NANO CARBON ANALOGUES, PROPERTIES AND SYNTHESIS

Gopika R.[a,b*], Muhamed Ashraf P.[a], Anjana C.S.[a]

gopikar198@gmail.com

a- ICAR- Central Institute of Fisheries Technology, Cochin, Kerala

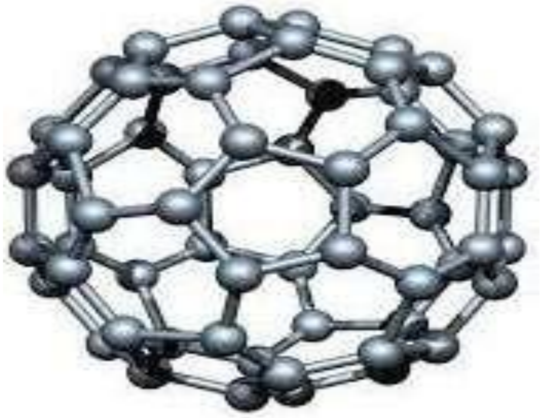
b- Cochin University of Science and Technology, Kerala

Introduction

Carbon stands as an unparalleled and essential element within our realm, ranking as the sixth most prevalent element in the cosmos, the fourth most abundant in the solar system, and the seventeenth most frequent component in the Earth's crust. Its occurrence is estimated to range from 180 to 270 parts per million, and notably, it claims the position of the second most prevalent element in the human body, trailing only oxygen. Despite its limited presence in the earth's crust, comprising only about 0.2% of the total planetary mass elemental carbon assumes aprofoundly vital role owing to its unique ability to engage in bonding interactions with both lighter elements and its own molecular entities. Prior to the invention of third allotrope of carbonit was believed that carbon exist only in two distinct form that is graphite and diamond. Carbon allotropes are; atomic and diatomic carbon, Graphite and its derivatives, diamond, amorphous carbon, nanocarbon, glassy carbon, carbon nanofoam, carbide derived carbons. Among these allotropes, nano carbon analogues are, fullerenes, carbon nano tubes, carbon nano horns and carbon dots. Carbon-based nanomaterials are a group of nanoparticles made from carbon, which have been studied a lot because of their unique properties. These materials can be altered to perform different function, which makes them interesting for new technologies and solving modern problems. During the modern era, nanotechnology has gained significant focus owing to its immediate potential in creating novel materials endowed with distinctive properties. Numerous attributes, including exceptional directionality, expansive surface area, and remarkable flexibility, render nanostructures highly suitable for a diverse array of applications. This fundamental reason drives the curiosity of researchers from various scientific disciplines towards these materials, given the pivotal roles they have assumed in various emerging technologies. Here we discuss about the historical background, synthesis and properties ofcertain selected nano carbon analogues.

Fullerenes

The identification of a molecule resembling a soccer ball, comprising 60 carbon atoms, emerged somewhat serendipitously during investigations into the composition of matter in outer space. In the course of their inquiry, Donald Huffman and Wolfgang Kratschmer postulated the existence of a molecule resembling a soccer ball, with 60 carbon atoms. However, at that time, no concreteevidence was available. With the help of infrared (IR) spectroscopy and mass spectroscopy, these two scientists subsequently substantiated the presence of this captivating new molecule, consisting 60 carbon atoms intricately bonded into a spherical configuration. The outcomes of this groundbreaking discovery were documented in the journal Nature in 1990. Kroto and Smalley bestowed the term "fullerene" upon the group of molecules detected in the gaseousphase experiments, owing to their likeness to the geodesic domes envisioned by R. Buckminster Fuller. The designation "buckminsterfullerene," commonly referred to as "buckyball," was specifically assigned to the C_{60} molecule, while the broader label "fullerene" encompassed C_n cage molecules constructed from an arrangement of hexagonal and pentagonal facets. They consist of 12 pentagonal and 20 hexagonal facets made up of 60 carbon atoms which are sp2 hybridized and bonded covalently. Buckyballs possess distinctive characteristics including notably elevated superconductivity (33K), icosahedral symmetry, and the ability to form monodisperse nanostructures that can be organized into both film and crystalline arrangements. C_{60} is soluble in benzene, single crystals of it can be grown by slow evaporation from benzene solution, they act as electrophile in chemical reactions, has property of ferromagnetism. 26% volume of face centered cubic fullerene unit cell is empty, doping with alkali atoms like potassium will generate K_3C_{60}. C_{60} is an insulator but when doped with alkali atom it becomes electrically conducting.



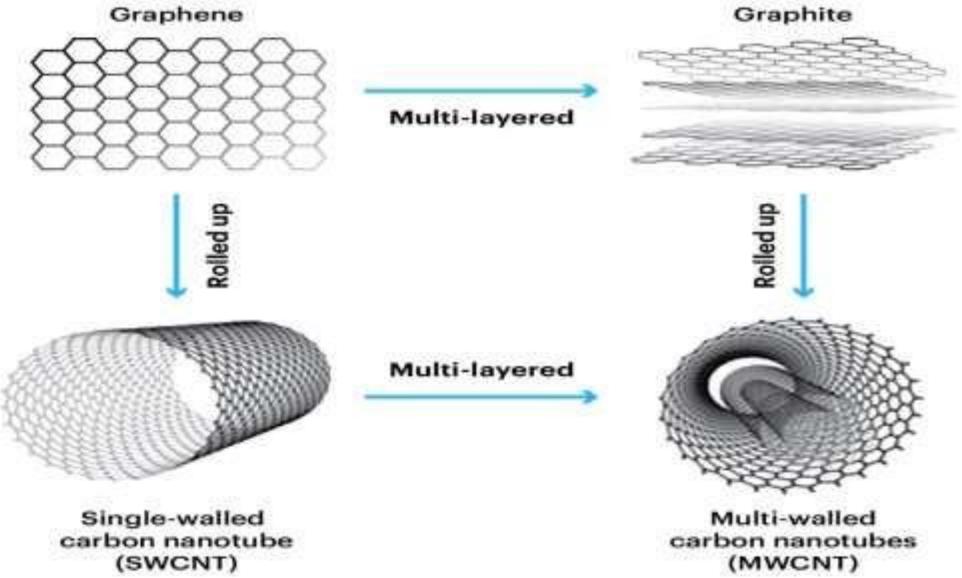
Structure of fullerene

Recently C_{60} is mainly synthesized by arc method in which a spark is generated between pieces of graphite in a chamber filled with helium gas. Later contact arc method was used in which flowof electricity is obtained by a smaller carbon rod touching a bigger fixed carbon rod. The heat generated at the contact point turns the graphite into tiny particles called soot and fullerenes. These particles stick to the walls of a cooled container. A special setup is used where the materials slide against each other. The container is kept in water to stay cool. This method can produce a good amount of C_{60}/C_{70} every day. The soot generated contain about 13% of C_{60}, 2% of C_{70} etc, which is separated by Soxhlet extraction. Typically C_{60} is separated from higher fullerenes by liquid chromatography and the fractions are identified by optical spectroscopy and nuclear magnetic resonance (NMR) spectroscopy data, which can also provide indication on purity. Fullerenes can be synthesized through various methods like arc discharge and laser ablation, enabling the exploration of their remarkable properties. Their exceptional stability, diverse electronic properties, and potential applications in fields ranging from nanotechnology and medicine to energy storage underscore their significance in modern science.

Carbon Nanotubes (CNT)

The discovery of fullerenes has shown us exciting things about nano carbon structures and by arranging sp^2 carbon atoms in a specific way, we can create new structures with unique properties. Carbon nanotubes serve as a best example, which was discovered exactly a decade after the discovery of fullerenes. Carbon Nanotube (CNT), also called bucky tubes, was initially found in 1991 accidently, while studying the surfaces of graphite electrodes used in an electricarc discharge. Later, in 1993, Iijima and Ichihashi successfully the synthesised of a single-wall carbon nanotube with a diameter of just 1 nanometer. But, in 1952 Radushkevich and Lukyanovich, two researchers, presented a clear picture of 50 carbon nanotubes in the Journal of Physical Chemistry while working in the Soviet Union. During the biennial 14th Carbon Conference at Pennsylvania State University in 1979, John Abrahamson provided supporting evidence for carbon nanotubes. Carbon nanotubes can be categorized into two main types based on their structures. The first type is single-walled carbon nanotubes (SWCNT), which consist of just one layer of graphite. The second type is multi-walled carbon nanotubes (MWCNT), which have multiple layers of graphite arranged concentrically. A SWCNT have a diameter of 2nm and a length of 100 μm, making it effectively a one-dimensional structure called nanowire. Three different structures based on orientation are possible for SWCNT, armchair, zigzag, chiralstructure. Nanotubes are commonly enclosed at both ends, and at the tube ends, metal particles are often discovered. This provides evidence for the catalytic function of these metal particles in the formation process.

Carbon nanotubes possess a fascinating trait: they can be either metallic or semiconducting, depending on the tube's diameter and chirality. Typically, the synthesis yieldsa blend of tubes, with approximately two-thirds is semiconducting and one-third is metallic. The metallic tubes have an armchair configuration. When in the metallic state, nanotubes exhibit remarkably high conductivity. It is approximated that they can conduct up to a billion amperes per square centimeter. Magnetoresistance is when a material's resistance changes when a magnetic field is applied to it. Carbon nanotubes show this effect at low temperature. Single- walled nanotubes (SWNTs) can have metallic properties, with resistivity ranging from $5.1 \times 10^{-6}$to 1.2×10^{-4} ohm cm. The hexagonal lattice structure of carbon atoms leaves one valence electron free in each unit, contributing to the electrical properties. Multi-walled carbon nanotubes (MWNTs) show diffusive or quasi-ballistic transport properties. CNTs exhibit exceptional strength in the axial direction. Their Young's modulus ranges from 270 to 950 GPa, and tensile strength varies between 11 and 63 GPa. CNTs show flexibility and resistance to breaking when bent, indicating relative softness in the radial direction. This radial elasticity influences mechanical properties, particularly in nanocomposites. CNTs remain intact even under significant deformation. They can withstand bending without fracturing and endure high pressures and shock waves without breaking. Mechanical properties of CNTs are influenced by their diameter. Smaller-diameter tubes can have theoretical Young's modulus values comparable to diamond, while increasing diameter enhances mechanical properties until they approach those of planar graphite. Reported values for Young's modulus range from 320 to 1470 GPa.

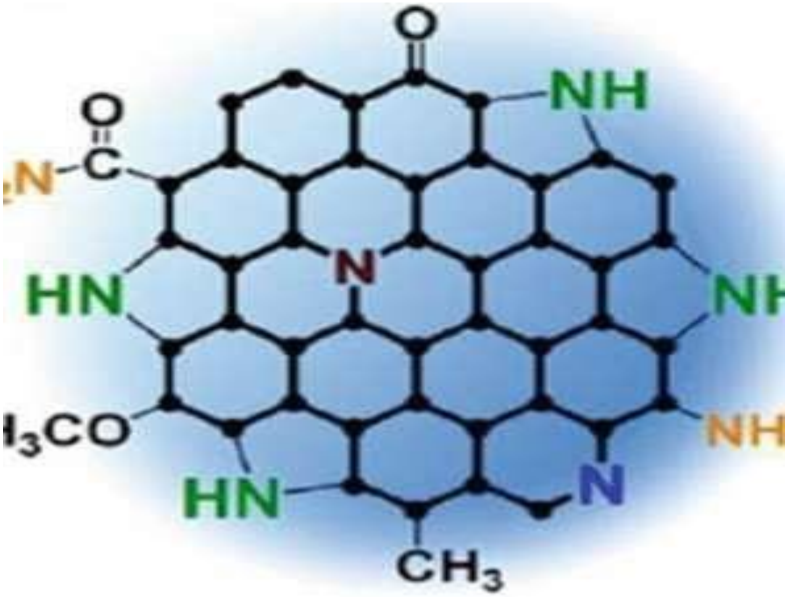


Graphical representation of SWCNT and MWCNT

CNTs can be synthesized mainly through 3 methods, arc discharge, laser ablation and chemical vapour deposition. The arc discharge method involves heating carbon atoms to high temperaturesuntil they become plasma. This happens in a specific pressure range with inert gas. An electricarc forms between close graphite electrodes. This creates carbon plasma at temperatures above 3000 degrees Celsius. To make better carbon nanotubes (CNTs), more research is needed on howthe plasma technique works. This method produces flexible CNTs with fewer defects. A mix of gases including argon, helium, nitrogen, carbon, cobalt, and nickel is used for this. Scientists have studied the properties of this plasma at different temperatures. These studies provideinsights for future CNT synthesis using plasma techniques. Laser ablation works like arc discharge but uses a laser to heat carbon. This vaporizes the carbon, and it condenses with a gas stream. A study looked at laser types for making SWCNTs. Laser strength affects SWCNT growth. UV laser has a narrower effective range than infrared. Changing laser fluence results in varied SWCNT diameters. A large amount of CNTs can be made at normal temperature and pressure using pulsed laser on graphite in metal nano-sol. Metal nano-sol acts as a catalyst in thisprocess. CVD for CNT synthesis needs a metal catalyst, often cobalt, nickel, copper, or iron. Chemical deposition is cost-effective, high-yield, and controllable. Some say CVD-made CNTs aren't as good as arc or laser ones. The catalyst helps split hydrocarbons into carbon andhydrogen at lower temperatures. Researchers, like Chen, used nano-MgNi to make MWCNTs via pyrolysis of CH4 gas. They optimized the reaction for methane conversion and carbon yield in CVD. Their unique properties, along with one-dimensional nature, hold promise for transformative applications in fields such as electronics, materials science, and nanotechnology.

Nano Carbon dots (CDs)

Fluorescent carbon dots were serendipitously discovered during the surface passivation of carbonnanotubes by Xu.et.al in 2004. This finding resulted from observing enhanced luminescence due to surface defects and dispersion efforts. The breakthrough occurred when a fast-moving fluorescent band with color-changing properties under UV light was accidentally observed during the electrophoretic purification of single-walled nanotubes. Analytical characterization revealed the composition: C 53.93%, H 2.56%, N 1.20%, and O 40.33%, composed mainly of carboxyl groups and entirely devoid of metals. C-dots are typically smaller than 10 nm in size. They possess abundant oxygen-containing groups, including sp3 carbon and hydroxyl-attached carbon groups. The interlayer spacing of C-dots measures 0.42 nm, exceeding the 0.33 nm of graphitic interlayer spacing. This suggests a lower degree of crystallinity compared to graphite. Different starting materials yield C-dots with varying structures, ranging from graphitic toamorphous. Non-toxicity and high biocompatibility, water solubility, an adjustable luminous range, high photo stability, an absence of light flicker, easy functionality, rich sources of cheap raw materials, easy large-scale synthesis, have resistance to photo bleaching etc. are the unique properties of CDs. Method of CDs synthesis can be divided into two categories top down and bottom up. In top- down approach, larger carbon precursors are broken down into smaller CDs bymethods like arc discharge, laser ablation, electrochemical oxidation, and so on. Commonly used carbon precursors are graphite, carbon nanotubes, carbon black, activated carbon and graphene oxide, etc. Summary of different synthetic methods given in table 1.



Hypothetical structure of Carbon nano dots

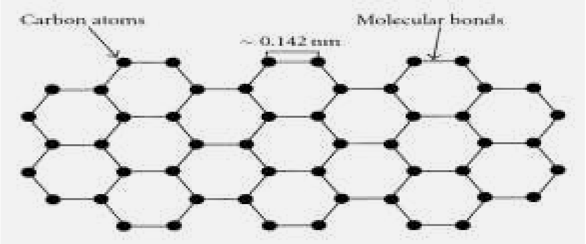
Table 1: summary of different methods synthesis of CDs

Method of synthesis	**advantages**	**disadvantages**	**remarks**
Arc Discharge	Small particle sizes	Complex composition and impurities	Intrinsic fluorescence, no surface modifications needed
Laser Ablation	Successful multi-photon imaging	Yields non-fluorescent carbon nanoparticles (CNPs)	Generates fluorescent CDs from carbon nanoparticles
Electrolysis	Water-soluble CDs from carbonaceous materials	Variable particle sizes	Achieved using different electrode setups
Combustion	Uses readily available raw materials	Requires oxidative acid treatment	Higher dispersibility in CDs
Template Method	Controlled synthesis process	Difficulty in template separation	Potential for uniform particle size

Pyrolysis	High PL quantum yield	Formation and separation challenges	Large-scale CDs obtained via oxidation of carbon precursors
Microwave Synthesis	Novel, green, and efficient	Non-uniform particle size distribution	Rapid synthesis within minutes
Hydrothermal/Solvothermal	High PL quantum yield in one step	Non-uniform CD size, impurities	Simple and controllable reaction

Facile synthesis techniques and remarkable properties of carbon dots have the potential to revolutionize diverse fields ranging from electronics and photonics to biomedicine and environmental remediation.

The groundbreaking discovery of graphene earned Andre Geim and Konstantin Novoselov the Nobel Prize in Physics in 2010. This serendipitous isolation of graphene using adhesive tape and its subsequent exploration ignited a wave of research and innovation across various industries. Graphene, a monolayer of carbon atoms arranged in a 2D honeycomb lattice with a C-C bond length of 0.142 nm, exhibits remarkable properties: high electron mobility of 250,000 cm^2/Vs, impressive thermal conductivity of 5000 W/m-K, and an exceptional Young's modulus of 1 TPa. Graphene serves as the fundamental building block for other carbon materials; stacked graphene forms graphite, while rolled-up sheets create carbon nanotubes. The quality of graphene significantly affects its electronic and optical attributes, necessitating high-quality, single- crystalline graphene for optimal performance in electronic applications. Different methods of graphene synthesis is summarized in table 2 given below.



Schematic representation of graphene sheet

Table: summary of different methods synthesis of graphene

Method of synthesis	**Advantages**	**Disadvantages**	**Product quality type yield**

Exfoliation	Initial method. Simple setup and equipment. Low cost method	Labor-intensive process Prone to structural defects and impurities	Developed by Nobel laureates Andre Geim and Konstantin Novoselov Yields monolayer graphene, but quality can be compromised Presence of defects affects electrical conductivity
Scotch Tape Method	Facilitates large-scale graphene production Easily accessible materials	Requires repetitive peeling Quality control is challenging	Effective for obtaining monolayer graphene structural defects observed through Raman spectroscopy Graphene structure not fully restored after thermal reduction
NMP Exfoliation	Potential for defect-free monolayer graphene	High cost and boiling point of solvent	Not recommended due to solvent expense
Fe-Assisted GNS Production	Eco-friendly alternative to toxic reducing agents	Method may have specific requirements	Utilizes Fe as a reducing agent toobtain GNS Avoids the use of poisonous gases. Like hydrazine and hydroquinone
Chemical Conversion of Graphite to GO	Economical alternative to graphene synthesis. Hydrophilic nature aids exfoliation	Oxygenation disrupts electronic structure. O behaves as an insulating material	Promising method due to cost-effectiveness. Chemical reduction could partially restore conductivity
Hummers Method for GO Synthesis	Established method for GO production	thicker GO films compared to pristine graphene	Utilizes oxidants like H2SO4, HNO3, and KMnO4. Involves oxidation of graphite
Thermal Reduction of GO	Removal of oxide functional groups	Loss of mass and structural defects	Heat treatment reduces rGO's functional groups. Dubin et al.'s low-temperature approach

Graphene a 2D wonder exhibits extraordinary properties, which enable it to open up an array of promising applications, from flexible electronics to advanced coatings and energy storage devices. With the ongoing innovations and collaborations across disciplines, graphene's journey from the laboratory to real-world applications is destined to reshape industries and enrich our technological landscape, driving us toward a more sustainable and interconnected future.

Conclusion

In the realm of nanocarbon analogues, the synthesis and properties of fullerenes, carbon nanotubes, carbon dots, and graphene have unveiled a universe of possibilities. These remarkablematerials, born from the world of nanotechnology, have displayed unparalleled properties that are reshaping industries and scientific frontiers alike. With fullerenes' unique molecular structure, carbon nanotubes' exceptional strength and conductivity, carbon dots' versatile luminescence, and graphene's two-dimensional wonder, the potential for innovation across fields such as electronics, materials, medicine, and energy is boundless. As we embrace the future, the ongoing exploration of these nano carbon analogues promises to usher in an era of unprecedented advancements, offering solutions to complex challenges and pushing the boundaries of what is achievable on the nanoscale.

Reference

1. Malik S. (1985). *Nature*, *318*: 162-163.
2. Nasir S., Hussein M.Z., Zainal Z. and Yusof N.A. (2018). *Materials*, *11*(2), : 295.
3. Baig N., Kammakakam I. and Falath W. (2021) *Materials Advances*, *2*(6), : 1821-1871.
4. Dresselhaus M.S., Dresselhaus G. and Eklund P.C. (1993). *Journal of materials research*, *8*(8),.2054-2097.
5. Chen J., Wei S. and Xie H. (2021). *Journal of Physics: Conference Series* (Vol. 1948, No. 1, :012184). IOP Publishing.
6. Himaja A.L., Karthik P.S. and Singh S.P.(2015). *The Chemical Record*, *15*(3), : 595-615.
7. Wang Y., Zhu Y., Yu S. and Jiang C. (2017). *RSC advances*, *7*(65),: 40973-40989.
8. Dasari B.L., Nouri J.M., Brabazon D. and Naher S. (2017). *Energy*, *140*, : 766-778.
9. Charles and Owens, Introduction to Nanotechnology, 2006, Wiley Student Edition.