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# Aqueous Solution Surface Chemistry of Carbon Nanotubes

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## 1. Introduction

Since the rediscovery of carbon nanotubes (CNTs) by Iijima in 1991, a plethora of applications have been developed in the fields of biomolecular science, catalysis, environmental chemistry and medicine. Relevant to the development of these new technologies, it is important to effectively characterize and tune the chemical and electronic structures of these materials for desired properties. Within the last 15 years, an array of surface characterization methods have been developed to assay the surface structures of single- (SWNTs) and multi-walled (MWNTs) carbon nanotubes, in particular as organic moieties and catalytically active metal nanoparticles are tethered to them. Distinctive physical, chemical, electrical and high thermal properties of CNTs make these materials suitable for widespread applications, such as fuel cells, semiconducting materials in electronics, atomic force microscopy probes, microelectrodes, adsorbents to remove pollutants from waste water, electrochemical sensing and drug carriers. Aqueous surface chemistry plays a vital role in determining the fate and transport of CNTs. A large fraction of the atoms in CNTs reside at or near the surface (Sayes et al., 2006; Bottini et al., 2006). Pristine carbon nanotubes are barely soluble in liquids. To introduce nanotubes in more easily dispersible forms, they require functionalization. These processes entail attaching various organic moieties to the sidewalls, which can be used to tether catalytically reactive nanoparticles. Biomolecules require electron mediators to promote electron transfer needed for effective biosensing (Sampath et al., 1998). Electrochemical metal ion sensors require certain functional groups which show potential affinity towards particular metal ions (Mojica et al., 2007). Surface electrostatic interactions in solution also influence the sorption properties of these materials to entrain environmental contaminants on the CNT sidewalls (Tavallai et al., 2012).

Historically, the synthesis, fabrication and characterization of carbon nanomaterials have been carried out in vacuum environments. As these materials proliferate in use, knowledge pertaining to their environmental impact (i.e., involving fate and transport in aqueous systems) becomes increasingly important (Cho et al., 2008). Furthermore, preparation and synthesis of these materials in non-vacuum conditions makes these processes more amenable for industrial scale up. Recent attention has focused on modifying SWNTs and MWNTs in solution media.

A review of recent advancements to modify CNT surfaces in aqueous media is described in this chapter. Changes in the material properties are often observed concomitant to alterations in surface structure, such as colloidal dispersion and electrocatalytic activity. In the introductory section, the strengths and weaknesses of various traditional CNT surface chemistry probes are presented. Following this, nanotubes that have been chemically modified via chemical oxidation and organic derivatization are discussed. The technique of electrochemical functionalization using carbon nanotubes as the working electrode surface is presented. The next section describes the applications of derivatized carbon nanotubes as it applies to catalysis (involving noble metal nanoparticles), sensing, and selective cancer cell destruction, in which the nanotube sidewall structure plays a key role. The use of transmission electron microscopy (TEM) in conjunction with point-of-zero charge (PZC) measurements for exploring structure-property relationships is shown. The final sections present the effects of CNT functionalization on properties pertaining to colloidal stability and isoelectric points relevant for applications in environmental chemistry, catalyst synthesis, and designing materials for the remediation of contaminated ground water.

## 2. Overview of analytical techniques: strengths and weaknesses

Traditional analysis methods of carbon nanotubes include Boehm titrations, settling speed measurements, atomic force microscopy (AFM), and quartz crystal microbalance (QCM) measurements, X-ray photoelectron spectroscopy (XPS), attenuated total reflection infrared spectroscopy (ATR-IR), transmission electron microscopy (TEM), Raman spectroscopy, thermogravimetric analysis (TGA) and temperature programmed desorption (TPD). Each of these techniques has its own advantages in the chemical/structural information that they can provide as well as drawbacks.

Wet chemical characterization methods provide a rapid means of characterizing the CNT surface structure. Settling speed measurements is a crude, but rapid technique for measuring the extent of CNT sidewall oxidation containing protic groups with which the solvent can undergo hydrogen bonding (Xing et al., 2005). In this simple experimental setup, the rate at which CNTs fall in a buret (by gravity) is measured and correlated with the extent of surface functionalization. However, no qualitative information regarding the identity of the

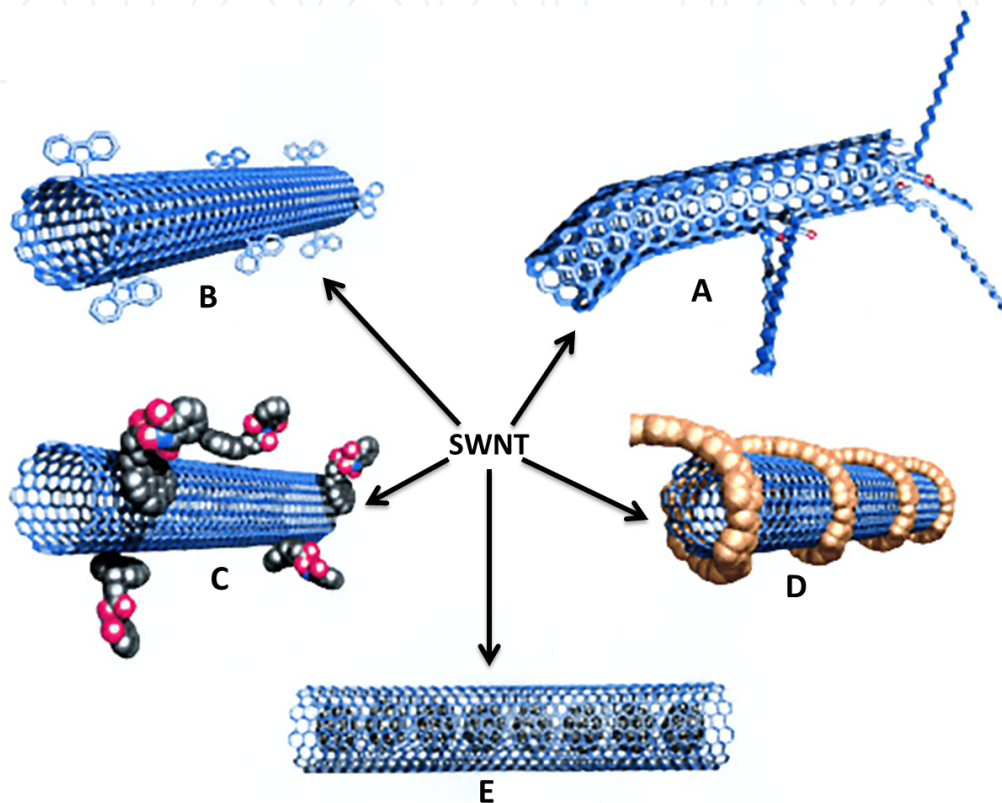
surface groups is available using this approach. Boehm titrations can be used to quantify the number of proton-containing functional groups (carboxylic acids, hydroxyl groups, lactones, etc.) on the CNT sidewall surface (Boehm et al., 1964). The titrant typically involves various bases ideal for each protic group, e.g.,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaOH}$ ,  $\text{NaHCO}_3$ , etc.), the acidity constants ( $\text{pK}_a$ ) of which differ by orders of magnitude, rendering the analysis selective to the functional group of interest. But, this technique is ineffective for characterizing CNTs functionalized with aprotic moieties.

ATR-IR, AFM, QCM and Raman spectroscopy can be performed in ambient environments (i.e., not requiring vacuum conditions for analysis). ATR-IR is useful for qualitative identification of CNT surface moieties; however, quantitation is not available and some modes are too small to be observed relative to background (Brundle et al., 1992). AFM offers the capability of probing changes in CNT surface morphology, sidewall surface coverage and CNT lengths. However, the technique is not amenable to subnanometric scales as thermal noise becomes a major interference at this lengthscale (Magonov et al., 1996). QCM provides a means of monitoring mass changes during the assembly process as CNTs undergo functionalization, but accurate mass measurements are readily hampered by changes in temperature or cavitation (i.e., during ultrasonication) (Brown and Gallagher, 2007). The “diamond” D and G band shifts observed in Raman spectroscopy at  $\sim 1300$  and  $\sim 1600$   $\text{cm}^{-1}$ , respectively, is a useful tool for assessing the degree of sidewall surface damage encountered in some functionalization methods (i.e., ultrasonication) as well as CNT purity and composition. D and G bands emanate from disordered and ordered  $\text{sp}^2$ -hybridized carbon from the graphene sheets, respectively, and are commonly used markers for elucidating covalent bond formation (Dresselhaus et al., 2001). However, spectral interpretation, involving relative D and G band intensity determinations can be complex (Brundle et al., 1992).

Vacuum-based characterization tools (the most cost-prohibitive class of these analytical methods), include electron spectroscopy, microscopy and mass analysis. XPS is an excellent tool for monitoring analyte surface oxidation states, and useful for elemental quantification and qualitative identification of surface functional groups. However, large amounts of sample ( $\sim 5$  mg) are needed for analysis and peakfitted interpretation can be complex. TEM offers powerful imaging capabilities of the CNT sidewalls to allow for observation of surface roughening that can result from either functionalization or the creation of surface defects. Material length, diameter and dispersion state can also be readily determined by TEM. In addition, spatial elemental analysis is available via energy dispersive X-ray spectroscopy (EDX), as it is often an available technique built into many TEM instruments. However, CNTs are susceptible to beam damage from TEM electrons. Another caveat is that variation in technique involving dispersing samples onto TEM grids and subsequent drying can skew observed results. TGA and TPD can be used to quantify the concentration of moieties tethered to the CNT sidewalls; but, limiting case assumptions, e.g., all of the mass lost (TGA) and bonding modes remain unchanged (TPD), need to be made for assessments, which may not be accurate if the CNT surface chemistry is complex. In addition, large amounts of sample ( $> 10$  mg) are required for TPD and TGA analysis.

### 3. Functionalizing carbon nanotubes

Both single- and multiwalled carbon nanotubes have a tendency to aggregate into bundles very efficiently via van der Waals interactions in solution. These bundles can be exfoliated by using ultrasonication in combination with suitable surfactants. Typically, the outer walls of pristine carbon nanotubes are chemically inactive. Two major functionalization routes are used to activate CNT sidewalls: (i) endohedral and (ii) exohedral functionalization.

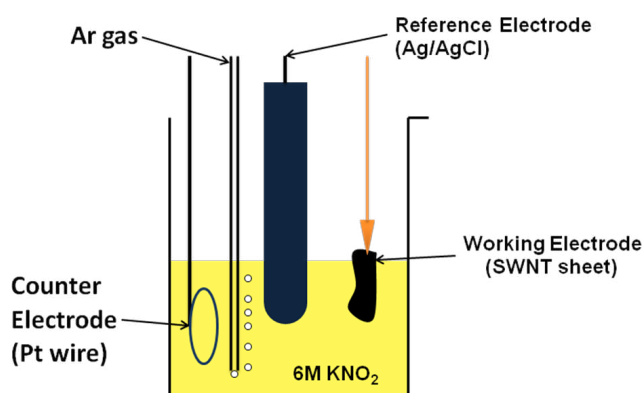


**Figure 1.** Functionalization pathways of SWNTs: A) defect-group functionalization, B) covalent sidewall functionalization, C) noncovalent exohedral functionalization with surfactants, D) noncovalent exohedral functionalization with polymers, and E) endohedral functionalization with, for example, C<sub>60</sub>. (Reprinted with permission from [Hirsch., 2002]. Copyright, WILEY-VCH Verlag).

Endohedral functionalization involves insertion of various nanoparticles into the inner walls (Fig. 1E) (Hirsch, 2002). This task can be achieved either by (i) spontaneous penetration with colloidal nanoparticle suspensions filling the inner walls by evaporation of the carrier solvent; or (ii) by wet chemistry, as compounds are introduced into the inner walls of the nanotubes where they are transformed into nanoparticles while maintaining predetermined thermal/chemical conditions. Various pathways for exohedral functionalization is summarized in Figs. 1A-D (Hirsch., 2002). These avenues include defect group functionalization (Fig. 1A), covalent sidewall functionalization (Fig. 1B), and noncovalent exohedral functionalization using surfactants (Fig. 1C) and polymers (Fig. 1D). Covalent functionalization, which typically damages the carbon framework and is an irreversible process, is achieved by attaching functional groups to the nanotube ends or defects (Hirsch, 2002; Banerjee et al.,

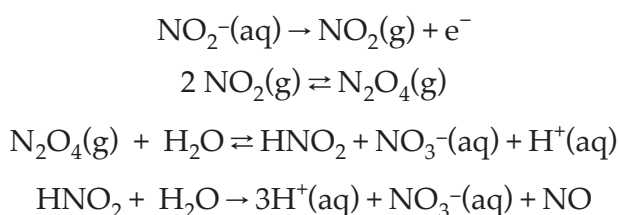
2005). Noncovalent exohedral functionalization, on the other hand, is achieved by wrapping nanotubes using polymers or surfactants (Hirsch, 2002). They leave the CNT carbon framework intact and, it is usually a reversible process.

Hu et al. (2005) exohedrally functionalized SWNTs with DNA (noncovalently) by wrapping the outer surface of dispersed SWNTs with single-stranded DNA (ss-DNA). The functionalized ss-DNA-SWNTs have a strong tendency to attach onto glass substrates, forming a uniform film. These behaviors make it possible for electrochemical analysis and sensing. The material is amenable for use as a working electrode, exhibiting good electrochemical voltammetric properties. The electrode has well-defined quasi-reversible voltammetric responses, showing rapid electron transfer properties for  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$  redox pair systems, important for biosensing as this redox couple has demonstrated the ability to traverse bilayer lipid membranes (Lu et al., 2008).



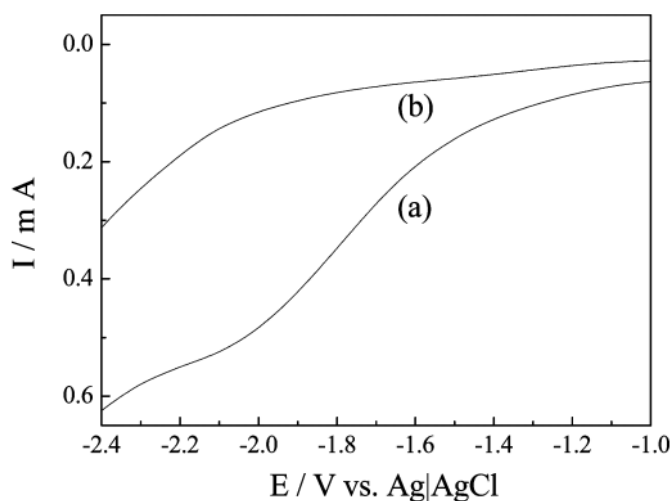
**Figure 2.** Arrangement of SWNT sheet in an electrochemical cell. The free-standing sheet of SWNTs underwent electrochemical oxidation upon reaction in potassium nitrite ( $\text{KNO}_2$ ) solution (McPhail et al., 2009).

CNTs can also be functionalized electrochemically. Fig. 2 shows the general arrangement of an electrochemical cell where a SWNT sheet is used as a working electrode. This particular set up has been used to functionalize pristine HiPco SWNTs with nitroso (NO) functional groups in which free-standing SWNT sheets were produced via ultrasonication in 1% Triton X-100 solution surfactant. Prior to use as a working electrode for the electrochemical NO group attachment reaction, the Triton X-100 surfactant is removed via thermal decomposition in a tube furnace while flowing inert Ar gas is heated to  $800^\circ\text{C}$ . The electrochemical reaction forms a  $\text{N}_2\text{O}_4$  dimer, which then dissociates into NO groups that attach to the SWNT sidewalls (Piela and Wrona, 2002; McPhail et al., 2009). The mechanistic scheme for the reaction is as follows:



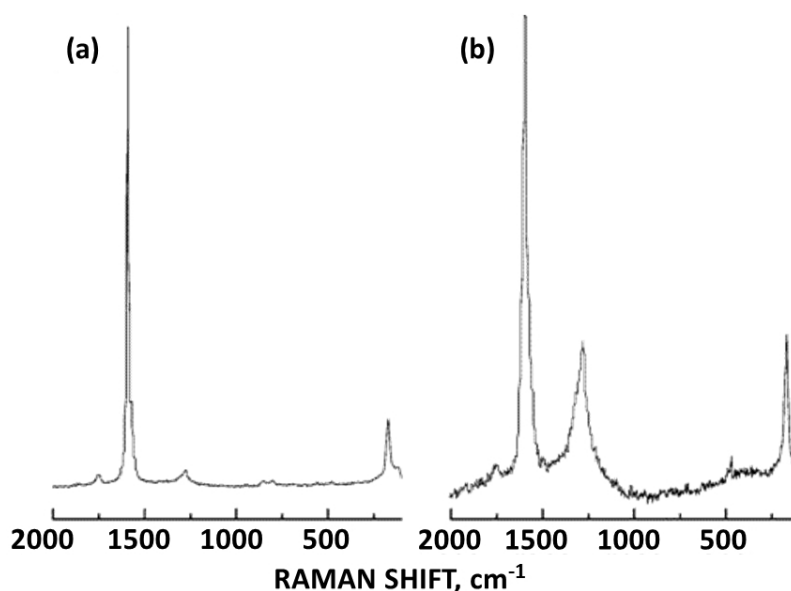
Nitric oxide (NO) is formed from nitrite ( $\text{NO}_2^-$ ), in which dimerization occurs and followed by disproportionation. The observed nitrogen dioxide ( $\text{NO}_2$ ) gas is liberated from the free standing SWNT working electrode during electrolysis. It should be noted that the fabrication technique for the free-standing sheet is not effective for homogeneously electrografting large quantities of SWNTs (with a  $\sim 2 \mu\text{m}$  thickness), hampering industrial scale-up.

This task can be accomplished by using room-temperature ionic liquid (RTIL) to fabricate a supported three-dimensional network of SWNTs as the working electrode (Zhang et al., 2005). In this design, N-succinimidyl acrylate (NSA) serves as a monomer dissolved in the supporting RTIL, 1-butyl-3-methylimidazolium hexafluorophosphate ( $\text{BMIMPF}_6$ ), electrografted onto the SWNTs. The resulting linear sweep voltammogram (LSV) for the oxidation of glucose is shown in Fig. 3. Voltage is applied to the three dimensional network SWNT electrode from 0 to  $-2.4 \text{ V}$  before and after the electrografting. The passivation peak due to the chemisorption (grafting) of an insulative polymer film on the cathode surface is observed at about  $-2.0 \text{ V}$  in the first scan. After electrografting, the passivation peak disappears, denoting electrografting saturation.



**Figure 3.** Linear sweep voltammograms of electrografting N-succinimidyl acrylate (NSA) at the three-dimensional network SWNT electrode in  $\text{BMIMPF}_6$  during the first scan (a) and the second scan after conditioning at the passivation potential for a period of 40 min. (b). Scan rate: 20 mV/s. (Reprinted with permission from [Zhang et al., 2005]. Copyright, American Chemical Society).

Raman bands (Fig. 4) at  $1591 \text{ cm}^{-1}$  (tangential modes) and at  $1278 \text{ cm}^{-1}$  (disorder mode) are observed in both pristine SWNTs (Fig. 4a) and the SWNTs tethered to poly-NSA (Fig. 4b), showing direct evidence of covalent electrografting. Raman spectra were collected at several different spots for each of these surfaces; no distinctive differences in spectral features were observed, confirming homogeneous functionalization. Control experiments without NSA addition showed no affect on the structure of pristine SWNTs, as observed by Raman spectroscopy.



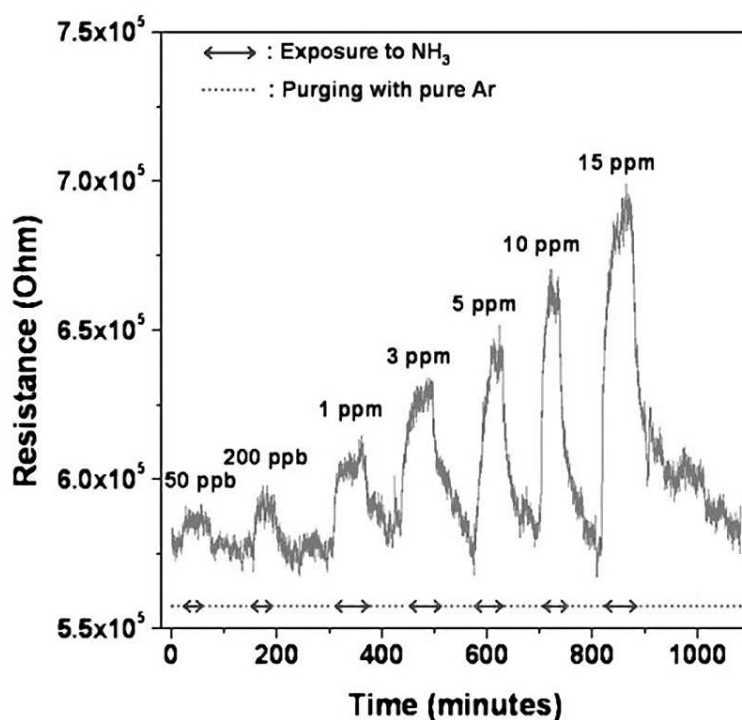
**Figure 4.** Normalized Raman spectra (the intensity of the strongest tangential modes) of pristine SWNTs (a) and SWNTs-poly-NSA (b). (Reprinted with permission from [Zhang et al., 2005]. Copyright, American Chemical Society).

Ultrasonication has become a standard technique for accelerating surface functionalization, employing the cavitation process from sound waves to facilitate acid oxidation. Defect sites are created during this process to facilitate sidewall functionalization (Fig. 1A). It should be noted that acid oxidized functionalization is more amenable to MWNTs than to SWNTs as robust conditions render the latter more susceptible to material decomposition. A sonochemical treatment method under acidic condition has been carried out to functionalize carbon nanotubes with  $-C=O$ ,  $-C-O-C-$ ,  $-COO-$ ,  $-C-OH$  groups, which serve as effective tethering points for attaching catalytically active Pt nanoparticles for improved direct methanol fuel cell performance (Xing et al., 2005; Hull et al., 2006; Chusuei and Wayu, 2011). Raman spectra of the D and G “diamond” bands indicate minimal surface damage of the underlying graphene sheet during the sonication process (applied up to 8 hours). Pt nanoparticles were deposited onto these functionalized surfaces via O-containing moieties resulting in the improved electrocatalytic activity. Hull et al. (2006) demonstrated from ATR-IR data that, specifically, the carboxylate oxygen atoms were responsible for effective tethering of the catalytically active nanoparticles. It should be noted, however, that while sonication improves and facilitates functionalization of the MWNT sidewalls, it is possible to overtreat the MWNT sidewalls using this process. In the study, catalytic activity improved when sonication was performed over a 1-hour period, maximizing after a 2-hour sonication treatment. At a 4-hour sonication treatment, however, performance (for the direct methanol fuel cell reaction) diminished. ATR-IR peaks indicated that carboxylate surface structure was damaged after prolonged treatment. These same surfaces also show signs of roughening in the TEM images (Xing et al., 2005), attributable to defect formation and an increased degree of functionalization. Well-defined MWNT sidewall surface structures of the MWNTs are paramount for effective catalytic performance (*vide infra*).



#### 4. Applications of functionalized carbon nanotubes

Functionalized CNTs have distinctive physicochemical properties, such as ordered structure with high aspect ratio, high mechanical strength, ultra-light weight, high electrical conductivity, high thermal conductivity, metallic or semi-metallic behavior and high surface area, which make them amenable for diverse applications (Ajayan, 1999). For example, Zhang et al. (2006) showed that electrochemically functionalized SWNT with polyaniline (PANI) can be used to fabricate chemical gas sensors. In monitoring ammonia gas with the PANI-SWNT composite, superior sensitivity and detection limits with good reproducibility were observed. Fig. 5 shows gas sensing response to various concentrations of  $\text{NH}_3$ , ranging from 50 ppm to 15 ppm, relative to initial baseline. It is clear from the graph that, after exposure to  $\text{NH}_3$ , the resistance of the PANI-SWNT sensor dramatically increased.

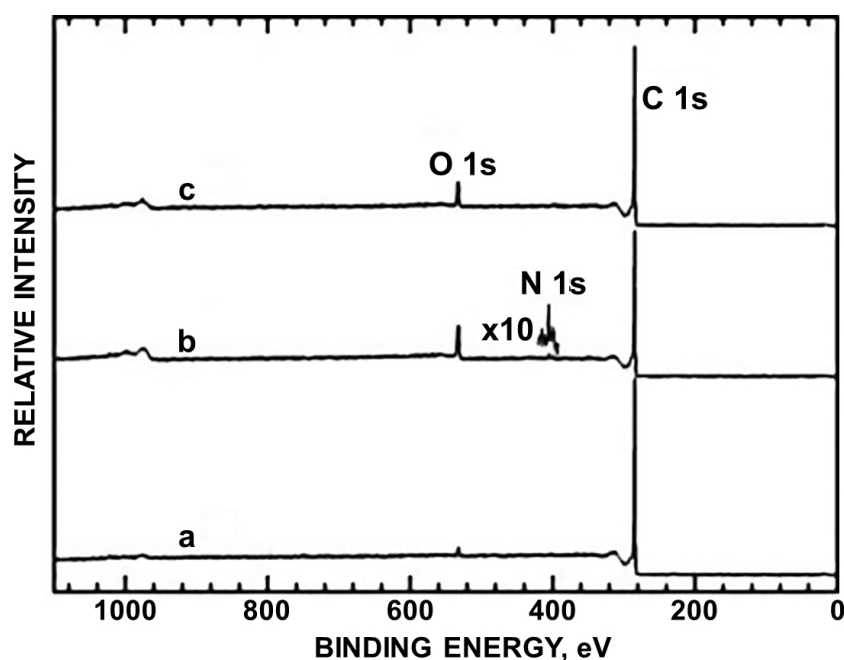


**Figure 5.**  $\text{NH}_3$  gas sensing results using polyaniline coated SWNTs. The arrows ( $\leftrightarrow$ ) show exposure times to  $\text{NH}_3$ . PANI was coated on SWNTs using a two electrode configuration at 0.8 V for 5 minutes. (Reprinted with permission from [Zhang et al., 2006]. Copyright, WILEY-VCH Verlag).

When comparing the performance of the functionalized MWNT surface for the direct methanol fuel cell reaction in the previous section (*vide supra*), catalysts with the functionalized MWNT support exhibited a 48% increase in electrocatalytic activity compared to Pt nanoparticles tethered to the more commercially used Vulcan XC-72 fibrous carbon black support (Xing, 2004). The increased activity was due to the finer dispersion of catalytically active Pt nanoparticles (~3.5 nm in diameter) tethered to the CNT sidewalls (as compared to carbon black) made available by uniform attachment of the Pt nanoparticle precursors to ester-like oxygen atoms (Hull et al., 2006). Hence, sonication in aqueous acid environment has been shown to be effective for creating functional tethering points for practical catalyst syn-

thesis. Overjero et al. (2006), similarly applied acidic (liquid phase) oxidation to MWNTs using nitric acid ( $\text{HNO}_3$ ) to tether catalytically active Pt, Cu, and Ru nanoparticles. The sturdy support provided by functionalized MWNTs (with oxygen-containing moieties) was responsible for the observed, enhanced catalytic activity.

In fact, aqueous solution acid treatments have been found to be more effective than oxygen plasma treatments to functionalize CNTs with oxygen containing moieties. Xia et al. (2007) showed that nitric acid treatment yielded a 60% higher surface oxygen concentration compared to plasma treatment. Fig. 6 shows XPS survey spectra of the intensity of nitric acid-treated and plasma-treated MWNTs were recorded to identify the chemical composition. There was no evidence of metallic impurities (i.e., FeCo used to synthesize the nanotubes) present. In addition, after the nitric acid treatment an N 1s peak was found. It can be clearly seen that the intensity of the O 1s peak increased, whereas the C 1s peak decreased due to the oxidizing treatment with nitric acid and plasma treatments. The atomic percent oxygen-to-carbon ratios (taking into account differences in instrumental atomic sensitivity factors in the XPS) for the as-received, nitric acid-treated and oxygen plasma-treated MWNTs were found to be 0.118, 0.214 and 0.052, respectively. The acid-treated MWNTs clearly yielded the higher density of surface oxygen.



**Figure 6.** XP survey spectra of the MWNTs: (a) as received; (b) treated with nitric acid; (c) treated with oxygen plasma. The N 1s region at around 400 eV in trace (b) is magnified 10 times. (Reprinted with permission from [Xia et al., 2007]. Copyright, Elsevier B.V.).

Functionalized SWNTs have also received attention for their potential applications in medicine. Carboxylic acid functionalization on SWNTs improves electrocatalytic reactivity towards the oxidation of an array of biomolecules, such as dopamine, ephinephrine and ascorbic acid (Luo et al., 2001). SWNTs functionalized with hydroxyl ( $-\text{OH}$ ) and carboxylic acid ( $-\text{COOH}$ ) exhibit antimicrobial properties, capable of inactivating bacterial pathogens. In a study by Arias et al. (2009), modified SWNTs inactivated both Gram-positive and

Gram-negative bacterial cells in deionized water and 0.9% NaCl solution regardless of cell shape. Antimicrobial activity increased with both increasing concentration of the CNTs (in colloidal suspension) and treatment time (Arias et al., 2009). In either deionized water or 0.9% NaCl aqueous solution, 200-250  $\mu\text{g/mL}$  of either OH-SWNTs or COOH-SWNTs have the ability to inactivate  $\sim 10^7$  cfu/mL *Salmonella* cells in 15 minutes. The oxygen-containing moieties attached to the cell surface facilitated inactivation. Functionalized SWNTs have also shown promise as near-infrared agents for selective cancer cell destruction (Kam et al., 2005). Engineering SWNTs for this purpose is achieved by tethering pristine SWNTs with folate groups using sonication and centrifugation, in which the HiPco SWNTs are incorporated into a solution of phospholipids with polyethylene glycol moieties and folic acid terminal groups. These folate-SWNTs selectively attach to the inside structures of cancer cells that contain folate receptor tumor markers. Cell death is then triggered using near infrared irradiation that thermally decompose cancer cells without harming normal cells, which are folate receptor-free. Kam et al. (2005) demonstrate that while biological systems are transparent to 700-to-1100-nm near-infrared light, there is a strong absorbance of SWNTs within this wavelength region resulting in selective thermal heating of cancer cells.

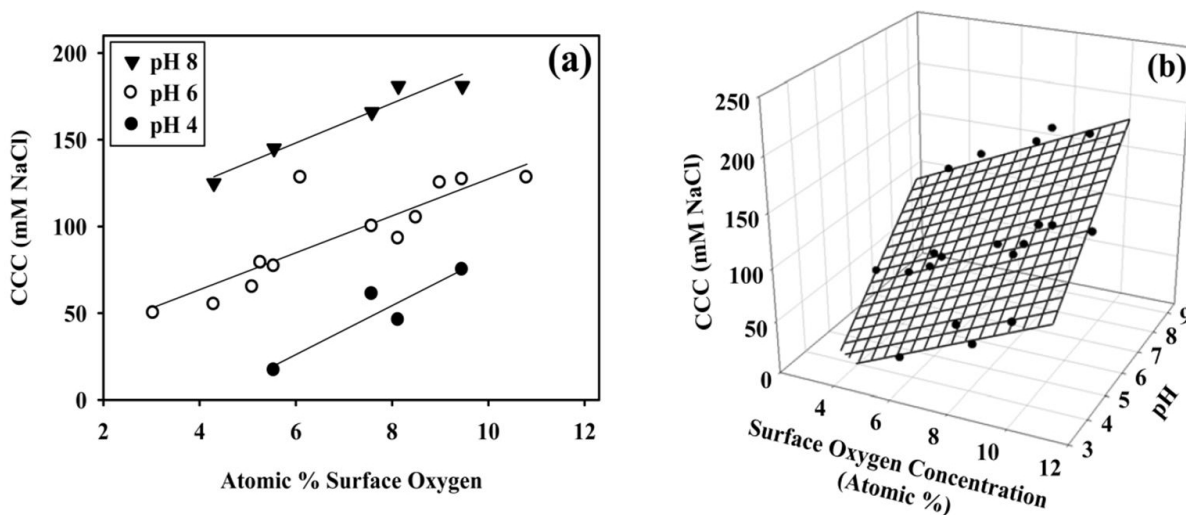
In applications pertaining to ground water remediation, -OH, -COOH, and carbonyl (-C=O) functionalized MWNTs have been shown to have high sorption capacities. In fact, carboxyl-carbon sites are 20 times more energetic for zinc sorption than unoxidized carbon sites (Cho et al., 2010). Along with Zn(II) and Cd(II) chemically modified MWNTs have also been used as sorbent material (Tavallai et al., 2012) for separation and preconcentration of trace amounts of Co(II) and Cu(II) in the environmental and biological samples. In this study, MWNTs were modified with thiosemicarbazide and found to be an easily prepared solid and cost effective sorbent. These MWNT materials can be used several times without marked loss in sorption capacity.

In another study by Shamspur and Mostafavi (2009), MWNTs were modified using the reagent, N,N-bis(2-hydroxybenzylidene)-2,2(aminophenylthio)ethane for applications in ground water remediation. The resulting composite (incorporated into column material) was found to be a useful sorbent for simultaneous separation and preconcentration trace amounts of Au(III) and Mn(II). The reagent remained in the column and its use could be cycled several times. Analytical ions were quantitatively recovered with detection limits and enrichment factors comparable or better than an array of commercially available matrices, such as Mberlite XAD-2000, silica gel/nanometer-sized  $\text{TiO}_2$ , Cu(II)-9-phenyl-3-fluorone, Kaolinite/5-Br-PADAP, and *Penicillium italicum*/Sepabeads SP 70 systems.

Furthermore, MWNTs can be modified using electrolysis. Unger et al. (2002) discovered that halogens, such as chlorine or bromine, can electrochemically be bonded to the nanotube lattice. Halogen gases are evolved from the anode and are attached to free-standing MWNT bucky sheets. These chlorine and bromine carbon nanotubes offer a pathway to a wide spectrum of nanotube derivatives. Oxygen-bearing functional groups, such as -OH and -COOH groups, are formed simultaneously, promoting solvation of the nanotubes in water or alcohol without any surfactant. Impurities and low grade modified nanotubes remain insoluble and can be filtered out. Since the functionalized nanotube structure is maintained, soluble material can readily be applied in aqueous solution to solid surfaces for applications, such as electric circuit patterning.

## 5. Effect of functionalization on colloidal stability

Without the use of sonication, pristine CNTs are generally hydrophobic in nature and cannot be dispersed in most solvents. The disparity of functionalized CNTs in colloidal particle depends on the nature of the functional groups and colloidal particles. Smith et al. (2009a; 2009b) found that the difference in the colloidal stability of the O-MWNTs was due to the effects of surface oxygen. Small changes of surface oxygen concentration, by as little as 1-to-5 percent results in drastic changes in the colloidal stability of O-MWNTs. The amount of oxygen incorporated onto the surface of nanotubes depends on the oxidizing agent used ( $\text{HNO}_3$ ,  $\text{KMnO}_4$ ,  $\text{H}_2\text{SO}_4/\text{HNO}_3$ ,  $\text{O}_3$ ,  $\text{H}_2\text{O}_2$ , etc.). Fig. 7a shows the relation between critical coagulation concentrations (CCC) for each O-MWNT with the surface oxygen concentration. The effect of pH with the above two parameters are also shown in Fig. 7b. These plots confirm that, for the vast majority of the O-MWNTs studied, CCC has a linear dependence on surface oxygen concentration over the pH range of 4-to-8).



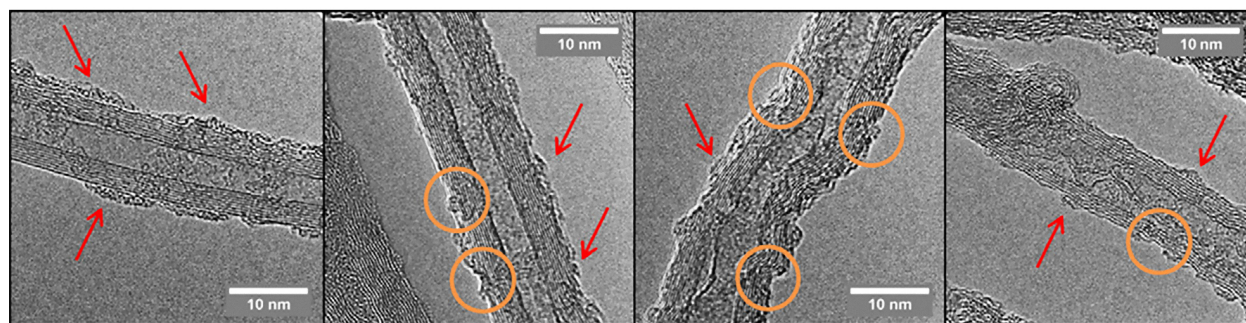
**Figure 7.** (a) Influence of surface oxygen concentration on the critical coagulation of O-MWNTs at pH = 4, 6 and 8; (b) three dimensional plot showing the functional interdependence of surface oxygen concentration, pH, and CCC of O-MWNTs. (Reprinted with permission from [Smith et al., 2009b]. Copyright, American Chemical Society).

Fig. 7 shows that for a given concentration of surface oxygen, the colloidal stability of O-MWNTs increases with increasing pH (Wepasnick et al., 2011). In the study, chemical derivatization was used in conjunction with XPS to quantify the distribution of oxygen containing functional groups (e.g.,  $-\text{OH}$ ,  $-\text{COOH}$ ,  $-\text{C}=\text{O}$ ) on the differently functionalized O-MWNTs. At high pH, the carboxylic acid group was the most predominant surface oxide present. This same result was observed by other researchers (Blanchard et al., 2007). Of the various MWNTs studied, the CCC correlated best with carboxylic acid group surface concentration. A significantly poorer correlation was found with both hydroxyl and carbonyl

group surface concentration. In terms of MWNT electrophoretic mobility, Smith et al. (2009a) observed that surface oxygen concentration had no measurable effect on electrophoretic mobility. No correlation was observed between colloidal stability of O-MWNTs and its electrophoretic mobility. However, in terms of environmental impact, it is noteworthy that CCC values fell within the range of salinity conditions in estuaries and other fresh water bodies, indicating that O-MWNTs are likely stable and prone to aggregate and/or settle prior to being transported to oceanic environments.

Colloidal stability of oxidized MWNTs also changes with pH and electrolytic composition. Smith et al. (2009a) found that the colloidal stability of O-MWNTs increases with increasing pH, which is consistent with previous UV-vis studies of acid treated CNTs (Shieh et al., 2007). CCC values of O-MWNTs vary with counter ion concentration and valence in a manner consistent with Derjaguin-Landau-Verwey-Overbeek (DLVO) theory (Derjaguin et al., 1941; Verwey and Overbeek, 1948). MWNT surface oxygen density also affected MWNT adsorption properties. For instance, when adsorption of naphthalene onto O-MWNTs were carried out with variable surface oxygen concentrations (Ball et al., 2008), the MWNTs with the most concentrated surface oxygen content had the least adsorption capacity in the series.

The selection of acid oxidant can have markedly different effects on MWNT sidewall oxidation, as shown by Wepasnick et al. (2011). In this study, MWNTs were treated with six commonly used wet chemical oxidants ( $\text{HNO}_3$ ,  $\text{KMnO}_4$ ,  $\text{H}_2\text{SO}_4/\text{HNO}_3$ ,  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ,  $\text{H}_2\text{O}_2$  and  $\text{O}_3$ ). Using XPS and EDX to characterize and quantify the extent of surface oxidation, density of  $-\text{OH}$ ,  $-\text{COOH}$ ,  $-\text{C}=\text{O}$  surface groups, and their distribution, these parameters were found to be independent of reaction conditions, but sensitive to identify the oxidant. As MWNTs were treated with  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ,  $\text{H}_2\text{O}_2$  and  $\text{O}_3$ , higher concentrations of carbonyl and hydroxyl functional groups were found to form on the surface. In contrast, as more aggressive oxidant agents ( $\text{HNO}_3$ ,  $\text{KMnO}_4$ ) were used, higher fractional concentrations of carboxylic acid groups formed. Fig. 8 shows representative transmission electron micrographs of pristine MWNTs exposed to various oxidants, comparing the effects of equal concentrations of  $\text{H}_2\text{O}_2$  and  $\text{H}_2\text{SO}_4/\text{HNO}_3$ .



**Figure 8.** Representative TEM micrographs (left to right): Pristine MWNTs (0.9%),  $\text{H}_2\text{O}_2$ -treated MWNTs (4.5% O), and  $\text{H}_2\text{SO}_4/\text{HNO}_3$ -treated MWNTs (5.3% O). Amorphous carbon is indicated with arrows, and sidewall defects are highlighted by circles. (Reprinted with permission from [Wepasnick et al., 2011]. Copyright, Elsevier Ltd.).

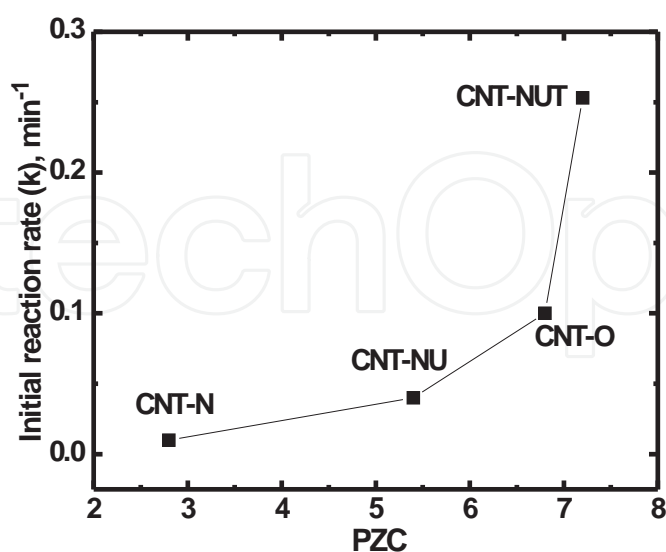
Noteworthy are the effects of the oxidants on amorphous carbon and sidewall defects. The long and straight outermost wall of MWNT denotes uniform and largely defect-free sidewall structure. The overall level of amorphous carbon was reduced during  $\text{H}_2\text{O}_2$  treatment, and few defects were generated on the sidewalls. On the other hand, treatment with  $\text{H}_2\text{SO}_4/\text{HNO}_3$  produced a distortion in the linearity of the MWNT structure. Following  $\text{KMNO}_4$  treatment, MWNTs exhibited a larger fraction of tethered COOH groups compared to other oxidized MWNTs with a relatively low amount of sidewall damage.

The identity of the CNT surface functional group has a large impact on the surface charge of the sidewalls. While using MWNTs as catalyst supports, the point-of-zero charge [PZC, defined as the pH at which the solid-aqueous solution interface is electrostatically neutral, according to the electrical double layer model described by Gouy-Chapman theory (Brown et al., 1999)] is an important parameter to consider when anchoring metal complex precursors to maximize dispersion and loading on the MWNT sidewalls. Lee et al. (2011) showed that the treatment of nitric acid-oxidized MWNTs by ethanol reduction at 20 atm and  $180^\circ\text{C}$  was an efficient method for producing a high surface density of  $-\text{OH}$  groups, which in turn provided effective tethering points for grafting metal acetylacetonate metal complexes to the MWNT surface. Since the tethering of cationic/anionic precursors is Coulombic in nature, the PZC can serve as a guide for electrostatic attachment of precursors to engineer the MWNT sidewalls.

Similarly, when functionalizing CNT sidewalls with specific moieties, the PZC is an important parameter for depositing finely dispersed metal nanoparticles from precursors in solution. McPhail et al. (2009) functionalized HiPco single-walled carbon nanotubes (p-SWNTs) with carboxyl acid (COOH-SWNT), nitroso (NO-SWNT), and maleic anhydride (MA-SWNT) groups. PZC values measured using a method described by Park and Regalbuto (1995) were found to be in the descending order: NO-SWNTs (7.5) > p-SWNTs (3.5) > MA-SWNTs (2.0) > COOH-SWNTs (1.2). The trend in measured PZC values correlated well with the electron withdrawing character of the moieties. Of the functional groups used, those with a greater electron donating character resulted in a higher PZC. By varying only the predetermined selection of the functional groups for sidewall attachment, the PZC of HiPco SWNTs could be tuned within a range of 6.3 pH units. Furthermore, UV-vis-NIR and Raman spectra showed that increasing electron withdrawing character of the functional groups led to greater selectivity for covalent attachment to those SWNTs with greater semiconducting character.

The extent of CNT surface oxidation has also been shown to directly impact catalytic reaction rate. Rocha et al. (2011) modified MWNTs using nitric acid at  $100^\circ\text{C}$  (boiling temperature), liquid phase urea at  $200^\circ\text{C}$ , and gas-phase nitrogen at  $600^\circ\text{C}$  in order to produce materials with different textural and chemical properties. In this example, a decrease in sidewall oxidation resulted in increased initial reaction rate for the decomposition of oxalic acid, an important reaction for the clean up of contaminated industrial waste waters. The modified MWNTs were directly applied for catalytic wet air oxidation (CWAO). No impregnated metals were used. This methodology is commonplace among other researchers for preparing Pt-based MWNT catalysts (Yang et al., 2007; Yang et al., 2008; Garcia et al., 2005). The

array of functionalized MWNTs studied by Rocha et al. (2011) were as follows. Original, untreated MWNTs (CNT-O) were oxidized in nitric acid and rinsed in distilled water until a neutral pH was attained, followed by drying (CNT-N). The resulting CNT-N was then treated with urea in a high pressure reactor. The MWNTs were then rinsed, dried, and subjected to gas phase thermal treatment under  $N_2$  flow at  $600^\circ C$  for 60 minutes to produce CNT-NUT. Excluding CNT-O, which was used as the starting material, the successive treatments resulted in a lowering of the density of oxygen-containing functional groups on the MWNT sidewalls in the descending order: CNT-N > CNT-NU > CNT-NUT. These catalyst surfaces were then examined for their ability to degrade oxalic acid. Fig. 9 shows the relationship between PZC values and initial reaction rate constants, as well as with the basicity (indicated by the decrease in PZC values). The decrease in reaction rates were as follows: CNT-NUT > CNT-O > CNT-NU > CNT-N. Accompanying reaction rate increase, the PZC increased with decreasing oxygen-containing moiety density. Noteworthy is the fact that the 1<sup>st</sup>-order rate constant for oxalic acid decomposition was elevated with increasing PZC while the density of oxygen-containing functional groups decreased. The data indicated that there were fewer oxygen-containing groups in the CNT-NUT than in the original untreated CNT-Os. The CNT-NUT MWNTs was the least acidic in this series of MWNT catalysts. Catalytic performance for oxalic acid decomposition in CWAO depends mostly on the acid/base nature of MWNTs. Weak activity for CNT-N (having the second largest available surface area in this series of catalysts) can be correlated to the acidic character of the nanotube sidewall surface. The result implies that MWNTs with lower acidic character are more efficient for decomposing oxalic acid.



**Figure 9.** Apparent first-order initial reaction rate constants ( $k$ ) (for the decomposition of oxalic acid) vs PZC for the original and treated MWNTs (Rocha et al., 2011).

## 6. Conclusions

In summary, the surface chemistry of CNT sidewalls markedly affects its properties relevant to an array of applications. Non-reversible, covalent functionalization often damages the carbon structure and/or creates defects for moiety attachment in order to make these surfaces chemically active. CNT sidewall surface structure, which can be engineered via surface functionalization in solution, can significantly affect heterogeneous catalytic properties. More recently, methods for electrochemical functionalization and manipulation of the solid surface isoelectric point have been developed to diversify our ability to engineer CNT sidewall structures. The effects of oxidizing agents on the colloidal stability of these materials and the role of the PZC have become increasingly important for engineering nanomaterials in aqueous solution environments. The direction of future research will undoubtedly involve detailed elucidation of structure-property relationships involving these parameters.

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