From Carbon to Buckypaper

Surabhi Potnis

This article aims to highlight the amazing properties and potential uses of the more recently developed allotropes of carbon such as carbon nanotubes, graphene, fullerene, and buckypaper. This is an area offering wide opportunity for research, especially due to the multidisciplinary nature of applications.

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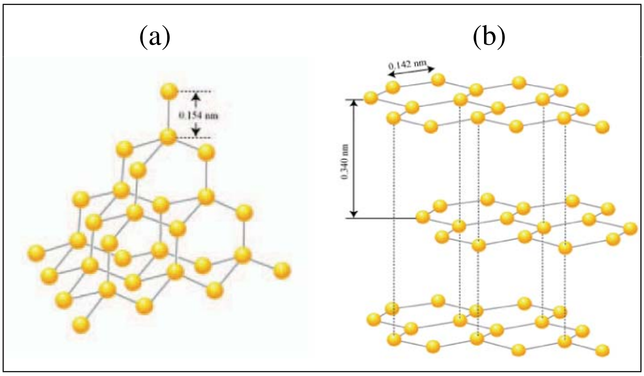
Carbon has always been acknowledged as an element essential to life as we know it. It exists in a variety of physical forms or allotropes that have been known for a long time – from the precious diamond and lubricant graphite, to the lowly soot, lampblack, coke, and charcoal. The more recently discovered and thereafter artificially developed forms such as fullerene, carbon nanotubes, and graphene are major landmarks in the field of material science, and hold out much promise for the future.

The difference in properties of the various forms of carbon originates primarily from their structural peculiarities. In a diamond, (*Figure* 1a) the carbon atoms have sp^3 hybridization and are tetrahedral, connected by covalent bonds, and forms a 3-dimensional network. The rigid structure thus formed is responsible for the extreme hardness of diamond. Graphite (*Figure* 1b), on the other hand, has carbon atoms in sp^2 hybrid state, and the hexagonal planar structure thus formed exists in a large number of parallel layers. This makes graphite softer, enables it to have lubricant properties, and to conduct electricity. Soot, lampblack, coal, coke, charcoal, etc., have no systematic arrangement of atoms and are therefore amorphous in nature.

Towards the end of the 20th century, much interest was generated by the discovery of hitherto unknown forms of carbon. Studies of mass spectrophotometric data by Kroto, Curl, and Smalley on laser-vaporized graphite, showed patterns similar to those seen in

Keywords
Allotropes, graphene, fullerene, buckypaper, carbon nanotubes.

Figure 1. Structures of naturally occurring allotropes of carbon. **(a)** Diamond **(b)** Graphite



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interstellar space, corresponding to long molecules of carbon [1]. Of these, the most prominent was seen to be C_{60}. The structure of this molecule was found to be a hollow sphere, rather like a soccer ball – a caged structure, so similar to the geodesic dome designed by Buckminster Fuller that it was named 'Buckminsterfullerene' or 'buckyball' (*Figure* 2a). It was stable, but could be converted to a wide range of derivatives, leading to a plethora of potential applications. The discovery of fullerene[1] Molecules in 1985, thus led to the award of the coveted Nobel Prize to Kroto, Curl, and Smalley in 1996. Subsequently, a whole range of similar molecules – the 'fullerenes', were obtained and studied, although the original buckyball remained the most significant one.

[1] Pradeep P Shanbogh and Nalini G Sundaram, Fullerenes Revisited: Materials Chemistry and Applications of C_{60}, *Resonance*, Vol.20, No.2, pp.123–135, 2015.

'Carbon nanotubes' (*Figure* 2b) constituted the next breakthrough. As early as the 1950s, a lot of interest was generated by papers showing hollow graphitic tubes and tube-like structures of carbon that had diameters of less than 200 nm. In 1960, Roger Bacon grew 'graphite whiskers' in an arc-discharge apparatus, and with the help of electron microscopy showed that the structure consisted of rolled up graphene sheets in concentric cylinders. The development of more sophisticated instruments enabled characterization of these entities.

In 1991, Sumio Iijima put a sample of soot from electric arc discharge under an electron microscope to take pictures of buckyballs (see *Box* 1). Some needle-like structures caught his attention, and he was able to determine the crystal structure of these carbon nanotubes [2]. Carbon nanotubes (CNTs) are extremely

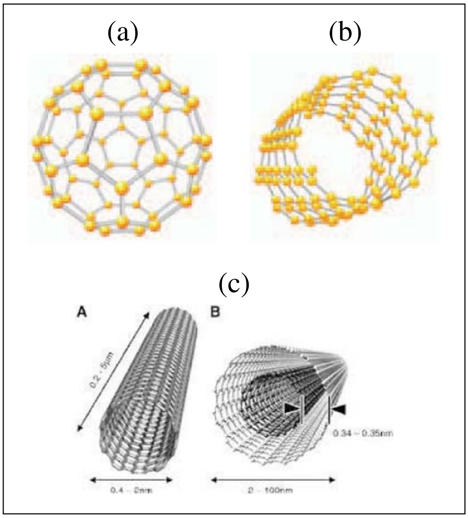


Figure 2. Structures of **(a)** Buckminsterfullerene **(b)** Carbon nanotube **(c)** Single walled and Multi walled carbon nanotubes (A) SWNT (B) MWNT

thin cylindrical tubes with diameter less than 200 nm, and much longer lengths. CNTs have extraordinary electrical conductivity and super high tensile strength. They are structurally related to fullerenes, and are cylindrical rather than spherical in shape. At one of the ends, usually the CNT is enclosed with a hemispherical structure like fullerene, hence are also called 'buckytubes'. The CNTs are further classified as 'single walled carbon nanotubes' (SWNT) that have thickness of a single layer of atoms; or 'multi walled carbon nanotubes' (MWNT) that have multiple cylinders fitted one inside another, forming two or more layers of atoms (*Figure* 2c).

A new form of carbon – 'graphene' (*Figure* 3), was isolated by Giem and Novoselov in 2004 [3,4] by laboriously separating layers a single atom thick from graphite, using scotchtape. Six years later, they were awarded the Nobel Prize in Physics in 2010 for their work [5].

Graphene [6] consists of a planar, hexagonal single sheet of carbon atoms, looking rather like chicken wire. This forms the structural basis of carbon nanotubes. In graphite, the layers of graphene are positioned parallel to one another, separated by 0.34 nm. Carbon nanotubes are made from graphene sheets consisting of a single atomic layer of carbon atoms arranged in hexagonal for-

Figure 3. **(a)** Structure of Graphene **(b)** Scanning probe microscopy image of graphene.

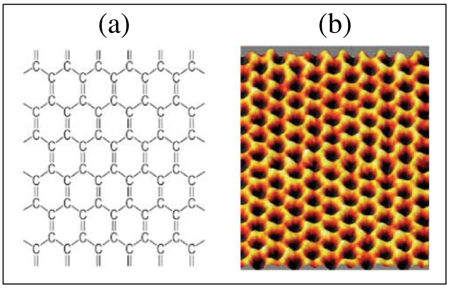
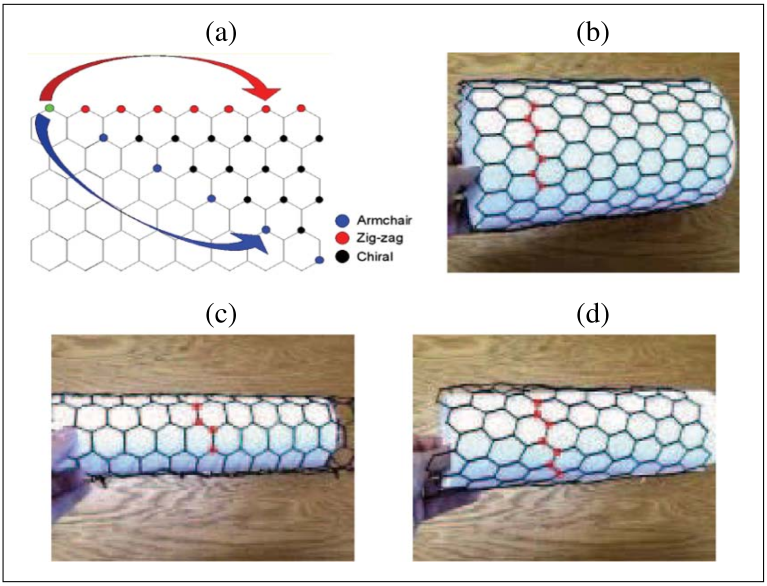


Figure 4. The graphene sheet can be rolled more than one way, producing different types of carbon nanotubes. **(a)** The three main types **(b)** zig-zag **(c)** armchair **(d)** chiral carbon nanotubes.



mation.

Carbon nanotubes are essentially rolled up versions of graphene (*Figure* 4)[2]. The manner in which the rolling up occurs affects the properties of the material, especially electrical conductivity.

[2]Mandar M Deshmukh and Vibhor Singh, Graphene–An Exciting Two-Dimensional Material for Science and Technology, *Resonance*, Vol.16, No.3, pp.238–253, 2011.

The discovery of these materials has initiated much research, resulting in the synthesis and study of a large number of compounds of fullerene and CNTs, and development of different forms of graphene having a wide range of applications. Some of the materials in this category [7] include:

• Fullerites, which represent a solid-state compact form of fullerene, consisting of polymerized single-walled carbon nanotubes. This material is incompressible and has hardness comparable to or even higher than that of diamond.

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• Nanotori (singular nanotorus), which are theoretically described carbon nanotubes bent into a torus or doughnut shape. Their unique properties, such as extremely high magnetic moment, thermal stability, etc., can be varied widely depending on radius of the torus and radius of the tube.

• Carbon nanobuds, which combine carbon nanotubes and fullerenes (*Figure* 5a). In this new material, fullerene-like 'buds' are covalently bonded to the outer sidewalls of the underlying carbon nanotube. This hybrid material has useful properties of both fullerenes and carbon nanotubes, and are found to be exceptionally good field emitters. In composite materials, the attached fullerene molecules may function as molecular anchors preventing slipping of the nanotubes, thus improving the composite's mechanical properties.

• Carbon fiber, (*Figure* 5b) most widely used in high-performance applications [9] is produced from a variety of precursors, including polyacrylonitrile (PAN), rayon, and pitch. The precursor fibers are heated and stretched to create the high-strength fibers. PAN-based carbon fibers are the most versatile and widely used. They are extremely strong, very stiff, and have low coefficient of thermal expansion. They are thus especially useful in spacecraft applications that require thermal management, such as electronic instrumentation housings. Carbon fibers are stronger than glass fibers, and can be used to make composites with plastics, producing 'carbon fiber reinforced polymer' (CFRP). CFRP is strong, lightweight, and impact-resistant, and this material is widely used in sports equipments, automobiles, and aircrafts.

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• Buckypaper (*Figure* 5c) is a macroscopic aggregate of carbon nanotubes leading to a material that is extremely strong, lightweight, and very highly conductive.

The main similarity among these different substances is that they have carbon in the sp^2 hybridized form and a predominantly hexagonal arrangement of carbon atoms. Fullerenes have a combina-

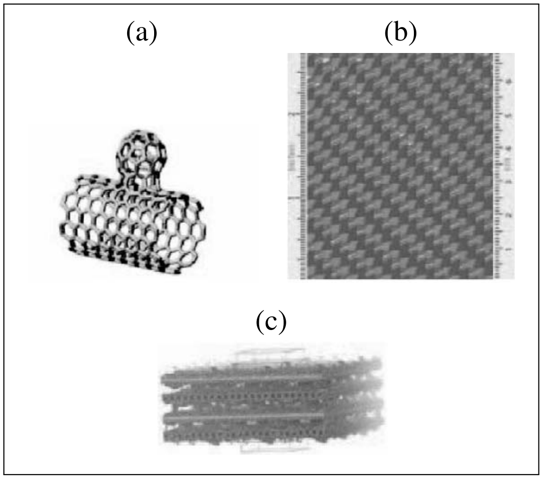

Figure 5. From left to right: **(a)** Carbon nanobud **(b)** Carbon fiber **(c)** Buckypaper

tion of 6-membered and 5-membered carbon rings that give the characteristic shape of a soccer ball. Graphene has 6-membered rings consisting of sp^2 hybrid carbons that are in a planar configuration. In all of these configurations, the carbon atoms in a specific layer are in a single plane, with electrons in the unhybridized pure p orbitals. These π electrons in the bonding molecular orbitals can be delocalized and constitute the valence band, while the antibonding molecular orbitals are available as the conduction band. This structural peculiarity can explain the amazing electrical properties[3] of these materials.

[3]CNTs are 100 times stronger than and 1/6th the weight of steel with a length-to-diameter ratio that can be as high as 132,000,000:1; a much higher thermal conductivity than diamond or graphite, and a low thermal expansion coefficient [10, 11]. They are flexible, elastic, and absorbent. Electrical conductivity of SWNTs vary; the armchair form is metallic, while the chiral form behaves as a semiconductor.

The amazing properties of fullerenes, graphene, and CNTs [13, 14] suggests a wide range of potential applications of these wondrous materials in pure chemistry, material science, pharmaceutical chemistry, and nanotechnology. They can form composites and can even be derivatized [12, 13], leading to a plethora of potential uses.

Applications

CNT-based polymer composite materials are being utilized in an increasing number of applications in various sectors [15, 16, 17].

1. Reinforcement of Composite Materials: Carbon fiber is most notably used to reinforce composite materials, particularly carbon fiber or graphite reinforced polymers. CNTs can be added to many other materials including thermosetting plastics and thermoplastics to form composites with enhanced strength, elasticity, toughness, and durability. Reinforced carbon-carbon (RCC) consists of carbon fiber-reinforced graphite, and is used structurally in high-temperature applications. The fiber also finds use in filtration of high-temperature gases, as an electrode with high surface area and impeccable corrosion resistance, and as anti-static, fire-resistant components in the electronics, automotive, and aerospace sectors.

2. Aerospace: Carbon fiber composites are gradually displacing aluminum from aerospace applications. CFRP is used in the manufacture of spacecraft and ultralight aircraft. The Airbus A380 was one of the first commercial airliner to have a central wing box made of CFRP [18].

3. Sports Equipment: CFRP is widely used in sports gears such as tennis racquets, hockey sticks, fishing rods, bicycle frames, etc. Carbon fiber containing up to 75% carbon is used in personal items like wallets and backpacks.

Box 1. Some Methods of Preparation [12]

1. **Arc Discharge:** The method originally used by Iijima, in which an electric arc is struck between two carbon rods placed end to end, in an enclosure filled with inert gas at low pressure. Vaporization of one electrode occurs, and nanotubes are formed on the other electrode.
2. **Laser Vaporization:** Carbon rods are vaporized using a dual-pulsed laser, resulting in the formation of fullerenes and CNTs. The material produced by this method appears as a mat of 'ropes', consisting primarily of SWNTs.
3. **Chemical Vapour Deposition (CVD):** In this method, an inert gas is passed through the heated solution of a hydrocarbon such as acetylene or methane, with a metal catalyst which will act as seeds for the growth of carbon nanotubes. The length and diameter of the CNTs can be controlled by manipulating the experimental conditions, and hence this method is most promising for large scale production of CNTs.
4. **Mechanical Exfoliation of Graphite:** The method originally used by Geim and Novoselov to isolate graphene, involves carefully peeling off layers of graphite on scotchtape, and transferring to a target surface. Although the material obtained is pure, the method is not very useful for large scale preparation, as the size and shape of the material obtained cannot be controlled.

4. Body Armor: Carbon nanotubes are said to have the strength of diamond, and potential uses include weaving them into clothes to create combat jackets, and stab-proof and bulletproof clothing. The nanotubes would effectively stop the bullet from penetrating the body.

5. Nano-Electronics: [19] CNTs find numerous applications in micro- and nano-electronics. The unique structural and bonding properties of carbon nanotubes enable the inner tubes of a multi-walled nanotube to slide within an outer tube. This might possibly enable such materials to function as tiny motors or ball bearings in nanomachines. Carbon nanotubes can be used in nanotransistors and nanoradios.

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6. Diamond Nano-Thread: Material scientists have obtained a one-dimensional diamond crystal capped with hydrogen, called a 'diamond nano-thread' [20]. The property of the nano-thread is that it can be tuned so that some parts of the thread can be made rigid, while others are entirely flexible. Potential applications include creation of extremely strong three-dimensional nano-architectures, and the much-discussed space elevator.

7. Stress Analysis: Electromechanical sensing and structural health monitoring of a CNT nanocomposite material is possible, as the resistivity of a CNT nanocomposite changes when subjected to a structural deformation caused by an external load. Strain sensing can be done using buckypapers and SWCNT-polymethylmethacrylate (PMMA) composites.

8. Thermo-Acoustics: A sheet of nanotubes can operate as a loudspeaker if an alternating current is applied. The sound is not produced through vibration but thermo-acoustically.

9. Solar Photo-Voltaics: Carbon nanotube complex, together with tiny carbon buckyballs are used in solar panels. Buckyballs trap the electrons and the current can then flow through the nanotubes.

10. Structural Composite Materials: CFRP can be used for strengthening concrete, masonry, steel, cast iron, and timber structures. Its use in industry can be either for retrofitting to strengthen an existing structure or as an alternative reinforcing (or pre-stressing) material instead of steel from the outset of a project.

11. Drug Delivery: Carbon nanotubes can be used as a vessel for transporting drugs into the body. The nanotube could effectively localize the distribution and hence lower the dosage of the drug.

12. Biosensors: [21] A single nanotube experiences a change in electrical resistance when experiencing stress or strain, which can be measured in order to accurately quantify the applied stress. A semi-random positioning of many overlapping nanotubes forming an electrically conducting network embedded within orthopaedic plates, clamps, and screws, and in bone grafts can help determine the state of bone healing by measuring the effect of a load on the plate, clamp, screw, or other fixation device attached to the bone, allowing the doctor to accurately assess healing. CNT biosensors can also be used for ultrasensitive glucose as well as DNA detection.

13. Gene Therapy and Cancer Therapy: Carbon nanotubes can be used to target tumors and as multifunctional biological transporters, and near-infrared agents for selective cancer cell destruction. Carbon nanotubes have been proposed as a possible gene delivery vehicle and for use in combination with radiofrequency fields to destroy cancer cells.

Buckypaper [22] is about 25-μm thick and made from CNT fibers about 1/50,000th the diameter of a human hair. Nobel Laureate Richard Smalley first produced buckypaper during the 1990s by filtering a nanotube suspension in order to prepare samples for various tests.

When sheets of buckypaper are stacked, the resulting composite material is 10 times lighter than steel but 250 times stronger. The implications for aero structures – increased payloads and improved fuel efficiency, are tantalizing.

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The possible uses for buckypaper that are being researched include:

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1. Fire Protection: A thin layer of buckypaper significantly improves fire resistance of material due to the efficient reflection of heat by the dense, compact layer of carbon nanotubes or carbon fibers.

2. Electrical Conduction: Buckypaper conducts electricity almost as well as silicon and disperses heat like steel. A coating of buckypaper on the surface of aircraft would enable dissipation of electrical charge in case of lightning strike without causing damage.

3. Electromagnetic Shielding: Buckypaper films can be employed for protection of electronic circuits and devices within airplanes from electromagnetic interference, which can damage equipment and alter settings. Similarly, such films could allow military aircraft to shield their electromagnetic ‘signatures’, which can be detected *via* radar.

4. Armor Plating: Produced in high enough quantities and at an economically viable price, buckypaper composites could serve as an effective armor plating.

5. Illumination: If exposed to an electric charge, buckypaper could be used to illuminate computer and television screens. It could be more energy-efficient, lighter, and could allow for a more uniform level of brightness than current cathode ray tube (CRT) and liquid crystal display (LCD) technology.

6. Thermal Conduction: Since individual carbon nanotubes are one of the most thermally conductive materials known, buckypaper lends itself to the development of heat sinks that would allow computers and other electronic equipment to disperse heat more efficiently than is currently possible, leading to even greater advances in electronic miniaturization.

The properties of the recently discovered allotropes of carbon, namely nanotubes, graphene, buckypaper, etc., potentially make them materials of the not-so-distant future.

7. Nanofiltration: Buckypaper could act as a filter membrane to trap microparticles in air or fluid. Because the nanotubes in buckypaper are insoluble and can be functionalized with a variety of functional groups, they can selectively remove compounds or can act as a sensor.

8. Biocomposites: Buckypaper can be used to grow biological

tissue, such as nerve cells. Buckypaper can be electrified or functionalized to encourage the growth of specific types of cells. This material could perhaps be used as artificial muscles.

Conclusion

The properties of the recently discovered allotropes of carbon, namely nanotubes, graphene, buckypaper, etc., potentially make them materials of the not-so-distant future. Toxicity of these materials needs to be investigated further. Manufacturing processes have to be improved to make them affordable. A multidisciplinary approach is required for best realization of the potential of these amazing materials.

Acknowledgement

Many thanks to Prof Prajval Shastri and the anonymous referee for their helpful comments that enabled me to improve this article.

Suggested Reading

[1] https://www.acs.org/content/acs/en/education/whatischemistry/landmarks/fullerenes.html

[2] Sumio Iijima, Helical microtubules of graphitic carbon, *Nature*, Vol.354, p.6348, pp.56–58, 7 November 1991.

[3] This Month in Physics History: October 22, 2004: Discovery of Graphene, *APS News*, Series II, Vol.18, No.9, p.2, 2009.

[4] http://www.graphene.manchester.ac.uk/explore/the-story-of-graphene/

[5] The Nobel Prize in Physics 2010, The Nobel Foundation. Retrieved 3 December 2013.

[6] http://www.nanowerk.com/what_is_graphene.php

[7] https://en.wikipedia.org

[8] S Gullapalli, M S Wong, Nanotechnology: A Guide to Nano-Objects (PDF), *Chemical Engineering Progress*, Vol.107, No.5, pp.2832, 2011.

[9] Bill Howard, (30 July 2013), BMW i3: Cheap, mass-produced carbon fiber cars finally come of age, Extreme Tech., Retrieved 31 July 2015.

[10] S B Sinnott, R Andrews, Carbon Nanotubes: Synthesis, Properties, and Applications, *Critical Reviews in Solid State and Materials Sciences*, Vol.26, No.3, pp.145–249.

[11] https://www.cheaptubes.com/carbon-nanotubes-applications/

[12] Albert G Nasibulin *et. al*., A novel hybrid carbon material (PDF), *Nature Nanotechnology*, Vol.2, No.3, pp.156–161, 2007.
[13] http://www.intechopen.com/books/carbon-nanotubes-synthesis-characterization-applications/smart-materials-and-structures-based-on-carbon-nanotube-composites
[14] http://www.azonano.com/article.aspx?ArticleID=1564
[15] discovermagazine.com/2009/jul.../09-ways-carbon-nanotubes-just-might-rock-world
[16] http://www.understandingnano.com
[17] http://www.zdnet.com/article/5-surprising-uses-for-carbon-nanotubes/
[18] Thermoplastic composites gain leading edge on the A380. Composites World, 3 January 2006, Retrieved 6 March 2012.
[19] J C Charlier and S Roche, Electronic and transport properties of nanotubes, *Reviews of Modern Physics*, Vol.79, No.2, pp.677–732, 2007.
[20] https://www.technologyreview.com/s/543631/forget-graphene-and-carbon-nanotubes-get-ready-for-diamond-nanothread/
[21] Pacios Pujadó, Mercè, Carbon Nanotubes as Platforms for Biosensors with Electrochemical and Electronic Transduction. Springer Heidelberg. pp.XX, 208, 2012.
[22] http://www.buckypaper.com/

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