

**Kurdistan regional government**

**Salahaddin University**

**College education**

**Chemical Department**

**4<sup>th</sup> stage**



## **Chemical functionzation & characterization of graphene-based materials**

**Supervising**

***Mrs. Suad Najmadin Mohialdin***

**Propertied by**

***Shanaz Omer Ramadan***

**2022/2023**

## Supervisor recommendation

I am the student's supervisor, ---**student full name**----**Shanaz Omer Ramadan**---. I support that the student has completed all the requirements for submitting the research drawn entitled --**title of project**-- **Chemical Functionzation & Characterization of Graphene Based materials** -- according to the numbered administrative order 3/1/5/1972 on 9<sup>th</sup> oct. 2022 in accordance with the instructions of Salahaddin university quality assurance and it is ready for discussion.

Supervisor full name with

Signature with date : 8/4/2023



Dr. Suad Najmaldin Mohiaedin

Research project lecturer

Dr. Dler D. Kurda

### ***Acknowledgement:***

In the name of Allah, I would like to express my special appreciation and thanks to my supervisor (Dr. Suad Najmadin Mohiaedin), Who have been a tremendous mentor for me. I would like to thank her for encouraging in work in this research project and for allowing me to be independent as a researcher. Herr advice on both research as well as on writing up have been appreciated. I would also like to thank to all teaching staff in my college and my friends in my class, for supporting me for everything. Finally thank my God for letting me through all the difficulties.

## **Abstract**

Graphene research, provide material advantages that bring about unique and novel applications rather than simply an improved substitute to existing materials. Significant progress are new approaches to its manufacture including combination with other atoms and nano bio composite materials that introduce new functional properties.

Functionalized graphene can interface with biomolecules to provide new health sector benefits in the form of highly sensitive biosensors that may offer continuous label-free measurement of key bioactive cell molecules, innovative nanoparticles for tissue targeted drug delivery and scaffolds for tissue engineering with previously unachievable qualities favoring tissue integration and biocompatibility.

We here describe graphene functionalization methods and provide recent examples of how graphene can be used to achieve biological interactions with innovative outcomes. These laboratory focused advances each contribute to an incrementally improved understanding of how different forms of graphene and its derivatives can best be tailored to meet biological demands. Much has yet to be discovered with regard to safety profiles and improved manufacture yet considering how carefully derived rational insights might be combined with computational biology to accelerate complex performance models, prospects that graphene-based biomaterials can achieve extraordinary real-world benefits are optimistically poised.

**Key words: Graphene, functionalized Graphene, nanoparticles, bioactive, biological**

<b>List of connect</b>	<b>Page number</b>
Acknowledgement	3
Abstract	4
Introduction	6
Functionalization	8
Covalent Functionalization Of Graphene	9
3 .Properties Of Functionalized Graphine	9
3.1 Chemical Properties	12
3.2 Mechanical Properties	12
3.3Electronics Properties	13
2.Materials Engineering	16
2.1. High Thermo mechanical Performance Materials	17
2.2.Antibiofouling Coatings	20
2.3.Lubricants	20
2.4.Flexible Electronics	21
Optical Limiters	24
Toxicity	25
Conclusions	26
References	27

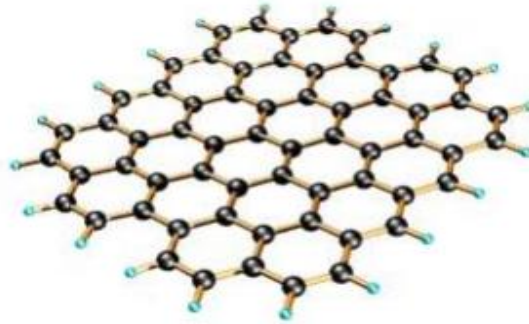
## 1. INTRODUCTION

Graphene is an allotrope of carbon consisting of a single layer of atoms arranged in a hexagonal lattice nanostructure. [(Mostofizadeh, Li et al. 2011)] The name is derived from "graphite" and the suffix -ene, reflecting the fact that the graphite allotrope of carbon contains numerous double bonds. Each atom in a graphene sheet is connected to its three nearest neighbors by a strong  $\sigma$ -bond, and contributes to a valence band one electron that extends over the whole sheet. This is the same type of bonding seen in carbon nanotubes and polycyclic aromatic hydrocarbons, and (partially) in fullerenes and glassy carbon. [(Abreu, Reber et al. 2014)] [(Harris 2018)] The valence band is touched by a conduction band, making graphene a semimetal with unusual electronic properties that are best described by theories for massless relativistic particles. Charge carriers in graphene show linear, rather than quadratic, dependence of energy on momentum, and field-effect transistors with graphene can be made that show bipolar conduction. Charge transport is ballistic over long distances; the material exhibits large quantum oscillations and large and nonlinear diamagnetism. [(Li, Chen et al. 2015)] Graphene conducts heat and electricity very efficiently along its plane. The material strongly absorbs light of all visible accounts for the black color of graphite; yet a single graphene sheet is nearly transparent because of its extreme thinness. The material is about 100 times as strong as would be the strongest steel of the same thickness [(Cao, Feng et al. 2020)] Photograph of a suspended graphene membrane in transmitted light. This one-atom-thick material can be seen with the naked eye because it absorbs approximately 2.3% of light.

Scientists theorized the potential existence and production of graphene for decades. It has likely been unknowingly produced in small quantities for centuries, through the use of pencils and other similar applications of graphite. It was possibly observed in electron microscopes in, but studied only while supported on metal surfaces. In the material was rediscovered, isolated and investigated at the University of Manchester by Andre Geim and Konstantin Novoselov. In 2010, Geim and Novoselov were awarded the Nobel Prize in Physics for their "groundbreaking experiments regarding the two-dimensional material graphene". [(O'Beirne 2001)] High-quality graphene proved to be surprisingly easy to isolate.

Graphene has become a valuable and useful nanomaterial due to its exceptionally high tensile strength, electrical conductivity, transparency, and being the thinnest two-dimensional material in the world.[1] The global market for graphene was \$9 million in. with most of the demand from research and development in semiconductor, electronics, electric batteries, [(Soldano, Mahmood et al. 2010)] and composites. The IUPAC (International Union for Pure and Applied Chemistry) recommends use of the name "graphite" for the three-dimensional material, and "graphene" only when the reactions, structural relations, or other properties of individual layers are discussed. A narrower definition, of "isolated or free-standing graphene" requires that the layer be sufficiently isolated from its environment. But would include layers suspended or transferred to silicon dioxide or silicon carbide. Graphene has a unique atom-thick two-dimensional structure, and excellent electrical, optical, chemical, thermal, and mechanical properties. It is an attractive material used for a variety of applications, including electronics. energy related systems, sensors actuators, composites, etc. To satisfy the requirements in practical applications, graphene has to be chemically modified frequently. First, pristine graphene is insoluble and

### **Idealized structure of a single graphene sheet**



## 2. Functionalization

The synthesis and applications of functionalized graphene materials have already been summarized in several reviews. However, few of them systematically discussed the chemistry related to the functionalization of graphene. In this section, we focus on the reaction mechanisms of graphene functionalization, and the structural and property changes of graphene upon functionalization. Fig. 1 schematically illustrates the chemical functionalization of graphene through a covalent or noncovalent approach. The edge sites of a graphene sheet with dangling bonds are more reactive than its basal plane. The dangling bonds can be used to covalently bond with various chemical moieties (Fig. 1a). These chemical moieties can increase the solubility and process ability of graphene, or provide reactive groups for further modification. Covalent functionalization of the graphene basal plane (Fig. 1b) causes the distortion of a p-p conjugation system. In contrast, the non covalent functionalization keeps the atomic and electronic structures of graphene (Fig. 1c). The asymmetric d electronic structures of graphene (Fig. 1c). The asymmetric functionalization on the two surfaces of a graphene sheet (Fig. 1d) can impart graphene with specific supra molecular behavior (Fig. 1e).

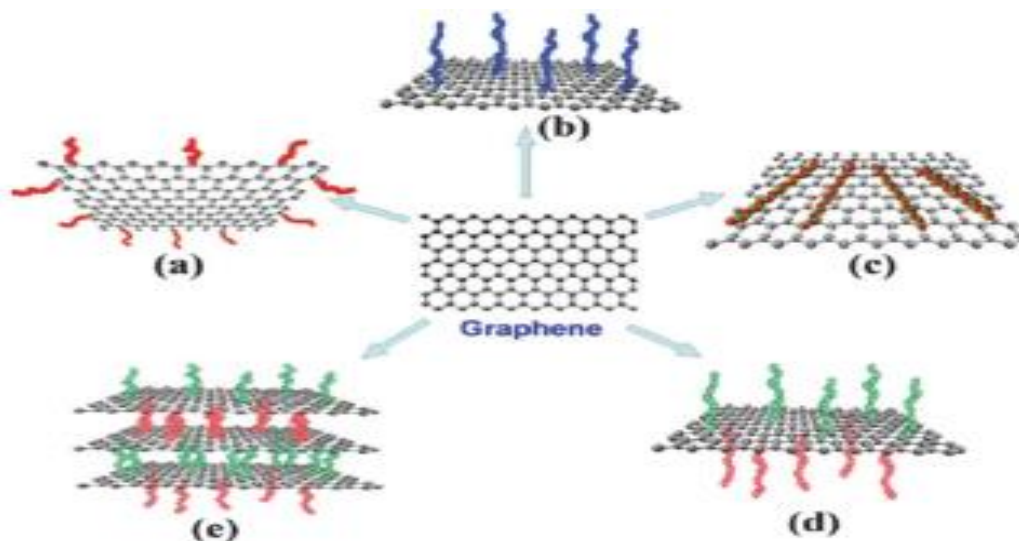


Fig. 1, covalent functionalization of graphene



## 2.1. Covalent functionalization of graphene basal plane

The basal plane of graphene is composed of  $sp^2$  carbons, which are chemically unsaturated. Intrinsically, it is possible to undergo covalent addition to change the carbon atoms from

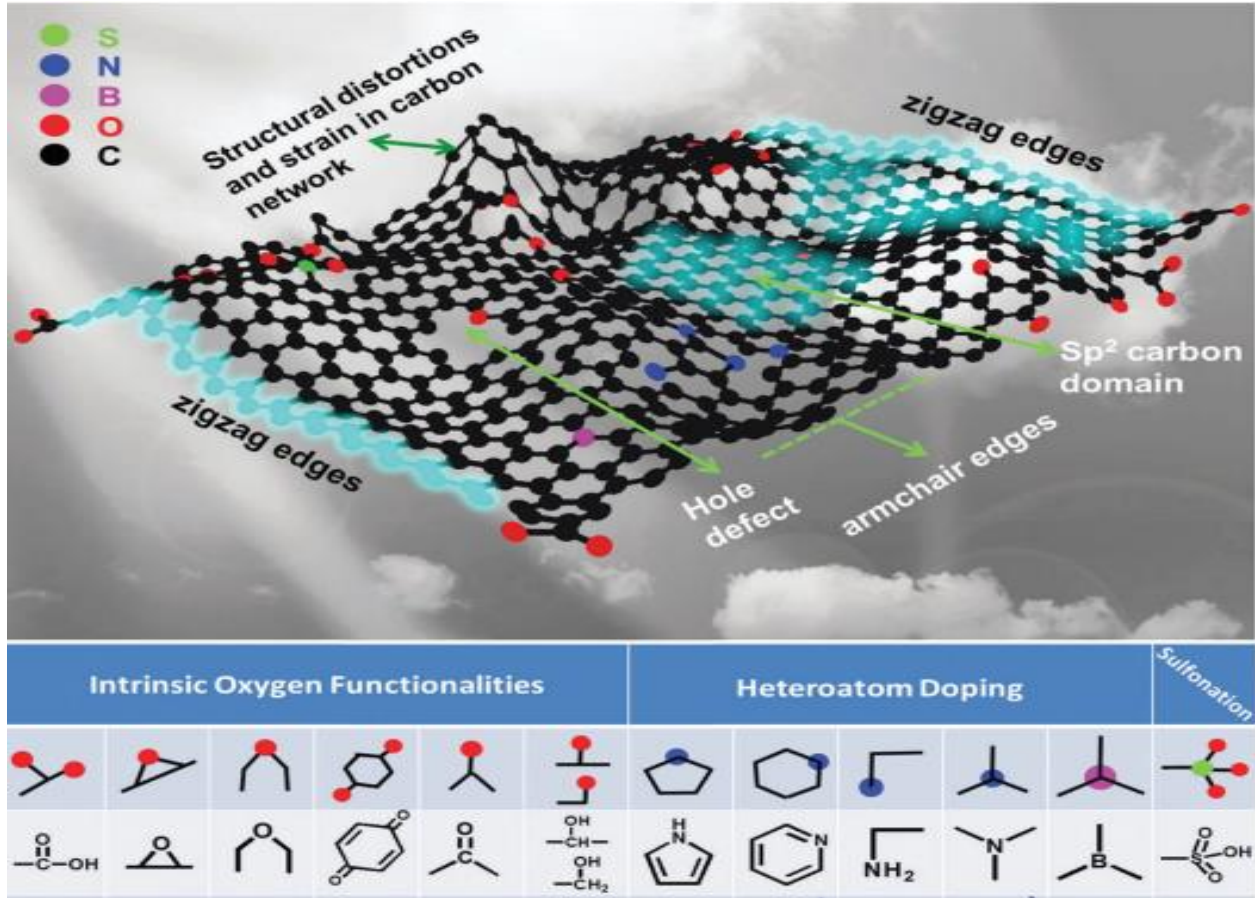


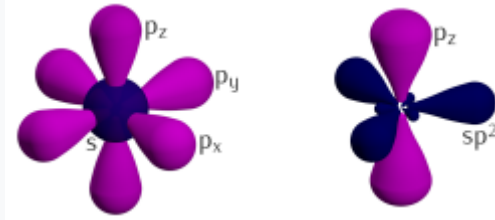
Fig.2 functionalization of graphene

## 3. Properties of functionalized Graphene

### Structure:

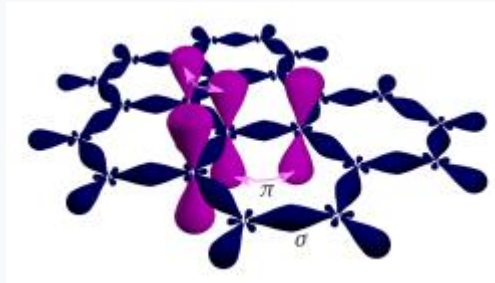
Graphene is a single layer (monolayer) of carbon atoms, tightly bound in a hexagonal honeycomb lattice. It is an allotrope of carbon in the form of a plane of  $sp^2$ -bonded atoms with a molecular bond length of 0.142 nanometers.

## Bonding



Carbon orbitals  $2s$ ,  $2p_x$ ,  $2p_y$  form the hybrid orbital  $sp^2$  with three major lobes at  $120^\circ$ .

The remaining orbital,  $p_z$ , is sticking out of the graphene's plane.



Sigma and pi bonds in graphene. Sigma bonds result from an overlap of  $sp^2$  hybrid orbitals, whereas pi bonds emerge from tunneling between the protruding  $p_z$  orbitals.

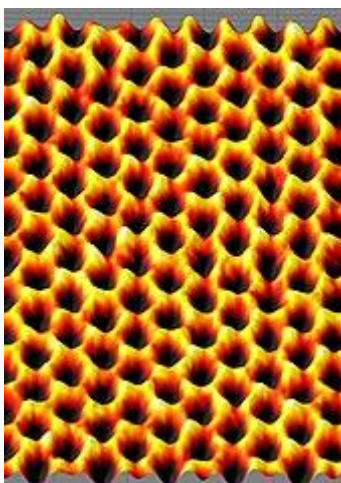
Three of the four outer-shell electrons of each atom in a graphene sheet occupy three  $sp^2$  hybrid orbitals – a combination of orbitals  $s$ ,  $p_x$  and  $p_y$  — that are shared with the three nearest atoms, forming  $\sigma$ -bonds. The length of these bonds is about 0.142 nanometers.(Cooper, D'Anjou et al. 2012)<sup>[1]</sup>(Abdelsalam, Teleb et al. 2019)<sup>[1]</sup>

The remaining outer-shell electron occupies a  $p_z$  orbital that is oriented perpendicularly to the plane. These orbitals hybridize together to form two half-filled bands of free-moving electrons,  $\pi$  and  $\pi^*$ , which are responsible for most of graphene's notable electronic properties.Recent quantitative estimates of aromatic stabilization and limiting size derived from the enthalpies of hydrogenation ( $\Delta H_{\text{hydro}}$ ) agree well with the literature reports.(Dixit and Singh 2019)

Graphene sheets stack to form graphite with an interplanar spacing of 0.335 nm (3.35 Å).

Graphene sheets in solid form usually show evidence in diffraction for graphite's (002) layering. This is true of some single-walled nanostructures. However, unlayered graphene with only (hk0) rings has been found in the core of pre-molar graphite onions. TEM studies show faceting at defects in flat graphene sheets and suggest a role for two-dimensional crystallization from a melt.

## Geometry



Scanning probe microscopy image of graphene

**Fig. 3 Scanning probe microscopy image of graphene**

The hexagonal lattice structure of isolated, single-layer graphene can be directly seen with transmission electron microscopy (TEM) of sheets of graphene suspended between bars of a metallic grid. Some of these images showed a "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. 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. The hexagonal structure is also seen in scanning tunneling microscope (STM) images of graphene supported on silicon dioxide substrates. The rippling seen in these images is caused by conformation of graphene to the substrate's lattice, and is not intrinsic.

## Stability

Ab initio calculations show that a graphene sheet is thermodynamically unstable if its size is less than about 20 nm and becomes the most stable fullerene (as within graphite) only for molecules larger than 24,000 atoms.

### 3.1 Chemical Properties

Graphene is the only form of carbon (and generally all solid materials) in which each single atom is in exposure for chemical reaction from two sides (due to the 2D structure). It is known that carbon atoms at the edge of graphene sheets have special chemical reactivity, and graphene has the highest ratio of edgy carbons (in comparison with similar materials such as carbon nanotubes). In addition, various types of defects within the sheet, which are very common, increase the chemical reactivity

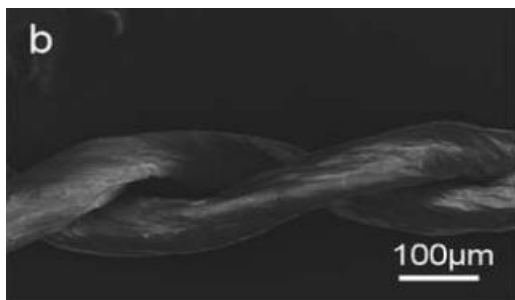


Figure 3 (b) the middle of the twisted fiber

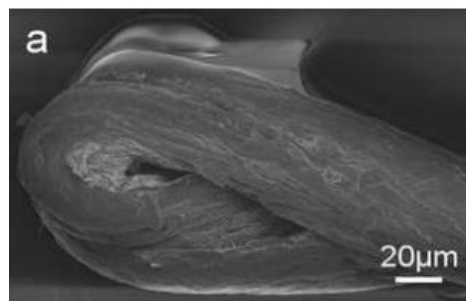
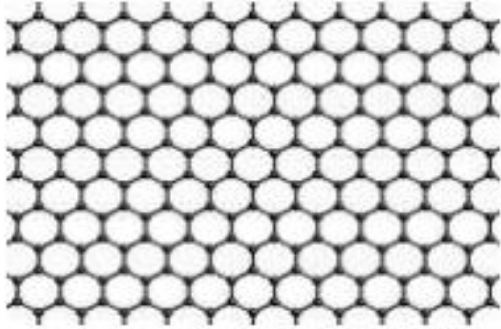


Figure 3 (a) the end of the twisted fiber

### 3.2 mechanical Properties

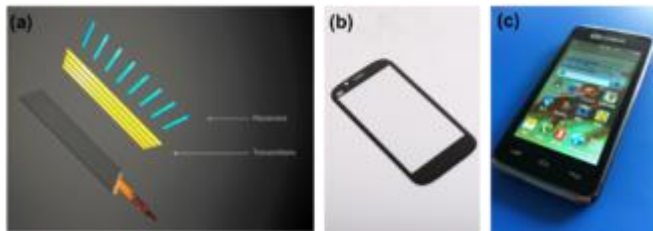
Another of graphene's stand-out properties is its inherent strength. Due to the strength of its 0.142 Nm-long carbon bonds, graphene is the strongest material ever discovered with an ultimate tensile strength of 130,000,000, extraordinarily strong, it is also very light at 0.77 milligrams per square meter (for comparison purposes, 1 square metre of paper is roughly 1000 times heavier). It is often said that a single sheet of graphene (being only 1 atom thick), sufficient in size enough yield, would weigh under 1 single gram. What makes this particularly special is that graphene also contains elastic properties, being able to retain its initial size after strain.



**Fig. 4 single Graphene sheet**

### **3.3 Electronics Properties**

Graphene is a semi-metal or zero-gap semiconductor. Four electronic properties separate it from other condensed matter systems. One of the most useful properties of graphene is that it is a zero-overlap semimetal (with both holes and electrons as charge carriers) with very high electrical conductivity



**Fig.5 The typical structure of a touch sensor in a touch panel. (Image courtesy of Synoptics, Incorporated.) (b) An actual example of 2D Carbon Graphene Material Co., Ltd.’s graphene transparent conductor-based touchscreen that is employed in (c) a commercial smartphone.**

### **Applications**

#### **Potential applications of graphene**

Graphene is a transparent and flexible conductor that holds great promise for various material/device applications, including solar cells, light-emitting diodes (LED), integrated photonic circuit devices, touch panels, and smart windows or phones. Smartphone products with

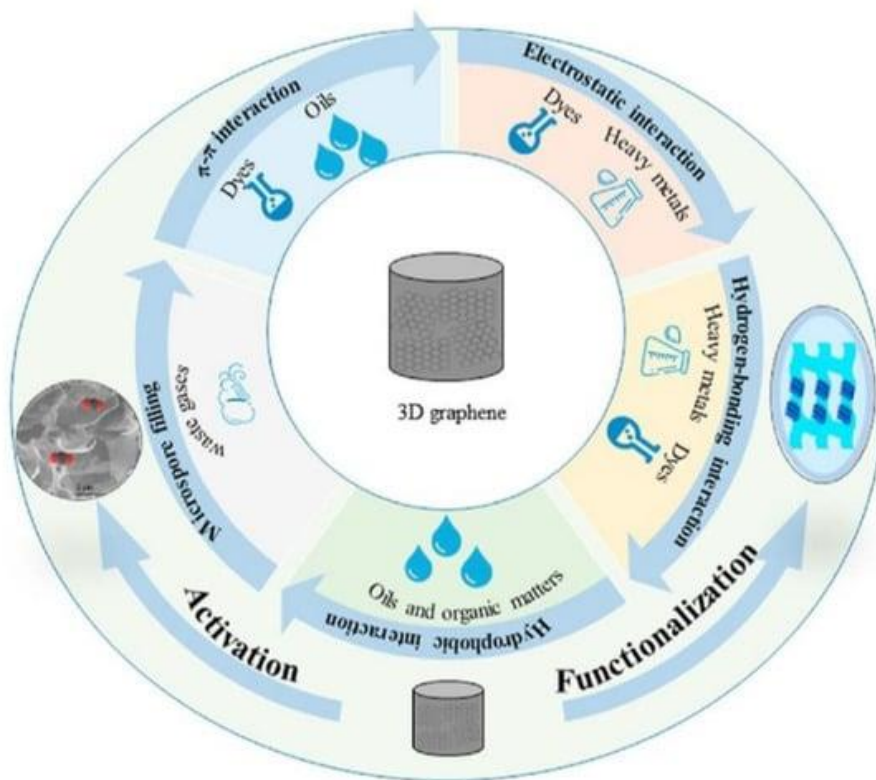
graphene touch screens are already on the market. In Head announced their new range of graphene tennis racquets.

As there is one product available for commercial use: a graphene-infused printer powder. Many other uses for graphene have been proposed or are under development, in areas including electronics, biological engineering, filtration, lightweight/strong composite materials, photovoltaics and energy storage. Graphene is often produced as a powder and as a dispersion in a polymer matrix. This dispersion is supposedly suitable for advanced composites. paints and coatings, lubricants, oils and functional fluids, capacitors and batteries, thermal management applications, display materials and packaging, solar cells, inks and 3D-printers' materials, and barriers and films.(Miller, Outlaw et al. 2011)On August 2, 2016, BAC's new Mono model is said to be made out of graphene as a first of both a street-legal track car and a production car.In graphene based spiral inductors exploiting kinetic inductance at room temperature were first demonstrated at the University of California, Santa Barbara, led by Kaustav Banerjee. These inductors were predicted to allow significant miniaturization in radio-frequency integrated circuit applications.

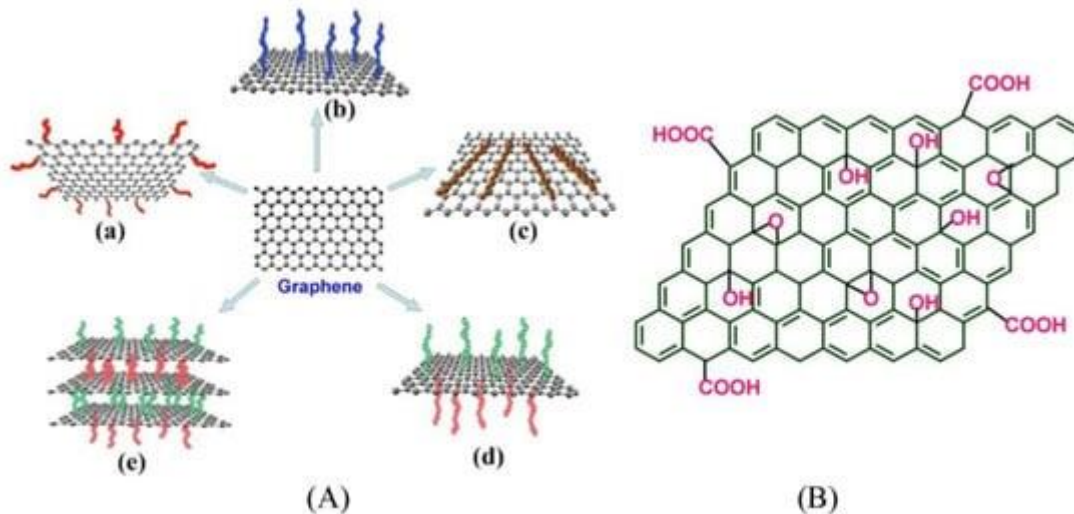
The potential of epitaxial graphene on SiC for metrology has been shown since 2010, displaying quantum Hall resistance quantization accuracy of three parts per billion in monolayer epitaxial graphene. Over the years precisions of parts-per-trillion in the Hall resistance quantization and giant quantum Hall plateaus have been demonstrated. Developments in encapsulation and doping of epitaxial graphene have led to the commercialization of epitaxial graphene quantum resistance standards. Novel uses for graphene continue to be researched and explored. One such use is in combination with water based epoxy resins to produce anticorrosive coatings. Therefore, GO attracts enormous interest especially for applications in biomedicine, and surfactants or lubricants, while graphene and GNP are often more suitable than GO for applications in flexible electronics and energy storage/conversion. All the graphemic materials demonstrate exceptional ability to trap other substances, thus being lately proposed as promising materials for environmental applications. In this latter case, the possibility to prepare graphene with tunable physicochemical characteristics is a key factor. In fact, modulation of oxidation level, size, and surface chemistry via derivatization allows for the removal of different classes of air and aqueous pollutants, including either polar or nonpolar aliphatic and aromatic molecules, waste gases, refractory organics, heavy metals, salts, oils, and so on. A generic representation of

the mechanisms that graphene materials exploit for the removal of various pollutants is provided in **Figure 6** [1].

GO is more prone to further derivatization reactions that encompass both non-covalent and covalent functionalization approaches, while graphene, due to the prevalence of  $sp^2$ -conjugated carbons, is preferably functionalized via  $\pi$ - $\pi$  stacking complexation or introducing specific moieties onto edge or basal planes, as depicted in **Figure 6** [2].



**Figure.6.1** Pictorial representation of the mechanisms involved during removal of various pollutants by using three-dimensional graphene materials. Reprinted with permission from [10], Copyright Elsevier, 2020.



**Figure.6.2 (A) Functionalization possibilities for graphene: (a) edge functionalization, (b) basal plane functionalization, (c) noncovalent adsorption on the basal plane, (d) asymmetrical functionalization of the basal plane, and (e) self-assembling of functionalized graphene sheets. (B) Chemical structure of graphene oxide. Reprinted with permission from. Copyright 2013, American Chemical Society. All the graphemic materials can be doped in an easy, tunable way, thus being suitable for energy storage applications.**

Graphene nanomaterials can be conveniently integrated into organic (e.g., polymers) and inorganic matrices and, thus, processed into thin films, sheets, fibers, membranes, foams, aerogels, and so on, leading to the possibility to attain 0D, 1D, 2D, and 3D materials, which can be even endowed with graded or hierarchical architecture in the last decade, hybrid structures of graphene and other nanocarbons, such as carbon nanotubes (CNTs), were proposed, aiming to exploit synergistic effects in mechanical, thermal, and electrical performance.

## 2. Materials Engineering

Over the last years, numerous applications in materials engineering have been conceived involving graphene or its derivatives, due to the interesting features in terms of mechanical, thermal, and electrical properties [(Amiri, Sadri et al. 2015),(Chatterjee, Nafezarefi et al. 2012) ,(Baby and Ramaprabhu 2010) ,(Sonvane, Gupta et al. 2015) ,(Yu and Zhang 2016) ,(Li, Bu et al. 2013) ,(Li, Wang et al. 2013)].



In the following, some relevant examples of actual materials engineering applications are described.

### **2.1. High Thermo mechanical Performance Materials**

One of the most desired goals in materials engineering is to achieve lightweight systems with enhanced mechanical and thermal resistance properties. From this point of view, the rise in graphene has sparked groundbreaking research, which has paved the way for quite promising developments [(Scaffaro and Maio 2019)]. Some relevant examples are cited in the following.

Gan et al. [(Gan, Shang et al. 2015)] succeeded in functionalizing graphene with D-glucose via esterification and preparing a nanocomposite with poly(vinyl alcohol) (PVA) and poly(methyl methacrylate) (PMMA) as matrices. They found that the functionalized graphene dispersed homogeneously in the matrices and led to significant improvements of thermomechanical properties, which are thought to be due to the strong hydrogen bond interactions between the polymer blend and D-glucose moieties attached onto fillers.

Chhetri et al. [(Chhetri, Adak et al. 2018)] functionalized GO nanoparticles with 3-amino-1,2,4-triazole (TZ) in KOH as catalyst and integrated such nanohybrids into epoxy resin by solution mixing. The resulting nanocomposites exhibited improved mechanical and thermal resistance. In detail, tensile strength and elastic modulus enhanced about 30% in comparison to those of composites containing pure GO, and fracture toughness doubled; TGA tests showed an approx. 30 °C increase in the onset degradation temperature.

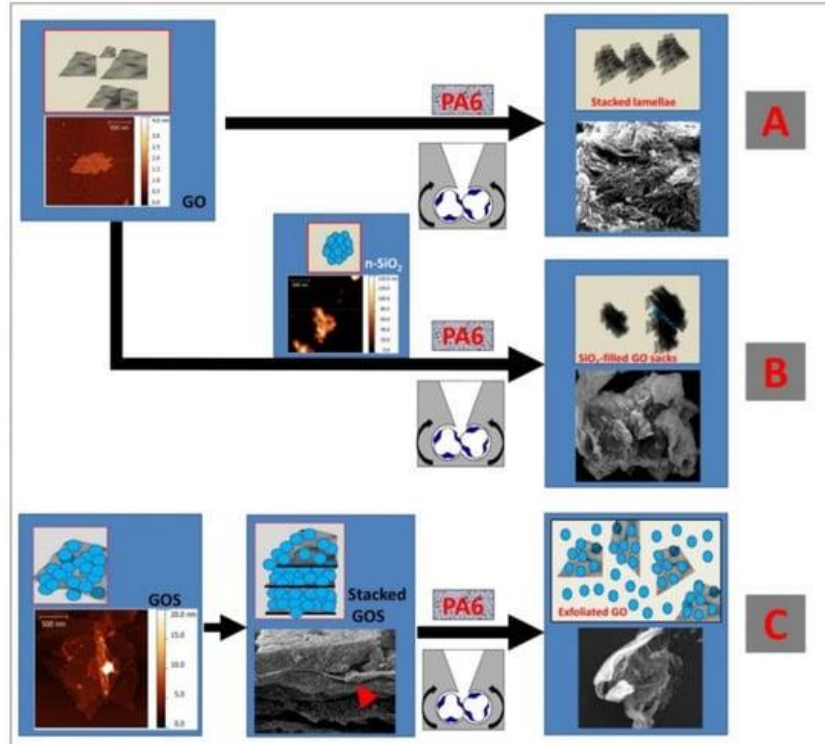
Yong et al. [(Qian, Wu et al. 2015)] fabricated nanocomposites from polyimide (PI) 3-aminopropylethoxysilane functionalized GO, via in situ polymerization and thermal imidization, finding significant improvements in the mechanical and thermal properties in comparison to the neat PI and depending on the functionalized GO amount: a bare 1.5 wt.% allowed them to obtain approx. 130% increment of the tensile modulus, 80% increase in the tensile resistance, and 200% increase in the thermal conductivity.

Bian et al. [(Bian, Wang et al. 2017)] prepared a complex system involving high-density polyethylene grafted with maleic anhydride (HDPE-g-MA), GO functionalized with ethylenediamine (GO-EDA) and oxidized carbon nanotubes (MWCNTs-COOH). GO-EDA and MWCNTs-COOH were coupled by L-aspartic acid, and the resulting hybrid network was integrated into HDPE-g-MA via melt compounding. Tensile, impact, and DMA characterization indicated that the properties underwent significant improvements in comparison to the neat

polymer matrix, while TGA showed that a bare 0.75 wt.% of hybrid loading allowed for an increase in the maximum decomposition temperature of about 11 °C.

Another important field where the use of graphene and derivatives may be of great interest is the packaging industry. In this case, the main applications are food packaging, which requires biodegradable materials due to the increasing environmental concerns related to waste disposal, and electronic packaging, which requires good barrier properties against gases and, especially, water vapor. In the latter case, the use of graphene seems particularly promising, thanks to its capability to improve mechanical properties, chemical durability, and barrier properties [(Gouvêa, Del Aguila et al. 2018),(Illyefalvi-Vitéz 2013)]. An example of application was provided by Gui et al. [(Gui, Yu et al. 2016),(Gui, Xiong et al. 2016)], who covalently immobilized polyurethane-imide and 4-allyloxy-biphenyl-4-ol onto GNP, with functionalization performed in ethanol for 30 min under ultrasonication, through the setting up of covalent bonding and  $\pi$ - $\pi$  interactions. Nanocomposites were then prepared with vinyl silicone resin prepolymer. They found that 1 wt.% of functionalized GNP allowed for the obtaining of a dramatic increase in the mechanical properties, i.e., about 500% of the original tensile strength, while 2 wt.% enhanced the elastic modulus up to 1000%. At the same time, higher functionalized GNP percentages (10–15%) lead to very remarkable improvements of the thermal conductivity (from 16 up to 38 times the original conductivity of the resin).

Non-covalently functionalized reduced graphene oxide nanoplatelets were used to grow in situ SiO<sub>2</sub> nanoparticles, thus giving rise to hierarchical structures. These latter were found to act as reinforcing agent for a hydrogenated nitrile butadiene rubber matrix, providing strong enhancement of both the static and the dynamic mechanical properties [(Wang, Wang et al. 2020)]. GO-SiO<sub>2</sub> nanohybrids can also be prepared via covalent bonding [(Maio, Agnello et al. 2016),(Maio, Agnello et al. 2016)]. Such nanoplateforms, prepared in water by either Fischer esterification or ethylenediamine-mediated coupling, were successfully tested as reinforcing fillers for thermoplastic polymers, including polyamide 6 (PA6) [(Maio, Agnello et al. 2016)], polylactic acid (PLA) [(Terzopoulou, Klonos et al. 2019)], and thermoplastic polyurethane (TPU) [(Ren, Zhou et al. 2018)]. **Figure 7** pictorially describes the outstanding exfoliation level of PA6 nanocomposites containing GO-silica nanohybrids (C), when compared to those containing GO (A) or a physical mixture of GO and silica (B) [36].



**Figure 7.** Schematics of the pathway followed and processing-structure relationship for nanocomposites A (direct melt mixing of PA6 and GO), nanocomposites B (melt mixing of PA6, GO, and Nano silica), nanocomposites C (synthesis of lasagna-like self-assembled GOS nanohybrids and melt mixing with PA6. AFM of nanomaterials and SEM of stacked GOS and polymer-based nanocomposites are provided together with the pictorial representation. Reprinted with permission from [36].

The intriguing thermal and heat transfer properties, which can be imparted by the presence of graphene and derivatives, also suggest the use for conventional working fluids, obviously in order to improve their thermal conductivity. For instance, Sadri et al. [(Sadri, Hosseini et al. 2017)] developed a route to fabricate highly water-soluble, functionalized GNP, based on free radical grafting of gallic acid onto GNP at 80 °C, 12 h, reflux conditions. The obtained nanofluid, containing just 0.05 vol% of nanoparticles, was found to possess approx. 25% higher thermal conductivity in comparison to the reference fluid.

## 2.2. Antibiofouling Coatings

Biologically generated fouling (biofouling) on marine equipment is a well-known issue related to the undesired growth of algae, plants, and microorganisms on submerged surfaces [(Maio, Scaffaro et al. 2019)]. Although it can also happen outside of marine environments, it is in those scenarios that it becomes more significant and annoying, blocking accesses and reducing the hydrodynamic performance of crafts (thus increasing fuel consumption) .Therefore, it is important to coat marine-submerged surfaces with suitable anti-biofouling products. Those, especially over the last years, need to be not only effective, but also with toxicity and environmental impact features as low as possible. For this reason, currently, the most used antifouling agents are based on  $\text{Cu}_2\text{O}$  and organic, environment-friendly biocides. On the other hand, biodegradable antifouling coatings would be of great interest, since they would lead, through degradation, to a “polishing” of the biofouling layer and to a “self-renewal” of the involved surfaces. Unfortunately, the actual application of these biodegradable coatings is undermined by the low values of degradation rate as well as of the adhesion strength. For instance, biodegradable polyurethanes (PU) and polylactides (PL) can find application in this field due to their good mechanical properties and biocompatibility, but on the other hand, especially with regard to PUs, they typically show slow hydrolysis kinetics and poor adhesion characteristics. Additionally, in this case, the literature suggests that the incorporation of graphene may significantly help in making the product more biodegradable and at the same time improve the antibacterial activity, while still keeping a reasonably long service life. Ou et al. prepared a biodegradable polyurethan, containing units of poly(L-lactic acid) as soft segments, and graphene. Phenol-derivatized graphene was used as an initiator for ring-opening polymerization of L-lactic acid and the resulting polymer grafted with graphene underwent condensation polymerization with diphenylmethane-diisocyanate to form polyurethan. They found it to be a suitable coating for smooth surfaces, with better antifouling behavior and hydrolysis capability in comparison to the neat PU.

### **2.3. Lubricants**

It is well known that most of the lubricants used for steel-based machinery and items are organic-based; on the other hand, environmental impacts considerations would require using more ecologically friendly systems, for instance based on water (which are already used in other fields). Unfortunately, water is not suitable as a lubricant for steel-based systems. Therefore, research has been carried out in order enhancing the tribological features of water, for instance by dispersing nanoparticle additives; in this context, graphene has been studied for use as a water-lubricating additive. One of the main limitations is due to carbon nanomaterials being hydrophobic; therefore, surface treatments are needed in order to impart hydrophilicity to this class of additives; at the same time, significant friction and wear reduction must be guaranteed.

One possibility is represented by carbon nanotube-ionic liquid (IL) and graphene-IL [88,89] hybrid lubricants, which showed intriguing friction and wear performance. Graphene-IL hybrid systems were added to polyethylene glycol (PEG) [(Khare, Pham et al. 2013)] to exploit the synergistic effect of graphene and ILs in reducing friction, with graphene covalently functionalized with methyl imidazolium oleate ([MIM][OL]), hexafluorophosphate ([MIM][PF<sub>6</sub>]), and bis(salicylato)borate ([MIM][BScB]) by means of suitable propyl trimethoxy silyl bridges. This led to significantly improved anti-wear behavior (increasing according to the above listing order) in comparison to the neat ILs-PEG systems. Significant anti-friction and wear properties were also found in systems prepared from GO and PEG subjected to  $\gamma$ -radiolysis in water [(Gusain, Mungse et al. 2016)].

Finally, also fluorinated graphene (FG) was taken into consideration, due to its excellent properties; on the other hand, its hydrophobicity strongly reduces its actual applicability. In this view, a trial was performed [(Gupta, Kumar et al. 2016)] to enhance its hydrophilicity via melt functionalization with urea. It was found that, after 4 h at 150 °C treatment, urea was covalently grafted onto FG, and that even small amounts of UFG (1 mg/mL) lead to significant reductions (up to approx. 60%) in the wear rate.

### **2.4. Flexible Electronics**

Flexible electronics is the terminology usually adopted to indicate electronic devices mounted on flexible substrates to obtain flexible electronic circuits [(Ye, Ma et al. 2016),(Salvatore, Münzenrieder et al. 2014)], which are, therefore, of any desired shape and, at the same time, can be bent during the operative use, finding application in consumer electronics

and medical devices, as depicted in **Figure 8**. [(Yao and Zhu 2015)]. More specifically, such a device should have features such as bendability, stretching ability, twistability, and stable electronic performance, and a flexible substrate is fundamental in obtaining a light, thin, and ductile device. In this perspective, functionalized graphene and derivatives can find application as fillers in a polymer matrix, improving the dielectric constant and keeping good flexibility and overall mechanical properties. Furthermore, it may be interesting to investigate the potential application of graphene in self-healing flexible electronics: self-healing substrates capable of repairing or recovering themselves after being subjected to use-related damages.



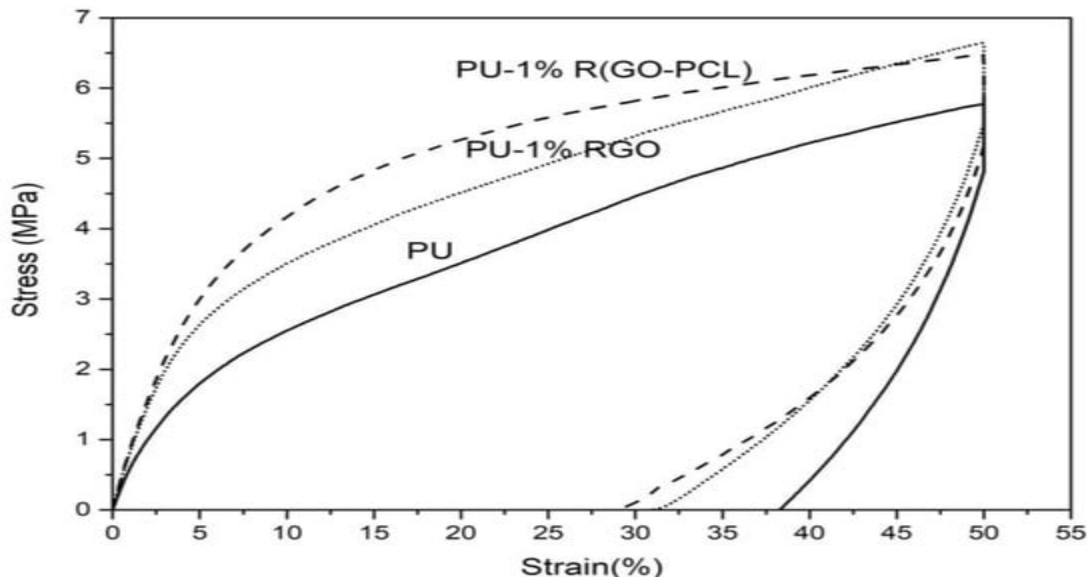
**Figure 8. Examples of possible applications of graphene-based flexible electronics.**

The literature reports some examples. Manna and Srivastava [(Zheng, Lee et al. 2020)] prepared, via solution mixing, nanocomposites based on carboxylated nitrile rubber (XNBR) and hexadecyl amine-functionalized graphene nanosheets (GNS-HDA). They found some very promising results, such as an approx. 60% increase in elongation at break and tensile strength, 13% reduction in the elastic modulus (and thus increased flexibility), 14-fold increased dielectric constant, and enhanced thermal stability, thus providing a suitable material for flexible dielectric devices.

Wu et al. [(Manna and Srivastava 2017)] prepared, through Diels-Alder chemistry, a composite based on polyurethane (PU), covalently bonded to RGO, showing good tenacity and IR-laser self-healing properties. They found that a bare 0.5 wt.% led to an improved stress at break equal to 36 MPa and, in particular, the ability to recover after breaking most of the initial properties, through laser irradiation (980 nm) for 60 s.

Another study also involving Diels-Alder chemistry was performed by Li et al. [(Wu, Li et al. 2017)], who prepared polyurethane composites covalently cross-linked with functionalized RGO. First, they modified GO with furfuryl amine in water (60 °C, 12 h) obtaining FRGO sheets, and then, they covalently crosslinked it with linear PU bearing furfuryl moieties by Diels-Alder cycloaddition reactions. They obtained, in summary, composites with improved mechanical properties and thermal stability and, moreover, healing efficiency by 5-minute microwave irradiation.

Lotfi Mayan Sofla et al. functionalized GO with polycaprolactone (PCL) and then added it to polyurethane to prepare shape memory nanocomposites [(Li, Zhang et al. 2017)]. Chemical bonding of PCL to GO was accomplished by the esterification reaction between OH groups of PCL and COOH groups of GO nanosheets. Results demonstrated that functionalized GO increased the shape recovery and mechanical properties of nanocomposites, as showed in **Figure 8.1**



**Figure 8.1 Thermomechanical cyclic behavior of neat PU and the related nanocomposites.**

## 2.5. Optical Limiters

The use of lasers is now widespread in several different fields, including medical treatments, optical communications, chemical measurements, and materials processing. On the other hand, the use of lasers also requires the utilization of suitable protections for sensitive optical apparatuses and human eyes, which involve the development of highly efficient optical limiters (OLs)

OL behavior has been found in some systems, such as organic dyes, metal nanoparticles, quantum dots, and carbon-based ones. In particular, graphene has been attracting considerable interest due to its OL properties deriving from its  $sp^2$ -conjugated carbon lattice and the linear dispersion of electronic band structure, which results in a nonlinear optical (NLO) characteristic. Furthermore, such behavior was also found in graphene-related composites

For instance, Xu et al. covalently functionalized RGO with three conjugated polymers containing carbazole, tetraphenyl ethylene, and phenyl moieties. They found an improved dispersion stability of RGO and, somehow unexpectedly, OL behavior strongly dependent on the type of polymer grafted onto nanoplateforms. In particular, two of them showed excellent OL performance, since they even responded to a 4  $\mu$ J input laser intensity.



Recently, decorating GO with nanoparticles such as metals and metal oxides is an emerging trend for the development of OL materials. In this context, Ren et al. adopted hydrothermal method to prepare TiO<sub>2</sub>/rGO nanohybrids that showed enhanced NLO and OL features with respect to starting components. Moreover, such a performance was found to improve upon decreasing the size of TiO<sub>2</sub>. With a similar approach, Nancy et al. developed a novel, green synthetic approach to decorate GO lamellae with laser-induced silver nanoparticles. The resulting nanohybrids gathered NLO behavior with antimicrobial properties, thus potentially serving as antibacterial OLs.

GO was incorporated into a silico-phosphate glassy matrix via the sol-gel method to construct films capable of exerting optical limiting functions for femtosecond laser pulses in the infrared-B spectral region. Additionally, fluorographene can be conveniently used in OL applications, and in this regard, Stathis et al. proposed a series of *N*-octylamine-modified fluorographene's with tunable NLO response.

### 3. Toxicity

One review on graphene toxicity published in 2016 by Lalwani et al. summarizes the in vitro, in vivo, antimicrobial and environmental effects and highlights the various mechanisms of graphene toxicity. Another review published in 2016 by Ou et al. focused on **graphene-family nanomaterials** (GFNs) and revealed several typical mechanisms such as physical destruction, oxidative stress, DNA damage, inflammatory response, apoptosis, autophagy, and necrosis.

A 2020 study showed that the toxicity of graphene is dependent on several factors such as shape, size, purity, post-production processing steps, oxidative state, functional groups, dispersion state, synthesis methods, route and dose of administration, and exposure times.

In 2014, research at Stony Brook University showed that 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. In 2013 research at Brown University found that 10 µm few-layered graphene flakes are able to pierce cell membranes in solution. They were observed to enter initially via sharp and jagged points, allowing graphene to be internalized in the cell. The physiological effects of this remain unknown, and this remains a relatively unexplored field.

## Conclusions

This review provides insight into the various ways to functionalize graphene and graphene derivatives, thereby expanding the number of potential applications for graphene-based materials. The functionalization modes can be classified according to the method and materials used and as such have been categorized as covalent functionalization, noncovalent functionalization, substitutional doping of graphene, and hybridization with nanoparticles, nanowires, and other materials. These various methods of functionalization offer various ways to expand on the current uses of graphene, that is, bioimaging or band gap opening, which can be used in electronics.

Graphene as a 2-D material still suffers from controlled synthetic growth conditions, especially when graphene derivatives are considered. It is imperative that these synthetic issues are addressed so that graphene and its derivatives can attain the highly promised application potential. With improved synthetic procedures graphene should be able to be employed far more easily in electronics as well as other applications that require fast electron transfer like photocatalytic applications toward renewable energy. The 3-D manipulation of the 2-D graphene material is another very important issue to be addressed as the manipulation of graphene into higher order nanostructures is already showing promise in super capacitors, fuel cells, water remediation, and drug delivery among others. However, as has been noted in the main text, the main applications of graphene and graphene composite materials will more than likely be in devices.

Whatever the future holds for graphene research, one can be assured that there will continuously be interesting topics because the material has already found interesting applications in fields as far apart as stem cell differentiation, highly selective separation, graphene–nanowire hybrid structure based photoconductive devices, graphene charge-doping based  $\pi$  plasmon control, and high-resolution spectroscopy. Looking toward the future use of graphene, it may be that in expanding on the already studied synthetic procedures lies a key to unlocking a new realm of opportunities for this material.

## References:

- Abdelsalam, H., et al. (2019). "First principles study of the adsorption of hydrated heavy metals on graphene quantum dots." Journal of Physics and Chemistry of Solids **130**: 32-40.
- Abreu, M. B., et al. (2014). "Does the 18-electron rule apply to CrSi<sub>12</sub>?" The Journal of Physical Chemistry Letters **5**(20): 3492-3496.
- Amiri, A., et al. (2015). "Synthesis of ethylene glycol-treated graphene nanoplatelets with one-pot, microwave-assisted functionalization for use as a high performance engine coolant." Energy conversion and management **101**: 767-777.
- Baby, T. T. and S. Ramaprabhu (2010). "Investigation of thermal and electrical conductivity of graphene based nanofluids." Journal of Applied Physics **108**(12): 124308.
- Bian, J., et al. (2017). "HDPE composites strengthened–toughened synergistically by l-aspartic acid functionalized graphene/carbon nanotubes hybrid nanomaterials." Journal of Applied Polymer Science **134**(29): 45055.
- Cao, K., et al. (2020). "Elastic straining of free-standing monolayer graphene." Nature communications **11**(1): 284.
- Chatterjee, S., et al. (2012). "Size and synergy effects of nanofiller hybrids including graphene nanoplatelets and carbon nanotubes in mechanical properties of epoxy composites." Carbon **50**(15): 5380-5386.
- Chhetri, S., et al. (2018). "Interface engineering for the improvement of mechanical and thermal properties of covalent functionalized graphene/epoxy composites." Journal of Applied Polymer Science **135**(15): 46124.
- Cooper, D. R., et al. (2012). "Experimental review of graphene." International Scholarly Research Notices **2012**.
- Dixit, V. A. and Y. Y. Singh (2019). "How much aromatic are naphthalene and graphene?" Computational and Theoretical Chemistry **1162**: 112504.

Gan, L., et al. (2015). "Covalently functionalized graphene with d-glucose and its reinforcement to poly (vinyl alcohol) and poly (methyl methacrylate)." RSC advances **5**(21): 15954-15961.

Gouvêa, R. F., et al. (2018). "Extruded hybrids based on poly (3-hydroxybutyrate-co-3-hydroxyvalerate) and reduced graphene oxide composite for active food packaging." Food packaging and shelf life **16**: 77-85.

Gui, D., et al. (2016). "Improved thermal and mechanical properties of silicone resin composites by liquid crystal functionalized graphene nanoplatelets." Journal of Materials Science: Materials in Electronics **27**: 2120-2127.

Gui, D., et al. (2016). "Liquid crystal functionalization of graphene nanoplatelets for improved thermal and mechanical properties of silicone resin composites." RSC advances **6**(42): 35210-35215.

Gupta, B., et al. (2016). "Effective noncovalent functionalization of poly (ethylene glycol) to reduced graphene oxide nanosheets through  $\gamma$ -radiolysis for enhanced lubrication." The Journal of Physical Chemistry C **120**(4): 2139-2148.

Gusain, R., et al. (2016). "Covalently attached graphene–ionic liquid hybrid nanomaterials: synthesis, characterization and tribological application." Journal of Materials Chemistry A **4**(3): 926-937.

Harris, P. J. (2018). "Transmission electron microscopy of carbon: a brief history." C **4**(1): 4.

Illyefalvi-Vitéz, Z. (2013). Graphene and its potential applications in electronics packaging- A review. Proceedings of the 36th International Spring Seminar on Electronics Technology, IEEE.

Khare, V., et al. (2013). "Graphene–ionic liquid based hybrid nanomaterials as novel lubricant for low friction and wear." ACS applied materials & interfaces **5**(10): 4063-4075.

Li, J., et al. (2017). "A covalently cross-linked reduced functionalized graphene oxide/polyurethane composite based on Diels–Alder chemistry and its potential application in healable flexible electronics." Journal of Materials Chemistry C **5**(1): 220-228.

- Li, W., et al. (2013). "The preparation of hierarchical flowerlike NiO/reduced graphene oxide composites for high performance supercapacitor applications." Energy & fuels **27**(10): 6304-6310.
- Li, Z., et al. (2015). "Field and temperature dependence of intrinsic diamagnetism in graphene: Theory and experiment." Physical Review B **91**(9): 094429.
- Li, Z., et al. (2013). "Control of the functionality of graphene oxide for its application in epoxy nanocomposites." Polymer **54**(23): 6437-6446.
- Maio, A., et al. (2016). "A rapid and eco-friendly route to synthesize graphene-doped silica nanohybrids." Journal of Alloys and Compounds **664**: 428-438.
- Maio, A., et al. (2019). Functionalization of graphene with molecules and/or nanoparticles for advanced applications. Handbook of Graphene, Scrivener Publishing LLC. **1**: 559-610.
- Manna, R. and S. K. Srivastava (2017). "Fabrication of functionalized graphene filled carboxylated nitrile rubber nanocomposites as flexible dielectric materials." Materials Chemistry Frontiers **1**(4): 780-788.
- Miller, J. R., et al. (2011). "Graphene electric double layer capacitor with ultra-high-power performance." Electrochimica Acta **56**(28): 10443-10449.
- Mostofizadeh, A., et al. (2011). "Synthesis, properties, and applications of low-dimensional carbon-related nanomaterials." Journal of nanomaterials **2011**: 1-21.
- O'Beirne, R. (2001). "Nobel Foundation." Reference Reviews **15**(8): 6-6.
- Qian, Y., et al. (2015). "In situ polymerization of polyimide-based nanocomposites via covalent incorporation of functionalized graphene nanosheets for enhancing mechanical, thermal, and electrical properties." Journal of Applied Polymer Science **132**(44).
- Ren, H., et al. (2018). "Enhanced mechanical properties of silica nanoparticle-covered cross-linking graphene oxide filled thermoplastic polyurethane composite." New Journal of Chemistry **42**(4): 3069-3077.

- Sadri, R., et al. (2017). "A novel, eco-friendly technique for covalent functionalization of graphene nanoplatelets and the potential of their nanofluids for heat transfer applications." Chemical Physics Letters **675**: 92-97.
- Salvatore, G. A., et al. (2014). "Wafer-scale design of lightweight and transparent electronics that wraps around hairs." Nature communications **5**(1): 2982.
- Scaffaro, R. and A. Maio (2019). "Optimization of two-step techniques engineered for the preparation of polyamide 6 graphene oxide nanocomposites." Composites Part B: Engineering **165**: 55-64.
- Soldano, C., et al. (2010). "Production, properties and potential of graphene." Carbon **48**(8): 2127-2150.
- Sonvane, Y., et al. (2015). "Length, width and roughness dependent thermal conductivity of graphene nanoribbons." Chemical Physics Letters **634**: 16-19.
- Terzopoulou, Z., et al. (2019). "Interfacial interactions, crystallization and molecular mobility in nanocomposites of Poly (lactic acid) filled with new hybrid inclusions based on graphene oxide and silica nanoparticles." Polymer **166**: 1-12.
- Wang, Y., et al. (2020). "Ultra-small SiO<sub>2</sub> nanoparticles highly dispersed on non-covalent functionalized reduced graphene oxide nanoplatelets for high-performance elastomer applications." Composites Science and Technology **198**: 108297.
- Wu, S., et al. (2017). "Ultrafast self-healing nanocomposites via infrared laser and their application in flexible electronics." ACS applied materials & interfaces **9**(3): 3040-3049.
- Yao, S. and Y. Zhu (2015). "Nanomaterial-enabled stretchable conductors: strategies, materials and devices." Advanced materials **27**(9): 1480-1511.
- Ye, X., et al. (2016). "Covalent functionalization of fluorinated graphene and subsequent application as water-based lubricant additive." ACS applied materials & interfaces **8**(11): 7483-7488.

Yu, Z. G. and Y.-W. Zhang (2016). "Electronic properties of mutually embedded h-BN and graphene: A first principles study." Chemical Physics Letters **666**: 33-37.

Zheng, Q., et al. (2020). "Graphene-based wearable piezoresistive physical sensors." Materials Today **36**: 158-179.