Therefore it is necessary to engineer band gaps in graphene.

Experiments have demonstrated the benefits of graphene as a platform for flash memory which show the potential to exceed the performance of current flash memory technology by utilizing the intrinsic properties of graphene.

- *Flexible, stretchable and foldable electronics*

Flexible electronics relies on bendable substrates and truly foldable electronics requires a foldable substrate with a very stable conductor that can withstand folding (i.e. an edge in the substrate at the point of the fold, which develops creases, and the deformation remains even after unfolding).

That means that, in addition to a foldable substrate like paper, the conductor that is deposited on this substrate also needs to be foldable. To that end, researchers have demonstrated a fabrication process for foldable graphene circuits based on paper substrates.

Graphene's remarkable conductivity, strength and elasticity has also made it a promising choice for stretchable electronics – a technology that aims to produce circuits on flexible plastic substrates for applications like bendable solar cells or robotic-like artificial skin.

Scientists have devised a chemical vapor deposition (CVD) method for turning graphene sheets into porous three-dimensional foams with extremely high conductivity. By permeating this foam with a siloxane-based polymer, the researchers have produced a composite that can be twisted, stretched and bent without harming its electrical or mechanical properties ("Graphene: Foaming for stretchable electronics").

- *Photodetectors*

Researchers have demonstrated that graphene can be used for telecommunications applications and that its weak and universal optical response might be turned into advantages for ultrafast photonics applications. They also found that graphene could be potentially exploited as a saturable absorber with wide optical response ranging from ultra-violet, visible, infrared to terahertz ("The rise of graphene in ultra-fast photonics").

There is a very strong research interest in using graphene for applications in optoelectronics. Graphene-based photo detectors have been realized before and graphene's suitability for high bandwidth photo detection has been demonstrated in a 10 GBit/s optical data link ("Graphene photo detectors for high-speed optical communications").

One novel approach is based on the integration of graphene into an optical micro cavity. The increased electric field amplitude inside the cavity causes more energy to be absorbed, leading to a significant increase of the photo response ("Micro cavity vastly enhances photo response of graphene photo detectors").

- *Coatings*

Coating objects with graphene can serve different purposes. For instance, researchers have now shown that it is possible to use graphene sheets to create a superhydrophobic coating material that shows stable superhydrophobicity under both static as well as dynamic (droplet impact) conditions, thereby forming extremely water repelling structures.

8. Looking towards the future

Is all of this hype justified? Graphene's properties are truly remarkable and versatile, but there are still some challenges that need to be addressed before the material enters consumers' lives. The rate of progress that graphene-based technology can hope to achieve is directly tied to manufacturing. Some applications require single-layer graphene with as few impurities as possible, but right now, the most effective methods (mechanical exfoliation and chemical vapor deposition) are not cost-effective enough yet to be suitable for production at scale. However, manufacturing of graphene flakes (few-layer or multi-layer) has started to get off the ground, which means less demanding applications could soon bring their graphene-based products to the market in increasing numbers.

Although it's been fifteen years since graphene was first isolated, the material is still in its 'baby years'. Most of the components in your smartphone, from the microprocessor to touchscreen, were first invented in the 1960s or prior to that time but it took many decades before the technology was mature enough to transition into the consumer market. In many respects, graphene research is growing at an astonishing rate with respect to other novel materials. For instance, there are now nearly 60,000 graphene-related patents, half of which were filed in the last three years.

Investments in graphene R&D are also riding an exponential curve. For instance, the European Commission has launched the Graphene Flagship initiative, which aims to bring together "academic and industrial researchers to take graphene from the realm of academic laboratories into European society in the space of 10 years." With a budget of €1 billion, the consortium consists of over 150 academic and industrial research groups in 23 countries.

Although graphene is still way ahead of its time, there are reasons to believe that it won't be very long before almost every industry is disrupted by it.

We should all be very excited about a future spearheaded by graphene.

9. Appendix

1. https://www.nanowerk.com/what_is_graphene.php [1]
2. https://www.lindau-nobel.org/blog-the-wonder-material-graphene/ [2]
3. https://www.graphene-info.com/graphene-introduction
4. https://www.theneweconomy.com/energy/graphene-is-the-new-wonder-material-transforming-the-energy-sector
5. https://www.techinstro.com/role-of-graphene-in-future-applications/
6. ISI essays: the reduction of graphene oxide
7. ISI essays: the graphene-based coating and healing materials

[1] By Michael Berger – Michael is author of three books by the Royal Society of Chemistry:
Nano-Society: Pushing the Boundaries of Technology,
Nanotechnology: The Future is Tiny, and
Nanoengineering: The Skills and Tools Making Technology Invisible

[2] Additional information: Graphene will be the main topic during a Science Breakfast at the 69th Lindau Nobel Laureate Meeting; this programme session will be hosted by the Graphene Flagship, Europe's biggest ever research initiative.