Surface affinity of graphene for health, energy and environmental safety applications

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ABSTRACT

This review focuses on the applications of graphene, and the effects of doping and functionalization on its properties. Though known for several years, the potential applications of graphene in various fields have only been recently realized. Remarkable research is going on in the various application based fields of graphene, such as in hydrogen storage, Li batteries, catalysis and many more. Its use as a sensor to detect various species at the molecular level is fascinating. Also, on account of its 2D structure, graphene has found promising applications in several adsorption phenomena. Various adsorption studies have been done on the graphene surface resulting in the chemisorption of the chemical species. This review focuses on the application of graphene for removal of hazardous substances, such as heavy metal ions and drug metabolites, from waste waters. Another class of substances, known as disinfection by-products (DBPs), formed during the disinfection of drinking water using chlorine, ozone, chloramines and chlorine dioxide as disinfectants, and the use of graphene for their removal, is also discussed. Use of graphene based materials as chemical and biosensors and its applications in various other fields is also briefly discussed. Copyright © 2013 VBRI press.

Keywords: Graphene; adsorption; sensor; pollutants.

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Introduction

Graphene, two-dimensional graphite, is a zero-gap semiconductor. The robust two-dimensional structure of graphene makes it an exciting material for applications in the present era. Single-layer graphene is a one-atom thick sheet of sp^2-carbon atoms, densely packed into a two-dimensional honeycomb lattice. All the graphitic forms of carbon, *viz.* zero-dimensional fullerenes, one-dimensional carbon nanotubes and three-dimensional graphite have emerged from graphene, as shown in **Fig. 1 [1].** Graphene has been studied for the past sixty years in order to describe the properties of various carbon-based materials [2-4]. It also provides an excellent condensed-matter analogue of (2+1)-dimensional quantum electrodynamics which makes graphene the most theoretically studied material in the recent years.

It exhibits the quantum Hall effect at room temperature [5-7] and also an ambipolar electric field effect, along with ballistic conduction of charge carriers [8]. Different studies have provided evidence for its tunable band gap [9] and high elasticity [10]. In graphene, the energy of the electrons is linearly dependent on the wave vector near the crossing points in the Brillouin zone which is a significant property of this upcoming material. In this 2D material, Dirac equation finds more utility compared to the frequently used Schrödinger equation to describe the charge carriers which imitate relativistic particles [1, 6, 8]. It is assumed to be a

planar surface but to reduce the effect of thermal fluctuations, ripples occur [1]. Graphene is a single-layer material but to study various phenomena on its surface, two or more layers are also considered as its model. So, on the basis of number of layers, three different types of graphenes are used nowadays *viz.* single-layer graphene (SG), bilayer graphene (BG), and few-layer graphene (FG, number of layers ≤10). Graphene was first formed using micro-mechanical cleavage [8] but at present a number of techniques have been developed for its synthesis [11]. To study the physical properties of graphene, its single layer structure formed by micro-mechanical cleavage is considered, but for its preparation in large quantities and also for the different types of graphene, other techniques have also been developed recently [12].
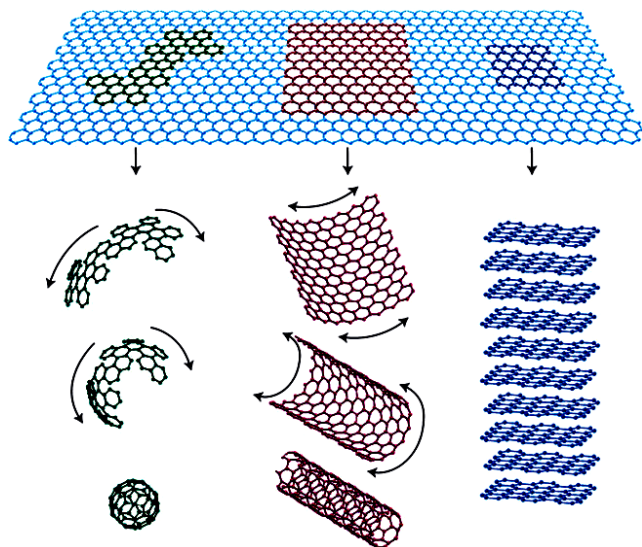

Fig. 1. Graphene: mother of all graphitic forms. It can be wrapped up into 0D buckyballs, rolled into 1D nanotubes or stacked into 3D graphite [Reprinted with permission from **Ref. 1**].

The widespread applications of graphene have interested scientists worldwide. Since, the synthesis of graphene has already been discussed in great detail [13-16], this article would primarily focus on applications of graphene and the effect of doping or functionalization on its properties.

Chemical species as environmental threats

Heavy metal ions present in water are threats for human beings, as well as for the ecosystem. They are found in industrial and agricultural waste water [17] and acidic leachate [18] from landfill sites in relatively high concentration. The heavy metals released to the environment were also detected in river water and the sediment accumulated to be managed as hazardous materials [17, 19-21].

Different organic compounds are also frequently present as polluting agents of continental waters. Among these, phenols and molecules that contain the phenolic group are relatively frequent as contaminants [22]. These pollutants appear in the water as a consequence of degradation of the phenolic compounds used in the synthesis of dyes, pesticides, insecticides, etc. These products are found frequently in the rivers, either by the action of the agriculturists or by dumping.

Other than the organic compounds, many drugs that are harmful for aquatic and human life are also present in water. These drugs are the pharmaceutical compounds with biological activity, developed to promote human health and well-being. Nevertheless, since a considerable amount of the dose taken is not absorbed by the body, a variety of these chemicals, including painkillers, tranquilizers, anti-depressants, antibiotics, birth control pills, chemotherapy agents, etc. find their way into the environment via human and animal excreta from disposal into the sewage system and from landfill leachate, which may impact groundwater supplies. Also, pesticide contamination of ground water and surface water has been recognised as a widespread and significant water quality concern [23, 24]. Pesticide-containing wastewaters have been mainly generated from applicator container rinsates, agrochemical industries, and formulating and manufacturing plants [24, 25]. Improper disposal of these wastes may increase the risk of contamination of the aqueous environment causing detrimental ecological and human health consequences. One example of such a contaminant, which is mainly employed as a household insecticide and as a tool for eradicating nuisance fish populations in lakes and enclosed waters [26, 27], is rotenone. It is a broad-spectrum, non-systemic botanical insecticide derived from the roots and bark of Derris, Tephrosia, Amorpha and Lonchocarpus, tropical plant species [28]. Its removal has been discussed later on in the article.

Apart from the above discussed hazardous species, there is a new class of harmful species, known as disinfectant by-products (DBPs) present in drinking water. DBPs are formed during disinfection of drinking water using chlorine, ozone, chloramines and chlorine dioxide as disinfectants. These species include trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles (HANs), halonitromethanes (HNMs), haloacetamides (HAcAms), nitrosamines (R_2NNO) and cyanogen halides (CNX) [29-31]. These DBPs are further categorized into two classes, carbonaceous DBPs (C-DBPs), which include THMs (major class) and HAAs (second major class), and nitrogenated DBPs (N-DBPs) which include the rest of the above mentioned DBPs. DBPs have adverse effects on human health since these are cytotoxic, genotoxic, mutagenic and teratogenic as reported by the different studies [32-34]. The concentration of N-DBPs in water is less than that of C-DBPs; still, their presence is a matter of concern due to their high toxicity [35, 36].

Hence, there is a need for efficient methods for removing these species from wastewaters as well as from drinking water because of their toxicities in relatively low concentrations and tendency towards bioaccumulation [37]. Among many conventional methods that are being used for this purpose, sorption of heavy metal ions onto various solid supports (ion exchange resins, activated charcoals, zeolites, and ion chelating agents immobilized on inorganic supports) is the most common route applied for decontamination of wastewater and industrial effluents, because the employed sorbent can be easily regenerated and because it is highly effective and economical [38, 39]. Moreover, solid sorbents can be easily incorporated into

automated analytical procedures for preconcentration and determination of trace metal ions in natural waters [40, 41]. However, efforts dedicated to exploring new effective sorbents continue to grow.

Can graphene be used for the removal of a variety of hazardous species?

The use of a suitable surface to remove hazardous materials through the adsorption process is a well-established technique. Carbonaceous materials like activated carbon (a common sorbent consisting of graphene sheets randomly substituted with heteroatoms) have proved to be effective sorbents for removal of metal ions, their complexes and other chemical species. Their large sorption capacity is linked to their well-developed internal pore structure, a large specific surface area, and the presence of a wide spectrum of surface functional groups. Activated carbon supplies adsorption sites for contaminated organic compounds, especially aromatics such as phenol and nitrobenzene [42-44]. Also, adsorption of organic compounds from the aqueous phase is a very important application of activated carbons, within the processes of decontamination of water, and it has been cited by the US Environmental Protection Agency (EPA) as one of the best available environmental control technologies [45]. Due to their versatility, activated carbons have been studied, not only as adsorbents, but also as catalysts and catalyst supports for many different purposes, such as the removal of pollutants from gaseous or liquid phases and for the purification or recovery of chemicals [46-48]. Further, activated carbon (AC) is also used in wastewater treatment plants at the tertiary stage from the last few decades for the removal of DBPs.

Among the activated carbons, graphene, in particular, is the most appropriate surface, since it is a two-dimensional material and its whole volume, *i.e.* all carbon atoms, is exposed to the analyte of interest [49]. Hence, it has maximum surface area, which is one of the major requirements of an adsorbent so as to adsorb maximum species on its surface. Over the last decade, both the intrinsic graphene and functionalized graphene were found to play significant roles, both for aromatics and for heavy metals adsorption [50-57]. So, if AC is replaced by the recently discovered graphene then the rate of adsorption can be increased to a large extent.

Detailed study of interactions of hazardous species with graphene

Nevskaia *et al.* [58] studied the adsorption behaviour of phenol, aniline and phenol-aniline mixtures in water on carbonaceous material surfaces (mesoporous high surface area graphite and microporous activated carbon). It was shown that the adsorption behaviour was affected by the pore size of the carbonaceous material and by the presence of a number of oxygen surface groups. Another group of researchers, Castillejos-López *et al.* [59] also studied the interactions of phenol, aniline and p-nitrophenol, adsorbed from aqueous solutions, with the surface of two activated carbons (with and without oxygen surface groups). It was found that, on the bare surface of an activated carbon, these

compounds were physically and chemically adsorbed, but a change in the adsorption/desorption behaviour resulted when oxygen surface groups were introduced on the carbon surface. In an attempt to remove organic pollutants such as formaldehyde (H_2CO), which is highly toxic, volatile and also a carcinogen [60], Chi and Zhao [61] investigated its adsorption on intrinsic and Al-doped graphene sheets using DFT calculations. They found that the adsorption energy is dependent on the orientation of H_2CO over the graphene surface. The most stable configurations of intrinsic graphene and Al-doped graphene found by them are shown in **Fig. 2**.
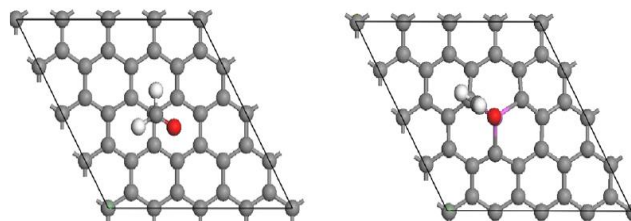

Fig. 2. Optimized most stable configurations of (a) intrinsic graphene and (b) Al-doped graphene. Grey, pink, red and white spheres are denoted as C, Al, O and H atoms, respectively. [Reprinted with permission from **ref. 61**].

The high binding energy values and short connecting distances for various orientations of H_2CO support chemisorption on the Al-doped graphene, which can hence be used as a novel chemical sensor for the H_2CO as well as an adsorbent for it, as compared with the intrinsic graphene. Further, the removal of an analgesic drug (acetaminophen, also known as paracetamol) from water has been investigated [62] using activated carbons prepared from various wastes, and the authors compared their adsorption capacity with that of commercially available carbonaceous adsorbents. The characterization of the materials revealed that the adsorption of acetaminophen is a complex process that depends strongly on the characteristics of the adsorbent (in terms of porosity and chemical composition). The analysis of the carbon samples after absorbing the analgesic showed that adsorbent-adsorbate affinity is stronger in hydrophobic carbons of basic character that contain a well-developed micro porosity. These characteristics are however not sufficient for an overall performance of a carbon in acetaminophen removal. The carbon must also have a well interconnected pore network (to facilitate the accessibility of acetaminophen molecules) and an adequate chemical composition, which ultimately leads to a high adsorption capacity. As discussed previously, among the activated carbons graphene is the most suitable adsorbent, so one can study the adsorption of such drugs on the graphene surface.

In the same direction of detoxifying chemical species by their adsorption over graphene, Cordero and Alonso [63] analysed the interaction between sulphuric acid and graphene. Four different coverages, ranging from a nearly isolated sulphuric acid molecule (one H_2SO_4 molecule per 32 C atoms) to a bilayer (one H_2SO_4 molecule per 4 C atoms) were studied using DFT calculations. Except for low coverage, the sulphuric acid molecules were found to be stable in their *trans* configuration, and results showed that the graphene sheet is protonated by the acid, in

accordance with experimental results for H_2SO_4 adsorbed onto highly oriented pyrolytic graphite. Furthermore, the removal of rotenone (an insecticide) from synthetic and real wastewaters using modified activated carbons has been investigated [64].

Apart from intrinsic graphene, modified graphene, such as graphene oxide, can also be used for the adsorption. Zhang *et al*. [65] performed a study using graphene oxide, cross-linked with ferric hydroxide for the effective removal of arsenate from contaminated drinking water. Arsenate (As (V)) is an inorganic form of As; it is more toxic than the organic form and is found in surface waters [66]. Drinking water contamination by arsenic remains a major public health problem around the world, especially in Bangladesh, India, USA, China, Mexico, Chile, etc. [67, 68]. The World Health Organization's (WHO) provisional guideline of 10 ppb (0.01 mg/L) for arsenic in drinking water has been adopted as the drinking water standard by most of the countries. In this study by Zhang *et al*. [65], the ferric hydroxide was homogenously impregnated onto graphene oxide sheets in amorphous form. These composites were evaluated as absorbents for arsenate removal from contaminated drinking water. For the water with arsenate concentration at 51.14 ppm, more than 95% of arsenate was absorbed by the composite of graphene oxide and iron with an absorption capacity of 23.78 mg arsenate g^{-1} of composite. Also, the efficiency of arsenate removal was found to be pH dependent and effective arsenate removal occurred in a wide range of pH from 4 to 9. Thus, graphene oxide stands for a new type of material as an excellent carrier matrix of ferric hydroxide for arsenate removal.

Till now we have taken the examples of organic species, drugs, insecticides and other chemical species. Some gaseous molecules are also present in the environment and high concentration of these gaseous molecules can also be harmful. The most commonly found gaseous molecules CO_2 and CH_4 are the two main greenhouse gases. Many industrial processes around the world produce these gases. The removal of these gases from the atmosphere is mainly done using amine baths. This process presents several problems. Among these are additional processing and corrosion control [69]. Another employed process is chemical capture of CO_2 using oxides [70]. Because of their drawbacks, adsorption processes to remove these greenhouse gases have been considered. Among the materials that have been studied for these processes, we have activated carbons, zeolites, and porous metal-organic frameworks [71, 72]. Carrillo *et al*. [73], using DFT and molecular dynamics calculations, studied the adsorption of these greenhouse gases on a titanium-graphene system with high metal coverage, and found that both adsorb on the considered system. **Fig. 3** shows the adsorption of CO_2 onto Ti-graphene.

It was found that CO_2 dissociates to CO and O when adsorbed, but CH_4 does not dissociate, and desorbs at 600 K. Another gaseous molecule, nitrogen dioxide, besides being a toxic industrial gas, is also considered as a main air pollutant contributing to the formation of photochemical smog and acid rain [74]. Its main source in the environment is from the photochemical oxidation of NO released from power plants and car engines during fossil fuel burning. NO_2 and NO are often referred to as NO_x. Since their

presence in the atmosphere also affects human health [75], the efforts continue towards controlling and minimizing the emissions of these gases. Adsorption and reduction of NO_2 at conditions close to ambient have been studied extensively on various adsorbents, including carbonaceous materials, such as activated carbon fibres [76], soot [77, 78], carbon black [79], char [80], carbon nanotubes [81], and activated carbon [75, 82-85]. Kante *et al*. [86] have shown that there is an increase in the reactivity of carbons towards immobilization of nitrogen dioxide when highly porous wood-based activated carbon is impregnated with cerium, lanthanum and sodium chlorides. On their surface, both carbonaceous matrix and inorganic phases are active. The latter is involved in the reduction of NO_2 to NO, leading to the incorporation of oxygen functional groups and -NO_2 in the graphene layers, resulting in an increase in surface acidity. The presence of water enhances this process via formation of nitrous and nitric acids, and the presence of chlorides also increases the capacity to interact with NO_2. Further, for the process of NO_2 removal, theoretical studies have been performed [87], where the charge transfer between the paramagnetic molecule and a graphene layer was calculated using *ab initio* methods. The results showed that the charge transfer crucially depends on the size of the super cell used in the calculations.
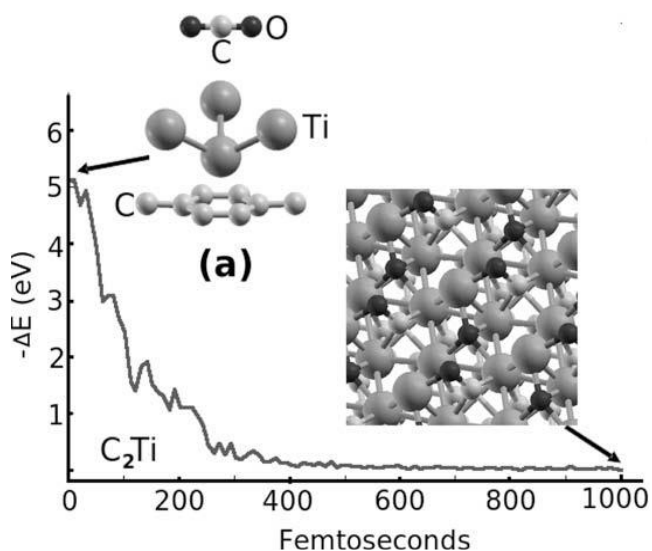

Fig. 3. CO_2 adsorption onto Ti–graphene (C_2Ti). The final configuration shows the dissociation of the molecule in CO and O. The initial orientation of the molecule has no influence on the result [Reprinted with permission from **ref. 73**].

As stated earlier, heavy metal ions are a threat to the environment, and mercury (Hg) is also one of these. Therefore, to design and fabricate effective control technologies for mercury detoxification, understanding the mechanism by which mercury adsorbs on the activated carbon is crucial. Padak and Wilcox [53] studied the possible binding mechanism of Hg and its chlorides, *i.e.*, HgCl and $HgCl_2$, on activated carbon and chlorine substituted activated carbon using *ab initio*-based calculations. It was concluded that both HgCl and $HgCl_2$ can be adsorbed dissociatively or non-dissociatively. In the case of dissociative adsorption, it is energetically favourable for atomic Hg to desorb and energetically

favourable for it to remain on the surface in the Hg^{1+} state, HgCl. The Hg^{2+} oxidized compound, $HgCl_2$ was not found to be stable on the surface. The most probable mercury species on the surface was found to be HgCl.

Interactions of graphene with metals, their ions and clusters

A number of elements and their compounds are present in soil and water bodies. Excess of these elements is hazardous to the environment, so there is a need to adsorb these elements on a desired surface. In order to adsorb these elements and their compounds on the graphene surface, there is a need to first understand the interactions between graphene and these species. Theoretical studies can aid in the understanding of these interactions. Upon interaction of these species on graphene, the electronic and magnetic properties, as well as the band gap of graphene, were found to be modified. Measurements of electronic transport properties can also be done by studying the interaction between metal atoms and the graphene surface. Hence, it becomes important to discuss these properties in detail.

Effect of adsorption on electronic properties

The metal-graphene interface plays a significant role in understanding the electronic transport through a graphene sheet [5, 88-90]. Several investigations on metal atom adsorption and impurities on graphene have been done by various research groups [89, 91-95]. The research on interaction between the atoms, molecules, and graphene is developing rapidly [96-105]. This is essential in controlling the modification of graphene.

The chemical adsorption of metallic atoms can alter the electronic properties of graphene. The electronic properties that result from adsorption depend strongly on the ionic and/or covalent character of the bonds formed between carbon and the metal and are sensitive to the doping of graphene with alkali or transition metals.

Uchoa *et al.* [94] studied the effects of metallic doping (K and Pd) on the electronic properties of graphene using DFT. The charge transfer from a single layer of potassium on the top of graphene was estimated, and it was found that when graphene is coated with a nonmagnetic layer of palladium, it leads to a magnetic instability in the coated graphene due to hybridization between the transition metal and the carbon orbitals. Further, the electronic and magnetic properties of graphene and graphene nanoribbons functionalized by $3d$ transition-metal (TM) atoms have been investigated [104]. It was found that the binding energy of adsorbed TM atoms depends on the type of TM involved and coverage density and it usually ranges between 0.10 and 1.95 eV. Except Cr, adsorption on the hollow site gave the minimum energy for all TM atoms and the properties of graphene and graphene nanoribbons could be strongly modified through the adsorption of $3d$ TM atoms. Graphene is found to become a magnetic metal after the adsorption of TM atoms. Chan *et al.* [97] investigated the adsorption of 12 different metal adatoms, including transition, noble, and Group IV metals on graphene, using DFT calculations, and found that the calculations are in

agreement with covalent bonding, and strong hybridization between the adatom and graphene.

The adsorption of Si and Ge on graphene has been studied [106] using first-principles plane wave calculations. While these atoms bind to graphene at the bridge site with significant binding energy, many other atoms bind at the hollow site above the centre of the hexagon. These adatoms induce important changes in the electronic structure of graphene, even at low coverage. For example, semimetallic graphene becomes metallized and attains a magnetic moment. In the same year, 2010, Subrahmanyam *et al.* [107] studied the interaction of Ag, Pd, Au and Pt nanoparticles with graphene, employing Raman spectroscopy and first-principles calculations, and their results demonstrated that there is significant electronic interaction between the nanoparticles and graphene, giving rise to changes in the Raman spectrum of graphene, showing meaningful trends with the ionization energies of the metals as well as the charge-transfer energies. First-principles calculations were found to support the conclusions from the Raman study and demonstrated the importance of charge-transfer between the metal particles and graphene.

It has been already stated that the electronic states of graphene can be customized by doping with alkali metals and the interaction of alkali ion with graphene is important in the development of new molecular devices of nano-carbon materials. In order to elucidate the nature of interaction between Na^+ and graphene, Tachikawa and Kawabata [108] performed DFT calculations, and the structures and electronic states of Na^+ trapped on the graphene were calculated. Calculations showed that the sodium ion is stabilized in the hexagonal site and is located at *ca.* 2.230 Å from the graphene surface. In case of Mg, [109], the same kind of results was found. Magnesium ion is also stabilized in the hexagonal site and is located at *ca.* 2.02 Å from the graphene surface. Electron transfer from graphene to the Mg atom, which is important in the interaction of Mg with the graphene, was also observed. There are several alternatives for changing the electronic behaviour of graphene, either by cutting the monolayer into nanoribbons [9, 110] or by the adsorption of foreign atoms [111, 102]. Using first-principles calculations, Medeiros *et al.* [112] investigated the electronic and structural properties of H, Li, Na, K and Rb that are adsorbed, in a regular pattern, on a graphene surface. Cohesive energies concluded that all of the studied systems are stable, with their stabilities descending in the order - graphane, Li-graphene, graphene, Na-graphene, K-graphene and Rb-graphene. The adsorption energies showed that, among the analysed cases, only Li-graphene and graphane could be spontaneously obtained. For all other systems, the adsorption process would take place only by providing the system with some energy.

Till now we have seen different studies which involve changes in the electronic properties of graphene upon adsorption of various species. A similar kind of study was performed by Alzahrani [113] using *ab initio* calculations and taking benzene and naphthalene as adsorbates on the graphene surface. It was found that both molecules adopt a planar geometry with a vertical distance of 3.52-3.54 Å above the graphene and the stack configuration is more

stable than the hollow structure. Results showed that the Dirac point of graphene upon benzene and naphthalene adsorption coincides with the Fermi level, indicating that no significant amount of electronic charge is transferred. Therefore, the electronic properties of graphene remain unchanged upon benzene and naphthalene adsorption.

Functionalization leads to tuning of the band gap

The energy gap in the electronic spectrum of graphene can be tuned in a controllable way [114] using various dopants. Tuned energy gap finds many potential applications, including that in an efficient carbon-based transistor. Different energy gaps could be achieved by chemical functionalization of bilayer graphene. Using various dopants, such as H, F, Cl, Br, OH, CN, CCH, NH_2, COOH, and CH_3, one can smoothly vary the gap between 0.64 and 3 eV. One-side doping, almost independent of the chemical nature of the dopants, leads to gaps of the order of 0.6-0.7 eV. Two-side doping makes possible to change the gap in much broader limits, while functionalization by halogens or their combination with hydrogen results in gap values in the range of 1-3 eV; however, this value cannot be fine-tuned. Using various groups formed by elements of the second period of the Periodic table, one can easily change the gap between 2 and 3 eV, with an accuracy of about 0.2 eV. Interaction between dopants and water can also change the gap by a value of the order of 0.2 eV. Thus, variations of solvents can also be used to tune the gap. In order to study the tuning of the band gap by chemical doping of monolayer and bilayer graphene with Al, Si, P and S, Denis [115] performed first principles periodic calculations. It was found that phosphorus can open the largest band gap in graphene, and just by varying the amount of P introduced, the band gap could be tuned from 0.66 to 0.1 eV. Si-doped graphene was found to have the lowest formation energy; however, it is not effective enough for opening a band gap in the band structure of graphene. Al-doped graphene was found to be very unstable owing to the largest formation energy and the longest Al-C bond distance. The formation of interlayer Al-Al, P-P and Si-Si bonds between different layers significantly lowers the formation energy of these materials and makes the synthesis of P and Si-doped bilayer graphene easier. Further, in the case of P, the magnetic moment was found to be quenched by weak covalent bond formation. The material has a band gap of 0.43 eV, making it very attractive to design field effect transistors.

The band gap also becomes tunable when Au_nPt_n clusters are adsorbed on graphene, and adsorption of these clusters changes the electronic properties of graphene, which is important in applications such as in gas sensors and electronic devices. Using the first-principles DFT-LDA/GGA method, Aktürk and Tomak [116] showed that the presence of Au_nPt_n clusters on graphene changes its electronic properties. It was concluded that graphene can be metallic or semiconducting, depending on the number of Au and Pt atoms in the cluster and the charge transfer between the cluster and the graphene. There is a downward shift of the Fermi level relative to the Dirac point for Au, AuPt, and Au_3Pt_3 on graphene, and an upward shift for Au_2Pt_2 and Pt on graphene.

Carara *et al*. [117] also performed a first-principles study of the electronic and structural properties of two-

dimensional arrays of Au_{38} nanoparticles, functionalized or not, by methylthiolate molecules in contact with a graphene layer. It was found that the interaction of functionalized nanoparticles with the graphene layer causes electronic structure modifications in it. This interaction does not lead to the opening of the band gap at the Dirac point, even in the case of charged nanoparticles or under an applied electric field. However, the interaction of bare nanoparticles with graphene causes a small band-gap opening at the Dirac point, for a moderate coverage of nanoparticles.

When Tachikawa *et al*. [118] studied the electronic structures of Li^+ doped graphene by means of DFT calculations, they found that the band gap of graphene slightly red-shifted. It could be explained on the basis of the interaction of graphene with the *sp*-hybrid orbital of the lithium ion. The Li^+ ion binds to a hexagonal site and its electronic configuration changes, suggesting that the *sp*-hybridization of lithium ion is important in its adsorption to the graphene surface. Further, using DFT, Mao *et al*. [102] investigated the functionalization of graphene by the addition of the transition metal atoms Mn, Fe and Co to its surface, and showed that on interaction with different metals, the conduction bands of graphene could be modified. The centre of the hexagonal ring formed by the carbons from graphene was found to be the most stable site for Mn, Fe, and Co. The conduction bands are modified, and move down due to the coupling between the Mn atom and graphene. The systems of Co and Fe adatoms on graphene also exhibit metallic and semi-half-metallic electronic structure, respectively. Thus, spin-polarized band structures and magnetic properties in adatom-graphene systems can be controlled, which helps in realizing graphene-based electronic and spintronic devices. If, one intends to measure the electronic transport through a graphene sheet, it becomes essential to have a full understanding of the physics of metal-graphene interfaces. Giovannetti *et al*. [89] used DFT calculations to study the doping of graphene induced by adsorption on metal (Al, Co, Ni, Cu, Pd, Ag, Pt, and Au) surfaces and developed a simple model that takes into account the electron transfer between the metal and graphene levels, driven by the work function difference and chemical interaction between graphene and the metal. In the same direction, Khomyakov *et al*. [119] studied the adsorption of graphene on metal substrates using first-principles calculations at the DFT level. It was found that the bonding of graphene to Al, Ag, Cu, Au, and Pt (111) surfaces is so weak that its unique "ultrarelativistic" electronic structure was preserved. A simple analytical model that describes the Fermi level shift in graphene in terms of the metal substrate work function was developed by these researchers, as the charge redistribution at the graphene-metal interface could be characterized experimentally by measuring the work function of the graphene-covered metal. The interaction and charge transfer between graphene and the metal substrate, and, in particular, the effects they have on the doping of graphene by the metal were focused, concluding that the crossover from *p*-type to *n*-type doping occurs for a metal with a work function ~5.4 eV, a value much larger than the work function of free-standing graphene, 4.5 eV. It was also found that graphene interacts with and binds more

strongly to Co, Ni, Pd, and Ti. This chemisorption involves hybridization between the graphene p_z states and metal d states that opens a band gap in graphene, and reduces its work function considerably.

Effect of adsorption on the magnetic properties

Upon interaction of different metal atoms with graphene, a change in the magnetic property of graphene and, in some cases, a change in the magnetic property of the metal atoms itself was observed. Wu *et al*. [95] studied the interaction of Cu single atom and dimer on graphene by first-principles calculations and found that Cu single-atom-adsorbed graphene showed magnetic moment, while Cu dimer-adsorbed graphene does not. It was also seen that the electronic structure of graphene could be modified via Cu adsorption and the Cu dimer, sitting parallel to the graphene plane above the C atoms, offers the possibility for the formation of Cu atom chain or wire on graphene, which might have potential nanoelectronic applications.

In another similar study, Zhou *et al*. [120] studied the magnetic properties and electronic structures of graphene with Cl, S, and P adsorption using *ab initio* calculations. The graphene exhibits the metallic state upon Cl adsorption, while S-absorbed graphene shows semiconducting behaviour. P adsorbed graphene exhibits a magnetic moment (0.86 μ_B), while no magnetic moment was observed after Cl and S adsorption. Results indicated that atom adsorption could modify magnetic properties and conductive behaviour of graphene. Particulary, P-absorbed graphene may be useful for spintronic applications, such as tunnelling magnetoresistance.

Further, Wang *et al*. [121] also studied the properties of an iron atom interacting with the Stone-Wales (SW) defect in graphene in terms of structural distortion, electronic structure, and magnetic properties using *ab initio* density functional calculations. The most stable site for iron atom adsorption was found to be the top site, on one of the bond-rotated carbon atoms. It was found that the distortion and the SW defect are two factors that contribute to the strong binding of the iron atom with graphene. These results could also be useful for spintronics applications and could be of help in the development of magnetic nanostructures. Also, the precise knowledge of the transition metal-graphene interaction is essential for understanding the role of implanted magnetic atoms such as Fe in the development of magnetic order in carbon materials [122] as the properties of transition metals can vary widely in various hosts [123]. It is not even clear whether substitutional transition metal atoms in the graphene sheet have magnetic moments or not. Using DFT calculations, Krasheninnikov *et al*. [93] calculated the atomic structure of transition metal atoms (Sc-Zn, Pt, and Au) adsorbed on pristine and defected graphene, containing single and double vacancies (SV and DV), and studied the stability of various defect configurations by comparing their relative energies and evaluating migration barriers. It was found that for most metals, the bonding is strong and the metal-vacancy complexes exhibit peculiar magnetic behaviour. In particular, a Fe atom on a SV is not magnetic, while the Fe atom on a DV has a high magnetic moment. Further, it was also found that Au and Cu atoms at SV are magnetic.

Graphene based sensors

Graphene has one of the most potential applications in sensors, including gas and biosensors. Sensors with high sensitivity for the industrial waste are required for environmental safety. An excellent gas sensor should have high sensitivity, robustness, should be easy to reactivate for reuse and have a wide range of applications with low cost and potential for miniaturization. In actual applications, solid-state gas sensors are popular and ubiquitous because of their high sensitivity to toxic gases [124, 125]. The operational principle of graphene based gas or bioelectronic sensor is based on the change of graphene's electrical conductivity (σ) due to adsorption of molecules on the graphene surface [10]. The change in conductivity can be attributed to the change in carrier concentration of graphene due to the absorbed gas molecules acting as donors or acceptors. Furthermore, some interesting properties of graphene aid to increase its sensitivity up to single atom or molecular level detection. Firstly, graphene is a two-dimensional (2D) material and its whole volume, *i.e.*, all carbon atoms are exposed to the analyte of interest [49]. Secondly, graphene is highly conductive with low Johnson noise (electronic noise generated by the thermal agitation of the charge carriers inside an electrical conductor at equilibrium, which happens regardless of any applied voltage); therefore, a little change in carrier concentration can cause a notable variation of electrical conductivity [49]. Finally, graphene has very few crystal defects [1, 5, 126-128] ensuring a low level of noise caused by thermal switching [6].

Chemical sensors

There are several reports on graphene based sensors. The first report on graphene sensing was given by Schedin *et al*. [49]. In this work, graphene demonstrated good sensing properties towards NO_2, NH_3, H_2O and CO. It was shown that the increase in graphene charge carrier concentration induced by adsorbed gas molecules could be used to make highly sensitive sensors [5, 127]. Furthermore, it was also demonstrated that chemical doping of graphene by both holes and electrons, in high concentration, did not affect the mobility of graphene [49]. In another work [129], the adsorption of H_2O, NH_3, CO, NO_2, and NO on a graphene substrate was investigated using first-principles calculations, as graphene can act as a sensor to detect individual gas molecules. The charge transfer between the considered adsorbates and graphene was found to be almost independent of the adsorption site but depends strongly on the orientation of the adsorbate with respect to the graphene surface. Charge transfer of two paramagnetic molecules, NO_2 and NO was compared, and it was found that NO_2 induces a relatively strong doping (-0.1e), but NO does not (<0.02e). When molecules adsorb on graphene, charge transfer occurs via two mechanisms. Small charge transfer takes place due to orbital hybridisation (orbital mixing) for all molecules. Large charge transfer takes place when the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the molecules lie close enough to the Dirac point. Further, Leenaerts *et al*. [100] investigated the mechanisms in detail for NH_3 and NO_2 adsorption on graphene using first-principles

calculations. Which mechanism is the dominant one depends on the magnetic properties of the adsorbing molecules. Mechanisms were explained through the density of states of the system and the molecular orbitals of the adsorbates. It is important to realize the difference between the different mechanisms when calculating charge transfers in order to get quantitatively reliable results.

In another related work, Ko *et al*. **[130]** demonstrated the applicability of graphene-based gas sensors by exploiting the charge transfer mechanism between NO_2 molecules and graphene. Graphene could selectively adsorb/desorb NO_x molecules at room temperature. The selectivity was tested under air and NO_2 gas ambients. This novel graphene-based gas sensor displayed good reproducibility when the ambient was alternated. The adsorption rate was much faster than the desorption rate due to the reaction occurring on the graphene surface. The sensitivity was 9% at 100 ppm NO_2 gas, which could be further improved by optimization of the sensor structure and by using a single layer of graphene.

Apart from small molecules, graphene can also detect large molecules like thiophene, as shown by Denis and Iribarne **[131]**, who investigated the adsorption of thiophene inside and outside Single Wall Carbon Nanotubes (SWCNTs) and onto graphene using DFT calculations. It was found that thiophene adopted a nearly parallel configuration with respect to the graphene plane, and the vibrational frequencies of thiophene were red-shifted when it was adsorbed on graphene; the intensity of the most prominent peak in the IR spectra increased by 34% and red-shifted by 14 cm^{-1}. Thus, the parallel mode could be used to detect stacked thiophenes on carbon nanostructures.

Effect of doping on sensitivity

The sensitivity of graphene to gas molecules can be enhanced by doping with metal atoms **[132]**. Metal doping in graphene can alter its electronic properties significantly, inducing a shift of the Fermi level and shallow acceptor states in graphene, which greatly extend its applicability **[89]**.The adsorption of CO molecules on the intrinsic and Al doped graphene was studied **[132]** using DFT calculations. While CO molecules were found to be only weakly adsorbed onto the intrinsic graphene, Al doped graphene strongly chemisorbed CO molecules. There was a large change in the electrical conductivity of Al doped graphene after the CO adsorption, due to the introduction of a large number of shallow acceptor states. These results were reinforced by Sun *et al*. **[133]**, who studied the adsorption of HF molecules on both intrinsic and Al-doped graphene sheets using first-principles calculations. They also found that Al-doped graphene has higher adsorption energy and shorter connecting distance to the HF molecule than intrinsic graphene. Thus, Al-doped graphene is an excellent candidate for sensing the gases CO, HF, as well as formaldehyde **[61]**.

It has been reported that the sensor material can also be reactivated by applying an external electric field **[134]**. For example, applying an external electric field to a fully hydrogenated graphene sheet could unload hydrogen atoms on one side **[120]**. Further studies were carried out **[135]** and the correlation of the applied electric field and the

adsorption/desorption behaviour of a CO molecule on Al-doped graphene was studied. A negative electric field strengthens the adsorption of the CO on the Al-doped graphene, while the adsorption reduces when a positive electric field was applied. Desorption of CO from Al-doped graphene occurred when an electric field of 0.03 a.u. was applied, which indicates that the used materials could be reactivated for repetitious application. Also, the HF molecules adsorbed on Al-doped graphene **[133]** could be reactivated by applying an external electric field of 0.013 a.u.

To compare the sensitivity of different kinds of graphene, Zhang *et al*. **[136]** studied the interactions between four different graphenes (including pristine, B- or N- doped and defective graphenes) and small gas molecules (CO, NO, NO_2 and NH_3) using DFT calculations. The structural and electronic properties of the graphene-molecule adsorption adducts were found to be strongly dependent on the graphene structure and the molecular adsorption configuration. All four gas molecules showed much stronger adsorption on the doped or defective graphene than on the pristine graphene. The defective graphene showed the highest adsorption energy with CO, NO and NO_2 molecules, while the B-doped graphene gave the tightest binding with NH_3. The transport behaviour of a gas sensor using B-doped graphene showed a sensitivity of two orders of magnitude higher than that of pristine graphene.

The sensitivity of the graphene based sensors is dramatically enhanced when a metal atom is introduced between the molecule and graphene, as shown by the adsorption energies, equilibrium molecule/graphene distance and charge transfer values obtained by Zhang *et al*. **[137]**, who investigated the binding of organic electron donor and acceptor molecules on graphene sheets using DFT calculations. Adsorption of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and tetrathiafulvalene (TTF) induced hybridization between the molecular levels and the graphene valence bands, transforming the zero gap semiconductor graphene into metallic graphene. Further, it was also found that iron modified graphene showed a sensitivity two orders of magnitude higher than that of pristine graphene.

Thus, it can be concluded from the above discussed studies that the sensitivity of graphene increases due to doping, which further enhances its applications in the field of chemical sensing.

Biosensors

Non-covalent interactions play an important role in understanding a range of biological problems such as base stacking and ligand binding to DNA and RNA. There is an increasing interest in the biological applications of graphene where its non-covalent interaction with aromatic amino acids is of particular importance. The development of graphene-based biosensors for the applications in biology requires knowledge of the interaction of peptides with graphene. A number of computational studies of the interaction of DNA bases and aromatic amino acids with both graphene sheets, and with polycyclic aromatic hydrocarbons of varying sizes, which may mimic graphene, have been performed by many researchers **[138-141]**. Such

studies are of fundamental interest and may also be compared with the corresponding complexes involving carbon nanotubes.

In the direction of development of graphene based biosensors, Rajesh *et al.* [139] investigated the interaction of phenylalanine (Phe), histidine (His), tyrosine (Tyr), and tryptophan (Tryp) molecules with graphene and single walled carbon nanotubes (CNTs) using DFT and the Møller-Plesset second-order perturbation theory (MP2). The equilibrium configurations of these complexes were found to be very similar, *i.e.*, the aromatic rings of the amino acids prefer to orient in parallel with respect to the plane of the substrates (shown in **Fig. 4**), which is due to weak π-π interactions. The binding strength follows the trend: His < Phe < Tyr < Tryp. Although the qualitative trend in binding energies was found to be almost similar for the graphene and nanotube structures, they differ in terms of the absolute magnitude. It was found that the binding strength of these molecules is weaker with the CNT as compared to the graphene sheet. Excellent correlation between the polarizability and the strength of the interaction was found; the higher the polarizability, greater is the binding strength. These results are useful for better understanding of the aminoacid interactions with planar and nonplanar carbon nanostructures, which has implications toward developing biosensors.
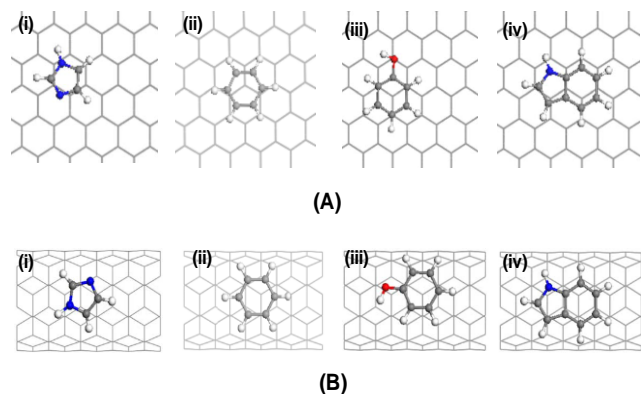
Fig. 4. (A) Equilibrium geometry of the rings of the aromatic amino acids on top of graphene: (i) Histidine, (ii) phenylalanine, (iii) tyrosine, and (iv) tryptophan. (B) Equilibrium geometry of rings of the aromatic amino acids on top of (5,5) CNT: (i) Histidine, (ii) phenylalanine, (iii) tyrosine, and (iv) tryptophan [Reprinted with permission from **ref. 139**].

Another study was performed [138] using DFT and *ab initio* molecular dynamics (AIMD) simulations to study the binding of collagen amino acids (AA, namely glycine, Gly; proline, Pro; and hydroxyproline, Hyp) to graphene, Ca-doped graphene and graphane. It was found that the binding of these acids to graphene and graphane is thermodynamically favourable, yet dependent on the amino acid orientation and always very weak (adsorption energies range from -90 to -20 meV). AIMD simulations revealed that room temperature thermal excitations induced detachment of Gly and Pro from graphene and of all the three amino acids from graphane. When graphene was doped with calcium atoms, it was found that collagen AA binding to graphene was enhanced dramatically (corresponding adsorption energies values decrease by practically two orders of magnitude with respect to the non-

doped case). This large difference in the binding energy was due to electronic charge transfers from the Ca impurity (donor) to graphene (acceptor) and the carboxyl group (COOH) of the amino acid (acceptor). Electronic density of states analysis was also performed to check the possibility whether graphene and graphane could be used as nanoframes for sensing collagen amino acids. It was found that graphene is hardly sensitive, but the electronic band gap of graphane could be modulated by attaching different number and species of AAs onto it. These results could be useful for developments in bio- and nanotechnology fields, as they provide fundamental insights on the quantum interactions of collagen protein components with carbon-based nanostructures.

Nowadays, selective detection of S-containing amino acids is expected imminently in biomedical and analytical communities due to the presence of S-containing cysteine and cysteine amino acids on the border of large proteins. Hence, they are especially interesting among biomolecules, as they can provide a link to anchor these proteins to inorganic supports. In this direction, Ma *et al.* [142] investigated by DFT the detection activity of Pt-embedded graphene and intrinsic graphene using the cysteine molecule as a model probe for sulphur-containing proteins. Particularly, Pt was chosen, because Pt/graphene has attracted a great deal of attention as a good catalyst, Pt atoms in layers consisting of one or two graphene planes have been monitored in real time at high temperature by high-resolution TEM [143]. Pt-doped graphene strongly adsorbs cysteine molecules as compared to the intrinsic graphene, supported by the higher binding energy value and shorter distance between the cysteine molecules and the graphene surface. The calculation of electron transfer and dipole moment also supports the fact that the electronic properties of Pt-doped graphene change more significantly than that of intrinsic graphene after the cysteine molecule is adsorbed. These calculations suggest that Pt-embedded graphene is a good candidate for sensors, with the possibility of detecting a variety of S-containing proteins and metalloenzymes.

Further, the nature of graphene allows its application to a new drug delivery system (DDS), contrast agent or tracer of biomedical imaging, as its structure can be regarded as a carbon capsule, and it is receiving much attention because the capsule has high chemical stability and the encapsulated materials, such as metals and metal oxides, are stable in air, water and acids. Though Gd^{3+} and Mn^{2+} are well-known effective contrast agents for magnetic resonance imaging (MRI), it is necessary to form a stable chelate for the agent [144, 146]. Therefore, elucidating the interaction of a metal ion with carbon materials is quantum mechanically important in order to develop new DDSs. Abe *et al.* [147] applied DFT calculations to the interaction system composed of graphene and Mn^{2+} ion in order to elucidate the electronic states of materials for DDS. The Mn^{2+} ion bound to a hexagonal site of the graphene sheet and a weak bond between Mn^{2+} and the carbon atom was formed. Also, the classical MD (molecular dynamics) calculations showed that the Mn^{2+} ion diffuses freely on the surface from the centre to the edge region at room temperature.

Graphene also has unique biological and medical properties [148-152], and it is expected that, in future,

biomaterials incorporating graphene will be developed for the graphene-based drug delivery systems and biomedical devices. Hence, there is a need of thorough investigation of the biomolecule-graphene system for the understanding and successful prediction of the intermolecular interactions. Qin *et al*. [153] performed DFT calculations and molecular dynamics (MD) simulations to investigate the interaction between L-leucine and graphene. The four different orientations of L-leucine on graphene, which were considered, are shown in **Fig. 5**.
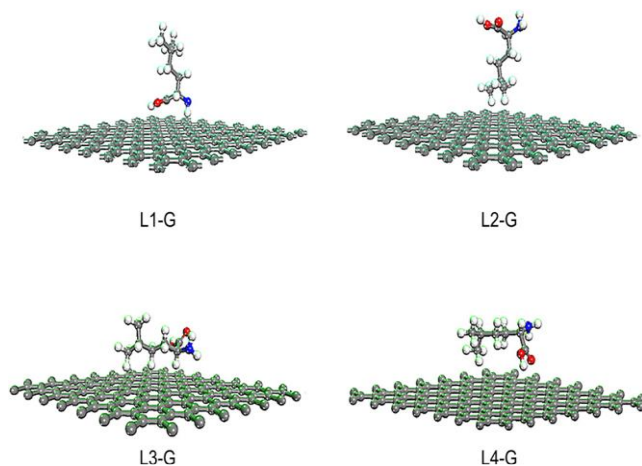
Fig. 5. Schematic view of L-leucine interacting with graphene sheet in four arrangements: L1-G: the functional group perpendicularly interacts to the surface; L2-G: methyl perpendicularly interacts to the surface; L3-G: fundamental chain with amino group of L-leucine parallelly interacts to the surface; L4-G: fundamental chain with carboxyl of L-leucine parallelly interacts to the surface [Reprinted with permission from **ref. 153**].

It was found that the electronic structure of graphene can be controlled by the adsorption direction of L-leucine. The binding energy corresponds to physisorption, and L-leucine prefers to parallelly arrange on the graphene surface. Further, MD simulations indicated that, under a certain range of temperature and pressure, the van der Waals interactions play an important role between L-leucine and graphene interactions during the adsorption process. Also, the L-leucine molecule could be adsorbed onto graphene spontaneously in aqueous solution, where the self-assembled structures of L-leucine molecules observed on the graphene surface were considered to be stabilized by a two-dimensional hydrogen-bonding network between the molecules. These results could provide helpful information for the molecular engineering of graphene-based nanoporous membranes, biomolecule delivery devices and medical diagnosis.

Furthermore, in the field of the biomedical application of graphene, Agarwal *et al*. [154] interfaced the living cells with chemically reduced graphene oxide (rGO) film and a network of single-walled carbon nanotubes (SWCNT-net), such as neuroendocrine PC12 cells, oligodendroglia cells, and osteoblasts. It was found that rGO is biocompatible with all these cell types, whereas the SWCNT-net is inhibitory to the proliferation, viability, and neuritegenesis of PC12 cells, and the proliferation of osteoblasts. This comparative study suggests that cells respond differently to these two types of nanocarbon substrates, likely due to their distinct nanotopographic features. The rGO film, the flat 2D nanocarbon structure analogous to a 2D cell membrane, is more biocompatible with all tested cells, which indicates its potential application in biology.

Other applications of graphene in various fields

Hydrogen storage

Hydrogen is an ideal energy carrier due to its abundance and environmental friendliness [155]. Developing efficient and stable hydrogen storage media is crucial for the hydrogen economy [156, 157]. However, its storage involves several technological and economic problems still not solved. Many different materials have been considered as attractive candidates for safe and economically feasible hydrogen storage media, such as liquid hydrogen [158], chemical hydrides [159] and advanced carbons [160-162]. Recently, special attention has been attracted to nanostructured materials because of their potentially high gravimetric hydrogen capacity, safety, and high efficiency of filling and delivering [163-165].

DFT calculations [166] showed that physisorption of H_2 on graphitic layers is possible. However, it was reported that the interaction between a hydrogen molecule and the bare graphite surface is so weak that the absorbed hydrogen molecule cannot remain on the surface [167].

In order to develop an efficient medium of hydrogen storage, carbon-based nanostructures functionalized by transition-metal atoms have been a subject of active study [167-171]. Recently, Yoon *et al*. [155] demonstrated that covering the surface of C_{60} with 32 Ca atoms can store 8.4 wt% hydrogen. In the year 2009, Ataca *et al*. [172] showed that Ca adsorbed on graphene can serve as a high-capacity hydrogen storage medium, which can be recycled by operations at room temperature. Further, the hydrogen storage capacity can be increased to 8.4 wt% by adsorbing Ca to both sides of graphene and by increasing the coverage to form the (2×2) pattern. Also, Chu *et al*. [173] explored the method based on first-principles plane-wave calculations with ethylene molecules and Ti, Li atoms intercalated into the graphite to open space for the physisorption of hydrogen. Results indicated that the interlayer distance of the graphene is close to the optimal physisorption of hydrogen.

Another theoretical study on the atomic and molecular hydrogen adsorption onto Pd-decorated graphene monolayers and carbon nanotubes was done [174] using a semiempirical tight-binding method. It was found that there is strong C-Pd and H-Pd bond formation during atomic hydrogen adsorption. Further, in the same direction, the characteristics of hydrogen adsorption on Li metal atoms dispersed on graphene with boron substitution were investigated [175] by DFT calculations. It was found that Li atoms are well dispersed on boron-substituted graphene forming a (2×2) pattern. One Li adatom dispersed on the double side of graphene can absorb up to 8 hydrogen molecules, corresponding to a 13.2% hydrogen storage capacity. To further extend their studies, Park and Chung [176] studied the bonding characteristics of Al and Ti on the boron-substituted graphene and the adsorption behaviour of H_2 on the Al and Ti dispersed on graphene. It was found that Al and Ti dispersed on graphene can bind

up to 8 hydrogen molecules resulting in a high hydrogen storage capacity of as much as 9.9 wt% and 7.9 wt%, respectively.

Batteries

The Li-ion battery has been a key component of hand-held devices, due to its renewable and clean nature. Graphite is usually employed as anode material in the Li-ion battery, due to its reversibility and reasonable specific capacity. However, to meet the increasing demand for Li-ion batteries with higher energy density and durability, new electrode materials with higher capacity and stability need to be developed. Among the carbonaceous materials, the graphene-based anode has been proposed as one of the promising alternatives in Li-ion batteries, as graphene has superior electrical conductivity, high surface area and chemical tolerance than graphitic carbon [110, 177-179].

The interaction of carbon with alkali metal atoms and ions is important in the field of secondary rechargeable batteries. In case of lithium ion (Li^+) and graphite, a theoretical maximum capacity of normal graphite material for the lithium ion (LiC_6) is 372 mAh g^{-1} [180]. When the carbon material was changed from graphite to amorphous carbon, this capacity increased to 500-1100mAh g^{-1} [181]. The elucidation of the diffusion processes of the alkali atom and ion on the graphene is one of the important themes in the development of higher performance secondary batteries. DFT calculations [182] on the Na atom-graphene system were carried out to elucidate the nature of Na-graphene interaction. The charge on the Na atom was found to be strongly dependent on the number of hexagonal rings of graphene. In the same study, using direct molecular orbital-molecular dynamics (MO-MD) calculations, it was shown that the diffusion rate of Na is slower than that of Na$^+$ ion on the graphene surface.

Further, the development of anode materials with high Li storage potential and small hysteresis is important for improving the properties of rechargeable Li-ion batteries [183]. Substitutions of atoms into carbon materials have been put in practice to modify the electronic properties and improve the anode material to satisfy the demand for high-energy and lightweight Li-ion batteries. Many heteroatom-substituted carbon species have been examined from the experimental [184-189] and theoretical [190] points of view. Boron substituted carbons [191, 192] have indicated very high Li storage capacity compared to a pristine carbon anode [193, 194]. Investigations [195] on the adsorption of Li ions on boron doped graphene revealed that more Li ions can be captured around boron doped centres than in pristine graphene. In particular, one boron atom doped into graphene can adsorb six Li ions, corresponding to a lithium storage capacity of 2271 mAh g^{-1}, which is six times that of graphite. Further, Velinova *et al.* [196] studied three series of Li complexes of aromatic hydrocarbons. The comparative study confirmed that pristine hydrocarbons are poorer anode materials. Further, for high-performance anodes, patterned B-substitution provided the most perspective candidates and results provide valuable information aiding the elucidation of the behaviour of larger systems, for example, Li intercalation in BN- or B-substituted carbon materials.

Halogen substitution and doping have also been examined in order to develop higher performance graphite materials [192]. Delabarre *et al.* [198] used fluorinated graphite as the cathode in primary lithium batteries. Higher capacity values were achieved for low temperature fluorinated graphite. In the same direction, Kawabata *et al.* [199] applied DFT and direct MO-MD methods to the diffusion dynamics of the Li$^+$ ion on the model surface of chlorinated graphene.

The theoretical estimates can facilitate controlled synthesis of novel modified carbonaceous materials with improved capacity for Li storage. Though few reports on application of graphene as electrode material in batteries are available, future research needs to concentrate more on understanding the mechanism of the electrochemical process in those systems and focus on application of a variety graphene based electrodes in Li-ion batteries.

Catalysis

Graphene has also a promising application in the field of catalysis. It can be used as a surface for many reactions or it can act as a support for some commonly used catalysts, such as Pt and Zr [200-204]. From DFT calculations, Kim *et al.* [205] found that the epoxide reduction by hydrazine on a single-layer graphene sheet predominantly follows a direct Eley-Rideal mechanism rather than a Langmuir-Hinshelwood mechanism. This study can aid in better understanding of atomistic mechanisms underlying the hydrazine reduction of graphene oxide sheets, as graphene based technology currently suffers from the lack of a method for high-yield production of graphene. Chemical reduction of exfoliated graphene oxide sheets with various reducing agents [206-208] is one of the promising approaches that has been extensively explored.

Some transition metal atoms and their clusters, which have a wide range of applications from catalysis to nanomagnetic devices [209], can also be adsorbed on graphene and research interest in this area is continuously growing. In particular, clusters of the ferromagnetic elements, Fe, Co, and Ni, are important in heterogeneous catalysis. Johll *et al.* [209] investigated the adsorption of Fe, Co, and Ni adatoms and homonuclear and heteronuclear dimers of these adatoms on graphene. Results show that the adatoms bind weakly to graphene, and binding of both homonuclear and heteronuclear dimers is found to be weaker than the respective adatoms.

Apart from the transition metal clusters, platinum on carbon black is a common catalyst/support combination, where modifying the support can increase the durability and activity of the catalyst. This combination is used for many reactions, including electricity generation using fuel cells [210, 211]. The carbon support is meant to stabilize Pt nanoparticles and increasing this interaction adds to the durability of the catalyst to resist any changes which would limit its efficiency. For example, the migration of the catalyst nanoparticles causes their potential accumulation into larger structures, which limits their availability and activity. Extending the lifetime of these catalysts would greatly reduce their cost and make them more appealing for a wider variety of applications which they may be better suited to fulfil. A two-fold increase in the binding energy was observed [200] when N-doped carbon structures were

used in Pt catalyst supports. Using DFT calculations, it was shown that N-doping of graphene increases the binding energy of a Pt atom to the substrate. This increase in binding energy is proportional to the number and proximity of nitrogen atoms to the carbon-platinum bond. Thus, graphene can mimic the common usage of carbon black for many catalyst supports used in fuel cells.

Also, unusually high catalytic activity of small Pt clusters supported on graphene has been observed in experiments [204]. Zhou *et al.* [212] studied the catalytic activity of small Au and Pt clusters supported on pristine or defective graphene using DFT calculations. It was found that single-carbon-vacancy defects in graphene greatly enhance the catalytic activity of Au_8 and Pt_4 clusters. The reaction barrier of CO oxidation catalyzed by Au_8 (Pt_4) clusters was estimated to be around 3.0 eV (0.5 eV) on a defect-free graphene sheet, and 0.2 eV (0.13 eV) on defective graphene.

Furthermore, zirconium is also used as catalyst in many reactions and some experiments [201-203] involving zirconium as catalyst and nanotube growth (with radii of several hundred Å) have revealed nanocrystalline structures with zirconia grains of about 15 Å in size in the outer wall of carbon nanotubes. These nanograins originate from the formation of a ZrC layer, and could be originally related to the clustering trend of Zr atoms on large radius nanotubes [213]. Sanchez-Paisal *et al.* [214] reported *ab initio* calculations of zirconium-coated graphene sheets at several coverages and geometries. It was shown that the Zr atoms have a trend to cluster when the Zr/C coverage ratio is increased.

Further, to explore the catalytic activity of graphene-metal systems, Li *et al.* [215] investigated the reaction of carbon monoxide with oxygen on Fe embedded in graphene, using first-principles calculations. It was found that the Fe atom can be constrained at a vacancy site of graphene with a high diffusion barrier (6.78 eV), and it can effectively activate the adsorbed O_2 molecule. The reaction between the adsorbed O_2 with CO was studied via both Langmuir-Hinshelwood (LH) and Eley-Rideal (ER) mechanisms and both the mechanisms were compared. The Fe embedded graphene shows good catalytic activity for the CO oxidation via the more favourable ER mechanism with a two-step route. The above discussed studies revealed that graphene play an important role in catalysis.

Conclusions

In merely eight years of its discovery the amount of research that has gone into graphene and   the fact that A. K. Geim and K. S. Novoselov have been awarded the Nobel Prize in physics in 2010 for their discovery of graphene, is indicative of the prospects of graphene as a material. Remarkable research is going on in the various application based fields of graphene, such as in hydrogen storage, Li batteries, catalysis and many more. Its use as a sensor to detect various species at molecular level is fascinating. Also, on account of its 2D structure, graphene has found promising applications in several adsorption phenomena. Various adsorption studies have been done on the graphene surface resulting in the chemisorption of the chemical species. Considering that graphene can serve as a surface to adsorb hazardous species that pose a threat to

mankind and environment, this material may indeed be referred to as the "material of the present era". However, there are gaps in the understanding of the involved mechanisms, which can be elucidated using theoretical calculations, in order to design more graphene based materials for use as chemical and biological sensors, batteries, and for removal of hazardous substances from the environment. In particular, the use of graphene for removal of hazardous substances, such as heavy metal ions and halogenated compounds, from water needs to be emphasized, given the strict EPA guidelines. Clearly more experimental and theoretical work, in particular, is needed to elucidate the mechanisms of adsorption and reaction of various species on graphene surfaces, so that better materials can be designed for environment protection.

Abbreviations

DBPs Disinfection by-products, **THMs** Trihalomethanes, **HAAs** Haloacetic acids, **HANs** Haloacetonitriles, **HNMs** Halonitromethanes, **HAcAms** Haloacetamides, **R₂NNO** Nitrosamines, **CNX** Cyanogen halides, **C-DBPs** Carbonaceous disinfection by-products, **N-DBPs** Nitrogenated disinfection by-products, **USEPA** United States Environmental Protection Agency, **AC** Activated carbon, **DFT** Density functional theory, **WHO** World Health Organisation, **SW** Stone-Wales, **SV** Single vacancy, **DV** Double vacancy, **SWCNTs** Single-walled carbon nanotubes, **AIMD** *ab initio* molecular dynamics, **AA** Amino acid, **TEM** Transmission electron microscopy, **DDS** Drug delivery system, **MRI** Magnetic resonance imaging, **MD** Molecular dynamics, **rGO** Reduced graphene oxide, **LH** Langmuir-Hinshelwood, **ER** Eley-Rideal.

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