Chapter 1

Introduction

Contents

In this chapter, a brief description of graphene and graphene oxide-based nanocomposites and the functionalization of graphene oxide has been incorporated in form of scope and motivation of the thesis.

1.1 Introduction

"Small is beautiful"

In last few years, the term nanotechnology has evolved in human life and grabbed much importance due to minimizations of dimensions. Nanotechnology is the leading scientific field as it combines knowledge from the fields of physics, chemistry and biology. The progress in the field results in significant discoveries that have practical applications [1].

During the past decades, nanomaterials have been a center of research due to its size and potential applications. All materials such as metals, semiconductor and insulators have size dependent physiochemical properties. Nanomaterials are defined as, materials having a very small size in the range of 1 – 100 nm. However, dimension is not the only factor in nanotechnology, the change in the material property at small dimensions is the important essence of nanotechnology. As displayed in **Figure 1.1**, objects with nanoscale range have always been present in our environment. The nanoworld is the intermediate between-the atoms and the large molecules with strong relation between surface and volume [2,3].

When size of materials reduced to nanoscale, the physical and chemical properties change and consequently the properties of newly formed materials, that is nanomaterials, changes dramatically. The effect of size is basically divided into two types, internal and external size effect. Internal size effect is determined as changes in the properties such as lattice parameters, melting point, hardness, bandgap, chemical activity, diffusion coefficient, etc. While external size effect arises when the interaction between different physical fields and matters results in decreasing their building units such as domain, grain and the particles. Thus, by reducing the size of materials, one can hope for the discovery of novel effects and properties. Within, this domain, carbon-based materials are one of the interesting nanomaterials and widely studied due to their unique properties and applications [1].

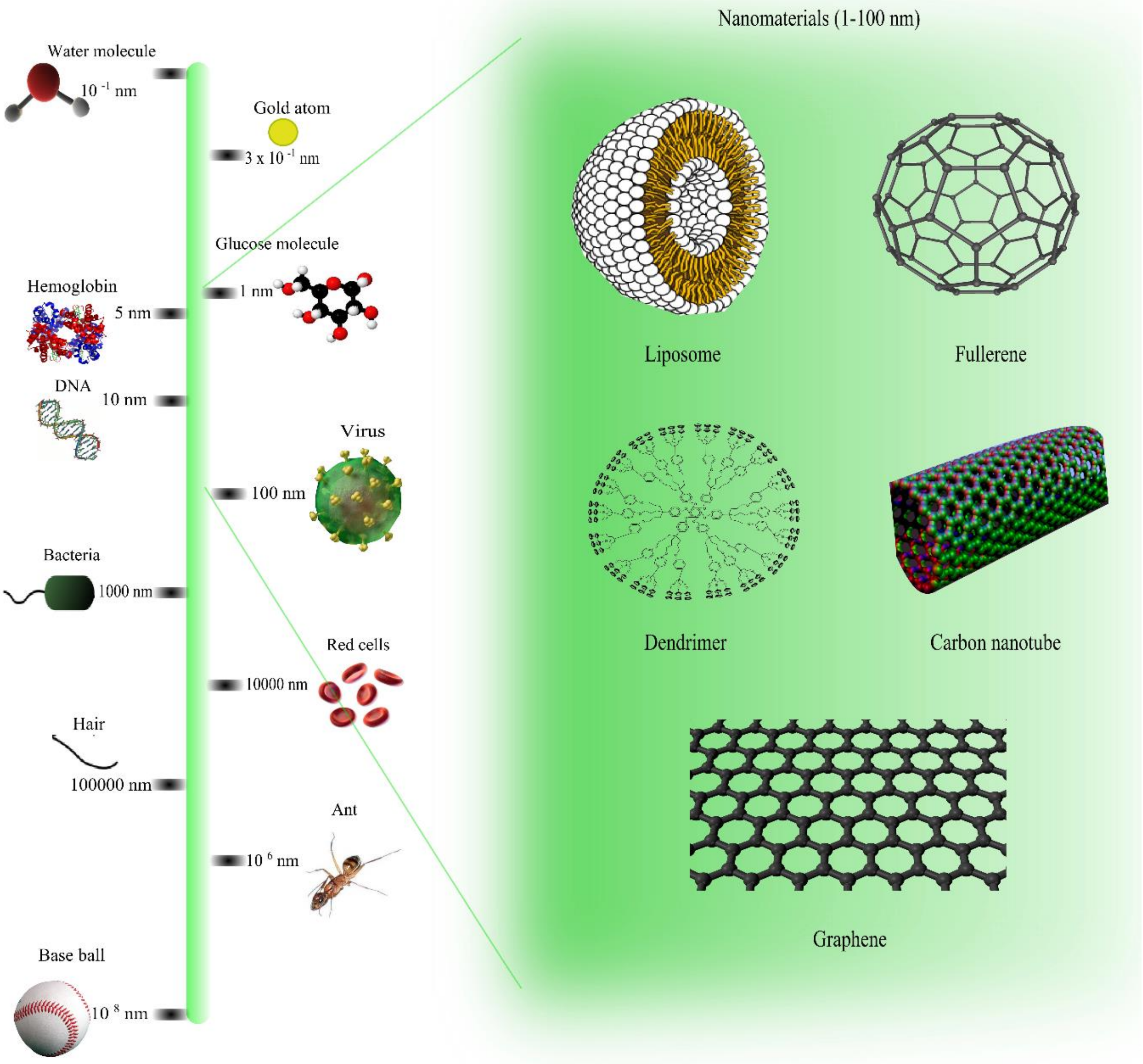


Figure 1.1: Examples of naturally occurring object in the nanoscale range [2]

1.1.1 Nanocomposites

The field of nanocomposite (NC) materials has been under close attention, imagination, and scrutiny of scientists and engineers in recent years. This scrutiny results from the simple premise that using building blocks with dimensions in the nanosize range makes it possible to design and create new materials with unprecedented flexibility and improvements in their physical properties. NCs and nanograined materials have been studied extensively mainly for improved physical properties [4].

Composites have been defined as “Multi-component material comprising multiple, different (non-gaseous) phase domains in which at least one type of phase domain is a continuous phase” and accordingly, NCs are composite materials in which at least one of the phase is a nanomaterial [5]. NCs refer to materials that are reinforced with nanoparticles consisting of at least two phases with one dispersed in another that is called matrix and forms a three-dimensional network, whereas nanograined materials are generally multi-grained single phase polycrystalline materials. These materials typically consist of an inorganic phase containing an organic phase or vice versa. Or they can consist of two or more inorganic/ organic phases in some combinatorial form with the constraint that at least one of the phases or features is in the nanosize [6]. To develop better NCs it is critical to be able to quantitatively describe the quality of the dispersion of the nanoparticles within the matrix. Homogeneous distribution of nanoparticles results in improved properties. But the tendency of particle agglomeration due to the weak Van der Waals forces between the nanoparticles results in deterioration in properties. For example, homogeneous dispersion of carbon nanotubes (CNTs), graphene, carbon nanofibers (CNFs), and clay in the polymer matrix improved mechanical, thermal, electrical, optical, gas barrier, and flame retardancy properties of NCs [7]. Surface modification and functionalization of nanomaterials improve the interfacial interaction or compatibility between the filler and matrix, which results in better dispersion which in turn facilitates effective stress transfer of the matrix and filler to develop high performance lightweight composites for advanced applications [8–11].

1.2 The carbon family

Carbon is the third most abundant material in the environment. It is the most fascinating element in the periodic table as it possesses ability to bind itself to the nearby elements [12]. Carbon based materials or nanostructures are most promising in nanotechnology as molecular sized diameter (~ 1 nm) with microscopic scale range results in amazing optical and electrical properties that can be used for the production of innovative devices [13,14]. In the field of science and technology, these materials have attracted much attention due to the existence of different forms of allotropes (shown in **Figure 1.2**) such as amorphous carbon, graphite, diamond, CNTs, carbon dots (GQDs), fullerene, graphene, graphene oxide (GO) and reduced graphene oxide (rGO).

The most common and naturally occurring form of carbon is graphite and diamond. Graphite consists of stacked sheets of carbon with hexagonal structure while under extremely high-pressure carbon forms diamond which is metastable form of carbon. Among all allotropes, graphite is considered as a promising material as different derivatives can be formed with different dimensionality [15,16]. In 2004 A. *Geim* and K. *Novoselov* discovered the existence of graphene [17]. It is a cutting-edge material due to its unique properties and exceptional applications. Some other derivatives like GO, rGO and GQD are also obtained by oxidizing both graphite and graphene [18]. Exploring the special features of GO from the carbon family, present work investigates its potential.

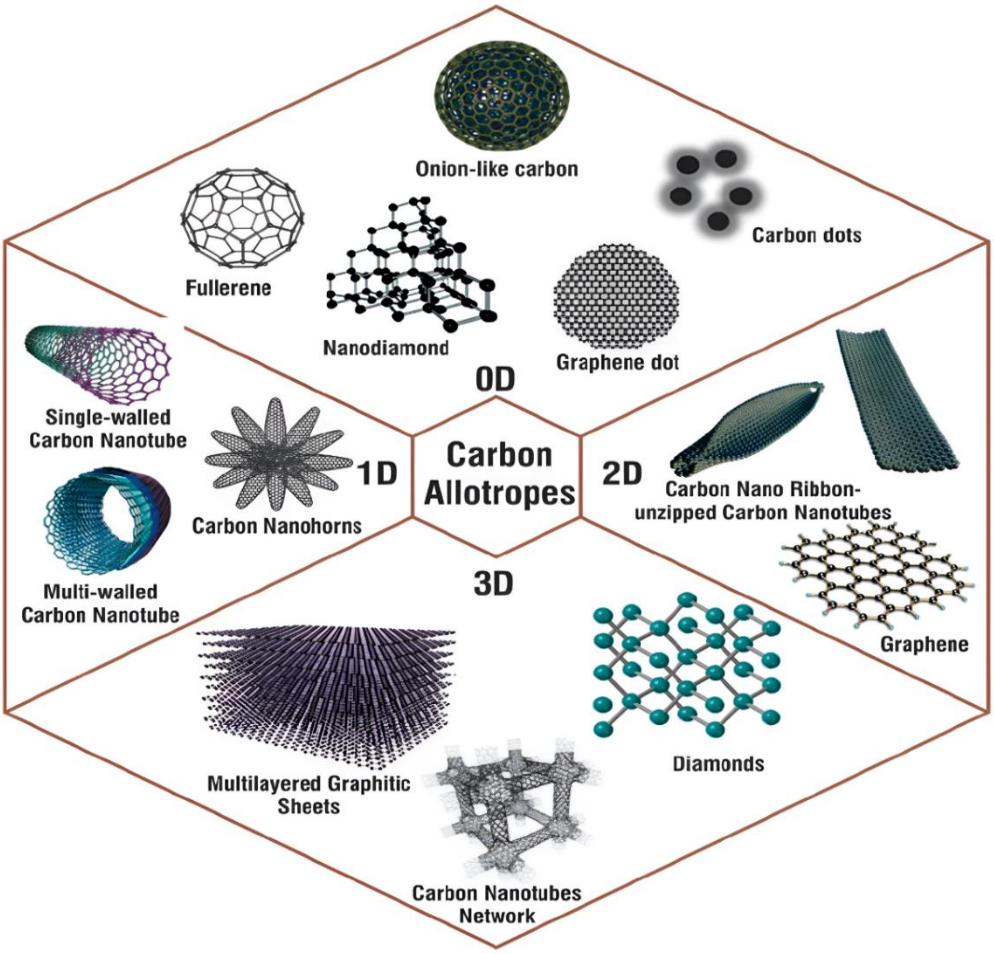


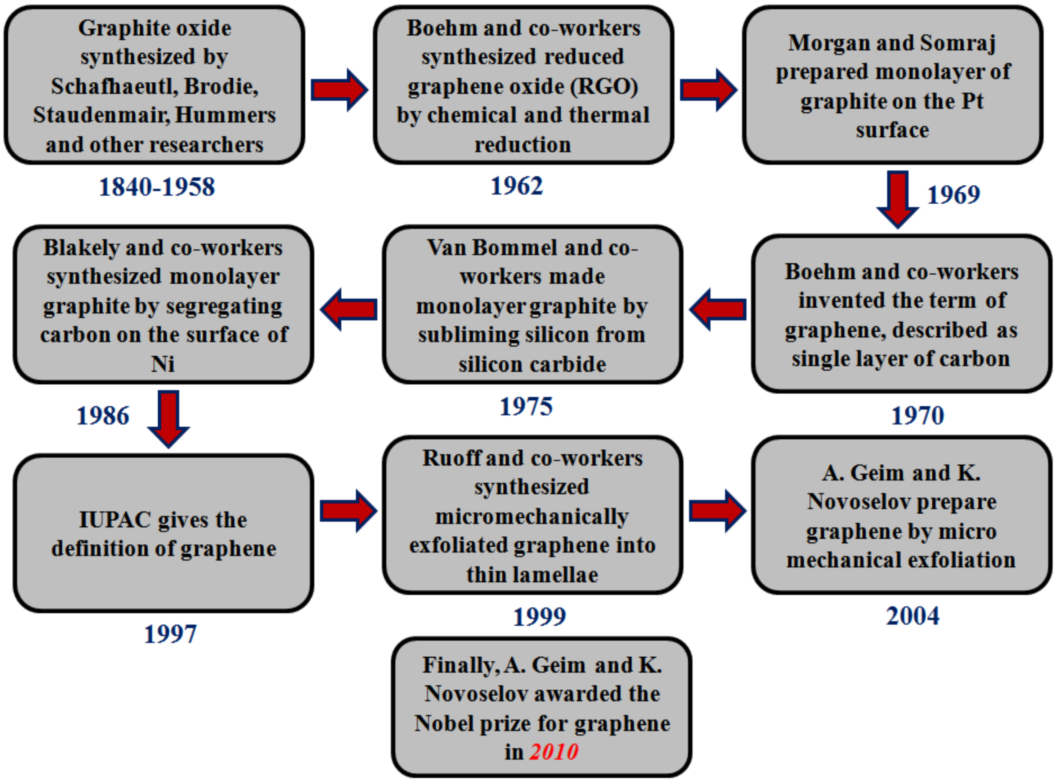
Figure 1.2: Illustration of carbon-based materials [19]

1.3 Graphene

Among the other allotropes, Graphene possesses unique properties due to its π-conjugated sp^2 hybridized network structure and very thin atomic thickness which yields extraordinary thermal, mechanical and electrical properties [20–22]. It is theoretically a nonmetal, but it is often referred to as a quasi-metal due to its properties being like that of a conducting metal [22]. It does not have an electronic band gap as the valence and conduction bands have a small overlap. Thus, the electrons travel through the graphene sheet as if they carry no mass, as fast as just one hundredth of the speed of light [23]. Accordingly, it possesses high electron mobility (15,000 $cm^2V^{-1}s^{-1}$) at room temperature, which leads to exceptionally good electrical conductivity. It is almost transparent, absorbs only 2.3% of the light intensity which is independent of the wavelength in the optical domain. The thermal conductivity of graphene is 5000 $Wm^{-1}K^{-1}$ and is 10 times better than copper (401 $Wm^{-1}K^{-1}$) [22].

Graphene has a breaking strength of 42 N/m which is 200 times stronger than the steel [20]. It is stretchable up to 20% of its initial length [23]. Graphene is chemically most reactive form of carbon. One atom thick sheet is hundred times more chemically reactive than the other. Carbon atoms at the edge of graphene sheets have special chemical [22]. The above-mentioned characteristics of graphene replaced CNT from various fields due to its all-in-one property which is superior comparison to CNT in all aspects and also cost effective than CNT.

Owing to its amazing properties graphene has become a material of choice since last few decades. Though, graphite was discovered in 1564 at Seathwaite (Borrowdale), North West England but, its structure was finally resolved in 1916 [17,24]. In 1859 *Benjamin Collins Brodie* has been reported the lamellar structure of thermally rGO [17,25]. Later *Kohlschutter* and *Haenni* reported the structure and properties of graphite oxide in the year 1918 [20]. In the year 1947, *P. R. Wallaee* presented a theory of graphene for understanding the electronic properties of 3D graphite. Transmission electron microscopic (TEM) image of few layers' graphite was first published by *G. Ruess* and *F. Vogt* in 1948 [26]. In 1990, an effort was made to make thin films of graphite by mechanical exfoliation. Finally, *A. Geim* and *K. Novoselov* successfully synthesized graphene by micro mechanical exfoliation from graphite in 2004. This revolutionary invention has bought them the Nobel Prize in 2010 (**Scheme 1.1**) [17].



Scheme 1.1: History of graphene as per the timeline.

1.4 Configuration and chemistry of graphene

Attractive properties of graphene arise from its intrinsic structure which consists of hexagonal carbon framework [23]. In graphene sheet, the three valence electrons of each carbon atom form C-C σ-bonds with each of its neighboring carbons whereas the fourth electron forms C=C π-bond that is oriented throughout the plane (**Figure 1.3**). The s, p_x and p_y atomic orbitals are involved in sp^2 hybridization which leads to a strong covalent C-C-C bond. The residual p_z orbitals of each carbon atom lies over the three adjacent carbons to form filled π-bonding orbitals and empty π* anti-bonding orbitals. Moreover, sp^2 hybridized planner skeleton with delocalized π-electrons throughout the sheet encourages its usability in different fields. This type of covalent attachment possibly opens a tunable band gap in graphene [22]. The delocalization of π-electrons makes graphene sheet extremely conductive, which creates great potential for graphene in various applications including electrodes, supercapacitor, composite materials, biomedical and sensors etc. [23,27,28]. Chemical functionalization is an effective approach to modify the structure and properties of graphene [27]. The different forms of graphene are GO, sulphonated graphene, fluorinated graphene, nitrogen doped graphene and polymer modified graphene [27,28]. Selective functionalization leads homogeneous dispersion of graphene in aqueous or different organic solvents. Due to its remarkable structural characteristics, graphene can grip a large variety of chemical functionalities on its planner surface and edge. However, the chemical reactivity of the graphene sheet is very weak in its surface because of large π-conjugation system, curve structure and the absence of dangling bonds. Thus, most of the chemical reactions can only take place at the edge of a graphene sheet as it found to be more reactive than its surface [28].

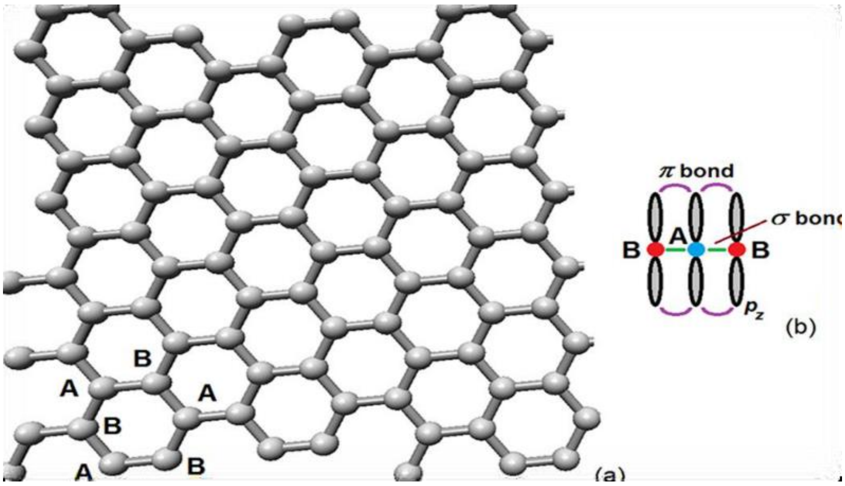


Figure 1.3: Structure (a) and bonding (b) of graphene [23].

1.5 Properties of graphene

Graphene possesses extraordinary properties such as high Young's modulus (~1.0 TPa) [29], large theoretical specific surface area (2630 m^2g^{-1}) [30], excellent thermal conductivity (~5000 $Wm^{-1}K^{-1}$) [31], high mobility of charge carriers (2×10^5 cm^2 V^{-1} s^{-1}) [23] and high optical transmittance (~97.7%) [32]. Electrical conductivity of single layer graphene is 6000 S/cm [33], which is higher than carbon nanotubes. The resistivity of graphene sheet is 10^{-6} Ω·cm which is found to be less than silver [26]. These astonishing properties make graphene as 'the supernatural projectile' in the research world and have opened up another skyline for the researchers.

Figure 1.4: Properties of graphene.

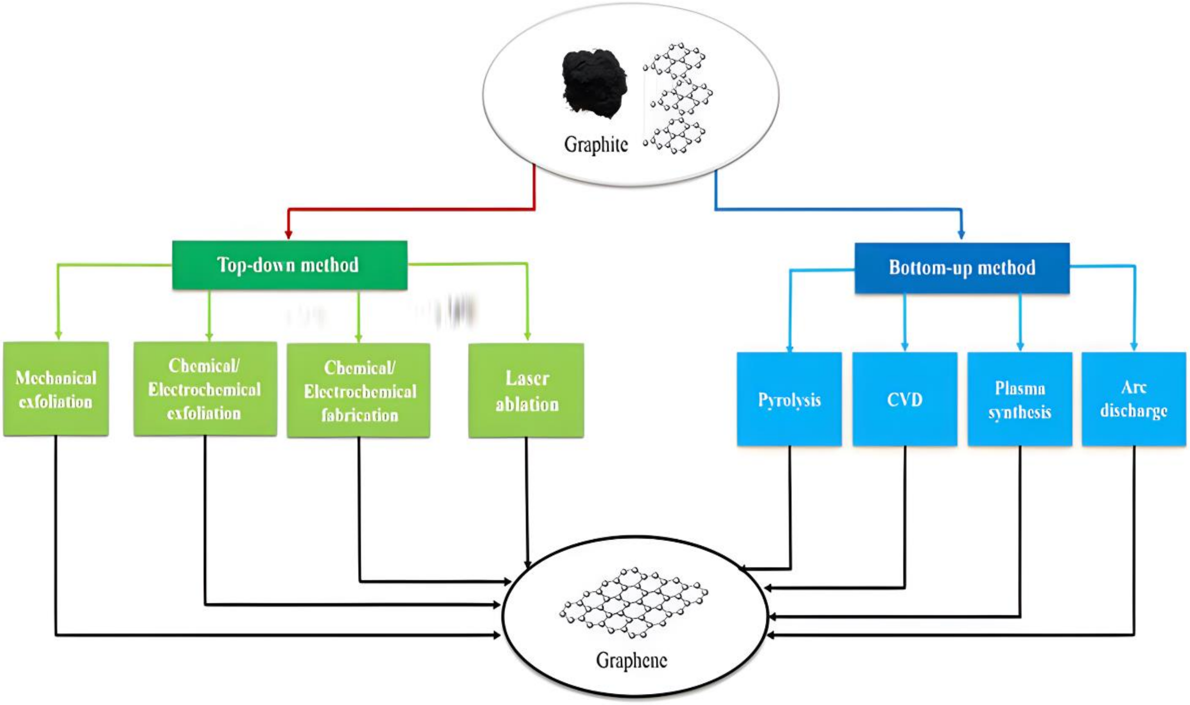
Table 1.1: At a glance view of properties of graphene

Structure	Graphene is basically two dimensional sp^2 hybridized, single atomic thin layer of graphite that is made up of very tightly bonded carbon atoms organized in to a hexagonal lattice. The thickness of graphite sheet is in the range from 3 nm to 100 nm.
Electronic	Graphene has high electron mobility (200000 cm^2/Vs) at room temperature which leads to higher electrical conductivity.
Thermal conductivity	Graphene with length and width of 3.6 μm and 5.52 μm possess 5000 W/mK thermal conductivity. Suspended single layer graphene's thermal conductivity measured at room temperature is ranging from 1500-5800 W/mK.
Mechanical	Pure graphene has high young modulus value of 1.0 TPa and it has a fracture strength (σ_t) of 130 GPa. The maximum stress and fracture strain (ε_f) of graphene in armchair direction is calculated to be 120 GPa and 0.13 respectively.
Optical	Single layer graphene sheet has a very high optical transmittance value of ~97.7%.

1.6 Synthesis of graphene oxide (GO) and reduced graphene oxide (rGO)

The discovery of graphene unlocked many challenges and make a new horizon to the researchers from all aspects owing to presence of its astonishing properties. Many attempts have been made to synthesize large scale defect free graphene sheets. Researchers have done extensive works on the large scale and high-quality production of graphene which includes both top down and bottom-up techniques for graphene synthesis (**Scheme 1.2**).

In 2004, A. *Geim* and K. *Novoselov* successfully prepared single layer graphene sheets by repeatedly peeling of graphene from graphite crystal using an adhesive tape and then they transferred the extracted graphite layer on to the silicon wafer [26,34]. Mechanical cleavage, direct sonication, electrochemical exfoliation, super acid dissolution, chemical reduction of colloidal GO and thermal exfoliation of GO are in the top-down category [35]. The bottom-up approach includes epitaxial growth using metal substrate, chemical vapor deposition (CVD), arc discharge and reduction of carbon monoxide [35].



Scheme 1.2: Flow-chart of graphene production [36].

- **Chemical exfoliation of graphene oxide**

The principle steps in the chemical exfoliation strategy are to build the interlayer separation of graphite, in this manner lessening the interlayer van der Walls forces and the shedding of intercalated graphite by breaking the frail van der Walls forces to form single layer graphene or GO. Previously, oxidation of graphite was done by $KClO_3$ and fuming HNO_3. Following 40 years of interlude, *Staudenmaier* changed the above strategy by utilizing mix acid (H_2SO_4 and HNO_3) and $KClO_3$ [37]. The most well-known strategy revealed in 1958 for the synthesis of GO is the *Hummer's* technique [38]. Till date, numerous methodologies have been executed so as to adjust the *Hummer's* technique which is designated as modified *Hummer's* technique [39,40]. The details about the technique have been discussed in the next chapters. Generally, reduction of GO is done by chemical reduction of the exfoliated GO in solvents such as water. Additionally, GO can be exfoliated in polar aprotic solvents by functionalization with organic compounds like isocyanate [41], octa-decylamine [42], and also using surfactants [42–44]. Various reducing agents are used for the synthesis of rGO such as hydrazine monohydrate [45], sodium borohydride [46], hydroquinone [47], strong alkali [48] and amines [49]. Among them, hydrazine hydrate is predominantly used because of its strong reducing ability for the removal of oxygen functionalities from GO. But the major drawback of hydrazine is its toxicity and explosiveness which retards its practical use.

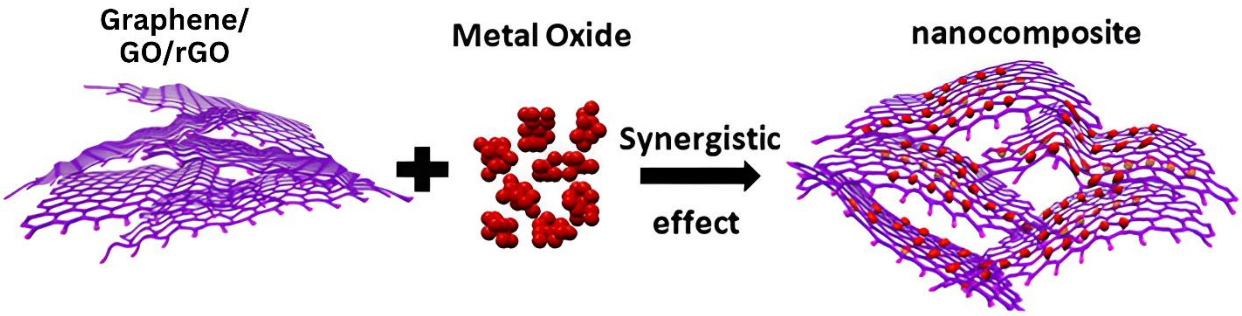
1.7 Graphene based nanocomposites

Because of graphene's exceptional thermal [50], mechanical [51], optical [52] and electronic properties [26], it stands out as the most promising candidate to be a major filling agent for composite applications [53]. Graphene NCs show substantial enhancements in their multifunctional aspects at very low loading, compared to conventional composites and their materials. This not only makes the material lighter with simple processing, but also makes it stronger for various multifunctional applications [53,54]. The advantages of graphene and GO NCs are: i) planar structure, ii) high surface area, iii) enhanced physical properties and iv) cost effectiveness. Graphene NCs are mainly classified as (a) graphene-inorganic nanocomposites and (b) graphene polymer nanocomposites.

1.7.1 Graphene-inorganic nanocomposites

Graphene/carbon/GO NCs also offers extraordinary properties like large surface area [55], high electrical conductivity [56], and unique mechanical strength [57]. Nanocomposites made of graphene and other carbon allotropes such as CNT, fullerene, carbon black (CB), carbon sphere and carbon nanofibers also shows improvement in various properties. Particularly, combination of graphene-CNT shows elevated electrical, thermal, mechanical and structural properties [58,59].

Graphene and GO based nonmetal NCs are very useful for the catalyst applications which are formed with the use of various non-metallic elements and compounds such as sulphur [60], silicon [61], silicon dioxide [62], silicon nitride [63], silicon oxy-carbide [64], cyanide [65] and carbon nitride [66]. These new types of composites are one of the substitutes in metal catalysts. It has been reported that graphene/C_3N_4 NC is a high-performance catalyst [66]. It activates molecular oxygen for selective oxidation of secondary C–H bonds in saturated alkanes into corresponding ketones [65,66].



Scheme 1.3: Schematic of the preparation of graphene/metal oxide NCs

The significant advantage of metal oxide NPs is: (i) structural changes that allow the altering of lattice symmetry and cell parameters, (ii) a change in electrochemical characteristics due to the quantum confinement effect, and (iii) change in surface properties leading to a drastic increase in the band gap that influences the conductivity and the chemical activity of the NPs. Another important property is their biocompatibility toward the immobilization of enzymes that aid in selective sensing of biomolecules [67].

In the last few decades, huge efforts have been made to synthesize graphene NCs with inorganic NPs, mostly based on transition metal and metal oxides [24,68], due to the improved properties and application possibilities of the NCs in different fields like super capacitor [69], optoelectronics, nanoelectronics [70], energy storage devices [71], biomedicine [72], catalysis [73], electro catalysis [74], photocatalysis [75], etc. There are two conventional methods for the preparation of graphene-based metal/metal oxide NCs. These are i) deposition method and ii) *in-situ* synthesis method [68]. In the former techniques, the metal NPs are adhered on the surface of graphene sheets either by physical adsorption, electrostatic binding or by charge transfer interactions whereas, in the *in-situ* synthesis method, the NCs are prepared at one stage by simultaneous reduction of GO and metal salt with suitable reducing agent [68]. Even though, this subsequent methodology is helpful in large scale productions, yet it is extremely difficult to maintain uniform particle size. There are different types of GO based metal/metal oxide NCs which can differ according to the use of different metal or metal oxide NPs like Ag, Au, Pt, Pd, CdO, ZnO, TiO_2, ZrO_2, SiO_2, Co_3O_4, Fe_3O_4 [76–80]. Other metal compounds like sulphides [81], selenides, nitride [82], and inorganic salts [83] are loaded with graphene to produce graphene/metal compound NCs. Since the combination of metal/metal oxide NPs with graphene sheets improves performances of the NCs, thus in this thesis will be focused on the synthesis of graphene oxide-based metal oxide NCs (such as GO@ZrO_2, GO@TiO_2, GO@ZnO, GO@SiO_2 NCs) studying their effects on physical and chemical properties through different applications. Details of this work have been discussed in separate chapters.

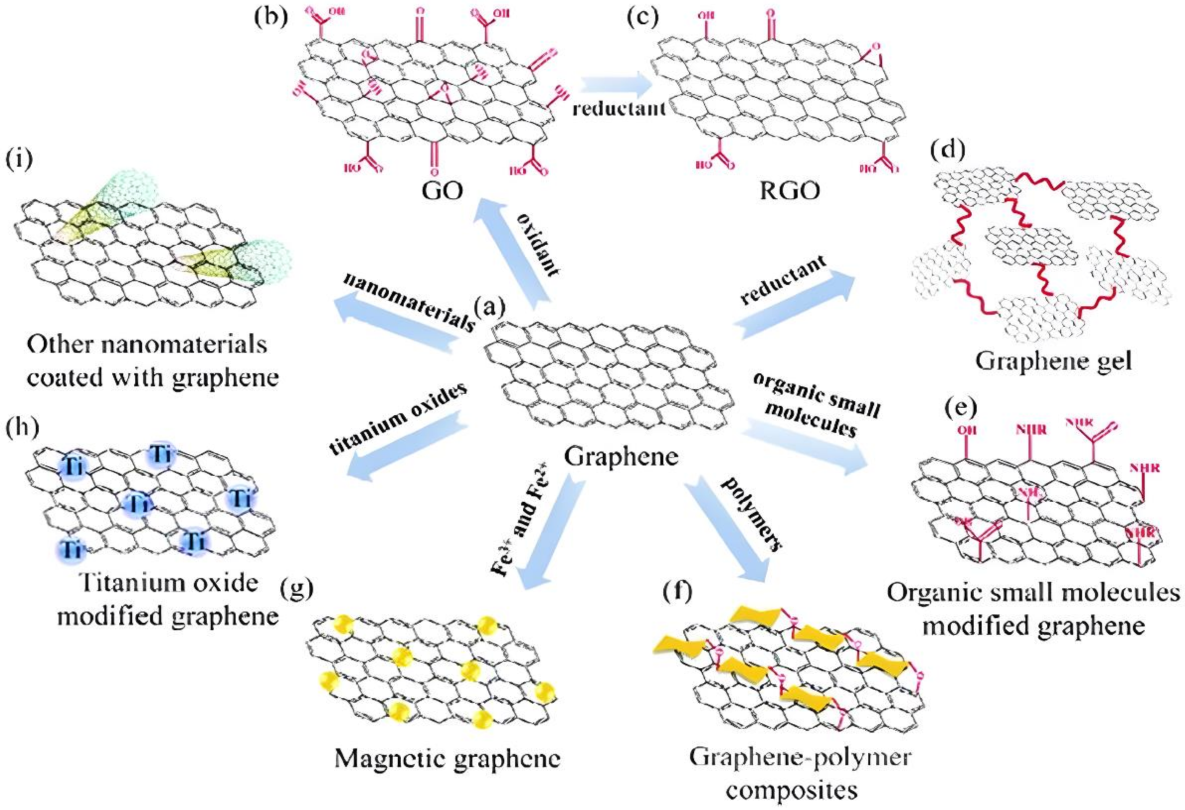
1.7.2 Graphene-polymer nanocomposites

GO-polymer nanocomposites are prepared to improve the properties of polymers such as electrical conductivity, thermal conductivity and mechanical strength [84,85]. It also increases chemical resistivity properties of the polymers at the lower concentration of graphene [84]. Kuilla *et al.* (2010), in their extensive review article on graphene-based polymer nanocomposites, have systematically explained the importance and the usage of graphene in various host materials. They also carried out a remarkable comparison of various nano fillers and listed their important applications in detail [85]. Mainly, three basic approaches have been utilized for making graphene based polymer nanocomposites, viz., are solution mixing, melt blending and *in-situ* polymerization technique [84,86]. Different polymers like poly-ethylene (PE) [54], poly-propylene (PPy) [84], poly-aniline (PANI) [85], poly-styrene (PS) [86], poly-vinyl alcohol (PVA) [54], poly-ethylene glycol (PEG) [86] have been explored for synthesizing NCs with graphene [68].

1.8 Functionalization of graphene oxide-based nanocomposites

The modification of GO can be achieved by the addition of other groups by covalent or noncovalent bonding. Covalent functionalization is possible for GO due to the presence of carboxylic, carbonyl groups at the edges and epoxy, hydroxyl at the surface. These functional groups can provide active sites for addition of other organic functionalities on the surface of GO [87]. To functionalize GO with organic molecules, the orthogonal reaction is an ideal condition for selective functionalization of one site over another [88]. Whereas, non-covalent functionalization can be achieved via intercalation and doping.

Small molecules have been one of most popular ways to functionalize graphene. Molecules such as surfactants [89], pyridine [90], proteins [91], DNA [92], RNA, peptide, deep eutectic solvents (DES) [76] and complex compounds such as anticancer drugs can be functionalized on graphene surfaces [93], to enhance solution processing capability, optical, electronic, and biological properties (**Scheme 1.4**) [24].



Scheme 1.4: Functionalization of graphene (a) Graphene; (b), (c), and (d) are GO, rGO and graphene gel; (e) and (f) are organic small molecules and polymers modified graphene materials; (g), (h), and (i) are NPs functionalized graphene materials [94].

- **Covalent functionalization**

In covalent functionalization a chemical bond is formed by sharing of electron between the atoms thereby producing σ bond. Basically, covalent interaction exists in various forms, viz., σ bond, π bond, three center two electron bond and metal to metal bonding [95]. The presence of oxygen containing functional groups in GO makes the possibilities for the formation of covalent attachments. A lot of research has been reported on covalent functionalization of GO with organic molecules [96,97]. The organic functional groups with active sites provide new properties that could be combined with GO for improving the conductivity, thermal property, dispersibility and absorbent properties of GO [98]. The functionalization of GO is an effective synthetic methodology currently gaining huge interest in materials research.

- **Non-covalent functionalization**

Non-covalent functionalization of GO with organic or inorganic molecules can be possible either via hydrogen bonding or Van der Waals forces [99]. These interactions occur due to the partial negative charge on oxygen containing functional groups on GO. The non-covalent functionalization is also possible either through intercalation or via doping of inorganic compounds in between the sheets of GO. The main advantage of non-covalent attachment is high solubility which can be achieved without altering the intrinsic structure of GO. Non-covalently functionalized GO has many applications in device fabrication and sensing [94,100]. Due to its wide range of applications, this thesis focuses on the functionalization of GO-based NCs with surfactants and DESs for various applications.

1.8.1 Functionalization of graphene oxide-based nanocomposite with surfactants

Material which drastically lowers surface tension/ interfacial tension of air (or oil)/ water interface, due to interface accumulation, comes under the category of surfactants or surface-active agents. Surfactants are usually organic compounds with the special molecular structure of two opposite solvent loving/ hating tendencies (water-loving or hydrophilic and water-hating or hydrophobic). Due to the above two functionalities (hydrophilic head group attached with hydrophobic hydrocarbon tail), the surfactants are also known as amphipathic, hetero-polar or polar-nonpolar substances. The general depiction of a surfactant molecule is shown in **Figure 1.5**. This polarity gradient in a typical molecular structure originates various phenomena / unique properties in solution [143–145].

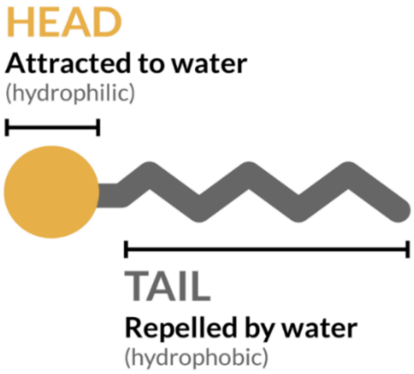


Figure 1.5: A typical structure of surfactant molecule.

1.8.1.1 Classification of surfactants

Surfactants can mainly be classified based on the head group charge (positive or negative or no charge). Types and structure of various surfactants are depicted in **Figure 1.6**.

- **Anionic Surfactants**: In surfactant solution, if the head group bears -ve charge then the surfactant is called anionic surfactant. Examples of anionic surfactants include linear or branched chain sulfonates, sulfates, phosphates or carboxylates. This is the oldest class of surfactant and widely used in cleaning formulations [101]. SDS is a well-known anionic surfactant and considered as the work horse of surfactant research.
- **Cationic Surfactants**: Similarly, if the head group bears +ve charge and attached to a long alkyl tail then the surfactant would be cationic in nature. The positively charged head groups are quaternary ammonium, immidazolium, pyridinium, esterified quaternaries, etc. [102] Among all head groups, quaternary ammonium surfactants are effective in neutral, alkaline as well as in acidic medium. A famous cationic surfactant in use is cetyltrimethylammonium bromide.
- **Non-ionic Surfactants**: If the head group is neutral (un-ionizable) then surfactant is known as non-ionic one. Non-ionic head groups are: alcohol ethoxylates; phenol ethoxylates; alkanolamides; alkanediols; mono- and disaccharides [102]. The hydrophobic part contains saturated/unsaturated fatty acid or fatty alcohols in the form of a hydrogenated/fluorinated chain. Polyoxyethylene (4) lauryl ether series compounds are well known non-ionic surfactants.
- **Zwitterionic Surfactants**: When both charges are present in a typical surfactant molecule then the surfactant is known as zwitterionic or amphoteric one [102]. Cocobetaine (CB) is a well-known surfactant of this category.
- **Gemini Surfactants**: 'Gemini surfactants' consist of two amphiphilic monomers linked at the level of polar heads by a chain of spacer [103,104]. Various properties in gemini solution depend on the distance between the polar heads decided by nature and length of the spacer [105]. Among geminis, cationic bis(alkyldimethylammonium)alkane dibromides (represented by m-s-m, where m is the number of carbon atoms in hydrocarbon chain and s is the number of carbon atoms in the spacer) have studied many a time. Gemini head group can be +ve (ammonium), -ve (phosphate or carboxylate), or neutral (polyether or sugar) [104,106,107]. Structural variation exists in the nature of the spacer which can be short or long; rigid or flexible, polar or nonpolar and cleavable or non-cleavable. It has been reported that the spacer hydrophobicity affects aqueous aggregate morphology [105].

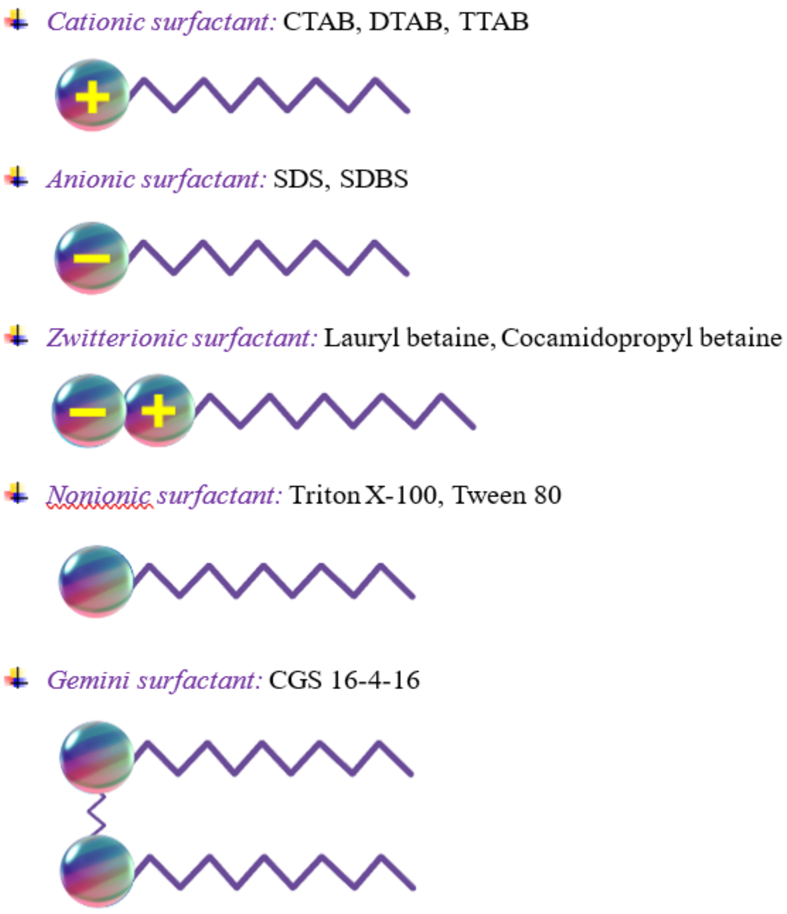


Figure 1.6 Types of surfactants.

1.8.1.2 Advantages of surfactants for functionalization

This thesis underscores the vital role of surfactants in (i) stabilizing GO in aqueous solutions, (ii) enhancing the even distribution of GO sheets, and (iii) shaping the characteristics of GO metal oxide NCs. However, the impact of ionic surfactants on the electrical conductivity and mechanical attributes of GO metal oxide NCs remains to be definitively established [108,109].

The widespread use of surfactants in NC synthesis aims to enhance the even distribution of fillers like GO/rGO, ensuring a more uniform incorporation into the polymer matrix [110–112]. However, the influence of these surfactants on intrinsic properties of NCs, such as electrical conductivity and mechanical and physicochemical attributes, remains not fully comprehended. Recent efforts have focused on understanding how different common surfactants interact with rGO and GO in aqueous dispersion, with a potential impact on the properties of rGO, GO, and their resulting polymeric NCs. Uddin *et al.* explored the aqueous dispersibility and electrical conductivity of rGO surface-functionalized with surfactants like SDS, sodium dodecyl benzene sulfonate (SDBS), and TX-100 [113]. Notably, a cationic gemini surfactant (CGS) has recently gained attention as a modification material [107,114,115]. CGSs are recognized for their improved structural and surface/solution properties compared to conventional cationic surfactants [116,117]. This thesis exclusively focuses on surfactants' potential to modify metal oxide or GO, facilitating adsorption, degradation, and various applications.

1.8.2 Functionalization of graphene oxide-based nanocomposite with DESs

DESs are one of the most interesting emerging research fields. This work highlights the great potential of DESs for synthesizing functional materials with controllable structures that have high performance for water treatment and other applications over other functionalizing agents.

1.8.2.1 DES and its types

Ever since in 2003 *Abbott et al.* defined a deep eutectic solvent (DES) as a liquid mixture of compounds that exhibits a significant decrease of melting point of more than 100 °C compared to its pure compounds [118], this new class of solvents has quickly attracted the scientific community. Straightforward preparation method of DESs which consists of simply mixing hydrogen-bond donors (HBDs) and hydrogen-bond acceptors (HBAs) is one of their big advantages over conventional solvents and especially ionic liquids (ILs) [119,120].

DESs are classified into five types based on the complexing agent. Types I, II, and IV DESs are deemed toxic because they contain non-hydrated metal halides, hydrated metal halides, and transition metals, respectively [121,122]. Type III DESs are free from metals and are perceived as environmental-friendly, non-toxic, and benign and are frequently synthesized by mixing choline chloride (ChCl, HBA) with biodegradable materials such as organic acids, alcohols, sugars, and natural compounds (HBDs) [118,121,123]. These DESs are usually less expensive, non-hazardous, and highly tunable for specific applications compared to other types [123]. Moreover, their synthesis procedures widely employ the principles of green chemistry and usually involve simple mixing and mild heating of HBAs and HBDs [121]. Type V DESs are a relatively new class, are synthesized by mixing non-ionic solid components, and exhibit strong negative deviations from thermodynamic ideality [124]. Moreover, the compounds used in preparation of DESs are abundant, inexpensive, biodegradable, biocompatible, and very often come from natural sources, as for example ChCl, carbohydrates, amino acids, among others. Another important property of DESs are their low melting point and volatility, ability to dissolve various substances, and “designer solvent” character [121,125]. The possibility of obtaining liquids just by mixing solid compounds with high melting points caused a big excitement among scientist, and thereafter the number of publications on DESs and their applications significantly increased. Over the years they have been applied in a diverse field, including analytical chemistry [126], biocatalysis [127], biomass processing [128], and also, they were used as extractants for biomolecules [129], traditional fuels [130], and specialty solvents in gas chromatography [131], pharmaceutical [132], and cosmetic industries [133].

1.8.2.2 Advantages of DESs for functionalization

DESs have emerged as novel, cheap, and biocompatible functionalization and synthesis agents for high-performing adsorbent materials for water treatment applications [134]. DESs' synthesis procedures widely embrace the principles of green chemistry, which are being used for synthesizing and functionalizing diverse adsorbents that include GO, CNTs [135], metal-oxide NPs [136], magnetic GO [137], cellulose nanofibers [138], and MOFs [139]. The effects of functionalizing these materials with DESs resulted in increased specific surface area, good chemical stability, and enhanced adsorption performance for various contaminants including micropollutants, dyes, and heavy metals from water and wastewater with high efficiency [134]. The wide range of available DESs with different functional groups, viscosity, dispersibility, and solubility allows functionalization of a wide range of materials and tuning of physicochemical properties of those adsorbents. The possible combination of thousands of DESs has huge potential for creating adsorbents with high selectivity, specificity, reusability, and adsorption efficiency [134].

Magnetic GO adsorbents were synthesized and functionalized using DES to adsorb mercury [140], lead [137], and methylene blue dye [137] from water. Chitosan beads were functionalized using ChCl-urea (Reline, 1:2 molar ratio) and ChCl-Gly (Glyceline, 1: molar ratio) DESs to adsorb copper ions (Cu (II)) from water. when carboxymethyl-β-cyclodextrin pre-functionalized magnetic (Fe_3O_4) chitosan is further functionalized with Glyceline, its adsorption capacity for anionic dye substantially increased from 9 mg/g to 114.8 mg/g [141,142]. Building upon these advantages, functionalizing GO metal oxide NCs with DES has been undertaken in this thesis.

1.8.3 Functionalization of graphene oxide-based nanocomposite with polymers

Even though polymers have high specific strength and flexibility, they face some drawbacks when utilized as such for industrial applications [143]. Hence, researchers ended up in developing polymer NCs to enhance the properties of pristine polymers. NCs are substances with more than one constituent, in which one of the constituents is in the nanoscale. Varieties of NPs such as silica, nanoclay and various other carbon NPs have been added to the polymer matrices in order to achieve enhancement in properties. Among them, graphene finds a unique place due to its abundance, cost effectiveness and exciting properties [84,144].

Galpaya *et al.* in their review about GO polymer NC have explained the three broad classifications of synthesis of polymer NCs namely (i) solution mixing, (ii) melt blending and (iii) *in-situ* polymerization [145]. In the first method, the nanofiller is dispersed in a suitable solvent by ultrasonication, followed by the addition of polymer. The solvent is then removed by either distillation or evaporation. In the second method, the polymer is heated to high temperatures so that it softens. The filler is then added in to the polymer with high force. Even though this method is free of toxic solvents, the dispersion is low due to high viscosity of the composites. The third method involves the conversion of a monomer into polymer by polymerization process. Initially, the liquid monomer is added with graphene and then a suitable initiator is dispersed. The polymerization process is initiated either by heat or by radiation. During polymerization, the monomer intercalates in to the graphene sheets, increasing the interlayer spacing, thus aiding in better dispersion of graphene into the polymer [145]. Within the framework of this thesis, NCs have undergone additional modification with polymers. This alteration aims to customize their properties for specific applications in gas separation and purification.

1.9 Applications of GO based NCs

Due to light weight, thin, flexibility, durability and all in one property enable the uses of graphene and GO based NCs in the various field of applications. The potential applications of GO include waste water treatment, microelectronics, display screens, electric or photonics circuits, energy storage devices such as solar cells, fuel cells etc., catalyst, photocatalyst and various medical, biological, industrial processes (**Figure 1.7**) [22,36,54,146].

- **Wastewater treatment**

GO based NCs exhibit exceptional promise in wastewater treatment, efficiently removing contaminants and dyes from water sources [76,89]. Their unique structural features, including a large surface area and abundant functional groups, enable strong adsorption capabilities. NCs effectively bind to a spectrum of pollutants, ranging from heavy metals to organic dyes, facilitating their removal from water matrices [147,148]. Through a combination of GO inherent adsorption properties and the synergistic effects of incorporated nanomaterials, these NCs offer a sustainable and versatile solution for environmental remediation. Their application holds significant potential for addressing water pollution challenges, providing a scalable and efficient means to enhance water quality and promote environmental sustainability.

- **Energy storage and green hydrogen production**

The green energy initiative delves into the transformative possibilities of polymer-modified GO nanocomposites for gas separation, targeting advancements in energy storage and green hydrogen production. By leveraging the unique properties of GO, combined with polymers, this research seeks to optimize gas separation efficiency. The goal is to pioneer sustainable energy storage solutions, addressing challenges in storing renewable energy. Additionally, the initiative aims to bolster green hydrogen production, fostering cleaner energy alternatives. Through interdisciplinary collaboration, this endeavor aspires to contribute to a greener future by harnessing the potential of innovative nanocomposite materials in shaping the landscape of sustainable energy technologies [149].

- **Biosensors**

Owing to the large specific surface area, high surface adsorption properties and low frequency noise of graphene, it is a promising material for sensor applications to detect a variety of molecules, biomolecules from gases. The charge transfer between the adsorbed molecule and GO is accountable for the chemical response. Different varieties of GO sensor have been made where the fluorescence and electrochemical properties of GO are mostly utilized [150,151].

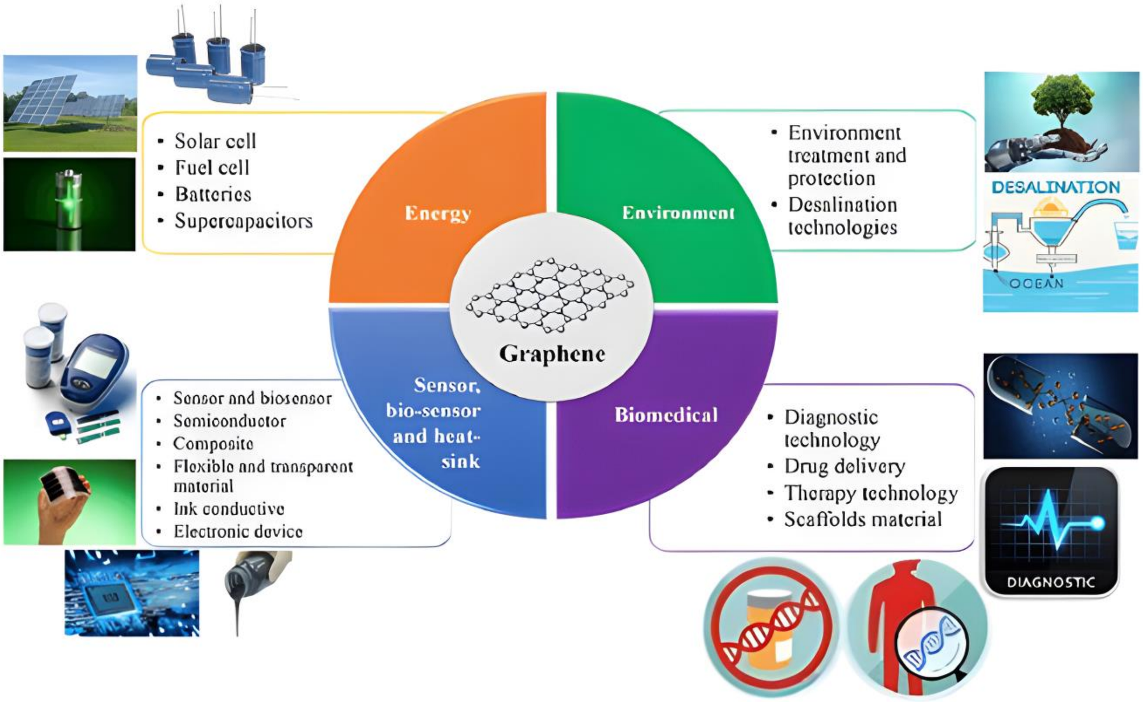


Figure 1.7: Application of GO [36].

- **Antibacterial potentiality**

In recent times, graphene and GO based NCs have appeared as talented antibacterial materials [152]. Chemically modified graphene such as GO and its reduced form could inhibit the growth of several clinically relevant pathogens which is mainly due to the favorable combination of physical structure and chemical functionality. Leading contact with such a nanostructure, membrane stress encouraged by the sharp edges of graphene nanosheets cause considerable physical damage to cell membrane and successive loss of bacterial membrane reliability and leakage of intracellular material.

- **Other applications**

GO-based NCs find versatile applications in supercapacitors, lithium-ion batteries, solar cells, electronic devices, fuel cells, catalysis, drug delivery, air purification, hydrogen storage, and cancer therapy as shown in **Figure 1.7**.

1.10 Aim and objectives of work

In the contemporary landscape, global concerns over environmental degradation have intensified, prompting an urgent revaluation of conventional practices, especially in the realm of water treatment. The discharge of industrial effluents laden with complex dye compounds into water bodies has become a pressing issue, posing serious threats to ecosystems and human health. The escalating demand for water resources, coupled with the adverse effects of climate change, underscores the critical need for innovative and sustainable solutions to address water pollution.

Against this backdrop, the primary objective of this thesis gains even greater significance. The synthesis of GO and the fabrication of composite materials through the integration of metal oxides represent a pivotal step towards the development of advanced materials with multifaceted applications. The integration of surfactants and DESs into these NCs adds a layer of sophistication, promising enhanced properties and improved environmental compatibility.

The core focus of this research lies in the assessment of these novel NCs efficacy in dye adsorption for wastewater treatment. The intricate chemical structure of industrial dyes poses a formidable challenge to conventional treatment methods, often rendering them ineffective. The utilization of GO-based NCs offers a novel and promising avenue to overcome these challenges. By exploring the adsorption capabilities of these materials, this work aims to provide practical solutions to mitigate the impact of dye pollutants on water ecosystems.

Moreover, the research extends its purview to investigate the versatility of these composites in gas separation applications. As concerns about air quality and greenhouse gas emissions continue to mount, there is a growing need for efficient gas separation technologies. The unique properties of GO-based NCs, especially when integrated with metal oxides and subjected to functionalization with DESs, hold the potential to revolutionize gas separation processes. This exploration aligns with the imperative to develop sustainable technologies capable of addressing contemporary environmental challenges.

Additionally, this work seeks to contribute to the broader field of materials science by conducting a comprehensive study of dye photophysics. Understanding the interactions between dyes and the fabricated composites at the molecular level is crucial for optimizing their performance in biosensor applications. This in-depth exploration of dye photophysics not only enriches our understanding of the fundamental science behind these materials but also lays the groundwork for tailoring their properties for specific applications.

In essence, the multifaceted approach of this research strives to advance our understanding of innovative materials and their potential applications. By addressing critical challenges in water treatment, environmental sustainability, and materials science, present investigation endeavours to make a substantial contribution to the global effort to safeguard water resources and promote a more sustainable future. In doing so, it underscores the role of cutting-edge materials and technologies in mitigating the environmental impact of industrial processes and advancing the collective goal of a cleaner, healthier planet.

Key Objectives:

- **Synthesize GO:** Employ a modified Hummer's method to synthesize graphene oxide.
- **Prepare GO-based Metal Oxide NCs:** Integrate metal oxides into GO to fabricate nanocomposites.
- **Functionalize GO NCs:** Apply surfactants and DES to functionalize graphene oxide nanocomposites.
- **Characterization of NCs:** Perform a thorough characterization of these nanocomposites, focusing on their structural, chemical, and optical properties.
- **Clean Water Approach:** Conduct dye adsorption experiments using these nanocomposites to assess their effectiveness in wastewater treatment.
- **Green Energy Initiative:** Explore the potential enhancement of gas separation using polymer-modified nanocomposites for applications in energy storage and green hydrogen production.
- **Fluorescent Sensors:** Investigate the photophysical modulation of dyes in DESs with or without additives, inspired by the use of graphene oxide and surfactants.

1.11 Constitution of the thesis

The thesis entitles "Investigation on Graphene Based Composites of Metal Oxides Functionalized by Surfactants" consists of seven chapters including: **Chapter 1:** General introduction; **Chapter 2:** Materials, methods, and characterization techniques; **Chapter 3:** Synthesis and characterization of surfactant/DES modified GO@ZrO_2 NC for adsorption of dye from aqueous background; **Chapter 4:** Synthesis and characterization of surfactant/DES modified GO@TiO_2 NC for adsorption of dye from aqueous background; **Chapter 5:** GO/surfactant-inspired photophysical modulation of dye in DESs with or without additives; **Chapter 6:** Polymer blend NCs for the separation and purification of gases for different applications; **Chapter 7:** Conclusion and future perspective.

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