Advances in chemistry of carbon nanotubes and their composites (nanomaterial): A Review

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Abstract. This review is about the commercial as well as some other applications of carbon nanomaterials as in recent past years their various beneficial properties (physical & chemical) have revealed. Carbon nanotubes are cylindrical bodies that are made by rolling single-layered carbons means graphene. They can be of one wall i.e., single walled (SWCNT) having diameter less than 1nm and also can be multilayered or multi walled (MWCNT). More & more nanotubes join concentrically to make themselves multilayered (diameter – more than 100nm). Previous strives on these nanotubes has revealed their various properties like high thermal conductivity, outstanding field emission properties & controlled electronic properties etc. It has been proven that carbon nanotubes are ideal model system for studying physics in one dimensional solid. Other aspects related to nanomaterials and its various derivatives can be better understood by glancing below.

1. Introduction

Out of all the known elements, only a few have the ability to form the allotropes. For knowing their different properties, the structural geometry of the atoms and the types of the bonding they show should be known. In this list, Carbon is the most important element having this special property of allotropy. Hard diamond and soft graphite come under the classical examples of carbon allotropes. The other existing carbon allotropes has come in technology after the discovery of several new low dimensional carbon forms [1]. The ideal nanomaterial of carbon includes,

- Carbon Nanotubes
- Fullerene
- Graphene
- Grapheme oxide
- Nanodiamonds
- Quantum dots

1.1 Carbon Nanotubes

The research on carbon nanotubes was launched in 1991. Their initial observation was from transmission electron microscopy (TEM) [2]. Initially, only physical properties of these nanotubes were known but over the past few years their chemical properties are also focused. A nanotube has three major regions- cap, wall & end. The caps are found more reactive than rest portions due to its curvature and first lost during any chemical reaction. These are considered as ultimate carbon fibers due to its all those properties mentioned above in the abstract. These are called unique as they lie in between traditional carbon fiber and its other forms like fullerenes [3]. Actually, these are seamless cylinders whose aspect ratio means diameter/length is so great. Normally, it has straight structure with six carbon atoms in each ring & no external strain. With their improving properties, decreasing cost and the increasing need for light weighted materials, carbon nanotube’s industrial use is increasing day by day. These are strong enough due to their hexagonal network (graphite structure) in longitudinal axis of carbon fiber. These can be prepared by, Carbonization of polymer fibers and disintegration of hydrocarbons in the companionship of catalyst[4]. Studies proved this that nanotubes can be either metallic or semiconductors & this not only depends on diameter but also gets affected by helicity. All achiral single-walled carbon nanotubes are metallic but rest are semiconductors which may be either small or having moderate band gap. We can say, as its properties was discovered day by day, the expectations for these nanotubes were running very high in 1992, but problem was that the carbon nanotubes were present in small abundance in deposits of carbon & it was very difficult for researchers to extract them for further studies. Each cylindrical shell consistssp² hybridized carbons which form hexagonal network. A carbon nanotube can be taken as microcrystal of tubular graphite. They have hierarchical structure in which nanotubes organized themselves into bundles and then bundles arrange themselves to form 50 μm fibers that can be seen as larger fibers.
Carbon nanotubes are said metallic & conducting in nature due to the presence of N and M in them. However, they can be any i.e., metallic or semiconductive. Conductivity is found complex in multi-walled nano tubes. It has been proved that armchair structured CNTs are more conducting as compared to other metallic CNTs. The behavior of changes its position on these nanotubes. After measuring the conductivity and resistivity of these ropes, the order of resistivity is found around 10-4-ohm cm at 27° C which suggests that these ropes are most conductive carbon fibers known till today. Graphite is like planar honeycomb lattice in which four atoms are connected to each other via strong chemical bonds. Due to these strong bonds, these are considered of high strength fibers. These are a bit stiffer than steel. On applying pressure to its tip, it bends & regain its original shape after removal of similar pressure. The carbon nanotubes are having a very high aspect ratio for all types of plastics means their very low loading is required than others to attain same electrical conductivity. These are proved to be excellent additives to provide electrical conductivity in plastics although plastics are non-conducting in nature [5].

1.2 Fullerences

These comprise of carbon atoms held together by means of single as well as double bonds and get a form of fused rings (of 5-7 atoms). They can be hollow sphere, tubes, ellipsoid or many other shape and sizes. Their discovery greatly expands the list of already known allotropes of carbon [6].

1.3 Graphene

It is a single, 2-dimensional sheet of graphite. In graphene, carbon atoms are sequence hexagonally to form honey comb lattices like structure. It is also known as ‘WONDER MATERIAL’ as it holds enormous group of properties. It is first discovered 2D material [7] and it has the structure as shown below:

1.4 Graphene oxide

The aromatic lattices of graphene get interrupted or trapped by epoxides, ketones, alcohols & carboxylic acids when the interlayer spacing in graphene (which is generally around 0.335nm) becomes more than 0.625nm, lattices get disrupted. Graphene oxides come out as offshoot of oxidation of graphite. After dissolving the oxidized compound in base solution in (water) the graphene oxide is formed [8]

1.5 Nanodiamonds

These diamonds are prepared from graphite. First successful publication of nanodiamond from graphite was in 1955. By varying the temperature and pressure (T=13,00-1800° C and P=5.0-7.0 GPa) and using suitable catalysts, nanodiamonds were produced. It had been noted that the graphite-diamond transformation coefficient increases with the increasing temperature and pressure. Now a days this transformation technique is called high-pressure-high-temperature (HPHT) synthesis & is a well suitable technique to produce gem-quality nanodiamonds [9]. The nanodiamonds majorly have biomedical applications due to its non-toxic behavior [10] as shown in below fig 1.

![Fig.1. properties of nanodiamonds](image)

1.6 Quantum Dots

Carbon quantum dots have gained their extensive position in the area of membrane technologies due to their solicitation in uncoupling operations. Their physiological properties are outstanding including extremist-miniatured sizes, ethical biocompatibility, chemical idleness, mellifluous hydrophilicity & antifouling characteristics. Major applications on the basis of membrane separation:

- Reverse osmosis (RO)
- Ultrafiltration (UF)
- Nano filtration (NF)
- Forward-osmosis (FO)
- Membrane distillation (MO)
- Organic solvent nano filtration (OSN) [11]

2 Literature Review

Carbon nanotubes were first announced by lijima(1991) but large-scale manufacturing was done by Ebbesen and Ajayan in 1992. Hamada et al. (1992) originated indexing method for single shells of these nanotubes [12]. In 1993 lijima, Ichihashi and Bethune et al. took around 2 years to unify SWCNT with the method of arc-discharge in the presence of metal catalyst[13]. An
alternative way of preparing SWCNT was discovered by Smalley’s group (1996) [14]. In 2001 the unique properties and applications of carbon nanotubes were discovered by Dresselhaus et al. [15].

2.1 Carbon Nanotubes

2.1.1 Arc Discharge

It is the senior method of production of carbon nanotubes as mentioned above that this was first employed by lijima at NEC’s Fundamental Research Laboratory to form finite needle shaped carbon structures/tubes. These structures/tubes were produced by using arc discharge evaporation method. The diameter of those needles was found around 4-30nm and length was 1mm. These were grown on carbon electrode used for DC arc discharge evaporation of carbon. A pressurized chamber, filled with gas mixture of 10 Torr methane and 40 Torr argon, having two electrodes in the center was used by lijima [16].

2.1.2 Laser Ablation Method

This technique was successfully evolved by Smalley et al. in 1996 for the ‘mass rendering’ of single walled carbon nanotubes [17]. Rest betterments was done by Thess Et. al. [18] and Rao et al. [19] by using double beam laser. This was believed that nanotubes produced by this method was more pure and better graphitized [20]. In the inert atmosphere and high temperature, we use laser beam for vaporization of graphite target. Then carbon species are produced which are then swept to cooled copper collector by flowing inert gas. What is the quality of the product and the yield of the same totally depends on temperature? By changing the laser, composition of catalyst, temperature, attributes of gases & gas pressure, the diameter and size allocation of the nanotubes can be diversified according to need. And if we add bitty quantity of transition metals such as Ni, Fe or Co then SWCNTs can be produced. In 2003, Chen M. et al. worked on this and found that the use of Ni-Y alloy can increase the diameter of SWNT whereas it gets reduced by Rh-Pd catalyst [21].

2.1.3 Chemical Vapor Deposition

In 1890, some scientists from France observed the growth of cyanobacteria on a hot white vitrified ceramic means porcelain. Then in 1896, it was investigated that this growth was due to the interactivity of molten iron with carbon containing gases. With the passing years, CVD became most common method of mass production and synthesis of CNTs. In terms of crystallinity, the CVD-grown MWCNT shows low crystallinity while it is high for SWCNT. As CVD produces more pure products with high yield, it is considered superior to arc and laser method. After the contact of hydrocarbon with metal nanoparticles, it first putrefies into hydrogen and carbon. This carbon dissolves in the metal catalyst. After a particular temperature, carbon stops itself from dissolving and then starts crystallizing to form CNTs. On the basis that how strong is the binding interaction between carbon and metal catalyst, two types of growths can be seen and as shown in below Fig 2 and Fig 3.

![Fig.2. Different types of growth of carbon nanotubes in CVD](image)

Now a days, CNTs have also involved themselves in pharma as well as in various therapies. CNTs are used as drug vectors, biomolecule, gene delivers. Basically, the surface area of CNTs is large enough for drugs to bind with themselves. Then the CNTs take that drug to target sites. The drugs can be attached by two methods either they get loaded into CNTs or simply attached to the surface. It has been noted that internalization is more effective than surface attachment [23].

2.2 Fullerenes

In 1985, an unknown pure carbon molecule, C60, was discovered by a team of scientists. In 1996, Robert Curl, Harold Kroto and Richard Smalley won the Nobel Prize in chemistry for the discovery of the fullerenes. It was observed that for the formation of fullerenes, environment depleted of Hydrogen was an essential condition. Fullerenes are considered exceedingly efficient as compare to graphene as it (graphene) gets easily vaporized in hydrogen-deficient atmosphere with helium as buffer gas (Kroto et al. 1985, Kratschmer et al. 1990) [24]. When graphite is heated in electric arc in the presence of helium or argon, fullerenes are formed. After condensation of C11, a sooty material is formed which consists mainly of C60, smaller extent of C70 and traces of C32, C50, C75, C84 etc. Hence fullerenes can be achieved simply by dissolving soot in benzene or other hydrocarbons. A wine-red colored solution is obtained from which finally we can crystallize mustard-colored crystals. These different fullerenes are then separated by chromatography. Out of all, C60 fullerenes are most stable [25]. A major stability defining character of
fullerenes is pentagonal carbon rings. In all known fullerenes, most stable one is Buckminster as it has 12 such rings which arrange themselves symmetrically to form icosahedral structure. The stability is only due to this icosahedral structure because in it all the rings are isolated from each other hence do not cause any instability. The number of structures increases with the size. Exception is this that there are some giant fullerenes that possess icosahedral symmetry for example C_{180} and C_{240}. The instability of C_{60} than other large ones were demonstrated by Mochida and Colleagues. After heating C_{60} and C_{70}, they showed that at around 900-1000°C, the cage structure was broken down whereas hollow-sphere (diameter 10-20nm) were formed at 2400°C [26].

Fig.3. Synthesis methods of fullerenes

Fullerenes have the capacity to show cytoprotective action which provide protection against UVA irradiation. The ultraviolet A when come in contact with human skin, oxygen species are produced that react with skin causing cell damage and cell death. It has been found that fullerene derivatives radial sponge can provide better protection than vitamin C and this is due to its ability to enter into depth of human skin as it is stable towards oxidative decomposition. Fullerenes have also shown their excellence in brain science or neuroscience. The brain’s ability to regenerate the damaged cells is limited and it cannot control the oxidative damage caused by free radicals. The fullerene derivatives are well able to stop the chain reaction of lipid peroxidation [27].

2.3 Graphene

Graphene has gained the title of strongest material. It can be considered as monomer for carbon nanotubes & large fullerenes. The property due to which it is anomalous is the lack of electronic band gap with electrons having zero effective mass where valence & conduction bands meet. It is neither a metal nor semiconductor. Various great properties of graphene are getting revealed day by day which includes quantum hall effect, ultrahigh electronic mobility, incensed conveyance, long electronic mean free paths, superior chief thermic response, considerable mechanical toughness, outstanding pliability etc as shown in below table 1 and Table 2.

Table 1. Methods for Graphene production [28]

<table>
<thead>
<tr>
<th>Methods</th>
<th>Electronic quality of layers</th>
<th>cost</th>
<th>Nature of graphene produced</th>
<th>precursor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechnical exfoliation</td>
<td>High</td>
<td>Low</td>
<td>Pristine</td>
<td>Graphite</td>
</tr>
<tr>
<td>Liquid-phase exfoliation</td>
<td>High</td>
<td>Low</td>
<td>Chemically modified</td>
<td>Graphite</td>
</tr>
<tr>
<td>Epitaxial growth by thermal distortion of Si-atom from the SiC surface</td>
<td>High</td>
<td>High</td>
<td>Pristine</td>
<td>Silicon carbide</td>
</tr>
<tr>
<td>Vapor deposition on transition metals</td>
<td>High</td>
<td>High</td>
<td>Pristine</td>
<td>Hydrocarbons</td>
</tr>
<tr>
<td>Solvothermal synthesis</td>
<td>Not available</td>
<td>Low</td>
<td>Chemically modified</td>
<td>Ethanol</td>
</tr>
<tr>
<td>Unzipping carbon-nanotubes</td>
<td>Inferior</td>
<td>Low</td>
<td>Chemically modified</td>
<td>Multiwalled carbon-nanotubes</td>
</tr>
</tbody>
</table>

The National Science Foundation (NSF) is one of the major entities in the United States for funding graphene research [28].
2.4 Graphene oxide

The properties of graphene oxide were first discovered by B.C. Brodie, a British Chemist. Due to its unique properties, graphene oxide was the most researched topic at that time.

Methods of synthesis:

2.4.1 Brodie method

Then in 1898, his work was carried by L. Staundenmaier. He replaced two-third of fuming Nitric acid with Sulphuric acid and introduced repeated oxidations in it [31]. After 40 years, again he discovered a new more practical & simple method which was not including repeated oxidations [32].

2.4.2 Hummer’s method

the most/widely used method to produce graphene oxide was put forward by chemist Hummer and Offeman in 1958 [33]. In this method, KMnO₄ replaced KClO₃ (so that spontaneous explosion could be avoided), HNO₃ got exchanged by NaNO₃ and, moreover, this process was taking only few hours to produce graphene oxide of high quality. The Hummer’s method was considered best at that time, however, still there was some drawback as it was producing toxic gases like NO₂ & N₂O₄ [34].

Previous works on GO have revealed its various applications in biomedical field. As GO has large surface area so various biomolecules are immobilized on it. GO also can act bio marker. Due to various functional groups present, GO can easily disperse in bio fluids. The hydrophobic GO loaded with drugs are being used in cancer treatment. If we talk about its cytotoxicity, the tenability of size and dose made GO nontoxic as well as biocompatible [35].

2.5 Nanodiamonds

Nanodiamonds have the properties of diamonds and because of these properties, the nanodiamonds have become an interesting topic for research. They have color centers which are point-defects, present in diamonds, responsible for fluorescence. The most studied color center is Nitrogen-Vacancy. It can occur in 2 forms- neutral (NVO) and negatively charged (NV). Out of these two, NV⁻ is most researched one.

Nanodiamonds can be synthesized via detonation synthesis, chemical vapor deposition, HPHT, pulsed laser ablation [36]. Detonation method for nanodiamond synthesis has reduced due to powerful explosions. These explosions occur when trinitrotoluene and hexogen get mixed in a shuttled chamber, the conditions of temperature and pressure are created at which diamonds are thermodynamically durable & get smoothly produces nanodiamonds. In 1987, Lewis et al. delayered that the nanodiamonds were discovered in meteorites. When the minerals, which were present in meteorites, were dissolved in strong acids, a whitish or grayish powder was recovered. This powder was producing diamond peaks in X-ray diffraction [37].
As shown in above Fig 4, Fig 5 and Fig 6, Nanodiamonds have proved their pre-eminence in medical field. And this is only due to their properties like negligible toxicity, chemical inertness, small size, low cost, robust fluorescence etc. these nanodiamonds are being used for drug delivery, diagnosis, bone surgery devices, tissue engineering, antivirals [39]. Bone morphogenetic proteins (BMPs) are majorly applied for cartilage and bone development. But its utility is getting limited by delivery method. So, these days, detonation nanodiamonds serving as delivery vehicle for BMP-2 and basic fibroblast growth factor (bFGF). BMP-2 and bFGF when loaded on nanodiamonds, they form a colloidal solution & then targeted to release in acidic conditions. Hence, we can say that nanodiamonds have provided an alternative for drug delivery in bone formation [40] carbon nanoparticles and received their name by Sun et al. in 2006 [41].

2.6 Quantum dots

Table 2. synthesis methods of quantum dots [42]

<table>
<thead>
<tr>
<th>Synthesis method</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical ablation</td>
<td>Ultimate attainability/sun dry authority</td>
<td>strident situation, immoderate process, various-styles, meager restraint over sizes</td>
</tr>
<tr>
<td>Electrochemical carbonization</td>
<td>Size and nanostructure are tractable, durable, single stepped</td>
<td>slight paltry forerunner molecules</td>
</tr>
<tr>
<td>Laser ablation</td>
<td>Hasty, impactful, surface states atonal</td>
<td>Low QY, poor control over sizes, alteration is required</td>
</tr>
<tr>
<td>Microwave irradiation</td>
<td>Fast, climbable, worthwhile, ecofriendly</td>
<td>Sises are not under control.</td>
</tr>
<tr>
<td>Hydrothermal/isothermal treatment</td>
<td>Practical, reliable and secure</td>
<td>One cannot modify the sizes accordingly.</td>
</tr>
</tbody>
</table>

Carbon quantum dots have electronic, physiochemical as well as optical properties. In all these properties, most researched & studied are optical activities. Researchers find it interesting to work on optical activities of CQDs. They also have their solicitation in biosensing and bioimaging. However, semiconductor quantum dot are considered highly toxic because of the heavy metals present in them as heavy metals are very much toxic even at their low levels. Hence CQDs have replaced these semiconductor QDs due to their low toxicity, low cost, chemical inertness. These CDQs were discovered (by a mere chance) by Xu et al. in 2004 during separation and purgation of SWCNTs. Earlier carbon quantum dots were called fluorescent High aspect ratio, transparency under visible light, electrical and environmental stability, quantum dots are being used in sensing. Immunosensors including QDs shows high selectivity for antigen detection. QDs are porous and can generate oxygen and this property makes it available to serve in photodynamic cancer therapy. The produced oxygen destroys the cancer cells. But this therapy makes the patient very sensitive towards daylight exposure. To prevent these side effects, a hydrophobic dye molecule is enclosed into QDs. This dye lowers the chance of leak & spread to other body parts [43].

3. Discussion

In the discussion segment, we will discuss about the applications of carbon nanomaterials that why they are being researched even in today’s time, how they are improving layman’s lifestyle, what are their roles in medical sciences.
xi. Graphene has its applications in biomedical field like biosensing, cell differentiation and growth, laser desorption [54].

xii. Graphene also has shown its importance in drug delivery and gene delivery in cancer therapy [55].

xiii. Graphene acts as constituents for the treatment of water and desalination film [56].

xiv. Graphene based nanomaterials are being making supercapacitors, double-layer capacitors, asymmetric supercapacitors [57].

xv. The additional groups on graphene oxide absorbs gas molecules and hence helping in making strong gas sensors [58].

xvi. Nanodiamonds have various applications in tribology, tissue engineering [59].

xvii. Nanodiamonds have significant role in separation and purification of proteins. It also has decreased the time of separation (30-40 minutes) [60].

xviii. Nanodiamonds help in diagnosis of infectious diseases [61].

xix. Nanodiamonds in fluorescence resonance energy transfer analysis [62].

Conclusion

Nanotechnology is the field that invents new devices or applications on the scale of atoms & molecules. In this review, we have talked about CNTs, fullerenes, graphene, graphene oxide, nanodiamonds, quantum dots. We have seen their properties, applications, structures, discoveries and many more. After studying all these things, we can conclude that CNTs & Graphene are best among others because they are strongest as well as lightest and most conductive too. The nanomaterials have their applications in electrical, mechanical, chemical and biomedical field also. Due to hard work and determination of our nanotechnologists, their many excellent properties have been revealed. This study is going on and will disclose many other qualities which will make our lives easier.

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