Graphene: The two-dimensional carbon nanomaterial

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ABSTRACT

Graphene, the name is given to the two-dimensional sheet of sp^2-hybridized carbon. Its extended honeycomb network is the basic building block of other important carbon allotropes; it can be stacked to form 3D graphite, rolled to form 1D carbon nanotubes, and wrapped to form 0D fullerenes. Therefore, graphene is called the mother of all graphitic carbon based nanomaterials. This review article summarizes the various aspects of graphene which includes synthesis, some of its amazing properties and its various applications ranging from sensors to energy storage devices.
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INTRODUCTION

Since the discovery of fullerene (C_{60}) in 1985 by Smalley and his co-workers, several novel carbon nanomaterials have been isolated[1]. In 1991, carbon nanotube (CNT) was discovered by Iijima[2], while graphene, a two dimensional form of graphite was isolated in 2004 by Geim and Novoselov of Manchester University, United Kingdom[3]. Graphene has become a new super-material due to its unique physical properties. This new kind of two dimensional carbon nanostructure has attracted tremendous attention both from fundamental and applied research point of view in physics, chemistry as well as materials science. It has high specific surface area, high chemical stability, high optical transmittance, high elasticity, high porosity, biocompatibility, tunable band gap and ease of chemical functionalization which actually helps in tuning its properties[4,5]. Graphene exhibits many exciting properties such as half-integer room-temperature quantum

Hall effect[6], long-range ballistic transport with almost ten times greater electron mobility than of silicon (Si), availability of charge carriers that behave as massless relativistic quasi particle (Dirac fermions)[7] and quantum confinement giving rise to finite band gap and Coulomb blockade effect. TABLE 1 illustrates some of the amazing physical properties of graphene.

Graphene is a flat single sheet from graphite, has the ideal two-dimensional (2D) structure with a monolayer of carbon atoms packed into a honeycomb crystal plane. Graphene is considered as the fundamental building block for graphitic materials of all other dimensions. It can be wrapped up into zero dimensional (0D) fullerenes, rolled into one dimensional (1D) nanotubes and stacked into three dimensional (3D) graphite. Therefore, graphene is called the mother of all graphitic carbon based nanomaterials.

The discovery of graphene or two-dimensional (2D) form of graphite in early 2000 has quickly grabbed the attention of physicists and engineers, who hope that it

might compete with silicon to be the material of choice for certain applications in electronics in the near future. Graphene exhibits amazing physical and electronic properties. The outstanding electronic property is crucial for many device applications and it is expected that graphene could eventually replace silicon (Si) as the substance for computer chips, offering the prospect of ultra-fast computers/quantum computers operating at terahertz speeds.

Graphene was experimentally discovered accidentally and unexpectedly by Geim and Novoselov of Manchester University in United Kingdom in the year 2004[3]. They were awarded Nobel prize in physics in the year 2010 for their ground breaking experiment on the discovery of graphene. Mechanically exfoliated single-layer graphene was developed using a technique called micromechanical cleavage. Typically, a cellophane tape is used to peel off graphene layers from a graphite flake, followed by pressing the tape against a substrate. Upon removing the tape, a single sheet of graphene is obtained. This is also called "Scotch tape" or "Peel-off" method.

The aim of this paper is to provide updated overview of graphene in terms of synthesis, some of the amazing properties and applications. Due to the space limitations, a complete review of all recent work on this important nanomaterial is not possible. However, only a few representative examples have been summarized. In this comprehensive review article, special attention has been paid on the potential use of graphene as energy storage devices such as hydrogen storage and supercapacitors.

SYNTHESIS OF GRAPHENE

Though in 2004, Novoselov and Geim extracted graphene by micromechanical cleavage of highly oriented pyrolytic graphite (Scotch-tape method) in small yield, the next seven to eight years have witnessed several different methods for the production of graphene. However, the low throughput of the mechanical exfoliation method largely limits its applications for mass production. Therefore, alternative methods involving a high yield of graphene are highly desirable.
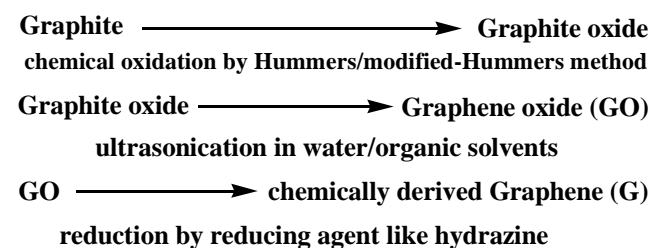
The various methods which have been reported in the literature so far to synthesize graphene sheets include micromechanical cleavage of graphite[3], unzipping of carbon nanotubes[8,9], chemical exfoliation of graphite[10], solvothermal synthesis[11], epitaxial growth on silicon carbide (SiC) surfaces and metal surfaces[12,13], chemical vapour deposition (CVD) of hydrocarbons on metal surfaces[14], bottom-up organic synthesis[15] and the reduction of graphene oxide obtained from graphite oxide by a variety of reducing agents[16-20]. The last mentioned protocol yields only chemically modified graphene.

The chemical method is considered as a scalable approach to obtain graphene at a large scale due to its simplicity, reliability and exceptionally low cost. This method has been used widely to synthesize chemically derived graphene. Graphite is first oxidized to graphite oxide using either the Hummers method[21] or the modified Hummers method[22] in the presence of strong acids and oxidants. Graphite oxide can be readily exfoliated as individual graphene oxide (GO) sheets by ultrasonication in water. GO, an oxidized form of graphene is decorated by hydroxyl and epoxy functional groups on the hexagonal network of carbon atoms with carboxyl groups at the edges. GO is highly hydrophilic and forms stable aqueous colloids due to presence of large number of oxygen-containing functional groups and electrostatic repulsions. It is electrically insulating and can be converted into conducting graphene by chemical reduction process. There have been reports in the literature on the reduction of GO in solution phases using different reducing agents such as hydrazine, dimethylhydrazine, hydroquinone, ethyleneglycol, sodium borohydride, lithium borohydride and in the vapour phase using hydrazine/hydrogen or just by thermal annealing. Therefore, GO is an excellent precursor to synthesize graphene nanosheets.

The following scheme shows the synthesis of graphene by chemical method.

TABLE 2 illustrates the various synthetic protocols employed for the synthesis of graphene.

Graphite ⟶ **Graphite oxide**
chemical oxidation by Hummers/modified-Hummers method

Graphite oxide ⟶ **Graphene oxide (GO)**
ultrasonication in water/organic solvents

GO ⟶ **chemically derived Graphene (G)**
reduction by reducing agent like hydrazine

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TABLE 1 : Some of the amazing properties of grapheme.

Some basic properties	Graphene
Young's modulus	~ 1100 GPa
Thermal Conductivity	~ 5000 $Wm^{-1}K^{-1}$
Mobility of charge carrier	2×10^5 cm^2 V^{-1} s^{-1}
Specific Surface area	2630 m^2g^{-1}

TABLE 2 : Various methods employed for the synthesis of grapheme.

Synthetic protocol	Yield
Micromechanical cleavage (Scotch-tape method)	low
Unzipping of carbon nanotubes (mechanical and electrochemical unzipping)	moderate
Chemical exfoliation of graphite (graphite intercalation compound)	moderate
Solvothermal synthesis	moderate
Bottom-up organic synthesis	high
Liquid-phase exfoliation of graphite	high
Chemical vapour deposition (CVD)	high
Thermal decomposition of SiC	high
Chemical reduction of graphene oxide obtained from graphite oxide by various reducing agents	high
Microwave, laser, plasmas, sonochemical, hydrothermal and photochemical techniques	moderate
Electrochemical method	high

SOME OF THE AMAZING PROPERTIES OF GRAPHENE

The amazing properties of graphene has been explored for versatile applications ranging from electronic devices to electrode materials. It exhibits outstanding electronic properties, permitting electricity to flow rapidly through the materials. In fact, it has been shown that electrons in graphene behave as massless particles similar to photons, zipping across a graphene layer without scattering. This outstanding electronic property is crucial for many device applications.

Graphene also exhibits outstanding optical property with high optical transmittance. The optical transmission through the graphene surface in the visible range is more than 95 %. This one-atom thick crystal can be seen with naked eye. Therefore, graphene has the ideal optical property of high optical transmission to be used as transparent electrodes in liquid-crystal displays (LCDs) as a replacement of indium-tin oxide (ITO) coated electrodes.

Graphene's unique properties arise from the collective behaviour of electrons. The interaction between electrons and the honeycomb lattice in graphene causes the electrons to behave as massless relativistic particles. Due to this reason, the electrons in graphene are governed by the Dirac equation, the quantum mechanical description of electrons moving relativistically. Therefore, these electrons in graphene are called Dirac fermions[7]. The relativistic behaviour of electrons in graphene was first predicted in 1947 by Canadian physicist Philip Wallace, long before the isolation of graphene[23]. We are already accustomed with massless Dirac fermions in neutrinos in high-energy particle physics. However, neutrinos have no electric charge and do not interact strongly with any kind of matter. In contrast, the Dirac fermions in graphene carry one unit of electric charge and can interact strongly with electromagnetic field. The manipulation of electrons in graphene using electromagnetic fields may allow us to go beyond the limits of silicon semiconductor technology.

Electrons in graphene move with an effective speed of light 300 times less than the speed of light in vacuum, allowing relativistic effects to be observed[7].

The electrons in graphene can travel long distances with scattering, making it the ideal material for the fabrication of fast electronic components.

Graphene also exhibits unusual "half-integer" quantum Hall effect (QHE), which distinguishes itself from an ordinary metal and semiconductor[6]. In the original Hall effect, a current flowing along the surface of a metal in the presence of a transverse magnetic field causes a potential drop. The ratio of potential drop to the current flowing is called the Hall resistivity, which is directly proportional to the applied magnetic field. In a 2D electron gas, the Hall resistivity becomes quantized at a temperature close to absolute zero. This is called QHE. The Hall resistivity is represented by h/ne^2, where h is Planck's constant, e is the electric charge and n is a positive integer. In case of graphene, QHE arises due to quantum-mechanical effect called a Berry's phase and the Hall resistivity should be quantized in terms of odd integers only. QHE is observed at room temperature in case of graphene, whereas it is only observed in ordinary metal at very low temperature.

Graphene has the property of fluorescence quenching[24]. It has the ability to quench the fluorescence emitted by aromatic molecules. The fluorescence quench-

ing of graphene is associated with photo-induced electron transfer.

APPLICATIONS OF GRAPHENE

It is expected that the remarkable electronic property of graphene will bring a new era in nanoelectronics. Despite the high expectation about graphene-based electronics, 'graphenium' microprocessors are unlikely to appear for the next few years. However, many other graphene-based applications are likely to be utilized.

The most direct application for graphene is probably its use in composite materials. Indeed, it has been demonstrated that by spreading a small amount of graphene throughout polymers, tough lightweight materials can be designed. The composites conduct electricity and can withstand much higher temperatures than the polymers. Recently, a mechanical engineering professor at Northwestern University, USA synthesized graphene-based polymer composite materials. These graphene based polymer composites could be ideal to make lightweight gasoline tanks and plastic containers. These composites can be potentially used to make lighter, more fuel-efficient aircraft and car parts, stronger wind turbines, medical implants and sports equipments.

Another option is the use of graphene powder in electric batteries that are already one of the main markets for graphite. A high surface-to-volume ratio and high conductivity provided by graphene powder can lead to improvements in the overall efficiency of batteries, taking over from the carbon nanofibres used in modern batteries.

High conductivity and high optical transparency makes graphene suitable for fabricating transparent conducting coating in LCDs and solar cells. Recently, researchers from Korea and USA developed ultraviolate (UV) nitride light-emitting diode which uses a few layer of graphene as a transparent conducting layer.

Graphene has extremely high specific surface area and high porosity, making them ideal for adsorption of different gases such as hydrogen (H_2), methane (CH_4) and carbon dioxide (CO_2). Graphene can be an ideal material for hydrogen storage owing to the light weight, high surface area and chemical stability. Hydrogen can be chemically stored in graphene by physisorption or chemisorption. However, practically it exhibits a low

hydrogen storage capacity at ambient temperatures and moderate pressures. For example, a single-layer graphene was shown to store 0.4 wt% hydrogen at 100 kPa pressure and cryogenic temperature. Therefore, chemical modification of carbon supports by metal or metal oxide nanoparticles is essential to enhance the hydrogen uptake efficiency. Pd has strong affinity towards hydrogen adsorption. The role of Pd nanoparticles on graphene can be enhanced by three times under moderate temperature and pressure. Therefore, graphene and its nanocomposites have a great potential in hydrogen storage, which can be employed in fuel cell technology with the fuel cell serving as the fuel source. Recently, Dhathathreyan et al.[25] have utilized the functionalized graphene sheets as catalyst support for the proton exchange membrane fuel cells. C. N. R. Rao and his group studied the chemical storage of hydrogen in few layer graphene[26].

The extraordinary mechanical, optical and electrical properties of graphene have been exploited by many scientists to develop actuators. Park et al. designed a bilayer paper composed of adjacent graphene oxide and multi-walled carbon nanotube layers and demonstrated a macroscopic graphene-based actuators[27]. Recently, Wu et al. developed a remote-controlled transparent, large area graphene based robot[28]. This graphene based actuator can curl and uncurl in the absence and presence of infrared (IR) radiation[28]. This remote-controlled based robot picks up any object, moves it to a desired location and drops it by the remote control of IR radiation. This is undoubtedly an elegant demonstration of photothermal energy transformation by graphene based actuators.

Current research and development on electrochemical power sources are mainly focused on fuel cells, batteries and electrochemical capacitors and are directed towards obtaining high specific energy, high specific power, long cycle life at relatively low cost. The high rate of pollution induced by electric vehicles and recent growth of portable electronic devices has facilitated the development of high-performance supercapacitor as flexible energy storage devices. Electrochemical capacitors, also called supercapacitors or ultracapacitors, store energy using either ion adsorption (electrochemical double layer capacitors) or fast surface redox reactions or faradaic reactions (pseudo-capacitors/redox-

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capacitors)[29,30]. They can complement or replace batteries in electrical energy storage and harvesting applications, when high power delivery or uptake is needed. Due to their high specific power, supercapacitors have applications including automobiles, electric vehicles and various hybrid electric vehicles. Recently, graphene based electrode material has been used for supercapacitor applications. In contrast to the conventional high surface materials, the effective surface area of graphene based materials as capacitor electrode materials does not depend on the distribution of pores at the solid state, which is different from the current supercapacitors fabricated with activated carbons and carbon nanotubes. Obviously, the effective surface area of graphene materials should depend highly on the layers. Therefore, the single or few layered graphene should be expected to exhibit higher effective surface area and thus better supercapacitor performance. Wang et al.[31] fabricated supercapacitor devices using graphene as electrode materials and investigated their performance. The single-layered graphene oxide sheets were reduced using gas-based hydrazine reduction at room temperature. The reduced graphene materials produced by this method have a lower degree of agglomeration than the chemically modified graphene prepared in aqueous solution at the high temperature. A maximum specific capacitance of 205 F g^{-1} at 1.0 V in aqueous electrolyte with energy density of 28.5 W h kg^{-1} has been obtained, which are the best results for graphene materials so far and also significantly higher than those of CNT-based supercapacitors. Furthermore, the power density of the capacitors reaches as high as 10 kW kg^{-1}, higher than that for CNT-based supercapacitors.

Subsequent development of graphene based nanocomposites using conducting polymers is an important step of improvisation in the area of nanoscience and nanotechnology. This kind of graphene-based polymer nanocomposites can be used as electrode material in supercapacitors. The main conductive polymer materials that have been investigated for the supercapacitor electrode are polyaniline (PANI), polypyrrole (PPY), polythiophene (PTH) and their derivatives.

Freestanding and flexible graphene/polyaniline composite paper was prepared by Wang et al.[32] employing an *in situ* anodic electropolymerization of polyaniline film on graphene paper. This graphene-based composite paper electrode, consisting of graphene/polyaniline composite sheets as building blocks, shows a favorable tensile strength of 12.6 MPa and exhibits a stable large electrochemical capacitance (233 F g^{-1} and 135 F cm^{-3} for gravimetric and volumetric capacitance). These values are much larger compared to many other currently available carbon-based flexible electrodes and is therefore particularly promising for flexible supercapacitors.

CONCLUSIONS

The discovery of graphene in 2004 triggered research activities at various experimental and theoretical aspects worldwide due to its extremely large surface area and unique material properties. Within few years of discovery, graphene based materials and their composites enjoy the status of being the new supermaterial on the horizon of materials science and condensed matter physics owing to their versatile applications in various fields. Different protocols have been employed for the synthesis of graphene[33]. It is expected that this new supermaterial will replace silicon to be the material of choice for certain applications in electronics in the near future.

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