Chapter

Recent Developments in *Nanocarbon-Polymer Composites* for Environmental and Energy Applications

Prateek Khare, Ratnesh Kumar Patel and Ravi Shankar

Abstract

Advancement in technology is brought up for both the industrialization and urbanization, which imitates the diverse pollutants as by-products to air-water ecosystem. Utilization of carbon is a very well-known age-old practice used for environmental remediation. In recent past years, a tremendous research inclination has been witnessed toward the sustainable development of nanocarbons specifically for environment remediation and energy applications. The new sustainable synthesis approached has been investigated for the development of sustainable nanocarbons. Tailoring the nanocarbon with polymer as a nanocomposite material has spotlighted a new class of environmentally benign bio-compatible materials. Herein, the present perspective is summarizing the basic-advanced research.

Keywords: nanocarbon, polymer composite, bio-polymer, environmental remediation

1. Introduction

Use of chemical products such as, conventional energy reserves, synthetic detergents, pharmaceuticals, dyes, fertilizers, polymers and composites, food additives, agrochemicals, etc., increases over period time across the developing and developed countries and simultaneously is very important for the development of any economy. The society is consuming such products at an exponential rate and thereby generating pollutant in terms of fuel combustion, waste generation in the process operation and waste disposal [1]. Till date, due to their maximum operational, and consumption of the conventional energy reserves including, fossil fuel, and coal are the prime factors of increasing the pollutions to the biosphere at such alarming rate. Moreover, their residue generates unwanted carbon like carbon soot interact ecosystem imparts their toxic nature and affects the ecology [2–4].

Developments of the green environmentally benign materials and its competent with technology advancement are very necessary and now have become a challenging task for the developing eco-friendly society in the biosphere. The concept of zero-waste production, waste prevention, and with use of efficient materials is the prime concerned for the industries, Therefore, for a healthy society, the role of green chemistry is significant, achieving these targets [5]. As it is a well-known mechanism that green chemistry offers a relatively lesser toxic synthesis approach, by reducing the harmful chemical substances in the designing the useful chemical products [6]. Nowadays, due to the unique properties of carbon-based nanomaterials like good electrical conductivity, ease in surface functionalization, high mechanical strength and good thermal stability of carbon-based fullerenes carbon nanotubes (CNTs), carbon quantum dots and graphene, attracted high interest toward research and used widely in many application purposes. Therefore, in the reported literatures, as wonder materials, carbon-nanomaterials have been used directly or modified for aforesaid applications [7]. Although, following complex techniques and expensive hydrocarbons or other specific hazardous source like laser are not easy to handle in different synthesis routes like chemical vapor deposition (CVD), plasma CVD, laser ablation used for the synthesizing the different carbon-based nanomaterials. There are some reported literatures in which an inexpensive and environmentally friendly approach is exploited for recovering the carbon based nanomaterials and experimentally particularly shown their applicability in remediation and sensing applications [8–14]. The synthesis of nanocomposites plays leading role in the current advanced applications purposes such as, energy storage, electronics parts, environmental remediation, biomedicine, etc. [15].

Present book chapter deals with production and potential applications of nanocarbon and nanocarbon-polymer composite materials, with special attention on the energy and environmental related sector and their significant role in enhancing the efficacy for the previously mentioned applications.

2. Classifications of carbon and carbon-based nanomaterials

Carbon have tendency to polymerize into the large molecular weight compounds with long chains due to its unique electronic construction and the smaller size in comparison of group IV that makes it capable of linking with other elements. As it contains four electrons in the valence layers, carbon can easily form covalent bonds with both metals and non-metals. Due to this property, carbon-based compounds can exist in diverse molecular forms, and same type of atoms can be arranged in the different shapes, with different properties known as allotropes. Graphite and diamond are two known natural occurring allotropes of carbon found in the ecology and formed other multiple allotropes of carbon from natural carbon sources for the different purposes. Furthermore, with the knowledge of top down and bottom up approaches of nanotechnology, a new family of carbon nanomaterials as wonder materials is introduced. In recent past years, the different types of carbon nanomaterials have been experimentally tested and successfully developed as advance materials in many engineering applications. In general, carbon nanomaterials exist in between 1 and 100 nm size range; therefore, the unique properties of carbon nanomaterials like good electrical, ionic conductivity, high mechanical and thermal stability at the nanoscale compared with other materials are exceptional and competent for many engineering applications [16]. Carbon nanomaterials are classified further based on their shape and geometrical structures, till dates different forms of carbon nanomaterials that are existing; horn-shaped as nanohorns, tube-shaped as carbon nanotube (CNT), ellipsoidal spherical shape carbon nanospheres (fullerenes), and zero-dimension dots exhibited quantum character as carbon quantum dots (CQDs). Because of excellent properties, carbon nanomaterials have now been extensively used synthesizing the nanocomposite materials that and used in many applications including microchannels, micro/nanoelectronics, textiles, paints, gas storage, composites, conductive plastics, displays, antifouling batteries with excellent durability during cycling-charge. The carbon quantum dots, as a newly emerging biocompatible material, have exhibited fluorescence properties and possess many other valuable excellent properties, such as high aqueous solubility, low cost, low toxicity, abundant surface functional groups and large active surface area for functionalization. Although, besides being used as bio compatible materials, such new class of (carbon quantum dots) nanomaterial are also applied as gas biosensors and heavy metal sensing applications [7, 17, 18]. In particular, the unique features of CQDs as up-converted photoluminescence (PL) behavior and photo-induced electron transferability of CQDs have proposed a new route for harvesting the sunlight from nonconventional reserve, to achieve efficient metal-free photocatalysts [19–21].

2.1 Fullerenes

Fullerene as a new class of carbon family had introduced by Kroto, Curl and Smalley [22] in 1985 and denoted as buckminsterfullerene (C60). It is an intermediate allotrope of carbon between graphite and diamond as it constitutes from the bunch of atomic C*n* repeating unit (*n* > 20) which are collectively composed to form a spherical surface having a hollow core, or empty region of space inside the molecule. Carbon atoms are usually located on the surface of the sphere at the vertices of pentagons and hexagons and linked by forming sp2-hybridizing covalent bonds. Generally, C60 has two bond lengths, in which double bonds for 6:6 ring bonds are shorter than the 6:5 bonds. The important distinct characteristic ofC60 is that the pentagonal rings resulted in poor electron delocalization. As a result, C60 behaves like an electron deficient alkene, and reacts readily with electron rich species. C60 is the odorless, and nonvolatile black solid having density 1.65 g/cm^3, standard heat of formation 9.08 kcal/mol with boiling point of 800 K [23]. Fullerenes, due to its excellent properties like superconductivity, radical scavengers and excellent durability, are frequently applied in medicinal and electronics field, also in solar cell, fuel cell, cosmetic products (low order fullerene such as, C28, C26, etc.), biological/medical area, catalysis and other relevant fields [24–26]. Furthermore, fullerene can be easily modified to tailor properties for nanocomposites synthesis. [27].

2.2 Carbon nanotubes

CNTs are one of the types of allotrope among carbon-based nanomaterials that have excellent mechanical and electrical properties. CNT are light-weighted, high strength material as compared to steel at nondimensional scale and discovered first by a Japanese scientist S. Ijimain 1991. Nowadays, due to its extraordinary graphic nature and high specific surface area have attracted attention and applied as a pillar material in many engineering applications like battery, electrochemical, pollutant remediation, and used as fillers for nanocarbon-polymer composites [28–30]. CNT exist broadly in two different shapes; cylindrical shaped is formed by rolling of the graphene sheets; and possessed cap fullerene structure appeared in half shape. Based on their geometrical configuration as proficiently qualified is experienced by high voltage electron microscopy techniques. CNT are further classified into two types (i) single-walled carbon nanotube (SWCNT), and (ii) multiwalled nanotube (MWCNT), Carbon nanotubes are prepared in rolled sheets of very few single layer carbon atoms (graphene) form cylindrical molecules. CNT with diameter 1–3 nm and length of few micrometers while for MWCNT, graphene sheets having 0.34 nm of inter-space distance, are stacked like concentric layers in cylindrical form of diameter 5–40 nm. Zhang et al. has been described in a reported literature, which is approximately 550 mm in length [31]. The properties of CNT are basically dependent upon the diameter, size and morphology. There are several methods are reported for CNT preparation like arc discharge, laser ablation, chemical CVD, and plasma CVD. Among the listed methods, arc discharge was the first technique used for the preparation of CNT while laser-ablation method was used to prepare the SWCNT. In the chemical CVD method, small amount of metallic catalysts (Ni and Co) are used to catalyze the hydro-carbon as source at relatively lower temperature for the growth of graphitic surface. The high enhanced electrical property of SWCNTs is due to the presence of the chirality or hexagon orientation with respect to the tube axis, however on bulk scale its synthesis process is very complex and not easy to control the layers. In contrast to the SWCNT, due to the presence of multiple layers, MWCNT possess high mechanical and thermal satiability. Further, based on SWCNTs morphology, it is classified into three subgroups: (i) armchair morphology exhibiting high electrical conductivity than the copper, (ii) zigzag morphology has good semiconductor property and (iii) chiral morphology has semi-conductive property.

2.3 Graphene

Graphene is two dimensional, single-atom layer of carbon atoms which are sp2 hybridized and fixed in a rigid hexagonal lattice like a flat plane. Graphene is also a primitive building element of graphite, fullerene and CNT, Graphene was discovered in 2004 by Canadian physicist Wallace. It is an allotropic form of carbon with bond length of 0.142 nm between neighboring atoms of carbon and layer by layer of graphene is stacked with an interplanar spacing of 0.335 nm. The layers of graphene in graphite are bounded by Van der Waal forces [32, 33]. The unique physical properties of graphene, such as, thermal stability, mechanical rigidity and electrical conductivity are higher for few layers of graphene than of their three-dimensional materials. Also, graphene conducts high heat because of high thermal conductivity of graphene in comparison with available excellent heat conductors such as, silver and copper, and much better than graphite and diamond [7, 33].

2.4 Carbon quantum dots

A new class of with unique fluorescent property of carbon nanoparticles discovered accidentally Xu et al. in [34] during purification of SWCNTs. Later in 2006, Sun et al. had given a name of such fluorescent materials as carbon quantum dots (CQDs) particle of size found less than 10 nm. Till date, due to its fascinating property (harvesting optical light and imparting multicolor tuned emission) of CQDs offers a surprising potential material in fields of bio-imaging, photo-degradation and catalysis applications [35]. In last decade, various chemical precursors like citric acid, ammonium citrate, ethylene glycol, benzene, phenylenediamine, phytic acid, and thiourea, have been used for synthesizing CQDs. In order to minimize energy consideration, various synthetic methods, including hydrothermal, solvothermal, electrochemical, microwave assisted pyrolysis, ultrasonication, and chemical oxidation, etc., have been tested to produce the fluorescent CQDs. A number of review and research papers have been focused on the synthesis of such CQDs [36–39]. However, to date there has not been a very few reviews which explicitly focused on green synthesis routes is discussed in details for sensing and bio-imaging of applications [40].

Figure 1 describes the different types classification of synthesis routes used in developing the different types of nanocarbons.

2.5 Naturally occurring synthesis nanocarbon

Nanocarbons occur naturally, but not available at abundant scale; therefore, this approach is not very conventional to control the number of graphitic layers,

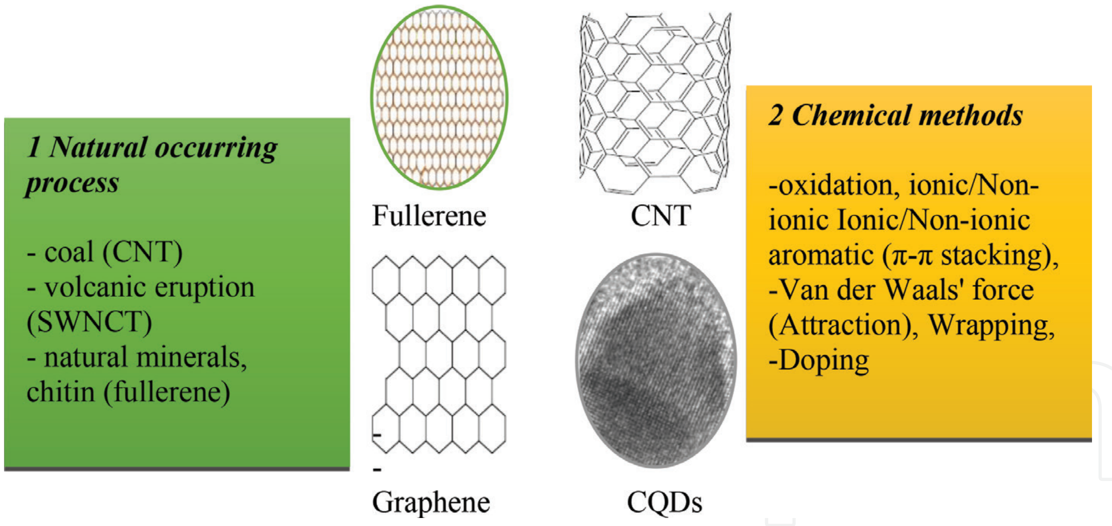

Figure 1.
Types of synthetic routes of different nanocarbons.

therefore their physical and chemical properties of nanocarbon may vary for engineering applications. There are different types of nanocarbon available from natural synthesis are reported in literature [41]. Velasco-Santos et al. described the existence of carbon nanotubes in the coal/petroleum mixture [42]. SWCNT can be synthesized by CVD, Su and Chen, 2007 and Mracek et al. 2011used metal oxide mixed volcanic lava as a substrate and catalyst [43, 44]. It was noted that process may provide indication for a probable creation of nanomaterials in natural conditions when the temperature rises extremely high, e.g., during volcano eruptions. Like CNT and SWCNT, fullerenes are also found in different ecological materials, for example in the natural mineral shungite from Karelia fullerene is found in low concentrations (2% w/w) [45] and also in meteorite samples of cosmic origin [46]. Chitin is one of the naturally occurring nanomaterials obtained from carbohydrate polymer. Synthesis of chitin nonmaterial considers the following factors such as, thermal dimensional stability, dispersibility, mechanical reinforcements, antibacterial activity etc. depending on the specific goals [47]. Natural nanomaterials can be obtained from polymer waste and its feasibility depends upon processing, recycling, transportation cost, etc. [48].

2.6 Chemically functionalized nanocarbons

Chemical functionalization process formed a huge distinct variety of carbon-based nanomaterials having different functionality, which are applied successfully in different sectors. As the surface functionalization means, carbon-based nanomaterials are added with other groups that ultimately changed its chemical and physical properties [49, 50]. There are many methods of functionalization available for carbon based nanomaterial, such as oxidation, ionic/non-ionic aliphatic aqueous (Hydrophobic), Ionic/Non-ionic aromatic (π-π stacking), Van der Waals' force (Attraction), Wrapping, doping, and direct deposition. The modification of surfaces is depending on the feasibility and degree of functionalization for the specific application. Therefore, in light of specific application, materials have been synthesized by following different mechanisms like non-covalent bonds, covalent bonds, electrostatic force, hydrogen bonds, Van-der Waals force etc. [51]. Some example of surface modification are as follows; Jiang et al. covered the CNT surface with active sulfate groups by using sodium dodecyl sulfate ($NaC_{12}H_{25}SO_4$) a common surfactant (anionic) for dispersing the sulfate groups [52]. In oxidation process CNT are exposed to mixture of acids via ultrasonic treatment method, during this process, carboxylic groups (–COOH) is attached with CNT surfaces. Oxidation of CNT is very important and creates oxygen carrying groups (–COOH and –OH), which makes CNT feasible for further functionalization without affecting their electrical and mechanical properties [7].

3. Potential applications of carbon-based nanomaterials

The outstanding physiochemical properties of nanocarbons have triggered interest, toward the applicability of nanocarbons, in multiple area including adsorption, photocatalyst, fertilizer, nanobiotechnology products, environmental materials, and renewable energy related application etc. De Volder et al. reported industrial scale production approximately up to several thousand tons of nanocarbon [17]. Properties like, high thermal stability and mechanical strength of nanocarbon make them suitable alternatively as fillers provides high aspect ratio for nanocomposites materials. Therefore, the prepared nanocomposites materials exhibited enhanced mechanical and other properties as compare to their starting primitive materials [53]. Nasibulin et al. reported the composite material based on cement matrix in which the addition of nanocarbon to original materials exhibited higher strength composite material [54]. Use of low weight, high strength materials in mechanical equipment improves the overall efficiency with low energy consumption. Regarding this use of nanocarbon based materials in energy generating machine such as, turbine as a lightweight and mechanically tough material is desirable [55, 56], and non-corrosive nature and insoluble nature of sp2 hybridized nanocarbon as fillers for marine turbines [57], various electronic applications [58], automotive industry [59], aviation [60], sport equipment allow to use strong and light weighted materials, which generates economical energy generation at optimal energy consumption. Fullerenes and composite based materials are frequently used in pharmaceutical industries [61]. Nowadays, graphene and its composite are frequently in high demands in various applications such as, electronics, solar cell, biochemical sensors [62]. Carbon based nanomaterials based composite materials having excellent properties like high tensile strength, flexibility and good electrical conductivity that make them more favorable for electronics applications [63]. Similarly, the graphene-carbon nanotube/polyvinyl alcohol based composite show high rigidity, strength, and ductility in comparison with conventional nanocarbon materials. Although there is a dramatically increase in the resistivity witnessed for graphene-carbon nanotube/polyvinyl alcohol-based composite, Therefore, such composite materials can be a suitable as a smart stretchable insulator devices using formed by combining the property of conductive nanocarbon materials with epoxy polymer [64].

3.1 Environmental applications of nanocarbon-polymer-based composites

Ecological balance is essential which is majorly affected by different pollutants. Therefore, it is difficult to check ecology balance simultaneously with the rapid growth of industrialization and civilization. In this regard, it is required to increase effectiveness by taking some corrective measures in pre-existing methods of controlling pollutions [65, 66]. In light of nanotechnology knowledge, advanced nanomaterial/composite materials can be developed that significantly enhanced the performance of different pre-existing treatment technologies [55, 57]. For example nanocarbon provide high specific surface area thus, carbon-based nanomaterial/composites provide high specific surface for the adsorption process [29, 30] oxidation process [67, 68], and electrochemical applications [69, 70]. Although, the nanocarbon is one of the most effective adsorbents used in the wastewater treatment because of its high surface area to weight ratio. But, it cannot be applied directly in flow or dynamics conditions [71]. Specific affinity of metal functionalized-nanocarbon based materials as adsorbent exhibited high adsorption capacity specific for different heavy metals (As, Fe, Pb, Cu), vitamin B12, nitrates, phosphates and show superior antibacterial activity than that of primitive activated carbon [72–77]. Moreover, after adsorption operation, specific adsorbate with nanocarbon based adsorbent can be separated by the mechanism of filtration and can be recycled [10]. But, high preparation cost of nanocarbon based materials and uncertainties regarding the leaching potential are the major challenges in the application of nanocarbon based materials. Silver coated carbon-based nanomaterials can be used as an antibacterial material and used in disinfection purposes, antimicrobial activity and preparation of biomedical devices [78]. Carbon nanotubes, activated with alcohol 1-octadecanol can also be used as better adsorbent for the absorption of microwaves because of its antibacterial characteristics. So, it can be used in the water purification technologies [79].

Moreover, nanocarbons are not only important in the pollution reduction in different ecological sections, but it has significant importance in the monitoring of pollution stages. Carbon-based nanomaterials and their composites can be used for the development of different and efficient sensors (biochemical) to detect very low concentrations of chemical compounds in different environments. For example, carbon nanotubes loaded with ZnO nanoparticles can be used for congo red dye reduction from aqueous solutions and showing that ZnO/MWCNTs is a promising, environmentally friendly and efficient adsorbent for wastewater treatment [80].

3.2 Energy applications of nanocarbon-polymer-based composites

Economy of any country is directly boom if they can produce and store energy particularly from renewable resource. In this viewpoint carbon-based nanomaterials and their composites can play an important role in the area of energy harvesting and energy storage. It is well known most of the nanocarbon composed of sp2 hybridization and possessed excellent properties such as, high pore size distribution, high surface area, with enhanced mechanical properties and improved electrical properties. In recent years, nanocarbon and nanocomposites are widely applied for developing energy storage and energy saving devices/instrument. Photovoltaic cells are commonly known as solar cell used as an alternative device for harvest renewable energy sources. Photovoltaic cells can be classified in two categories such as, thin films and crystalline silicon photovoltaic cells. Earlier, silicon, cadmium, copper-based compounds are used in the semiconductors used [81, 82] applied in energy storage devices. Nowadays thin-film group photovoltaic cells used platinum-based semiconductor for high band width/specific related applications. But, high cost and availability of platinum increases overall cost of an instrument. In this case carbon-based nanomaterials/composites can play an alternative role of platinum-based materials due to its superior properties [83]. Generally, nanomaterials prepared from graphene are used to enhance electron carriage and boost the efficiency of solar energy conversion [84]. Graphene-based materials can also be used in fuel cells and batteries due to its favorable properties.

Supercapacitors are used for energy storage devices applied in electric vehicles, hybrid electric vehicles, backup power cells, and portable electronic devices due to its advanced properties such as, high-power density, very short charging time, and high cycling stability. The main mechanism of storage of energy in super capacitors are pseudo capacitance and electrochemical double-layer capacitance. In pseudo capacitor, faradic reactions mechanism is responsible for charge transfer processes.

	SN	Nanomaterials	Method	Materials used	Conditions	Application	Ref
Environmental Application	1	Multiwall carbon nanotube	Oxidation, filtration, drying	H_2SO_4: HNO_3 (3:1)	Sonicated; 3 h; 40°C	Heavy metal removal (Cadmium reduction)	[67]
	2	Oxidized multiwall carbon nanotube	EDA, N - HATU, filtration, drying	NH_2 materials	Sonicated; 4 h; 40°C	Heavy metal removals (Cadmium and lead reduction)	[68]
	3	Multiwall carbon nanotube	Oxidation/reduction/pyrolysis	Ethanol/ferrocene/thiophene	Airflow, 400°C, argon flow, 600–900°C	ciprofloxacin reduction from aqueous solution	[90]
	4	Graphitic oxide	Oxidation, filtered; washed; dispersed	$NaNO_3$, H_2SO_4, $KMnO_4$, H_2O_2	Vigorous agitation 20–66°C, dilution: 98°C, 15 min	Wastewater treatment	[91]
	5	Graphite Oxide	Oxidation, sonicated; washed; dried	$Na_2S_2O_3$	Sonicated; 1 h, disproportionation; 30 min	Heavy metal removal (mercury Hg^{2+} reduction)	[92]

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	SN	Nanomaterials	Method	Materials used	Conditions	Application	Ref
Energy Application	6	Graphite powder	Heating, drying, filtration, mixing	$K_2S_2O_8$, P_2O_5, H_2SO_4, $KMnO_4$, H_2O_2	Heating: 80°C, ice bath: 20–35°C, mixing: 35°C for 2 h	Fabricating of various microelectrical devices	[93]
	7	Graphene oxide, graphene nanoplatelets	Heating, drying, filtration, mixing	Polyethylene glycol, H_3PO_4, $KMnO_4$, H_2SO_4, HCl, H_2O_2	Mixing: 50-0 °C for 12 h, Drying: 50°C, sonicated; 1 h	To prepare higher thermal energy storage material	[94]
	8	Single wall carbon nanotube	Absorption, drying, Nitration	HNO_3, Ag/AgCl electrode, methylene blue	Nitration: 10 h, methylene blue doping: 3 h	Application in biofuel.	[95]
	9	carbon nanotubes	Melting/heating, sonicated	graphite nanoplatelets, phase change materials	Heating: 60°C, ultrasonicated at pulse velocity of 25 m/s for 20 min	To prepare enhanced thermal conductive material	[96]
	10	Porous carbon and hydrous RuO_2	Oxidation, absorption	Sulfuric acid		Supercapacitor for energy storage	[97]

Table 1.
Application of nanocarbon based materials in energy and environmental field.

Many metals/oxides/conducting polymers are good examples of the pseudo capacitance process. While, in electrochemical double-layer capacitance processes, charges are accumulated at the interface by the mechanism of adsorption/desorption process of electrolyte ions on a large surface area electrode materials. So, in this regards carbon-based nanomaterials can play an important role in the supercapacitor preparations [85]. Supercapacitors based on nanocarbon have many advantages over conventional (metal-based) supercapacitor, such as, high cycling stability, high power density and low energy density limits for their applications in batteries [86].

Excellent mechanical and electrical properties of nan0carbon-based materials (carbon nanotube) offer an exposed surface to functionalize and make them suitable for energy storage. But, it has some disadvantages such as, moderate capacitance due to low density of nanomaterials [87]. The lithium-ion battery is alternative type of energy storing substance, which holds energy as a chemical energy. It has many advantages over capacitors such as, high power density, and less greenhouse gas emissions possibilities [88]. Nanocarbon materials/composites are used in the lithium batteries because structure of the nanocarbon-based material usually express some common factors such as, the amount of lithium that is reversibly incorporated into the carbon lattice, the faradic losses during the first charge–discharge cycle, and the voltage profile during charging and discharging.

Carbon based nanomaterials such as, carbon nanotubes, activated carbons, and graphene based nanosheets are suitable for sustainable energy storage devices, because, carbon materials have many favorable properties such as, light weight, low cost, easy processability, adaptable porosity, and simplicity of chemical modification [89]. Generally, higher specific surface area and pore size distribution of nanocarbon structures allow them to increase the performance of electrochemical capacitance in terms of both the power delivery rate and the energy storage capacity. Some nanocarbon based materials used in the environmental and energy application are shown in **Table 1**.

4. Conclusion

This book chapter has focused on the application of nanocarbon-based materials/composites in the environmental and energy relevant area. Numerous exceptional properties of nanocarbon based such as, outstanding pore size distribution, large surface area, ease of porous texture modification, mechanical, thermal stability and chemical deformation make them appropriate for the different application. Overall functional group related to nanocarbon attached with specific materials/metals and increases the electrical, thermal and other desirable properties of the composite. Modified nanocarbon-based materials with enhanced electronics properties can be used for the different electronics devices in energy relevant area such as energy storage, conduction, radiation, etc., and environment relevant area such as, pollution parameter detecting devices. Higher surface area of nanocarbon based materials in comparison with conventional materials can be used in the pollution remediation application. Antibacterial nature of nanocarbon based materials can also be used in wastewater treatment for disinfection process and it can be used in preparation of biomedical relevant area to minimize bacterial contamination.

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