Synthesis of Nitrogen-doped Carbon From Palm Flowers

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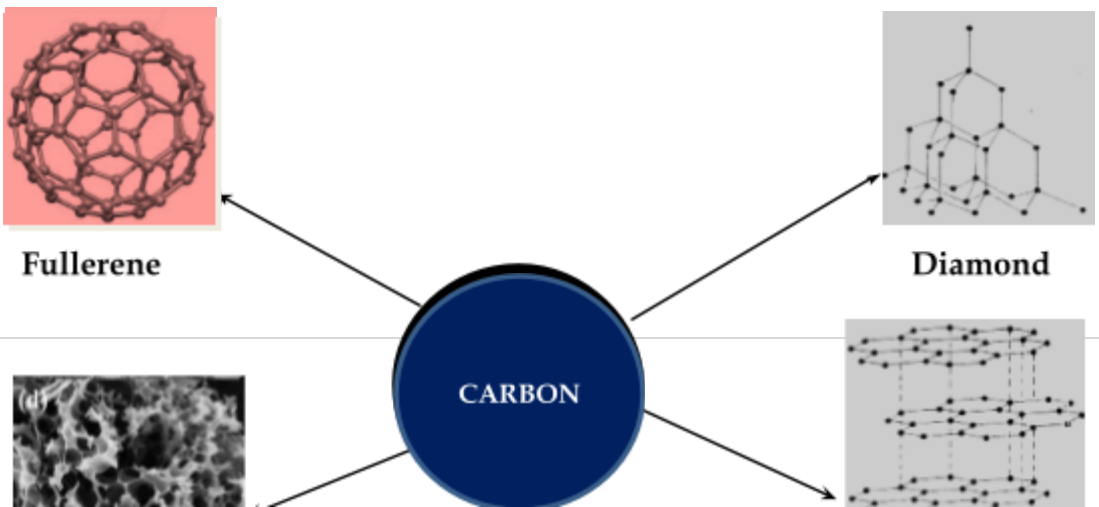
Abstract

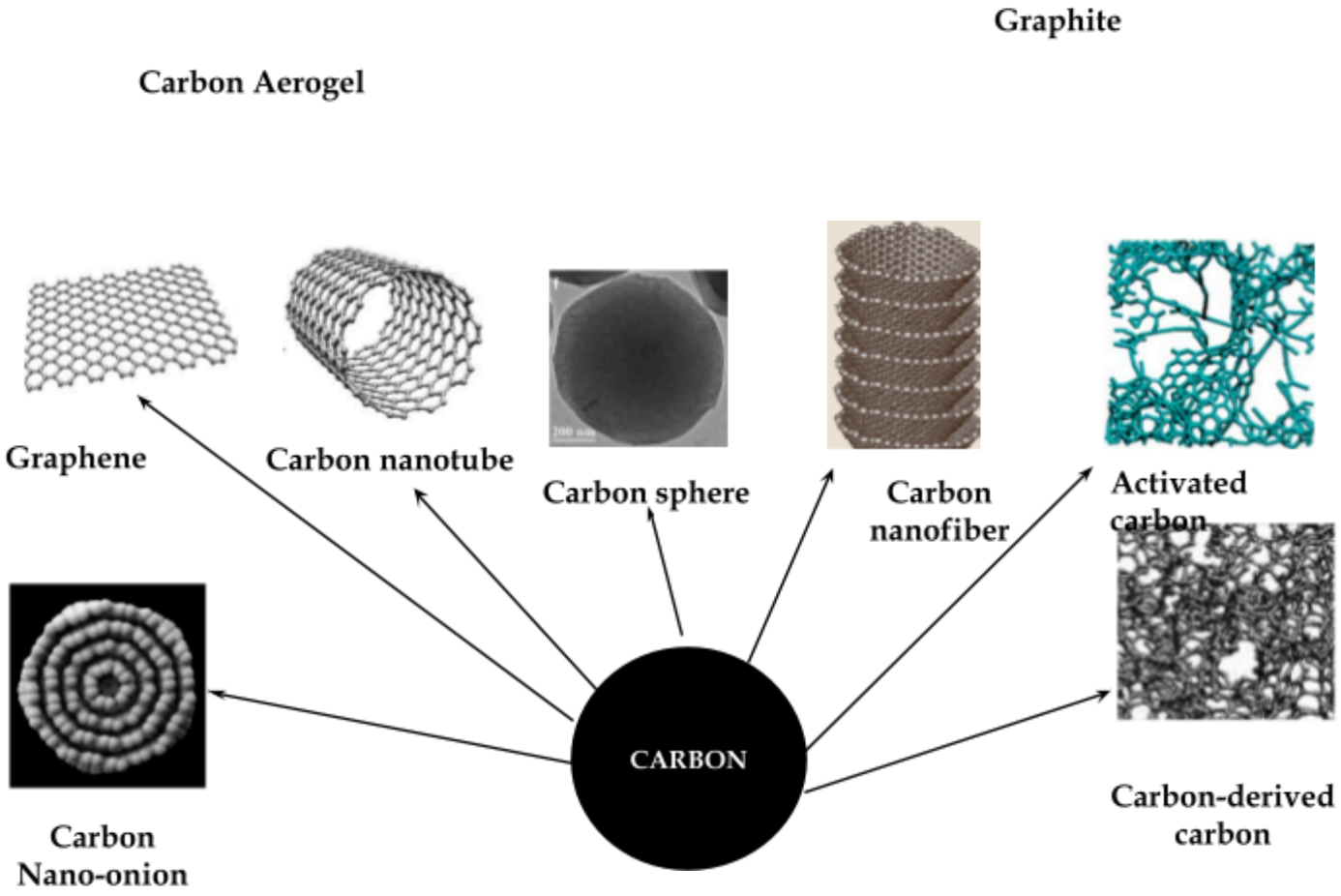
Biomass-derived carbon possesses immense potential in terms of its ecological ramifications, relative ease of synthesis and abundance. Carbon and its many allotropes offer a wide range of properties that can be used for various purposes. Carbon doped with heteroatoms in particular, can show excellent electrochemical applications, such as high capacitance, conductance, etc.

In this report, the diversity of carbon and its unique properties are put forth, followed by its applications in chemistry (including, but not limited to: electrochemistry, surface chemistry etc.) A particular case study of extracting carbon from palm flowers and doping it with nitrogen is taken up subsequently and various methods of synthesis employed are discussed.

1: Introduction

Carbon is the element of life. It is the fourth most abundant element in the universe by mass. It has unique properties due to its electronic configuration [He] $2s^2$ $2p^2$ which gives it its tetravalency, that is, the ability to form four covalent bonds with itself or other elements to fill its valence shell. Its ability to covalently bond with itself lends to the fact that it forms various **allotropes.** Allotropes are defined as different structures for the same element [1] in the same physical state, i.e., the only variation is in the chemical bonding and the link between atoms. Illustrated below are a few allotropes of carbon.





Allotropes of carbon exhibit variation in physical properties owing to their different structures. For example, diamond is considered to be one of the hardest substances, shines due to total internal reflection, and exhibits very poor electrical conductivity. On the other hand, graphite, another allotrope of carbon, is amorphous, is blackish in colour and an excellent conductor of electricity.

However, carbon is not limited to just these two allotropes. In addition to this, a host of allotropes and forms of carbon are present or can be synthesized, each with its own desirable property that can be exploited. A few of these are mentioned below.

1.1: Graphite

Graphite has a simple, planar, multilayered structure. It consists of only carbon atoms such that each carbon atom is surrounded by three other carbon atoms. Out of the three bonds formed by a carbon atom, two are single bonds and one is a double bond. This double bond consists of a sigma bond and a π bond – the π bond is weaker and electrons present in this bond are delocalized across the plane of the

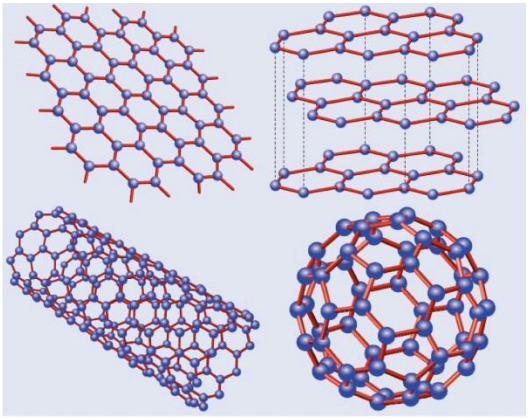
The golden-yellow KC_8

layer. Hence, graphite conducts electricity across the plane but not perpendicular to it.

There also exist van der Waals forces between the layers that are weak in nature, therefore, the layers slide past each other with relative ease and graphite is generally amorphous.

Graphite has multiple industrial and chemical uses. It is used in refractories for making crucibles to hold molten metal. It is also used in brake shoes and also as a lubricant. Graphite is further used as a primary source of carbon in zinc-carbon batteries. A mixture of graphite and clay is used in the deceptively-named lead pencils. Certain graphite-intercalation compounds have also been created, wherein host molecules or atoms get sandwiched between layers of graphite. This allows for interesting compounds which can exhibit superconductivity [2] such as KC_8.

1.2: Graphene



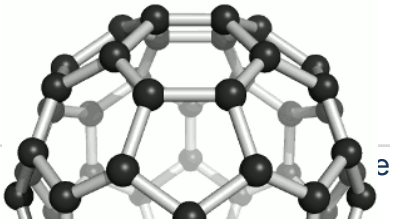
Graphene is a planar allotrope of carbon which has a hexagonal "honeycomb" lattice structure. It can be considered as an individual layer of graphite. Graphene is composed solely of sp^2 hybridised carbons, which have a delocalized cloud of π electrons, as in the case of graphite. Graphene is, in a sense, the fundamental allotrope. This is because graphene can be stacked, rolled or bent into various configurations to form other allotropes of carbon. For example, stacked graphene layers form graphite, rolled graphene sheets form single-walled carbon nanotubes etc. as illustrated on the right.

It was first isolated in the UK in the University of Manchester by Andre Geim and Konstantin Novoselov using Scotch Tape to peel off layers of graphite. They received the Nobel Prize in Physics for the same in 2010. The most widely-used process for the synthesis of graphene today is **mechanical exfoliation**, which is the extraction of individual layers of graphite. It is not very cost-effective and hence, newer, economically-viable methods of graphene isolation are being discovered.
Graphene has numerous potential applications in a variety of fields ranging from medicine, biology, electronics, energy generation and storage to environmental science. Among them, the most significant are listed as follows:

- Introduction of graphene nanoflakes into the polymerase chain reaction has increased the production of DNA and reduced PCR cycles by upto 65% [3]. This is largely attributed to the increased thermal conductivity that graphene provides.
- Graphene is extensively used in touchscreens, LCDs, organic photovoltaic cells, OLEDs etc. because of its high electrical conductivity and its transparency. [4]
- Graphene-based water filters could potentially perform much better than the current conventional desalination and purification methods. [5]
- Graphene's high electric conductivity can be harnessed to produce Li-ion batteries which can last over a week on merely fifteen minutes of charging.

1.3: Buckminsterfullerene

Buckminsterfullerene is a member of the fullerene family of carbon molecules. It was originally synthesized in 1985 by Robert Curl, Harold



Kroto and Richard Smalley. They used a solid rotating graphite disk as a source of carbon from which they produced vapours using a technique of plasma laser vaporisation. The carbon species thus produced was cooled and clusters of C_{60} were formed. Now-a-days fullerene is synthesised by an arc process between graphite electrodes in a helium atmosphere, a process developed by physicists Wolfgang Krätschmer, Konstantinos Fostiropoulos, and Donald R. Huffman in 1989.[6]

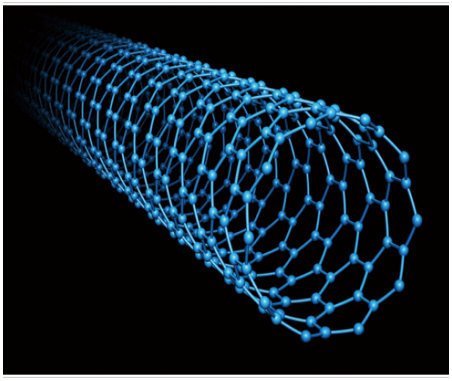
The structure of the Buckminsterfullerene has 60 vertices and 32 faces (20 hexagons and 12 pentagons where no pentagons share a vertex). The molecule is extremely stable with the ability to withstand high pressures and temperatures. The exposed surface can react with selective species while maintaining its spherical structure. Atoms and small molecules can fit inside the fullerene molecule and not react with it. Fullerenes are sparingly soluble in aromatic solvents like toluene and insoluble in water. A pure sample in solution is purple in colour and turns brown when evaporated.

Fullerene exhibits superconductivity at some of the highest transition temperatures when doped with alkali metals. The highest superconducting transition temperature of 33 K at ambient pressure is reported for Cs_2RbC_{60}.[7]

Although there are no commercial applications for fullerene currently, its properties have been harnessed in various research fields. For example, the optical absorption properties of C_{60} suggest that C_{60}-based films could be useful for photovoltaic applications. Moreover, due to its high electronic affinity it is one of the most common electron acceptors used in donor/acceptor based solar cells. Conversion efficiencies up to 5.7% have been reported in C_{60}–polymer cells.[8]

1.4: Carbon Nanotubes

Carbon nanotubes are perhaps the most crucial allotropes of carbon used in nanotechnology. As their name suggests, they possess a tubular, cylindrical structure which is made of a layer of graphene that has been rolled up. This cylindrical structure is extremely pronounced; carbon nanotubes can exhibit a length to diameter ratio of up to 132,000,000:1. [9] These materials can also show extremely high tensile strength, being one of the strongest materials known today, with certain multi-walled carbon nanotubes having a tensile strength of 63 GPa [10]. The nanotubes are obtained by “rolling” graphene sheets at specific angles called **chiral angles.** The chiral angle and the radius of the nanotube determine its structure, and therefore, its properties.



Carbon nanotubes are classified into two – single-walled carbon nanotubes (SNWTs) and multi-walled carbon nanotubes (MWNTs). The distinction between the two is based on the number of cylindrical structures present, and as evident from their names, SNWTs have only one tubular structure while MNWTs may have multiple such structures. Carbon nanotubes do not respond to all kinds of stresses in the same manner; they are best suited to withstanding longitudinal stress. Any kind of torsional or normal stress causes buckling, by virtue of the material (as it is hollow from within).

The route for the synthesis of MWNTs differs from that of SWNTs in the fact that MWNTs can be synthesised directly from graphite sources whereas SWNTs require the presence of nickel. However, the common methods for their synthesis include Chemical Vapour Deposition (CVD), laser ablation, arc discharge, high pressure CO disproportionation etc.

In laser ablation, a laser is used to vapourise the carbon source (usually a graphite target) at very high temperatures in a reactor into which an inert gas is constantly supplied to prevent any reaction/interference. This vapour then reaches the cooler parts of the reactor and condenses. This technique yields about 70% but is fairly expensive compared to the others. Arc discharge method uses over 100 Amperes of current on a graphite electrode that leads to the formation of carbon nanotubes. CVD is the most widely-used method, and involves passing a carbon-containing gas over a nickel/cobalt substrate, wherein the carbon breaks out of the gas supplied at high temperatures of over 700˚C and forms deposits of carbon nanotubes on the substrate.

While the synthesis of this allotrope has been studied, its applications have still not been realised to the fullest. For example, CNTs can be used for pure-carbon scaffolding to pave the way for future capacitors, cells, photovoltaics etc. These may also be made into electrically-conducting "yam". Further, they may be used to replace copper as a feasible material for winding.

1.5: Diamond

Diamond is a metastable allotrope of carbon which is formed at extremely high pressure and temperature conditions. It is known for its superlative physical qualities attributed to the strong covalent bonds between its atoms. It has the highest hardness and thermal conductivity of any bulk material. Diamond, unlike other allotropes of carbon does not conduct electricity. This arises as a consequence of the unique crystal lattice of diamond which has an absence of delocalised π electrons.

Diamond can also be synthesised in the laboratory. It is primarily synthesised through two methods – high temperature high pressure (HTHP) and chemical vapour deposition (CVD). In HTHP, the carbon source is kept in molten metal at over 1400˚C, and kept in a device called a press, which pressurises the sample. The carbon source dissolves in the molten metal, and is then precipitated out by keeping them in diamond seeds.

CVD is used to synthesise diamond from a hydrocarbon mixture. In the chamber, various gases (mainly a carbon-containing gas such as methane and also a non-carbon containing gas such as hydrogen) are fed in and a substrate is placed. The chamber is heated to over 800˚C. The gaseous species are ionised or made into free radicals through various processes and the pure carbon is converted into diamond.

Diamond has a variety of applications including using for cutting purposes, heating etc. But its primary application remains to be in jewellery and ornamentation.

1.6: Carbon Quantum Dots (CQDs)

Carbon quantum dots were discovered during the synthesis of single-walled carbon nanotubes. [11] CQDs are primarily fluorescent carbon nanomaterials. Their fluorescence is attributed to a number of possible reasons, some of which include:

a. The emission arises from the transition of electrons across energy levels from the core of the quantum dots;
b. Defects in carbon nanostructure;
c. Surface-charges recombine;
d. Coupling between core and surface electronic states, etc.

Their synthesis is achieved through various methods. The top-down method involves breaking down of larger carbon allotropes using processes such as laser ablation, arc discharge etc. The bottom-down method involves hydrothermally treating carbohydrate or citrate nanocomposites.
CQDs can extensively be used in bioimaging, biosensing, etc.

2: Methods of Synthesising Heteroatom-Doped Carbon from Bio-sources in Literature

There are various methods for the isolation of carbon from natural precursors. Some of the most common methods are explained in this section.

I: From Chitosan-derived Aerogel [12]

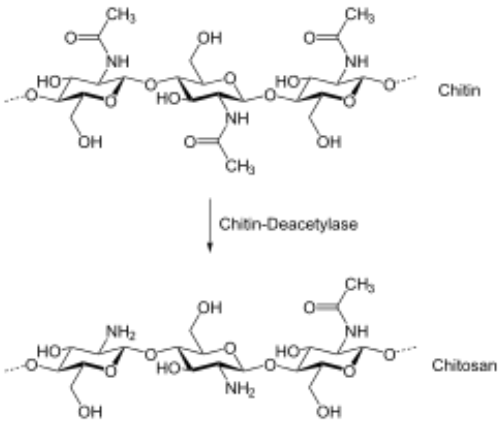
- Aerogels were made by freeze-drying a viscous mixture of chitosan (derived from crustaceans), distilled water and acetic acid. These aerogels were pyrolysed in a furnace at 800˚C for 3 hours, with a nitrogen atmosphere and the carbon doped with nitrogen was derived.
- KOH: chitosan aerogel carbonised extract was mixed in the ratio 3:1, and the sample was heated at various temperatures in a nitrogen atmosphere.

II: From Gelatin Biomolecule [13]

- A solution of H_2SO_4 was made by adding 0.168 g of acid to 5 g of deionised water. To this, previously calcined mesoporous silica was added.
- This mixture was heated and dried for 6 h at 100˚C, and then at 160˚C for 6 h. The silica composite and gelatin mixture was treated with the same heating again, followed by addition of 0.75 g of gelatin, 0.12 g of sulphuric acid, and 5 g of deionised water.
- Finally, the mixture was pyrolysed in an Argon atmosphere at 600˚C, then treated with HCl that dissolved the silica framework, leaving behind the N-doped carbon.

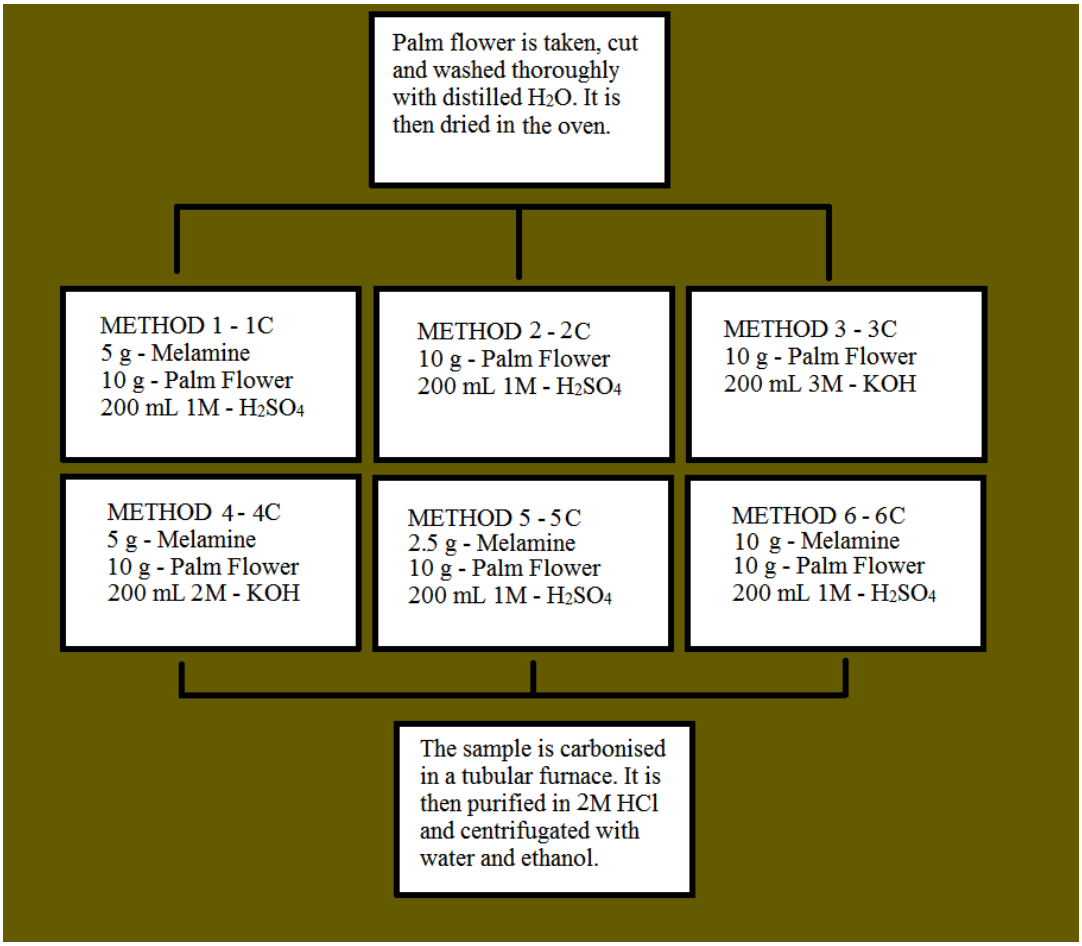
III: From Corn Cobs [14]

- Corn cob was obtained and cut into smaller pieces, washed and dried in sunlight and in an oven at 108˚C for 2 hours.
- The material was transferred to a muffle furnace where it was heated at the rate of 20˚C/min to 500˚C where it was maintained at that temperature for 2 hours.
- The burnt material obtained was then crushed into particles of different sizes and kept in alumina boats and carbonised in a tubular furnace with nitrogen gas flow to 700˚C, after which nitrogen supply was cut off and replaced by carbon dioxide for 1.5 h.
- The material is then allowed to cool in a nitrogen atmosphere again.



3: Synthesis of N-doped Carbon from Palm Flower: Methods Used

Given below is a simplified representation of the various methods followed.



Samples of palm flower were obtained, cut into small pieces, rinsed thoroughly with distilled water and kept in an oven at 100˚C for 36 hours to dry completely. Various methods were employed for the isolation of carbon and the doping of nitrogen in the same. The methods and the associated steps taken are as follows –

Palm Flower (C Precursor)

Autoclave Treatment

Palm Flower-Melamine Mixture

Method 1: Dissolved 5 g of melamine in 200 mL of 1 M H_2SO_4 solution. The mixture was stirred for one hour and then 10 g of palm flower pieces were added to it followed by stirring for another 2 h. Then, the solution was transferred into a 200 mL capacity autoclave and heated in an oven at 160 °C for 12 h. After cooling, the solution was filtered in a G4 crucible and dried in a hot air oven for 12 h. Then the partialized carbon particles were carbonised in an Argon atmosphere for two hours at 800 °C in a tubular furnace at the rate of 5˚C/minute (1Ab). After calcination, the sample was collected and dissolved in 2M HCl solution for 8h followed by centrifugation of the solution while washing with water and ethanol. (1C)

Method 2: Dissolved 10 g of palm flower pieces in 200 mL of 1 M H_2SO_4 solution followed by stirring for 2 h. The solution was then transferred into a 200 mL capacity autoclave and heated in an oven at 160 °C for 12 h. After cooling, the solution was filtered in a centrifuge machine and dried in a hot air oven. After drying, the partialized carbon particles were carbonised in an Argon atmosphere for two hours at 800 °C in a tubular furnace at the rate of 5˚C/minute. After calcination, the sample was collected and dissolved in 2M HCl solution for 6 h, followed by centrifugation of the solution while washing with water and ethanol. (2C)

Method 3: Prepared 3 M KOH solution by dissolving 39.5g of 85% KOH pellets in 200 mL distilled water. To this 10 g of palm flower pieces were added, followed by stirring for 2 h. Poured this solution in an autoclave and kept in an oven at 180˚C for 12 h. Centrifuged it several times with water, then kept it in a hot air oven for 12 h. Calcined the powder at 800 °C for 2h (5 °C/min). After calcination, collected the sample and dissolved in 2M HCl solution for 6 h, followed by centrifugation of the solution while washing with water and ethanol. (3C)

Method 4: Prepared 2 M KOH solution in 200 mL distilled water. To this 5 g of melamine and 10 g of palm flower pieces were added and set aside to dissolve for a few minutes. Poured this solution in an autoclave and kept in an oven at 160˚C for 12 hours. Centrifuged it several times with water, and kept it

in a hot air oven for 12 h; then, calcined the powder at 800 °C for 2h (5 °C/min). After calcination, collected the sample and dissolved in 2M HCl solution for 12 h. (4C)

Method 5: 1 M H_2SO_4 solution was prepared in 200 mL of water and 2.5 g of melamine and 10 g of palm flower pieces were added to it, followed by stirring for 2 h. The solution was then transferred to a 200 mL capacity autoclave and kept it in an oven at 160˚C for 12 h. After cooling, the solution was filtered in a centrifuge and dried in a hot air oven. After drying, the partialized carbon particles were carbonised in an Argon atmosphere for two hours at 800˚C in a tubular furnace at the rate of 5˚C/minute. After calcination, the sample was collected and dissolved in 2M HCl solution for 6 h. (5C)

Sample Before Carbonisation

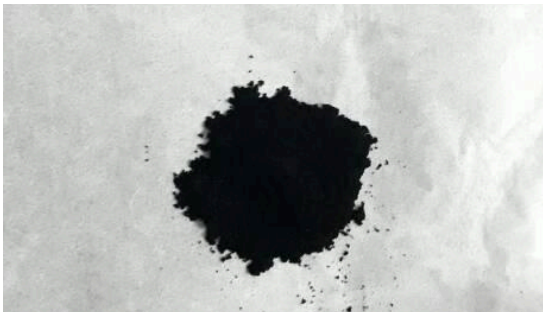
Stirring Carbonised Sample+HCl

Unusual Filtrate (Centrifugation)

During the centrifugation process in this method, an unusual-looking substance was obtained, with a lustrous, silver-like shine in a golden-yellow solution. Due to unfortunate time constraints, this sample could not be identified, but our hypotheses is that it could be a carbon-intercalation compound such as the aforementioned KC_8.

Method 6: Dissolved 10 g of melamine in 200 mL of 1 M H_2SO_4 solution. The mixture was stirred for one hour and then 10 g of palm flower pieces were added to it followed by stirring for another 2 h. The

solution was then transferred into a 200 mL capacity autoclave and kept it in an oven at 160 °C for 12 h. After cooling, the solution was filtered in a G4 crucible and dried in a hot air oven for 12 h. Then the partialized carbon particles were carbonised in an Argon atmosphere for two hours at 800 °C in a tubular furnace at the rate of 5˚C/minute (1Ab). After calcination, the sample was collected and dissolved in 2M HCl solution for 8h followed by centrifuging the solution by adding water and ethanol several times. (6C)



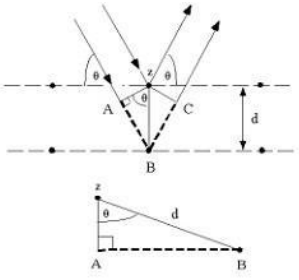
Carbonised Sample

Tubular Furnace

4: Characterisation of N-doped Carbon Samples, a Brief Introduction to X-Ray Diffraction and Infrared Spectroscopy

4.1. X-Ray Diffraction Spectroscopy

X-Ray Diffraction Spectroscopy uses the fact that x-ray radiation, when it strikes a crystal lattice, undergoes diffraction as well as reflection. The part of the radiation that is reflected is separated by a distance from the radiation that does not get reflected at the previous point and is reflected at some later point. The two separated waves undergo constructive interference if the separation between them is an integral multiple of the wavelength of the radiation, i.e., the waves are in phase. As a result, the following result is obtained, called the Bragg's law:



$$n\lambda = 2dsin\theta$$

Since AB=BC and $\sin\theta=\frac{AB}{d}$, therefore, AB=BC=dsinθ

Path travelled by wave is AB+BC=2AB=2dsinθ.

Therefore, the given relation between wavelength, the angle of incidence (diffraction) and the interplanar distance is valid.

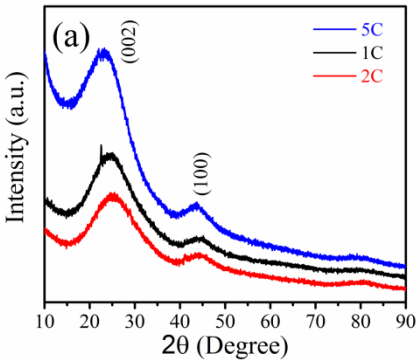
XRD spectra are plotted as intensity vs. 2θ values. A typical XRD spectrum will consist of bands and peaks, but the behaviour of these spectra is largely dependent on the nature of the solid in question.

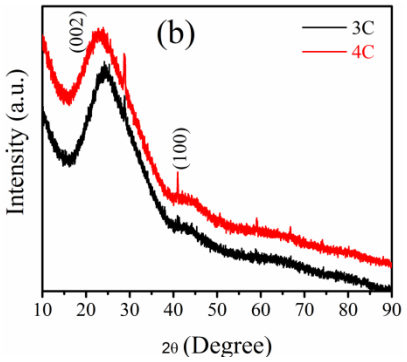
Amorphous solids do not have a definite crystalline structure, and possess no regularity. This calls for a wide range of values of 2θ wherein the intensity could vary; therefore, the spectrum consists of broad peaks. Perfectly crystalline solids, on the other hand, possess near-perfect regularity. As a result, the 2θ values do not exhibit as much variance for the same peak. This results in a sharp peak observed at that point. XRD spectra can be used to interpret the nature of the crystals of the solid, like their general structure, Miller indices etc. This can help in terms of characterising the physical attributes of the compound.

4.2. XRD Characterisation of N-doped Carbon Samples

All carbon samples show the most relevant characteristic peaks at 2θ = 23.7° and 43.7° arising from (002) and (100) planes of carbon sheets consisting of graphitized carbon obtained by carbonization. The d_{002} value of all carbons is about 0.36 nm, larger than that of graphite (0.33 nm). This suggests that all the carbons are made up of random combination of graphitic and turbostratic stacking of carbon layers. The d value can be calculated by using the previously mentioned Bragg's equation.

Similarly, the XRD spectrum can also be used to detect the elements present in the sample by comparing the 2θ values of the peaks with sources available in literature.





The labels 1C, 2C and so on represent the same labels as before.

4.3. Infrared Spectroscopy

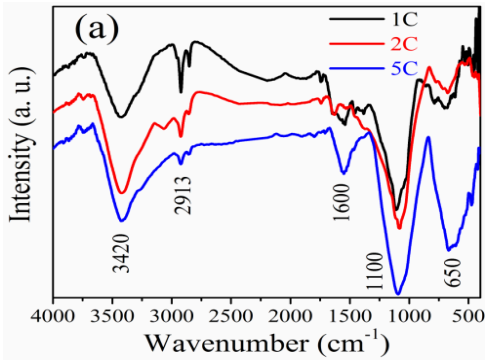
Infrared spectroscopy uses infrared radiation on molecules to determine which functional groups and elements are present in the sample. When molecules are irradiated with infrared light, they start to vibrate and show various vibrational modes, stretching, bending of bonds, etc. It is with these vibrational modes that the various peaks are identified and their corresponding sources detected. Further, each molecule has a characteristic spectrum or a "signature" that further aids in identifying the chemical structure of the sample. IR absorption peaks can be compared to data available. A sample data table is given for reference.

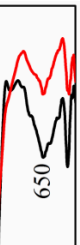
Functional Group	***Characteristic Absorption(s)*** **(cm^{-1})**
Alkyl C-H Stretch	2950 - 2850 (m or s)
Alkenyl C-H Stretch	3100 - 3010 (m)
Alkenyl C=C Stretch	1680 - 1620 (v)

Alkynyl C-H Stretch Alkynyl C≡C Stretch	~3300 (s) 2260 - 2100 (v)
Aromatic C-H Stretch Aromatic C-H Bending Aromatic C=C Bending	~3030 (v) 860 - 680 (s) 1700 - 1500 (m,m)
Alcohol/Phenol O-H Stretch	3550 - 3200 (broad, s)
Carboxylic Acid O-H Stretch	3000 - 2500 (broad, v)
Amine N-H Stretch	3500 - 3300 (m)
Nitrile C≡N Stretch	2260 - 2220 (m)
Aldehyde C=O Stretch Ketone C=O Stretch Ester C=O Stretch Carboxylic Acid C=O Stretch Amide C=O Stretch	1740 - 1690 (s) 1750 - 1680 (s) 1750 - 1735 (s) 1780 - 1710 (s) 1690 - 1630 (s)
Amide N-H Stretch	3700 - 3500 (m)

4.4. IR Characterisation of N-doped Carbon Samples

In the FTIR spectrum, the peaks at 685 cm^{-1} and 1100 cm^{-1} correspond to the C—H stretching of the α-linkage in pyrrole ring and C—N stretching vibrations, respectively. The strong band at 1400 cm^{-1} is assigned to C=C backbone stretching vibration of the aromatic groups. The band at 1626 cm^{-1} and at 2913 cm^{-1} are ascribed to the vibration of phenylene conjugated C=C and CH_2 stretching vibration. The broad band at 3100-3400 cm^{-1} is corresponding to N—H stretching vibrations.





Bibliography

[1] IUPAC. Compendium of Chemical Terminology, 2nd ed. (the "Gold Book"). Compiled by A. D. McNaught and A. Wilkinson. Blackwell Scientific Publications, Oxford (1997)

[2] Superconductivity in Graphitic Compounds N. B. Hannay, Phys. Rev. Lett. 14, 225.

[3] Abdul Khaliq R et al 2012 Nanotechnology 23 455106

[4] Wang, X.; Zhi, L; Müllen, Klaus (2007). "Transparent, Conductive Graphene Electrodes for Dye-Sensitized Solar Cells". Nano Letters. 8 (1): 323–7

[5] Cohen-Tanugi, David; Grossman, Jeffrey C. (2012). "Water Desalination across Nanoporous Graphene". Nano Letters. 12 (7): 3602–3608.

[6] The infrared and ultraviolet absorption spectra of laboratory-produced carbon dust: evidence for the presence of the C60 molecule

[7] Tanigaki, K.; Ebbesen, T. W.; Saito, S.; Mizuki, J.; Tsai, J. S.; Kubo, Y.; Kuroshima, S. (1991). "Superconductivity at 33 K in Cs_xRb_yC60"

[8] Katz, E. A. (2006). "Fullerene Thin Films as Photovoltaic Material" In Sōga, Tetsuo

[9] Wang, X.; Li, Qunqing; Xie, Jing; Jin, Zhong; Wang, Jinyong; Li, Yan; Jiang, Kaili; Fan, Shoushan (2009). "Fabrication of Ultralong and Electrically Uniform Single-Walled Carbon Nanotubes on Clean Substrates" Nano Letters. 9 (9): 3137–3141

[10] Yu, M.-F.; Lourie, O; Dyer, MJ; Moloni, K; Kelly, TF; Ruoff, RS (2000). "Strength and Breaking Mechanism of Multiwalled Carbon Nanotubes Under Tensile Load". Science. 287 (5453): 637–640.

[11] Xiaoyou Xu, Robert Ray, Yunlong Gu, Harry J. Ploehn, Latha Gearheart, Kyle Raker and Walter A. Scrivens – "Electrophoretic Analysis and Purification of Fluorescent Single-Walled Carbon Nanotube Fragments", Journal of the American Chemical Society 2004 126 (40), 12736-12737.

[12] Pin Hao, Zhenhuan Zhao, Yanhua Leng, Jian Tian, Yuanhua Sang, Robert I. Boughton, C.P. Wong, Hong Liu, Bin Yang; "Graphene-based nitrogen self-doped hierarchical porous carbon aerogels derived from chitosan for high performance supercapacitors", Nano Energy, 15: 9-23

[13] Dhawale, D. S., Mane, G. P., Joseph, S., Anand, C., Ariga, K. and Vinu, A. (2013), Enhanced Supercapacitor Performance of N-Doped Mesoporous Carbons Prepared from a Gelatin Biomolecule. ChemPhysChem, 14: 1563–1569.

[14] S. Nethaji, A. Sivasamy, A.B. Mandal, "Preparation and characterization of corn cob activated carbon coated with nano-sized magnetite particles for the removal of Cr(VI)", Bioresource Technology, 134: 94-100