Study the Graphene derivatives

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ABSTRACT

Nanotechnology is improving our everyday lives by enhancing the performance and efficiency of everyday objects. It provides a clean environment by providing safer air and water, and clean renewable energy for a sustainable future. Nanotechnology has gained a wide attention where more investment is made for the research and development by top institutions, industries and organisations. Nanotechnology has established to be an advanced field of science where extensive research is carried out to implement the technology. It is being tested for various new applications to increase the efficiency and performance of the object or process and subsequently reduce the cost so that it is accessible for everyone. The nanotechnology has a great future due to its efficiency and environmental friendly property.

Nanotechnology has gained huge attention over time. The fundamental component of nanotechnology is the nanoparticles. Nanoparticles are particles between 1 and 100 nanometres in size and are made up of carbon, metal, metal oxides or organic matter. The nanoparticles exhibit a unique physical, chemical and biological properties at nanoscale compared to their respective particles at higher scales. This phenomena is due to a relatively larger surface area to the volume, increased reactivity or stability in a chemical process, enhanced mechanical strength, etc. These properties of nanoparticles has led to its use various applications. The nanoparticles are generally classified into the organic, inorganic and carbon based.And we sum arize the recent progress in synthesizing graphene and its derivatives. the effect of synthesis on the froperties of the materials, and the promising applications related to those propertis. Include graphene derivatives (GO , Fluorographene , Graphyne , Graphdiyne and Graphane) Graphene derivatives have proven to be effective fillers in polymer nano composite materials thanks to their ideal material properties and dispersibility in polymer matrices, which has led to many applications, the tight packing of sp^2 carbon atoms has been shown to serve as anear-perfect barrier to gas molecules, which demonstats its use in packaning materials, protection for sensitive electronic devices, or even corrosion resistant materials. For similar reasons, the fin – tuning of the filler content in nano composites can be used to adjusts the selectivity of certain- sized molecules to generate superior membrane technologies

Keywords: Graphene derivatives, Nanotechnology, chemical process

Introduction

Nanotechnology has gained huge attention over time. The fundamental component of nanotechnology is the nanoparticles. Nanoparticles are particles between 1 and 100 nanometres in size and are made up of carbon, metal, metal oxides or organic matter(1). The nanoparticles exhibit a unique physical, chemical and biological properties at nanoscale compared to their respective particles at higher scales. This phenomena is due to a relatively larger surface area to the volume, increased reactivity or stability in a chemical process, enhanced mechanical strength, etc. (2) These properties of nanoparticles has led to its use various applications.

The nanoparticles differs from various dimensions, to shapes and sizes apart from their material(3). A nanoparticle can be either a zero dimensional where the length, breadth and height is fixed at a single point for example nano dots, one dimensional where it can possess only one parameter for example graphene, two dimensional where it has length and breadth for example carbon nanotubes or three dimensional where it has all the parameters such as length, breadth and height for example gold nanoparticles.

The nanoparticles are of different shape, size and structure. It be spherical, cylindrical, tubular, conical, hollow core, spiral, flat, etc. or irregular and differ from 1 nm to 100 nm in size. The surface can be a uniform or irregular with surface variations. Some nanoparticles are crystalline or amorphous with single or multi crystal solids either loose or agglomerated (4)

Numerous synthesis methods are either being developed or improved to enhance the properties and reduce the production costs. Some methods are modified to achieve process specific nanoparticles to increase their optical, mechanical, physical and chemical properties. A vast development in the instrumentation has led to an improved nanoparticle characterisation and subsequent application. The nanoparticles are now used in every objects like from cooking vessel, electronics to renewable energy and aerospace industry. Nanotechnology is the key for a clean and sustainable future.

Classification of Nanoparticles

The nanoparticles are generally classified into the organic, inorganic and carbon based.

1- Organic nanoparticles

Dendrimers, micelles, liposomes and ferritin, etc. are commonly knows the organic nanoparticles or polymers. These nanoparticles are biodegradable, non-toxic, and some particles such as micelles and liposomes has a hollow core (Figure1), also known as nanocapsules and are sensitive to thermal and electromagnetic radiation such as heat and light (5). These unique characteristics makes them an ideal choice for drug delivery. The drug carrying capacity, its stability and delivery systems, either entrapped drug or adsorbed drug system determines their field of applications and their efficiency apart from their normal characteristics such as the size, composition, surface morphology, etc. The organic nanoparticles are most widely used in the biomedical field for example drug delivery system as they are efficient and also can be injected on specific parts of the body that is also known as targeted drug delivery.

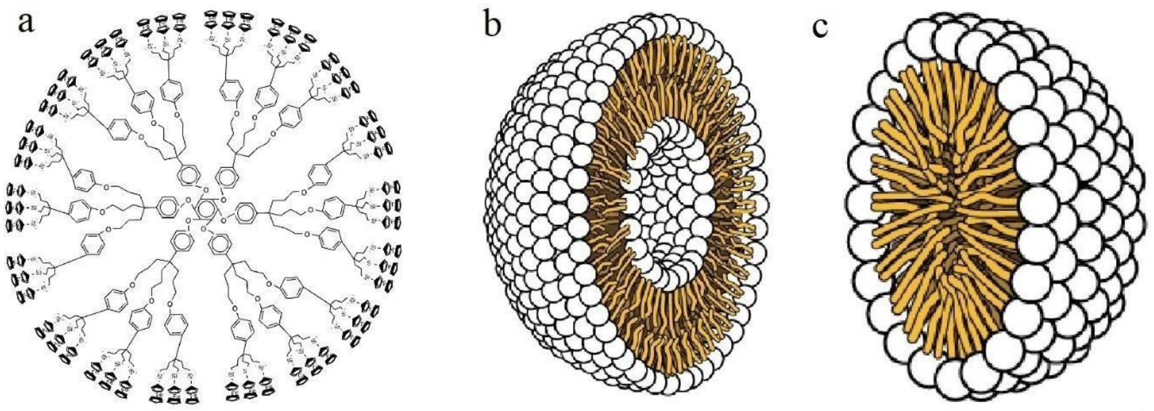


Figure 1. Organic nanoparticles: a – Dendrimers, b – Liposomes and c – micelles.

2- Inorganic nanoparticles

Inorganic nanoparticles are particles that are not made up of carbon. Metal and metal oxide based nanoparticles are generally categorised as inorganic nanoparticles

2.1-Metal based. Nanoparticles that are synthesised from metals to nanometric sizes either by destructive or constructive methods are metal based nanoparticles. Almost all the metals can be synthesised into their nanoparticles (6) The commonly used metals for nanoparticle synthesis are aluminium (Al), cadmium (Cd), cobalt (Co), copper (Cu), gold (Au), iron (Fe), lead (Pb), silver (Ag) and zinc (Zn). The nanoparticles have distinctive properties such sizes as low as 10 to 100nm, surface characteristics like high surface area to volume ratio, pore size, surface charge and surface charge density, crystalline and amorphous structures, shapes like spherical and cylindrical and colour, reactivity and sensitivity to environmental factors such as air, moisture, heat and sunlight etc.

2.2-Metal oxides based. The metal oxide based nanoparticles are synthesised to modify the properties of their respective metal based nanoparticles, for example nanoparticles of iron (Fe) instantly oxidises to iron oxide (Fe_2O_3) in the presence of oxygen at room temperature that increases its reactivity compared to iron nanoparticles. Metal oxide nanoparticles are synthesised mainly due to their increased reactivity and efficiency (7). The commonly synthesised are Aluminium oxide(Al_2O_3),

Cerium oxide (CeO_2), Iron oxide (Fe_2O_3), Magnetite (Fe_3O_4), Silicon dioxide (SiO_2), Titanium oxide (TiO_2), Zinc oxide (ZnO). These nanoparticles have possess an exceptional properties when compared to their metal counterparts.

3- Carbon based

The nanoparticles made completely of carbon are knows as carbon based (8). They can be classified into fullerenes, graphene, carbon nano tubes (CNT), carbon nanofibers and carbon black and sometimes activated carbon in nano size and are presented in Figure2.

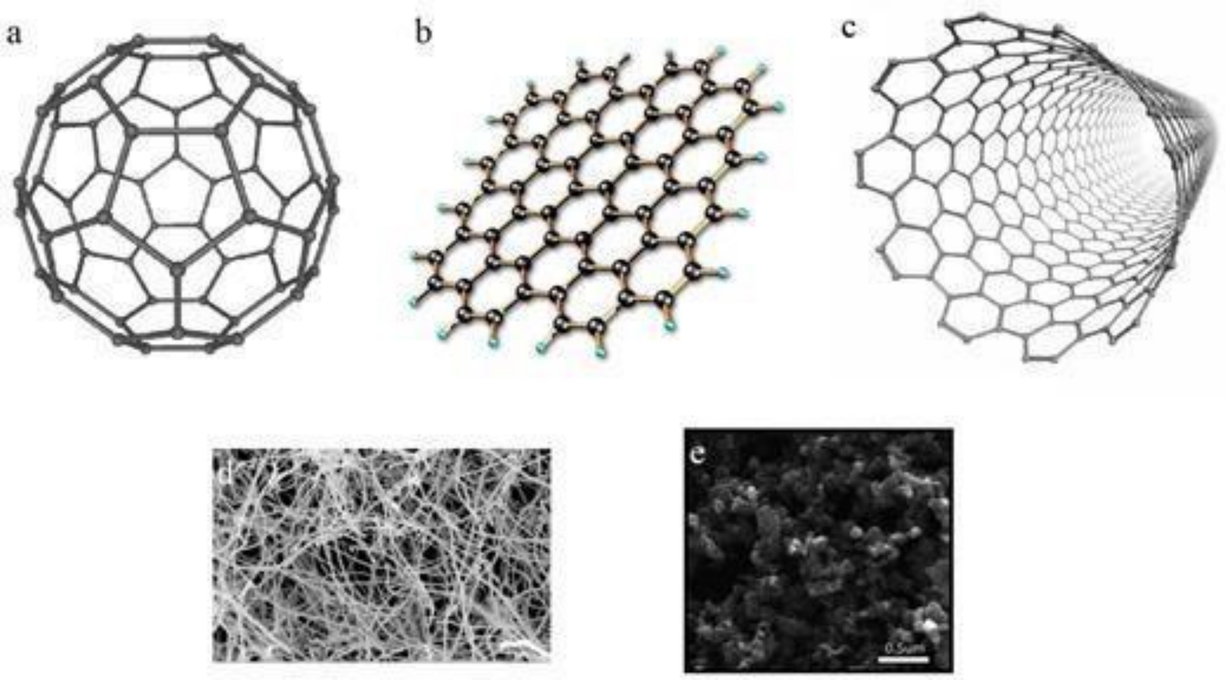


Figure2. Carbonbasednanoparticles:a– fullerenes,b– graphene,c– carbonnanotubes,d– carbon nanofibers and e – carbon black

3.1-Fullerenes. **Fullerenes** (C_{60}) is a carbon molecule that is spherical in shape and made up of carbon atoms held together by sp^2 hybridization. About 28 to 1500 carbon atoms forms the spherical structure with diameters up to 8.2 nm for a single layer and 4 to 36 nm for multi-layered fullerenes.

3.2-Graphene. **Graphene** is an allotrope of carbon. Graphene is a hexagonal network of honeycomb lattice made up of carbon atoms in a two dimensional planar surface. Generally the thickness of the graphene sheet is around 1 nm.

***3.3-Carbon Nano Tubes** (CNT)*. Carbon Nano Tubes (CNT), a graphene nanofoil with a honeycomb lattice of carbon atoms is wound into hollow cylinders to form nanotubes of diameters as low as 0.7 nm for a single layered and 100 nm for multi-layered CNT and length varying from a few micrometres to several millimetres. The ends can either be hollow or closed by a half fullerene molecule.

3.4-Carbon Nanofiber. The same graphene nanofoils are used to produce carbon nanofiber as CNT but wound into a cone or cup shape instead of a regular cylindrical tubes.

3.5-Carbon black. An amorphous material made up of carbon, generally spherical in shape with diameters from 20 to 70 nm. The interaction between the particles are so high that they bound in

Organic Nanoparticles

Organic nanoparticles/nanobeads are of major interest in the material and life sci- ences. Their small size provides them with unique properties putting them at the forefront of emerging technologies. They are highly useful in bioanalysis and basic science as model systems to study single molecule behavior, molecular rec- ognition, signal transduction, and protein-mediated membrane fusion processes once functionalized/associated with biological entities (such as DNA or anti- bodies) as catalytic interfaces, for sensor applications, for drug delivery, as well as other applications. There are a multitude of possible applications of fabricated nanoparticles in biotechnology, fundamental and clinical research, and in medi- cine. While nanobiotechnology deals with the development of electronic circuits, molecular ―switches,‖ biosensors, and nanosized microchips, nanomedicine focuses on disease treatment, diagnosis/monitoring, and rational delivery and tar- geting of pharmaceutical, therapeutic, and diagnostic agents. Rather than using inorganic matrices, biopolymer nanoparticles may provide some significant advantages. They have been primarily developed for drug delivery to overcome the risk of chronic toxicity due to the intracellular and/or tissue overloading of nondegradable polymers. The need for developing such nanoparticles (liposome, virus-like particle, protein, polysaccharide, etc.) not only as effective drug delivery devices but also for immunoassays was realized years ago.(9) Indeed, in addition to the general advantages of nanoparticles, biopolymer nanoparticles in particular offer several advantages, which include the ease of their preparation from well-understood biodegradable polymers and their high stability in biolog- ical fluids and during storage.(10)

Organic nanoparticles already play an important role in many biotechnology applications and promise to take center stage for many new and emerging applications in the coming years. Interesting future developments include not only biomedical applications such as improved delivery of drugs to tumor cells and the use of dendrimers for regenerative medicine but also fields such as water purification and disinfection, food production, and packaging.

For example, it may be possible to circumvent the anti-apoptotic mecha- nism of the Bcl-2/Bax system, which contributes to the survival and drug resistance of tumoral cells, by introducing proapoptotic molecules into the cells using nanoparticles, aiding in the escape from lysosomes and thus sensitizing cancer cells to the induction of apoptosis by several therapeutic agents. As an example, lipid nanocapsules used as nanocarriers have been shown to improve the activity of a number of anticancer hydrophobic compounds and to transport drugs in the close vicinity to mitochondria.(11) The capability of obtaining nanocarriers that recognize mitochondria is a major improvement to introduce into cell drugs which have subcellular compartment as a target.

In addition, dendrimers may be useful in the field of regenerative medicine. The use of dendrimers as support biomaterial for the generation of new tissue may play an increasingly important role, whether for the forma- tion of scaffolds to allow for cell growth or the generation of bioartificial tissues.(12)

Organic nanoparticles may also play an increasingly important role in water treatment and disinfection. Although disinfection methods currently used in drinking water treatment can effectively control microbial pathogens, research in the past few decades has revealed a dilemma between effective disinfection and formation of harmful disinfection by products, many of which are carcinogens. Nanomaterials are excellent adsorbents, catalysts, and sensors due to their large specific surface area and high reactivity. Inter- estingly, naturally occurring chitin and certain peptides have been long recognized for their antimicrobial properties toward bacteria, viruses, and fungi. Chitosan prevents the multiplication of bacteriophages in bacteria and induces resistance toward viral diseases in plants.(13) Recently, these materials have been engineered into nanoparticles.(14) Nanoscale chitosan has potential drinking water disinfection applications as an antimicrobial agent in mem- branes, sponges, or surface coatings of water storage tanks.

Nanoparticles are now also starting to be used for all stages of food production. Nanotechnology is being applied in areas such as food security and quality, development of new products and packaging. Reducing the particle size of materials to that of NPs has been used to enhance emulsification, gelation, foaming, water-binding capacity. Nanoparticles are also being used to deliver vitamins or other nutrients in food and beverages without affecting the taste or appearance. These nanoparticles actually encapsulate the nutrients and carry them through the stomach into the bloodstream.(15) Nanopackaging has also started to impact food storage by increasing the shelf life of fresh foods and carbonated beverages, and many other food packaging products are currently under development.(16)

As the number of biotechnological applications of organic nanoparticles continues to expand, the use of this technology promises to play an increasingly important role in the biomedical and industrial arenas, affecting the lives of all of us.

Graphene

Carbon-based nanostructures have made very high impacts for science and a large variety of technological applications more than 30 years since buckminsterfullerene (C_{60}) was discovered in 1985. Due to its valency, carbon nanostructures can be formed to various allotropes ranging from fullerene or graphene quantum dot (0D), carbon nanotubes (1D), graphene nanoribbons (2D), to pillared graphene (3D). Each carbon nanostructure has unique properties. For example, a single-walled carbon nanotube (SWCNT) can be up to 100 times stronger than steel with the same weight. The Young's modulus of SWCNTs is up to 1 TPa, which is five times greater than steel (230 GPa). The thermal conductivity (2000 WUm^{21}UK^{21}) is five times greater than that of copper (400 WUm^{21}UK^{21})(17). Graphene exhibits an exceptionally large thermal conductivity of approximately 5300 WUm^{21}UK^{21}, remarkable electron mobility at room temperature (excess of 15,000 cm^{2}UV^{21}Us^{21}), one atomic layer thickness, zero- overlap semimetal, ultimate tensile strength, and plasmonics effects (18,19). The 3D pillared graphene possesses a high surface area/volume ratio, higher electrical conductivity, and better structural mechanical stability over carbon nanotubes and graphene. In the case of 0D graphene quantum dots represented as one to few layers of graphene with a size less than 30 nm, the conductivity of graphene quantum dots is higher than that of graphene oxide. The graphene quantum dots show high transparency, high surface area, good hole transporting ability, low toxicity, stable photoluminescence, chemical stability, and quantum confinement effect as a result of direct influence of ultra-small length scale on the energy band structure(20). Comparative properties of carbon-based nanostructures are summarized in Table.1. and fig3(21).

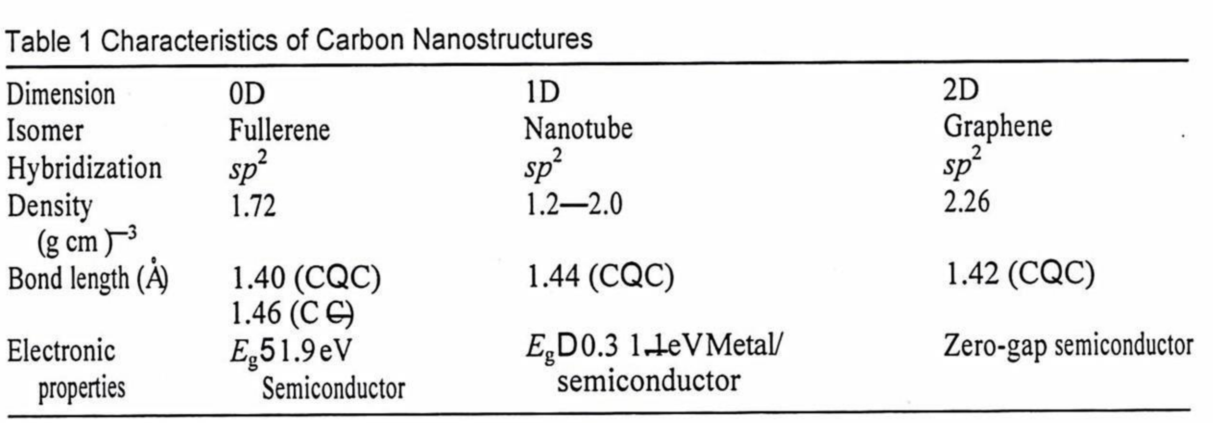


Table 1 Characteristics of Carbon Nanostructures

Dimension	0D	1D	2D
Isomer	Fullerene	Nanotube	Graphene
Hybridization	sp^2	sp^2	sp^2
Density (g cm)$^{-3}$	1.72	1.2—2.0	2.26
Bond length (Å)	1.40 (CQC) 1.46 (C C)	1.44 (CQC)	1.42 (CQC)
Electronic properties	E_g51.9eV Semiconductor	E_gD0.3 1.1eVMetal/ semiconductor	Zero-gap semiconductor

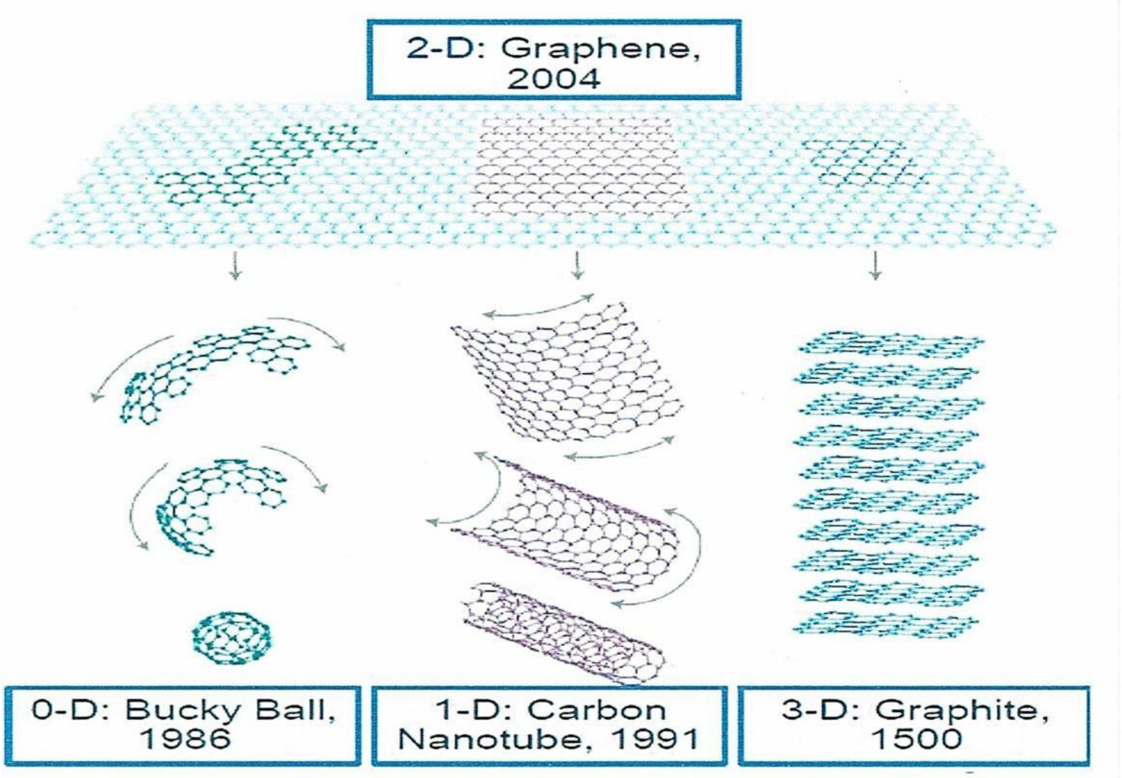


Fig. 3 Mother of all graphene forms. Graphene is a 2D building material for carbon material of all other dimensionalities. It can be wrapped up into 0D buck balls, rolled into 1D nanotubes or stacked into 3D graphite

3:1:Properties of Graphene(22)

1. Electronic properties.
2. Optical properties.
3. Mechanical properties.
4. Thermal properties.

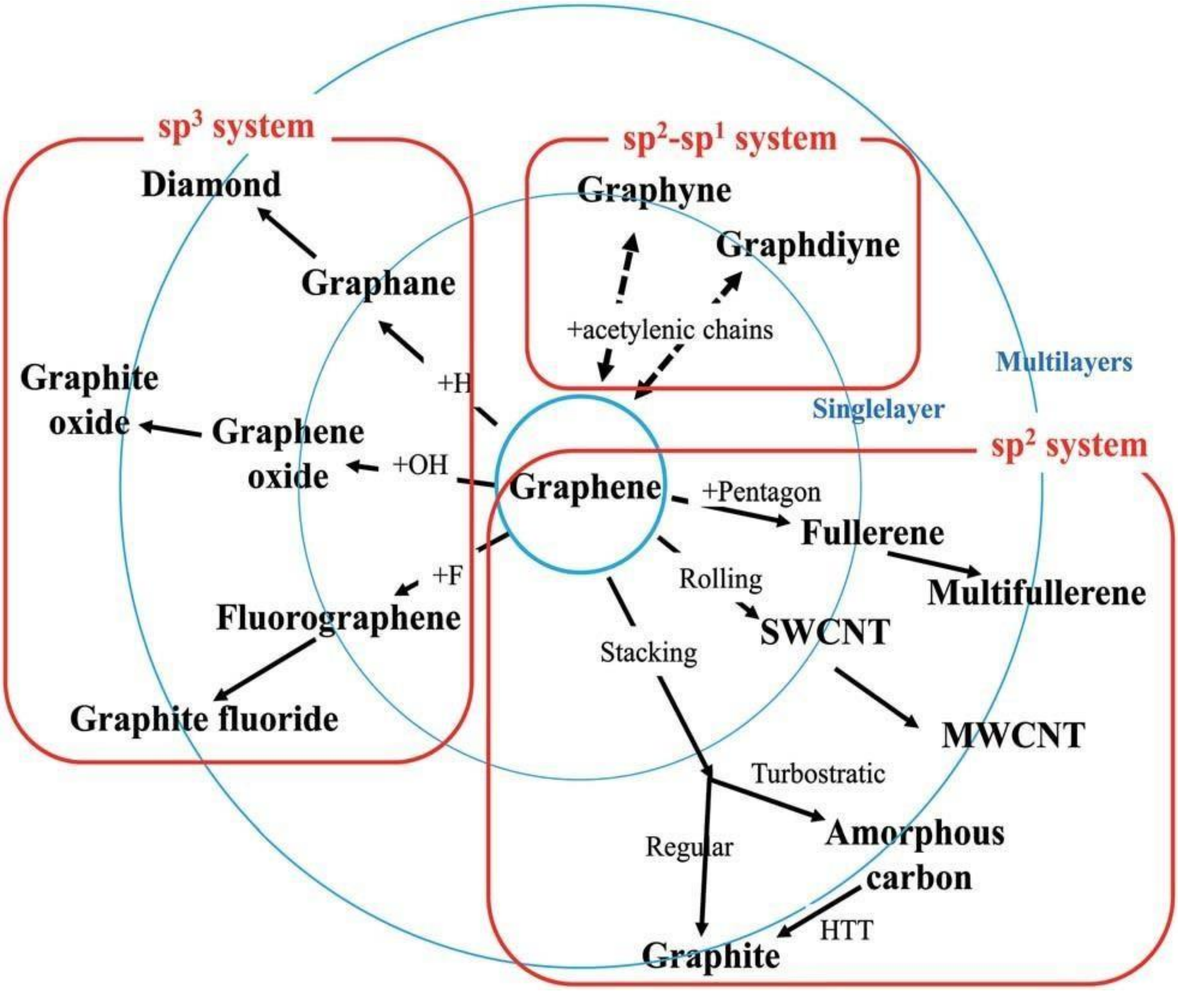
Applications of graphene(22)

1. Flexible transparent conductors (FTCs).
2. High-frequency transistors.
3. Energy storage systems.
4. Light–emitting devices.
5. Photovoltaics devices.

6. Photodetectors.
7. Fuel cells.

Graphene derivatives

New carbon materials have recently been derived from graphene theoretically and experimentally, hydrogenated graphene (graphane), fluorinated graphene (fluorographene), oxidized graphene (graphene oxide), and graphene introduced by acetylenic chains (graphyne and graphdiyne), which may be called graphene derivatives.



Figer:4 Graphene derivatives

1- Graphene Oxide (GO)

GO is derived on oxidation of neutral graphite. It is characterized to be a lamellar solid with unoxidized aromatic regions and aliphatic regions containing phenolic, carboxyl and epoxide groups as a result of oxidation(23). Thus the GO platelets are strongly hydrophilic and dispersible inwatertoformmonolayercolloidaldispersions(24)

Graphene derivatives (GO, rGO, GQDs) have proven to be effective fillers in polymer nanocomposite materials thanks to their ideal material properties and dispersibility in polymer matrices[25,26] .which has led to many applications.

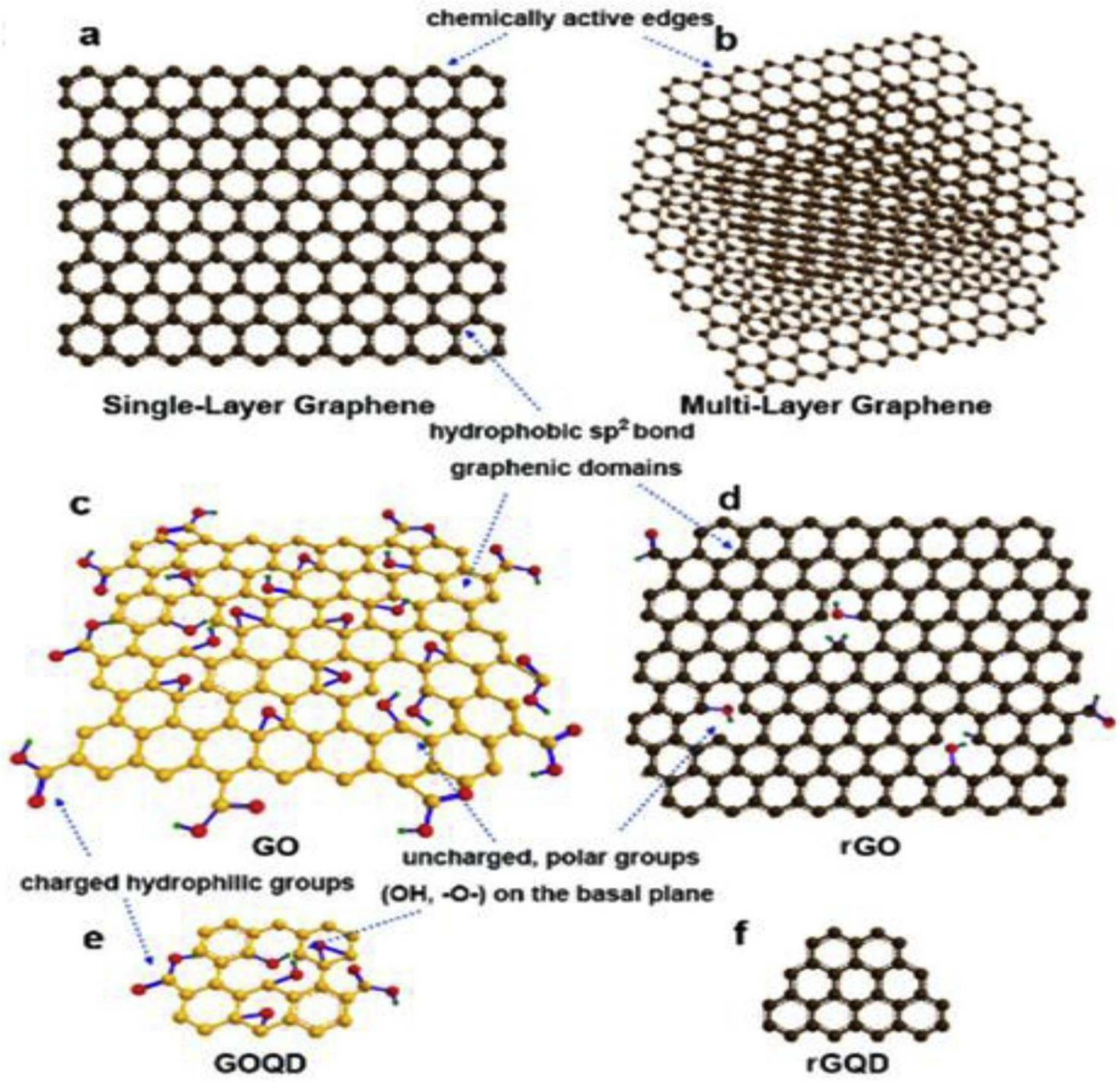


Fig.5. Forms of graphene and its derivatives: (A) single-layer graphene, (B) multilayer graphene, (C) GO, (D) rGO, (E) GOQD, (F) rGQD. (25,)

Properties of graphene oxide:

1- Mechanical properties. 2-Electrecal Properties. 3-Thermal properties.

Applications of GO and rGO

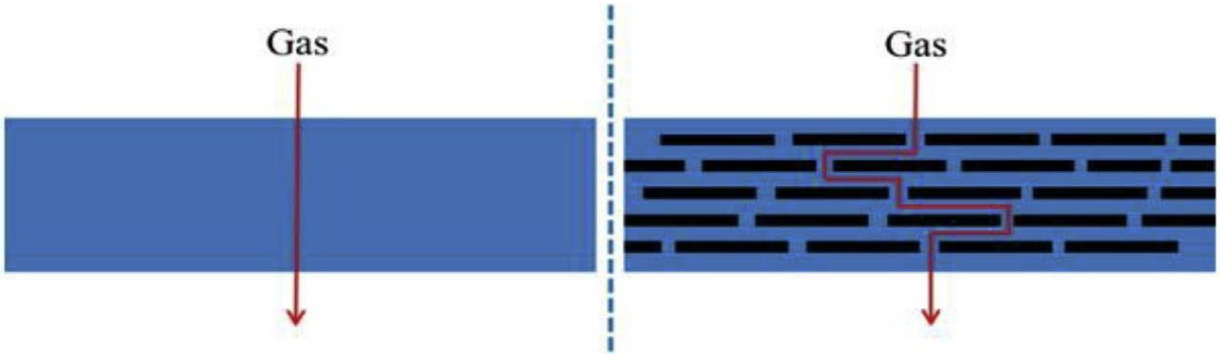
1- Membranes and coatings

1.1 Gas transport

Owing to GO's negatively-charged surface and large aspect ratio nanosheet structure giving exceptional impermeability to most gases, GO-based membranes have found wide application in gas barrier nanocomposites(27,28). Numerous reviews on polymer nanocomposites exist which compile many instances of barrier property improvements by graphene derivatives as fillers(29,30,31).As in the rest of research done in the field of high-gas-barrier properties of polymer nanocomposites (32,33), it is generally regarded that 2D fillers can be oriented in a polymer matrix to create a ―tortuous‖ path for gas molecules (Fig. 6). This involves GO and rGO nanosheets aligned in a nacre-like structure, taking advantage of the fillers' high aspect ratio and surface functionalization by oxygen groups.

In a typical example, Kausar was able to produce rGO/polyamide nanocomposite films which showed great improvements in barrier properties(34). Their GO was produced by a modified Hummer's method and subsequently reduced to rGO using hydrazine hydrate in an aqueous solution.

Fig. 6. Comparison of gas molecule passing through a neat polymer film (left) and a polymer film containing a high concentration of well-aligned impermeable nanosheets (right). Reproduced with permission from the



American Chemical Society(35).

Due to its exceptional ability considered for gas separation processes. However, in recent work researchers were able to demonstrate the remarkable ability of GO-based membranes to generate atomically- thin highly selective gas transport membranes with selective structural defects to allow for the transport of small molecules. Li et al.(36) developed GO membranes with thicknesses as thin as 1.8 nm through a facile vacuum filtration process

1.2-Water treatment

GO membranes are widely considered promising materials for water treatment application because of their high water permeance (37,38) and stability in water(39). As a result, significant progress has been made during the past few years in developing high permeance mem- branes while maintaining high rejection rates. For example, Thebo et al.(40)

fabricated GO sheets on polydopamine modified PES supports with tannic acid and theanine amino acid as crosslinking agents. These membranes demonstrated water permeance over 10,000 L m^{-2} h^{-1} bar^{-1} with dye rejection of ~100% for rhodamine B and methylene blue. Bano et al(41). developed a GO/polyamide nanocomposite which showed a 12 fold increase in water flux over the base polyamide membrane while maintaining high salt rejection with the incorporation of 0.2 wt. % GO in the polyamide by improving the hydrophilicity of the nanocomposite membrane.

The use of GQDs has also been reported in membrane technology thanks to their high dispersibility in water, high specific surface to form high barrier films to most small molecular weight species, GO is often not area, hydrophilicity, and antifouling performance(42,43). Zhang et al. developed a nanofiltration membrane by incorporating GQDs synthe- sized

2- Stimuli-responsive materials

2.1-Humidity actuation

As is well discussed, GO films have a strong affinity for water whereupon the oriented GO nanosheets swell as water enters between them. In addition, GO/polymer nanocomposites have improved mechanical properties, providing structural stability in humid environ- ments. For sufficiently thick hydrophilic films exposed to water, there results an asymmetric swelling causing bending of films that results in reversible actuation of polymer films upon hydration/dehydration cycling(44,45). Zhang et al. demonstrated a biomimetic film actuator by combining GO with CS(46), a hydrophilic polymer, to form a nacre-like structure that shows continuous flipping when exposed to humidity from one side. Even though CS is hydrophilic, a film on its own has insufficient mechanical properties to demonstrate any actuation performance. When combined with GO, The results show that there is potential for these GO/CS films to turn humidity induced actuation into usable mechanical work.

2.2-Thermal/light responsive actuation

As is well documented, GO is efficient in photothermal conversion of light in nanocomposites (47,48). As such, it has proven an excellent filler to add to polymer nanocomposites to develop actuators that respond to heat and near-infrared light (NIR)(49,50). For example, Kim et at(51). developed a thermally responsive GO fiber that showed torsional and tensile actuation upon heating. The GO was mixed with a nylon-6,6 polymer by wet spinning and showed two different types of actuation depending upon the fabrication of the fiber which could be twisted and wound to form coils with a homochiral structure or hetero- chiral structure. The fibers undergo volume expansion upon heating showing 80% contraction for the homochiral direction and heterochiral elongation of 75%. The fibers are capable of lifting 100 times their own mass and can even withstand temperatures above the melting tempera- ture of the nylon.

In another report, Zhao et al. (52)designed multiple bionic hydrogel actuators with GO and N-isopropylacrylamide and 4-hydroxybutyl acrylate as a monomer and crosslinking agent

2.3-Electromechanical actuation

As well discussed, rGO shows exceptional electrical conduction properties when encapsulated in polymer matrices. So, it is no surprise that this endows rGO/polymer nanocomposites with excellent electrical stimuli-responsive actuation (53,54)

2.4-Multi-stimuli actuation

With the diverse properties of GO/rGO showing excellent application in various stimuli- responsive actuation materials, it is then desirable to explore the different combinations of the actuating stimuli. For example, Chen et al(55). developed a multi-responsive actuator responding to both humidity and NIR by making a nanocomposite of GO and biaxially oriented polypropylene (BOPP). For this nanocomposite, the GO layer is very hygroscopic and thus highly sensitive to ambient humidity, while the BOPP is inert to humidity. This provided the GO/BOPP film with excellent humidity-driven actuation based on the large asymmetric swelling generated from the two layers.

adsorbs the light. As a result of GO and BOPP's difference in coefficient of thermal expansions (0.85 ppm K^{-1} for GO and 137 ppm K^{-1} for BOPP), the films would bend upon exposure to NIR light. When exposed on the BOPP side the actuator would bend towards the GO side within 10 s with a bending curvature of 2.8 cm^{-1}.

Ji et al. (56) developed a similar bilayer actuator responding to humidity and NIR with a polydopamine-modified rGO layer and a Norland Optical Adhesive (NOA)-63 layer. The NOA is responsive to neither humidity or NIR, thus imbuing the bilayer actuator with fast and reversible bending and unbending under the stimuli. The film rolled up at 7% RH and unrolled when exposed to 80% RH in 46 s and showed reversible rolling up in 53 s when returned to 7% RH for at least 7 cycles. The authors were also able to develop a walking device driven by NIR, by attaching PET plates onto opposite ends of the film with a complete cycle of bending and unbending taking 3.8 s and moving ~4–5 mm per cycle.

stimuli-responsive actuators are not just limited to humidity and NIR. Jiang et al(57). formed a nanocomposite actuator with rGO and polypyrrole (PPy) that responds to humidity and electro- mechanical stimuli. The authors used a self-oxidation reduction strategy to form the film in which GO acted as the oxidant to polymerize pyrrole into PPy, thus being partially reduced and forming cross-links between rGO and PPy. At low RH, the film exhibited little to no curvature; as the RH was raised, the film curled up and reached a maximum curvature of 330° at an RH of 65%. The actuator could also be driven by electrochemical potential, actuating to both sides depending upon the potential applied.

The above results suggest the versatile nature of GO-based actuators, offering a promising material for stimuli-responsive actuation. The diverse properties of GO will allow for the development and incorpora- tion of GO into multi-stimuli-responsive smart materials for use in highly humid environments and touchless sensing technology with electrome- chanical responses.

2.5-Corrosion resistance

Graphene derivatives show promise for anti-corrosive polymer coat- ings thanks to their 2D morphology and high chemical inertness(58). Polymers alone are permeable to chloride, sulfites, water and other chemicals that would be harmful to substrate metals(59), but graphene and its derivatives could be used as fillers to prevent the diffusion of harmful materials to a metal surface or even promote the generation of a passivation layer(60). Ghauri et al. compared the abilities of GO (by improved Hummer's method) and rGO (by hydrazine reduction) in epoxy nanocomposites on steel substrates(58). Electrical impedance

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spectroscopy (EIS) showed that the modulus of impedance (Z) of the GO coating was 6.36 kΩ cm^2 and that of the rGO coating was 3.48 kΩ cm^2 after 24 h of exposure to a Cl— ion electrolyte flux. rGO showed a higher resistivity to electrolyte flux after 1 h due to its hydrophobicity and closer interlayer spacing; however, because the rGO was more conductive than GO for migration of Cl— and $\mathrm{Fe}^{3\text{þ}}$ ions through the coating and at the metal/coating interface, which might accelerate the process of a subsequent accumulation

Singhbabu et al. proposed that the largest obstacle to reliable gra- phene oxide corrosion of corrosion products (Fig 7) barriers is defect formation(61). They reflected on several studies done by other groups and developed a methodology of deriving rGO from shellac bio-polymer. Citing the previous literature where the heating of shellac bio-polymer in an inert atmosphere resulted in graphene oxide, they directly dip-coated cold rolled steel (CRS) with shellac solution in isopropanol, then heated the coating in a hydrogen atmosphere at 710 °C for 24 h. To prevent exposure of the metal surface to any defects in the resulting coating.

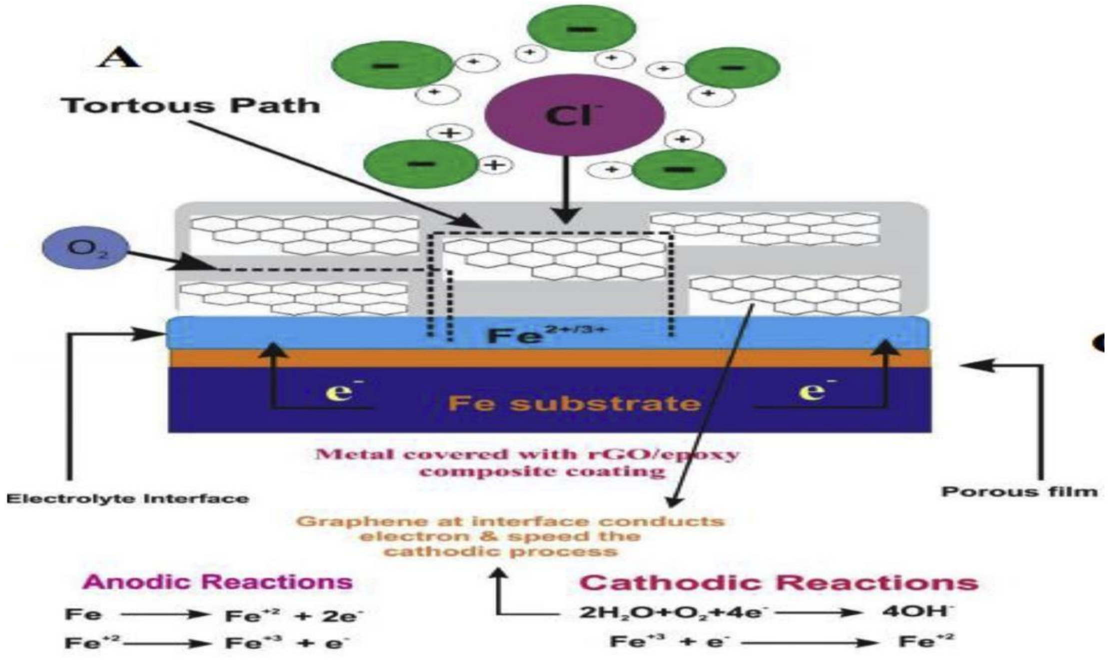

Fig. 7 Schematic of electrochemical response of rGO coatings in chloride containing media

2.6-Energy storage

With rGO's superior electrical properties, rGO has become a prom- ising material for many energy applications, such as in supercapacitors(62,63), lithium ion batteries (LIBs)(64,65), and stretchable electronics (66,67,68).

Because of their long cycle lifetime and high-power density, super- capacitors have become a highly important area of research for energy storage devices. As such, it is no surprise that rGO materials have become important to the recent study of supercapacitors. A problem with GO is that it will tend to agglomerate during processing, greatly reducing its theoretical high surface area thus limiting its supercapacitance perfor- mance. Xu et al(69). was able to design a sponge templated GO supercapacitor electrode by combining GO with a PU sponge. This ma- terial exhibited a specific capacitance of 401 F g^{-1} in aqueous electrolytes and an energy density of 89 W h kg^{-1} due to creating a shorter ion transport distance with the 3D structure and inner porosity. Zhao et al.
designed a supercapacitor electrode of GO/NaCl/Urea film, which upon hydrothermal treatment was reduced to rGO. During the hydro- thermal treatment the NaCl acts to prohibit restacking of the graphene sheets and urea results in nitrogen doping improving the capacitance over rGO alone. The film exhibited a specific capacitance of 425 F g^{-1} and a volumetric specific capacitance of 693 F cm^{-3} at 1 A g^{-1} in 1M H_2SO_4.

In other energy storage applications, rGO based materials have found success in LIBs(70). Wang et al. reported a method to design folded paper like rGO electrode decorated with Tin Oxide (SnO_2) for use as the electrode for LIBs.

Besides LIBs, rGO has also been shown to work with sodium-ion batteries (SIBs), which are a potential alternative to lithium due to lower environmental impact and lower cost(71). Wang et al. combined VS_4 with rGO as an effective nanocomposite anode for SIBs. The authors explored two procedures to achieve high-specific capacity and stable cycling performances.

2- Fluorographene

Fluorographene(FG)was predicted as a stablegraphene derivative by sofo and cowrkers in 2007 and prepared by fluorographene(72)and mechanical or chemeical exfoliation of graphite fluoride three years later.

was considered the thinnest insulator and counterpart of poly- tetrafluoroethylene (Teflon ®), because it is perfluorinated hydrocarbon. Since its discovery , physical and chemical proper- ties of fluorographene have been thoroughly analyzed. Numerous studies show that FG is not chemically inert and undergoes vari- ous chemical reactions under ambient conditions. The chemistry of fluorographene is now a budding discipline because it can lead to various graphene derivatives and represent efficient strategy for synthesis of tailored graphene derivatives with a high degree of functionalization(73).

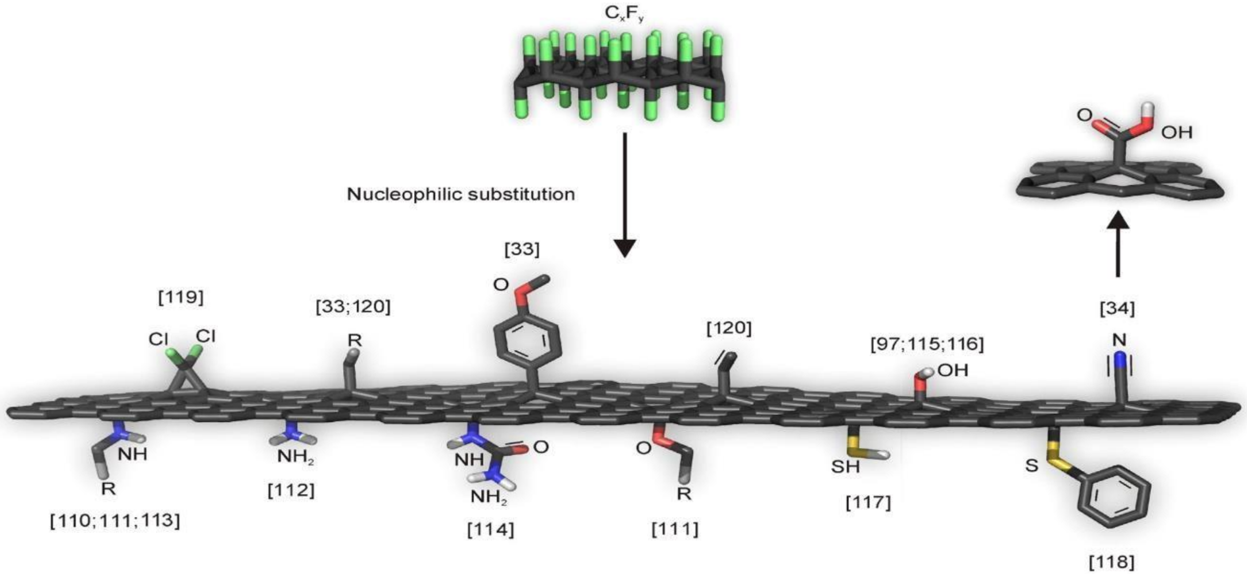

Fig. 8. Reactions of fluorographene lead to a wide portfolio of graphene derivatives.

1-Applications

GrF and organosiloxane derivatized GrF were studied as solid lubricants and lubricant additives since ’60 s and ’70 s, in place of other 2D materials such as graphite and MoS_2. At that time, there were no reports on the use of single sheets of FG. Neverthe- less, the layered nature, low surface energy, and facile exfoliation of GrF plays a significant role in lubrication(74). GrF, with theoretical specific capacity for Li of 865 mAh g^{-1}, which is substantially more than that for pure graphene (372 mAh g^{-1}), was also utilized as cathode material for primary and secondary Li-ion bat- teries, improving the discharge and shelf-life characteristics of the battery cells. An overview of many other properties and application of GrF, e.g., in batteries, is given in a book(75).

In the case of batteries as well, intercalation and even reactions (i.e., defluorination and transformation of GrF to conductive carbon(76)) take place in between the single layers. Therefore, eventu- ally, the mechanisms in these processes exploit the properties of FG and not of the bulk GrF material only. Application of FG in batteries still provokesresearch interest(77).

The applications of FG were extended to solar cell technolo- gies by Das et al. (78)in 2011.

FG, considered as one of the thinnest 2D insulators, is also explored in electronic applications as gate dielectric material and modified layer in organic field effect transistors (FETs)(79).

FG has also found applications in the field of biomedicine. In 2012, Wang et al. (80)studied the differentiation of the mesenchy- mal stem cells on fluorinated graphene surfaces,

Finally, in 2012, two independent reports appeared studying the non-linear optical properties of FG (81) and FGO with the open-aperture Z-scan technique. Important third order non-linear optical response was recorded in aqueous colloids of FG, prepared by exfoliation of GrF with the aid of a perfluorinated surfactant and sonication(82). In addition, non-linear optical limiting (one order of magnitude higher than that of GO) was identified in aqueous dis- persions of FGO(83). Such properties predispose these materials for optoelectronic and photonic applications.

3- Graphane

1- Applications

graphane is a hydrogenated sheet of gra- phene, where a primitive graphane cell contains two carbon atoms and two hydrogen atoms.(84) The difference in this case is that the graphene sheet is 100% hydrogenated as opposed to 50% hydrogenated. However, the structural parameters are similar. There is roughly a 5° difference in the CCCbondangle while there is less than 0.1 Å difference in the C–

C bond lengths. As can be seen in Figure 13, the most notable difference is that each carbon in graphane is bound to a single hydrogen atom resulting in complete sp3 hybridization, as opposed to graphone's mixture of sp2 and sp3 hybridized bonds or graphene's sp2 hybrid structure. Another difference from previous structures is that at finite temperatures, graphane does not exhibit intrinsic thermal ripples that are present in graphene.(85) Furthermore, graphane has been successfully synthesized, and various studies have been per- formed on graphane investigating its electronic,(86,87) optical,103 mechanical,(89,88) and thermal109 properties. Graphane is an attractive material due, in part, to the fact that the hydrogena- tion of graphene into graphane can be reversed through anneal- ing at high temperatures, thus restoring the original properties of graphene.(90) The applications for graphane have also been examined in the areas of hydrogen storage,(91,92) biosensing, transistors, and spintronic devices.

examine the stability, electronic structure, and hydrogen stor- age capacity of strain-induced stabilization of lithium doped graphane. Two symmetries, hexagonal and rectangular, in the dispersion of lithium on graphane were examined and their relative stabilities were compared. Furthermore, the effects of lithium stabilization on the enhancement of hydrogen storage capacity of lithium doped graphane were discussed.

For their choice of the supercell, Hussain et al replaced two hydrogen atoms with lithium, resulting in a doping concen- tration of 25%. Upon geometry optimizations of the system, the two lithium atoms centered above the bond between two carbon atoms as seen in Figure 9.

Furthermore, the binding energies of the adsorbed hydrogen molecules are consistently between 0.15 eV and 0.20 eV, regardless of how many hydrogen molecules are adsorbed. This study provides a potential application of graphane for hydrogen storage using lithium dopants.

2- Biosensing

Another possible application of graphane is for use in biosensing. In experimental work by Tan et al, the prop- erties of graphane were compared with graphene for use in electrochemical oxidation of biomarkers by using a ferro/ ferricyanide probe via cyclic voltammetry and electro- chemical impedance spectroscopy. The use of graphane in biosensing could be a novel use for carbon based devices in biotechnological applications.

To perform their electrochemical measurements, the synthesized graphene and hydrogenated graphene structures were dispersed in dimethylformamide by sonication. After sonication, the aliquot of the suspension was placed onto a glassy carbon electrode that had been previously polished. The deposited material was then allowed to dry.

3- Spintronics

Although by no means a complete list of applications for graphane, a final aspect we examine is its spintronic device applications. In a study by Da et al, a number of different transition metals were embedded within graphane. This tran- sition metal atom replaces both the carbon atom that would normally be in that position as well as the bound hydrogen. The result of these embedded transition metal atoms is that there are varying amounts of net magnetization within the systems studied. Furthermore, it was shown that by designing a heterojunction structure with nickel and vanadium embed- ded within graphane, the spin current can be effectively manipulated. As a result, one spin current, which in this work has been deemed the spin down current, can be completely suppressed when a negative bias voltage is applied, result- ing in a perfect spin filter and spin current diode.

References:

1. Hasan S 2015 A Review on Nanoparticles : Their Synthesis and Types Biosynthesis : Mechanism **4** 9–11
2. Assessment R 2007 Nanoparticles in the Environment
3. Cho E J, Holback H, Liu K C, Abouelmagd S A, Park J and Yeo Y 2013 Nanoparticle characterization : State of the art , challenges , and emerging technologies
4. Machado S, Pacheco J G, Nouws H P A, Albergaria J T and Delerue -Matos C 2015 Characterization of green zero-valent iron nanoparticles produced with tree leaf extracts Sci. Total Environ. **533** 76–81
5. TiwariDK, Behari J andSenP2008ApplicationofNanoparticlesinWaste WaterTreatment 3 417–33
6. Salavati-niasari M, Davar F and Mir N 2008 Synthesis and characterization of metallic copper nanoparticles via thermal decomposition Polyhedron **27** 3514–8
7. Tai C Y, Tai C, Chang M and Liu H 2007 Synthesis of Magnesium Hydroxide and Oxide Nanoparticles Using a Spinning Disk Reactor 5536–41
8. Bhaviripudi S, Mile E, Iii S A S, Zare A T, Dresselhaus M S, Belcher A M and Kong J 2007 CVD Synthesis of Single-Walled Carbon Nanotubes from Gold Nanoparticle Catalysts 1516–7
9. Roth CM, Sundaram S. Engineering synthetic vectors for improved DNA delivery: insights from intracellular pathways. Annu Rev Biomed Eng 2004;6:397–426.
10. (a) Sundar S, Kundu J, Kundu SC. Biopolymeric nanoparticles. Sci Technol Adv Mater 2010;11(1):014104–17. (b) Nayak S, Lyon LA. Soft nanotechnology with soft nanoparticles. Angew Chem Int Ed 2005;44(47):7686–708.
11. (a) Kommareddy S, Amiji M. Preparation and evaluation of thiol-modified gelatin nanopar- ticles for intracellular DNA delivery in response to glutathione. Bioconjug Chem 2005;16 (6):1423–32. (b) Lemieux P, Guerin N, Paradis G, Proulx R, Chistyakova L, Kabanov A, Alakhov V. A combination of poloxamers increases gene expression of plasmid DNA in skeletal muscle. Gene Ther 2000;7(11):986–91.
12. (a) Bhavsar MD, Amiji MM. Polymeric nano- and microparticle technologies for oral gene delivery. Expert Opin Drug Deliv 2007;4(3):197–213. (b) Morille M, Passirani C, Vonarbourg A, Clavreul A, Benoit J-P. Progress in developing cationic vectors for non-viral systemic gene therapy against cancer. Biomaterials 2008;29(24–25):3477–96.
13. Tabatt K, Kneuer C, Sameti M, Olbrich C, Muller RH, Lehr CM, Bakowsky U. Transfection with different colloidal systems: comparison of solid lipid nanoparticles and liposomes. J Control Release 2004;97(2):321–32.

14. (a) Schwarz C, Mehnert W, Lucks JS, Muller RH. Solid lipid nanoparticles (SLN) for con- trolled drug-delivery. 1. Production, characterization and sterilization. J Control Release 1994;30(1):83–96. (b) Muller RH, Mader K, Gohla S. Solid lipid nanoparticles (SLN) for controlled drug delivery—a review of the state of the art. Eur J Pharm Biopharm 2000;50 (1):161–77. (c) Vighi E, Ruozi B, Montanari M, Battini R, Leo E. Re-dispersible cationic
15. Gazit E. Self-assembled peptide nanostructures: the design of molecular building blocks and their technological utilization. Chem Soc Rev 2007;36(8):1263–9.
16. M. Terrones, Science and technology of the twenty-first century: synthesis, propertypes, and applications of carbon nanotubes, Annu. Rev. Mater. Res. 33 (2003) 419 501.
17. C. Soldano, A. Mahmood, E. Dujardin, Production, properties and potential of graphene, Carbon 48 (2010) 2127 2150.
18. M. Xu, T. Liang, M. Shi, H. Chen, Graphene-Like Two-Dimensional Materials, Chem. Rev. 113 (5) (2013) 3766 3798.
19. X. Huang, Z. Yin, S. Wu, X. Qi, Q. He, Q. Zhang, et al., Graphene-Based Materials: Synthesis, Characterization, Properties, and Applications, Small 7 (2011) 1876 1902.
20. S. Bak, D. Kim, H. Lee, Graphene quantum dots and their possible energy applications: A review, Current Applied Physics 16 (2016) 1192 1201.
21. Y. Cui, S.I. Kundalwal, S. Kumar, Gas Barrier Performance of Graphene/polymer Nanocomposites, Pergamon, 2016, pp. 313
22. B.M. Yoo, H.J. Shin, H.W. Yoon, H.B. Park, Graphene and graphene oxide and their uses in barrier polymers, J. Appl. Polym. Sci. 131 (1) (2014) (n/a-n/a).
23. C. Cheng, S. Li, A. Thomas, N.A. Kotov, R. Haag, Functional graphene nanomaterials based

architectures: biointeractions, fabrications, and emerging biological applications, Chem. Rev. 117 (3) (2017) 1826–1914.

24. B. Tan, N.L. Thomas, A review of the water barrier properties of polymer/clay and polymer/graphene nanocomposites, J. Membr. Sci. 514 (2016) 595–612.
25. F.A. Ghauri, M.A. Raza, M.S. Baig, S. Ibrahim, Corrosion study of the graphene oxide and reduced graphene oxide-based epoxy coatings, Mater. Res. Express 4 (12) (2017), 125601-125601.