Graphene Nanocomposite Anchored Scientific Research to a New Perspective

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Abstract:- The graphene nanocomposite considered as the most emerging research field in science due to superior catalysis, photo-catalysis and electro-catalysis properties etc. like Large specific surface area, high electrical conductivity, superlative mechanical strength, high thermal conductivity, ballistic mobility of charge carriers, good optical transparency and quantum Hall effect at room temperature. Here we discussed briefly the beneficiary synthesis methods, challenging engineering properties and its wide applications.

Keywords:- *Graphene, Nanoparticles, Organic synthesis, Field-Effect devices, Biosensor, Photo-catalytic, Antibacterial.*

I. INTRODUCTION

Graphene considered as a promising allotrope element of carbon and nanoparticles are the tiniest particles of crystalline solid. These extraordinary properties of graphene crowned it in the field of Nobel prize since the 2010 for “ground breaking experiments regarding the two-dimensional (2D) material graphene” [1]. Graphene is a two dimensional sheet with sp^2 hybridized carbon bonded together and assembled over to form graphite.

Graphene possesses high specific surface area, high intrinsic mobility, high Young’s modulus, high thermal conductivity, high optical transparency, enhanced quantum hall effect with fracture strength of values 2630 $m^2 g^{-1}$, 200000 $cm^2 v^{-1} s^{-1}$, ~1.0 TPa, ~5000 $Wm^{-1} K^{-1}$,~97.7%, and 125 GPa) [1-4].These remarkable properties of graphene make itself as a different from other carbon based allotrope materials. Graphene acts as a unique precursor in the field of energy conversion materials, biosensors, organic synthesis, photochemical reactions and many more [5,6]. Graphene has zero band gap between conduction and valence band, mobility value of ~10 000 $cm^{-2} s^{-1}$ in room temperature and its absorbs approx. 2.3% towards the visible light [7-10].

Graphene having oxygen functional groups named Graphenoxide is light yellow in colour and on reduction of oxygen based functional group turns to black graphene [11]. Graphite oxidised by oxidising agent’s forms Graphenoxide and then on reduction forms graphene. Graphenoxide have lower conductivity, thermal stability than graphene. Graphene shows carbon-carbon Vander Waal’s force of attraction bond length of value 1.42 Å [12]. The separation of multiple stacked sheets layer of graphite by exfoliation method employed at first to form graphene [13-17] and then organic precursors used in situ for synthesis of graphene [18-21].

Mean while different methods like electrochemical [22, 23], photo chemical [24, 25], thermal [26, 27], laser irradiation [28-30], microwave reduction [31, 32], reduction by different reducing agents [33, 34] are employed to form graphene from graphite. Apart from all the methods Hummers method is proposed to be the most efficient, safe and high quality with quantity of Graphene oxide is produced from graphite by this method [35]. In this method, oxidising agents such as sulphuric acid (H_2SO_4), potassium permanganate ($KMnO_4$) and then hydrogen peroxide is used for insertion of oxygen containing functional groups. The 2D graphene sheets are folded over for increasing catalytic properties into graphene quantum dots with zero dimensional, graphene nano meshes and ribbons (GNRs) [36, 37].

Further, the graphene on combination with nanoparticles possesses remarkable and outstanding properties than single graphene sheets and nanoparticle. This extra increase fascinating in activity of nanocomposite is caused due to compatibility and long range π electron conjugation resonances in hexagonal dramatically arrangement [35,38]. The properties of combined graphene and nanoparticles can be enhanced by the different shaped of nanoparticles. The increase in electrochemically active surface area (ECAS) of nanocomposite illustrates that graphene acts as a best transducer for supporting nanoparticles [39-41]. The fascinating combination of graphene nanoparticles and their unique properties attracts a huge research area of interest in catalytic research [35-38].

The research based on graphene nanocomposite privileged in wide range applications worldwide at an incredible rate. It’s a difficult task to embody all the information related to this nanocomposite in a single platform. Still the importance of this article is that, various synthesis methods and large fields of applications in practical means have been discussed, which will provide a better platform for future research scope [42]. In particular demand for study of this review is that the nanocomposite overview towards graphene based photo catalytic activity, biosensor, energy conversion, antibacterial & biomedical and organic synthesis applications and explain the quantum Hall Effect, band gap, Dirac points, Klein tunneling properties etc. are the intense interest of this review [43]. The challenging engineering of nanocomposite are anchored engineering science to a new level. This technology is able to make novel devices with low cost, high quality and designing photo catalytic technology [44]. Hence the graphene supported nanoparticles grabbed a new engineering in field of scientific community.

II. OVERVIEW ON GRAPHENE NANOCOMPOSITE PROPERTIES

The structurer and elemental detection at first suggested by Hofmann and Holst [45] and later on that modified by Scholz and Boehm [46] then Nakajima and Matsuo [47]. Recent reports suggested for structural illustration of graphene by using different kinds of techniques like high-resolution transmission electron microscopy (HRTEM), atomic force Microscope (AFM). These techniques suggested the presence of spliting in the position of functional group and more thickness of graphene oxide than graphene respectively. The general concept of different theory suggested that the σ bonds and π bonds of carbon element formed by three valence orbitals (S and 2Px,2Py)and the un-hybridized fourth 2Pz forms π bond with other carbon atom. The electronic features of graphene illustrated by ultra-high scanning tunneling microscopy (UHSTM), which shows all six carbons in graphene have completely equivalent with equal intensity [48].

The experimental value observed from raman techniques, atomic force emission (AFM), young's modulus and absorbance value considered graphene as the hardest material than diamond and the key objective for its optoelectronics applications [49-53]. The unique quantum Hall effect (QHE) and Klein tunneling properties of graphene confirms the high speed movement of electron in graphene medium even that speed of light [54]. This suggests exceptional electronic arrangement and caused for electrons in graphene medium move 100 times faster than light.

Recently Behera *et al*. [35,38] synthesized and characterized graphene, graphene nanocomposite by different techniques like TEM, XRD, AFM, XPS methods. They suggested the kinetics of electron transfers is more faster in nanocomposite than single graphene and suggested the graphene nanocomposite plays excellent materials for biosensor and fuel cell energy conversion applications.

III. APPLICATIONS

The extraordinary properties graphene and its composite developed a wide range of applications in many fields. The king like catalytic potential properties of composite grabbed itself in wide applications like photo-catalysis, biosensor, fuel cell energy conversion, organic synthesis, pharmaceutical fields, electronic engineering fields and many more.

IV. PHOTO-CATALYTIC

Photo catalysis, a renewable and green technology acts as a rising star for the transfer of renewable energy (i.e., solar light) into chemical fuels. Near future this method is an alternative effective, low cost and environmental benign method to solve the environmental and energy crisis. The whole photo catalytic process is summarized basically three steps such as absorption of light to generate charge carriers, disassociations of charge carriers and consumption of charge carriers. Various materials have been developed over the past for this energy application but all have their own limitations like high cost, large set up instruments, poor operational with storage stability and the most important one its inability to use visible light efficiently for energy conversion. As per the literature survey, Graphene/Graphene oxide photo-catalysts are unable to generate H_2 and O_2 by the photocatalytic reaction using water. This is because of it's oxidation potential is not high enough to oxidize water for O_2 evolution. Further, their reaction kinetics did not support the evolution of H_2. Graphene/Graphene oxides cannot generate electron-hole pair, but only helps in transportation of electrons or holes in the photocatalytic process. The impurities in the form of co-catalyst or the generation of defects in the Graphene/Graphene oxide structure can help in improvement in photocatalytic application.

Apart from this Graphene has strong visible light-photon absorption and have improved separation efficiency of photo generated charge carriers and also exhibits adsorption of organic pollutants due to strong π-π interactions. The outrageous work function activity of graphene ($\Phi = 4.42$ eV) permits the effective extraction of photoelectrons and make GO/rGO as prominent photo-catalyst for H_2 evolution.

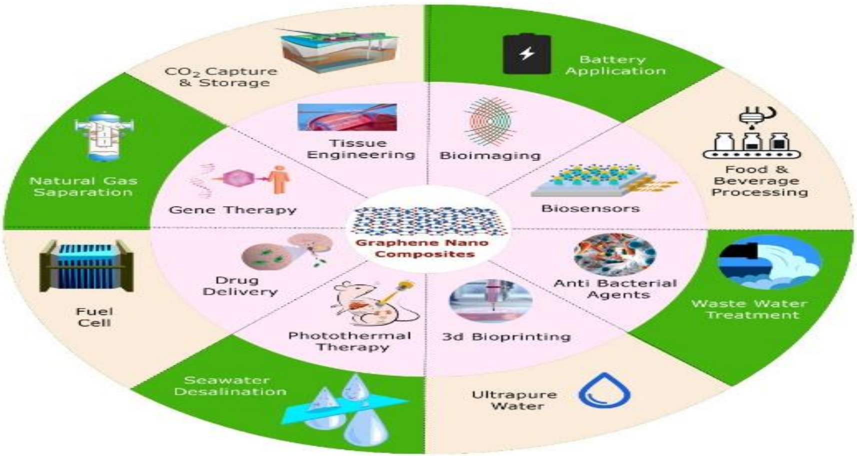

Fig. 1: A brief overview of the contribution of Graphene nanocomposite to various applications and different fields.

The flexible GO decorated (FGC) $Ni(OH)_2$ exhibited H_2 evolution rate of 75 μmol h^{-1} under UV / Vis irradiation. This increased value of evolution rate of the composite was due to the overlapping of π orbital of the polymer, GO and the carboxylic group on the surface of FGC leads to the formation of active sites. This excitation generates the electron-hole pair and reacts with water molecule to produce H_2. Again the presence of co-catalyst Ni $(OH)_2$ act as a trapping center and helps in absorbing UV light and enhanced the H_2 evolution by reducing the electron-hole recombination [55]. Graphene acts as a co-catalyst for H_2-evolution can greatly improve photocatalytic activity in various compounds like MoS_2/GO photocatalysts [56], CZTS (Cu_2ZnSnS_4)/GO [57], TiO_2/Au/rGO hybrid structure [58], bimetallic plasmonic Ag/Au decorated GO [59], RGO/Co_2P [60], flexible Pt/GO foil [61], rGO@$SrTiO_3$ [62] and Ni-doped ZnS decorated graphene[63], CdS/Co9S8-RGO [64] etc.

Again, the conversion of atmospheric CO_2 into fuel through photocatalytic process is the most popular research area in the near future. This technique has the potential to reduce the overall carbon footprint and global warming. Numerous studies have made for the reduction of CO_2 because of excellent performance of graphene-based composites. 2D π electron cloud of graphene conjugated with CO_2 π-conjugated electrons. This leads to an establishment of π-π interaction between grapheneand CO_2 molecule and significantly enhance the CO_2 adsorption on to the GO/RGO based composites. Notably the strong conjugation interaction (π-π) between CO_2 molecule and graphene causes activation and destabilization of CO_2 and that leads to good photo catalytic reduction of CO_2. Figure 2 represents different chemical product formed due to CO_2 conversion. Moreover, different methods such as porous hyper crosslinked polymer TiO_2/GO composites was used for CO_2 conversion. [65], Zn based electro-catalyst (ZnO/rGO) reduced CO_2 to CO [66], RGO/CdS [67], RGO/Cu_2O [68,], RGO/ZnO [69], etc. also exhibits unique photo reduction of CO_2.

High oxygen containing functional groups in graphene/graphene oxide possesses outstanding hydrophilicity. This leads to easy dispersion in water to form stable colloidal suspensions, enable the semiconductors to be modified in aqueous medium [70]. The high electron mobility of graphene/graphene oxide than other general conductors create its own identity. This is because of the large specific surface area, high chemical stability improves the adsorption capacity and hence promotes the PC degradation performance. In PC degradation, the effective separation of the photogenerated charges occur due to the anode bias was applied to the film (graphene/graphene oxide) electrodes.

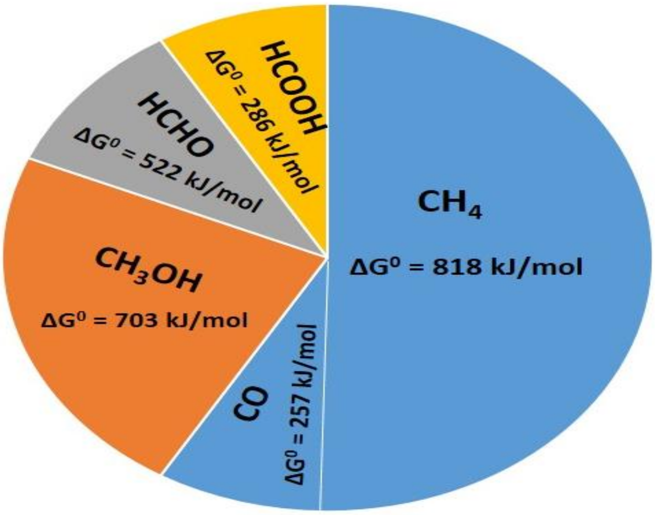

Fig. 2: Different chemical products formed the conversion of CO_2

This promotes the flow of e^-s and h^+s in the opposite directions per unit time. At the same time at photoelectrode the anodic reaction of the h^+s ($OH^•$) reacts with the dye and improves the PC quantum yield and efficiency of pollutant degradation. From this it is clear that because of electrical conductivity, charge transportation and large specific surface area, graphene/ graphene composites in small weight percentage increases the efficiency of semiconductors in photoelectrodes. In addition to this, numbers of yearly publications on photoelectro-catalysis (PEC) of graphene enhance the value of graphene to another step. Metal oxide in combination with graphene possesses excellent photoelectro-catalysis activity than the single one metal oxide. For example, PECdye degradation of Rhoda mine B was done by Zhao et al. usingGO/Ag_3PO_4/Ni film electrode. The active oxide species generated ($OH^•$, $O_2^{•-}$, and h^+) during PEC process are responsible for the increase the photodegradation efficiency [71].

Other different catalysts showed their potential towards PEC dye degradation are $YAlO_3$/rGO/TiO_2 electrode for methylene blue degradation [72], GO/TiO_2 film electrode for reactive brilliant red dye X-3B [73].Despite these superiorities of graphene in photocatalytic field, several challenges remain in the synthesis, solar fuel generation and defect engineering in photocatalytic materials are observed. So, more research in this field under being proceeding for a better green environment.

V. ORGANIC SYNTHESIS

In organic synthesis, the use of catalytic metals like Pd, Ni, Cu causes high expensive and hazardous. Carbon based material graphene acts as a best heterogeneous catalyst in organic reactions due to their high quality properties [74]. Graphene appear as commitment materials to full fill all the demands as heterogeneous catalysts and phase transfer catalyst. Introductions of functional group like nitro, hydroxyl, carboxyl, halogen and amine groups in organic synthesis and material designed anchored more future synthetic research work. Functional group reactivity on the graphene sheet was often modified as a result of the proximity to the graphene plane. Take the example of Suzuki coupling reaction [74], in which phenyl bromide on the graphene surface did not reacts with covalent carbon- carbon bonds and yields aldehyde, epoxy and vinyl groups on the graphenenano particle surface in high product. Graphene plays high versatile functionality in organic reactions like Suzuki-Miyaura cross coupling reactions [75], coupling reaction uses chiral palladium nanoparticles bound to the thiol groups, styrene functionalized yielded a homogeneous and stable magnetic hydrogel etc.

Wang and his co-workers prepared graphene oxide in co-junction with n-butyl ammonium bromide (TBAB) for aldol coupling/aza-Michael reaction. The $\pi-\pi^*$ cloud and acidic group in graphene oxide caused for high catalytic activity in organic reactions [76]. Zarnegaryan et al. was designed paladium (Pd) modified GO catalyst (GO/N_2S_2) through covalent attachment for Suzuki –Miyaura reaction. The coupling of Phenyl boronic acid with aryl halides in presence of K_2CO_3 has been performed by palladium graphene oxide catalyst [77]. GO co-ordinated inorganic and organic metal complex of nickel-metformin i.e. Ni (0) (GO-Met-Ni) was fabricated by Raoufi and his team for Suzuki-Miyauracross coupling reaction of various aryl halides (chlorine, bromine and iodine) and phenyl boronic acid. They have taken phenyl boronic acid and iodobenzene as the model reaction. The reaction mechanism of Suzuki-Miyaura mainly depends on the three steps (oxidative addition, trans metallation, and reductive elimination) to get the desired product and again with the due course of reaction Ni (0) was generated to continue the cyclic reaction and enhances the efficiency [78].

Likewise, different GO modified catalysts are used in various organic transformation reactions such as: diethylenetri-aminefunctionalized GO decorated Fe_3O_4 nanoparticle (Fe_3O_4/DETA/GO) for Knoevenagel reaction [79], Au/Pd nano alloy modified reduced graphene (RGO) showed its potential towards oxidation of benzyl alcohol and reduction of nitro aromatics [80]. Clay-GO nanocomposite for solvent free multicomponent Biginelli reaction [81]

VI. BIO-SENSORS AND ANTIBACTERIAL

The device which converts a biological response into an electrical signal called biosensor. Biosensor have great application in field of clinical, pharmaceutical, enzymatic since the detection of bio-analytes in micro molar or Nano-molar range is highly necessary for a healthy society.

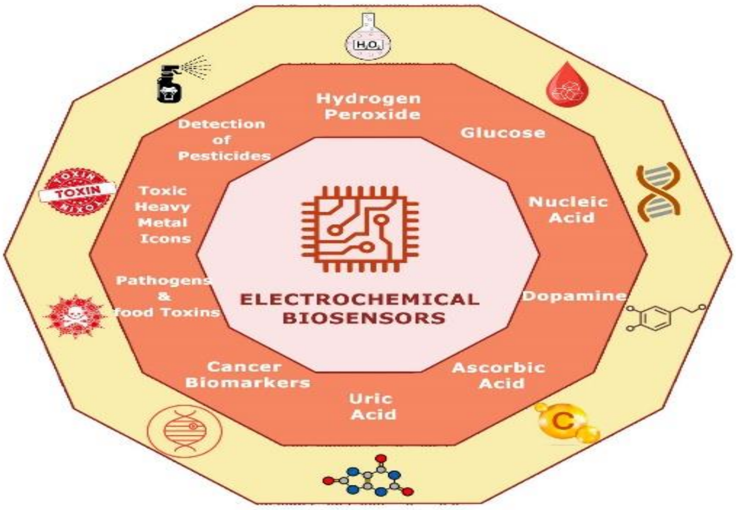

Fig. 3: Electrochemical biosensor applications for detection of different bio-analytes.

For the detection of bio-analytes, electrochemical method able to detect sub nano-molar range than any other methods [82,83]. This nano molar level detection is due to amazing engineering of nanoparticles on surface of graphene. Behera et al. modified Pt on graphene surface (GPtNs) and employed for bio-sensing of hydrogen peroxide [35]. Here the composite acts as an excellent transducer for nano molar detection of hydrogen peroxide bio-analytes. Here, modified electrode shows oxidised potential value of +0.37 V for hydrogen peroxide oxidation with sensitivity value of 811.26 $\mu A/mm\ cm^2$ and limit of detection (LOD) value of 5 nm. Again Behera *et al* fabricated RGO-Pd electrode for detection of hydrogen peroxide also. It is shown that over graphene surface, porous Palladium nanoparticles are uniformly disturbed and created remarkable morphology. This morphological combination caused for very low limit of detection of hydrogen peroxide.

In the recent year's antibiotics and anti microbial agents decreased infectious diseases but still it rises as a global challenging issues. So far creating and exploring novel materials is always being a matter of concern. Graphene has received much research attention since it covers up the lacuna, due to its jubilant size controllability, ability to tune their property and high dis-persibility in water. Recently functionalized graphene used for bio-selective detection of bacteria at cellular levels are attracted more research intrest. The excellent antibacterial properties of graphene supported nano composites like RGO-Ag [84], RGO-Au [85], RGO-Cu [86] Nps attracted long range of employment in antibacterial health care.

VII. ELECTRONIC APPLICATIONS

In high quality graphene, the conduction band and valence bands touch to dirac point and hence does not possess a band gap, that means it is a great conductor (it can't be switched off). The finite minimum conductance of graphene is due to relatively low current ratio ($I_{\text{on}} / I_{\text{off}} <\sim 30$ at 300 K) [87,88]. Recent studies revealed that in graphene the band gap can be monitored by applying strain on keeping constant G and 2D bands tracks [89]. This reduces its electron mobility in it as in strained silicon films. The band gap value approximately found of 300 Mev on applying strain in graphene film [91]. However, these band gaps have no experimental evidences and more research needs to be done in place of silicon in electrical fields.

For a single layer of mechanically exfoliated graphene have high qualities of 2D crystal lattice with carrier mobility of 200,000 $\text{cm}^2/$ (V s). Graphene possess strong ambipolar electric field effect with metallic characteristics. These qualities make graphene to show extraordinary electronic properties and able to replace silicon films in many electronics applications. The employment of silicon and indium tin oxide (ITO) in some materials as electrode has limitations like brittle nature, costly, and insufficient element resources. Graphene used as conductor in touch screen table computers and smart phones etc and indium tin oxide as commercial product used extensively electrode in solar cells and OLEDs as transparent conductor. It also extensively used as an unbreakable screen guard coating to improve current in touch screens, used to make the circuitry for our computers to make them incredibly faster. IBM researchers designed a high speed graphene circuit in 2011 including protecting of the ultra-thin graphene layer during the etching process with electron beam lithography. This IBM team researcher masterly operate graphene transistor at twice the speed of a comparable silicon transistor. In addition to this graphene also emerged its use in field of memory devices. Composites of graphene-polymer used for production of memory devices through a trustworthy and cost-effective synthesis process [92]. These memory devices show low switching threshold voltage (0.5–1.2 V) with high $I_{\text{on}} / I_{\text{off}}$ ratio (10^4–10^5). Graphene acts as a semiconductor although it has zero band gaps. In graphene, both holes and electrons move very fast, which provide an advantage over conventional semiconductors [87-90]. It has created global research interest as a semiconductor. The unique properties like thinness, at just one atom thick and conductivity at room temperature could be best alternative semiconductor materials for computer chips. Although it is the prototype stage of graphene in electronics field, yet it has the potential to stand as the next-generation new electronics material king.

VIII. SUMMARY

The nanotechnology is the combination of physics, chemistry and its application to energy conversion fuel cell, organic synthesis, biosensor, electronics, healthcare and medicine in biology etc. appreciated high attention worldwide. The challenging engineering properties of nanocomposite shows excellent tensile strength, young's modulus, high conductivity, excellent quantum Hall effect (QHE) and Klein tunneling properties. The future energy deficiency can be quenched by the nanoparticles supported graphene surface. The good quality manufacturing of graphene in huge scale will lead the nanocomposite closer to human being's society and now a day's it still a challenging factor and more research should be done.

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