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REVIEW ARTICLE

FUTURE OF ENVIRONMENT WITH CARBON ALLOTROPES

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ABSTRACT

Carbon and its allotropes have been regarded as a fantastic invention that solved several chemical, biological and physical problems. Carbon nanomaterial fabrication and applications have emerged as a highly intriguing and rapidly evolving field of study in the last few decades. In the present review, the carbon materials found have been presented thoroughly according to their crystal structures, taking into account the type of hybridization. Carbon and its bonding properties, along with special applications of the carbon allotropes, have been discussed so far including various future scopes of the carbon allotropes in an array of suggested strategies to inhibit metal corrosion, in storage of energy with cutting-edge synopsis and emphasis on sodium and lithium ion batteries, elimination of organic pollutants from waste water through catalysis. Furthermore, their usage as core materials in new generation optoelectronic gadgets and biomedical cell scaffolds, gene therapy, newly discovered allotropes like graphdiyne and its applications as promising for energy resources due to its exceptional physicochemical characteristics, which include non-uniform electron distribution, uniform pore distribution, great electron mobility, and elevated chemical stability, etc. are discussed. In summary, the environment's future would be much more sustainable using carbon allotropes and their derivatives effectively. Therefore, the purpose of this review is to offer a suitable path for empowering advancements in ongoing research that will strengthen applications in the future and help this field overcome its current constraints.

Keywords. Carbon, Allotropes, Environment, Graphene, Carbon nanotubes.

INTRODUCTION

With the discovery of the carbon atom or organic compounds, science and technology have witnessed a significant revolution in the field of chemistry.[1] Among all the elements in the periodic table, carbon has been found with excellent versatility and forms different allotropes depending on its hybridization state and atomic arrangement.[2] Nano-chemistry of carbon has played a significant role and is immensely useful in the expansive and dynamic study fields of nanoscience and nanotechnology. The field was initiated by the discovery of Fullerene C60 in 1985, for which Robert F. Curl, Jr., Harold W. Kroto, and Richard E. Smalley were awarded the Nobel prize in chemistry in 1996.[3]

CARBON ALLOTROPES

Carbon bonds to electropositive, electronegative elements and bonds to itself (catenation) through single, double, or triple bonds. It has been found to form the allotropes like diamond, graphite, fullerenes, and carbon nanotubes. Recently discovered structures include carbon onions, atomically thin films, and nanofoams.[4,5] The schematic representation of different types carbon allotropes have been presented in **Figure 1** and some their key properties have been highlighted in **Table 1**.[6,7]

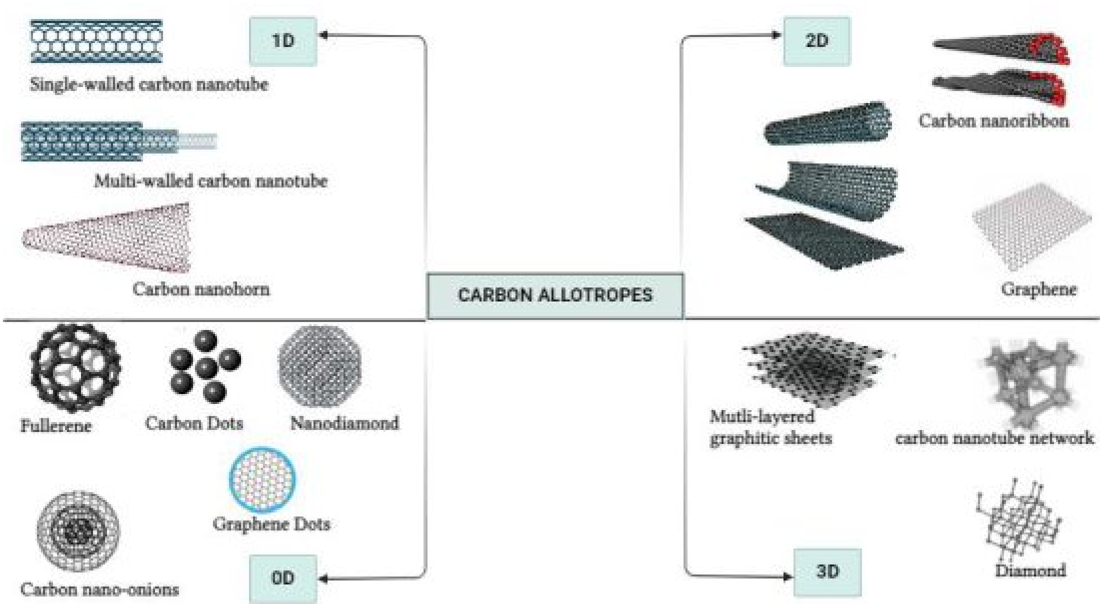

Figure 1: Types of Carbon Allotropes

Table 1. Properties of Different Allotropes of Carbon.

Allotrope	Structure	Appear-ance	Hardness (Mohs)	Electrical Conduc-tivity	Thermal Conduct-ivity (W/mK)	Melting Point (°C)	Density (g/cm^3)	Chemical React-ivity
Diamond	Cubic	Transparent, colorless	10	Insulator	1200	3550	3.51	Low
Graphite	Hexagonal	Black, opaque	1-2	Conductor	180-280	Sublimes at 3650	2.26	Low
Graphene	Single layer of hexagonal graphite	Transparent	-	Conductor	5300	-	2.2	High
Fullerenes (e.g., C60)	Spheres, tubes, other shapes	Variable	-	Variable	-	-	-	High
Carbon nanotubes	Cylindrical tubes of graphene	Black, opaque	Variable (5-7)	Variable (metallic or semiconducting)	6000	-	Variable	High
Charcoal	Amorphous	Black, opaque	Variable (0-2)	Variable (conductor or insulator)	10-40	-	Variable	Medium
Amorphous carbon (e.g., soot)	Irregular, disordered	Black, opaque	Variable (0-2)	Variable (conductor or insulator)	-	-	Variable	Medium
Lonsdaleite	Hexagonal diamond-like	Black, opaque	8-9	Insulator	900	1600	3.33	Low
Carbyne	Linear chains of *sp*-hybridized carbon	Metallic to semiconducting	Variable	Variable	Variable	-	-	Very high
Graphene nanoribbons	Narrow strips of graphene	Variable	-	Variable	-	-	-	High
Carbon aerogels	Ultralight networks of carbon fibers	Black, opaque	Variable (0-2)	Variable (insulator or conductor)	Variable	-	Variable	Medium
Diamond nanorods	Tiny needle-like structures of diamond	Transparent	Very hard	Insulator	High	-	-	Variable

The hardest known substance, diamond, has each sp^3 hybridised carbon covalently bonded to the other three carbons in tetrahedral form, whereas graphite comprises sp^2 hybridized carbon atoms.[8] Diamond transforms to graphite at lower pressures, above temperatures 1500 °C under an inert atmosphere. Lately, there has been a lot of interest in diamond as a platform for quantum electronics and its many potentials uses due to the steady nitrogen vacancy (NV) and other defect facilities. Diamonds are usually found in 2–3 nm clusters, with a diamond core encircled by a network resembling fullerene. Diamond traces have even been found in meteorites.[9] Bucky tubes, also known as carbon nanotubes (CNTs), are cylindrical molecular graphene forms that possess unique characteristics.[10] They can be further classified into two types: single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). CNTs have a thermal capacity twenty times greater than steel, which is why they are employed in bridges, chemical industries, aerospace materials, bulletproof jackets, and other applications. Carbon nanotubes have several uses in energy, health care, the environment, electronics, and materials. Since CNT is dispersed throughout the cement matrix, it performs stronger. CNT is a filler that gives concrete a self-sensing quality and increases its electrical conductivity.[11] Graphene is the newly discovered carbon allotrope with intrinsic carrier mobility and has excellent thermal conductivity with a honeycomb hexagonal structure along with sp^2 hybridization.[12,13] The outstanding properties of the carbon allotropes give way to various applications and scopes.[14,15] Because of its excellent adsorption capacity and ability to fine-tune its surfaces to meet specific properties, graphene aerogel is a material of choice for researchers. Their formation can be attributed to the interaction between van der Waals-generated 2-D graphene sheets, which have a relatively low density and a high surface area of 1300 m^2 g^{-1}.[16] Conical carbon nanostructures made from a sp^2 carbon sheet are called carbon nanohorns (also known as nanocones).[17] Nanohorns have a single closed end with a horn-like, cone-shaped cap, whilst CNTs have two closed ends with cap-like structures at each end. Organic solvents and water do not dissolve the same by nature.[18] Nanohorns can be created in large quantities and don't need a metal catalyst to be created. Studies on the use of nanohorn dahlia as drug carriers, biofuel cells, highly sensitive devices, and drug delivery systems have already been conducted.[18] carbon quantum dots (CQDs) are quasi-spherical nanoparticles made primarily of graphitic carbon, also known as sp^2 carbon or graphene and graphene oxide sheets joined by sp^3 hybridised carbon insertions that resemble diamonds, have amorphous to nanocrystalline cores, and are gaining popularity in research for carbon dots (CDs) based nanozymes in biosensing, photocatalysis, theragnostic, biomedicine, and catalytic treatment.[19–21] Hia *et al.*

reorganised CQDs into four categories: (i) graphene quantum dots (GQDs); (ii) carbon quantum dots (CQDs); (iii) carbon nanodots (CNDs); and (iv) carbon polymeric dots (CPDs), taking into account the basic structure and shell organisation. The other CD classification that was used was based on characteristics like their functionalities, association with metal frameworks, biomolecules, and nanostructures, as well as their fluorescence emission wavelength.[22]

Recent research has demonstrated that faster thermal processes can create conductive carbon films from pyrolyzed photoresists. Radiofrequency sputtering technique is found to be potent in creating ultra-smooth carbon films and carbon films with incorporated nanoparticles.[23] Inter-synthetic-carbon-allotrope (SCA) structures are produced by integrating several carbon allotropes, including the extensively studied 0D-fullerene, 1D-carbon nanotubes (CNTs), and 2D-graphene. Additionally, cross-dimensional hybrids are produced by combining 0D-fullerenes (both empty and endohedral fullerenes) with 2D-graphene/1DCNTs.[24] The remarkably diverse chemical composition of carbon nanospheres can be modified to incorporate more diverse chemical mixtures, like heteroatom-doping or the addition of noble/transition metal nanoparticles for specific applications (like oxygen reduction processes and heterogeneous catalysis). Electrocatalytic applications are already making use of recent advances in carbon nanostructures, such as carbon nano leaves, carbon sheets, carbon cages, and hollow carbon nanococoons.[25] Mesoporous carbon derivatives like mesoporous carbon nitrides [MCNs], mesoporous heteroatom-doped carbons, and mesoporous carbon-metal nanoparticle hybrids, have dramatically contributed to several of sectors because they can be endowed with a variety of desirable features.[26,27] There are many techniques available now for creating carbon nanoparticles. Nevertheless, in recent years, those that use energy-saving processes and economical starting materials have garnered the most emphasis.[28]

Carbon is generated by a wide range of techniques, including liquid phase exfoliation of graphite, chemical vapour deposition (CVD), epitaxial growth on SiC substrates, chemically exfoliated elimination of graphene oxide, micromechanical cleavage, and unzipping of carbon allotropes.[29] In the chemical vapour deposition process, hydrocarbons like acetylene, ethylene, propylene, methane, benzene, and toluene are pyrolyzed along with other carbon feedstocks like carbon monoxide and polymeric materials that have been mixed in the furnace system’s stream of inert gas. In comparison to other synthesis techniques, it also provides superior influence over growth parameters. The three primary elements influencing CNT growth in CVD are growth the outside temperature, the supply of carbon, catalyst, and environment.[30] The first practical method for producing graphene was micromechanical cleavage, which has been used to substances like MoS^2.[31] The Scotch tape is placed to the HOPG (highly ordered pyrolytic graphite) surface and so applies a normal force according to the exfoliation mechanics of micromechanical cleavage in this procedure. The graphitic layer gets thinner and thinner if one is very careful to repeatedly apply this normal force, eventually becoming single-layer graphene.[32] Several teams have been successful in reproducibly producing single-crystalline monolayer (ML) graphene SiC on a large scale. Rather than being grown directly on top of the substrate, graphene layer is developed on a complicated, non-conductive, carbon-rich interfacial layer that is only partially covalently attached to the SiC framework beneath it.[33] Between the graphene films and the SiC support, this intermediate layer serves as an electrical "buffer" film coating and serves as a matrix for further graphene expansion, which is identified by scanning tunnelling microscopy.[34]

As for carbon atoms, sp is the third possible hybridization. While it is now widely accepted that C atoms have sp^2 and sp^3 hybridizations, and that several of their derivatives exist and have been demonstrated through theory and research, the same may not be true for the still-speculative C allotrope with a sp hybridization. Carbon-atom wires (CAW) are real 1D wires of finite length, whereas Carbyne is a (speculative) 1D substance composed of single carbon atom chains with sub-nanometric diameter and infinite length.[35] Carbyne, also known as polyyne, is a carbon allotrope made up of one-dimensional linear chains of carbon atoms with alternating single and triple bonds; chains with only double bonds between the carbon atoms are known as cumulene.[36] Subsequently, using a polymer dehydro-hydrohalogenation and graphite sublimation process, Korshak *et al*. synthesised carbon materials that resembled carbyne and measured their auger and electron energy loss spectra. By using the fast-cooling carbon vapour method in the lab, Tanuma and co-workers produced carbyne-like crystals known as "carbolite" in 1995 and published the corresponding X-ray diffraction (XRD) data.[37]

Amorphous allotropes have an unordered structure and are not like crystalline materials like diamonds. They are champions of adsorption due to their large surface area, easily absorbing pollutants in water filters or storing gases for renewable energy. Since their properties are the same in all directions, unlike their crystalline siblings, they are isotropic and can be used in a wide range of applications.[38] The first free-standing amorphous carbon (MAC) monolayer has been discovered recently. A network of hybridised carbon atoms with a broad distribution of bond length and bond angle values makes up the amorphous material known as MAC. These atoms resemble sp^2 and sp^3 in nature. Rings with five to eight members make up

MAC.[39] Tetrahedrally bonded amorphous carbon (ta-C) is amorphous carbon with a very high sp^3 fraction (up to approximately 88%) that has a high percentage of tetrahedral bonding. The only form of ta-C that is currently accessible is in thin film form, which is typically grown using a variety of film deposition methods that involve energetic ions or plasma beams.[40]

SCOPE AND APPLICATIONS OF CARBON ALLOTROPES

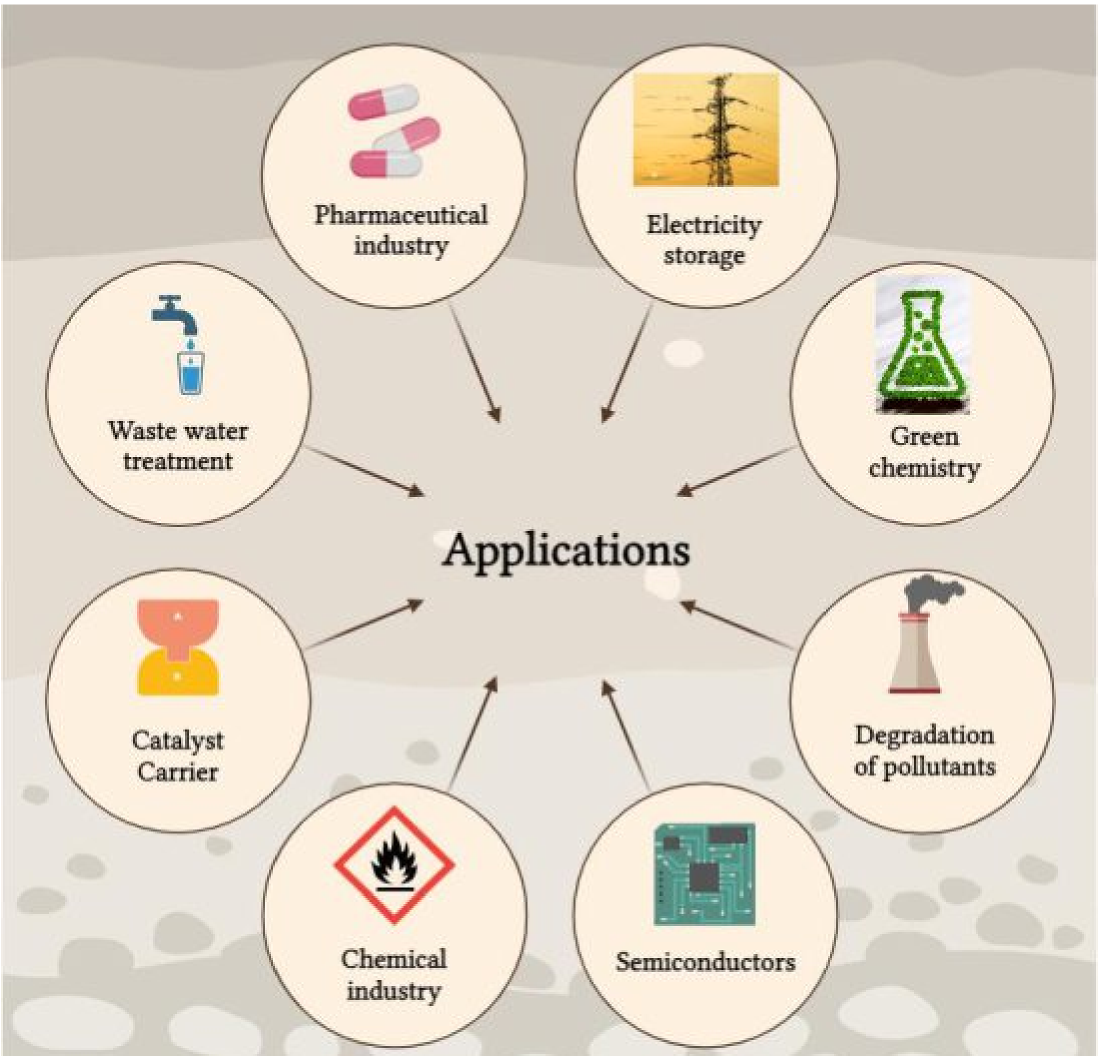

Figure 2: Recent Developments and Advancements in the Applications of Carbon Allotropes.

The carbon allotropes have found several applications in the field of pharmaceutical industry, storage of electricity, green chemistry, degradation of pollutants, semiconductors, chemical industry, catalysts, waste-water treatment, etc. The schematic representation on the scope and applications of the carbon allotropes have been presented in **Figure 2.**

Corrosion Inhibitors

Graphene has been used as corrosive protective layers on different metal substrates by including it with paints or wet-transferred graphene films on Cu and Ni foils. Graphene has excellent anti-corrosion and anti-oxidant potential in marine or salinity environments because of its amazing chemical inertness, ultrathin nanostructures, and higher stability up to 400 ºC in an ambient atmosphere.[41] The graphene layers on the surface of Ni wire improve the resistance against corrosion by acting as an ultrathin impermeable barrier by preventing direct contact between the shielded metal and corrosive substances and creating a more complicated channel for the penetrating solution. The application of graphene as a barrier on Cu or Ni foils against the hostile environment was mainly performed for the material created making the use of the popular chemical vapor deposition method.[42]

Energy Storage

Carbon compounds, being inexpensive, and having super conductance with sufficient stability, have been exhaustively checked for their scope as electrode materials for the storage of electrochemical energy with the construction of nanosheets into 3D arrangements allowing the direct molecule transfer and the large reactive surface.[43] Vlad and co-workers have recently found the application of vanadium oxides loaded on reduced graphene oxides (rGO) nanocomposites in the extensive use of electrochemical devices or lithium-ion batteries.[44] [45] T-carbon, a newly synthesized carbon allotrope, has been the potential material for next-generation energy devices in thermoelectric, hydrogen storage, lithium-ion batteries, etc. It has been a fluffy type of carbon material with high space between atoms, being a good application of hydrogen storage. In the future, T-carbon based rechargeable energy storage devices can be quickly charged due to the high diffusivity of Li ions.[46] Graphdiyne has been made up of benzene rings and butadiyne. It can be regarded as the novel allotrope of carbon as it possesses higher conductivity/ specific surface area/ specific porosity and high charge density.[47] Thus, it has applications in energy storage, catalytic reaction, phase separation, and optoelectronic devices.[48] Graphdiyne (GDY) can store Li^+ ions and Na^+ ions in the batteries because of the conductive and electron-rich layered structure with tunable cavities.[49] The prototypical GDY was created by catalysing hexaethynyl-benzene (HEB) cross-coupling reactions with copper, pyridine, and a relatively low temperature.[50] The manufacture of ultrathin GDY has since received a lot of focus, ranging from implementation of a metal catalyst-free method to interface reaction engineering.[51] For electrochemical energy storage applications, nano porous carbons (NPCs) with tailored pore size ranges and high surface areas are promising. Metal-organic frameworks (MOFs) with large pore volumes and high surface areas have been shown to make good precursors for synthesizing NPC materials.[52]

Applications of Graphene

The components built around graphene have significant functions in electrochemical energy storage devices such as super capacitors, fuel cells, metal-air batteries, light emitting diodes (LED) bulbs, antennas, and fabric sensors being cheaper and having ultra-high capacitances.[28,53] Further, they have been applied in biomedical engineering, especially in gene delivery, bioimaging in cancer therapy, diagnostics, and tissue engineering.[53,54] They have been used in printing technology, textile engineering, aerospace, etc.[53] Their higher optical, thermal, and electronic properties have been used to catalyze organic transformations through electron transport in redox processes alongside organic molecule adsorption/activation through π–π and electrostatic interactions.[55]

Waste water Treatments

Water contamination and pollution have been among the most worrying and significant problems on the earth due to releasing harmful industrial effluents into rivers.[56] Owing to their low density, good chemical stability, structural diversity, and suitability for large-scale production, carbon-based materials have been thoroughly investigated for adsorption applications.[57] Additionally, graphene has been known to play the role of an antibacterial agent not only by the damage to the metabolic pathway of the bacterial cell but also by disruption of its membrane via its sharp edges. This antibacterial property during waste-water treatment can be enhanced under solar irradiation for the complex metal oxide-based graphene and graphene derivatives-based nanocomposites.[58] (**Fig. 3 and Fig. 4**).

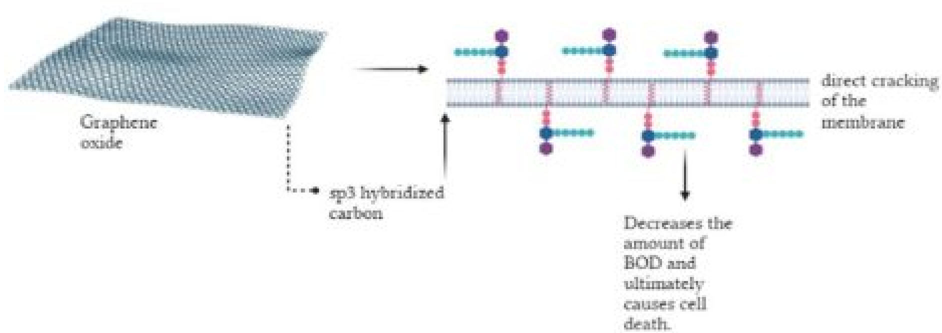

Figure 3: Waste Water Filtration using Graphene Oxide

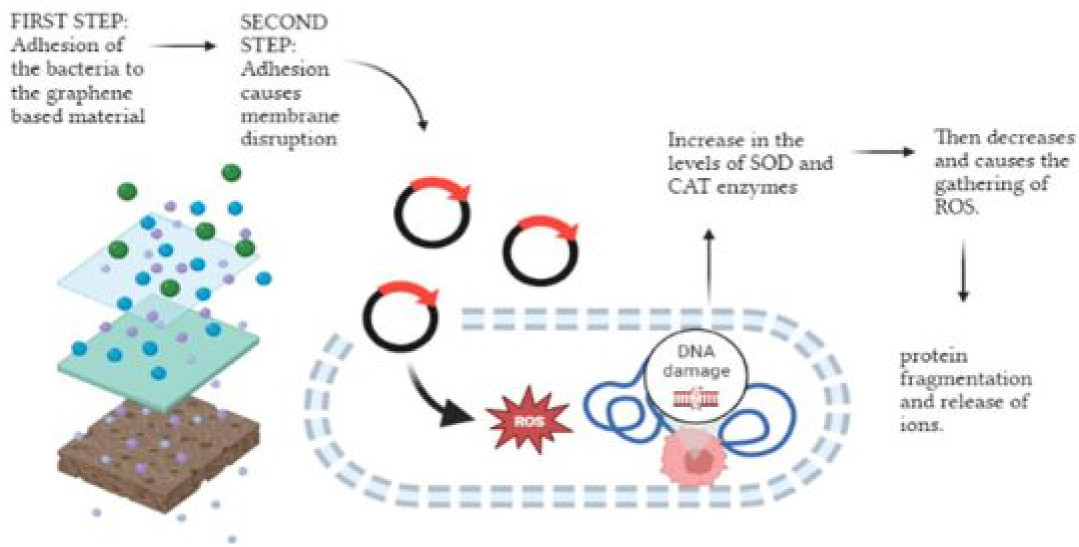

Figure 4: Mechanism of Action of Water Purification

Environmental Applications

Due to its properties like high mechanical resistance and charge generation, graphene and its derivatives are used in green environmental chemistry. Due to their high effectiveness, excellent stability, durability, and cost-effectiveness, nanomaterials become good candidates for catalysis in green chemistry.[59] Superior iron oxide core binding strength, excellent resilience to organic solvents, and strong mass exchange kinetics are all benefits of silica coated nanoparticles.[60,61] Graphdiyne, a 2D carbon nanomaterial allotrope of carbon, has been applied within the domain of energy storage, transformation, and environmental protection.[62]

For the creation of different biosensors, the interaction of quantum dots (QD) with carbon allotropes has been studied by several research groups for their applications in biomedical imaging and environmental applications. The DNA sensing might be accomplished via the hydrophobic and π-stacking interactions between graphene oxide (GO) and the nucleobases of QD-labelled oligonucleotide probes. The combined usage of QDs and graphene has also been explored for the real-time imaging of targeted live cell/tumour and cancer treatment.[63] Further, such graphene and magnetic graphene nanoparticles have been appointed as adsorbents for heavy metal ions as well as organic pollutants by Wang and co-workers. Many transition-metal oxide graphene hybrids have been used to degrade harmful organic pollutants, along with creating a few sensor devices to analyse pollution using graphene-based materials.[64]

Others

Graphene oxide and related materials have been used in biorefinery-related conversions as catalysts for converting biomass-derived resources.[65] Graphene and its biomaterials have found a lot of biomedical applications, e.g., transplant devices, invasive instruments, implants, biosensors, etc., owing to its higher conductance. Further, graphene nanosheets have also found enough inhibitory potential against *E. coli* and suppression of its catabolism and anabolism (< 13%).[66–68] MiRNA electrochemical detection makes extensive use of a variety of carbon nanomaterials, including CNTs, g-C_3N_4, CDs, and graphene QDs, as well as graphene and its derivatives.[69] Recently, inorganic nanoparticles (NPs), such as those made of metals (such as gold, silver), semiconductors (such as quantum dots), carbon dots, carbon nanotubes, or oxides (such as iron oxide), have been thoroughly studied for application in oncology.[70] Target analytes of concern, such as viral infections, proteins, DNA, and volatile chemicals, have size scales that are comparable to those of nano-electronic devices based on 1-D and 2-D nanoscale materials. This allows for recognition down to the single molecule level and biological sensor functionality.[71] We may now learn more about meningitis using new tools and perspectives provided by nanomedicine, which may also give meningitis patients renewed hope.[72] Nanoparticles offer an advantage for meningitis and brain infection patients in early diagnosis by permeating the blood brain barrier and provide targeted drug action.[73] Recent progressive research done on the combination of the magnetic nanoparticles (MNPs) and carbon nanotubes (CNTs) to generate structurally and physiochemically different hybrid materials that have varied applications in magnetic material organization, magnetic resonance imaging, therapeutic hyperthermia and newer drug delivery systems.[74] Currently research has been focused on the advanced radiology techniques involving the synergistic effects of radioisotopes and nanomaterials. β-rays emitting radioisotopes like radioactive ^{131}I and radioactive gold particles are used for the drug delivery systems in cancer therapies.[75] The generation and applications of luminous nanoparticles (LNPs) for chemical and biological investigation and imaging is the current focus of research. [76]

Nanocellulose, having good mechanical strength, thermal and electrical conductivity, flexibility, and nano porous nature with good adsorption properties, has been used as a dispersing agent which disintegrates the carbon nanoparticles in the aqueous phase.[77] It has been used in biomedical fields along with water purification, construction of fire retardants, etc.[78] Nanoparticles (NPs) can communicate with internal organelles and different metabolites when they infiltrate plant cells. Both carbon nanotubes and fullerenes have the potential to alter the level of gene expression in plant-specific metabolism. As a result, they can act as powerful inducers of a variety of commercially significant specialized metabolites (SMs), which are crucial for plants to adapt to harsh environments. A large number of these SMs are also biologically active and have many uses.[79]

Liquid crystal displays (LCD) used in electronic devices such as television, mobile phones, etc., have been made from indium tin oxide. Its shortage has necessitated the production of indium tin oxide-free optoelectronic devices. Due to their transmittance and sheet-resistant properties, carbon-based materials have also found applications in manufacturing such home-entertainment devices.[80,81]

The surfaces of instruments or devices and places can be safeguarded by the antibacterial metal matrix nanocomposites (MMNCs) coatings with a view to prevention of germs from adhering to the surface as the growth of bacterial strains may be slow on smooth surfaces. This can be achieved by discharging the chemicals, harming the bacteria on MMNC coatings, or using graphene-based antibacterial and tribomechanical nanofiller.[82]

Graphene-based nanomaterial has also found applications in sustainable catalysis,[83] photocatalysis, and environmental chemical science.[84] The larger surface area, low costing manufacturing process, and sufficient stability have attracted considerable attention to sustainable catalysts.[84] The discovery of nitrogen-doped carbon nanotubes (NCNTs) as highly potent electrocatalysts for oxygen reduction reactions (ORR) in alkaline fuel cells, along with their use as effective catalyst supports and metal-free catalysts.[85,86] Since carbon quantum dots (CQDs) have strong electrical and optical properties, they are non-toxic and safe green materials with the potential to enhance photocatalysis.[87] The functions played by CQDs as photocatalysts are primarily split into two categories: the first is the up-conversion effect, and the second is the ability to transport electrons, or both.[88] Novel application of the carbon nano lubricants that uses the carbon nanotubes as better antifriction material as compared to various commercially available lubricating oils. The physical interaction between the nanoparticles and the rubbing surfaces was primarily to be related to the anti-friction qualities. The primary reason for this is that, under specific stress circumstances, the spherical form of carbon nanomaterials can reduce the sliding contact area and stickiness.[89]

SUMMARY

The present work reports the applications of allotropes of carbon considering their future for the environmental applications with their broad applicability and versatility in futuristic and environmental fields such as energy storage, wastewater treatment, corrosion inhibitors, biomedical, etc. Despite the several advantages of graphene-based materials, it has been known to possess some limitations regarding their toxicity and safety concerns in pharmaceutical and medical components due to the generation of free radicals, physical toxicity, and adsorptive properties.

Graphene allotrope and its materials have found use in various sectors, including energy storage devices, biomedical engineering, printing, textile engineering, aerospace, and other fields. In marine or salt conditions, graphene possesses strong anti-corrosion and anti-oxidant properties. The layers of graphene on the exterior of Ni wire have been found to increase corrosion resistance. T-carbon has been recognized as a viable substance for energy-related devices of the future such as thermoelectric, hydrogen storage, lithium-ion batteries, etc. Because of the high diffusivity of Li ions, T-carbon-based rechargeable energy storage devices can be charged fast ultimately. In the light of its conductive as well as electron-rich layered framework with adjustable cavities, graphdiyne can store Li^+ and Na^+ ions in batteries, illustrating their application in sodium or lithium-ion cells. The ability of graphene to serve as an antibacterial agent in wastewater treatment has been demonstrated through both harm to the metabolic pathway of the bacterial cell and rupture of the cell's membrane due to its sharp edges. Even it found its use in catalysis, photocatalysis, degradation of organic pollutants, chemical, environmental science, etc. Carbon allotropes will play a significant role in creating a green future for the newer generation.

COMPETING INTERESTS

The authors declare no competing financial interest.

DATA AVAILABILITY

No new data has been generated in this manuscript.

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