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High Performance Hybrid Graphene Nano Filters as a Total dissolved solid remover

Renuka Sharma*, Pratyush Shekhar
Department of RISE,Chandigarh group of Colleges,Landran,Mohali.
Department of biotechnology,Chandigarh College of Technology, Landran,Mohali.
Email Id: *renuka.rise@cgc.edu.in

Abstract: **Graphene, a single-layer carbon sheet with its distinctive two-dimensional (2D) single-atomic-thick sp2 hybridized hexagonal packed lattice structure which is nearly friction less with high chemical inertness, and pliability which can be manufactured sustainably in great amounts with less expense, has shown many unique properties, Graphene has attracted tremendous research interest in recent years, owing to its exceptional properties. The scaled-up and reliable production of graphene derivatives, such as graphene oxide (GO) and reduced graphene oxide (GO), offers a wide range of possibilities to produce nano-filters containing graphene membrane which is capable to remove ninety percent of the heavy contaminants from different sources of water and to reduce the level of total dissolved solids, salinity, and neutralizes the pH level further inorganic membrane used in synergism with graphene oxide shows improved efficiency and reduction in cost of production of separation membranes. In this review, we demonstrated real world application of graphene, Fabricated with Several Metal Oxides in synergism to illustrate enhanced photocatalysis properties, Flexural strength and anti-fouling characteristics of the material in comparisons to conventional membrane, photocatalytic metal oxides nanoparticles such as Titania TiO2, Zirconia ZrO2, Alumina Al2O3, and Silica SiO2 functions in the presence of Multiple Spectrums of Light by absorbing photons and releasing Oxygen Radical which degrades harmful water pollutants into less harmful substances.**

Nano-Filters, Graphene membrane, Metal Oxides, Oxygen Radicals (*Keywords*)

I. INTRODUCTION

It is estimated that ninety-eight percent of all surface water present on earth is unsuitable for human drinking rest of two percent freshwater source in which 3/4th of it tend to be frozen and rest remains in the liquid phase known as drinkable groundwater, groundwater sources are under great threat of pollutants and pathogens because of rapid industrialization and urbanization [1]. With the increase in urban population, there has been exponential growth in the release of untreated hazardous chemical loaded sewage into rivers and oceans causing harmful contaminations to water resources [2]. Many conventional polymer water separation filters have been developed for the removal of total dissolved solids but utilizes a lot of the energy in the filtration process which is not sustainable in long term. Nanotechnology has shown the most relevant and promising long-term solutions for complete removal of total dissolved solids and to reduce the hardness of freshwater source without utilizing energy through graphene based nano filters [3] [4] developed highly efficient particle separation membranes which showcased high resistance to halogens compounds, resistance to high pressure and high temperature also it showed no corrosion contamination in filtered water [5]. Conventional polymeric membranes are of low cost, easily operable, and takes less maintenance, although with all these practical advantages these polymeric membranes show fouling effect which is not suitable [6]. Novel graphene Nano filters show great resistance towards Organic solvents, Halogen contaminants [7]. It can survive in high acidity and high alkalinity environments without corrosion because of its strong mechanical agility and strength, with its distinctive two-dimensional (2D) single-atomic-thick sp2 hybridized hexagonal lattice structure Fig 1. which is nearly frictionless with high chemical inertness, and pliability which can be manufactured sustainably in great amounts with less expense, although the graphene crystal is not the ultimate 2D plane, ridges of about 1 nm in size are also contained in the lattice Fig.2.

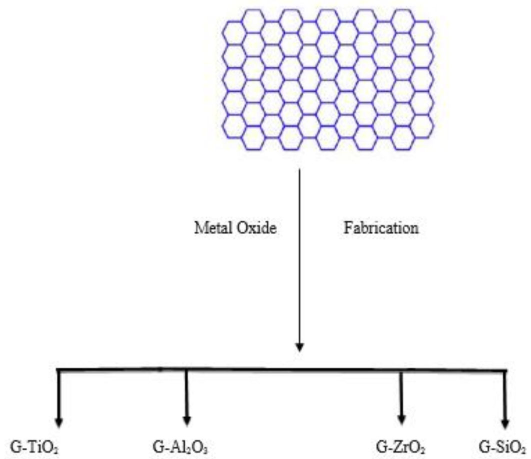

Fig.1 Stinctive two dimensional single atomic thick sp2 hybridized hexagonal lattice structure.

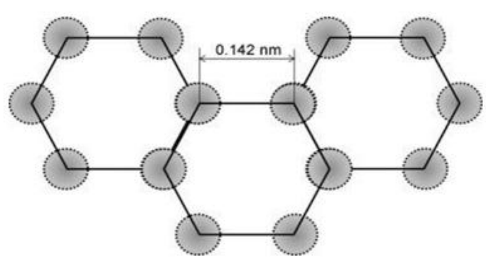

Fig. 2 Honeycomb hexagonal lattice formed by sp^2 hybridized bonds. (Zhen et al., 2018)

II. GRAPHENE OXIDE SYNERGISM AND FABRICATION

GO is a single-layered material made of carbon, hydrogen and oxygen molecules, which eventually becomes reasonably affordable yet plentiful [8]. With the development in research in separation of graphene oxide, we can now use this carbon based material in synergism with many other capable membranes, extensive findings

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suggest inorganic membrane used in synergism with graphene oxide shows improved efficiency and reduction in cost of production of separation membranes [9] produced a fabricated graphene oxide with nanocomposite polyacrylonitrile to increase the thickness of graphene oxide to achieve less water flux based on the assumption of increased mass transfer resistance eventually creating a novel nano fiber mat of graphene oxide polyacrylonitrile membrane, but according to non-ideal fluid dynamics based on Hagen-Poiseuille theory, the flow of the fluid is directly depended on the number of physical factors: the viscosity (n) of the passing fluid, the radii (r) of the graphene oxide porous, also [10] suggest a new concept of hydrophilicity and hydrophobicity sections of graphene oxide nanosheet they called this hydrophilicity gates as a defective sections of graphene oxide nanosheet this theory was supported by [3] which mentions graphene oxide is the mere structure of carbon wall existing as a 2D sheet consisting of a gap between layers of carbon atoms these gaps were named as a channel through which fluid passes contains hydrophilic gates where fluid slips into, due to hydrophobicity of carbon wall responsible for higher water flux, however [11] showed it experimentally that the Graphene oxide net thickness reached 34nm and calculated maxm water flux around (8.2 L.m-2-h-1-bar-1) which is (1.6) times more than the graphene oxide film of 33nm with the calculated water flux around (5.0 L.m-2-h-1.bar-1) clearly explaining higher water flux of previous Graphene Oxide sheets phase inversion is another method to prepare high performance filtration membrane used by [12] to increase hydrophilicity by mixing novel poly-ether sulfone (PES) with graphene oxide nanosheet further addition of casting solution increased flexibility of the nanocomposite the final findings where that the graphene oxide in Synergism with novel poly-ether sulfone (PES) performed much efficiently with more dye removing capability and more reproducibility throughout the filtration with pursuing of refinements in the field of separation membrane for water treatment and quality up gradation, graphene based synergistic nanocomposite has a great potential of research selected two nanoparticles reduced Graphene oxide and silver based nanoparticles to enhance hydrophilicity gates, and expansion of graphene oxide 2D channel influencing water flux resulting in a 200 percent surge from the previous versions of nanosheet

i. Graphene in synergism with Titania nanoparticles

Titania (titanium dioxide) generally exist in nature in the minerals known as anatase and rutile additionally high-pressure rare polymorph of TiO2Akaogiite which exist as monoclinic crystals another orthorhombic form of TiO2 commonly called Brookite has been recognized till date in nature TiO2 exist in three metastable crystal systems (Tetragonal, Monoclinic, and Orthorhombic) nanoparticles gives an impression of black hexagonal crystals and can exist as both nanocrystals and nanodots, with notably bigger surface area, titania nanoparticles have excellent magnetic character, titanium dioxides are also colloquially termed as Rutile, Flamenco. [11]Xu et al., 2013, prepared graphene oxide-Titanium dioxide composite films as shown in Fig. 3 redefining a great potential as a separation membrane and many other filtration application they found these composites were able to maintain a stable suspension in water and were capable to separate dye molecules rhodamine B, methyl orange [13] also studied the antibacterial property of titanium dioxide due to photocatalysis reaction in presence of Ultraviolet Light it generates Oxygen Radicals which acts on organic substances present in the membranes of bacterial cells. Based on the studies conducted by [14] chromium (VI) tends to be extremely poisonous to humans and animals also highly water soluble in comparisons to chromium (III) [15] used TiO2 nanoparticles in the treatment of chromium (VI) contaminated water due to photo-reduction catalysis chromium (VI) is reduced to less toxic insoluble Cr (III). Wang has well documented the chemical nature of Chromium (VI) and material importance for adsorption of Chromium (VI) [16]. TiO2 used in the recombination of Graphene oxide synergise the water treatment process with increased efficiency in photo reduction catalysis, separation membrane also attains antifouling properties making the photocatalysis process less expensive than before [17] suggested Titania photo catalyst used with graphene oxide is much more economical in production and usage compared to other materials graphene oxide provides relatively more stability due to abundant availability and a sharp cutback in graphene oxide production cost because of less-expensive elemental components fabrication of TiO2 nanoparticles over Graphene sheets surged essential photocatalytic properties which were selectively absent in pure TiO2 nanoparticles, when compared to pure form [18], illustrated a test through linear sweep voltammetry to analyse the rate of recombination and charge transfer efficiencies to demonstrate carrier generation and recombination, the locomotion of electron from Graphene sheets to Titanium dioxide by the interfacial potential gradient of the nanocomposite conduction bands reduced charge recombination rate of electron hole pair, the photocatalytic action of the graphene titanium oxide caused by the transference of electron into the binary heterojunction, Graphene Titania hybrid nanoparticles have larger circumference area with extra active sites thus increasing photocatalytic activity.

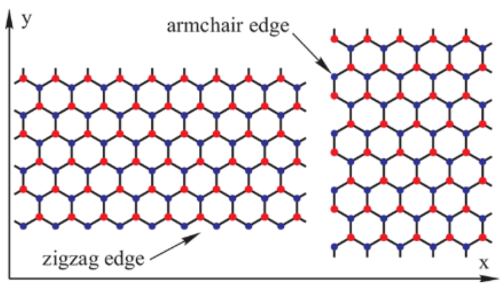

Fig. 3 Graphene lattice with zigzag and armchair edges [1]

ii. Graphene in synergism with Zirconia nanoparticles

Zirconium dioxide is a white crystalline powder which generally occurs in three phases Monoclinic <1170 °C increasing temperature between 1170 °C and 2370 °C and forms Cubic <2370 °C zirconia (ZrO2) shows high thermal stability in comparisons TiO2 nanoparticles with six coordinated titanium centres. zirconium nanoparticles has seven coordinated.

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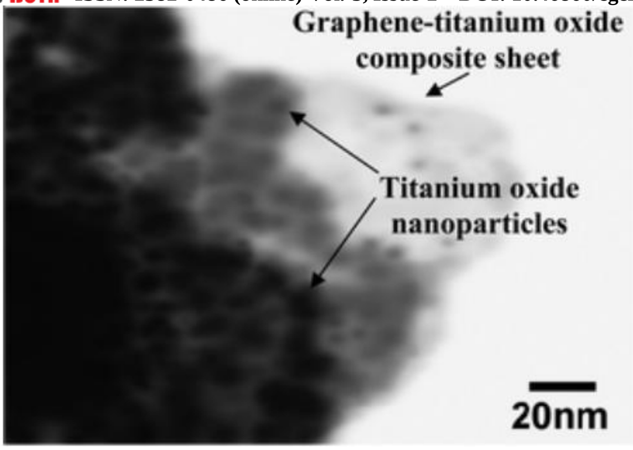

Figure 4: Synergistic Graphene Titanium Oxide Composite Sheet [19].

Zirconium in all discoverable phases [20] zirconium dioxide also known as Baddeleyite which commonly forms monoclinic prismatic crystals, based on the chemical and physical properties of monoclinic prismatic crystal [21] observed Zirconia has higher oxygen diffusivity, higher rigorousness, Corrosive resistance and a potential thermal insulator, due to its distinctive optical properties [22] documented refractive index of cubic zirconia around 2.2 which was higher than any other metal oxide, Recently [23] investigated transparent ZrO2 where they mentions unique properties of Yttria (Y2O2) when combined with Zirconia further [24] prepared yttria stabilized Zirconia (YSZ) and proved combination of yttrium dioxide with Zirconia nanoparticles has improved ionic conductivity and stabilized tetragonal structures of Zirconia through the presence of oxygen vacancies, now polycrystalline transparent cubic (Zirconium dioxide-yttrium dioxide) c-YSZ are extensively been used for its unique photocatalytic applications [21] graphene Zirconium Oxide Nanocomposites exhibit exceptional Chemical resistance, optimum heat resistance and high electronic conductivity, highly resilient, non-brittle, [25] noted High thermal coefficient and high thermal stability these properties of Graphene Zirconium oxide nanocomposite which makes it an ideal separation membrane according to [16] heterogenous photocatalytic membranes has lower efficiency because rapid recombination of electron-hole pair semiconductor based photocatalytic has several advantages over heterogenous membrane due to less recombination rate of electron-hole pairs. Graphene Zirconia nanoparticles appears to be a quasi-spherical in shape, in comparisons to other heterogenous membranes Graphene-ZrO2 nanoparticles have larger surface area [26] used three Organic dyes Rhodamine B (Rhb), Methyl Blue (MB) and methyl orange (MO) and showed degradation of this dyes under Ultra-Violet irradiation via UV-Vis spectra using heated Graphene-Zirconium Oxide and also noted Graphene-ZrO2 tend to be more effective than any of the nanocomposites used thus far.

iii. Graphene in synergism with Alumina Nanoparticles

Aluminium (III) oxide (α-Al2O3) is an amphoteric oxide of aluminium widely known as Alumina, AL oxide, or Alundum based on their existence in nature aluminium oxide generally occurs as mineral corundum which is the most common crystalline polymorphic form. Aluminium Oxide has relatively higher thermal conductivity but poor conductor of electricity [27] bending strength and hardness generally relies upon two factors density and surface area of the nanocomposite [28] conducted sets of experiments to observe bending strength of alumina nanoparticle drastically excelled by addition of reduced graphene oxide in small amount further addition of graphene in higher amounts resulted in reduction of bending strength because when the amount of graphene is incremented, pores formation took place due to agglomeration and overlapping of molecules which further reduced density of nanocomposites therefore weakening flexural strength, their maximum flexural strength calculated at (671.8 MPa) observed at 0.4 percent addition amount of reduced graphene oxide in comparisons to pure Al2O3 which approximates around 415.8 MPa, this shows significance rise in strength of the nanocomposite [29] suggest a great demand for photocatalytic materials for environmental purposes due to high energy consumption of conventional technologies, graphene oxide termed out to be the most effective contender as photocatalytic material for TDS degradation which gives synergistic effect with recombination with highly photocatalytic substance Al2O3 [30] graphene oxides sheets function as excellent sheet for combination for metal oxides [31] conducted an experiments to document a novel approach to create Graphene-Aluminium oxide nanocomposites which showcased a successful degradation of organic dyes p-hydroxy benzoic acid(BA), methylene blue(MB), Methyl Orange(MO) because the Graphene-Al2O3 nanocomposites were successfully modulated to enhance light absorption capability of multiple solar spectrum here graphene-Al2O3 nanocomposites were also compared to pure Graphene oxide and γ-Al2O3 overall graphene oxides electronic properties were effective between transportation of electrons in graphene oxide framework, through novel dry sol-gel method, fabrication of Al2O3 microstructures on Graphene sheets increased vital photocatalytic properties which was selectively absent in pure Al2O3 particles. [32]Kanwal et al., 2020 carried a photocurrent test by using linear sweep voltammetry to evaluate rate of recombination and charge transfer efficiencies to illustrate electron-hole pair separation, the transfer of electron from Graphene sheets to Al2O3 by interfacial potential gradient of the nanocomposite conduction bands reduced charge recombination rate of electron-hole pair the photocatalytic action of the graphene aluminium oxide caused by transference of electron in the binary heterojunction, synergistic hybrid nanoparticles have extended surface area with additional active sites augmenting photocatalytic activity.

iv. Graphene in synergism with silica nanoparticles

Silicon dioxide are the oxides of silicon which is one of the most abundant material in the earth crust exists in many minerals but most commonly as a hard-crystalline mineral known as quartz silicon dioxide can be traced in many crystalline polymorphous forms orthorhombic metastable form exist as α-tridymite, tetragonal metastable form exist as α-cristobalite and keatite, cubic phase exist as β-cristobalite whereas monoclinic phase exist as moganite and coesite, hexagonal phase can also be traced in bilayer sheet like structure known as 2D silica. Unlike several other Metal Oxides Silicon dioxide inclines to be toxic and can be hazardous to human and animals if inhaled in high dosages [33] silicon dioxide has numerous optical properties with refractive index calculated at 1.456 of fused quartz silicon dioxide photocatalytic experiments in efficient degradation of methyl orange and rhodamine blue expresses a great potential as photocatalytic agent further modified membranes of silicon dioxide also displayed great efficiencies [34] silicon dioxides remains stable when combined with several other metal oxides and might show synergism. [35] Hofrichter et al., 2010 demonstrations of graphene oxide fabrication with silicon oxide displays a noteworthy favourable photocatalytic activity in presence of Ultra violet radiation Scanning electron microscope (SEM) analysis showed a successful combination of G-SIO2 microporous structure [21] used a innovative dry sol-gel method for fabrication of silicon dioxide and graphene and documented improved hydrothermal stability and high degradation of organic dyes rhodamine blue. methylene blue and methyl orange further multiple spectrum light adsorption capabilities were also improved the fabricated Graphene silicon dioxide was also compared to reduced graphene oxide and silicon dioxide which suggested transference rates of electron through binary heterojunction were enhanced and the hybrids of graphene silicon dioxide have considerably more surface area then pure form therefore reducing corrosion rates of hybrid nanoparticles [36]. Flexural strength considerably improved when [37] incorporated silicon dioxide nanoparticles graphene matrix interphase and checked its further relevant effects and applications as TDS remover.

III. FUTURE PERSPECTIVE

Major developments are being done in graphene-metal oxide TDS removing process and technologies breakthrough are making Graphene metal oxide membrane inexpensive by which water purification can be achieved efficiently. By the end of year 2024, 14 percent of the world's population will experience water scarcity which makes graphene metal oxide purification very significant. And therefore, this technology could come to the households soon hydrophilic nature of graphene oxide makes it the ideal material for desalination and purification of fluids, as shown in Fig.5 However, making pores on graphene oxide nano sheets by ion bombardment is not a practical solution. Another way of making pores is by stacking GO sheets and tuning the distance and creating separation in them. So, water passes through it automatically by capillary action [38]. Variety of dissolved solids and other impure sources in ionic state i.e., Na+ and Cl-. So, when these salt ions are in water, they hydrate and as they are charged, they attract surrounding molecules of water in concentric shells, thus, increasing the salt ion diameter. So, the pore size of graphene oxide membrane is designed accordingly to block these hydrated ions [37]. A conventional RO membrane removes around 80-85 percent dissolved and impurities whereas Graphene oxide membranes remove around 97 percent dissolved solids Graphene oxide membranes due to their high tensile strength and higher affinity to water are perfect candidates for purification. In RO, we need to reverse a naturally occurring process using external energy, therefore electrical energy required for pumps accounts for approximately 44 percent of RO plant's total cost, the graphene oxide on the other hand is a naturally occurring filtration process, hence GO membranes will definitely save a lot of power.

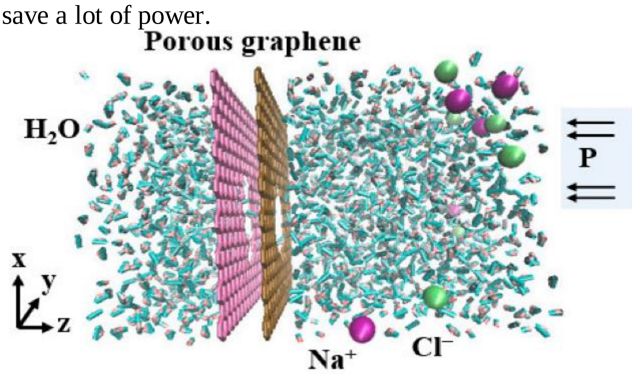

Figure 5 Separation of Dissolved NaCl Particle through porous graphene

IV. CONCLUSION

Recent advances in material-blending technologies and fabrication of metal oxide over graphene surfaces to synergise the nanomaterial properties are in development further organic-inorganic recombination has created polymeric modified nanoparticles with the facile process ability metal oxides such as Zinc Oxide, Titanium-Silicon Dioxide, Ferrous Oxide, Silver Oxide, and Zeolites are under sight for their advance high performance photocatalytic activities in recombination with single atomic layer graphene with high mechanical strength these nanocomposites were also analysed for anti-microbial properties, anti-pollution properties and potentially high water flux graphene derivatives are assembled based on molecule separation requirements generally three types are in experimental phase assembled graphene laminates porous graphene layer, and graphene-based nanocomposites. All metal oxides mentioned in this paper show at least 80 percent photo degradation efficiency production of these fabricated membranes considerably releases very less Carbon footprint and harmful environmental pollution.

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