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Brief review of developments in graphene, PVA and future opportunity for PVA- graphene composite

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Abstract
Graphene due to its unique properties and versatile nature has emerged as the most likable material among the new nanostructured carbonaceous species. Graphene due to its properties like light weight, electrical conductivity, mechanical robustness, large surface area can be explored in numerous applications in the engineering and scientific field. Graphene is many times stronger compared to same mass of steel thereby has provided us with light weight and yet strong alternative compared to other conventional materials that are presently in use. This review work aims to present a brief overview of the main characteristics of graphene and most recent advances made in application of graphene and graphene related materials in electronic and optoelectronic devices, chemical sensors, nanocomposites, and energy storage devices. We have also reviewed the progress in the field of graphene functionalization, various synthesis processes for graphene and its future perspective. The work also states brief introduction of properties of PVA and its crosslinking processes and agents used for crosslinking with their applications ine various fields. The article concludes with a brief discussion on limitations and future prospects of graphene, PVA and the future of PVA based composite reinforced with functionalized graphene in today's rapidly emerging material science field.

Keywords: Graphene, functionalization, poly vinyl alcohol, crosslinking.

Introduction

Graphene is an allotrope of carbon, consisting of single layer of atoms arranged in a 2-D honeycomb lattice [1, 2] nanostructure [3]. Graphene has become a valuable and useful nanomaterial due to its uniquely high tensile strength, electrical conductivity, transparency. It is thinnest two-dimensional material discovered [3]. Graphene's structure can be seen using transmission electron microscopy (TEM) [6] and scanning tunnelling microscope (STM) [7].

Since electron waves propagate within a single-atom layer, graphene is sensitive to the presence of high-κ dielectrics, super conductors, and ferromagnetic materials. Thermal properties of graphene is an active area of research. Thermal conductivity of suspended graphene was found to have surprisingly large thermal conductivity values up to 5300 W·m−1·K−1 [8], as compared to that of pyrolytic being 2000 W·m−1·K−1 at room temperature [9].

Graphene is one of the strongest material tested [10, 11] and it is almost 100 times stronger than steel of same amount of weight. Researchers of Rice University and the Georgia Institute of Technology in 2014 have found that graphene is relatively brittle, and has fracture toughness of about 4 MPa√m. [12].

Graphene's specific surface area (SSA) is 2630 m2/g which is much larger compared to carbon black (<900 m2/g) or carbon nanotubes (100 to 1000 m2/g) and is similar compared to activated carbon [13]. Graphene is a carbon form that offers every atom for chemical reaction from two sides (due to the 2D structure). Physicists form Stanford University in 2013 reported that single-layer graphene is a many times more reactive chemically than multilayer sheets [14].

When exposed to molecules containing carbon, such as hydrocarbons graphene can self-repair holes in its sheets by bombarding it with pure carbon atoms, holes are filled as the the atoms perfectly align into hexagons structure [15, 16]. Researchers of Graphene Research Centre at the National University of Singapore (NUS) in 2011 discovered graphene can accelerate the osteogenic differentiation of human Mesenchymal Stem Cells without biochemical inducers [17].
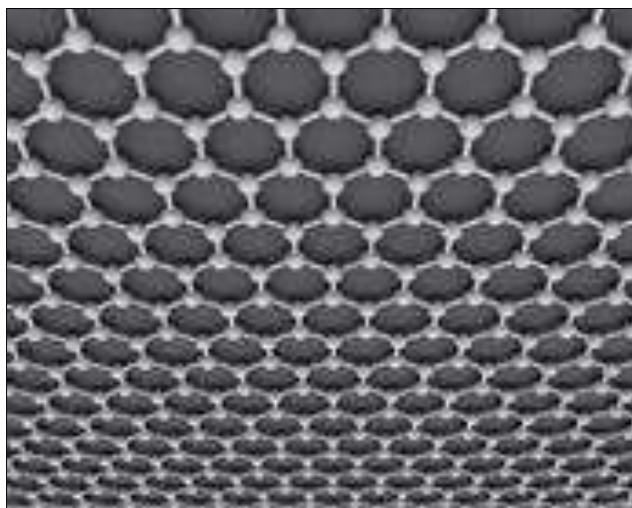
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Fig 1: Atomic structure of graphene

PVA is a water soluble biodegradable synthetic polymer which is popular for its properties like film forming, emulsification and its adhesive quality.

It possess no odour, is resistant to grease, oils, and solvents and mostly its non-toxic. It is ductile material yet has moderate strength.

Crosslinking of PVA

Crosslinking is process of the polymer chain bonding with each other to enhance the properties of polymers. Reagents with multi-functional groups are used for crosslinking of polymer chains. PVA has been crosslinked using dialdehydes, dicarboxylic acids, tricarboxylic acids, and boric acid etc. depending on its application.

Table 1: Different crosslinking agents and their functional groups attached according to the applications of PVA

S. No.	Crosslinking reagent	Functional groups		Structure	Application
1	Glutaraldehyde	Two-CHO groups		Aliphatic dialdehyde	Reducing oxygen permeability [18]
					Drug delivery [19]
					Proton exchange membrane [20]
					Pervaporation systems [21, 22]
					Ultrafiltration membranes [23, 24]
					coating [25]
2	Maleic acid	Two groups	-COOH	Aliphatic dicarboxylic acid	Separation process [26]
3	Fumaric acid	Two groups	-COOH	Aliphatic dicarboxylic acid	Pervaporation systems [27]
4	Malic acid	Two groups	-COOH	Aliphatic dicarboxylic acid	Pervaporation systems [28]
5	Sulfosuccinic acid	Two groups	-COOH	Aliphatic dicarboxylic acid	Proton and methanol transport [29]
6	Pthalic acid	Two groups	-COOH	Aromatic dicarboxylic acids	Development of polysulfone membranes [30]
7	Iso-pthalic acid	Two groups	-COOH	Aromatic dicarboxylic acids	
8	Terepthalic acid	Two groups	-COOH	Aromatic dicarboxylic acids	
9	Aconitic acid (cis and trans)	Three groups	-COOH	Aliphatic Tricarboxylic acids	
10	Citric acid	Three groups	-COOH	Aliphatic Tricarboxylic acids	Support membrane for PS [31]
11	Hexamethylene diisocyanate	Two groups	-NCO	Aliphatic di-isocyanates	Improved
12	Boric acid	Three groups	-OH	Non linear	Improved melting behaviuor of PVA [33]

Above table summarises the findings of different authors using different crosslinking reagents. Figueiredo KCS,et. al. (2009) crosslinked PVA using glutaraldehyde under mild conditions and found there was reduction in oxygen permeability. Campos E. et.al. (2013) employed an improved method for preparing glutaraldehyde crosslinked chitosan Poly (vinyl alcohol) microparticles and found their application in drug delivery. Beydaghi H. et.al. (2014) crosslinked Poly (vinyl alcohol) /sulfonated nonporous silica hybrid membrane for proton exchange in membrane fuel cell. Huang RYM and Rhim JW (1993) Modified Poly (vinyl alcohol) using maleic acid and used it for separation of acetic acid - water mixtures by pervaporation technique. Heydari M et.al. (2013) determined the effect of crosslinking time on the thermal and mechanical properties and pervaporation performance of poly (vinyl alcohol) membrane crosslinked

using fumaric acid used for dehydration of isopropanol. Işıklan N and Şanlı O (2005) used poly (vinyl alcohol) membranes modified with malic acid for separation characteristics of acetic acid–water mixtures by pervaporation. Rhim J- W et.al. (2004) crosslinked poly (vinyl alcohol) membranes using sulfosuccinic acid containing sulfonic acid group. Dlamini DS et.al. (2013) determined effect of crosslinking agent (pthalic acid) chemistry and coating conditions on physical, chemical, and separation properties of PVA-Psf composite membranes. Jian S and Xiao Ming S (1987) Crosslinked PVA-PS thin-film composite membrane using aio-pthalic acid for reverse osmosis. Krumova M et.al. (2000) determined effect of crosslinking using Hexamethylene diisocyanate on the mechanical and thermal properties of poly (vinyl alcohol). Miyazaki T et.al. (2010) used boric acid for a poly (vinyl alcohol) film as a crosslinking agent.

Applications of Polyvinyl alcohol

Polyvinyl alcohol is used to provide strength to textile yarn and papers, and to make them more resistant to oils and grease. PVA can be used to coat food supplements because it does not pose any risk to human health and it is non-poisonous. Density of crosslinking gives resistance to moisture and increases its usability in the supplement coating application.

PVA is used for the developing other resins such as polyvinyl butyral (PVB) or polyvinyl formal (PVF). PVB is a water-resistant, plastic film with adhesive properties therefore it can be used to laminate safety glass for vehicles and other materials. PVF is mostly used to insulate wires. PVA finds extensive application when interested in development of new materials with certain required properties.

Graphene Synthesis

The current production methods for graphene include liquid exfoliation, chemical vapor deposition (CVD), annealing of silicon carbide, and ultrahigh vacuum processes. There are other methods also which are used for scalable graphene synthesis and are listed in table below.

Table 2: Synthesis process of graphene by different scientists

S. No.	Researcher	Synthesis method and Process	Remarks
1	Dijkkamp et al. 1987 [46]	Pulsed Laser Deposition: A stoichiometry transfer occurs between ablated target and substrate where the material is deposited	Most versatile growth approach. No carbide formation occurs at the interface of graphene and the metal
2	Kammler et al., 2001 [44]	Flame synthesis: The particles are collected by placing a transmission electron microscopy grid 2 cm above the tip of the burner for 10– 50 ms. The most commonly used flame types include premixed, normal diffusion, inverse diffusion, and co-flow	Process can produce commercial quantities of nanoparticles. Cost effectiveness.
3	Novoselov et al., 2005 [34]	Micromechanical exfoliation: peel-highly ordered pyrolytic graphite (HOPG) using adhesive tape	Simplest method Not for large-scale graphene growth
4	Zhu et al., 2007 [40]	Plasma enhanced CVD (PECVD): plasma sources used are microwave (MW) [41], radio frequency (RF) [42], and direct current (dc) arc discharge [43].	This process enables the growth of graphene at lower temperatures and shorter duration
5	Hernandez et al., 2008 [35]	Liquid-phase exfoliation (LPE): Solvent (acetic acid, sulfuric acid, and hydrogen peroxide [36] is used to exfoliate graphite by ultrasonication	Process can be used to producr graphene nanoribbon (GNRs) with width <10 nm [37]. Large scale film growth is challenging.
6	Reina et al., 2008 [38]	Chemical vapor deposition: Transition metals (nickel (Ni) and copper (Cu)) are used to enables a low-energy pathway by forming intermediate compounds for the growth of graphene.	Cu has the lowest carbon solubility therefore it is ideal metal for growing single layer graphene.
7	Mattevi et al., 2011 [39]	Roll-to-roll CVD	High quality graphene is produced
8	Park et al., 2011 [47]	Laser-Based Chemical Vapor Deposition: precursor gases (methane and hydrogen) are used with Ni foil as the substrate.	Process can be used for graphene lithography
9	Yannopoulos et al. 2012 [45]	Epitaxial Growth on Silicon Carbide Substrate: Thermal decomposition of SiC surface provides epitaxial growth of graphene	Stacking order of epitaxial graphene can be controlled Process does not involve any pre-treatment step or high- vacuum process.
10	Wei and Xu 2012 [48]	Laser Growth Directly on Silicon and Quartz Substrates	If the laser power was below the melting point of silicon, there was no graphene grown.

Novoselov, K. S. et al. (2005). Used micromechanical exfoliation method for graphene extraction it's the simplest method but not suited for large-scale graphene growth. Hernandez Y. et al. (2008). Used high-yield production of graphene by liquid-phase exfoliation of graphite. Reina et al., (2008) used Chemical vapor deposition for graphene production. Transition metals (nickel (Ni) and copper (Cu)) are used to enables a low-energy pathway by forming intermediate compounds for the growth of graphene. Zhu H. et al. (2008). Chemically derived, ultra smooth graphene nanoribbon semiconductors.

Krivchenko V.A. et al. (2012) studied evolution of carbon film structure during its catalyst-free growth in the plasma of direct current glow discharge. Carbon N. Y. 50, 1477-1487. Kammler H. K. et.al. (2001). Used flame synthesis of graphene nanoparticles. The particles are collected by placing a transmission electron microscopy grid 2 cm above the tip of the burner for 10–50 ms. The most commonly used flame types include premixed, normal diffusion, inverse diffusion, and co-flow. Yannopoulos S. N. et.al. (2012). Used CO2-Laser-induced growth of epitaxial graphene on 6H-SiC. Stacking order of epitaxial graphene was controlled Process and does not involve any pre-treatment step or high-vacuum process. Dijkkamp D. et al. (1987). Prepared Y-Ba-Cu oxide superconductor thin films using pulsed laser evaporation from high Tc bulk materials. Park J. B. et al. (2011). Developed fast growth of graphene patterns by laser direct writing. Wei, D. and Xu, X. (2012) employed Laser direct growth of graphene on silicon substrate.

Application of Graphene in functional devices

Graphene finds application in various fields and some of its application in the field of functional devices is listed in table 3 given below.

Table 3: Applications of graphene in different devices

S. No.	Device	Application
1	Photovoltaic Cell	Graphene-based solar cells have been demonstrated in dye- sensitized PV cells. [49] Power conversion efficiency (PCE) of graphene- electrode organic solar cells are higher.
		graphene-based organic bulk-heterojunction PV cells and hybrid ZnO/poly(3-hexylthiophene) (P3HT) PV cells was demonstrated by Li et al. [50, 51]
2	Transparent and Flexible Electronics	Pentacene-based organic FETs-devices were elaborated onto a flexible substrate [54]. carrier mobility of 0.01 and 0.12 cm2/Vs were systematically estimated for the (Transfer-Patterning) and (Patterning-Transfer) processes, respectively [55]

3	Thermoelectric Application	Thermoelectric Power of 80 µV/K was recently measured in graphene at room temperature (300 K) [56]
		Very large TEP values have been predicted for GNRs, 4 mV/K for a 1.6 nm wide ribbon [57].
4	Shape Memory Materials	Han and Chun prepared a graphene/PU composite material by functionalizing graphene with diazonium salts carrying phenethyl
		Alcohol. [59] Material showed shape fixity up to 98 with 94% shape recovery ratio after four cycles.
		Rana *et al*. prepared a flexible and conductive shape memory composite based on PU and functionalized (using phenyl isocyanate and poly diol) graphene sheets. [60] Composite resulted in 97% shape recovery and 95% shape fixity
		Thakur *et al*. have demonstrated that castor oil-modified hyperbranched PU and graphene-oxide (without functionalization) [61] Composite resulted in a shape recovery of ~99.5% with shape Fixity of ~90%.
5	Self-Healing Materials	Dong *et al*. synthesized a composite material of poly (acrylamide) (PAM), poly (acrylic acid) (PAA), and graphene (10–30wt %) self-healing ability [62].
		Huang *et al*. have demonstrated the use of FLG with thermoplastic polyurethane (TPU) as self-healing material initiated using an electric stimulus [63].
		Wang *et al*. and Sullivan *et al*. have recently reported the fabrication of a composite based on a cross-linked hydrogen bonding polymer with graphene oxide [64, 65].
6	Photomechanical Actuators	Single walled CNT and multiwalled CNT based composites have been reported to undergo photomechanical actuation [66] (Dreyer *et al*., 2010).
7	Piezoelectric Materials	Luk'yanchuk *et al*. have reported an extraordinary two-dimensional piezoelectric effect, both on a strained and unstrained graphene junction [67].
8	Electrorheology Materials	Zhang *et al*. prepared colloidal r-GO using a modified Hummers method, which was used to prepare a nanocomposite material comprising of GO and polyaniline (PANI) [68]. Material showed Adjustable electrical conductivity.
9	Nanocomposite Foams for space applications	These composites help replacing heavy copper wiring, with low density carbon-based wiring cables.

Graphene and graphene-based materials find a major application in photovoltaic cell. Graphene- based organic bulk-heterojunction PV cells and hybrid ZnO/poly(3-hexylthiophene) (P3HT) PV cells was demonstrated by Li *et al*. and Si based PV cells demonstrated by Shim *et al*. Gomez De Arco demonstrated InGaN p-i-n PV cells. It was found that Power conversion efficiency (PCE) of graphene-electrode organic solar cells is higher. Other applications include shape memory alloys Han and Chun prepared a graphene/PU composite material by functionalizing graphene with diazonium salts carrying phenethyl alcohol and achieved shape fixity up to 98 with 94% shape recovery ratio. Rana *et al*. prepared a flexible and conductive shape memory composite based on PU and functionalized (using phenyl isocyanate and poly diol) graphene sheets which resulted in 97% shape recovery and 95% shape fixity. Thakur *et al*. have demonstrated that castor oil-modified hyperbranched PU and graphene-oxide (without functionalization). Single walled CNT and multiwalled CNT based composites have been reported to undergo photomechanical actuation by Dreyer *et al*. Luk'yanchuk *et al*. have reported an extraordinary two-dimensional piezoelectric effect, both on a strained and unstrained graphene junction. Zhang *et al*. prepared colloidal r-GO using a modified Hummers method, which was used to prepare a nanocomposite material comprising of GO and polyaniline (PANI). Nanocomposite Foams are used for space applications and help replacing heavy copper wiring, with low density carbon-based wiring cables.

Functionalization of graphene and graphene oxide
The proper functionalization of graphene and graphene oxide is done to prevent agglomeration during the reduction process [69], helps retain inherent properties and new functional groups attached give them new characteristics.

Covalent functionalization
In covalent bond functionalization graphene is attached to newly introduced groups through covalent bonding hence the name given to the process. The oxygen-containing groups which are present on the surface of graphene oxide makes covalent bond functionalization easier for GO than that of graphene. Different types of covalent functionalization are explained below.

Carbon skeleton functionalization
In this process the functional modification of the carbon skeleton is performed by the C C bond [70-72]. Fig 2 shows the functionalization process.

Hydroxy functionalization
Graphene oxide contains many reactive hydroxyl groups the process involves reaction of amide or isocyanate with graphene oxide to produce esters, and then further functional modification using different groups [74].

Carboxyl functionalization
Carboxyl groups present at the edge of graphene oxide is a highly reactive group, and thus has been greatly studied for the functionalization of graphene oxide [76, 77] The reagents commonly used for carboxyl reaction are thionyl chloride (SOCl2) [78], 2-(7-aza-1*H*-benzotriazole-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate,[79] *N,N*-dicyclohexylcarbodiimide (DCC) [80], and 1-ethyl-3- (3-dimethylaminopropyl)-carbodiimide (EDC) [81].

Non-covalent functionalization
The non-covalent bond functionalization results in the formation of a composite material due to interaction between hydrogen bonds and electrostatic forces of graphene and functional molecules, the beneficial point of which is that the bulk structure is maintained and the dispersibility and stability of material is improved.

π–π bond interaction
Song *et al*. [82] produced a super tough artificial nacre through the synergistic interface interactions of p–p interaction and hydrogen bonding between graphene oxide (GO) nanosheets and sulfonated styrene–ethylene/butylene–styrene copolymer synthesized using multifunctional benzene.

Hydrogen bond interaction
He *et al*. [83]. Studied the fabrication of reduced graphene-oxide aerogel membranes via the reduction- induced self-assembly of rGO through hydrogen bond mediation (mediator used was polyethylene glycol (PEG)). Hydrogen

bonding interactions of PEG-rGO partly replaced the interlayer p–p and hydrophobic interactions and rGO laminate size in 2D stacking was reduced.

Ion interaction
Choi *et al.* [84] executed a stable dispersion of reduced graphene was achieved in various organic solvents via noncovalent ionic interaction functionalization with amine-terminated polymers.

Electrostatic interaction
Electrostatic repulsion between the same types of charge is another strategy to improve the dispersion of graphene.

Bhunia *et al.* [85] used hydrazine as a reducing agent to control the reduction to remove the functional groups such as hydroxyl groups and epoxy bonds and retain the carboxyl anion, which is well dispersed due to charge repulsion.

Element doping
Element doping generally uses annealing heat treatment, ion bombardment and arc discharge as means to incorporate different elements into graphene. The process results in the substitution defects and vacancy defects in graphene but maintains the intrinsic two-dimensional structure of graphene. Process modifies surface properties to give new performances [87-90].

Table 4: Summary of different process for functionalization of graphene

Modification type	Modified group	Modification agent		Interaction type	
Covalent functionalization	–C C–	4-Propargyloxydia- zobenzenetetrafluoroborate		Diazotization	
	–OH	2-Bromoisobutyryl bromide, NaN3, HC≡C–PS		Esterification	
	–COOH	SOCl2		Esterification	
	–OH	N2H4, DNA		Addition esterification	
Non-covalent functionalization	Carbon six- membere d	Sulfonated ethylene/butylene–styrene copolymer	styrene–	Copolymerization	
	Carbon six- membere d ring	Tetrapyrene derivative		π–π	
	–OH	DNA		Hydrogen interaction	bond
	–OH	DXR		Hydrogen interaction	bond
	–COOH	Amine-terminated polymers		Ion interaction	
	–COOH	SDBS		Ion interaction	
	–COO–	Hydrazine		Electrostatic interaction	
Element doping	–C–	B, P, and N		—	

Table 4 above summarizes all the functionalization process which were studied and the functional groups added to the structure of graphene and the agents used in the process. The interactions which occur between the introduced group and the original graphene the type of modification in the lattice structure and the property which is changed due to the introduction of functional group.

Future prospects of graphene
Graphene has many unique and prominent physical and chemical properties (large specific surface area, high transparency due to its special structure, and thus has wide application potential in many fields. There are several problems which limits the application of graphene some of them are listed below.
▪ Graphene is difficult to disperse in water and organic solvents, known as the agglomeration phenomenon of graphene
▪ Functionalized target groups are difficult to control.
▪ Synthesis of graphene is complicated.
▪ Separation and purification is difficult.

All the limitations provide us with opportunities for further research in this field. For future work we can lay our focus on
▪ Developing new functional modification methods.
▪ Separating particles of different size while working on new material synthesis to optimize the required parameter.
▪ We can develop a relation between microstructure and properties of graphene and graphene oxide so we can better exploit the desired properties in engineering field.

▪ Functionalization of graphene can be studied in deep details so as to reduce the gaps between inherited properties and properties we want to achieve.

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