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Review Article

Carbon Nanotubes (CNTs) from Synthesis to Functionalized (CNTs) Using Conventional and New Chemical Approaches

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Carbon nanotubes (CNTs) have emerged worldwide because of their remarkable properties enlarging their field of applications. Functionalization of CNTs is a convenient strategy to tackle low dispersion and solubilization of CNTs in many solvents or polymers. It can be done by covalent or noncovalent surface functionalization that is briefly discussed regarding the current literature. Endohedral and exohedral are conventional methods based on covalent and van der Waals bonding forces that are created through CNT functionalization by various materials. In this paper, a review of new approaches and mechanisms of functionalization of CNTs is proposed, including amidation, fluorination, bromination, chlorination, hydrogenation, and electrophilic addition. Our analysis is supported by several characterization methods highlighting recent improvements hence extending the range of applicability of CNTs.

1. Introduction

Nanotechnology is a branch of material science in which nanoparticles with specific intended properties are synthetized or produced by the application of chemical and physical processes. Besides the most famous carbon forms like amorphous carbon [1], diamond [2], graphite [3], or lonsdaleite [4], more exotic allotropes of carbon were successively discovered such as fullerene (C_{60}) [5], fullerenes C_{20}, C_{240}, C_{540}… [6], carbon nanotube and graphene [7], carbon nanotorus [8], carbon nanobud [9], peapod [10], cup-stacked carbon nanotube [11], nanodiamond [12], and carbon nano-onions [13]. The carbon nanotube (CNT) represents one of the best novel nanostructures. Its discovery was made in 1991 by Sumio lijima by arc-discharge method [14]. It is presented as multiwalled carbon nanotubes (MWCNTs) defined as allotropes of carbon, tubular in shape and made of graphite containing at least two layers with a spacing of 4 to 30 nm in diameter whereas single-walled carbon nanotubes (SWCNTs) were fabricated two years later in 1993 consisting of a single seamless cylinder of graphene generally closed at each end [15]. Mostly, physical properties of carbon nanotubes are derived from graphene regarding their simplest synthesis approaches and chemical composition [16]. Carbon nanotubes have emerged worldwide, because of their remarkable properties, dimensions, strength, and physical properties providing a very unique material with large applications: extended new scientific results are published continuously in all CNT application fields and disciplines [17–19] such as medical applications [19], coatings and films, microelectronics, energy storage, environment and biotechnology [20], and

CNT cotton super fiber materials [21]; CNTs are also used as composite membrane [22], transparent electrodes [23], and catalysis [24] and can act as a transistor [16, 25].

Chemical stability is an important part of CNT properties. CNTs have high chemical and environmental stability; the chemistry of carbon nanotubes focuses on the purification, solubilization [19], dispersion, and functionalization [26]. Chemical functionalization is a new promising approach that enlarges the application field of CNTs by developing novel nanomaterials based on value added by several materials to CNT armature that can be realized by the mean of multiple strategies.

Several authors reviewed chemical modification of CNTs for a precise field of application such as in the removal of dyes from wastewater [27] medical diagnostics and drug delivery [28]. Kamran et al. focused on the strategies and methods of functionalization or modification of carbon-based materials and highlighted their applications in electronic devices [29]. Syntheses of different CNT structural types including CNT functionalization strategies are reviewed by Verma and Balomajumder applied for removal of aqueous heavy metal [30]. Xu et al. have additionally reviewed the technical preparation of functionalized CNTs and graphene by several mechanisms for adsorption of heavy metal from water [31]. The two major techniques of functionalization are described by covalent and noncovalent interactions of CNTs, and different material groups were reported for a specified application such as drug delivery and biosensor devices [32, 33]. Among the available tools for functionalization of CNTs, the use of polymers as a class of materials in interfacial CNT functionalization is reviewed by Chen et al. [34]. Grafting the surface of SWCNTs by oxidative procedure offers opportune properties correlated to optical properties of modified SWCNTs [35].

By reviewing all the previous articles, we believe that CNTs going from synthesis to functionalization encompassing the conventional methods and new approaches were not properly discussed despite of the number of publications on these nanostructures. Their recent advancements in this field have not yet reviewed. In this review, we focalize in giving an overview on carbon nanotube structure and synthesis; then, we cover the different methods of functionalization of CNTs based on endohedral and exohedral conventional methods using different functional materials going from functional groups, surfactants, oligomers, and polymers aiming for CNTs to cover a specified application. We present in details recent chemical approaches according to Figure 1 with the functionalization of CNTs including practical uses of functionalized CNTs in many fields of applications. In the light of this fact, we have an intention to do a throughout study reviewing exclusively the recent advances in CNT functionalization which will provide researchers a global insight of the main functionalization strategies of carbon nanotube nanostructures [36, 37].

2. Basic Structure and Morphology of CNTs

Carbon is the chemical element of atomic number (A = 6); it is tetravalent making four electrons available to form covalent chemical bonds; their electrons occupy $1s^2 2s^2 2p^2$ atomic orbital. It can hybridize in sp, sp^2, or sp^3 forms. Carbon nanotubes (CNTs) are made of hexagonal sheets of carbon atoms rolled up into tubular structure having different helicities seamless of graphitic sheets cylindrical; the structure of CNTs is composed of sp^2 bonds [38], and each end is capped with half a fullerene molecule having stronger bond than sp^3 bonds compared with diamond that provides them unique strength [21, 39]. CNTs can be merged under high pressure and changing some sp^2 bonds for sp^3 bonds [18, 40].

Carbon nanotubes can be divided into two categories: single walled (SWCNTs) or multiple walled carbon nanotubes (MWCNTs) [1]. SWCNT is formed by rolling up a piece of graphene with a diameter of (1-2 nm) while MWCNT consists of many SWCNTs; it has concentric cylinders placed around a common central hollow with a spacing of 0.34 to 0.39 nm between the layers, slightly larger than the single-crystal graphite value of 0.335 nm [41–43]. Due to severe geometric constraints in these tubes presented during the formation of seamless concentric cylinders, the quality of CNTs depends on the exact method and conditions of production as reported elsewhere [21, 44–46].

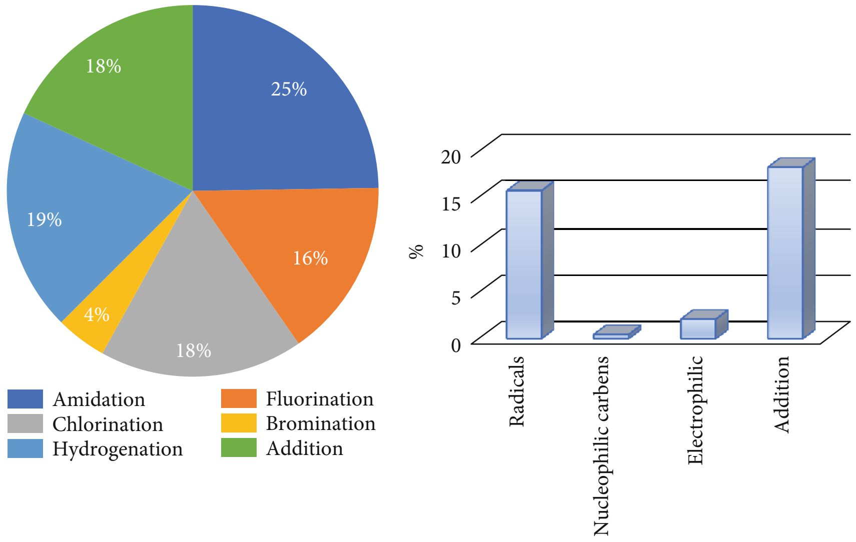
All possible ways how the graphene sheet can be rolled up to the cylinder can be represented by a pair of integer numbers or chiral indices n and m that predefine the chiral vector ($\overrightarrow{c_h}$). Chiral angle (θ) and chiral vector ($\overrightarrow{c_h}$) can be classified into three categories as zigzag, armchair, and chiral in terms of the chiral vector $\overrightarrow{c_h}$ as shown in Figure 2 [47, 48].

MWCNTs and SWCNTs have similar properties. The sp^2 bonds between the individual carbon atoms in CNTs give carbon nanotube intrinsic mechanical properties; this bond is even stronger than the sp^3 bond found in diamond; for this reason, carbon nanotubes are considered the strongest materials [18, 51]. CNTs have remarkable flexibility and resilience due to the high anisotropy of graphite. Their Young's modulus is superior to all carbon fibers, greater than 1 TPa; compared to steel, it is approximately 5 times higher. This specific characteristic gives carbon nanotubes a possible use in composite materials with improved mechanical properties [18, 32, 40].

CNTs have high thermal conductivity: SWCNTs up to 3500 W/m.k and MWCNTs more than 3000 W/m.k [40, 52]. Their densities can be draw up or below 1.3 g/cm^3 [51]. Elasticity is another special property of carbon nanotubes; when they are exposed to great axial compressive forces and under high force, CNTs can bend, twist, kink, and buckle, and they will return to their original structure with preserving their properties presenting a Newtonian behavior, providing that powerful force presses are not greater than the limit elasticity force of nanotubes [18]. CNTs have also extraordinary electronic properties comparable to copper. They have high electrical conductivity, because of the chirality (the chiral angle between hexagons and the tube axis); CNT can be metallic or semiconducting; in another way, the energy gap decreases with increasing tube diameter [18, 52].

3. Fundamental Methods of Synthesis of CNTs

A variety of techniques have been developed to synthesize high quality CNTs with different structure and morphology



(a)

(b)

Figure 1: (a) Statistical published papers on CNT functionalization using new approaches. (b) Different types of CNT addition approach in 2020.

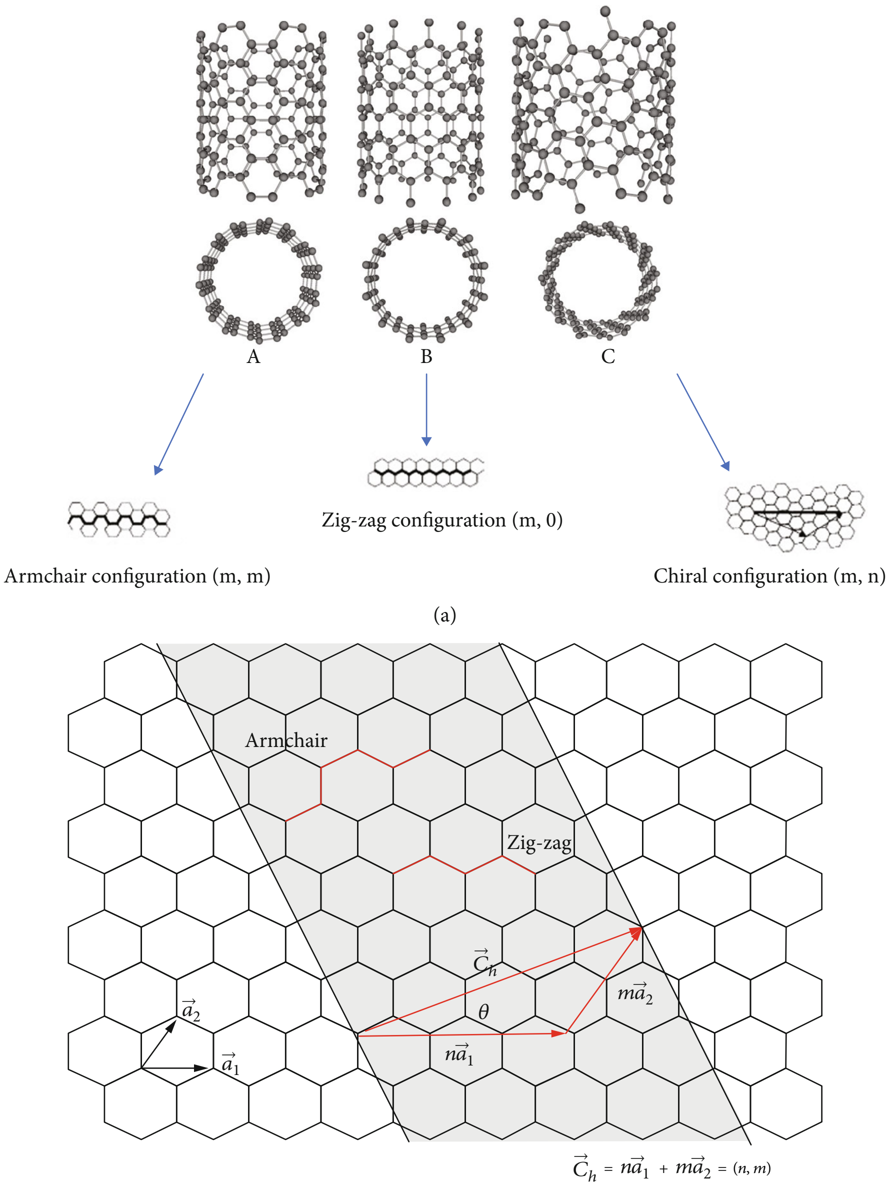
for both fundamental and technological applications. CNTs are generally produced using three main techniques: arc discharge, laser ablation, and chemical vapor deposition (CVD).

3.1. Arc Discharge Method. Arc discharge is the oldest and most common technique to produce CNTs. It also produces carbon soot material which is formed of fullerene molecules. This method relies on the electrical breakdown of a gas to generate plasma. It uses higher temperatures (above 1700°C) to evaporate carbon atoms in plasma providing the growth of CNTs with minimum structural defects in comparison with other techniques. A schematic of an arc discharge chamber is shown in Figure 3. The chamber consists of two electrodes, one of which is anode and the other is cathode. The anode is filled with a mixture of graphite powder and catalyst. The catalyst favors the growth of SWNTs rather than MWNTs [35]. The cathode consists of a pure graphite rod. Initially, electrodes are kept independent under a gaseous atmosphere (typically argon/hydrogen mixture); then, distance between the electrodes is reduced, and an electric arc of 60–100 A or 50–150 A intensity is applied associated to a potential drop of 25 V [19, 53]. The inert gas flow is maintained at 50–600 Torr; the temperature in the interelectrode zone is above 1700° to 4000°C. The electrodes become red hot, and a plasma is formed, so carbon sublimes from the positive anode that is consumed and condenses as filamentous carbon product on the cathode due to the temperature gradient. The reaction takes up from 30–60 seconds to 2–10 minutes. At the final stage of reaction, the machine is left for cooling. Later, CNTs and soot deposited on the walls of chamber are collected then purified and finally observed under an electron microscope to investigate their morphology. Flow rate, inert gas pressure, and metal concentration are the fundamental process parameters to obtain high yield of CNTs. Generally, short tubes with diameters ranging from 0.6 to 1.4 nm and 10 nm for SWCNTs and MWCNTs, respectively, are formed [53]. The disadvantages of this method are the use of high temperature in the fabrication process, low pressure, and expensive noble gasses [39]. Hosseini et al. synthetized CNTs by arc discharge method, immersing the graphite electrodes in a sodium chloride (NaCl) solution in the presence of Fe and Ni catalyst particles; they have obtained CNTs having 100-300 nm in length and 25-30 nm in diameter [54]. Maria and Mieno synthesized SWCNTs by low-frequency bipolar pulsed arc discharge method using a newly developed bipolar pulsed current circuit, having constant current and constant pulse; they found that the rate of produced soot increases with increasing frequency whereas the quality of the produced SWNTs remains almost the same [55].

3.2. Laser Ablation. Laser ablation (LA) is one of the superior methods to produce SWNTs; however, this method is not very much interesting for the synthesis of MWNTs because of its expensive cost [51]. LA has the advantage of producing good quality, higher yield, and high purity of SWNTs through few moments: 500 mg of SWCNTs in 5 min with up to 90% purity [57]. In 1995, Smalley's group at Rice University demonstrated that the efficient route to synthesis SWCNTs with narrow distribution is by LA [58].

A schematic representation of an LA setup is shown in Figure 4. Generally, the lasers used for the ablation are YAG and continuous wave- (cw-) CO_2; reaction chamber is in a quartz tube having as dimensions: diameter 25 mm and length 1000–1500 mm [57], situated in the center of the furnace containing a catalyst metal-graphite composite targeted for SWNTs; catalyst transition metals are generally Ni, Co, Cu, Pt, Co/Ni, Co/Pt, Co/Cu, Ni/Pt, Rh/Pd in small concentration (1%, 2%), and pure graphite for MWNTs [59, 60].

Laser irradiation focuses on to the target through the window and under high temperature (800-1400°C) [19] or mostly 1200°C [42, 59] and an inert gas flow or mixed gas composition inside the quartz tube (Ar, N_2). The pressure



(a)

(b)

Figure 2: (a) Configuration of nanotubes (A) armchair, (B) zigzag, and (C) chiral. (b) Representation of the schematic diagram of the chiral vector $\vec{c_h}$ and the chiral angle (θ), this vector can be decomposed in two components $\vec{a_1}$ and $\vec{a_2}$, $\vec{c_h} = n\vec{a_1} + m\vec{a_2}$, where the integration pair (n, m) are the indices of translation which decide the winding of tube [47, 49, 50].

is between 200 and 400 Torr [53] allowing the evaporation of the target rod which swept by inert gas and deposit the soot on a water-cooled collector located at the exit of the furnace which filters them to deposit CNTs.

The properties of CNTs prepared by the LA process are strongly dependent on different parameters: the laser properties, the composition of the target material, the chamber temperature, pressure, and the chemical composition, flowing buffer gas [43]. Chrzanowska et al. have studied the effect of laser wavelength on SWCNT synthesis yield and properties by using a double pulse Nd:YAG laser, working at a wavelength of 355 or 1064 nm. They have found that properties of synthesized CNTs depend much more on the laser fluence, and the SWCNT synthesis is favored at narrower UV laser radiation fluence [61]. However, Kuo et al. successfully synthesized MWCNTs with very small diameters (5–10 nm) at room temperature by using high energy laser pulses (193 nm, 5 J/cm^2, and 20 ns) which are much stronger than carbon nanotubes produced by conventional techniques thanks to its size and multiwalled nature [62]. Ismail et al. have recently synthetized a new nanostructured MWCNT from graphite target in water by pulsed laser ablation process using different wave lengths (532 and 1064 nm). The authors have reported that optical absorption property

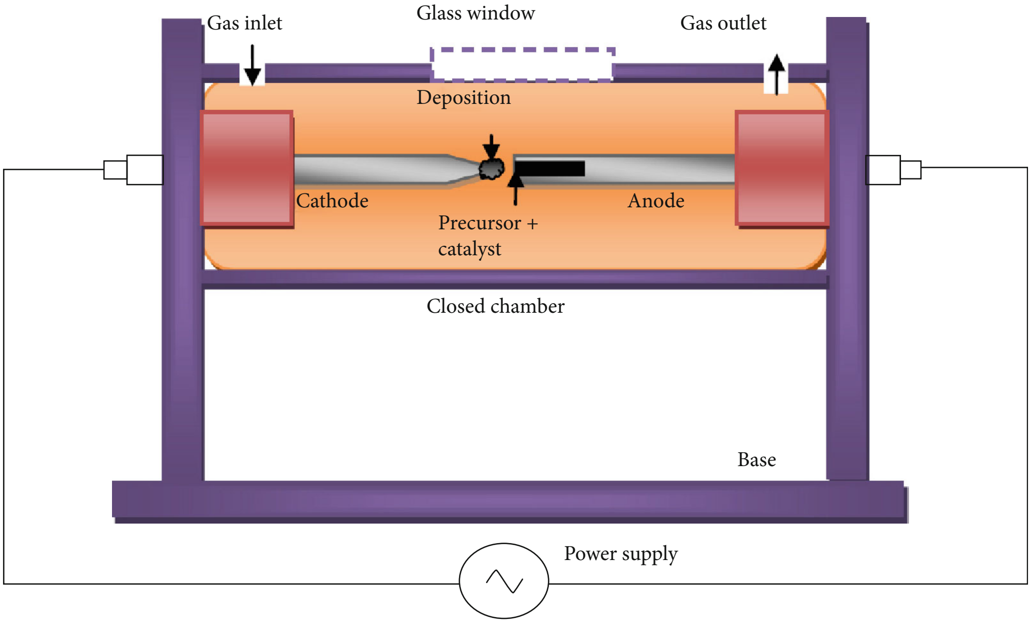


Figure 3: Schematic of an arc discharge chamber [56].

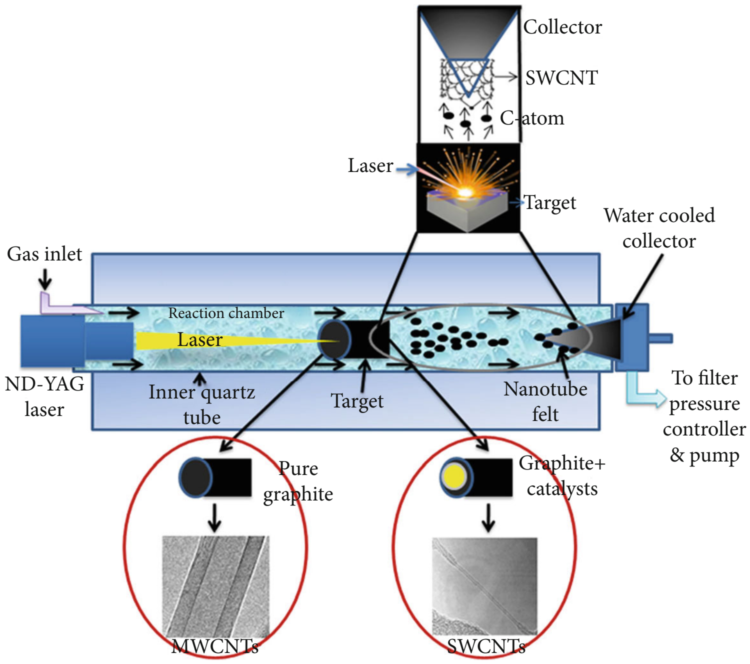


Figure 4: Schematic representation of an LA setup using ND:YAG laser system [57].

of MWCNTs is strongly dependent on the diameter and length of the nanotubes which are in turn related to the laser wavelength. Their work has been realized in the absence of the catalyst which can be considered as a new approach of producing a new morphology of polycrystalline CNTs [63].

3.3. Chemical Vapor Deposition (CVD). Actually, chemical vapor deposition method is considered as the most important and suitable process for the manufacturing of various products, including powders, fibers such as CNT, and monolithic semiconductor electronic components. Heterogeneous chemical reaction in CVD method is an irreversible process because of the heterogeneous chemical reaction through a deposition of solid from a gas or a mixture of gases.

There are different CVD techniques such as plasma enhanced (PECVD), microwave plasma (MPECVD) [64] or radiofrequency CVD (RF-CVD) [65], hot-filament

(HFCVD) [43], oxygen assisted CVD [66] and water assisted CVD [67], and floating catalyst (FCCVD) method [21]. Recently, CVD is considered as an uncomplicated and flexible technology used in the synthesis of CNTs compared to arc discharge and laser ablation. The main advantages of CVD are easy control of the reaction, high yield, low impurity production and low cost of CNT, and relatively low operating temperature lower than 1200°C [68]. The choice of catalyst is one of the most important parameters influencing growth and morphology of the CNTs, because the structure of CNTs has been determined by the size and chemical composition of the metal catalysts [51]. Transition metals in the form of nanoparticles less than 3 nm, Pt [69], Fe [42], Pd, Mn [70], and aluminum isopropoxide [71] are considered as effective catalysts. Figure 5 shows a diagram of CVD to produce CNTs. Firstly, the catalyst is placed in a ceramic or quartz boat which is put into a quartz tube and heated to the sufficient reaction temperature in the range 500–1200°C [72]. Then, the reaction mixture containing a source of hydrocarbon such as methane, acetylene, ortho-xylene, carbon monoxide [73, 74], and an inert gas flow (nitrogen, hydrogen, argon) [75] is passed over the catalyst bed, and the chemical reactions pass on or near the hot surfaces in inert atmosphere. After decomposition of the carbon precursor, carbon atoms are generated, and CNTs grow on the catalyst particle and thin film deposed on the surface. Finally, the system is cooled to room temperature, and CNTs are collected from walls and supported surfaces [76]. The nature and yield of CNTs obtained by CVD method are controlled by varying different parameters such as hydrocarbon sources [77], the nature of the metals and the supports [78], the gas flow [79], the reaction temperature, and the reaction time [80].

CVD process parameters (deposition time, temperature, and gas flow rate) can be independently utilized to produce CNTs with similar or different dimensions and characteristics with distinctive advantages [80]. The increase in reaction temperature and flow rate of precursor gas increases the mean diameter of MWCNTs while increasing processing time decreases the diameter. Additionally, the diameter distribution and quality of MWCNTs are strongly influenced by the diameter of the catalyst particles [81]. High hydrogen content can induce catalytic hydrogenation of carbon and lead to surface modification of CNTs as a result the mean and core diameters. Crystallinity of the graphene walls and length of CNTs are greatly influenced by the hydrogen flow [56]. Recently, it has been reported that hydrocarbons are not the only source for synthesis of CNTs. Bhongade et al. reported the synthesis of MWCNTs using waste toner powder as carbon source by CVD method then confirmed that waste toner is a good source of carbon for the synthesis of CNTs [82].

The difference between these conventional methods is in the quality and purity of the obtained CNTs although scientists are searching for other possibilities, i.e., more economic ways to grow nanotubes, but they had less success. The main causes can be summed up in reaction in the devices, reaction conditions (pressure, temperatures of liquid nitrogen), and cost of the catalyst material. Arc discharge method is a top-down approach which is called for making down of solid materials into small pieces by applying external force. In this approach, physical forces provide the necessary energy for a nanoparticle formation; however, with this method, it is difficult to achieve expected nanosized particles [83]. Although laser ablation leads to the release of harmful byproducts, it is difficult to have control over the surface chemistry, size, and structure of the nanoparticles [84]. Nevertheless, a bottom-up approach can produce nanoparticles starting from a simple molecule to the cluster and then to the nanoparticles, inducing greater control of the shape and size of the nanoparticles. The synthesis of CNT nanoparticles can be also realized by a biological approach when the source of electrons is an organism [85]. Researchers in the field of nanotechnology are turning towards it to gain inspiration to develop novel nanomaterials for nanoparticle synthesis; physical and chemical method of synthesis uses hazardous chemical in their protocol, and therefore, green biological of nanoparticles is a possible alternative to chemical and physical methods.

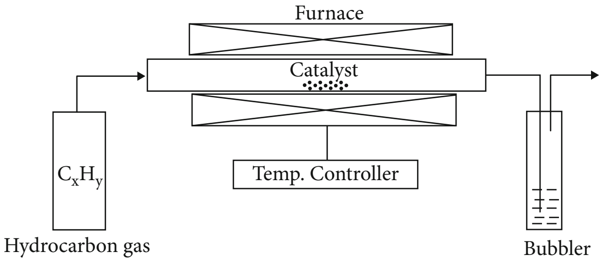


Figure 5: Diagram of CVD to produce CNTs [86].

3.4. New Synthesis Approaches: Green Synthesis. Green synthesis is a bottom-up approach; it is similar to a chemical reduction where an expensive chemical reducing agent is replaced by an extract of a natural product. Green synthesis uses environmentally ecofriendly reagents as reducing agents decreasing the risk of releasing toxic residues into the environment [87]. Wang et al. have developed a new synthesis green method based on the use of MnO_2 as initiator to convert polypyrrole-co-polyaniline (PPy-co-PAni) into hollow structured carbon nanotubes (HPCNTs) with a high surface area 1419 m^2g^{-1} through a simple carbonization treatment at 900°C for 10 h. This hollow porous nanomaterial can be utilized in high-efficient energy storage applications [88]. Tripathi et al. presented an unconventional growth synthesis of CNTs using green catalysts derived from plants in CVD process at low temperature (575°C) producing high yield of CNTs [89]. Hakim et al. synthetized CNTs with 123 nm average diameter having irregular distributions through coconut shell waste by one step water assisted quenching method at a temperature of 700°C, presenting by this study the possibility to produce CNTs at a large-scale using plant and their extract [90]. Hamid et al. have synthetized SWCNTs with a diameter around 27 nm using a pyrolysis of mixed oil as precursor and $NiCl_2$ catalyst supported on Si wafer substrate; well graphitized grown nanotubes are produced at 700°C [91]. Paul and Samdarshi have synthetized MWCNTs with diameter of 80-90 nm by CVD method under optimum conditions by evaporating natural green precursor (coconut oil) transported by N_2 inert gas; this reaction was carried out in the presence of iron catalyst assuring the growth of the nanotubes [92].

4. Modification Strategies and Functionalization of CNTs

4.1. Conventional Methods. Dispersion and dissolution of all CNT forms in aqueous solution, water, most organic, and aqueous solvents are hard to achieve because of CNT chemical nature. To overcome these problems, extensive research has been done in order to enhance chemical properties of CNT [39, 93]. CNT surface functionalization can be performed by covalent and noncovalent (van der Waals bonds); this strategy depends on the linkage between CNTs and functional molecules [93].

4.1.1. Covalent Functionalization. Nejabat and Rayati have prepared Fe/Mn bimetallic heterogenized catalyst by the simultaneous attachment of Mn and Fe porphyrins onto the surface of functionalized multiwalled carbon nanotubes. This new bimetallic nanohybrid displays a superior catalytic performance in comparison with their analogous monometallic counterparts [94]. Functional groups (OH, COOH, NH_2) are attached to sp^2 carbon armature. Generally, for covalent functionalization, these entities are attached to the surface of carbon nanotubes [95, 96]. As a result, their solubility and dispersion are improved in different solvents such as water, dimethylformamide, ethyl alcohol, 1,3-dimethyl-2-imidazoleidinone, dimethyl sulfoxide, and chloroform [97]. Palacin et al. have successfully functionalized CNTs with porphyrin dendrons via click chemistry using the covalent linkages between SWNT and ZnP [98]. On the other hand, Sanders and O'Bryan studied covalent surface modification of CNTs by exploring oxidation, cycloaddition, and radical reactions to determine their success at covalently altering the CNT surface [99]. Voiry et al. [100] prepared monolayered transition metal dichalcogenides by phase engineering using covalent functionalization; the same method has been applied and highlighted by Abo-Hamad et al. indicating that modified-CNTs presented different dispersibility resulting in the change in hydrophilicity after functionalization so that the suspension stability is improved considerably compared to pristine CNT, hence making them applicable in electrochemical sensing [101]. Consequently, Rajaura et al. used them ultimately in hydrogen storage field; chemical changes are responsible factors to enhance the hydrogen storage density due to the presence of surface defects that offer enhanced surface area for hydrogen adsorption [102].

4.1.2. Noncovalent Functionalization. Noncovalent functionalization is mainly based on van der Waals force: π-π interactions [103]. Noncovalent functionalization confers the advantageous conservation of the structure and original properties of CNTs after modification [104, 105]. Tran et al. [106] have reported noncovalent modification of carbon nanotubes with pyrene-functionalized nickel complexion followed by thermodynamic study showing the relation between nanotube diameter and porphyrin molecules, indicating that strong binding of tetraphenyl-porphyrin molecules is preferential to larger diameter nanotubes. The thermodynamic study of noncovalent functionalization of CNT with porphyrin without complexion is presented by Vialla et al. [107].

Alpatova et al. [108] studied the dispersion of SWCNTs in water using a range of natural and synthetic dispersing agents that noncovalently attach to the CNT surface via different physisorption mechanisms. The toxicity of SWCNT suspensions depends on the toxicity of the dispersant and recommends the potential of noncovalent functionalization with nontoxic dispersants.

While Lu et al. applied an effective purification method for SWNTs based on a combination of oxidative acid treatment and reversible noncovalent functionalization with 1-pyreneacetic acid which allows complete removal of residual metal catalysts and carbonaceous impurities while highly pure SWNTs remained dispersible in solvent [109]. On the other hand, Ghosh et al. reported noncovalent functionalization, solubilization of graphene, and single-walled carbon nanotubes explored in nonpolar organic solvents with aromatic donor and acceptor molecules. The aromatic surfaces of electron-donor and acceptor molecules are present onto the surface of the graphene/SWNTs through p–p stacking interactions whereas the alkyl chains as well as the glycol chains on the aromatic molecules promote the solubility [110].

The surface modification of the CNTs can be performed also by other methods such as creating defects, sidewall functionalization, noncovalent bonds with surfactants, and noncovalent exohedral polymers. Defect-group functionalization signifies the presence of defects sites, in the presence of irregularities on the benzene forming the motif frame of nanotube. These defects can be situated on the ends, and sidewalls are formed during the preparation and purification steps. The presence of carboxylic and pentagon groups are examples of defects in addition to the presence of five- and seven-membered rings instead of six-membered rings and the rehybridization of carbon atoms from sp^2 to sp^3 that leads to a local change in the nanotube structure increasing by that the CNT performances [111, 112].

4.1.3. Direct Sidewall Functionalization. Direct sidewall functionalization is related to hybridization of carbon atom from sp^2 to sp^3 by cycloaddition and electrophilic or nucleophilic attack on the aromatic rings. Consequently, carbon atoms loss their conjugations [104, 112]. Covalent sidewall functionalization of SWCNTs can be realized via one-electron reduction [113]. The reaction of a potassium atom with a benzophenone molecule resulted in transferring one electron from the potassium to the benzophenone [114]. Thermal treatment of the sidewall functionalized SWCNTs involves a spoilage of created bonds on the SWCNT sidewall and does not restore the original electronic structure of the SWNTs [115].

Sidewall functionalization can be applied through different approaches for covalent attachment of carboxylic acid groups to the sidewalls of single SWCNTs as reported by Darabi et al. [116]. Gebhardt et al. reported sidewall functionalization of

SWCNTs with lithium alkynylides. Variation of different reaction parameters such as solvent or temperature has been carried out, yielding more soluble SWCNT derivatives. This study demonstrated that the addition reaction was found to preferentially take place on smaller diameter SWCNTs [117]. Gebhardt et al. reported an innovative, efficient, and controllable synthesis of covalent sidewall functionalized SWCNT using the chemical postfunctionalization of polycarboxylated SWCNT-$(COOH)_n$, characterized by the preservation of the integrity of the entire σ-framework of SWCNTs and the possibility of achieving very high degrees of addition [118]. Then, the functionalization of MWCNTs can be performed by the Diels-Alder method as reported by Diyuk et al. [119]. Saini et al. [120] reported covalent sidewall functionalization of SWCNTs via attachment of alkyl groups to the sidewalls of nanotubes. Carbon/alkyl group ratio is up to 10.0 wt.% by using n-Hexyl; whereas for a higher degree of SWCNT functionalization, the smaller diameter tubes (about 1.0 nm) are alkylated more easily.

4.1.4. Surface Modification to Noncovalent State with Surfactant and Polymers. The noncovalent surface functionalization is generally produced in presence of amphiphilic surfactants usually organic compounds, exhibiting both polar hydrophilic head group and nonpolar hydrophobic fractions or tail group that usually consists of one or few hydrocarbon chains. Surfactants are classified according to the charge of their head groups, thus cationic, anionic, nonionic, or zwitterionic. Noncovalent surface modification with surfactants improves the dispersion of carbon nanotubes. This behavior of the surfactants is similar to that of dispersing solid particles [121].

Surfactants or amphiphilic molecules diffuse in water and adsorb at interfaces between immiscible phases, air, and water or at the interface between oil and water or particles and solution [122]. Surfactants ensure the dispersion of CNTs in different solvents via physical adsorption. It presents a nonsolubilization since the main surfactant's property is a stable dispersion of solids in solvents thanks to an accumulation at surfaces or interfaces [123, 124].

Kaur et al. reported the noncovalent functionalization of graphene with poly (diallyldimethylammonium) chloride (PDDA), a polyelectrolyte containing nitrogen, using a very simple method. The addition of a nonionic surfactant (Triton X-100) during functionalization improved the interactions between graphene and PDDA [125].

Madni et al. [126] investigated a novel method to prepare highly dispersed MWCNTs using the mixture of cationic surfactant dodecyl trimethylammonium bromide (DTAB), anionic surfactant, and sodium octanoate (SOCT) and the dispersive effects achieved by surface-active agents on MWNTs. The stable dispersion is obtained at low total surfactant concentration as compared to their concentration when used alone.

Noncovalent functionalization with polymers is considered as a major key to solve the poor solubility of CNTs in aqueous and organic solvents without damaging their unique structure and their intrinsic properties. The main advantage of using polymers is the reduction of the entropic penalty of micelle formation instead of small molecular surfactants [122, 127].

Gan et al. [128] synthetized functionalized CNTs through the self-polymerization of tannins (TA) finding their application in removal of methylene blue (MB). The CNT-TA showed much higher MB adsorption capacity for the functional groups on the surface of CNT-TA.

Cao et al. [105] reported a green and direct functionalization of poly-ethylene glycol-grafted on the surface of SWCNTs in aqueous media through Diels-Alder (DA) click reaction. The functional copolymer was simply grafted on SWCNTs by DA reaction in addition. The hybrid materials possessed a high drug loading capacity (DLC) of doxorubicin reaching up to 279.9 wt.% of DLC; then, it has showed no cytotoxicity against the normal HEK293 cell line. However, Tunckol et al. [129] studied the effect of the synthetic strategy on the noncovalent functionalization of MWCNTs with polymerized ionic liquids which does not allow a uniform surface functionalization. Hence, the dispersion of MWCNTs is changed and showed dependency to polymer type used for functionalization.

4.2. Endohedral Functionalization. The inner environment of the carbon nanotubes presents a nano space where many reactions may take place which do not happen outside the tube. Endohedral functionalization is aimed at exploiting the inner cavity of the tubes [130, 131]. The CNTs can encapsulate molecules or atoms within their central concave space like as fullerenes and other organic molecules through a variety of synthetic methods [132, 133]. Regarding CNT stability towards thermal decomposition, the inner cavity of the tubes has even been exploited as nano-reactor environments for production of simple molecules [134]. Iglesias and Melchionna [135] reported carbon nanotube endohedral catalysis; they have mentioned the recent major advancements of catalysis conducted within the CNTs, starting from the synthesis of the catalytic composite and discussing the most notable catalytic processes that have been reported in the last decade. Endohedral functionalization is limited by the tube inner diameter, which for the largest tubes used for optical experiments can reach up 0.7-2 nm [136]. Kharlamova et al. indicated that diameter and metal-dependent growth properties of inner tubes inside metallocene-filled SWCNTs through filling of single-walled with ferrocene molecules occur during vacuum annealing at temperatures between 500 and 1000°C [137]. As well as Kuznetsov reviewed stereochemistry and noncovalently bonding of atoms and simple molecules inside nanotube fullerenes [138]. Juan and Perez. [133] presented an overview of some of the most prominent examples of encapsulation of molecules inside carbon nanotubes.

4.3. Exohedral Functionalization. Exohedral functionalization is considered as a feasible approach for CNT functionalization in order to purify, solubilize, and improve the properties of CNTs. It is submitted to less limitation compared to endohedral functionalization. Exohedral approaches can be divided into two main classes [131, 136]:

(i) Covalent functionalization

(ii) Noncovalent functionalization

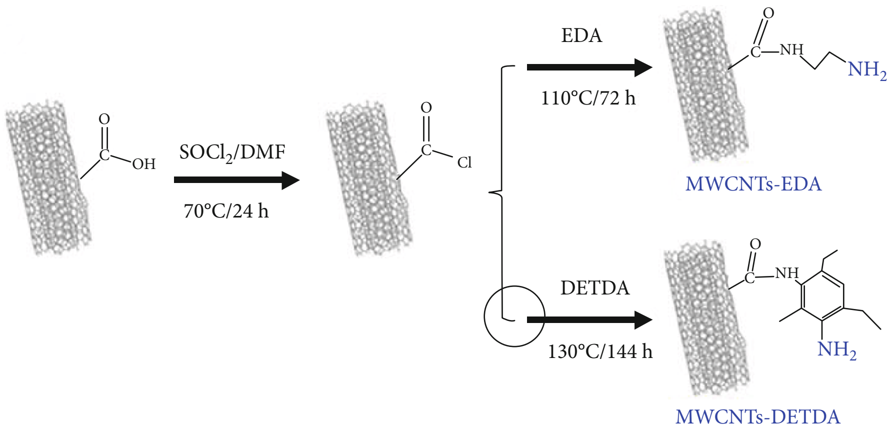


Figure 6: Reaction scheme for amino-functionalized multiwalled carbon nanotubes (MWCNTs-NH2) through surface grafting ethylenediamine and diethyltoluenediamine (EDA, DETDA) [154].

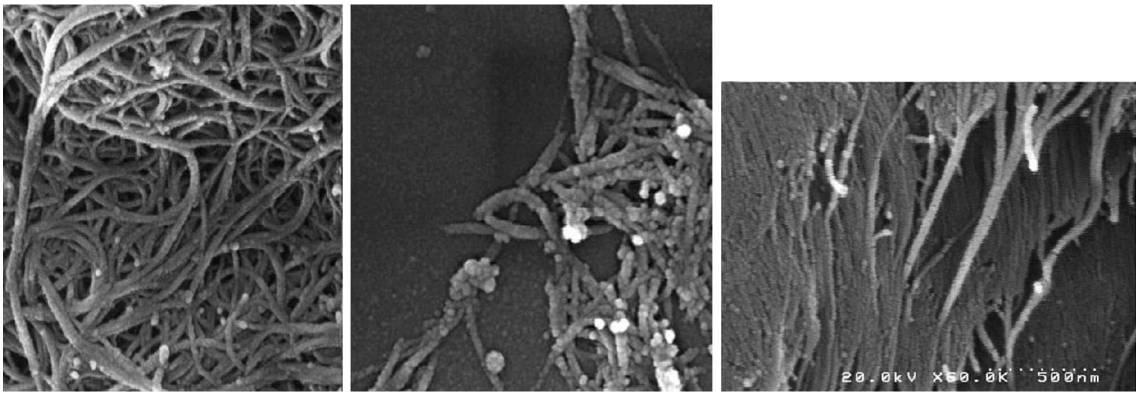


Figure 7: SEM images of SWCNT functionalization [153].

Table 1: The FT-IR results of (SWCNTs) with chloride SOCl2 and NH3 [153].

Absorption nature rays	Range	Chemical groups
Strong absorption	1,450–1,650 cm^{-1}	Aromatic ring
Stretching absorption peak	1,600–1,660 cm^{-1}	C–H
Absorption bands	3,000–3,500 cm^{-1} (3,440)	Hydroxyl group (O–H tensional vibration)
Peak	1,737 cm^{-1}	Carbonyl group C=O (C=O stretching)
Peak	1,311 cm^{-1}	–COOH carboxylic acid group (C–O stretching vibration)
Peak	1,778 cm^{-1}	Converting of the carboxylic acid groups (SWCNTCOOH)
Broad band	1,630–1,380 cm^{-1}	(C=O stretch) of the amide and peaks at 3,180; 3,480; and 1,640 cm^{-1} for NH (N–H tensional) of amid group
Sharp peak	1,098 cm^{-1}	(C–N) amines

4.3.1. Covalent Exohedral Functionalization. The covalent approach consists of attaching the desired groups onto the tubes. This covalent functionalization involves the modification of the carbon atom hybridization from sp^2 to sp^3 due to the functional group attachment [139]. The double covalent functionalization of MWCNTs was achieved by attaching hydrophilic units of cyclodextrins and branched polyethyleneimine (PEIs) [140]. Functionalization of SWNTs via atom-transfer radical addition in the presence of copper (I/II) redox systems allows for covalent attachment of a variety of different groups such as carboxylate and aryl [141]. However, Jafer et al. [142] covalently functionalized 5-10-15-20-tetra (4-aminophenyl) porphyrinatonickel (II) (Ni-TAP) with MWCNTs through an amide linkage; the results

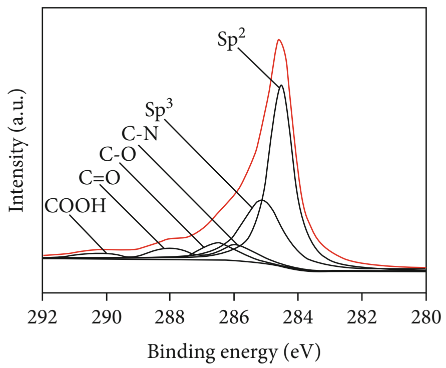


Figure 8: The XPS spectra of XPS form MWCNTs-HEA [155].

showed that not only metal ion substitution increases the defect peak in Raman, but it is also depending on the method of acylation. Covalent functionalization of carbon nanotubes with polyhedral oligomeric silsequioxane for superhydrophobicity (POSS) and flame retardancy indicated that POSS particles were chemically grafted to MWCNT; thus, grafting of POSS onto MWCNT enhanced the dispersion of POSS particles in the hybrid buckypaper; then, a stable and superhydrophobic surface characteristic was observed for the buckypaper made of MWCNTs grafted with POSS (MWCNT-g-POSS) even after an exposure to a high-humidity environment over a long time period [127]. Polyether and epoxide group covalently attached to the sidewalls of CNTs are indicating that the polyether was successfully grown from the CNT surface, with final product having a polymer weight percentage of 14-74 wt.%. The oxygen-carbon O/C ratio of CNTs increased significantly from 5.1% to 29.8% after surface functionalization of CNTs [143]. On other hand, supramolecular approach reported by Bosch et al. [144] allowed facile solubilization and separation of covalently functionalized SWCNTs. The combination of an electronic-type selective diazonium-based attachment onto CNT framework and a supramolecular approach of a cyanuric acid derivative indicating fine homogeneity of the functionalized material resulted in increased dispersibility of the functionalized SWCNTs in chloroform, and by a simple low-speed centrifugation step (3000 rpm, 5 min), functionalized SWCNTs can be separated from their unfunctionalized counter parts.

4.3.2. Noncovalent Exohedral Functionalization. The noncovalent approach is based on the physisorption of chemical moieties on the graphitic surfaces of nanotubes through the π–π-stacking interactions and polymer wrapping mechanisms [127, 129, 145] or micellar forces [146]. Among noncovalent exohedral functionalization techniques, the microemulsion method is reported by Al-Jammal et al. consisting of changing the surface structure of MWCNTs by attaching a hydrocarbon tail on its surface; microemulsion functionalization can be combined with in situ oxidative polymerization methods to form OH-MWCNT [93]. The beneficial effect of microemulsion functionalization on the hydrophobic properties of MWCNT is to solve the main problem regarding the functionalization of MWCNTs [147] in addition to preserving the mechanical and electrical properties of carbon nanotubes [148]. On the other hand, Basiuk et al. have demonstrated the possibility of fast and efficient solvent-free noncovalent functionalization of MWCNTs by using three representative amines of different structure. The highest amine content was found for octadecylamine, and the lowest one was observed for 1,5-diaminonaphthalene [148]. Basiuk et al. reported the noncovalent functionalization of SWCNT and MWCNT with Ni(II) tetramethyldibenzotetraaza[14]-annulene (NiTMTAA) in the gas phase at 220 and 270°C, without the use of organic solvents. NiTMTAA influenced the morphology of SWNTs functionalized at 220°C. The tubular structure of both SWNTs and MWNTs becomes totally (for functionalization at 220°C) or partially (at 270°C) masked with an amorphous layer of NiTMTA [149].

5. New Strategies of Functionalization of CNTs

5.1. Amidation: Formation of Nanotube. The carboxyl groups introduced on the CNT surface can be used to produce amino functionalized CNTs. The CNT amidation is performed by oxidative procedure [150]. Structural analysis of the amine-functionalized products showed the covalent grafting of amine nitrogen to CNTs as shown in Figure 6 [151]. Shen et al. [152] realized the functionalization by amidation of MWCNTs by attaching the carboxylic (COOH) and amine (N-H) groups at a temperature below 600°C to the outer tube of MWCNTs. Furthermore, Abjameh et al. [153] studied the synthesis of functionalized SWCNTs with amide group using thionyl chloride (SOCl$_2$) and NH$_3$. The FTIR analysis confirmed the presence of –COOH carboxylic acid and amid groups through the broad band of the amide and peaks for (NH) of amid group and carbon to amines (C–N), respectively. Both SEM images of SWCNT-CONH$_2$ and SWCNT-COOH (Figures 7(b) and 7(c)), respectively, showed a thin layer of organic compounds (amide) on the surface resulting an increase in diameter of the nanotubes compared to SWCNT microstructure represented in Figure 7(a).

FT-IR spectroscopy and SEM image are among analysis methods performed to identify all new chemical bonding products by identification of the chemical groups that were attached to SWCNTs as shown in Table 1 and Figure 6, respectively. In addition, the study of surface morphology by SEM image of prepared samples represents the difference in dispersion and adhesion of a thin layer of organic compounds (amide) on the surface of SWCNT-COOH.

However, Wang et al. [155] have taken the advantage of amidation of carboxylated MWCNTs to prepare a new class of hydrophilic MWCNTs after undergoing the Michael addition reactions [149] with hydroxyethyl acrylate (HEA), acryloyl morpholine (ACMO), and acrylamide (AM). The attachments of -NH, -OH, C-N, C=O, and amid groups are confirmed FTIR and XPS spectroscopies analyses as shown in Figure 8. Functionalized MWCNT properties were investigated through the preparation of water polyurethane (WPU) composites via homogenously dispersion; functionalized MWCNTs showed stronger interfacial adhesion with

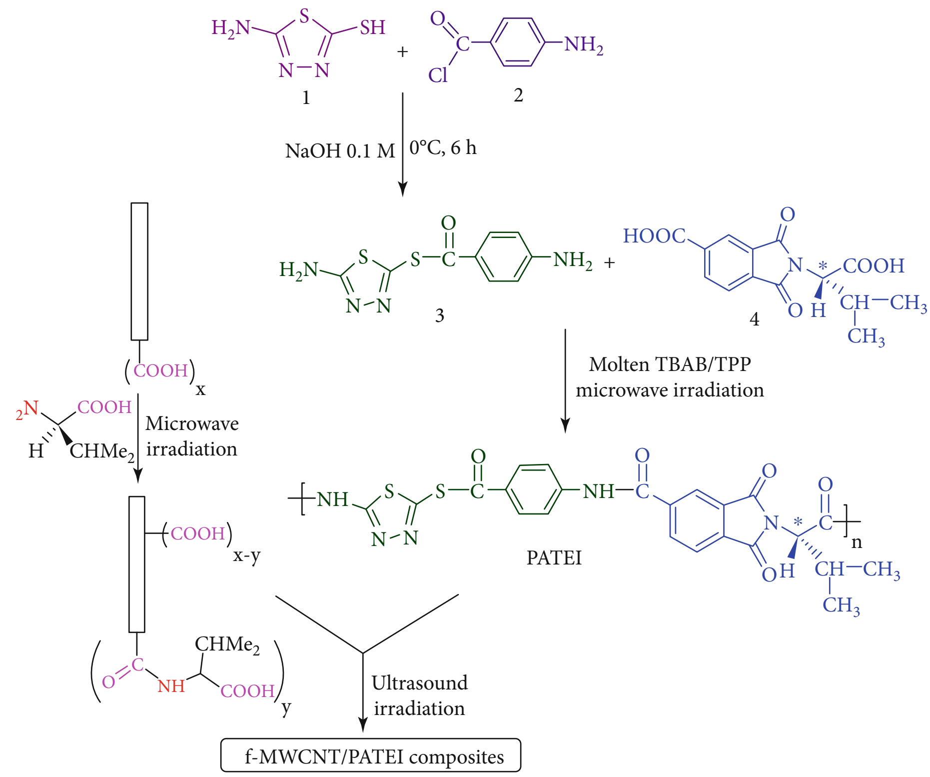


Figure 9: Schematic of the preparation process of f-MWCNT/PATEI composites [156].

WPU macromolecules in comparison with pristine MWCNTs hence increasing the mechanical properties, hydrophilicity, and electronic conductivity of the composites. Unlikely to them, Mallakpour and Zadehnazari [156] chose another parameter for functionalization of MWCNTs with amino acid molecules by microwave irradiation followed by reaction with a carboxylic acid; direct attachment by an amide bond and functionalized MWCNTs (f-MWCNTs) were dispersed throughout a thiadiazol and amino acid containing poly(amidethioester-imide) (PATEI) as shown in Figure 9. This process is fast and simple and resulted a high degree of functionalization in addition to high dispersion in organic solvents.

Desired functionalization of MWCNT by amino acid is evident through f-MWCNT FTIR results, whereas the bands appeared at 3433 cm^{-1}, 2923 cm^{-1}, and 1629 cm^{-1} refer to presence of O-H stretching, aliphatic sp^3 (C-H), and C=O stretching vibration. Furthermore, the appeared band at 1383 cm^{-1} and 3408–3451 cm^{-1} and the peak at around 1627 cm^{-1} referred to the C-N-C axial stretching bands and C=O of amide and acid bonds, respectively, as shown in Figure 10 [156].

Functionalized CNTs by amidation were used for biological studies as reported by Ng et al. who performed a conjugation of insulin onto the sidewalls of single-walled carbon nanotubes through functionalization and diimide-activated amidation as depicted in Figure 11. Insulin was successfully incorporated on the surface of functionalized SWCNTs through the formation of amide bonds with the esterified carboxylic groups [157].

On the other hand to understand the structure of the synthesized amidoamine-MWCNTs, the mechanism and selectivity of interaction between metal ions and MWCNT, Deb et al. [158] applied a theoretical study using density functional theory (DFT) in their work highlighting the use of functionalized MWCNTs for removal of mercury (II) ions from wastewater in presence of both amide (-CONH-) and amine (-NH2) units (amidoamine-MWCNTs) on the surface of nanotubes. Through theoretical study, amidoamine group attached on the surface of the SWNT may covalently relate with the sp^2 carbon atom situated on the sidewall or at the open end of the nanotube.

Functionalization of carbon nanotubes by amidation is depending on various parameters as using different type of amine [159] and catalyst allowing high degrees of surface functionalization by attachment of functional groups on CNT surface [151]. Recently, Soubaneh et al. [160] used wet method to prepare [14C]-label amide MWNTs by successive reactions of carboxylation, chloroacylation, and amidation using [14C]-labeled ethanolamine for ecotoxicological study. This method showed high functionalization degree and good f-CNT distribution illustrating a new use of CNTs in this type of studies.

5.2. Fluorination. Fluorination is one of the methods authorizing an efficient functionalization of carbon nanotubes. Fluorination of CNTs is a very important way to improve the surface chemical properties as well as polarization [161] and structural and electrical properties [162]. Direct

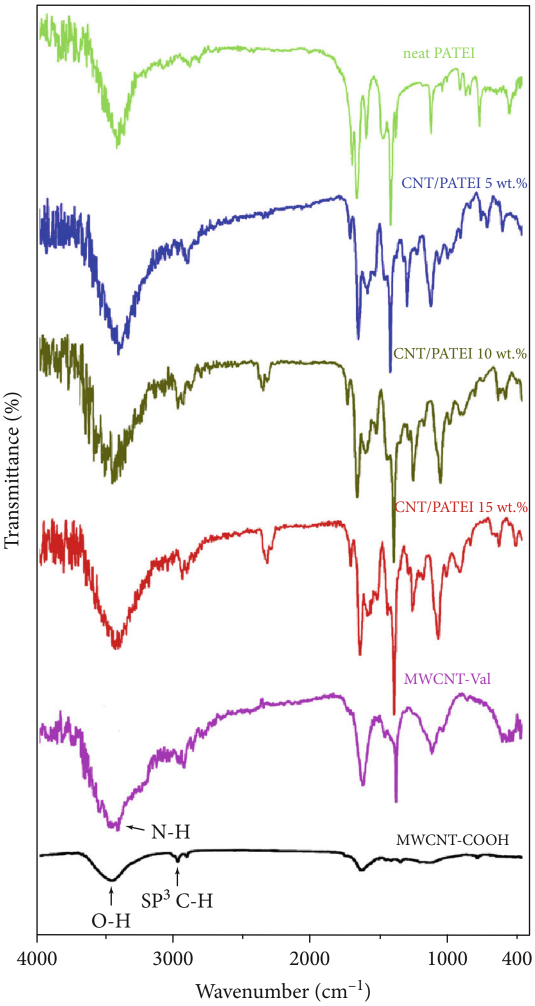


Figure 10: FT-IR spectra of carboxyl and amino acid-functionalized MWCNT amidation [156].

fluorination is a famous method for the fluorination of CNTs [163]. Fluorination process consists of a covalently attachment of fluorine on the surface of CNTs [161, 163] to form covalent C-F bands [161, 164]. This process depends on various parameters. For the objective of knowing the effect of temperature on the fluorination of CNTs, Mickelson et al. have applied fluorination of SWCNTs under several temperatures: 150, 250, 325, and 600°C using F_2 gas. According to the IR spectroscopy results, the addition of fluorine to the tube wall requires temperature up than 150°C shown by appearance of peak at 1225-1250 cm^{-1} for the samples fluorinated at 250°C [165]. On the other hand, Jung et al. reported the thermal fluorination of MWCNTs at temperatures 30, 100, 200, and 400°C with Fe catalyst exposed on MWCNTs. The MWCNTs were thermally fluorinated at 100°C with high capacitance of 94 F/g at a current density of 0.2 A/g due to the increase of surface area and surface polarity. However, the fluorine content decreased at the temperature of 400°C as a result of increased of thermal energy adequate to break the CF bond [161].

The effect of fluorination agents on CNT surfaces and properties is also obvious. For this reason, Zhang et al. have studied the effect of fluorination agents on SWCNTs using molecular fluorine (F_2) and xenon difluoride (XeF_2) as fluorination agents. These methods correspond to fluorination by molecular fluorine F_2 and atomic fluorine F, respectively. As a result, the two methods presented the similar fluorine content but with different morphologies as shown by TEM image in Figure 12 [166] and also confirmed by Park et al. study where it is shown that the structural changes of SWCNT resulted by fluorination include increased diameters and changes in chirality [162] then indicated a homogenous dispersion of fluorine atom on the wall of nanotube and little surface damaged unlike fluorinated parts by conventional method with F_2 which present high concentration of fluorine [162].

Fluorination technique presents an important role in carbon nanotube fluorination. Bulusheva et al. used three different techniques to fluorinate DWCNTs: fluorine F_2 at 200°C, gaseous BrF_3 at room temperature, and CF_4 radio-frequency plasma functionalization. As a result, all methods allowed the formation of covalent C-F liaison as shown by IR spectrum in Figure 13. Then, each technique allowed a distinct local surrounding of the attachment of fluorine which demonstrates the different possible structuration [164].

Furthermore, Bulusheva et al. studied the stability of fluorinated DWCNT produced by different techniques using F_2 at 200°C, a mixture of BrF_3 and Br_2 at room temperature and radio frequency CF_4 plasma. After heating in vacuum at 70°C for 10 h or 120°C for 20 h, the results demonstrated that the technique using gaseous F_2 at 200°C is the best due to high stability of fluorinated DWCNTs whereas the temperature of decomposition is higher than 350°C [167]. Another method reported by Fedoseeva et al. consists of fluorination of DWCNT containing oxygen at outer surface using BrF_3 at room temperature. Fluorine attachment is shown near the oxygen groups on the nanotube as shown in Figure 14 with double concentration of sidewall fluorine in the oxygenated DWCNTs, which confirms that physical and chemical properties of CNT scan be changed through fluorine and oxygen groups [168].

5.3. *Chlorination.*

CNTs can be functionalized by different halogenated compounds. Nevertheless, CNTs are also used for decomposition treatment for halogenated compounds as proposed by Yamaura et al. [169]. Though, Desforges et al. reported functionalization of CNTs by high temperature oxygen/chlorine gas treatment to improve their stability and possibility to use them in various fields. This method allowed the move of metal-based impurities from catalyst residue without destruction of CNTs arising from the presence of chlorine functional groups on the carbon nanotube surface [170]. While Qian et al. proposed a simple synthesis of halogenated MWCNT carbon nanotubes using $SOCl_2$, Br_2, and I_2 as halogen sources under high pressure and high temperature. For chlorination of MWCNTs, the concentration of Cl on MWCNTs is reached up to 3-8% in weight. In addition, this study confirmed clearly the attachment of Cl to the nanotube surface (Cl-MWCNTs) by means of

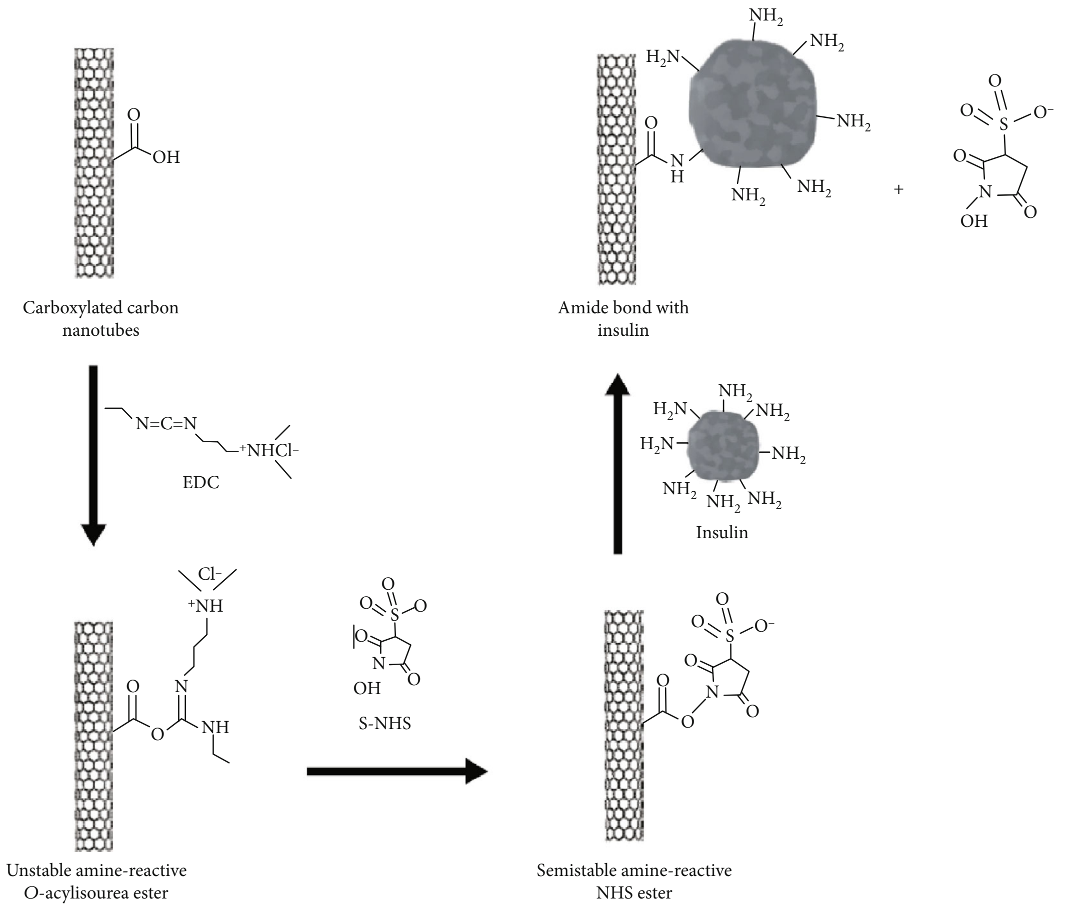
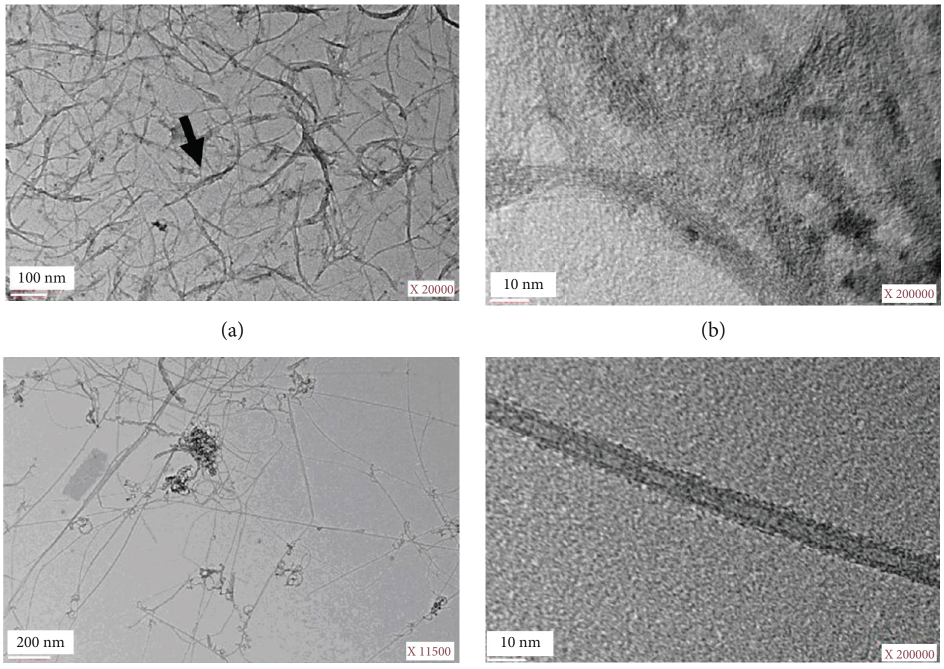


Figure 11: Reaction pathway for the formation of insulin-conjugated SWCNT [157]. EDC: 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride; S-NHS: *N*-hydroxysulfosuccinimide; SWCNT: single-walled carbon nanotube.



(a) (b) (c) (d)

Figure 12: TEM images of F-SWCNT fluorinated by direct method with F_2 (a, b) and controlled method with XeF_2 (c, d) [166].

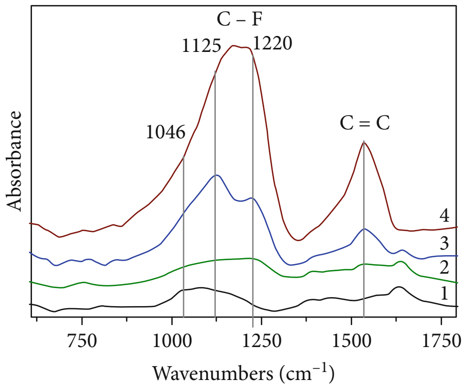


Figure 13: IR spectra of pristine DWCNTs (1) and DWCNTs fluorinated with CF_4 plasma (2), BrF_3 (3), and F_2 (4) [164].

different analysis methods [171]. As well, Abdelkader et al. exposed the chlorination of CNTs through carbon tetrachloride cold plasma treatment as a new way to covalently bind Cl-MWCNTs as proved by XPS spectra shown in Figure 15; this treatment involves several factors such as preparation method of plasma, temperature of treatment, and time. The treatment of MWCNTs with helium prior to addition of CCl_4 plasma at shorter time allows a high concentration of chlorine on surface without changing the textural characteristic of the nanotube; however, long-time exposure of MWCNTs to CCl_4 plasma has influenced significantly the Cl concentration as shown in Figure 15 [172].

To upgrade the ability of using carbon nanotubes, Pełech et al. proposed functionalization and purification of CNTs from metal particles. The metal particles are present as Fe, Co, and Fe/Co catalysts from carbon nanotube synthesis. The chlorination is carried out in gas phase, and the process was kept at 50, 250, and 450°C; XPS and EDS results showed the presence of chlorine on MWCNT surface as presented in Tables 2 and 3. The authors concluded that chlorination is dependent from temperature and confirmed remaining catalyst particles by TGA [173].

Otherwise, to study the effect of chlorine on morphology of MWCNTs, Maboya et al. synthetized chlorinated carbon nanomaterials using different chlorine sources: chlorobenzene (CB), dichlorobenzene (DCB), trichlorobenzene (TCB), dichloroethane (DCE), trichloroethane (TCE), and tetrachloroethane (TTCE) over a Fe-Co/$CaCO_3$ catalyst. The increase of inner and outer diameters of MWCNTs was observed due to increase content of chlorine resulting in bamboo structure, showing that MWCNT is strongly generated between TCE and TTCE [174]. Furthermore, to understand the chlorine behavior, Ma et al. reported adsorption and desorption of chlorinated compounds to MWCNTs using trichloroethylene (TCE), 1,1,1-trichloroethane (1,1,1-TCA), and 1,s3,5-trichlorobenzene (1,3,5-TCB), so adsorption capacities of chlorinated compounds to MWCNTs are depending on molecular structure of reactant up to 96.8% for TCA and the treatment technique [175]. Bulusheva et al. developed a chemical process for functionalization of DWCNTs; this treatment increased dispersibility of DWCNTs and covalent attachment of chlorine on surface of DWCNTs with a special decoration through creation of holes in outer walls granting to use DWCNTs for relative humidity sensor over repeatable good response to humid environment [176].

5.4. Bromination. Bromination is another way to modify and purify carbon CNTs using halogenous compounds inferring changes in their electronic structure and chemical reactivity [177]. Bulusheva et al. synthetized DWCNTs then functionalized them by bromine vapor at room temperature. The interaction of DWCNTs with Br_2 is represented by C-Br bonding [178]. With the purpose of understanding the functionalization procedure of MWCNTs, Diyuk et al. applied thermogravimetric on the functionalization of MWCNTs with bromine Br_2 vapor at high temperature 200-500°C showing the chemisorption of bromine at the temperature range 300-500°C. Furthermore, bromination of MWCNTs is carried out at two regimes, fast reaction of bromine vapor with MWCNTs at 30-350 min causes chemisorption of bromine, and the slow process of bromination appears at 120 min where bromine reacts with micropores at the MWCNT surfaces [119]. Moreover, Abdelkader et al. performed covalent bromination of MWCNTs through a reaction with solution of IBr in CCl_4 and CH_3Br cold plasma. This study showed that bromination of CNTs is depending on the treatment, whereas the degree of bromination by the reaction with solution of IBr in CCl_4 mild temperature is reached up to 3.5% with 96% of bromine covalent bonds and no increasing in the oxygen content of nanotubes. While by CH_3Br cold plasma, 4.9% bromination is reached through 10 min with 99% of bromine covalent bonds [179]. In addition, Colomer et al. have reported synthesis and characterization of DWCNTs under microwave-assisted conditions. The bromine was successfully attached covalently on DWCNT walls (Br-DWCNTs) with 5.8% in weight as shown by different characterizations methods of Br–DWCNTs [180]. Then, Bulusheva et al. similarly reported the effect of ultrasound pretreatment on bromination of DWCNTs using Br_2 vapor with or without pretreatment a bromine water at room temperature. The result demonstrated that ultrasound pretreatment changed the chemical state of bromine in DWCNT walls. This result is interpreted by calculation of CNT-Br_2 models using density functional theory proposing the electronic state of Br_2 molecules on adsorption site [178]. On the other hand, Moradi and Etesami proposed a new route for bromination of MWCNTs using N-bromosuccinimide (NBS), NH_4 NO_3/NBS, and Br_2 under thermal and UV conditions; Figures 16 and 17 represent the possible mechanism for the bromination of CNT. IR spectroscopy results confirmed the attachment of Br on the MWCNT surface, and electron scanning microscopy (SEM) showed no damage in MWCNT structures after bromination for two cases due to the mild condition. The simplicity of procedure relies on short reaction times conferring the advantage to develop this method for functionalization of CNT surfaces [181].

5.5. Hydrogenation. Hydrogenation mainly causes changes in CNT physical properties as conductivity of the metallic nanotubes [182] and chemical properties as electronic structures [183]. Park et al. have studied theoretically using

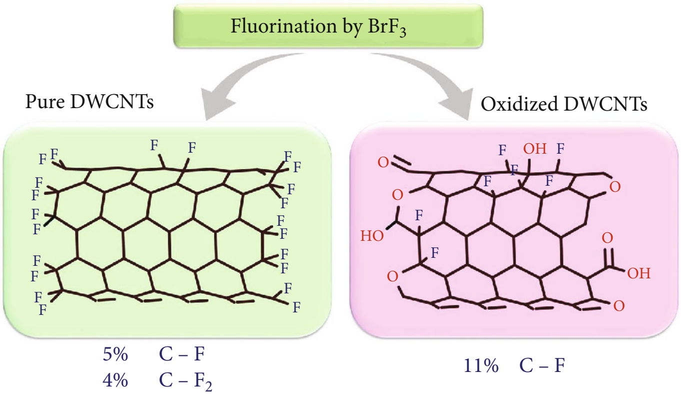


Figure 14: Distribution of fluorine on pure and oxidized DWCNT sidewall [168].

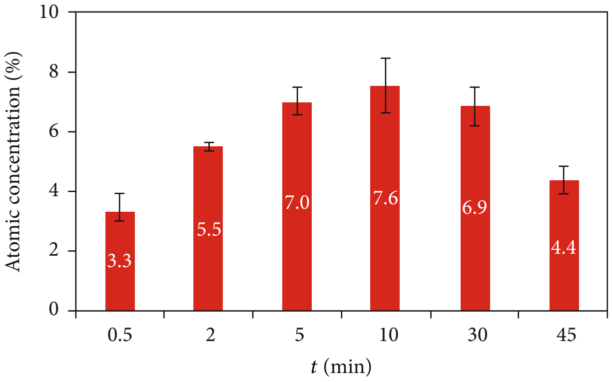


Figure 15: Influence of exposure time on the XPS chlorine atomic concentration [172].

Table 2: EDS result of surface composition of the samples after chlorination [173].

Sample	C *K* -line	O *K* -line	Cl *K*-line %at.	Fe *K* -line	Co *K* -line
FeCo	92.8	3.1	—	2.0	1.4
$FeCo_{50}Cl$	91.6	4.7	0.5	1.5	1.3
$FeCo_{250}Cl$	92.3	4.0	1.4	1.4	0.7
$FeCo_{450}Cl$	90.6	5.5	2.3	0.3	0.9

density functional calculation the atomic and electronic structure of hydrogen chemisorbed SWCNTs [184]. Nikitin et al. proved the formation of C-H bonds by chemical interaction in the nanotube walls through hydrogenation of SWCNTs with atomic hydrogen. Those bonds can be completely broken at 600°C; nanotube hydrogenation is up to 65 ± 15% of carbon atoms in the SWCNTs, and this process is reversible [185]. Pekker et al. prepared hydrogenated SWCNTs and MWCNTs using metal reduction method in liquid ammonia according to the following reactions reported in equations (1)–(5):

Table 3: XPS result of composition of the samples after chlorination [173].

Sample	C	O	Cl %at.	Fe	CO
FeCo	97.8	2.2	—	—	—
$FeCo_{50}Cl$	94.2	3.4	1.3	1.1	—
$FeCo_{250}Cl$	94.4	3.8	1.0	0.8	—
$FeCo_{450}Cl$	97.8	—	2.2	—	—
$Fe_{450}Cl$	94.3	4.8	0.8	—	—
$Co_{450}Cl$	92.1cc	4.5	1.4	—	—

(1+2) Solution of lithium in ammonia and the formation of its carbanion complex

(3) Formation of a covalent hydrogenated carbon derivative

(4) Formation of hydrogen

(5) Reaction of the excess ammoniated electron with methanol

$$\mathrm{Li} + \mathrm{nNH_3} \longrightarrow \mathrm{Li^+} + \mathrm{e^-(NH_3)_n} \tag{1}$$

$$\mathrm{e^-(NH_3)_n} + \mathrm{C} \longrightarrow \mathrm{nNH_3} + \mathrm{C^-} \tag{2}$$

$$\mathrm{C^-} + \mathrm{CH_3OH} \longrightarrow \mathrm{CH} + \mathrm{CH_3O^-} \tag{3}$$

$$\mathrm{C^-} + \mathrm{CH_3OH} \longrightarrow \mathrm{C} + \mathrm{CH_3O^-} + \frac{1}{2}\mathrm{H_2} \tag{4}$$

$$\mathrm{e^-(NH_3)_n} + \mathrm{CH_3OH} \longrightarrow \mathrm{nNH_3} + \mathrm{CH_3O^-} + \frac{1}{2}\mathrm{H_2} \tag{5}$$

As result, thermal stability of hydrogenated products is up to 400°C. The hydrogenated derivatives are thermally stable up to 400°C. A characteristic decomposition and simultaneous formations of hydrogen and a small amount of methane were showed above 400°C. A disorder on the nanotube walls due to hydrogenation is shown by transmission electron microscopy (TEM) (see image Figure 18) [186]. On the other hand, Talyzin et al. showed the multifunction of molecular hydrogen through hydrogenation, purification, and unzipping of carbon nanotubes; hydrogenation of nanotubes is realized at 400-

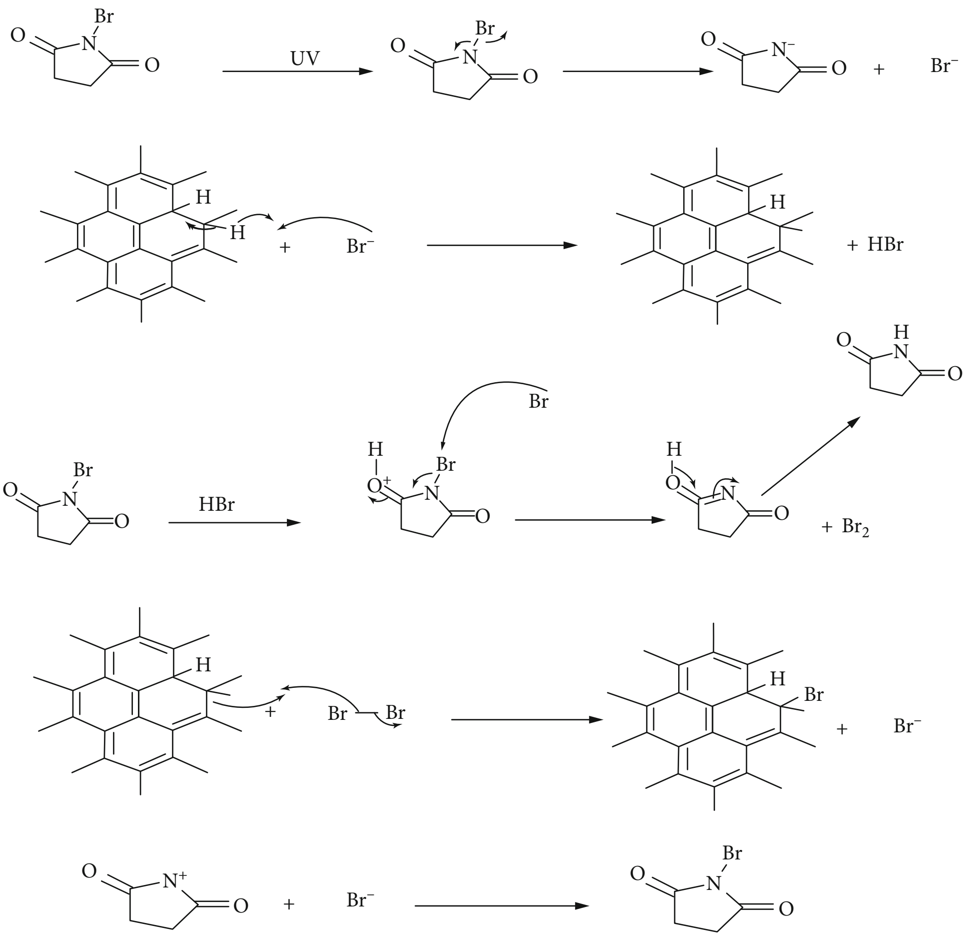


Figure 16: The mechanism of bromination of CNTs using NBS/UV condition [181].

450°C with 1/3 of carbon atoms forming C-H bonds [187]. Nikitin et al. studied the hydrogen chemisorption in SWCNTs; this study demonstrated that nanotube diameter is the main variable for hydrogenation degree of the nanotube whereas a value of around 2.0 nm for the diameter makes the nanotube hydrogen complexes close to 100% hydrogenation [188]. In addition, Mohammadi et al. interpreted this change in the CNT diameter by the incorporation of H atom into CNT structure [189]. Advanced research related to CNTs relies that on increasing their properties including different CNTs forms as spaghetti MWCNTs using hydrogenation, as reported by Kazemi et al., thanks to MWCNT structure and wettability [190].

5.6. Addition of Radicals, Nucleophilic Carbenes, and Sidewall Functionalization through Electrophilic Addition. Addition of different species on the surface of CNTs as radicals can also functionalize CNTs. Umek et al. synthetized functionalized SWCNTs via addition of carbon radicals generated by thermal decomposition of diacyl (LP) and dibenzoyl peroxides (DBP) resulting in undecyl and phenyl radicals as shown in Figure 19; the attachment of radicals in the nanotube wall is shown by UV-visible spectra results of SWNTs and products SWNT + LP and SWNT+ DBP as seen in Figure 20, through complete loss of the van Hove singularities related to covalent modification of the nanotubes. The authors confirmed their results by FTIR spectroscopy [191].

Vanhorenbeke et al. reported a new approach using xanthates as radical precursors for carbon nanotube covalent functionalization; these radical precursors react with carbon-carbon bonds as represented in Figure 21; as a result, the moiety grafted on the tube surface contains no sulfur in addition to introducing ester groups on the CNTs [192].

Several other chemical functionalization techniques were reported such as addition of nucleophilic carbenes and sidewall functionalization through electrophilic addition [193, 194]. Controlling the electronic properties and increasing their dispersibility are the main advantages of functionalization of carbon nanotubes by carbene derivatives. Luksirikul et al. have explored functionalization of single- and double-walled carbon nanotubes with different diaryldiazomethane derivatives using the actinic irradiation to insert the intermediate carbenes to the carbon nanotube structure as shown in Figure 22. The functionalization of CNTs is observed through Raman and FTIR spectroscopy results whereas the increase of the D/G bands intensity ratio related to SWCNT–R–N(CH3)2 and SWCNT–R–OCH_3 samples

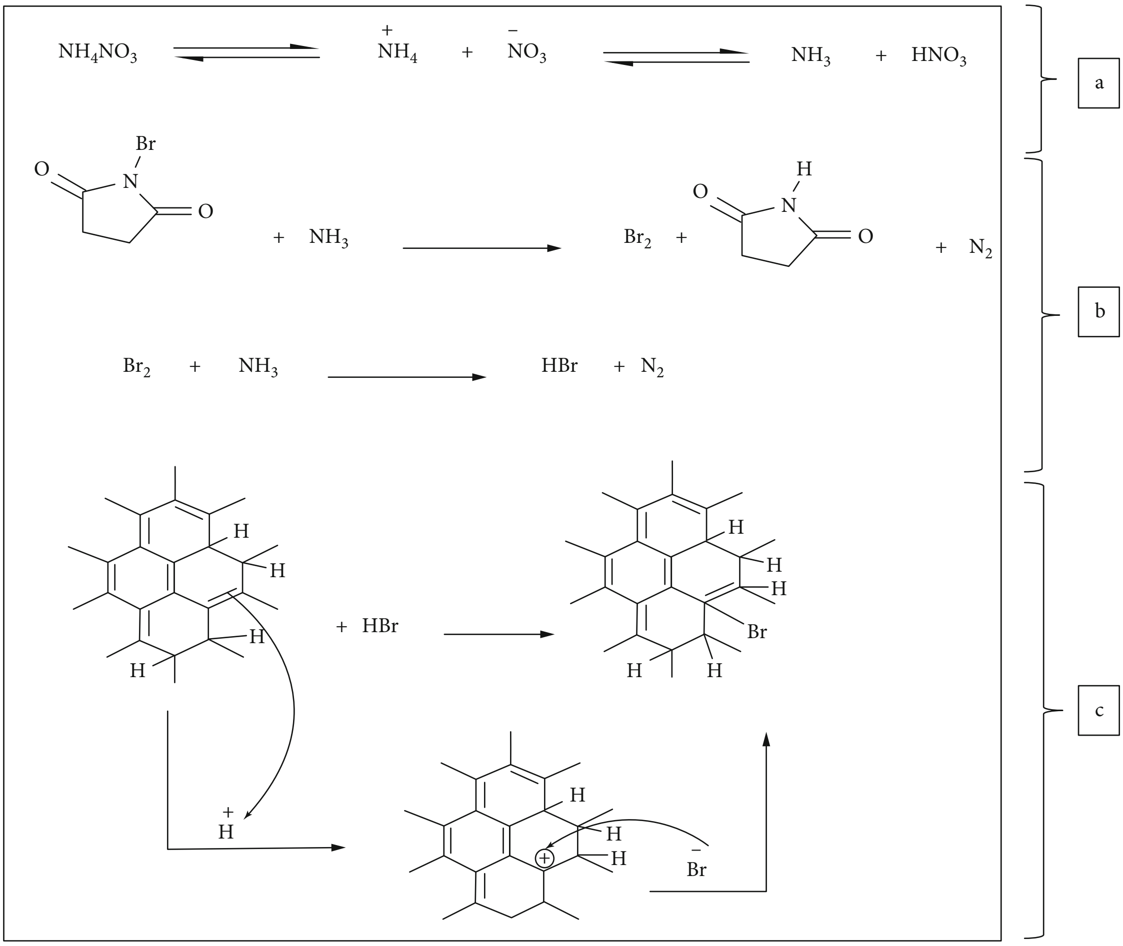
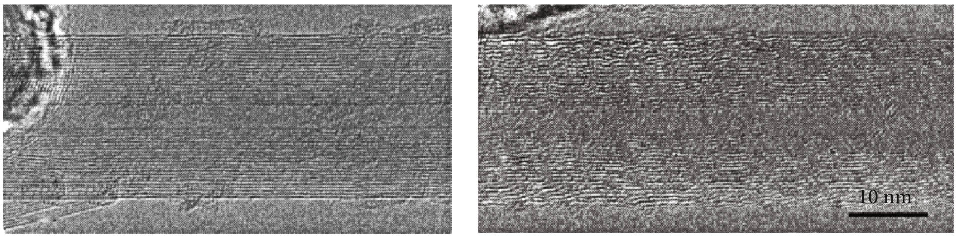


Figure 17: Bromination of carbon nanotubes using NBS/NH_4NO_3 under thermal condition [181].



(a)

(b)

Figure 18: TEM images of (a) individual pristine MWCNTs and (b) hydrogenated MWCNTs [186].

demonstrates the cycloaddition of carbenes on the sidewalls and tips of carbon, therefore an appearance of new bands in FTIR spectra confirmed by Raman results as shown in Figure 23 [195].

Zeng et al. reported the electrophilic substitution reactions on phenylated CNTs. A new functionalization of CNT sidewalls was realized by including diphenyl ketone, benzenesulfonyl chloride, benzyl chloride, and thiophenol as shown in Figure 24 [196]. Then, Tagmatarchis et al. have successfully functionalized SWCNTs through electrophilic addition of chromoform SWCNTs followed by hydrolysis which is allowing the addition of hydroxyl groups to the surface of the nanotubes [197]. On the other hand, Xu et al. reported the microwave-induced electrophilic addition of SWNTs with alkyl halides [198], whereas Tian et al. used microwave irradiation for electrophilic addition of alcohol to SWCNTs which resulted in the attachment of various alkyl or alcoholic groups to the surface of the nanotubes [199].

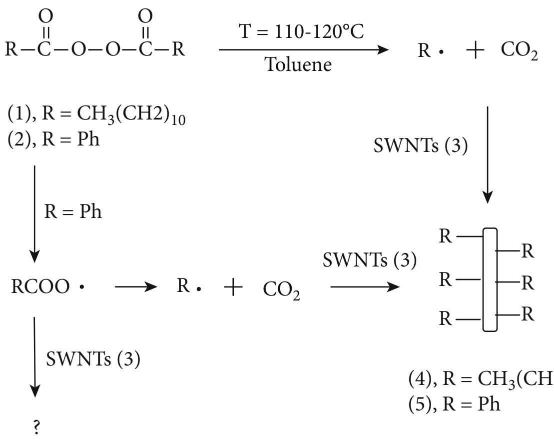


Figure 19: The reaction pathway of thermal decomposition of LP (1) and DBP (2) [191].

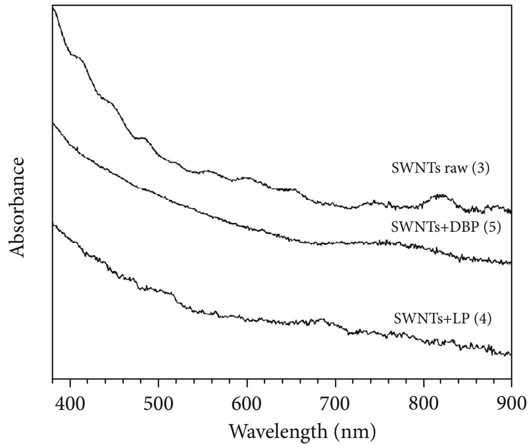


Figure 20: UV-Visible spectra of raw SWNTs (3), SWNTs+LP (4), and SWNTS+DBP (5) [191].

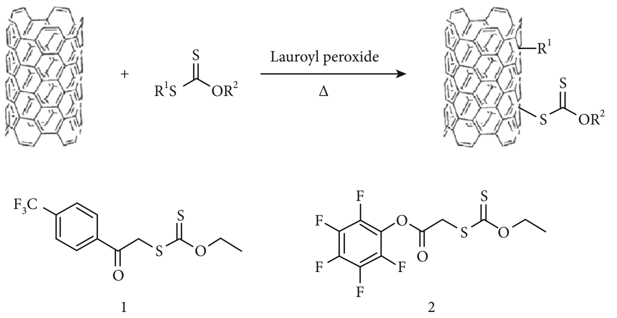


Figure 21: Functionalization of CNTs by xanthates 1 and 2 [192].

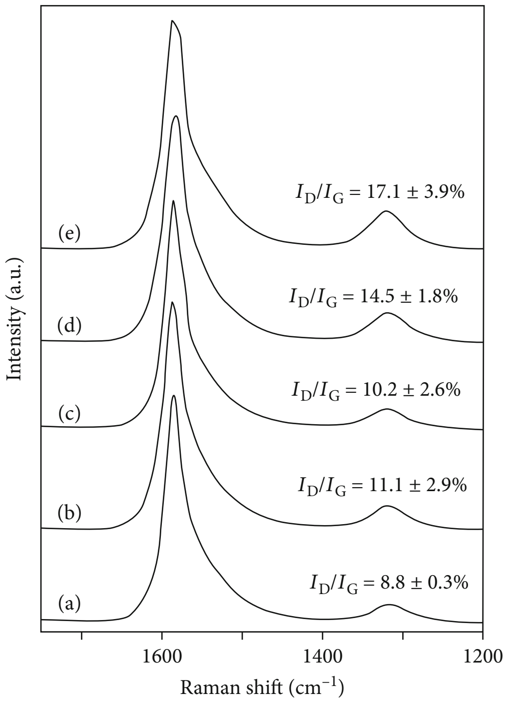


Figure 22: Raman spectra of samples (a) purified SWCNTs, (b) SWCNT–R–N(CH_3)$_2$, (c) SWCNT–R–OCH_3, (d) SWCNT–R–CH_2OH, and (e) SWCNT–R–I [195].

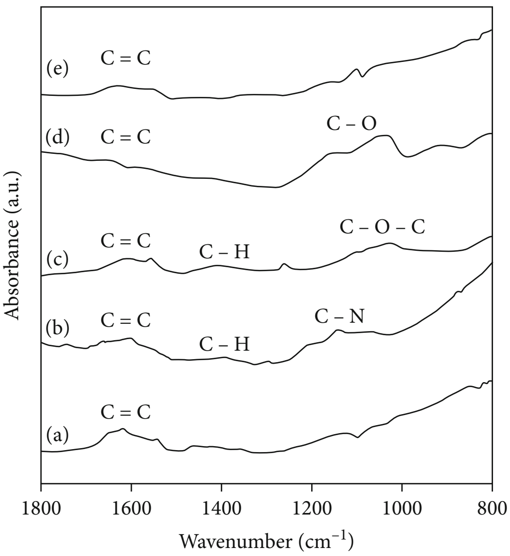


Figure 23: FTIR spectra of (a) purified SWCNTs, (b) SWCNT–R–N(CH_3)$_2$, (c) SWCNT–R–OCH_3, (d) SWCNT–R–CH_2OH, and (e) SWCNT–R–I [195].

6. Properties of Functionalized CNTs

Functionalization of CNTs can be done by new methods as discussed beforehand; these new approaches differ mainly in the functionalization agent, operating temperature and the presence of the catalyst during the functionalization process. These main parameters are presented in Table 4 for amidation type functionalization of CNTs for multiple applications. The optimization and the control of these parameters known to affect strongly the CNT surface armature are the main purpose of researchers involved in enhancing the properties of CNTs by functionalization.

Singh et al. [200] and Peng and Liu [201] have explained the change in the CNT structure by a change in the nature of

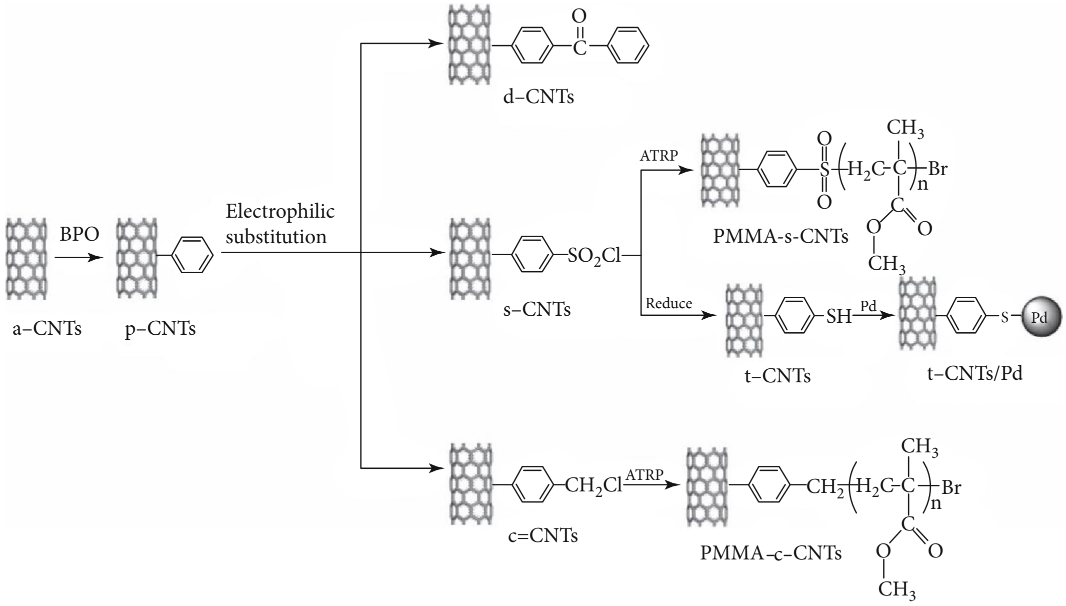


Figure 24: Schematic procedure for the electrophilic substitution reaction on p-CNTs and the applications in making hybrid materials [196].

the bonding and the formation of surface functional groups, presenting new nanostructured nanotubes produced by functionalization and having different properties than pristine CNTs. Steimecke et al. [202] have presented new functionalized CNTs with an increased surface area and an outer diameter between 5 and 30 nm. While Yaragalla et al. [203] have studied the effect of MWCNT functionalization, they have clearly indicated by TEM characterization an increase of the diameter of F-MWCNT by 120% compared to neat MWCNTs. Functionalization of CNTs affects the mechanical properties as well as reported by Garg and Sinnott [204]. Chemical functionalization degrades the mechanical strength of the CNTs by an average value of 15%; the same conclusion has been reported by Steiner et al. [205], while Zhang et al. [206] reported also a decrease in ductility and strength of CNTs after functionalization. Milowska and Majewski [207] have reported the decrease of the elastic modulus with increasing the adsorbent concentration resulting in a change of the geometry of CNTs, and hence, the elasticity of the nanotubes is diminished. Considering hydrogen (–H), hydroxyl (–OH), carboxyl (–COOH), and amine (–NH2) as functional groups, for each functional group and 20% functionalization, Young's modulus and the shear modulus are decreased by about 34% and 43%, respectively [208]. Ansari et al. [209] have reported that functionalization of SWCNTs caused chemisorption of atomic oxygen and -hydroxyl and reduces Young's modulus and critical strain while increases the critical force of CNTs. Thermal conductivity is also dropped by a factor of 1.5 after functionalization of CNTs [210]. Stability and thermal conductivity of F-CNTs is better explained by concentric functional group parameter presented in the nanotube [211]. Marcelino et al. reported that unmodified CNTs presented a conductivity of 510 S/m which decreased as the functionalization degree increased [212]. In contrast, Lau et al. [213] reported that electrical conductivity of MWCNTs increases with functionalization. Electrical conductivity depends on the technique of functionalization and not on the functionalization degrees. Bromination of SWCNTs using bromine liquid at 100°C allowed the insertion of bromine without altering the crystallinity of SWCNTs providing a new possibility to use F-CNTs as an electrolyte redox capacitor as reported by Clancy et al. [214]. The alignment of CNT arrays has been investigated by Lu et al. [215] during the process of functionalization in radio frequency tetrafluoromethane (CF_4) plasma for different times; polar components, such as C-O bonds, C=O bonds, semi-ionic covalent CeF bonds, and covalent CeF bonds, were introduced, and nonpolar $CF_2=CF_2$ bonds were further introduced over 120 s adhesion strength of vertical aligned carbon nanotube (VACNT) that was continuously raised until 90s; due to the introduction of polar groups, the height of the array is almost unchanged, and the carbon nanotubes are straightly aligned vertically. The increase in the temperature from 600 to 750°C during functionalization of CNTs in 2-dichlorobenzene (DCB) in the presence of Fe-Co/$CaCO_3$ catalyst with an increase in the synthesis temperature chlorine plays a role in creating defect in CNT surface; the best surface for growth is formed at 700°C, and the inner diameter of the CNTs is changed from 5 to 10 nm [216].

7. Comparative Performance of CNTs and Functionalized CNTs by New Approaches

The morphology and structure of CNTs are strongly depending on the type of bromination and the type of the catalyst as reported by Zeynalov et al. [229]; the bromine functionalization of MWCNTs is done by plasma chemical functionalization in the presence of Lewis acid catalyst where the sp transition configuration of MWCNTs is

Table 4: Main parameters for amidation type functionalization of CNTs for multiple applications.

Author	CNT type	Functionalization agent	T	Catalyst	Properties	Application	Ref
Antolín-Cerón et al.	CNT	(1) H_2SO_4:HNO_3 (2) Dimethylformamide (3) 4 aminobenzoic acid	60°C 80°C 130°C	—	f-CNTs present low thermal stability due to the presence organic substituent	Nanocomposites (reinforcement agent for polyurethane (PU))	[217]
Wang et al.	MWCNT	N, N0-Dicyclohexylcarbodiimide (DCC) and p-phenylenediamine	50°C	—	Diameter of carbon nanotubes is ~20 nm	Water-dispersible electrochormic nanocomposites	[218]
Bahramnia et al.	MWCNT	3-(Triethoxy silyl) propyl amine (TESPA) with different concentration 150, 75, and 25 wt.%	80°C	TEA	(i) Presence of amide in functionalized MWCNTs (ii) Modification of MWCNTs with respect to the pristine MWCNTs morphology (iii) The measurable mean diameter sizes of 25 wt.%, 75 wt.%, and 150 wt.% TESPA MWCNTs were 41.6, 49.2, and 80.38 nm	The effect of 3-(triethoxy silyl) propyl amine concentration on surface modification of multiwall carbon nanotubes	[219]
Blaskievicz et al.	CNT	1-(3-Aminopropyl)imidazole	Room temperature	—	After reduction of functionalized CNT, the carbons attached to oxygenated groups did not return to the sp^2 hybridization or restore a typical hexagonal graphitic structure No variation in the interlayer distance	Nanocatalysts derived from magnetic carbon nanotubes	[220]
Janudin et al.	CNT	Dodecylamine	80°C	H_2SO_4	Diameter distribution of CNT-amide was slightly decreased which was in the range of 10 to 109 nm, and the mean diameter was 32.16 nm with a standard deviation of 17.01 The functionalized CNTs are better aligned and denser because of the insertion of a new functional group	Effect of functionalized carbon nanotubes in the detection of benzene at room temperature	[221]
Anandhi and Benial	MWCNT	L-Alanine	Room temperature	—	(i) Rough surface morphology because of the attachment of the alanine (ii) Larger diameter for the functionalized MWCNTs (mean diameter 84.80 nm) (iii) No agglomeration for functionalized MWCNTs (iv) Helix form of structure of functionalized MWCNTs	Biomedical	[222]
Gao et al.	MWCNT-COOH	Ethylenediamine (EDA)	—	—	(i) The boundary of MWCNTs-A was blurry, and thin films were adhered to the tubes (ii) Surface of MWCNTs-A is rougher than that of MWCNTs-COOH	Improving thermal, electrical, and mechanical properties of fluoroelastomer/amino functionalized multiwalled carbon nanotube composite	[223]
Jang et al.	MWCNT		80°C	—			[224]

Table 4: Continued.

Author	CNT type	Functionalization agent	T	Catalyst	Properties	Application	Ref
		3-Aminopropyltriethoxysilane			(i) The BET surface area 112.52 m^2 g-1 containing both micro- and meso-porous structure (ii) Increased diameters as well as rougher, more corrugated surfaces (iii) Interlayer spacing of the modified MWCNTs was estimated to approximately 14 nm	Removal of cesium from aqueous solution	
Al-Shuja'a et al.	MWCNT	Thylene diamine (EDA) and O-phenylenediamine (OPDA)	90°C	—	(i) Formation of Poly (MWCNT/amide) with electrical conductivity in the range 4.5×10-6-5.3×10-6 S/cm	New strategy for chemically attachment of amide group on multiwalled carbon nanotube surfaces	[225]
Prabhavathi et al.	MWCNT	5,10,15,20-Mesotetra(4-aminophenyl) porphyrin	130°C	—	(i) MWCNT surface became bumpy after TAP functionalization (ii) Electronic properties of MWCNTs were improved in the hybrid compared to raw MWCNTs	Synthesis, characterization, and photoluminescence properties of tetra(aminophenyl) porphyrin	[226]
Topcu et al.	CNT	Folic acid	0°C	—	(i) The diameter of the carbon nanotubes increased after grafting with folic acid molecules accompanied by the reducing aggregation of the carbon nanotubes	Potentiometric sensor	[227]
Zhou et al.	MWCNT	Polyethyleneimine (PEI)	80°C	—	(i) The PEI loading was dependent on both total functional group loading and the surface area of CNT (ii) The maximum PEI loading could be obtained on CNT material with the highest total functional group loading (7.8 wt.%) and surface area (171.3 m^2/g)	Carbon dioxide capture	[228]

changed from sp^2 to sp^3 reinforced state. This change affects as well the C-C bond angle presenting a shift from 120° in plane to 109.5° out of plane for sp^2 and sp^3, respectively.

DWCNTs are fluorinated by molecular fluorine and a mixture of F_2 and hydrogen fluoride at 200°C; DWCNT has preserved its structure after fluorination presenting an interlayer distance of 0.34 nm in both fluorinated agents making this research promising for the use of additive hydrogen fluoride as agent of functionalization [230]. In the other hand, Wang et al. investigated the use of HF solution in functionalization of CNTs in a free catalyst solution at ambient temperature. This process has not changed the tubular structure of CNTs presuming that fluorination of CNTs may be take place at the sp^3 presenting F-CNTs that retain a highly graphitic ordered structure [231]. Min et al. have functionalized CNTs at 140°C in a mixed HF+Urea free catalyst solution; as the modification reaction progresses, the wall surfaces of F-CNTs and UF-CNTs become relatively rougher than pure CNTs; new layers are formed on the tube wall of UF-CNTs, acting as water-based lubricant additives having good dispersibility in water [232].

Hu et al. have synthetized fluorinated films from functionalization of SWCNTs by xenon difluoride (XeF_2) gas at room temperature; these functionalized films showed a higher conductivity, higher work function, and higher areal density than pristine SWCNT films. The electrical conductivity of fluorinated carbon materials is closely related to the type of C–F bonding, and the surface of the F-SWCNT film is smoother than that of the pristine SWCNT film. The F-SWCNT film has a surface root-mean-square roughness of 5.89 nm, which is smaller than that of the pristine SWCNT film (7.79 nm) providing a new nanomaterial for solar cells [233].

Wulan et al. have functionalized MWCNTs by chlorination approach using hydrophilic acid (HCl) with various molarities between 1 and 6 M and a mixture of sulfuric acid (H_2SO_4) and nitric acid (HNO_3) at room temperature. High amount of functional groups presented in CNT armature adds more hydrophilicity to the nanotubes; hence, more impurities presented in water are cleaned due to the best dispersion of F-MWCNTs; least surface damages and no impurities allow F-MWCNTs by chlorination to be used in drug delivery systems [234]. In contrast, Bulusheva et al. have functionalized DWCNTs in CCl_4 vapor phase at 650°C; his approach has showed a decrease in the content of residual metal and in the bundles size from 3 to 10 nm in chlorinated nanotubes leading to a high repeatable response to humid environment [176]. Mao et al. have synthesized f-MWCNTs by addition of radicals using powder and $NaBH_4$ via ultraviolet irradiation. As a result, thiol functionalized MWCNTs (SH-MWCNTs) with limited damages of conjugated structure are formed. Thiol groups are decomposed at relatively higher temperatures that can go from 350 to 400°C, and the tube of MWCNTs became relatively smooth whereas the atomic percentage of thiol groups in SH-MWCNTs could reach 0.53% after 2 h of exposure to UV radiation [235]. Sadri et al. functionalized MWCNTs by clove plant at 80°C; CMWCNT is attacked directly by hydroxyl radicals forming –OH groups on MWCNT surface; higher number of hybridized sp^3 carbons reinforces the occurrence of an electrophilic addition reaction characterized by the intensity ratio of the D and G bands (ID/IG = 0.8) [236]. CNTs are functionalized by the introduction of diarylcarbene at 100-120°C by nucleophilic carbene addition; covalent bonding between CNTs and diarylcarbene showed better dispersion and remarkable increase in CNT diameter with an average thickness of around 10 nm of the enwrapped PS layers. Das et al. have functionalized MWCNTs via sidewall functionalization through electrophilic addition by using HNO_3; this technique showed the presence of tubular network with MWCNT diameters in the range of 20-30 nm with a graphitic structure having a d-spacing of 0.34 nm [237]. On the other hand, Santangelo has functionalized CNTs by HNO_3 vapors at 135°C; the oxidants attack the graphene structure by electrophilic reactions and generate active sites, such as -C-OH then transform it into –C=O groups or breaks up to carboxyl groups in stronger oxidative environment [58]. In addition to the production of smaller tube and deterioration of the crystalline structure, loss of smoothness is observed in the tube wall [233].

8. Conclusion

A review on the synthesis and different strategies of functionalization of carbon nanotubes going from conventional to recent new approaches of functionalization of CNT nanostructures was presented and discussed. As summary, the nature of the linkage between CNT armature and functional molecules is ensured by the creation of covalent bonds or van der walls forces between the group entities and CNTs at its surface conferring to CNT new structural properties. CNT nanostructure is largely conserved by noncovalent functionalization where the properties are the same as pristine CNT, but solubility of f-CNTs in different systems is more promoted due to functionalization process by different materials as presented in this review. The hybridization of CNT carbon from sp^2 to sp^3 is performed by direct covalent sidewall functionalization by several functional groups via a specified reaction mechanism; CNT functionalization could be also realized by surfactants and grafted polymers on CNTs by noncovalent surface modification that depends on exploiting the cavity of the nanotube in an endohedral or exohedral technical processing. For the purpose to upgrade the applicability circle of CNTs, new strategies are presented mainly differing in the type of agent of functionalization, temperature, and the presence of a catalyst in CNT functionalization process; functionalization affects mainly the structural properties of CNTs as assessed by the new chemical approaches in which amidation of CNTs is performed by oxidative procedure through attaching carboxylic group (COOH) and amine (N-H) groups on the CNT surface. This process resulted in a high degree of functionalization and dispersibility in organic solvents. Bromination is realized via the attachment of Br on the CNTs using halogeneous compounds to change their electronic structure and chemical reactivity. Their main advantage summarized in simplicity of procedure, short reaction times. Chlorination is distinct by the attachment of Cl and the presence of chlorine functional group on the nanotube surface through creation of holes in the outer walls of CNTs. Moreover, fluorination process consists of covalently attachment of fluorine on the surface of CNTs. Each fluorination technique demonstrates the different possibilities of structuration and improves the surface chemical properties as well as polarization. Hydrogenation proved the formation of C-H bonds by chemical interaction in the nanotube walls through hydrogenation of CNTs whereas addition of radicals, nucleophilic carbenes, and sidewall functionalization through electrophilic addition is related to covalent modification of the nanotubes by grafting moieties on the tube surface.

Overall, amidation and fluorination are among the best strategies for CNT functionalization because of their easiest reaction process, the cost of the required materials, and the time of functionalization unlike addition by nucleophilic carbenes that requires a complicated process.

Data Availability

The data used to support the findings of this study are available from the corresponding authors upon reasonable request.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

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