

A Review on Defect Engineering of Graphene

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ABSTRACT

“Defect Engineering” is a term, which means the application of controlled defects in the ultrathin arrangement of 2D materials to improve its structure and various properties. Graphene a 2D single atom thick layer allotrope of carbon shows outstanding crystalline structure, various physicochemical properties, remarkable optoelectronic properties, a very good thermal conductivity, charge transport performance, optical transparency, electronic characteristics and extraordinary band gap structure is regarded as the building material for fifth generation electronic and optoelectronic devices. The highly ordered lattice of graphene displays extraordinary device performance, but during growth and processing development of structural defects decreases the performances of the material in the devices. However, these defects can be modified by applying several advanced techniques, so that to realize better performances for device applications. Hence, “Defect engineering of Graphene” actually means perfection of the structure as well as the properties of graphene in order to enhance the functions by using organized defects. In nanotechnology, it is growing towards the route of a perfect material with superior properties for better device performances. This review briefly describes the recently applied advanced techniques that are useful for defect engineering of graphene i.e. Electron beam irradiation, plasma, chemical treatment and doping.

Key words: Graphene, functionality, bandgap, e-beam irradiation, plasma, chemical treatment, doping.

1. Introduction

Recently 2D materials have gained much attention owing to its ultrathin, highly ordered crystalline structure and extraordinary optical, electronics and optoelectronics properties [1]. It has a wide range of application in transistors [2], light emitting diodes (LED) [3], photo detector [4], modulator [5] and have a plentiful usage in numerous fields. However experimentally it is realized that the intrinsic defects associated within the two dimensional material structure displays inferior structural properties, which decrease the performances of the device as, predicted theoretically. According to the Mermin - Wagner theorem [6, 7] a 2D crystalline structure is unstable by longer wavelength fluctuations. Elastic theory [8, 9] states the thickness of the crystal film is unsteady at temperature greater than 0 K. This uncertainty of stability in 2D crystalline material accelerates researchers the discovery of contemporary 2D crystalline material for better stability and device applications. Graphene an ultrathin stable monolayer of carbon atoms with 2D crystalline structure is isolated by mechanical exfoliation by Novoselov in 2004[10] after its discovery. It stimulates researchers for various applications in numerous fields due to several fascinating properties. It has sp^2 hybridised honeycomb lattice structure with thickness of about 0.335nm [11] possess extraordinary physicochemical properties i.e.

high surface area, superior stiffness and strength [12], high electron mobility, thermal conductivity [13], half-integer quantum hall effect and quantum tunnelling effect [14]. Graphene has also attracted worldwide attention as a promising electronic material due to its intrinsic high crystal quality [15, 16] and massless Dirac fermions [17]. Because of exceptional Dirac cone band structure near Fermi level it shows extremely high density charge carrier and ballistic electron transport properties. Due to these properties, graphene is also termed as zero-gap semiconductor [18]. The quantum effect of graphene at room temperature is due to the movement of massless electrons in the hexagonal lattice at sub-micrometre distance without scattering [19]. The aforesaid unusual properties triggered a wide range of application of graphene in various fields i.e. in micro-nano devices, reinforcing materials and thermal applications[20,21], energy applications viz. solar cells, lithium ion batteries, supercapacitors [22] , biological sensing and glucose detection[23] etc. Figure.1 shows a schematic diagram of the application of graphene in various fields.

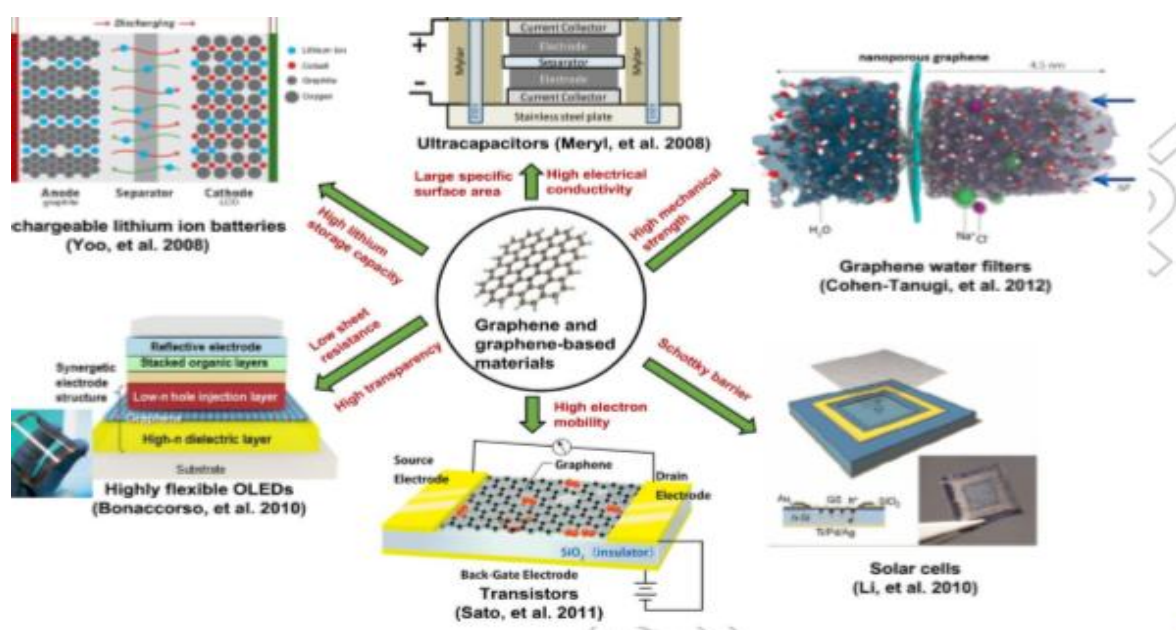


Figure:1 Various applications of graphene and graphene-based materials [18].

Generally, no material in nature is perfect. It the second law of thermodynamics that commands the defect and disorder present in crystalline material. Graphene possess different defects during its synthesis and processing and these defects affects the properties of the crystal, crystal topology, structure [24] along with its thermal, mechanical and electronic properties [25]. The structural defects like pentagons and heptagons are obtained during graphene synthesis by chemical vapour deposition (CVD) [26, 27], Graphene Oxide (GO) reduction [28] and epitaxial growth [29, 30]. Meanwhile, introduction of energetic particle irradiation and chemical treatment methods on the as-synthesized graphene creates higher structural disorders. The structural defects in graphene exhibit different dimensionalities i.e. 0D, 1D and 2D. The 0D point defects possess vacancies, adatoms, and substitutions. Vacancies may create different polygons in the sp^2 hybridised hexagonal structure of graphene and increases the reactivity of the structure. It acts as adsorption site for atoms, molecules and cluster of graphene due the absence of dangling bonds. Foreign atoms could be introduced in the structure by substitutions. Stone- Wales (SW) defect a 0D defect arises due to the C-C bond rotation without losing or

gaining atoms. Dislocations and grain boundaries (GB) are 1D line defects arise from bulk crystals that reduces the dimensionalities of graphene due to abnormal atomic arrangements. 2D defect like stacking faults is also developed in graphene few layers [31]. A diagram given below shows the various defects in graphene.

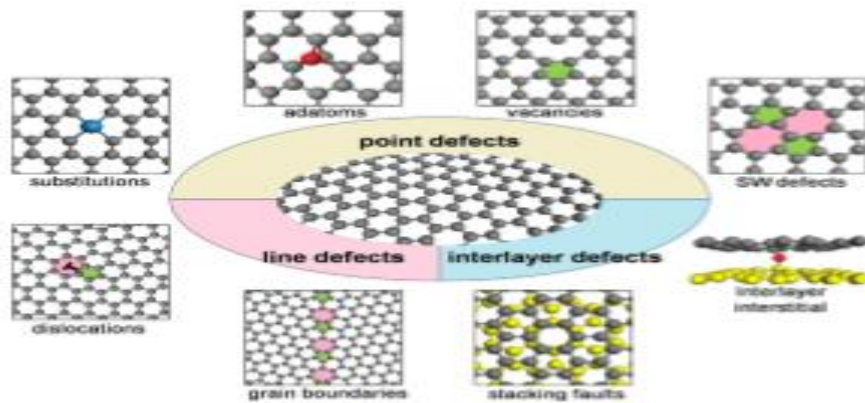


Figure: 2 Defects in graphene [31]

The structural defects in graphene have some disadvantageous effect on the properties of graphene. For instance, in graphene different defects created by vacancies, dopant atoms, the scattering electrons and phonons, decreases the electrical and thermal conductivity, mechanical strength, Young's modulus and various physicochemical properties. Table: 1 gives a brief description of comparative performances of various properties of structurally perfect and defect graphene.

Table: 1 performance properties of structurally perfect and defect graphene.

Properties	Perfect graphene	Defect graphene	Reference
Young Modulus(TPa)	~ 1	0.15-0.95	[31]
Fracture strength(GPa)	90-130	47-117	
Electrical conductivity(S/m)	10^8	$1-10^5$	
Electron mobility($\text{cm}^2/\text{V/s}$)	10^5-10^6	$1-10^4$	
Thermal conductivity(W/m/K)	10^3-10^4	$10-10^3$	

The advanced tools used for investigating the defect formation, its structural transformation, and localization of defects with high atomic resolution are Transmission Electron Microscope (TEM) with optical aberration corrector [32] and Scanning Tunneling Microscope (STM). Given below, the STM and TEM images of an isolated single vacancy in graphene. In the figure, the STM image shows a spot at single vacancy as local density of states increased due to dangling bonds around the single vacancy [33]. Table 2 describes various pattern and properties of defects observed under TEM and STM.

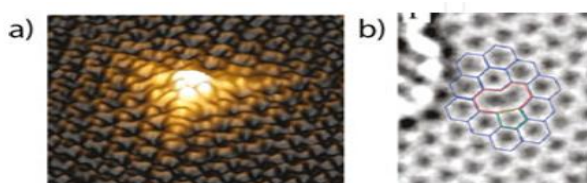


Figure: 3(a) STM image of single isolated vacancy in graphene. (b) TEM image of reconstructed single vacancy with atomic configurations in graphene [33].

Table 2 Pattern and Properties of various defects in graphene.

Defect Pattern	Formation energy(ev)	Migration energy(ev)	Energy per dislocation(5-7 pair) (eV)	References
SW (55-77)	4.9	10	2.5	[18]
Inverse SW (57-57)	5.8		2.9	
SV (5-9)	7.3 - 7.5	1.2 - 1.4		
Di vacancy (5-8-5)	7.2 - 7.9	7		
Di vacancy (555-777)	6.4 - 7.5	6		
Dislocation $\mathbf{b} = (1,0)$	7.5			
Linear GB $\theta = 21.8^\circ$	0.338 eV/Å		2.2	
Linear GB $\theta = 32.2^\circ$	0.284 eV/Å		1.3	
Adatom	6 - 7	0.4		
Adatom-SV pair	14			

However, the defects can also have beneficial effects upon various applications. To get the desired properties and enhanced functionalities in graphene-based devices, the defects can be modified by recognizing the specific type of disorder formed during growth and processing or by other methods. This is known as graphene defect engineering. For example, Graphene in the process of self-doping [34-37] increases its electronic properties. Because of its two dimensional arrangement it can easily add, remove and move carbon atoms from its structure to get a tuned structure. The extended defects in graphene, such as Stone-Thrower-Wales defect (STW) and di-vacancy defect are developed from localized defects. Matthias Batzill et.al [38] introduced alternative STW and di-vacancy defect on the epitaxial layer of graphene on a nickel substrate, which create an extended defect of paired pentagons and octagons. This is a type of line defect acts as a conductive nanowire in graphene based electronic devices [39]. Other defect engineering approaches in 2D crystalline lattice of graphene includes electron beam irradiation (e-beams), plasma, chemical treatment, ozone treatment, doping and laser. Therefore it is essential to have a better understanding on recent progress on defect engineering of graphene trigger by these methods and the knowledge of defect generation, its structural and

phase transitions, and new structure fabrication, so that it will be beneficial for researchers to fix up the surface structure and properties for better performance and device application.

2. Defect engineering process and recent techniques

2.1. Formation of defects during growth and processing

Defects are sometimes created knowingly to tailor the properties of graphene. Nevertheless, during growth and processing defects are generally created in pristine graphene. Large-scale production of graphene is essential due to its numerous application in different fields and generally two methods i.e. top down and bottom up methods are assessed for this purpose. Top down method includes mechanical exfoliation and reduction of graphene oxide whereas bottom up method are epitaxial growth and CVD. Among the two top down method reduction of graphene oxide is a low cost and large-scale production process. Mechanical exfoliation by scotch tape method produces monolayer free standing graphene but the method is labour intensive and unfeasible for large scale production of graphene. Defects such as point defects, line defects, adsorption of functional groups etc. are introduced during the oxidation, exfoliation and reduction processes. Bottom up methods such as epitaxial growth and CVD are two large-scale synthesis approaches of graphene. In CVD growth of graphene at high temperature facilitates annealing of defects hence shows less defect than at low temperatures. Due to high formation energy of vacancies and fast-migrated adatoms isolated vacancies are developed in graphene after growth. During growth grain boundaries are formed which generate polycrystallinity of structure. Grain boundaries and topological defects produces ripples and wrinkles. Crumples are formed when multidirectional forces are applied on graphene during rapid evaporation [18].

2.2. Electron beam Irradiation

Generally, electron beam irradiation creates higher structural disorders and destroys the properties of the 2D material. Nevertheless, it can easily detect the point defects in the defective lattice, its phase transition and structural transformations at a time with high-resolution atomic image when the same electron beam is introduced. The 2D crystal lattice of graphene is highly anisotropic and is very sensitive to electron beam irradiation. Owing to its unique properties, graphene can renovate the defects when electron beam is irradiated on its structure. Even at a lower voltage, it can either generate defects or make possible for the rearrangement of atoms to acquire new structures and morphologies. However, when the electron beam irradiation is coupled with thermal annealing it shows advantageous effect. The atomic point defects can cause atomic displacement in the lattice when the induced electron energy is higher than the targeted atoms threshold energy. Likewise, when the transference energy of electron beam is nearly equal to atomic binding energy, the irradiation causes migration, agglomeration and reconstruction of the point defects. If the electron beam is irradiated in a controlled manner [1] (energy, its dose and irradiation area) on the surface of 2D material different nanostructures such as nanopores [40-42], quasi one dimensional structure i.e. atomic chains, nanowires, and nanotubes [43-47] are formed for various beneficial applications. Therefore it is essential to have a better knowledge about the techniques involved in electron beam irradiation on 2D crystalline material so that the structure -property relationship along with high atomic resolution images are reasonably known to modify the properties for better device performance. Scanning Tunnelling Microscope (STM) and Transmission Electron Microscope (TEM)

are the two advanced tool used for imaging. In STM, the atomic resolution is determined by measuring the tunnelling current to an atomic sharp tip but it is time consuming and needs harsh environmental condition. In this regard, TEM performs the best in which the atomic resolution image is better than $1\text{\AA}$, even in low voltage [48, 49].

Advantages of TEM on 2D materials

- TEM easily detects the structural growth in 2D material at individual atomic level and modify the structure with higher accuracy and precision.
- It can tailor the 2D materials when the electron beam and specimen interaction is specifically controlled.
- TEM is associated with aberration corrected technique and possess energetic electrons to give high atomic resolution imaging.
- It can attain better spatial resolution than $1\text{\AA}$ even at low operating voltage.
- The creation of point defects is realized in real time with the same electron beam with atomic resolution.
- The renovation of lattice occurs in 2D atomic plane at individual atomic level without any prediction artefacts.

2.2.1. Electron beam induced process on 2D material

When energetic electron beam falls on the sample of 2D material electrostatic deflection causes elastic and inelastic scattering. Elastic scattering is the coulombic interaction between the induced electron beam and the nucleus of the specimen whereas inelastic scattering is the coulombic interaction between the incident electron beam and the electrons surrounding each atomic nucleus of the sample. At first the electrostatic charging occurs from both electron-nucleus and electron-electron scattered interactions. The net charge which builds up in the material during the interaction is mainly depends on sample, electron energy and electron beam current density. This interactions causes various changes in the crystal lattice such as the atomic displacement, knock-on-damage, structural changes, heat generation and mass loss. By following the conservation of energy and momentum, very small amount of energy from the electron beam can be transferred to the atoms on the material structure and creates collisions. In electron-nucleus collision, the transferred energy from the electron beam exceeds slightly greater than the threshold energy of an atom. Hence the atoms from the normal lattice gets deviated or displaced or simply leave the atomic site. This causes knock-on-damage or sputtering of atoms in the structure. Here the displacement rate of the atom directly depends on the electron beam current density [1, 50]. For instance, in graphene generally low voltage TEM studies are carried out with an electron acceleration voltage of 80kV but for surface atoms, the knock-on-damage threshold occurs at an electron acceleration voltage of 86kV [51, 52] while for edge atoms it is 56kV [53]. On the other hand in electron-electron interaction, the transfer energy from electron beams only rises the temperature of the specimen as the transfer energy is lower than the knock-on-damage threshold energy. This leads to atomic ionization, bond breaking, heat generation and mass loss rather than atomic displacement that create damage in the structure. Another one is electron beam induced deposition. It is formed during electron-electron collision where the hydrocarbons at the surface of material polymerized and causes low surface mobility and vapour pressure [50, 54].

Figure 4 shows flow-chart for electron beam induced processes on the sample.

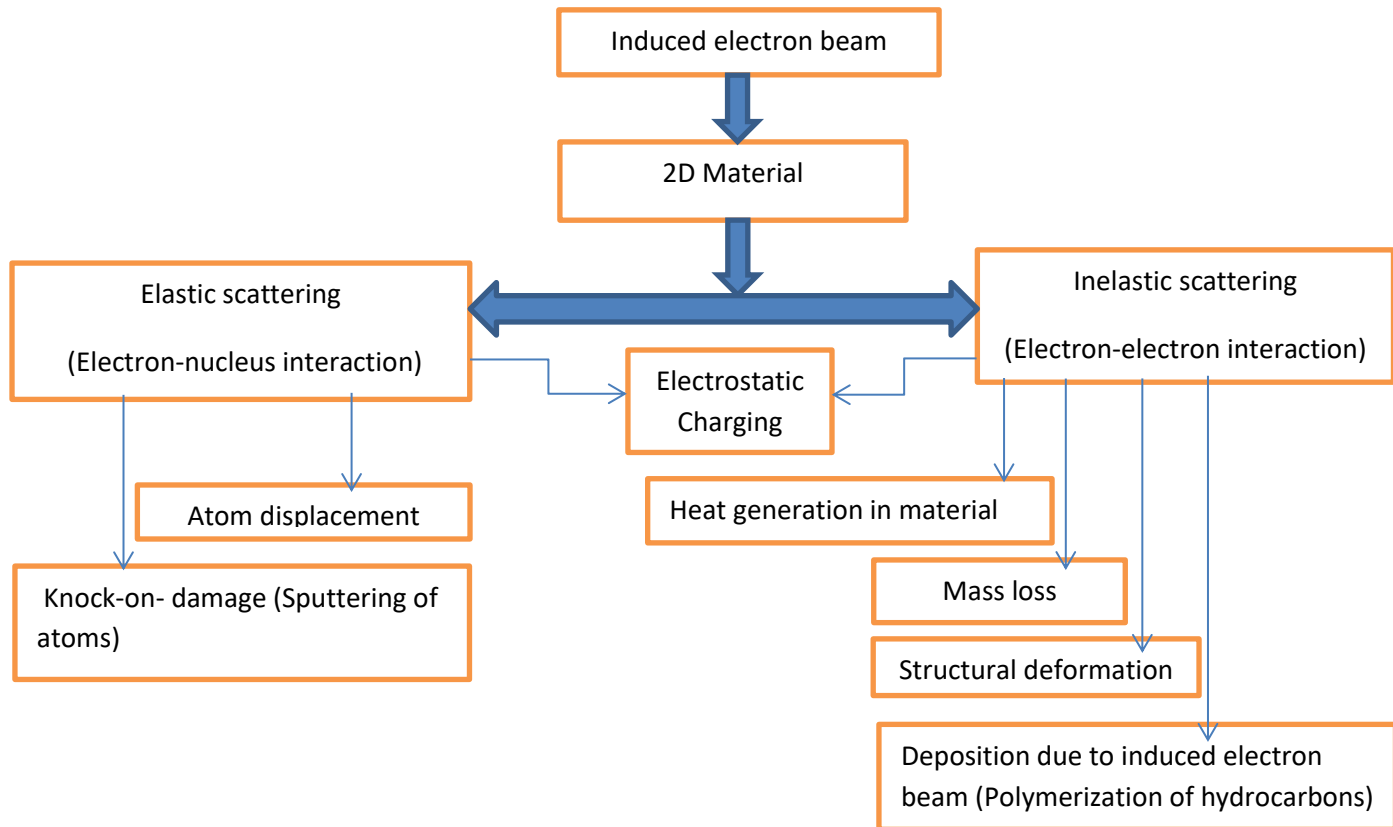


Figure: 4 Electron beam driven processes on material [54]

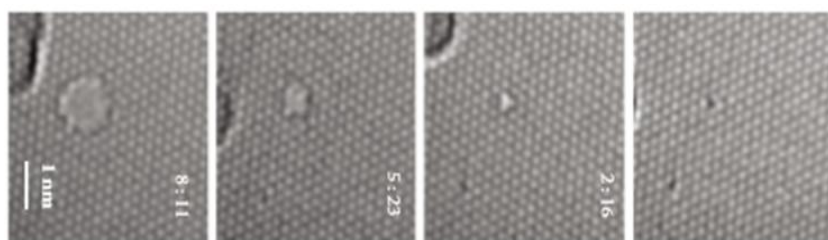
2.2.2. Defects dynamics of graphene under electron beam irradiation

Electron beam irradiation encourages the generation, migration, aggregation, or reconstruction of defects in the 2D lattice of graphene. Hence a good understanding of the defects formed under electron beam irradiation is useful for fabricating different nanostructures in graphene to increase its various properties for better device performances. Under electron beam irradiation the structure of the stable graphene may changes to polycrystalline or amorphous while the majority are the point defects, which includes vacancies and stone-wales (SW) defects. Vacancies are due to the ballistic ejection of carbon atoms from the surface. The carbon atoms are ejected or adsorbed on the graphene surface and move as an adatom [18, 55]. The defect generation mainly depends upon the knock-on-damage threshold energy. When electron beam induced energy exceeds the knock-on-damage threshold energy of an atom creates displacement of atom in the structure. Usually pristine graphene is stable at the electron acceleration voltage of 80kV. Different TEM studies proved defects can also be generated by lowering the knock-on-damage threshold of graphene or even at acceleration voltage of 80kV. For example, vacancy can be generated on graphene surface at 80kV [56] (Fig-5 A) and this is due to the reaction of surface adsorbates and graphene when the electron beam is introduced. The presence of unsaturated bond in graphene also decreases the knock-on-damage threshold energy and creates a hole on its structure at 80kV which indicates the knock-on-damage threshold depends upon the atomic arrangement of crystal [1].

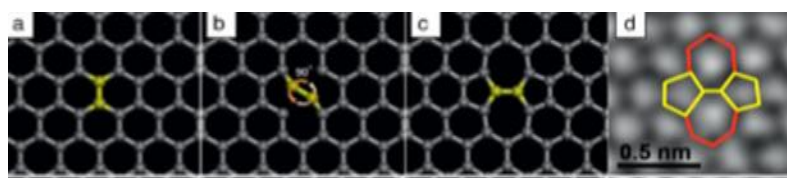
Another type of point defect is Stone-Wales defect (Fig-5 B) which is formed by the in plane 90° rotations of C-C bond and here the atomic number remains constant under electron beam irradiation. Here the four adjacent hexagons of

graphene are converted to two pentagons and heptagons at an activation energies 9-10eV which is lower than knock-on-damage threshold energy [49, 57]. Stone-Wales bond rotation also convert divacancies into different configurations such as 5-8-5, 555-777, and 5-7-7-5 under electron beam irradiation (Fig-5 C) and flower defects are also formed in graphene structure at 80kV electron beam irradiation [58, 59]. The flower defect with a core of seven hexagons is due to 30° C-C bond rotations, it is less disordered state and converted to original graphene due to C-C bond rotations [1]. 5-8-8 divacancy can develop 5555-7777 configurations via 555-777 by Stone-Wales bond rotation [48].

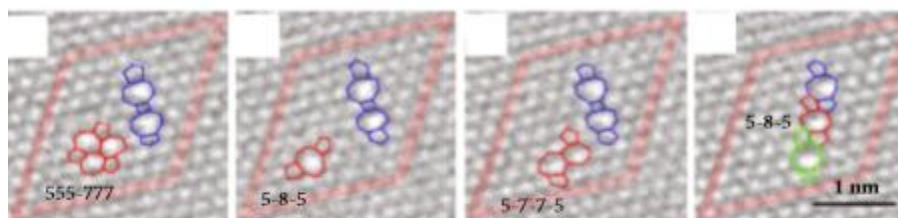
Figure: 5 Generation of defects on graphene by electron beam irradiation



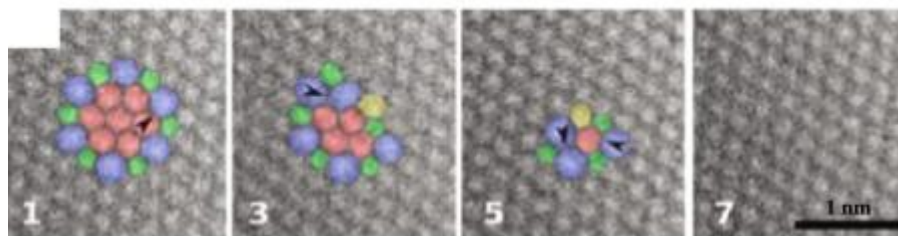
(A) Vacancy at 80kV electron beam irradiation: [1]



(B) Stone-Wales Defect at 80kV electron beam irradiation [49]



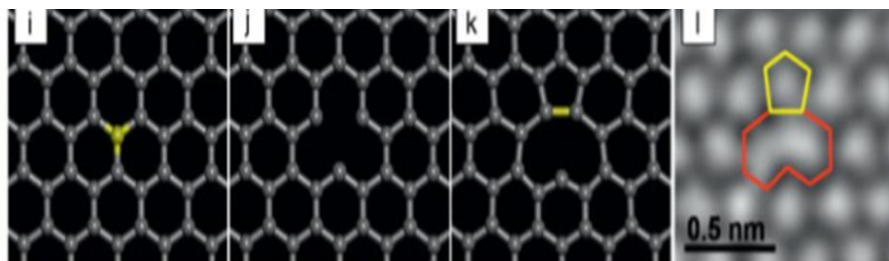
(C) Divacancy at 80kV electron beam irradiation [1]



(D) Flower defect at 80kV electron beam irradiation [1]

The TEM images of graphene explain the formation and reconstruction of graphene lattice in many ways. Normally the defect formation in graphene at 80kV is due to the movement of adatoms on the surface of graphene. They interact with graphene under electron beam irradiation and interrupt the hexagonal lattice. Hence any perturbation in the lattice makes the bonds weaker and the atoms leave from their original site in the hexagonal lattice at lower energies creating

vacancies. But the complex defect structure formation at energy 80kV can be explained by taking a single vacancy. The single vacancy undergoes Jahn-Teller distortion and lowers its energy. Two of the three dangling bonds around the missing atom are saturated. The Jahn-Teller distortion lowers the overall energy of the system, removes electronic degeneracies and leads to the formation of a pentagon and a nonagon [57, 60] but the nonagon contains a dangling bond. The Jahn-Teller distortion energy is very small and the three reconstructed structures can easily rotate among these three configurations [49]. Fig 5 E shows the atomic models of the formation of a reconstructed single vacancy.



(E) Atomic models showing the formation of a reconstructed single vacancy. The yellow atom is the one removed, and the yellow bond indicates the reconstructed bond. (l) AC-TEM image of a reconstructed single-vacancy defect [49]

Recent TEM studies showed that Jahn-Teller reconstructed single vacancy is stable up to one minute and it is due to the attachment of hydrogen atom to the dangling bonds of C atom or presence of N atom in place of C atom at the vacant site [60]. Several TEM studies show the stability of single vacancy at 80kV is valid up to some minutes. This is due to the quenching of single vacancy by trapped mobile adsorbates such as C, N, Fe or Si [61-63]. Divacancies are formed by coalesce of two migrating single vacancy or when an atom next to single vacancy is displaced. They do not have any dangling bonds in the reconstructed lattice. Larger and more complex vacancy defect configurations are created by removal of atoms. Generally vacancies with even no of missing atoms are energetically more favourable than odd no of missing atoms with at least one open bond [64]. Quasi amorphous structure of graphene is due to the large density of vacancies in the structure [65, 66]. Recent research revealed that tetravacancies are also formed due to the bond rotations or linear defects along armchair direction of graphene [67]. Vacancies in graphene also behave as trapping site for foreign atoms [68]. Substitution defects are formed with nearby uncoordinated carbon atoms via covalent bond and generally B and N atom are used for this purpose as they have same atomic radius as C carbon atom which are detected by TEM by applying a Gaussian low-pass filter [69]. Other than B and N, Si [70] and transition metals [71] are also used in substitutional doping although they have larger size. These images are easily detected by HRTEM [48].

Bond rotations in graphene form dislocation glide and migration of di vacancies. The dislocation cores can migrate in the lattice by climbing or gliding (Fig 5F). In climb motion the atoms are added or removed next to the dislocation core while in gliding motion the Stone-Wales transformation occurred in zigzag direction and the movement of dislocation is 0.25nm [48, 72].

Electron beam irradiation also causes impurity sites without atomic loss. The foreign adatoms are stuck in the graphene structure (Fig 5 G) in the meantime an attractive interaction occurred between the defect and foreign atom over a region of 1-2nm. Although these substitution defects are stable, sometimes the foreign atoms can migrate under electron beam irradiation. For example, oscillation of pyridinic-N between equivalent bonding sites across a single vacancy [73], the movement of Si substitution via out-of-plane bond inversion [74] and the rotation of a Si trimer in a divacancy [75]. A tungsten atom can jump back and forth between two defective sites at a distance of 0.5–1.4 nm. A biaxial strain of 1% in the graphene lattice increases the adsorption energy for transition-metal adatoms by 0.06–0.16 eV, depending on the metal species and the adsorption site.

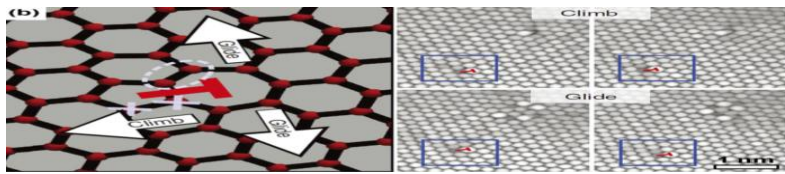


Fig 5F Migration of dislocation core by climbing or/and gliding [48]

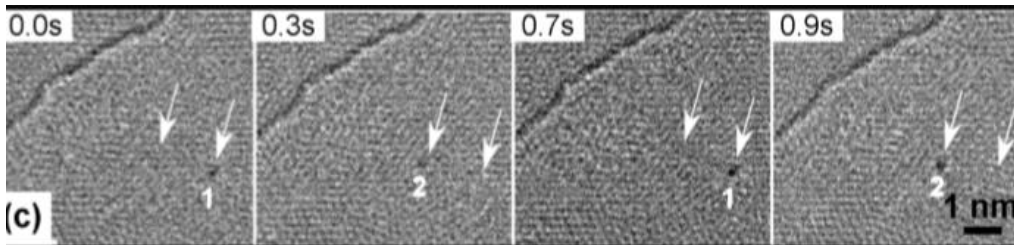


Fig 5G Oscillations of a W atom between two trapping centres 1 and 2 on a few-layer graphene at 480°C [48]

The functional properties of graphene are also affected by electron beam irradiation. Insulated fluorinated graphene can be made conducting or semiconducting structure by electron beam irradiation. The resistance of fluorinated graphene decreases with increasing channel width and resistance decreases to 7 orders of magnitude and increases the conductance. In electronic devices the fluorinating graphene acts as insulating host and defluorinating graphene as metallic interconnect in devices [76].

One dimensional defects in 2D crystalline structure of graphene like line defect of dislocation type at edges also appeared under electron beam irradiation [77-80]. In this defect the zigzag chain [81] of carbon atoms is removed creating pentagon-heptagon pair or distorted hexagons which are either straight line or twisting till the end of sheet. Dislocation can migrate either by bond rotations or by removal or addition of two carbon atoms. The strain induced caused the out-of-plane distortion and creates defect in the structure.

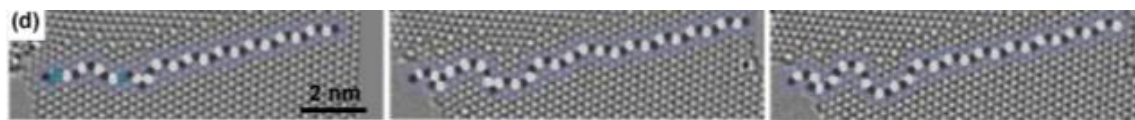


Fig.5H Bond rotation-mediated configurational changes of a graphene GB with low overall curvature [48].

Intense irradiation creates holes along with unsaturated bond [82-84] and the edges of holes may be zigzag, armchair or reconstructed lines [85-88]. Defective edges are also due to the removal of atoms from the structure [89]. Electron beam irradiation damage when coupled with temperature creates defects. For example, when temperature higher than 300°C is applied on electron beam induced graphene damage structure single vacancy become mobile. This defect annealing [90] causes formation of non-hexagonal ring and the migration of carbon interstitials or vacancies, followed by Frenkel pair recombination.

2.2.3. Innovative structure fabrication by electron irradiation

During electron beam irradiation process mass loss and mass gain are the occurred in 2D material either by the sputtering of atoms or polymerization of hydrocarbons on the surface. The process not only creates defects but also modify the structure and properties of the defective material which are essential for novel structure fabrication if the irradiation region and irradiation beam current density is controlled when applied on material through a probe-corrected TEM. The fabricated structures have various applications in many areas of graphene related devices. Nanopores with ultrathin membrane are used in DNA sequencing and single molecule analysis [91]. Here the device performance depends upon the pore geometry and size. To get desired size electron beam can be focussed on a spot of less than 1 Å⁰

in a controlled manner to interact with target atoms in order to sculpture a nanopore with atomic precision. The fabricated nanopores do not meet always the requirements for single molecule analysis. The area surrounding the spot is damaged or converted to amorphous structure due to focussed electron beam. The reconstruction of this structure is carried out by thermal excitation and at high temperature the area around the pore become crystalline so that the size of the as-sculpted nanopore is modified (Fig. 6A).

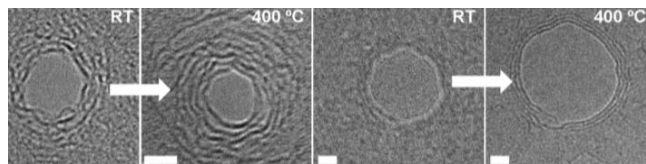


Fig. 6A Size evolution of graphene pores under thermal excitation. The scale bar is 2nm. [48].

Subnanometer quasi one dimensional structure of 2D materials which are the building blocks of future electronics devices are generally prepared from top-down method are also prepared from electron beam irradiation by controlling irradiation area and electron beam dose. The desired sized thin quasi 1D nanoribbons can be fabricated by controlling the electron beam irradiation dose between two adjacent pores. Continuous irradiation cause sputtering of carbon atoms [92] and forms very narrow structures or atomic chains (Fig 6 B). The atomic chain shows conductive behaviour but compared to ideal unstrained chain it is lower due the presence of local strain. Under strain the 1D structure behave as semiconducting polyyne chain with alternative single and triple bond and if it is unstrained it is a metallic cumulene chain having same length double bonds [48, 93].

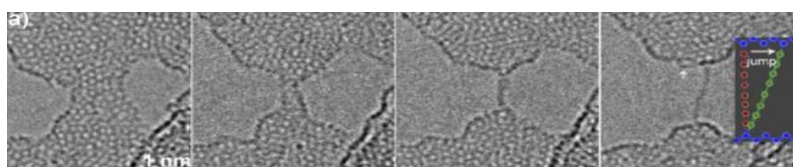


Fig 6 B Formation of free-standing carbon atomic chain in graphene through continuous electron beam irradiation (120 kV, 4 A/cm²) [48]

A three-electrode device was prepared from a continuous graphene sheet where the third electrode operates as a side gate in a field-effect transistor (FET) [94]. The sculpted graphene nanoribbon was suspended between the sources and drain electrodes and served as a FET channel where the carrier density can be modulated by the side-gate potential. Although the e-beam provides the possibility, in situ EM fabrication of nanodevices remains challenging due to the lack of operational flexibility.

With activation energy transferred from the electron beam, adatoms or clusters on 2D sheets can be assembled into crystalline monolayers, showing a path to form quasi 2D structures. For instance, metal oxide monolayers such as single-atom-thick CuO membrane can be fabricated from CuOx clusters on graphene substrates and inside graphene nanopores [Fig. 6(C)]. If one half of O atoms are further removed by electron beam irradiation, monolayer CuO may transform into another stable oxide (Cu₂O) with direct bandgap [95].

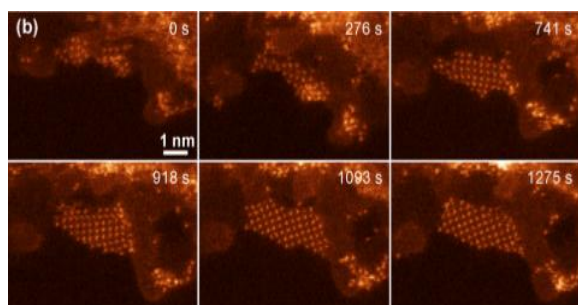


Fig. 6(C) : Growth of CuO monolayer on graphene substrate [95]

2.3. Ion Irradiation Process

Ion irradiation not only creates defects in graphene structure but also pattern graphene sheets by using a focused ion beam [18, 96]. The defects such as interstitial, vacancies are created over a large area on graphene by controlling dose of irradiation. The damage which are formed are depends upon the intensity of dose and sputtering of atoms in the lattice.

The dependence of vacancies created with intensity of ion irradiation was observed by Kalbac et al. by Raman spectroscopy [97]. They created interstitials and vacancies on isotopically labelled bilayer graphene sheets by Ar^+ ion irradiation with various doses and their experimental results indicates that the number of the vacancies created shows a positive dependence on the intensity of ion dose, and the final defect density in the bottom layer was lower than that in the top layer [Fig 7].

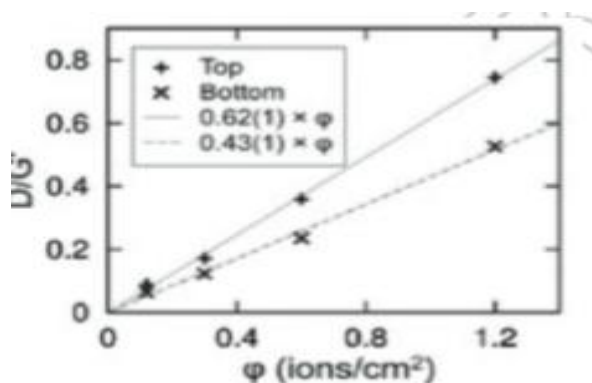


Fig 7 : D/G' intensity ratios as functions of Ar^+ ion irradiation fluence (in 10^{13} ions/cm²) [97]

He^{2+} ion irradiation creates sufficient number of vacancies and these vacancies are responsible for hole doping in graphene which increases the work function of graphene. The hole doping is due to the charge interaction between the broken carbon bonds and ambient oxygen molecule. The increase of work function due to hole doping showed a logarithmic behavior with respect to the irradiation dose [98]. Buchheim et al [99] irradiated He^+ ions at energies (10-30 keV) and the results were corroborated by Raman spectroscopy. They found these ions allows the passage of more than 97% He^+ particles without creating vacancies on the hexagonal lattice of freestanding graphene. But the large Ga^+ ions at energies (5-30 keV) collide with the graphene lattice, and impart a notable higher sputter yield of ~50% [18].

Fluorination is another process to functionalize graphene well described by Halder et al.[33].The fluorination of graphene is a site-selective-fluorination process [100] in which the focus ion beam is used under XeF_2 environment in high vacuum or the graphene surface is radicalized using high-energy ion irradiation under fluorine contained precursor molecule. The defected structures were created by Ga^+ ions with 30kV and an irradiation dose of 10^{13} ions cm⁻² (Fig. 8). Although it is not the threshold energy to displace atoms completely from their normal site, still some of the damaged part forms defects such as vacancies. The fluorination process and its mechanism were verified by X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, scanning tunnelling microscopy (STM), and density functional theory (DFT) calculations. XPS shows the fluorinated graphene exhibits a clear signal of F 1 s peak. Raman spectra show the intensity of the D-peak (at 1350 cm⁻¹) increases after irradiation and the intensity of the 2D-peak decreases sharply which indicates the translational symmetry of sp² bond is broken. In fluorinated graphene, the ID/IG is lower than the defected

graphene which implies that fluorinated graphene contains less structural disorder. STM shows various defects along with corrugations on the fluorinated graphene surface. Standing waves with different structures near the defect area form these corrugations. Figure: 9 shows the STM images at low voltage of -75 mV at Fermi level having the irradiation area of 20×20 nm². According to their *ab initio* density functional theory (DFT) calculation, the adsorption energy of the fluorine adatoms on pristine graphene is very high than the di-vacancy and the hole defects. It implies that the fluorine atoms are prone to react with the carbon atom surrounding the defect sites.

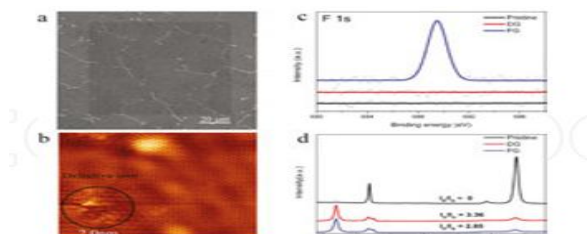


Figure:8. Characterization of pristine graphene, defected graphene (DG) and fluorinated graphene (FG). (a) Scanning electron microscope (SEM) image of local functionalization of graphene ($100 \mu\text{m} \times 100 \mu\text{m}$) with ion doses of 10^{13} ions/cm² and simultaneous 167 s gas exposure. (b) Scanning tunneling microscopy image of DG under the same ion dosage. (c) X-ray photoelectron spectroscopy spectra of F 1 s peak of pristine graphene, DG and FG. FG reveals a distinguished F 1 s peak, and the F 1 s spectrum of pristine graphene as well as DG is given as a reference. (d) Raman comparison of pristine graphene, DG and FG. Lower ID/IG in FG in contrast to DG indicates lower degree of defects density and larger crystalline size [33].

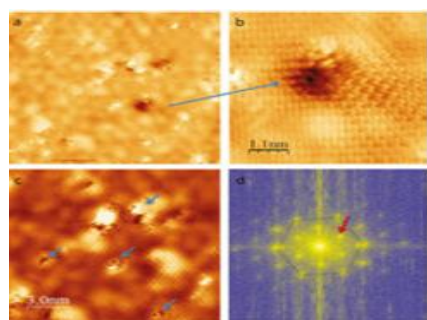


Figure: 9. STM images of fluorinated graphene. (a) 20×20 nm² area. (b) Zoom in image of a hole defect showing standing waves pattern. (c) Other area 15×15 nm² showing bright feature decorating holes (blue arrows) attributed to fluorine atoms. (d) FFT of (a). It reveals the first Brillouin zone with hexagonal lattice and K points (red arrows) associated to the standing waves pattern due to intervalley scattering. [33].

Graphene has potential application in gas sensing devices due to its 2D structure, high conductivity and electrical noise. The gas molecules acts as electron donors or acceptors, modify the carrier density of graphene and changes its electrical resistance [33]. By measuring the electrical resistance changes, graphene can be used as a gas sensing device [101,102]. The gas sensing properties of graphene especially NO₂ gas detection is determined by creating defects under Ga⁺ ion irradiation. The defects were created in the pristine graphene by irradiation with 30 keV Ga⁺ ions in a vacuum chamber under $\sim 10^{-6}$ mbar pressure. The area of irradiation is $20 \times 20 \mu\text{m}^2$ and one single irradiation consists of an ion dose of $\sim 10^{12}$ ions cm⁻². The defect formation was confirmed by Raman spectra analysis and atomic force microscopy. The analysis results showed graphene is bilayer and the D-peak appeared at 1352 cm⁻¹ which indicates the formation of defects in graphene. The appearance of D-peaks is due to the breathing modes of sp² rings. The intensity of D-peak increases after the second irradiation and also D'-peak appears at 1626 cm⁻¹ which suggest an increase of defects in graphene (Fig 10).

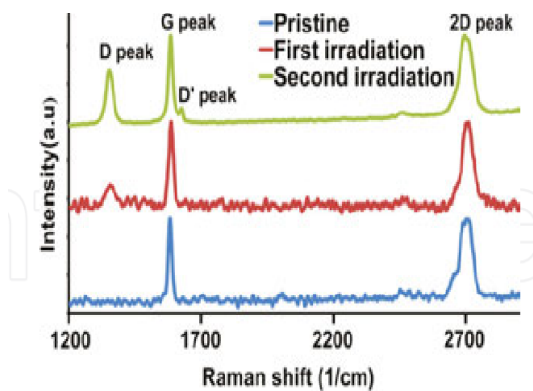


Figure 10. Evolution of Raman spectra with respect to ion irradiation of graphene. [103]

The defected graphene shows higher conductivity in the presence of NO_2 gas compared to the pristine graphene. In pristine graphene, the electrons are transferred from graphene to NO_2 molecules and increases the hole density in graphene. Hence conductivity increases after first irradiation. But the gas sensing properties decrease after the second irradiation due to the increase of defects, which increases the number of scattering states and reduces the conductance. Hence the defected graphene has higher sensitivity in gas detection [33]. (Fig 11). The *ab initio* density functional calculations showed that NO_2 gas molecules bind strongly with SW defects (binding energy 0.72 eV) in graphene compare to other defects (binding energy ~ 0.3 eV) such as monovacancy, divacancy (585 defect), 686 structure [104]. The SW defects with NO_2 gas changes the local electronic structure and enhances the transport properties.

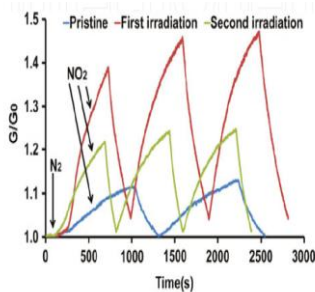


Fig 11. Normalized conductance (G/G_0) response of the graphene gas sensor. The exposure of the NO_2 gas started after 110 s in all three cases. The average rise times for pristine, first, and second defected graphene (during NO_2 exposure) are 500, 328, and 420 s respectively. [103]

2.4. Chemical Treatment Methods

2.4.1 Chemical reactions

The surface of graphene sheet can be modified by different chemical reaction methods and the overall result is the formation of vacancies or sp^3 defects in the structure. These are due to the interaction of graphene with different chemical species. During graphene oxide formation different oxidizing agents such as H_2SO_4 and HNO_3 are used in Hummers method and oxygenation occurs in graphene surface with different functional groups like hydroxyl, carboxyl and epoxy group. The presence of these functional group increases its functionalities but with chemical inhomogeneity and irreversibility of graphene oxide. For reversible and uniform oxidation of epitaxial graphene on SiC(0001) atomic

oxygen is used in vacuum and the oxidation degree of epitaxial graphene can be tuned by controlling oxygen exposure. Again this adsorbed oxygen can be reversibly removed from the surface either by heating the surface at 260°C or by irradiation of energetic electrons from the STM tips of Scanning Tunneling Microscope [18, 105].

Cycloaddition reactions are useful for surface modification of graphene which creates defects by converting sp^2 to sp^3 hybrid orbitals. The cycloaddition reaction on graphene by depositing maleimide derivatives at room temperature shows that both (1, 4) and (1, 2) cycloadditions are possible on freestanding graphene, but only the (1, 2) cycloaddition could be activated for SiC (0001)-supported graphene. The (1, 2) cycloaddition reaction results the grafting of covalent bond to graphene surface and the breakage of covalently bonded sp^2 carbon atoms and formation of sp^3 bond. Again the perturbation of the graphene lattice by grafted molecules results the anisotropic standing-wave pattern in the graphene lattice which are confirmed by STM [106].

2.4.2 Doping

Effective doping of graphene lattice with various dopants is an efficient chemical treatment method generally used to modify the surface of graphene. The efficient doping of the material provides low damage to the structure and modulates different set up states in optoelectronic devices. Nitrogen doped graphene sheets shows a remarkable high conductivity in plasma treatment methods. Plasma treatment in ammonia gas is an effective nitrogen doping method in the graphene lattice in which the nitrogen containing radicals form stable covalent bonds with carbon to form pyridine like carbon linkages which are stable after heating. Some research groups used nitrogen/hydrogen gas mixture as substrate in plasma treatment of graphene and they found that the defects are reduced due to the formation of high substrate temperature and most of the nitrogen atoms are pyridine like in carbon networks [107]. Some suggested the properties of N-doped graphene lattice depends upon its defect sites, amount of defects, plasma treatment exposure time and flow rate. For instance the covalent functionalization with amine groups occurs usually at edges or defective sites of graphene layer [108]. An efficient N- doping is substitution of carbon atoms by NH radical in which the nitrogen doping level can be finely tuned by controlling exposure time, flow rate and transport measurements. The work function of N-doped graphene can be modified by plasma treatment by Akada et al [109]. They found the nitrogen atoms at edge site or pyridinic or a pyrrolic site of N-doped graphene shows higher work function than at graphitic site and suggested the work function of graphene can be tuned from 4.3 eV to 5.4 eV by adjusting plasma treatment time and the amount of initial defects. Further the N-doped RGO sheets with high conductivity are synthesized by thermal annealing of RGO sheets in ammonia environment [110].

Graphene doping by electron beam irradiation is used for fabrication and testing of graphene based electronics. For instance, Zhou et al [111] reported a site specific reversible bipolar doping with high mobility by focussing scanning electron beam. The doping profile is explained by selecting the location, dose of electron beam irradiation and it is erasable. Hence both n-type and p-type doping is achieved along and its erasable nature enables the fabrication of multiple logic gates using the same graphene flakes. They extended their study with MoS₂ which explains the nature of field effects in 2D devices and provides a new path to prototype 2D logical devices for future electronics applications. Here the results briefly shows how by controlling the electron beam irradiation the electrical transport properties of a graphene field effect transistor (FET) can be modified. According to their results pristine graphene shows an ambipolar gate response with Dirac point near -2V having a low n-type carrier concentration of $1.5 \times 10^{-11} \text{ cm}^{-2}$ without gate biasing. But after the graphene is exposed to a 2 keV e-beam, the gate response shifted to the left i.e. The Dirac point moves from -2 V to -55 V after an irradiation dose of $10^{14} \text{ e}^-/\text{cm}^2$ which indicates strong n-type doping with a doping level of $\sim 4 \times 10^{12} \text{ cm}^{-2}$. Again a 30 keV e-beam with a dose of $10^{15} \text{ e}^-/\text{cm}^2$ shifts the Dirac point of the same graphene FET to +11 V producing hole doping. The zero-gate conductance of graphene increases with the increase of Dirac point shift which indicates the doping level. The doping level can be controlled by regulating the electron dose. A dose of $10^{12} \text{ e}^-/\text{cm}^2$ shifts the Dirac point from -2 V to -22 V. As the irradiation dose increases, the doping level becomes higher and the Dirac point is shifted to -50V after a dose of $5 \times$

$10^{13} \text{ e}^-/\text{cm}^2$. The carrier concentration increases rapidly under a low dose below $10^{13} \text{ e}^-/\text{cm}^2$, but saturates to a value of $4 \times 10^{12} \text{ cm}^{-2}$ when dose is increased to $10^{14} \text{ e}^-/\text{cm}^2$. (Fig 11A)

The retention times for n-type and p-type doping address its stability. The high n-type doping level can be maintained in vacuum for a long period of time (over 16 hours at a base pressure of $2 \times 10^{-5} \text{ mbar}$) with a small decay rate of $1.9 \times 10^7 \text{ cm}^{-2} \cdot \text{s}^{-1}$. The p-type doping state decays much faster with decay rate $> 9 \times 10^{10} \text{ cm}^{-2} \cdot \text{s}^{-1}$. The gate sweep affects the doping states i.e. for the n-type doping induced by a 2 keV beam with a dose of $10^{13} \text{ e}^-/\text{cm}^2$, the Dirac point slightly shifts a further $\sim 2 \text{ V}$ after 3 cycles of back gate sweep between -60 V and 60 V , indicating the n-type doping is stable under the gate operation. For the p-type doping induced by a 30 keV e-beam with a dose of $10^{14} \text{ e}^-/\text{cm}^2$, the Dirac point shifts from $\sim +8 \text{ V}$ to -13 V after 3 cycles of gate sweep.

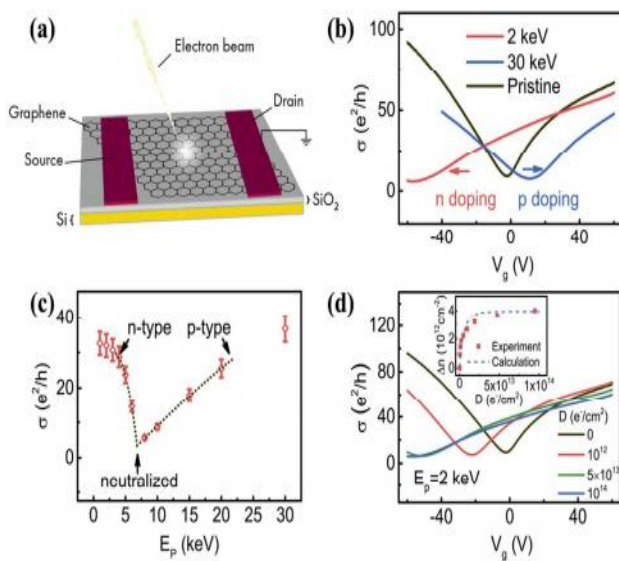


Fig. 11 (A) Electron beam induced doping in graphene. (a) e-beam irradiation of a graphene device in a field effect geometry. (b) Control of doping type by varying e-beam energies. (c) Zero gate conductivity as a function of beam energy. The two dashed lines are the polynomial fittings to the data from 1- 6 keV and 8-20 keV respectively. (d) Control of doping level with different irradiation doses using a 2 keV e-beam. (Evolution of carrier concentration with increasing dose; red squares are the experimental data, the blue dashed line is the theoretical calculation. 101x71mm (300 x 300 DPI) [111]

2.5. Engineering the properties of graphene

Graphene possesses different physical and chemical properties. By using the different defect engineering techniques the properties of graphene are modified. In this section some experimental results of engineering the properties of graphene are discussed which will be helpful to understand how the properties can be improved by defect formation.

2.5.1. Mechanical property

Plasma treatment method is a highly efficient, tunable and non-chemical process which produces surface defects in graphene due to the presence of highly charged particles like reactive ions, electrons and free radicals in plasma. The mechanical property of graphene and graphene /Cu composite was studied by plasma treatment method [112]. The plasma treated graphene showed higher strength and stability compared to untreated graphene indicating plasma

treatment is an efficient approach to enhance the mechanical properties of graphene. Fig. 12 shows a schematic diagram for the preparation method of plasma- reduced graphene oxide-Cu composite.

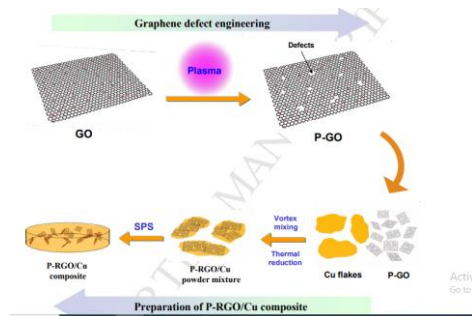
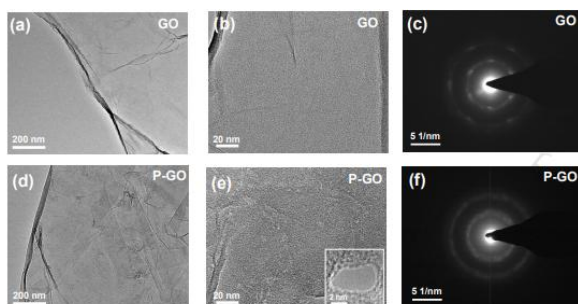


Fig.12 Graphene defect engineering and preparation of P-RGO/Cu composite [112].

The TEM study shows the presence of 5-10nm nanopores on the basin structure of P-GO which are not found in original GO and the nanopores are obtained by the surface structure damage of P-GO due to plasma irradiation. SAED pattern displays hexagonal spots for GO and intense diffraction rings for P-GO, suggesting more structural defects on P-GO due to plasma-etched nanopores on P-GO. Nitrogen adsorption measurements shows that the P-GO possess a higher specific surface area and more meso-pores than GO. Raman spectra analysis shows that the I_D/I_G ratio for P-GO is 1.13 and GO is 1.01. This value represents the defect level of P-GO which is higher than GO. XPS analysis gives the chemical structure of the sample. Both the GO and P-GO possess C1s and O1s peak but O1s peak at P-GO is reduced than that of GO, which suggest the oxygen containing groups removed in P-GO during plasma treatment process. The deoxygenation of P-GO was also examined by XRD pattern of GO and P-GO. The 2θ angle for P-GO is found at 10.7° along with a small graphene peak at $2\theta = 25.8^\circ$ which is a little bit different than GO peak at $2\theta = 10.1^\circ$. Given below the picture of different morphological study. The XPS survey shows the C/O ratio for P-GO is 5.2% a low content which enables P-GO disperse in water as well as shows a high electrostatic affinity to Cu powder (Fig.14). The P-RGO/Cu powder shows a flaky morphology in figure 14.a whereas in 14.b & c thin and wrinkled structure shows the uniform adhesion, compatibility and electrostatic interaction of P-RGO and Cu powder. Fractographs 14.d & e shows the individual existence of P-RGO sheets without visible P-RGO restacks.

Fig.14.f shows the Raman I_D/I_G ratio of P-GO after thermal annealing, blending and sintering processes. The P-RGO possesses a higher I_D/I_G ratio (1.21) than original P-GO (1.13), and it is due to the GO reduction. This reduction can cause a reduced size of the sp^2 domains and an increased number of these domains [113]. It is seen that the I_D/I_G varies slightly for P-RGO/Cu powder (1.24) and P-RGO/Cu composite (1.15) with respect to P-RGO (1.21), suggesting that no additional defects are introduced during the blending and sintering processes. The decrease in I_D/I_G ratio (1.15) in P-RGO/Cu composite compared to P-RGO/Cu powder (1.24) suggests the in situ formation of Cu_xO_y nanoparticles at the defects (nanopores) of P-RGO which indicates the suppression of D-band vibration and a decreased I_D/I_G [114].



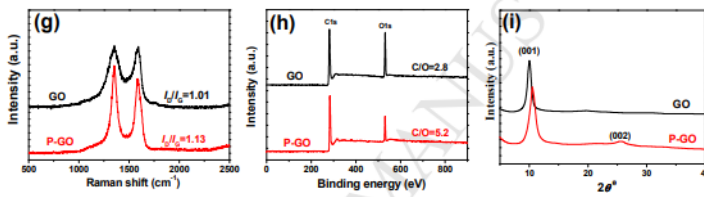


Fig 13. (a, b) TEM images of GO and corresponding SAED pattern (c). (d, e) TEM images of P-GO and corresponding SAED pattern (f). Inset of (e) is the HRTEM image of a plasma-etched nanopore. (g) Raman spectra of GO and P-GO. (h) XPS survey spectra of GO and P-GO. (i) XRD patterns of GO and P-GO. [112]

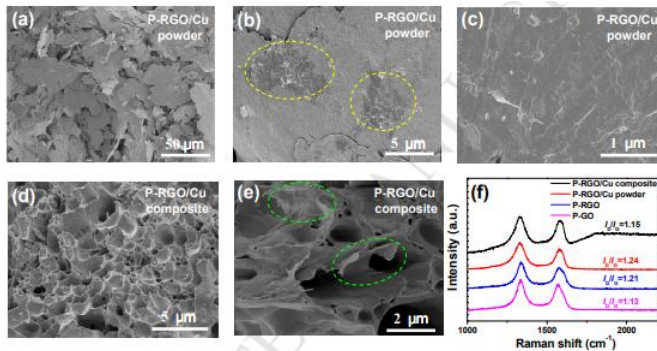


Fig.14. (a-c) Morphologies of 1 vol% P-RGO/Cu powder and corresponding (d, e) fractographs of 1 vol% P-RGO/Cu composite. (f) Raman spectra of P-GO, P-RGO, 1 vol% P-RGO/Cu powder and 1 vol% P-RGO/Cu composite [112]

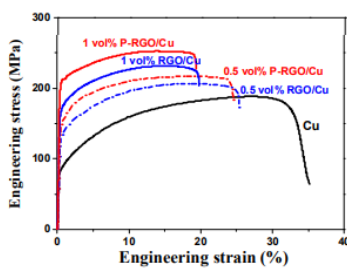


Fig. 15. Engineering stress–strain curves of unreinforced Cu, RGO/Cu and P-RGO/Cu composites.[112]

Fig. 15 shows the engineering stress-strain curves of unreinforced Cu, RGO/Cu and P-RGO/Cu composites. The mechanical data are listed in Table 3.

Table: 3 (Mechanical data) [112]

Sample	Relative density (%)	Average grain size (μm)	Yield strength(MPa)	Tensile strength(MPa)	Elongation (%)
Cu	99.6	2.75	82± 4.8	190 ± 3.4	35 ± 1.1
0.5 vol% RGO/Cu	98.8	2.38	128 ± 4.8	206 ± 6.1	25 ± 0.9
0.5 vol% P-RGO/Cu	99.1	2.56	146 ± 7.5	214 ± 8.8	23 ± 1.8
1 vol% RGO/Cu	98.5	2.29	170 ± 8.4	228 ± 9.2	19 ± 1.3
1 vol% P-RGO/Cu	98.2	2.13	209 ± 9.5	251 ± 7.6	18 ± 0.8

It can be seen that the 0.5 vol% P-RGO/Cu composite exhibits a yield strength of 146 MPa, ~78% and ~14% higher than that of unreinforced Cu and 0.5 vol% RGO/Cu composite, respectively. When the graphene loading is increased to 1 vol%, the yield strength of P-RGO/Cu composite is further increased to 209 MPa, corresponding to ~155% and ~23% enhancements over the Cu and 1 vol% RGO/Cu composite, respectively. These results indicate that the P-RGO is a more powerful reinforcement than RGO for improving the strength of Cu matrix. The elongations of RGO/Cu and P-RGO/Cu composites are moderately lower than that of unreinforced Cu, and the 1 vol% P-RGO/Cu composite shows a 16.8% uniform elongation suggesting a remarkable strength-ductility balance of P-RGO/Cu composites.

2.5.2. Biological property

Structural defects in nanomaterials affect the biological properties and the impact of these defects are studied by molecular dynamics simulations. For example, the chicken villin headpiece subdomain (HP35) denaturation was studied by interaction with defective graphene (D-Gra) [115] and described below. For this ideal graphene (I-Gra) was taken as a control. The edges of defective graphene consist of twelve carbon atoms alternative with carboxyl group and hydrogen atoms. I-Gra has same dimension as D-Gra i.e. ($12.48 \times 12.72 \text{ nm}^2$ with nine vacancy defects, each of which is ~1 nm in diameter) but without defects. The two systems are used to investigate the influence of ionic concentration and valence state on the unfolding degree of HP35 on D-Gra. As HP35 composed of α -helices a simulations of β -sheet constructed using the YAP65 WW domain and D-Gra to test the unfolding degree of the β -sheet protein on D-Gra. In all the simulation system the HP35 was placed over D-Gra/I-Gra with a separation distance of 1.2 nm to allow the free motion of protein and to avoid its interaction with nanomaterials at the initial stage. Three independent trajectories with different velocities and HP35 orientations were conducted. After 500ns, HP35 adsorbed onto both D-Gra and I-Gra surfaces. Results showed that HP35 lost its total structural integrity in all three trajectories (fig.16 B-D). All aromatic residues (Phe-6, Phe-10, Phe-17, Trp-23 and Phe-35) bound to the defect-free regions of D-Gra through the formation of π - π stacking with the sp^2 -hybridized carbon atoms, while most charged residues (Lys-7, Arg-14, Lys-24 and Lys-29) bound to the defects. But all the three trajectories of the system with I-Gra, both secondary and tertiary structures of HP35 were maintained whereas the aromatic residues Trp-23 and Phe-35 in helix-3 involved in interfacial binding (fig.16 E-G). This indicated the defects in graphene denatures the protein structure. Again it is seen that the aromatic residues i.e. (Phe-6, Phe-10 and Phe-17) which were initially buried in the hydrophobic core of HP35 exposed into the solvent after binding with defective graphene whereas with I-Gra remained as such in the core. The protein denature by the defects for longer time scale measurement, the HP35/D-Gra was examined in 1000ns. In which at $t=500\text{ns}$ HP35 has severe structural deformation losing its secondary structure but after $t=500\text{ns}$ the secondary structure remained same and binding conformation showed limited fluctuation, suggesting 500ns simulations detects the unfolding of HP35.

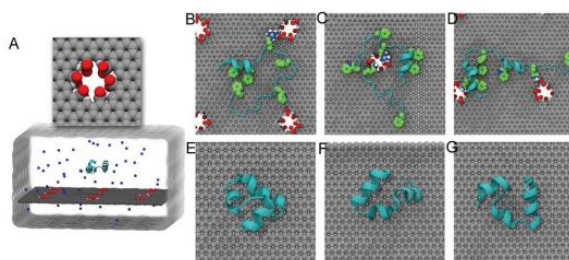


Fig. 16 (A) The simulation model of HP35 on defective graphene (D-Gra). Na^+ ions (blue spheres). The HP35 protein is shown in ribbon representation. The water boundaries are shown as gray surfaces. The inset depicts the structure of a defect. The carbon, oxygen and hydrogen atoms of D-Gra are shown as gray, red and white spheres, respectively. (B–D) Last snapshots of HP35 on D-Gra from three independent trajectories at 500 ns (E–G) Snapshots of HP35 on ideal graphene (I-Gra) from three independent trajectories at 500 ns [115]

In order to examine the effect of ionic concentration and valence state on HP35 unfolding on D-Gra another simulation of HP35/ D-Gra system in 0.15 M NaCl and MgCl₂ solutions were performed. Under 0.15 M NaCl solution the structure of HP35 showed that α -helices disappeared partially with some aromatic residue packing on the defect free regions of D-Gra and a lysine (Lys-29) contacting a defect . This defect attracts Na⁺ ions through electrostatic interactions, weaken the lysine binding and leads to the weaker unfolding of the protein. Again in 0.15 M MgCl₂ solution the unfolding of HP35 is weaker than in fig 16 B-D. As defective graphene shows different unfolding capacities to HP35 in different solutions so deformation of helices occurred which suggest D-Gra unfold α -helices. The β -sheet YAP65 protein denaturation also occurred in D-Gra but the levels of denaturation were different. The root mean square deviation (RMSD) study showed the quantitative binding process of HP35 on D-Gra/I-Gra. The number of contacts between protein and nanomaterials calculated and the protein structural change was assessed by calculating RMSD of backbone carbon atom of HP35. A contact was defined when heavy atom in protein is within 6Å⁰ of a carbon/oxygen atom in D-Gra/I-Gra. It is seen that the initial loading stage of HP35 on D-Gra/I-Gra completed within a few nanoseconds suggesting strong binding of graphene with the protein whereas for the system with I-Gra the number of contacts reached a plateau with relatively small fluctuations after 20ns. The RMSD showed stable binding without major changes of the protein structure. When the number of contacts increased 200 in 50ns for the system of D-Gra there is larger fluctuations of RMSD indicating deformation of protein structure. The structural changes of the protein HP35 on binding with D-Gra/I-Gra was investigated and secondary and tertiary structures were assessed during simulation. Original HP35 has three helical segments having 88.6% protein sequence, but upon binding with D-Gra it lost 72.7%, 63.4%, and 50.7% of its helical segments in three independent trajectories but upon binding with I-Gra it lost 8.1%, 0.3%, and 4.0%, respectively. The change of tertiary structure of HP35 was investigated by quantifying the native contact (Q) with simulation time t. The results showed that Q of HP35 with D-Gra decreased sharply to a value of 0.34-0.44 by 40ns and afterwards decreased at a slower rate but at 500ns simulations the native contact was lost around 69.3% to 72.9%. The Q of HP35 with I-Gra fluctuated around 0.94–0.99 during the entire simulations, and the loss of native contacts was only 1% to 6% at the end of the simulations. Contact maps of HP35 gives the change in tertiary structure during simulation. The contact map of protein with D-Gra indicated helix-2 and helix-3 are completely unfolded and helix-1 is moderately stable. The mechanism of denaturation of HP35 on D-Gra was studied by taking one of trajectories of HP35/D-Gra where helix-2 is denatured in a short period of time (~4 ns; from 8.8 ns to 12 ns in the simulation). Figure 17 describes the helix denaturation. Fig A is the snapshot at 8.8 ns right before the helix denaturation. In which the side chain of Arg-14 formed an electrostatic interaction with the carboxyl oxygen atoms of the defect and Phe-17 has a conformation where the phenyl sidechain pointed to helix-3. The helix-2 unfolded completely at 12 ns. and Phe-17 formed face-to-face π - π stacking with the carbon atoms at the defect free regions of D-Gra, while Arg-14 remained restrained, acting like an “anchor” of the protein at the defective region (Fig. 17B). The strong electrostatic interaction between the side chain of Arg-14 and the carboxyl groups at the defective site played an important role in anchoring (Fig. 17C). The Coulomb energy was found to be around -40 kcal mol⁻¹ and at some time points it increases sharply and reached ~0 kcal mol⁻¹ (e.g. t = 9.0 ns) due to transitory movements of Arg-14 on the defect-free region. The interaction energies are calculated. It is seen that the Coulomb energy between Arg-14 and the defect was ~40% of the total interaction energy between HP35 and D-Gra suggesting the Coulomb energy between Arg-14 and the defect was important to the anchoring of HP35 to D-Gra. The total interaction energy of anchoring was ~-54.6 kcal mol⁻¹ while the total potential energy of HP35 (helix-2) unfolding was ~-136.2 kcal mol⁻¹, which suggests the importance of anchoring to unfolding from an energy view. The exposure level of HP35 core (i.e., Phe-6, Phe-10 and Phe-17) to solvent was analysed during unfolding. The average number of first shell solvation water molecules around the three aromatic residues from 7.8 ns to 8.8 ns was 18.9 whereas the number increased to 22.5 from 12.0 ns to 13.0 ns, suggests the local unfolding near the defects had caused exposure of the core residues to the solvent.

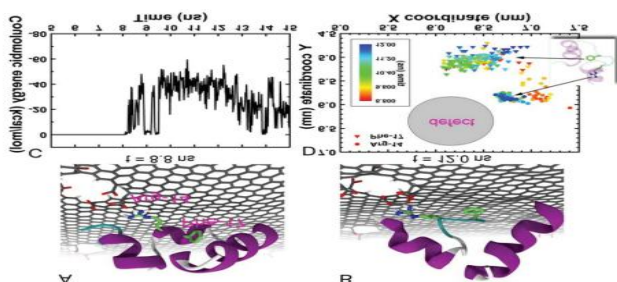


Fig. 17 The unfolding process of helix-2 from 8.8 ns to 12.0 ns in the simulation. (A–B) Snapshots of HP35 on D-Gra at 8.8 ns and 12.0 ns, respectively. Two key residues (Arg-14 and Phe-17) that played important roles in the unfolding process are highlighted. (C) The Coulomb energy between Arg-14 and the defect of D-Gra. (D) The trajectories of Arg-14 (circles) and Phe-17 (triangles) projected on the surface of D-Gra. The colors represent the time from 8.8 ns to 12.0 ns. The gray circle indicates the position of the defect [115]

The authors suggests here the role of defects upon HP35 (biomolecules) which are helpful in engineering the structure of nanomaterials for applications in drug-carriers, bio-imaging agents, and therapeutics.

3. Defect engineering of graphene for electrocatalysis

3.1 Energy conversion in fuel cell

Cleaner energy production in eco-friendly way is the focus point for the technologist of the carbon constrained globe. Hence for the purpose of continuous and low carbon power supply, direct alcohol fuel cells (DAFCs) are regarded as the encouraging sources [116]. In DAFCs generally either methanol or ethanol is electrochemically oxidised at anode to produce H^+ ions which migrates towards cathode through proton exchange membrane. Upon combination with OH^- ions which are due to the electrochemical reduction of oxygen at cathode generates heat, water and electricity [117,118]. For commercialization issues fuel cells are considered as a non-stop, less carbon energy producing system. But as the overall conversion efficiency of fuel cell completely depends on the kinetics of oxidation of alcohol, it is crucial to use highly active catalysts at low operating temperatures. Platinum is used as a best electro-catalyst which adsorbs energy efficiently as well as exchange current density, but due to high instability of Pt catalyst [119], cost and heavy Pt loadings [120] during the system performances it is desirable to improve a durable and highly efficient electro-catalyst. Various attempts such as dispersion of Pt on conducting supports [121-123] or combination with other metals [124, 125] are employed in fuel cell reactions for Pt utilisation. An appropriate and efficient fuel cell supports offers a high surface- to- volume ratio of metal particles for electrochemical reactions. Hence in the state-of-art Carbon, reduced graphene oxide (RGO) sheets are considered as a cutting-edge electro-catalyst in DAFCs owing to its 2D structure [126], high surface area for one atomic thick layer ($2630 \text{ m}^2\text{g}^{-1}$), large surface- to- volume ratio, high specific capacitance (550Fg^{-1}), intrinsic redox ability and fast electron transfer rate, so it disperse Pt nanoparticles as well as possess faster charge and mass transport properties [127-129]. Still π - π restacking in RGO sheets due to weak van der waals interaction reduces the Pt availability. This causes low catalyst utility and transport pathways for reaction. Material processing techniques reduces the agglomeration in RGO sheets by changing the physiochemical properties. Development of intercalation composites [130, 131], geometrical modification approaches [132] are some pathways which improves the use of supported Pt catalysts for electro-catalysis. The electronic properties of RGO can be achieved by tuning the band gap near Dirac point of the C-C double bonded structure. For the electronic properties modification of RGO increase of catalyst activity is required and this may be achieved by fine-tuning the interaction between support and catalyst surface. In this regard various defect engineering approaches in RGO i.e. heteroatom doping, size controlled vacancy formation, 3D structure assembly, surface metal complexation methods are employed to prepare support materials with desired characteristics for fuel cell catalysis. Some electrode materials tailored by these methods are discussed here.

3.1.1 Structure assembly for mass transfer

A 3D assembled RGO based platinum catalyst was synthesized by Kwok et al. [133] for methanol oxidation. They synthesized a platinum-decorated RGO aerogel porous framework in solvothermal method and the RGO aerogel porous framework is optimised by changing GO concentration in gelation process. The ultra- fine platinum nano-particles ranging 1.5 to 3nm size increases the electrochemically active surface area to 8.92 times greater than the standard Pt/C catalyst and the specific power increases to 358%. Qiu et al [134] synthesized platinum nanoparticles on 3D reduced graphene oxide hollow nanospheres to enhance the activity of methanol oxidation reaction in which the microporous structure exposes active sites and promotes the ion and mass transfer process. The activity of the electrocatalyst also increased by increasing the electronic effect of platinum which is done by alloying Pt with other transition metals. Thus the platinum loading of the fuel cell decreases. Wang et al. [135] prepared three dimensional structure of polyaniline (PANI) functionalized RGO sheets which prevent RGO sheets from restacking. The synergistic effect of the porous frame work facilitates the mass and electron transfer and acts as a superior electrode material for methanol electrooxidation. The conductivity of RGO is due to the conductive polymeric network structure with PANI. Radhakrishnan et al. [136] prepared a 3D platinum nanostructure with (100) plane on RGO by co-electrodeposition method. The morphology, active site, and electrochemical activity of the catalyst were very much dependent on the number of electrochemical cycling used for deposition and the prepared nanocomposite showed a high mass activity towards methanol oxidation reaction. Honma et al [137] synthesized platinum nanoparticles supported on graphene nanosheets (GNS) for methanol oxidation reaction. For this they used $\text{Pt}(\text{NO}_2)_2 \cdot \text{NH}_3$ as Pt precursor and GNS powder, which were annealed at 400 °C in Ar /H₂ (4:1 v/v) for 2 h. By inductively coupled plasma (ICP) analysis the Pt cluster loading in GNS was measured and the Pt loading amount is 20% which is approximately similar to Pt on activated carbon (Pt/C). In high-angle-annular-dark-field scanning-transmission electron microscope (HAADF-STEM) two types of Pt nanoparticles (0.5nm and 1.5nm) are observed. 0.5nm Pt nanoparticles possess more available surface area and the Pt/GNS cluster has current density of about 0.6 mA/cm² at the over-potential of 0.6 V vs. RHE, than commercial Pt/C. The i-t curve result of the Pt/GNS at 0.6 V vs. RHE for 30 min, showed 4 times higher current density (0.12 mA/cm²) than that of commercial Pt/C (0.03 mA/cm²). Pt/rGO composites [138] were prepared by chemical reduction of GO and H₂PtCl₆ using NaBH₄ as reducing agent. The ECSA of the Pt/rGO and commercial Pt/C are 44.6 and 30.1 m² /g, respectively. The higher ECSA of Pt/rGO is favourable for methanol oxidation reaction (MOR). The current density of Pt is found to be 199.6 mA/mg at the potential of 0.652 V (vs. Ag/AgCl), while for Pt/C the peak current density is 101.2 mA/mg at 0.664 V. The Pt/rGO displays nearly double current density, but it has 12 mV lower over-potential than that of Pt/C indicating the better performance of Pt/rGO for the MOR. Liu et.al [139] prepared functionalized graphene sheets (FGSs) via thermal expansion of GO in which Pt nanoparticles having diameter 2nm were uniformly loaded on FGSs by impregnation methods. The Pt/FGS shows high current density and good retention on electrochemically active surface area (ECSA) and ORR activity compared with the commercial Pt/C. After 5000 cycles, ECSA values of both Pt/FGS and commercial Pt/C have retained about 62.4 and 40%, respectively, of the initial values and in ORR activity, Pt/FGS retains 49.8% of its initial value, whereas the commercial Pt/C maintains 33.6% indicating Pt/FGS is much more stable than commercial Pt/C. After 5000 cycles, an average particle size of Pt/FGS is increased from 2 to 5.5 nm with more than 75% of Pt particles retaining its size below 6.9 nm. On the other hand, an average particle size of Pt/C is increased from 2.8 nm to 5.5 nm, and more than 45% of the particles have its size over 6.9 nm indicated that the higher ECSA and ORR activity of Pt/FGS is due to smaller particle size in Pt/FGS.

Bimetallic nanoparticles showed enhanced catalytic properties than single nanoparticles. For instance ethylene glycol prepared Pt-Ru/graphene [140] shows high electrocatalytic activity for methanol and ethanol oxidation than Pt-nanoparticles. Cyclic voltammogram study shows that the methanol oxidation potential of Ru-Pt/graphene is shifted to 0.50 V compared with 0.65 V for Pt/graphene, suggesting the addition of Ru can improve the methanol oxidation and Pt-Ru/ graphene performs better catalytic activity than Pt/graphene. Wang et al. [141] synthesized Pt- on- Pd bimetallic nonodendrites supported on graphene nanosheets (TP-BNGN) through wet-chemical approach.

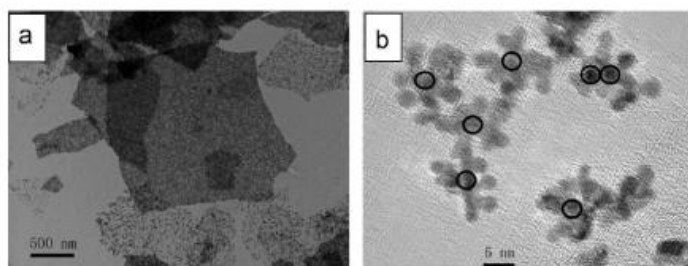


Fig 18 TEM (a) and HR-TEM (b) images of TP-BNGN. The circled parts in panel B denotes as Pd nanoparticles [141]

It is seen in the figure that Pt nanobranches on Pd cores, with an average size of 15 nm are directly grown onto the surface of graphene nanosheets. The ECSA of TP-BNGN ($81.6 \text{ m}^2/\text{g}$) exhibits higher than those of Pt/C ($54.7 \text{ m}^2/\text{g}$) and Pt/CB ($19.2 \text{ m}^2/\text{g}$). This is due to the structure of bimetallic nanodendrites and high surface area and better dispersion on the graphene nanosheets. The number of branches for Pt-on-Pd bimetallic nanodendrite on the surface of graphene nanosheets could be easily controlled by changing the reaction parameters, resulting in the tunable catalytic properties. The bimetallic nanodendrite/graphene hybrids show about 3.0 and 9.5 times higher electrocatalytic activity for MOR than those of commercial Pt/C and Pt/CB catalysts.

Ternary alloy systems possess superior catalytic activity and stability than binary alloys. Wang et al [142] prepared Pt–Pd–Au/rGO catalyst via simply ethylene glycol-water reduction from GO and Pt, Pd and Au precursor salts. The onset potential of MOR on Pt–Pd–Au/rGO shifted to the more negative values with low over-potential in the electrooxidation reaction. The forward current density (I_f) of Pt–Pd–Au/rGO was 1.5, 2.3 and 2.8 times higher than those of Pt–Pd/rGO, Pt–Au/rGO and Pt/rGO, respectively. Compared with Pt–Pd/rGO and Pt–Au/rGO, the Pt–Pd–Au/rGO electrode it shows lowest onset potential and high current density of electrooxidation. The high catalytic activity of ternary system in alkaline is due to the combination of the third metal. The linear relationship between the current density and the square root of scan rate indicates the MOR activity of Pt–Pd–Au/rGO catalysts is a diffusion controlled process.

3.1.2 Heteroatom doping for charge transfer

The efficiency of fuel cell can be improved by designing and developing metal free cathode catalyst in place of Pt catalyst as it possess some drawbacks such as high cost, scarcity of platinum metal, time dependent drift, CO poisoning. Heteroatom doped reduced graphene oxide has been proved to be an efficient metal free electrocatalyst for oxygen electrocatalysis. Generally the recent graphene derivatives suffer from low intrinsic conduction as fuel catalyst supports and current carriers. To enhance the conduction support in graphene and its derivatives, heteroatom doping is an encouraging topic as it replace some carbon atoms by heteroatoms like N, B, O, P, S, Cl, Se, Br, and I etc. Recent works shows that the heteroatom doping provides proper nanoparticle dispersion, size-controlled active sites, and regulates catalyst d-band to achieve superior catalyst for electrochemical activity [143, 144]. Although numerous reports are studied on heteroatom doping of graphene but in particular N- doping graphene has relevant importance because quaternary N atoms or substitutional N-doping(Fig) introduce high positive charge distribution to nearby C atoms due to the high electron withdrawing ability of N [145] so that the defective sites can efficiently attach catalyst nanoparticles. The substitutional defects in the 2D network acts as electron donors and provides n-type conductivity [146] which could enhance the electron transport from support to the attached nanoparticles and increases catalyst tolerance to poisoning.

Zhao et al. [143] prepared a 3D structure of N-doped RGO by a simple one pot hydrothermal process using melamine-cyanurate as N source and pore forming agent. The interconnected porous microstructure expose sufficient accessible active site. The ECSA increased by 1.16 times greater than the benchmark Pt/C catalyst. Hence, the platinum on rGO could enhance the MOR activity by approximately three times compared to platinum on carbon black. Kanninen et al

[147] co-doped RGO with nitrogen and sulphur atoms by a thiol-ene approach and the co-doping changes the platinum supporting interaction and improves the ethanol oxidation reaction(EOR) than the Pt supported undoped RGO. The induced defective sites increases the stability of supported nanoparticles and their durability which are confirmed by potential cycling experiment. After 500 potential cycles, ECSA decreases in the order as: Pt/C ($-12.3 \text{ m}^2 \cdot \text{g}^{-1}$) > Pt/rGO ($-3.8 \text{ m}^2 \cdot \text{g}^{-1}$) > Pt/rGO/ double-walled carbon nanotube (DWCNT) ($-2.7 \text{ m}^2 \cdot \text{g}^{-1}$) > Pt/NS-rGO-DWCNT ($-2.0 \text{ m}^2 \cdot \text{g}^{-1}$). The mixing double-walled carbon nanotubes (DWCNT) prevent the restacking of the rGO sheets and leads to faster mass transfer.

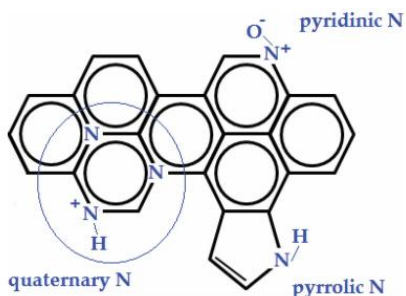


Figure: 19 Schematic diagram of nitrogen dopant configuration in the 2D carbon—carbon network. [116]

Rethinasabapathy et al [144] prepared platinum nanoparticle interconnected porous N-doped RGO through hydrothermal method using urea as nitrogen source. The doped nitrogen atoms breaks the 2D symmetry and creates induced defective sites for platinum nanoparticle attachment. The prepared electrode shows higher catalytic activity towards MOR than nitrogen free RGO nanoparticle support. The higher catalytic activity is due to smaller particle size, narrower size distribution, and better dispersion of nanoparticles. The synergetic effect of N doping improves the electronic conductivity, facilitates charge transfer from platinum-support interface to the strongly adsorbed MOR intermediates.

3.1.3 Oxygen reduction reaction (ORR)

To attain low material cost, high electrical conductivity, excellent corrosion resistance electrocatalst in fuel cell for ORR, graphene based materials are chosen as active electrocatalyst by nitrogen atom doping. N-doping of graphene by chemical vapour deposition method (CVD) possess high electrocatalytic activity, but the mass production in CVD is limited [148]. Hence a metal free N- doped graphene films are prepared by solution casting and heat treatment of edge selectively functionalized graphite (EFG) with 4-aminobenzyl moieties and acts as sources for carbon and nitrogen for C-welding and N-doping. The EFG solution in NMP is dip-coated on a glassy carbon electrode and heat treated at 900°C for 3 hours under an argon atmosphere to give N-graphene/GC electrode. The electrocatalytic activity of the electrode is confirmed by cyclic voltammetric study. The oxygen reduction peak appeared at the potential of -0.15V in oxygen saturated solution. The nitrogen content of N- graphene from EFG is 1.7 at% which is lower than the nitrogen content 4.0 at% of the N-graphene from CVD. SEM analysis showed that the welded boundary have wrinkled structure and contained higher concentration of nitrogen. The larger surface area and effective active sites at edges are responsible for high ORR activity [149].

Dai et al [150] suggested a hybrid material i.e. Co_3O_4 nanocrystals grown on RGO ($\text{Co}_3\text{O}_4/\text{RGO}$) and N- doped RGO ($\text{Co}_3\text{O}_4/\text{N-RGO}$) prepared by heat treatment by using NH_4OH and used as bifunctional catalyst for ORR and OER.

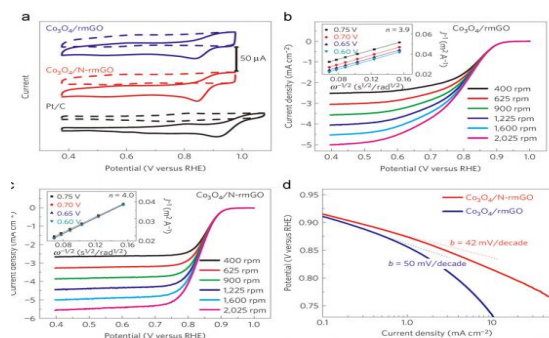


Figure 20 (a) CV curves of Co₃O₄/rGO hybrid, Co₃O₄/N-rGO hybrid and Pt/C on glassy carbon electrodes in O₂-saturated (solid line) or Ar-saturated 0.1 M aqueous KOH solution (dash line); (b) rotating-disk voltammograms of Co₃O₄/rGO hybrid; (c) Co₃O₄/N-rGO hybrid in O₂-saturated 0.1 M aqueous KOH solution with a sweep rate of 5 mV/s at the different rotation rates indicated. The insets in (b) and (c) show corresponding Koutecky–Levich plots (j^{-1} vs. $\omega^{-0.5}$) at different potentials; (d) Tafel plots of Co₃O₄/rGO and Co₃O₄/N-rGO hybrids derived by the mass-transport correction of corresponding RDE data [150]

Figure 20. (a) Showed Co₃O₄/RGO possess higher positive onset potential (0.88 V vs. RHE) and higher cathodic current than Co₃O₄ and RGO alone. Figure 20 (b), (c) showed the Koutecky–Levich plots and the slopes indicates that the electron transfer number of CO₃O₄/rGO is ~ 3.9 and CO₃O₄/N-RGO is ~ 4 . The CO₃O₄/N-RGO hybrid catalyst also exhibit excellent ORR activity (Fig20 (d)) with much smaller Tafel slope of 42 mV/decade at low over-potentials than that measured with CO₃O₄/rGO hybrid (54 mV/decade) in 0.1 M aqueous KOH solution. In 1M and 6M KOH, the current density of CO₃O₄/N-RGO catalyst showed same performance as freshly loaded Pt/C catalyst and showed a positive shift in the ORR onset potential from 0.1M KOH electrolyte solution. The Tafel slope of kinetic current is less than 37mV/decade for CO₃O₄/N-RGO in 1 M KOH which is the smallest Tafel slope for ORR catalyst. The CO₃O₄/N-RGO hybrid exhibits superior durability to Pt/C catalyst in 0.1–6 M aqueous KOH electrolytes. The Pt/C catalyst exhibits 20– 48% decrease in catalytic activity in 0.1–6 M aqueous KOH electrolytes, giving lower long-term ORR current than the stable currents sustained by the CO₃O₄/N-RGO.

Platinum nanotubes with N-doped graphene (Pt NTs/NG) showed ultra-high activity and durability towards ORR in acidic medium and the half wave potential for Pt NTs/NG catalyst is 0.903V vs. RHE whereas the Pt/C catalyst shows 0.875V vs. RHE [151]. Xie et al. [152] dispersed Pt nanocrystals (Pt NCs) with diameter 2.8nm in 3D mesopore rich N-doped graphene aerogel (NGA). The PtNCs@NGA possess a large surface area of 1750 m²g⁻¹, rich in mesopores and high N content (3.93 at %), acts as good electrocatalyst for ORR.

Platinum free ORR electrocatalysts are also developed by Wang et al [153]. They developed FeNx/graphene flakes and the catalytic activity increased to 30 times per gram and 100 times per metal atom compared to Pt/C catalyst. Wu et al. [154] prepared N, S co-doped 3D graphene aerogels which showed good ORR activity and it is due to the exposure of more electrocatalytically active sites exposure in interconnected porous network, synergistic effects originated from the doped N, S in the graphene sheet. Edges in graphene possess highly active sites than basal plane [155]. An edge rich, dopant free graphene electrocatalyst [156] for ORR activity was prepared by plasma etching and it showed excellent ORR electrocatalytic activity with high positive half wave potential 0.737V vs RHE than pristine graphene(0.572V vs RHE). The durability and stability of the electrode is much higher than Pt/C catalyst. It showed a long term stability with 12% decrease of current density after 20000 test cycles.

The above reviewed current methodologies describes the synthesis and design of high performance RGO fuel cells support materials and current carriers. The performance of the electrocatalyst can be determined by higher current density, lower onset potential and higher ECSA compare with Pt/C.

3.1.4 Metal-Organic Frameworks (MOFs): superior ORR electrocatalyst

A highly efficient, crystalline material and superior oxygen electrocatalyst is MOFs (Metal-organic frameworks) due to its awesome properties like large surface area ($1000\text{-}10000\text{m}^2/\text{g}$), structure tunability and high porosity (pore size smaller than 100nm). MOFs are designed as a group of inorganic-organic hybrid porous material consist of inorganic metal ions or cluster and organic linkers through co-ordination bonds. Despite numerous utilization, single MOFs possess some defects which constrains their application to a greater extent. In electrochemistry it shows inferior performance in electrical conduction with a poor ability and stability. Hence MOF-based composites are the best alternatives than single MOFs which can overcome the aforesaid shortcomings. Graphene based materials are the promising candidate to improve the conduction performances and stability in MOFs because of its unique properties, structure and low toxicity. Assembly of graphene and graphene based materials with MOFs shows extraordinary characteristics in which the MOF-composite shows the unique properties of both the material that reduces the shortcomings of each component and provides high conductivity, selectivity and better stability. The presence of ionic groups and SP^2 hybridised aromatic domain in graphene and graphene based materials helps in providing the structural arrangement as well as enhances the bonding interactions which are more active in MOFs. Generally the carboxylate and pyridine groups of graphene based materials plays an important role for heterostructure assembly which can enhance the coordination bonding and guide the growth of MOFs to provide more beneficial structure. For better ORR kinetics and to replace platinum catalyst graphene based MOFs acts as the best electrocatalyst in which the oxygen species enters the pores with higher chance of contact with the active sites due to the high surface area in MOFs. Because high active site density, faster transfer rates of electrons and reagents, and good durability are important features for ORR mechanism [116, 157,158].

Sohrabi et al. [159] prepared a porous coordination network-pyridine-functionalized graphene (PCN-222-G-py) as a catalyst for the reduction of oxygen. G-Py was formed by the diazonium reaction between graphene nanosheet and with the pyridinium moiety. PCN-222 was prepared by solvothermal method using DMF and ethanol as solvent. The CV results of the PCN-222-G-py (25 wt%)-GCE electrode showed that the oxygen reduction was irreversible. The peak current and the scan rate showed a linear relationship indicating the reduction process was adsorption controlled. The stability and the recyclability was confirmed by immersing PCN-222-G-py-GCE in an O_2 -saturated $0.5\text{ m H}_2\text{SO}_4$ solution several times, and the same CVs results were obtained. Jahan et al. [160] synthesized Cu-MOF@GO by solvothermal method. They compared the ORR performances of pure Cu-MOF and Cu-MOF@GO (GO amounts of 2, 4, 6, 8, and 20 wt%). The results suggested that the composites combining GO possessed a better electrocatalytic performance than the pure MOF, and the composite with 8 wt% GO amount had the best performance than that with 20 wt% GO.

Zeolitic imidazolate frameworks (ZIFs) with ligands having high nitrogen content are the most studied frameworks for the preparation of nitrogen-doped porous carbon. Zhong et al. [161] prepared the ORR electrocatalyst for alkaline media using nitrogen doped porous carbon sheets (GNPCSS) derived from graphene and ZIF-8. It possesses a large amount of micropores and meso/macropores due to the retention of micropores in ZIF-8 and removal of Zn. The best resultant GNPCSS-800 shows better ORR activity than the conventional Pt/C. The catalyst shows an outstanding tolerance to methanol and superior durability, and it is due to the close contact between N-doped porous carbon and N-doped graphene. Wei et al. [162] prepared a framework for ORR which possess higher active site with nanoporous carbon /graphene sandwich structure having high specific surface area of $1170\text{ m}^2\text{ g}^{-1}$ and a high onset potential of 0.92 V vs RHE and a large limiting current density of 5.2 mA cm^{-2} at 0.60 V .

N- Coordinated transition metal NPs-doped carbon materials (M-N-C) possess excellent ORR electrocatalytic activity both in acidic and alkaline media. Cobalt imidazolate frameworks are the earliest studied MOFs for ORR. The high ORR activity is due to the high density Co-N_4 centers after calcination. Wei et al [163] prepared a nanoporous $\text{Co-N}_x/\text{graphene}$ material which is derived from ZIF-67/GO via the carbonization at 700°C and acid leaching process. This catalyst exhibited higher ORR catalytic activity, better methanol tolerance and superior stability than Pt/C under both

alkaline and acidic conditions. Compared with ZIF-700-AL and ZIF-67/rGO-700, ZIF-67/rGO-700-AL had the advantageous limiting current density and onset potential, because rGO was beneficial for high catalytic performance and acid leaching can remove CoO and part of Co nanoparticles in contact with the solution from the carbon skeleton matrix. The porosity of the carbon framework increased with increase in active site and transportation efficiency of mass and charge enhanced. The structure with layered pores and high interconnectivity increases the ORR performances due to the increase in density and exposure of highly active sites. Xia et al. [164] prepared CoO_x hollow NP/N-doped graphene aerogels (NG-A) from Co-MOFs/NG-A with calcination in Ar and air respectively. The catalyst possessed excellent ORR activity with a more positive onset potential of 1.019 V and a half-wave potential of 54 mV, which was identical to that of Pt/C. Nitrogen adsorption desorption test showed CoO_x/NG-A exhibited a high BET surface area (1359 m² g⁻¹) and large pore volume (7.2 cm³ g⁻¹). These holes with larger pore volumes promoted the transport of substances in the triple-phase reaction.

M-N-C shows higher catalytic performance when doped with heteroatoms P and S. This is due to the redistribution of the charge on the carbon atoms which reduces the potential needed for ORR and weakens the O-O bonding [165]. There are two main approaches of doping heteroatoms to MOFs-derived carbon materials. One is to select MOFs with organic linkers that contain heteroatoms, the other is to introduce heteroatoms in MOFs or GO before or during carbonization. It is important to note that both the type and degree of doping can significantly affect the corresponding catalytic performance. Huang et al. [166] prepared nitrogen, sulfur-codoped cobalt oxides/graphene utilizing ZIF-67 and sulfur-functionalized graphene oxide by a simple two-step method. CoO@Co₃O₄/NSG-650 showed a half-wave potential of +0.79 at -3.0 mA cm⁻², which was very close to the value of Pt/C, and a low Tafel slopes of 366.7 mV dec⁻¹, similar with that of IrO₂ (396.4 mV dec⁻¹). Fe- based MOFs also showed higher intrinsic ORR activity due to their highly active Fe-N_x moiety in acidic electrolyte [167]. Liang et al. [168] prepared a framework of Fe₃O₄@NGA from MIL-88B-NH₂ by hydrothermal reaction. The TEM image showed that Fe₃O₄ have exposed edge active sites which promotes the oxygen adsorption and activation. The CV curves of Fe₃O₄@NGA was taken from N₂-saturated and O₂-saturated KOH. The O₂ saturated CV curve showed an enhanced cathodic peak potential than N₂ saturated line. LSV curve showed Fe₃O₄ @NGA possessed an onset potential of 0.96 V and half-wave potential of 0.81 V which were comparable to those of 20% Pt/C.

Bimetallic MOF crystals also achieved a particular interest as the single metallic MOFs has some limitation i.e. presence of single active site, poor conductivity and aggregation at high temperature during calcination. Bimetallic MOF crystals contains both active metals i.e. Co and Fe and inactive metals i.e. Mg, Zn, and Al. The inactive metals contribute to high surface area and homogeneous dispersion of active metals in MOFs then the two active metals are used for ORR. Niu et al. [169] prepared a sandwich like Fe/Co-N/rGO from FeCo-MOFs/GO after a high-temperature carbonization. At Fe/Co molar ratio 0.40, the Fe-Co-N-rGO-AL catalyst showed a high onset potential of 0.98 V, a halfwave potential of 0.84 V. The methanol tolerance of the catalyst was better than that of 20 wt% Pt/C in 0.1 M KOH. The result showed the ORR performance of FeCo-MOFs was much better than single-metal Fe-MOFs and Co-MOFs. Catalysts with rich exposure of metal active sites and defects acts as superior electrocatalyst for ORR. In this regard Fang et al. [170] synthesized core-shell structured nitrogen-doped CoCx/FeCo@C/rGO hybrid derived from Fe-doped Co₃ [Co (CN)₆]₂. The long term stability of this catalyst is due to the CoCx/FeCo and RGO bond and large surface area. The N-doped CoCx/FeCo@C/rGO possessed an onset potential of 1.0183V, a half wave potential of 0.9653 V, and a Tafel slope of 99.09 mV dec⁻¹ which is close to the Pt/C (73.05 mV dec⁻¹). The strong binding affinity of Fe easily broke the O-O bond and the nanoparticles has strong electron transfer ability. These two increases the ORR performance of the catalyst. Given below briefly the performance of electrocatalysts discussed for fuel cell electrocatalysis. (Table-4).

Table:4 (Performances of various electrocatalysts)

Catalyst	Current Density (mA.Cm ⁻²)	Onset Potential(V)	ECSA(m ² /g)	Remark	Reference
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Pt/GO	-	-	188(8.92 times more than Pt/C)	MOR	[133]
Pt/3D-GNs(PANI)	550 mA/mg(3.5 times more than Pt/C)	-	48(2.4 times more than Pt/C)	MOR	[135]
RGO/Pt	2.5K(mA/mg) 2.5 times more than Pt/C)	-	>6K(3 times more than Pt/C)	MOR	[136]
Pt/GNS	0.6 at 0.6V	0.6 vs RHE	-	MOR	[137]
Pt/RGO	199.6 mA/mg at 0.652V	-	44.6	MOR	[138]
Pt/FGS	-	-	108	PEMFC	[139]
Pt-Ru/graphene	16.5 at 0.5V	-	-	DMFC	[140]
Pt-Pd/graphene	647.2 mA/mg	-	81.6	DMFC	[141]
Pt-Pd-Au/graphene	27.1	-0.642 vs SCE	-	DMFC	[142]
Pt/N-RGO	20 mA/mg(3 times more than Pt/C)	-	60.6(1.16 times more than Pt/C)	MOR	[143]
PtRuFe/N-graphene	-	-	96 (2 times more than PtRuFe/rGO)	MOR	[144]
Pt/NS-rGO-DWCNT	-	-	-2.0(After 500 potential cycles)	EOR	[147]
N-graphene	-1.3 at 0.8V	-	-	ORR	[149]
Co ₃ O ₄ / N-RGO	52.6	0.88 V vs. RHE	-	ORR,OER	[150]
Porous Carbon/graphene framework	5.2 at 0.60 V	0.92 V vs RHE	-	ORR	[162]
CoO@Co ₃ O ₄ /NSG-650	-3.0 at 0.79V	-	-	ORR	[166]
Fe-Co/N-rGO-AL	-	0.98 V	-	ORR	[169]
N-doped CoCx/FeCo@C/rGO	-	1.0183V	-	ORR	[170]

MOR: Methanol Oxidation Reaction, PEMFC: polymer electrolyte membrane fuel cell, DMFC: Direct Methanol Fuel Cell

CONCLUSION

In summary, in this chapter the recent research progress in defect engineering of graphene has been described. The defect formation, its transformation and novel structure fabrication by electron beam irradiation on graphene surface are briefly explained. Other than electron beam irradiation other active processes described are ion irradiation, doping and chemical reaction methods. Introduction of point defects such as vacancies, SW defects, substitutional impurities on graphene and from these defects the fabrication of novel structures like nanoribbon, nanochains, nanowires by electron beam irradiation are described. Effect of defect on the mechanical and biological properties are

explained by Plasma treatment method. The plasma treatment on the biomolecules changes or finely tuned the biological effects of nanomaterials. The study suggests the structural engineering of nanomaterials and these structured materials could be used in various applications like drug-carriers, bio-imaging agents, and in therapeutics. In the last section the application of graphene defect engineering for energy conversion in fuel cell is discussed. The importance of a fuel cell in electrocatalysis is due to structure of the electrode. A perfect fuel cell electrode must possess highly porous structure, exhibit extremely conductivity property and could have accessible surface active site for mass and charge transfer. Hence recent research techniques regarding 3D structure assembly for mass transfer, heteroatom doping for charge transfer are discussed in which the materials are graphene supported Pt, Pt alloy and graphene based metal free catalyst. This demonstrates the enhanced electrocatalytic activity with high cyclic stability and durability for fuel cells. Lastly the graphene based materials composites/MOFs are the topic of interest as these overcomes the shortcomings of single MOFs i.e. the stability, selectivity, electroconductivity are enhanced to a greater extent which are useful for various applications specially we emphasize here the ORR activity for fuel cells. Hence by ensuing these defect engineering methodological approaches, the issues triggered by energy conversion concerns in direct alcohol fuel cells could be resolved. Still the technology of graphene defect engineering deserve further research for better achievements in future in energy conversion as well as storage systems to meet the challenges of energy crisis across the globe alternative to fossil fuel.

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