



## Review

## Functionalizing carbon nanotubes for proton exchange membrane fuel cells electrode

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## ABSTRACT

In recent years, carbon nanotubes (CNTs) have been increasingly considered as an advanced metal catalyst support for proton exchange membrane fuel cells (PEMFCs), owing to their outstanding physical and mechanical characteristics. However, the effective attachment of metal catalysts, uniformly dispersed onto the CNT surface, remains a formidable challenge because of the inertness of the CNT walls. Therefore, the surface functionalization of CNTs seems necessary in most cases in order to enable a homogeneous metal deposition. This review presents the different surface functionalization approaches that provide efficient avenues for the deposition of metal nanoparticles on CNTs, for the application of catalyst supports in PEMFCs with improved reactivity.

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## 1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are considered to be efficient and clean energy sources for automotive and portable applications, as well as for stationary ones [1]. The development of a durable, low cost, and highly active oxygen reduction reaction electrocatalysts is one of the critical remaining challenges for the successful introduction of PEMFCs into mass markets [2,3]. In state

of the art PEMFCs, the most often used electrocatalyst is Pt (or Pt alloy) nanoparticles supported on high surface area carbon materials. In spite of the high surface area of the carbon black particles, the carbon black-based electrocatalyst support has two main problems: (i) it induces significant mass transfer limitations due to its dense structure, leading to a very low Pt utilization [4] and (ii) carbon black is known to undergo electrochemical oxidation, forming surface oxides such as –OH, –COOH and –C=O, reacting finally to CO<sub>2</sub> at the cathode of the fuel cell [5]. The formation of CO<sub>2</sub> is promoted at lower pH, and higher potential, humidity and temperature (~80 °C) [6]. As carbon corrodes, noble metal nanoparticles (e.g., Pt) will detach from the carbon black and aggregate into larger particles resulting in the loss of Pt surface area, which subsequently lowers the performance of PEMFCs [5,7,8]. Since the cost of conventional

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electrocatalyst accounts for a significant amount (30–45%) of the total cost of a PEMFC, the performance reduction associated with low Pt utilization must be avoided, although there should be no sacrifice in cell and stack operating lifetime. The concept of ultra-low Pt loading is becoming one of the most important issues for PEMFC, and carbon nanotubes-supported electrocatalysts can help in this respect.

In the last several years, considerable efforts have been made to develop new catalyst support materials to improve both catalytic activity and stability [9–15]. Normally the performance degradation contributed from the catalyst support is mainly due to carbon corrosion. Nanostructured materials can be of assistance to overcome from carbon corrosion due to their unique chemical and physical properties, which are dependant on their size and shape [16]. One such nanostructured material is carbon nanotubes (CNTs). Due to their fascinating structure and electrical/mechanical properties, CNTs are ideal supporting material for metal nanoparticles [17–19].

CNTs can be divided essentially into two categories: single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) [20]. SWCNTs are formed by rolling a perfect graphene sheet, i.e., a polyaromatic mono-atomic layer consisting of a hexagonal arrangement of  $sp^2$  hybridized carbon atoms, into a cylinder along an  $(m,n)$  lattice vector in the graphene plane. The  $(m,n)$  indices determine the diameter and chirality, which are key parameters of a nanotube. SWCNTs have a relatively small diameter, as low as 0.4 nm, whereas the length can range from a few microns to several millimeters, and could be metallic or semiconducting in nature depending on their structure. Multiple rolled sheets that result in a concentric set of cylinders with a constant interlayer separation of 0.34 nm result in MWCNTs; these have relatively large diameters, from a few nanometers to tens of nanometers, and are conducting materials. The electronic properties of perfect MWCNTs are similar to those of perfect SWCNTs because the coupling between the cylinders is weak in MWCNTs. Table 1 shows a summary of physical attributes of CNTs.

A large number of studies have shown that Pt (or Pt alloys) supported on CNTs exhibit better performance for the electro-oxidation of methanol [21–23] and oxygen reduction [14,24–30] and a better durability than that on a carbon black support [31–33]. However, the effective attachment of uniformly dispersed Pt nanoparticles remains a formidable challenge, due to the inertness and hydrophobic properties of the CNT surface [34–38]. In order to obtain a more controlled and specific nucleation of metal nanoparticles on the surface of CNT supports, it is necessary to modify the surface through oxidation to introduce anchoring sites. Therefore, it is important to develop proper techniques to improve adhesion through surface modification of CNTs before metal deposition [39].

In this review paper, recent advances in the development of reliable methods for the functionalization of CNTs will be described, with the aim to use CNTs as catalyst supports for PEMFCs.

## 2. A brief overview of carbon nanotubes

Since their discovery in the early-1990s [40], CNTs have become one of the most active fields of nanoscience and nanotechnology, due to the exceptional properties that make them very attractive candidates for fuel cell applications [23,24,26,41,42]. Many reviews are available dealing with the synthesis of CNTs and their characteristics as a novel catalyst support [43–45]. The synthesis of CNTs can be accomplished via a wide variety of methods that involve the catalytic decomposition of carbon source materials either in gas or solid phase. Some of the most common techniques are chemical vapor deposition (CVD), arc discharge, and laser vaporization

**Table 1**  
Summary of physical attributes of CNTs [107].

Attributes	Comments
Electrical conductivity: $10^8 \Omega^{-1} \text{ m}^{-1}$	Comparable to that of copper
Thermal conductivity: $10^4 \text{ W m}^{-1} \text{ K}^{-1}$	Greater than that of diamond
Young's modulus: 1 TPa	Stiffer than any other known material
Tensile strength: 150 GPa	600 times the strength/weight ratio of steel

synthesis [46,47]. The synthesis conditions (temperature, pressure, carrier gas, etc.), metal catalyst type (most commonly iron, nickel, cobalt, or yttrium), and carbon source (graphite or hydrocarbon) have all been shown to influence the properties of the resulting CNTs [46,48,49]. After synthesis, the purification step is important to eliminate the trace amounts of catalyst remaining. Rocco et al. [50] achieved the best result using an aqueous HCl solution ( $3 \text{ mol L}^{-1}$ ) over a 24 h reflux. Han et al. [51] used a mild and less destructive medium like polyphosphoric acid (PPA), with or without phosphorous pentoxide ( $\text{P}_2\text{O}_5$ ) at various temperatures such as 130, 160 and 190 °C, for both purification and functionalization of CNTs. The process was claimed to be an efficient method of removing persistent metallic impurities in CNTs with or without little damage to the CNT framework.

The CNTs produced in the above steps are high molecular weight, and have strong hydrophobic forces keep them aggregated together in bundles. Such a bundling effect leads to a poor dispersion of metal particles on CNTs and limits the overall electrocatalytic activity. The CNTs produced in the above ways are also inert and hardly support any precious metals like Pt. CNTs are not wetted by liquids with surface tensions higher than 100–200  $\text{mN m}^{-1}$ , thereby excluding most metals (and other elements) in the periodic table. The one approach is to deposit the metals through a chemical reaction on the inner or outer surfaces of the tubes [52]. A major challenge in the synthesis of CNTs as supports for Pt electrocatalysts is to control the size and distribution of the Pt nanoparticles. Since the dispersion and particle size of Pt on the support material can strongly affect its utilization and catalytic activity [53], the synthesis of Pt nanoparticles supported by CNTs is of clear practical importance [24,26,27,34,54,55]. A useful review on the synthesis of CNTs- and nanofiber-supported Pt electrocatalysts by Lee et al. [56], described various synthesis methods. The deposition, distribution, and crystalline size of Pt nanoparticles supported on CNTs are significantly affected by oxidation treatment of CNTs which will be addressed later in this article.

## 3. Methods of functionalizing of carbon nanotubes

A great deal of research has been conducted over the past decade studying the surface modification of CNTs. These efforts basically fall into two categories: covalent and non-covalent modification. Covalent surface modification of the reinforcing material involves a permanent change to the material surface, such that it is functionalized with reactive groups which can later form a covalent bond with another molecule [57,58]. Non-covalent surface modification does not involve the formal chemical bond formation between a molecule and the surface of CNT. Examples of this type of interaction include van der Waals forces, electrostatic forces, hydrogen bonding, and other attractive forces [59].

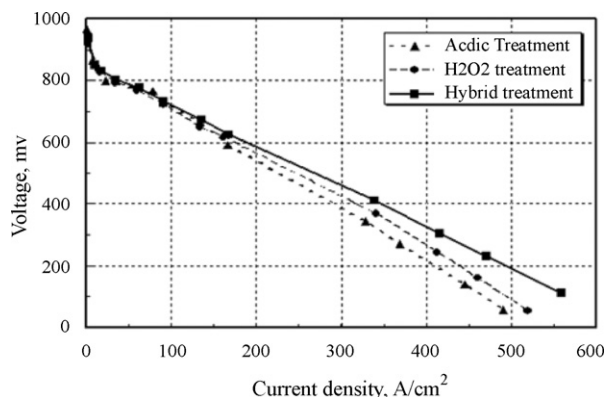
### 3.1. Covalent functionalization

#### 3.1.1. Oxidative treatment of carbon nanotubes surfaces

Among the various methods of modifying the CNT surface, surface oxidation is probably the most widely used [60]. This treatment of CNTs can be performed by using different oxidants such

**Table 2**  
Oxidative treatment of carbon nanotubes surfaces.

Chemicals used and concentration	Particle size (nm)	Comments	Reference
HNO <sub>3</sub> (70%)	3–5	Homogeneous distribution of smaller Pt particles	[25]
Glacial acetic acid (99.8%)	2–4	Producing a high density of oxygen-containing functional groups	[30]
HNO <sub>3</sub> (2.6 M)	1–2	Deposition of smaller Pt particles	[54]
H <sub>2</sub> SO <sub>4</sub> – HNO <sub>3</sub> and H <sub>2</sub> O <sub>2</sub> solution	3	Pt nanoparticles are fine enough and distribute homogeneously	[62]
Concentrated HNO <sub>3</sub> –H <sub>2</sub> SO <sub>4</sub> mixture (1:1, v/v)	2–4	H <sub>2</sub> SO <sub>4</sub> –HNO <sub>3</sub> is more efficient than HNO <sub>3</sub>	[68]



**Fig. 1.** Catalytic performance of the different Pt nanoparticles/CNTs materials in a PEMFC.

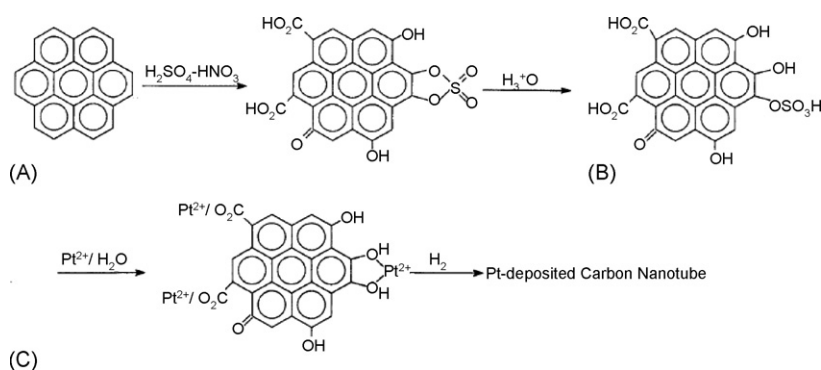
as HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, KMnO<sub>4</sub>, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, polyphosphoric acid [51] and H<sub>2</sub>O<sub>2</sub> [61–64]. Table 2 shows the different oxidative treatment of CNTs. Electrochemical method for surface modification of CNTs [65,66] can also be included in this category. As a result of this treatment, the aromatic conjugate ring system of the CNT surface can be modified, and the CNTs can be functionalized with groups such as hydroxyl (–OH), carboxyl (–COOH) and carbonyl (–C=O) [25,67]. These surface functional groups have strong attraction forces toward metal ions that cause them to cling to the CNTs surface; some functional groups even have ion exchange capabilities, such as the formation of carboxylic acid groups. These groups therefore serve as metal-anchoring sites to facilitate metal nuclei formation and electrocatalyst deposition. The influence of the treatment method on the deposition of Pt nanoparticles was investigated by Xu et al. [62]. They reported that the reflux with the mixture of H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> solutions followed by the immersion in the H<sub>2</sub>O<sub>2</sub> solution are effective pretreatment methods for the depositing of Pt nanoparticles on the CNT's surface. This process is called hybrid process. Pt nanoparticles with a size of 3 nm can be obtained on the CNT's surface using this process. The catalytic properties of CNTs with Pt particles deposited by different methods in a PEMFC are summarized in Fig. 1. The nanoparticles produced by the hybrid method exhibit the best catalytic proper-

ties, which indicates that they are relatively small and distributed homogeneously on CNTs.

Rajalakshmi et al. [25] also investigated the influence of the surface treatment on the deposition of Pt nanoparticles. The author functionalized the CNT surface by sonication and pretreatment with 70% nitric acid. According to their results, a more uniform distribution of Pt nanoparticles, with sizes of about 3–5 nm, was obtained for surface treated CNTs. The particle size may be correlated with the oxidation of the CNTs, indicating that the efficient deposition of Pt nanoparticles is due to a strong interaction between the metal salt precursor and the functional surface group. The Pt treated CNTs were tested in a polymer electrolyte membrane fuel cell to examine the oxygen reduction reaction. The electrode, prepared with a catalyst pretreated with HNO<sub>3</sub>, gave a cell voltage of 680 mV at 500 mA cm<sup>–2</sup>, whereas the other electrodes, with catalysts treated by sonication, gave a 40 mV lower performance.

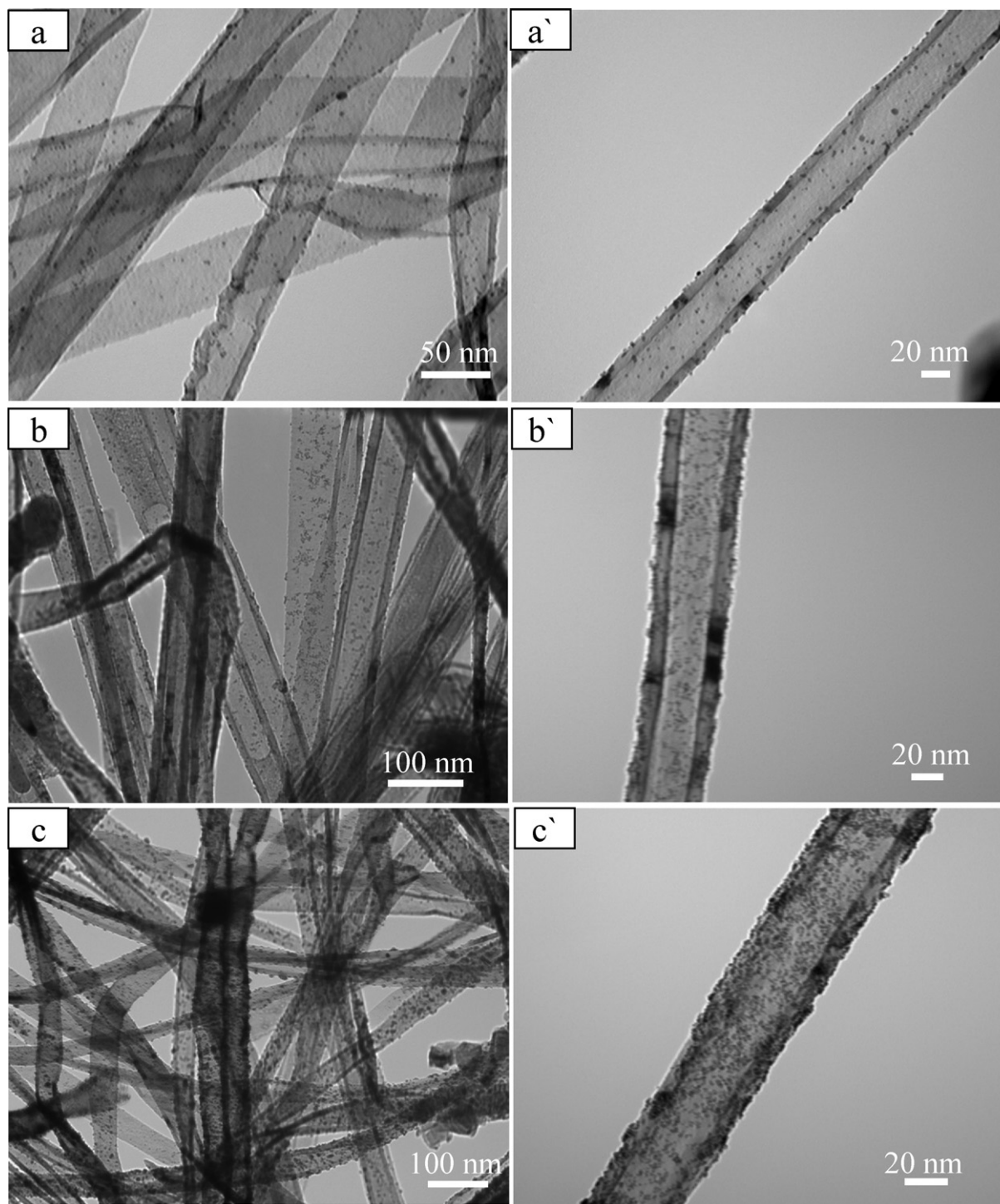
Yu et al. [68] treated CNTs by using mixed acids (HNO<sub>3</sub>–H<sub>2</sub>SO<sub>4</sub>). They proposed a mechanism of Pt deposition on the CNTs as shown in Fig. 2. When CNTs are refluxed with a mixture of HNO<sub>3</sub>–H<sub>2</sub>SO<sub>4</sub>, the surface graphitic layers would react with the oxidants and produce a high density of various surface functional groups, such as carboxyl, carbonyl and phenolic groups. When the Pt ions were introduced into the system, they would interact with and attach to these surface functional groups through an ion exchange or coordination reaction, and serve as nucleation precursors. A well-dispersed deposition of the Pt metal nanoparticles on the surface of CNTs was obtained after the reduction of the surface Pt<sup>2+</sup> ions by hydrogen.

The synthesis of highly dispersed Pt nanoparticles with controlled loading on CNTs remains a tough challenge because of the inertness of the CNT surface [56]. Recently, Saha et al. [30] developed a novel synthetic method for preparing uniformly dispersed high loading Pt nanoparticles on CNTs which were grown directly on carbon paper. The method consists of the treatment of the CNTs with glacial acetic acid which reduces the Pt ion onto the CNTs surface. The CNTs were synthesized in a CVD reactor by decomposing a hydrocarbon gas on catalytic Co–Ni particles deposited on the fibers of the carbon paper [30]. Platinum acetylacetonate was added into glacial acetic acid and was agitated in an ultrasonic bath for 10 min at room temperature. The CNTs, which were grown on carbon paper, were then added to the solution and sonicated for 2 min.



**Fig. 2.** A schematic diagram for dispersion of Pt on CNTs surface.





**Fig. 3.** TEM images of Pt nanoparticles deposited on the CNTs/carbon paper from different concentrations of Pt precursor: (a) 1 mM, (b) 2 mM and (c) 4 mM in glacial acetic acid. (Right panel) Pt nanoparticles deposited on single CNT. The corresponding Pt loadings on the CNTs are 0.11, 0.24 and 0.42 mg<sub>Pt</sub> cm<sup>-2</sup>.

The beaker was placed on a hot plate and heated at a temperature of 110–120 °C for 5 h under constant stirring. Afterward, the CNTs containing the Pt nanoparticles were washed with deionized water and dried at 90 °C overnight in a vacuum oven. The monodispersed Pt particles on the surface of the CNTs have a size between 2 and 4 nm depending on the concentration of the Pt precursor as shown in Fig. 3. X-ray photoelectron spectroscopy analysis indicates that the glacial acetic acid, which acted as a reducing agent, had the capability to produce high density, oxygen-containing functional groups on the surface of CNTs, leading to high density and monodispersed

Pt nanoparticles. They reported that Pt/CNT/carbon paper composite electrodes exhibit higher electrocatalytic activity for methanol oxidation reaction and higher single-cell performance in a H<sub>2</sub>/O<sub>2</sub> fuel cell in comparison with standard Pt/C electrode.

### 3.1.2. Sonochemical treatment

Sonochemical treatment can also be an effective method of functionalizing the CNT surface [67,69]. For example, Xing et al. [67] have shown that Pt nanoparticles deposited on sonochemically treated CNTs result in a much higher catalytic activity than those

supported on carbon black when used in PEMFCs. In a typical experiment, the purified CNTs were added to a flask containing 9.4 mL of HNO<sub>3</sub> (69%), 8.0 mL of H<sub>2</sub>SO<sub>4</sub> (96.2%), and 0.6 mL of deionized H<sub>2</sub>O. The solution was stirred using a vortex mixer for about 1 min and then placed in an ultrasonic bath for 5 min to promote dispersion of the carbon nanotubes. This mixing and dispersion process was repeated twice to ensure the disruption of large carbon nanotube aggregates. The flask was then placed into the ultrasonic bath which was maintained at 60 °C for 2 h. The surface treated CNTs were centrifugally separated from the acids and then thoroughly washed with deionized water. Pt nanoparticles were deposited by reduction of the Pt salt precursor in an ethylene glycol–water solution. The sonochemically treated CNTs were placed in a flask containing a 15.0 mL aliquot of ethylene glycol–water solution (2:1 volume ratio) and a 0.01 M aqueous solution of the metal precursor. The flask was then heated on a hot plate with magnetic stirring. The reduction reaction was performed under reflux conditions (ca. 125 °C) for 2 h. The Pt treated CNTs were then separated from the ethylene glycol solution in a centrifuge and rinsed with deionized water for five times. In this way, a high loading of well-dispersed Pt nanoparticles was obtained on the CNTs.

### 3.1.3. Silane-assisted treatment

Several groups have reported the chemical functionalization of CNTs using silane coupling agents [28,70–72]. For example, Sun et al. [70], used a silane derivative to functionalize the CNT surface with SO<sub>3</sub>H group for the deposition of Pt nanoparticles. The deposition of the Pt particles was carried out by immersing the CNTs in a solution containing PtCl<sub>2</sub>, a silane derivative and water in ethanol [70]. Upon hydrolysis, the silane derivative formed a sulfonic acid-silicate, permitting the exchange of H<sup>+</sup> for the Pt<sub>2</sub><sup>+</sup> ions. After 2 h of immersion, the CNTs with the Pt precursor were removed from the solution and chemically reduced in a flow of H<sub>2</sub> and Ar. Fig. 4 shows the TEM images of Pt nanoparticles deposited on CNTs in the absence and the presence of the silane precursor. It was observed in Fig. 4 that the functionalization with silane derivative facilitates the uniform deposition of Pt on the CNT's surface. Also, much smaller Pt particles (1.2 ± 0.3 nm) were obtained using the silane derivative procedure to adsorb Pt ions onto the nanotubes.

### 3.1.4. Ionic liquids treatment

Recently, ionic liquids have attracted a high degree of technological and scientific interest, as they represent a group of solvents that consist only of ions and remain in the liquid state at low temperatures (<100 °C). They possess high thermal stability and ionic conductivity, and these inherent characteristics make them highly suitable as room temperature electrolytes for electrochemical devices and reactions, and also as solvents and catalysts [73]. Ionic liquids were used to prepare CNT supported Pt catalysts for the first time by Zhao et al. [74]. In their experiment, MWCNTs were prepared by catalytic CVD using nano-sized Co as the catalyst, then pretreated in concentrated HNO<sub>3</sub> at 120 °C for 2 h to produce active functional groups. The monodispersed Pt nanoparticles from H<sub>2</sub>PtCl<sub>6</sub> on pretreated CNTs were prepared from a microwave heated ethylene glycol solution with ionic liquids. The ionic liquids were 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, respectively. The ionic liquids are thought to contribute to the formation of small, homogeneous Pt nanoparticles and to suppress agglomeration of CNTs. It was reported that the electrochemical surface area of the Pt nanoparticles prepared using these methods is 21% higher than the commercial Pt/C catalyst.

### 3.1.5. Electrochemical modification

The surface of the CNTs can also be functionalized by covalent bond formation via electrochemical coupling of aromatic

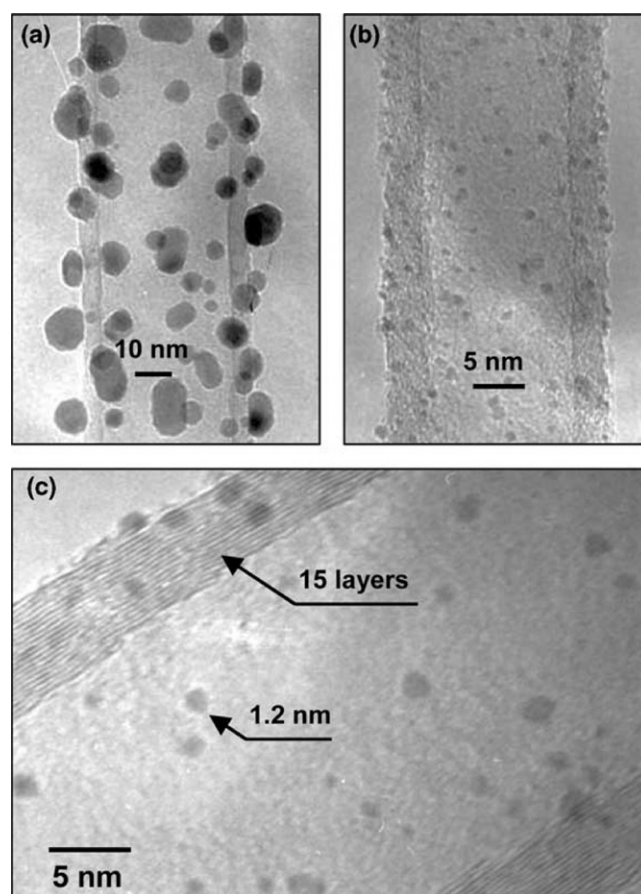


Fig. 4. TEM images of Pt nanoparticles deposited on CNTs: (a) in the absence of the silane precursor; (b) in the presence of the silane precursor; (c) higher magnification TEM of (b).

diazonium salts and phenyl residues [75,76]. For example, Guo and Li [65] developed a method for deposition of Pt nanoparticles through covalent modification of CNTs with 4-aminobenzene. They first purified the as-produced CNTs by magnetically stirring in 12 M HCl for 24 h. After the acid treatment, the CNTs were filtered and washed with distilled water until the filtrate was of neutral pH. CNT paste electrodes were prepared by mixing CNTs and mineral oil. Subsequently, an ordered 4-aminobenzene monolayer was grafted onto the paste electrode by electro-reduction of 4-nitrobenzenediazonium tetrafluoroborate by scanning between 1.1 and –0.3 V (vs. SCE). The electrode was then successively rinsed in 0.1 M H<sub>2</sub>SO<sub>4</sub> and water to remove the physically adsorbed materials. PtCl<sub>6</sub><sup>2-</sup> was adsorbed onto the 4-aminobenzene monolayer-modified electrode surface by electrostatic interaction. Finally, Pt nanoparticles could be obtained through pulsed potentiostatic reduction. The potential was stepped from 700 to –300 mV for 100 ms and returned to 700 mV. They concluded that forming a 4-aminobenzene monolayer on the CNT surface has several advantages: (1) the 4-aminobenzene group is attached to the CNT surface via a C–C covalent bond, which is strong and suitable for the deposition of nanoparticles, (2) covalent bonding of two-dimensional 4-aminobenzene on a CNT surface provides a uniform functional layer, which can effectively prevent the desired nucleation process on the surface of the CNT itself and (3) the specific electrostatic interaction between the substrate and the adsorbed atoms can cause particle size distributions to be considerably narrower than in the case of random nucleation.



### 3.2. Non-covalent functionalization

Non-covalent functionalization of CNTs is particularly attractive because it offers the possibility of attaching chemical handles without affecting the electronic network of the tubes [77,78]. Various species of polymers [79,80], polynuclear aromatic compounds [81], surfactants [82,83] and biomolecules [84] can non-specifically bind with the external surface of CNTs without using covalent coupling. The non-covalent interaction is based on van der Waals forces or  $\pi$ - $\pi$ -stacking interactions [58,85,86]. Yang et al. [85] reported a method for the functionalization of CNTs with benzyl mercaptan as an interlinker for Pt nanoparticles. In their experiment [85], the CNTs were dispersed in deionized water by sonication for 1 h. Then the CNTs were mixed with benzyl mercaptan dissolved in ethanol, and the solution was sonicated for a further 30 min to obtain a well-dispersed CNT mixture. The Pt nanoparticles were deposited either by evaporation in the preparation chamber with an electron-beam evaporator or by the addition of separately produced nanoparticles prepared by the wet chemical reduction of equal volumes of  $\text{H}_2\text{PtCl}_6$  by  $\text{HCOOH}$ . The functionalized CNT surface interacts strongly with Pt nanoparticles through the formation of Pt-S bonds and results in very high Pt nanoparticles loadings, with both good dispersion and a narrow size distribution.

### 3.3. Nitrogen-doped carbon nanotubes as surface modification

The chemical modification of the surface of CNTs by acid treatment reduces considerably the mechanical and electronic performance of the tubes due to the introduction of large numbers of defects. The doping of CNTs with other elements (e.g., nitrogen) could be a particularly interesting way to modify their electrical and mechanical properties [87–89]; for example, the additional electrons contributed by nitrogen atoms provide electron carriers for the conduction band [90]. The addition of atoms other than carbon into the walls of the CNTs was first performed by Stephen et al. [91], who doped them with nitrogen (and boron) using arc discharge procedures. The introduction of N modifies the structure of the CNT leading to: (i) high surface areas [92], (ii) a high density of defects [92], (iii) chemically active impurity sites [93,94], and (iv) narrow tubes (the numbers of walls decrease with N inclusion) [94]. Nitrogen-doped nanotubes are found to be either metallic or narrow energy gap semiconductors [95,96], thus offering the possibility of greater electrical conductivity as compared to pure carbon nanotubes.

The development of catalysts with high activity and high durability is a key issue for PEMFCs and N-doped CNTs and their composites have great potentiality in PEMFC catalyst applications. Shao et al. [105] have reviewed N doping strategies to manipulate the electrocatalytic properties of CNTs using nitrogen. Recently, nitrogen-doped CNTs (N-CNTs) were reported as being used as support materials in fuel cell catalysts, utilizing the enhanced dispersion of Pt nanoparticles [97–103]. N-CNTs contain nitrogenated sites (substitutional and pyridinic nitrogen) that are chemically active. The N sites in N-CNTs are reported to bind strongly to metals, leading to excellent metal dispersion in metal/N-CNT materials [104]. The surface modifications induced in CNTs by N doping can thus enhance the reactivity and the selectivity of carbon supported catalysts in many catalytic applications [105]. Therefore, it should be possible to avoid functionalization processes that use strong acid treatments, as it is relatively easy to deposit metal catalysts onto N-CNTs [97–101]. For example, Maiyalagan et al. [100] used N-CNTs as supports for Pt electrocatalysts in methanol oxidation applications. Nitrogen containing carbon nanotubes was synthesized by impregnating polyvinylpyrrolidone inside an alumina membrane template, and subsequently inducing carbonization of the polymer [100]. Platinum nanoparticles were supported on the N-CNTs

by the impregnation method. They observed that the Pt particles were homogeneously dispersed on the nanotubes with particle sizes of 3 nm. An enhanced catalytic activity and stability toward methanol oxidation was observed with Pt/N-CNTs in comparison with commercial Pt/C catalyst supplied by E-TEK. The enhanced electrocatalytic activity was tentatively attributed the following factors, which still require further investigation: (1) the higher dispersion of Pt nanoparticles on the N-CNTs increases the availability of electrochemically active surface area, (2) the appearance of the specific active sites at the metal-support boundary and (3) strong and specific metal-support interaction.

A recent report by Saha et al. [106] described a 3D composite electrode consisting of Pt nanoparticles supported on N-CNTs grown directly on the carbon paper. In their experiments, the N-CNTs were grown from the metal catalyst precursor,  $[\text{Fe}(\text{acetylacetonate})_3]$ , dissolved in a mixture of acetonitrile and tetrahydrofuran with atomic C/N ratio of  $\sim 6$ , by using aerosol-assisted chemical vapor deposition (AA-CVD) method [106]. Pt nanoparticles were deposited on the CNTs by the impregnation method. The superior performance with this catalyst as a cathode in PEMFCs may be explained by the possibility of better dispersion of Pt nanoparticles, i.e., smaller size (around 2–3 nm) and higher electrochemical Pt surface area.

## 4. Conclusions

The recent advances in the development of reliable methods for the chemical functionalization of the CNTs are critically reviewed. The doping of CNTs with other elements (e.g., nitrogen) could be a particularly interesting way to modify their electronic and mechanical properties. However, it is important to improve the quality of the CNTs, with particular emphasis on the uniformity of the catalyst metal for further development of this research area. Furthermore, comparative studies on individual nanotubes before and after functionalization are necessary, so that both the dependence of reactivity on electronic structure and the effect of chemical modification on the electrical and mechanical properties can be determined.

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