

Graphene

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Abstract: Graphene is an allotrope form of carbon consisting of a single layer of carbon atoms arranged in a hexagonal lattice. It is a semimetal with small overlap between the valence and the conduction bands. There are many other allotropes of carbon, such as graphite, diamond, charcoal, carbon nanotubes and fullerenes. The graphene can be considered as an indefinitely large aromatic molecule, the ultimate case of the family of flat polycyclic aromatic hydrocarbons. Graphene is the strongest, thinnest material as we know now, and it can conduct electricity and heat better than anything else, and also one of the most pliable. Only a single atom thick, it has been called the wonder material. This article introduces recent research reports as references in the related studies.

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Introduction

Graphene is an allotrope form of carbon consisting of a single layer of carbon atoms arranged in a hexagonal lattice. It is a semimetal with small overlap between the valence and the conduction bands. There are many other allotropes of carbon, such as graphite, diamond, charcoal, carbon nanotubes and fullerenes. The graphene can be considered as an indefinitely large aromatic molecule, the ultimate case of the family of flat polycyclic aromatic hydrocarbons. Graphene is the strongest, thinnest material as we know now, and it can conduct electricity and heat better than anything else, and also one of the most pliable. Only a single atom thick, it has been called the wonder material.

The following introduces recent reports as references in the related studies.

Carbon is a chemical element with symbol C and atomic number 6. It is nonmetallic and tetravalent — making 4 electrons available to form covalent chemical bonds. It belongs to group 14 of the periodic table. Three isotopes occur naturally, ^{12}C and ^{13}C being stable, while ^{14}C is a radionuclide, decaying with a half-life of about 5,730 years. Carbon is one of the few elements known since antiquity.

Carbon is the 15th most abundant element in the Earth's crust, and the 4th most abundant element in the universe by mass after hydrogen, helium, and oxygen. Carbon's abundance, its unique diversity of organic compounds, and its unusual ability to form polymers at the temperatures commonly encountered on Earth enables this element to serve as a common element of all known life. It is the second most abundant element in the human body by mass (about 18.5%) after oxygen.

The atoms of carbon can bond together in different ways, termed allotropes of carbon. The best

known are graphite, diamond, amorphous carbon and graphene. The physical properties of carbon vary widely with the allotropic form. For example, graphite is opaque and black while diamond is highly transparent. Graphite is soft enough to form a streak on paper, while diamond is one of the hardest naturally occurring materials known. Graphite is a good electrical conductor while diamond has a low electrical conductivity. Under normal conditions, diamond, carbon nanotubes, and graphene have the highest thermal conductivities of all known materials. All carbon allotropes are solids under normal conditions, with graphite being the most thermodynamically stable form at standard temperature and pressure. They are chemically resistant and require high temperature to react even with oxygen. The most common oxidation state of carbon in inorganic compounds is +4, while +2 is found in carbon monoxide and transition metal carbonyl complexes. The largest sources of inorganic carbon are limestones, dolomites and carbon dioxide, but significant quantities occur in organic deposits of coal, peat, oil, and methane clathrates. Carbon forms a vast number of compounds.

Graphene has many uncommon properties. It is the strongest material ever tested, conducts heat and electricity efficiently, and is nearly transparent. Graphene shows a large and nonlinear diamagnetism, greater than that of graphite, and can be levitated by neodymium magnets. It had been produced unintentionally in small quantities for centuries through the use of pencils and other similar graphite applications. It was observed originally in electron microscopes in 1962, but only was studied while supported on metal surfaces. The graphene was later rediscovered, isolated, and characterized in 2004 by Andre Geim and Konstantin Novoselov at the University of Manchester. This work resulted in the

two winning the Nobel Prize in Physics in 2010 for groundbreaking experiments regarding the two-dimensional material graphene.

Graphene is a combination of graphite and the suffix -ene, named by Hanns-Peter Boehm and colleagues, who produced and observed single-layer carbon foils in 1962. Boehm et al. introduced the term graphene in 1986 to describe single sheets of graphite. Graphene can be considered an infinite alternant polycyclic aromatic hydrocarbon. Graphene is a crystalline allotrope of carbon with 2-dimensional properties. Its carbon atoms are packed densely in a regular atomic-scale chicken wire (hexagonal) pattern. Each atom has 4 bonds: one σ bond with each of its 3 neighbors and 1 π -bond that is oriented out of plane. The atoms are about 1.42 Å apart. Graphene's hexagonal lattice can be regarded as two interleaving triangular lattices. This perspective was successfully used to calculate the band structure for a single graphite layer using a tight-binding approximation. Graphene's stability is due to its tightly packed carbon atoms and a sp^2 orbital hybridization – a combination of orbitals s , p_x and p_y that constitute the σ -bond. The final p_z electron makes up the π -bond. The π -bonds hybridize together to form the π -band and π^* -bands. These bands are responsible for most of graphene's notable electronic properties, via the half-filled band that permits free-moving electrons.

Graphene sheets in solid form usually show evidence in diffraction for graphite's layering. This is true of some single-walled nanostructures. However, unlayered graphene with only rings has been found in the core of presolar graphite onions. TEM studies show faceting at defects in flat graphene sheets and suggest a role for 2-dimensional crystallization from a melt. Graphene can self-repair holes in its sheets when exposed to molecules containing carbon, such as hydrocarbons. Bombarded with pure carbon atoms, the atoms perfectly align into hexagons, completely filling the holes. The atomic structure of isolated, single-layer graphene is studied by TEM on sheets of graphene suspended between bars of a metallic grid. Electron diffraction patterns showed the expected honeycomb lattice. Suspended graphene showed rippling of the flat sheet, with amplitude of about one nanometer. These ripples may be intrinsic to the material as a result of the instability of two-dimensional crystals, or may originate from the ubiquitous dirt seen in all TEM images of graphene. Atomic resolution real-space images of isolated, single-layer graphene on SiO_2 substrates are available via scanning tunneling microscopy (STM). Photoresist residue, which must be removed to obtain atomic-resolution images, may be the adsorbates observed in TEM images, and may explain the observed rippling. Rippling on SiO_2 is caused by conformation of graphene to the underlying

SiO_2 and is not intrinsic.

Analogs (artificial graphene) are two-dimensional systems that exhibit similar properties to graphene. Analogs can be systems in which the physics is easier to observe and to manipulate. In those systems, electrons are not always the chosen particles—they might be optical photons, microwave photons, plasmons, microcavity polaritons or even atoms. Also, the honeycomb structure in which those particles evolve can be of a different nature than carbon atoms in graphene. It can be, respectively, a photonic crystal, an array of metallic rods, metallic nanoparticles, a lattice of coupled microcavities or an optical lattice.

Graphene is a zero-gap semiconductor, because its conduction and valence bands meet at the Dirac points, which are six locations in momentum space, on the edge of the Brillouin zone, divided into two non-equivalent sets of 3 points. The 2 sets are labeled K and K'. The sets give graphene a valley degeneracy of $g_v = 2$. By contrast, for traditional semiconductors the primary point of interest is generally Γ , where momentum is zero. However, if the in-plane direction is confined, in which case it is referred to as a nanoribbon, its electronic structure is different. If it is zig-zag, the bandgap is zero. If it is armchair, the bandgap is non-zero. The corresponding resistivity of graphene sheets is less than the resistivity of silver, the lowest otherwise known at room temperature. However, on SiO_2 substrates, scattering of electrons by optical phonons of the substrate is a larger effect than scattering by graphene's own phonons. Superconductivity has been observed in twisted bilayer graphene.

Graphene's unique optical properties produce an unexpectedly high opacity for an atomic monolayer in vacuum, absorbing $\pi\alpha \approx 2.3\%$ of red light, where α is the fine-structure constant. This is a consequence of the unusual low-energy electronic structure of monolayer graphene that features electron and hole conical bands meeting each other at the Dirac point which is qualitatively different from more common quadratic massive bands. Based on the Slonczewski–Weiss–McClure (SWMcC) band model of graphite, the interatomic distance, hopping value and frequency cancel when optical conductance is calculated using Fresnel equations in the thin-film limit. Although confirmed experimentally, the measurement is not precise enough to improve on other techniques for determining the fine-structure constant.

Multi-parametric surface plasmon resonance was used to characterize both thickness and refractive index of chemical-vapor-deposition (CVD)-grown graphene films. The measured refractive index and extinction coefficient values at 670 nm wavelength are 3.135 and 0.897, respectively. The thickness was

determined as 3.7 Å from a 0.5 mm area, which agrees with 3.35 Å reported for layer-to-layer carbon atom distance of graphite crystals.

The method can be used for real-time label-free interactions of graphene with organic and inorganic substances. The existence of unidirectional surface plasmons in the nonreciprocal graphene-based gyrotropic interfaces has been demonstrated theoretically. By efficiently controlling the chemical potential of graphene, the unidirectional working frequency can be continuously tunable from THz to near-infrared and even visible. Particularly, the unidirectional frequency bandwidth can be 1–2 orders of magnitude larger than that in metal under the same magnetic field, which arises from the superiority of extremely small effective electron mass in graphene.

The optical response of graphene nanoribbons is tunable into the terahertz regime by an applied magnetic field. Graphene/graphene oxide systems exhibit electrochromic behavior, allowing tuning of both linear and ultrafast optical properties. Such unique absorption could become saturated when the input optical intensity is above a threshold value. This nonlinear optical behavior is termed saturable absorption and the threshold value is called the saturation fluence. Graphene can be saturated readily under strong excitation over the visible to near-infrared region, due to the universal optical absorption and zero band gap. This has relevance for the mode locking of fiber lasers, where fullband mode locking has been achieved by a graphene-based saturable absorber. Due to this special property, graphene has wide application in ultrafast photonics. The optical response of graphene/graphene oxide layers can be tuned electrically. Saturable absorption in graphene could occur at the Microwave and Terahertz bands, owing to its wideband optical absorption property. The microwave saturable absorption in graphene demonstrates the possibility of graphene microwave and terahertz photonics devices, such as a microwave saturable absorber, modulator, polarizer, microwave signal processing and broad-band wireless access networks. Under more intensive laser illumination, graphene could possess a nonlinear phase shift due to the optical nonlinear Kerr effect.

Several techniques can prepare nanostructured graphene, e.g., graphene quantum dots (GQDs); these techniques mainly include electron beam lithography, chemical synthesis, electrochemical preparation, graphene oxide (GO) reduction, C60 catalytic transformation, the microwave assisted hydrothermal method (MAH), the Soft-Template method, the hydrothermal method, and the ultrasonic exfoliation method. Thermal transport in graphene is an active area of research which has attracted attention because of the potential for thermal management applications.

It has been suggested that the isotopic composition, the ratio of ^{12}C to ^{13}C , has a significant impact on thermal conductivity. For example, isotopically pure ^{12}C graphene has higher thermal conductivity than either a 50:50 isotope ratio or the naturally occurring 99:1 ratio. It can be shown by using the Wiedemann–Franz law, that the thermal conduction is phonon-dominated. However, for a gated graphene strip, an applied gate bias causing a Fermi energy shift much larger than $k_{\text{B}}T$ can cause the electronic contribution to increase and dominate over the phonon contribution at low temperatures. The ballistic thermal conductance of graphene is isotropic.

Despite its 2-D nature, graphene has 3 acoustic phonon modes. The two in-plane modes (LA, TA) have a linear dispersion relation, while the out of plane mode (ZA) has a quadratic dispersion relation. Due to this, the T^2 dependent thermal conductivity contribution of the linear modes is dominated at low temperatures by the $T^{1.5}$ contribution of the out-of-plane mode. Some graphene phonon bands display negative Grüneisen parameters (GPs). At low temperatures (where most optical modes with positive GPs are still not excited) the contribution from the negative GPs will be dominant and thermal expansion coefficient (which is directly proportional to GPs) negative. The lowest negative GPs correspond to the lowest transverse acoustic ZA modes. Phonon frequencies for such modes increase with the in-plane lattice parameter since atoms in the layer upon stretching will be less free to move in the z direction. This is similar to the behavior of a stretched string that has vibrations of smaller amplitude and higher frequency. This phenomenon, named membrane effect, was predicted by Lifshitz in 1952.

A prediction that was published in 2015 suggested a melting point of ≈ 4125 K. Recent and more sophisticated modelling has increased this temperature to at least 5000 K. At 6000 K (the sun's surface having an effective temperature of 5,777 K) graphene melts into an agglomeration of loosely coupled doubled bonded chains, before becoming a gas. Large-angle-bent graphene monolayer has been achieved with negligible strain, showing mechanical robustness of the two-dimensional carbon nanostructure. Even with extreme deformation, excellent carrier mobility in monolayer graphene can be preserved.

As is true of all materials, regions of graphene are subject to thermal and quantum fluctuations in relative displacement. Although the amplitude of these fluctuations is bounded in 3D structures (even in the limit of infinite size), the Mermin–Wagner theorem shows that the amplitude of long-wavelength fluctuations grows logarithmically with the scale of a 2D structure and would therefore be unbounded in

structures of infinite size. Local deformation and elastic strain are negligibly affected by this long-range divergence in relative displacement. It is believed that a sufficiently large 2D structure, in the absence of applied lateral tension, will bend and crumple to form a fluctuating 3D structure. Ripples have been observed in suspended layers of graphene. It has been proposed that the ripples are caused by thermal fluctuations in the material. As a consequence of these dynamical deformations, it is debatable whether graphene is truly a 2D structure. In 2014 it was shown that these ripples, if amplified through the introduction of vacancy defects, can impart a negative Poisson's ratio into graphene, resulting in the thinnest auxetic material known. Graphene nanosheets can be incorporated into a nickel matrix through a plating process to form Ni-graphene composites on a target substrate. The enhancement in mechanical properties of the composites is attributed to the high interaction between Ni and graphene and the prevention of the dislocation sliding in the Ni matrix by the graphene.

In 2011 graphene was shown to accelerate the osteogenic differentiation of human mesenchymal stem cells without the use of biochemical inducers. In 2015 graphene was used to create biosensors with epitaxial graphene on silicon carbide. The sensors bind to 8-hydroxydeoxyguanosine (8-OHdG) and is capable of selective binding with antibodies. The presence of 8-OHdG in blood, urine and saliva is commonly associated with DNA damage. Elevated levels of 8-OHdG have been linked to increased risk of several cancers. A commercial version of a graphene biosensor has been used as a protein binding sensor platform. In 2016 uncoated graphene was shown to serve as a neuro-interface electrode without altering or damaging properties such as signal strength or formation of scar tissue. Graphene electrodes in the body stay significantly more stable than electrodes of tungsten or silicon because of properties such as flexibility, bio-compatibility and conductivity. A production unit produces continuous monolayer sheets of High Strength Metallurgical Graphene (HSMG). The process is based on graphene growth on a liquid metal matrix.

Bilayer graphene displays the anomalous quantum Hall effect, a tunable band gap and potential for excitonic condensation. Bilayer graphene typically can be found either in twisted configurations where the two layers are rotated relative to each other or graphitic Bernal stacked configurations where half the atoms in one layer lie atop half the atoms in the other. Stacking order and orientation govern its optical and electronic properties. One synthesis method is chemical vapor deposition, which can produce large bilayer regions that almost exclusively conform to a Bernal stack geometry. Superconductivity has been

observed in twisted bilayer graphene. Graphene nanoribbons, at low temperatures, show spin-polarized metallic edge currents, which suggest spintronics applications.

In 2013, a three-dimensional honeycomb of hexagonally arranged carbon was termed 3D graphene. Self-supporting 3D graphene was produced that year. Three dimensional bilayer graphene was reported in 2012 and 2014. In 2016, a box-shaped graphene (BSG) nanostructure resulted from mechanical cleavage of pyrolytic graphite has been reported. The discovered nanostructure is a multilayer system of parallel hollow nanochannels located along the surface that displayed quadrangular cross-section. The thickness of the channel walls is approximately equal to 1 nm, the typical width of channel facets makes about 25 nm. In 2017, freestanding graphene gyroids with 35 nm and 60 nm unit cells were fabricated via controlled direct chemical vapor deposition. They represent the smallest free standing periodic graphene 3D structures yet produced with a pore size of tens of nm. A graphene gyroid has five percent of the density of steel, yet is ten times as strong with an enormous surface area to volume ratio. An aerogel made of graphene layers separated by carbon nanotubes was measured at 0.16 milligrams per cubic centimeter. The material has superior elasticity and absorption: it can recover completely after more than 90% compression, and absorb up to 900 times its weight in oil, at a rate of 68.8 grams per second. Multiple production techniques have been developed. Isolated 2D crystals cannot be grown via chemical synthesis beyond small sizes even in principle, because the rapid growth of phonon density with increasing lateral size forces 2D crystallites to bend into the third dimension. In all cases, graphene must bond to a substrate to retain its two-dimensional shape.

As of 2014, exfoliation produced graphene with the lowest number of defects and highest electron mobility. Geim and Novoselov initially used adhesive tape to pull graphene sheets away from graphite. Achieving single layers typically requires multiple exfoliation steps. After exfoliation the flakes are deposited on a silicon wafer. Alternatively a sharp single-crystal diamond wedge cleave layers from a graphite source. Another method is reduction of graphite oxide monolayer films, e.g. by hydrazine with annealing in argon/hydrogen with an almost intact carbon framework that allows efficient removal of functional groups. Measured charge carrier mobility exceeded 1,000 centimetres (393.70 in)/Vs. Burning a graphite oxide coated DVD produced a conductive graphene film (1738 siemens per meter) and specific surface area (1520 square meters per gram) that was highly resistant and malleable. Dispersing graphite in a liquid medium can produce graphene by sonication

followed by centrifugation. The addition of dispersants (e.g., graphene quantum dots) can facilitate the exfoliation process, forming aqueous graphene dispersion with high yield. Such process is straightforward, low-cost, and environmentally friendly. Sonicating graphite at the interface of two immiscible liquids, most notably heptane and water, produced macro-scale graphene films. Graphite particles can be corroded in molten salts to form a variety of carbon nanostructures including graphene. Electrochemical synthesis can exfoliate graphene. Varying a pulsed voltage controls thickness, flake area, number of defects and affects its properties. The process begins by bathing the graphite in a solvent for intercalation. The process can be tracked by monitoring the solution's transparency with an LED and photodiode. Graphene has been prepared by using a sugar (e.g. glucose, sugar, fructose, etc.) This substrate-free bottom-up synthesis is safer, simpler and more environmentally friendly than exfoliation. The method can control thickness, ranging from monolayer to multilayers, which is known as Tang-Lau Method.

Epitaxial graphene may be coupled to surfaces weakly enough (by Van der Waals forces) to retain the two dimensional electronic band structure of isolated graphene. A normal silicon wafer coated with a layer of germanium (Ge) dipped in dilute hydrofluoric acid strips the naturally forming germanium oxide groups, creating hydrogen-terminated germanium. CVD can coat that with graphene. A two-step CVD process is shown to grow graphene directly on TiO₂ crystals or exfoliated TiO₂ nanosheets without using a metal catalyst. The atomic structure of metal substrates including ruthenium, iridium, nickel and copper has been used as substrates for graphene production. Commercial copper foils have been used for graphene production, reducing substrate costs by 100-fold. Gaseous catalyst-assisted CVD paves the way for synthesizing high-quality graphene for device applications while avoiding the transfer process. Gram quantities were produced by the reduction of ethanol by sodium metal, followed by pyrolysis and washing with water. Growing graphene in an industrial resistive-heating cold wall CVD system was claimed to produce graphene 100 times faster than conventional CVD systems, cut costs by 99% and produce material with enhanced electronic qualities. Experiments with precise control of process parameters during cold wall CVD provided conclusive insight into the classical surface-mediated two dimensional nucleation and growth mechanism of graphene grown using catalytic CVD under conditions sought out in the semiconductor industry.

In applications where the thickness and packing density of the graphene layer need to be carefully controlled, the Langmuir-Blodgett method has been

used to produce single layer films of graphene and graphene oxide which can then be reduced to graphene. Some of the benefits of Langmuir-Blodgett deposition include accurate control over the layered architecture of the graphene, that the layer-by-layer deposition process allows assembling any combination of thin carbon layers on a substrates, and that the assembly process is performed at room temperature and produces greater throughputs while being amenable to automation and mass production. Graphene is the only form of carbon (or solid material) in which every atom is available for chemical reaction from two sides (due to the 2D structure). Atoms at the edges of a graphene sheet have special chemical reactivity. Graphene has the highest ratio of edge atoms of any allotrope. Defects within a sheet increase its chemical reactivity. The onset temperature of reaction between the basal plane of single-layer graphene and oxygen gas is below 260 °C (530 K). Graphene combusts at 350 °C (620 K). Graphene is commonly modified with oxygen- and nitrogen-containing functional groups and analyzed by infrared spectroscopy and X-ray photoelectron spectroscopy. However, determination of structures of graphene with oxygen- and nitrogen-functional groups requires the structures to be well controlled.

Contrary to the ideal 2D structure of graphene, chemical applications of graphene need either structural or chemical irregularities, as perfectly flat graphene is chemically inert. In other words, the definition of an ideal graphene is different in chemistry and physics. Graphene placed on a soda-lime glass (SLG) substrate under ambient conditions exhibited spontaneous n-doping ($1.33 \times 10^{13} \text{ e/cm}^2$) via surface-transfer. On p-type copper indium gallium diselenide (CIGS) semiconductor itself deposited on SLG n-doping reached $2.11 \times 10^{13} \text{ e/cm}^2$. Various graphene derivatives, e.g., cyanographene and graphene acid, can be prepared via elegant chemistry of fluorographene. Cyanographene and graphene acid have high degree of functionalization (~15%), open band gap and are hydrophilic providing stable colloids in water.

Graphene is a transparent and flexible conductor that holds promise for various material/device applications, including solar cells, light-emitting diodes (LED), touch panels and smart windows or phones. Graphene has also been used in other fundamental electronic devices, such as capacitors and Field Effect Transistors (FETs), in which it can act as an atomically thin channel. In the same framework, fluorine-doped graphene has shown to have insulating properties and it can be used as a passivation layer in graphene FETs, leading to a substantial increase in carrier mobility. Other early commercial uses of graphene include fillers such as a graphene-infused

printer powder.

Graphene supercapacitors serve as energy storage alternative to traditional electrolytic batteries. Among advantages are fast charging, long life span and environmentally friendly production. Graphene supercapacitors produced by Skeleton Technologies have been commercially available since around 2015 and were first used in some specialized applications instead of traditional batteries. By 2017, commercial graphene supercapacitor units were available for industrial power applications, with maximal power output of 1500 kW. In 2016, Adgero announced a regenerative braking system (KERS) for large trucks that employed a graphene-based supercapacitor.

A joint effort from the University of Pennsylvania, Shanghai Institute of Ceramics, Queensland University of Technology, and Rice University has led to the development of carbon nanotube supercapacitors that can offer three times the energy density of most carbon-based nanomaterials. The scientists on this team utilized silicon and graphene to develop carbon nanotubes 4-6 nm wide and then doped the carbon atoms with nitrogen. This process causes a chemical reaction which allows the material to store up to three times more energy without compromising their power density. Fuqiang Huang, a researcher on this project, reports that the fabricated carbon nanotube integrated supercapacitors are able to store up to 41 Wh/kg of energy; for comparison, an average lead acid battery has an energy density of 33 - 42 Wh/kg. Additionally, the supercapacitors offer a substantially higher power density of 70 - 250 Wh/kg compared to average lead acid battery which is capable of 2 - 1 Wh/kg. This breakthrough demonstrates that supercapacitors can provide a performance that matches, and even supersedes, of conventional energy storage methods. To put this achievement into perspective, a materials scientist from University of Pennsylvania, I-Wei Chen, stated that the implementation of these supercapacitors would allow an average bus to make 25 km trips with a recharge time of only 30 seconds.

In 2016, Henrik Fisker announced development of an electric car that will use graphene supercapacitor instead of lithium-ion batteries.¹ Its low energy density as compared to lithium-ion batteries is being addressed. The planned electric car would target a minimum range of 400 miles (640 km). It has been announced later that the electric car produced by Fisker Inc. will still use lithium-ion batteries, but research in graphene supercapacitors will continue by Nanotech Energy Inc. BAC's 2016 Mono model is said to be made out of graphene as a first of both a street-legal track car and a production car. The first company to use graphene-made structural parts on a production model was Spania GTA, which unveiled a version of its Spano

supercar fitted with graphene in 2015. The global market for graphene reached \$9 million by 2012 with most sales in the semiconductor, electronics, battery, energy storage or conversion, and composites industries.

The toxicity of graphene has been extensively debated. A review on graphene toxicity summarized the *in vitro*, *in vivo*, antimicrobial and environmental effects and highlights the various mechanisms of graphene toxicity. Nanotubes of graphene could reproduce the effects of asbestosis. The toxicity of graphene depends on its shape, size, purity, post-production processing steps, oxidative state, functional groups, dispersion state, synthesis methods, route, dose of administration, and exposure times. Graphene nanoribbons, graphene nanoplatelets, and graphene nano-onions are non-toxic at concentrations up to 50 µg/ml. These nanoparticles do not alter the differentiation of human bone marrow stem cells towards osteoblasts (bone) or adipocytes (fat) suggesting that at low doses graphene nanoparticles are safe for biomedical applications. 10 µm few-layered graphene flakes were able to pierce cell membranes in solution. They were observed to enter initially via sharp and jagged points, allowing graphene to enter the cell. The physiological effects of this remain uncertain, and this remains a relatively unexplored field.

A lump of graphite, a graphene transistor, and a tape dispenser, a tool that was used for the exfoliation of single-layer graphene from graphite in 2004. Donated to the Nobel Museum in Stockholm by Andre Geim and Konstantin Novoselov in 2010. The theory of graphene was first explored by Wallace in 1947 as a starting point for understanding the electronic properties of 3D graphite. The emergent massless Dirac equation was first pointed out by Semenoff, DiVincenzo and Mele. The earliest TEM images of few-layer graphite were published by Ruess and Vogt in 1948. An early, detailed study on few-layer graphite dates to 1962 when Boehm and colleagues reported producing monolayer flakes of reduced graphene oxide. Efforts to make thin films of graphite by mechanical exfoliation started in 1990, but nothing thinner than 50 to 100 layers was produced before 2004. Initial attempts to make atomically thin graphitic films employed exfoliation techniques similar to the drawing method. Multilayer samples down to 10 nm in thickness were obtained.

One of the first patents pertaining to the production of graphene was filed in October 2002 and granted in 2006. Two years later, in 2004 Geim and Novoselov extracted single-atom-thick crystallites from bulk graphite and transferred them onto thin silicon dioxide (SiO₂) on a silicon wafer, which electrically isolated the graphene. The cleavage

technique led directly to the first observation of the anomalous quantum Hall effect in graphene, which provided direct evidence of graphene's theoretically predicted Berry's phase of massless Dirac fermions. The effect was reported by Geim's group and by Kim and Zhang, whose papers appeared in *Nature* in 2005. Geim and Novoselov received awards for their pioneering research on graphene, notably the 2010 Nobel Prize in Physics. In 2013, the European Commission funded the large-scale research project Graphene Flagship with a total budget of €1 billion, involving 150 partner organizations. Commercialization of graphene proceeded rapidly once commercial scale production was demonstrated. By 2017, 13 years after creation of the first laboratory graphene electronic device, an integrated graphene electronics chip was produced commercially and marketed to pharmaceutical researchers by Nanomedical Diagnostics in San Diego.

In Aamir's study (Aamir, M. A., et al., 2018), the combination of a field-tunable band gap, topological edge states, and valleys in the band structure makes insulating bilayer graphene a unique localized system, where the scaling laws of dimensionless conductance g remain largely unexplored. They showed that the relative fluctuations in $\ln g$ with the varying chemical potential, in strongly insulating bilayer graphene (BLG), decay nearly logarithmically for a channel length up to L/ξ approximately 20, where ξ is the localization length. This "marginal" self-averaging, and the corresponding dependence of $\ln g$ on L , suggests that transport in strongly gapped BLG occurs along strictly one-dimensional channels, where ξ approximately $0.5 \pm 0.1 \mu\text{m}$ was found to be much longer than that expected from the bulk band gap. Their experiment revealed a nontrivial localization mechanism in gapped BLG, governed by transport along robust edge modes.

In Al-Shahrani's recent study (Al-Shahrani, D., et al., 2018). Lignin's immiscibility with most polymers along with its unknown association behaviors are major factors that contribute to its disposal and processability for the production of materials. To fully utilize lignin, an improved understanding of its interaction with other materials is needed. In this study, they investigated the morphological and physicochemical properties upon the addition of reduced graphene oxide (rGO) as a function of material composition in a tertiary system comprised of lignin, cellulose and xylan. The main motivation for this work is to understand how the lignin molecule associates and behaves in the presence of other natural macromolecules, as well as with the addition of reduced graphene oxide. The fabricated biocomposites with and without rGO were investigated using Attenuated Total Reflectance

Fourier Transform Infrared spectroscopy (ATR-FTIR), Scanning Electron Microscope (SEM) techniques, Thermogravimetric Analysis (TGA), and Differential Scanning Calorimetry (DSC). The results demonstrated that the regenerated films' structural, morphological and thermal character changed as a function of lignin-xylan concentration and upon the addition of rGO. They also observed a dramatic change in the glass transition temperature and topography. Final analysis showed that the addition of rGO prevented the macromolecules to self-assemble through a reduction of pi-pi aggregations and changes in the cellulose crystallinity.

In Adeel's study (Adeel, M., et al., 2018). Graphene-based nanomaterials have gained high research interest in different fields related to proteins and thus are rapidly becoming the most widely investigated carbon-based materials. Their exceptional physicochemical properties such as electrical, optical, thermal and mechanical strength enable graphene to render graphene-based nanostructured materials suitable for applications in different fields such as electroanalytical chemistry, electrochemical sensors and immobilization of biomolecules and enzymes. The structural feature of oxygenated graphene, i.e., graphene oxide (GO) covered with different functionalities such as epoxy, hydroxyl, and carboxylic group, open a new direction of chemical modification of GO with desired properties. This review describes the recent progress related to the structural geometry, physicochemical characteristics, and functionalization of GO, and the development of graphene-based novel carriers as host for enzyme immobilization. Graphene derivatives-based applications are progressively increasing, in recent years. Therefore, from the bio-catalysis and biotransformation viewpoint, the biotechnological perspective of graphene-immobilized nano-bio-catalysts is of supreme interest. The structural geometry, unique properties, and functionalization of graphene derivatives and graphene-based nanomaterials as host for enzyme immobilization are highlighted in this review. Also, the role of GO-based catalytic systems such as microfluidic bio-catalysis, enzyme-based biofuel cells, and biosensors are also discussed with potential future perspectives of these multifaceted materials.

Choi's studies (Choi et al, 2018) showed that soft bioelectronic devices provided new opportunities for next-generation implantable devices owing to their soft mechanical nature that leads to minimal tissue damages and immune responses. However, a soft form of the implantable optoelectronic device for optical sensing and retinal stimulation has not been developed yet because of the bulkiness and rigidity of conventional imaging modules and their composing

materials. They described a high-density and hemispherically curved image sensor array that leverages the atomically thin MoS₂-grapheneheterostructure and strain-releasing device designs. The hemispherically curved image sensor array exhibits infrared blindness and successfully acquires pixelated optical signals. They corroborated the validity of the proposed soft materials and ultrathin device designs through theoretical modeling and finite element analysis. Then, they proposed the ultrathin hemispherically curved image sensor array as a promising imaging element in the soft retinal implant. The CurvIS array was applied as a human eye-inspired soft implantable optoelectronic device that can detect optical signals and apply programmed electrical stimulation to optic nerves with minimum mechanical side effects to the retina.

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1/21/2019