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Surface Functionalization of Carbon Nanotubes for Energy Applications

Mohamed R. Berber, Inas H. Hafez and Mohamad Y. Mustafa

Abstract

Carbon nanotubes (CNTs) are receiving a great deal of attention as a catalyst support for different energy applications, due to their high surface area and high conductivity. Recent literature studies have shown that the application of CNTs mainly depends on their surface functionalization process. Typically, pristine CNTs (as produced) have no functional groups, which is usually considered as an obstacle to their widespread application. In this chapter, we highlight the different techniques used to functionalize the surface of CNTs, including physical and chemical functionalization processes. We show the advantages and the drawbacks of the different functionalization processes. Additionally, we explain in detail the different techniques used to characterize the CNTs before and after functionalization processes. Furthermore, we focus on polymer wrapping techniques of CNTs to create active nanocomposite materials for energy applications, in particular the applications in the agriculture field to fight pollution and make farming activity easier and more efficient.

Keywords: physical functionalization, chemical functionalization, carbon nanotubes, polymers, fuel cells, energy applications for agriculture engineering

1. Introduction

The birth of nanoscience has emerged new pathways for developing new materials with new target properties for different energy applications. Among these promising materials are the carbon nanotubes (CNTs).

CNTs have been discovered by Iijima in 1991 [1]. They are made of graphene sheets which are rolled up to form nanostructured tubes (**Figure 1**). CNTs are receiving a great deal of attention for energy applications due to their high electrical conductivity, low density, large specific surface area, high chemical and thermal stability, as well as their remarkable mechanical properties [2]. CNTs are synthesized by various techniques, including chemical vapor deposition [3] (**Figure 2a**) and arc-discharge method [4] (**Figure 2b**). The as-produced (pristine) CNTs possess a hydrophobic nature due to the high interaction forces (van der Waals force and bundling) between the nanotubes (formation of aggregates). The presence of these aggregates in addition to the low solubility of CNTs shows major drawbacks for engineering useful materials based on CNTs. Thus, a functionalization process is required to overcome the CNT bundle structure which is usually obstacle their real world applications.

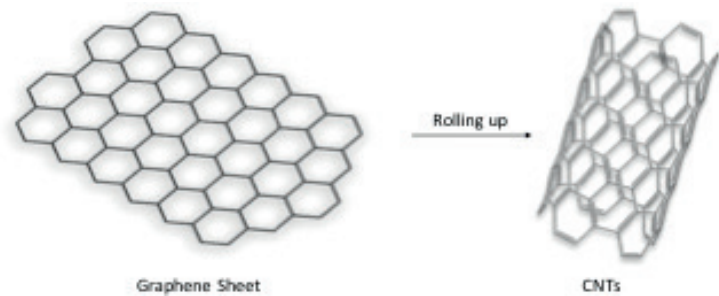


Figure 1.
CNT construction from graphene sheets.

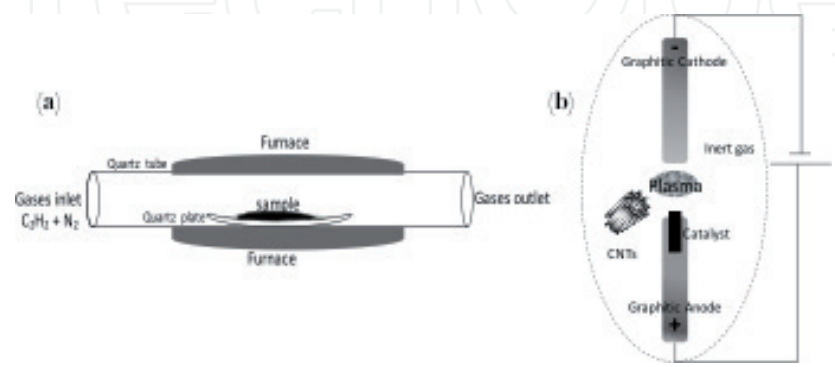


Figure 2.
Schematic illustration of (a) CVD method for preparation of CNTs and (b) arc-discharge method for preparation of CNTs.

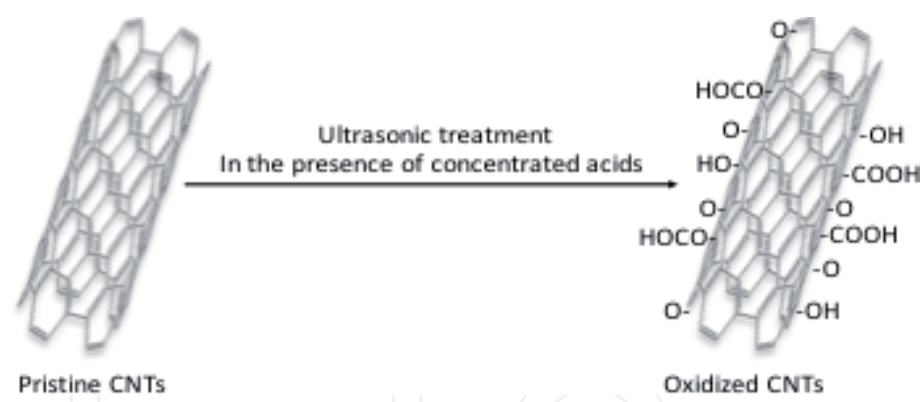


Figure 3.
Oxidation process of CNTs under harsh conditions.

Surface functionalization of CNTs is a promising technique to overcome their bundle structure and to offer a step forward for their real field application. In this chapter, we highlight the current research progress of CNT functionalization. We show the advantages and the drawbacks of the different functionalization processes. Additionally, we present and explain in details the different techniques used to characterize the CNTs. Moreover, we focus on fuel cell and supercapacitor applications of polymer functionalized CNTs. Finally, we show the future prospective of CNTs.

2. Chemical functionalization of CNTs

2.1 Activation of CNT surface via oxidation processes

CNTs are usually functionalized through a harsh oxidation process using harsh materials (e.g., nitric acid and/or sulfuric acid, permanganate using a phase transfer

catalyst, or hydrofluoric acid) under ultrasonic treatment conditions [5–7]. The oxidation-functionalization process usually produces small CNT fragments with side-walls containing different oxygen functional groups (e.g., hydroxyl, carbonyl, and carboxylic acids) [8] that will be able to create covalent bonding with other groups (e.g., polymeric reagents, metal oxides, amino acids, and enzymes) (see **Figure 3**) [9].

A novel chemical activation process for CNTs is the oxidation through a silanization process. This method introduces different organo-functional groups attached to the surface of CNTs, improving the CNT chemical compatibility with specific polymers for producing new CNT-based composites. As an example, oxygen-functionalized CNTs were coupled with 3-methacryloxypropyltrimethoxysilane as an organo-functional silane agent to get double-bond-functionalized CNTs that will be used for copolymerization with vinyl monomers. The produced CNT material has been explored to achieve an improvement for CNT compatibility with other polymers and also to improve their solubility [10].

2.2 Photo-irradiation functionalization of CNTs

Photo-irradiation technique was also used to generate active species (such as nitrene) on the surface of CNTs [11]. Osmylation, for example, is one of the processes in which CNTs were photoactivated through a UV light irradiation process. Typically, CNTs are exposed to osmium tetroxide (OsO_4) under a UV light irradiation (see **Figure 4**). As a result, a photoinduced cycloaddition process of OsO_4 to the $\text{C}=\text{C}$ bonds of CNTs was observed, leading to surface-functionalized CNTs, which facilitate the formation of an intermediate charge-transfer complex for further uses and applications [12].

2.3 Electrochemical activation of CNT surface

In a clean, nondestructive, and a controlled process, the surface of CNTs is functionalized using electrochemistry. Typically, a constant potential is applied to a CNT electrode which is immersed in a solution that contains a suitable active reagent in order to produce radical species. These radical species show a tendency to react or to polymerize, providing a surface-functionalized CNT [13].

In addition of being simple, electrochemical activation process is quite efficient in that they allow for an accurate control over the extent of film deposition thickness through the choice of suitable electrochemical conditions, i.e., duration of deposition and the magnitude of the applied potential. Moreover, by utilizing reagents containing appropriate substituents, the surface properties of the coated CNTs can be tailored [13].

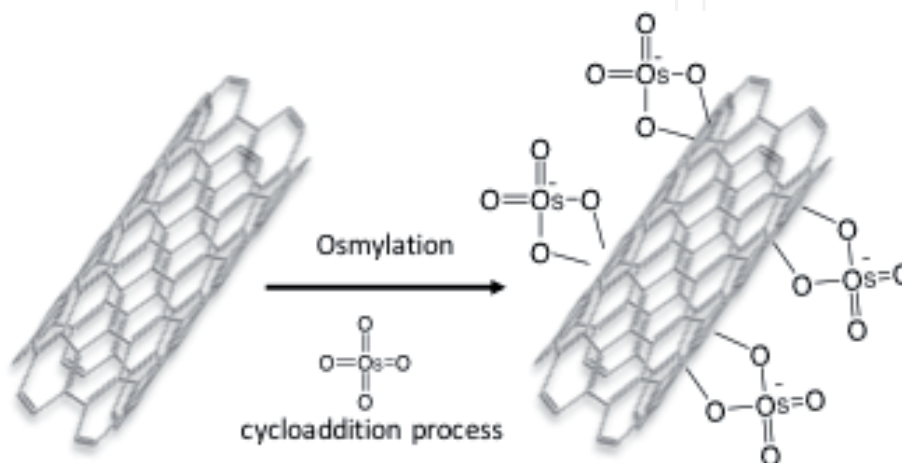


Figure 4.
Schematic illustration of cycloaddition osmylation process of CNTs using osmium tetroxide.

Using this technology, Zhang et al. [13] have electrochemically grafted CNTs in large quantities at room temperature using ionic liquids (see **Figure 5**). In their work, CNTs were considerably untangled in the ionic liquid to greatly increase the effective surface area of the electrode. Then, *N*-succinimidyl acrylate (a model monomer) was dissolved in the supporting ionic liquid and was electrochemically grafted onto CNTs. As an application example, glucose oxidase was covalently anchored on the *N*-succinimidyl acrylate/CNTs assembly, and accordingly the electrocatalytic oxidation of glucose in this assembly was investigated, showing an improvement.

In another study by Bahr et al., CNTs were functionalized via electrochemical reduction process of aryl diazonium salts. In this study, different diazonium salts were used in order to provide conducive materials for further elaboration after attachment to the CNTs [14].

2.4 Characterization of oxidized CNTs

To identify the surface functional groups of the oxidized CNTs, Fourier Transform Infrared spectroscopic analysis was applied (see **Figure 6**). The oxidized CNTs have showed the OH functionality at around 1380 cm^{-1} (bending deformation) and around 3500 cm^{-1} (stretching). The C—O (stretching) was observed at 1160 cm^{-1} , while the C = O functionality of COOH group was observed at 1730 cm^{-1} . Such absorption spectroscopic investigations have provided a strong evidence of the surface functionalization of CNTs [15].

Raman spectroscopy is also considered as a powerful technique to provide information concerning CNT purity. The Raman spectra of **Figure 7** have showed three bands at around $1340\text{--}1350$, $1550\text{--}1600$, and $2600\text{--}2700\text{ cm}^{-1}$. These bands are assigned for structural defects of CNTs (D band), graphitized carbon atoms of CNTs, and a secondary D band (2D band), respectively. To detect the changes occurred in the structure of CNTs after functionalization process, the ratio of D and G band (I_D/I_G) was applied in order to determine the purity factor. As a result of the oxidation process of CNTs, the I_D/I_G has increased. The increasing ratio mainly depends on the oxidation parameters [16].

X-ray photoelectron spectroscopy (XPS) is a surface characterization tool to identify the surface functional groups [15]. For CNTs, it is used to detect the surface changes resulting from the oxidation process. **Figure 8** shows the XPS spectra of C1s of pristine CNTs (top spectrum) and oxidized CNTs (bottom spectrum). As seen, the spectra have revealed six peaks related to carbon satellite peaks, carbonates groups due to carbon dioxide adsorption, carbonyl groups of carboxylic acid groups and lactone, hydroxyl groups of phenolic and alcoholic moieties, sp^2 hybridized carbon. As a result of chemical oxidation of CNTs, the ratio of these carbon functional groups has changed. As reported, longer oxidation times usually lead to higher oxygen content in the oxidized form of CNTs.

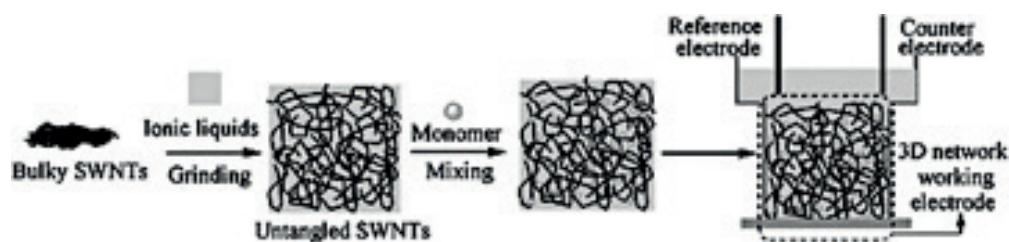


Figure 5. Schematic illustration of electrochemical functionalization of CNTs using ionic liquids and monomer grafting. Reproduced with a permission from Ref. [13].

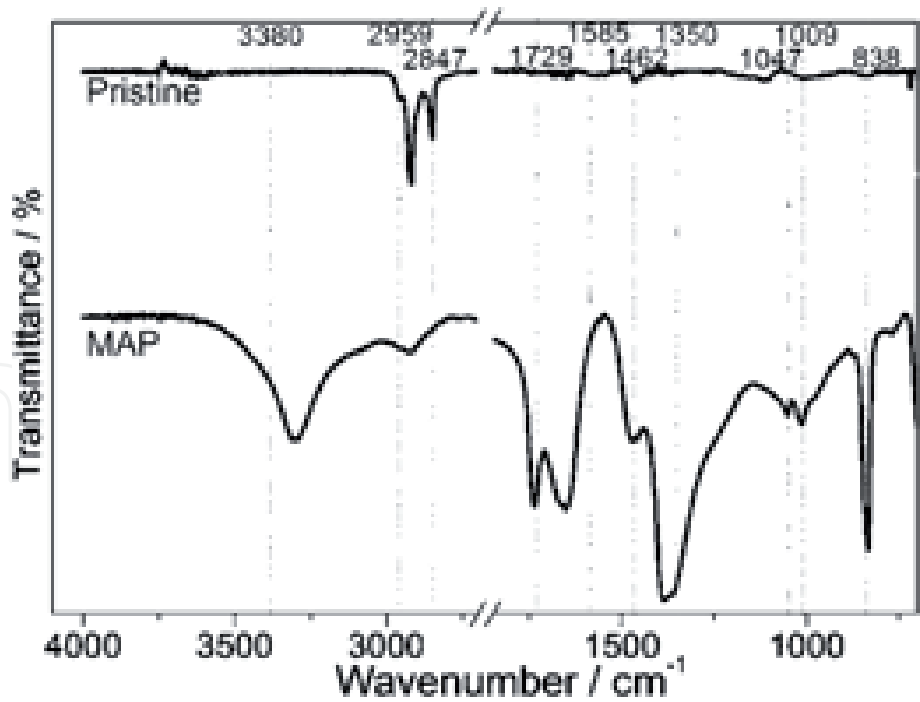


Figure 6.
Fourier Transform Infrared spectra of pristine CNTs (top spectrum) and oxidized/purified CNTs (bottom spectrum). Reproduced with a permission from Ref. [15].

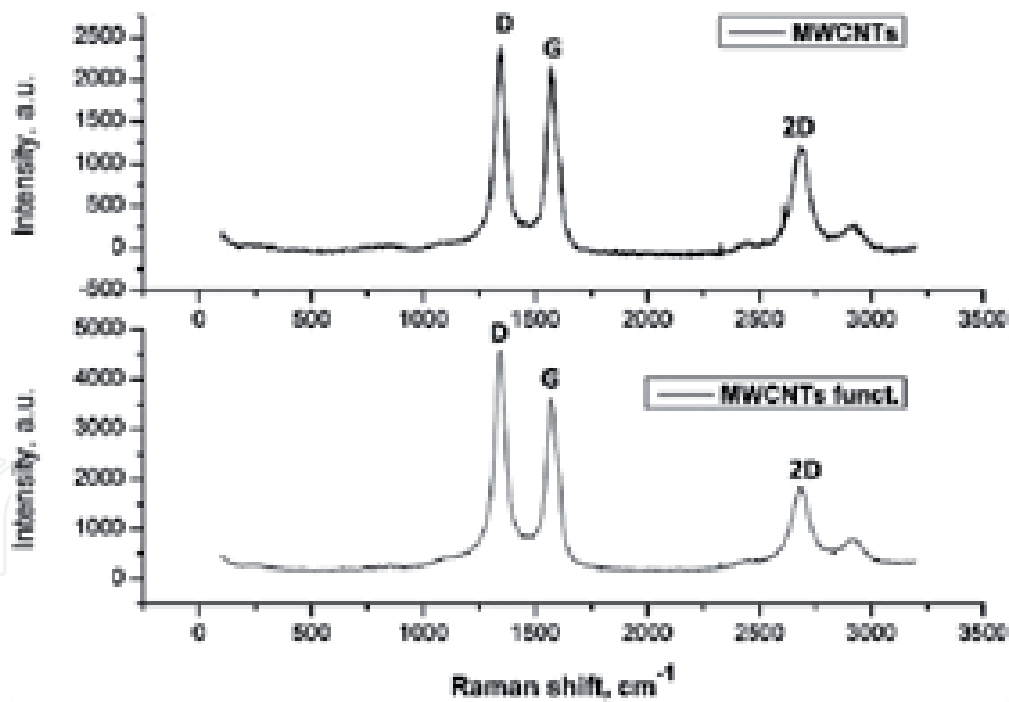


Figure 7.
Raman spectra of pristine CNTs (top spectrum) and oxidized CNTs (bottom spectrum). Reproduced with a permission from Ref. [16].

The XPS of oxygen atoms (O1s spectrum) was also an important result to provide information about the surface functionalization of CNTs. As seen from **Figure 9**, four peaks related to adsorbed water, carboxylic acid groups, hydroxyl groups, and carbonyl moieties were emerged. The ratio of these peaks has changed as a result of oxidation-functionalization process of CNTs. Hence, XPS is a powerful technique to confirm the different functionalities produced by oxidation of CNTs [17].

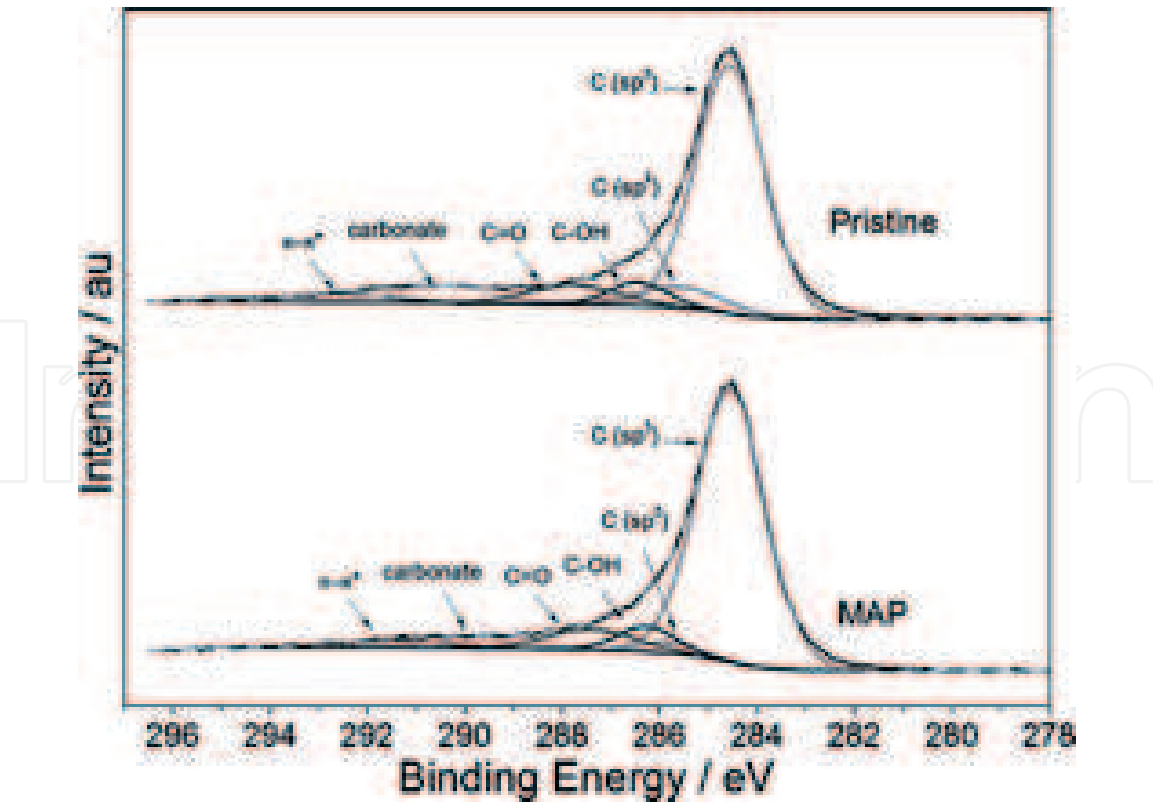


Figure 8.
XPS of C1s spectrum of pristine CNTs (top spectrum) and oxidized/purified CNTs (bottom spectrum).
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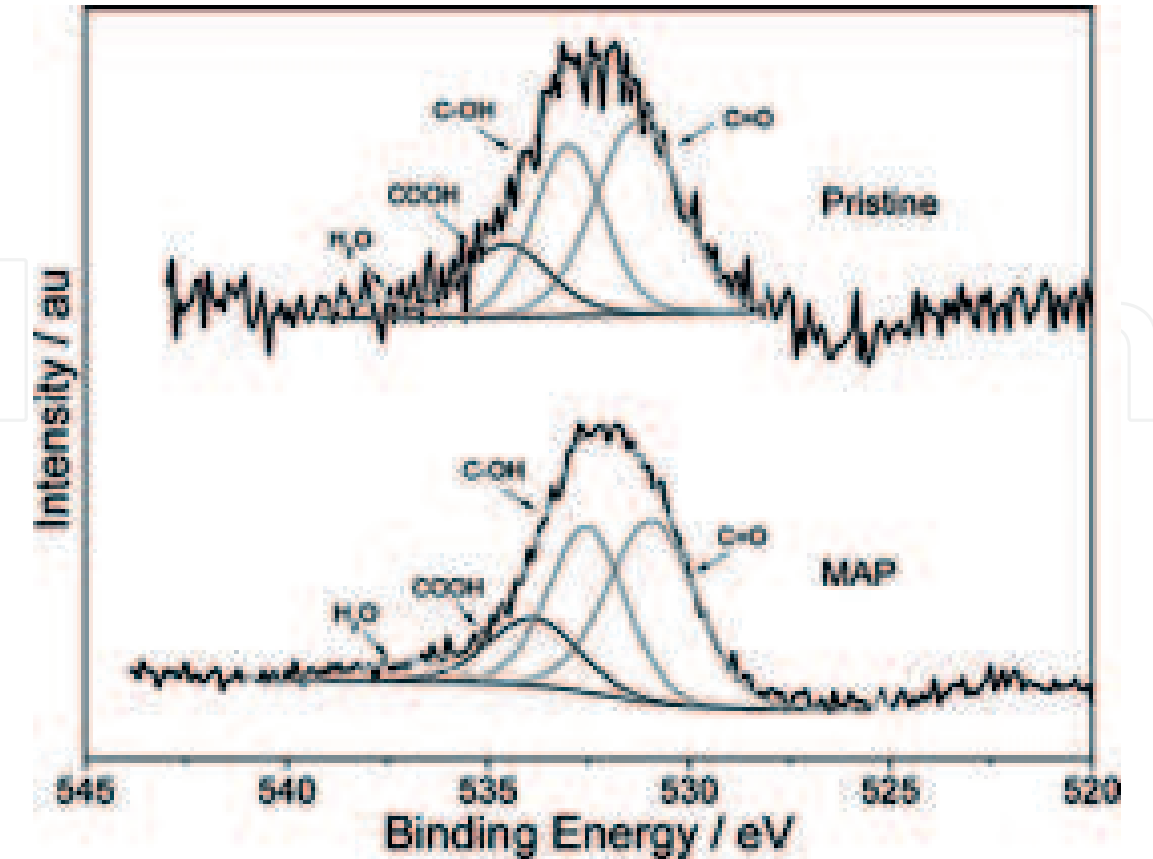


Figure 9.
XPS of O1s spectrum of pristine CNTs (top spectrum) and oxidized/purified CNTs (bottom spectrum).
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3. Physical functionalization of CNTs

The noncovalent functionalization of CNTs has received a great deal of attention because the properties of CNTs can be tailored while maintaining their intrinsic properties. Physical functionalization of CNTs is a process in which CNTs are noncovalently activated through a π - π interaction between π bonds of sp^2 -hybridized carbon atoms of CNTs and the π bonds of macromolecules, surfactants, or functional polymers that are used to activate the surface, forming supramolecular complexes. This hybrid technique usually keeps the original electronic structure and properties of CNTs.

3.1 Small molecule anchoring of CNTs

Through a nondestructive hybrid formulation process, CNTs were functionalized by a simple technique in which CNTs were assembled with a variety of small molecules. This technique has enabled a convenient process to efficiently assemble a wide variety of nanoscale particles on the surfaces of CNTs and accordingly has led to the construction of different nanoscale hetero structures with new functionalities [18].

In a study by Li et al. [18], pristine CNTs were assembled with aminopyrene molecules using the well-known π - π stacking process [19] between the pyrenyl groups of aminopyrene and the sp^2 carbon rings of the CNTs (see **Figure 10**). The resulting CNT hybrid was then used to adsorb different nanoparticle precursors through an electrostatic interaction under appropriate conditions. This unique approach has showed a wide variety of nanoparticles decorated on the surface of CNTs with high efficiency and specificity for different applications.

In a similar study, Li et al. [20] have achieved noncovalently amino-functionalized CNTs by the adsorption of amino ethanol on CNTs surface. The prepared epoxy composite of the noncovalently functionalized CNTs has showed promising mechanical properties while persevering the electrical properties of pristine CNTs.

CNTs were also physically functionalized with cytochrome to construct a new bioanalytical platform for building biosensors. The sensitivity of the resulting biosensor toward glucose has showed a high reproducibility and a successful determination of glucose in commercial beverages [21].

The amino molecules of tetrazine compounds were also attached on CNT surface by a noncovalent process. The amino groups of the functionalized CNTs have generated chemical bonds with the epoxide groups in the epoxy matrices, resulting in a homogenous dispersion of the CNTs. The electrical conductivity of the amino-functionalized CNTs/epoxide composites was significantly higher than that of the pristine CNTs/epoxide composites at the same CNT content [22].

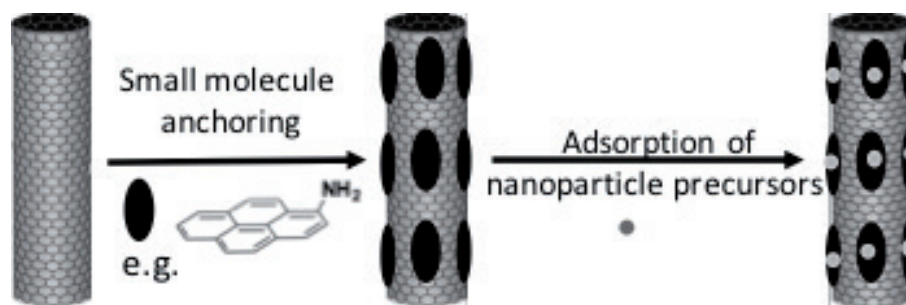


Figure 10.
Schematic illustration of small molecule anchoring onto CNTs.

3.2 Polymer anchoring of CNTs

Polymer functionalization of CNTs is generally introduced to enhance the CNT solubility and dispersion as well as synthesize new CNT composites with advanced properties. The conventional techniques used for the polymer functionalization of CNTs are the covalent attachment processes (grafting from or grafting onto). In “grafting from” technique, the polymer is added to the CNT surface through an in situ polymerization process of the previously attached monomers on the surface of CNTs in the presence of an initiator, while in “grafting onto” technique, the whole polymer is covalently added to CNTs through the surface functional groups which were previously introduced onto the CNT structure [23]. These conventional polymer functionalization techniques have been reported to be not suitable for preparing controlled and pure CNT polymer composites where the residual catalysts and the impurities removal from the reaction medium are problematic issues. Hence, advanced polymer functionalization techniques of CNTs are still required to cover the sensitive and broad application of CNTs [24].

Noncovalent functionalization of CNTs by polymer wrapping is a feasible technique to disperse CNTs, causing no changes in the electronic properties of CNTs. One of the advantages of this technique is the possibility to remove the unbound polymer while leaving the stacked polymer layer on the CNT surface [25]. **Figure 11** shows a schematic illustration of polymer wrapping of CNTs using π -conjugated polymer where a π - π stacking occurs.

Polymers such as polyvinyl alcohol and polymethyl methacrylate [26, 27] have been reported to disperse CNTs through a wrapping mechanism. The results of these studies have showed the importance of the CH- π interaction bonding for the dispersion of the nonaromatic polymers [27].

Polybenzimidazole (PBI, **Figure 12**) is one of the most promising polymers for CNT wrapping, especially for fuel cell applications since it possesses remarkable conducting properties [28]. Using PBI, we fabricated a novel electrocatalyst assembly with CNTs, for high-temperature fuel cells. The obtained PBI/CNT assembly has showed a good dispersibility (see **Figure 13**) and a high utilization efficiency of the loaded metal catalyst compared to the pristine CNTs (see **Figure 14**).

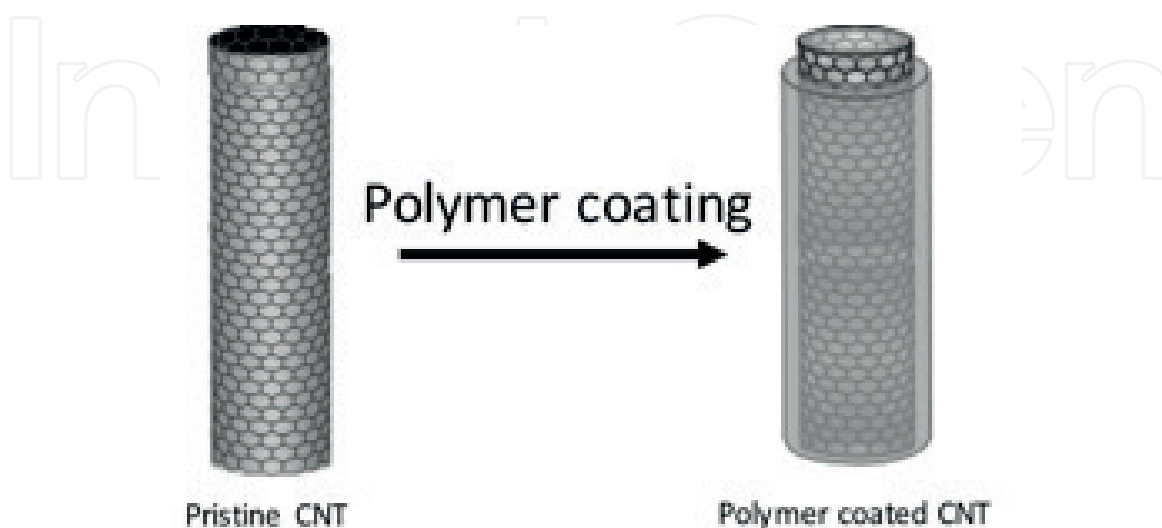


Figure 11.
Schematic illustration of polymer coating of CNTs.

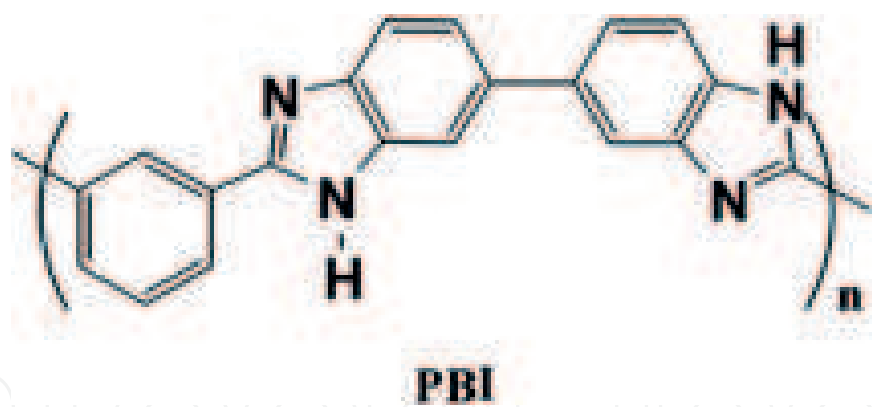


Figure 12.
The structure of polybenzimidazole polymer (PBI).

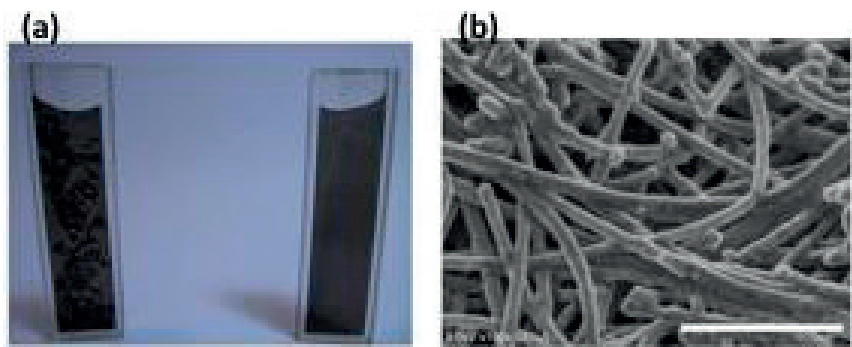


Figure 13.
(a) Photo image of CNT solution before polymer coating (left) and after polymer coating (right) and (b) TEM image of polymer-coated CNTs. Reprinted with a permission from Ref. [28].

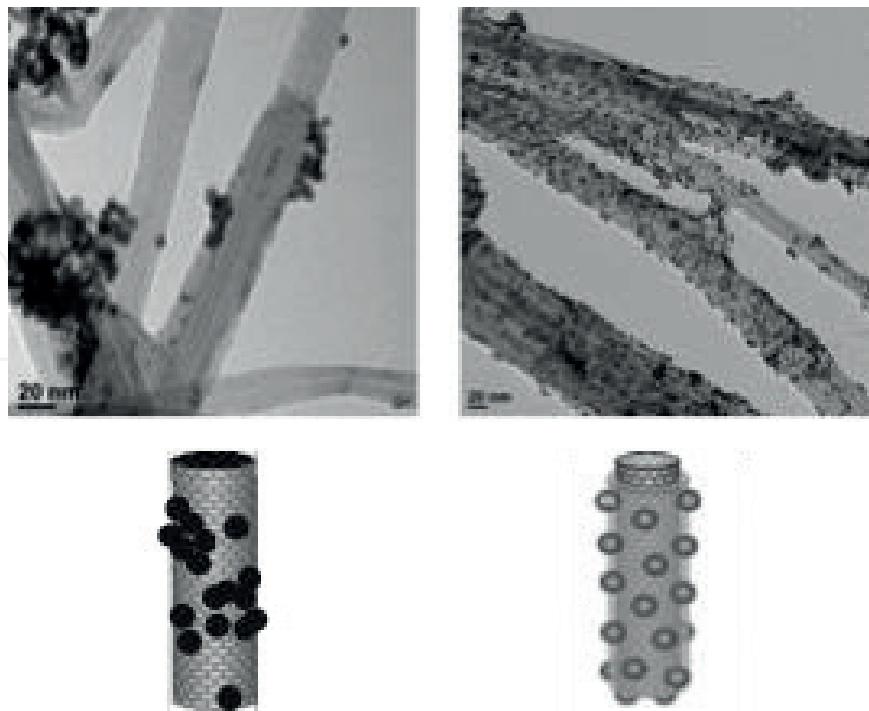


Figure 14.
TEM image of pristine CNTs loaded with metal catalyst (left) and polymer/CNT composite loaded with metal catalyst (right), reprinted with a permission from Ref. [29].

As reported in the literature, the stability of the formed polymer/CNT hybrid depends on the polymer structure [25]. The literature studies have correlated the relation between the binding strength and the length of the oligomers [30].

3.3 Applications of polymer-wrapped CNTs in fuel cells

Polymer-based fuel cell is considered as one of the best sources to realize a green energy source for many applications. It consists of two carbon-based electrodes and a conducting polymer membrane (see **Figure 15**). The carbon-based electrodes are usually composed of a carbon material decorated with a platinum metal catalyst. CNTs are considered as a good supporting material for fuel cell electrocatalysts because they possess a high electrical conductivity and a good electrochemical durability compared to other carbon-supporting materials like, for example, carbon black. The durability and cost of electrodes are the two major roadblocks to commercialize the polymer-based fuel cells. To overcome these obstacles, novel electrocatalysts with high efficiency are required.

For this target, we described a new approach to grow homogeneously platinum nanoparticles in a controllable size manner on a polymer (polybenzimidazole, PyPBI)-wrapped CNT hybrid (see **Figure 16**). A fuel cell employing this polymer-wrapped CNTs composite has exhibited eight times higher mass activity than the current state-of-the-art CNT fuel cells (see **Figure 17**) [31]. With the decrease of platinum nanosize on the polymer-wrapped CNTs, further enhancement in platinum mass activity is observed.

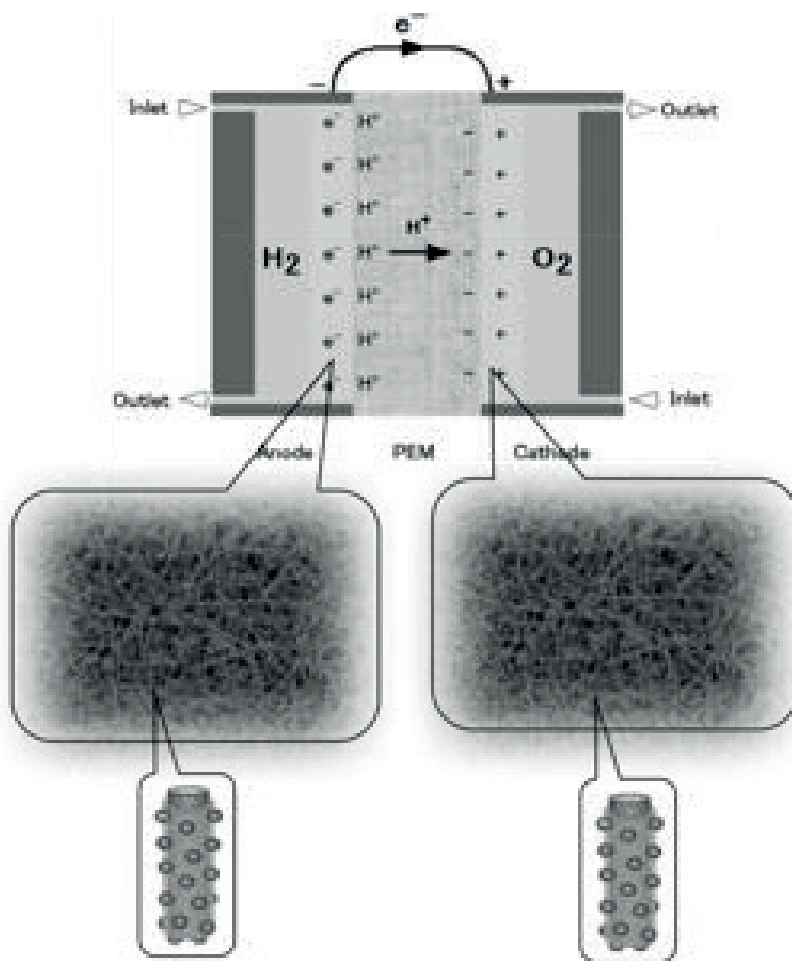


Figure 15. Schematic illustration of polymer-based fuel cell and its components. Polymer-wrapped CNTs were used as anode and cathode electrodes.

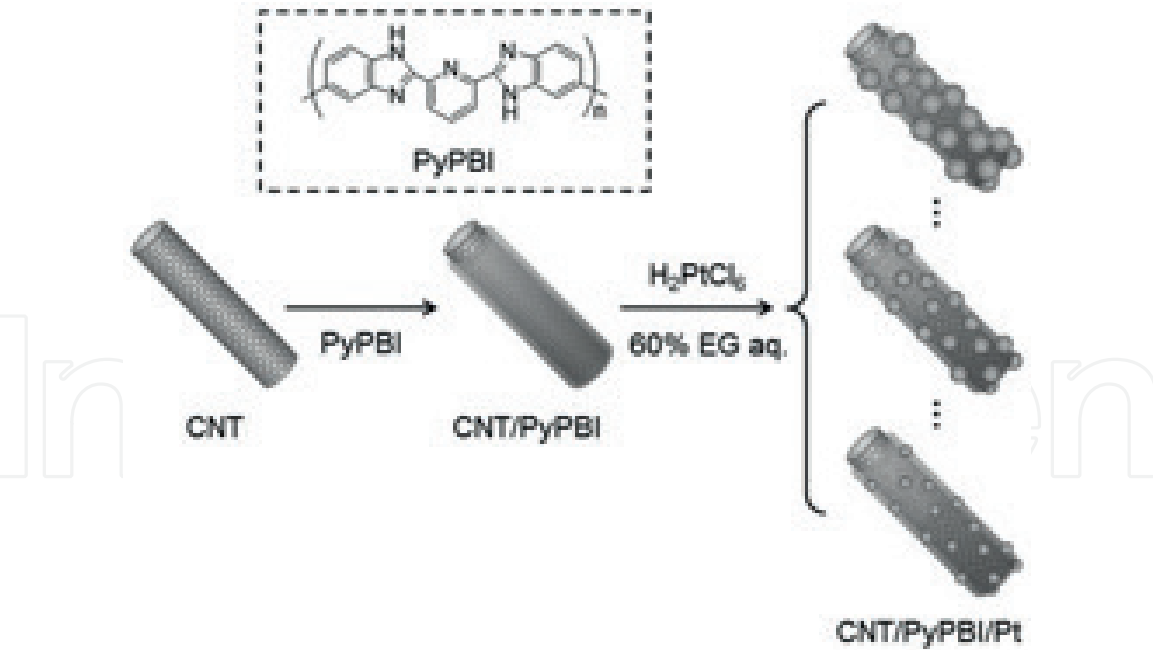


Figure 16.
Schematic illustration of polymer wrapping and platinum deposition on CNTs. The figure shows how the authors have controlled the deposition of the platinum nanoparticles. Reprinted with a permission from Ref. [31].

From the stability point of view, the assembled platinum-/polymer-wrapped CNT nanocomposite has showed a remarkable durability even at very small platinum nanosize (see **Figure 18**), thanks to the PyPBI functional polymer which offered a strong binding sites (the nitrogen atoms of the imidazole units of PyPBI) for the platinum nanoparticles. Thus, polymer wrapping technique of CNTs has offered an effective solution to use efficiently the pristine CNTs in fuel cells, keeping their high electrical properties and their stability.

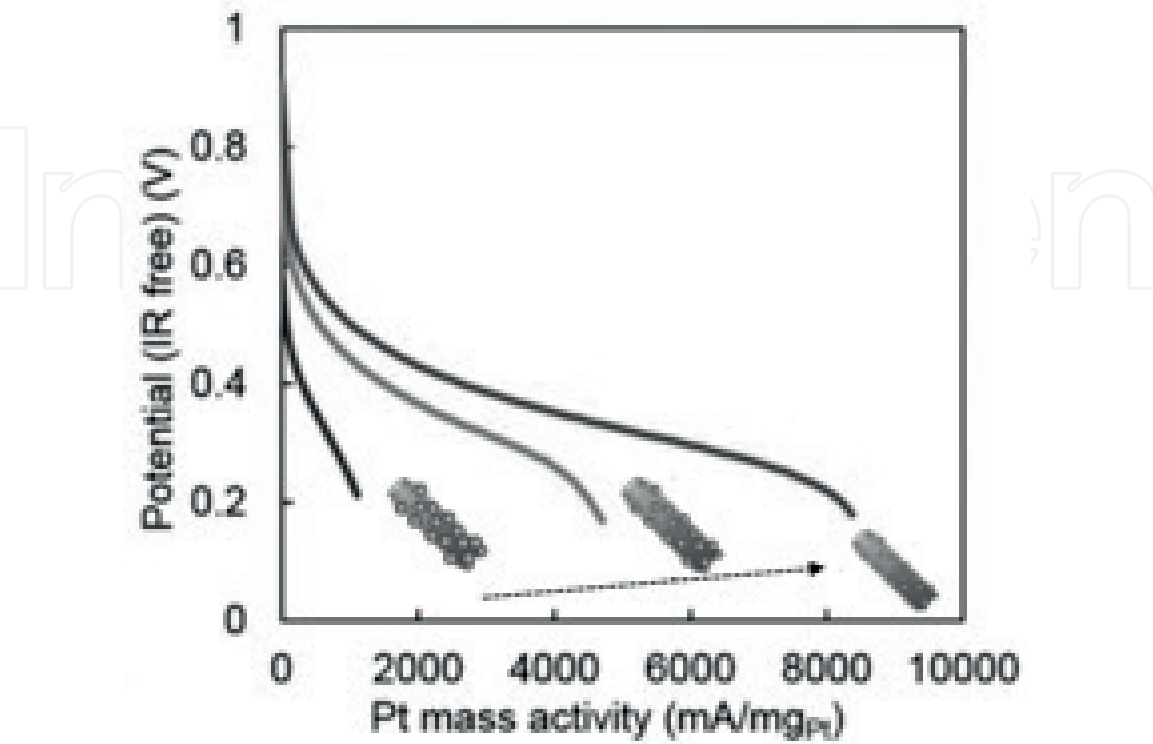


Figure 17.
Potential curves as a function of platinum (Pt) mass activity. Reprinted with a permission from Ref. [31].

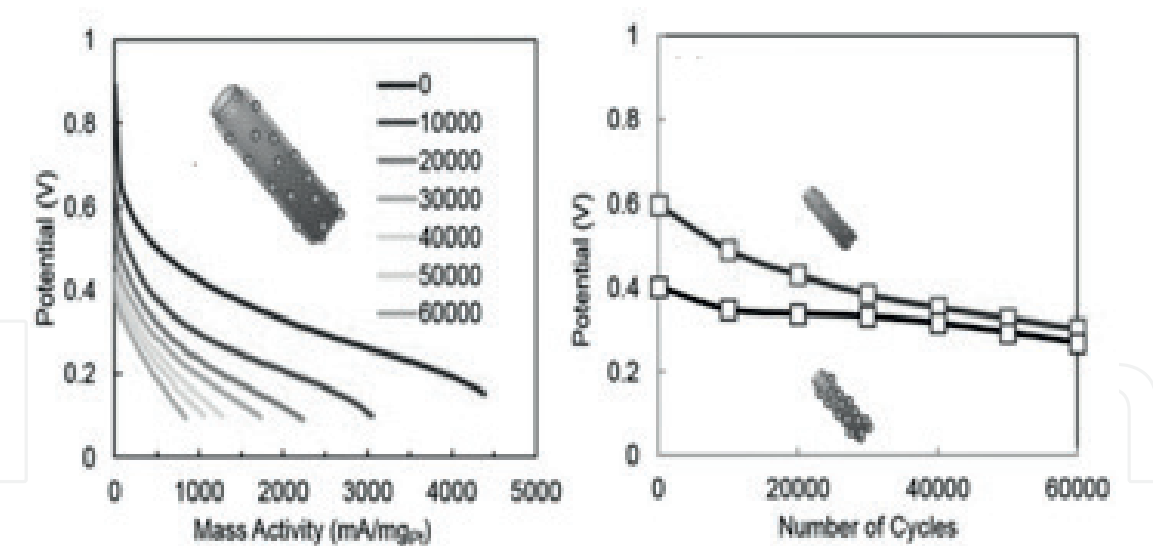


Figure 18. Durability potential curve test using MEA10 (small platinum nanosize). The polarization curves were measured after every 1000 cycles. For convenience, the data were plotted every 10,000 cycles (c). Plots of the cell voltage at 200 mA mgPt-1 for the MEA50 and MEA10.

3.4 Fuel cell-based tractors

The agricultural sector needs to decrease its use of fossil fuels in order to diminish the global warming and to lower environmental impact. **Figure 19** shows a schematic illustration of the new fuel cell tractor built by New Holland company (<http://www.newholland.com/Pages/index.html>). The figure shows also the photo image of the fuel cell tack used in the tractor. The volume and the design of the fuel cell stack depend on the required power from the tractor.

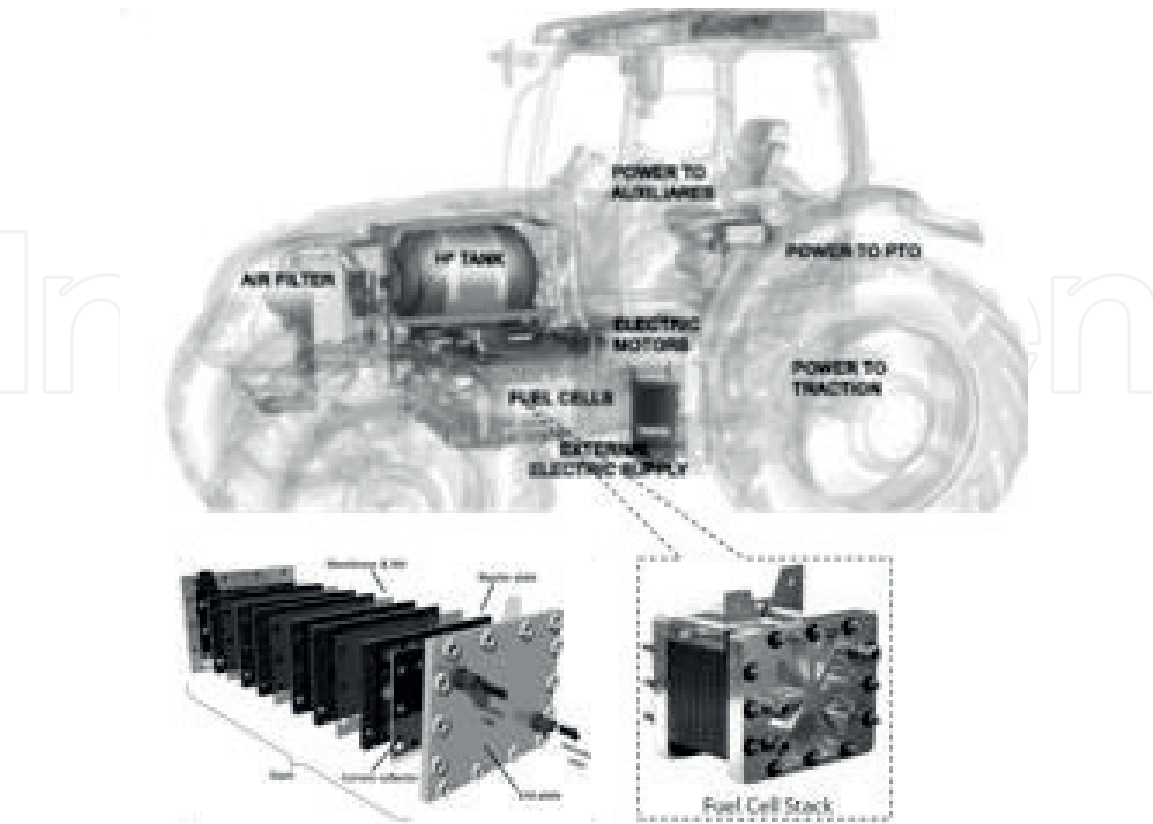


Figure 19. Schematic illustration of fuel cell tractor built by New Holland (photo courtesy of New Holland). The fuel cell stack depends on the required power.

The current research of fuel cell tractors focuses on serving the farmer to find better, smarter, and faster ways to make the fuel cell technology simple, accessible, and easy to use. Also let farmers free from the cost of purchased fossil fuel and allow them to achieve fuel autonomy.

The new fuel cell tractors offer greater reliability than the fossil-based tractors because the use of fewer moving parts and also the replacement of the hydraulic and the mechanical systems with electrical parts.

3.5 Applications of polymer-wrapped CNTs in supercapacitor

CNTs are being tested as electrodes in supercapacitors because of their remarkable electrical and mechanical properties as well as their high specific surface area. In order to provide high-performance supercapacitor-based devices with potential applications, CNTs need to be perfectly functionalized to maintain their intrinsic properties mentioned above. The introduction of conducting polymers on the surface of CNTs is envisioned to increase the specific capacitance of the supercapacitors. Hence, a suitable engineering process is required to achieve this target, keeping the stability of the supercapacitor [32].

It has been reported that CNT composites with conducting polymers like polyaniline or polypyrrole show a high specific capacitance and a high conductivity, leading to a high power density because the entangled mesoporous network of CNTs in the polymer composite can adapt to the volume change avoiding shrinkage. Accordingly, a more stable capacitance with cycling is obtained [33]. Another important advantage of the polymer/CNT composite is the remarkable volumetric energy coming from the high density of conducting polymer/CNT composite that facilitates the accessibility of the electrode/electrolyte interface, allowing a quick charge propagation in the composite material and an efficient reversible storage of energy in the conducting polymer/CNT composite during subsequent charging/discharging cycles [34].

4. Drawbacks of chemical and physical functionalization of CNTs

As reported in the literature, covalent functionalization usually demolishes the CNT electrical properties due to the transformation of the sp^2 -hybridized carbon atoms to sp^3 -hybridized atoms in the CNT framework. Thus, it is not the appropriate technique to activate the structure of CNTs for electronic device applications [35].

While the physical functionalization keeps the electronic properties of the CNTs, this technique suffers from a major drawback which is the stability of the produced assembly. Typically, the molecules adsorbed on the surface of CNTs can more or less be desorbed depending on the conformation and/or the size of the attached molecules when for example the solvent is changed or the CNTs are filtered, and then redispersed in another medium. Hence, there is a need for an advanced process to overcome the current drawbacks of the chemical and physical functionalization processes of CNTs.

5. A bridge method between physical and chemical activation processes

In a recent study, a new functionalization process of CNTs was introduced to gather the advantages of both covalent and noncovalent activation techniques, avoiding their principal drawbacks. This process is based on a controlled polymerization of hydrophobic molecules onto CNTs dispersed in micelles. This approach

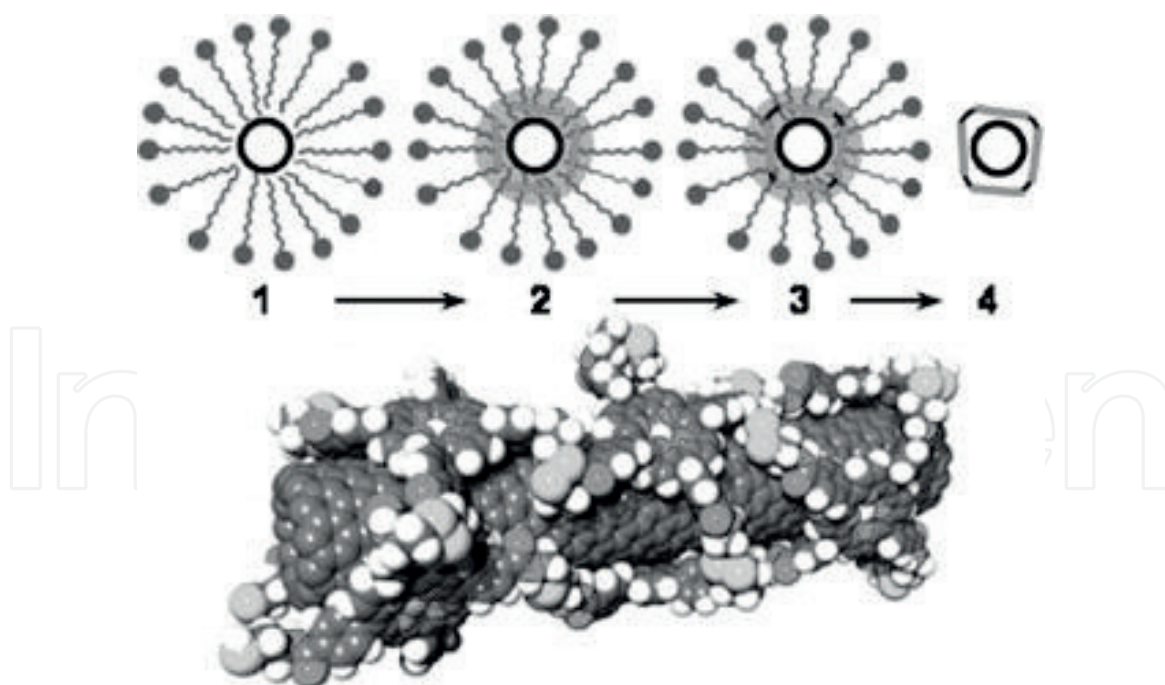


Figure 20.

Schematic illustration of the covalent/noncovalent functionalization of CNTs. (1) The CNTs dispersed in micelles, (2) dispersion of porphyrins on the CNT surfaces, (3) crosslinking of porphyrin around the CNTs, and (4) purification of CNTs via filtration and extensive washing to remove the surfactants, reagents, and unbound porphyrin moieties. Reproduced with a permission from Ref. [36].

permits to obtain CNT hybrids exhibiting high stability while preserving their π -conjugated system responsible for their outstanding optical and electrical properties. The obtained CNT hybrids can be purified, manipulated, and dispersed in various solvents without losing their functionality (see **Figure 20**) [36].

6. Conclusion and outlook

It is important to note that CNTs are now in the way of commercial production in large quantities. Also, the literature has reported many purification and functionalization processes, which maintain the original and intrinsic properties of CNTs, in addition to providing many interesting properties based on hybridization and complexation processes with other functional materials including polymers. Despite all these efforts, structural details of functional CNTs especially in the atomic level still remain to be demonstrated. In this chapter, we have highlighted the different functionalization process of CNTs including chemical, photo-irradiation, electrochemical, and physical activation processes. In addition, we have highlighted the different characterization tools used to characterize the functionalized CNTs and have indicated the drawbacks of the functionalization processes of CNTs, showing a bridge method to avoid these roadblocks that prevent the wide applications of CNTs. Finally, we have paid attention to the CNT energy applications, especially in fuel cells and supercapacitors.

To date, further work is still required to understand how the amount of the functional groups, their type, and their distribution affect the efficiency of the CNTs in its target application.

From the application point of view, CNT-based fuel cells are the future engine for the transport sector, which currently depends on the fossil fuel that causes many environmental problems. A special focus is on hydrogen- and biodiesel-based vehicles used in the agriculture field to fight pollution and make farming activity

easier and more efficient. This pioneering spirit led us to look always forward in the research of fuel cells, anticipating the evolution of farming by designing effective farm vehicles.

Acknowledgements

“The publication charge for this article has been funded by a grant from the publication fund of UiT, The Arctic University of Norway”.

Conflict of interest

The authors declare no “conflict of interest.”

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