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Chemically Modified Carbon Nanotubes: Derivatization and their Applications

Malingappa Pandurangappa and Gunigollahalli Kempegowda Raghu
Department of Chemistry, Bangalore University,
Central College Campus, Bangalore
India

1. Introduction

Nanotechnology and Nanoscience is the fastest emerging and developing field of science, which find technological importance and intense interest to many researchers. The unique chemical, physical, electronic (metallic or semiconducting) and high thermal properties of carbon nanotubes (CNTs) made them interesting materials for widespread application in the fields such as electrochemical sensors, biosensors, supports for heterogeneous metal catalysts in organic synthesis, fuel cells, semiconductors, batteries, random access memory cells, field effect transistor, field emission display, atomic force microscopy probes, microelectrodes, specific adsorbents to remove organic pollutants from water and waste water and as a potential drug carriers in cancer therapy. The poor solubility of carbon nanotubes in organic solvents restricts them to be used as drug delivery agents into living systems in drug therapy. Hence many modification approaches like physical, chemical or combined have been exploited for their homogeneous dispersion in common solvents to improve their solubility [1-4]. The reports appeared till now in the literature reveals that the modification is required to control the dispersion and such modification introduces specific functionalities as molecular wedges onto the surface of the carbon nanotubes. Thus the functional groups present on the surface control the lateral interactions between the bundles and separate indivisual tubes. Hence homogeneous dispersion can be achieved by breaking the close lateral contact between them which enhances the affinity towards solvents and other related matrices [2]. Due to these specific properties, many research groups explored the development of novel methods for the modification of nanotubes and investigated the mechanistic aspects of these new class of novel materials called chemically modified carbon nanotubes (CMCNTs).

Many applications require covalent modification to meet specific requirements i.e. in case of biosensors the biomolecules require electron mediators to promote electron transfer [5]. Similarly electrochemical metal ion sensors require specific functional groups which show potential affinity towards particular metal ion [6]. The chemical modification of a carbon substrate material was first reported by Murray et. al. in 1970s [7]. The modification protocol was generally achieved by attaching specific molecule or entity which imparts chemical specificity to the substrate material [8]. These chemical modifications can be easily achieved in many ways but in this chapter the modification routes are mainly classified into two

types namely surface modification and bulk modification. The surface modification includes electrochemical induced method, polymer grafting and metal nanoparticle deposition. The later includes chemical reduction of diazonium salts using hypophosphorous acid as a reducing agent, thermally activated covalent modification, microwave assisted modification and ball milling modification.

2. Derivatization methodologies

2.1 Electrochemically assisted covalent modification

Electrochemically assisted covalent modification of carbon substrate material has become a new era in the field of chemically modified electrodes which involves the formation of covalent bond between the substrate and the modifier molecule which had been reviewed by Alison J Downard [9]. Two strategies have been reported in the literature, one is the reductive strategy which involves the electrochemical reduction of aromatic diazonium salts and the other includes the oxidation of aromatic amines [10] which have been discussed elaborately in reviews appeared recently [9,11].

The reductive strategy was initially developed by Jean Pinson and co-workers in 1990 [12] and later developed by a number of workers including McCreery [13] and Downard group [9]. The basic mechanism involved in this modification is the generation of aryl radical at the solution/electrode interface by one electron electroreduction of corresponding diazonium salt and its subsequent attachment on the surface of carbon nanotubes which results in the formation of covalent bond between carbon atom of substrate and carbon atom of the modifier molecule. The schematic modification of the carbon surface has been shown in the figure 1[12].
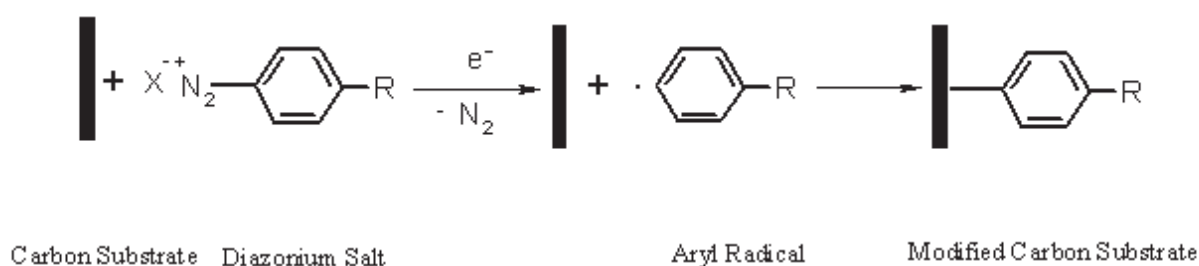

Fig. 1. Schematic representation of electrochemical reduction of aromatic diazonium salt [12]

Electrochemical modification can be achieved easily using techniques like cyclic voltammetry [14] or controlled potential electrolysis [15] either in non aqueous or in aqueous solutions of pH less than 3 [16]. The thickness of the modifying molecule on the surface of CNTs can be controlled by varying the experimental variables like applied potential or current, length of modifier molecule, concentration and scan rate. McCreery et.al. have predicted that the concentration less than 1 mM of modifier forms monolayer and greater than 1 mM concentration results multilayer formation [10, 17]. Very low reduction potentials have to be applied typically around 0 V vs SCE, to generate radical because of electron withdrawing nature of diazonium group. The C - C bond formed in this strategy is significantly stronger than the gold - thiol bond and they can withstand temperature upto 700 K without being lost from the surface [18]. It is quite stable over wide potential window in the range 2.6 - 5.6 V depending on the substituents on the para position [19]. In contrast to

the enhanced stability, formation of these layers on electrode surfaces are less controlled than for the alkane-thiol system. The aryl radicals generated electrochemically are captured by the carbon surface, a fraction of aryl radicals generated in the reaction may bound on the carbon surface, rest of them goes into solution. Allongue et.al. have reported that 84% of radicals form bonds with a glassy carbon surface while only 56% form bonds with the basal planes of highly oriented pyrolytic graphite (HOPG) [18]. The order and coverage of the modifier molecules in the modification layer also depends on the type of modifier as well as the substrate surface. This has been illustrated by McCreery and co-workers [20] where the diazonium salt of nitroazobenzene gave well ordered monolayers on glassy carbon but not on the basal planes of HOPG or diamond where the coverage was only between 50 - 70% of a monolayer [21].

Steven et.al. has modified the indivisual single walled carbon nanotubes(SWCNTs) by the electrochemical reduction of diazonium salt of p-nitro phenol in a home built miniaturized electrochemical cell equipped with platinum wire as counter electrode and pseudo-reference electrodes. Based on experimental results they concluded that the covalent bond formation occurs between the lattice of carbon nanotubes and carbon atom of substituted phenyl groups. The detailed investigations revealed that the degree of functionalization of the carbon nanotubes was as high as 5% of carbon atoms bearing a functionalized moiety, implying that it is not only the ends but also the sidewalls of the SWCNTs that were susceptible to radical attack [10]. Another way of electrochemical modification involves the oxidation of amines. The carbon substrate surfaces like CNTs, graphitic carbon, carbon fibers and glassy carbon spheres were functionalized with amines by their oxidation which forms surface attached layers on the electrode surface. Several mechanisms pertaining to the modification of carbon surfaces by the oxidation of amines have been reported in the literature. One such modification proceeds through stepwise manner wherein the proton loss occur after amine gets attached to the surface (Fig. 2A) and the other way involves the formation of amine cation radical with a loss of proton before the amine gets attached on the surface (Fig. 2B) [12].

A variety of primary amines such as 6-aminohexanol, 4-aminobenzoic acid, 4-aminoethyl pyridine, β-alanine, 2-amino-2-methylpropane, butylamine, octylamine, decylamine, dodecylamine, cysteine, dopamine, aspartic acid, 4-aminomethyl phenylboronic acid, 3-nitro benzylamine, octadecylamine, triethylene tetramine, hexamethylene tetramine, 2-amino anthraquinone, 2-amino-4-methyl thiazole, 1,7-diaminoheptane, 1,10-diaminodecane and 4-amino butyl-H_3PO_4 have been covalently attached onto the rigid surfaces of glassy carbon, carbon fiber and graphitic carbon based electrodes respectively. This kind of modification can also be carried out with secondary and tertiary amines also. Comparing the oxidation of primary, secondary and tertiary amines, the tertiary amines undergo oxidation easily compared to primary and secondary amines which were confirmed by the strong, sharp, irreversible oxidation peaks appear at least positive potentials. This kind of observed behavior might be due to the stabilization of amine cation radical by the presence of alkyl substituents [22,23]. The lifetimes of the radical cation formed increases from primary, secondary to tertiary amines. Although the ease of amine oxidation decreased from tertiary, secondary and primary, primary amines were found to give the highest modifier surface concentration when compared to secondary amines. However in case of tertiary amines the attachment was very poor and sometimes not detectable due to stearic hindrance of bulky substituents at the nitrogen atom which prevents the tertiary amine to undergo oxidation and get attached to the carbon surface. Attachment of primary amines on the electrode
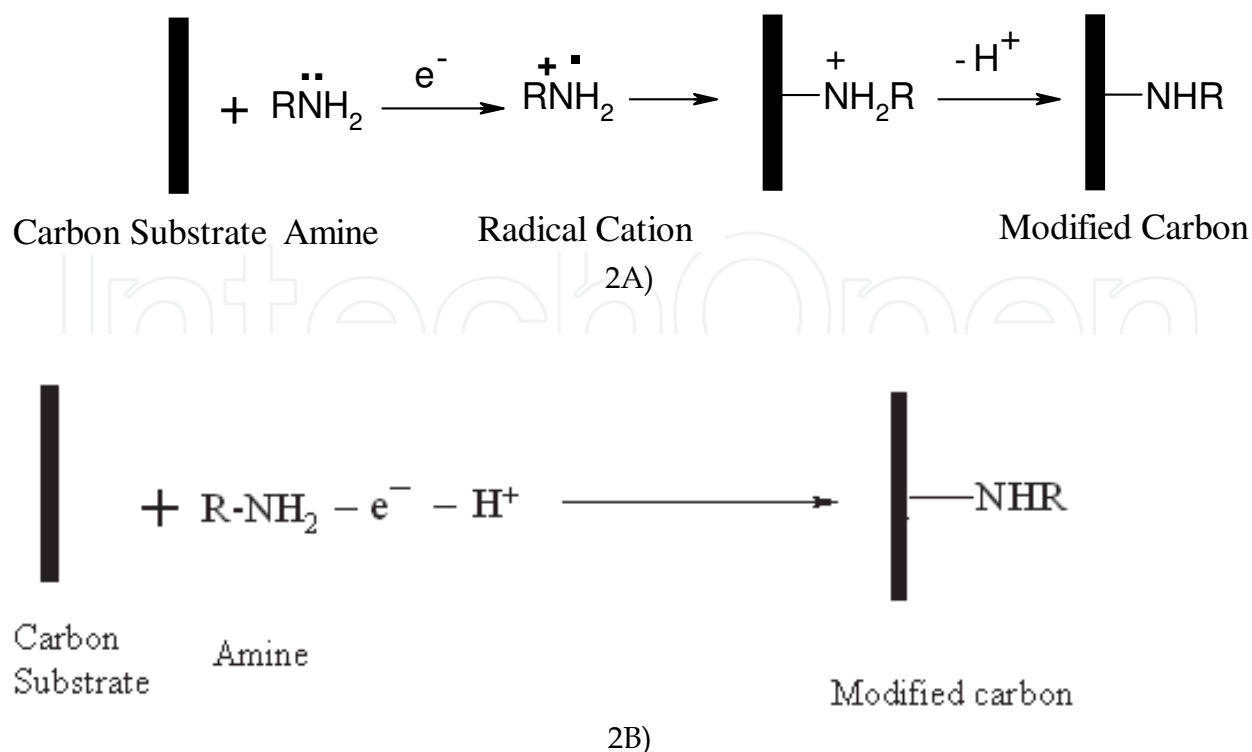
Fig. 2. Schematic representation of carbon modification through amine oxidation.

surface was supported by an observation that the irreversible oxidation peak disappears and the currents decreased significantly with the increase of number of cycles in cyclic voltammetry (CV), whereas for secondary and tertiary amines the height of the oxidation peak remained relatively unchanged. The attachment of amine to carbon surface through its oxidation preferably requires either primary or secondary amines but not tertiary amines. The amine oxidation mechanism has an H group eliminated during the oxidation process, which is not possible with tertiary amines. The reaction occurs with a monoamine modifier however in case of diamine modifiers it is possible that both amines attach to the surface. In one study that investigated the attachment of ethylene diamines to carbon fibers, it was proposed that the single oxidation peak observed accounted for two single electron processes. The two identical and electronically independent amines were oxidized at closely spaced potentials [24, 12]. The coupling of 4-fluorobenzoyl chloride, the conformation of the ethylene diamines monolayer attached to carbon fibers was suggested to be 75% coverage in the looped arrangement where both amines were surface bound and the remaining 25% were attached via one amine [12]. In another study two irreversible oxidation peaks were observed for modification of carbon fibers with ethylene diamines. The peaks were attributed to the corresponding mono and dication radicals respectively. The potentiometric titrations of modified carbon fibers with HCl has revealed that the majority of the ethylene diamines modifiers were attached to the carbon fibers by oxidation of the two amines which subsequently led to form a polymeric multilayer chain and also a looped configuration. The longer diamines like 1, 7-diaminoheptane 1, 10-diaminodecane and 1, 12-diaminododecane has resulted that only one amine of the diamines was covalently attached to the glassy carbon surface where as the other amine is not surface bound [25]. Steven et.al. modified the indivisiual SWCNTs by the electrochemical oxidation of substituted amino phenol [10].

2.2 Polymer grafting

Polymers with its inherent tunable chemical properties like good stability, number of active sites, strong adherence, homogeneity, electronic properties makes these materials interesting. In addition to these properties, polymers reduces the adsorption phenomena by the selective exclusion of interfering species and also due to the presence of large number of active sites which can preconcentrate the analyte molecules. They are also semipermiable hence only selective analytes can diffuse towards it hence high specificity towards particular analyte can be achieved. The combination of all these properties of polymers and the properties of nanotubes make them a very important class of synthetic materials which mimic the molecular recognition by natural receptors. CNTs modification with polymers can be achieved mainly in three ways, the first one involves simple soaking of the electrode material in a polymer solution the other involves chemical approach which inherently requires an oxidant further it gets converted into a reducing product and the last approach involves electrochemical approach i.e. electropolymerization either by potential cycling or under galvonostatic conditions. Electropolymerization on rigid electrode has got considerable attention in recent years due to the possibility of having great control over the thickness of the polymer layer on the surface of CNTs [26-28]. In this way MWCNTs were modified with polydiphenylamine(PDPA), Poly(acrylic acid), Quinone - o – phenylenediamine, Osmium (4,4 – dimethyl – 2, 2 – bipyridine) chloride and also with most popular electron-conducting polymers like polyaniline(PANI), polypyrrole (PPy) and the derivatives of polythiophene(PTh). Similarly SWCNTs were modified with poly(styrene sulphonic acid) sodium salt, poly(1, 2-diamino benzene) (PABA) [29,30]. These modified materials have been designed as sensing surfaces that are capable of interacting with simple anions, metal ions and small organic molecules.
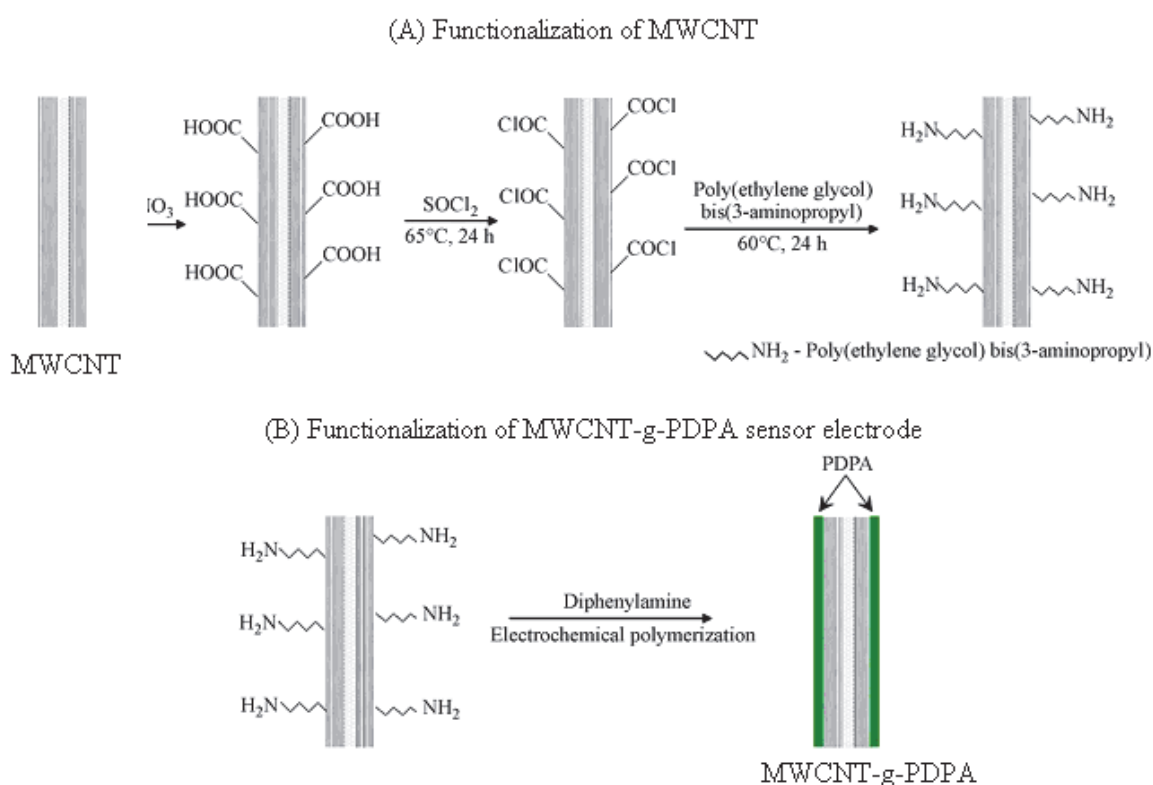

Fig. 3. Modification of MWCNTs-Polydiphenylamine A) amine functionalization of MWCNTs B) fabrication of MWCNTs-PDDA sensor [30]

2.3 Nanoparticle modified carbon nanotubes

Nanoparticles (NPs) in particular metal and semiconductor NPs are the building blocks of nanodevices since from the time of Faraday who proposed that the ruby red color of gold colloid has been the consequence of its small particle size [31]. The size dependent properties have given rise to enormous applications that have emerged in the last few decades [32]. Data storage, sensing devices, catalysis, biological interfaces, quantum dots, nanoelectromechanical devices and nanotribology are some of the areas where the impact has been very substantial and also in several areas from chemistry to physics to material science to biology and medicine [33].

On the other hand, owing to the excellent thermal, electrical, chemical and mechanical properties of CNTs (both SWCNT and MWCNT) they have been intensively studied and gained great deal of attention for their applications in various areas like sensing, biosensing, catalysis due to their inherent properties like high surface area, high electronic conductivity, outstanding chemical and electrochemical stability [34]. The modification of CNTs with nanoparticles for the construction and designing of nanoarchitectures would enhance the electrocatalytic efficiency of many electrochemical processes giving rise to several significant applications like sensors, biosensors, heterogeneous catalysts for fuel cells and nanotechnology [29].

Many methods are reported in the literature for the modification of CNTs with NPs which are associated with their own advantages and disadvantages. As a result of this, here we have focused selective and advanced methods such as electrochemical modification or electrodeposition, electroless deposition and modification through covalent attachment[35].

2.4 Electrodeposition

Electrochemical method is a powerful tool for the modification of nanotubes with NPs through electrodeposition because the method has great control over the nucleation and growth of NPs by varying nucleation potential, deposition time and the concentration of noble metal complexes.

Electrochemical deposition of NPs onto the CNTs is generally performed by the reduction of noble metal salts like $H[AuCl_4]$, $H_2[PtCl_4]$ and $(NH_4)_2[PdCl_4]$ mostly through van der walls interactions which is sufficient enough to provide good adhesion with the tubes [36].

He et.al. modified the nanotubes with Pt-Ru bimetallic nanoparticles with diameter 60-80 nm potentiostatically followed by the electrochemical oxidation in a solution containing various ratios of Pt to Ru in 0.5M H_2SO_4 [37].The developed composite showed a significant electrocatalytic activity towards methanol oxidation and the process is free from commonly interfering problem like CO adsorption which blocks the catalytic sites and it follows bifunctional mechanism as shown below.

$$Pt + CH_3OH \;\rightarrow\; Pt\text{-}CO_{ads} + 4H^+ + 4e^-$$

$$Ru + H_2O \;\rightarrow\; Ru\text{-}OH + H^+ + e^-$$

$$Ru\text{-}OH + Pt\text{-}CO_{ads} \rightarrow\; Ru + Pt + CO_2 + H^+ + e^-$$

Day et.al. electrochemically deposited the Pt and Pd NPs onto the surface of tubes at various potentials with different times and from the experimental results they found the strong dependence of deposition potential and time on the size, density and distribution of NPs on the surface of carbon nanotubes [38]. Afterwards they have further extended the

methodology for the electrodeposition of Ag and Pt on high density SWCNT networks and determined the complete dependence of dispersion of NPs in the form of nanowires or in the form of individual nano particles. The driving potential required for the deposition of metal nanoparticles varies with respect to the distance from the metal contact electrode. The potential for deposition decreases with increase of distance from the metal contact electrode therefore the rate of nanoparticles nucleation and growth increased at close proximity to the contact electrode, resulting in continuous nanowires, rather than separate NPs, near the contact electrode.

Chen et.al. have investigated the control on the size of Pt nanoparticles to 2-3 nm by varying the viscosity of the electrolyte and adjusting the potential pulses during course of deposition. Aqueous solutions of $H_2[PtCl_6]$ were used as working solution and its viscosity was varied by adding different quantities of glycerol then it is easily removed simply by rinsing with hot water. The results showed that the particle size of Pt NPs could be easily controlled by adjusting the diffusion of electrolyte and number of potential pulses [39]. Arai et.al.have reported electrodeposition of Cu and Ni nanoparticles on carbon nanotubes [40]. They demonstrated the selective deposition of Ni at ends and defect sites of MWCNTs which can be attributed to their high electrical conductivity in the axial direction and fast electron transfer kinetics at defect sites. Ni coated SWCNT nanowires were also prepared by electrodeposition on SWCNTs supported on alumina membranes. Lee et.al. have used drop coating method using acid treated tubes on a Ni working electrode using Pt wire & saturated calomel as counter and reference electrodes respectively [41]. Under potentiostatic condition at 0.4 V, they have deposited $MnSO_4$ at pH 5.6 as larger aggregates preferentially at the tips of nanotubes. Frank et.al. galvonostatically deposited the Ti from $TiCl_3$ precursor on the pristine SWCNT working electrode at pH 2.5. Similar modifications were also carried out to deposit NiO or RuO_2 via potential cycling by Kim et.al. They have found that the gas atmosphere during post annealing process had a significant effect on the morphology loss of the RuO_2. Further heating in argon atmosphere produced more uniform, spherical nanoparticles while annealing in O_2 atmosphere resulted in elliptical RuO_2 nanoparticles [42,43]. Qu et.al. reported the modification of nanotubes with Pt nanoparticles and [tetrakis (N methylpyridyl) porphyrinato] cobalt as a hybrid thin film electrode. In this case the platinum nanoparticles were generated by chloroplatinic acid in 0.5 M H_2SO_4, then adsorbed onto [tetrakis(N-methylpyridyl)porphyrinato]cobalt modified nanotubes through electrostatic interaction and then the platinate complex was reduced potentiostatically at -0.7V [44]. Tsai et.al. synthesized Pt (Pt-Ru) NPs/CNTs monohybrids by electrochemical deposition in ethylene glycol in presence of H_2SO_4 as supporting electrolyte. They have successfully obtained Pt (Pt-Ru) nanoparticles with 4.5 nm for Pt and 4.8-5.2 nm for Pt-Ru with uniform distribution on the surface of the tubes. Ethylene glycol not only enhanced the dechlorination of Pt and Ru precursor salts but also acts as stabilizing agent preventing the agglomeration of nanoparticles during electro deposition process which results in the better dispersion of small diameter Pt or Pt-Ru NPs [45,46]. Xia et.al. have used a novel methodology by using ultrasonic energy which involves the usual electrodeposition strategy to synthesize bimetallic Au-Pt NPs on the surface of MWCNTs in ionic liquids [47].

2.5 Electroless deposition (ELD)

This method involves the incorporation of NPs onto the surface of nanotubes without any external aid like reducing agent or applied potential for the reduction of metal ions as opposed

to that of electrochemical deposition or chemical reduction methods. The driving force beyond the modification involves the direct redox reaction between the tubes and NPs. For the first time Dai et.al. modified the nanotubes with Pt and Au NPs using this method [48]. ELD can be carried out only when the metal ions having higher redox potentials than nanotubes, hence Au, Pt, Pd metal ions can be used to modify tubes through this method but not metal ions like Ag, Ni and Cu because of their lower redox potentials than that of the nanotubes. The atomic force microscopy (AFM) and Fermi level diagram of SWCNTs is shown in the following figure 4 [48]. In order to overcome the above limitations, Qu and Dai further developed a novel process known as substrate enhanced electroless deposition (SEED) [49]. In this strategy CNTs were supported by a metal substrate having lower redox potential than that of NPs and the deposition of metal NPs was achieved through the redox reaction of a galvanic cell wherein the carbon nanotubes acts as a cathode for metal deposition by the reduction of metal ions in solution and the metal substrate serves as an anode where the metal atoms are oxidized to the corresponding ions and dissolved in solution. The schematic representation of the reaction pathway is shown in the following figure 5 [49].
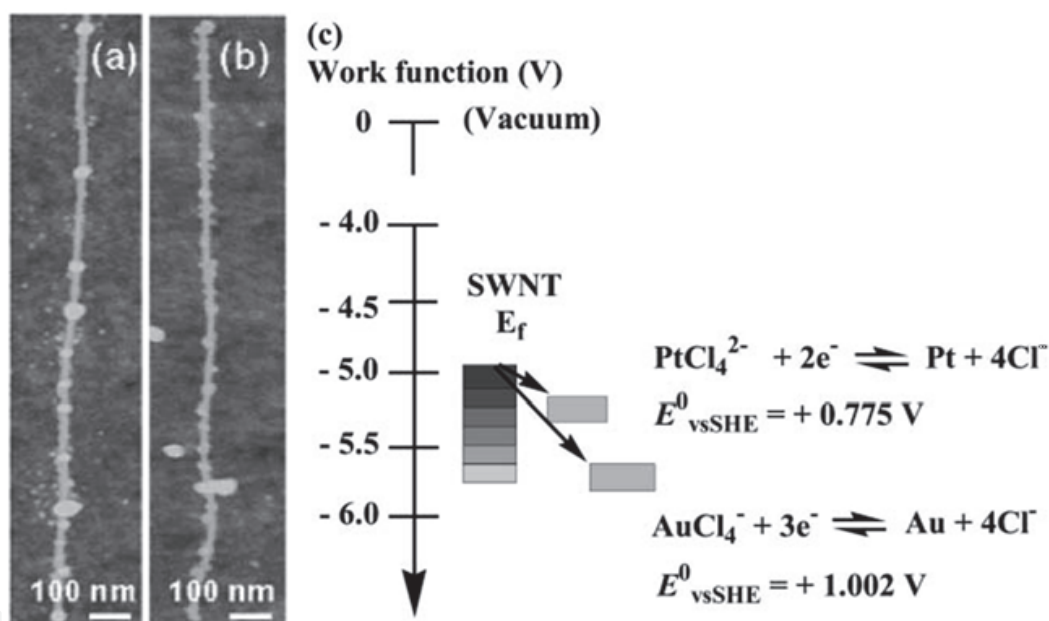

Fig. 4. AFM images of (a) Au and (b) Pt NPs on SWCNTs. (c) Diagram of the Fermi energy (EF) of a SWCNT, and the reduction potentials of Au^{3+} and Pt^{2+} vs. SHE respectively [48].
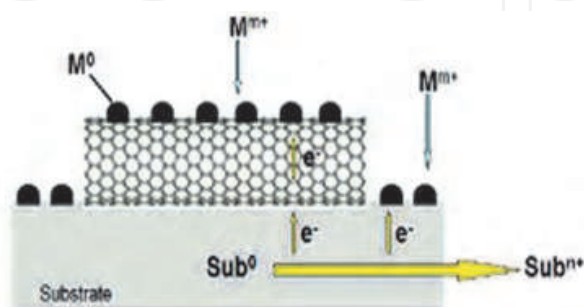

Fig. 5. Schematic illustration of metal nanoparticles deposition on carbon nanotubes through electroless deposition process [49].

2.6 Modification through covalent attachment

Heterogeneous catalytic reactions encounter completely on the surface of supporting substrates, hence surface structure play a very important role in heterogeneous catalysis. In recent years NPs decorated carbon nanotubes are used as catalytic supports but simple deposition of metal NPs results in a poor dispersion and hence least stability due to insufficient binding sites present on the surface of carbon nanotubes. Hence in order to achieve highly stable and uniformly dispersed nanoparticles, the surface of nanotubes must be modified via a proper functionalization procedure which involves the formation of covalent bond with the use of linker. The strength of the modification determines the distribution and concentration of the metal nanoparticles on the surface of carbon nanotubes [50].

Covalent modification of nanotubes can be achieved by many ways which has been reviewed in the literature [51]. The main perspective of this modification involves the generation of oxygen containing functionalities more specifically, carboxylic groups commonly called as surface oxides by the aggressive oxidation treatment using strong acids. The resulting carboxylic acid groups are used to anchor and disperse the NPs on the surface of tubes but it is hard to achieve smaller particle size and high degree of loadings [52]. In order to overcome this drawback, the carboxyl functionalized carbon nanotubes could be further grafted with functional moieties with terminal amine or thiol groups which can effectively control the particle size and dispersion of noble metal NPs on the surface of tubes. Niu and co-workers have proposed the above modification procedure recently [53]. They modified the carboxylated nanotubes with amine terminated ionic liquids through amide bond formation and subsequently attached the gold NPs through electrostatic interaction and ion exchange. The resulting modified CNTs showed nano sized and uniform distribution of NPs. Similarly Guo et.al. have modified the nanotubes using imidazolium salt based ionic liquids (IS-ILs) as linkers. Further they found the enrichment of $PtCl_6{}^{2-}$ by coupling effect which promotes the nucleation of Pt NPs due to low interface energy [54]. Lu and Imae et.al. have modified the MWCNTs covalently with fourth generation NH_2-terminated poly(amidoamine) (G4-PAMAM) dendrimers (CNT/DEN) and used as support for Au NPs. The particle size of Au NPs could be concisely controlled by tuning the ratio of $H[AuCl_4]$ to the covalently bonded dendrimers on the surface of CNTs (Fig.6) [55].

These results revealed that the Au NPs interacts with the dendrimers in two possible ways. One is the coordination of NPs at outside the dendrimers and the other is the encapsulation of NPs inside the dendrimers [55]. Further, Ag, Cu, Pt and Ag@Au NPs were also successfully synthesized in situ on the surface of CNT/DEN with a great control on its particle size. The Pd NPs were also deposited on the surface of MWCNTs which were initially functionalized with thiol [56], benzenesulfonic [57] and ionic liquid functionalized MWCNTs [58]. Banerjee et.al. have functionalized the CNTs with CdSe QDs through p-mercaptobenzoic acid using ethylenediamine as linker between oxidized CNTs and p-mercaptobenzoic acid. In a similar way, thiol stabilized ZnS capped CdSe QDs were protected with 2-aminoethanethiol and linked to the acid terminated carbon nanotubes in presence of a coupling agent like EDC (Fig. 7) [59]

In contrast to this, metal oxides can be attached to the carboxyl groups without any linker due to their hydrophilic nature as recently demonstrated for MnO_2, MgO, TiO_2 and Zr $(SO_4)_2$. However, the authors observed only weak interactions between the oxides and the acid-terminated nanotubes resulting in rather nonuniform distributions of the NPs. Better adhesion was observed when capping agents were used. Sainsbury and Fitzmaurice produced capped TiO_2 and SiO_2 nanoparticles ($d \approx 4\text{-}5$ nm) via a standard sol-gel process using titanium tetraisopropoxide (TTIP) and tetraethyl orthosilicate (TEOS) as precursors with cetyltrimethyl ammonium bromide (CTAB) as the capping agent (Fig. 8) [60].
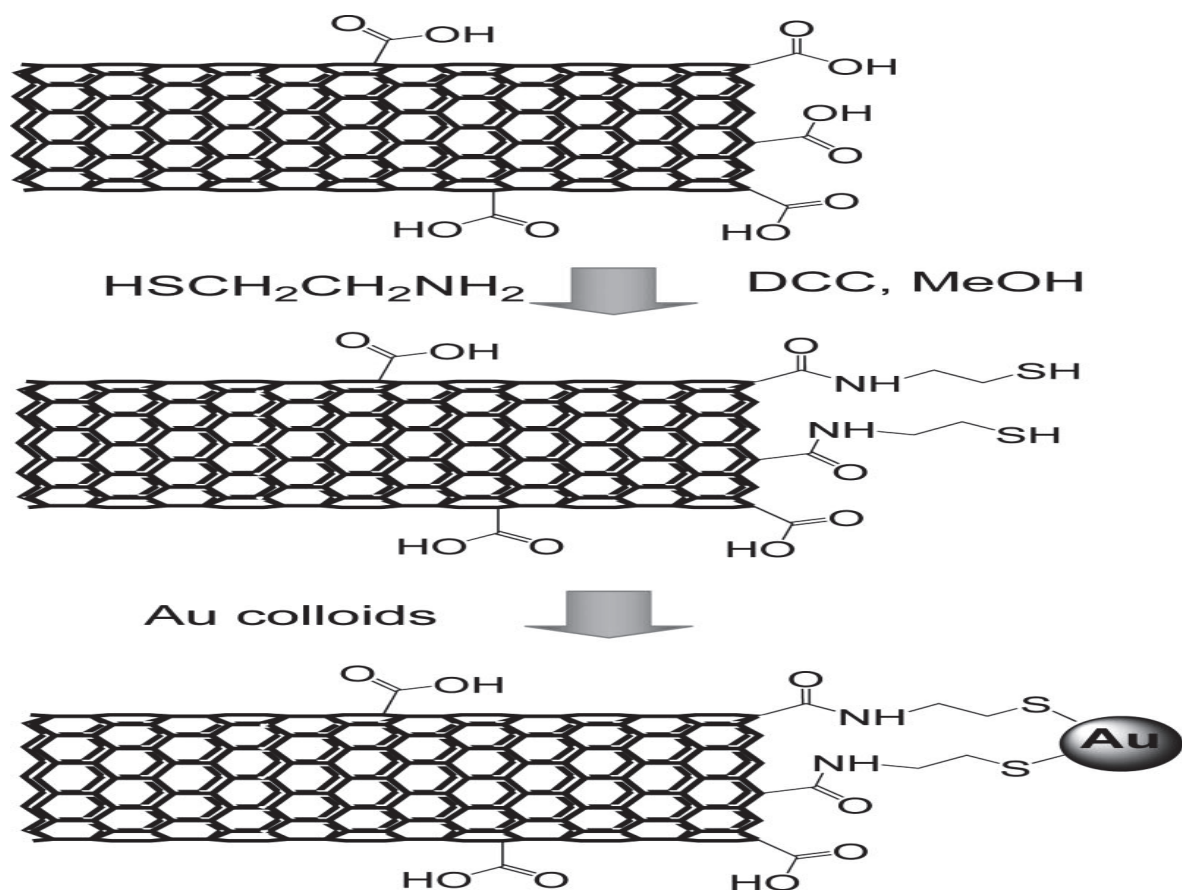
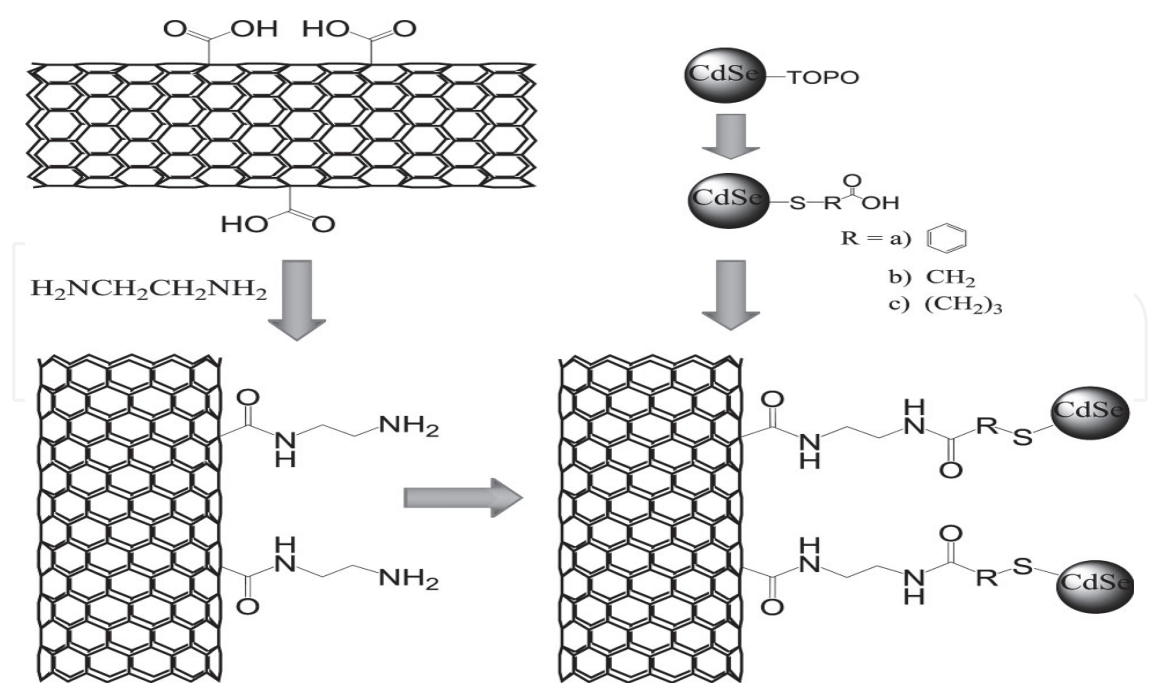Fig. 6. Covalent attachment of Au nanoparticles to amino or mercapto terminated CNTs [55].

Fig. 7. Multistep process for linking modified CdSe QDs to CNTs via amide bonds, involving oxidation of CNTs and functionalization with ethylenediamine and thiolization of CdSe and termination with acid groups [59].
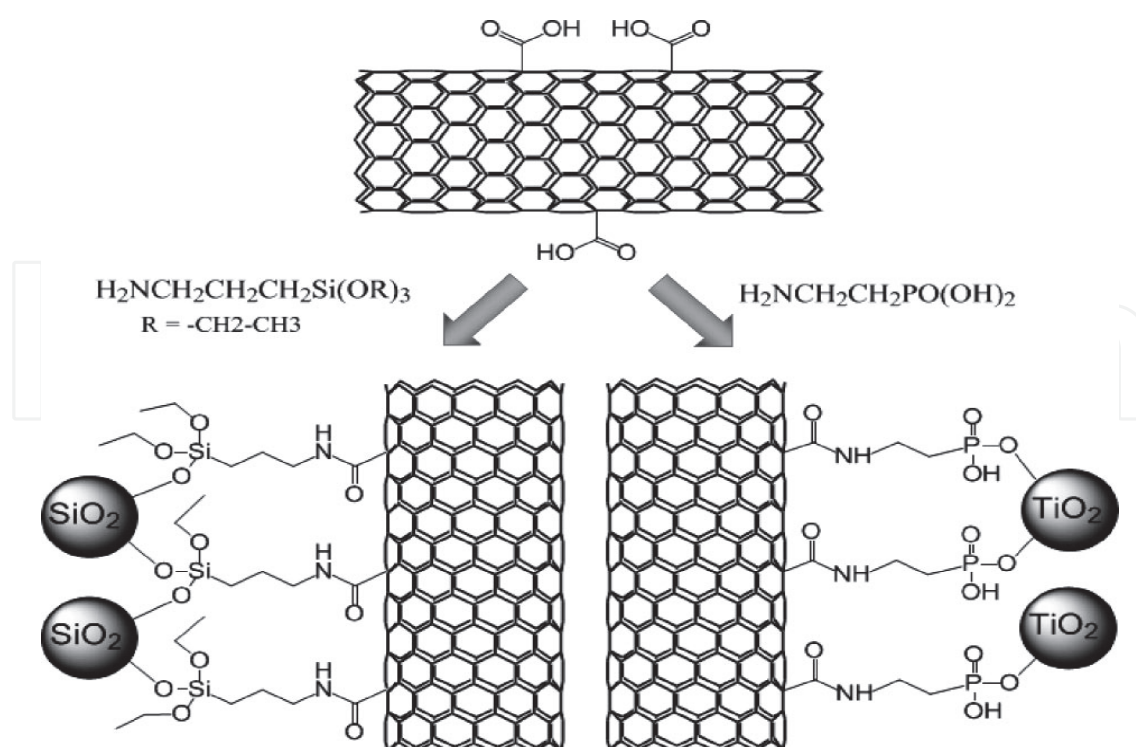
Fig. 8. Modification of carbon nanotubes with SiO_2 and TiO_2 nanoparticles via silane and phosphonic acid bonds [60].

2.7 Modification through chemical reduction of diazonium salts

This class of modification involves one electron chemical reduction of aromatic diazonium salts in presence of hyphophosphrous acid as a reducing agent. The reduction yields molecular nitrogen and a highly reactive aryl radical which subsequently attached to the carbon surface and forms covalent bond between carbon and the modifier molecule. General scheme and modification mechanism has been shown in the figure 9 [61].
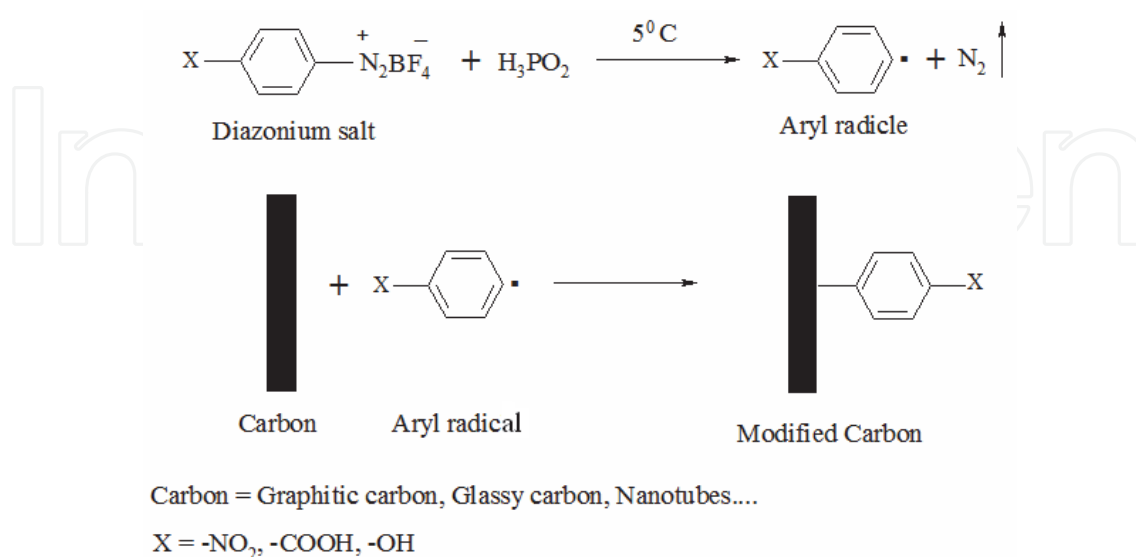

Fig. 9. General scheme of modification of carbon substrates using hypophosphorous acid as a reducing agent.

This method of modification is a simple and convenient for the preparation of gram quantities of modified carbon nanotubes and offers high degree of functionalization which results in bulk modified carbon substrate material. This bulk modified carbon substrate material can be utilized as a thin film to fabricate chemically modified electrodes or it can be compressed into pellets before using as electrode material for various applications [61].

The general procedure of this modification involves the addition of H_3PO_2 into a mixture of carbon substrate material and diazonium salt solution with occasional stirring at 0-5^{0}C for about 30 minutes. Then the resulting mixture is filtered, washed thoroughly with acetonitrile to remove any unreacted diazonium salt and with ample quantities' of water to remove the excess of acid. Finally the modified carbon has been dried by placing in a fuming hood for 12 hours and stored in an air tight container [61]. Using this strategy, Heald et.al. have prepared 1-anthraquinone functionalized MWCNTs and studied their electrochemical behaviour. These electrochemical studies revealed that the modified MWCNTs undergoes two electron, two proton transfer which results in a quasi reversible cyclic voltammograms corresponding to quinine/hydroquinone redox couple which has been confirmed by the pH study (Fig. 10).
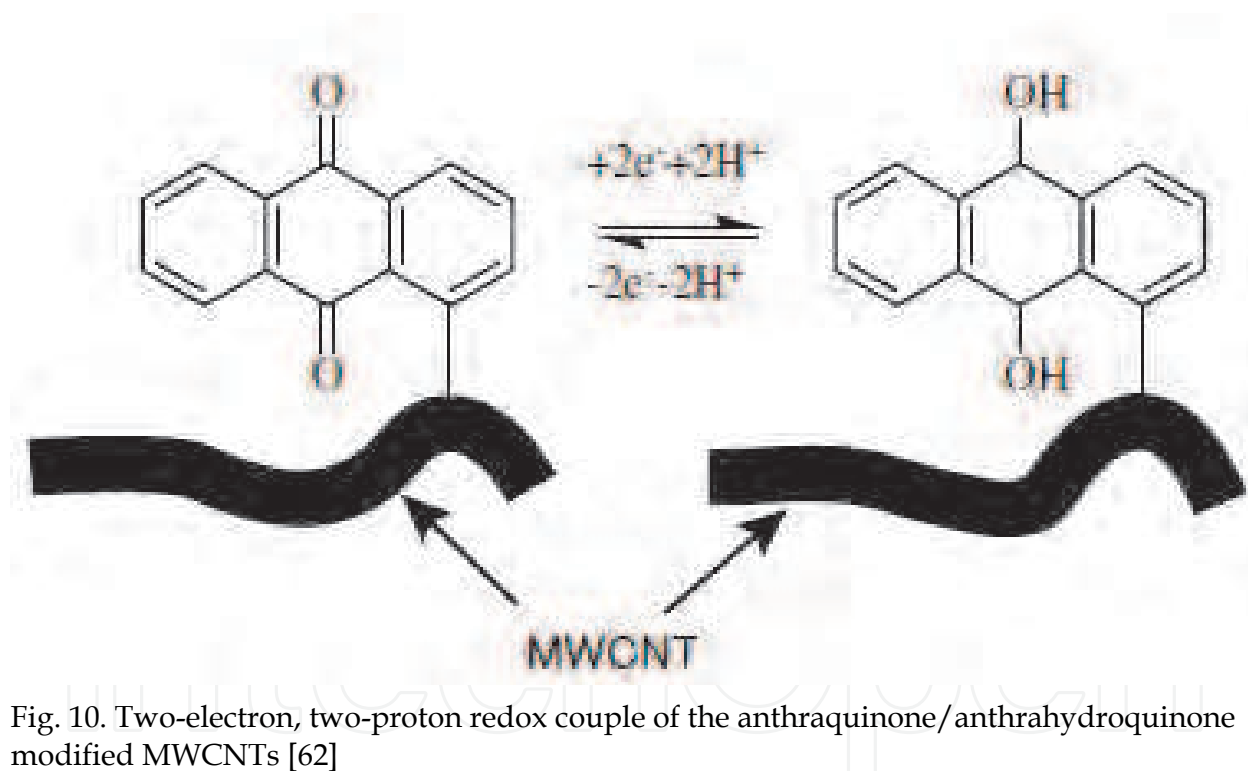

Fig. 10. Two-electron, two-proton redox couple of the anthraquinone/anthrahydroquinone modified MWCNTs [62]

Masheter et.al. have extended the derivatization method of Heald et.al. using nanotubes of different morphologies like b-MWCNTs, h-MWCNTs and SWCNTs and proposed the following modification strategy[63]. In case of MWCNTs, the majority of anthraquinonyl radicals modify the edge-plane like sites at the tube ends than that of the basal planes, whereas a greater degree of sidewall functionalization occurs for the SWCNTs, which reflect their greater reactivity. Masheter et.al. have attached the anthraquinone species covalently onto the surface of graphitic powder after attaching nitrophenyl groups and reducing it to aniline species then coupling with anthraquinone-2-carboxylic acid which results AQ-AN modified CNTs (Fig. 11) [63].
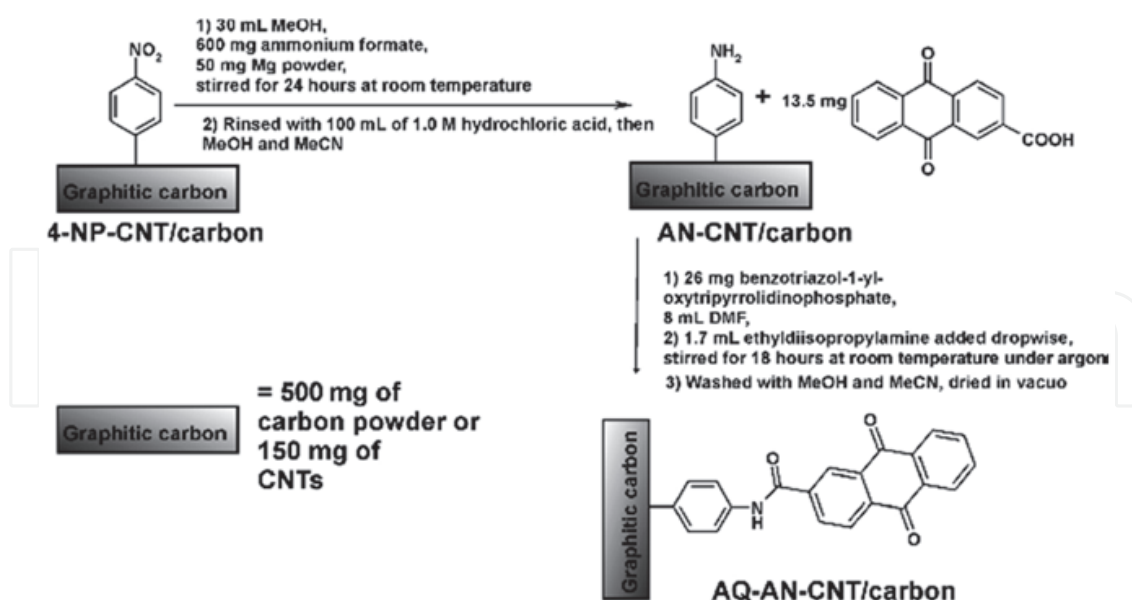
Fig. 11. Derivatization of graphitic carbon using anthraquinone-2-carboxylic acid [63]

This coupling method has the effect of attaching the anthraquinone center to the graphitic surface through a ''spacer'' molecule extending the anthraquinone group farther from the surface of the carbon material into the solution phase. Similar modification was also carried out by Abiman et.al. using MWCNTs of different morphologies in order to study the detailed mechanistic path way of chemical modification [64]. In this regard MWCNTs were derivatized in presence and absence of hypophosphorous acid as a mild reducing agent and the resulting materials were characterized using cyclic voltammetry. The observed peak potentials for the modified materials were found to differ depending on the derivatization conditions (presence/absence of hypophosphorous acid, diazonium salt concentration and temperature) and these differences were interpreted mechanically. The experimental results suggest that in the absence of hypophosphorous acid, the derivatization mechanism likely to proceed through a cationic intermediate, where as in the presence of the hypophosphorous acid the mechanism probably involves either a purely radical intermediate or a mixture of radical and cationic species depending on the concentration of a reducing agent and the reaction temperature (Fig. 12) [64].

Polymerization of the nitro phenyl groups on the surface of nanotubes was studied using different concentrations of 4-nitrobenzenediazonium tetraflouroborate and was found to increase with increasing concentration of cationic intermediates. The effect of the reaction temperature on the derivatization procedure was explored over a range of temperatures from 5 to 50⁰C and the optimum derivatization temperature was determined in the presence and absence of hypophosphorous acid. It was found to be 20⁰C and 35⁰C in presence and absence of hypophosphorous acid respectively. The modified tubes both in presence and in absence of hyphophosphrous acid were physically immobilized onto the surface of MWCNTs and were electrochemically characterized using cyclic voltammetry in order to confirm the modification by utilizing the electroactivity of nitro groups. The cyclic voltammogram clearly shows an irreversible reduction wave of reduction of nitrophenol to hydroxy phenyl amine which corresponds to a four electron and four protons transfer and a quasireversible wave of oxidation of hydroxy phenyl amine to nitroso phenyl groups corresponds to the two protons and two electron processes. The possible mechanism along with cyclic voltammogram has been shown in the figure 13 [64].
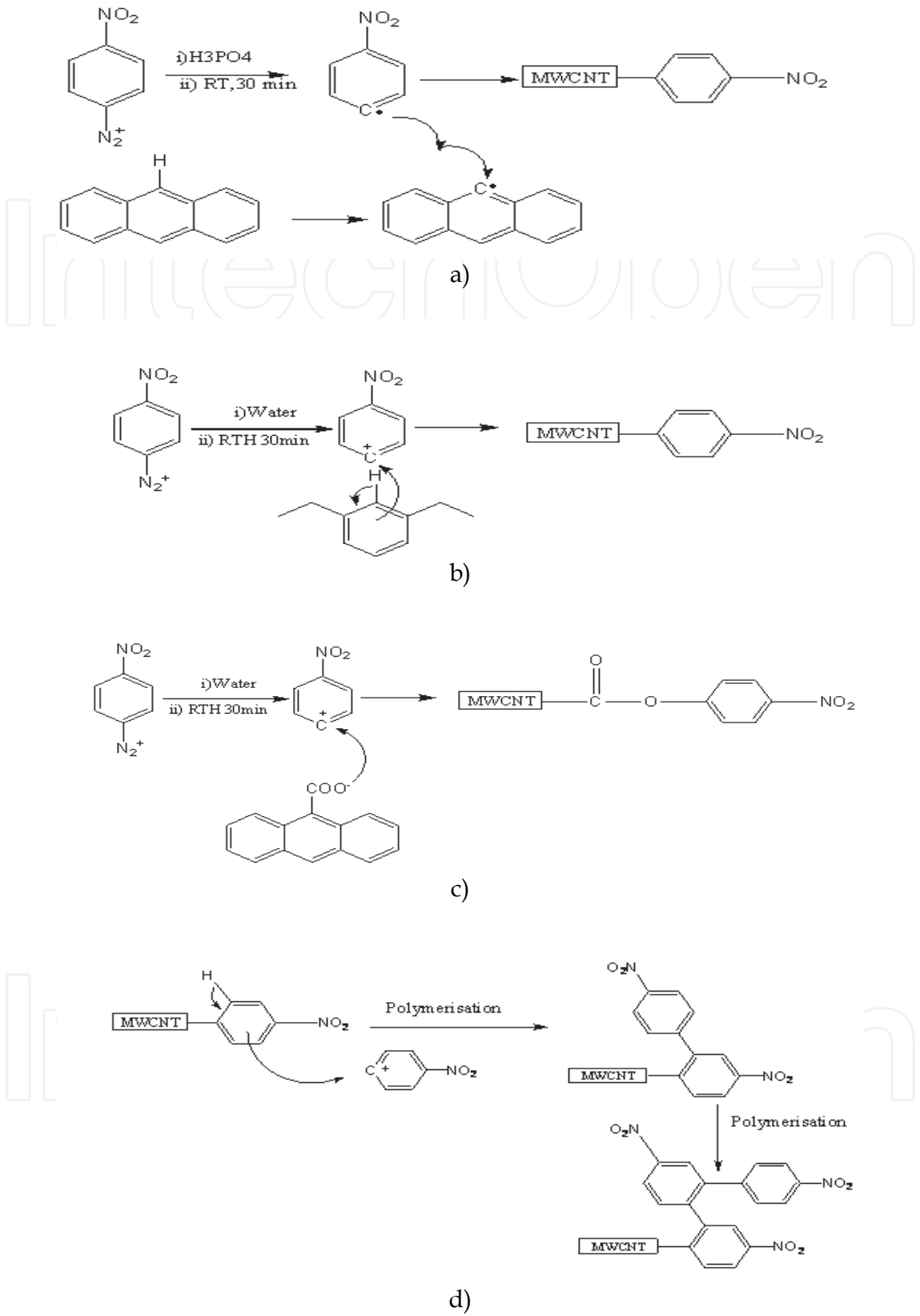
Fig. 12. Proposed mechanistic pathways for the derivatization of MWCNTs through a) radical intermediate; b) cationic intermediate; c) reaction of cationic intermediate with carboxylic group; d) polymerization of cationic intermediates [64].
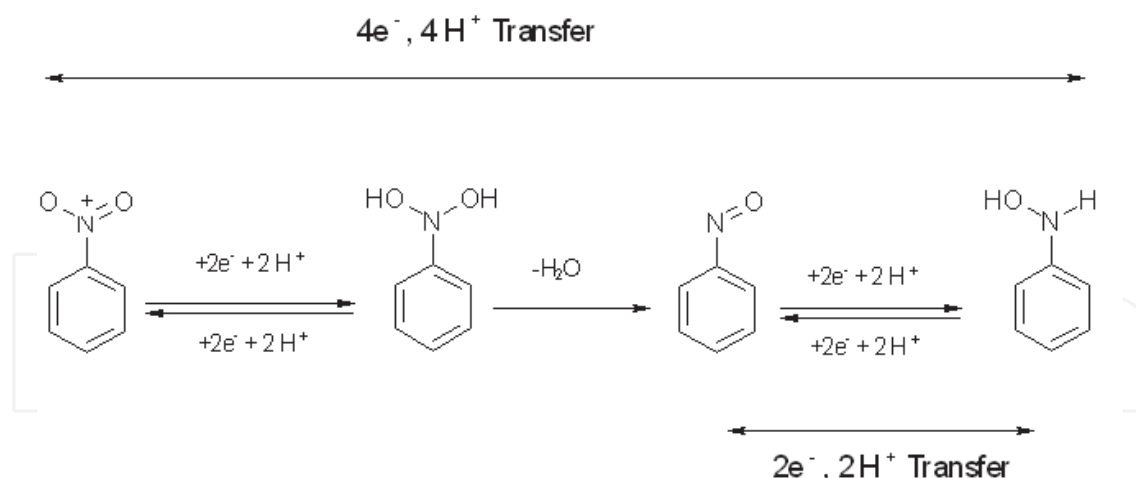
Fig. 13. Mechanistic pathway of electrochemical reduction of aryl nitro group under aqueous condition.

Recently Pandurangappa et.al. have modified SWCNTs using H_3PO_4 as a reducing agent and studied the stability of the modified substrate material by examining the electrochemical behaviour of indicator species for a period of one year [65]. In order to understand the stability of the modifier molecule on the substrate material, it has been examined the cyclic voltametric behaviour at different time intervals. Even after one year the electrochemical behavior of the functionalized CNTs remains more or the less same and the wave shapes are symmetrical with a slight variation in peak currents which might be due to the difference in the quantity of immobilized species drawn on the surface of the electrode during electrochemical study (Fig. 14) [65].
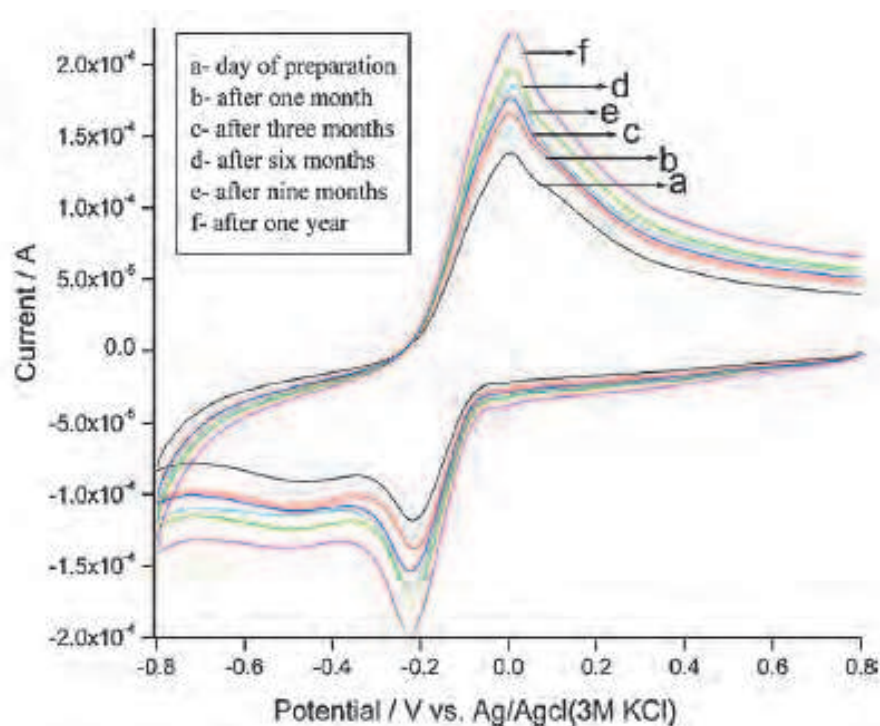

Fig. 14. Overlaid voltammograms of the covalently modified CNTs with anthraquinone species at different time intervals [65].

2.8 Thermally activated chemical covalent functionalization

This type of modification proceeds through three steps that are chemical oxidation, activation and amidation reactions. This multi step process results in highly stable modification with high surface coverage. Following this methodology Hsieh et.al. have reported the amino functionalized carbon nanotubes/carbon paper electrodes which have showed not only hydrophilic coverage for the formation of double layer (double layer capacitance) but also active sites for redox reaction. These materials pocesses higher capacitance, high rate capability and capacitance stability with high columbic efficiency compared to fresh and oxidized carbon nanotube/carbon paper capacitor materials [66,67]. Bifeng Pan et.al. have prepared the MWCNT nano hybrids initially by the oxidative pretreatment of CNTs with 3:1 H_2SO_4/HNO_3 mixture then they were activated using $SOCl_2$ and finally acyl chloride was coupled with ethylene diamine. The resulted MWCNTs were again modified with mercaptoacetic acid coated QDs [68]. Gabriel et.al. modfied the single walled carbon nanotubes similarly with different amines and explored two types of modification schemes. The first scheme involves the usage of $SOCl_2$ and in the second scheme without $SOCl_2$. From the experimental evidences they have concluded that the first scheme is the most efficient method for the functionalization of carbon based substrates which might be due to the increased degree of formation of carboxylic groups. The following scheme illustrates the two different modification strategies [69].
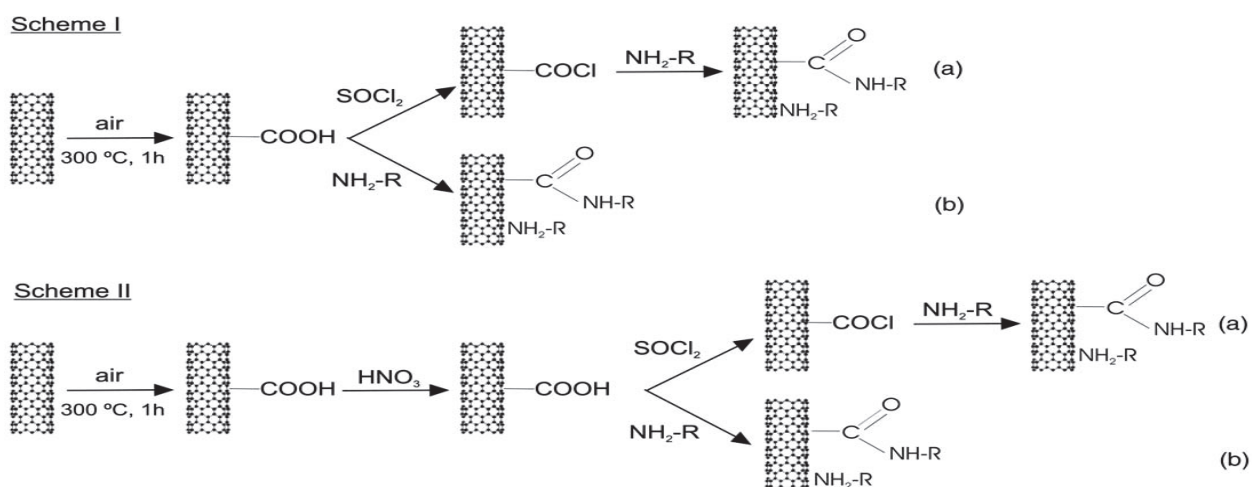

Fig. 15. Schemes illustrating the different strategies used to functionalize SWCNTs [69].

Kai et.al. have modified the MWCNTs with triethylenetetramine with three methods of acid treatments in order to determine the extent of carboxylic groups onto the surface of CNTs [70]. The first method involves the treatment of MWCNTs with 3:1 mixture of concentrated H_2SO_4/HNO_3 under sonication at 40^0C for 10 h. After acid treatment the CNTs were washed with ample quantities of water until the pH value of the washings reaches pH 7, then dried at 80^0C for 24 h. The second method was carried out as that of first method but without H_2SO_4. Similarly the third method was carried out as that of second but at a temperature of 90^0C. Then the acid activated MWCNTs were stirred for about 24 hours at 70^0C in presence of $SOCl_2$. The resulted acyl chlorides were further reacted with TETA at 12^0C under magnetic stirring for 96 h (Fig. 16) [70].
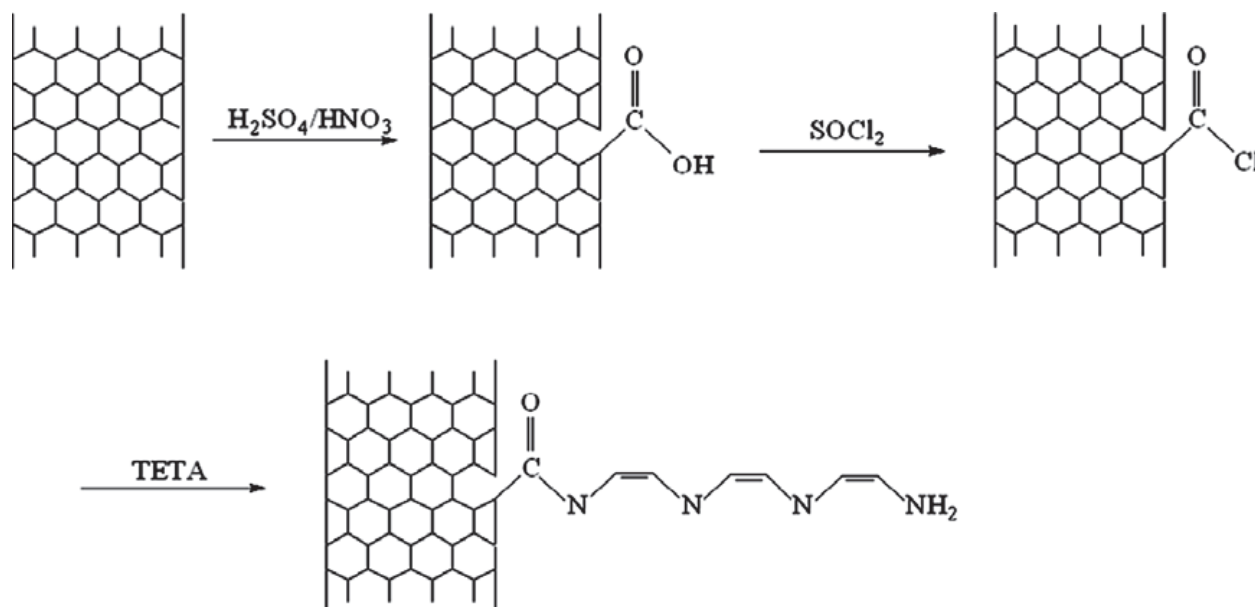
Fig. 16. Schematic representation of TETA grafting on the MWCNTs surface [70].

2.9 Microwave induced modification

Application of Microwave technology is relatively a new area in the field of chemical synthesis as evidenced by number of papers and reviews appearing in the literature in recent years. The chemistry under microwave radiation is known to be faster and more efficient than the conventional methods. Microwave assisted synthesis has been exploited in various fields of organic synthesis including heterocyclic, organometallic, combinatorial chemistry, synthetic transformations, radical reactions, organocatalysis, cycloaddition, metathesis and metal mediated transformations etc. due to the possibility of controlling the reaction by tuning pressure and temperature. These reactions have become significant ones in recent years as it reduces time, volume of solvents, quantity of reactants required for the completion of reaction and results in high purity, good selectivity and yield. The basic principle lying in this method is that when the molecules with permanent dipole moment are subjected into the electric field, the molecules get aligned with respect to the field. Molecular oscillations results as soon as the field oscillations begins and the molecules align and realign continuously giving rise to an intense internal heat energy which in turn agitates the molecules leading in the formation of product molecules [71,72].

Prato et.al. have described a new strategy for the multifunctionalization of nanotubes by the combination of two different addition reactions, 1, 3-dipolar cycloaddition of azomethine ylides and the addition of diazonium salts [73]. Then Ramanath and co-workers have demonstrated a novel strategy in combination with the polyol reduction of a metal salt to derivatize nanotubes with Au NPs in a single step [74]. Y. Wang et.al. have functionalized the SWCNTs with 2, 6-dinitroaniline through 1,3-dipolar cycloaddition initially through microwave irradiation in presence of conc. HNO$_3$ to produce carboxylic groups and coupling with 2, 6-dinitroaniline using DMF as solvent. Based on these facts they concluded that microwave assisted covalent functionalization can minimize the number of steps and the reaction could be completed within 15 minutes when compared to conventional methods which require long duration [75,76]. Jie Liu had showed the possibility of modifying the nanotubes through radical addition under microwave method using 4-methoxy phenylhydrazine hydrochloride as modifier molecule (Fig. 17) [77].
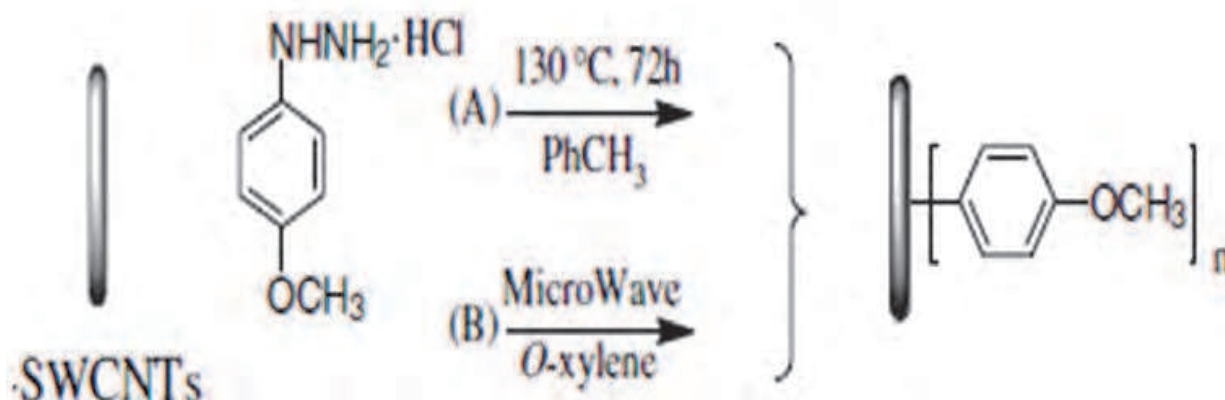
Fig. 17. Functionalization of SWCNTs by 4-methoxy phenylhydrazine through a classical thermal reaction (A) and a microwave assisted reaction (B) [77].

Raghuveer et.al. have demonstrated a novel strategy of combining microwave radiation with polyol reduction of a metal salt to derivatized tubes with Au nanoparticles in a single processing step. It is believed that exposing carbon nanotubes to microwave irradiation results in the formation of defects and functional groups on the tubes surface. These functional groups serve as preferred nucleation points for reducing metal ions from solution by a microwave reduction reaction yielding uniformly gold nanoparticles decorated nanotubes [74]. Nikolaos Karousis et.al. have modified the external wall of C_{60} encapsulated SWCNT peapods by insitu generated aryl diazonium salts using microwave irradiation [78]. Recently Jun Liu et.al. have reported the scalable and economical strategy for the effective transformation of Cu-complex to fabricate CuS CNTs based on the preferential chemical transformation and crystalline process and they have controlled the diameter of CuS/CNT composite by tuning the chemical reaction parameters [79]. This simple and convenient approach opens up a new way to synthesize CNT hetero structures that could be used in developing device concepts, novel catalysts and composites.

2.10 Modification through ball milling
Ball milling is a methodology in which solvent usage is very minimum or almost nil in the organic synthesis as well as in the surface modification reactions. Ball milling methods make the synthesis simple and very efficient phenomenon under green protocols. It is an established method for the generation of active centers on the substrate material surface during functionalization process under solvent free conditions. Simple ball mill grinding facilitates the activation of substrate material and subsequent modification with suitable indicator species often used in inorganic and material chemistry. This kind of modification has been extensively used in the preparation and modification of solids at laboratory and industrial scale levels [80]. The basic principle involved in this process is the generation of frictional forces by the collision between the surfaces of the reactants which results in the increased internal energy, temperature and pressure. In chemical synthesis, ball milling approach provides the required conditions very efficiently thereby the chemical reactions takes place in a very shortest time intervals. The mechanism of modification takes place either by changing the reactivity of the reagents or by breaking the molecular bonds [80]. Pierard et.al. have evaluated the effect of grinding on the structure of single walled carbon nanotubes using a ball mill and found the decreased length of CNTs and increased surface area which is a primary and necessary

condition for heterogeneous catalytic supports [81]. Welham et.al. have examined the effect of extended ball milling on the chemisorption of gases and its dependence on the extent of milling. Similarly Yu Feng Sun reported the adsorptive behavior of aniline in aqueous solution using milled nanotubes compared to unmilled nanotubes [82, 82a]. Li et.al. have reported the functionalization of SWCNTs with alkyl and aryl groups using the high speed vibration mill which have showed that the modified carbon surfaces with long alkyl chains are remarkably soluble in common organic solvents [83]. Peng et.al. have proposed a chemomechanical method for the insitu functionalization of nanotubes in presence of ammonium bicarbonate to introduce amine and amide groups. They have also observed that the conversion of semiconducting behaviour of tubes takes place from p-type to n-type [84]. Konya et.al. have shortened the MWCNTs using ball milling under ambient conditions and proposed different mechanisms for the cleavage of tubes based on the morphology of broken ends [85]. They have modified the MWCNTs with thiol, amine, amide, carbonyl and chlorine in presence of specific atmosphere through milling. The SWCNTs were modified with hydroxyl groups using a simple solid phase mechanochemical reaction at room temperature in presence of potassium hydroxide (Fig. 18) [86]. Recently Yi Liu et.al. have deposited the metal NPs onto the surface of carbon nanotubes by simple mechanochemical process within 10 minutes [87].
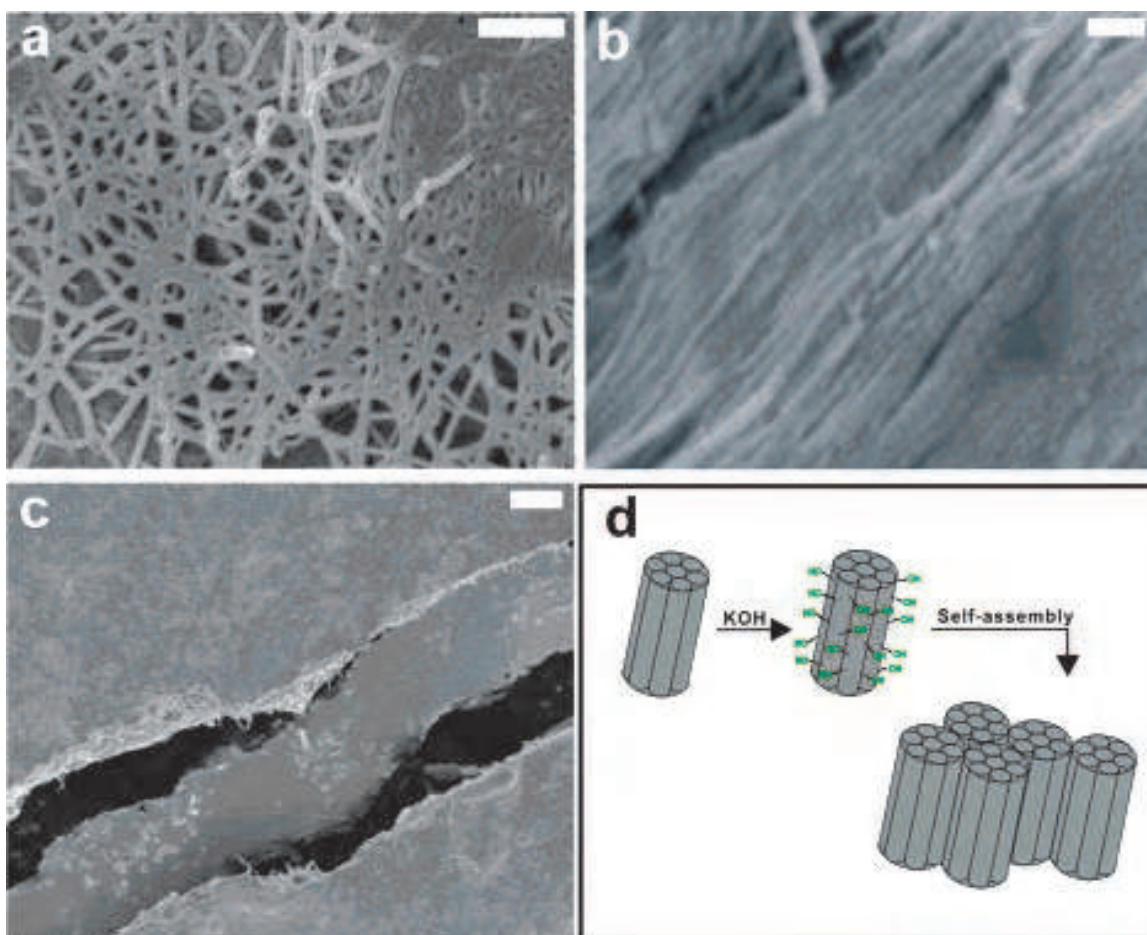

Fig. 18. SEM images of a) native SWCNTs (scale bar, 100nm) b) cross-sectional view of the self assembled SWCNTol sample shown in c) (scale bar, 100nm) c) top view of the self assembled SWCNTol sample (scale bar, 1000 nm) d) schematic representation of the self-assembled process [86].

3. Applications

3.1 Biosensors

Biosensors are the simple analytical devices composed of a sensing element, transducer and a detector which results a biological response in the form of a detectable and quantifiable analytical signal [88]. Several comprehensive reviews and articles have appeared over past few decades on the biosensors. Here only few emerging trends in the design of biosensors appeared in the literature have been discussed.

Since from their discovery, CNTs have been extensively studied and successfully used in fabricating biosensor because of the fact that they play a dual role as a substrate to immobilize the suitable matrix for biomolecules and also acts as a transducer. In addition to these, CNT based electrode materials allows efficient electron shuttling between electrodes and redox centers of the enzymes [89]. The land mark paper using carbon nanotubes as an electrode material in the field of biosensors began with the pioneering work of Britto and co-workers in 1996 by exploring the possibility of electrochemical oxidation of dopamine [90]. Then Joseph Wang has modified the glassy carbon with the suspension of CNT in suitable organic solvent and successfully determined NADH molecule [91]. This concept was extended by several research groups to sense many biomolecules like insulin, uric acid, catechol, morphine, brucine, cytochrome C, galactose, glucose, nitric oxide and horseradish peroxidase as well as hydrogen peroxide[92]. The enzymes like horseradish peroxidase and glucose oxidase (GOx) were immobilized on the surface of nanotube modified GCE which allowed direct electron transfer between them and has resulted symmetrical redox peaks [93]. Similar to that GCE modified with microperoxidase has also showed an enhanced electrocatalytic activity towards the reduction of H_2O_2 and O_2 molecules. This kind of behaviour was also noticed with catalase[94]. The GOx modified MWCNTs composite electrode exhibited high catalytic activity towards glucose molecule with a long term stability [95]. The conjugated monolayer of nanotube cyctochrome C (Cyt C) were prepared and stabilized at air-water interface. The electrochemical measurements showed well resolved redox peaks for modified Cyt C when compared to pure Cyt C due to the fact that the fast electron transfer takes place at the nanotube supports [96]. An amperometric third generation H_2O_2 biosensor based on the immobilization of hemoglobin on MWCNTs and gold colloidal nanoparticles has been reported [97]. The hemoglobin/gold nanoparticles multilayer films were assembled onto hemoglobin/MWCNT film through layer-by-layer assembly technique. The unmodified electrode substrate requires high overvoltage and suffers from electrode fouling due to the formation of radical intermediates [98]. In order to overcome the problem of high over voltage and electrode fouling, mediator modified electrodes have been prepared and applied for different analyte molecules [99]. Rutin modified MWCNTs on the surface of GCE were prepared and used towards the electrooxidation of hydroxylamine [100]. SAMs of SWCNTs with cobalt (II) tetraminophthalocyanine on gold electrode have been prepared and applied in the determination of dopamine and epinephrine [101,102]. Phenothiazine derivatives, Azure C and MWCNTs co-immobilized in the chitosan matrix were used to develop amperometric sensor for the determination of NADH [103]. Similar sensors were also developed using toludine blue, thin layer of 4-aminobenzene sulphonic acid on the substrate of MWCNTs in the determination of tyrosine [104]. MWCNTS/Co-Salophene carbon composites were used in the determination of tryptophan in serum, uric acid and ascorbic acid [105,106,107].

Next type of biosensors involves the use of NPs modified CNTs. The attractive physical and chemical properties of metal NPs have been widely used in exploring the possibility of various sensing applications [108]. NPs in conjunction with nanotubes have been found to enhance the electrocatalytic activity towards many electrochemical processes. Pt-nanoclusters/MWCNTs-GCE were used in the determination of estrogens and also in the oxidation of estradiol, estrone and estriol [109]. The dispersed Pt nanoparticles on 4-aminobenzene functionalized MWCNTs showed a good electrocatalytic activity towards methanol oxidation [110]. A novel nano-silver coated MWCNT composite was prepared on a GCE and applied in the determination trace level of thiocyanate in urine and saliva samples from smokers and nonsmokers [111]. Tri-metallic (Gold, silver and palladium) NPs/MWCNTs composites on GCE were prepared and explored their sensing ability using the model systems like hydrazine, bromide and Tl(I). Metal nanoparticles (Pt, Au or Cu) together with MWCNTs or SWCNTs solubilized in Nafion have been used to form nanocomposite for electrochemical detection of trinitrotoluene (TNT) and several other nitro aromatics. Similarly Cu modified CNTs were used to detect TNT in ppb levels [112]. An amperometric biosensor based on self-assembling of glutamate dehydrogenase and poly(amidoamine) dendrimer encapsulated platinum nanoparticles onto MWCNTs has been developed for the determination of glutamate [113]. Pt nanoparticles encapsulation scheme has been employed to construct an amperometric glucose biosensor based on layer-by-layer electrostatic adsorption of GOx and the dendrimers-encapsulated nanoparticles on MWCNTs. Composites prepared with CNTs and gold nanoparticles (Au-NPs) have demonstrated to possess special properties for biosensors detection due to the coupling of Au-NPs which are having capability to adsorb proteins with no loss of bioactivity, with the electrocatalytic ability of CNTs towards molecules of biochemical interest. A multilayer gold nanoparticles/MWCNTs/GOx membrane was prepared by electrostatic assembly using positively charged poly(dimethylallylammonium chloride) to connect them layer-by-layer and the membrane showed excellent electrocatalytic ability for glucose biosensing at a relatively low potential (−0.2 V) [113]. Polypyrrole modified CNTs were used in the determination of glutamate with high sensitivity, rapid response and low detection limit at 0.2 V [115]. A biosensor with improved performance was also developed through the immobilization of HRP onto electropolymerized PANI films doped with nanotubes [116]. It was found that the use of CNTs in the biosensor system could increase the amount and stability of the immobilized enzyme and greatly enhanced the biosensor response when compared with the biosensor without tubes. A mediator glucose biosensor has been constructed by immobilizing GOx at electropolymerized poly(toludine blue O) film on a CNTs-modified GCE. The toludine blue O moieties served as redox mediators for enzymatic glucose oxidation and as polymeric network to maintain the biosensor activity. Great enhancement in current response was observed for the glucose biosensor and the detection potential could be decreased to −0.1V (vs Ag/AgCl), where common interferences such as ascorbic acid, uric acid and acetamidophenol were not oxidized [117]. Nanofibrous glucose bioelectrodes were fabricated by the immobilization of GOx into an electrospun composite, membrane consisting of polymethylmethacrylatedispersed with MWCNTs wrapped by a cationic polymer (poly (diallyldimethylammonium chloride)). Nanofibrous electrode exhibited excellent electrocatalytic activity towards hydrogen peroxide with a pronounced oxidation current at +0.1 V [118]. Glucose biosensors were also prepared with electropolymerized polyphenylendiamine films, CNTs and GOx [119]. Glucose dehydrogenase(GDH) and its cofactor NAD+ were covalently attached to polyamino-

saccharide chains of chitosan. Electron conducting films of such macro complexes were prepared on GCE by adding tubes and evaporating the water. These bioelectrodes acted as oxygen independent reagentless biosensors in contrast to the oxidase based electrodes [120]. MWCNTs/polysulfone biocomposite membrane modified thick-film screen-printed electrochemical biosensors have been constructed by the incorporation of HRP by phase inversion technique which facilitated into fabrication of disposable biosensors [121]. The ability of poly(vinyl alcohol) to solubilize the tubes provides a useful way for preparing CNTs binder composite modified electrodes for a wide range of sensing applications. Using this approach a novel amperometric ethanol biosensor was constructed with NADH physically immobilizing within a PVA-MWCNTs composite obtained by a freezing thawing process [122].

3.2 Electrochemical metal ion sensors

Metal ion sensors require specific functionalities on the surface of carbon substrates which showed potential affinity towards particular metal ions. This can be achieved by modifying the electrode surface with suitable indicator species [6,7]. Many electrode materials have been used in the detection and quantification of metal ions but in this chapter the focus has been on the use of CNT as an electrode material. Modified MWCNTs/Nafion films on GCE provided suitable stripping responses for Cd (II) and Pb (II) ions [123]. A similar approach was followed to determine Europium (III) [124]. A SWCNT modified GCE was also employed to determine Cd (II) in water samples [125]. A thiol-tethered-MWCNTs chemically modified gold electrode has been prepared for As (III) speciation and Bi (III) determination at trace levels in natural and high salinity waters [126]. Gold NPs modified nanotubes were used to determine As (III) via anodic stripping voltammetry [127].

3.3 Heterogeneous catalysis

One of the most significant applications of SWCNT/NPs materials is in the area of catalysis [128]. The nanometer scale dimensions of metal nanoparticles facilitate enhanced diffusion rates and fast electron transfer kinetics. Therefore various research groups have done extensive studies on the effect of using carbon nanotube as catalyst. Pt nanoparticles supported on SWCNT electrodes have shown improved catalytic properties for both methanol oxidation and oxygen reduction reactions [129]. SWCNTs deposited on optically transparent electrodes (OTEs) were used as substrates and Pt nanoparticles were electrodeposited on these SWCNTs and used in the oxidation of methanol [129]. Cui et.al. have studied the electrocatalytic oxygen reduction reaction by Pt nanoparticles electrodeposited on MWNTs and found the positive shift in reduction potential and increased current and also showed high electron transfer rate towards methanol oxidation [130]. Use of bimetallic catalysts such as Pt-Ru has been commonly accepted in order to improve the poisoning effects of CO and also to increase the catalytic efficiency. In this direction, He et.al. first studied the electrodeposition of Pt-Ru on SWCNTs and carried out the methanol oxidation with maximum current density [131]. Highly dispersed Pd nanoparticles prepared by electrodeposition on SWCNT bundles have exhibited high catalytic activity for hydrazine oxidation and indicated that if SWCNTs are used as a support, the loading of precious metal catalysts could be minimized [132]. Use of MWCNT as a Pt catalyst supports were investigated by Wang et.al. [133]. Based on their investigations, they have concluded that with smaller sized Pt particles (2.5 nm), the performance of fuel cells could be improved. Most of the studies involved in the use of

random networks, bundles or SWCNT paste electrodes. Aligned networks of SWCNTs will enable better control over the density and distribution of NPs. An interesting liquid phase lamellar flow deposition technique to align carbon nanotubes has been demonstrated by Lay et.al. [134]. For instance one of the current highest values of anodic currents for Pt-C has been reported by Motorola with 40 mA/cm^2 for 2.5 mg Pt/cm^2, while Pt-CNT catalysts exhibited currents as high as 54 mA/cm^2 for 0.43 mg Pt/cm^2 and 25 mA/cm^2 for 10 μg Pt/cm^2. Fu et.al. synthesized hydrous RuO_2 nanoparticles supported on CNTs via a homogeneous oxidation-precipitation method using H_2O_2 as both the oxidant and precipitant at room temperature [135]. The hybrid was very active in the aerobic oxidation of various aromatic, saturated and cyclic alcohols and quite selective towards the corresponding aldehydes/ketones in liquid phase under mild conditions. The CNT-RuO_2 hybrid showed the lowest onset peak potentials of all tested catalysts, indicating the highest activity for the electrooxidation of methanol [136]. Huang et.al. Investigated the activity of V_2O_5 catalysts towards the selective catalytic reduction of NO with NH_3 in the presence of excess oxygen and also for skeletal isomarization reactions [137]. Further, the CNT-WO_3 hybrids exhibited very high skeletal isomerization selectivity exclusively toward olefin reactions. In this example, the improved performance of the CNT-WO_3 hybrid was not only attributed to a more uniform dispersion of WO_3 but also to CNTs due to the fact that the CNTs prevent the complete reduction of WO_3 to metallic tungsten (W) [137]. Another example of a successful application of CNT hybrids has been demonstrated by Chen et.al. who has investigated the catalytic performance of CNT-VO_x in the partial oxidation of *n*-butane. Such dehydrogenation reactions are often highly exothermic and the heat is typically released to the catalyst surface causing sintering of the particles and decreased catalytic activities. Because of their high thermal conductivity, the CNTs can act as a heat sink thus keeping the crystal size small [138].

3.4 Batteries and fuel cells

Fuel cells generate electricity through an electrochemical process in which the energy stored in a fuel is converted directly into electricity. Fuel cells combine the molecules of a fuel and oxidant chemically without burning, dispensing with the inefficiencies and pollution of traditional combustion. Unlike a battery, a fuel cell does not run down or require recharging. It will produce electricity as long as fuel and oxidants are supplied. Pt-based NPs/CNTs nanohybrids showed higher electrocatalytic activity for the methanol oxidation and oxygen reduction reaction than the commercial Pt-based NPs/C catalysts due to its one dimensional structure, excellent electronic conductivity and good electrochemical properties of CNTs [139,140]. Wei et.al. have prepared 1-Pt/FMCNTs and 2-Pt/FMCNTs nanohybrids by spontaneous reduction deposition of Pt NPs on the FMCNTs after or before film membrane CNTs(FMCNTs) coated on the teflon boned carbon electrodes [141]. The two types of nanohybrids exhibited higher electrochemical activity than commercial Pt/C catalyst. They found that the utilization of Pt in electrodes of 1-Pt/FMCNTs, 2-Pt/FMCNTs, and Pt/C were 75.6%, 44.6%, and 39.2% respectively. Electrodes of 2-Pt/FMCNTs and Pt/C were fabricated by the same procedure, but the former has a 5.4% Pt utilization higher than the later, which can be ascribed to a much better connected electron path contributed by FMCNTs in 2-Pt/FMCNTs than that in Pt/C electrode. It is well known that oxygen reduction in cathode of proton exchange membrane fuel cell (PEMFCs) must be able to easily access the surface of the catalyst particles, a pathway for proton diffusion must exist in the proximity of the active sites on catalysts and an electronic conducting pathway from

the catalyst to the electrode is required for electron transport. Yin et.al. have synthesized two kinds of Pt-Au/CNTs nanohybrids with different structures, one contained the separated Pt and Au NPs (Pt/Au/CNTs) and another composed with alloy-like Pt-Au NPs (PtAu/CNTs). Compared with the Pt/CNTs nanohybrids, the two Pt-Au/CNTs nanohybrids showed a lower overpotential for O_2 reduction in the presence of methanol. The Pt/Au/CNTs catalyst with separated Au and Pt NPs exhibited significantly higher methanol tolerance than the alloy like PtAu/CNTs nanohybrids, which should be ascribed to the less methanol absorption on Pt surface due to the effect of Au NPs [142]. In recent years the durability of PEMFCs has also been recognized as one of the most important issues to be addressed before the commercialization of the PEMFCs. Li et.al. have developed a route to stabilize Pt NPs supported on CNTs by anchoring Pt NPs on hydrofluoric acid treated CNTs [143]. Matsumori et.al. have used silica protection layer to improve the stability of Pt NPs supported on CNTs [144]. However the former method involves the use of a nonenvironmental friendly chemical (hydrofluoric acid), which has resulted in some structural damage and loses its conductivity [145,146]. The latter one would reduce the active surface area of the catalysts, resulting in the decrease of the catalytic activity of the catalysts. Chen et.al. have overcome this by developing a novel method to stabilize the CNTs supported Pt NPs by ionic liquid polymer thin film and the long-term operation stability of the obtained nanohybrids (PIL/PtNPs/AP-CNTs) for methanol electrooxidation. This modification has improved the stability of the electrode due to the mechanical isolation of PIL thin layer between PtNPs [147].

4. Conclusions

Carbon nanotubes have been the subject of discussion in recent years due to their diversified structures, properties and variety of applications. Chemically modified carbon nanotubes not only provide selectivity but also specificity for the detection of a wide variety of analyte molecules from all domains. They find widespread application in sensor technology, catalysis, drug delivery agents and as a composite material in high engineering applications.

5. Acknowledgement

6. References

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Carbon Nanotubes Applications on Electron Devices

Edited by Prof. Jose Mauricio Marulanda

Carbon nanotubes (CNTs), discovered in 1991, have been a subject of intensive research for a wide range of applications. In the past decades, although carbon nanotubes have undergone massive research, considering the success of silicon, it has, nonetheless, been difficult to appreciate the potential influence of carbon nanotubes in current technology. The main objective of this book is therefore to give a wide variety of possible applications of carbon nanotubes in many industries related to electron device technology. This should allow the user to better appreciate the potential of these innovating nanometer sized materials. Readers of this book should have a good background on electron devices and semiconductor device physics as this book presents excellent results on possible device applications of carbon nanotubes. This book begins with an analysis on fabrication techniques, followed by a study on current models, and it presents a significant amount of work on different devices and applications available to current technology.

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